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Synthesis of porous carbon nanotubes foam composites with a high accessible surface area and tunable porosity

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The macroscopic shaping of carbon nanostructure materials with tunable porosity, morphologies, and functions, such as carbon nanotubes (CNT) or carbon nanofibers (CNF), into integrated structures is of great interest, as it allows the development of novel nanosystems with high performances in filter applications and catalysis. In the present work, we report on a low temperature chemical fusion (LTCF) method to synthesize a self-macronized carbon nanotubes foam (CNT-foam) with controlled size and shape by using CNT as a skeleton, dextrose as a carbon source, and citric acid as a carboxyl group donor reacting with the hydroxyl group present in dextrose. The obtained composite has a 3D pore structure with a high accessible surface area ($>350 \text{ m}^2 \text{ g}^{-1}$) and tunable meso- and macro-porosity formed by the addition of a variable amount of ammonium carbonate into the starting mixture followed by a direct thermal decomposition. The as-synthesized CNT-foam also exhibits a relatively high mechanical strength which facilitates its handling and transport, while the nanoscopic morphology of the CNT significantly reduces the problem of diffusion and contributes to an improvement of the effective surface area for subsequent applications. These CNT-foams are successfully employed as selective and recyclable organic absorbers with high efficiency in the field of waste water treatment.

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1 Introduction

Carbon nanotubes (CNT) possess a nanoscopic dimension with a high specific surface area ($>100 \text{ m}^2 \text{ g}^{-1}$), high thermal conductivity and high thermal resistance under an inert atmosphere, and high chemical and environmental stability.^{1,2} The surface character of these materials can also be fine-tuned, *i.e.* hydrophilic or hydrophobic character, depending on the downstream application.^{3,4} Due to the exceptional physical and chemical properties cited above, CNT have been a subject of ever increasing scientific and industrial interest during the last few decades,⁵ especially in the field of catalysis,^{6–10} electrochemical energy storage^{11–13} and waste water treatment.^{14–16} For these applications, a nanoscopic size of carbon nanotubes significantly reduces the problem linked with mass transfer limitations while the high specific surface area provides a large number of anchorage sites either to adsorb pollutants (waste water treatment) or to host active nanoparticles (catalysis). As a consequence, the overall

adsorption capacity or catalytic activity per unit of volume of such materials is significantly improved. The nanoscopic size, however, is a main drawback, as it renders the handling and transport of the materials and the recovery of used materials difficult, especially in a liquid medium, due to the problem of filter plugging.¹⁷ The development of hybrid materials that can efficiently combine the nanoscopic properties with a macroscopic shape is therefore of great interest.^{17–20} According to the literature reports, CNT can be efficiently deposited on several macroscopic supports such as alumina²¹ or carbon,²² allowing their direct use in conventional systems. However, it is worth noting that up to now works dedicated to self-macronization of CNT are relatively scarce.^{17,23} It is expected that such self-macronization of CNT can additionally open new application fields for this material.

Here we report on a facile and simple approach to synthesize a macroscopic 3D interconnected carbon nanotubes foam (CNT-foam) with a high accessible surface area and relatively high mechanical strength for subsequent use in the field of waste water treatment. In the case of waste water treatment the foam is pre-treated under appropriate conditions in order to obtain a hydrophobic-type surface which can selectively adsorb organic compounds present in a water medium. The pore size of the foam can also be fine-tuned by changing the content of a pore-forming agent or by adding a removable template, *i.e.* alumina or silica powder. The synthesis method is easy for up-scaling and the final size and shape of the composite can be tailored at will depending on the downstream applications.

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2 Experimental

2.1 Synthesis of porous CNT-foam composites

Multi-walled carbon nanotubes (CNT) are selected as a raw material for the foam synthesis. The carbon nanotubes were synthesized by a Chemical Vapour Deposition (CVD) process using Fe/ γ -Al₂O₃ as a growth catalyst and a mixture of C₂H₆ and H₂ as a carbon source.^{24,25} The synthesis was carried out at 750 °C for 2 h and the black product containing CNT and the residual growth catalyst was collected from the ceramic boat. The product was submitted to a basic and acid treatment at 110 °C in order to remove as much of the residual growth catalyst as possible before further processing. The specific surface area of purified CNT, measured by the BET method, was around 190 m² g⁻¹. Such a value is in good agreement with those reported nowadays in the literature for multi-walled carbon nanotubes synthesized by a CVD technique.^{17,25}

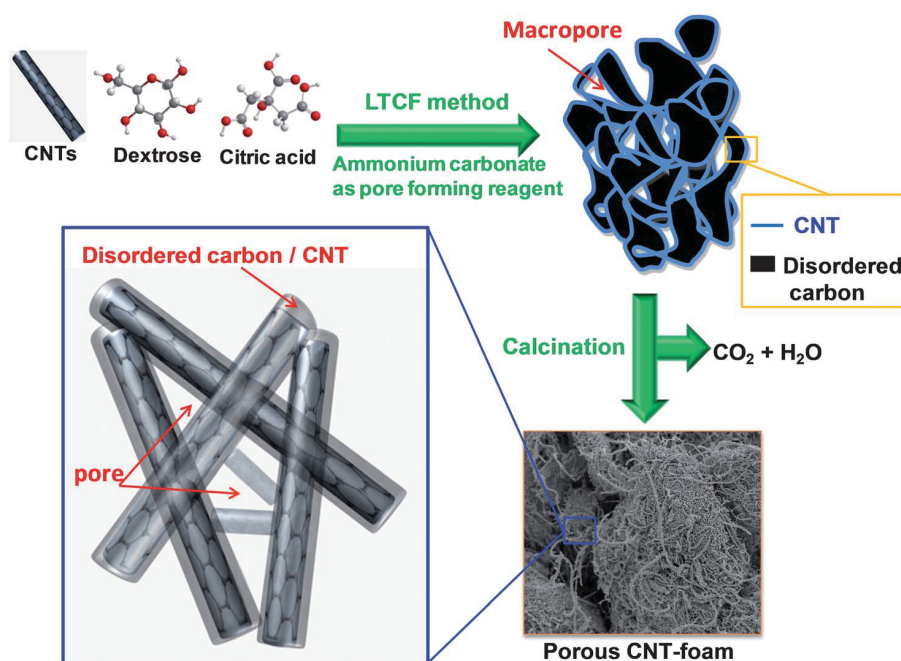
Self-macronized carbon nanotubes foam (CNT-foam) composites with controlled size and shape were synthesised by the low temperature chemical fusion (LTCF) method. In the synthesis procedure, 1 g of CNTs was mixed with 4 g of dextrose and 6 g of citric acid by mechanical crushing at room temperature. Then, a known amount of ammonium carbonate (*i.e.* 2 g) was added *via* mechanical mixing to obtain a homogeneous solid mixture. Dextrose and citric acid were employed to generate a porous CNT-foam composite by the low temperature chemical fusion (LTCF) method as illustrated in Scheme 1. In the procedure dextrose is used as a carbon source while citric acid offers carboxyl groups to react with hydroxyl groups present in dextrose. The ammonium carbonate is used as a pore forming agent during the LTCF treatment which, during the thermal treatment, undergoes decomposition into gaseous products

