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Sonochemical decoration of multi-walled carbon nanotubes with nanocrystalline tin

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A simple sonication route to decorate multi-walled carbon nanotubes (MWCNTs) with crystalline tin nanoparticles is reported. The sonication process results in a uniform decoration of nanoparticles over the entire outer surface of the nanotubes. Acid-treated MWCNTs were exposed to ultrasonic radiation in a solution of $SnCl_2$ in ethylene glycol under an N_2 atmosphere. The products were characterized by X-ray powder diffraction measurements, differential scanning calorimetry, transmission electron microscopy, and high-resolution transmission electron microscopy. The decoration is composed of metallic tin nanocrystals of size less than 5 nm. This technique is suggested as a general versatile method for decorating carbon nanotubes with other nanoparticles.

Introduction

Carbon nanotubes (CNTs) have been the focus of much significant research activity because of their properties of high mechanical strength, chemical stability and, particularly, one-dimensional morphology. In addition to the many potential applications of CNTs, decorated CNTs are widely suggested for their use in heterogeneous catalysis.[1–3] CNTs have been used as the support materials for decoration by Ni, Cu, Au, Pt, Ag, W, Se, SnO_2 and Co–B nanoparticles. Various methods were employed to deposit these materials, such as electroless plating,[4–6] physical vapor deposition,[7,8] chemical reduction of precursors,[9–13] colloidal chemistry combined with electrostatic interactions[14] and also combined with sonication in aqueous solutions.[13,15] Rao *et al.* [13] have managed to deposit Au clusters on the nanotubes by refluxing 25 mg of acid-treated nanotubes with 5 mg of $HAuCl_4{\cdot}H_2O$ in 10 ml water for 4 h in the presence of alkaline THPC. The size of the gold clusters decreased from the range of 1–7 nm to less than 2 nm in diameter when mild sonication was utilized during the refluxing process.[13] All these deposition routes share one common requirement, that is the CNTs should have active sites on the outer surfaces. It is known that refluxing CNTs with nitric acid not only opens the closed caps of the tubes, but also creates acidic sites on their surfaces that helps in the deposition of various nanoparticles.[16,17] In this paper we report a simple, effective sonochemical route to decorate multi-walled carbon nanotubes (MWCNTs) with crystalline tin nanoparticles (∼5 nm).

Sonochemistry has been widely used in the synthesis of nanoparticles due to the ultrasonic cavitation process that includes the formation, growth and collapse of microbubbles in a liquid.[18] The collapse of the bubbles creates temperatures and pressures inside the cavities that can reach 4200–5000 K and 20–50 MPa, respectively.[19] Furthermore, microbubbles imploding near a solid surface result in microjets and shock waves. Our aim is to make use of these microjets to push and anchor the *in situ* produced nanoparticles of tin onto the surfaces of the CNTs.

Metallic tin is of great interest to electrochemists because of its high theoretical capacity and its ability to alloy with lithium.[20] Though sonochemical preparation of nanosized tin oxides and sulfides from an aqueous medium have been reported,[21–23] due to the hydrolysis of Sn^{2+} or Sn^{4+} ions in aqueous solutions or the lack of a suitable reducing agent, synthesis of nano-sized Sn particles has not yet been reported. Over the past two decades, the polyol process has been largely studied and well-adapted to the preparation of powders of metals[24] and binary alloys.[25] The polyol process consists of the reduction of metallic compounds such as oxides, hydroxides and salts in a liquid alcohol medium, at moderate temperatures. Based on thermodynamic arguments, SnO cannot be reduced to metallic tin by ethylene glycol (EG) at its boiling temperature.[26] It is also pointed out that in the polyol process the Gibbs free energy for the reduction of SnO by EG decreases slowly as the temperature is raised and may become negative at higher temperatures. In the sonochemical process, extremely high temperatures are achieved that allows Sn(II) to be reduced by EG. As a result, we have employed a combination of sonochemical and polyol processes to reduce tin(II) salts. Acid-treated MWCNTs were exposed to ultrasonic radiation in a solution of $SnCl_2$ in EG under an N_2 atmosphere. To the best of our knowledge, this is the first report of decorating MWCNTs with tin nanoparticles (∼5 nm) reduced *in situ* from tin salts by a polyol process combined with a sonochemical method. The sonochemically prepared samples are termed "as-prepared samples" and characterized by thermal, structural and morphological techniques. This combination of polyol and sonochemical processes is suggested as a general versatile method for decorating CNTs with other metallic nanoparticles.

