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Synthesis of Self-Supported Multi-Walled Carbon Nanotubes

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Abstract

Carbon nanotubes are generally synthesized in a fine powder with a very high specific volume and a low apparent density, which render their manipulation extremely difficult and hazardous. Here we demonstrate a simple and reliable method for the direct synthesis of multi-walled carbon nanotubes (MWCNTs) supporting each other in a controlled macroscopic shape and size by applying an external constraint on the reactor during the synthesis. The MWCNTs are highly entangled allowing a natural compacting of the macroscopic pieces without fine formation, making subsequent handling easier. The present synthesis method addresses many critical problems encountered with the use of carbon nanotubes as a macroscopic building-block materials.

INTRODUCTION

Carbon nanotubes have recently received increasing interest due to their exceptional physical and chemical properties [1, 2]. During their growth, MWCNTs are highly entangled and interconnected, forming a dense and elastic network generally on a microscopic scale which render their direct use complicated because of their fluffy character. Thus, a post-synthesis treatment is needed to obtain a macroscopic shape. Such a post-treatment generally requires to mix the as-synthesized carbon nanotubes with a polymer or a chemical agent before processing the macroscopic shape.

Processing carbon nanotubes with macroscopic shapes to obtain materials with practical use is nowadays a major challenge in the field of advanced materials. Most of the works on such macroscopic shaping of carbon nanotubes has been devoted to the synthesis of macroscopic fibres of either single-walled or multi-walled carbon nanotubes by adding foreign agents to the nanotubes or by modifying the synthesis method [3–7]. Zhu *et al.* [3] have reported the synthesis of a 20 cm long thread of carbon nanotubes, using a pyrolysis process of a mixture of hexane, ferrocene, and thiophene. Windle and co-workers [5] have reported the direct spinning of fibres made of carbon nanotubes from hot zone chemical vapour deposition (CVD). Fibres made of SWCNTs, with microscopic diameters were successfully obtained by Ericson and co-workers [7] using concentrated SWNTs dispersed in superacid, extrusion and coagulation in a liquid medium. From this technique, a continuous spool of microscopic SWNT fibres with well-aligned orientation were obtained with a relatively simple process. Hata *et al.* [8] have reported the synthesis of aligned SWCNTs in millimeter size bundles on a silicon wafer, using the catalytic decomposition of ethylene in the presence of a controlled amount of steam. Ribbons of carbon nanotubes were also produced by recondensation of carbon nanotubes dispersed in surfactant solution in a flow of polymer solution [9]. However, as far as the macroscopic shaping of carbon nanotubes is concerned, there is almost no process dealing with the one-step synthesis of carbon nanotubes with three-dimensional macroscopic shape.

In the present work, we report the synthesis of pure MWCNTs self-supported in a macroscopic shape. The synthesis method is extremely simple, based on a conventional CVD method which allows easy scaling-up with minimum cost investment. The as-synthesized self-supported MWCNTs were subsequently used as a reversible adsorber for the removal of organic pollutants from water [10].

EXPERIMENTAL

Experimentally, a medium temperature (640 °C), a relatively low C_2H_6/H_2 molar ratio (60/40), a flow rate (100 ml/min) and a reaction time (4 h) were found to produce almost exclusively MWCNTs (>98 %, determined by statistical image analysis) with a yield in mass carbon/catalyst close to 1000 %. Hydrogen seems to play an important role to avoid the formation of carbon nanoparticles along with carbon nanotubes [5, 11].

