AO 120 (Rev. 08/10)

TO:	Mail Stop 8 Director of the U.S. Patent and Trademark Office P.O. Box 1450 Alexandria, VA 22313-1450	REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT OR TRADEMARK

In Compliance with 35 U.S.C. § 290 and/or 15 U.S.C. § 1116 you are hereby advised that a court action has been filed in the U.S. District Court District of Delaware on the following

☐ Trademarks or ☑ Patents. (☐ the patent action involves 35 U.S.C. § 292.):

DOCKET NO.	DATE FILED	U.S. DISTRICT COURT
	8/29/2022	District of Delaware

PLAINTIFF	DEFENDANT
Molecular Rebar Design, LLC and Black Diamond Structures, LLC	LG Chem, Ltd., LG Energy Solution, Ltd., LG Energy Solution Michigan, Inc., and LG Electronics, Inc.

PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1 US 8,475,961 B2	7/2/2013	Molecular Rebar Design, LLC and Black Diamond Structures, LLC
2 US 9,636,649 B2	5/2/2017	Molecular Rebar Design, LLC and Black Diamond Structures, LLC
3 US 10,608,282 B2	3/31/2020	Molecular Rebar Design, LLC and Black Diamond Structures, LLC
4		
5		

In the above---entitled case, the following patent(s)/ trademark(s) have been included:

DATE INCLUDED	INCLUDED BY ☐ Amendment ☐ Answer ☐ Cross Bill ☐ Other Pleading	
PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1		
2		
3		
4		
5		

In the above---entitled case, the following decision has been rendered or judgement issued:

DECISION/JUDGEMENT

CLERK	(BY) DEPUTY CLERK	DATE

Copy 1---Upon initiation of action, mail this copy to Director Copy 3---Upon termination of action, mail this copy to Director
Copy 2---Upon filing document adding patent(s), mail this copy to Director Copy 4---Case file copy

LGES 1002

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/881,071	03/31/2020	10608282	MRE012NP2C / 277190	2885

130577 7590 03/11/2020
Hunton Andrews Kurth LLP/HAK TX
600 Travis Street
Suite 4200
Houston, TX 77002

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 149 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

MOLECULAR REBAR DESIGN, LLC, Austin, TX;
Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;
Milos Marinkovic, San Antonio, TX;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

IR103 (Rev. 10/09)

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

130577 7590 12/18/2019
Hunton Andrews Kurth LLP/HAK TX
600 Travis Street
Suite 4200
Houston, TX 77002

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)

(Signature)

(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/881,071	01/26/2018	Clive P. Bosnyak	MRE012NP2C / 277190	2885

TITLE OF INVENTION: Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	03/18/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
SMITH, JEREMIAH R	1723	429-144000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 Gregory L Porter
2 Hunton Andrews Kurth LLP
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: Molecular Rebar Design, LLC

(B) RESIDENCE: (CITY and STATE OR COUNTRY): Austin, Texas

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

☒ Electronic Payment via EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 50-0206

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☒ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /Gregory L. Porter/ Date 2020-02-18

Typed or printed name Gregory L. Porter Registration No. 40131

Electronic Patent Application Fee Transmittal

Application Number:	15881071
Filing Date:	26-Jan-2018
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Filer:	Gregory L. Porter/Jeanne Dunn
Attorney Docket Number:	MRE012NP2C / 277190

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
UTILITY APPL ISSUE FEE	2501	1	500	500

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**500**

Electronic Acknowledgement Receipt	
EFS ID:	38620294
Application Number:	15881071
International Application Number:	
Confirmation Number:	2885
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	130577
Filer:	Gregory L. Porter/Jeanne Dunn
Filer Authorized By:	Gregory L. Porter
Attorney Docket Number:	MRE012NP2C / 277190
Receipt Date:	18-FEB-2020
Filing Date:	26-JAN-2018
Time Stamp:	18:07:06
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$500
RAM confirmation Number	E20202HI07191258
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	IssueFeeTrans.pdf	138210 3caaff45417e333383fe139b3bf1ba9ea20b3a60	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30575 b7fa30cb683a41b0ac31e180a949bc3d638a23ee	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	168785		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

130577 7590 12/18/2019
Hunton Andrews Kurth LLP/HAK TX
600 Travis Street
Suite 4200
Houston, TX 77002

EXAMINER
SMITH, JEREMIAH R

ART UNIT	PAPER NUMBER
1723	

DATE MAILED: 12/18/2019

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/881,071	01/26/2018	Clive P. Bosnyak	MRE012NP2C / 277190	2885

TITLE OF INVENTION: Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	03/18/2020

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

130577 7590 12/18/2019
Hunton Andrews Kurth LLP/HAK TX
600 Travis Street
Suite 4200
Houston, TX 77002

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)

(Signature)

(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/881,071	01/26/2018	Clive P. Bosnyak	MRE012NP2C / 277190	2885

TITLE OF INVENTION: Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	03/18/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
SMITH, JEREMIAH R	1723	429-144000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1_____
2_____
3_____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑Issue Fee ❑Publication Fee (if required) ❑Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/881,071	01/26/2018	Clive P. Bosnyak	MRE012NP2C / 277190	2885

130577 7590 12/18/2019
Hunton Andrews Kurth LLP/HAK TX
600 Travis Street
Suite 4200
Houston, TX 77002

EXAMINER
SMITH, JEREMIAH R

ART UNIT	PAPER NUMBER
1723	

DATE MAILED: 12/18/2019

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 15/881,071	Applicant(s) Bosnyak et al.	
	Examiner JEREMIAH R SMITH	Art Unit 1723	AIA (FITF) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to 10/18/19.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-16 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 12/13/19.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☑ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/JEREMIAH R SMITH/
Primary Examiner, Art Unit 1723

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. Application 15/881071 "BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES" is a continuation of application 14/390902, which is the national stage entry of a PCT application filed on 6/21/13 and claims priority from a provisional application file on 6/22/12.

The present application is being examined under the pre-AIA first to invent provisions.

This Office Action is in response to communication filed on 10/18/19.

EXAMINER'S AMENDMENT

2. An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in an interview with Gregory Porter on 12/13/19.

The application has been amended as follows:

CLAIMS

8. (Currently Amended) The ~~binder composition of claim 2~~ composition of claim 2, further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. (Currently Amended) The composition of ~~claim 9~~ claim 1, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

13. (Currently Amended) The composition of ~~claim 13~~ claim 12, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

14. (Currently Amended) The composition of ~~claim 14~~ claim 12, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

16. (Currently Amended) The composition of ~~claim 16~~ claim 15, wherein the electrolyte comprises a polymer or a liquid.

Allowable Subject Matter

3. Claims 1-16 are allowed.

4. The examiner's statement of reasons for allowance:

Claim 1 as filed on 10/18/19 is amended to include features of claims 17 and 18 indicated as allowable in the 10/17/19 Non-Final Rejection. As stated in the previously mailed Non-Final Rejection, the closest prior art (Bosynak, Johnson, Gu and Schaefer, all of record) does not appear to teach or fairly suggest the limitations of now cancelled claims 17 and 18, (i.e. a distribution of carbon nanotube aspect ratios, wherein 40 to 90 % of the nanotubes have an aspect ratio of 30 to 70, and wherein 1 to 30% of the

carbon nanotubes have an aspect ratio of 80 to 140) in combination with the features of the corresponding independent claim and intervening claims. Therefore, the previously presented rejection based on the closest prior art is withdrawn.

Upon an updated search, no new and closer prior art has been discovered which cures this deficiency of the previously presented combined embodiment, or which independently fairly teaches or suggests the above described features of claim 1, in combination with the balance of the features of claim 1. Accordingly, claim 1 and all dependent claims are found to be allowable.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to JEREMIAH R SMITH whose telephone number is (571)270-7005. The examiner can normally be reached on Mon-Fri: 9 AM-5 PM (EST).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Milton Cano can be reached on 571-272-1398. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/JEREMIAH R SMITH/
Primary Examiner, Art Unit 1723

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/881,071	Bosnyak et al.
	Examiner	**Art Unit**
	JEREMIAH R SMITH	1723

CPC - Searched*		
Symbol	**Date**	**Examiner**
H01M2/14 H01M2/1606 H01M2/1613 H01M2/162 H01M2/1633 H01M2/164 H01M2/1653 (all keyword searched for carbon nanotube)	12/13/2019	J.R. Smith

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	**Date**	**Examiner**
Considered IDS	10/11/2019	J.R. Smith
Considered history of parent 14/390902	10/11/2019	J.R. Smith
H01M2/14 H01M2/1606 H01M2/1613 H01M2/162 H01M2/1633 H01M2/164 H01M2/1653 (all keyword searched for carbon nanotube)	10/11/2019	J.R. Smith
further text based searching	10/11/2019	J.R. Smith
relevant searches updating, sear		

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
interference	see EAST search history	12/13/2019	J.R. Smith

/JEREMIAH R SMITH/ Primary Examiner, Art Unit 1723	

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/881,071	Bosnyak et al.
	Examiner	**Art Unit**
	JEREMIAH R SMITH	1723

/JEREMIAH R SMITH/ Primary Examiner, Art Unit 1723	

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/881,071	Bosnyak et al.
	Examiner	**Art Unit**
	JEREMIAH R SMITH	1723

CPC						
Symbol					**Type**	**Version**
H01M	/	10	/	0565	F	2013-01-01
H01G	/	9	/	035	I	2013-01-01
H01M	/	10	/	056	I	2013-01-01
H01M	/	4	/	14	I	2013-01-01
H01M	/	2	/	1613	I	2013-01-01
H01G	/	11	/	38	I	2013-01-01
H01G	/	11	/	52	I	2013-01-01
H01M	/	2	/	1653	I	2013-01-01
H01M	/	4	/	625	I	2013-01-01
H01M	/	4	/	621	I	2013-01-01
H01G	/	11	/	54	I	2013-01-01
H01G	/	9	/	022	I	2013-01-01
H01G	/	9	/	02	I	2013-01-01
H01G	/	11	/	36	I	2013-01-01
H01G	/	11	/	56	I	2013-01-01
H01M	/	4	/	20	I	2013-01-01
H01M	/	4	/	622	I	2013-01-01
H01M	/	10	/	052	I	2013-01-01
H01M	/	10	/	08	I	2013-01-01
Y10T	/	428	/	249921	A	2015-04-01
Y02E	/	60	/	13	A	2013-01-01
Y02T	/	10	/	7022	A	2013-01-01
Y10T	/	428	/	2918	A	2015-01-15
Y10T	/	428	/	24995	A	2015-04-01
H01M	/	2	/	145	A	2013-01-01
H01M	/	4	/	663	A	2013-01-01
H01M	/	4	/	96	A	2013-01-01
H01M	/	10	/	06	A	2013-01-01
Y02E	/	60	/	122	A	2013-01-01
Y02E	/	60	/	126	A	2013-01-01

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 16	
/JEREMIAH R SMITH/ Primary Examiner, Art Unit 1723 (Primary Examiner)	13 December 2019 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

U.S. Patent and Trademark Office

Part of Paper No.: 20191213

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/881,071	Bosnyak et al.
	Examiner	**Art Unit**
	JEREMIAH R SMITH	1723

CPC Combination Sets								
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE (Assistant Examiner) (Date)		**Total Claims Allowed:** 16	
/JEREMIAH R SMITH/ Primary Examiner, Art Unit 1723 (Primary Examiner) (Date)	13 December 2019	O.G. Print Claim(s) 1	O.G. Print Figure 1

U.S. Patent and Trademark Office Part of Paper No.: 20191213

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/881,071	Bosnyak et al.
	Examiner	**Art Unit**
	JEREMIAH R SMITH	1723

INTERNATIONAL CLASSIFICATION				
CLAIMED				
H01M	/	10	/	052

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	SUBCLASS

CROSS REFERENCES(S)						
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					

NONE (Assistant Examiner) (Date)		Total Claims Allowed: 16	
/JEREMIAH R SMITH/ Primary Examiner, Art Unit 1723 (Primary Examiner) (Date)	13 December 2019	O.G. Print Claim(s) 1	O.G. Print Figure 1

U.S. Patent and Trademark Office Part of Paper No.: 20191213

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/881,071	Bosnyak et al.
	Examiner	**Art Unit**
	JEREMIAH R SMITH	1723

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	10	10		19										
2	2	11	11		20										
5	3	12	12												
7	4	13	13												
8	5	14	14												
6	6	15	15												
3	7	16	16												
4	8		17												
9	9		18												

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 16	
/JEREMIAH R SMITH/ Primary Examiner, Art Unit 1723 (Primary Examiner)	13 December 2019 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

U.S. Patent and Trademark Office Part of Paper No.: 20191213

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	12	((nt nanotube) near3 carbon cnt) near4 ("aspect ratio") same "aspect ratio" near4 (percent percentage amount "%" wt number weight).clm.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/12/13 16:15
L4	534034	@pd>"20191011"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/12/13 16:21
L5	121	((nt nanotube) near3 carbon cnt).ab. and ((nt nanotube) near3 carbon cnt) near4 ("aspect ratio") and "aspect ratio" near4 (percent percentage amount "%" wt number weight)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/12/13 16:40
L6	2	4 and L5	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/12/13 16:40
L7	92	Bosnyak near2 Clive.in. Swogger near2 Kurt.in. Marinkovic near2 Milos.in.	US-PGPUB; USPAT	OR	ON	2019/12/13 16:48
L8	24	L7 and "aspect ratio".clm. and open.clm.	US-PGPUB; USPAT	OR	ON	2019/12/13 16:48
L9	0	4 and L8	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/12/13 16:48
S1	1	14/390902.app.	US-PGPUB; USPAT	OR	ON	2017/05/22 10:33
S2	11	("20080111110" | "6555945" | "20110163274" | "7070753" | "7070753" | "20090176082" | "20090200517" | "20110294013" | "20120068125" | "20100075231" | "20110311876" | "20050224764").PN.	US-PGPUB; USPAT	OR	ON	2017/05/22 10:34
S5	1	"WO 2010117392"	DERWENT	OR	ON	2017/05/22 10:38
S6	12	("20110104551" "20090317710" "7429371" "20050006623" "6114068" "6878361" "20070048619" "20070259994" "20090142666" "20080038635" "20090142665").pn. "20110294013"	US-PGPUB; USPAT	OR	ON	2017/05/22 10:39
S7	11	("20080111110" | "6555945" |	US-	OR	ON	2017/05/22

		"20110163274" | "7070753" | "7070753" | "20090176082" | "20090200517" | "20110294013" | "20120068125" | "20100075231" | "20110311876" | "20050224764").PN.	PGPUB; USPAT			10:40
S8	7	"WO 2009155267" "WO 2012083358" "WO 2013011516" "WO 2011163129" "ep 1665446" "ep 1845124" "ep 2415839"	DERWENT	OR	ON	2017/05/22 10:44
S9	6	("20070104981" "20090317710" "20120068125" "20120183770" "20140127565" "20140162111").pn.	US-PGPUB; USPAT	OR	ON	2017/05/22 10:47
S10	1	"CA 2747728"	DERWENT	OR	ON	2017/05/22 14:52
S11	1	"8993161".pn.	US-PGPUB; USPAT	OR	ON	2017/05/22 15:02
S12	3	lead near3 acid near3 battery and (anode negative) same "polyvinyl alcohol" and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:49
S13	7	lead near3 acid near3 battery and (anode negative) same "polyvinyl alcohol" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:52
S14	9	(anode negative) same "polyvinyl alcohol" and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:57
S15	84	lead near3 acid near3 battery and (anode negative) same "polyvinyl alcohol"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:58
S16	1445	lead near3 acid near3 battery and (anode negative) same "sulfuric"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:58
S17	190	lead near3 acid near3 battery and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:59
S18	56	lead near3 acid near3 battery and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:59
S19	31	lead near3 acid near3 battery and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube" and (anode negative) same paste	US-PGPUB; USPAT	OR	ON	2017/05/22 15:59
S20	8	lead near3 acid near3 battery and (anode negative) same "sulfuric" same "carbon nanotube" same paste	US-PGPUB; USPAT	OR	ON	2017/05/22 16:01
S21	1	"20130157118"	DERWENT	OR	ON	2017/05/22 17:16
S22	1	"20120328940"	DERWENT	OR	ON	2017/05/22 17:37
S23	1	"20130022860"	DERWENT	OR	ON	2017/05/22 18:11
S24	113	"429".clas. and battery and "carbon	US-	OR	ON	2017/05/23

		nanotube" and nanotube with "aspect ratio"	PGPUB; USPAT			11:03
S25	113	"429".clas. and battery and "carbon nanotube" and nanotube with "aspect ratio" and "aspect ratio"	US-PGPUB; USPAT	OR	ON	2017/05/23 11:04
S26	126	"429".clas. and battery and "carbon nanotube" and (cnt nt nanotube) with "aspect ratio" and "aspect ratio"	US-PGPUB; USPAT	OR	ON	2017/05/23 11:06
S27	1	"20150064538"	DERWENT	OR	ON	2017/05/23 11:39
S28	50	battery and "carbon nanotube" and (cnt nt nanotube) with "aspect ratio" and "aspect ratio"	EPO; JPO; DERWENT	OR	ON	2017/05/23 11:52
S32	27318	(H01M2/004, H01M2/04, H01M2/027, H01M2/1613 H01M4/14, H01M4/26, H01M4/38, H01M4/027, H01M4/622, H01M4/625 H01M10/24, H01M10/056, H01M10/05658 H01G4/16, H01G9/035, H01L31/022425).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:54
S33	7531	(H01L31/022425).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:54
S34	611	(H01G9/035,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:54
S35	26	(H01G4/16,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S36	0	(H01M10/05658).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S37	1358	(H01M10/056,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S38	942	(H01M10/24,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S39	7097	(H01M4/625).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S40	4503	(H01M4/622,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55

S41	0	(H01M4/027,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S42	4900	(H01M4/38,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S43	909	(H01M4/26,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S44	813	(H01M4/14,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S45	892	(H01M2/1613).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S46	514	(H01M2/027,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S47	597	(H01M2/04,,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S50	2809	S32 and battery and (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:58
S51	2760	S32 and battery near3 (lead acid)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:58
S52	470	S50 and S51	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:58
S53	1816781	@pd>"20170523"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:09
S54	29368	(H01M2/004, H01M2/04, H01M2/027, H01M2/1613 H01M4/14, H01M4/26, H01M4/38, H01M4/027, H01M4/622, H01M4/625 H01M10/24, H01M10/056, H01M10/05658 H01G4/16,	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:10

		H01G9/035, H01L31/022425).cpc.				
S55	3116	S54 and battery and (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:10
S56	383	S53 and S55	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:10
S57	464	lead near3 acid near3 battery and (cathode anode electrode) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/10/17 12:13
S58	45	(lead near3 acid near3 battery).clm. and (cathode anode electrode) with "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/10/17 12:13
S59	46	(lead near3 acid near3 battery).clm. and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT	OR	ON	2017/10/17 12:14
S60	88	(lead near3 acid near3 battery) and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon).clm.	US-PGPUB; USPAT	OR	ON	2017/10/17 12:15
S61	120	S59 S60	US-PGPUB; USPAT	OR	ON	2017/10/17 12:16
S63	15	(S59 S60) and "aspect ratio"	US-PGPUB; USPAT	OR	ON	2017/10/17 12:17
S64	14009	H01M4/625.cpc. H01M4/14.cpc. H01M10/06.cpc. H01M4/663.cpc. H01M4/96.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S65	7767	H01M4/625.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S66	869	H01M4/14.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S67	1737	H01M10/06.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S68	1606	H01M4/663.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:47
S69	2967	H01M4/96.cpc.	US-PGPUB; USPAT;	OR	ON	2017/10/17 12:47

			EPO; JPO; DERWENT			
S70	2343	H01M4/14.cpc. H01M10/06.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:47
S71	21	S70 and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon).clm.	US-PGPUB; USPAT	OR	ON	2017/10/17 12:47
S72	44	S70 and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT	OR	ON	2017/10/17 12:47
S73	5	S70 and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon) and (nanotube near3 carbon cnt nt near3 carbon) with ("aspect ratio" aspect$1ratio)	US-PGPUB; USPAT	OR	ON	2017/10/17 12:48
S77	1	15/881071.app.	US-PGPUB; USPAT	OR	ON	2019/10/07 17:03
S78	91	Bosnyak near2 Clive.in. Swogger near2 Kurt.in. Marinkovic near2 Milos.in.	US-PGPUB; USPAT	OR	ON	2019/10/08 12:07
S79	24	S78 and "aspect ratio".clm. and open.clm.	US-PGPUB; USPAT	OR	ON	2019/10/08 12:08
S80	7	S78 and "aspect ratio".clm. and open.clm.	USPAT	OR	ON	2019/10/08 12:08
S82	1	"cn 101734650"	DERWENT	OR	ON	2019/10/08 15:11
S83	39852	(H01M2/004, H01M2/04, H01M2/027, H01M2/1613 H01M4/14, H01M4/26, H01M4/38, H01M4/027, H01M4/622, H01M4/625 H01M10/24, H01M10/056, H01M10/05658 H01G4/16, H01G9/035, H01L31/022425).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/08 16:12
S84	5062	S83 and battery and ((nt nanotube) near3 carbon cnt)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/08 16:12
S85	203	S83 and (separator electrolyte) near4 ((nt nanotube) near3 carbon cnt)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/08 16:13
S86	4	"20080254362"	US-PGPUB; USPAT	OR	ON	2019/10/08 16:49
S87	1	"wo 2009148959"	DERWENT	OR	ON	2019/10/08 17:07
S88	2	"20110220574"	US-PGPUB; USPAT	OR	ON	2019/10/08 17:08
S89	33	("2011/0220574").URPN.	USPAT	OR	ON	2019/10/08 17:09
S90	4	S89 and battery	US-	OR	ON	2019/10/08

			PGPUB; USPAT			17:09
S91	2352	H01M2/14.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:08
S92	416	H01M2/1606.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:08
S93	1267	H01M2/1613.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:08
S94	2869	H01M2/162.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S95	427	H01M2/1633.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S96	319	H01M2/164.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S97	8719	H01M2/1653.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S98	13771	H01M2/14.cpc. H01M2/1606.cpc. H01M2/1613.cpc. H01M2/162.cpc. H01M2/1633.cpc. H01M2/164.cpc. H01M2/1653.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S99	690	S98 and ((nt nanotube) near3 carbon cnt)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:10
S100	90	S99 and (inorganic near4 filler)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:10
S101	133	S98 and (inorganic with strength near4 separator)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:23
S102	48	S98 and (inorganic with strength near4 separator) and inorganic with (transition metal)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:23
S103	11	S98 and (graphene near4 separator)	US-PGPUB; USPAT	OR	ON	2019/10/10 14:08
S104	0	("2009117467" "2012045688" "2011183180" "2012251881").pn.	US-PGPUB;	OR	ON	2019/10/10 14:13

			USPAT			
S105	4	("20090117467" "20120045688" "20110183180" "20120251881").pn.	US-PGPUB; USPAT	OR	ON	2019/10/10 14:13
S107	2719	jeremiah.xp,xa. igloo	US-PGPUB; USPAT	OR	ON	2019/10/11 09:25
S108	1	jeremiah .xp,xa. and igloo	US-PGPUB; USPAT	OR	ON	2019/10/11 09:26
S109	204	jeremiah near2 smith .xp.	US-PGPUB; USPAT	OR	ON	2019/10/11 09:29
S110	39876	(H01M2/004, H01M2/04, H01M2/027, H01M2/1613 H01M4/14, H01M4/26, H01M4/38, H01M4/027, H01M4/622, H01M4/625 H01M10/24, H01M10/056, H01M10/05658 H01G4/16, H01G9/035, H01L31/022425).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 10:54
S111	13771	H01M2/14.cpc. H01M2/1606.cpc. H01M2/1613.cpc. H01M2/162.cpc. H01M2/1633.cpc. H01M2/164.cpc. H01M2/1653.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 10:54
S113	50661	(S110 S111)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 10:54
S114	124	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 10:55
S115	1	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio" and bimodal with "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:54
S116	1	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio" and (bi$1mod$3 bimodal) with "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:55
S117	1	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio" and (bi$1modal bimodal) with "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:55
S118	9	S113 and ((nt nanotube) near3 carbon cnt) with "aspect ratio" and (bi$1modal bimodal) same "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:57
S119	10	("20110294013" | "20050224764" | "20080111110" | "20110163274" | "20100075231" | "6555945" | "20090200517" | "20120068125" | "20110311876" | "7070753").PN.	US-PGPUB; USPAT	OR	ON	2019/10/11 12:02

S120	6	((nt nanotube) near3 carbon cnt).ab. and ((nt nanotube) near3 carbon cnt) near4 ("aspect ratio" near4 distribution)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 12:23
S121	1440	((nt nanotube) near3 carbon cnt).ab. and ((nt nanotube) near3 carbon cnt) near4 ("aspect ratio")	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 12:31
S122	119	((nt nanotube) near3 carbon cnt).ab. and ((nt nanotube) near3 carbon cnt) near4 ("aspect ratio") and "aspect ratio" near4 (percent percentage amount "%" wt number weight)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 12:32
S123	2	14/390902.app.	US-PGPUB; USPAT	OR	ON	2019/12/13 13:26

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L2	12	((nt nanotube) near3 carbon cnt) near4 ("aspect ratio") same "aspect ratio" near4 (percent percentage amount "%" wt number weight).clm.	US-PGPUB; USPAT	OR	ON	2019/12/13 16:16
L3	0	(binder electroltye separator) same ((nt nanotube) near3 carbon cnt) near4 ("aspect ratio") same "aspect ratio" near4 (percent percentage amount "%" wt number weight).clm.	US-PGPUB; USPAT	OR	ON	2019/12/13 16:17
S74	29	(lead near3 acid near3 battery).clm. and (cathode anode electrode) with "carbon nanotube"	US-PGPUB	OR	ON	2017/10/17 12:13
S75	30	(lead near3 acid near3 battery).clm. and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB	OR	ON	2017/10/17 12:15
S76	60	(lead near3 acid near3 battery) and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon).clm.	US-PGPUB	OR	ON	2017/10/17 12:15

12/13/2019 5:06:41 PM
C:\Users\jsmith10\Documents\EAST\Workspaces\15881071 con 14390902.wsp

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15881071
	Filing Date	2018-01-26
	First Named Inventor	Kurt W. Swogger
	Art Unit	
	Examiner Name	
	Attorney Docket Number	108892.0277190

U.S.PATENTS

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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U.S.PATENT APPLICATION PUBLICATIONS

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20110163274	A1	2011-10-07	Plee et al.	

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FOREIGN PATENT DOCUMENTS

Examiner Initial*	Cite No	Foreign Document Nu	Country Code[2] ¡	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2011163129	WO	A1	2011-12-29	Bosnyak et al.		☐

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

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	1	XIANKE ET AL., "Layered and interfacially blended polyelectrolyte multi-walled carbon nanotube composites for enhanced ionic conductivity", 520 Thin Solid Films (Sep. 16, 2011), pgs. 1872-1879	☐

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Examiner Signature	/JEREMIAH R SMITH/	Date Considered	12/13/2019

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	Art Unit	
	Examiner Name	
	Attorney Docket Number	108892.0277190

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☐ See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Gregory L. Porter/	Date (YYYY-MM-DD)	2019-12-13
Name/Print	Gregory L. Porter	Registration Number	40131

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Bibliographic Data

Application No: 15/881,071

Foreign Priority claimed: ○ Yes ◉ No

35 USC 119 (a-d) conditions met: ☐ Yes ☑ No | ☐ Met After Allowance

Verified and Acknowledged: /JEREMIAH R SMITH/ | [ ]

Examiner's Signature | Initials

Title: Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

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FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
01/26/2018 **RULE**	429	1723	MRE012NP2C / 277190

APPLICANTS

MOLECULAR REBAR DESIGN, LLC, Austin, TX, UNITED STATES

INVENTORS

Clive P. Bosnyak Dripping Springs, TX, UNITED STATES

Kurt W. Swogger Austin, TX, UNITED STATES

Milos Marinkovic San Antonio, TX, UNITED STATES

CONTINUING DATA

This application is a CON of 14390902 10/06/2014 PAT 9912009

14390902 is a 371 of PCT/US2013/047029 06/21/2013

PCT/US2013/047029 has PRO of 61663513 06/22/2012

PCT/US2013/047029 has PRO of 61662393 06/21/2012

FOREIGN APPLICATIONS

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	1	20110163274	A1	2011-10-07	Plee et al.	

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	1	2011163129	WO	A1	2011-12-29	Bosnyak et al.		☐

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SIGNATURE

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Signature	/Gregory L. Porter/	Date (YYYY-MM-DD)	2019-12-13
Name/Print	Gregory L. Porter	Registration Number	40131

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(71) Applicant *(for all designated States except US)*: **DESIGNED NANOTUBES, LLC** [US/US]; 4211 Waters Edge Cove, Austin, TX 78731 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BOSNYAK, Clive, P.** [US/US]; 12001 Settlers Trail, Dripping Springs, TX 78620 (US). **SWOGGER, Kurt, W.** [US/US]; 4211 Waters Edge Cove, Austin, TX 78731 (US).

(74) Agents: **DUNSTAN, Amy, Ulfers** et al.; Jackson Walker L.L.P., 901 Main Street, Suite 6000, Dallas, TX 75202 (US).

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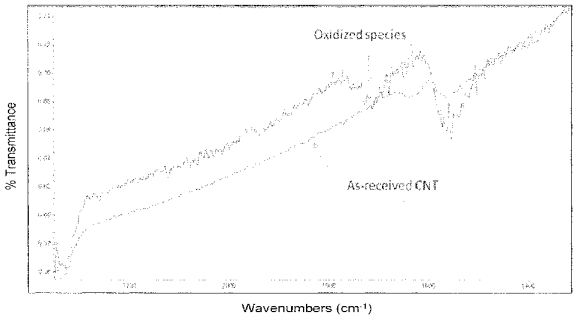

Figure 13

(57) Abstract: The present invention relates to the exfoliation and dispersion of carbon nanotubes resulting in high aspect ratio, surface-modified carbon nanotubes that are readily dispersed in various media. A method is disclosed for their production in high yield. Further modifications by surface active or modifying agents are also disclosed. Application of the carbon nanotubes of this invention as composites with materials such as elastomers, thermosets and thermoplastics are also described.

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MODIFIED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States Provisional Patent Application No. 61/357,420, filed June 22, 2010, entitled MODIFIED CARBON NANOTUBES, METHODS FOR PRODUCITON THEREOF AND PRODUCTS OBTAINED THEREFROM, , the entire content of which is hereby incorporated by reference. This application also incorporates by reference the entire content of each of the following applications: PCT patent application PCT/US09/68781 filed December 18, 2009, which claims priority to U.S. provisional patent applications 61/138,551, filed December 18, 2008, and 61/139,050, filed December 19, 2008.

BACKGROUND

[0002] The present invention relates to the exfoliation and dispersion of carbon nanotubes resulting in high aspect ratio, surface-modified carbon nanotubes that are readily dispersed in various media. Also, the present invention pertains to methods for production of such carbon nanotubes in high yield. These carbon nanotubes are further modified by surface active or modifying agents. This invention also relates to the carbon nanotubes as composites with materials such as elastomers, thermosets and thermoplastics.

[0003] Carbon nanotubes in their solid state are currently produced as agglomerated nanotube bundles in a mixture of chiral or non-chiral forms. Various methods have been developed to debundle or disentangle carbon nanotubes in solution. For example, carbon nanotubes may be shortened extensively by aggressive oxidative means and then dispersed as individual nanotubes in dilute solution. These tubes have low aspect ratios not suitable for high strength composite materials. Carbon nanotubes may also be dispersed in very dilute solution as individuals by sonication in the presence of a surfactant. Illustrative surfactants used for dispersing carbon nanotubes in solution include, for example, sodium dodecyl sulfate and PLURONICS. In some instances, solutions of individualized carbon nanotubes may be prepared from polymer-wrapped carbon nanotubes. Individualized single-wall carbon nanotube solutions have also been prepared in very dilute solutions using polysaccharides, polypeptides, water-soluble polymers, nucleic

acids, DNA, polynucleotides, polyimides, and polyvinylpyrrolidone. The dilution ranges are often in the mg/liter ranges and not suitable for commercial usage.

[0004] A number of uses for carbon nanotubes have been proposed including, for example, energy storage devices (e.g., ultracapacitors, supercapacitors and batteries), field emitters, conductive films, conductive wires and membrane filters. Use of carbon nanotubes as a reinforcing agent in polymer composites is another area in which carbon nanotubes are predicted to have significant utility. However, utilization of carbon nanotubes in these applications has been hampered due to the general inability to reliably produce individualized carbon nanotubes. For example, load transfer to carbon nanotubes in polymer composites is typically less than would be expected than if the carbon nanotubes were fully exfoliated as individual nanotubes.

[0005] Likewise, in applications involving electrical conduction, conductivity is lower than anticipated due to reduced access to the carbon nanotube surface when the carbon nanotubes are agglomerated as opposed to being dispersed as individuals. As noted above, current methods for producing exfoliated carbon nanotubes usually results in severe shortening and/or functionalization of the nanotubes. Without proper individual separation of the carbon nanotubes, it is also likely that non-uniform functionalization of the tube surface results. Such shortening, functionalization or non-uniform functionalization also generally results in reduced conductivity, which is also disadvantageous for applications where high electrical conductivity is beneficial.

[0006] In view of the foregoing, solid exfoliated carbon nanotubes and methods for efficiently exfoliating carbon nanotubes are of considerable interest in the art. Such exfoliated carbon nanotubes are likely to exhibit considerably improved properties in applications including, for example, energy storage devices and polymer composites. Further surface modification of the tubes for enhanced bonding to a material or attaching electroactive materials are facilitated by exfoliation. These further surface modified carbon nanotubes are considered advantageous for energy applications such as batteries and capacitors and photovoltaics, and material-composite applications such as tires, adhesives, and engineering composites such as windblades.

SUMMARY

[0007] In various embodiments, a plurality of carbon nanotubes is disclosed comprising single wall, double wall or multiwall carbon nanotube fibers having an aspect ratio (the ratio of length of the nanotube to the diameter of the nanotube) of from about 25 to about 500, preferably from about 60 to about 250, and a oxidation level of from about 3 weight % to about 15 weight %, preferably from about 5 weight% to about 12 weight % and most preferably 6 weight% to about 10 weight% (weight % is the ratio of the weight of a component divided by the total weight expressed as a percentage). Preferably, a neutralized water treatment of the fibers results in a pH of from about 4 to about 9, more preferably from about 6 to about 8. The fibers can have oxidation species comprising of carboxylic acid or derivative carboxylate groups and are essentially discrete individual fibers, not entangled as a mass.

[0008] In other embodiments, the fibers comprise a residual metal concentration of less than about 1000 parts per million, ppm, and preferably less than about 100 ppm. The fibers can be open-ended and the matt of fibers has an electrical conductivity of at least 0.1 Siemens/cm and as high as 100 Siemens/cm.

[0009] In another embodiment, the fibers can be mixed with a material such as, but not limited to, an elastomer or thermoplastic or thermoset to form a material-carbon nanotube composite.

[0010] In yet other embodiments, the fibers have an average diameter of from about 0.6 nanometers to about 30 nanometers, preferably from about 2 nm to about 15 nm and most preferably 6-12 nm. The fibers have an average distribution length of from about 50 nanometers to about 10000 nanometers, preferably from about 400 nm to about 1200 nm.

[0011] In another embodiment, a method for preparing carbon nanotube fibers is disclosed, said method comprising suspending entangled non-discrete multi-wall carbon nanotube fibers in an acidic solution, optionally agitating said composition, sonically treating said suspended nanotube fiber composition to form discrete carbon nanotube fibers and isolating the resultant discrete carbon nanotube fibers from the composition using solid-liquid methods such as filtration or centrifugation prior to further treatment.

[0012] In another embodiment, the method for preparing carbon nanotube fibers includes an acidic solution which comprises a solution of sulfuric acid and nitric acid wherein the nitric acid is present in a dry basis of from about 10 wt % to about 50 wt %, preferably from about 15 wt % to about 30 wt %.

[0013] In another embodiment, the method for preparing carbon nanotube fibers includes the carbon nanotube fibers are present in a concentration of from greater than zero to less than about 4 weight percent of the suspended nanotube fiber composition.

[0014] In another embodiment, the method for preparing carbon nanotube fibers includes wherein the sonic treatment is performed at an energy input of from about 200 to about 600 Joules/gram of suspended composition, preferably from about 250 to about 350 Joules/gram of suspended composition.

[0015] In other various embodiments, the method for preparing carbon nanotube fibers includes wherein the suspended discrete nanotube fiber composition in the acidic solution is controlled at a specific temperature environment from about 15 to about 65°C, preferably from about 25 to about 35°C.

[0016] In another embodiment, the method for preparing carbon nanotube fibers comprises a batch, semi-batch or continuous method.

[0017] In another embodiment, the method for preparing carbon nanotube fibers includes wherein the composition is in contact with the acidic solution from about 1 hour to about 5 hours, preferably from about 2.5 to about 3.5 hours.

[0018] In yet another embodiment, the method for preparing carbon nanotube fibers includes wherein said isolated resultant discrete carbon nanotube fibers from the composition prior to further treatment comprises at least about 10 weight percent water.

[0019] In another embodiment, the discrete carbon nanotube fibers are made in at least a 30% yield from the initial charge of as-received non-discrete nanotubes with the preferred yield >80%.

[0020] In some embodiments, the fibers are at least partially (> 5 %) surface modified, or coated, with at least one modifier, or at least one surfactant.

[0021] In some embodiments, the fibers are completely (>80%) surface modified, or coated.

[0022] In some embodiments, the fibers are at least partially surface modified or coated wherein the surfactant or modifier is hydrogen bonded, covalently bonded, or ionically bonded to the carbon nanotube fibers.

[0023] In some embodiments, the completely surface modified or coated fibers include wherein said surface modification or coating is substantially uniform.

[0024] In other embodiments, at least partially, or fully surface modified fibers are further mixed or blended with at least one organic or inorganic material to form a material-nanotube fiber composition.

[0025] In another embodiment, the material-nanotube fiber composition includes wherein the fiber surface modifier or surfactant is chemically bonded to the material and/or fiber.

[0026] In another embodiment, the at least partially, or fully surface modified fibers are further mixed or blended with at least one elastomer to form an elastomer nanotube fiber composition.

[0027] In another embodiment, the elastomer nanotube fiber composition includes wherein the fiber surface modifier or surfactant is chemically bonded to the elastomer and/or fiber.

[0028] In another embodiment, the elastomer nanotube fiber composition, particularly materials made from elastomers, commonly called either natural or synthetic rubber or rubber compounds which can include fillers such as carbon or silicon compounds, includes wherein the fiber surface modifier or surfactant is chemically or physically (or both) bonded to the elastomer and/or the isolated fibers and/or any fillers present.

[0029] In another embodiment, the at least partially, or fully surface modified fibers are further mixed or blended with at least one epoxy to form an epoxy nanotube fiber composition.

[0030] In another embodiment, the epoxy nanotube fiber composition includes wherein the fiber surface modifier or surfactant is chemically bonded to the epoxy and/or fiber.

[0031] In an additional embodiment, the elastomer nanotube fiber composition has a fatigue crack failure resistance of at least 2 to about 20 times the fatigue crack failure resistance of the elastomer tested without carbon nanotubes.

[0032] In an another embodiment, the epoxy nanotube fiber composition has a fatigue crack failure resistance of at least 2 to about 20 times the fatigue crack failure resistance of the epoxy tested without carbon nanotubes.

[0033] In another embodiment, the epoxy/nanotube fiber composition has a coefficient of expansion in at least one dimension of at least 2/3 to 1/3 that of the epoxy tested without carbon nanotubes in the same dimension.

[0034] In yet other embodiments the material-nanotube fiber composition exhibits superior adhesion or cohesion to a substrate by at least a factor of two compared to the same material without the nanotube tested similarly.

[0035] In another embodiment the nanotube fibers are further mixed or blended and/or sonicated with at least one elastomer and an inorganic nanoplate to form an elastomer nanotube fiber and nanoplate composition.

[0036] The foregoing has outlined rather broadly various features of the present disclosure in order that the detailed description that follows may be better understood. Additional features and advantages of the disclosure will be described hereinafter, which form the subject of the claims.

[0037] In various embodiments, compositions of fully and high aspect ratio exfoliated carbon nanotubes are disclosed herein. The exfoliated carbon nanotubes are dispersed in the solid state such as, for example, a mat of dispersed carbon nanotubes. The exfoliated carbon nanotubes are maintained in a dispersed state without being dispersed in a continuous matrix such as, for example, a polymer matrix dispersant or a solution.

[0038] In other various embodiments, methods for preparing exfoliated carbon nanotubes are disclosed herein.

[0039] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a first quantity of a nanocrystalline

material, precipitating a first quantity of exfoliated carbon nanotubes from the solution and isolating the first quantity of exfoliated carbon nanotubes.

[0040] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0041] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanorod material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0042] In some embodiments, the methods for preparing exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in a superacid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter.

[0043] In still other various embodiments, energy storage devices containing exfoliated carbon nanotubes are disclosed herein. In some embodiments, the energy storage device is a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes contains exfoliated carbon nanotubes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0044] For a more complete understanding of the present disclosure, and the advantages thereof, reference is now made to the following descriptions to be taken in conjunction with the accompanying drawings describing specific embodiments of the disclosure, wherein:

[0045] FIGURE 1 shows an illustrative arrangement of the basic elements of a Faradaic capacitor;

[0046] FIGURE 2 shows an illustrative arrangement of the basic elements of an electric double layer capacitor;

[0047] FIGURE 3 shows an illustrative arrangement of the basic elements of a battery;

[0048] FIGURE 4 shows an illustrative electron micrograph of hydroxyapatite plates having diameters of 3 – 15 μm;

[0049] FIGURE 5 shows an illustrative electron micrograph of hydroxyapatite nanorods having lengths of 100 – 200 nm;

[0050] FIGURE 6A shows an illustrative electron micrograph of as-received multi-wall carbon nanotubes; FIGURE 6B shows an illustrative electron micrograph of multi-wall carbon nanotubes exfoliated using hydroxyapatite nanorods;

[0051] FIGURE 7A shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes; FIGURE 7B shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes after acid washing;

[0052] FIGURE 8 shows an illustrative electron micrograph of exfoliated multi-wall carbon nanotubes after precipitation and washing;

[0053] FIGURE 9 shows an illustrative electron micrograph of exfoliated carbon nanotubes obtained from 3:1 H_2SO_4:HNO_3;

[0054] FIGURE 10 shows an illustrative electron micrograph of exfoliated double-wall carbon

nanotubes following acid exfoliation and treatment with sodium dodecyl sulfate; and

[0055] FIGURE 11 shows an illustrative electron micrograph of exfoliated carbon nanotubes decorated with copper oxide nanoparticles.

[0056] FIGURE 12 shows a thermogravimetric plot of carbon nanotubes of this invention with oxidation species of various levels;

[0057] FIGURE 13 shows an illustrative fourier transform infra red spectrum of an untreated carbon nanotube and of an oxidized carbon nanotube of this invention in the wavenumber range 2300 to 1300 cm^{-1};

[0058] FIGURE 14. Representative engineering stress strain curves for the unfilled and fiber filled SBR; and

[0059] FIGURE 15. Engineering Stress-engineering strain curves for a polypropylene-ethylene copolymer with 1% wt carbon nanotubes of this invention and without carbon nanotubes.

DETAILED DESCRIPTION

[0060] In the following description, certain details are set forth such as specific quantities, sizes, etc., so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be evident to those of ordinary skill in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

[0061] While most of the terms used herein will be recognizable to those of ordinary skill in the art, it should be understood, however, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of ordinary skill in the art. In cases where the construction of a term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition, 2009. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification or if the incorporation is necessary for maintaining validity.

[0062] Various embodiments presented hereinbelow reference carbon nanotubes. In particular, in various embodiments, bundled or entangled carbon nanotubes can be debundled or unentangled according to the methods described herein to produce exfoliated carbon nanotube solids. The carbon nanotubes being debundled or unentangled can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis (HiPco). The bundled or entangled carbon nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled or entangled carbon nanotubes may be of any length, diameter, or chirality. Carbon nanotubes may be, semi-metallic, semi-conducting or non-metallic based on their chirality and number of walls. In various embodiments, the bundled and/or exfoliated carbon nanotubes may include, for example, single-wall carbon nanotubes (SWNTs), double-wall carbon nanotubes (DWNTs), multi-wall carbon nanotubes (MWNTs), shortened carbon nanotubes, oxidized

carbon nanotubes, functionalized carbon nanotubes, and combinations thereof. One of ordinary skill in the art will recognize that many of the specific embodiments referenced hereinbelow utilizing a particular type of carbon nanotube may practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

[0063] Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof. In some embodiments, the carbon nanotubes may be functionalized before, during and after being exfoliated.