leaving behind a porous material. However, it is worth noting that part of the dextrose and citric acid also undergo decomposition during the thermal treatment, and thus, also significantly contribute to the pore size generation in the final composite.

According to the LTCF method, the mixture was reacted in an oven at 130 °C for 5 h, and then, the carbon nanotubes foam precursor was decomposed by heating up to 450 °C under air flow for 3 h. After the calcination step, the CNT-foam was annealed in helium at 900 °C for 2 h in order to obtain the final hydrophobic composite employed further in the waste water treatment.

2.2 Characterization techniques

The crystallinity of the sample was evaluated by means of the powder X-ray diffraction (XRD) technique in a $\theta/2\theta$ mode on a Bruker D-8 Advance diffractometer. Thermal gravimetry analysis (TGA) was performed on a Setaram apparatus at an air flow rate of 25 mL min⁻¹ and a heating rate of 10 °C min⁻¹, from room temperature to 1000 °C. The specific surface area of the different samples was measured by a BET method using N₂ as an adsorbent at liquid nitrogen temperature (TriStar sorptometer). Before measurements, the samples were outgassed at 250 °C overnight in order to desorb moisture and impurities from their surfaces. The XPS measurements of the support were performed on a MULTILAB 2000 (THERMO VG) spectrometer equipped with an Al K α anode ($h\nu = 1486.6$ eV) with 10 min of acquisition. Peak deconvolution was made with the "Avantage" program from Thermoelectron Company. The C 1s peak at 284.6 eV was used to correct charging effects. Shirley backgrounds were subtracted from the raw data to obtain the areas of the C 1s peak. The gross morphology of the carbon and ceramic materials was observed



Scheme 1 Illustration of a low temperature chemical fusion (LTCF) method for the synthesis of porous CNT-foam composites.

by scanning electron microscopy (SEM) on a JEOL F-6700 FEG with a lattice resolution of 5 nm, at an accelerating voltage of 10 kV. The sample was covered by a thin layer of gold in order to decrease the problem of charging during the analysis. Transmission electron microscopy (TEM) observations were made on a JEOL 2100F microscope working at an accelerated voltage of 200 kV with a point-to-point resolution of 0.17 nm. The sample was ultrasonicated in ethanol solution and a drop was deposited onto a copper grid covered with a holey carbon membrane for observation.

3 Results and discussion

3.1 Characteristics of porous CNT-foam composites

The representative SEM micrographs of the as-synthesized foam-structured carbon composite are presented in Fig. 1. The SEM micrograph (Fig. 1a) shows a complete embedding of CNT by a thick layer of carbon species, which were generated from the thermal decomposition of dextrose after the low temperature chemical fusion (LTCF) process. Further heat treatment in air at 450 °C leads to the decomposition of gaseous products within a solid layer and to the formation of the CNT-foam precursor (Fig. 1c). The low magnification SEM image of the CNT-foam (Fig. 1c) confirms the open microstructure of the sample with fully accessible porosity. For comparison, the

foam-structure carbon composite precursor is also calcined in air at lower temperature, *i.e.* 350 °C (Fig. 1b). The SEM micrograph shows the formation of a poorly porous structure, which indicates that the carbon source precursor was incompletely decomposed at lower temperature and indicates that the air calcination treatment at around 450 °C is the most appropriate to form a well opened porous foam. Indeed, higher thermal treatment temperature shows almost no influence on the porosity of the final composite. The developed synthesis method also allows us to synthesize CNT-foams with different sizes, ranging from a few millimetres to several centimetres, and shapes (Fig. 1e), depending on downstream applications, *i.e.* waste water treatment or catalytic processes. As shown in Fig. 1f, CNT-foams can withstand a relative weight load without any changes and the stress tests show that the CNT-foams can withstand a stress pressure of about 1.39 MPa.

Thermal analysis results for a purified CNT precursor and the corresponding foam-structured nano-carbon materials after different thermal treatments are displayed in Fig. 2. The purified CNT sample is stable below 500 °C and a complete weight loss was observed at a temperature of around 650 °C due to the oxidation of CNT by oxygen.²⁶ The corresponding TGA/DTG curves recorded on the sample after heat treatment at 130 °C in air contain several peaks which indicate the presence of several carbon-based species within the sample. As can be seen in Fig. 2b, three weight loss areas located at 200–300 °C, 512 °C and 654 °C, respectively, are found in a DTG curve. The weight loss area between 200 and 300 °C is attributed to the reaction between the functional groups from citric acid (–COOH) and dextrose (–OH), which is responsible for the formation of the foam-structured nano-carbon composite. The two weight loss areas appearing at 512 and 654 °C are ascribed to the oxidation of non-graphitic and graphitic carbon in the composite, respectively. The TGA/DTG curves of samples after calcination in air at 350 and 450 °C are presented in Fig. 1c and d and indicate that a large part of the disordered carbon species, formed during the low temperature treatment of the foam precursor, were removed during the calcination step at 450 °C. For the sample calcined at 350 °C two peaks are observed in a DTG which could be attributed to the oxidation of disordered carbon (low temperature peak) and CNT (high temperature peak) (Fig. 2c). The sample after calcination at 450 °C exhibits only a single peak with a shoulder (Fig. 2d). It is worth noting that for both samples the high temperature peaks are shifted to a higher temperature region, *i.e.* 674 °C and 654 °C instead of 611 °C for the pristine CNT (Fig. 2a). Such a change could be attributed to a homogeneous coating of CNT by a layer of carbon with different crystallinity which could hinder the oxidation process, leading to higher combustion temperature. The high oxidative resistance observed in the sample could also be attributed to the large diameter of the CNT coated with a layer of carbon which results in higher combustion temperature.