The self-sustained MWCNTs were made by placing the powder catalyst inside a quartz cylinder with both ends closed by a gas-permeable disk of carbon felt from Carbone Lorraine Ltd. The powder catalyst was either pilled at the bottom of the quartz cylinder or deposited on its walls. The catalyst ($Fe(NO_3)_3 \cdot 9H_2O$) was deposited onto alumina (particle size: 40–80 μm) with a loading rate of 20 mass % in iron, then calcinated at 350 °C, and finally reduced *in situ* under hydrogen flow (100 ml/min) at 400 °C for 1 h. The hydrogen flow was then replaced by a mixture of C_2H_6 and H_2 and the temperature was rapidly increased from 400 to 640 °C. These conditions were maintained for 4 h and the resulting solid was cooled under He down to room temperature. The as-synthesized MWCNT blocks were purified in two steps: firstly, the alumina support was removed by heating the sample in an aqueous solution of NaOH (20 mass %) under reflux at 80 °C for 12 h. The sample was recovered by filtration and washed several times with distilled water and then treated with an aqueous solution of HNO_3 (4 M) at 110 °C for 2 h in order to remove the iron-based catalyst.

RESULTS AND DISCUSSION

Optical micrographs of the carbon nanotubes synthesized without constraint and the ones synthesized under constraint are presented in Fig. 1.

As one can see, the constraint synthesis allows a significant increase of the apparent density without any need of post-treatment or foreign agent addition as usually reported in the literature. This apparent density after synthesis under constraint is typically close to 200 kg/m (in comparison with 20 kg/m when synthesized without constraint). The shaped carbon nanotube pieces display a mechanical resistance high enough to be handled without any breakage or significant fine formation. Mechanical properties are actually under investigation and are directly related to the apparent density of the block: this density is mainly dependent of the amount of catalyst and of the reaction time.

The corresponding SEM image of the self-supported MWCNT pieces after purification to remove the catalyst is provided in Fig. 2. The carbon nanotubes formed were relatively homogeneous in size, ca. 30–50 nm, with lengths up to several micrometers leading to an aspect ratio of about 100–200 which is within the values reported up to now in the literature. The as-synthesized carbon nanotubes were also extremely pure as almost no trace of carbon nanoparticles was observed in the

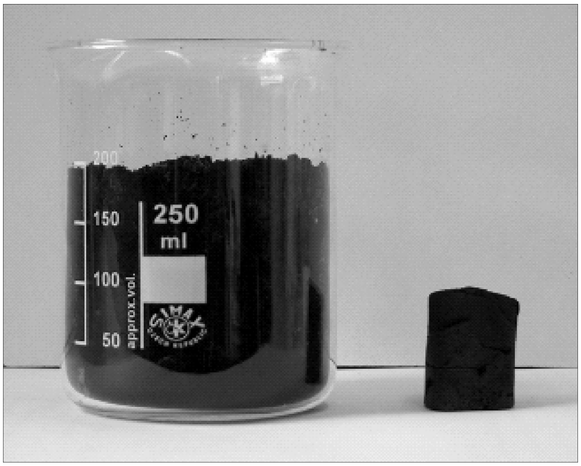

Fig. 1. Comparsion of the volume filled by the free-grown and grown under consraint MWNTs (for the same mass: 7 g).

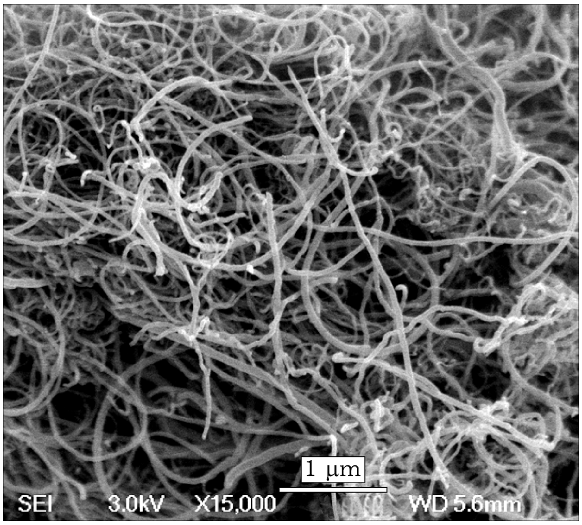

Fig. 2. SEM picture of self-supported MWNTs after HNO_3 and NaOH washing.