[0064] In various embodiments, a plurality of carbon nanotubes is disclosed comprising single wall, double wall or multiwall carbon nanotube fibers having an aspect ratio of from about 25 to about 500, preferably from about 60 to about 200, and a oxidation level of from about 3 weight % to about 15 weight %, preferably from about 5 weight% to about 10 weight %. The oxidation level is defined as the amount by weight of oxygenated species covalently bound to the carbon nanotube. In FIGURE 12 is an example of a thermogravimetric plot illustrative of the method of determination of the % weight of oxygenated species on the carbon nanotube. The thermogravimetric method involves taking about 5 mg of the dried oxidized carbon nanotube and heating at 5 °C/minute from room temperature to 1000 degrees centigrade in a dry nitrogen atmosphere. The % weight loss from 200 to 600 degrees centigrade is taken as the % weight loss of oxygenated species. The oxygenated species can also be quantified using fourier transform infra-red spectroscopy, FTIR, FIGURE 13 and energy-dispersive X-ray (EDX) analyses.

[0065] Preferably, a neutralized water treatment of the fibers results in a pH of from about 4 to about 9, more preferably from about 6 to about 8. The pH of the matt of oxidized carbon nanotubes can conveniently adjusted using an alkaline solution such as aqueous ammonium hydroxide. A certain residual time is allowed for the acid or alkaline molecules from the internal regions of the carbon nanotube to diffuse out or in. The fibers can have oxidation species comprising of carboxylic acid or derivative carbonyl containing species and are essentially

discrete individual fibers, not entangled as a mass. The derivative carbonyl species can include ketones, quaternary amines, amides, esters, acyl halogens, metal salts and the like.

[0066] As-made carbon nanotubes using metal catalysts such as iron, aluminum or cobalt can retain a significant amount of the catalyst associated or entrapped within the carbon nanotube, as much as 5% by weight. These residual metals can be deleterious in such applications as electronic devices because of enhanced corrosion. In other embodiments, the oxidized fibers comprise a residual metal concentration of less than about 1000 parts per million, ppm, and preferably less than about 100 ppm. The metals can be conveniently determined using EDX.

[0067] In another embodiment, the fibers can be open-ended to allow transport or storage of small molecules such as ethane or propane.

[0068] In yet another embodiment, the matt of fibers has an electrical conductivity of at least 0.1 Siemens/cm and as high as 100 Siemens/cm. A convenient measurement of conductivity is made using a digital ohmmeter with copper strips 1cm apart on a matt of the fibers compressed with hand pressure between two polystyrene discs.

[0069] In another embodiment, the fibers can be mixed with an organic or inorganic material to form a material-carbon nanotube composite. Organic materials can include such as, but not limited to, an elastomer, thermoplastic or thermoset or combinations thereof. Examples of elastomers include, but not limited to, polybutadiene, polyisoprene, polystyrene-butadiene, silicones, polyurethanes, polyolefins and polyether-esters. Examples of thermoplastics include amorphous thermoplastics such as polystyrenics, polyacrylates, and polycarbonates, and semi-crystalline thermoplastics such as polyolefins, polypropylene, polyethylene, polyamides, polyesters, and the like. The exfoliated carbon nanotube fibers of this invention impart significant strength and stiffness to the materials even at low loadings. These new elastomer nanotube filler materials can improve or affect the frictional, adhesive, cohesive, noise and vibration, rolling resistance, tear, wear, fatigue and crack resistance, hysteresis, large strain effects (Mullins effect), small strain effects (Payne effect) and oscillation or frequency properties and swelling resistance to oil of the elastomers and elastomer compounds. This change in

properties will be beneficial for applications such as tires or other fabricated rubber or rubber compounded parts.

[0070] In yet other embodiments, the carbon nanotube fibers have an average diameter of from about 0.6 nanometers to about 30 nanometers, preferably from about 2 nm to about 15 nm and most preferably 6-12 nm. Single wall carbon nanotubes have diameters as low as 0.6nm and the interwall dimension is about 0.34 nm. The fibers have a length of from about 50 nanometers to about 10,000 nanometers, preferably from about 400 nm to about 1,200 nm.

[0071] In other embodiments, a method for preparing carbon nanotube fibers is disclosed of suspending entangled non-discrete multi-wall carbon nanotube fibers in an acidic solution over time , optionally agitating said composition, while sonically treating the suspended nanotube fiber composition to form discrete carbon nanotube fibers and isolating the resultant discrete carbon nanotube fibers from the composition using solid/liquid separation such as filtration or centrifugation prior to further treatment. The acidic solution comprises a mixture of sulfuric acid and nitric acid where the nitric acid is present in a dry basis of from about 10 wt % to about 50 wt %, preferably from about 15 wt % to about 30 wt. %. The method also includes the carbon nanotube fibers being present in a concentration of from greater than zero to less than about 4 weight percent of the suspended nanotube fiber composition with a preference of 1 to 2 %. Above about 2% by weight the carbon nanotubes interact with each other such that the viscosity rises rapidly and stirring and sonication can become non-uniform, which can result in non-uniform oxidation of the fibers.

[0072] In another embodiment, the method for preparing carbon nanotube fibers includes wherein the sonic treatment is performed at an energy input of from about 200 to about 600 Joules/gram of suspended composition, preferably from about 250 to about 350 Joules/gram of suspended composition. If there is a large excess of sonic energy much above about 600 joules/gram of suspended composition this excess energy can lead to the fibers being damaged and too short in length for optimum performance in applications such as material-fiber composites.

[0073] In other various embodiments, the method for preparing carbon nanotube fibers includes wherein the suspended nanotube fiber composition in the acidic solution is controlled at a

specific temperature environment from about 15 to 65°C, preferably from about 25 to about 35°C. Above about 65°C in the acid medium, the rate of oxidation is very rapid and not well-controlled leading to severe degradation of the tube length and great difficulty in filtering the fibers. Below about 15°C the rate of oxidation can be too slow for economic production of the fibers.

[0074] In another embodiment, the method for preparing carbon nanotube fibers comprises a batch, semi-batch or continuous method. The continuous method can involve using temperature controlled sonicator cells in conjunction with circulating pumps with different energy inputs and a centrifuge for filtering and washing of the exfoliated carbon nanotube product.

[0075] In other embodiments, the method for preparing carbon nanotube fibers includes wherein the composition is in contact with the acidic solution from about 1 hour to about 5 hours, preferably from about 2.5 to about 3.5 hours. The choice of the time and temperature interval are given by the degree of oxidation of the exfoliated carbon nanotubes required for the end-use application After isolated resultant discrete carbon nanotube fibers from the acid composition prior to further treatment the mats can contain at least about 10 weight percent water. This method facilitates the subsequent exfoliation in other materials. The discrete carbon nanotube fibers are made in at least a 30% yield from the initial charge of nanotubes as-received with the preferred yield >80%.

EXAMPLE 1

[0076] An illustrative process for producing oxidized carbon nanotubes follows: 3 liters of sulfuric acid, 97% sulfuric acid and 3% water, and 1 liter of concentrated nitric acid containing 70% nitric acid and 30% water, are added into a 10 liter temperature controlled reaction vessel fitted with a sonicator and stirrer. 400 grams of non-discrete carbon nanotubes, grade Flowtube 9000 from CNano corporation, are loaded into the reactor vessel while stirring the acid mixture and the temperature maintained at 25 °C. The sonicator power is set at 130-150 watts and the reaction is continued for 3 hours. After 3 hours the viscous solution is transferred to a filter with a 5 micron filter mesh and much of the acid mixture removed by filtering using a 100psi pressure. The filter cake is washed 1 times with 4 liters of deionized water followed by 1 wash of 4 liters of an ammonium hydroxide solution at pH > 9 and then 2 more washes with 4 liters of

deionized water. The resultant pH of the final wash is > 4.5. A small sample of the filter cake is dried in vacuo at 100 °C for 4 hours and a thermogravimetric analysis taken as described previously. The amount of oxidized species on the fiber is 8% weight.

EXAMPLE 2

[0077] An example of the control of carbon nanotube oxidation for a different carbon nanotube grade, Flowtube 20000 is given in FIGURE 12 which shows the weight loss of Flowtube 20000 at various times in contact with an acid mixture at 25 °C and after being separated from the acid mixture, washed with deionized water and dried.

[0078] In some embodiments, the fibers are at least partially or fully surface modified or coated with at least one modifier or at least one surfactant. The surface modifier or coating or surfactant is hydrogen bonded, covalently bonded, or ionically bonded to the carbon nanotube fibers. Suitable surfactants include, but are not limited, to both ionic and non-ionic surfactants, sodium dodecyl sulfate, sodium dodecylbenezene sulfonate, and PLURONICS. Cationic surfactants are chiefly used for dispersion in non-polar media, such as, for example, chloroform and toluene. Other types of molecules such as, for example, cyclodextrins, polysaccharides, polypeptides, water soluble polymers, DNA, nucleic acids, polynucleotides, and polymers such as polyimides and polyvinyl pyrrolidone, can be used to redisperse the oxidized carbon nanotubes. Furthermore, the surface modification or coating can be substantially uniform.

[0079] In other embodiments, at least partially, or fully surface modified fibers are further mixed or blended and/or sonicated with at least one organic or inorganic material to form a material-nanotube fiber composition. As illustrative examples carbon nanotubes are oxidized to a level of 8% weight, with an average tube diameter of 12 nm and average length 600nm and mixed into various materials. In one example the 1% weight fiber is mixed with commercial styrene-butadiene, SBR, polymer obtained from Goodyear. This is labeled SBR 1% MWNT in Table 1. In another approach, a master-batch, MB, is made of a concentrate of SBR and 10% weight fiber, followed by melt mixing with more SBR to give 1% weight fiber content. This is labeled SBR 1% MWNT MB in FIGURE 14 and in Table 1. A control of SBR without fiber is made under exactly the same thermal history and with the same curing package. The curing package contains zinc oxide, stearic acid, sulfur and t-butyl benzothiazole sulfonamide.

[0080] After curing the films are tested in tension at 25 °C using a tensile tester with an initial strain rate of $1x10^{-2}$ s^{-1} at 25°C. Tensile modulus is the ratio of engineering stress to strain at the beginning of the tensile test. Engineering Stress is the load divided by the initial cross-sectional area of the specimen. Strain is defined as the distance traversed by the crosshead of the instrument divided by the initial distance between the grips.

Table 1. Tensile properties of cured SBR and SBR with MWNT.

Material	Average Modulus (MPa)	Average Strength (MPa)	Average Strain to Break
SBR	1.22	0.64	2.8
SBR+1% MWNT	1.58	0.94	2.4
SBR+1% MWNT MB	1.63	0.97	1.7

[0081] A 30% increase in the values of tensile modulus and 50% increase in the tensile strength are gained using 1% weight of the oxidized carbon nanotubes of this invention. These attributes are important elements that will lead to improved wear.

[0082] Using another elastomer, in this case a semi-crystalline propylene-ethylene copolymer, Versify resins from The Dow Chemical Co, after melt mixing and solidification the elastomer containing 1% weight modified tubes gave an improvement in strength of about 50%, see FIGURE 15.

[0083] In another embodiment, the elastomer nanotube fiber composition, particularly materials made from elastomers commonly called either natural or synthetic rubber or rubber compounds (with the addition of fillers such as carbon or silicon) includes wherein the fiber surface modifier or surfactant is chemically or physically (or both) bonded to the elastomer and/or the isolated fibers or the filler in the compounds.

[0084] In another embodiment, the material-nanotube fiber composition includes wherein the fiber surface modifier or surfactant is chemically bonded to the material and/or fiber. As an example, oleylamine (1-amino-9-octadecene) can be reacted with carbon nanotubes containing carboxylic groups to give the amide. On addition of the amide modified carbon nanotube fiber to a vinyl containing polymer material such as styrene-butadiene followed by addition of

crosslinking agents comprising such as peroxides or sulfur, the vinyl containing polymer can be covalently bonded to the amide functionality of the carbon nanotube.

[0085] In another embodiment, the at least partially, or fully surface modified fibers are further mixed or blended with at least one epoxy to form an epoxy nanotube fiber composition. In this example the oxidized carbon nanotubes are dispersed in a bisphenol F epoxy at high temperature using a sonicator and mechanical mixer. The epoxy is cured at 110 °C for 2 hours using tetraethylene tetraamine. Results of tensile testing are shown in Table 2.

Table 2

Sample	%CNT	Modulus psi	Stress bk	Elong Bk %
Bisphenol F	0	152330	10040	10.7
Bisphenol F + 0.4%wt fiber	0.4	194190	12275	12

[0086] The fatigue properties of the material-carbon fiber composites of this invention also show a fatigue crack failure resistance of at least 2 to about 20 times the fatigue crack failure resistance of the material tested without carbon nanotubes. A usual test procedure for fatigue crack failure resistance is to take a dogbone specimen and introduce a razor notch 1/10 the width of the specimen in the center of the length of the specimen. The specimen is subjected to oscillation with a maximum stress less than the yield stress determined under monotonic loading to break. The number of cycles to break under a given loading history is recorded.

[0087] In another embodiment, the epoxy/nanotube fiber composition has a coefficient of expansion in at least one dimension of at least 2/3 to 1/3 that of the epoxy tested without carbon nanotubes in the same dimension. As an illustrative example follows; ERL 4221, a cycloaliphatic epoxy resin, Dow Chemical Co., is mixed with 1% weight of the oxidized fiber of this invention. It was then mixed and cured with an anhydride ECA 100, Dow Chemical Co., at 180 °C for 2 hours. The plaque gave a through thickness linear thermal coefficient of expansion of 4.5×10^{-5} m/m/°C compared to a control similarly cured, but with no carbon nanotube fiber which gave a value of 8.4×10^{-5} m/m/°C.

[0088] In another embodiment the nanotube fibers are further mixed or blended and/or sonicated with at least one material and an inorganic nanoplate to form a material nanotube fiber and nanoplate composition. The materials can be elastomers, thermoplastics and thermosets. The nanoplates can be, for example, clays, transition metal containing phosphates or graphene structures. The nanoplates have an individual plate thickness less than 20nm. The nanotube fibers of this invention can disperse between the individual nanoplates.

[0089] The oxidized and exfoliated carbon nanotubes of the present disclosure take advantage of physical properties offered by individual carbon nanotubes that are not apparent when the carbon nanotubes are aggregated into bundles. For example, in various embodiments, the oxidized and exfoliated carbon nanotubes may be advantageously used in a wide range of applications including capacitors, batteries, photovoltaics, sensors, membranes, static dissipators, electromagnetic shields, video displays, pharmaceuticals and medical devices, polymer composites, various adhesives, and gas storage vessels. In various embodiments, the oxidized and exfoliated carbon nanotubes may also be used in fabrication and assembly techniques including, for example, ink-jet printing, spraying, coating, melt extruding, thermoforming, blow-molding, film blowing, foaming and injection molding.

ADDITIONAL EXAMPLES

[0090] Various embodiments presented herein below reference carbon nanotubes. In particular, in various embodiments, bundled carbon nanotubes can be debundled according to the methods described herein to produce exfoliated carbon nanotube solids. The carbon nanotubes being debundled can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis (HiPco). The bundled carbon nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting or non-metallic based on their chirality and number of walls. In various embodiments, the bundled and/or exfoliated carbon nanotubes may include, for example, single-wall carbon nanotubes (SWNTs), double-wall carbon nanotubes (DWNTs), multi-wall carbon nanotubes (MWNTs), shortened carbon nanotubes, oxidized carbon nanotubes, functionalized carbon nanotubes, and

combinations thereof. One of ordinary skill in the art will recognize that any of the specific embodiments referenced hereinbelow utilizing a particular type of carbon nanotube may practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

[0091] Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof. In some embodiments, the carbon nanotubes may be functionalized before being exfoliated. In other embodiments, the carbon nanotubes are functionalized after being exfoliated.

[0092] In some embodiments, the carbon nanotubes may be further associated or functionalized with an electroactive material. In some embodiments, an electroactive material may be oxides of transition metals such as, for example, Ru, Ir, W, Mo, Mn, Ni and Co. In some embodiments, the electroactive material may be a conducting polymer such as, for example, polyaniline, polyvinylpyrrole or polyacetylene. In some embodiments, the electroactive material may be a nanoparticle or plurality of nanoparticles bound to the carbon nanotubes. For example, in some embodiments, an electroactive nanoparticle may include materials such as SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof. Carbon nanotubes associated or functionalized with an electroactive material may be particularly advantageous for applications involving electrical conductivity.

[0093] Any of the embodiments herein referencing carbon nanotubes may also be modified within the spirit and scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure. In various embodiments, the nanotubes may include elements such as, for example, carbon, silicon, boron and nitrogen. In further embodiments, the inorganic or mineral nanotubes may also include metallic and non-metallic elements. For example, in some embodiments, the inorganic or mineral nanotubes can be associated with

metals, organic compounds, and inorganic compounds. Association may be on the interior or exterior of the inorganic or mineral nanotubes. Exterior association may be a physical association, such as, for example, van der Waals association. Exterior association of these materials may also include either ionic or covalent bonding to the nanotube exterior.

[0094] In various embodiments, the present disclosure describes compositions containing exfoliated carbon nanotubes. The exfoliated carbon nanotubes are not dispersed in a continuous matrix that maintains the carbon nanotubes in an exfoliated state. Illustrative continuous matrices include, for example, a solution or a polymer matrix that maintains the carbon nanotubes in at least a partially or substantially exfoliated state. In various embodiments, the exfoliated carbon nanotubes comprise a carbon nanotube mat. As such, the exfoliated carbon nanotubes of the present disclosure are distinguished over exfoliated carbon nanotubes presently known in the art, which may re-agglomerate once removed from solution.

[0095] The exfoliated carbon nanotubes of the present disclosure take advantage of physical properties offered by individual carbon nanotubes that are not apparent when the carbon nanotubes are aggregated into bundles. For example, in various embodiments, the exfoliated carbon nanotubes may be advantageously used in a wide range of applications including capacitors, batteries, photovoltaics, sensors, membranes, static dissipators, electromagnetic shields, video displays, pharmaceuticals and medical devices, polymer composites and gas storage vessels. In various embodiments, the exfoliated carbon nanotubes may also be used in fabrication and assembly techniques including, for example, ink-jet printing, spraying, coating, melt extruding, thermoforming, blow-molding and injection molding.

[0096] In various embodiments, the exfoliated carbon nanotubes may be single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes and various combinations thereof. In some embodiments, the carbon nanotubes are full-length carbon nanotubes.

[0097] In some embodiments, the carbon nanotubes are substantially free of catalytic residues, non-nanotube carbon and various combination thereof. In some embodiments, the carbon nanotubes are purified to remove catalytic residues and non-nanotube carbon. Such purification may take place either before or after the exfoliation of the carbon nanotubes takes place.

[0098] In various embodiments, exfoliated carbon nanotubes generally have a diameter of between about 0.7 nm and about 20 nm. Single-wall carbon nanotubes are generally about 0.7 nm to about 10 nm in diameter, whereas multi-wall nanotubes are generally greater than about 10 nm in diameter and up to about 100 nm in diameter in some embodiments. In some embodiments, the exfoliated carbon nanotubes have a diameter between about 1 nm and about 10 nm. In some embodiments, the exfoliated carbon nanotubes have a diameter between about 10 nm and about 100 nm.

[0099] The carbon nanotube length varies between about 500 nm and about 10 mm in some embodiments, between about 500 nm and 1 mm in some embodiments, between about 500 nm and 500 μm in some embodiments, between about 500 nm and 1 μm in some embodiments and various subranges thereof. In some embodiments, the exfoliated carbon nanotubes have an average length that is not substantially different than that of the bundled carbon nanotubes from which they are produced. That is, in some embodiments, the carbon nanotubes are full length carbon nanotubes that are not shortened during exfoliation. In some embodiments, the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes, and the exfoliated carbon nanotubes have a narrower distribution of lengths than do the bundled carbon nanotubes. That is, a subrange of exfoliated carbon nanotube lengths may be obtained from a population of bundled carbon nanotubes having a distribution of lengths.

[00100] The carbon nanotubes have a length to diameter ratio (aspect ratio) of least about 60 in some embodiments and at least about 100 in other embodiments. In some embodiments, the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes, and the exfoliated carbon nanotubes have a narrower distribution of diameters than do the bundled carbon nanotubes. That is, a subrange of exfoliated carbon nanotube diameters may be obtained from a population of bundled carbon nanotubes having a distribution of diameters.

[00101] In various embodiments, the exfoliated carbon nanotubes are further separated by chirality. For example, in the process of exfoliating bundled carbon nanotubes, exfoliated carbon nanotubes of a specific chirality or range of chiral forms may be produced. For example, in some embodiments, the exfoliated carbon nanotubes produced may be metallic, semi-metallic or semiconducting.

[00102] In some embodiments, the exfoliated carbon nanotubes are further functionalized. Functionalization may take place either before or after exfoliation. However, Applicants envision that functionalization after exfoliation may be advantageous to take advantage of the greater surface area available in the exfoliated carbon nanotubes compared to their bundled counterparts. In some embodiments, the exfoliated carbon nanotubes are functionalized to include an electroactive material bound to the carbon nanotubes, as set forth in more detail hereinabove.

[00103] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a first quantity of a nanocrystalline material, precipitating a first quantity of exfoliated carbon nanotubes from the solution and isolating the first quantity of exfoliated carbon nanotubes.

[00104] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[00105] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanorod material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[00106] In some embodiments of the methods, the carbon nanotubes may be further oriented in an alignment step after isolating the exfoliated carbon nanotubes. In some embodiments, the exfoliated carbon nanotubes may be shaped into a form such as, for example, a mat, film, fiber, cloth, non-woven fabric or felt.

[00107] An illustrative process for exfoliating carbon nanotubes follows. Carbon nanotubes can be effectively exfoliated using nanoplate of zirconium phosphate treated with a surfactant such as t-butylammonium hydroxide. The carbon nanotubes and the nanoplates are sonicated for short times to obtain full exfoliation of the carbon nanotubes in aqueous media. By controlling the ionic strength of the mixture after sonication, exfoliated carbon nanotubes can be obtained by simple separation techniques such as, for example, centrifugation. The carbon nanotubes after centrifuging and separating exist in a disordered but non-aggregated state and

can easily be resuspended with other surfactant addition. Suitable surfactants for resuspension include, for example, both ionic and non-ionic surfactants, such as, for example, polyvinyl pyrrolidone, sodium dodecyl sulfate and PLURONICS. Cationic surfactants may be used for dispersion in non-polar media, such as chloroform and toluene. Application of an electric potential to the suspension may be used alternatively to or in combination with adjusting the ionic strength.

[00108] Although the above process may be used to cleanly separate single-wall carbon nanotubes, multi-wall carbon nanotubes and particularly oxidized multi-wall carbon nanotubes may not be separated as cleanly due to their broader range of ionic potentials. As a result, it is difficult to achieve separation of zirconium phosphate from the exfoliated carbon nanotubes when multi-wall carbon nanotubes are used. Furthermore, zirconium phosphate is particularly difficult to dissolve in acids (solubility = 0.12 mg/L in 6 M HCl), and it cannot typically be removed by simple acid washing even after isolating the exfoliated carbon nanotubes.

[00109] In various embodiments, the methods for preparing exfoliated carbon nanotubes further include utilizing a solution that contains both a surfactant and a quantity of a nanocrystalline material. Surfactants are well known in the carbon nanotube art to aid in solubilization. Without being bound by theory or mechanism, Applicants believe that when a surfactant is used in preparing exfoliated carbon nanotubes, the surfactant may aid in the initial solubilization or suspension of the carbon nanotubes. Precipitation of exfoliated carbon nanotubes takes place thereafter. In various embodiments of the present disclosure, the surfactant may include, for example, sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, or tetralkylammonium hydroxide. In some embodiments, the surfactant may also modify the surface of the nanocrystalline material used for exfoliating the carbon nanotubes.

[00110] In general, exfoliated carbon nanotubes are prepared according to embodiments of the present disclosure by precipitating exfoliated carbon nanotubes from a solution containing a nanocrystalline material. In some embodiments, the ionic strength of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, the electrical potential of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In

some embodiments, the pH of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes.

[00111] In some embodiments, the methods for exfoliating carbon nanotubes include adding a release species to the carbon nanotube suspension to adjust the ionic strength and precipitate exfoliated carbon nanotubes. In some embodiments, the ionic strength can be adjusted with an ionic species such as, for example, a solution of KCl. Although one of ordinary skill in the art will recognize the benefits of using an ionic species for adjustment of ionic strength, non-ionic species such as organic compounds may be used for ionic strength adjustment as well. In some embodiments, an electromagnetic field can be applied to the suspension of exfoliated carbon nanotubes in lieu of or in combination with adjustment of the ionic strength with a release species to induce precipitation of the exfoliated carbon nanotubes. Release species may be organic or inorganic compounds.

[00112] After precipitation, exfoliated carbon nanotubes can be isolated by simple separation techniques such as, for example, centrifuging, filtering or settling. The separated, exfoliated carbon nanotubes exist in a disordered but non-aggregated state and can be easily redispersed in various media such as, for example, a liquid or polymer melt. In some embodiments, the redispersion may be aided by addition of a surfactant. Suitable surfactants include, but are not limited, to both ionic and non-ionic surfactants, sodium dodecyl sulfate, sodium dodecylbenezene sulfonate, and PLURONICS. Cationic surfactants are chiefly used for dispersion in non-polar media, such as, for example, chloroform and toluene. As noted above, other types of molecules such as, for example, cyclodextrins, polysaccharides, polypeptides, water soluble polymers, DNA, nucleic acids, polynucleotides, and polymers such as polyimides and polyvinyl pyrrolidone, can be used to redisperse the exfoliated carbon nanotubes in some embodiments.

[00113] In some embodiments, a second quantity of exfoliated carbon nanotubes may be precipitated from the suspension of carbon nanotubes. For example, in an embodiment, adding a second quantity of nanocrystalline material to the suspension results in precipitation of a second quantity of exfoliated carbon nanotubes. In some embodiments, the first quantity of carbon nanotubes and the second quantity of carbon nanotubes have different properties from one

another such as, for example, different average lengths, diameters or chiralities. Repeated precipitation of carbon nanotube fractions may be repeated as many times as desired.

[00114] In some embodiments, the methods further include removing residual nanocrystalline material from the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes remain exfoliated after removing the nanocrystalline material. Hence, once the carbon nanotubes become fully exfoliated, they are no longer prone to becoming bundled. In some embodiments, the nanocrystalline material may be removed by washing the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be washed with an acid to remove the nanocrystalline material.

[00115] The redispersability of the carbon nanotubes after removal of the nanocrystalline material may be controlled by changing the surfactant concentration and the rate of addition of the release species. Hence, the redispersibility may be controlled by changing the rate of precipitation of exfoliated carbon nanotubes. In other words, in some embodiments the kinetic rate of carbon nanotube precipitation influences the rate of their redissolution following removal of the nanocrystalline material.

[00116] In various embodiments of the present disclosure, carbon nanotubes are exfoliated from bundles of carbon nanotubes using a nanocrystalline material having a crystalline form such as, for example, nanorods, nanoplates, or nanowhiskers, to intersperse between individual carbon nanotubes with addition of energy such as sonification. Nanorods include any inorganic or organic compound that may be induced to crystallize in a rod-like crystalline form. Nanowhiskers include any inorganic or organic compound that may be induced to crystallize in a whisker-like crystalline form. In various embodiments, the nanocrystalline material may include, for example, clays, graphite, inorganic crystalline materials, organic crystalline materials and various combinations thereof.

[00117] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes with subsequent treatment.

[00118] In various embodiments, the nanocrystalline material may be, for example, hydroxyapatite and hydroxyapatite derivatives. Hydroxyapaptite derivatives include, for example, fluorapatite. In some embodiments, the hydroxyapatite has a crystalline form such as, for example, nanorods, nanoplates and nanowhiskers. In some embodiments, the methods further include removing the hydroxyapatite from the exfoliated carbon nanotubes. In some embodiments, removing can be accomplished, for example, through washing the exfoliated carbon nanotubes with an acid after their being isolated.

[00119] Various sizes of the nanocrystalline material may be used to exfoliate the carbon nanotubes. In some embodiments, the nanocrystalline material may be equal to or larger in size than the longest carbon nanotube present in the sample before exfoliation. In such embodiments, the exfoliated carbon nanotubes can be obtained in discrete fractions following addition of a release species such as, for example, KCl. In other embodiments, the nanocrystalline material has a size that is equal to or less than the longest carbon nanotube present in the sample before exfoliation. In this case, carbon nanotubes equal to or less than the size of the nanocrystalline material may be separated from the carbon nanotube suspension. In various embodiments, larger or smaller sizes of nanocrystalline material can be added to the carbon nanotube suspension to exfoliate carbon nanotube fractions having various carbon nanotube sizes.

[00120] In various embodiments, the exfoliated carbon nanotubes are further purified to remove impurities such as, for example, residual metal catalyst and non-nanotube carbon residue. With exfoliated carbon nanotubes, further purification is more easily conducted than like purifications conducted on bundled carbon nanotubes due to the comparatively greater surface area present in the exfoliated carbon nanotubes. Purification techniques include conventional techniques such as, for example, oxidation at elevated temperature (e.g., about 200°C to about 400°C) or acid extraction to remove metallic impurities. Illustrative acids that may be used to extract metallic impurities from the exfoliated carbon nanotubes include, for example, various concentrations of hydrochloric, hydrobromic, nitric, chlorosulfonic and phosphoric acids and various combinations thereof. In general, the acid and impurities are removed from the exfoliated carbon nanotubes by rinsing with water, organic solvents or combinations thereof. In some embodiments, supercritical fluids such as, for example, highly

compressed CO_2 or hydrocarbons such as, for example, propane or butane, may also be employed to remove impurities from the exfoliated carbon nanotubes.

[00121] In various embodiments, the methods for producing exfoliated carbon nanotubes further include derivatization of the exfoliated carbon nanotubes with at least one functional group. Derivatization may occur either before or after exfoliation has occurred. Numerous methods to derivatize carbon nanotubes are known to those of ordinary skill in the art. For example, diazonium chemistry can be utilized to introduce alkyl or aryl groups, either of which may bear further functionalization, on to the carbon nanotubes. In additional embodiments, treating nanotubes with lithium in liquid ammonia, followed by reaction with an alkyl halide may be used to alkylate carbon nanotubes. Reaction of fluorinated carbon nanotubes with ammonia or amines in the presence of a catalyst such as, for example, pyridine, may be used to functionalize the nanotubes through amine-bearing functionalities. Likewise, fluorinated carbon nanotubes may be functionalized with hydroxyl-containing moieties, which may be functionalized to bear an ether linkage OR, wherein R may be any combination of alkyl, aryl, acyl, and arylacyl groups. Furthermore, R may be further functionalized, for example, with halogens, thiols, amino groups and other common organic functionalities. In addition, the carbon nanotubes may be directly functionalized with thiols, alkyl substituted thiols, aryl substituted thiols, and halogens.

[00122] In some embodiments, the first quantity or second quantity of exfoliated carbon nanotubes are selectively precipitated by a physical property such as, for example, chirality, diameter or length. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanoplates and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanorods and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanowhiskers and then further separated by chirality, nanotube length, or nanotube diameter. Regardless of how the exfoliated carbon nanotubes are prepared, separation by chirality, length or diameter may be more facile after the carbon nanotubes are isolated.

[00123] In some embodiments, a direct separation of carbon nanotubes by chirality, length or diameter may be accomplished by choice of the nanocrystalline material in combination with additional agents. For example, using a nanocrystalline material either alone or in combination with chiral surfactants and/or polymers may allow exfoliated carbon nanotubes to be separated based on length, diameter, chirality, type, and functionality such as, for example, oxidation state and/or defect structure.

[00124] In some embodiments, the suspension of carbon nanotubes further includes a chiral agent, resulting in selective precipitation of exfoliated carbon nanotubes by chirality. Chiral agents include, for example, surfactants, polymers and combinations thereof. Chiral agents include molecules such as, for example, R,R-tartaric acid, which have been useful for separation of enantiomeric drugs in electrokinetic chromatography, and enantiomers of polylactic acid. In some embodiments, the chiral agents may be used to separate exfoliated carbon nanotubes of a single chirality or a limited number of chiral configurations from a mixture of carbon nanotubes containing a range of carbon nanotube chiralities. In some embodiments, the chiral agent may be a surfactant that both helps disperse the carbon nanotubes and facilitates the chiral separation. The chiral agent may be associated with or chemically bound to the carbon nanotube surface. In some embodiments, carbon nanotubes separated by chirality also are separated by electronic type (i.e., metallic, semi-metallic and semiconducting).

[00125] By using polymers and/or surfactants having a defined chirality, separated populations of exfoliated metallic, semi-metallic, or semi-conducting carbon nanotubes can be obtained. Without being bound by mechanism or theory, Applicants believe that polymers and/or surfactants of defined chirality preferentially wrap a carbon nanotube of a complementary chirality type. By selective carbon nanotube precipitation as described hereinabove, carbon nanotubes may be separated by chirality. Selective carbon nanotube precipitation may occur either in the presence or absence of a nanocrystalline material. Separation techniques such as, for example, solvent/non-solvent addition, co-surfactant addition, and differential temperature gradients may be used to selectively precipitate a chiral population of carbon nanotubes. In various embodiments, the chiral polymers and/or surfactants may be mixtures of tactic molecules. By using tactic polymers with a low thermal degradation temperature such as, for example, polypropylene carbonate, the isolated, exfoliated carbon nanotubes can be easily

recovered by thermal degradation of the polymer. For example, polypropylene carbonate can be thermally degraded at less than about 300°C without damaging carbon nanotubes. In further embodiments, the tactic molecules may be a mixture dissolved in a hydrocarbon solvent such as, for example, toluene or decalin. Illustrative tactic polymers include, for example, atactic polystyrene, iostactic polystyrene, syndiotactic polystyrene, d and l polylactic acid, d and l polypropylene carbonate and the like. Further, the carbon nanotubes in polymers can be oriented to be aligned by various methods known to those of ordinary skill in the art.

[00126] The technique of separating carbon nanotubes by chirality by using a chiral polymer may be further extended to a chromatography column for continuous separation. For example, carbon nanotubes wrapped in a chiral polymer may be applied to a chromatography column and then be separated by chirality. Alternatively, a suspension of exfoliated carbon nanotubes lacking a chiral agent may be applied to a chromatography column having a chiral stationary phase. In the alternative embodiments, separation by chirality is on a selective interaction of the chiral stationary phase with the various carbon nanotube chiralities.

[00127] In still further embodiments, exfoliated carbon nanotubes either with or without a wrapping chiral polymers and/or surfactants may be separated by electronic type by applying an electric potential to a solution of exfoliated carbon nanotubes. For example, exfoliated metallic carbon nanotubes will migrate toward the potential for collection and separation.

[00128] In some embodiments of the present disclosure, alternative methods for producing exfoliated carbon nanotubes not utilizing a nanocrystalline material are disclosed. In some embodiments, the methods for producing exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in a superacid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, the superacid is chlorosulfonic acid or a nitrating system.

[00129] Filtration of a superacid solution of exfoliated carbon nanotubes produces a mat of exfoliated carbon nanotubes on the filter. The mat of exfoliated carbon nanotubes may be further modified on the filter in some embodiments of the present disclosure. For example, the mat of exfoliated carbon nanotubes may be functionalized while on the filter or treated with a surfactant to maintain the carbon nanotubes in an exfoliated state. In addition, the exfoliated

carbon nanotubes may be processed according to any of the methods described hereinabove for further processing of exfoliated carbon nanotubes.

[00130] The exfoliated carbon nanotubes prepared by the techniques described hereinabove are typically longer than are carbon nanotubes exfoliated using existing technology. For instance, as described previously, other separation techniques result in carbon nanotube damage and shortened carbon nanotube lengths. In certain applications, particularly those involving electrical conduction or mechanical reinforcement, shorter carbon nanotubes may not provide adequate electrical conductivity or structural reinforcement. For example, by having at least a portion of longer carbon nanotubes present with electrical devices such as energy storage device, a higher degree of connectivity at a carbon nanotube volume fraction can be obtained. Furthermore, longer carbon nanotube lengths may increase the toughness of the polymer composites over those made with shorter carbon nanotubes.

[00131] The present disclosure also relates to improved energy storage devices and particularly to ultracapacitors and batteries having components containing exfoliated carbon nanotubes. The improved energy storage devices include components such as, for example, current collectors, electrodes, insulators, electrolytes and separators containing exfoliated carbon nanotubes. The improved energy storage devices have a high energy density and power density and better discharge and charge capabilities. The improved energy storage devices have at least one of at least two electrodes containing exfoliated carbon nanotubes. The improved energy storage devices also include a dielectric medium or electrolyte, each optionally including carbon nanotubes.

[00132] FIGURE 1 shows an illustrative arrangement of the basic elements of a Faradaic capacitor. As shown in FIGURE 1, current collectors **1** and **5** contact with electrodes **2** and **4**, which are separated by electrode **3**. In an embodiment of the present disclosure, at least one of the electrodes **2** and **4** contains exfoliated carbon nanotubes. In various embodiments, current collectors **1** and **5** can be metals such as, for example, copper and other highly conductive metals. In some embodiments, the current collectors can contain conductive exfoliated carbon nanotubes. For example, in an embodiment, the carbon nanotubes may be full length exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic

carbon nanotubes. In various embodiments, at least one of electrodes **2** and **4** contains exfoliated carbon nanotubes.

[00133] FIGURE 2 shows an illustrative arrangement of the basic elements of an electric double layer capacitor. As shown in FIGURE 2, current collectors **11** and **17** contact electrodes **12** and **16**, and electrolytes **13** and **15** contact electrodes **12** and **16**. Non-conducting separator **14** separates electrolytes **13** and **15** and is permeable to ions flowing between the electrodes **12** and **16**. In some embodiments, current collectors **11** and **17** can be metals such as, for example, copper and like conductive metals. In some embodiments, current collectors **11** and **17** contain exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic carbon nanotubes. At least one of electrodes **12** and **16** contains exfoliated carbon nanotubes. Electrolytes **12** and **16** may be fully intermixed with the electrodes **2** and **6**, or they may contact along a surface such as, for example, a plane. In various embodiments, non-conducting separator **4** may contain non-conducting carbon nanotubes. In various embodiments, the separator **4** may be made from porous polyethylene or fiberglass mats. In various embodiments, electrolytes **13** and **15** can contain exfoliated carbon nanotubes, which may be exfoliated conductive carbon nanotubes in some embodiments. conductive nanotubes in various embodiments.

[00134] FIGURE 3 shows an illustrative arrangement of the basic elements of a battery. As shown in FIGURE 3, electrodes **21** and **23** contact electrolyte **22**. The electrolyte **22** conveys ions between electrodes **21** and **23**. In an embodiment, the ions are metal ions such as, for example, lithium ions. Hence, the present disclosure describes a lithium battery containing exfoliated carbon nanotubes. In some embodiments, at least one of the electrodes contains exfoliated carbon nanotubes. In some embodiments, the electrolyte contains exfoliated carbon nanotubes.

[00135] In various embodiments of the present disclosure, the energy storage device containing exfoliated carbon nanotubes is a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes contains exfoliated carbon nanotubes.

[00136] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are multi-wall carbon nanotubes. In some embodiments, the at least one electrode containing exfoliated carbon nanotubes is the anode.

[00137] In various embodiments of the energy storage devices, the electrode may contain exfoliated carbon nanotubes dispersed in a polymer or viscous liquid. After forming the electrode, in various embodiments, the may be laminated to another medium such as, for example, a dielectric or electrolyte.

[00138] In various embodiments, the electrolyte of the energy storage devices can be a solid or a fluid. Electrolytes are generally chosen to minimize internal electrical resistance. Aqueous electrolytes such as potassium hydroxide or sulfuric acid are generally employed in conventional batteries and capacitors. Due to water's low electrochemical decomposition potential of 1.24 volts, the energy density is limited with these types of electrolytes. Organic electrolytes such as, for example, organic carbonates and tetraalkylammonium salts provide good solubility and reasonable conductivity. In general, organic electrolytes have lower conductivity than aqueous electrolytes, but they can operate at higher voltages, for example, up to about 5 volts. Other electrolytes can be of a polymer-gel type such as, for example, polyurethane–lithium perchlorate, polyvinyl alcohol-KOH-H_2O and the related systems. Organnic electrolytes such as, for example tetraethylammonium tetrafluoroborate and tetrabutylammonium tetrafluoroborate, can simultaneously serve as an electrolyte and surfactant for dispersing and exfoliating carbon nanotubes in embodiments where carbon nanotubes are contained in the electrolyte. Electrolyte salts may also be used for dispersing the carbon nanotubes or maintaining exfoliated carbon nanotubes in an exfoliated state.

[00139] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are modified with an electroactive material. In some embodiments, the electroactive material is a transition metal or transition metal oxide. Electroactive transition metals include, for example, Ru, Ir, W, Mo, Mn, Ni, and Co. In some embodiments, the electroactive material may be a conducting polymers such as, for example, polyaniline, polyacetylene and polyvinylpyrrole. In some embodiments, the electroactive material is a nanomaterial bound to

the exfoliated carbon nanotubes. In some embodiments, the nanomaterial may be, for example, SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof.

[00140] In other various embodiments, the present disclosure describes layered structures containing exfoliated carbon nanotubes suitable for use in energy storage devices. For example, co-extrusion of liquids or melts containing exfoliated carbon nanotubes through multilayer dies or multilayer generators may be used in making the energy storage devices of the present disclosure. The resultant layered structures can be stacked and connected in series to give higher voltages in energy storage devices. In other embodiments, the components of the energy storage devices may be processed from a solution of exfoliated carbon nanotubes by solvent casting, spraying, paste spreading, compression stretching, or combinations thereof.

[00141] In some embodiments, the present disclosure also relates to an ion diffusion separator of electrical double-wall capacitors. In various embodiments, the separator contains non-metallic single-wall carbon nanotubes. In some embodiments, insulators of the energy storage devices contain non-metallic single-wall carbon nanotubes. In some embodiments, when the insulator contains carbon nanotubes, the dielectric constant of the insulator/carbon nanotube mixture is greater than that of the insulator alone.

[00142] In various embodiments, exfoliated carbon nanotubes can be aligned in forming electrodes for use in the energy storage devices. In some embodiments, the alignment may occur through melt extrusion.

[00143] In some embodiments, incorporation of exfoliated carbon nanotubes to electrodes, electrolytes or dielectrics of the present energy storage devices provides enhanced strength and ruggedness to the device. These features allow further shaping of the device for functioning under demanding environments, such as high vibration or extreme thermal cycling environments.

Experimental Examples

[00144] The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments

of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

[00145] Example A: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates and t-Butylammonium Hydroxide Surfactant. A dispersed solution of carbon nanotubes was prepared from 10 mg of multi-wall carbon nanotubes placed in 2 mL of a solution of $Zr(HPO_4)_2 \cdot H_2O$ nanoplates and t-butylammonium hydroxide (5 wt% $Zr(HPO_4)_2 \cdot H_2O$; 1:0.8 ratio of $Zr(HPO_4)_2 \cdot H_2O$:t-butylammonium hydroxide). The solution was subsequently diluted to 30 mL and then sonicated for 2 hours. The solution was stable for at least 24 hours. An aliquot of 0.01 M KCl was added, resulting in precipitation of a quantity of exfoliated multi-wall carbon nanotubes. The precipitated fraction was removed by centrifugation. The quantity of isolated nanotubes was approximately 1/10 the mass of carbon nanotubes originally suspended. The filtrate was treated with another aliquot of 0.01 M KCl, resulting in a second precipitation of multi-wall carbon nanotubes. The precipitation/centrifugation process was repeated until substantially all nanotubes had been precipitated from the suspension.

[00146] Example B: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates of Varying Sizes. The experimental procedure described in Example A hereinabove was repeated, except the nanoplate size was about 1/10 the length of the longest carbon nanotube present in the sample. After removal of the first precipitation fraction following addition of 0.01 M KCl, a second quantity of nanoplates of a different size was added. The second quantity of nanoplates fractionated a second quantity of nanotubes following addition of 0.01 M KCl. The second precipitation fraction of nanotubes had a different length distribution than did the first precipitation fraction. The precipitation/centrifugation process was repeated with progressively larger nanoplates until substantially all nanotubes had been precipitated from the suspension.

[00147] Example C: Synthesis of Hydroxyapatite Plates. Hydroxyapatite nanoplates of controlled sizes were synthesized by dissolving 10 g of hydroxyapatite (Sigma Aldridge reagent grade) in 400 mL of dilute nitric acid (pH = 2) at room temperature, followed by very slow dropwise addition of 48 mL of 1% v/v ammonium hydroxide. Crystals collected at pH = 4

and pH = 5 were found by microscopy to be plates having an aspect ratio about 7 to 8 and a diameter ranging between 3 – 15 μm. FIGURE 4 shows an illustrative electron micrograph of hydroxyapatite plates of 3 – 15 μm diameter. Increasing the addition rate of the 1% v/v ammonium hydroxide reduced the average HAp plate size.

