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Carbon nanotube research developments in terms of published papers and patents, synthesis and production

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Abstract Progress of carbon nanotube (CNT) research and development in terms of published papers and patents is reported. Developments concerning CNT structures, synthesis, and major parameters, in terms of the published documents are surveyed. Publication growth of CNTs and related fields are analyzed for the period of 2000–2010. From the explored search term, "carbon nanotubes", the total number of papers containing the CNT concept is 52,224, and for patents is 5,746, with a patent/paper ratio of 0.11. For CNT research in the given period, an annual increase of 8.09% for paper and 8.68% for patents are resulted. Published papers for CNT, CVD and CCVD synthesis parameters for the period of 2000–2010 are compared. In other research, publications for CNT laser synthesis, for the period of 2000–2010, are reviewed. Publications for major laser parameters in CNT synthesis for the period of 2000–2010 are described. The role of language of the published references for CNT research for the period of 2000–2010 is also investigated. Published papers/patents in English, Japanese, Chinese, Russian, German, French, Polish, and Spanish languages are compared. As expected, the number of paper/patent publications in English dominates other languages.

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1. Introduction

The introduction of carbon nanotubes (CNTs) and recent developments have revolutionized the new field of nanotechnology and made great contributions to both basic science and engineering, as given by Ding et al. (2011) [1] and Coiffic et al. (2007) [2]. For this reason, most developed countries have made huge investments in CNT and nanomaterial research programs, and have found many interesting results. This motivated more and more research in this field, but, the limited budget for all science projects encouraged different countries to spend optimally in this area. The scientific impact on nations, in terms of publications and research spending, is reported by King (2004) [3].

In a previous study, the trend of CNT research and development for the period of 1999–2003 is reported by Golnabi (2006) [4]. The share of top nations in scientific publications, and, in particular, carbon nanotube publications, in terms of their gross domestic product (GDP), is presented in that article. It was noted that four countries, including the USA, Japan, Germany and China, have a paper publication contribution of 67%, while the rest of the world, including 189 countries, contributed 33%. The USA leads all nations in the number of scientific publications and citations for carbon nanotube publications; however, in terms of accepted CNT patents, Japan showed a big lead.

Following that research study, the goal here is to follow up on the progress of carbon nanotube research for the period of 2000–2010. A good figure of merit for such evaluation is the number of peer reviewed papers published in prestigious journals. Another important parameter, in this respect, is the number of citations referred to by other researchers in such scientific publications. The number of referenced patents is also important, which can lead to innovations and technological breakthroughs. Thus, a number of scientific publications, including journal papers and patents, are considered for the analysis. By comparing the results obtained here, a precise evaluation can be made for the real progress in carbon nanotube research over the past 11 years (2000–2010). Since the role of nations in such contributions remains almost the same, in this

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report, more emphasis is put on advancements made in the scientific aspect of CNTs and their production.

Using the Science Finder (ScinFinder Reference Explorer option) [5] search engine, the numbers of explored references cited in databases of this engine are surveyed. SciFinder is a research tool that allows the user to explore Chemical American Society (CAS) databases containing literature from many scientific disciplines, including biomedical sciences, chemistry, engineering, materials science, agricultural science, and etc.. However, it must be pointed out that these numbers are not the complete list of all publications in this field. Because some of the published documents are not peer reviewed papers, they may not be included in this database. Also, the search results depend upon the search date and time, and upon the "search term", and some errors in definition of the proper terms are conceivable. It is, however, a good and reliable source that illustrates the historical growth for the purpose of this study. In comparison with other search engines, it represents a reasonable indexing and is well suited as a comparison tool for the present study. The research survey offers information about the progress of carbon nanotube publications made since the year 2000 up to the end of 2010 (11 years).

2. Publication progress of CNT research

During past years, there have been considerable achievements, and, as an example, carbon nanotube research progress for fourteen years, from 1990 to 2003, is described by Golnabi et al. (2006) [4]. Considerable efforts have been made in the development of new synthesis methods of nanotube production and related test equipment for fabrication of high quality nanotubes and nanofibers. From the explored search under the topic "carbon nanotubes", the total number of publications for the period of 1990–2003 (14 years) was 351,824 papers and 48,448 patents, with a patent/paper ratio of 0.137.

Similar research is accomplished here for the period of 2000–2010 (11 years), and, in Figure 1, the number of references for the search term "carbon nanotubes" is shown. It must be mentioned in such a search that there are two numbers. The first one shows the document containing the exact term "carbon nanotubes", while the second number indicates the number of references containing the concept of "carbon nanotubes". In the given analysis, the second number containing the concep of the search term is used for the review. From the explored search under the given topic, the total number of publications for the period of 2000–2010, at a recorded date and time, is 52,224 papers. For the same period, the total number of accepted patents is 5746 items. The ratio of published patents to papers for this period is 0.11. As can be seen in Figure 1, the number of publications in journals in the year 2000 is 980, while it is increased to 8930 in 2010. An annual increase rate of 8.09% (722.72) is noted for this period. On the other hand, for the referenced patents in year 2000, the number is only 48, which is increased to 1067 in the year 2010. For the referenced patents, an annual increase of 8.68% (92.63) is obtained for this recorded period. As a result, a sharp growth in the number of referenced journal papers and filed patents is observed for this period. However, the growth rate for the patents is higher than that of the published papers in the journals.

In order to compare annual progress in CNT publications, in Table 1, the number of explored references for published papers, patents, and patent/paper ratio are listed for the period of 1991–2010 (20 years). From Table 1, consider the periods of 1991–2000 and 2001–2010, both for 10 years. For 1991–2000,

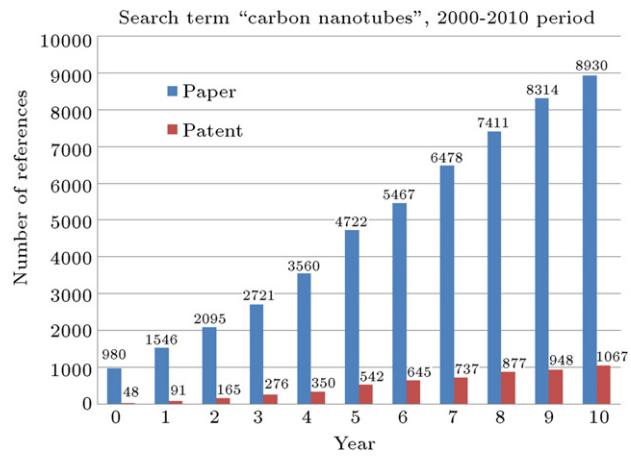

Figure 1: Growth of the carbon nanotube references for the period of 2000–2010.

Table 1: CNT published papers, patents, ratio (patent/paper) for the period of 1991–2010 (20 years).