solid according to the statistical SEM images analysis. These results clearly indicate that the decomposition of the carbon source and the growth of the carbon nanotubes were finely balanced, which significantly reduced the formation of non-fibrous particles along with the nanotubes. Statistical SEM observation also reveals that the MWCNT network was more densified when compared to that observed on the bundle of MWCNTs synthesized without external macroscopic constraint. The macroscopic shape of the sample in the present work depended on the shape of the confining reactor. The high purity of the sample was also confirmed by the relatively sharp oxidation peak observed during the temperature-programmed oxidation (TPO) analysis (Fig. 3). The combustion range of the self-supported carbon nanotubes ranged between 550 and 650 °C with a maximum at 565 °C which was very similar to that observed for traditional carbon nanotubes synthesized without external constraint with a purity up to 98 % as described elsewhere [12, 13].

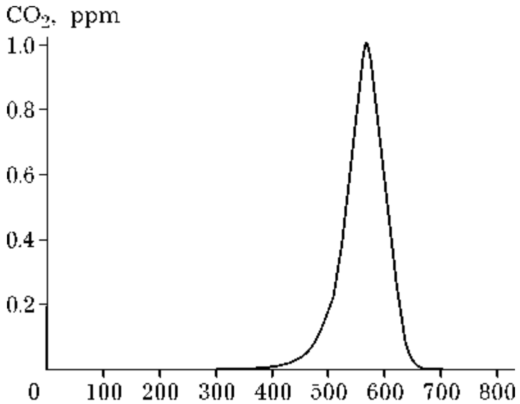

Fig. 3. Temperature-programmed oxidation of self-supported MWNTs.

The as-synthesized self-supported MWCNTs were used as a selective and reversible adsorber for the removal of organic pollutants from water. The experiment was carried out with a mixture of water containing 10 vol. % of benzene. In order to allow the easy visualization of the two liquid phases, a small amount of boradiazaindacene (BODIPY®) compounds was dissolved in benzene leading to the formation of a bright yellow colour. A piece of self-supported MWCNTs (a cylinder with the following dimensions: length, 30 mm; diameter, 20 mm) was plunged in the mixture. As soon as the MWCNTs piece was in contact, the organic phase was ad- or absorbed onto or into the carbon nanotubes (as typically observed with activated carbons) and the yellow colour of the organic fraction was no longer observed. At saturation the amount of benzene ad- or absorbed was about 8 g per gramm of carbon nanotubes. After adsorption the MWCNTs piece was removed and plunged into an acetone (or ethanol) bath. The colourless acetone became yellow, indicating the release of the benzene trapped by the carbon nanotubes: such a shifting of benzene by acetone has not been observed in case of activated carbon (Merck activated charcoal). The most surprising is the fact that if this piece is plunged again in a solution of water with benzene at its surface, the benzene is ad(ab)sorbed again with a removal of acetone. This clearly indicates the reversible ad(ab)sorption character of the self-supported MWCNTs for the selective removal of benzene or organic compounds in an aqueous medium. Quantitatively, the reversibility of the adsorption is equal to about 80 % (whatever the number of cycles) of the initial mass uptake of benzene after immersion during 15 min of the MWCNTs in every bath. Experiments are in progress to quantify kinetic parameters of such a reaction but also to try to understand ad(ab)sorption or superficial tension phenomena.

Similar "depollution" phenomena were observed with other water pollutants than benzene. Gazoline, for instance, was removed from water without difficulty. In all cases the amount of remaining organic pollutants was below the maximum of solubility of these compounds in water.

CONCLUSION

In summary, by using a constrained synthesis, self-supported carbon nanotubes with a homogeneous size can be synthesized in controlled macroscopic forms which make their handling easier without the problems linked to the manipulation of these nanomaterials. The method is applicable for the synthesis of MWCNT blocks of various size and shape depending on the downstream utilization. The reversible adsorption and desorption of organic compounds inside these nanomaterials make them extremely interesting for use in the purification of water polluted by traces of organic compounds in several areas of the existing industry without facing the problems linked to the manipulation of solid powder. It is worth noting that the as-synthesized self-supported MWCNTs can be also infiltrated with liquid resin in order to prepare a high mechanical strength and light-mass composite, which can find several applications in the field of advanced materials.

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