

Decorating multiwalled carbon nanotubes with zinc oxide nano-crystallines through hydrothermal growth process

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Multiwalled-carbon nanotubes coated with nano-crystalline zinc oxide (ZnO) was prepared by in situ growth of nano zinc oxide on the surfaces of carbon nanotubes through hydrothermal method. X-ray diffraction, transmission electron microscopy and scanning electron microscopy analysis techniques were used to characterize the samples. It was observed that a layer of nano-crystalline ZnO with the wurtzite hexagonal crystal structure was uniformly coated on the nanotube surfaces with good adhesion, which resulted in the formation of a novel ZnO-nanotube nano composite. In this work, the carbon nanotubes decorated by metal oxide nanoparticles were synthesized by a simple chemical-solution route which is suitable for the large-scale production with low cost.

carbon nanotubes, transmission electron microscopy, zinc oxide, hydrothermal growth

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1 Introduction

Since their discovery, carbon nanotubes have continuously attracted strong interest from many areas of science and technology due to their well-defined 1D structure, nano-scaled diameters, superior electronic, mechanical, and chemical properties [1]. The physical properties of carbon nanotubes can be dramatically influenced by surface modification with selected organic, inorganic, and biological species [2–5]. Such functionalization can lead to a significant enhancement of properties that are relevant to technological applications. Semiconductor nanoparticles have been one of the interested research area during the past decade due to their unique size-tunable chemical and physical properties [6]. These nanoparticles have shown potential

applications in molecular electronics, nonlinear optics, catalysis, and photoelectrochemical cells. They also represent ideal building blocks for the construction of nanostructured materials [7]. Several semiconductor nanoparticles such as tin oxide [8, 9], cadmium selenide [10–12], zinc sulfide [11], titanium oxide [10, 13], and silicon oxide [14, 15] have been bound to the surfaces of carbon nanotubes.

ZnO is an n-type non-toxic inorganic semiconductor with a wide energy gap that potentially offers salient features as large electron channel mobility, excellent environmental stability and high transparency. It plays a key role in applications such as conductive electrodes, field-effect transistor, heterojunction solar cells and chemical sensors [16–19]. The deposition techniques of ZnO include sputtering, pulsed laser deposition, chemical vapor deposition, sol-gel and hydrothermal chemical bath deposition, etc. [20–24].

Here we report a simple and efficient low temperature solution chemical route using zinc nitrate as precursor and

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hexamethylenetetramine as structure-directing agent to coat carbon nanotubes fully with a nominally uniform layer of nano ZnO. This work is motivated by potential applications of the combined nanotube/ZnO system.

2 Experimental procedure

Multiwalled carbon nanotubes were produced by catalytic decomposition of propylene over Ni/diatomite catalysts [12, 13]. Transmission electron microscopy (TEM, JEOL-200CX) image (Figure 1) shows that the diameters of the as produced multiwalled carbon nanotubes are different, the larger diameters of them are about of 80 nm, the lengths of the carbon nanotubes are several microns to several tens of microns. Before use, the carbon nanotubes were first annealed in air at 500°C for 20 minutes [25], and then boiled by concentrated HNO₃ (acid modification) for one hour [26].

Aqueous solutions of zinc nitrate and hexamethylenetetramine (Wako) were prepared at room temperature by dissolving zinc nitrate hydrate [Zn(NO₃)₂·6H₂O, Wako] and hexamethylenetetramine in deionized water (molar ratio of [Zn²⁺] : [hexamethylenetetramine] = 1 : 1, [Zn²⁺] = 0.05 M). The prepared solutions were filtered through a membrane with 0.5 μm pores before use.

A full mixture of carbon nanotubes and polytetrafluoroethylene (PTFE), prepared by mixing carbon nanotubes with PTFE suspending liquid in ethanol (weight ratio of carbon nanotubes to PTFE was 100: 5), was agitated and blown by a hot-air generator. When most solvent was volatilized, the mixture, becoming slush state, was uniformly coated on cotton-linen fiber cloth (template) by the blade, and then dried up at 100°C. The fixed type carbon nanotubes were gained.