Year	Papers	Patents	Ratio
1991	0	0	0
1992	20	0	0
1993	65	0	0
1994	135	1	0.007
1995	161	3	0.018
1996	222	6	0.027
1997	269	13	0.048
1998	475	5	0.010
1999	617	16	0.025
2000	980	48	0.048
2001	1546	91	0.058
2002	2095	165	0.078
2003	2721	276	0.101
2004	3560	350	0.098
2005	4722	542	0.114
2006	5467	645	0.117
2007	6478	737	0.113
2008	7411	877	0.118
2009	8314	948	0.114
2010	**8930**	1067	0.119

the averaged annual increase rate for papers is 10.0% and for patents is 10.0%. For the 2001–2010 interval, an annual increase rate for papers is 8.26%, while, for patents, is 9.14%. A growth in the number of referenced journal papers and filed patents is observed for both periods. However, the growth rate for patents is higher than that of published papers.

In comparing laser publications for the 1991–2000 period with the recent period (2001–2010), two points can be noted. First, as described for the period 1991–2000, an annual paper increase rate of 10.0% and patent increase of 10.0% are noted. On the other hand, for the recent period of 2001–2010, the annual paper increase rate is 8.26%, while, for patents, the increase is 9.14%. Such a comparison indicates that for the recent period, the averaged annual growth for papers and patents is slower than for the earlier period. Second, the patent to paper ratio factor for the earlier period shows an increase from 0 to 0.048 (0.048), while, for the recent one, there are increases from 0.059 to 0.119 (0.06). This means that there is a higher innovation increase in the recent period.

In another study, the role of the language of published references in carbon nanotube research for the period of 2000–2010 is investigated. Table 2 shows the number of published papers and patents in searched languages of English, Japanese, Chinese,

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Table 2: CNT publications in different languages for the period of 2000–2010.

Language	Papers	Patents	Ratio
English	**52,224**	**5746**	0.11
Japanese	1,071	4580	4.27
Chinese	3,763	3214	0.85
Russian	466	136	0.29
German	80	543	6.78
Polish	52	3	0.05
French	34	318	**9.35**
Spanish	20	18	0.90

Russian, German, French, Polish, and Spanish. Two important facts can be deduced from the listed numbers for each category. First, as expected, the publications in English dominate other languages, because it is a well established international language. This is in agreement with given results for the earlier period of 1990–2003, Golnabi (2006) [4]. This is true for both journal papers (302,749) and published patents (29,923). Second, and perhaps the most important fact, is consideration of the patent/paper ratio for each language, as indicated in Table 2. For the documents published in French, the patent/paper ratio is 9.35, which is much higher than that of the Polish language ratio (0.05). Considering such an important factor, French documents with a ratio of 9.35 are superior, then German (6.78) and Japanese documents show a high ratio of (4.27), while, for English language publications, this ratio is only 0.11. For the reported results in the remainder of this article, the English option is used for all searches.

3. CNT synthesis

A meaningful progress in nanotechnology requires a thorough knowledge of carbon nanotube structure, properties, and synthesis aspects. Historically, the first carbon nanotube material was discovered by Iijima (1991) [6]. The structure of CNTs can be single-walled carbon nanotubes (SWNT), double-walled carbon nanotubes (DWNT), and multi-walled carbon nanotubes (MWNT), see results in Figure 2. Carbon nanotubes (CNT) are generally produced using five main techniques: ARC discharge, laser ablation, chemical vapor deposition (CVD), catalyst chemical vapor deposition (CCVD) and template-directed synthesis. Although scientists are searching for more economic ways to produce these structures, nanotubes self-assemble from the resulting carbon vapor in different ways. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon-containing feedstock gas (methane or carbon monoxide). At the moment, laser ablation produces a small amount of clean nanotubes, whereas arc discharge methods generally produce large quantities of impure material. Explored published papers and patents for the common search parameters are investigated. For example, for the search term "effect of temperature in carbon nanotube synthesis" the publication index is 492 papers and 33 patents, with a ratio of 0.67 for the period of 2000–2010; for tube diameter: 272, 2, and 0.007, respectively; for tube chirality: 220, 26, and 0.118, respectively: and finally for tube length: 106, 3, 0 and 028, respectively. As can be seen in all synthesis methods, parameter temperature plays an important role.

A research is accomplished here for the period of 2000–2010 (11 years) for different terms, as shown in Figure 3. The

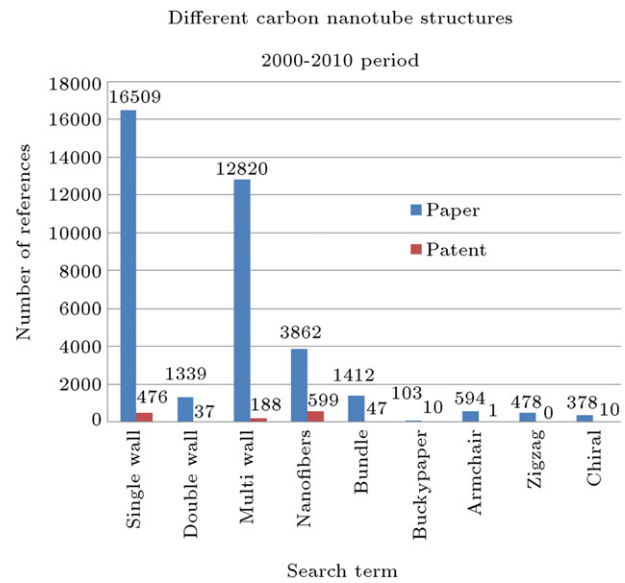

Figure 2: Publications for different CNT structures for the period of 2000–2010.

first one shows the document containing the exact terms "carbon nanotube production yield", "carbon nanotube growth rate" and "production cost", while the next terms indicate the number of references for different synthesis methods for CNT preparation. The major search terms are "Chemical Vapor Deposition" (CVD), "chemical methods", "arc discharge" (arc), "laser ablation", and, finally, the Catalyst Chemical Vapor Desposition (CCVD) method. In the given analysis, as can be seen in Figure 2, there is more concern about the CNT production yield with a publication index of 371 papers, 30 patents, and ratio 0.08. The second important parameter in CNT preparation is growth rate, with the reference index of 203,11, and 0.054. From the explored search, it is noted that there are more publications as a result of the CVD method, with the reference index of 88, 13 and 0.147. However, the ratio is higher for general chemical methods, which show more published patents using this method of CNT preparation.