Experimental

The arc-grown MWCNTs were supplied by MER (Materials and Electrochemical Research Corporation). The declared dimensions of the tubes are 2–15 nm in diameter, 1–10 µm long, with 5–20 graphitic layers. MWCNTs were refluxed for 30 h in a concentrated solution of HNO_3 to remove carbon impurities. The precipitate was separated by centrifugation, washed 4 times with deionized water and dried under vacuum for 10 h. One hundred milligrams of the acid-treated MWCNTs were mixed in a 50 mL sonication vessel with a

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solution of 0.1 g $SnCl_2$ (99.9%, Alfa Aesar) in 40 mL of ethylene glycol (95%, Aldrich). The solution was de-oxygenated by bubbling pure nitrogen through the solution for 30 min before its exposure to ultrasonic radiation. The solution was sonicated with a high-intensity ultrasonic probe (Vibra cell VCX 600 Sonifier, 20 kHz) for 1.5 h at room temperature under nitrogen atmosphere by direct immersion of a titanium horn (diameter 1.13 cm, 200 W cm^{-2}). The resulting black mixture was separated by centrifugation at a speed of 10 000 rpm for 10 min, washed 4 times with absolute ethanol and dried under vacuum at room temperature.

X-Ray diffraction (XRD) patterns were collected at a scanning rate of 0.015° s^{-1} in the 20° to 80° range using a Bruker AXS D8 Advance Powder X-Ray Diffractometer (Cu–Kα radiation, wave length ~1.5406 Å). EDX (energy dispersive X-ray analysis) was probed by using the attached function to a scanning electron microscopy (JSM-840 SEM). Differential scanning calorimetry (DSC) measurements of the dried as-prepared product was carried out on a Mettler DSC-25 instrument at a heating rate of 10 °C min^{-1} under nitrogen at a flow rate of 40 mL min^{-1} in an aluminium pan. The morphology of the as-prepared product was determined by transmission electron microscopy (TEM; JEM-1200EX) and high-resolution transmission electron microscopy (HRTEM; JOEL 2010), working at acceleration voltages of 80 and 200 kV, respectively. Samples for TEM and HRTEM were prepared by ultrasonically dispersing the products into absolute ethanol, then placing a drop of this suspension onto a copper grid coated with an amorphous carbon film and then drying in air.

Results and discussion

XRD, DSC and EDX studies

We have used both MWCNTs treated with acid and MWCNTs without any treatment for the decoration with tin nanoparticles. In both cases, the detected XRD patterns are almost the same. A typical XRD pattern of the sonochemically as-prepared samples is presented in Fig. 1. XRD results show the presence of graphite (JCPDS Card No. 75-1621), related to the MWCNTs. Other diffraction peaks were observed at 30.6°, 32,0°, 43.8°, 44.9°, 55.3°, 62.5°, 64.6°, 72.4°, 73.2° and 79.5°. The cell constants calculated from these values are $a = 5.83$, $b = 5.83$, $c = 3.18$ Å. These values are in good agreement with the diffraction peaks and cell parameters of crystalline tin (JCPDS Card. No. 04-673). The crystal structure of the synthesized Sn can be indexed to a body-centered tetragonal phase. The XRD results definitely indicate that the ultrasonic radiation process leads to the reduction of $SnCl_2$ to metallic tin in EG solution.

The DSC pattern of the as-prepared sample (trace a in Fig. 2) reveals a distinct endothermic peak centered at 231.5 °C. For comparison, we also measured the DSC (trace b in Fig. 2) for metallic tin particles (<325 mesh, purchased from Aldrich Chemical Co. and used as received). The melting point for the 325 mesh particles is observed at 233.9 °C. The lowering of the melting point of the tin in the as-prepared sample by about 2.4 °C should be attributed to nanosize effects.[27] The comparison of the DSC curve with that of $SnCl_2$ (trace c in Fig. 2) shows that the latter has disappeared in the sonication and is completely converted to Sn. Comparison with previous DSC measurements of SnO[21] also eliminates the possibility of its presence. Furthermore, the EDX pattern (not shown) of the sample shows that the as-prepared sample does not contain any chlorine. We can therefore conclude that the as-prepared sample contains neither $SnCl_2$ nor SnO, but only nanosized metallic tin.

