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Coating of multi-walled carbon nanotubes with thick layers of tin(IV) oxide

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Carbon nanotubes (CNTs) have been the most actively studied materials in the past few years due to their unique electrical, mechanical and chemical properties [1–4]. To optimize the use of CNTs in many of these applications, there is a need to attach functional groups to their surface or attach other nanostructures to the nanotubes. The development of novel nanometer-scale integrated systems incorporating multi-walled carbon nanotubes (MWNTs) will likely require covalent attachment of the MWNTs to another nanometer-sized material in a reliable and robust manner. A lot of the direct covalent functionalization methods have been based on the acid oxidation of CNTs [5]. Treating CNTs with nitric acid or other oxidants could create various functional groups at both tips and sidewalls, such as COOH, OH, and CO, which can act as nucleation sites for metal clusters. Covalent modifications of CNTs with metal colloids [6] (for low resistance ohmic contacts) and semiconducting quantum dots [7,8] (for light-emitting diodes) have been reported. However, little work about the coating of CNTs with thick layers of different materials has been reported.

SnO_2 and CNTs are both well known as active components in molecular detection and transudation systems, suggesting nanoscale sensor applications for SnO_2 functionalized CNTs. Chen et al. [9] obtained SnO–CNT composites by a sol–gel method as anode material for lithium-ion batteries. Han and Zettl [10] have coated single-walled carbon nanotubes with a thin SnO_2 layer (about 4 nm) by a chemical-solution route. Both synthesis methods use $SnCl_2$ as the starting materials. However, it is well known that the residual chlorine ions are very difficult to be rinsed off [11]. We report here the surface coating of MWNTs with a thick SnO_2 layer by a new and simple one-step wet chemical method without chlorine ions. The growth behavior and the morphology of the coating layer are discussed in detail.

MWNTs, prepared by the catalytic decomposition of CH_4, were kindly provided by Shengzhen Nanotech Port Ltd. Co (Shengzhen, China) with the purity 95–98% and used as received. The typical procedure employed here was described as follows. First, 200 mg granulated tin was carefully dissolved in 100 ml nitric acid (7 mol l^{-1}) and obtained a translucent solution; then 200 mg MWNTs were added into the above solution and refluxed for 3 h in an oil bath maintained at 140 °C. The mixture solution was cooled to the ambient temperature and was continued vigorously stirring for different time. The resulting products were filtered out, rinsed repeatedly and then dried at 100 °C.

The XRD patterns of the pristine MWNTs and SnO_2 coated MWNTs (Fig. 1) were obtained by powder X-ray diffraction (D/max 2550 V). The diffraction angles at $2\theta = 26.56°, 32.28°, 51.49°, 37.25°$ (Fig. 1b), can be assigned to (1 1 0), (1 0 1), (2 1 1), (2 0 0) planes of the cassiterite structure of SnO_2, respectively. The broad peaks in the XRD pattern indicate that the crystalline portion of the SnO_2 particles are very small. The mean particle

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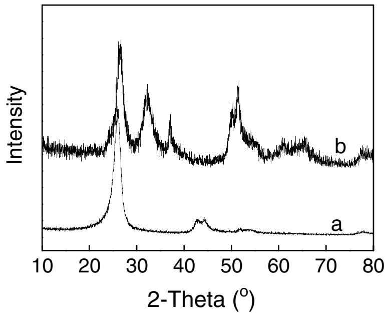

Fig. 1. XRD patterns of (a) pristine MWNTs and (b) hybrid MWNTs reacted for 70 h.

size of SnO_2 calculated by Scherrer equation is about 5 nm. It is hard to elicit the characteristic peaks of MWNTs from the spectrum of SnO_2 coated MWNTs because of the good crystallization of cassiterite SnO_2 and their fine coating on the MWNTs. Meantime, the crystal structure of MWNTs may suffer some damage during the refluxing process in nitric acid. Elemental analysis by EDS indicates the atomic ratio of O to Sn is approximately 2:1.

Zeta potentials (Fig. 2) of the pristine MWNTs and the nitric acid-oxidized MWNTs in the absence of tin were measured using KNO_3 with the ionic strength 10^{-3} M, respectively. The pristine MWNTs are negatively charged. Oxidation of MWNTs in nitric acid further decreases the zeta potential values for all pH values studied. It means that refluxing in nitric acid to modify the MWNTs surface according to an established procedure [12] can generate functional groups on the surface graphite layers of MWNTs.