The fixed type 0.05 g carbon nanotubes (fixed on 5 mm

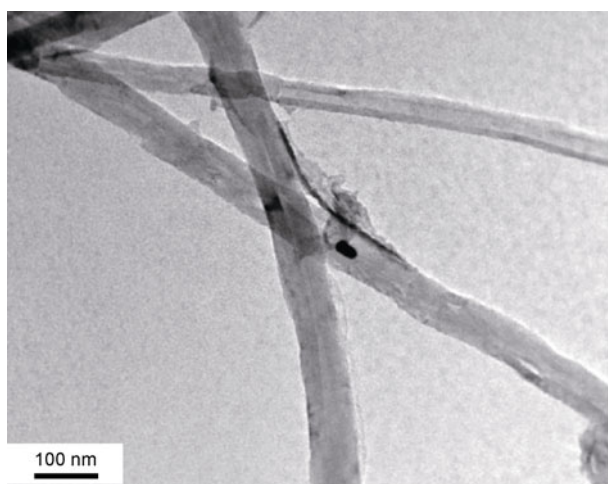


Figure 1 Transmission electron microscopy (TEM) of the as produced carbon nanotubes.

×5 mm template) were put on the bottom of a 100 mL thermostatic vessel, a 70 mL solution of 0.05 M Zn²⁺ was transferred to the vessel. Under uniform shaking, the reaction vessel was heated to ~ 80°C at a rate of 0.5°C/min, and the temperature was maintained at 80°C for 30 min. Then the reaction was quenched by cooling the vessel in an ice bath. The sample was cleaned in distilled water and dried at 60°C for 0.5 h.

The structure and surface characteristics were analyzed by transmission electron microscopy (TEM, JEOL-200CX), field emission scanning electron microscopy (FE-SEM, AMRAY-1910), X-ray diffraction (XRD, Rigaku D_{max} γA X-ray diffractometer with Cu-Kα radiation, λ = 0.154178 nm) and “PERKINELMER Spectrum GX FTIR System Jeol-200CX” infrared spectrometer.

3 Results and discussions

Modifying CNTs with acid effectively modified the surface characteristics of the CNTs, and the nature of the surface groups was characterized with FTIR, as shown in Figure 2. In IR spectra, the signature of >C=O functional groups in carbonyls, carboxyls or carboxylic anhydrides is evident at about 1710 cm⁻¹ [27] and -OH functional groups appear at about 3430 cm⁻¹. The peak at 1575 cm⁻¹ reflects the vibration of carbocyclic plane of CNTs. The signal at about 1624 cm⁻¹ is associated with >C=O functional groups in quinones or ketones [28]. The peak centered on 1200 cm⁻¹ is associated with C-O stretching in ethers, hydroxyls or carboxylic anhydrides [28]. It is evident that there are many more carbonyl groups, carboxylic groups, hydroxyl groups, etc. in acid modified CNTs than in as produced CNTs.

Annealing CNTs in air changed the surface structures of

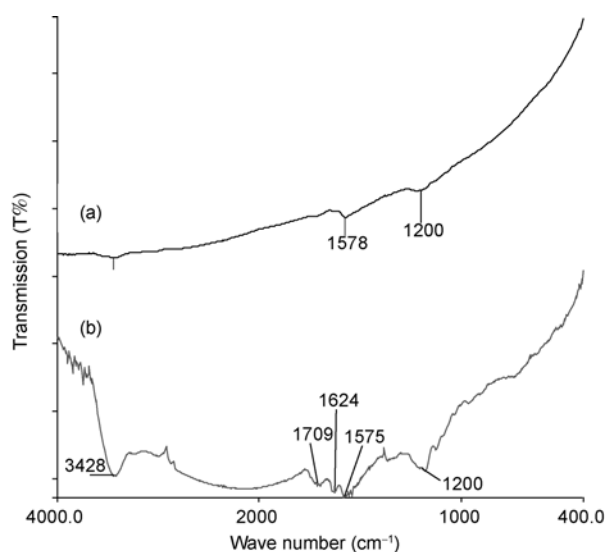


Figure 2 Infrared transmission spectra. (a) As produced CNTs; (b) acid modified CNTs.

the CNTs. When the CNTs are oxidized by air, carbon reacts with air to generate CO_2 . But the reactivities of the structures with pentagons and heptagons and the parts with amorphous structures of the CNT surfaces are greater than that of the cylindrical walls of CNTs structured by hexagonal graphite layers [29], air molecules can more effectively oxidize these metastable structure parts. As shown in Figure 3, during the annealing process, oxygen attacked the walls of CNTs, resulting in rough "convex-concave" surface structure of the CNT walls.