[00148] **Example D: Synthesis of Hydroxyapatite Nanorods.** 2 g of hydroxyapatite was first dissolved in 40 mL of dilute nitric acid (pH = 2) containing a 3:1 ethanol:water ratio. The mixture was then quenched into 80 mL of 5 vol% ammonium hydroxide, also in a 3:1 ethanol:water ratio. The resultant pH was 8.5. A milky, jelly-like precipitate resulted. The resulting mixture containing the precipitate was then heated at between 70°C and 80°C on a magnetic stirrer hotplate for 24 hours. Thereafter, hydroxyapatite crystals were filtered, washed with deionized water and dried. Electron microscopy showed that hydroxyapatite nanorods having an aspect ratio of about 25 and lengths between 100 – 200 nm were formed. FIGURE 5 shows an electron micrograph of hydroxyapatite nanorods having 100 – 200 nm lengths.

[00149] **Example E: Exfoliation of Carbon Nanotubes Using Hydroxyapatite.** 0.5142 g hydroxyapatite nanorods were added to 50 mL water and 0.8280 g t-butylammonium hydroxide (Sigma Aldrich reagent grade; TBAH; 1:1 molar ratio of hydroxyapatite:TBAH). The resultant mixture was sonicated for one hour at 25°C then diluted with deionized water to give a 0.2 wt% solution based on hydroxyapatite content. Multi-wall carbon nanotubes (CNano Ltd;) were received as a powder that contained highly entangled bundles having a grain size of 1 – 10 μm in diameter. The lengths of the individual multi-wall carbon nanotubes were found to be in excess of 1 μm, and the diameters were found to be 10 – 20 nm.

[00150] 1 g of multi-wall carbon nanotubes was added to 50 mL of a mixture of concentrated sulfuric and nitric acid in a 3:1 volume ratio. The mixture was placed in a sonicator bath (Branson sonicator, model 250) and oxidized for two hours while sonicating at temperature of 25 – 35°C. The mixture was then filtered using a polyvinylidene fluoride microporous filter (5 μm pore size), followed by washing of the resultant solid with deionized water until the pH of the filtrate was 4.5. The oxidized multi-wall carbon nanotubes were then dried in vacuo for 2 hours at 80°C.

[00151] Samples were prepared by adding the dried multi-wall carbon nanotubes to the hydroxyapatite/TBAH solution prepared above to give carbon nanotube:hydroxyapatite weight ratios of 1:1, 1:2, 1:3, 1:4 and 1:5. The mixture was sonicated at room temperature for 2 hours and then left for 24 hours. At weight ratio of 1:1, a portion of the multi-wall carbon nanotubes settled out as agglomerated particles. At a 1:2 weight ratio the solution had a few multi-wall carbon nanotube particles present after 24 hours. All higher weight ratios examined gave stable dispersions for at least 24 hrs. A control experiment at a weight ratio of 1:3 multi-wall carbon nanotubes:TBAH with no hydroxyapatite present showed mostly aggregated carbon nanotubes settling after 24 hours. FIGURE 6A shows an electron micrograph of as-received multi-wall carbon nanotubes, and FIGURE 6B shows multi-wall carbon nanotubes exfoliated using hydroxyapatite nanorods.

[00152] The precipitated exfoliated multi-wall carbon nanotubes contained residual hydroxyapaptite as evidenced by energy-dispersive X-ray spectroscopy. FIGURE 7A shows an EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes. As shown in the EDX spectrum, strong Ca and P signals indicated the presence of hydroxyapatite. The precipitated multi-wall carbon nanotubes were subsequently washed with 50 mL of 1 N nitric acid, followed by 250 mL of deionized water, which removed substantially all the hydroxyapatite as evidenced by EDX. FIGURE 7B shows an EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes after acid washing. In contrast, the exfoliated multi-wall carbon nanotubes of Example 1 contained residual $Zr(HPO_4)_2 \cdot H_2O$, which could not be removed by washing with acids such as nitric, hydrochloric or sulfuric acids.

[00153] Unentangled multi-wall carbon nanotubes were obtained after exfoliation, precipitation and washing. FIGURE 8 shows an electron micrograph of the exfoliated multi-wall carbon nanotubes after precipitation and washing. Exfoliation of the multi-wall carbon nanotubes could be conducted equivalently using hydroxyapatite plates.

[00154] **Example F: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions.** 40 mg of multi-wall carbon nanotubes were added to 40 mL of a 3:1 sulfuric:nitric acid mixture and sonicated for 60 minutes at 25 °C. A drop of the mixture was placed on a PVDF filter and allowed to dry. FIGURE 9 shows an electron micrograph of exfoliated carbon

nanotubes obtained from 3:1 H_2SO_4:HNO_3. As shown in FIGURE 9, exfoliation was maintained after removal of the acid by drying.

[00155] Example G: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions, Followed by Surfactant Addition. A 1% by weight double-wall carbon nanotube solution in 3:1 sulfuric:nitric acid was oxidized for 2 hours as described previously. After filtering the concentrated acid solution to immobilize the double wall carbon nanotubes, the immobilized carbon nanotubes were washed with deionized water until the washings were pH = 4.5. While still wet, the PVDF filter paper and the double-wall carbon nanotubes were sonicated for 30 minutes with a 0.2 % by weight sodium dodecyl sulfate (SDS) solution in deionized water such that the weight of double-wall carbon nanotubes to SDS was 1:3. The mixture was stable for at least 24 hours. A drop of the mixture was placed on a carbon tape and dried for examination by electron microscopy, which showed exfoliated carbon nanotubes. FIGURE 10 shows an electron micrograph of exfoliated double-wall carbon nanotubes following acid exfoliation and treatment with sodium dodecyl sulfate.

[00156] Example H: Epoxy Composite Containing Exfoliated Carbon Nanotubes. 5 mg of oxidized multi-wall carbon nanotubes were placed in 10 mL of tetraethylenetetramine (TETA), and various additions of sodium dodecylsulfate (SDS) were added such that the weight ratio of multi-wall carbon nanotubes to SDS was 5, 2.5, 1, and 0.33 to 1. The mixture was sonicated at 30 °C for 30 minutes and allowed to stand. After 7 days the 1:1 and 1:0.33 ratio was seen to be stable toward precipitation.

[00157] 49 g of Bisphenol F epoxy was admixed with 0.242 g of oxidized multi-wall carbon nanotubes and sonicated for 10 minutes at 60 °C. The mixture was cooled to 25°C and then degassed for 10 minutes at 25 inches Hg. 7 g of TETA containing 0.5% wt oxidized multi-wall carbon nanotubes and 0.5% wt. SDS was sonicated and degassed separately as above. The two degassed mixtures were then carefully mixed and poured into a mold. The mold was cured for 2 hours at 100 °C. Controls were prepared as above without carbon nanotubes (control 1) and with as-received multi-wall carbon nanotubes (control 2).

[00158] Table 3 shows the mechanical strength improvement in the epoxy composite containing exfoliated multi-wall carbon nanotubes. Kq is a the maximum stress before failure on

tensile testing a notched specimen at 0.01.min initial strain rate. Relative fatigue lifetime improvement is the lifetime of the notched specimen counted as the number of cycles to failure at 1 Hz, at about 16.7 MPa maximum tensile stress with stress amplitude of 0.1 (stress minimum/stress maximum.)

Table 3: Mechanical Properties of Carbon Nanotube Composites

Material	Relative Kq improvement	Relative fatigue lifetime improvement
Control 1	1	1
Control 2	1.2	1.1
Example 1	1.5	4.7

[00159] Example I: Capacitor Containing Exfoliated Multi-Wall Carbon Nanotubes. Control 1: 10 g of poly(ethylene oxide) (PEO; 1500 molecular weight) was melted, and 1 mL of 4 N potassium hydroxide added to make the electrolyte. 1 wt % of as-received multi-wall carbon nanotubes were added to the electrolyte mixture and sonicated for 15 minutes in a sonicator bath. Approximately 2.1 g of the mixture was poured into one part of a polystyrene petri dish 6 cm in diameter with a strip of copper adhered as the current collector. A piece of clean writing paper was then placed on the molten liquid electrolyte, and 2 g of the electrolyte was poured on to the paper, taking care not to weep at the edges. The other side of the petri dish with a copper strip adhered was then inserted to make a capacitor. After cooling to room temperature for 15 minutes the capacitance was measured using an HP 4282A capacitance meter. The measured capacitance was 0.0645 microfarads. Control 2: Control 2 was prepared as for control 1, except as-received graphene (Rice University) was substituted for the multi-wall carbon nanotubes. The measured capacitance was 0.176 microfarads. Exfoliated carbon nanotube capacitor: The capacitor was prepared as for control 1, except oxidized multi-wall carbon nanotubes were used in place of as-received multi-wall carbon nanotubes. The measured capacitance was 0.904 microfarads, a 14-fold improvement over control 1 and a 5.1-fold improvement over control 2.

Example J: Exfoliated Carbon Nanotubes Decorated with Copper Nanoparticles. 102 mg of oxidized multi-wall carbon nanotubes were added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture was sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37%

solution) and 500 mg of sodium hydroxide were added to bring the pH to 12.2. The mixture was stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. FIGURE 11 shows an electron micrograph of exfoliated carbon nanotubes decorated with copper oxide nanoparticles obtained from the mixture.

[00160] From the foregoing description, one of ordinary skill in the art can easily ascertain the essential characteristics of this disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt the disclosure to various usages and conditions. The embodiments described hereinabove are meant to be illustrative only and should not be taken as limiting of the scope of the disclosure, which is defined in the following claims.

CLAIMS

We claim:

1. A plurality of carbon nanotubes comprising carbon nanotube fibers having an aspect ratio of from about 25 to about 500, and a oxidation level of from about 3 weight % to about 15 weight %.

2. The fibers of claim 1 wherein a neutralized water treatment of the fibers results in a pH of from about 3 to about 9, preferably from about 4 to about 8.

3. The fibers of claim 1 wherein the oxidation species comprises carboxylic acid or derivative carboxylate groups.

4. The fibers of claim 1 wherein the fibers are discrete individual fibers, not entangled as a mass.

5. A plurality of carbon nanotubes comprising discrete carbon nanotube fibers having an aspect ratio of from about 25 to about 250 and a oxidation level of from about 3 wt % to about 15 wt %, wherein the fibers are mixed, blended, sonicated, or a combination step thereof, with at least one epoxy resin to form an epoxy/nanotube composite.

6. A plurality of carbon nanotubes comprising discrete carbon nanotube fibers having an aspect ratio of from about 25 to about 250 and a oxidation level of from about 3 wt % to about 15 wt %, wherein the fibers are mixed, blended, sonicated, or a combination step thereof, with at least one rubber compound to form a rubber/nanotube composite.

7. The fibers of claim 1 comprising a residual metal concentration of less than about 1000 ppm.

8. The fibers of claim 1 comprising a residual metal concentration of less than about 100 ppm.

9. The fibers of claim 1 comprising open ended carbon nanotube fibers.

10. The fibers of claim 1, wherein a mat of said fibers are electrically conductive.

11. The fibers of claim 10, wherein said mat has an electrical conductivity of at least 0.1 Siemens/cm and as high as about 100 Siemens/cm.

12. The fibers of claim 1, wherein said fibers have an average diameter of from about 0.6 nanometers to about 30 nanometers.

13. The fibers of claim 1, wherein said fibers have an average length of from about 50 nanometers to about 10000 nanometers.

14. A method for preparing carbon nanotube fibers, said method comprising:

a) suspending entangled non-discrete multi-wall carbon nanotube fibers in an acidic solution for a time period ;

b) optionally agitating said composition;

c) sonically treating said suspended nanotube fiber composition to form discrete carbon nanotube fibers; and

d) isolating the resultant discrete carbon nanotube fibers from the composition prior to further treatment using solid/liquid separations, wherein said separations comprise, filtration and centrifugation.

15. The method of claim 14, wherein the acidic solution comprises a solution of sulfuric acid and nitric acid.

16. The method of claim 15, wherein the nitric acid is present in a dry basis of from about 10 weight % to about 50 weight %, preferably from about 15 weight % to about 30 weight %.

17. The method of claim 14, wherein the sonic treatment is performed at an energy input of from about 200 to about 600 Joules/gram of suspended composition.

18. The method of claim 14, wherein the non-discrete carbon nanotube fibers are present in a concentration of from greater than zero to less than about 4 weight percent of the suspended nanotube fiber composition.

19. The method of claim 14, wherein the suspended discrete nanotube fiber composition in the acidic solution is controlled at a specific temperature environment.

20. The method of claim 19, wherein the specific temperature environment is from about 15 to 65°C, preferably from about 25° to about 35°C.

21. The method of claim 14, wherein said method comprises a batch, semi-batch, or continuous method.

22. The method of claim 14, wherein the composition is in contact with the acidic solution from about 1 hour to about 5 hours.

23. The method of claim 14, wherein said isolated resultant discrete carbon nanotube fibers from the composition prior to further treatment comprises at least about 10 weight percent water.

24. The fibers of claim 1, wherein the fibers are at least partially surface modified or coated with at least one surfactant.

25. The fibers of claim 1, wherein the fibers are completely surface modified or coated.

26. The fibers of claim 1, wherein the fibers are at least partially surface modified or coated with at least one modifier.

27. The fibers of claim 1, wherein the fibers are completely surface modified or coated.

28. The fibers of claim 24, wherein the surfactant or modifier is hydrogen bonded, covalently bonded, or ionically bonded to the carbon nanotube fibers.

29. The fibers of claim 24, wherein said coating is substantially uniform.

30. The fibers of claim 24, wherein the fibers are further mixed, blended, sonicated, or a combination method thereof, with at least one elastomer to form an elastomer nanotube fiber composition.

31. The fibers of claim 30 wherein the elastomers comprises natural rubber, synthetic rubber, or rubber compounds comprising fillers of carbon or silicon compounds, and wherein a fiber surface modifier or the surfactant is chemically, physically, or both, bonded to the elastomer, an isolated fibers, or any fillers present.

32. The elastomer nanotube fiber composition of claim 30 wherein said modifier or surfactant is chemically bonded to said elastomer, said nanotube fiber, or both.

33. The fibers of claim 24, wherein the fibers are further mixed, blended, sonicated, or a combination method thereof, with at least one other material to form a material/nanotube fiber composition.

34. The material nanotube fiber composition of claim 32, wherein said modifier or surfactant is chemically bonded to said material or said nanotube fiber.

35. The fibers of claims 24, wherein the fibers are further mixed, blended, sonicated, or a combination method thereof, with at least one epoxy to form an epoxy/nanotube fiber composition.

36. The epoxy/nanotube fiber composition of claim 35, wherein said modifier or surfactant is chemically bonded to said epoxy, said nanotube fiber, or both.

37. The epoxy/nanotube fiber composition of claim 35, wherein said composition has a fatigue crack failure resistance of at least 2 to about 20 times the fatigue crack failure resistance of the epoxy tested without carbon nanotubes.

38. The epoxy/nanotube fiber composition of claim 35, wherein said composition has a coefficient of expansion in at least one dimension of at least 2/3 to 1/3 that of the epoxy tested without carbon nanotubes in the same dimension.

39. The elastomer/nanotube fiber composition of claim 30, wherein said composition has a fatigue crack failure resistance of at least 2 to about 20 times the fatigue crack failure resistance of the elastomer tested without carbon nanotubes.

40. A material-nanocomposite fiber composition of claim 32 bonded to a substrate, wherein said composition has an adhesive or cohesive strength of at least two times greater that of the material without carbon nanotubes tested similarly.

41. An elastomer-nanocomposite fiber composition of claim 30 bonded to a substrate, wherein said composition has an adhesive or cohesive strength of at least two times greater that of the elastomer without carbon nanotubes tested similarly.

42. An epoxy-nanocomposite fiber composition of claim 35 bonded to a substrate, wherein said composition has an adhesive or cohesive strength of at least two times greater that of the epoxy without carbon nanotubes tested similarly.

43. An epoxy-nanocomposite fiber composition of claim 35 bonded to a substrate, wherein said composition has an adhesive or cohesive strength of at least two times greater that of the epoxy without carbon nanotubes tested similarly.

44. The fibers of claims 24 wherein the fibers are further mixed, blended, sonicated, or a combination method thereof, with at least one elastomer and an inorganic nanoplate to form an elastomer nanotube fiber and nanoplate composition.

45. The elastomer nanotube fiber and nanoplate composition of claim 30, wherein the carbon nanotube and/or nanoplate is chemically bonded to said elastomer .

46. A cyano-acrylate containing material containing fibers of claims 24 bonded to a substrate wherein said composition has an adhesive or cohesive strength of at least two times greater that of the cyano-acrylate containing material without carbon nanotubes tested similarly.

47. The carbon nanotube fibers of claim 1 comprising single, double, or multi-wall fibers.

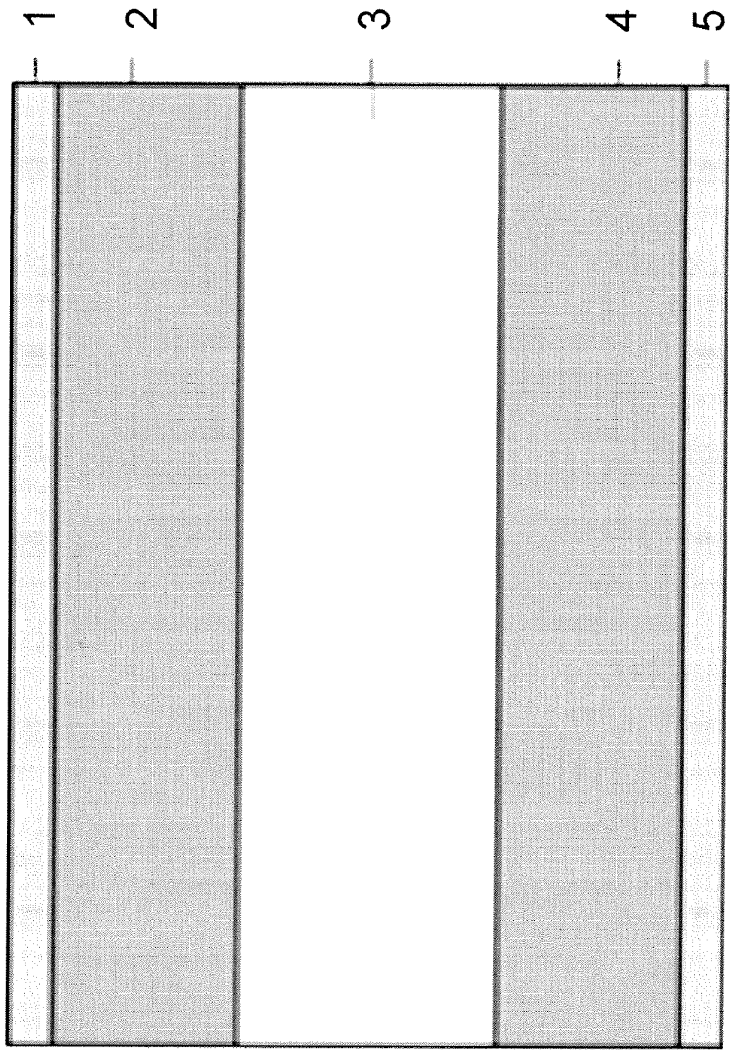


Figure 1

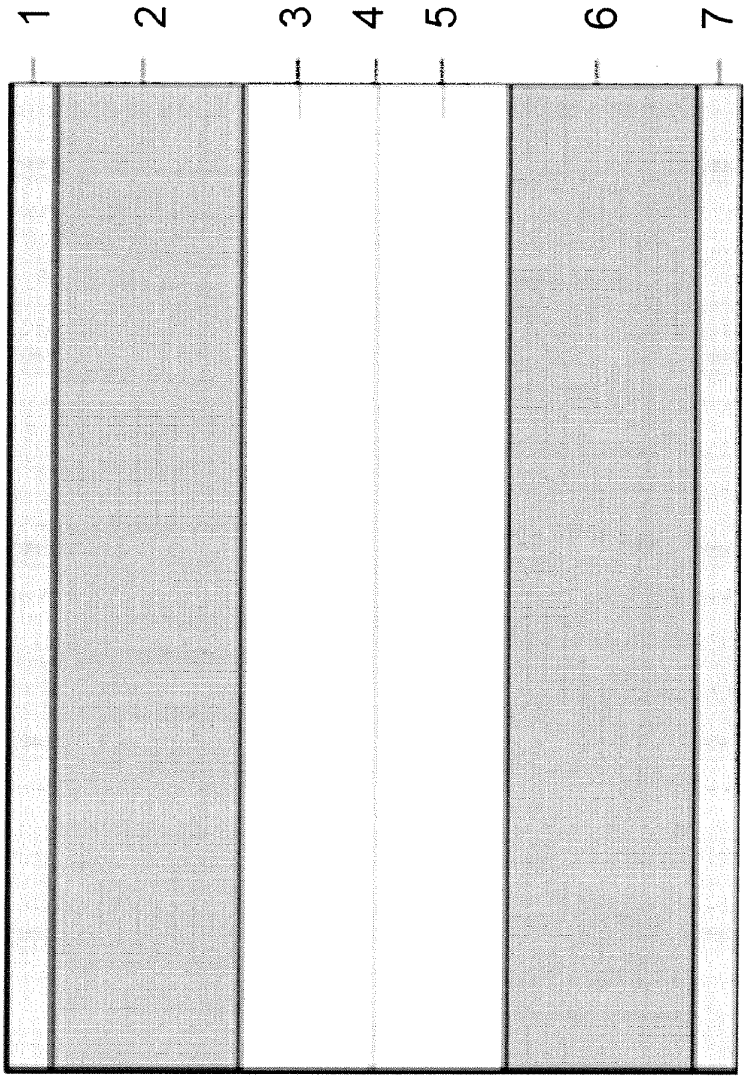


Figure 2

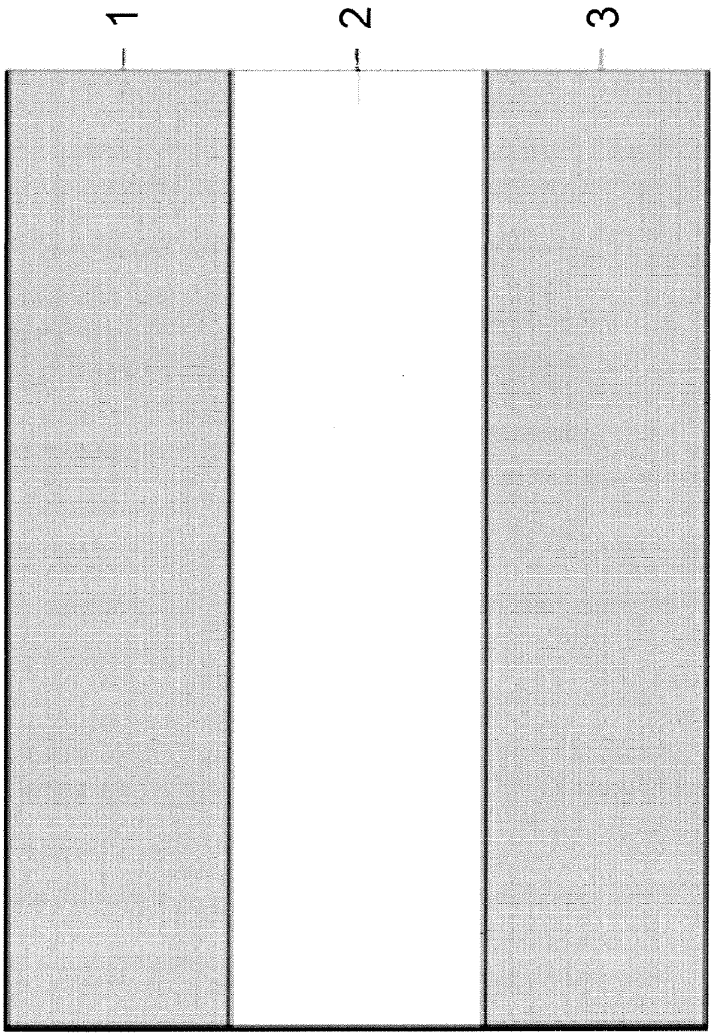


Figure 3

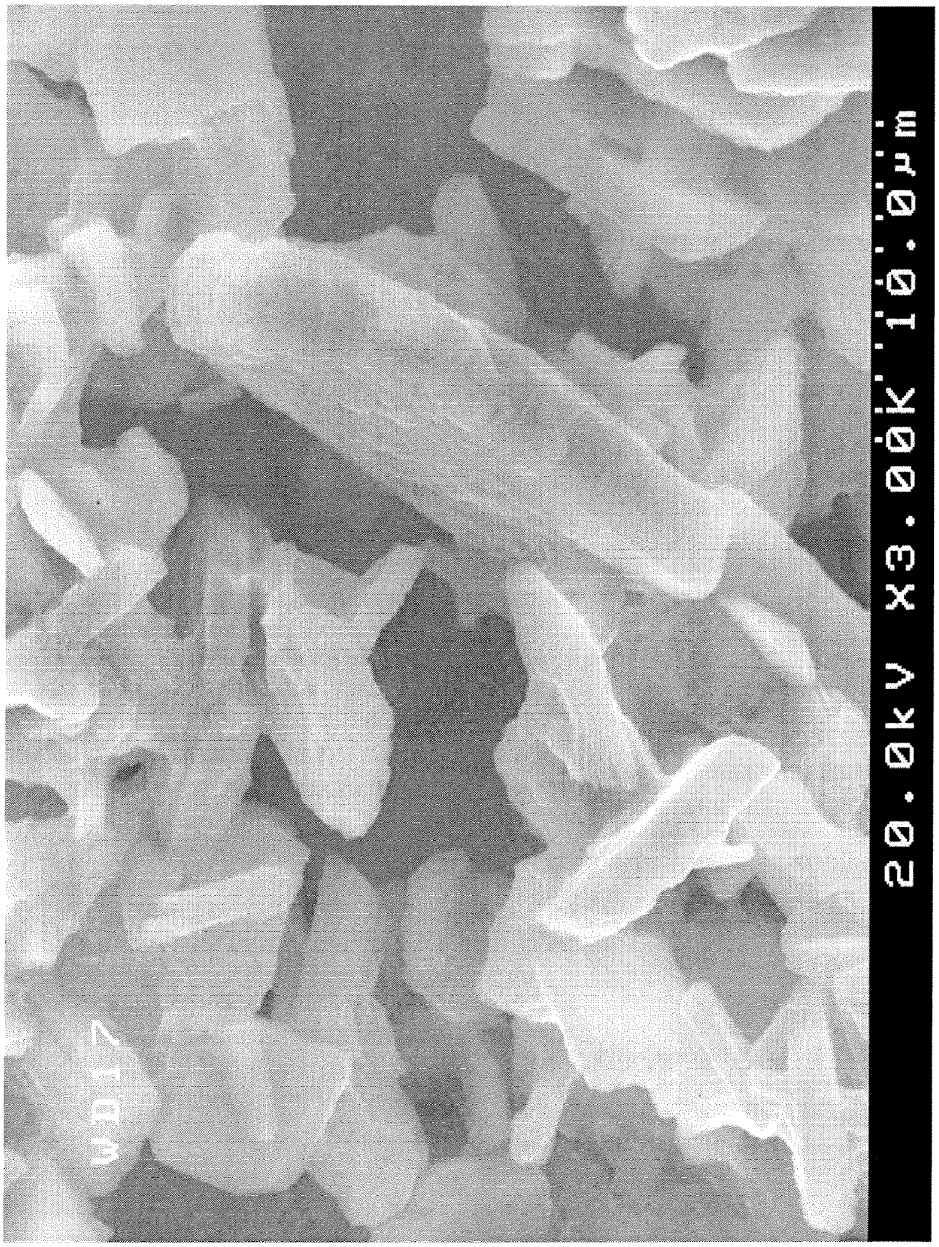
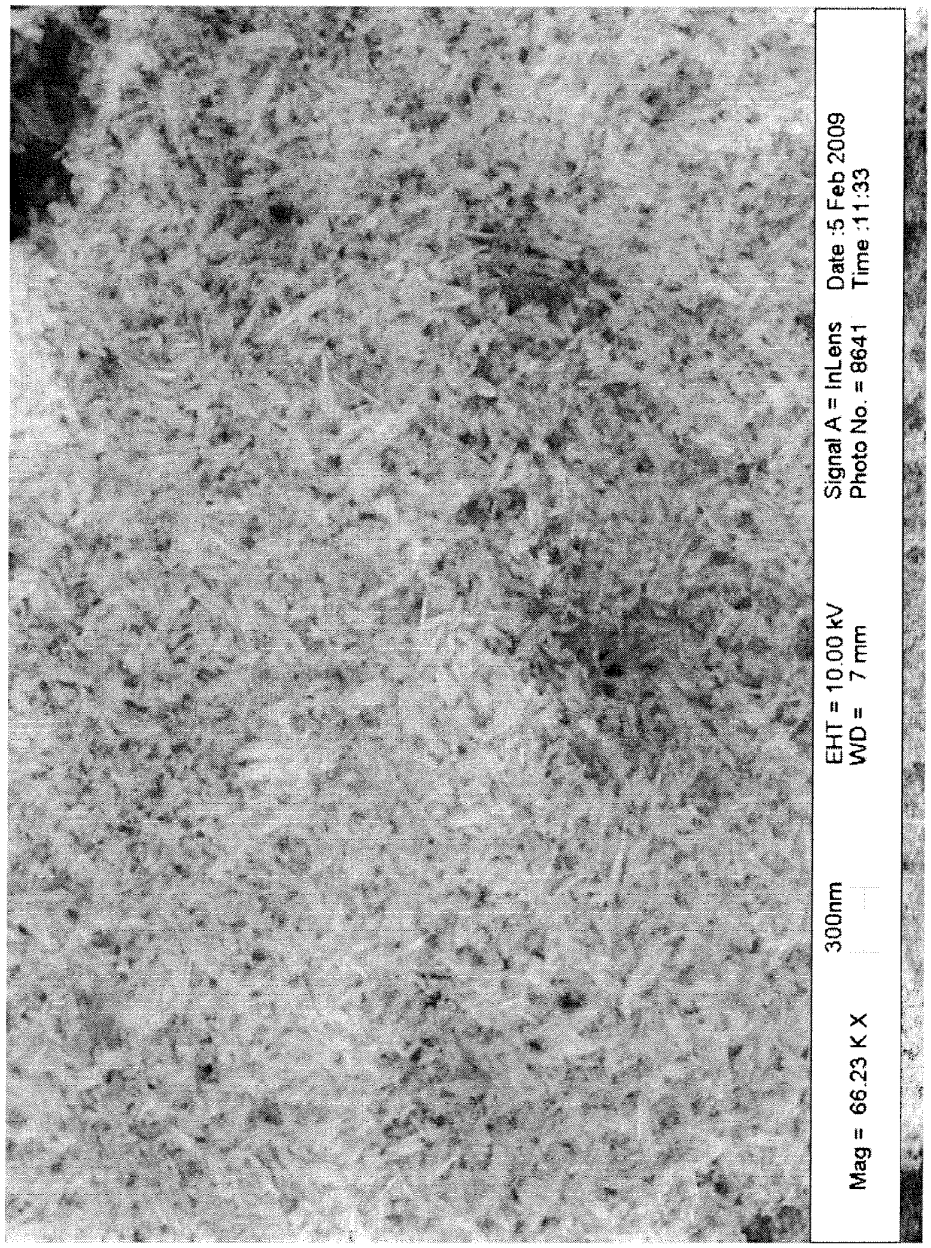


Figure 4


Mag = 66.23 K X
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EHT = 10.00 kV
WD = 7 mm
Signal A = InLens
Photo No. = 8641
Date :5 Feb 2009
Time :11:33

Figure 5

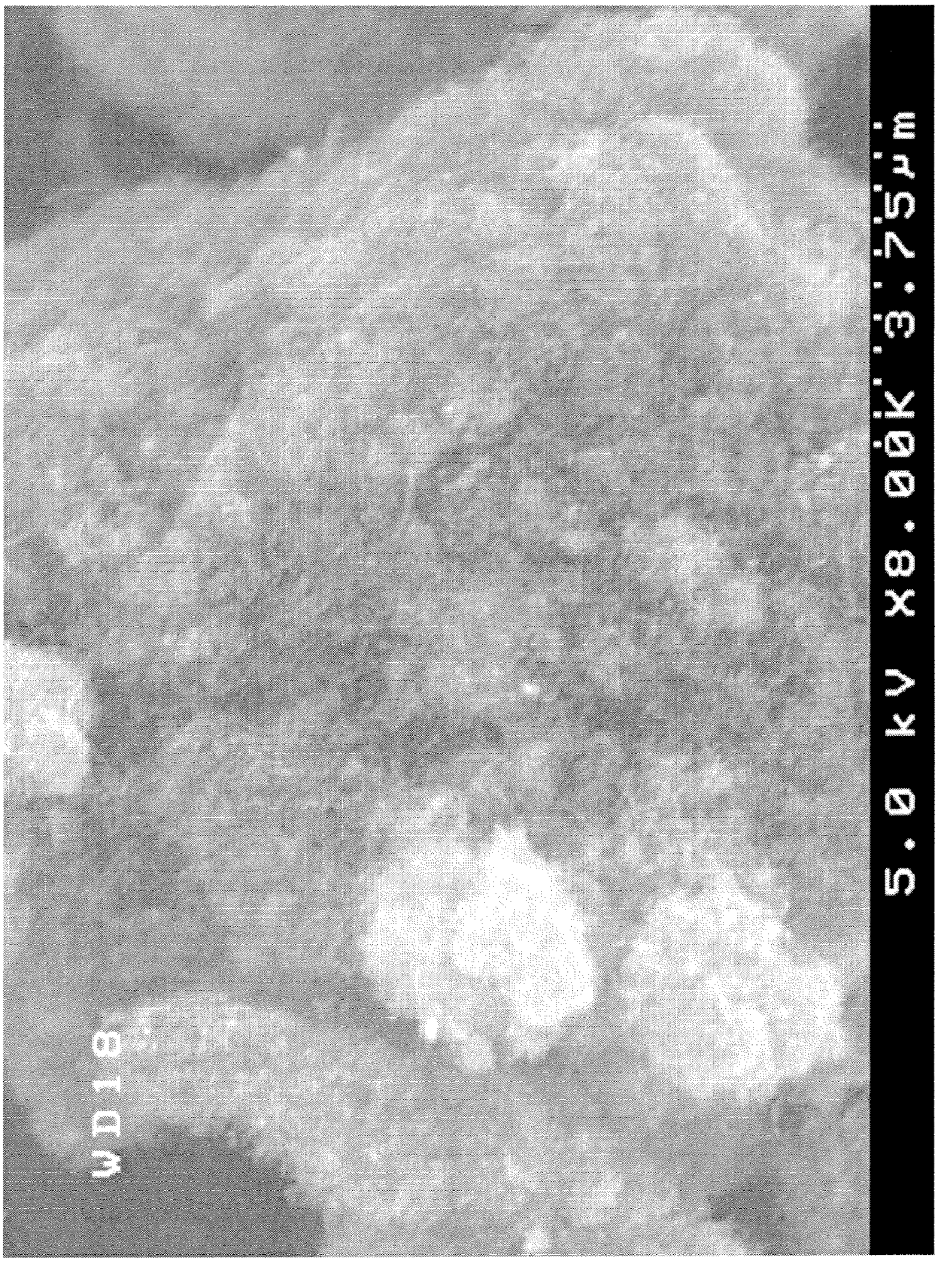

Figure 6A

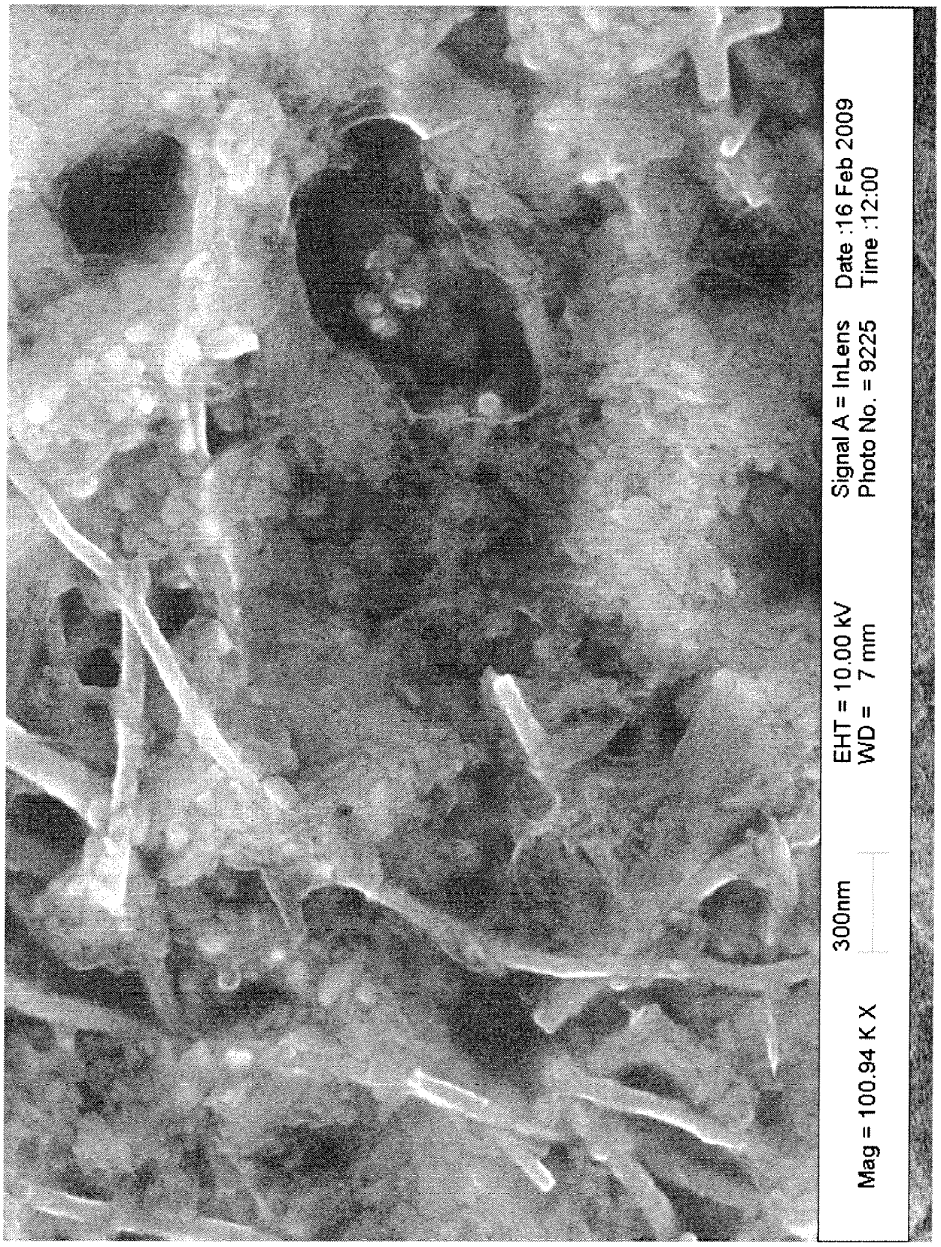
Mag = 100.94 K X
300nm
EHT = 10.00 kV
WD = 7 mm
Signal A = InLens
Photo No. = 9225
Date :16 Feb 2009
Time :12:00

Figure 6B

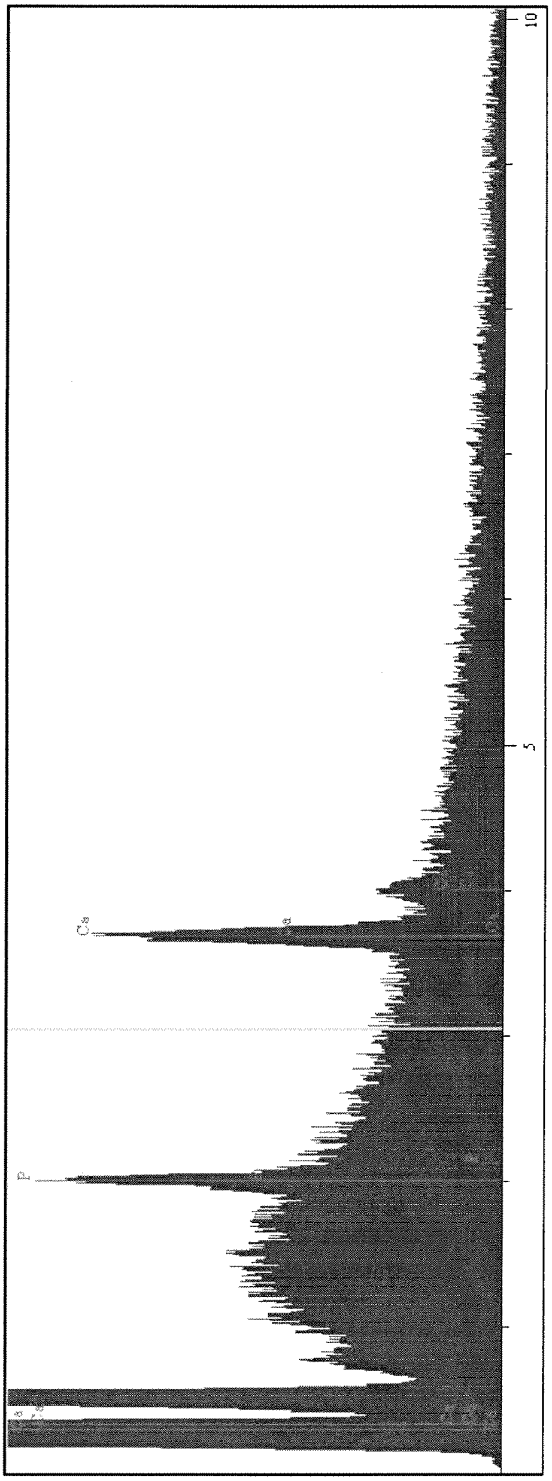

Figure 7A

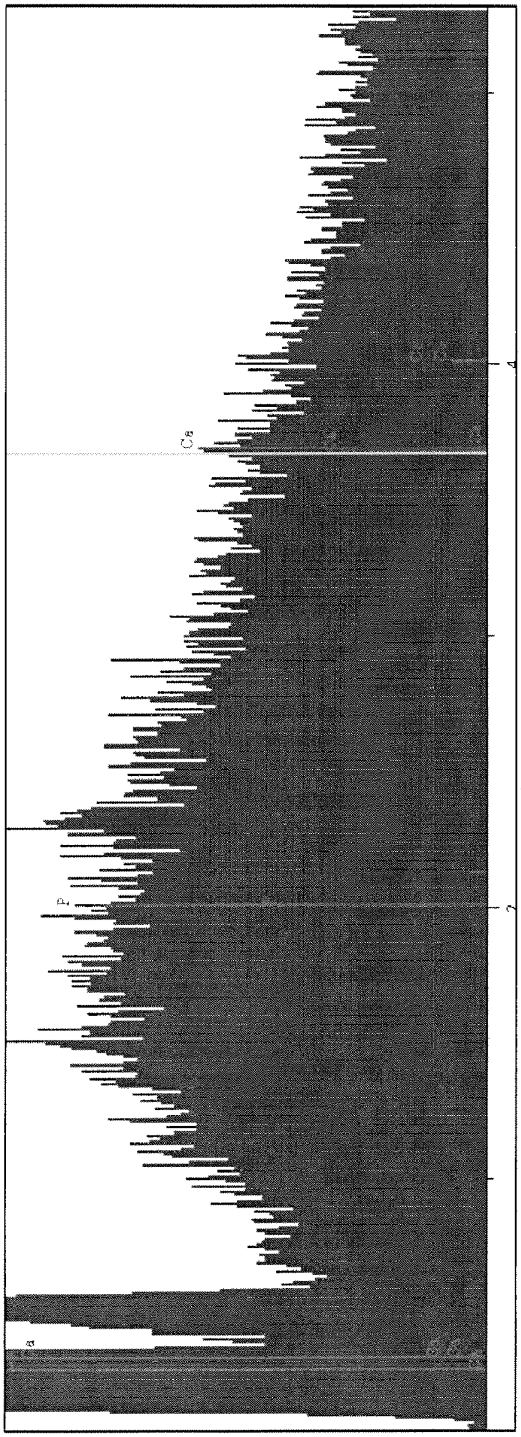

Figure 7B

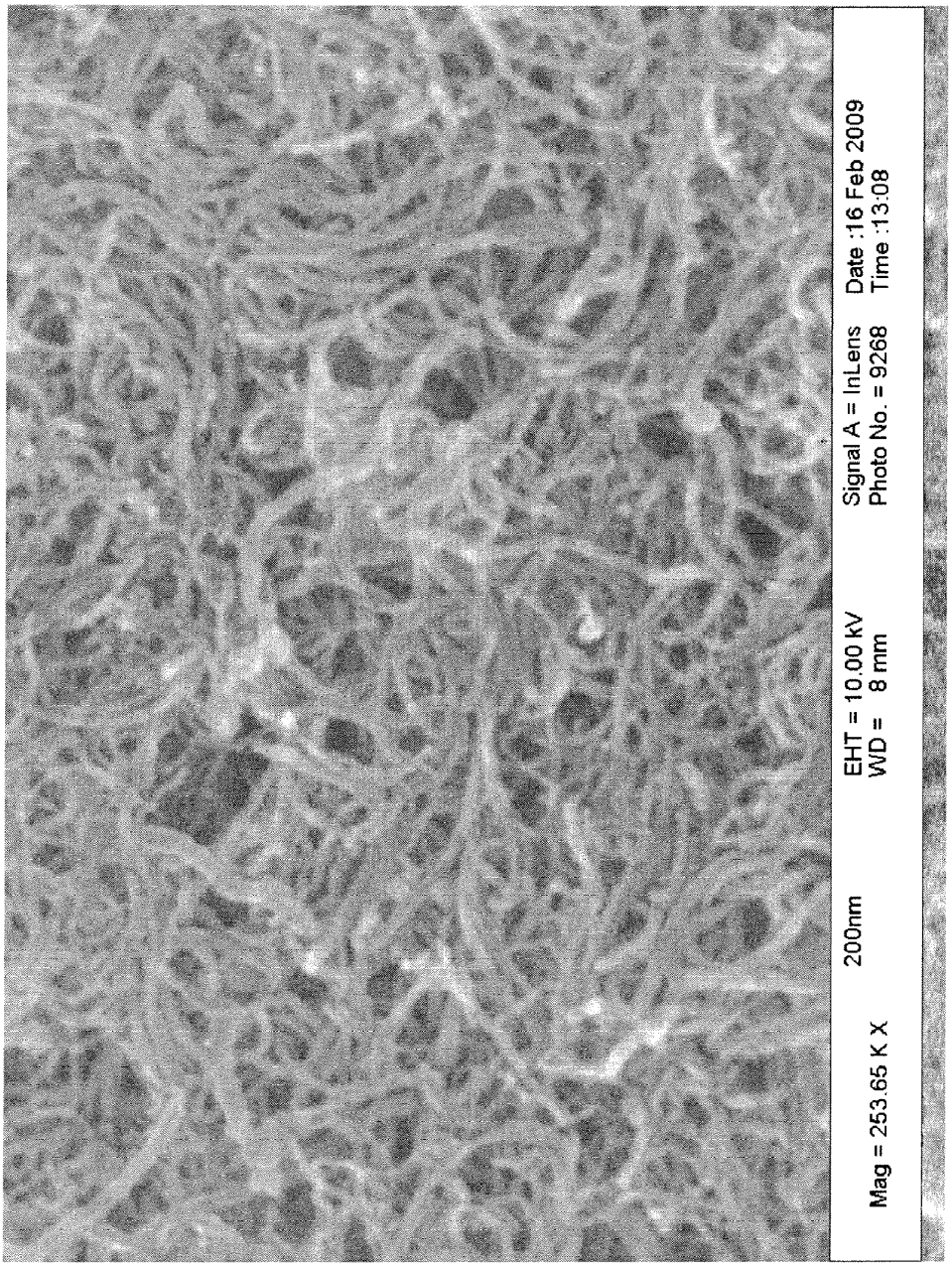
Mag = 253.65 K X
200nm
EHT = 10.00 kV
WD = 8 mm
Signal A = InLens
Photo No. = 9268
Date :16 Feb 2009
Time :13:08