3.1. Arc discharge

Arc discharge is a well known method for CNT synthesis. However, it is difficult to control the morphology of CNTs, such as length, diameter, and number of layers, because the mechanisms of CNT production by the arc discharge method are complicated. Knowing the importance of the method, progress in this technique, in terms of explored publications for major parameters, is reported. Synthesis of DWNT films and their field emission properties are reported by Wang et al. (2010) [7]. Continuous DWNT films are synthesized using a Fe–Mo catalyst, which has improved the purity and selectivity of the product. TEM results indicate that outer and inner diameters are 1.9–4.7 and 1.2–3.8 nm, respectively.

In another study, heat convection in the synthesis of SWNTs by arc vaporization is described by Tan and Mieno (2010) [8]. The cooling rate of carbon clusters and the temperature distribution of the He buffer gas are calculated. The effects of three factors: gravity (g, $2g$, and $3g$, where g is normal gravity), input power ($P = 500$, 1000, 2000, and 3000 W), and buffer gas pressure ($p = 40$, 50, 80, and 100 kPa) are given. The next study considers CNT synthesis by arc discharge in water using metal cathodes. CNT arc discharge in water can yield

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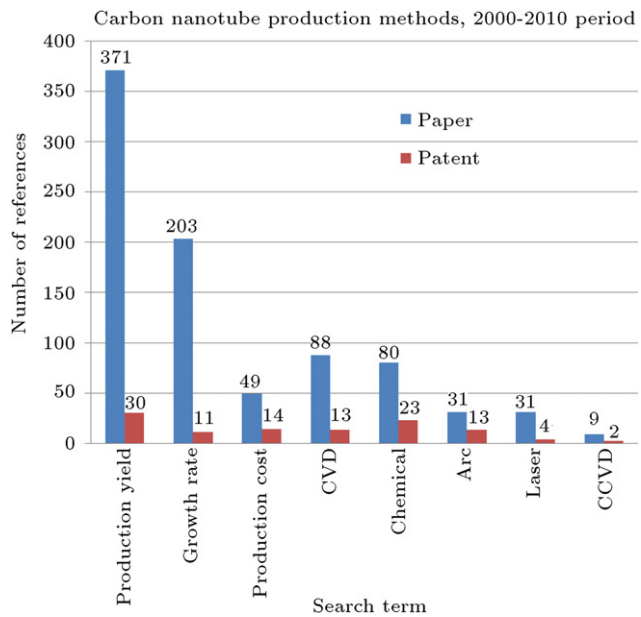

Figure 3: Publications for different CNT synthesis terms for the period of 2000–2010.

high-crystallinity. Plasma enhanced techniques are widely used for synthesis of CNTs. The mechanism is discussed by Keidar et al. (2010) [9]. Experimental and theoretical advances in the understanding of the single-wall carbon nanotube (SWNT) synthesis mechanism in arcs are reported, and the relationship between plasma parameters and SWNT characteristics is discussed. Tailored distribution of SWNTs from arc plasma synthesis using magnetic fields is described by Volotskova et al. (2010) [10]. They report a method for tuning the distribution of single-wall carbon nanotubes (SWCNTs) produced by the arc production method via the application of a non-uniform magnetic field. Application of the non-uniform magnetic field, 0.2–2 kG, results in a broadening of the diameter range of SWCNTs produced towards decreased diameters (1.3 nm, at the highest field). In the next study, CNT synthesized by CVD on nickel coatings deposited with a vacuum arc is reported by Escobar et al. (2010) [11]. Nanotubes and nanofibers were grown on Ni coatings deposited by plasma generated with a pulsed vacuum arc on Si wafers using 3 different bias conditions: at floating potential (+30 V respect to the grounded cathode), at ground potential, and at −60 V. The morphology of carbonaceous species depends on Ni films characteristics. In another study, current and arc pushing force effects on the synthesis of SWNTs by arc discharge are described by Zhao et al. (2010) [12]. The current and arc pushing force of arcing process effects on the synthesis of SWNTs was investigated by a temperature-controlled arc discharging furnace with Co–Ni alloy powder as catalyst at 600 °C. The appropriate conditions included the current, and the arc pushing force of the arcing process was 100 and 80 A, respectively (buffer gas helium pressure is at 500 torr). Another report considers the preparation of DWNTs from fullerene waste soot by arc discharge given by Qiu et al. (2010) [13]. Fullerene waste soot (FWS) was used as raw material to produce double-walled carbon nanotubes (DWCNTs) by arc discharge in a mixture of Ar and H_2 (2:1, vol./vol.) at 300 torr.

As mentioned, the production of carbon nanotubes (CNTs) has various methods. These methods generally require, besides catalyst particles, a vacuum environment and special ambient gas to protect the carbon from high temperature oxidation. The production of CNTs by a single-pulse discharge in air is reported by Tsai et al. (2009) [14]. The micro electro-discharge system is made with a transistor circuit to offer a discharging time of microseconds and a peak current of several amperes.

Considering the different described parameters, a publication research is accomplished here, for the period of 2000–2010, for different paramerers involved in arc CNT synthesis. The search performed for the document contained the exact terms "effect of temperature carbon nanotube arc synthesis", "effect of plasma discharge in carbon nanotube arc synthesis" and "effect of magnetic field carbon nanotube arc synthesis". Also, the next search terms indicate "effect of catalyst in carbon nanotube arc synthesis", "effect of electrode materials carbon nanotube arc synthesis", "DC voltage carbon nanotube arc synthesis", "effect of pulse discharge carbon nanotube arc synthesis", "effect of electrode structure carbon nanotube arc synthesis", "effect of discharge medium carbon nanotube arc synthesis" and "CNT quantity in carbon nanotube arc synthesis". The numbers of published journal papers for different terms involved in arc synthesis methods are shown in Figure 4. The numbers in descending order, as shown in Figure 4, are temperature (127), plasma discharge (34), magnetic field (15), and catalyst material (12). Other paper numbers for search terms are electrode material (11), DC voltage (8), pulsed discharge (8), electrode structure (5), discharge medium (3) and, finally, the produced CNT quantity (1). In the given analysis, as seen in Figure 4, there are more paper publications with the concept of temperature parameters in CNT production (127 papers). The second important parameter in arc CNT preparation is plasma enhaced discharge, with a publication index of (34).