Fig. 3 shows the FTIR spectra of pristine MWNTs (a), MWNTs refluxed in nitric acid in the absence of tin (b) and hybrid MWNTs (c). The peak at ~1581 cm^{-1} in curves a, b and c can be assigned to the carbon skeleton, and the peaks near 1631 and 3433 cm^{-1} correspond to the bending vibrations of adsorbed molecular water and stretching vibrations of OH groups. The peaks at 1389 and 1168 cm^{-1} in Fig. 3c may be due to adsorbed nitrate anion. After refluxing in nitric acid (Fig. 3b), new peaks around 1709 cm^{-1} corresponding to the carboxyl groups occur, which is consistent with previous work and the result of zeta potentials. When SnO_2 is coated on the surface of oxidized MWNTs (Fig. 3c), the characteristic peak of carboxyl group shifts from 1709 to 1744 cm^{-1} and its relative intensity decreases significantly. The peaks assigned to the carbon skeleton still exist and exhibit no shift, and the characteristic peaks assigned to the SnO_2 also appear below 1000 cm^{-1}. The shift to higher frequency and the decrease of relative intensity probably result from the binding of carboxyl groups onto the SnO_2 nanoparticles. These results show that the outer surface of MWNTs can be modified with the surface functional groups after a period of oxidation, and can act as specific sites for metal particle nucleation. We propose a tentative mechanism of SnO_2 deposition via the oxidation of nitric acid under acidic conditions, that is, the surface graphitic layers of MWNTs can react with the oxidants and produce a high density of functional carboxyl groups. Tin ions in the system then attach to and interact with the surface carboxyl groups by electrostatic attraction and serve as nucleation precursors. The possible chemical reaction for the formation of SnO_2 can be expressed as following:

$$Sn^{2+} + 2HNO_3 \rightarrow SnO_2 + 2NO_2 \uparrow + 2H^+$$

The tin ions in the solution are adsorbed to the surface of the functionalized MWNTs with the carboxyl groups due to electrostatic attraction, and then in situ oxidized to be SnO_2 nanocrystals; subsequently, the tin ions continuously adsorb on the as-originated SnO_2 coating layer and slowly crystallize to SnO_2 nanoparticles. The particles decorated around the MWNTs attach one another to minimize their overall surface potential energy.

Transmission electron microscopy (JEM200CX) was performed to observe the attachment of SnO_2 nanoparticles to the MWNTs (Fig. 4). After reacting for 20 h (sample A), a thick coating layer of the SnO_2 nanoparticles with a thickness of ~40 nm is observed (Fig. 4a and

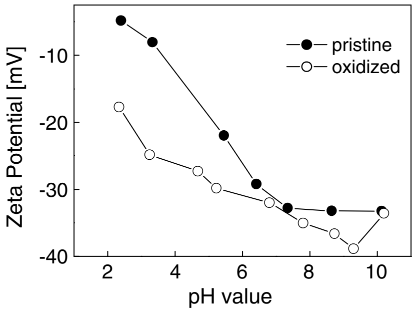

Fig. 2. Zeta potential values at various pH of pristine and nitric acid oxidized MWNTs.

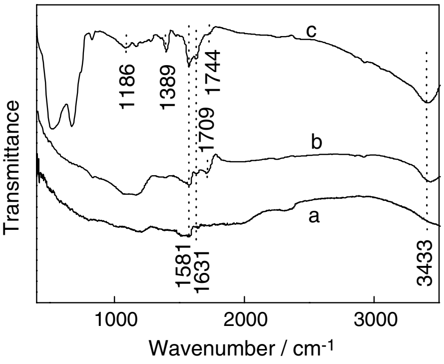

Fig. 3. FTIR spectra of (a) pristine MWNTs; (b) MWNTs refluxed in concentrated nitric acid (c) hybrid MWNTs.

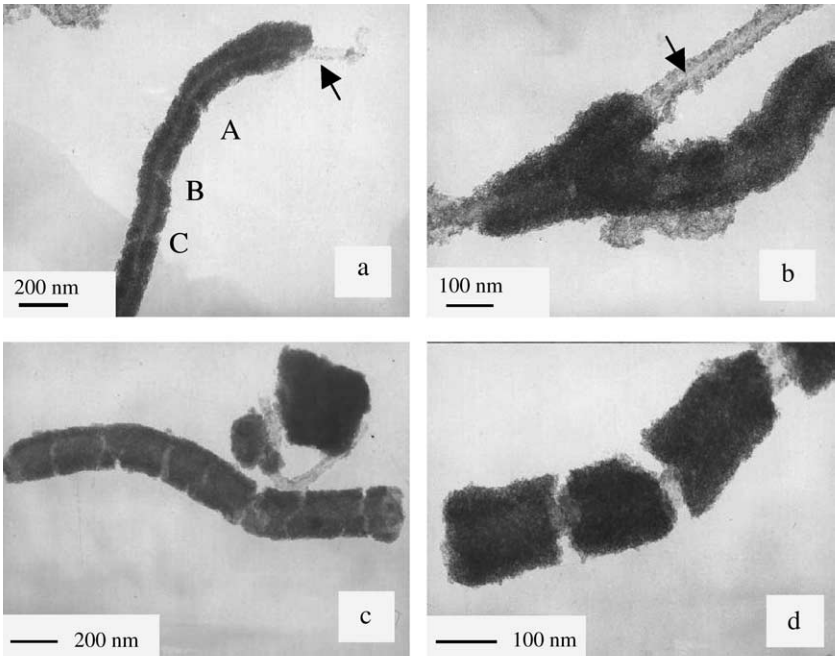

Fig. 4. TEM micrographs of hybrid MWNTs reacted for 20 h (a and b); 70 h (c and d).