Figure 8

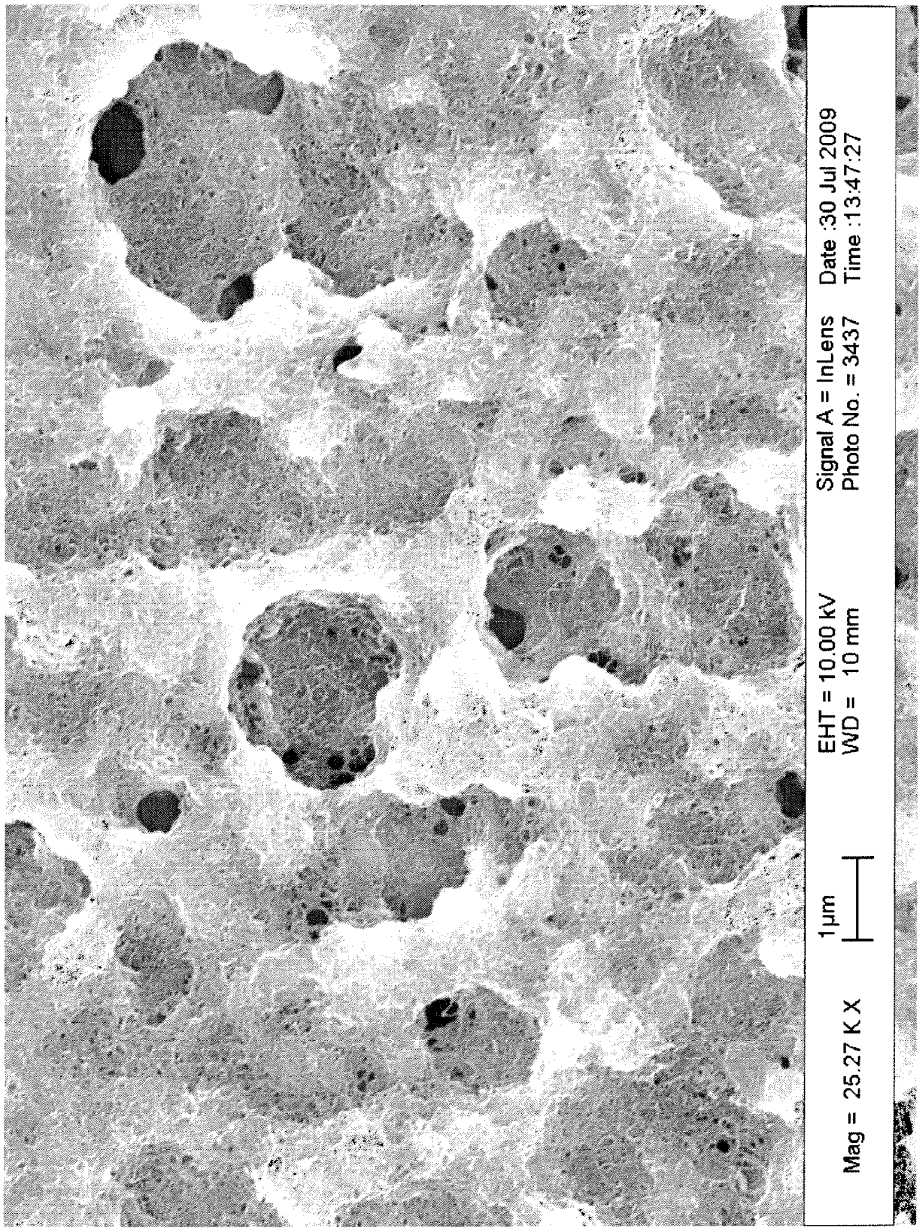
Mag = 25.27 K X
1 µm
EHT = 10.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 3437
Date :30 Jul 2009
Time :13:47:27

Figure 9

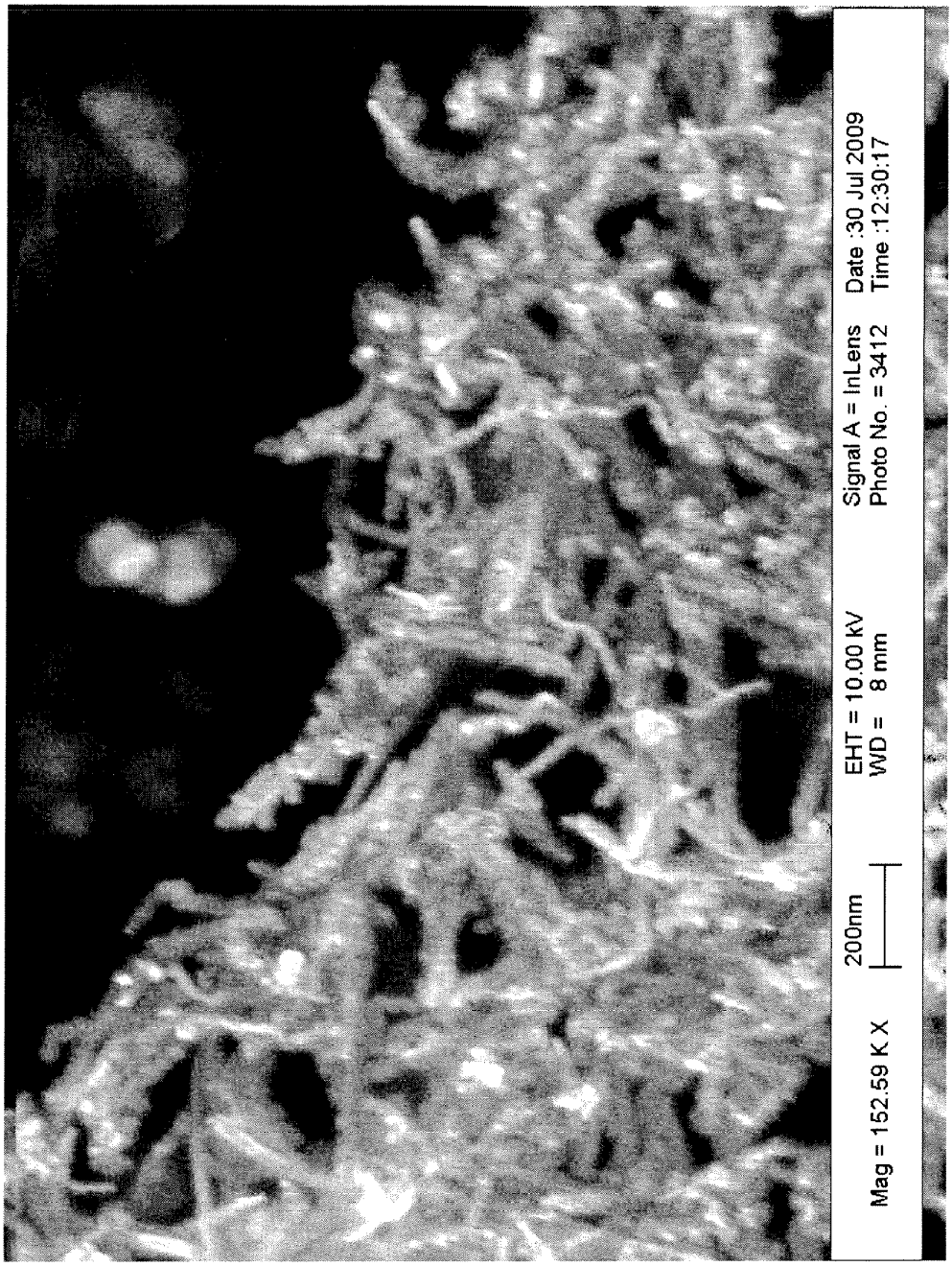
Mag = 152.59 K X
200nm
EHT = 10.00 kV
WD = 8 mm
Signal A = InLens
Photo No. = 3412
Date :30 Jul 2009
Time :12:30:17

Figure 10

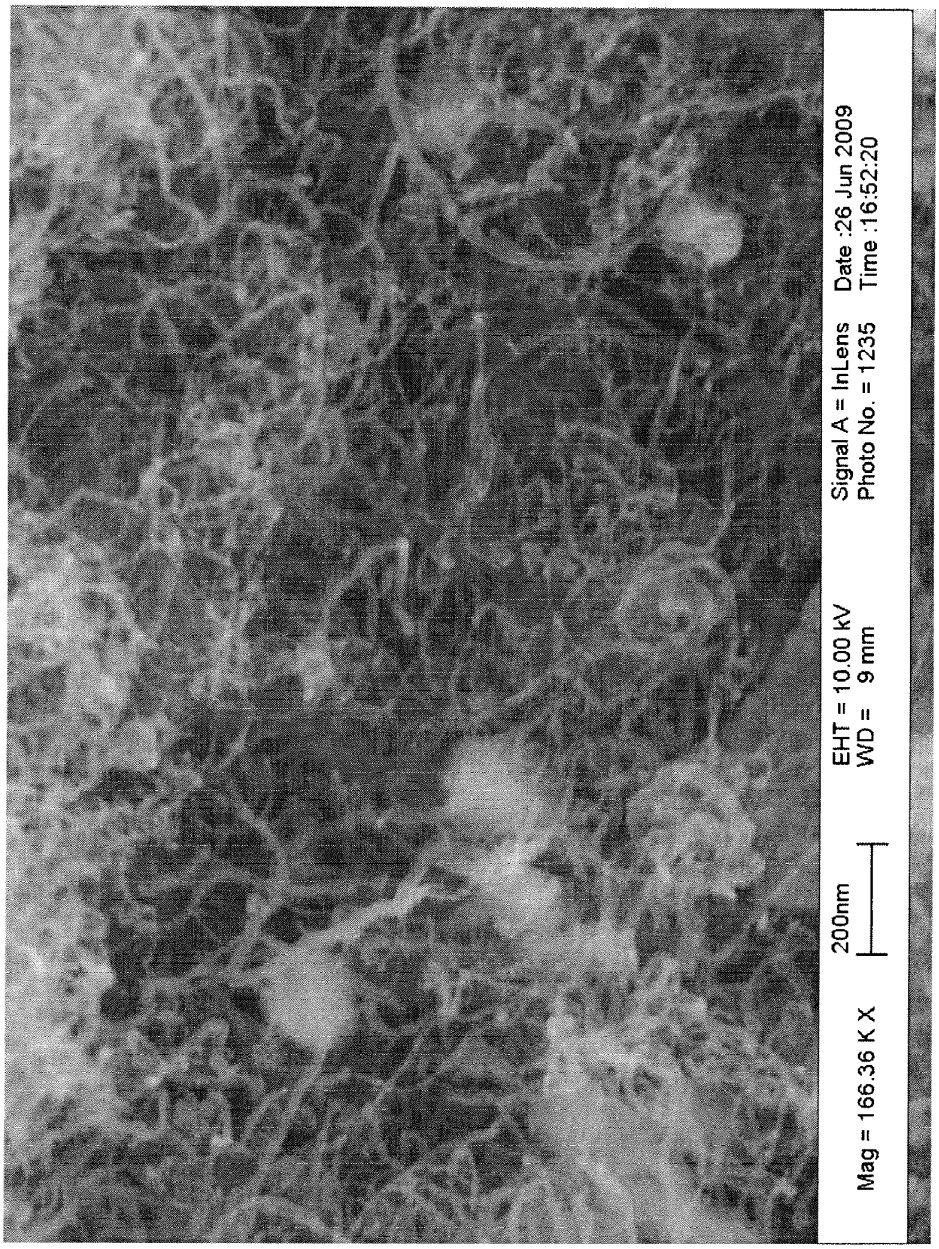
Mag = 166.36 K X
200nm
EHT = 10.00 kV
WD = 9 mm
Signal A = InLens
Photo No. = 1235
Date :26 Jun 2009
Time :16:52:20

Figure 11

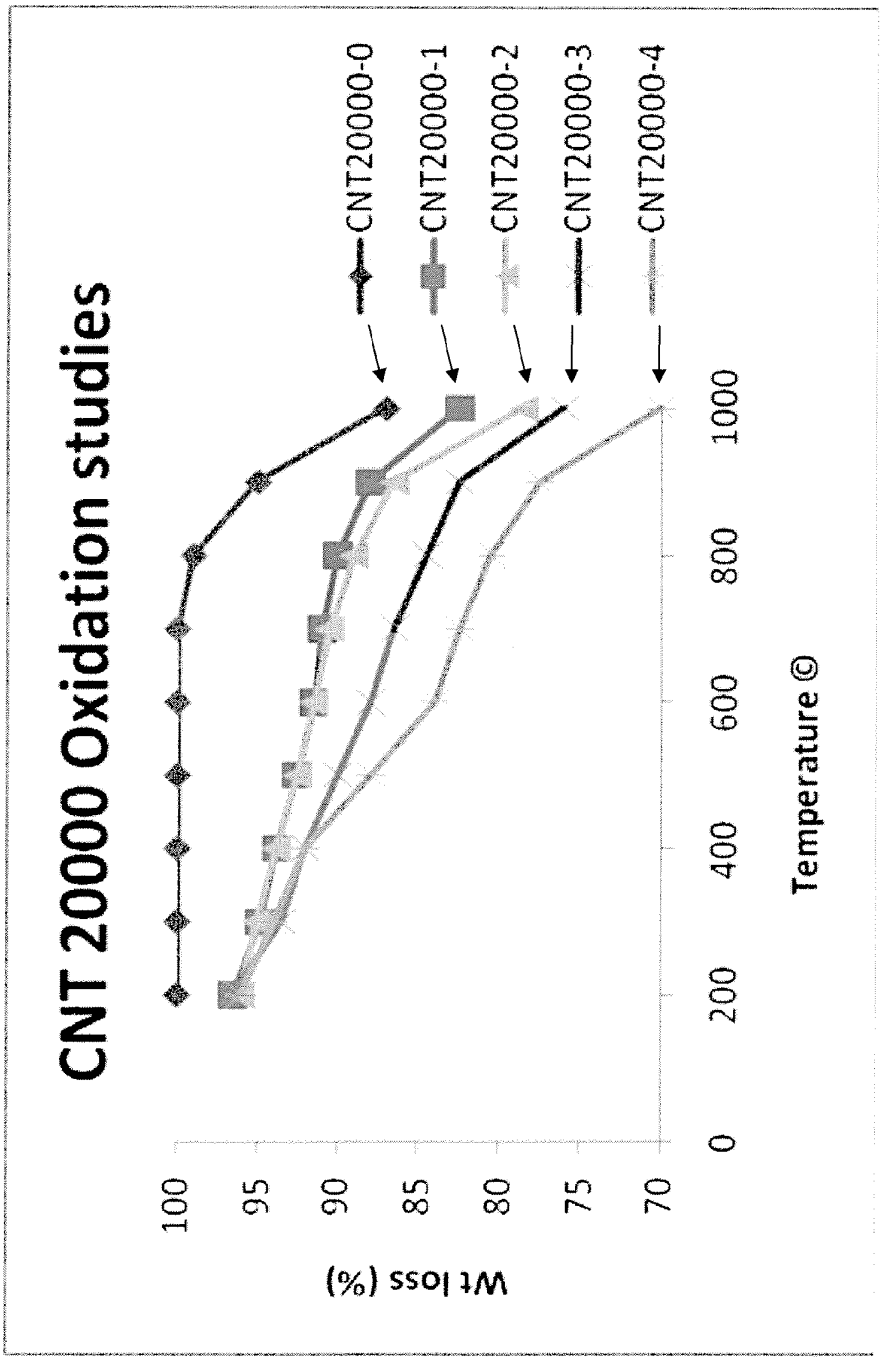
CNT 20000 Oxidation studies
Wt loss (%)
100
95
90
85
80
75
70
0
200
400
600
800
1000
Temperature ©
CNT20000-0
CNT20000-1
CNT20000-2
CNT20000-3
CNT20000-4

Figure 12

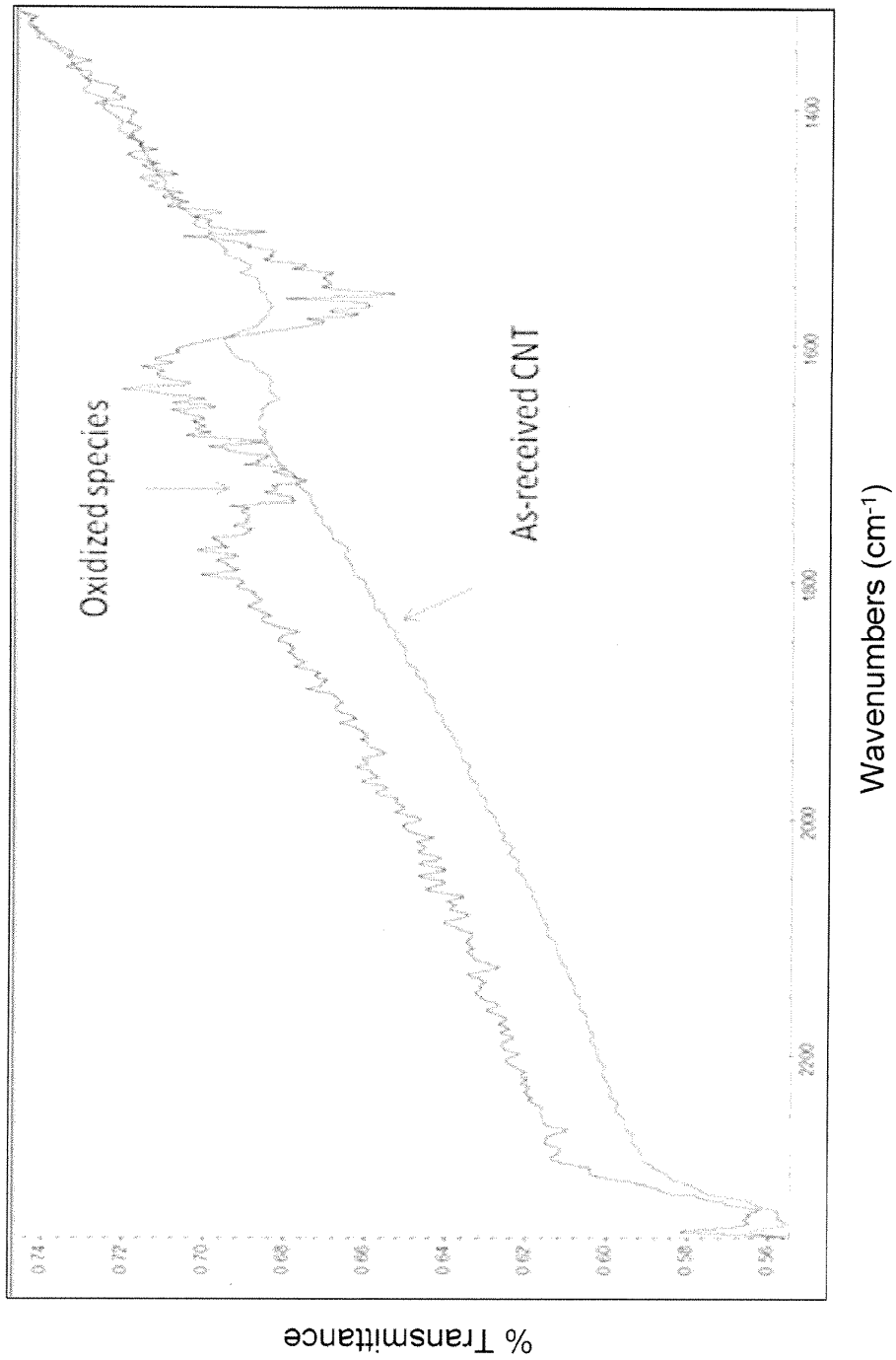
Oxidized species
As-received CNT
% Transmittance
0.74
0.72
0.70
0.68
0.66
0.64
0.62
0.60
0.58
0.56
2200
2000
1800
1600
1400
Wavenumbers (cm-1)

Figure 13

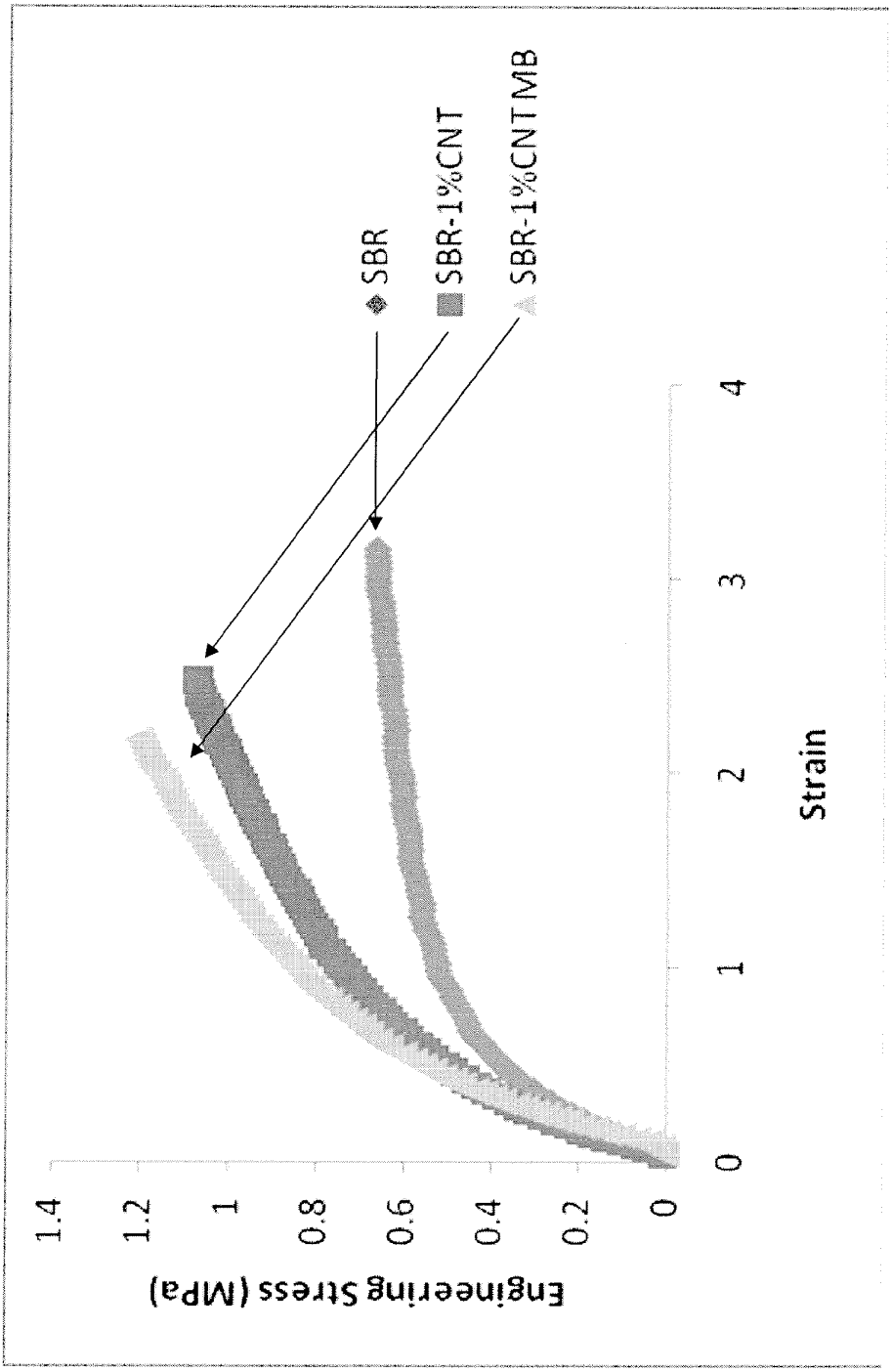
Engineering Stress (MPa)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
Strain
SBR
SBR-1%CNT
SBR-1%CNT MB

Figure 14

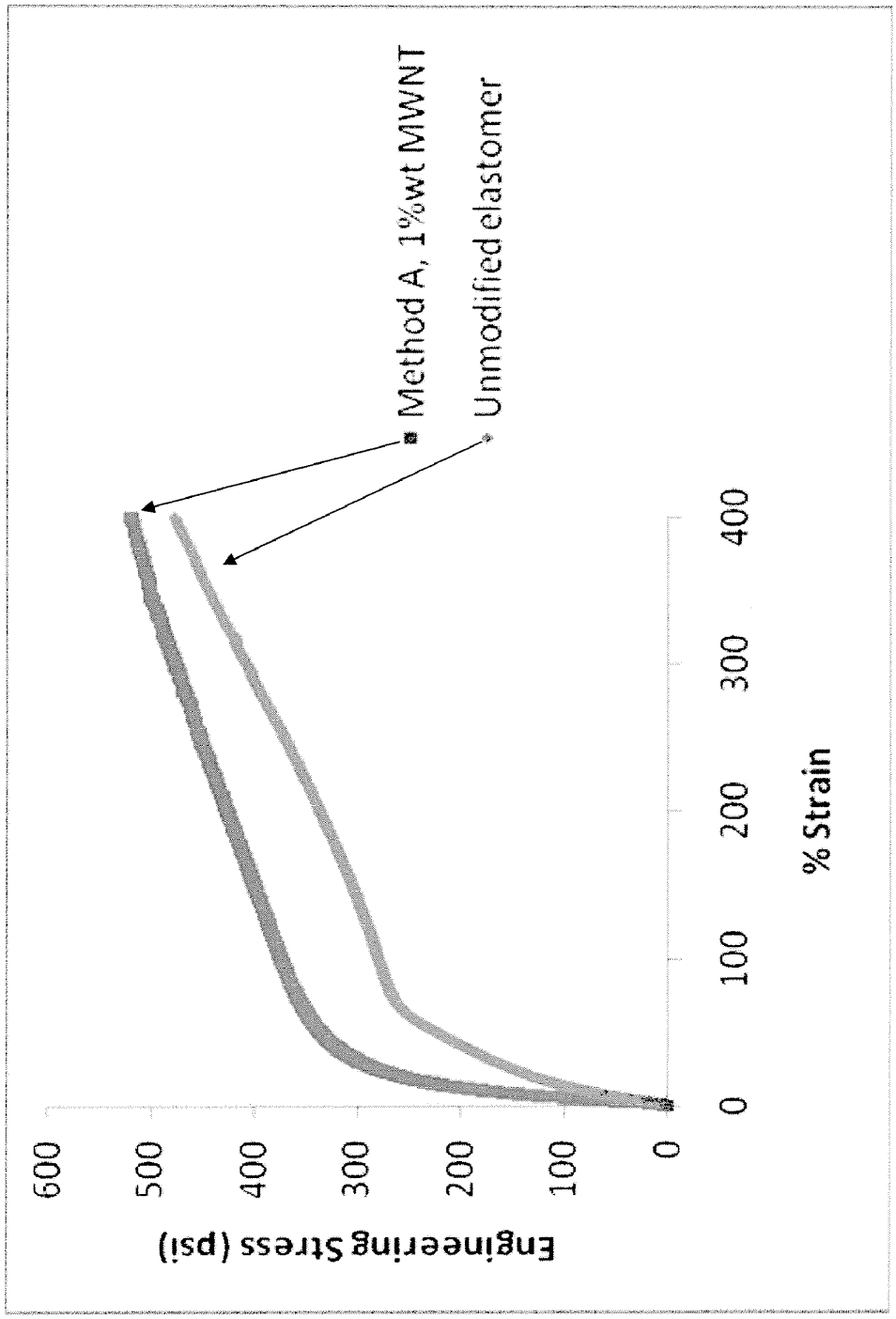
Engineering Stress (psi)
600
500
400
300
200
100
0
0
100
200
300
400
% Strain
Method A, 1%wt MWNT
Unmodified elastomer

Figure 15

Electronic Patent Application Fee Transmittal

Application Number:	15881071
Filing Date:	26-Jan-2018
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Filer:	Gregory L. Porter/Jeanne Dunn
Attorney Docket Number:	MRE012NP2C / 277190

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
SUBMISSION- INFORMATION DISCLOSURE STMT	1806	1	240	240
		Total in USD ($)		**240**

Electronic Acknowledgement Receipt	
EFS ID:	38026800
Application Number:	15881071
International Application Number:	
Confirmation Number:	2885
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	130577
Filer:	Gregory L. Porter/Jeanne Dunn
Filer Authorized By:	Gregory L. Porter
Attorney Docket Number:	MRE012NP2C / 277190
Receipt Date:	13-DEC-2019
Filing Date:	26-JAN-2018
Time Stamp:	15:02:01
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$240
RAM confirmation Number	E2019BCF02271611
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	SuppIDS.pdf	77246 91e43167b93e75351e8a18078f55fed4119eb24f	no	4
Warnings:					
Information:					
This is not an USPTO supplied IDS fillable form					
2	Foreign Reference	WO_2011_163129.pdf	12171891 555116a4b8b8c25ca468fea15541f0e195d5ebab	no	63
Warnings:					
Information:					
3	Non Patent Literature	Xianke.pdf	995798 8c23118d219c6f0ccb440c33fa9b3b8e94815223	no	8
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Information:					
4	Non Patent Literature	CASrchRpt.pdf	300120 c785745cb77b9b901c3810bc9ceae355aa06c1aa	no	4
Warnings:					
Information:					
5	Fee Worksheet (SB06)	fee-info.pdf	30797 9d4dd09cb9ae4f3692cbd7cb24cbd7d5ba344a70	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	13575852	

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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/881,071	Filing Date 01/26/2018	☐ To be Mailed

ENTITY: ☑ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $100 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $460 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

AMENDMENT	10/18/2019	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 16	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	*** 3	= 0		x $460 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/JAMES W TUNSTALL/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

REMARKS

Applicant confirms election of Group I, Claims 1-18 without traverse. Unelected Claims 19-20 have been cancelled.

Independent Claim 1 has been amended to incorporate the subject matter of Claim 18 which was indicated as having allowable subject matter on page 11 of the Office Action. Claims 17-18 have been cancelled.

Claim 15 has been amended to moot the 112 rejection of Claims 15-16.

It is believed that the amendments place Claims 1-16 in condition for allowance and Applicant requests reconsideration and withdrawal of the rejections. Please charge any fee required for the entry of this paper or to avoid abandonment of this application to Deposit Account No. 50-0206 referencing attorney docket no. 108892.0277190. The Examiner is invited to call the undersigned attorney at 713-220-4621 if a telephone call could help resolve any item.

Respectfully submitted,

/Gregory L. Porter/
Gregory L. Porter
Registration No. 40,131

Date: October 18, 2019

Hunton Andrews Kurth LLP
600 Travis, Suite 4200
Houston, Texas 77002
713/220-4621 (office)
Customer No. 23,444

Electronic Acknowledgement Receipt

EFS ID:	37494171
Application Number:	15881071
International Application Number:	
Confirmation Number:	2885
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	130577
Filer:	Gregory L. Porter/Jeanne Dunn
Filer Authorized By:	Gregory L. Porter
Attorney Docket Number:	MRE012NP2C / 277190
Receipt Date:	18-OCT-2019
Filing Date:	26-JAN-2018
Time Stamp:	10:09:51
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		ROA_10172019.pdf	84036 aa33a3187b84ea46a78d588a9a878739f4be45a7	yes	6

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment Copy Claims/Response to Suggested Claims	1	4
	Applicant Arguments/Remarks Made in an Amendment	5	6
Warnings:			
Information:			
	Total Files Size (in bytes):	84036	

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New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	Clive P. Bosnyak	**Confirmation No.**:	2885
Serial No.:	15/881,071	**Art Unit:**	1726
Filed:	January 26, 2018	**Examiner:**	
For:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	**Atty. Dkt. No.:**	MRE012NP2C / 277190

Mail Stop Amendment
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO OCTOBER 17, 2019 OFFICE ACTION

Responsive to the outstanding October 17, 2019 Office Action, reconsideration is respectfully requested in view of the arguments presented herein.

Listing of the Claims begins on page **2** of this paper.

Remarks begin on page **5** of this paper.

LISTING OF THE CLAIMS

The following listing of claims will replace all prior versions and listings of claims in the application.

1. (Currently amended) A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:

   a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended and

wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70 and wherein from 1% to 30% by number of discrete carbon nanotubes have an average aspect ratio 80-140.

2. (Original) The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.
3. (Original) The composition of claim 1, further comprising at least one polymer.
4. (Original) The composition of claim 1, wherein the carbon nanotubes are further functionalized.
5. (Original) The composition of claim 1, further comprising at least one dispersion aid.
6. (Original) The composition of claim 3, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate),

poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

7. (Original) The composition of claim 2, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.
8. (Original) The binder composition of claim 2 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.
9. (Original) The composition of claim 9, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.
10. (Original) The composition of claim 1, wherein the binder material has an impedance of less than or equal to about one billion ohm-m.
11. (Original) The composition of claim 1, where the electrolyte material or separator film has a charge transfer resistance of less than or equal to about 10 million ohm-m.
12. (Original) The composition of claim 1, wherein the carbon nanotubes are oriented.
13. (Original) The composition of claim 13, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

14. (Original) The composition of claim 14, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

15. (Currently amended) The composition of claim 1, which further ~~wherein a portion of open ended tubes~~ comprises electrolyte.

16. (Original) The composition of claim 16, wherein the electrolyte comprises a polymer or a liquid.

17. Cancelled.

18. Cancelled.

19. Cancelled.

20. Cancelled.

.

UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/881,071	01/26/2018	Clive P. Bosnyak	MRE012NP2C / 277190	2885

130577 7590 10/17/2019
Hunton Andrews Kurth LLP/HAK TX
600 Travis Street
Suite 4200
Houston, TX 77002

EXAMINER
SMITH, JEREMIAH R

ART UNIT	PAPER NUMBER
1723	

NOTIFICATION DATE	DELIVERY MODE
10/17/2019	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

patenttrademarks@andrewskurth.com

PTOL-90A (Rev. 04/07)

Office Action Summary	Application No. 15/881,071	Applicant(s) Bosnyak et al.	
	Examiner JEREMIAH R SMITH	Art Unit 1723	AIA (FITF) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 6/7/18.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☑ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-20 is/are pending in the application.

5a) Of the above claim(s) 19-20 is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-17 is/are rejected.

8) ☑ Claim(s) 18 is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☑ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date 6/7/18.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. Application 15/881071 "BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES" is a continuation of application 14/390902, which is the national stage entry of a PCT application filed on 6/21/13 and claims priority from a provisional application file on 6/22/12.

The present application is being examined under the pre-AIA first to invent provisions.

This Office Action is in response to communication filed on 6/7/18.

Election/Restriction

2. Restriction to one of the following inventions is required under 35 U.S.C. 121:

I. Claims 1 -18, drawn to a composition classified in H01M 10/00

II. Claim 19, drawn to an electrode past, classified in H01M 4/002.

III. Claim 20, drawn to a method for making a composition, classified in H01M 2/145.

3. The inventions are distinct, each from the other because of the following reasons:

4. Inventions I and III are related as process of making and product made. The inventions are distinct if either or both of the following can be shown: (1) that the process as claimed can be used to make another and materially different product or (2) that the product as claimed can be made by another and materially different process

(MPEP § 806.05(f)). In the instant case the composition as claimed can be made by another and materially different process, for example manual mixing rather than vigorous mixing such as with a sonicator. Alternatively the method as claimed can be used to make a materially different product such as carbon fiber parts for automobile parts.

5. Inventions I and II are directed to related products The related inventions are distinct if: (1) the inventions as claimed are either not capable of use together or can have a materially different design, mode of operation, function, or effect; (2) the inventions do not overlap in scope, i.e., are mutually exclusive; and (3) the inventions as claimed are not obvious variants. See MPEP § 806.05(j). In the instant case, the inventions as claimed do not overlap in scope, they are 2 different products which are not connected. The inventions are 2 different distinct products, the composition of claim 1 requires a plurality of discrete carbon nanotube fibers with an aspect ratio of from about 10 to about 500 while the composition for claim 19 requires carbon nanotubes with an average length of about 400 to about 1400 nm. Furthermore, the inventions as claimed do not encompass overlapping subject matter and there is nothing of record to show them to be obvious variants.

6. Inventions II and III are unrelated. Inventions are unrelated if it can be shown that they are not disclosed as capable of use together and they have different designs, modes of operation, and effects (MPEP § 802.01 and § 806.06). In the instant case, the different inventions the method of claim 20 is directed to making a composition for use as a binder material, an electrolyte material or a separator film where claim 19 claims an electrode paste. Claim 20 does not discuss an electrode paste. The inventions are not

discussed as capable of being used together. The composition of the material of claim 20 may not be useful as claim 19's electrode paste.

7. During a telephone conversation with Gregory Porter on 9/6/19 a provisional election was made without traverse to prosecute the invention of Group I, claims 1-18.

8. **Affirmation of this election must be made by applicant in replying to this Office action.** Claims 19 and 20 are withdrawn from further consideration by the examiner, 37 CFR 1.142(b), as being drawn to a non-elected invention.

Claim Rejections - 35 USC § 112

9. The following is a quotation of 35 U.S.C. 112(b):

> (b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:

> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

10. Claims 15-16 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

11. Regarding these claims, it is unclear what is meant by "a portion of open ended tubes comprise electrolyte". More specifically, the term comprise is normally used to describe the make-up of a thing. In this case, the nanotubes are taught in the specification to be made up of carbon, not electrolyte, making the claim as worded

generally inconsistent with the remainder of the detailed description. Applicant may have intended the claim to instead require that electrolyte is contained within the hollows of the nanotubes. Since multiple interpretations are possible, the claim as worded is ambiguous and therefore indefinite.

12. Additionally, it is noted that "tubes" is not used previously in the base claims and therefore lacks defined meaning and proper antecedent basis.

Claim Rejections - 35 USC § 103

13. The following is a quotation of pre-AIA 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

14. Claims 1, 4-5 and 12-16 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Bosynak (CA 2747728, published 8/14/10; citations taken from US 2011/0294013).

15. Alternatively, claims 1, 4-5 and 12-16 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Bosynak (CA 2747728, published 8/14/10; citations taken from US 2011/0294013) in view of Johnson (US 2011/0104576).

16. Claim 17 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Bosynak (CA 2747728, published 8/14/10; citations taken from US 2011/0294013) in view of Johnson (US 2011/0104576).

17. **Regarding claim 1,** Bosnyak teaches a composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device (this description of intended use is found to be nonlimiting. For completeness of record, Bosynak does appear to teach this feature at paragraph [0074, 0077]), comprising: a plurality of discrete carbon nanotube fibers ("exfoliated carbon nanotubes", paragraph [0074]), said fibers having an aspect ratio of from about 10 to about 500 (paragraphs [0041-0042] suggests an aspect ratio a range which overlaps the claimed range), and wherein at least a portion of the discrete carbon nanotube fibers are open ended (paragraph [0038]).

Bosnyak does not expressly teach the fibers must have an aspect ratio of from about 10 to about 500. However, paragraphs [0041-0042] suggests an aspect ratio a range which overlaps the claimed range. As described in MPEP 2144.05, a prima facie case of obviousness exists when the range disclosed by the prior art overlaps the claimed range.

18. **Regarding claim 4,** Bosnyak further teaches wherein the nanotubes are functionalized (paragraph [0032-0033]).

19. **Regarding claim 5,** Bosnyak further teaches including a dispersion aid (paragraph [0054]).

20. **Regarding claim 12-14,** Bosnyak further teaches wherein the carbon nanotubes are oriented (paragraph [0048]) and the composition may be in the form of a sheet or

film (paragraph [0048]; paragraph [0074] noting that battery separators are conventionally in the form of films which separate electrodes as illustrated in Figure 3). Claim 14 is a product-by-process claim which includes a plurality of optional manufacturing methods, but does not set forth any additional structural features to distinguish from the prior art.

21. **Regarding claim 15-16,** Bosnyak further teaches that the carbon nanotubes may be contained in a liquid electrolyte (paragraph [0081]), appearing to read on the "tubes comprise electrolyte" limitation.

22. **Regarding claim 17, and alternatively regarding the aspect ratio related limitation of claim 1**, Bosynak does not appear to teach the carbon nanotubes wherein 40 to 90% of the carbon nanotubes have an aspect ratio of 30 to 70.

In the battery art, Johnson teaches that carbon nanotubes for use in battery applications are known to have aspect ratios in the range of 20 to 100 (paragraph [0028]). Note that the range disclosed by Johnson lies completely within the range disclosed in claim 1.

It would have been obvious to a person having ordinary skill in the art at the time of invention to size the carbon nanotubes in accordance with the teachings of Johnson, as Johnson describes typical aspect ratios for carbon nanotubes as used in the art. Such a selection would yield only predictable effect. It is noted that the range disclosed by Johnson substantially overlaps the claimed aspect ratio range; therefore, a prima facie case of obviousness exists in accordance with MPEP 2144.05. The 40 to 90%

claimed range is found to be obvious, considering that a distribution of carbon nanotube sizes around the intended aspect ratio would be expected due to limitations on experimental technique.

Finally, it is noted that aspect ratio merely describes a statement of scale and relative proportions in the carbon nanotubes. It has been held that generally differences in size or scale do not patentably distinguish a claimed invention from the prior art, absent a showing of criticality associated with the claimed scaling (MPEP 2144 IVA).

23. Claims 2, 3 and 6 and 10-11 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over the combination of Bosynak (CA 2747728, published 8/14/10; citations taken from US 2011/0294013), Johnson (US 2011/0104576) and Gu ("Layered and interfacially blended polyelectrolyte…"; Thin Solid Films 520 2012 1872-1879; Published 9/16/11).

24. **Regarding claims 2, 3 and 6,** Bosynak teaches carbon naotubes as a constituent of an electrolyte material, but does not expressly teach the carbon nanotubes being ion conducting or the material further comprising a polymer among those recited in claim 6.

In the battery art, Gu teaches an electrolyte material comprising carbon nanotubes and a polymer from among those recited in claim 6 (see Gu abstract). Gu further teaches that the nanotubes themselves may be ion conducting (Section 3.3.3, 3rd paragraph).

It would have been obvious to a person having ordinary skill in the art at the time of invention to combine the carbon nanotubes with a polymer, such as a species among

those recited in claim 6, for the benefit of providing an electrolytic material having desirable ion conductivity as taught by Gu. Moreover, it would have been obvious to a skilled artisan at the time of invention to utilize carbon nanotubes which are ion conducting, as taught by Gu, for the benefit of enhancing the conductivity of the composite ion conducting electrolyte material.