3.2. CVD method

In a recent study, growth of carbon nanomaterial on granular activated carbon is described by Onundi et al. (2011) [15]. In another report, a study of the electrical and mechanical properties of epoxy nanocomposites reinforced by CVD and arc-grown MWCNTs is given by Sumfleth et al. (2010) [16]. Three

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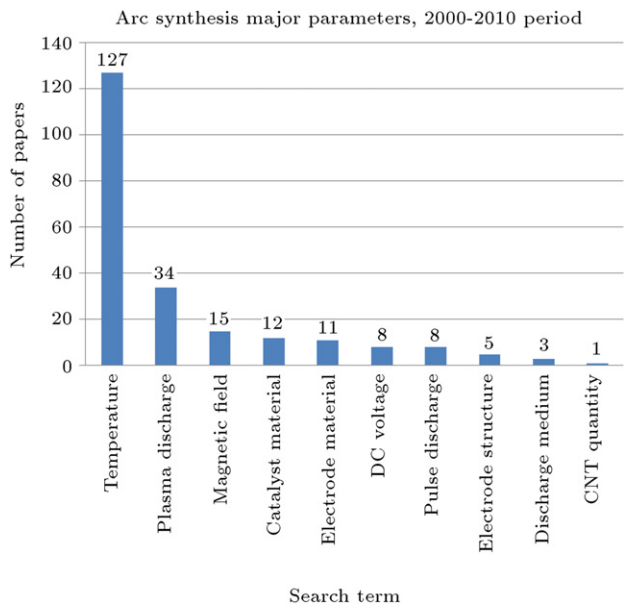

Figure 4: Published papers for CNT arc synthesis parameters for the period of 2000–2010.

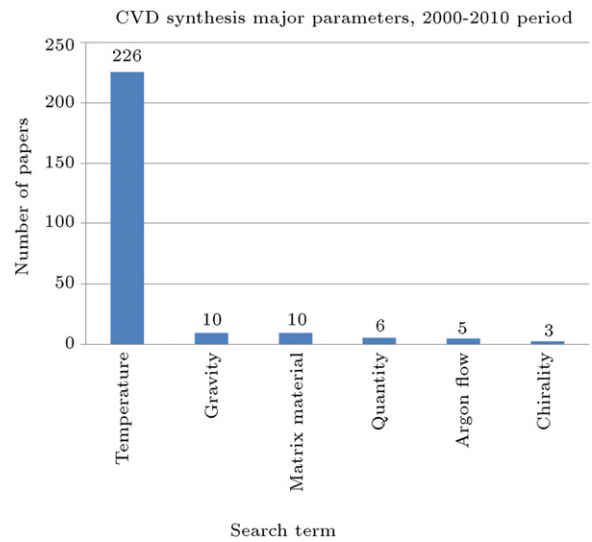

Figure 5: Publications for CNT CVD synthesis for the period of 2000–2010.

different types of MWCNT are compared as nanostructured reinforcements in epoxy polymers. The nanocomposites properties were characterized by means of electron microscopy and mechanical methods. Magnetic amphiphilic composites, based on CNTs and nanofibers grown on an inorganic matrix, are reported by Oliveira et al. (2010) [17]. New magnetic amphiphilic composites are prepared by the catalyst Carbon Vapor Deposition (CVD) growth of CNTs and nanofibers, using ethanol as the carbon source and red mud waste as the catalyst. In one research, the growth of CNTs in a calcium phosphate matrix with different Ca/P molar ratios is given by Lu et al. (2011) [18]. They report that CNTs can be successfully grown from a calcium phosphate matrix without an additional catalyst of transition metal by CVD, using acetylene as the carbon source. There is a large difference in CNT growth in the matrices prepared with different Ca/P molar ratios.

A similar publication research is accomplished for CVD CNT synthesis for the period of 2000–2010. The exact search terms are "effect of temperature in carbon nanotube CVD synthesis", "effect of gravity in carbon nanotube CVD synthesis", and "effect of matrix materials in carbon nanotube CVD synthesis", while the next terms indicate "CNT quantity in carbon nanotube CVD synthesis", "effect of argon flow rate in carbon nanotube CVD synthesis", and finally, "CNT chirality in carbon nanotube CVD synthesis". The number of published papers for different terms involved in the CVD synthesis method are shown in descending order in Figure 5. The number of published papers is: temperature (226), gravity (10), matrix material (10), CNT quantity (6), argon flow rate (5) and produced CNT chirality (3), respectively. As can be seen in Figure 5, there are more paper publications with the concept of temperature parameters in CNT production using the CVD method. More details on this subject can be found in a review report by Kumar and Ando (2010) [19] on growth mechanisms and mass production of CNTs using the CVD method.

3.3. CCVD method

Considered the most suitable technique for the large scale and low-cost production of MWNTs, CCVD is currently the most flexible and economically attractive method for the growth of CNTs. Although its principle is simple, the precisely controlled growth of carbon nanotubes remains very complex, because many different parameters influence the growth process. Carbon nanotubes from camphor by the CCVD method are described in an early report by Kumar et al. (2002) [20]. In a study, MWNT growth on an iron-sprayed catalyst using the CCVD method under atmospheric pressure is reported by Hosseini and Taleshi (2010) [21]. Fe powder is spread on quartz substrate as a catalyst by a simple method and then heated under Ar atm. Carbon products are prepared by the decomposing of ethylene gas and the deposition of carbon on the Fe catalyst particles in Ar atm. at 930 °C. Another study considers the catalyst deactivation during MWNT synthesis using the CCVD process, and the influence of hydrogen. Initial specific reaction rate, relative specific productivity and catalyst deactivation are studied. The carbon source is ethylene and a bimetallic iron–cobalt catalyst supported on alumina is used for that study.

Effects of argon flow rate and reaction temperature on synthesizing SWNTs from ethanol is investigated by Liu et al. (2009) [22]. The effects of Ar flow rate and reaction temperature on synthesizing SWNTs by means of the CCVD are investigated. The SWCNTs sample, which was synthesized by this equipment at 950 °C with Ar flow rate 150 sccm, exhibited high quality. CCVD synthesis of CNTs with W/Co–MgO catalysts is also reported. CNTs were prepared from a H_2–CH_4 mixture with a W/Co–MgO catalyst using the CCVD method. It was observed that both the number of walls and the diameter of CNT increased with the proportion of tungsten. High crystallinity MWNTs synthesized by inductive heating CCVD are reported by Biris et al. (2008) [23]. CNTs were synthesized by CCVD with inductive heating from acetylene on a Fe–Co/CaO catalyst obtained from the thermal decomposing of the Fe:Co:CaCO3 catalyst in nitrogen, previous to the growth process. MWCNTs were synthesized at 750, 850 and 950 °C, and characterized. The nanotubes presented a ratio of outer to inner diameters between 2 and 3, and 90% of them all have diameter values ranging from 5 to 25 nm, with an aspect ratio in the order of hundreds.

A novel synthesis process of r.f.-catalytic CVD (r.f.-CCVD) was used for the synthesis of pelletized ceramic carbon nanotube composites. The surface resistance of the insulating MgO was found to drop dramatically as the result of the

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graphitic nanostructures formed within the ceramic matrix after the catalytic process. The influence of the catalyst drying process is also investigated. The effect of the preproduction process and of the support particle size on catalyst efficiency, conversion yield of the carbon source and diameter of the nanotubes produced, was studied. When 50 nm calcite $CaCO_3$ particles support the Fe_2Co nanoparticles and when the catalyst is freeze dried to avoid the particles agglomeration, 85% of acetylene is converted into MWNTs, and by this rotary tube furnace, 1200 g of MWNTs can be produced per day. The effect of reaction temperature on the diameter distribution of CNT grown from ethylene decomposition over a Co–La–O catalyst is also considered.