In the solution reaction system of this work, the ZnO crystal nuclei were slowly generated under heating. The formation of the nanodomain crystalines was led by multi-nucleation and subsequent growth on crystals [30]. As the growth rate is slow at low temperatures, this behavior might occur with nucleation and multi-dimensional growth of nanodomains on the substrates and newly formed nanodomains, leading to the formation of hexagonal crystals. When carbon nanotubes were added, they became the substrates of zinc oxide crystal nuclei generated by the hydrothermal reaction process. The carbon nanotubes were annealed in air before use for reason that oxygen can attack the cylindrical walls of carbon nanotubes, giving rough nanotube-surfaces. The roughness of nanotube-surfaces increases the effective surface area and affords the graphene edges with a higher wettability for catching zinc oxide crystal nuclei and fixing ZnO phases. In addition, the acid treatment to carbon nanotubes after annealing in air can add many functional groups on the surfaces of carbon nanotubes. These functional groups can strongly absorb the metal ions in aqueous solution, thus are benefit for the deposition of nano-phase metal salts on the surfaces of carbon nanotubes in aqueous solution [26]. As the reaction temperature slowly increased, ZnO crystals gradually grew vertically with respect to the nuclei planes, which led to a nanophase of ZnO hexagonal crystal structure. Crystal growth lateral to the

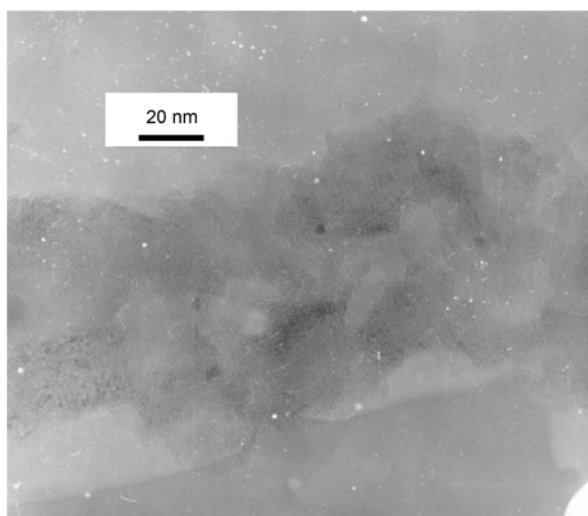


Figure 3 TEM image of the CNTs annealed in air.

nanotube surfaces spread and continued mutually, leading to dense nanocrystals coating on the nanotube surfaces.

Figure 4 shows the TEM image of the carbon nanotubes decorated by ZnO nanoparticles; ZnO nanoparticles with the diameters about several tens nanometer were homogeneously and densely coated on the surfaces of carbon nanotubes. Figure 5, a SEM image, also shows that the carbon nanotubes were effectively decorated by zinc oxide nanoparticles. An X-ray diffraction (XRD, Rigaku $D_{\text{max}} \gamma A$ X-ray diffractometer with Cu-K α radiation, $\lambda = 0.154178$ nm) pattern of the nanotube-ZnO heterostructure is shown in Figure 6, where the distinct peaks at 26.2° , 31.8° , 34.4° and 36.3° represent respectively the (002) crystal plane of carbon nanotubes [31], the (100), (002) and (101) crystal planes of ZnO, revealed a wurtzite hexagonal crystal structure with high crystallinity ($P6_3mc$, $a = 3.248$ Å, $c = 5.207$ Å, JCPDS No. 36-1451)[32]. The crystallite dimensions of ZnO were calculated using Scherrer's equation [33, 34].