Electron microscopic studies

The morphologies of the acid-treated MWCNTs and the decorated nanotubes were examined by TEM measurements. The samples were dispersed in absolute ethanol in an ultrasonic bath and dropped onto carbon-coated copper grids for a TEM test. Fig. 3(A) shows that the acid-treatment process indeed removed the caps of the CNT (marked by an arrow). Multi-layered polygonal carbon nanoparticles are also observed in the image. The acid treatment removed most of the amorphous carbon particles that existed initially in the purchased sample. In fact, the treatment not only purified the sample and opened the caps, but also produced defects on the surfaces. According to our interpretation, these defects are associated with the formation of functional groups such as COOH and OH. These functional groups are more active towards the sonication products than the initial inert nanotubes. They act as nucleation points in the decoration or coating processes. In our present decorated sample [Figs. 3(B) and 3(C)], nanoparticles are anchored on the outer surfaces of the MWCNTs and in some places along the tube they aggregate and pile up on the surface of the CNTs. Most of the CNTs are decorated with tin nanoparticles. The sonochemical coating is independent of the tube diameter or morphology. This differentiates the sonication process from the electroless plating process where the coating of MWCNT by Co–B was found to be strongly dependent on the nanotube diameter.[10] In ref. 10, decoration by Co–B was achieved only for nanotubes with large diameters (> 45 nm), but failed for nanotubes having smaller diameters. The images observed at higher magnification [see Fig. 3(C)] show that the CNTs are densely decorated with uniform tin nanoparticles whose diameters are less than 5 nm.

To probe whether the decorating particles are strongly adhered to the surface of the CNTs, we sonicated the dried, as-prepared product in an ultrasonic bath for various times (up to 60 min) to see if tin nanoparticles that were not well-anchored to the CNTs could be easily removed from the tubes' outer surfaces. The TEM image in Fig. 3(C) was measured after 60 min of sonication. It shows that the tin nanoparticles strongly adhered to the outer surfaces. We believe that both the acid treatment and the ultrasonic radiation form active sites on the outer surfaces of the nanotubes.[16,28,29] Thus, the entire surfaces of the tubes are almost completely covered with nanoparticles. To the best of our knowledge, such a

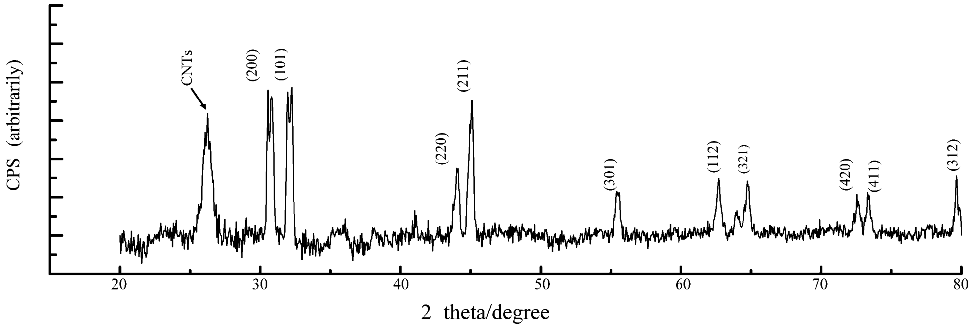

Fig. 1 XRD pattern of the tin-decorated MWCNTs.

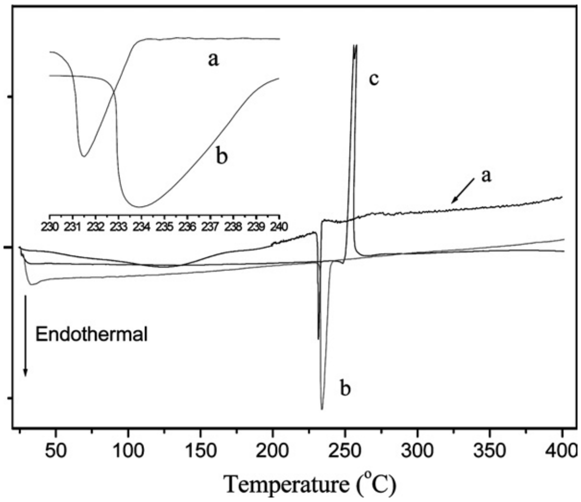

Fig. 2 DSC patterns of (a) the as-prepared sample, (b) pure metallic tin particles (less than 325 mesh) and (c) pure $SnCl_2$ (anhydrous). The inset is the expanded *x* scale for samples (a) and (b).

complete coverage has not been achieved by other methods. In addition to the decorated MWCNTs, we observed that some of the tin was separated from the CNT. This is because the asymmetric collapse of the bubble near a solid surface ejected most of the product towards the CNTs, but some were dispersed in other directions as well.