High-yield catalytic synthesis of thin MWNTs and their field emission characteristics is investigated. They have synthesized thin MWCNTs using a FeMoMgO catalyst. The number of nanotube walls was 2–6 with corresponding diameters of 3–6 nm. They obtained a high production yield of over 3000 wt% compared to the weight of the supplied catalyst. These thin MWCNTs revealed the intermediate structural characteristics between SWNTs and MWNTs.

In another study, enhanced photoluminescence from very thin DWNTs synthesized by the Zeolite-CCVD method is described. Photoluminescence (PL) from purified (>90%) DWNTs, which have been synthesized by zeolite catalyst-supported chemical vapor deposition (zeolite-CCVD) of very small diameters (0.8-nm av. inner tube) is reported. After the extensive high-temperature oxidation at 700 °C, high-purity (>90%) DWNTs of ∼0.8 nm inner diameter are obtained, and most of these correspond to the DWNTs having inner tubes with chiralities of (7, 5), (7, 6) and (9, 4). For different described parameters, similar publication research is accomplished here for the period of 2000–2010, for different paramerers involved in CNT synthesis using the CCVD method. The search documents containing the exact terms "effect of temperature in carbon nanotube CCVD synthesis", "effect of catalyst materials in carbon nanotube CCVD synthesis", "effect of pressure in carbon nanotube CCVD synthesis", "RF-CCVD in carbon nanotube CCVD synthesis", "effect of argon flow rate in carbon nanotube CVD synthesis" and finally "effect of inductive heating in carbon nanotube CCVD synthesis" are considered in this analysis. The number of references for different terms involved in the CCVD synthesis method in descending order are shown in Figure 6. The numbers are temperature (12), catalyst (12), pressure (11), argon flow rate (11), radiofrequency chemical vapor desposition (RF-CCVD) (3) and role of inductive heating (1). In the given analysis, as can be seen in Figure 6, there are more paper publications with the concept of temperature and catalyst parameter in CNT production with an equal number of paper publications.

3.4. Laser ablation

A process very useful to obtain many kinds of nanoparticles, including SWNTs. Effects of vaporization temperature on the diameter and chiral angle distributions of SWNTs are reported by Nikolaev et al. (2010) [24]. Pulsed laser vaporization preparation of single-wall carbon nanotubes on Co/Ni and Rh/Pd catalysts was explored, with respect to variations in the production temperature. The nanotube type populations were determined via photoluminescence, UV-VIS-NIR absorption and Raman spectroscopy. Lowered production temperature leads to smaller nanotube diameters and exceptionally narrow (n, m) type distributions, with marked preference towards large

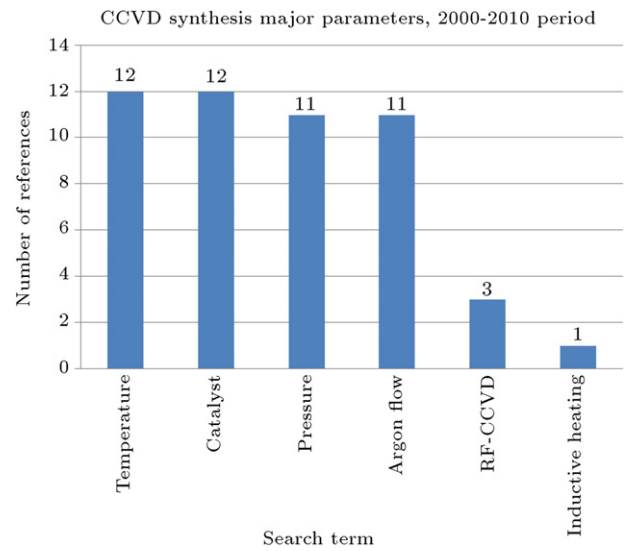

Figure 6: Publications for CNT CCVD synthesis parameters for the period of 2000–2010.

chiral angles for both catalysts. Interestingly, larger nanotube diameters tend to be associated with larger chiral angles.

An analytical solution to predict laser ablation rate in a graphite target is given by Marchiori et al. (2010) [25]. An analytical method to predict the ablation rate is a starting point for setting up experimental conditions, to allow the predefinition of the nanoparticles produced with laser ablation. An ablation method using a pulsed Nd:YAG laser is carried out to ablate a target of graphite. Spectroscopic characteristics of differently produced SWNTs are described by Li et al. (2009) [26]. Four differently produced SWNT materials (by arc discharge, HiPco, laser ablation, and CoMoCat method), with diameters ranging from 0.7 to 2.8 nm, are investigated using Raman scattering, optical absorption, and X-ray absorption near the edge structure, along with X-ray photoemission. The vibrational spectroscopy revealed that the diameter distribution and the character of metallic and semiconducting tubes of SWNT materials are strongly affected by the synthesis methods.

Preparation of SWNT by pulsed laser vaporization is also reported by Stuerzl et al. (2009) [27]. A procedure is described to obtain SWNTs in gram quantities. The procedure is based on sintering to obtain graphitic targets from common available amorphous C-powder doped with nickel and cobalt metals. This method provides a high degree of conversion of the initial carbon material into nanotubes. The impact of nanometal catalysts on the laser vaporization of SWNT's is given by Schauerman et al. (2009) [28]. The effects of catalyst particle size on the purity, yield, and purification efficiency of SWCNTs produced by pulsed laser vaporization are investigated. The purity of as-produced SWCNT material prepared using Ni and Co nanometal (∼13 nm diameter) catalyst particles was compared to material preparation using conventional micro metal (2–3 μm diameter) particles. The SWCNT material from nanometal catalysts demonstrated a 50% increase in SWCNT purity. The process and properties of the CNT assisted $LiCoO_2$ thin-film battery electrode by pulsed laser deposition are reported. A pulsed laser deposition process is described to deposit a CNT assisted LiCoO2 electrode to improve its power. The electrodes were deposited on Pt-coated Si substrates with Ar and O_2 as sputtering gases and $LiCoO_2$ + C as the target. Comparative NEXAFS examination of SWNTs