$$D = 0.9\lambda / B \cos \theta, \quad (1)$$

where λ is the wavelength of the X-ray, B is the full width

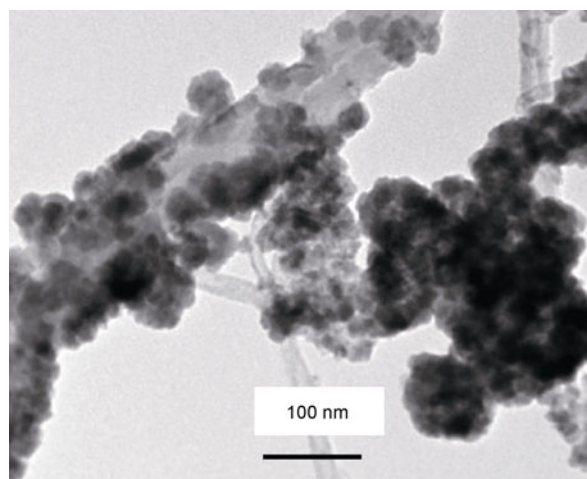


Figure 4 TEM image of ZnO decorated CNTs; the CNTs were treated only by air oxidation and acid modification.

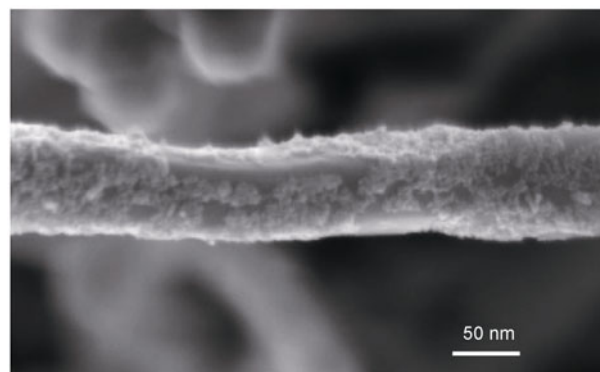


Figure 5 SEM image of ZnO decorated nanotubes; the CNTs were treated only by air oxidation and acid modification.

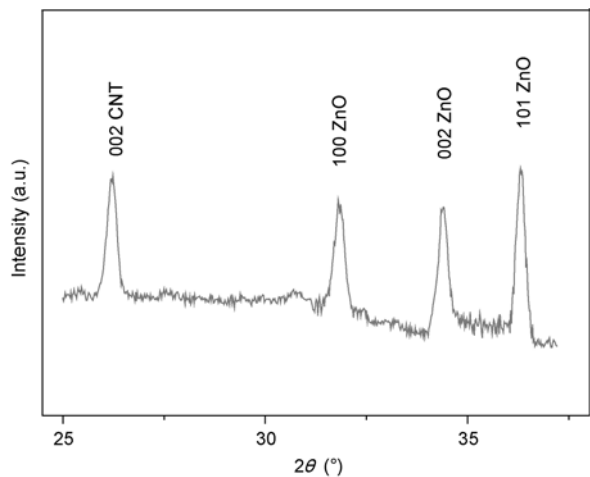


Figure 6 XRD pattern of the ZnO-nanotube hetero-structure.

at half maximum, and θ is the Bragg angle (degree). The calculated crystallite size of ZnO nanophase is around 20 nm.

As a contrast experiment, the CNTs, which were not modified by acid though oxidized by air, were used in the same experiment process. It was observed that the ZnO-nanotube hetero-structure nanotubes were not effectively generated, as shown in Figure 7, only some ZnO particles were trapped in the CNT network. The reason should be that these CNTs have little oxygen-containing functional groups and thus have a weak adsorption capability for Zn^{2+} , and it was difficult for ZnO nuclei to be formed on CNTs' surfaces. The ZnO particles were only generated in solution phase during the hydrothermal process and mixed with the CNTs. When the reaction of hydrothermal process was finished, the sample was cleaned with distilled water, most ZnO deposition was removed during the water washing, only some residual ZnO particles were maintained in CNT network.

The CNTs, which were not oxidized by air though modi-

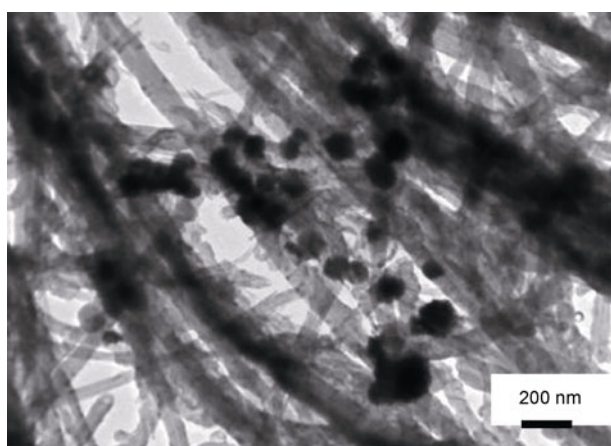


Figure 7 TEM image of ZnO decorated CNTs; the CNTs were treated only by air oxidation.

fied by acid, were used in the same experiment process. The TEM image (Figure 8) shows that the ZnO-nanotube hetero-structure nanotubes were also not effectively generated, and that sparse ZnO nano particles were grown on CNT surface. The reason lies in that the smooth CNT surfaces can not effectively fix the ZnO crystal phase.