We could not, however, find MWCNTs filled with tin. Sonication was found to be an excellent method for the insertion of nanoparticles into mesoporous structures.[30] The main reasons why the uncapped tubes are not filled with nanosized tin may be the following: (1) in our case, according to the dimension range of the tubes, the ratio of the outer surface of an individual tube to its cross sectional area on both open ends can be as high as 10^3–10^5; (2) the *in situ* formed particles with sizes similar to the openings may block the open end and there is no strong force to drive them further into the tubes.

HRTEM and ED studies

Fig. 4 shows HRTEM images of tin-decorated MWCNTs. The conventional dark fields reveal the sizes and crystallization mode of the nanoparticles anchored on the MWCNTs. The decorating particles are unambiguously nanocrystalline. Their lattice fringes, from which the distances of the diffraction planes are precisely measured, are very clear. The decorating particles are made up of well-defined, rounded and randomly deposited nanoparticles with a fairly narrow size distribution (3–5 nm). Stacks of lattice fringes are observed with spacings of 0.295 nm, in good agreement with the (200) planes of body-centered tetragonal bulk Sn. A very few fringes spaced by 0.207 nm are also detected. This spacing corresponds to the (220) diffraction plane of tin. Furthermore, it is worth noting that the fringes of the nanocrystals are randomly directed with respect to the MWCNT's axis. This implies that the growth of the nanoparticles is not controlled by the organized parallel walls of the MWCNTs, but rather that nucleation is determined by the defects created by ultrasound radiation, as well as by acid treatment.[13,16,17,28,29] These active sites, which were exposed to the *in situ* created tin, act as either a reaction center or nucleation center for the freshly produced metal clusters.[10] The inset to Fig. 4(B) is the corresponding selected area electron diffraction pattern of the decorated MWCNTs. It reveals the local Sn structure in detail, which can be indexed to body-centered tetragonal Sn. The two unclear polycrystalline rings correspond to the (200) and (220) crystal faces of Sn, while the clear spot ED pattern corresponds to MWCNT, which is in accordance with the above measurements of the lattice fringe spacing.

A possible mechanism

In our case, we have combined a sonochemical process with the polyol process to reduce $SnCl_2$ into nanosized metallic tin. For the reduction mechanism of tin we first adopt and modify the kinetic steps proposed for the reduction of $Ni(OH)_2$ and $Co(OH)_2$ by EG.[27,31] The polyol process leads to the reduction of ethanol into aldehyde, which then acts as the reducing agent for Sn(II) in the following sonochemical process. The possible reduction of tin ions to metallic tin follows these intermediate reactions.

$$CH_2OH{-}CH_2OH \rightarrow CH_3CHO + H_2O \qquad (1)$$

$$SnCl_2 + 2H_2O \rightarrow Sn(OH)_2 + 2HCl \qquad (2)$$

$$2CH_3CHO + Sn(OH)_2 \rightarrow CH_3COCOCH_3 + Sn + 2H_2O \qquad (3)$$

We must point out, on the basis of thermodynamic arguments,[27] that SnO cannot be reduced to metallic tin in an EG medium by refluxing. However, it was further predicated that in the polyol process the Gibbs free energy of reduction slowly decreases as the temperatures increase and may become negative at high temperatures. As explained above extremely high temperatures can be obtained upon the bubble's collapse.[19] The calculated Gibbs free energy for the reduction of SnO by EG at its boiling temperature is close to zero. It is reasonable to suppose that the Gibbs free energy might, on the other hand, be negative at sonochemical temperatures. Even at the interfacial region of the exploded bubbles, and not in the center of the bubble, the temperatures are high enough to drive reaction (3) towards the right to form metallic tin.

Another application of this method

We applied a similar sonochemical process to the decoration of MWCNTs with nanoparticles of Fe. Acid-treated MWCNTs were mixed with a solution of $Fe(CO)_5$ (Aldrich, used as purchased) in decalin. The slurry was de-oxygenated and exposed to high-density ultrasonic irradiation under an atmosphere of