TGA analysis also indicates the presence of unburnt compounds which amount to about 5 to 8 wt% in the sample. Such species could be attributed to the residual iron catalyst which was buried under graphitic layers (2–3 wt%) and was not removed from the CNT during the purification process, and also

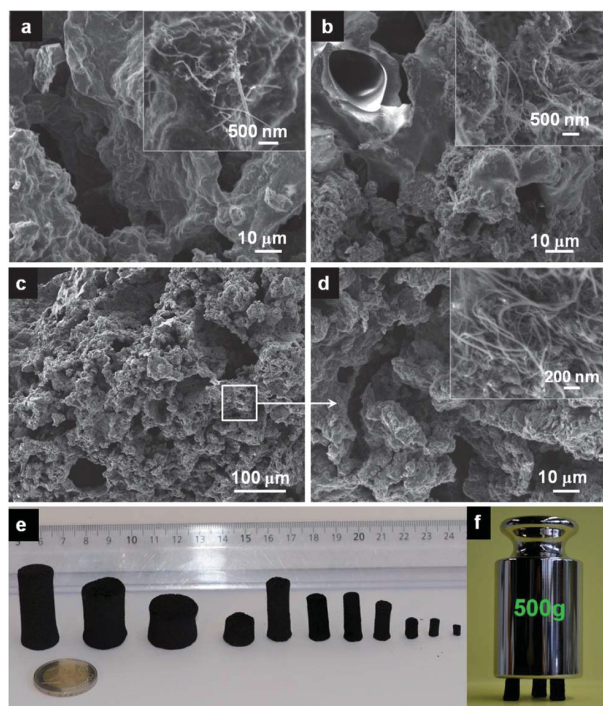


Fig. 1 (a) SEM micrographs of the CNT-foam precursor after the low temperature chemical fusion method. (b) SEM micrographs of the CNT-foam obtained from calcination in air flow at 350 °C for 3 h. (c and d) SEM micrographs of the CNT-foam obtained from calcination in air flow at 450 °C for 3 h showing the presence of large voids within the foam and CNT entanglement. (e) Optical photos of representative CNT-foams with different shapes for various applications. (f) Optical photo that shows three CNT-foam cylinders supporting 500 g weight without any changes.

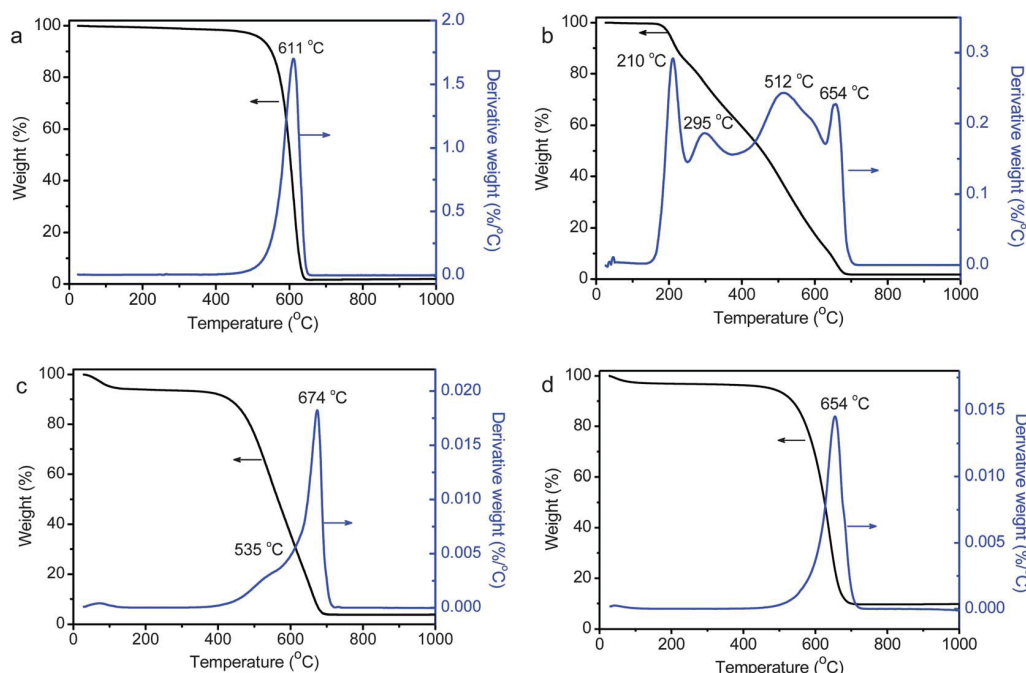


Fig. 2 Thermogravimetric analysis (TGA) curves. (a) The initial CNT after removal of the growth catalyst. (b) The mixed CNT, dextrose and ammonium carbonate powder after heat treatment at 130 °C overnight in the oven. (c and d) The CNT-foam precursor from (b) after calcination in air at 350 °C and 450 °C for 3 h.

to the SiO₂ phase, originating from the impurities that were present in the starting raw materials and were further converted into SiO₂ during the calcination process (see also XPS results below). It is worth noting that for the waste water treatment these unburnt residues are just playing the role of spectator species and are not involved in any way in the adsorption process.