25. **Regarding claim 10-11**, Bosynak does not expressly teach that the composition has an impedance of less than or equal to one billion ohm-m, or alternatively a charge transfer resistance of less than 10 million ohm-m.

Gu further teaches compositions having impedance [inverse of combined electronic + ionic conductivity] and charge transfer resistance [inverse of mixed conductivity] values within the claimed range as desirable for ensuring sufficient ionic transport (Introduction; Section 3.2).

It would have been obvious to a person having ordinary skill in the art at the time of invention to configure the material to have an impedance of less than or equal to one billion ohm-m, and a charge transfer resistance of less than 10 million ohm-m, for the benefit of providing desirable or at least adequate ionic conductivity as taught by Gu. Thus, the claimed range is found to be prima facie obvious since the range disclosed by the prior art overlaps within the claimed range, or otherwise is obvious as a matter of normal optimization as suggested by a section of Gu drawn to optimization of ionic conductivity. Note that the characterization of the material as a “binder” in claim 10 is found to be a non-limiting recitation of intended use because the claim does not recite

any additional structural or compositional features which cause the composition to perform as a binder.

26. Claims 7 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over the combination of Bosynak (CA 2747728, published 8/14/10; citations taken from US 2011/0294013), Johnson (US 2011/0104576), Gu ("Layered and interfacially blended polyelectrolyte…"; Thin Solid Films 520 2012 1872-1879; Published 9/16/11) and Rogers (USP 6143042).

27. **Regarding claims 7,** the cited art remains as applied to claim 2. Bosynak does not expressly teach the composition further including inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

In the battery art, Rogers teaches including inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements in a composition in order to enhance physical strength, melt viscosity and/or increase the level of electrolyte solution absorption of the composition (c7:33-38).

It would have been obvious to a person having ordinary skill in the art at the time of invention to include inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements in the composition of Bosynak in order to enhance physical strength, melt viscosity and/or increase the level of electrolyte solution absorption of the composition as taught by Rogers.

28. Claims 8-9 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over the combination of Bosynak (CA 2747728, published 8/14/10;

citations taken from US 2011/0294013), Johnson (US 2011/0104576), Gu ("Layered and interfacially blended polyelectrolyte…"; Thin Solid Films 520 2012 1872-1879; Published 9/16/11) and Schaefer (US 2013/0244119).

29. **Regarding claims 8-9,** the cited art remains as applied to claim 2. Bosynak does not expressly teach the composition wherein the carbon nanotubes are interspersed between graphene or graphene plates.

In the battery art, Schaefer teaches including graphene in a composition in order to increase mechanical stability (paragraph [0006, 0011]).

It would have been obvious to a person having ordinary skill in the art at the time of invention to interdisperse graphene particles or flakes between the carbon nanotubes of Bosynak for the benefit of improving mechanical stability at taught by Schaefer.

Allowable Subject Matter

30. Claims 18 is objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

31. The following is a statement of reasons for the indication of allowable subject matter: Regarding claim 18, the closest prior art is include in the art rejections above. The cited art does not does not appear to teach or fairly suggest the limitations of claims 18, (i.e. a distribution of carbon nanotube aspect ratios, wherein 40 to 90 % of the nanotubes have an apect ration of 30 to 70, and wherein 1 to 30% of the carbon

nanotubes have an aspect ratio of 80 to 140) in combination with the features of the corresponding independent claim and intervening claims.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to JEREMIAH R SMITH whose telephone number is (571)270-7005. The examiner can normally be reached on Mon-Fri: 9 AM-5 PM (EST).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Milton Cano can be reached on 571-272-1398. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a

USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/JEREMIAH R SMITH/
Primary Examiner, Art Unit 1723

Notice of References Cited	Application/Control No. 15/881,071	Applicant(s)/Patent Under Reexamination Bosnyak et al.	
	Examiner JEREMIAH R SMITH	Art Unit 1723	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-6143042-A	11-2000	Rogers; Marc W.	C08J7/02	29/623.1
*	B	US-20110104576-A1	05-2011	JOHNSON; Christopher S.	B82Y30/00	429/405
*	C	US-20110294013-A1	12-2011	Bosnyak; Clive P.	B82Y30/00	429/231.1
*	D	US-20130244119-A1	09-2013	Schaefer; Tim	H01M2/162	429/249
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N	CA 2747728	08-2010	CA	Bosynak	H01M4/625
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Gu ("Layered and interfacially blended polyelectrolyte…"; Thin Solid Films 520 2012 1872-1879; Published 9/16/11) (Year: 2011)
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/881,071	Bosnyak et al.
	Examiner	**Art Unit**
	JEREMIAH R SMITH	1723

CPC - Searched*		
Symbol	**Date**	**Examiner**

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	**Date**	**Examiner**
Considered IDS	10/11/2019	J.R. Smith
Considered history of parent 14/390902	10/11/2019	J.R. Smith
H01M2/14 H01M2/1606 H01M2/1613 H01M2/162 H01M2/1633 H01M2/164 H01M2/1653 (all keyword searched for carbon nanotube)	10/11/2019	J.R. Smith
further text based searching	10/11/2019	J.R. Smith

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**

/JEREMIAH R SMITH/ Primary Examiner, Art Unit 1723	

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	14/390902.app.	US-PGPUB; USPAT	OR	ON	2017/05/22 10:33
S2	11	("20080111110" | "6555945" | "20110163274" | "7070753" | "7070753" | "20090176082" | "20090200517" | "20110294013" | "20120068125" | "20100075231" | "20110311876" | "20050224764").PN.	US-PGPUB; USPAT	OR	ON	2017/05/22 10:34
S5	1	"WO 2010117392"	DERWENT	OR	ON	2017/05/22 10:38
S6	12	("20110104551" "20090317710" "7429371" "20050006623" "6114068" "6878361" "20070048619" "20070259994" "20090142666" "20080038635" "20090142665").pn. "20110294013"	US-PGPUB; USPAT	OR	ON	2017/05/22 10:39
S7	11	("20080111110" | "6555945" | "20110163274" | "7070753" | "7070753" | "20090176082" | "20090200517" | "20110294013" | "20120068125" | "20100075231" | "20110311876" | "20050224764").PN.	US-PGPUB; USPAT	OR	ON	2017/05/22 10:40
S8	7	"WO 2009155267" "WO 2012083358" "WO 2013011516" "WO 2011163129" "ep 1665446" "ep 1845124" "ep 2415839"	DERWENT	OR	ON	2017/05/22 10:44
S9	6	("20070104981" "20090317710" "20120068125" "20120183770" "20140127565" "20140162111").pn.	US-PGPUB; USPAT	OR	ON	2017/05/22 10:47
S10	1	"CA 2747728"	DERWENT	OR	ON	2017/05/22 14:52
S11	1	"8993161".pn.	US-PGPUB; USPAT	OR	ON	2017/05/22 15:02
S12	3	lead near3 acid near3 battery and (anode negative) same "polyvinyl alcohol" and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:49
S13	7	lead near3 acid near3 battery and (anode negative) same "polyvinyl alcohol" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:52
S14	9	(anode negative) same "polyvinyl alcohol" and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:57

S15	84	lead near3 acid near3 battery and (anode negative) same "polyvinyl alcohol"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:58
S16	1445	lead near3 acid near3 battery and (anode negative) same "sulfuric"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:58
S17	190	lead near3 acid near3 battery and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:59
S18	56	lead near3 acid near3 battery and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/05/22 15:59
S19	31	lead near3 acid near3 battery and (anode negative) same "sulfuric" and (anode negative) same "carbon nanotube" and (anode negative) same paste	US-PGPUB; USPAT	OR	ON	2017/05/22 15:59
S20	8	lead near3 acid near3 battery and (anode negative) same "sulfuric" same "carbon nanotube" same paste	US-PGPUB; USPAT	OR	ON	2017/05/22 16:01
S21	1	"20130157118"	DERWENT	OR	ON	2017/05/22 17:16
S22	1	"20120328940"	DERWENT	OR	ON	2017/05/22 17:37
S23	1	"20130022860"	DERWENT	OR	ON	2017/05/22 18:11
S24	113	"429".clas. and battery and "carbon nanotube" and nanotube with "aspect ratio"	US-PGPUB; USPAT	OR	ON	2017/05/23 11:03
S25	113	"429".clas. and battery and "carbon nanotube" and nanotube with "aspect ratio" and "aspect ratio"	US-PGPUB; USPAT	OR	ON	2017/05/23 11:04
S26	126	"429".clas. and battery and "carbon nanotube" and (cnt nt nanotube) with "aspect ratio" and "aspect ratio"	US-PGPUB; USPAT	OR	ON	2017/05/23 11:06
S27	1	"20150064538"	DERWENT	OR	ON	2017/05/23 11:39
S28	50	battery and "carbon nanotube" and (cnt nt nanotube) with "aspect ratio" and "aspect ratio"	EPO; JPO; DERWENT	OR	ON	2017/05/23 11:52
S32	27318	(H01M2/004, H01M2/04, H01M2/027, H01M2/1613 H01M4/14, H01M4/26, H01M4/38, H01M4/027, H01M4/622, H01M4/625 H01M10/24, H01M10/056, H01M10/05658 H01G4/16, H01G9/035, H01L31/022425).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:54
S33	7531	(H01L31/022425).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:54
S34	611	(H01G9/035,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:54
S35	26	(H01G4/16,).cpc.	US-	OR	ON	2017/05/23

			PGPUB; USPAT; EPO; JPO; DERWENT			12:55
S36	0	(H01M10/05658).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S37	1358	(H01M10/056,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S38	942	(H01M10/24,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S39	7097	(H01M4/625).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S40	4503	(H01M4/622,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S41	0	(H01M4/027,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:55
S42	4900	(H01M4/38,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S43	909	(H01M4/26,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S44	813	(H01M4/14,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S45	892	(H01M2/1613).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S46	514	(H01M2/027,).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:56
S47	597	(H01M2/04,,).cpc.	US-	OR	ON	2017/05/23

			PGPUB; USPAT; EPO; JPO; DERWENT			12:56
S50	2809	S32 and battery and (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:58
S51	2760	S32 and battery near3 (lead acid)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:58
S52	470	S50 and S51	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/05/23 12:58
S53	1816781	@pd>"20170523"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:09
S54	29368	(H01M2/004, H01M2/04, H01M2/027, H01M2/1613 H01M4/14, H01M4/26, H01M4/38, H01M4/027, H01M4/622, H01M4/625 H01M10/24, H01M10/056, H01M10/05658 H01G4/16, H01G9/035, H01L31/022425).cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:10
S55	3116	S54 and battery and (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:10
S56	383	S53 and S55	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:10
S57	464	lead near3 acid near3 battery and (cathode anode electrode) same "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/10/17 12:13
S58	45	(lead near3 acid near3 battery).clm. and (cathode anode electrode) with "carbon nanotube"	US-PGPUB; USPAT	OR	ON	2017/10/17 12:13
S59	46	(lead near3 acid near3 battery).clm. and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT	OR	ON	2017/10/17 12:14
S60	88	(lead near3 acid near3 battery) and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon).clm.	US-PGPUB; USPAT	OR	ON	2017/10/17 12:15
S61	120	S59 S60	US-PGPUB; USPAT	OR	ON	2017/10/17 12:16
S63	15	(S59 S60) and "aspect ratio"	US-PGPUB;	OR	ON	2017/10/17 12:17

			USPAT			
S64	14009	H01M4/625.cpc. H01M4/14.cpc. H01M10/06.cpc. H01M4/663.cpc. H01M4/96.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S65	7767	H01M4/625.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S66	869	H01M4/14.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S67	1737	H01M10/06.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:46
S68	1606	H01M4/663.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:47
S69	2967	H01M4/96.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:47
S70	2343	H01M4/14.cpc. H01M10/06.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2017/10/17 12:47
S71	21	S70 and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon).clm.	US-PGPUB; USPAT	OR	ON	2017/10/17 12:47
S72	44	S70 and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB; USPAT	OR	ON	2017/10/17 12:47
S73	5	S70 and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon) and (nanotube near3 carbon cnt nt near3 carbon) with ("aspect ratio" aspect$1ratio)	US-PGPUB; USPAT	OR	ON	2017/10/17 12:48
S77	1	15/881071.app.	US-PGPUB; USPAT	OR	ON	2019/10/07 17:03
S78	91	Bosnyak near2 Clive.in. Swogger near2 Kurt.in. Marinkovic near2 Milos.in.	US-PGPUB; USPAT	OR	ON	2019/10/08 12:07
S79	24	S78 and "aspect ratio".clm. and open.clm.	US-PGPUB; USPAT	OR	ON	2019/10/08 12:08
S80	7	S78 and "aspect ratio".clm. and open.clm.	USPAT	OR	ON	2019/10/08 12:08

S82	1	"cn 101734650"	DERWENT	OR	ON	2019/10/08 15:11
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S84	5062	S83 and battery and ((nt nanotube) near3 carbon cnt)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/08 16:12
S85	203	S83 and (separator electrolyte) near4 ((nt nanotube) near3 carbon cnt)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/08 16:13
S86	4	"20080254362"	US-PGPUB; USPAT	OR	ON	2019/10/08 16:49
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S88	2	"20110220574"	US-PGPUB; USPAT	OR	ON	2019/10/08 17:08
S89	33	("2011/0220574").URPN.	USPAT	OR	ON	2019/10/08 17:09
S90	4	S89 and battery	US-PGPUB; USPAT	OR	ON	2019/10/08 17:09
S91	2352	H01M2/14.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:08
S92	416	H01M2/1606.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:08
S93	1267	H01M2/1613.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:08
S94	2869	H01M2/162.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S95	427	H01M2/1633.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S96	319	H01M2/164.cpc.	US-PGPUB; USPAT;	OR	ON	2019/10/10 11:09

			EPO; JPO; DERWENT			
S97	8719	H01M2/1653.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S98	13771	H01M2/14.cpc. H01M2/1606.cpc. H01M2/1613.cpc. H01M2/162.cpc. H01M2/1633.cpc. H01M2/164.cpc. H01M2/1653.cpc.	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/10 11:09
S99	690	S98 and ((nt nanotube) near3 carbon cnt)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:10
S100	90	S99 and (inorganic near4 filler)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:10
S101	133	S98 and (inorganic with strength near4 separator)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:23
S102	48	S98 and (inorganic with strength near4 separator) and inorganic with (transition metal)	US-PGPUB; USPAT	OR	ON	2019/10/10 11:23
S103	11	S98 and (graphene near4 separator)	US-PGPUB; USPAT	OR	ON	2019/10/10 14:08
S104	0	("2009117467" "2012045688" "2011183180" "2012251881").pn.	US-PGPUB; USPAT	OR	ON	2019/10/10 14:13
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S109	204	jeremiah near2 smith .xp.	US-PGPUB; USPAT	OR	ON	2019/10/11 09:29
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S113	50661	(S110 S111)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 10:54

S114	124	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 10:55
S115	1	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio" and bimodal with "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:54
S116	1	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio" and (bi$1mod$3 bimodal) with "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:55
S117	1	S113 and ((nt nanotube) near3 carbon cnt) near4 "aspect ratio" and (bi$1modal bimodal) with "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:55
S118	9	S113 and ((nt nanotube) near3 carbon cnt) with "aspect ratio" and (bi$1modal bimodal) same "aspect ratio"	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 11:57
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S120	6	((nt nanotube) near3 carbon cnt).ab. and ((nt nanotube) near3 carbon cnt) near4 ("aspect ratio" near4 distribution)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 12:23
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S122	119	((nt nanotube) near3 carbon cnt).ab. and ((nt nanotube) near3 carbon cnt) near4 ("aspect ratio") and "aspect ratio" near4 (percent percentage amount "%" wt number weight)	US-PGPUB; USPAT; EPO; JPO; DERWENT	OR	ON	2019/10/11 12:32

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
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S75	30	(lead near3 acid near3 battery).clm. and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon)	US-PGPUB	OR	ON	2017/10/17 12:15
S76	60	(lead near3 acid near3 battery) and (cathode anode electrode) with (nanotube near3 carbon cnt nt near3 carbon).clm.	US-PGPUB	OR	ON	2017/10/17 12:15

10/ 11/ 2019 4:12:27 PM
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(71) Demandeurs/Applicants:
BOSNYAK, CLIVE P., US;
SWOGGER, KURT W., US

(72) Inventeurs/Inventors:
BOSNYAK, CLIVE P., US;
SWOGGER, KURT W., US

(74) Agent: KIRBY EADES GALE BAKER

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(54) Title: EXFOLIATED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

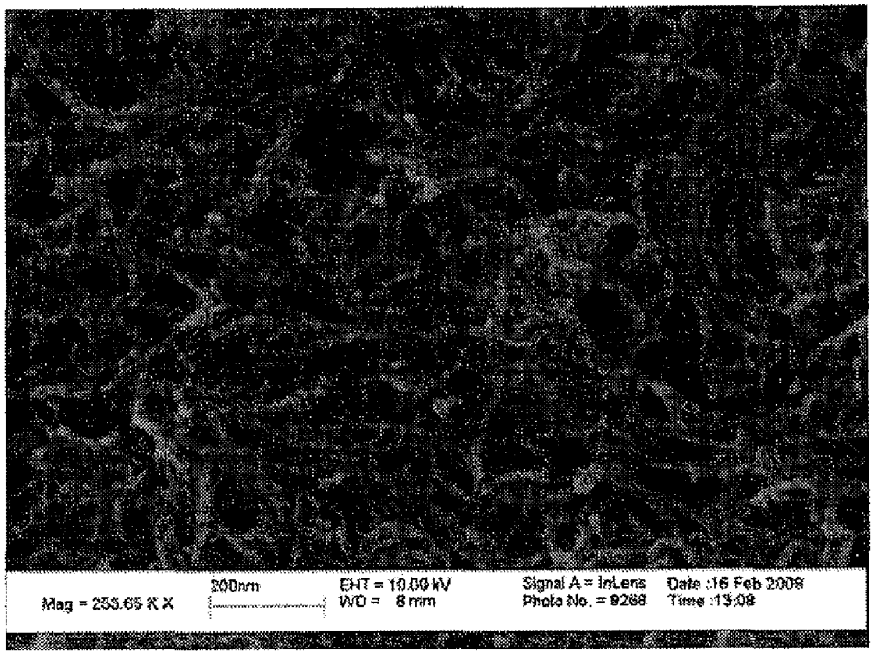

FIGURE 8

(57) Abrégé/Abstract:
In various embodiments, exfoliated carbon nanotubes are described in the present disclosure. The carbon nanotubes maintain their exfoliated state, even when not dispersed in a medium such as a polymer or a liquid solution. Methods for making the exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanocrystalline material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes. Nanocrystalline materials may include nanorods, hydroxyapatite and various hydroxyapatite derivatives. In some embodiments, methods for making exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated

(57) **Abrégé(suite)/Abstract(continued):**
carbon nanotubes on the filter. In some embodiments, a concentration of carbon nanotubes in the acid is below the percolation threshold. In other various embodiments, energy storage devices and polymer composites containing exfoliated carbon nanotubes are described herein. The energy storage device may be a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes in the energy storage device advantageously contains exfoliated carbon nanotubes. The polymer composites are prepared by mixing exfoliated carbon nanotubes with a polymer material. After being mixed in the polymer material, the carbon nanotubes maintain their exfoliated state.

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(72) Inventors; and
(71) Applicants : **BOSNYAK, Clive, P.** [US/US]; 12001 Settlers Trail, Dripping Springs, TX 78620 (US). **SWOGGER, Kurt, W.** [US/US]; 4211 Waters Edge Cv., Austin, TX 78731 (US).

(74) Agent: **THRASH, Thomas, P.**; Winstead Pc, P.O. Box 50784, Dallas, TX 75201 (US).

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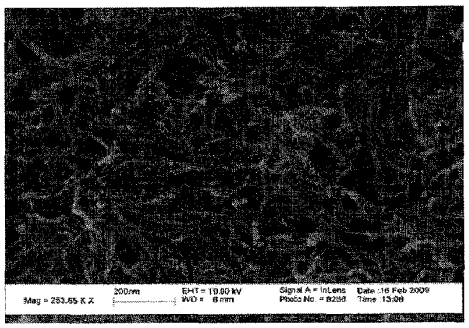

FIGURE 8

(57) Abstract: In various embodiments, exfoliated carbon nanotubes are described in the present disclosure. The carbon nanotubes maintain their exfoliated state, even when not dispersed in a medium such as a polymer or a liquid solution. Methods for making the exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanocrystalline material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes. Nanocrystalline materials may include nanorods, hydroxyapatite and various hydroxyapatite derivatives. In some embodiments, methods for making exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, a concentration of carbon nanotubes in the acid is below the percolation threshold. In other various embodiments, energy storage devices and polymer composites containing exfoliated carbon nanotubes are described herein. The energy storage device may be a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes in the energy storage device advantageously contains exfoliated carbon nanotubes. The polymer composites are prepared by mixing exfoliated carbon nanotubes with a polymer material. After being mixed in the polymer material, the carbon nanotubes maintain their exfoliated state.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PATENT APPLICATION

EXFOLIATED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

INVENTORS:

Clive P. Bosnyak
Citizen of the United States

Kurt W. Swogger
Citizen of the United States

Filed Via EFS-Web on December 18, 2009

EXFOLIATED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States provisional patent applications 61/138,551, filed December 18, 2008, and 61/139,050, filed December 19, 2008, each of which is incorporated by reference herein in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] Not applicable

BACKGROUND

[0003] Carbon nanotubes in their solid state are currently produced as agglomerated nanotube bundles in a mixture of chiral forms. Current technologies cannot fully exfoliate bundles of carbon nanotubes to produce individualized carbon nanotubes in the solid state without significant chemical and physical property modifications taking place to the carbon nanotubes. Additionally, there are currently no effective methods to separate carbon nanotubes on a bulk scale by length, diameter, chirality, or a combination thereof.

[0004] Various methods have been developed to debundle carbon nanotubes in solution. For example, carbon nanotubes may be shortened by oxidative means and then dispersed as individual nanotubes in solution. Carbon nanotubes may also be dispersed in solution as individuals by sonication in the presence of a surfactant. Illustrative surfactants used for dispersing carbon nanotubes in solution include, for example, sodium dodecyl sulfate and PLURONICS. In some instances, solutions of individualized carbon nanotubes may be prepared from polymer-wrapped carbon nanotubes. Individualized single-wall carbon nanotube solutions have also been prepared using polysaccharides, polypeptides, water-soluble polymers, nucleic acids, DNA, polynucleotides, polyimides, and polyvinylpyrrolidone.

[0005] A number of uses for carbon nanotubes have been proposed including, for example, energy storage devices (e.g., ultracapacitors, supercapacitors and batteries), field emitters, conductive films, conductive wires and membrane filters. Use of carbon nanotubes as a

reinforcing agent in polymer composites is another area in which carbon nanotubes are predicted to have significant utility. However, utilization of carbon nanotubes in these applications has been hampered due to the general inability to reliably produce individualized carbon nanotubes. For example, load transfer to carbon nanotubes in polymer composites is typically less than would be expected than if the carbon nanotubes were fully exfoliated as individual nanotubes.

[0006] Likewise, in applications involving electrical conduction, conductivity is lower than anticipated due to reduced access to the carbon nanotube's surface when the carbon nanotubes are agglomerated as opposed to being dispersed as individuals. Furthermore, when mixtures of conducting and non-conducting or semiconducting carbon nanotubes (i.e., carbon nanotubes having a mixture of chiralities) are used in applications involving electrical conduction, conductivity is less than could be achieved were all the carbon nanotubes electrical conductors. As noted above, current methods for producing exfoliated carbon nanotubes usually results in shortening or functionalization of the nanotubes. Such shortening or functionalization also generally results in reduced conductivity, which is also disadvantageous for applications where high electrical conductivity is beneficial.

[0007] In view of the foregoing, solid exfoliated carbon nanotubes and methods for efficiently exfoliating carbon nanotubes without nanotube damage are of considerable interest in the art. Such exfoliated carbon nanotubes are likely to exhibit considerably improved properties in applications including, for example, energy storage devices and polymer composites. Further separation of the exfoliated carbon nanotubes by chirality, length, diameter, or a combination thereof would also be of considerable interest in the art to further take advantage of their properties.

SUMMARY

[0008] In various embodiments, compositions of exfoliated carbon nanotubes are disclosed herein. The exfoliated carbon nanotubes are dispersed in the solid state such as, for example, a mat of dispersed carbon nanotubes. The exfoliated carbon nanotubes are maintained in an exfoliated state without being dispersed in a continuous matrix such as, for example, a polymer matrix dispersant or a solution.

[0009] In other various embodiments, methods for preparing exfoliated carbon nanotubes are disclosed herein.

[0010] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a first quantity of a nanocrystalline material, precipitating a first quantity of exfoliated carbon nanotubes from the solution and isolating the first quantity of exfoliated carbon nanotubes.

[0011] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0012] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanorod material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0013] In some embodiments, the methods for preparing exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter.

[0014] In still other various embodiments, energy storage devices containing exfoliated carbon nanotubes are disclosed herein. In some embodiments, the energy storage device is a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes contains exfoliated carbon nanotubes.

[0015] In yet additional various embodiments, methods for making a polymer composite are disclosed herein. The methods include a) providing exfoliated carbon nanotubes and b) mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite. The exfoliated carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

[0016] The foregoing has outlined rather broadly various features of the present disclosure in order that the detailed description that follows may be better understood. Additional features and advantages of the disclosure will be described hereinafter, which form the subject of the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] For a more complete understanding of the present disclosure, and the advantages thereof, reference is now made to the following descriptions to be taken in conjunction with the accompanying drawings describing specific embodiments of the disclosure, wherein:

[0018] FIGURE 1 shows an illustrative arrangement of the basic elements of a Faradaic capacitor;

[0019] FIGURE 2 shows an illustrative arrangement of the basic elements of an electric double layer capacitor;

[0020] FIGURE 3 shows an illustrative arrangement of the basic elements of a battery;

[0021] FIGURE 4 shows an illustrative electron micrograph of hydroxyapatite plates having diameters of 3 – 15 μm;

[0022] FIGURE 5 shows an illustrative electron micrograph of hydroxyapatite nanorods having lengths of 100 – 200 nm;

[0023] FIGURE 6A shows an illustrative electron micrograph of as-received multi-wall carbon nanotubes; FIGURE 6B shows an illustrative electron micrograph of multi-wall carbon nanotubes exfoliated using hydroxyapatite nanorods;

[0024] FIGURE 7A shows an illustrative EDX spectrum of precipitated exfoliated, multi-wall carbon nanotubes; FIGURE 7B shows an illustrative EDX spectrum of precipitated, exfoliated multi-wall carbon nanotubes after acid washing;

[0025] FIGURE 8 shows an illustrative electron micrograph of exfoliated multi-wall carbon nanotubes after precipitation and washing;

[0026] FIGURE 9 shows an illustrative electron micrograph of exfoliated carbon nanotubes obtained from 3:1 H_2SO_4:HNO_3;

[0027] FIGURE 10 shows an illustrative electron micrograph of exfoliated double-wall carbon

nanotubes following acid exfoliation and treatment with sodium dodecyl sulfate; and

[0028] FIGURE 11 shows an illustrative electron micrograph of exfoliated carbon nanotubes decorated with copper oxide nanoparticles.

DETAILED DESCRIPTION

[0029] In the following description, certain details are set forth such as specific quantities, sizes, etc. so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be evident to those of ordinary skill in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

[0030] Referring to the drawings in general, it will be understood that the illustrations are for the purpose of describing particular embodiments of the disclosure and are not intended to be limiting thereto. Drawings are not necessarily to scale.

[0031] While most of the terms used herein will be recognizable to those of ordinary skill in the art, it should be understood, however, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of ordinary skill in the art. In cases where the construction of a term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition, 2009. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification or if the incorporation is necessary for maintaining validity.

[0032] Various embodiments presented hereinbelow reference carbon nanotubes. In particular, in various embodiments, bundled carbon nanotubes can be debundled according to the methods described herein to produce exfoliated carbon nanotube solids. The carbon nanotubes being debundled can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis (HiPco). The bundled carbon

nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting or non-metallic based on their chirality and number of walls. In various embodiments, the bundled and/or exfoliated carbon nanotubes may include, for example, single-wall carbon nanotubes (SWNTs), double-wall carbon nanotubes (DWNTs), multi-wall carbon nanotubes (MWNTs), shortened carbon nanotubes, oxidized carbon nanotubes, functionalized carbon nanotubes, and combinations thereof. One of ordinary skill in the art will recognize that many of the specific embodiments referenced hereinbelow utilizing a particular type of carbon nanotube may practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

[0033] Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof. In some embodiments, the carbon nanotubes may be functionalized before being exfoliated. In other embodiments, the carbon nanotubes are functionalized after being exfoliated.

[0034] In some embodiments, the carbon nanotubes may be further associated or functionalized with an electroactive material. In some embodiments, an electroactive material may be transition metals or oxides of transition metals such as, for example, Ru, Ir, W, Mo, Mn, Ni and Co. In some embodiments, the electroactive material may be a conducting polymer such as, for example, polyaniline, polyvinylpyrrole or polyacetylene. In some embodiments, the electroactive material may be a nanoparticle or plurality of nanoparticles bound to the carbon nanotubes. For example, in some embodiments, an electroactive nanoparticle may include materials such as SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof. Carbon nanotubes associated or functionalized with an electroactive material may be particularly advantageous for applications involving electrical conductivity.

[0035] Any of the embodiments herein referencing carbon nanotubes may also be modified within the spirit and scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure. In various embodiments, the nanotubes may include elements such as, for example, carbon, silicon, boron and nitrogen. In further embodiments, the inorganic or mineral nanotubes may also include metallic and non-metallic elements. For example, in some embodiments, the inorganic or mineral nanotubes can be associated with metals, organic compounds, and inorganic compounds. Association may be on the interior or exterior of the inorganic or mineral nanotubes. Exterior association may be a physical association, such as, for example, van der Waals association. Exterior association of these materials may also include either ionic or covalent bonding to the nanotube exterior.

[0036] In various embodiments, the present disclosure describes compositions containing exfoliated carbon nanotubes. The exfoliated carbon nanotubes are not dispersed in a continuous matrix that maintains the carbon nanotubes in an exfoliated state. Illustrative continuous matrices include, for example, a solution or a polymer matrix that maintains the carbon nanotubes in at least a partially or substantially exfoliated state. In various embodiments, the exfoliated carbon nanotubes comprise a carbon nanotube mat. As such, the exfoliated carbon nanotubes of the present disclosure are distinguished over exfoliated carbon nanotubes presently known in the art, which may re-agglomerate once removed from solution.

[0037] The exfoliated carbon nanotubes of the present disclosure take advantage of physical properties offered by individual carbon nanotubes that are not apparent when the carbon nanotubes are aggregated into bundles. For example, in various embodiments, the exfoliated carbon nanotubes may be advantageously used in a wide range of applications including capacitors, batteries, photovoltaics, sensors, membranes, static dissipators, electromagnetic shields, video displays, pharmaceuticals and medical devices, polymer composites and gas storage vessels. In various embodiments, the exfoliated carbon nanotubes may also be used in fabrication and assembly techniques including, for example, ink-jet printing, spraying, coating, melt extruding, thermoforming, blow-molding and injection molding.

[0038] In various embodiments, the exfoliated carbon nanotubes may be single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes and various combinations thereof. In some embodiments, the carbon nanotubes are full-length carbon nanotubes. That is, in embodiments having full-length carbon nanotubes, the exfoliated carbon nanotubes are about the same length as the as-grown carbon nanotubes from which they are produced, and the carbon nanotube ends are generally closed in certain various embodiments. However, in other various embodiments, the carbon nanotubes are full-length carbon nanotubes that have open ends.

[0039] In some embodiments, the carbon nanotubes are substantially free of catalytic residues, non-nanotube carbon and various combinations thereof. In some embodiments, the carbon nanotubes are purified to remove catalytic residues and non-nanotube carbon. Such purification may take place either before or after the exfoliation of the carbon nanotubes takes place.

[0040] In some embodiments, the exfoliated carbon nanotubes are selectively precipitated by diameter. In various embodiments, exfoliated carbon nanotubes generally have a diameter of between about 0.7 nm and about 20 nm. Single-wall carbon nanotubes are generally about 0.7 nm to about 10 nm in diameter, whereas multi-wall nanotubes are generally greater than about 10 nm in diameter and up to about 100 nm in diameter in some embodiments. In some embodiments, the exfoliated carbon nanotubes have a diameter between about 1 nm and about 10 nm. In some embodiments, the exfoliated carbon nanotubes have a diameter between about 10 nm and about 100 nm.

[0041] In some embodiments, the exfoliated carbon nanotubes are selectively precipitated by length. The carbon nanotube length varies between about 500 nm and about 10 mm in some embodiments, between about 500 nm and 1 mm in some embodiments, between about 500 nm and 500 μm in some embodiments, between about 500 nm and 1 μm in some embodiments and various subranges thereof. In some embodiments, the exfoliated carbon nanotubes have an average length that is not substantially different than that of the bundled carbon nanotubes from which they are produced. That is, in some embodiments, the carbon nanotubes are full length carbon nanotubes that are not shortened during exfoliation. In some embodiments, the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes, and the exfoliated carbon

nanotubes have a narrower distribution of lengths than do the bundled carbon nanotubes. That is, a subrange of exfoliated carbon nanotube lengths may be obtained from a population of bundled carbon nanotubes having a distribution of lengths.

[0042] The carbon nanotubes have a length to diameter ratio (aspect ratio) of least about 100 in some embodiments and at least about 1000 in other embodiments. In some embodiments, the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes, and the exfoliated carbon nanotubes have a narrower distribution of diameters than do the bundled carbon nanotubes. That is, a subrange of exfoliated carbon nanotube diameters may be obtained from a population of bundled carbon nanotubes having a distribution of diameters.

[0043] In various embodiments, the exfoliated carbon nanotubes are further separated by chirality. For example, in the process of exfoliating bundled carbon nanotubes, exfoliated carbon nanotubes of a specific chirality or range of chiral forms may be produced. For example, in some embodiments, the exfoliated carbon nanotubes produced may be metallic, semi-metallic or semiconducting.

[0044] In some embodiments, the exfoliated carbon nanotubes are further functionalized. Functionalization may take place either before or after exfoliation. However, Applicants envision that functionalization after exfoliation may be advantageous to take advantage of the greater surface area available in the exfoliated carbon nanotubes compared to their bundled counterparts. In some embodiments, the exfoliated carbon nanotubes are functionalized to include an electroactive material bound to the carbon nanotubes, as set forth in more detail hereinabove.

[0045] Methods for exfoliating carbon nanotubes are also described herein. In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a first quantity of a nanocrystalline material, precipitating a first quantity of exfoliated carbon nanotubes from the solution and isolating the first quantity of exfoliated carbon nanotubes.

[0046] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0047] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanorod material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0048] In some embodiments of the methods, the carbon nanotubes may be further oriented in an alignment step after isolating the exfoliated carbon nanotubes. In some embodiments, the exfoliated carbon nanotubes may be shaped into a form such as, for example, a mat, film, fiber, cloth, non-woven fabric or felt.

[0049] An illustrative process for exfoliating carbon nanotubes follows. Carbon nanotubes can be effectively exfoliated using nanoplates of zirconium phosphate treated with a surfactant such as, for example, tetrabutylammonium hydroxide. The carbon nanotubes and the nanoplates are sonicated for short times to obtain full exfoliation of the carbon nanotubes in aqueous media. By controlling the ionic strength of the mixture after sonication, exfoliated carbon nanotubes can be obtained by simple separation techniques such as, for example, centrifugation. The carbon nanotubes after centrifuging and separating exist in a disordered but non-aggregated state and can easily be resuspended with other surfactant addition. Suitable surfactants for resuspension include, for example, both ionic and non-ionic surfactants, such as, for example, polyvinyl pyrrolidone, sodium dodecyl sulfate and PLURONICS. Cationic surfactants may be used for dispersion in non-polar media, such as chloroform and toluene. Application of an electric potential to the suspension may be used alternatively to or in combination with adjusting the ionic strength.

[0050] Although the above process may be used to cleanly separate single-wall carbon nanotubes, multi-wall carbon nanotubes and particularly oxidized multi-wall carbon nanotubes may not be separated as cleanly due to their broader range of ionic potentials. As a result, it is difficult to achieve separation of zirconium phosphate from the exfoliated carbon nanotubes when multi-wall carbon nanotubes are used. Furthermore, zirconium phosphate is particularly difficult to dissolve in acids (solubility = 0.12 mg/L in 6 M HCl), and it cannot typically be

removed by simple acid washing even after isolating the exfoliated carbon nanotubes. However, other various embodiments of the present disclosure are particularly applicable for exfoliating multi-wall carbon nanotubes.

[0051] In various embodiments, the methods for preparing exfoliated carbon nanotubes further include utilizing a solution that contains both a surfactant and a quantity of a nanocrystalline material. Surfactants are well known in the carbon nanotube art to aid in solubilization. Without being bound by theory or mechanism, Applicants believe that when a surfactant is used in preparing exfoliated carbon nanotubes, the surfactant may aid in the initial solubilization or suspension of the carbon nanotubes. Precipitation of exfoliated carbon nanotubes takes place thereafter. In various embodiments of the present disclosure, the surfactant may include, for example, sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, or tetralkylammonium hydroxide (e.g., tetrabutylammonium hydroxide). In some embodiments, the surfactant may also modify the surface of the nanocrystalline material used for exfoliating the carbon nanotubes.

[0052] In general, exfoliated carbon nanotubes are prepared according to some embodiments of the present disclosure by precipitating exfoliated carbon nanotubes from a solution containing a nanocrystalline material. In some embodiments, the ionic strength of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, the electrical potential of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, the pH of the solution is adjusted to induce precipitation of exfoliated carbon nanotubes. In some embodiments, a combination of ionic strength, electrical potential and/or pH is adjusted to induce precipitation of exfoliated carbon nanotubes.

[0053] In some embodiments, the methods for exfoliating carbon nanotubes include adding a release species to the carbon nanotube suspension to adjust the ionic strength and precipitate exfoliated carbon nanotubes. In some embodiments, the ionic strength can be adjusted with an ionic species such as, for example, a solution of KCl. Although one of ordinary skill in the art will recognize the benefits of using an ionic species for adjustment of ionic strength, non-ionic species such as organic compounds may be used for ionic strength adjustment as well. Release species may be organic or inorganic compounds. In some embodiments, an electromagnetic field can be applied to the suspension of exfoliated carbon nanotubes in lieu of or in combination

with adjustment of the ionic strength with a release species to induce precipitation of the exfoliated carbon nanotubes.

[0054] After precipitation, exfoliated carbon nanotubes can be isolated by simple separation techniques such as, for example, centrifuging, filtering or settling. The separated, exfoliated carbon nanotubes exist in a disordered but non-aggregated state and can be easily redispersed in various media such as, for example, a liquid or polymer melt. In some embodiments, the redispersion may be aided by addition of a surfactant. Suitable surfactants include, but are not limited, to both ionic and non-ionic surfactants, sodium dodecyl sulfate, sodium dodecylbenezene sulfonate, and PLURONICS. Cationic surfactants are chiefly used for dispersion in non-polar media, such as, for example, chloroform and toluene. As noted above, other types of molecules such as, for example, cyclodextrins, polysaccharides, polypeptides, water soluble polymers, DNA, nucleic acids, polynucleotides, and polymers such as polyimides and polyvinyl pyrrolidone, can be used to redisperse the exfoliated carbon nanotubes in some embodiments.

[0055] In some embodiments, a second quantity of exfoliated carbon nanotubes may be precipitated from the suspension of carbon nanotubes. For example, in an embodiment, adding a second quantity of nanocrystalline material to the suspension results in precipitation of a second quantity of exfoliated carbon nanotubes. In some embodiments, the first quantity of carbon nanotubes and the second quantity of carbon nanotubes have different properties from one another such as, for example, different average lengths, diameters or chiralities. Repeated precipitation of carbon nanotube fractions may be repeated as many times as desired.

[0056] In some embodiments, the methods further include removing residual nanocrystalline material from the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes remain exfoliated after removing the nanocrystalline material. Hence, once the carbon nanotubes become fully exfoliated, they are no longer prone to becoming bundled. In some embodiments, the nanocrystalline material may be removed by washing the exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be washed with an acid to remove the nanocrystalline material.

[0057] The redispersability of the carbon nanotubes after removal of the nanocrystalline material may be controlled by changing the surfactant concentration and the rate of addition of the release species. Hence, the redispersibility may be controlled by changing the rate of precipitation of exfoliated carbon nanotubes. In other words, in some embodiments the kinetic rate of carbon nanotube precipitation influences the rate of their redissolution following removal of the nanocrystalline material.

[0058] In general, the nanocrystalline materials of the present disclosure include any amorphous or crystalline material of nanometer-scale dimensions. In general, according to embodiments of the present disclosure, a nanocrystalline material is of nanometer-scale dimensions if it has at least one measured dimension that is less than about 1000 nm. In various embodiments of the present disclosure, carbon nanotubes are exfoliated from bundles of carbon nanotubes using a nanocrystalline material having a crystalline form such as, for example, nanorods, nanoplates, or nanowhiskers, to intersperse between individual carbon nanotubes. Nanorods include any inorganic or organic compound that may be induced to crystallize in a rod-like crystalline form. Nanowhiskers include any inorganic or organic compound that may be induced to crystallize in a whisker-like crystalline form. In various embodiments, the nanocrystalline material may include, for example, clays, graphite, inorganic crystalline materials, organic crystalline materials and various combinations thereof.

[0059] In some embodiments, the methods for preparing exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing hydroxyapatite, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes.

[0060] In various embodiments, the nanocrystalline material may be, for example, hydroxyapatite and hydroxyapatite derivatives. Hydroxyapaptite derivatives include, for example, fluorapatite. In some embodiments, the hydroxyapatite has a crystalline form such as, for example, nanorods, nanoplates and nanowhiskers. In some embodiments, the methods further include removing the hydroxyapatite from the exfoliated carbon nanotubes. In some embodiments, removing can be accomplished, for example, through washing the exfoliated carbon nanotubes with an acid after their being isolated.

[0061] Various sizes of the nanocrystalline material may be used to exfoliate the carbon nanotubes. In some embodiments, the nanocrystalline material may be equal to or larger in size than the longest carbon nanotube present in the sample before exfoliation. In such embodiments, the exfoliated carbon nanotubes can be obtained in discrete fractions following addition of a release species such as, for example, KCl. In other embodiments, the nanocrystalline material has a size that is equal to or less than the longest carbon nanotube present in the sample before exfoliation. In this case, carbon nanotubes equal to or less than the size of the nanocrystalline material may be separated from the carbon nanotube suspension. In various embodiments, larger or smaller sizes of nanocrystalline material can be added to the carbon nanotube suspension to exfoliate carbon nanotube fractions having various carbon nanotube sizes.

[0062] In various embodiments, the exfoliated carbon nanotubes are further purified to remove impurities such as, for example, residual metal catalyst and non-nanotube carbon residue. With exfoliated carbon nanotubes, further purification is more easily conducted than like purifications conducted on bundled carbon nanotubes due to the comparatively greater surface area present in the exfoliated carbon nanotubes. Purification techniques include conventional techniques such as, for example, oxidation at elevated temperature (e.g., about 200°C to about 400°C) or acid extraction to remove metallic impurities. Illustrative acids that may be used to extract metallic impurities from the exfoliated carbon nanotubes include, for example, various concentrations of hydrochloric, hydrobromic, nitric, chlorosulfonic and phosphoric acids and various combinations thereof. In general, the acid and impurities are removed from the exfoliated carbon nanotubes by rinsing with water, organic solvents or combinations thereof. In some embodiments, supercritical fluids such as, for example, highly compressed CO_2 or hydrocarbons such as, for example, propane or butane, may also be employed to remove impurities from the exfoliated carbon nanotubes.

[0063] In various embodiments, the methods for producing exfoliated carbon nanotubes further include derivatization of the exfoliated carbon nanotubes with at least one functional group. Derivatization may occur either before or after exfoliation has occurred. Numerous methods to derivatize carbon nanotubes are known to those of ordinary skill in the art. For example, diazonium chemistry can be utilized to introduce alkyl or aryl groups, either of which may bear further functionalization, on to the carbon nanotubes. In additional embodiments, treating

nanotubes with lithium in liquid ammonia, followed by reaction with an alkyl halide may be used to alkylate carbon nanotubes. Reaction of fluorinated carbon nanotubes with ammonia or amines in the presence of a catalyst such as, for example, pyridine, may be used to functionalize the nanotubes through amine-bearing functionalities. Likewise, fluorinated carbon nanotubes may be functionalized with hydroxyl-containing moieties, which may be functionalized to bear an ether linkage OR, wherein R may be any combination of alkyl, aryl, acyl, and arylacyl groups. Furthermore, R may be further functionalized, for example, with halogens, thiols, amino groups and other common organic functionalities. In addition, the carbon nanotubes may be directly functionalized with thiols, alkyl substituted thiols, aryl substituted thiols, and halogens.