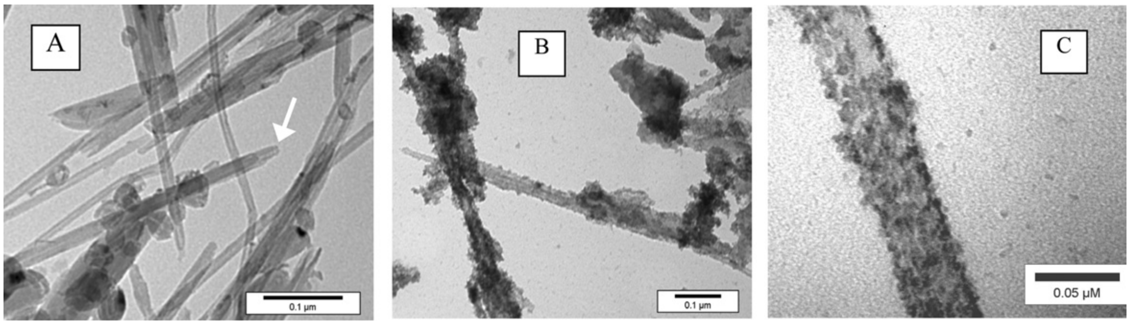

Fig. 3 TEM images of (A) the acid-treated MWCNTs, (B) the acid-treated MWCNTs coated with tin nanoparticles and (C) decorated acid-treated MWCNT shown at higher magnification.

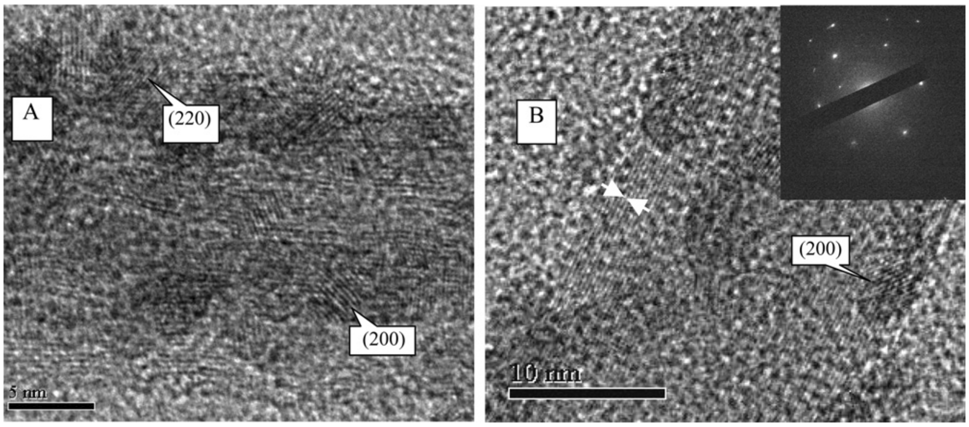

Fig. 4 HRTEM images of two randomly selected tin-decorated MWCNTs at magnifications of (A) 650 and (B) 390 k. The fringes of the nanocrystals on the surfaces of the CNTs are spaced by about 0.295 and 0.207 nm. The lattice spacing of the CNTs fringes is measured as 0.339 nm (indicating by the arrows), which is in good agreement with the standard value of 0.34 nm. Inset shows electron diffraction pattern of the tin-decorated sample.

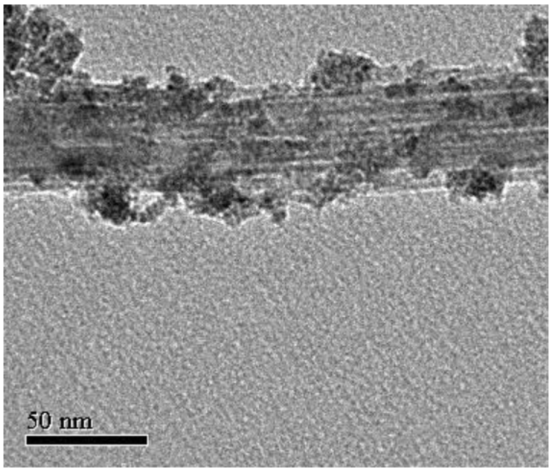

Fig. 5 TEM image of one Fe-decorated MWCNT.

N_2. The TEM image shows that the MWCNTs were successfully decorated with nanoparticles of Fe (Fig. 5). But HRTEM and XRD characterizations (corresponding data are not given here) show that the decorating Fe is not crystalline but amorphous nanoparticles. This difference from the case of decorating with Sn nanocrystals may lie in the formation mechanism of the two types of nanoparticles. Obviously, both cases have demonstrated that the sonochemical process is suitable for the decoration of MWCNTs with nanoparticles.

Conclusions

In summary, we report here on a novel, simple, effective method to decorate MWCNTs with metallic tin nanocrystals by ultrasonic radiation. The MWCNTs were pretreated by refluxing in concentrated HNO_3 acid, which resulted in purified and functionalized nanotubes. We have successfully demonstrated the decoration of MWCNTs with metallic tin nanoparticles (3–5 nm) by sonicating a mixture of MWCNTs with a solution of $SnCl_2$ in EG.

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