

溶胶-凝胶法可控制备氧化锡纳米晶包覆碳纳米管

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摘要: 采用溶胶-凝胶法制备了氧化锡纳米晶包覆的碳纳米管。自由 Sn⁴⁺ 离子从稳定的 Sn 柠檬酸配合物中缓慢释放出来, 迁移到碳纳米管上, 并在碳纳米管上沉积形成了 SnO₂ 纳米晶, 沉积过程完全为异相成核方式, 在碳纳米管外并没有发现单独的 SnO₂ 纳米晶。这种溶胶-凝胶方法还可以用来制备无氯离子污染的、低团聚的纯 SnO₂ 纳米晶。

关键词: 氧化锡; 碳纳米管; 纳米复合材料; 溶胶-凝胶制备

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SnO₂ Nanocrystals Coated Carbon Nanotubes Synthesized by Sol-gel Method

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Abstract: The free Sn⁴⁺ ions are released from the stable Sn-CA complexes and migrate to the surface of the carbon nanotubes to form SnO₂ nanocrystals by heterogeneous nucleation in a well controllable manner. No SnO₂ nanocrystals are observed away from the carbon nanotubes. The sol-gel method in this work can also be utilized to synthesize pure SnO₂ nanocrystals with low degree of agglomeration.

Key words: SnO₂; carbon nanotube; nanocomposites; sol-gel preparation

Tin oxide coated carbon nanotube composite materials have received much attention due to the integration of properties of SnO₂ (wide bandgap semiconductor, chemical and mechanical stabilities) and carbon nanotubes (mechanical, electrical, thermal and chemical stabilities). Many new applications of these materials have been reported, such as gas sensors^[1-4], biosensors^[5], Li-ion batteries^[6-7], supercapacitors^[8], catalysts for organic wastewater^[9] and fuel cells^[10].

Several strategies have been utilized to synthesize SnO₂ coated carbon nanotubes, such as precipitation or sol-gel from the starting materials SnCl₂^[5-6,8,11-12], SnCl₄^[7,9]

and tin alkoxides^[1-3], chemical vapor deposition (CVD) with SnCl₄^[13] and SnH₄^[14], dip coating with SnO₂ sol^[10], supercritical fluid deposition (SCFD) with SnCl₂^[15], and oxidization of Sn by HNO₃^[16]. Tin chlorides have the advantages of low cost, easy processing. But the residual chlorine ions are easily doped into the SnO₂ lattice, thus changing electronic properties of the materials. Tin alkoxides are good choice to avoid from chlorine ions, but they are comparatively expensive, moisture sensitive. Precipitation is a simple and economic method to obtain oxide nanoparticles, but the synthesis process is hard to control because hydrolysis

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of metal ions is fast, nucleation and growth complete within seconds. Complexation is a popular method to modify the metal ions. Carboxylic or β -diketones are most frequently used as modifying ligands to control the hydrolysis, nucleation and growth of oxide nanocrystals^[1]. The motivation of the present work was to find a method for the synthesis of tin oxide coated multiwall carbon nanotubes (MWNTs) in a controllable manner free from contamination of chlorine ions.

1 Experimental

A typical procedure was as follows: 1 g of MWNTs (Shenzhen Nanotech Port Co. Ltd.) was added to 30 mL of nitric acid (63wt%) and refluxed at 140 °C for 4.5 h under stirring. The acid-treated MWNTs were rinsed with distilled H₂O until pH value of the rinsed water reached 7 and then dried at 60 °C. 0.2 g of tin powder (99.999% purity) was added to 6 mol·L⁻¹ HNO₃ in ice water bath until a clear green solution, then citric acid (CA) (molar ratio of CA/tin was set at 2:1) was added to complex with tin ions. Acid treated MWNTs (0.2 g) were added to tin solution and stirred for 2 h. Tertiarybutyl alcohol was added dropwise to the

solution, which turned slowly into translucent colloid when volume of alcohol was six times of the tin solution, another two folds alcohol was added while stirring stopped. The resulting colloidal sol was filtered, washed with absolute alcohol, dried at 100 °C for 5 h and annealed at 500 °C for 2 h. For comparison, precipitation method was also used to obtain SnO₂ coated MWNTs composite. No citric acid was added and NH₃H₂O solution was added to precipitate tin ions. The morphologies of the MWNTs and SnO₂ coated MWNTs were observed by transmission electron microscopy (TEM, JEOL-2100F, Tokyo, Japan).

2 Results and discussion

Fig.1 shows TEM micrographs of the pristine and acid treated MWNTs. The as received MWNTs show outer diameter of 30~60 nm and the wall thickness of 10~15 nm, some catalyst particles and carbon particles are also observed. After HNO₃ refluxing, the particles are dissolved, the surfaces are very smooth, and the ends of the nanotubes are open. MWNTs are no longer twisted and dispersity is greatly improved. Fig.1 (c) exhibits a long single nanotube.