[0064] In some embodiments, the first quantity or second quantity of exfoliated carbon nanotubes are selectively precipitated by a physical property such as, for example, chirality, diameter or length. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanoplates and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanorods and then further separated by chirality, nanotube length, or nanotube diameter. In various embodiments, carbon nanotubes are exfoliated using a nanocrystalline material in the form of nanowhiskers and then further separated by chirality, nanotube length, or nanotube diameter. Regardless of how the exfoliated carbon nanotubes are prepared, separation by chirality, length or diameter may be more facile in some instances after the carbon nanotubes are exfoliated.

[0065] In some embodiments, a direct separation of carbon nanotubes by chirality, length or diameter may be accomplished by choice of the nanocrystalline material in combination with additional agents. For example, using a nanocrystalline material either alone or in combination with chiral surfactants and/or polymers may allow exfoliated carbon nanotubes to be separated based on length, diameter, chirality, type, and functionality such as, for example, oxidation state and/or defect structure.

[0066] In some embodiments, the suspension of carbon nanotubes further includes a chiral agent, resulting in selective precipitation of exfoliated carbon nanotubes by chirality. Chiral agents include, for example, surfactants, polymers and combinations thereof. Chiral agents include

molecules such as, for example, R,R-tartaric acid, which has been useful for separation of enantiomeric drugs in electrokinetic chromatography, and enantiomers of polylactic acid. Other molecules which are conventionally used in chiral separations also lie within the spirit and scope of the present disclosure. In some embodiments, the chiral agents may be used to separate exfoliated carbon nanotubes of a single chirality or a limited number of chiral configurations from a mixture of carbon nanotubes containing a range of carbon nanotube chiralities. In some embodiments, the chiral agent may be a surfactant that both helps disperse the carbon nanotubes and facilitates the chiral separation. The chiral agent may be associated with or chemically bound to the carbon nanotube surface. In some embodiments, carbon nanotubes separated by chirality also are separated by electronic type (i.e., metallic, semi-metallic and semiconducting).

[0067] By using polymers and/or surfactants having a defined chirality, separated populations of exfoliated metallic, semi-metallic, or semi-conducting carbon nanotubes can be obtained in some embodiments of the present disclosure. Without being bound by mechanism or theory, Applicants believe that polymers and/or surfactants of defined chirality preferentially wrap a carbon nanotube of a complementary chirality type. By selective carbon nanotube precipitation as described hereinabove, carbon nanotubes may be selectively separated by chirality. Selective carbon nanotube precipitation may occur either in the presence or absence of a nanocrystalline material. In some embodiments, separation techniques such as, for example, solvent/non-solvent addition, co-surfactant addition, and differential temperature gradients may be used to selectively precipitate a chiral population of carbon nanotubes.

[0068] In various embodiments, chiral polymers and/or surfactants may be mixtures of tactic molecules. By using tactic polymers with a low thermal degradation temperature, isolated, exfoliated carbon nanotubes can be easily recovered by thermal degradation of the polymer. Illustrative tactic polymers include, for example, atactic polystyrene, iostactic polystyrene, syndiotactic polystyrene, d and l polylactic acid, d and l polypropylene carbonate and the like. For example, polypropylene carbonate can be thermally degraded at less than about 300°C without damaging carbon nanotubes. In further embodiments, the tactic molecules may be a mixture dissolved in a hydrocarbon solvent such as, for example, toluene or decalin. In still further embodiments, the carbon nanotubes in the polymers can be oriented or aligned by various methods known to those of ordinary skill in the art.

[0069] The technique of separating carbon nanotubes by chirality by using a chiral polymer may be further extended to a chromatography column for continuous separation. For example, carbon nanotubes wrapped in a chiral polymer may be applied to a chromatography column and then be separated by chirality. Alternatively, a suspension of exfoliated carbon nanotubes lacking a chiral agent may be applied to a chromatography column having a chiral stationary phase. In these alternative embodiments, separation by chirality is based on a selective interaction of the chiral stationary phase with the various carbon nanotube chiralities.

[0070] In still further embodiments, exfoliated carbon nanotubes either with or without a wrapping of chiral polymers and/or surfactants may be separated by electronic type by applying an electric potential to a solution of exfoliated carbon nanotubes. For example, exfoliated metallic carbon nanotubes will migrate toward the potential for collection and separation.

[0071] In some embodiments of the present disclosure, alternative methods for producing exfoliated carbon nanotubes not utilizing a nanocrystalline material are disclosed. In some embodiments, the methods for producing exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, the acid is sulfuric acid. In some embodiments, the acid is a mixture of nitric acid and sulfuric acid. In some embodiments, the acid is a superacid. In some embodiments, the superacid is chlorosulfonic acid.

[0072] In general, the acid solutions used in preparing dispersed carbon nanotubes have a concentration of carbon nanotubes that is below the percolation threshold of carbon nanotubes in the acid. Filtration of such acid solutions of exfoliated carbon nanotubes produces a mat of exfoliated carbon nanotubes on the filter in various embodiments of the present disclosure. Although some acids and superacids are known to dissolve and exfoliate bundles of carbon nanotubes in solution, particularly when a liquid crystalline phase is formed, Applicants believe that there has been no recognition in the art the exfoliation can be maintained upon removal of the acid solvent. The mat of exfoliated carbon nanotubes may be further modified on the filter in some embodiments of the present disclosure. For example, in some embodiments, the mat of exfoliated carbon nanotubes may be modified by functionalizing or treating with a surfactant to maintain the carbon nanotubes in an exfoliated state. The exfoliated carbon nanotubes may be

subsequently removed from the filter. In addition, the exfoliated carbon nanotubes may be further processed according to any of the methods described hereinabove.

[0073] The exfoliated carbon nanotubes prepared by the techniques described hereinabove are typically longer than are carbon nanotubes exfoliated using existing technology. For instance, as described previously, other separation techniques often result in carbon nanotube damage and shortened carbon nanotube lengths. In certain applications, particularly those involving electrical conduction or mechanical reinforcement, shorter carbon nanotubes may not provide adequate electrical conductivity or structural integrity. For example, by having at least a portion of longer carbon nanotubes present with electrical devices such as energy storage device, a higher degree of electrical connectivity at a fixed carbon nanotube volume fraction can be achieved. Furthermore, longer carbon nanotube lengths may increase the toughness of the polymer composites over those made with shorter carbon nanotubes.

[0074] The present disclosure also relates to improved energy storage devices containing exfoliated carbon nanotubes and particularly to capacitors, supercapacitors, ultracapacitors and batteries having components containing exfoliated carbon nanotubes. The improved energy storage devices include components such as, for example, current collectors, electrodes, insulators, electrolytes and separators, each capable of containing exfoliated carbon nanotubes. In some embodiments, the improved energy storage devices have at least one of at least two electrodes containing exfoliated carbon nanotubes. The improved energy storage devices also include a dielectric medium or electrolyte, each optionally including carbon nanotubes. The improved energy storage devices have a high energy density and power density.

[0075] FIGURE 1 shows an illustrative arrangement of the basic elements of a Faradaic capacitor. As shown in FIGURE 1, current collectors **1** and **5** contact with electrodes **2** and **4**, which are separated by dielectric **3**. In an embodiment of the present disclosure, at least one of the electrodes **2** and **4** contains exfoliated carbon nanotubes. In various embodiments, current collectors **1** and **5** can be metals such as, for example, copper and other highly conductive metals. In some embodiments, the current collectors can contain conductive exfoliated carbon nanotubes. In an embodiment, the carbon nanotubes may be full length exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic carbon

nanotubes. In various embodiments, at least one of electrodes **2** and **4** contains exfoliated carbon nanotubes.

[0076] FIGURE 2 shows an illustrative arrangement of the basic elements of an electric double layer capacitor. As shown in FIGURE 2, current collectors **11** and **17** contact electrodes **12** and **16**, and electrolytes **13** and **15** contact electrodes **12** and **16**. Non-conducting separator **14** separates electrolytes **13** and **15** and is permeable to ions flowing between the electrodes **12** and **16**. In some embodiments, current collectors **11** and **17** can be metals such as, for example, copper and like conductive metals. In some embodiments, current collectors **11** and **17** contain exfoliated carbon nanotubes. In some embodiments, the carbon nanotubes may be separated metallic carbon nanotubes. In various embodiments, electrolytes **13** and **15** can contain exfoliated carbon nanotubes, which may be exfoliated conductive carbon nanotubes in some embodiments. In various embodiments, at least one of electrodes **12** and **16** contains exfoliated carbon nanotubes. Electrolytes **13** and **15** may be fully intermixed with the electrodes **12** and **16**, or they may contact along a portion of the electrodes. For example electrolytes **13** and **15** may contact along a single side of electrodes **12** and **16** along a plane. In various embodiments, non-conducting separator **4** may contain non-conducting carbon nanotubes. In various embodiments, the non-conducting separator **4** may be made from porous polyethylene or fiberglass mats.

[0077] FIGURE 3 shows an illustrative arrangement of the basic elements of a battery. As shown in FIGURE 3, electrodes **21** and **23** contact electrolyte **22**. The electrolyte **22** conveys ions between electrodes **21** and **23**. In an embodiment, the ions are metal ions such as, for example, lithium ions. Hence, the present disclosure describes a lithium battery containing exfoliated carbon nanotubes. In some embodiments, at least one of the electrodes **21** and **23** contains exfoliated carbon nanotubes. In some embodiments, the electrolyte **22** contains exfoliated carbon nanotubes.

[0078] In various embodiments of the present disclosure, the energy storage device containing exfoliated carbon nanotubes is a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes contains exfoliated carbon nanotubes.

[0079] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are multi-wall carbon nanotubes. In some embodiments, the exfoliated carbon nanotubes are single-wall carbon nanotubes. In some embodiments, the at least one electrode containing exfoliated carbon nanotubes is the anode.

[0080] In various embodiments of the energy storage devices, the electrode may contain exfoliated carbon nanotubes dispersed in a polymer or viscous liquid. In various embodiments, the electrode may be laminated to another medium such as, for example, a dielectric or an electrolyte.

[0081] In various embodiments, the electrolyte of the energy storage devices can be a solid or a fluid. Electrolytes are generally chosen to minimize internal electrical resistance. Aqueous electrolytes such as potassium hydroxide or sulfuric acid are generally employed in conventional batteries and capacitors. Due to water's low electrochemical decomposition potential of 1.24 volts, the energy density is limited with these types of electrolytes. Organic electrolytes such as, for example, organic carbonates and tetraalkylammonium salts provide good solubility and reasonable conductivity. In general, organic electrolytes have lower conductivity than aqueous electrolytes, but they can operate at higher voltages, for example, up to about 5 volts. Other electrolytes can be of a polymer-gel type such as, for example, polyurethane–lithium perchlorate, polyvinyl alcohol-KOH-H_2O and the related systems. Organic electrolytes such as, for example tetraethylammonium tetrafluoroborate and tetrabutylammonium tetrafluoroborate, can simultaneously serve as an electrolyte and surfactant for dispersing and exfoliating carbon nanotubes in embodiments where carbon nanotubes are contained in the electrolyte. Electrolyte salts may also be used for dispersing the carbon nanotubes or maintaining exfoliated carbon nanotubes in an exfoliated state.

[0082] In some embodiments of the energy storage devices, the exfoliated carbon nanotubes are modified with an electroactive material. In some embodiments, the electroactive material is a transition metal or transition metal oxide. Electroactive transition metals include, for example, Ru, Ir, W, Mo, Mn, Ni, and Co. In some embodiments, the electroactive material may be a conducting polymers such as, for example, polyaniline, polyacetylene and polyvinylpyrrole. In some embodiments, the electroactive material is a nanomaterial bound to the exfoliated carbon

nanotubes. In some embodiments, the nanomaterial may be, for example, SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and various combinations thereof.

[0083] In other various embodiments, the present disclosure describes layered structures containing exfoliated carbon nanotubes suitable for use in energy storage devices. For example, co-extrusion of liquids or melts containing exfoliated carbon nanotubes through multilayer dies or multilayer generators may be used in making the energy storage devices of the present disclosure. The resultant layered structures can be stacked and connected in series to give higher voltages in energy storage devices. In other embodiments, the components of the energy storage devices may be processed from a solution of exfoliated carbon nanotubes by solvent casting, spraying, paste spreading, compression stretching, or combinations thereof.

[0084] In some embodiments, the present disclosure also relates to an ion diffusion separator of electrical double-wall capacitors. In various embodiments, the separator contains non-metallic single-wall carbon nanotubes.

[0085] In some embodiments of the present disclosure, insulators of the energy storage devices contain non-metallic single-wall carbon nanotubes. In embodiments where the insulator contains carbon nanotubes, the dielectric constant of the insulator/carbon nanotube mixture may be greater than that of the insulator alone.

[0086] In various embodiments, exfoliated carbon nanotubes can be aligned in forming electrodes for use in the energy storage devices. In some embodiments, the alignment may occur through melt extrusion.

[0087] In some embodiments of the energy storage devices of the present disclosure, incorporation of exfoliated carbon nanotubes to electrodes, electrolytes or dielectrics of the energy storage devices provides enhanced strength and ruggedness to the device. These features allow further shaping of the device for functioning under demanding environments, such as high vibration or extreme thermal cycling environments.

[0088] In still additional embodiments of the present disclosure, polymer composites containing exfoliated carbon nanotubes and methods for making such polymer composites are described

herein. Polymer composites of the present disclosure are advantageous over those conventionally prepared in the art by having fully exfoliated carbon nanotubes dispersed in the polymer matrix. As such, the polymer composites of the present disclosure are advantageous in having all of the carbon nanotube surface area being available for load transfer when the composite is placed under stress. Further, the exfoliated state of the carbon nanotubes allows the carbon nanotubes to be easily mixed into the polymer matrix in a non-exfoliated state, as opposed to high shear mixing techniques which are used conventionally to disperse carbon nanotubes in polymer composites.

[0089] In some embodiments, methods for making polymer composites according to the present disclosure include providing exfoliated carbon nanotubes and mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite. The carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

[0090] In some embodiments of the methods for making polymer composites, the polymer material is an epoxy. In some embodiments, the methods further include curing the epoxy. In some embodiments, the polymer material is a monomer of a thermoplastic material, which is subsequently polymerized. In some embodiments, the polymer material is a polymer melt, which is hardened after mixing the exfoliated carbon nanotubes.

Experimental Examples

[0091] The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

[0092] Example 1: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates and Tetrabutylammonium Hydroxide Surfactant. A dispersed solution of carbon nanotubes was prepared from 10 mg of multi-wall carbon nanotubes placed in 2 mL of a solution of $Zr(HPO_4)_2 \cdot H_2O$ nanoplates and tetrabutylammonium hydroxide (5 wt% $Zr(HPO_4)_2 \cdot H_2O$; 1:0.8

ratio of $Zr(HPO_4)_2 \cdot H_2O$:tetrabutylammonium hydroxide). The solution was subsequently diluted to 30 mL and then sonicated for 2 hours. The solution was stable for at least 24 hours. An aliquot of 0.01 M KCl was added, resulting in precipitation of a quantity of exfoliated multi-wall carbon nanotubes. The precipitated fraction was removed by centrifugation. The quantity of isolated nanotubes was approximately 1/10 the mass of carbon nanotubes originally suspended. The filtrate was treated with another aliquot of 0.01 M KCl, resulting in a second precipitation of multi-wall carbon nanotubes. The precipitation/centrifugation process was repeated until substantially all nanotubes had been precipitated from the suspension.

[0093] Example 2: Exfoliation of Carbon Nanotubes Using $Zr(HPO_4)_2 \cdot H_2O$ Nanoplates of Varying Sizes (Prophetic Example). The experimental procedure described in Example 1 hereinabove will be repeated, except with a nanoplate size of about 1/10 the length of the longest carbon nanotube present in the sample. After removal of the first precipitation fraction following addition of 0.01 M KCl, a second quantity of nanoplates of a different (larger) size will be added. The second quantity of nanoplates will fractionate a second quantity of nanotubes following addition of 0.01 M KCl. The second precipitation fraction of nanotubes may have a different length distribution than did the first precipitation fraction. The precipitation/centrifugation process will be repeated with progressively larger nanoplates until substantially all carbon nanotubes have been precipitated from the suspension.

[0094] Example 3: Synthesis of Hydroxyapatite Nanoplates. Hydroxyapatite nanoplates of controlled sizes were synthesized by dissolving 10 g of hydroxyapatite (Sigma Aldridge reagent grade) in 400 mL of dilute nitric acid (pH = 2) at room temperature, followed by very slow dropwise addition of 48 mL of 1% v/v ammonium hydroxide. Crystals collected at pH = 4 and pH = 5 were found by microscopy to be plates having an aspect ratio about 7 to 8 and a diameter ranging between 3 – 15 μm. FIGURE 4 shows an illustrative electron micrograph of hydroxyapatite plates of 3 – 15 μm diameter. Increasing the addition rate of the 1% v/v ammonium hydroxide reduced the average plate size.

[0095] Example 4: Synthesis of Hydroxyapatite Nanorods. 2 g of hydroxyapatite was first dissolved in 40 mL of dilute nitric acid (pH = 2) containing a 3:1 ethanol:water ratio. The mixture was then quenched into 80 mL of 5 vol% ammonium hydroxide, also in a 3:1

ethanol:water ratio. The resultant pH was 8.5. A milky, jelly-like precipitate resulted. The resulting mixture containing the precipitate was then heated at between 70°C and 80°C on a magnetic stirrer hotplate for 24 hours. Thereafter, hydroxyapatite crystals were filtered, washed with deionized water and dried. Electron microscopy showed that hydroxyapatite nanorods having an aspect ratio of about 25 and lengths between 100 – 200 nm were formed. FIGURE 5 shows an illustrative electron micrograph of hydroxyapatite nanorods having lengths of 100 – 200 nm.

[0096] Example 5: Exfoliation of Carbon Nanotubes Using Hydroxyapatite. 0.5142 g hydroxyapatite nanorods were added to 50 mL water and 0.8280 g tetrabutylammonium hydroxide (Sigma Aldrich reagent grade; TBAH; 1:1 molar ratio of hydroxyapatite:TBAH). The resultant mixture was sonicated for one hour at 25°C and then diluted with deionized water to give a 0.2 wt% solution based on hydroxyapatite content.

[0097] Multi-wall carbon nanotubes were received as a powder that contained highly entangled nanotube bundles having a grain size of 1 – 10 μm in diameter. The lengths of the individual multi-wall carbon nanotubes were found to be in excess of 1 μm, and the diameters were found to be 10 – 20 nm. 1 g of the multi-wall carbon nanotubes was added to 50 mL of a mixture of concentrated sulfuric and nitric acid in a 3:1 volume ratio. The mixture was placed in a sonicator bath (Branson sonicator, model 250) and treated for two hours while sonicating at temperature of 25 – 35°C. The mixture was then filtered using a polyvinylidene fluoride microporous filter (5 μm pore size), followed by washing of the resultant solid with deionized water until the pH of the filtrate was 4.5. The multi-wall carbon nanotubes were then dried in vacuo for 2 hours at 80°C. The multi-wall carbon nanotubes were not substantially shortened by the acid treatment.

[0098] Samples were prepared by adding the dried multi-wall carbon nanotubes to the hydroxyapatite/TBAH solution prepared above to give carbon nanotube:hydroxyapatite weight ratios of 1:1, 1:2, 1:3, 1:4 and 1:5. The mixture was sonicated at room temperature for 2 hours and then left for 24 hours. At a weight ratio of 1:1, a portion of the multi-wall carbon nanotubes settled out as agglomerated particles. At a 1:2 weight ratio the solution had a few multi-wall carbon nanotube particles present after 24 hours. All higher weight ratios examined gave stable dispersions for at least 24 hrs. A control experiment at a weight ratio of 1:3 multi-wall carbon

nanotubes:TBAH with no hydroxyapatite present showed mostly aggregated carbon nanotubes settling after 24 hours. FIGURE 6A shows an illustrative electron micrograph of as-received multi-wall carbon nanotubes, and FIGURE 6B shows an illustrative electron micrograph of multi-wall carbon nanotubes exfoliated using hydroxyapatite nanorods.

[0099] The precipitated exfoliated multi-wall carbon nanotubes contained residual hydroxyapaptite as evidenced by energy-dispersive X-ray (EDX) spectroscopy. FIGURE 7A shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes. As shown in the EDX spectrum, strong Ca and P signals indicated the presence of hydroxyapatite. The precipitated multi-wall carbon nanotubes were subsequently washed with 50 mL of 1 N nitric acid, followed by 250 mL of deionized water, which removed substantially all the hydroxyapatite as evidenced by EDX. FIGURE 7B shows an illustrative EDX spectrum of precipitated exfoliated multi-wall carbon nanotubes after acid washing. In contrast, the exfoliated multi-wall carbon nanotubes of Example 1 contained residual $Zr(HPO_4)_2 \cdot H_2O$, which could not be removed by washing with acids such as nitric, hydrochloric or sulfuric acids.

[0100] Unentangled multi-wall carbon nanotubes were obtained after exfoliation, precipitation and washing. FIGURE 8 shows an illustrative electron micrograph of the exfoliated multi-wall carbon nanotubes after precipitation and washing. Exfoliation of the multi-wall carbon nanotubes could be conducted equivalently using hydroxyapatite plates.

[0101] Example 6: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions. 40 mg of multi-wall carbon nanotubes were added to 40 mL of a 3:1 sulfuric:nitric acid mixture and sonicated for 60 minutes at 25 °C. A drop of the mixture was placed on a PVDF filter and allowed to dry. FIGURE 9 shows an illustrative electron micrograph of exfoliated carbon nanotubes obtained from 3:1 H_2SO_4:HNO_3. As shown in FIGURE 9, exfoliation was maintained after removal of the acid by drying.

[0102] Example 7: Exfoliation of Carbon Nanotubes Using Concentrated Acid Solutions, Followed by Surfactant Addition. A 1% by weight double-wall carbon nanotube solution in 3:1 sulfuric:nitric acid was treated for 2 hours as described previously. After filtering the concentrated acid solution to immobilize the double wall carbon nanotubes, the immobilized carbon nanotubes were washed with deionized water until the washings were pH = 4.5. While

still wet, the PVDF filter paper and the double-wall carbon nanotubes were sonicated for 30 minutes with a 0.2% by weight sodium dodecyl sulfate (SDS) solution in deionized water such that the weight of double-wall carbon nanotubes to SDS was 1:3. The mixture was stable for at least 24 hours. A drop of the mixture was placed on a carbon tape and dried for examination by electron microscopy, which showed exfoliated carbon nanotubes. FIGURE 10 shows an illustrative electron micrograph of exfoliated double-wall carbon nanotubes following acid exfoliation and treatment with sodium dodecyl sulfate.

[0103] Example 8: Epoxy Composite Containing Exfoliated Carbon Nanotubes. 5 mg of acid-treated multi-wall carbon nanotubes were placed in 10 mL of tetraethylenetetramine (TETA), and various additions of sodium dodecylsulfate (SDS) were added such that the weight ratio of multi-wall carbon nanotubes to SDS was 5, 2.5, 1, and 0.33 to 1. The mixture was sonicated at 30°C for 30 minutes and allowed to stand. After 7 days the 1:1 and 1:0.33 ratio was seen to be stable toward precipitation.

[0104] 49 g of Bisphenol F epoxy was admixed with 0.242 g of acid-treated multi-wall carbon nanotubes and sonicated for 10 minutes at 60°C. The mixture was cooled to 25°C and then degassed for 10 minutes at 25 inches Hg. 7 g of TETA containing 0.5% wt treated multi-wall carbon nanotubes and 0.5% wt. SDS was sonicated and degassed separately as above. The two degassed mixtures were then carefully mixed and poured into a mold. The mold was cured for 2 hours at 100°C. Controls were prepared as above without carbon nanotubes (control 1) and with as-received multi-wall carbon nanotubes (control 2).

[0105] Table 1 shows the mechanical strength improvement in the epoxy composite containing exfoliated multi-wall carbon nanotubes. Kq is the maximum stress before failure on tensile testing of a notched specimen at 0.01/min initial strain rate and 1 mm razor notch. Relative fatigue lifetime improvement is the lifetime of the notched specimen counted as the number of cycles to failure at 1 Hz, at about 16.7 MPa maximum tensile stress with stress amplitude of 0.1 (stress minimum/stress maximum). As shown in Table 1, significant mechanical property enhancement was observed when exfoliated carbon nanotubes were used.

Table 1: Mechanical Properties of Carbon Nanotube Composites

Material	Relative Kq improvement	Relative fatigue lifetime improvement
Control 1	1	1
Control 2	1.2	1.1
Exfoliated Carbon Nanotubes	1.5	4.7

[0106] Example 8: Capacitor Containing Exfoliated Multi-Wall Carbon Nanotubes. Control 1: 10 g of poly(ethylene oxide) (PEO; 1500 molecular weight) was melted, and 1 mL of 4 N potassium hydroxide added to make the electrolyte. 1 wt % of as-received multi-wall carbon nanotubes were added to the electrolyte mixture and sonicated for 15 minutes in a sonicator bath. Approximately 2.1 g of the mixture was poured into one part of a polystyrene petri dish 6 cm in diameter with a strip of copper adhered as the current collector. A piece of clean writing paper was then placed on the molten liquid electrolyte, and 2 g of the electrolyte was poured on to the paper, taking care not to weep at the edges. The other side of the petri dish with a copper strip adhered was then inserted to make a capacitor. After cooling to room temperature for 15 minutes the capacitance was measured using an HP 4282A capacitance meter. The measured capacitance was 0.0645 microfarads. Control 2: Control 2 was prepared as for control 1, except as-received graphene (Rice University) was substituted for the multi-wall carbon nanotubes. The measured capacitance was 0.176 microfarads. Exfoliated carbon nanotube capacitor: The capacitor was prepared as for Control 1, except exfoliated multi-wall carbon nanotubes were used in place of as-received multi-wall carbon nanotubes. The measured capacitance was 0.904 microfarads, a 14-fold improvement over control 1 and a 5.1-fold improvement over control 2.

[0107] Example 9: Exfoliated Carbon Nanotubes Decorated with Copper Nanoparticles. 102 mg of exfoliated multi-wall carbon nanotubes were added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture was sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide were added to bring the pH to 12.2. The mixture was stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. FIGURE 11 shows an illustrative electron

micrograph of exfoliated carbon nanotubes decorated with copper oxide nanoparticles obtained from the mixture.

[0108] From the foregoing description, one of ordinary skill in the art can easily ascertain the essential characteristics of this disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt the disclosure to various usages and conditions. The embodiments described hereinabove are meant to be illustrative only and should not be taken as limiting of the scope of the disclosure, which is defined in the following claims.

CLAIMS

What is claimed is the following:

1. A composition comprising exfoliated carbon nanotubes,
wherein the exfoliated carbon nanotubes are not dispersed in a continuous matrix that maintains the carbon nanotubes in an exfoliated state.

2. The composition of claim 1, wherein the composition comprises a mat of exfoliated carbon nanotubes.

3. The composition of claims 1 or 2, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes and combinations thereof.

4. The composition of any one of claims 1 – 3, wherein the carbon nanotubes are full-length carbon nanotubes.

5. The composition of any one of claims 1 – 4, wherein the carbon nanotubes are substantially free of impurities selected from the group consisting of catalytic residues, non-nanotube carbon and combinations thereof.

6. The composition of any one of claims 1 – 5, wherein the exfoliated carbon nanotubes are separated by chirality.

7. The composition of any one of claims 1 – 6, wherein the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes;
wherein the exfoliated carbon nanotubes have a narrower distribution of lengths than do the bundled carbon nanotubes.

8. The composition of any one of claims 1 – 7, wherein the exfoliated carbon nanotubes are prepared from bundled carbon nanotubes;
wherein the exfoliated carbon nanotubes have a narrower distribution of diameters than do the bundled carbon nanotubes.

9. The composition of any one of claims 1 – 8, wherein the exfoliated carbon nanotubes are further functionalized.

10. The composition of any one of claims 1 – 9, wherein the exfoliated carbon nanotubes further comprise an electroactive material bound to the carbon nanotubes.

11. A method for preparing exfoliated carbon nanotubes, said method comprising:

a) suspending carbon nanotubes in a solution comprising a first quantity of a nanocrystalline material;

b) precipitating a first quantity of exfoliated carbon nanotubes from the solution; and

c) isolating the first quantity of exfoliated carbon nanotubes.

12. The method of claim 11, wherein the solution further comprises a surfactant.

13. The method of claims 11 or 12, wherein precipitating further comprises adjusting the ionic strength of the solution.

14. The method of any one of claims 11 – 13, wherein precipitating further comprises applying an electrical potential to the solution.

15. The method of any one of claims 11 – 14, wherein precipitating further comprises adjusting the pH of the solution.

16. The method of any one of claims 11 – 15, wherein the solution further comprises a chiral agent; and

wherein the first quantity of exfoliated carbon nanotubes is selectively precipitated by chirality.

17. The method of claim 16, wherein the chiral agent is selected from the group consisting of a surfactant, a polymer and combinations thereof.

18. The method of any one of claims 11 – 17, wherein the exfoliated carbon nanotubes are selectively precipitated by length.

19. The method of any one of claims 11 – 17, wherein the exfoliated carbon nanotubes are selectively precipitated by diameter.

20. The method of any one of claims 11 – 15, further comprising:
adding a second quantity of nanocrystalline material to the solution; and
precipitating a second quantity of exfoliated carbon nanotubes.

21. The method of claim 20, wherein the first quantity of exfoliated carbon nanotubes and the second quantity of exfoliated carbon nanotubes have different properties from one another.

22. The method of any one of claims 11 – 21, wherein the nanocrystalline material has a crystalline form selected from the group consisting of nanoplates, nanorods and nanowhiskers.

23. The method of any one of claims 11 – 22, wherein the nanocrystalline material is selected from the group consisting of clays, graphite, inorganic crystalline materials, organic crystalline materials, and combinations thereof.

24. The method of any one of claims 11 – 23, wherein the nanocrystalline material is selected from the group consisting of hydroxyapatite and hydroxyapatite derivatives.

25. A method for preparing exfoliated carbon nanotubes, said method comprising:
a) suspending carbon nanotubes in a solution comprising hydroxyapatite;
b) precipitating exfoliated carbon nanotubes from the solution; and
c) isolating the exfoliated carbon nanotubes.

26. The method of claim 25, wherein the hydroxyapatite has a crystalline form selected from the group consisting of nanorods, nanoplates and nanowhiskers.

27. The method of claims 25 or 26, further comprising:
removing residual hydroxyapatite from the exfoliated carbon nanotubes.

28. The method of claim 27, wherein removing comprises washing the exfoliated carbon nanotubes with an acid after their being isolated.

29. A method for preparing exfoliated carbon nanotubes, said method comprising:
    a) suspending carbon nanotubes in a solution comprising a nanorod material;
    b) precipitating exfoliated carbon nanotubes from the solution; and
    c) isolating the exfoliated carbon nanotubes.

30. A method for preparing exfoliated carbon nanotubes, said method comprising:
    a) preparing a solution of carbon nanotubes in an acid; and
    b) filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter.

31. The method of claim 30, wherein a concentration of carbon nanotubes in the acid is below a percolation threshold of the carbon nanotubes in the acid.

32. The method of claims 30 or 31, wherein the acid comprises a superacid.

33. The method of claim 32, wherein the superacid comprises chlorosulfonic acid.

34. The method of any one of claims 30 – 33, further comprising:
    c) modifying the exfoliated carbon nanotubes on the filter.

35. The method of claim 34, wherein modifying comprises functionalizing the exfoliated carbon nanotubes.

36. The method of claim 34, wherein modifying comprises treating the exfoliated carbon nanotubes with a surfactant.

37. An energy storage device comprising:
    a) at least two electrodes;
        wherein at least one of the electrodes comprises the exfoliated carbon nanotubes of claim 1; and
    b) an electrolyte in contact with the at least two electrodes.

38. The energy storage device of claim 37, wherein the exfoliated carbon nanotubes are modified with an electroactive material.

39. The energy storage device of claim 38, wherein the electroactive material comprises a transition metal.

40. The energy storage device of claim 38, wherein the electroactive material comprises a nanomaterial bound to the exfoliated carbon nanotubes.

41. The energy storage device of claim 40, wherein the nanomaterial is selected from the group consisting of SnO_2, $Li_4Ti_5O_{12}$, silicon nanotubes, silicon nanoparticles and combinations thereof.

42. The energy storage device of any one of claims 38 – 42, wherein the exfoliated carbon nanotubes comprise multi-wall carbon nanotubes.

43. The energy storage device of claim 37, wherein the at least one electrode comprising the exfoliated carbon nanotubes is the anode.

44. A method for making a polymer composite, said method comprising:

a) providing the exfoliated carbon nanotubes of claim 1; and

b) mixing the exfoliated carbon nanotubes in a polymer material to form a polymer composite;

wherein exfoliated carbon nanotubes remain in an exfoliated state after being mixed in the polymer material.

45. The method of claim 44, wherein the polymer material comprises an epoxy.

46. The method of claim 45, further comprising:

curing the epoxy.

FIGURE 1

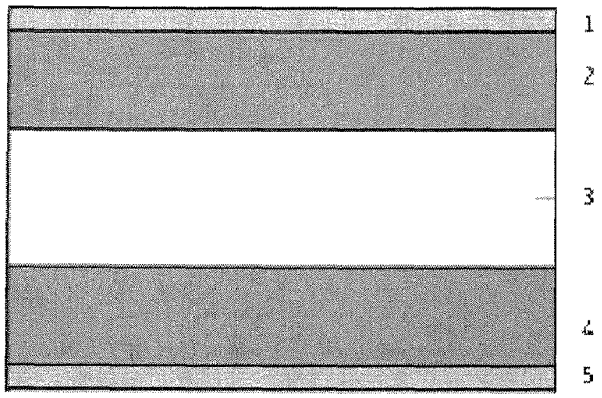


FIGURE 2

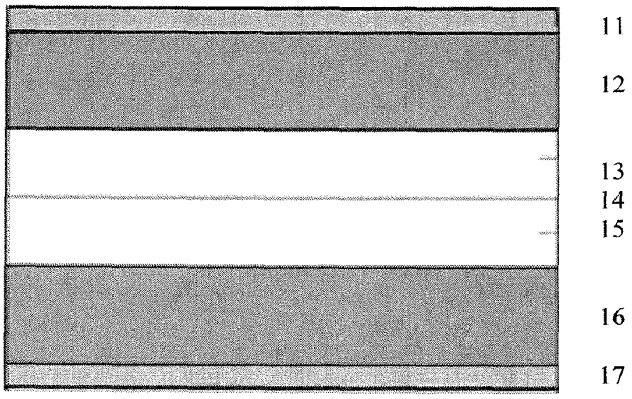


FIGURE 3

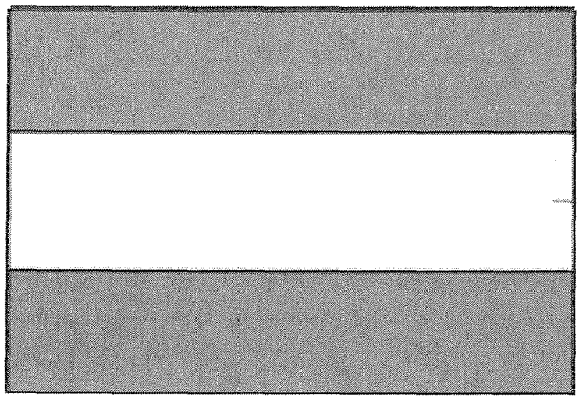


FIGURE 4

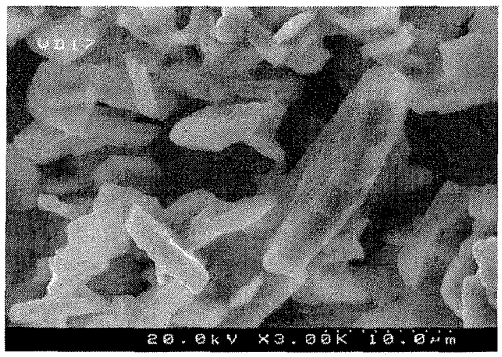
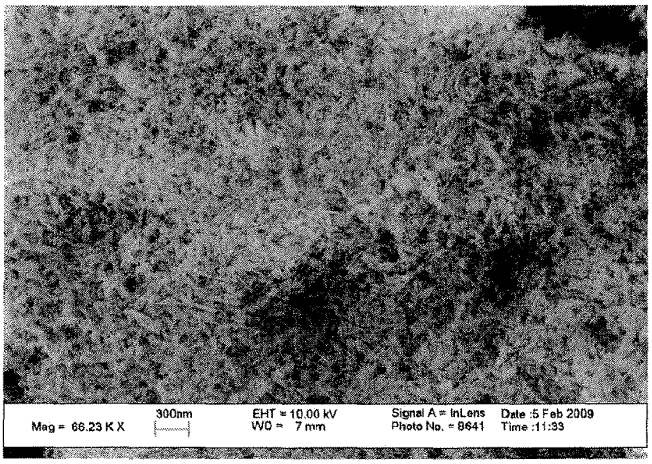
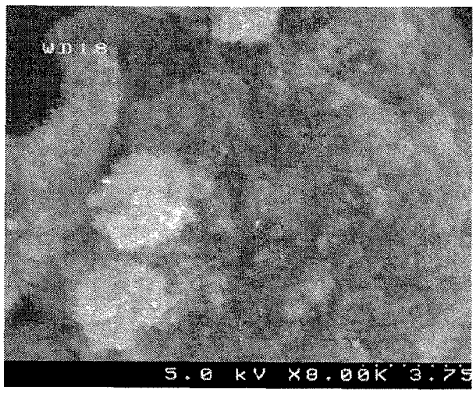


FIGURE 5



FIGURES 6A and 6B



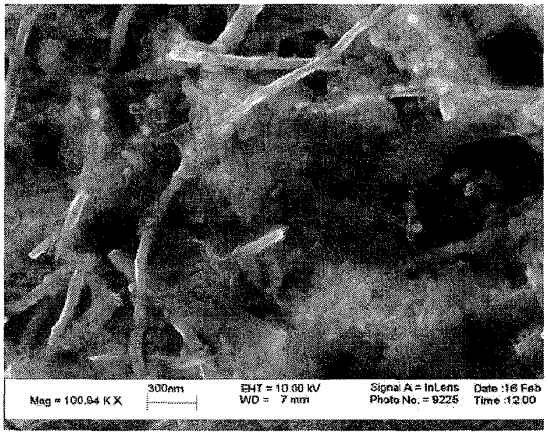


FIGURE 6A

FIGURE 6B

FIGURES 7A and 7B

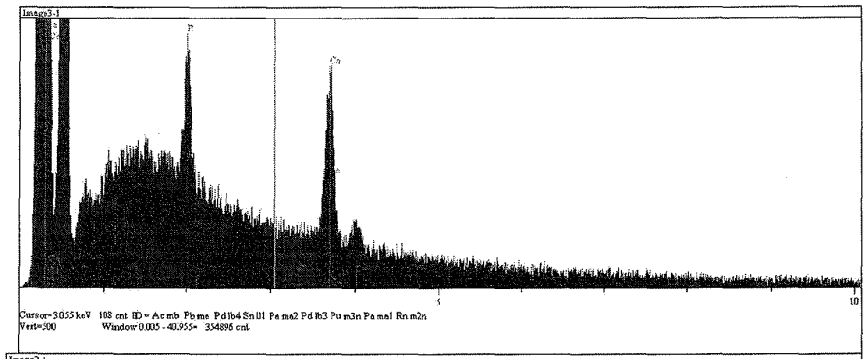


FIGURE 7A

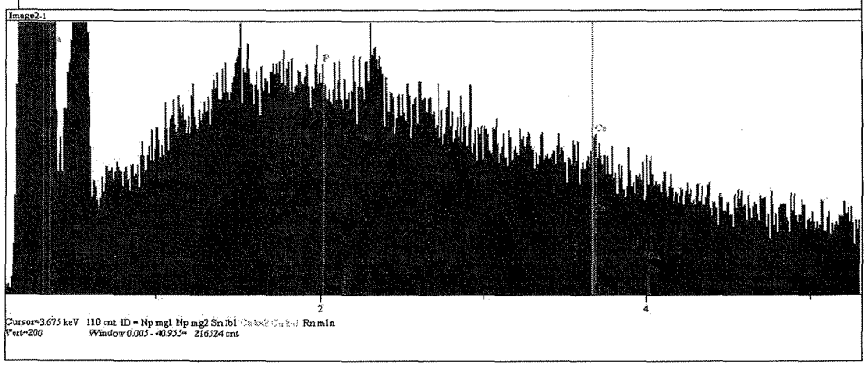


FIGURE 7B

FIGURE 8

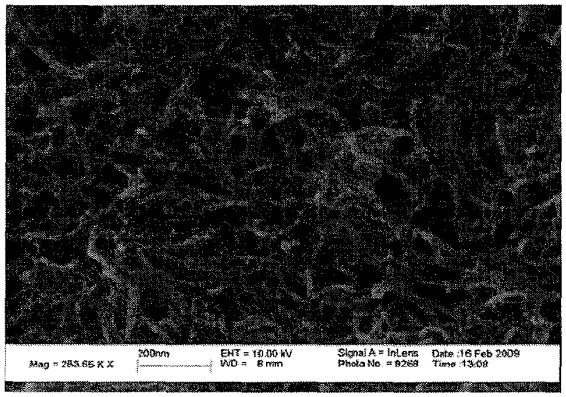


FIGURE 9

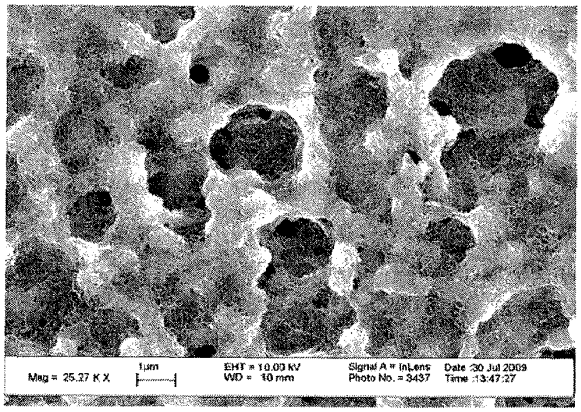


FIGURE 10

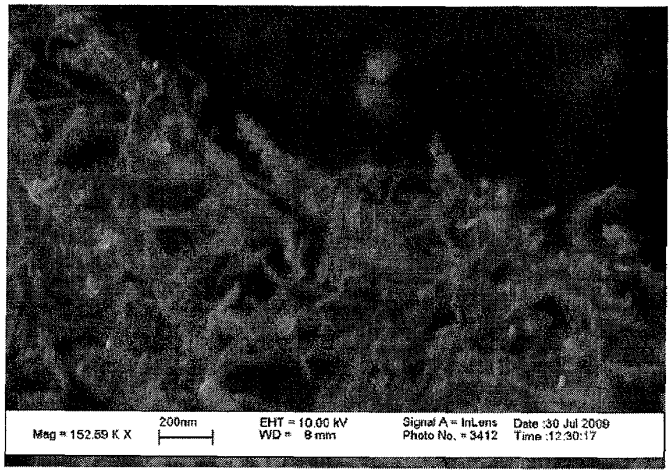
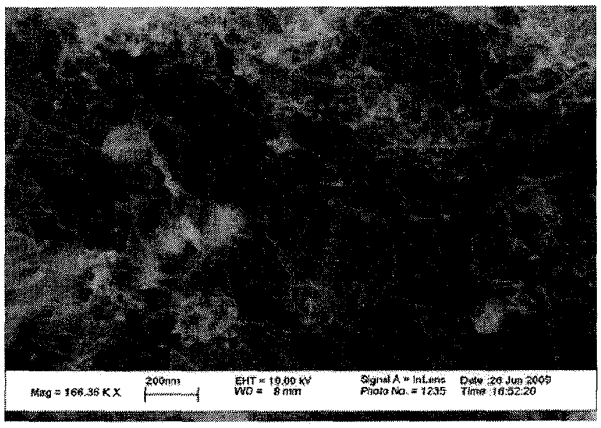


FIGURE 11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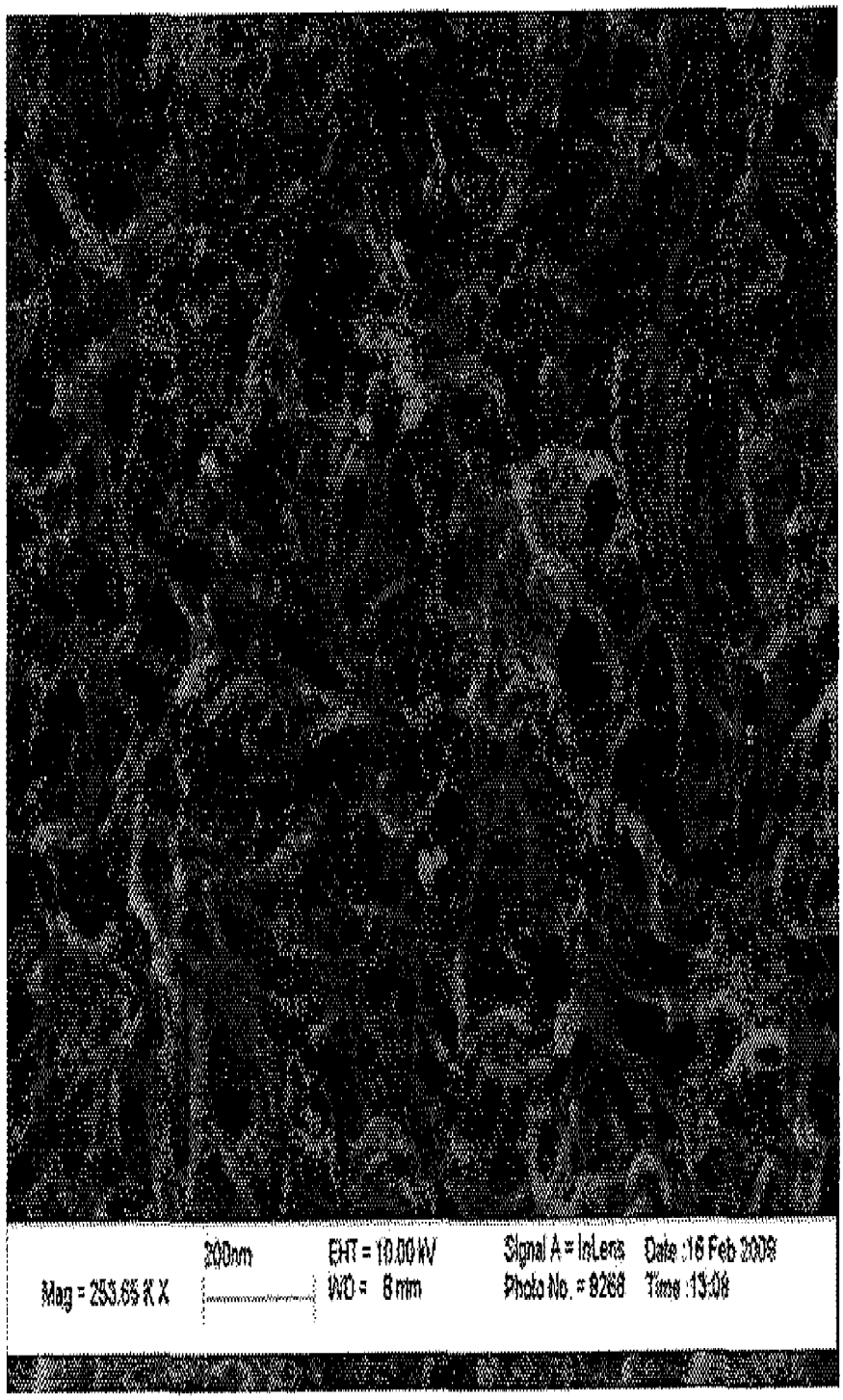
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FIGURE 8

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-10)
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	Filing Date	2018-01-26
	First Named Inventor	Kurt W. Swogger
	Art Unit	
	Examiner Name	
	Attorney Docket Number	MRE012NP2C / 277190

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	1	101734650	CN	A	2010-06-16	Univ. Shenyang Jianzhu		

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15881071
	Filing Date	2018-01-26
	First Named Inventor	Kurt W. Swogger
	Art Unit	
	Examiner Name	
	Attorney Docket Number	MRE012NP2C / 277190

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Examiner Signature	/JEREMIAH R SMITH/	Date Considered	10/11/2019

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	Art Unit	
	Examiner Name	
	Attorney Docket Number	MRE012NP2C / 277190

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OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Gregory L. Porter/	Date (YYYY-MM-DD)	2018-06-07
Name/Print	Gregory L. Porter	Registration Number	40131

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/881,071	01/26/2018	Clive P. Bosnyak	MRE012NP2C / 277190

CONFIRMATION NO. 2885

130577
ANDREWS KURTH KENYON LLP
600 Travis Street
Suite 4200
Houston, TX 77002

PUBLICATION NOTICE

OC000000102295804

Title: Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

Publication No.US-2018-0261884-A1
Publication Date:09/13/2018

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	Filing Date	2018-01-26
	First Named Inventor	Kurt W. Swogger
	Art Unit	
	Examiner Name	
	Attorney Docket Number	MRE012NP2C / 277190

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Signature	/Gregory L. Porter/	Date (YYYY-MM-DD)	2018-06-07
Name/Print	Gregory L. Porter	Registration Number	40131

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CN text

No documents available for this priority number.