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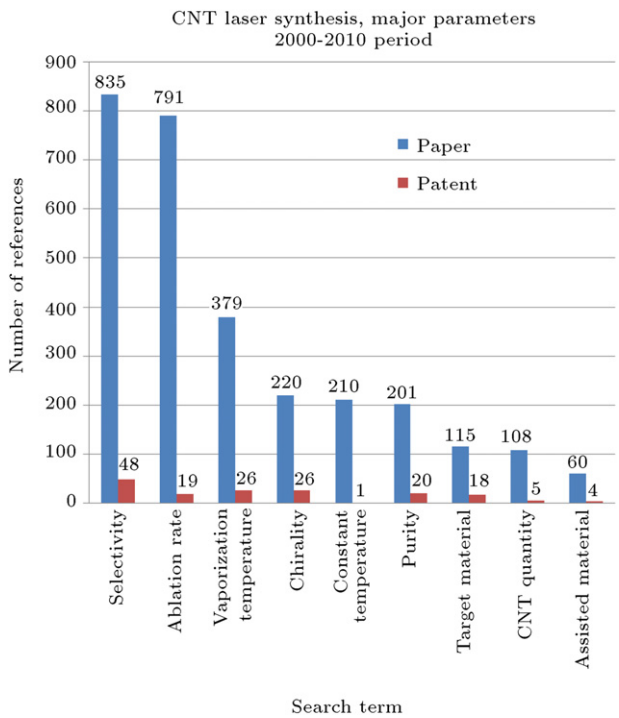

Figure 7: Publications for CNT laser synthesis parameters for the period of 2000–2010.

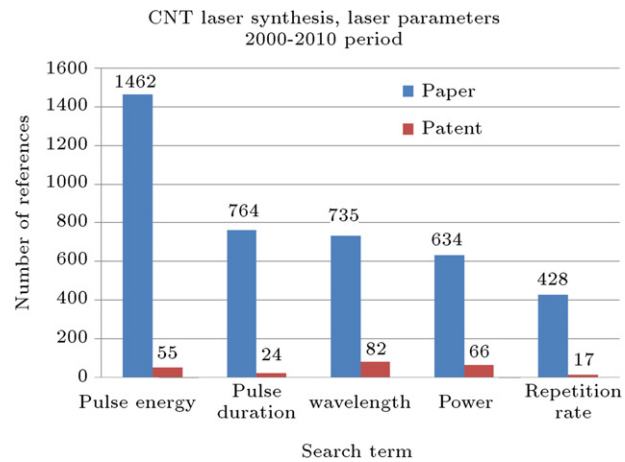

Figure 8: Publications for laser parameters in CNT synthesis for the period of 2000–2010.

produced by different methods is also reported. Three types of SWNTs were comparatively studied using near carbon K-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The tested samples were produced by laser vaporization, CVD, and super growth methods, and contained SWNTs with diameters of 1.2, 2.4 and 4.0 nm, respectively.

Considering different described parameters, a publication research is accomplished here for the period of 2000–2010 for different parameters involved in laser CNT synthesis. The terms, as shown in Figure 7, are selectivity, ablation, vaporization temperature, and CNT chirality. Other terms are: operation at a constant temperature, CNT purity, target material, CNT quantity, and finally, the effect of assisted material in laser ablation. The first one shows the document containing the exact terms "effect of CNT selectivity in laser ablation of carbon nanotubes", "effect of vaporization temperature in laser ablation of carbon nanotubes" and "effect of CNT chirality in laser ablation of carbon nanotubes", while the next terms indicate "effect of constant temperature in laser ablation of carbon nanotubes", "effect of CNT purity in laser ablation of carbon nanotubes", "effect of targer material in laser ablation of carbon nanotubes", "effect of CNT quantity in laser ablation of carbon nanotubes", "effect of electrode structure carbon, and "effect of assisted materials in laser ablation of carbon nanotubes". The number of references for different terms involved in laser ablation CNT synthesis is shown in Figure 7.

In the given analysis, as can be seen in Figure 7, there are more paper publications with the concept of CNT selectivity parameters in CNT production (835 paper, 48 patent, ratio 0.057). The second important parameter in laser CNT prepration is laser ablation discharge, with a publication index of 791, 19, and 0.024. From the explored search, it is noted that there are more publications as a result of the laser method, considering CNT selectivity, with a reference index of 88, 13, and 0.147. However, the ratio is higher for the vaporization temperature, which shows more published patents considering this parameter in given CNT preparation.

In this study, the publications for different parameters involved in laser ablations are given. However, laser parameters involved in efficient laser ablations are not considered in the laser synthesis process. Here, a publication research is accomplished for the period of 2000–2010 for different laser parameters involved in laser CNT synthesis. Terms, as shown in Figure 8, are: laser pulse energy, pulse duration time, wavelength, power, and laser repetition rate. The first one shows the document containing the exact terms "effect of pulse energy in laser ablation of carbon nanotubes", "effect of pulse duration in laser ablation of carbon nanotubes", "effect of wavelength in laser ablation of carbon nanotubes", while the next terms indicate "effect of power in laser ablation of carbon nanotubes", and "effect of repetition rate in laser ablation of carbon nanotubes". The number of references for different terms involved in laser ablation CNT synthesis is shown in Figure 8. In the given analysis, as can be seen in Figure 8, there are more paper publications with the concept of laser pulse energy in CNT production (1462 paper, 55 patent, ratio 0.037). The second important parameter in laser CNT prepration is laser pulse duration, with a publication index of 764, 24, and 0.031. However, the ratio is higher for the laser wavelength (735, 82, 0.111), which shows more published patents considering this laser parameter in given CNT preparation.

4. Progress in CNT productions

A variety of production methods for CNTs are available, and now, chemical modification, functionalization, and characterization of individual CNTs are possible.

4.1. Microstructure variation

Growth of MWNTs with a three-dimensional network microstructure is reported by Sadeghian (2009) [29]. MWNTs were grown by spray pyrolysis of acetylene as the carbon source in the presence of Au–Co as catalyst precursors. A high yield of network-shaped carbon nanotubes (CNTs) with further purification has been obtained under optimal conditions. The optimum synthesis parameters included a synthesis temperature of 700 °C, growth time of 30 min, and a flow rate of acetylene and hydrogen of 40 and 300 sccm, respectively. The morphology

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and structure features of the MWCNTs are characterized using SEM, transmission electron microscopy, and energy dispersive spectra.

Capillarity-assisted assembly of CNT microstructures with organized initiations is given by Lim et al. (2010) [30]. Three different capillary-assisted techniques for the formation of large-scale (MWNT)-based microstructures were presented. Using laser induced artificial vacancies, new insights into the effect of laser power, densities of MWNTs, and oxidation process dependencies for the creation of MWNT polygons were presented. Structural modification in CNT by boron incorporation is reported by Handuja et al. (2009) [31]. They synthesized boron-incorporated CNTs by decomposition of ferrocene and xylene in a thermal CVD set up, using boric acid as the boron source. Studies of the synthesized CNT samples showed that there was deterioration in crystallinity and improvement in alignment of the CNTs as the boron content in the precursor solution increased from 0% to 15%.