The CNT content in weight percent in the final composite, determined by the difference between the starting weight of the CNT and the final weight of the composite, amounts to 50–70% while that of the disordered carbon is about 50–30%. According to the results, about 10–30% of the dextrose and citric acid mixture was converted into solid carbon after the thermal treatment. According to the results one can state that part of the dextrose and citric acid also contributes to the pore size generation in the final composite along with the ammonium carbonate compounds.

The pore size distribution and specific surface area of the pristine CNT and CNT-foam, after calcination at 450 °C in air, are measured by means of the N₂ adsorption using the BET method. Typical nitrogen adsorption-desorption isotherms for both samples are shown in Fig. 3a and could be classified as Langmuir IV type isotherms.²⁷ The adsorption line demonstrates an ascending trend without observable inflexion or flatness in the relative pressure P/P_0 up to 0.85 and 0.50 for CNT and CNT-foam, respectively. When the relative pressure increases, the adsorption isotherm lines grow faster, and an obvious abruptness of adsorption and desorption lines appears.²⁸ The CNT-foam exhibits a significant pore size distribution change compared to the pristine CNT (Fig. 3b). Indeed, the introduction of a carbon phase from dextrose

leads to a significant shift of pore size from a large macropore network (CNT precursor) to a mesoporous region. The final foam-structured composite after thermal treatment in air at 450 °C exhibits a specific surface area of 357 m² g⁻¹ compared to 190 m² g⁻¹ for the pristine carbon nanotubes, based on N₂ adsorption-desorption. The specific surface area mostly consists of meso- and macropores and no micropores (<5 nm) are observed in the sample.

Such results are of high potential for waste water treatment or catalytic applications, where the presence of micropores is detrimental to the access of reactants and product desorption. The abruptness point of the isotherm curves confirms that the CNT-foam has a lower condensation at a given relative pressure compared with CNT, resulting in a lower specific surface area of the CNT.²⁸ According to the results presented in Fig. 3b, the increase in the specific surface area, from CNT to CNT-foam, is attributed to a partial carbonization of the dextrose compound on the external surface of carbon nanotubes leading to the formation of a new meso- and macro-porous carbon network with a high effective surface area.

The existence of mesopores is also confirmed by the location of the inflection point at the relative pressure (P/P_0) of the N₂ adsorption and desorption branching which started between 0.4 and 0.6.¹¹ The XRD spectra of CNTs and foam-structured composites revealed that the main crystalline phase at 26° and 43° is graphite-2H (Fig. 3c).²⁹

The pore size of the composite can be tuned by changing the composition of the reactant mixture followed by the same thermal treatment as shown in Fig. 4. According to the results one can see that by changing the reactant concentrations, macroscopic composites with different pore size distributions

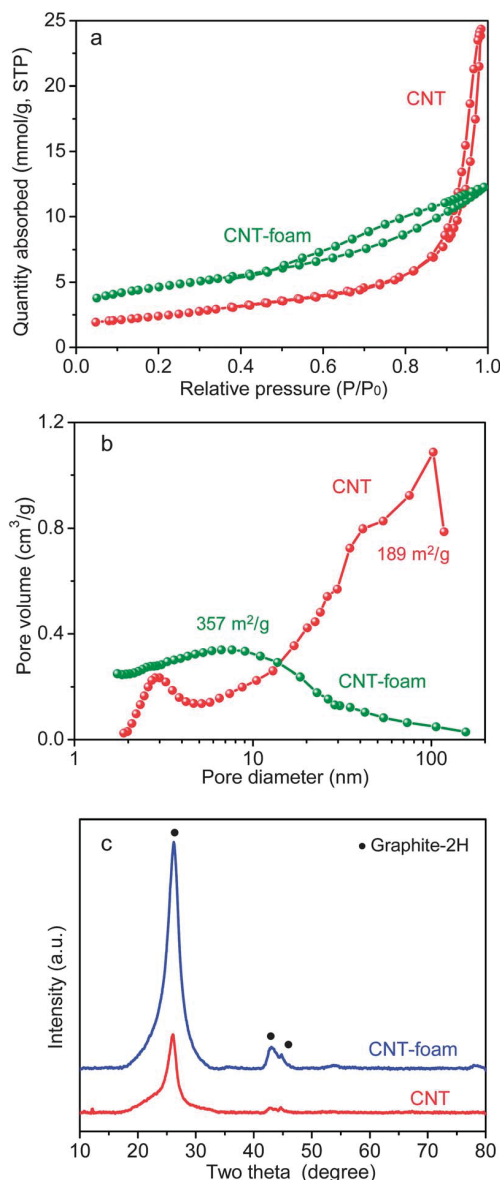


Fig. 3 (a) N₂ adsorption isotherms of the pristine CNT and the final foam. (b) Pore size distribution of the pristine CNT and after foam shaping, determined from a desorption branch of the isotherm showing a large change in the micro- and meso-pores contribution after shaping. (c) XRD patterns of carbon nanotubes and carbon nanotubes foam.

and specific surface areas can be obtained for different downstream applications, *i.e.* absorber or catalyst support.

The microstructure of the as-synthesized foam-structured composite was investigated by TEM and the corresponding results are presented in Fig. 5. A low resolution TEM micrograph clearly shows the presence of disordered carbon species within the mixture, which bridges CNT leading to the formation of a new porous network. According to the TEM results one could state that in the CNT-foam composite CNT play the role of a network allowing the anchorage of disordered carbon species formed from dextrose and citric acid transformation. The high resolution TEM image (Fig. 5b) indicates that the disordered

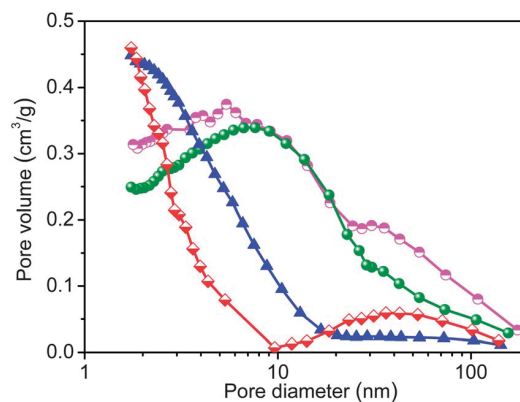


Fig. 4 Pore size distribution derived from N₂ desorption isotherms using the BJH method for CNT-foams prepared under different preparation conditions.