In addition, fixing nanotubes on the vessel bottom was more benefit for the deposition of ZnO nano crystals on nanotube surfaces compared to dispersing carbon nanotubes in the solution. The fixed CNTs become the stable substrates for the nucleation and growth of ZnO crystals, dense ZnO nuclei can be formed on CNT surfaces, and uniformly growth of ZnO nano crystals can be proceeded on CNT surfaces. As a contrast experiment, the CNTs which were treated by air oxidization and acid modification were used in the same experiment process, and the CNTs were not fixed but suspended in the solution. The TEM image (Figure 9) shows that many ZnO big particles were disorderly folded on the CNT bundles. During the the hydrothermal reaction process, the CNTs suspended in solution drifted



Figure 8 TEM image of ZnO decorated CNTs; CNTs were treated only by acid modification.

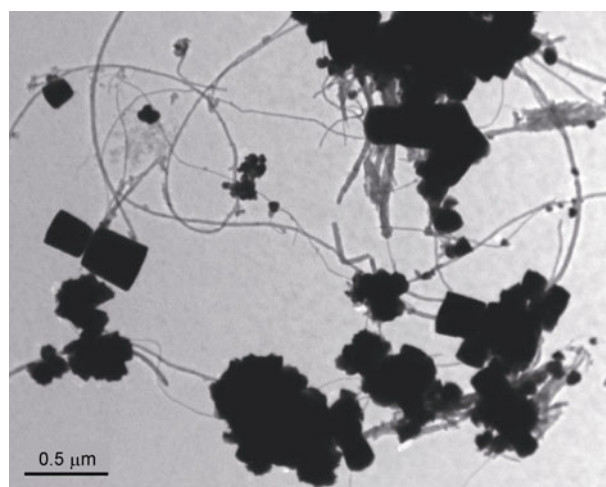


Figure 9 TEM image of ZnO decorated CNTs; CNTs were suspended in the solution during the hydrothermal process.

under the shake of the vessel and it was difficult for them to combine with the generated ZnO nanophase. The drifted CNTs only randomly entangled with some big ZnO particles in the solution, formed disordered fold of ZnO big particles on CNTs.

Finally, the temperature and number of ions are essential factors controlling the formation of crystals. When the concentration of zinc ions and the heating rate were low, smaller crystals were formed on the nanotube substrates. Crystal gradually grew and spread on CNT surfaces, leading to dense and continuous nanocrystals coating on the CNT surfaces. The observed growth process produced well-crystallized oxide layers coating nanotubes at slowly increased temperatures and low concentration. Therefore, this process is exceedingly important as a novel synthesis route for dense oxide films on various substrate materials. This method will be applicable to fabricating various nanostructured ZnO devices.

4 Conclusions

In this work, through the hydrothermal growth process of low temperature, low cost and non-toxic, we have realized the formation of thin, uniform, and uninterrupted coverage ZnO nanoparticles on carbon nanotubes. ZnO is one of the few oxides that can be grown as a polycrystalline material at relatively low temperatures on a variety of substrates. The large-scale production with low cost can be realized with this synthesis method. ZnO and carbon nanotubes are both well known as active components in molecular detection and transduction systems, so functionalized carbon nanotubes are suitable for nanoscale sensor applications. The possible formation of Zn-C bonds on the interface of ultra-fine nanoparticles of ZnO and nanotubes might change the localized electron system. We anticipate that the ZnO thin coating with ultra-fine ZnO nanoparticles produced in this work might also exhibit other interesting physical and chemical properties relevant to potential applications, such as the photocatalytic degradation of organic compounds [35], the electrodes of DSSCs [36] and the detection of components in gas phase [37].

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