Tailoring carbon nanotube microstructures using pH-responsive polymers in aqueous suspensions is also reported. In the reported work, significant tailoring of carbon nanotube dispersion in water is achieved with pH responsive Poly Acrylic Acid (PAA). Micro structural changes as a function of pH were observed. The pH-dependent interactions between PAA and carbon nanotubes were observed with Raman spectroscopy. In another research, tailoring carbon nanotube microstructures through non-covalent interactions is described. That work describes preparation of a single walled carbon nanotube-polyacrylic acid composite. Poly acrylic acid is an effective non-covalent stabilizer of carbon nanotubes in water, whose level of interaction can be tailored by altering pH. Tailoring of CNT microstructures using Poly Acrylic Acid (PAA) and Poly Allylamine Hydrochloride (PAH) is reported. PAA and PAH were used to tailor the microstructure of SWNTs in both aqueous solutions and dry composite films.

4.2. CNT composites

CdS-decorated MWNTs as a material for new devices are reported. Cadmium Sulfide (CdS) nanoparticles were successfully grown on MWNTs via a simple chemical reaction. The CdS-MWNTs sample was afterwards characterized with SEM/TEM and X-ray Diffraction (XRD). The obtained images show clearly the decoration of MWNTs by the CdS nanoparticles, and the XRD measurements indicate the CdS structure as a Zinc blend type.

Microstructure and properties of polyurethane nanocomposites reinforced with methylene-bis-ortho-chloroanilline-grafted MWNT is also described. Methylene-bis-ortho-chloroanilline (MOCA) is an excellent cross-linker, widely used to prepare cured polyurethane (PU) elastomer with high performance. PU/carbon nanotube (CNT) nanocomposites were prepared by incorporation of the MOCA-grafted CNT into the PU matrix. In another study, the strengthening phases in the production of Al2024-CNTs composites by a milling process are reported. Hardness results are given for the new composite material. CNTs synthesized by a CVD method and the 2024 aluminum alloy (Al2024) are used in the production of Al2024-CNTs composites. A homogeneous dispersion of CNTs into the aluminum matrix is achieved by a mechanical milling processing. Nitrogen doped CNTs synthesized from aliphatic diamines for an oxygen reduction reaction is reported by Higgins et al. (2011) [32]. N doped N-CNTs were synthesized using three different aliphatic diamines as N–C precursor solutions with varying C chain lengths, to elucidate the effect of a precursor solution on the overall N content and ORR activity of the synthesized materials. In another report, the Boron-doped CNTs were synthesized by a microwave plasma chemical vapor deposition (MWCVD) method. Obtained CNTs were evaluated by scanning electron microscope (SEM), transmission electron microscope (TEM), and Raman spectroscopy. Development of carbon/carbon composites with carbon nanotubes as reinforcement, and chemical vapor infiltration carbon as the matrix, is investigated. Carbon nanotube based carbon/carbon composites were prepared by infiltration of purified aligned carbon nanotube (ACNTs) film with pyrolytic carbon.

4.3. Growth rate

Another important parameter in CNT production is the growth rate. Influence of the Ni catalyst layer and TiN diffusion barrier on CNT growth rate is described by Kpetsu et al. (2010) [33]. Dense, vertically aligned multiwall carbon nanotubes were synthesized on TiN electrode layers for IR sensing applications. Microwave plasma-enhanced CVD and a Ni catalyst were used for nanotubes synthesis. Since the length of the CNTs influences sensor characteristics, they studied the effects of changing Ni and TiN thickness on the physical properties of the nanotubes.

The next study (by Geohegan et al. (2003) [34]) considers in situ growth rate measurements and length control during CVD of vertically aligned MWNT. Time-resolved reflectivity is employed as an in situ diagnostic in the thermal CVD of vertically aligned arrays of multiwall C nanotubes (VAA-MWNT). Fabry–Perot interference fringes and attenuation of a reflected HeNe laser beam are used to measure the length of VAA-MWNT throughout the 1st 3–8 μm of growth, yielding in situ measurements of growth rates and kinetics and the capability to observe the onset and termination of growth. VAA-MWNT growth is characterized between 565 and 750 °C on Si substrates with evaporated Al/Fe/Mo multilayer catalysts and acetylene feedstock.

In a study, silica supported Fe catalysts were prepared by different methods in order to obtain varying Fe particle sizes. The CNT growth from CO disproportionation was studied in order to establish a relationship between the CNT growth rate and the particle size. They found that there is an optimum catalyst particle size at around 13–15 nm, which will lead to maximum growth rate. The role of surface species in chemical vapor deposited CNT is reported. CVD of CNTs has been investigated using a coupled gas phase and surface chemical model. CNT growth rate is a function of reactor wall temperature such that deposition would occur in the transition region between the hydrogen abstraction and hydrocarbon adsorption limited regimes. Catalytic CVD synthesis of carbon nanotubes with high yield at low temperature growth is also described, and the role of the catalyst and the catalyst support is investigated. Effects of temperature and the role of the Mo top layer on the growth of carbon nanotubes are also given. CNTs were synthesized by a thermal CVD method using a three-layer Al/Fe/Mo metal catalyst. All metal layers were deposited by dc sputtering. The results showed that the growth temperature is an important parameter for the synthesis of CNTs.

4.4. Functionalized carbon nanotubes

New nitrene functionalization onto sidewalls of carbon nanotubes and their spectroscopic analysis is given by Leinonen

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et al. (2010) [35]. The reactivity of *p*-toluenesulfonyl, methylsulfonyl and trimethylsilyl nitrene, derived from the corresponding azides, was studied towards SWCNT prepared by arc or high-pressure CO conversion methods. The functionalized SWCNTs were analyzed by Raman, IR, and VIS/NIR spectroscopy.

Polymeric foams (or porous polymeric materials) are one of the most widely used materials in a variety of applications due to their inherent advantages. Excellent strength-to-weight ratio, light weight, materials savings, and flexibility of generating desired morphologies to meet applications, such as thermal insulation, acoustic attenuation and vibration damping to absorb and membrane for separation. Polymer composites based on functionalized carbon nanotubes and graphene are also reported. A review of polymer composites, based on functionalized carbon nanotubes and grapheme, is given. Functionalization of carbon nanotubes includes liquid-phase activation and ball milling. Functionalization of graphene includes chemical modification and electrochemical modification. Diffusion of ionic liquids into elastomer/carbon nanotubes composites and the tensile mechanical properties of the resulting materials are described. In order to ensure better elastomer/functionalized MWNT compatibility and to enhance dispersion, a series of ionic liquids has been tested in regard to an improved interaction between elastomer and functionalized carbon nanotubes.