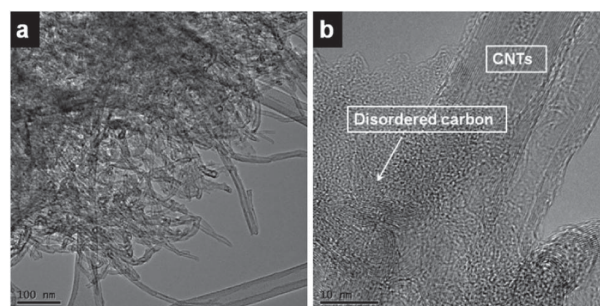


Fig. 5 Representative TEM micrographs of the CNT-foam showing the presence of a thin coating layer of disordered carbon, issued from dextrose decomposition, on the CNT surface.

carbon species are well anchored on the CNT wall and link the CNT like solid glue, which explains a relatively high mechanical strength of the final composite. It is worth noting that the HR-TEM analysis also confirms the complete retention of the CNT microstructure during the synthesis.^{30,31}

3.2 CNT-foam for an absorption application

3.2.1 XPS spectroscopy. An X-ray photoelectron spectroscopy (XPS) technique was utilized to get access to the contents of carbon species and oxygen groups in both CNTs and the hydrophobic phase porous CNT-foam. This provides useful information on the nature of functional groups and the presence of structural defects on the nanotube surface and the corresponding spectra are presented in Fig. 6.

To be efficiently used as a selective absorbent for organic phases (species) dispersed in water, the foam structured composite was annealed in helium at 900 °C (CNT-foam-900) in order to eliminate the oxygen functional groups on its surface and to obtain a solid with a hydrophobic character. Indeed, previous works have shown that an annealing step at a relatively high temperature leads to a selective removal of oxygen functional groups from a CNT surface and confers to the material a hydrophobic surface character.³² As can be seen in Fig. 6a, survey scan spectra of prepared materials show C 1s and O 1s

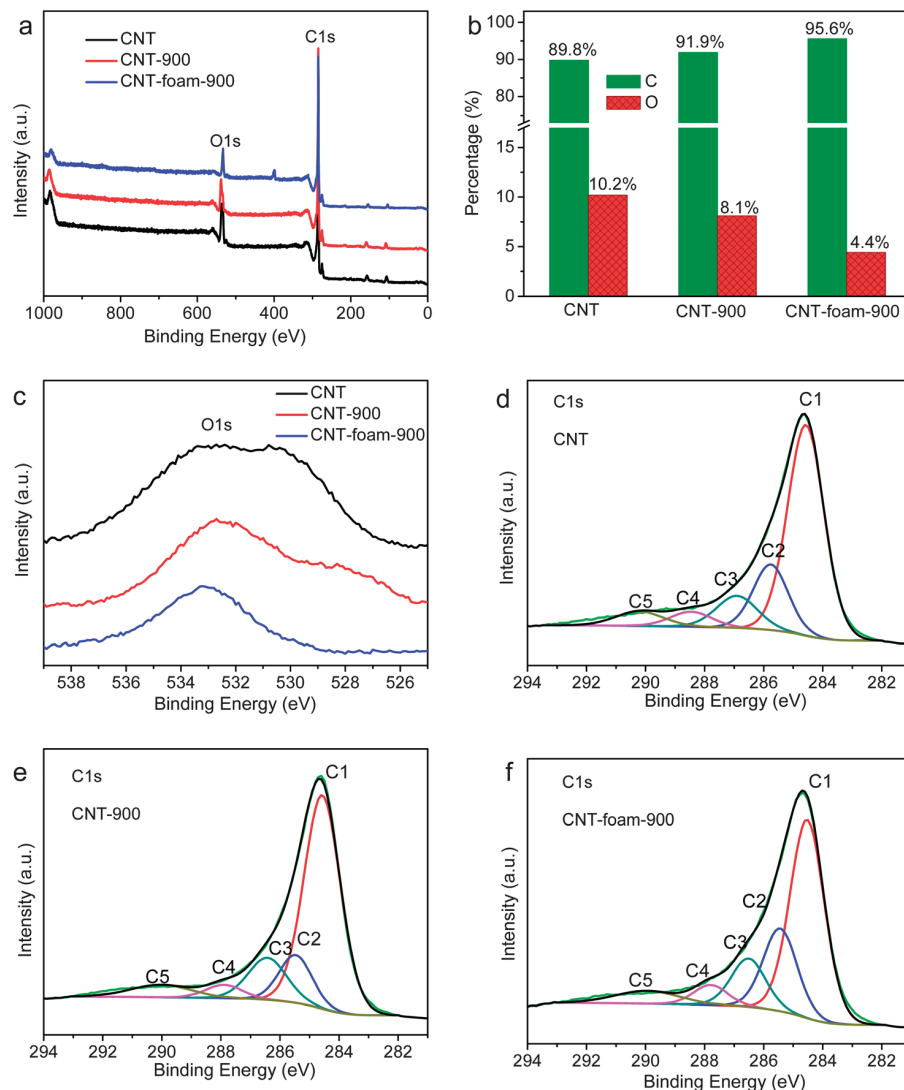


Fig. 6 XPS spectra of CNT and CNT-foam. (a) XPS survey scan, (b) calculated atomic concentration, (c) O 1s high-resolution XPS spectra and C 1s high-resolution XPS spectra of (d) CNT, (e) CNT annealed in helium at 900 °C (CNT-900) and (f) CNT-foam annealed in helium at 900 °C (CNT-foam-900).

photoelectron peaks at around 285 eV and 533 eV, respectively. The contribution of Si 2p and 2s peaks at about 102 and 153 eV, respectively, indicates the presence of Si-based species (Fig. 6a). Such silicon species could originate from traces of residual silicon oxide impurities in the raw materials used for the synthesis. As shown before, these impurities are thermally stable and therefore difficult to remove by the annealing treatment.³³ The XPS analysis also evidences the presence of nitrogen species on the composite surface at around 400 eV (Fig. 6a). Such nitrogen species could be generated from the ammonium carbonate and the detailed investigation of its origin is underway.