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Bibliographic data: CN101734650 (A) — 2010-06-16

Method for preparing graphene-carbon nano tube hybrid composite

Inventor(s):	JINHONG DU; PENGFEI LIU; YU TONG; YOU ZENG; JINBO ZHAO; LONG ZHAO ± (DU JINHONG, ; LIU PENGFEI, ; TONG YU, ; ZENG YOU, ; ZHAO JINBO, ; ZHAO LONG)
Applicant(s):	UNIV SHENYANG JIANZHU ± (SHENYANG JIANZHU UNIVERSITY)
Classification:	**- international:** ***B82B3/00; C01B31/02*** **- cooperative:**
Application number:	CN20091248681 20091223
Priority number (s):	CN20091248681 20091223
Also published as:	CN101734650 (B)

Abstract of CN101734650 (A)

The invention provides a method for preparing a graphene-carbon nano tube hybrid composite and relates to a method for preparing a functional high molecular material and a device thereof. The method comprises the following steps of: carrying out the stirring and sonic oscillation treatment on graphene and carbon nano tubes to preform an entangled network structure, thoroughly mixing the entangled network structure and polymer particles, and thus obtaining an uniformly-mixed system in which the graphene-carbon nano tube network is coated on the surfaces of the polymer particles after removing the solvent; and putting the uniformly-mixed system in a mould, hot-compacting, and obtaining the graphene-carbon nano tube hybrid composite after cooling and demoulding.; By mingling the graphene and the carbon nano tubes in advance to form the communicated network structure, the method realizes the advantage complementation of the graphene and carbon nano tube structures and enables the hybrid composite to have favorable electric conduction and heat conduction properties. The method can be widely used in the fields such as aviation, transportation and communication, electronic industry, civil facilities, construction, chemical industry and the like, can be produced in the industrial scale, and has the advantages of low cost and environmental friendliness.

Last updated: 13.03.2013 Worldwide Database 5.8.6.6; 92p

No documents available for this priority number.

Espacenet

Bibliographic data: CN101734650 (A) — 2010-06-16

Method for preparing graphene-carbon nano tube hybrid composite

Inventor(s): JINHONG DU; PENGFEI LIU; YU TONG; YOU ZENG; JINBO ZHAO; LONG ZHAO ± (DU JINHONG, ; LIU PENGFEI, ; TONG YU, ; ZENG YOU, ; ZHAO JINBO, ; ZHAO LONG)

Applicant(s): UNIV SHENYANG JIANZHU ± (SHENYANG JIANZHU UNIVERSITY)

Classification: - international: *B82B3/00; C01B31/02*
- cooperative:

Application number: CN20091248681 20091223

Priority number (s): CN20091248681 20091223

Also published as: CN101734650 (B)

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Last updated: 18.03.2013 Worldwide Database 5.5.6.6; 92p

(19)中华人民共和国国家知识产权局

(12)发明专利

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(45)授权公告日 2012.06.20

(21)申请号 200910248681.2
(22)申请日 2009.12.23
(73)专利权人 沈阳建筑大学
地址 110168 辽宁省沈阳市浑南新区浑南东路9号沈阳建筑大学
(72)发明人 曾尤 赵龙 杜金红 刘鹏飞 佟钰 赵金波
(74)专利代理机构 沈阳技联专利代理有限公司 21205
代理人 王德荣
(51)Int.Cl.
C01B 31/02(2006.01)
B82B 3/00(2006.01)

(56)对比文件
CN 1704447 A,2005.12.07,说明书第5页实施例1.
CN 1982370 A,2007.06.20,说明书第6页实施例1.
US 7449133 B2,2008.11.11,说明书第5栏实施例5.
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审查员 李翔

权利要求书1页 说明书4页

(54)发明名称

一种石墨烯-碳纳米管混杂复合材料的制备方法

(57)摘要

一种石墨烯-碳纳米管混杂复合材料的制备方法,涉及一种功能高分子材料及器件的制备方法。将石墨烯和碳纳米管经搅拌、超声振荡处理预先形成缠结的网络结构,将其与聚合物颗粒进行充分混合、去除溶剂后,获得石墨烯-碳纳米管网络包裹于聚合物颗粒表面的均匀混合体系,将其放入模具中,热压成型、冷却脱模后得到石墨烯-碳纳米管混杂复合材料。本方法通过石墨烯与碳纳米管预先混杂形成连通网络结构,实现了石墨烯和碳纳米管结构上的优势互补,使得该混杂复合材料具有较好的导电、导热性能。本发明可以在航空航天、交通运输、电子工业、民用设施、建筑及化工等方面具有广泛的应用,并能够工业化规模生产、成本低廉且环境友好。

CN 101734650 B

1. 一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于所述制备方法的工艺步骤如下：

（1）配制包含石墨烯、碳纳米管、分散溶剂的悬浮体系，经搅拌，超声振荡使得石墨烯和碳纳米管相互穿插、缠绕形成连通的网络结构；

（2）加入聚合物颗粒，经搅拌和超声振荡，使得聚合物颗粒表面被石墨烯－碳纳米管交织网络所包裹；

（3）去除溶剂后，形成石墨烯－碳纳米管包裹于聚合物颗粒表面的均匀混合体系；

（4）将所述混合体系放入模具中，经升温热压成型、冷却脱模后制得石墨烯－碳纳米管混杂复合材料。

2. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于所用的石墨烯是指单层石墨片、多层石墨片或它们的混合物；所用的碳纳米管是指直径为 5-200 纳米、长度为 0.1-100 微米的中空管状碳材料。

3. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于所用的分散溶剂为无水乙醇、丙酮、甲苯和苯乙烯。

4. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于经超声振荡后使得石墨烯和碳纳米管预先形成一种交织、缠绕的网络结构。

5. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于聚合物颗粒为聚乙烯、聚氯乙烯、聚丙烯、聚酰胺、聚苯乙烯、聚甲醛、聚四氟乙烯、聚碳酸酯、聚苯醚、聚砜。

6. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于去除溶剂是通过加热或者真空抽滤方法实现的。

7. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于石墨烯－碳纳米管网络包裹在聚合物颗粒表面，形成沿聚合物颗粒表面分布的连通网络。

8. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于热压温度高于聚合物熔点或软化点 20℃以上，成型压力大于 10MPa，冷却脱模温度低于 60℃。

9. 根据权利要求 1 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，其特征在于原料的初始用量重量配比为：

石墨烯：0.1-10 份；

碳纳米管：0.1-10 份；

聚合物：100 份；

分散溶剂：100-500 份。

一种石墨烯－碳纳米管混杂复合材料的制备方法

技术领域

[0001] 本发明涉及一种功能高分子材料及器件技术领域的制备方法，特别是涉及一种石墨烯－碳纳米管混杂复合材料的制备方法。

背景技术

[0002] 石墨烯（graphene，详见：Novoselov K S，et al.Electric field effects inatomically thin carbon films.Science，2004，306：666-119）是由单层碳原子紧密堆积成二维蜂窝状晶格结构的一种碳质新材料，它是构建其它维度碳质材料（如零维富勒烯、一维碳纳米管、三维石墨）的基本单元。石墨烯具有优异的电学性能和热学性能，其室温电子迁移率可达 $15000cm^2V^{-1}S^{-1}$，热导率可达 $3000Wm^{-1}K^{-1}$；此外，石墨烯价格低廉、原料易得，其独特的二维结构能够进行有效的电热传输，有望在高性能电子器件、场发射材料、气体传感器及能量存储等领域获得广泛应用。但由于石墨烯具有二维的片状结构，其在使用过程中特别容易卷曲和高度皱折；尤其是采用熔融共混法制备聚合物复合材料时，石墨烯在剪切力作用下更容易发生卷曲和高度皱折，不利于在基体内形成高效的输运网络。碳纳米管（carbon nanotube，CNT）是 1991 年由 Iijima 发现的一种新型碳材料，它可以看成是由石墨烯卷成的无缝中空管体，其长度为数微米至数毫米，直径在几纳米到几十纳米之间。由于其独特的结构，碳纳米管在力学增强和电子长程传输等方面具有显著的优势；但存在易于团聚和成本高等缺点。

[0003] 关于石墨烯混杂聚合物复合材料制备技术已有报道，例如：中国专利，CN200910067708.8 陈永胜等，《石墨烯与碳纤维复合材料及其制备方法》，其主要特征包括：它是以石墨烯和碳纤维材料为原料，通过涂覆的方法在碳纤维材料表面涂覆石墨烯涂层制备而成，涂层的厚度为 1 纳米 -5 微米。中国专利，CN101474897 陈永胜等，《石墨烯－有机材料层状组装膜及其制备方法》，其主要特征包括：以石墨烯材料和有机材料为原料，利用石墨烯与有机材料之间的静电、氢键、配位键或电荷转移等相互作用，通过旋涂、喷涂、浸渍－提拉等薄膜制备方法层层叠加成膜。中国专利，CN101474899 陈永胜等，《石墨烯－无机材料复合多层薄膜及其制备方法》，其主要特征包括：以石墨烯材料和无机材料为原料，通过喷涂、旋涂、浸渍、化学沉积等常用薄膜制备方法层层叠加成膜，每层膜厚可根据需要控制在 10 纳米 -2 毫米。以上方法中，都没有提及利用石墨烯和碳纳米管混杂技术形成缠绕交织网络，而且制备中多采用旋涂技术形成复合薄膜。

发明内容

[0004] 本发明的目的在于提出一种石墨烯－碳纳米管混杂复合材料的制备方法，通过在溶剂中搅拌和超声振荡使得碳纳米管与石墨烯形成混杂穿插结构，可以有效地防止石墨烯的卷曲或折皱，充分发挥石墨烯优异的二维电热传输特性；这种石墨烯－碳纳米管的混杂输运网络，可以使石墨烯和碳纳米管在结构和功能设计上形成互补，在满足导热、导电功能的同时，显著降低功能填料的掺量、降低复合材料的成本。此外，由于其输运网络结构可以

根据使用要求进行预先设计和构建，具有较大的设计自由度。

[0005] 本发明所采用的技术方案是：

[0006] 一种石墨烯－碳纳米管混杂复合材料的制备方法，该制备方法的工艺步骤如下：

[0007] (1) 配制包含石墨烯、碳纳米管、分散溶剂的悬浮体系，经搅拌、超声振荡使得石墨烯和碳纳米管相互穿插、缠绕形成连通的网络结构；

[0008] (2) 加入聚合物颗粒，经搅拌和超声振荡，使得聚合物颗粒表面被石墨烯－碳纳米管交织网络所包裹；

[0009] (3) 去除溶剂后，形成石墨烯－碳纳米管包裹于聚合物颗粒表面的均匀混合体系；

[0010] (4) 将所述混合体系放入模具中，经升温热压成型、冷却脱模后制得石墨烯－碳纳米管混杂复合材料。

[0011] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，所用的石墨烯是指单层石墨片、多层石墨片或它们的混合物；所用的碳纳米管是指直径为 5-200 纳米、长度为 0.1-100 微米的中空管状碳材料。

[0012] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，所用的分散溶剂为无水乙醇、丙酮、甲苯和苯乙烯。

[0013] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，经超声振荡后使得石墨烯和碳纳米管预先形成一种交织、缠绕的网络结构。。

[0014] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，聚合物颗粒为聚乙烯、聚氯乙烯、聚丙烯、聚酰胺、聚苯乙烯、聚苯乙烯、聚甲醛、聚四氟乙烯、聚碳酸酯、聚苯醚、聚砜。

[0015] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，去除溶剂是通过加热或者真空抽滤方法实现的。

[0016] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，石墨烯－碳纳米管网络包裹在聚合物颗粒表面，形成沿聚合物颗粒表面分布的连通网络。

[0017] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，热压温度高于聚合物熔点或软化点 20℃以上，成型压力大于 10MPa，冷却脱模温度低于 60℃。

[0018] 所述的一种石墨烯－碳纳米管混杂复合材料的制备方法，原料的初始用量配比（质量百分数）为：

[0019] 石墨烯 0.1-10 份；

[0020] 碳纳米管 0.1-10 份；

[0021] 聚合物：100 份；

[0022] 分散溶剂：100-500 份。

[0023] 本发明的有益效果是：

[0024] 1. 本发明采用石墨烯－碳纳米管混杂技术，通过超声振荡使得碳纳米管与石墨烯进行相互穿插和缠绕，利用石墨烯成本低、电学性能优异的优势，借助碳纳米管刚度大、长径比高的特点来防止二维石墨烯片的卷曲；充分发挥石墨烯和碳纳米管的结构特点、形成优势互补，有助于形成高效的三维电热输运网络。

[0025] 2. 通过预先设计和构建输运网络，可以有效地避免传统熔融共混制备过程中出现的聚合物对功能填料的包裹、填料间接触电（热）阻增加、导电（热）性能降低的局限性。

本发明中输运网络的预先构建有助于形成功能填料间的有效搭界、提高输运网络的电、导热传输效率。

[0026] 3. 结合石墨烯－碳纳米管网络与聚合物颗粒的混杂技术，使得石墨烯－碳纳米管网络包裹在聚合物颗粒表面，形成三维的输运网络，显著提高填料在电热传输增强方面的有效利用率，只需要很低的掺量，混杂复合材料就能够具有较好的导电（热）性能，显著降低复合材料的成本。此外，若采用高结晶性聚合物的基体，混杂复合材料会具有一定的正温度系数效应，可以在热敏电阻及器件领域得到广泛的应用。。

[0027] 4. 本发明将石墨烯－碳纳米管导电网络与聚合物基体通过溶剂共混、热压成型的方式制备混杂复合材料，设备简单，操作流程简易，可用于多种热塑性聚合物与石墨烯－碳纳米管混杂复合材料的制备。选择不同基体材料、颗粒分布以及填料用量，可根据实际使用需求，预先设计并制造具有特定网络结构的功能性复合材料，具有极大的设计自由度。

具体实施方式

[0028] 实施例 1：

[0029] 将 0.01 克石墨烯和 0.01 克碳纳米管分散于 10 克无水乙醇中，超声 2 小时后形成稳定的悬浮液；将 10 克高密度聚乙烯超细粉末加入到该悬浮液中，超声 30 分钟，待石墨烯－碳纳米管包裹在高密度聚乙烯粉末表面并形成均匀混合体系时，升温至 60℃进行干燥以除去溶剂。将其转移至模具中，升温至 170℃，并于 10MPa 条件下热压成型 5 分钟，冷却至室温、脱模得到石墨烯－碳纳米管混杂复合材料。测量复合材料体积电阻，计算其电阻率为 7.09×10^{6}ohm·cm。

[0030] 实施例 2：

[0031] 将 0.1 克石墨烯和 0.1 克碳纳米管分散于 10 克丙酮中，超声 2 小时后形成稳定的悬浮液；将 10 克聚丙烯颗粒加入到该悬浮液中，超声 30 分钟，待石墨烯－碳纳米管包裹在高密度聚丙烯颗粒表面并形成均匀混合体系时，于常温下进行真空抽滤除去溶剂。将其转移至模具中，升温至 200℃，并于 10MPa 条件下热压成型 5 分钟，冷却至室温脱模、得到石墨烯－碳纳米管混杂复合材料。测量复合材料体积电阻，计算其电阻率为 2.00×10^{4}ohm·cm。

[0032] 实施例 3：

[0033] 将 0.5 克石墨烯和 0.5 克碳纳米管分散于 25 克无水乙醇中，超声 2 小时后形成稳定的悬浮液；将 10 克聚甲基丙烯酸甲酯颗粒加入到该悬浮液中，超声 30 分钟，待石墨烯－碳纳米管包裹在聚甲基丙烯酸甲酯颗粒表面并形成均匀混合体系时，于常温下进行真空抽滤以除去溶剂。将其转移至模具中，升温至 180℃，并于 10MPa 条件下热压成型 5 分钟，冷却至室温脱模、得到石墨烯－碳纳米管混杂复合材料。测量复合材料体积电阻，计算其电阻率为 8.84×10^{2}ohm·cm。

[0034] 实施例 4：

[0035] 将 1 克石墨烯和 1 克碳纳米管分散于 50 克无水乙醇中，超声 2 小时后形成稳定的悬浮液；将 10 克聚苯乙烯颗粒加入到该悬浮液中，超声 30 分钟，待石墨烯－碳纳米管包裹在聚苯乙烯颗粒表面并形成均匀混合体系时，升温至 60℃进行加热干燥以除去溶剂。进一步转移至模具中，升温至 160℃，并于 10MPa 条件下热压成型 5 分钟，冷却至室温脱模、得到石墨烯－碳纳米管混杂复合材料。测量复合材料体积电阻，计算其电阻率为

4.55×10^{1}ohm·cm。

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Application: 200910248681

1. A method of preparation that graphite alkene - carbon nano tube hybrid composites, the technology step that characterized in said method of preparation as follows:(1)The preparation contains the suspension system of graphite alkene, carbon nano tube, dispersion solvent, and through the stirring, the sonic oscillation makes graphite alkene and carbon nano tube alternate, twine the network structure that forms the intercommunication each other;(2)Add the polymer granule, through stirring and sonic oscillation, make polymer granule surface interweaved the network by graphite alkene - carbon nano tube and wrap up;(3)Behind the removal of solvent, graphitization alkene - carbon nano tube wraps up in the surperficial homogeneous mixing system of polymer granule;(4)Put into the mould with said mixed system, make graphite alkene - carbon nano tube hybrid composites behind intensification hot-forming, cooling depanning.

2. The method of preparation that graphite alkene - carbon nano tube hybrid composites according to claim 1, characterized in that used graphite alkene individual layer graphite flake, multiply graphite flake or their mixture; Used carbon nano tube is that the diameter is 5-200 nanometer, the length tubular material with carbon element of cavity for the 0.1-100 micron.

3. The method of preparation that graphite alkene - carbon nano tube hybrid composites according to claim 1, characterized in that used dispersed solvent is pure alcohol, acetone, toluene and styrene.

4. The method of preparation that graphite alkene - carbon nano tube hybrid composites according to claim 1, characterized in making behind the sonic oscillation graphite alkene and carbon nano tube preform one kind interweave, winding network structure.

5. The method of preparation that graphite alkene - carbon nano tube hybrid composites according to claim 1, characterized in that the polymer granule is polyethylene, polyvinyl chloride, polypropylene, polyamide, polystyrene, polystyrene, polyformaldehyde, polytetrafluoroethylene (PTFE), Merlon, polyphenylene oxide, polysulfone (PSO).

6. The method of preparation that graphite alkene - carbon nano tube hybrid composites according to claim 1, characterized in that the removal of solvent that by heating or vacuum filtration method realize.

7. The method of preparation that graphite alkene - carbon nano tube hybrid composites according to claim 1, characterized in that graphite alkene - carbon nano tube network parcel is surperficial at the polymer granule, form along the connected network of polymer granule surface distribution.

8. The method of preparation that graphite alkene - carbon nano tube hybrid composites according to claim 1, characterized in that the hot pressing temperature is higher than polymer fusing point or softening point more than 20 DEG Cs, the briquetting pressure is greater than 10MPa, and cooling depanning temperature is less than 60 DEG Cs.

Plain Text Translation Description

Translation By Page Page Translation

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Application:
200910248681

A method of preparation that graphite alkene - carbon nano tube hybrid composites

The technical field

The present invention relates to a method of preparation that functional polymer and device technology field, especially relates to the method of preparation of graphite alkene - carbon nano tube hybrid composites.

The background art

Graphite alkene (graphene seen: Novoselov K S for details, et al.Electric field effects inatomically thin carbon films Science, 2004,306: 666-119) a carbonaceous new material of closely piling up into twodimentional cellular lattice structure by the individual layer carbon atom, it is the elementary cell that makes up other dimension carbonaceous materials (like zero dimension fullerene, one-dimensional carbon nano tube, three-dimensional graphite).Graphite alkene has excellent Electrical property and thermal, its room temperature electron mobility can reach 15000cm^{2}V^{-1}S^{-1}, Thermal conductivity can reach 3000Wm^{-1}K^{-1}In addition, graphite alkene low price, raw materials are easy, and its unique two-dimensional structure can carry out the transmission of effectual electric heat, is expected to obtain the wide application in fields such as high performance electronic device, field emission material, gas sensor and energy storages.Nevertheless because graphite alkene has two-dimensional sheet structure, it is curling and high fold easy very much in the use: When especially adopting melt-compounding method preparation polymer composites, graphite alkene is easier under the shearing force effect to be taken place curlingly and high fold, is unfavorable for forming the efficient and transports the network in the base member.Carbon nano tube (carbon nanotube, CNT) is the new carbon material by the Iijima discovery in 1991, and it can be regarded as by the seamless cavity body of graphite alkene coiled, and its length amounts to extremely several millimeters microns, and the diameter is in how many nanometers to between tens nanometers.Because its unique structure, carbon nano tube have remarkable advantage in the aspect of mechanics reinforcing and the transmission of electron long-range etc. ; Nevertheless there is easily shortcoming such as reunion and high costs.

It has had the report to mix the polymer composites technology of preparing about graphite alkene, for example: Chinese patent, and the old Yongsheng of CN200910067768.8 etc., " graphite alkene and carbon-fibre composite and method for making same ", its leading features includes: it uses graphite alkene and carbon fibre material as the raw materials, is prepared from in carbon fibre material surface coating graphite alkene coating by the deposited method, the thickness of coating is 1 nanometer - 5 micron.China's patent, the old Yongsheng of CN101474897 etc., " graphite alkene - organic material layer form equipment membrane and method for making same ", its leading features includes: use graphite alkene material and organic material as the raw materials, utilizes the interactions such as static, hydrogen bond, coordinate bond or charge transfer between graphite alkene and the organic material, by film preparation methods such as spin coating, spraying, flooding - carry the draw film forming that superposes layer upon layer.China's patent, the old Yongsheng of CN101474899 etc., " the compound multilayer film and method for making same of

graphite alkene - Inorganic Materials ", and its leading features includes: use graphite alkene material and Inorganic Materials as the raw materials, by film preparation methods commonly used such as spraying, spin coating, flooding, the electroless deposition film forming that superposes layer upon layer, every tunic thickness can be controlled in 10 nanometers - 2 millimeter as required. In the above method, do not mention all that it twines the network that interweaves to utilize graphite alkene and carbon nano tube to mix technique formation, and adopt the spin-coating to form the coextruded film more in the preparation.

The disclosure of the invention

A purpose of the present invention is to provide the method of preparation of graphite alkene - carbon nano tube hybrid composites, make the carbon nano tube form with graphite alkene through stirring in the solvent and sonic oscillation and mix the interlude structure, can prevent curling or pincher types of graphite alkene effectively, give full play to the two-dimentional electric heat transmission characteristics of graphite alkene excellence; Mixing of this kind of graphite alkene - carbon nano tube transports the network, and it is complementary to make graphite alkene and carbon nano tube form on the structure and function designs, when satisfying heat conduction, electrically conductive function, notably reduces the Blending quantity of function filler, the cost of reduction composite. In addition, because it transports the network structure and can predesign and found according to the operation requirement, has the great design degree of freedom.

The technical scheme that the invention was adopted is:

A method of preparation that graphite alkene - carbon nano tube hybrid composites, the technology step of the method of preparation as follows:

(1)The preparation contains the suspension system of graphite alkene, carbon nano tube, dispersion solvent, makes graphite alkene and carbon nano tube alternate, twine the network structure that forms the intercommunication each other through stirring, sonic oscillation;

(2)Add the polymer granule, through stirring and sonic oscillation, make polymer granule surface interweaved the network by graphite alkene - carbon nano tube and wrap up;

(3)Behind the removal of solvent, graphitization alkene - carbon nano tube wraps up in the superficial homogeneous mixing system of polymer granule;

(4)Put into the mould with said mixed system, make graphite alkene - carbon nano tube hybrid composites behind intensification hot-forming, cooling depanning.

The method of preparation of said graphite alkene - carbon nano tube hybrid composites, used graphite alkene are individual layer graphite flake, multiply graphite flake or their mixture; Used carbon nano tube is that the diameter is 5-200 nanometer, the length tubular material with carbon element of cavity for the 0.1-100 micron.

The method of preparation of said graphite alkene - carbon nano tube hybrid

composites, used dispersed solvent is pure alcohol, acetone, toluene and styrene.

The method of preparation of said graphite alkene - carbon nano tube hybrid composites, make behind the sonic oscillation graphite alkene and carbon nano tube preform one kind interweave, winding network structure.

The method of preparation of said graphite alkene - carbon nano tube hybrid composites, the polymer granule is polyethylene, polyvinyl chloride, polypropylene, polyamide, polystyrene, polystyrene, polyformaldehyde, polytetrafluoroethylene (PTFE), Merion, polyphenylene oxide, polysulfone (PSO).

The method of preparation of said graphite alkene - carbon nano tube hybrid composites, removal of solvent are that by heating or vacuum filtration method realize.

The method of preparation of said graphite alkene - carbon nano tube hybrid composites, graphite alkene - carbon nano tube network parcel is surperficial at the polymer granule, forms along the connected network of polymer granule surface distribution.

The method of preparation of said graphite alkene - carbon nano tube hybrid composites, hot pressing temperature are higher than polymer fusing point or softening point more than 20 DEG Cs, and the briquetting pressure is greater than 10MPa, and cooling depanning temperature is less than 80 DEG Cs.

The method of preparation of said graphite alkene - carbon nano tube hybrid composites, the initial quantity ratio (mass percent) of raw materials is:

Graphite alkene 0.1-10 part;

Carbon nano tube 0.1-10 part;

Polymer: 100;

Dispersion solvent: 100-500 part.

The beneficial effect of the invention is:

1. The invention adopts graphite alkene - carbon nano tube to mix the technique, makes carbon nano tube and graphite alkene alternate each other and twine by the sonic oscillation, utilizes the advantage that graphite alkene is with low costs, the Electrical property is excellent, and characteristics big with the help of carbon nano tube rigidity, the major diameter relative altitude prevent the curling of two-dimentional graphite alkene piece; Give full play to structural feature, the formation of graphite alkene and carbon nano tube and have complementary advantages, help forming the three-dimensional electric heat of efficient and transport the network.

2. Transport the network by predesigning with the structure, parcel that the polymer that can avoid effectively appearing in traditional melting blend Preparative processes packed to the function, pack between contact electricity (heat) hinder the limitation that increases, electrically conducts (heat) performance degradation.Ii

helps forming the function and effectively has a common boundary, improves the electricity, the heat conduction transmission efficiency that transport the network between packing to transport founing in advance of network in the invention.

3. Combine the technique that mixes of graphite alkene - carbon nano tube network and polymer granule, make graphite alkene - carbon nano tube network parcel surperficial at the polymer granule, form the three-dimensional network that transports, the remarkable effective rate of utilization of packing in the aspect of electric heat transmission reinforcing that improves, the blending quantity that the only need is very low, the hybrid composites just can have better (heat) the performance of electrically conducting, notably reduces the cost of composite. In addition, if adopt the base member of high crystalline polymer, the hybrid composites can have certain positive temperature coefficient effect, can obtain extensive application at thermal resistor and device field.

4. The hybrid composites is prepared with electrically conductive network of graphite alkene - carbon nano tube and the mode that the polymeric matrix passes through solvent blend, hot-forming to the invention, and equipment is simple, and the operating process is simple and easy, can be used to the preparation of multiple thermoplastic polymer and graphite alkene - carbon nano tube hybrid composites. Select different matrix materials, particle distribution and filler quantity, can predesign and manufacture the functional composite that has specific network structure according to the in-service use demand, have the very big design degree of freedom.

The detailed description of the invention

Embodiment 1:

Be scattered in 10 grams in the pure alcohols with 0.01 gram graphite alkene and 0.01 gram carbon nano tube, the supersound forms stable suspension after 2 hours. In adding the suspension with 10 gram high density polyethylene (HDPE) superfineas, the supersound is 30 minutes, treats that graphite alkene - carbon nano tube parcel is surperficial and when forming the homogeneous mixing system at the high density polyethylene (HDPE) powder, intensilies to 60 DEG Cs to carry out drying with except that desolvating. In its transfer to mould, heat up to 170 DEG Cs, and under the 10MPa condition hot-forming 5 minutes, cool off to room temperature, depanning and obtain graphite alkene - carbon nano tube hybrid composites. Measure the composite bulk resistance, calculate its resistivity and be 7.09 10^0Omcm.

Embodiment 2:

Be scattered in 10 grams in the acetone with 0.1 gram graphite alkene and 0.1 gram carbon nano tube, the supersound forms stable suspension after 2 hours; in adding the suspension with 10 gram polypropylene granules, the supersound is 30 minutes, treats that graphite alkene - carbon nano tube parcel is surperficial and when forming the homogeneous mixing system at high density polypropylene granule, carries out the vacuum filtration and remove and desolvate under normal atmospheric temperature. In its transfer to mould, heat up to 200 DEG Cs, and under the 10MPa condition hot-forming 5 minutes, cool off to the room temperature depanning, obtain graphite alkene - carbon nano tube hybrid composites. Measure the composite bulk resistance, calculate its

resistivity and be 2.00 10^4Ohmcm.

Embodiment 3:

Be scattered in 25 grams in the pure alcohols with 0.5 gram graphite alkene and 0.5 gram carbon nano tube, the supersound forms stable suspension after 2 hours; In adding the suspension with 10 gram polymethyl methacrylate granules, the supersound is 30 minutes, treats that graphite alkene - carbon nano tube parcel is surperficial and when forming the homogeneous mixing system at the polymethyl methacrylate granule, carries out the vacuum filtration and desolvate in order to remove under normal atmospheric temperature. In its transfer to mould, heat up to 180 DEG Cs, and under the 10MPa condition hot-forming 5 minutes, cool off to the room temperature depanning, obtain graphite alkene - carbon nano tube hybrid composites. Measure the composite bulk resistance, calculate its resistivity and be 8.84 10^2Ohmcm.

Embodiment 4:

Be scattered in 50 grams in the pure alcohols with 1 gram graphite alkene and 1 gram carbon nano tube, the supersound forms stable suspension after 2 hours; In adding the suspension with 10 gram polystyrene granules, the supersound is 30 minutes, treats that graphite alkene - carbon nano tube parcel is surperficial and when forming the homogeneous mixing system at the polystyrene granule, intensifies to carry out the heat drying to 60 DEG Cs and desolvate in order to remove. In the further transfer to mould, heat up to 160 DEG Cs, and under the 10MPa condition hot-forming 5 minutes, cool off to the room temperature depanning, obtain graphite alkene - carbon nano tube hybrid composites. Measure the composite bulk resistance, calculate its resistivity and be 4.55 10^1Ohmcm.

Method for preparing graphene-carbon nano tube hybrid composite

Application Number	200910248681	**Application Date**	2009.12.23
Publication Number	101734650A	**Publication Date**	2010.06.16
Priority Information			
International Classification	C01B31/02;B82B3/00		
Applicant(s) Name	Shenyang Jianzhu University		
Address			
Inventor(s) Name	Du Jinhong;Liu Pengfei;Tong Yu;Zeng You;Zhao Jinbo;Zhao Long		
Patent Agency Code	21205	**Patent Agent**	wang derong

Abstract

The invention provides a method for preparing a graphene-carbon nano tube hybrid composite and relates to a method for preparing a functional high molecular material and a device thereof. The method comprises the following steps of: carrying out the stirring and sonic oscillation treatment on graphene and carbon nano tubes to preform an entangled network structure, thoroughly mixing the entangled network structure and polymer particles, and thus obtaining an uniformly-mixed system in which the graphene-carbon nano tube network is coated on the surfaces of the polymer particles after removing the solvent; and putting the uniformly-mixed system in a mould, hot-compacting, and obtaining the graphene-carbon nano tube hybrid composite after cooling and demoulding. By mingling the graphene and the carbon nano tubes in advance to form the communicated network structure, the method realizes the advantage complementation of the graphene and carbon nano tube structures and enables the hybrid composite to have favorable electric conduction and heat conduction properties. The method can be widely used in the fields such as aviation, transportation and communication, electronic industry, civil facilities, construction, chemical industry and the like, can be produced in the industrial scale, and has the advantages of low cost and environmental friendliness.

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Electronic Acknowledgement Receipt

EFS ID:	32835901
Application Number:	15881071
International Application Number:	
Confirmation Number:	2885
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	130577
Filer:	Gregory L. Porter/Jeanne Dunn
Filer Authorized By:	Gregory L. Porter
Attorney Docket Number:	MRE012NP2C / 277190
Receipt Date:	07-JUN-2018
Filing Date:	26-JAN-2018
Time Stamp:	16:12:36
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	IDS.pdf	527881 e557704c37a1fe46cbe8debe9a583bdd4e50d566	no	4

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2	Foreign Reference	CN_101734650.pdf	1416690 b8a3a58afccc486a9f9a68910927a0942653 8d5d	no	15
Warnings:					
Information:					
			Total Files Size (in bytes):	1944571	

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/881,071

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	660
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	20 minus 20 =	*			OR	x 100 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1720

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
AMENDMENT A	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
AMENDMENT A	Application Size Fee (37 CFR 1.16(s))									
AMENDMENT A	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
AMENDMENT B	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
AMENDMENT B	Application Size Fee (37 CFR 1.16(s))									
AMENDMENT B	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/881,071	01/26/2018	1726	1720	MRE012NP2C / 277190	20	3

CONFIRMATION NO. 2885

UPDATED FILING RECEIPT

130577
ANDREWS KURTH KENYON LLP
600 Travis Street
Suite 4200
Houston, TX 77002

OC000000099936403

Date Mailed: 06/04/2018

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;
Milos Marinkovic, San Antonio, TX;

Applicant(s)

MOLECULAR REBAR DESIGN, LLC, Austin, TX;

Assignment For Published Patent Application

MOLECULAR REBAR DESIGN, LLC, Austin, TX

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 14/390,902 10/06/2014 PAT 9912009
which is a 371 of PCT/US2013/047029 06/21/2013
which claims benefit of 61/663,513 06/22/2012
and claims benefit of 61/662,393 06/21/2012

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 02/23/2018

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/881,071**

Projected Publication Date: 09/13/2018

Non-Publication Request: No

Early Publication Request: No

Title

Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

Preliminary Class

429

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	Clive P. Bosnyak	**Confirmation No.:**	2885
Serial No.:	15/991,071	**Art Unit:**	1726
Filed:	January 26, 2018	**Examiner:**	
For:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	**Atty. Dkt. No.:**	MRE012NP2C / 277190

Mail Stop Missing Parts
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO NOTICE TO FILE CORRECTED APPLICATION PAPERS

In response to the Notice to File Corrected Application Papers, dated February 27, 2018, applicant has enclosed a replacement drawing sheet 1/1. A two-month request for extension of time is also being submitted along with the requisite extension fee.

Applicant does not believe any other fee is necessary for this submission. However, if a fee is required, the Commissioner is hereby authorized to charge any required fee to the Hunton Andrews Kurth LLP Deposit Account (referencing matter MRE012NP2C / 277190). Any questions regarding this application should be directed to the attorney below.

Dated:

Respectfully submitted,

/Gregory L. Porter/
Gregory L. Porter
Regis. No. 40131
HUNTON ANDREWS KURTH LLP
600 Travis St., Suite 4200
Houston, Texas 77002
Tel: (713) 220-4621
Fax: (713) 238-4285
Pat-tmk@andrewskurth.com

ATTORNEYS FOR APPLICANT

HOU:3890925.1

1/1

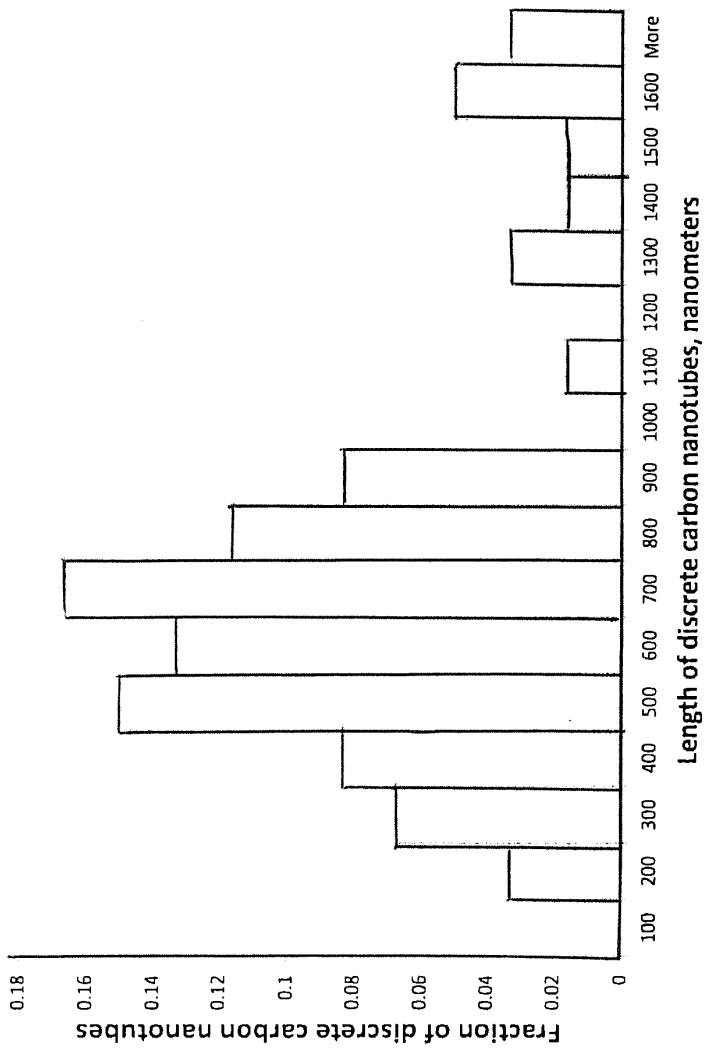
Fraction of discrete carbon nanotubes
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
More
Length of discrete carbon nanotubes, nanometers

Figure 1

Electronic Patent Application Fee Transmittal

Application Number:	15881071
Filing Date:	26-Jan-2018
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Filer:	Gregory L. Porter/Jeanne Dunn
Attorney Docket Number:	MRE012NP2C / 277190

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension - 2 months with $0 paid	1252	1	600	600
Miscellaneous:				
			Total in USD ($)	**600**

Electronic Acknowledgement Receipt	
EFS ID:	32754547
Application Number:	15881071
International Application Number:	
Confirmation Number:	2885
Title of Invention:	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	130577
Filer:	Gregory L. Porter/Jeanne Dunn
Filer Authorized By:	Gregory L. Porter
Attorney Docket Number:	MRE012NP2C / 277190
Receipt Date:	30-MAY-2018
Filing Date:	26-JAN-2018
Time Stamp:	11:48:18
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$600
RAM confirmation Number	053018INTEFSW00011753502849
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Applicant Response to Pre-Exam Formalities Notice	RNFCAP.pdf	18319 b6fdb5a2d51e85dfe2dea786c257da2a5a3f7e96	no	1
Warnings:					
Information:					
2	Drawings-only black and white line drawings	ReplacementDrwgSheet.pdf	364628 37f811cb93be80cd0851297215351f31e55f52f2	no	1
Warnings:					
Information:					
3	Fee Worksheet (SB06)	fee-info.pdf	30928 64fdca3e24eaf03686a44b78949bc9490fe6ae15	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	413875		

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/881,071	01/26/2018	Clive P. Bosnyak	MRE012NP2C / 277190

CONFIRMATION NO. 2885

130577
ANDREWS KURTH KENYON LLP
600 Travis Street
Suite 4200
Houston, TX 77002

FORMALITIES LETTER

OC000000097629303

Date Mailed: 02/27/2018

NOTICE TO FILE CORRECTED APPLICATION PAPERS

Filing Date Granted

An application number and filing date have been accorded to this application. The application is informal since it does not comply with the regulations for the reason(s) indicated below. Applicant is given TWO MONTHS from the date of this Notice within which to correct the informalities indicated below. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

The required item(s) identified below must be timely submitted to avoid abandonment:

- Replacement drawings in compliance with 37 CFR 1.84 and 37 CFR 1.121(d) are required. The drawings submitted are not acceptable because:
  - The drawings have a line quality that is too light to be reproduced (weight of all lines and letters must be heavy enough to permit adequate reproduction) or text that is illegible (reference characters, sheet numbers, and view numbers must be plain and legible) see 37 CFR 1.84(l) and (p)(1)); See Figure(s) 1.

Applicant is cautioned that correction of the above items may cause the specification and drawings page count to exceed 100 pages. If the specification and drawings exceed 100 pages, applicant will need to submit the required application size fee.

Replies must be received in the USPTO within the set time period or must include a proper Certificate of Mailing or Transmission under 37 CFR 1.8 with a mailing or transmission date within the set time period. For more information and a suggested format, see Form PTO/SB/92 and MPEP 512.