4.5. Catalyst effect

In a study, the decomposition of ethylene on an iron catalyst to obtain CNTs and their purification system is reported. That paper describes the preproduction and characterization of carbon nanotubes using ethylene as a carbon source and iron as a catalyst. An additional purification procedure of carbon nonmaterial is presented, and the purification was conducted in two stages. Effects of confinement in carbon nanotubes on the performance and lifetime of fischer-tropsch iron nano catalysts are reported by Tavasoli et al. (2010) [36]. The effects of confinement in carbon nanotubes on Fischer-Tropsch (FT) activity, selectivity and lifetime of CNT supported iron catalysts are reported. A method was developed to control the position of the catalytic sites on either inner or outer surfaces of carbon nanotubes. TEM analyses revealed that more than 80% of iron oxide particles can be controlled to be positioned at inner or outer surfaces of the CNTs. Deposition of iron oxide inside the nanotube pores decreased the average size of the iron oxide particles from 14 to 7 nm.

Comparative studies on the effect of iron oxide doped alumina-based catalysts via sol–gel and LFS methods on CNTs growth by methane decomposition are reported. Using the sol–gel technique and the liquid flame spray method (LFS), three different iron oxide doped alumina-based catalysts were prepared. X-ray diffraction, TEM and the nitrogen adsorption/desorption test were used to compare the three different catalysts and discuss their influence on the formation of the MWNTs. Electrochemical behavior of resorcinol on a gold nanoparticle/carbon nanotube composite modified glassy carbon electrode is described. A gold nanoparticle/carbon nanotube composite modified glassy carbon electrode was fabricated using a simple casting method and was used to study the electrochemical behavior of resorcinol under neutral pH conditions.

In the last study, publications for different parameters involved in CNT preparation are given. However, there are other

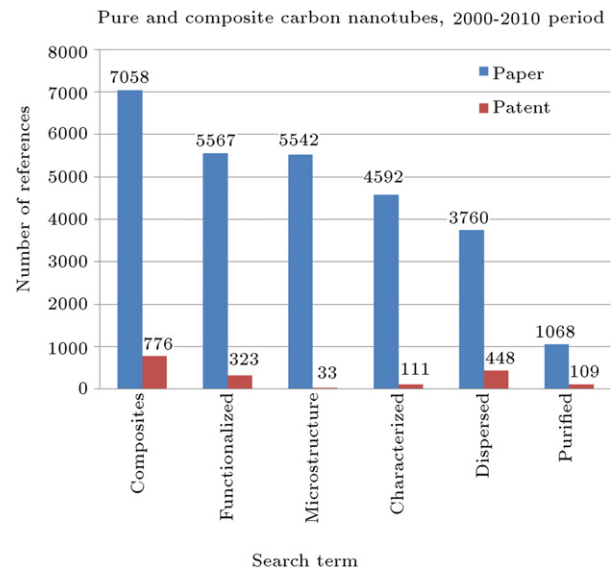

Figure 9: Publications for pure and composite CNTs for the period of 2000–2010.

parameters involved in the efficient production and preparation of special type CNTs. Here, a publication research is accomplished for the period of 2000–2010, for different critical parameters involved in CNT synthesis. The terms, as shown in Figure 9, are CNT composites, functionalized CNT material, microstructures, CNT characterization, dispersed CNTs, and CNT purification. The first one shows the document containing the exact terms "carbon nanotube composites", "functionalized carbon nanotubes", and "carbon nanotube microstructures", while the next terms indicate "characterization of carbon nanotubes", "dispersed carbon nanotubes" and "carbon nanotube purification". The number of references for different terms involved in CNT synthesis and chracterization is shown in Figure 9. In the given analysis, as can be seen in Figure 9, there are more paper publications with the concept of CNT composites in CNT production (7058 paper, 776 patent, ratio of 0.109). The second important parameter in CNT preparation is functionalized carbon nanotubes with a publication index of 5567, 323 and 0.058. From the explored search, it is noted that there are more publications as a result of composite materials, with a reference index of 7058, 776 and 0.109. However, the ratio is higher for the dispersed CNTs (3760, 448, 0.119), which shows more published patents considering this feature in the given special CNT preparation.

5. Conclusions

The concluding remarks related to this study are:

(a) In general, there is a correlation between published scientific documents in the open literature and CNT advances and developments. Except in strategic areas (military and high advanced technology), a good correlation is noted between the trends of CNT development and the number of published papers and filed patents.

(b) The main point is the rate increase in the number of published papers in journals in comparison with documented patents. For the period of 2000–2010, the annual increase rate for patents is slightly higher (8.68%) than that of journal papers (8.09%). This indicates that there is a higher tendency towards application of CNTs rather than basic research. As a result, a

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gradual growth in the number of referenced papers and filed patents is observed for both periods. However, the growth rate for patents is higher than that of published papers in journals.

(c) The third point is to compare the results of this study for the period of 2001–2010 with the results for the earlier period of 1991–2000. For 1991–2000, the averaged annual increase rate for paper is 10% and for patents is 10%. For the recent period of 2001–2010, an annual increase rate for journal paper publications is 8.26%, while for patent publications it is 9.14%. For the two mentioned periods two points can be made. As described for the period 1991–2000, the annual increase rate is a little higher than that of the recent period (2001–2010). This means that the subject was a really hot issue for the first decade of CNT discovery. The patent to paper ratio factor for the earlier period shows an increase of 0.048, while for the recent one, such an increase is 0.061. This means that more innovations are introduced and, as a result, a larger ratio increase is observed. The increase in the number of given references in the field of CNTs promises new advances in high technology.

(d) Progress in nanotechnology requires a thorough knowledge of carbon nanotube structure, properties, and synthesis aspects, and a meaningful advancement has been made during the recent period (2000–2010). Published papers for CNT arc synthesis parameters for the period of 2000–2010 are compared. Publications for CNT, CVD and CCVD synthesis for the period of 2000–2010 are described. In another research, the publications for CNT laser synthesis parameters for the period of 2000–2010 are reviewed. Publications for laser parameters in CNT synthesis for the period of 2000–2010 are described in detail. Parameter optimizations of the CVD, CCVD, ARC, and finally, the laser ablation method, are described.

(e) In another study, the role of the language of the published references for CNT research, for the period of 2000–2010, is investigated (Table 2). The number of published papers and patents in the searched languages of English, Japanese, Chinese, Russian, German, French, Polish, and Spanish is investigated. Two important facts can be seen from the listed numbers for each category. First, as expected, publications in English dominate other languages. Second is the consideration of the patent/paper ratio for each language, as indicated in Table 2. For the documents published in the French language, the patent/paper ratio is 9.35, which is much higher than that of the Polish language ratio (0.05). Considering such an important factor, French documents, with a ratio of 9.35, are superior, then German (6.78) and Japanese documents show a high ratio of 4.27, while, for English language publications, this ratio is 0.11.

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