The carbon and oxygen atomic ratios calculated by the high resolution C 1s and O 1s core level spectra are presented in Fig. 6b. It should be noted that reference SiO₂ samples were measured in order to subtract the contribution of SiO₂ impurities from the overall O 1s spectrum. Therefore the oxygen

atomic ratio presented in Fig. 6b is exclusively due to oxygen species attached to carbon. The oxygen content in the CNT sample is calculated to be about 10 at.%. Such high oxygen content was attributed to the post-synthesis acid treatment of the sample. After an annealing treatment under a helium atmosphere at 900 °C (CNT-900), the oxygen content in the CNT material slightly decreases, from 10 to 8 at.%. On the other hand, the oxygen content in the CNT-foam-900, after a similar annealing treatment, is about 4 at.%, which is the lowest amount among the analyzed samples. The observed results indicate that oxygen desorption is easier from the foam-structured composite compared to the pristine CNT material. This phenomenon is attributed to the presence of a porous disordered carbon structure on the topmost surface of CNT which binds oxygen in a loose manner.

The XPS O 1s peaks of the CNT, CNT-900 and CNT-foam-900 composite presented in Fig. 6c evidence a remarkable decrease

in the oxygen content at the low binding energy side (about 530 eV) when compared to that of CNT before the annealing process. The oxygen component at about 533 eV, which is practically unaffected by the annealing treatment, is linked to the SiO₂ impurities in accordance with previous studies.³³

Fig. 6d–f shows the C 1s XPS spectra of purified and annealed CNT and CNT-foam-900 composites. Deconvolution of the C 1s peak of purified and annealed CNT and CNT-foam-900 reveals five peaks. One main peak (C1) of sp² hybridized C=C (284.5–284.6 eV) is attributed to the graphitic structure, a secondary peak (C2) of sp³ hybridized C–C (285.4–285.8 eV) corresponds to defects in the nanotube structure and carbon nanoparticles in the CNT-foam,³⁴ and the other three accompanying peaks result from C–O or C=O (C3) at around 286.4–286.9 eV, –COO (C4) at 287.8–288.5 eV, and the shake-up π – π^* transition of carbon (C5) at 290–290.2 eV.^{35,36} The C 1s peak of the foam-structured composite shows higher intensity of sp³ C–C compared to that of the annealed CNT (CNT-900) which could be directly linked with the disordered carbon species introduced by dextrose transformation in the composite.

3.2.2 Morphological characteristics of the hydrophobic CNT-foam composite. Representative SEM micrographs of the CNT-foam composite material after annealing under helium at 900 °C (CNT-foam-900) are presented in Fig. 7a and b. Even after annealing under helium at 900 °C, the formed CNT-foam maintains its general morphology which confirms a high thermal resistance of this carbon–carbon composite. The low magnification SEM micrograph (Fig. 7a) shows a homogeneous dispersion of CNT within the composite along with the clear presence of both meso- and macroporous networks. High-magnification observation indicates that the foam-structured composite is constituted by highly entangled CNT well covered by disordered carbon species (see grey arrows (red online) in Fig. 7b) forming a dense network with a large connected porosity. The corresponding TEM images (Fig. 7c and d) confirm the facts observed from the SEM analysis and clearly show the presence of disordered carbon species around the

CNT network. It is also worth noting that annealing under helium also slightly decreases the overall specific surface area of the composite, from 357 m² g^{−1} to about 293 m² g^{−1}, which is still high enough for the targeted downstream applications in the field of waste water treatment or heterogeneous catalysis. Such specific surface area decrease could be attributed to the partial re-organization of a disordered carbon phase into a more graphitic one in the composite during the high temperature annealing.

3.2.3 Absorption ability of CNT-foam-900 for waste water treatment. The CNT-foam-900 with a hydrophobic surface character was further employed as a selective adsorbent for the waste water treatment. The high thermal resistance of the material also allows it to be easily regenerated by a simple thermal treatment. The last advantage relies on a controlled macroscopic shaping and high mechanical strength of the material which facilitates its manipulation and transport. The absorption capacities of the CNT-foam are expressed in terms of kilogram of organic compounds adsorbed per cubic meter of absorber materials (kg m^{−3}). The higher absorption capacity was obtained on a CNT-foam for lighter-density liquids (*i.e.* toluene) and higher-density liquids (*i.e.* chloroform) (Fig. 8a). For comparison, we also tested macroscopic CNT-beads which were earlier shaped from CNT by our group.¹⁷ For the waste water treatment the CNT-foam-900 was dropped into a mixture containing toluene (labelled with a ferrocene compound) and water. As soon as the CNT-foam-900 was put in contact with the mixture, the mixture became colourless which indicates that the organic solvent was steadily and completely adsorbed on the CNT-foam-900 (Fig. 8c and d). The efficient adsorption was attributed to the hydrophobic character and to the porous structure of the composite which significantly improve the contact surface between an organic phase and the CNT-foam-900.