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/lqchau/

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/881,071

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	660
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	20 minus 20 =	*			OR	x 100 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1720

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
AMENDMENT A	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
AMENDMENT A	Application Size Fee (37 CFR 1.16(s))									
AMENDMENT A	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
AMENDMENT B	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
AMENDMENT B	Application Size Fee (37 CFR 1.16(s))									
AMENDMENT B	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/881,071	01/26/2018	1726	1720	MRE012NP2C / 277190	20	3

CONFIRMATION NO. 2885

FILING RECEIPT

130577
ANDREWS KURTH KENYON LLP
600 Travis Street
Suite 4200
Houston, TX 77002

Date Mailed: 02/27/2018

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;
Milos Marinkovic, San Antonio, TX;

Applicant(s)

MOLECULAR REBAR DESIGN, LLC, Austin, TX;

Assignment For Published Patent Application

MOLECULAR REBAR DESIGN, LLC, Austin, TX

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 14/390,902 10/06/2014 PAT 9912009
which is a 371 of PCT/US2013/047029 06/21/2013
which claims benefit of 61/663,513 06/22/2012
and claims benefit of 61/662,393 06/21/2012

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 02/23/2018

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/881,071**

Projected Publication Date: To Be Determined - pending completion of Corrected Papers

Non-Publication Request: No

Early Publication Request: No

Title

Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes

Preliminary Class

429

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

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Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

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BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES

CROSS REFERENCE TO RELATED APPLICATIONS

[1] This patent application claims priority from USSN 61/662393 filed June 21, 2012 and USSN 61/663513 filed June 22, 2012; and is related to USSN 13/164456 filed June 20, 2011; USSN 12/968151 filed December 14, 2010; USSN 13/140029 filed December 18, 2009; USSN 61/500561 filed June 23, 2011; USSN 61/500560 filed June 23, 2011; and USSN 61/638454 filed April 25, 2012; the disclosures of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[2] Not applicable

BACKGROUND

[3] Many energy storage devices like batteries, capacitors and photovoltaics can utilize a binder and/or an electrolyte and separator film to provide enhanced performances in mechanical stabilization, improved electrical conduction of the powder used in cathodes or electrodes and ion transport in the electro-or photoactive material and electrolyte.

[4] Lithium ion batteries are used extensively for portable electronic equipment and batteries such as lithium ion and lead-acid are increasingly being used to provide electrical back-up for wind and solar energy. The salts for the cathode materials in lithium ion

batteries are generally known to have poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Both cathode and anode materials in many battery types such as lithium ion based batteries exhibit swelling and deswelling as the battery is charged and discharged. This spatial movement leads to further separation of some of the particles and increased electrical resistance. The high internal resistance of the batteries, particularly in large arrays of lithium ion batteries such as used in electric vehicles, can result in excessive heat generation leading to runaway chemical reactions and fires due to the organic liquid electrolyte.

[5] Lithium primary batteries consist, for example, of lithium, poly(carbon monofluoride) and lithium tetrafluoroborate together with a solvent such as gamma-butyrolactone as an electrolyte. These lithium primary batteries have excellent storage lifetimes, but suffer from only being able to provide low current and the capacity is about one tenth of what is theoretically possible. This is ascribed to the poor electrical conductivity of the poly(carbon monofluoride). In some cases a portion manganese dioxide is added to aid in the electrical conductivity and power of the lithium battery.

[6] Attempts to overcome the deficiencies of poor adhesion to current collectors and to prevent microcracking during expansion and contraction of rechargable batteries have included development of binders. Binders such as polyacrylic acid (PAA), for cathodes, poly(styrene butadiene), carboxymethylcellulose (CMC), styrene-butadiene (SBR), for anodes, and particularly polyvinylidene fluoride (PVDF) for cathodes and anodes, are used in lithium based batteries to hold the active material particles together and to maintain contact with the current collectors i.e., the aluminum (Al) or the copper (Cu) foil. The PAA and SBR are used as aqueous suspensions or solutions and are considered more

environmentally benign than organic solvent based systems such as n-methyl 2 pyrrolidone (NMP) with PVDF.

[7] A cathode electrode of a lithium ion battery is typically made by mixing active material powder, such as lithium iron phosphate, binder powder, i.e., high molecular weight PVDF, solvent such as NMP if using PVDF, and additives such as carbon black, into a slurry (paste) and pumping this slurry to a coating machine. An anode electrode for a lithium ion battery is made similarly by typically mixing graphite, or other materials such as silicon, as the active material, together with the binder, solvent and additives. The coating machines spread the mixed slurry (paste) on both sides of the Al foil for the cathode and Cu foil for the anode. The coated foil is subsequently calendared to make the electrode thickness more uniform, followed by a slitting operation for proper electrode sizing and drying.

[8] For zinc-carbon batteries, the positive electrode can consist of a wet powder mix of manganese dioxide, a powdered carbon black and electrolyte such as ammonium chloride and water. The carbon black can add electrical conductivity to the manganese dioxide particles, but is needed at high weight percentages in the range about 10 to 50% by weight of manganese dioxide. These high amounts of carbon black needed for improved electrical conductivity, or reduced impedance of the battery, diminish the capacity per unit volume of the battery as less manganese dioxide can be employed per unit volume of the positive paste mix. Thus, in general, there is a need to improve the impedance of a battery while maximizing the amount of active material per unit volume.

[9] For a lead-acid battery the anode can be made from carbon particles together with a binder to provide higher specific capacity (capacity per unit weight). The anode of a zinc-carbon battery is often a carbon rod typically made of compressed carbon particles,

graphite and a binder such as pitch. The carbon particle anodes tend to have poor mechanical strength leading to fracture under conditions of vibration and mechanical shock.

[10] The characteristics of the binder material are important for both manufacturing and performance of the battery. Some of these characteristics of relevance are electrical and ionic conductivity, tensile strength and extensibility, adhesion to particles as well as the foils, and swelling of electrolyte. Improvement of electrical and ionic conductivity is needed for improved battery capacity and power. Materials such as lithium manganese oxide for cathodes and silicon particles for anodes exhibit much lower practical specific capacity than theoretically available. A higher electrical and ionic conductivity binder material would be most beneficial to achieve specific capacities closer to their theoretical values. It is desirable to improve the tensile and adhesive strength of binders so that less binder material can be employed and also improve the battery cycling lifetime. Addition of conductive particles, such as carbon black decreases the tensile strength and extensibility of binders. Controlled swelling of the binder in electrolyte is also important. If too much swelling occurs, this separates the particles and significantly increases the inter-particle ohmic resistance. Also, since the particles of the anode or cathode are coated with binder, the layer thickness of the binder can be as thin as 50 to 100 nanometers. This layer thickness precludes uniform distributions of particles of sizes larger than the binder layer thickness. For example, multiwall carbon nanotubes as usually made in a gas phase reactor consist of bundles with diameters ranging from about 50 to 500 microns in diameter and would therefor reside only at the interstitial spaces between the particles.

[11] Impurities, such as non-lithium salts, iron, and manganese to name a few, with the binder can also be highly deleterious to battery performance. Typically, high purity of the binder material, and other additives comprising the binder material such as carbon black to

improve electrical conductivity, is an important factor to minimize unwanted side reactions in the electrochemical process. For example in alkaline-manganese dioxide batteries the total iron in the manganese dioxide is less than 100 ppm to prevent hydrogen gassing at the anode. Commercially available carbon nanotubes such as Baytubes® (Bayer AG) or Graphistrength® (Arkema) can contain as much as ten percent or more by weight of residual metal catalysts and are not considered advantageous for batteries at these levels of impurity.

[12] For photovoltaics, lines of conductive paste ink, made from solvents, binders, metal powder and glass frit, are screen-printed onto solar panel modules. The binders are usually polymer based for improved printability, such as ETHOCEL™ (Dow Chemical Company). During the burning off of the polymer and cooling the lines can crack due to shrinkage forces and so increase impedance. It is highly desirable to have a more robust conductive paste ink to prevent cracking during heating and cooling.

[13] Efforts to improve the safety of lithium ion batteries have included using non-flammable liquids such as ionic liquids, for example, ethyl-methyl-imidazolium bis-(trifluoromethanesulfonyl)-imide (EMI-TFSI), and solid polymer, sometimes with additional additives, for example, polyethylene oxide with titanium dioxide nanoparticles, or inorganic solid electrolytes such as a ceramic or glass of the type glass ceramics, $Li_{1+x+y}Ti_{2-x}Al_xSi_yP_{3-y}O_{12}$ (LTAP). The electrical conductivity values of organic liquid electrolytes are in the general range of 10^{-2} to 10^{-1} S/cm. Polymer electrolytes have electrical conductivity values in the range of about 10^{-7} to 10^{-4} S/cm, dependent on temperature, whereas inorganic solid electrolytes generally have values in the range 10^{-8} to 10^{-5} S/cm. At room temperature most polymer electrolytes have electrical conductivity values around 10^{-5} S/cm. The low ionic conductivities of polymer and inorganic solid electrolytes are presently a limitation to their general use in energy storage and collection devices. It is thus

highly desirable to improve the conductivity of electrolytes, and particularly with polymer and inorganic electrolytes because of their improved flammability characteristics relative to organic liquids. Also, it is desirable to improve the mechanical strength of solid electrolytes in battery applications requiring durability in high vibration or mechanical shock environments, as well as in their ease of device fabrication.

[14] In alkaline batteries the electrolyte is typically potassium hydroxide. Alkaline batteries are known to have significantly poorer capacity on high current discharge than low current discharge. Electrolyte ion transport limitations as well as polarization of the zinc anode are known reasons for this. An increase in the electrolyte ion transport is highly desirable.

[15] Amongst new generation thin film photovoltaic technologies, dye sensitized solar cells (DSSCs) possess one of the most promising potentials in terms of their cost-performance ratio. One of the most serious drawbacks of the present DSSCs technology is the use of liquid and corrosive electrolytes which strongly limit their commercial development. An example of an electrolyte currently used for DSSCs is potassium iodide/iodine. Replacement of the presently used electrolytes is desirable, but candidate electrolytes have poor ion transport.

[16] Typical electrolytic capacitors are made of tantalum, aluminum, or ceramic with electrolyte systems such as boric acid, sulfuric acid or solid electrolytes such as polypyrrole. Improvements desired include higher rates of charge and discharge which is limited by ion transport of the electrolyte.

[17] A separator film is often added in batteries or capacitors with liquid electrolytes to perform the function of electrical insulation between the electrodes yet allowing ion transport. Typically in lithium batteries the separator film is a porous polymer film, the

polymer being, for example a polyethylene, polypropylene, or polyvinylidene fluoride. Porosity can be introduced, for example, by using a matt of spun fibers or by solvent and/or film stretching techniques. In lead-acid batteries, where used the separator film is conventionally a glass fiber matt. The polymer separator film comprising discrete carbon nanotubes of this invention can improve ion transport yet still provide the necessary electrical insulation between the electrodes.

[18] The present invention comprises improved binders, electrolytes and separator films for energy storage and collection devices like batteries, capacitors and photovoltaics comprising discrete carbon nanotubes, methods for their production and products obtained therefrom.

SUMMARY

[19] In one embodiment, the invention is a composition comprising a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the composition comprises a binder material, an electrolyte material or a separator film of an energy storage or collection device.

[20] In another embodiment, the composition comprises a plurality of discrete carbon nanotube fibers have a portion of discrete carbon nanotubes that are open ended and ion conducting. The composition can further comprise at least one polymer. The polymer is selected from the group consisting of vinyl polymers, preferably poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene) and the like, poly(styrene-isoprene), poly(methacrylic acid), poly(acrylic acid), poly(vinylalcohols), and poly(vinylacetates), fluorinated polymers, preferably poly(vinylidine difluoride) and poly(vinylidene difluoride) copolymers, conductive polymers, preferably poly(acetylene), poly(phenylene), poly(pyrrole), and poly(acrylonitrile), polymers derived from natural sources, preferably alginates, polysaccharides, lignosulfonates, and cellulosic based materials, polyethers, polyolefines, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

[21] In yet another embodiment of this invention, the plurality of discrete carbon nanotube fibers are further functionalized, preferably the functional group comprises a molecule of mass greater than 50g/mole, and more preferably the functional group comprises carboxylate, hydroxyl, ester, ether, or amide moieties, or mixtures thereof.

[22] A further embodiment of this invention comprising a plurality of discrete carbon nanotube fibers further comprising at least one dispersion aid.

[23] In a yet further embodiment of this invention, the plurality of carbon nanotubes further comprise additional inorganic structures comprising of elements of the groups two through fourteen of the Periodic Table of Elements.

[24] Another embodiment of this invention comprises a plurality of carbon wherein the composition has a flexural strength of at least about ten percent higher than a comparative composition made without the plurality of discrete carbon nanotubes.

[25] Yet another embodiment of this invention is a binder, electrolyte or separator film composition comprising a plurality of discrete carbon nanotube fibers having a portion of discrete carbon nanotubes that are open ended and ion conducting further comprising non-fiber carbon structures. The non-fiber carbon structures comprise components selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes and mixtures thereof. Preferably the graphene or oxidized graphene have at least a portion of discrete carbon nanotubes interspersed between the graphene or oxidized graphene platelets.

[26] A yet further embodiment of this invention is a composition comprising a plurality of discrete carbon nanotube fibers where the binder material has an impedance of less than or equal to about one billion (1×10^9) ohm-m and the electrolyte material has a charge transfer resistance of less than or equal to about 10 million (1×10^7) ohm-m.

[27] Another embodiment of this invention comprises an electrolyte or separator film composition comprising a plurality of discrete carbon nanotube fibers wherein the carbon nanotubes are oriented. The orientation is accomplished by fabrication techniques such as in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or

fiber spinning fabrication method. The orientation may also be made via post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

[28] A further embodiment of this invention is a composition comprising a plurality of discrete carbon nanotubes wherein the portion of open ended tubes comprise electrolyte. For an electrolyte comprising polymer, the polymer is preferred to comprise a molecular weight of the polymer less than 10,000 daltons, such that the polymer can enter within the tube. The electrolyte may contain liquids.

[29] An additional embodiment of this invention comprises a composition including a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, preferably wherein 40% to 90% by number of the carbon nanotubes have an aspect ratio of 30-70, and more preferably aspect ratio of 40-60, and 1% to 30% by number of aspect ratio 80-140, most preferably an aspect ratio of 90 to 120. In statistics, a bimodal distribution is a continuous probability distribution with two different modes. These appear as distinct peaks (local maxima) in the probability density function. More generally, a multimodal distribution is a continuous probability distribution with two or more modes. The discrete carbon nanotubes can have a unimodal, bimodal or multimodal distribution of diameters and/or lengths. For example, the discrete carbon nanotubes can have a bimodal distribution of diameters wherein one of the peak values of diameter is in the range 2 to 7 nanometers and the other peak value is in the range 10 to 40 nanometers. Likewise, the lengths of the discrete carbon nanotubes can have a bimodal distribution such that one peak has a maximum value in the range of 150 to 800 nanometers and the second peak has a maximum value in the range 1000 to 3000 nanometers. That composition is useful in binders and electrolytes of the invention.

[30] In yet another embodiment, the invention is an electrode paste, preferably an anode paste, for a lead acid battery, the paste comprising discrete carbon nanotubes having an average length from about 400 to about 1400 nm, polyvinyl alcohol, water, lead oxide and sulfuric acid. Preferably, the carbon nanotubes, polyvinyl alcohol and water form a dispersion, and the dispersion is then contacted with lead oxide followed by sulfuric acid to form the electrode paste.

BRIEF DESCRIPTION OF FIGURES

[31] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

[32] Figure 1 shows discrete carbon nanotubes of this invention with a bimodal length distribution where the maximum of one peak is about 700 nanometers and the maximum of the second peak is about 1600 nanometers. The lengths were determined by deposition of the discrete carbon nanotubes on a silicon wafer and by using scanning electron microscopy.

DETAILED DESCRIPTION

[33] In the following description, certain details are set forth such as specific quantities, sizes, etc., so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be evident to those of ordinary skill in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

[34] While most of the terms used herein will be recognizable to those of ordinary skill in the art, it should be understood, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of ordinary skill in the art. In cases where the construction of a term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition, 2009. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification.

[35] In the present invention, discrete oxidized carbon nanotubes, alternatively termed exfoliated carbon nanotubes, are obtained from as-made bundled carbon nanotubes by methods such as oxidation using a combination of concentrated sulfuric and nitric acids and sonication. The bundled carbon nanotubes can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis. The bundled carbon nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes

may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting, or non-metallic based on their chirality and number of walls. They may also include amounts of nitrogen within the carbon wall structure. The discrete oxidized carbon nanotubes may include, for example, single-wall, double-wall carbon nanotubes, or multi-wall carbon nanotubes and combinations thereof. The diameters and lengths of the discrete carbon nanotubes can be determined by deposition of the discrete carbon nanotubes from dilute solution on a silicon wafer and by using scanning electron microscopy.

[36] One of ordinary skill in the art will recognize that many of the specific aspects of this invention illustrated utilizing a particular type of carbon nanotube may be practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

[37] Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof.

[38] Any of the aspects disclosed in this invention with discrete carbon nanotubes may also be modified within the spirit and scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure, such as

nitrogen. The nanotubes may include or be associated with organic or inorganic elements or compounds from elements such as, for example, carbon, silicon, boron and nitrogen. The inorganic elements can comprise of elements of the groups two through fourteen of the Periodic Table of Elements, singly or in combination. Association may be on the interior or exterior of the inorganic or mineral nanotubes via Van der Waals, ionic or covalent bonding to the nanotube surfaces.

[39] Dispersing agents to aid in the dispersion of discrete carbon nanotubes or other components of this invention are, for example, anionic, cationic or non-ionic surfactants, such as sodium dodecylsulfonate, cetyltrimethyl bromide or polyethers such as the Pluronic made by BASF. They can be physically or chemically attached to the discrete carbon nanotubes. In some cases the dispersing aid can also act as a binder. For example, with lead-acid batteries polyvinylalcohol can be used to disperse discrete carbon nanotubes of this invention in water among the paste particles then on addition of sulfuric acid the polyvinylalcohol is considered to deposit on the paste particle and act as a binder, The polyvinylalcohol is preferred to have an average molecular weight less than about 100,000 daltons.

[40] In some embodiments, the present invention comprises a composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising a plurality of discrete carbon nanotube fibers The nanotube fibers may have an aspect ratio of from about 10 to about 500, and at least a portion of the discrete carbon nanotube fibers may be open ended. The portion of discrete carbon nanotubes that are open ended may be conducting.

[41] In some embodiments of the present invention, the composition may further comprise at least one polymer. The polymer may be selected from the group consisting of vinyl polymers, such as poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

[42] In further embodiments, the composition of the present invention may comprise carbon nanotubes which are further functionalized. The composition of the present invention may comprise additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements. The composition of the present invention may further comprise at least one dispersion aid.

[43] The composition of the present invention may further comprise an alcohol, such as polyvinyl alcohol.

[44] In some embodiments, the present invention comprises a binder material further comprise non-fiber carbon structures, for example carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof. In some embodiments, at least a portion of discrete carbon nanotubes are interspersed between graphene and/or oxidized graphene plates. In this embodiment, the binder material may have an impedance of less than or equal to about one billion ohm-m.

[45] In further embodiments, the composition of the present invention comprises an electrolyte material or separator film. The composition may have a charge transfer resistance of less than or equal to about 10 million ohm-m.

[46] In further embodiments, the carbon nanotubes of the present invention are oriented, for example in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method. Orientation may be accomplished using post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

[47] In some embodiments of the present invention, a portion of open ended tubes comprise electrolyte. The electrolyte may comprise a polymer or a liquid.

[48] In further embodiments of the invention, 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70. In other embodiments, 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

[49] In some embodiments, the present invention comprises an electrode paste for a lead-acid battery comprising discrete carbon nanotubes having an average length from about 400 to about 1400 nm. The electrode paste may further comprise an alcohol, for example polyvinyl alcohol.

[50] The present invention also comprises a method for making a composition for use as a binder material, an electrolyte material or a separator film material for an energy storage or collection device. The method comprises the steps of a) adding carbon nanotubes to a liquid, solvent or polymer melt b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and c) optionally adding further materials, such as PVDF, and inorganic fillers such as carbon black and continued mixing until a homogenous dispersion is

obtained. The mixture can then be further fabricated into shapes by such methods as film extrusion, fiber extrusion, solvent casting, and thermoforming. The method may further comprise adding a polymer, a dispersion aid, additional inorganic structures, or an alcohol, such a polyvinyl alcohol.

Electrolytes

[51] The term electrolyte is defined as a solution able to carry an electric current. An ionic salt is dissolved in a medium which allows ion transport. Ion transport is defined as the movement of ions through the electrolyte. The ions are preferably a single type of ion, but can be a mixture of types of ions. The medium can be solid, liquid or semi-solid, for example gelatinous. For example, in a lead-acid battery the electrolyte medium is preferred to be liquid or gelatinous. For a lithium based battery the electrolyte medium is preferred to be gelatinous and more preferably a solid at use temperature to prevent high concentrations of flammable organic liquids which could escape on battery failure by shorting or penetration. The electrolyte has to be sufficiently non-electrically conductive to prevent poor storage stability or shorting.

[52] A separator film is often added in batteries with liquid electrolytes to perform the function of electrical insulation between the electrodes yet allowing ion transport. Typically in lithium batteries the separator film is a porous polymer film, the polymer being, for example a polyethylene, polypropylene, or polyvinylidene fluoride. Porosity can be introduced, for example, by using a matt of spun fibers or by solvent and/or film stretching techniques. In lead-acid batteries, where used the separator film is conventionally a glass

fiber matt. The separator film comprising discrete carbon nanotubes of this invention can improve ion transport yet still provide the necessary electrical resistivity. The degree of electrical conductivity can be controlled by the amount of discrete carbon nanotubes within the binder or separator film medium. In a binder it may be advantageous to use higher levels of discrete carbon nanotubes, for example in the range 10 to 50% by weight of the binder medium, for the optimum balance of low electrical resistivity, for example, less than $1x10^7$ ohm-m, with strength, than for the electrolyte medium or separator film where it may be advantageous to use less than 10% weight of discrete carbon nanotubes to maintain electrical resistivity greater than about 1 $x10^7$ ohm-m. The use of discrete carbon nanotubes to improve the strength and ease of battery assembly of the thin electrolyte or separator films is also considered valuable.

[53] The flexural strength or resistance to cracking of the solid electrolytes can be determined by flexural bending of a film or sheet of the solid electrolyte on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The resistance to deformation and stress to crack the solid electrolyte through the solid electrolyte film thickness is recorded. Units are in MPa.

[54] Ionic salts can be added to a polymeric medium such as polyethylene oxide to produce electrolytes. For example, for lithium ion batteries ionic salts, such as lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfate, lithium bistrifluoromethanesulfonimide, lithium bisoxalatoborate can be added to the polymer, by solvent or to the polymer melt. Solvents can be those that are retained as an electrolyte medium, for example, ethylene carbonate, propylene carbonate, or solvents which are then

removed by drying such as acetonitrile.

[55] The electrolyte or separator film containing polymeric material may have a polymer, or a combination of polymers that are dissimilar by molecular weight and or by type. For example, in an electrolyte containing polyethylene oxide a portion of the polyethylene oxide can be of molecular weight above about 200,000 daltons and a portion less than about 10,000 daltons. As another example, the polyethylene oxide can be partially replaced by another polymer, such as polyvinylidene fluoride, polyvinylpyrrolidone, or polymethylmethacrylate.

Procedure for impedance and swelling evaluation of binder materials

[56] Each dried sample film is obtained using a 22mm diameter punch. Films are also obtained saturated with neat electrolyte (a 50/50 composition of ethylene carbonate and propylene carbonate) and electrolyte and 50% by weight of lithium perchlorate by immersing the films for 1-20 days at room temperature. The films are evaluated for swelling by weight increase and tested for impedance using an LCR meter, (Agilent 4263B) at 25 degrees centigrade and under about 70 psi, (0.483 MPa) pressure at 1 Khz. The units of impedance are usually given as ohm-meter.

[57] The flexural strength or resistance to cracking of the pastes can be determined by flexural bending of the paste on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The stress to crack the paste through the paste thickness is recorded. Units are in MPa.

[58] The adhesive strength of the pastes can be determined by using lap shear strength procedures and the Instron Tensile Testing Machine. The test is analogous to EN 1465. The specimen consists of two rigid substrates, for example aluminum sheets or copper sheets, bonded together by the paste in a lapped joint. This causes the two ends of the specimen to be offset from the vertical load line of the test. The paste is placed between two strip of material, The stress to failure on pulling the lapped specimen is recorded. Units are in MPa.

Procedure for charge transfer resistance evaluation of electrolyte materials

[59] Electrolyte films are placed between two electrodes the resistance and reactance determined at frequencies of 100 Hz, 120 Hz, 1 KHz, 10 KHz and 100 KHz using an LCR meter, (Agilent 4263B) at 25 degrees centigrade and a 2volt dc bias with a sinusoidal test level of 20mv. A Nyquist plot is contructed of the real and imaginary components of the impedance from which the charge transfer resistance is obtained.

EXAMPLES 1-3

Compositions consisting of discrete carbon nanotubes in poly(vinylidene fluoride) for binders and separator films.

[60] **General procedure.** A dispersion of discrete carbon nanotubes in n-methyl-2-pyrrolidone (NMP) is first made by adding carbon nanotubes of about 2% weight of oxidized moieties and average aspect ratio about 60 to NMP under vigorous stirring. Following addition, sonication is applied for about 15 minutes to exfoliate the carbon nanotubes. An amount of PVDF is slowly added to the system over a period of 30 minutes to obtain the desired weight fraction of carbon nanotube to PVDF. Vigorous stirring

and sonication is continued until a homogenous dispersion was obtained. A uniform black colored film of PVDF is obtained by removing the NMP *in vacuo* to constant weight.

[61] Examples 1-3 are dried PVDF films containing discrete carbon nanotubes in the weight percentage 2.5, 7.5 and 10%, respectively, and are shown in Table 1.

[62] Control 1 is made in a similar manner as Example 1 except that no discrete carbon nanotubes are added. The resultant dried film is a pale yellow. The impedance measurements of the dry films and films swollen for 20 days in a mixture of ethylene carbonate and propylene carbonate 50/50 and 50% by weight of lithium perchlorate are provided in Table 1.

[63] The results shown in Table 1 demonstrate that Examples 1-3 with discrete oxidized carbon nanotubes of this invention in PVDF gave significantly lower values of impedance than the control 1 of PVDF film alone. Furthermore, inclusion of carbon nanotubes of this invention in PVDF demonstrate higher mass uptake of the $LiClO_4$ solvent mixture which enables improved ion transport. These improved properties on addition of discrete carbon nanotubes of this invention should lead to much enhanced performance as a binder or separator film.

Table 1.

PVDF	% wt Carbon nanotubes	% mass uptake in ECO/PCO and $LiClO_4$	Volume resistivity Dry Ohm-m	Volume resistivity swollen with ECO/PCO & $LiClO_4$, ohm-m
Control 1	0	6	1.579×10^{12}	3.035×10^{11}
Example 1	2.5	7	1.315×10^{11}	1.403×10^{10}
Example 2	7.5	9	3.326×10^{7}	1.239×10^{9}
Example 3	10	14	1.216×10^{8}	3.694×10^{8}

EXAMPLES 4 AND 5

Binder composition of discrete carbon nanotubes (w/w) in SBR Latex

[64] A polyether (BASF, Pluronic F-127) as a dispersing aid for the discrete carbon nanotubes is dissolved in water cleaned by reverse osmosis at a weight ratio of 1.5 to 1 of the polyether to dry oxidized carbon nanotubes, then oxidized carbon nanotubes are added at a concentration of 1.5 weight/volume carbon nanotubes to water and sonicated for a period of 30 minutes to disperse the oxidized carbon nanotubes. SBR latex (Dow Chemical Company, grade CP 615 NA, 50% solids content) is added directly to the exfoliated carbon nanotubes at the desired carbon nanotube to SBR weight ratio and stirred vigorously until homogenous. A black film is obtained on drying the mixture in air, followed by drying in vacuo until constant weight of the film is obtained.

[65] Example 4 is made with five weight percent of discrete carbon nanotubes to dry SBR.

[66] Example 5 is made with seven point five weight percent of discrete carbon nanotubes to dry SBR.

[67] Control 2 is made as example 4 and 5 except no discrete carbon nanotubes are added. The film is clear.

[68] The impedance measurements of the dry films and films swollen for 2 days in a mixture of ethylene carbonate, ECO, and propylene carbonate, PCO, 50/50 and 50% by weight of lithium perchlorate are provided in table 2. The results demonstrate inclusion of

discrete carbon nanotubes of this invention with SBR provide a significant reduction in impedance.

Table 2.

SBR	% weight carbon nanotubes	% mass uptake* ECO/PCO $LiClO_4$	Volume resistivity Ohm-m
Control 2	0	-3	9.99×10^{11}
Example 4	5	-2	4.241×10^{11}
Example 5	7.5	-2	1.073×10^{11}

*2 day swell

EXAMPLE 6

Formation of a solid electrolyte contained discrete carbon nanotubes wherein the tubes are further functionalized with polyethylene oxide.

[69] Oxidized carbon nanotube fibers are made by first sonicating the carbon nanotube fiber bundles (CNano, grade 9000) at 1% w/v in a mixture of concentrated sulfuric acid/nitric acid for 2 hours or more at about 30 °C. After filtering and washing with water the pH of the final washing is about 4.The oxidized carbon nanotube fibers are dried in vacuo for 4 hours at about 80 °C. The resultant oxidized tubes generally contain about 1.5-6% by weight of oxygenated species as determined by thermogravimetric analysis in nitrogen between 200 and 600 °C and at least a portion of the tubes are open ended as determined by secondary electron microscopy. The residual ash after burning the oxidized carbon nanotubes in air to 800 °C is about 0.5 to 2% w/w. Monohydroxy poly(ethylene glycol), PEG-MH, of molecular weight about 1900 daltons (Sigma Aldridge) is added in excess to the dried oxidized nanotubes together with a small amount of sulfuric acid as a catalyst and

the mixture heated to 100 °C while sonicating for about 1 hour. After cooling and addition of water the functionalized carbon nanotubes are filtered followed by washings to remove excess PEG-MH and sulfuric acid. The functionalized carbon nanotubes are dried in vacuo at 40°C overnight. 0.5% w/w of the carbon nanotubes reacted with PEG-MH are added to PEG-MH, heated to 60°C and sonicated for 30 minutes. A uniform black liquid is obtained which on examination while in the liquid state by optical microscopy up to 150X magnification revealed no discernible aggregates of carbon nanotubes, i.e. the tubes are discrete and dispersed On cooling, the PEG-MH with discrete carbon nanotubes the PEG-MH is observed to crystallize and carbon nanotubes are observed to be between crystal lamellae, i.e., in the amorphous regions of the solid polymer. This is considered very advantageous as ions are recognized to travel preferentially in the amorphous regions.

EXAMPLES 7-15

Solid electrolyte compositions with discrete carbon nanotubes

[70] Discrete carbon nanotubes of oxidation about 2% and an average aspect ratio of 60, with a portion of the carbon nanotubes being open-ended are dried in vacuo at 80 °C for four hours. Compositions are made up as detailed in table 3 by first making solutions of the components using acetonitrile (Sigma Aldridge, 99.8% anhydrous) as a solvent; a 1% w/v solution of the discrete carbon nanotubes, a 2.5% w/v of polyethylene oxide, PEO, (Alfa Aesar) consisting of a ratio of two PEO's, one of molecular weight 300,000 daltons and the other molecular weight 4000 daltons in the weight ratio 1:0.23, respectively, and 5% w/v solution of lithium trifluoromethanesulfate (Aldrich). The dried discrete carbon nanotubes are first sonicated in acetonitrile for 30 minutes using a sonicator bath. The solutions are made to the various compositions (parts per hundred of PEO) given in Table 3, then

sonicated for 30 minutes at around 30 °C in a sonicator bath (Ultrasonics). The mixtures are then transferred to a glass dish and the acetonitrile evaporated for 4 hours to give films. The films are dried in vacuo at 50 °C for 2 hours followed by compression molded at 120 °C for 3 minutes and 20 tons platen pressure between polyethylene terephthalate sheets, cooled to room temperature and stored in a dessicator before testing.

[71] The results in Table 3 show that significant improvements are gained in the conductivity of the solid electrolyte films with addition of discrete carbon nanotubes of this invention compared to the controls. The electrolyte films made with discrete carbon nanotubes are also seen to have higher strength than the controls as judged by their ability to be handled without tearing.

Table 3.

	$LiCF_3SO_3$ phr	PEO phr	Discrete Carbon nanotubes phr	Conductivity at 10 KHz, 25 °C , S/cm
Control 3	15	100	0.0	3.89×10^{-5}
Control 4	20	100	0.0	1.49×10^{-5}
Control 5	30	100	0.0	4.90×10^{-6}
Example 7	15	100	1.5	6.21×10^{-4}
Example 8	20	100	1.5	5.74×10^{-4}
Example 9	30	100	1.5	4.32×10^{-4}
Example 10	15	100	2.0	1.27×10^{-4}
Example 11	20	100	2.0	2.27×10^{-4}
Example 12	30	100	2.0	2.67×10^{-4}
Example 13	15	100	3.0	3.62×10^{-4}
Example 14	20	100	3.0	1.11×10^{-4}
Example 15	30	100	3.0	2.89×10^{-4}

EXAMPLE 16

Paste composition containing discrete carbon nanotubes for lead-acid battery

[72] The compositions for making an anode paste for a lead acid battery for control 6 and example 16 is shown in Table 4. The expander (Hammond) is a composition of lignin sulfonate, barium sulfate and carbon black in the weight ratio 1:1:0.5, respectively. The expander is added to the dry powder of lead oxide, then water is added and mixed, followed by slow addition and mixing of acid (sulfuric acid, 1.4 specific gravity) while maintaining the temperature below 55 °C. In example 16, discrete carbon nanotubes of average length 700 nanometers and oxidation level about 2% and polyvinyl alcohol, PVA, (Sigma Aldridge, average molecular weight 30,000 to 70,000 daltons, 87 to 90% hydrolyzed) are admixed with water and sonicated to give a dispersion of discrete carbon nanotubes of 2.25% by weight and PVA of 3.375% by weight. The discrete carbon nanotube solution is added together with the water to the lead oxide followed by slow addition of the sulfuric acid. The anode material is pasted to a lead grid and assembled into a battery with a lead oxide cathode, followed by standard battery formation as recorded elsewhere, i.e., Lead-Acid Batteries: Science and Technology: Science and Technology, Elsevier 2011. Author: D. Pavlov. The weight % of discrete carbon nanotubes to dry lead oxide in the anode paste is 0.16.

[73] Relative to Control 6, Example 16 showed a higher charge efficiency of at least 30% at 14.2v charging voltage, an increase rate of charge of at least 200% and at least 50% lower

polarization between 14 and 15 volts. Polarization is the difference between the voltage of the battery under equilibrium and that with a current flow.

Table 4.

	Control 6	Example 16
	Kg	Kg
Lead Oxide	230	230
Fiber flock	0.15	0.15
Expander	1.4	1.4
Discrete carbon nanotubes	0	0.368
Polyvinylalcohol	0	0.552
Water	27	27
Sulfuric acid 1.4 sg	23.1	23.1

CLAIMS

What is claimed is the following:

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:

   a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended.

2. The composition of claim 1, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

3. The composition of claim 1, further comprising at least one polymer.

4. The composition of claim 1, wherein the carbon nanotubes are further functionalized.

5. The composition of claim 1, further comprising at least one dispersion aid.

6. The composition of claim 3, wherein the polymer is selected from the group consisting of vinyl polymers, poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

7. The composition of claim 2, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

8. The binder composition of claim 2 further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

9. The composition of claim 9, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim 1, wherein the binder material has an impedance of less than or equal to about one billion ohm-m.

11. The composition of claim 1, where the electrolyte material or separator film has a charge transfer resistance of less than or equal to about 10 million ohm-m.

12. The composition of claim 1, wherein the carbon nanotubes are oriented.

13. The composition of claim 13, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

14. The composition of claim 14, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

15. The composition of claim 1, wherein a portion of open ended tubes comprise electrolyte.

16. The composition of claim 16, wherein the electrolyte comprises a polymer or a liquid.

17. The composition of claim 1, wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70.

18. The composition of claim 18, wherein from 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

19. An electrode paste for a lead-acid battery comprising:

discrete carbon nanotubes having an average length from about 400 to about 1400 nm; and polyvinyl alcohol.

20. A method for making a composition for use as a binder material, an electrolyte material, or a separator film material, comprising the steps of:

a) adding carbon nanotubes to a liquid, solvent or polymer melt;

b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and

c) continued mixing until a homogenous dispersion is obtained.

1/1

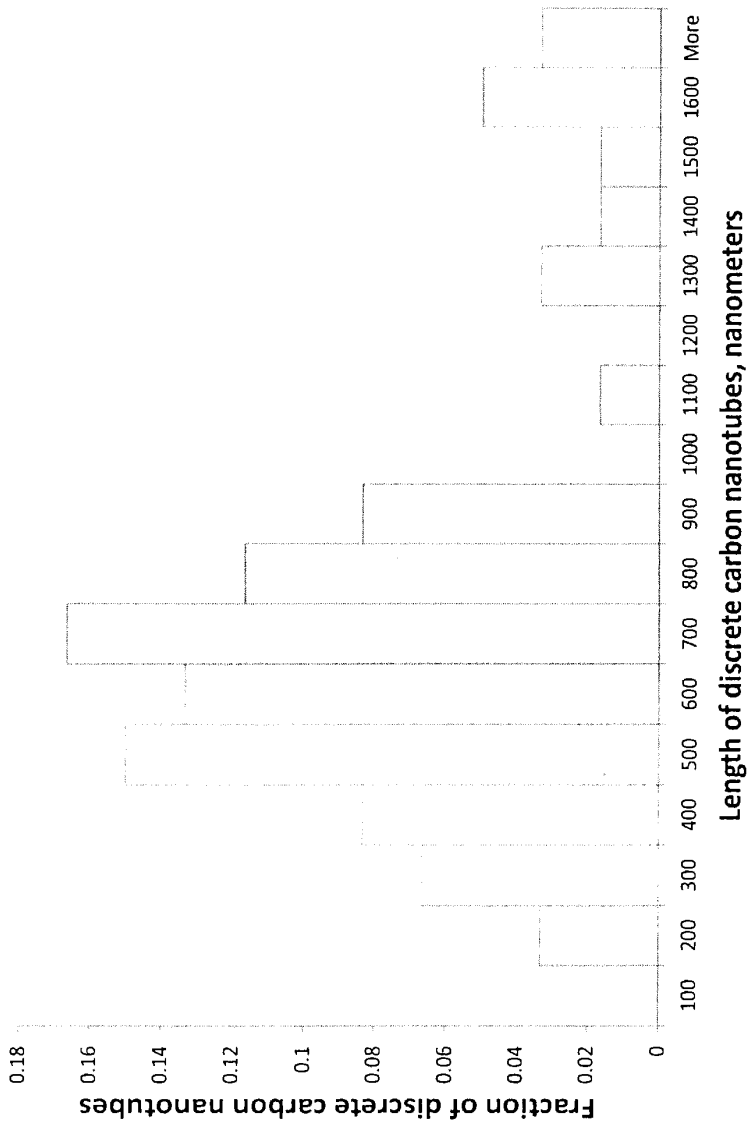
Fraction of discrete carbon nanotubes
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
More
Length of discrete carbon nanotubes, nanometers

Figure 1

ABSTRACT

In various embodiments an improved binder composition, electrolyte composition and a separator film composition using discrete carbon nanotubes. Their methods of production and utility for energy storage and collection devices, like batteries, capacitors and photovoltaics, is described. The binder, electrolyte, or separator composition can further comprise polymers. The discrete carbon nanotubes further comprise at least a portion of the tubes being open ended and/or functionalized. The utility of the binder, electrolyte or separator film composition includes improved capacity, power or durability in energy storage and collection devices. The utility of the electrolyte and or separator film compositions includes improved ion transport in energy storage and collection devices.

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Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

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	Clive	P.	Bosnyak	

Residence Information (Select One) ● US Residency Non US Residency Active US Military Service

City	Dripping Springs	State/Province	TX	Country of Residence i	US

Mailing Address of Inventor:

Address 1	12001 Settlers Trail
Address 2	
City	Dripping Springs
State/Province	TX
Postal Code	78620
Country i	US

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Kurt	W.	Swogger	

Residence Information (Select One) ◉ US Residency Non US Residency Active US Military Service

City	Austin	State/Province	TX	Country of Residence i	US

Mailing Address of Inventor:

Address 1	4211 Waters Edge Cove
Address 2	
City	Austin
State/Province	TX
Postal Code	78731
Country i	US

Inventor 3 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Milos		Marinkovic	

Residence Information (Select One) ◉ US Residency Non US Residency Active US Military Service

PTO/AIA/14 (11-15)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	MRE012NP2C / 277190
	Application Number	
Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

City	San Antonio	State/Province	TX	Country of Residence i	US

Mailing Address of Inventor:

Address 1	5201 Brouette Ct.		
Address 2			
City	Plano	**State/Province**	TX
Postal Code	78215	**Country** i	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	130577		
Email Address	pat-tmk@andrewskurth.com	Add Email	Remove Email

Application Information:

Title of the Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes		
Attorney Docket Number	MRE012NP2C / 277190	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	1	**Suggested Figure for Publication (if any)**	1

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country i

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	MRE012NP2C / 277190
	Application Number	
Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	◯ Limited Recognition (37 CFR 11.9)
Customer Number	130577		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Continuation of	14390902	2014-10-06
Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
14390902	a 371 of international	PCT/US2013/047029	2013-06-21
Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
PCT/US2013/047029	Claims benefit of provisional	61663513	2012-06-22
Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
PCT/US2013/047029	Claims benefit of provisional	61662393	2012-06-21

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	MRE012NP2C / 277190
	Application Number	
Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	MRE012NP2C / 277190
	Application Number	
Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	MRE012NP2C / 277190
	Application Number	
Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section. Clear

● Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.	Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	MOLECULAR REBAR DESIGN, LLC		
Mailing Address Information For Applicant:			
Address 1	13477 Fitzhugh Road		
Address 2			
City	Austin	**State/Province**	TX
Country	US	Postal Code	78736
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	MRE012NP2C / 277190
	Application Number	
Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☒

Organization Name	MOLECULAR REBAR DESIGN, LLC

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1	13477 Fitzhugh Road		
Address 2			
City	Austin	**State/Province**	TX
Country i	US	Postal Code	78736
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

Remove

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Gregory L. Porter/			Date (YYYY-MM-DD)	2018-01-26
First Name	Gregory	Last Name	Porter	Registration Number	40131

Additional Signature may be generated within this form by selecting the Add button. Add

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	MRE012NP2C / 277190
	Application Number	
Title of Invention	Binders, Electrolytes and Separator Films for Energy Storage and Collection Devices Using Discrete Carbon Nanotubes	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1 The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3 A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent CooperationTreaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number PCT/US2013/047029 filed on June 21, 2013.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Clive P. Bosnyak Date (Optional) 8/29/14

Signature: Clive P. Bosnyak

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE
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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number PCT/US2013/047029 filed on June 21, 2013.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Kurt W. Swogger Date (Optional): 9/29/2014

Signature: [signature]

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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This declaration is directed to: ☐ The attached application, or

☒ United States application or PCT international application number PCT/US2013/047029

filed on June 21, 2013

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

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LEGAL NAME OF INVENTOR

Inventor: Milos Marinkovic Date (Optional): 10.01.14

Signature: [signature]

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Filer:	Gregory L. Porter/Jeanne Dunn
Attorney Docket Number:	MRE012NP2C / 277190

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPLICATION FILING	1011	1	300	300
UTILITY SEARCH FEE	1111	1	660	660
UTILITY EXAMINATION FEE	1311	1	760	760
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**1720**

Electronic Acknowledgement Receipt	
EFS ID:	31619162
Application Number:	15881071
International Application Number:	
Confirmation Number:	2885
Title of Invention:	BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	130577
Filer:	Gregory L. Porter/Jeanne Dunn
Filer Authorized By:	Gregory L. Porter
Attorney Docket Number:	MRE012NP2C / 277190
Receipt Date:	26-JAN-2018
Filing Date:	
Time Stamp:	15:11:16
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$1720
RAM confirmation Number	012918INTEFSW00001619502849
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		Application.pdf	669963 8ed9751861b5d813f479adb105dfeb6dc4e71134	yes	32
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Specification		1	28	
	Claims		29	31	
	Drawings-only black and white line drawings		32	32	
Warnings:					
Information:					
2	Abstract	Abstract.pdf	9475 9c4bef1cd4069f54dc54e6fe0b4ce7e78bcb6c67	no	1
Warnings:					
Information:					
3	Application Data Sheet	ADS.pdf	1823664 ac1fa09544a4fd7fdfa4c2083a693d6626fdb48b	no	9
Warnings:					
Information:					
4	Oath or Declaration filed	Declarations.pdf	178229 9e86c603e55062f20baa3d193036c54dd2eb97f7	no	3
Warnings:					
Information:					
5	Fee Worksheet (SB06)	fee-info.pdf	34916 37efdc87a6fc1f9065b5705333fa50ca820cf7d7	no	2

Warnings:	
Information:	
Total Files Size (in bytes):	2716247

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.