b). The thick layer of SnO_2 nanoparticles decorated around the surfaces of MWNTs is uniform except for a few gaps (such as A, B and C in Fig. 4a). After reacting for 70 h (sample B), the thickness of the SnO_2 coating layer is ~50 nm (Fig. 4c and d). The remarkably large thickness of the coating layer can be attributed to the continuous adsorption of tin ions on the as-originated SnO_2 coating layer and its slow crystallization. It can also explain why the thickness of the SnO_2 coating layer was related to the reaction time, that is, the shorter the reaction time, the thinner the SnO_2 coating layer. Compared with sample A, it is clear that the coating layer of sample B is more smooth and uniform, which may be ascribed to the mode of the nanocrystals attaching one another to reduce the surface potential energy furthest. However, part of the image of sample A (arrows indicated) reveals a thin uniform layer about 10 nm instead of a thick layer on the surface of the MWNTs. For sample B, more cracks in the thick SnO_2 coating of the MWNTs are depicted compared with sample A, and even some broken segments are observed. The broken segments of the SnO_2 matrix (Fig. 4d) are shifted apart by ca. 15–30 nm and held together by the MWNTs. A thin SnO_2 layer of about 10 nm coat on the MWNTs of the broken segments instead of the bare MWNTs, which is inconsistent with the thin uniform layer of sample A. Just as described by FTIR, the tin ions are adsorbed on the surface of the functionalized MWNTs by the carboxyl groups due to electrostatic attraction, and then in situ oxidized to become SnO_2 nanocrystals. The interaction between the tin ions and MWNTs is quite strong, which indicates the inner SnO_2 nanoparticles immobilized on the MWNTs are stable. However, the internal structure of the coating, which is conglomerated to conquer the surface potential energy of the individual nanocrystals, is 'looser' and less cross-linked. As a result, gaps on the outer SnO_2 coating layer are formed, and in some cases whole outer layer shell off to leave a thin uniform inner layer about 10 nm (arrows indicated for sample A) when subjected to some outside force. When the thickness of the coating layer is high (approximately 50 nm for sample B in our experiment), spontaneous defoliation of the coating is likely to occur and form the brittle network, which tends to fracture due to local stress raisers. By contrast, the inner coating with the thickness less than 10 nm retains their flexibility and stress resistance.

In conclusion, we herein introduce a simple and effective one-step scheme to coat the MWNTs with very thick SnO_2 layers (>40 nm) using granulated tin as starting material. With the longer reaction time, the thickness of the coating layer increases and the morphology of the coating layer becomes more smooth and uniform. The inner SnO_2 nanoparticles immobilized on the MWNTs are stable, while the internal structure of the coating is 'looser' and less cross-linked. When the thickness of the SnO_2 layer is high, the coating with internal 'looser' and less cross-linked structure tends to fracture due to the accumulation of local stresses. Both SnO_2 and MWNTs are well known as active components in molecular detection and transudation systems, so the new hybrid material of MWNTs with 'looser' internal individual SnO_2 nanoparticles may foreshow potential applications in future nanoscale sensor devices.

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Bulk production of nanocarbon allotropes by a gas outflow discharge approach

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Fullerenes and nanotubes were discovered two decades ago, and like their older carbon brothers diamonds and graphite, have unusual properties and show promise of being used in different industries. But wide application of fullerenes and nanotubes is undermined by an inability to produce them inexpensively in bulk. An arc discharge method [1] developed by Krätschmer's group in 1990 remains until now the major tool for synthesizing fullerenes. There are essential pitfalls inherent in this method. These include the following: (1) slow removal of carbon vapour from a hot plasma zone, (2) long residence of carbon vapour in the electrode gap, (3) carbon vapour exposure to harmful UV irradiation resulting in photochemical decomposition/polymerization of fullerenes and fullerene precursors, (4) the precipitation of carbon vapour on a relatively cold cathode surface taking away as much as 40–60% by mass of carbon from the evaporated anode [2]. Another drawback of the arc discharge method is the necessity of maintaining pressure in the reactor below atmospheric pressure in order to provide sufficiently fast quenching rates of carbon vapour, which for the most successful fullerene formation must be in the range of 1000–2500 K/s [3]. All these factors prevent the arc discharge method from being commercialised.

There have been several attempts to increase fullerene productivity by applying buffer gas either perpendicular [4] or coaxial [5] to the electrodes, but productivity has achieved only minor improvements, and fullerene processing technology still remains non scalable.

Here we report a novel technique of fullerene production based on the arc discharge method. Substantial enhancement can be achieved by an entirely simple solution of introducing a gas outflow approach using a

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