The maximum organic solvent weight adsorbed by the CNT-foam-900, when toluene was used, is about 650 kg m^{−3} (Fig. 8a). Organic solvents trapped by the CNT-foam-900 were further removed by dipping the foam into a solution containing ethanol

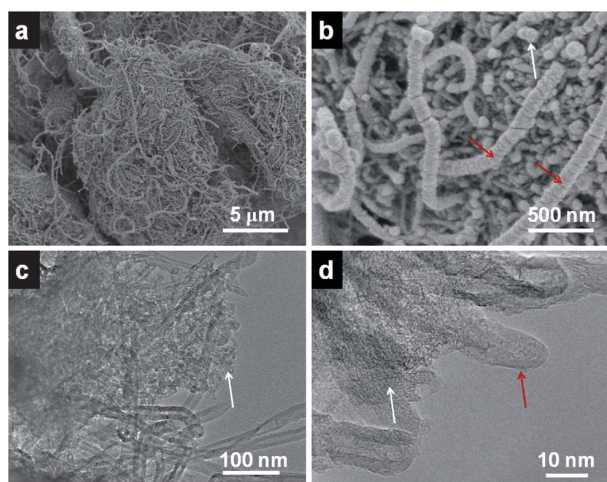


Fig. 7 (a and b) SEM micrographs and (c and d) TEM images of the carbon nanotubes foam composite after annealing in helium at 900 °C.

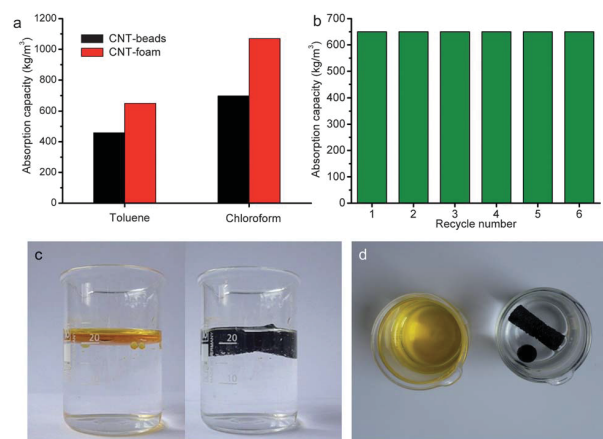


Fig. 8 (a) Adsorption capacity of the annealed CNT-foam and annealed CNT-beads of toluene and chloroform. (b) Regeneration capacity of the CNT-foam-900 for toluene adsorption. (c and d) Photographs showing adsorption of toluene by the CNT-foam-900. The toluene was colored with ferrocene for the sake of clarity.

followed by drying in an oven before re-using. The CNT-foam-900 exhibits an extremely high regeneration capacity as shown in Fig. 8b, as almost 100% of the adsorption capacity was maintained after several adsorption-regeneration cycles. The adsorption capacity varies with the density of adsorbed solvents as shown in Fig. 8a. In any case, the adsorption capacity was retained up to several adsorption-regeneration cycles regardless of the nature of the adsorbed organic solvent which highlighted the advantage of using these composites in the field of oil spills recovery where long-term stabilization is a prerequisite. The advantage of using such CNT-foam-900 for waste water treatment or oil spill recovery is the relatively high density of the material which significantly reduces the volume of the composite for a given weight. In the case of ultralight materials³⁷ which can absorb organic compounds several hundred times their own weight, the main problem is linked to the apparent volume of the composite. Indeed, for an ultralight composite with a density of 2.1 mg cm^{-3} and a capacity of adsorption of about 20 000%, the total weight adsorbed is about 420 kg m^{-3} , lower than the one obtained with the CNT-foam-900 in the present work, *i.e.* 650 kg m^{-3} .

4 Conclusions

In summary, a new macroscopic shaping method has been developed to make CNT-foams with a high accessible surface area ($>350 \text{ m}^2 \text{ g}^{-1}$) and tunable meso- and macroporosity. The porosity can be tuned by adding ammonium carbonate (pore former) in various amounts into the starting mixture, followed by a direct thermal decomposition. The CNT-foam exhibits a relatively high mechanical strength which facilitates its handling and transport, while the nanoscopic morphology of the carbon nanotubes significantly reduces the problem of diffusion and contributes to an improvement of the effective surface area for adsorption. *These high effective surface area and open porosity CNT-foams can also be synthesized with controlled shape, i.e. extrudates, discs, spheres, and size depending on the downstream applications.* These CNT-foams can be successfully employed as selective and recyclable organic absorbers in the field of waste water treatment. The low temperature chemical fusion (LTCF) method developed in the present work will be applied to the preparation of hybrid composites containing a mixture of CNTs and a few-layer graphene which can show improved efficiency in the field of waste water treatment. Work is under way to use such hierarchical foams, made from either CNT or nitrogen-doped CNT with enhanced basic sites, as absorbers for removing the trace amounts of metals present in waste water, and also as a structured catalyst support for reactions with high mass and heat transfer such as the Fischer-Tropsch synthesis.³⁸

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Notes and references

- 1 H. J. Dai, *Top. Appl. Phys.*, 2001, **80**, 29–53.
- 2 P. Serp, M. Corrias and P. Kalck, *Appl. Catal., A*, 2003, **253**, 337–358.
- 3 J. P. Tessonnier, O. Ersen, G. Weinberg, C. Pham-Huu, D. S. Su and R. Schlogl, *ACS Nano*, 2009, **3**, 2081–2089.
- 4 T. Kanyo, Z. Konya, F. Bergen, I. Dekany and I. Kiricsi, *Chem. Commun.*, 2003, 2746–2747.
- 5 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787–792.
- 6 J. P. Tessonnier and D. S. Su, *ChemSusChem*, 2011, **4**, 824–847.
- 7 J. Zhang, R. Wang, E. Z. Liu, X. F. Gao, Z. H. Sun, F. S. Xiao, F. Girgsdies and D. S. Su, *Angew. Chem., Int. Ed.*, 2012, **51**, 7581–7585.
- 8 J. P. Tessonnier, L. Pesant, G. Ehret, M. J. Ledoux and C. Pham-Huu, *Appl. Catal., A*, 2005, **288**, 203–210.
- 9 H. B. Zhang, X. L. Pan, J. Y. Liu, W. Z. Qian, F. Wei, Y. Y. Huang and X. H. Bao, *ChemSusChem*, 2011, **4**, 975–980.
- 10 H. Zhang, C. Lancelot, W. Chu, J. P. Hong, A. Y. Khodakov, P. A. Chernavskii, J. Zheng and D. G. Tong, *J. Mater. Chem.*, 2009, **19**, 9241–9249.
- 11 S. M. Bak, K. H. Kim, C. W. Lee and K. B. Kim, *J. Mater. Chem.*, 2011, **21**, 1984–1990.
- 12 S. Bose, T. Kuila, A. K. Mishra, R. Rajasekar, N. H. Kim and J. H. Lee, *J. Mater. Chem.*, 2012, **22**, 767–784.
- 13 B. P. Vinayan, R. Nagar, V. Raman, N. Rajalakshmi, K. S. Dhathathreyan and S. Ramaprabhu, *J. Mater. Chem.*, 2012, **22**, 9949–9956.
- 14 X. C. Gui, Z. P. Zeng, A. Y. Cao, Z. Q. Lin, H. Q. Zeng, R. Xiang, T. Z. Wu, Y. Zhu and Z. K. Tang, *J. Mater. Chem.*, 2012, **22**, 18300–18305.
- 15 X. C. Gui, J. Q. Wei, K. L. Wang, A. Y. Cao, H. W. Zhu, Y. Jia, Q. K. Shu and D. H. Wu, *Adv. Mater.*, 2010, **22**, 617–621.
- 16 Z. Y. Sui, Q. H. Meng, X. T. Zhang, R. Ma and B. Cao, *J. Mater. Chem.*, 2012, **22**, 8767–8771.
- 17 Y. F. Liu, L. D. Nguyen, T. H. Tri, Y. Liu, T. Romero, I. Janowska, D. Begin and C. Pham-Huu, *Mater. Lett.*, 2012, **79**, 128–131.
- 18 B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Paillet, C. Journet, P. Bernier and P. Poulin, *Science*, 2000, **290**, 1331–1334.
- 19 J. Amadou, D. Begin, P. Nguyen, J. P. Tessonnier, T. Dintzer, E. Vanhaecke, M. J. Ledoux and C. Pham-Huu, *Carbon*, 2006, **44**, 2587–2589.
- 20 C. Pham-Huu and M. J. Ledoux, *Top. Catal.*, 2006, **40**, 49–63.
- 21 Y. H. Chin, J. L. Hu, C. S. Cao, Y. F. Gao and Y. Wang, *Catal. Today*, 2005, **110**, 47–52.
- 22 C. Pham-Huu, R. Vieira, B. Louis, A. Carvalho, J. Amadou, T. Dintzer and M. J. Ledoux, *J. Catal.*, 2006, **240**, 194–202.

- 23 L. D. Nguyen, K. Chizari, K. Wang, M. Houille, I. Janowska, M. S. Moldovan, O. Ersen and C. Pham-Huu, *Mater. Lett.*, 2011, **65**, 2482–2485.
- 24 B. Louis, G. Gulino, R. Vieira, J. Amadou, T. Dintzer, S. Galvagno, G. Centi, M. J. Ledoux and C. Pham-Huu, *Catal. Today*, 2005, **102**, 23–28.
- 25 G. Gulino, R. Vieira, J. Amadou, P. Nguyen, M. J. Ledoux, S. Galvagno, G. Centi and C. Pham-Huu, *Appl. Catal., A*, 2005, **279**, 89–97.
- 26 M. F. Ran, W. J. Sun, Y. Liu, W. Chu and C. F. Jiang, *J. Solid State Chem.*, 2013, **197**, 517–522.
- 27 X. Tao, X. Chen, Y. Xia, H. Huang, Y. Gan, R. Wu, F. Chen and W. Zhang, *J. Mater. Chem. A*, 2013, **1**, 3295–3301.
- 28 Y. F. Liu, C. F. Jiang, W. Chu, W. J. Sun and Z. K. Xie, *React. Kinet., Mech. Catal.*, 2010, **101**, 141–151.
- 29 J. Y. Kim, K. Park, S. Y. Bae, G. C. Kim, S. Lee and H. C. Choi, *J. Mater. Chem.*, 2011, **21**, 5999–6005.
- 30 K. Wang, K. Chizari, Y. Liu, I. Janowska, S. M. Moldovan, O. Ersen, A. Bonnefont, E. R. Savinova, L. D. Nguyen and C. Pham-Huu, *Appl. Catal., A*, 2011, **392**, 238–247.
- 31 A. Deneuve, K. Wang, I. Janowska, K. Chizari, D. Edouard, O. Ersen, M. J. Ledoux and C. Pham-Huu, *Appl. Catal., A*, 2011, **400**, 230–237.
- 32 W. Baaziz, S. Begin-Colin, B. P. Pichon, I. Florea, O. Ersen, S. Zafeiratos, R. Barbosa, D. Begin and C. Pham-Huu, *Chem. Mater.*, 2012, **24**, 1549–1551.
- 33 T. C. R. Rocha, A. Oestereich, D. V. Demidov, M. Havecker, S. Zafeiratos, G. Weinberg, V. I. Bukhtiyarov, A. Knop-Gericke and R. Schlögl, *Phys. Chem. Chem. Phys.*, 2012, **14**, 4554–4564.
- 34 F. Yu, J. Ma and Y. Q. Wu, *J. Hazard. Mater.*, 2011, **192**, 1370–1379.
- 35 Y. K. Kim and H. Park, *Energ Environ. Sci.*, 2011, **4**, 685–694.
- 36 S. Kundu, Y. M. Wang, W. Xia and M. Muhler, *J. Phys. Chem. C*, 2008, **112**, 16869–16878.
- 37 Y. Zhao, C. G. Hu, Y. Hu, H. H. Cheng, G. Q. Shi and L. T. Qu, *Angew. Chem., Int. Ed.*, 2012, **51**, 11371–11375.
- 38 Y. Liu, T. Dintzer, O. Ersen and C. Pham-Huu, *Journal of Energy Chemistry*, 2013, **22**, 279–289.