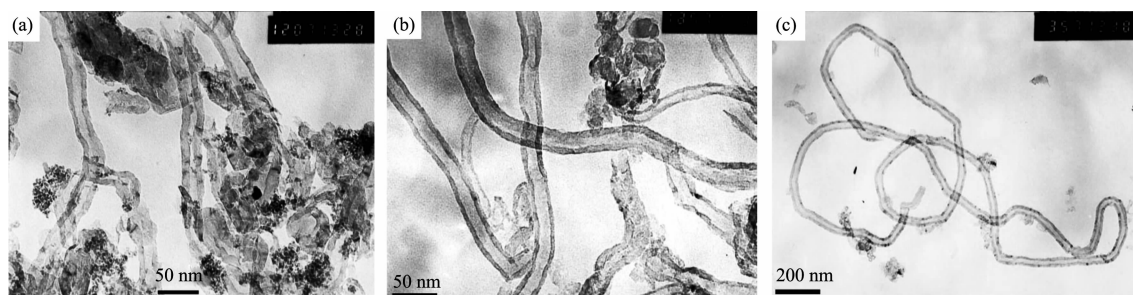


Fig.1 TEM photographs of the pristine (a), and acid treated MWNTs (b), (c)

Fig.2 shows micrographs of the SnO₂ coated MWNTs by the sol-gel method. All of the SnO₂ nanocrystals with mean diameter of 3~7 nm are deposited on the surfaces of the MWNTs and no SnO₂ are observed in the micrographs independently. In Fig.2 (a), the points A and B have higher SnO₂ density than other parts of the nanotube. Fig.2 (b) shows that SnO₂ nanocrystals are deposited discontinuously on the surface of the carbon nanotube, large amounts of SnO₂ particles gather at the broken part C, forming a nanochain and extending away from the nanotube. The

carbon nanotube in Fig.2 (c) is coated with SnO₂ nanocrystals completely. Without using CA as complexing ligands, we find different results. Fig.3 shows micrographs of the SnO₂ coated MWNTs by precipitation method. SnO₂ nanoparticles with size of 3~8 nm are randomly aggregated together and only a few SnO₂ particles are deposited on the carbon nanotubes.

The formation mechanism of the SnO₂ coated MWNTs by the sol-gel and precipitation methods can be described as follows. Treating MWNTs with nitric acid not only removes the catalyst and carbon particles,

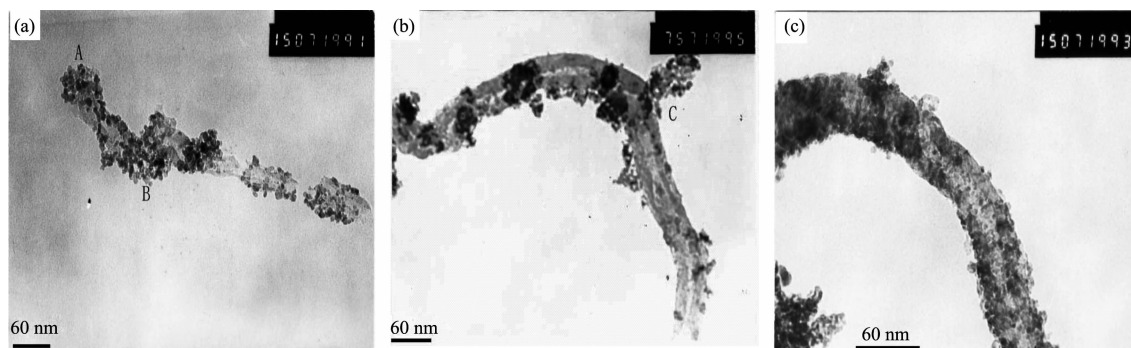


Fig.2 TEM photographs of SnO_2 nanocrystals coated MWNTs by the sol-gel method

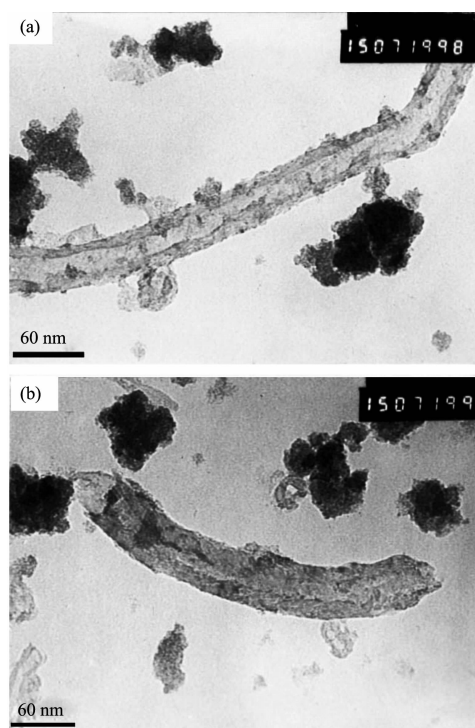
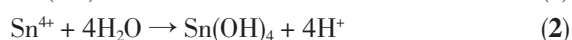


Fig.3 TEM photographs of SnO_2 nanocrystals coated MWNTs by precipitation method

but also oxidizes the defect sites of the nanotubes and creates various functional groups as $-\text{COOH}$, $-\text{OH}$ and CO [2,5,12]. These groups are negatively charged and adsorbed Sn^{4+} ions when MWNTs are immersed in Sn^{4+} solution. In the case of sol-gel method, the concentration of free Sn^{4+} is lower than the critical concentration for hydrolysis because most of the Sn^{4+} ions are complexed by CA ligands. When Tertiarybutyl alcohol is added to the solution, the Sn^{4+} -CA complexes begin to dissociate, the concentration of free Sn^{4+} ions increase gradually and start to hydrolysis:



The $\text{Sn}(\text{OH})_4$ nuclei are formed on the preexisting carbon nanotube surfaces. This heterogeneous nucleation decreases the energy barrier of nucleus formation as compared with homogeneous nucleation [17]. The Sn^{4+} ions in the mother liquor migrate continuously to the surfaces of the $\text{Sn}(\text{OH})_4$ nuclei, and the nuclei grow, leading to a sol-gel transition, and transform to SnO_2 nanocrystals when annealed at 500°C . Because the opened tips and broken bend have higher density of functional groups than the surface of the carbon nanotubes, so we find more SnO_2 nanocrystals deposited at the sites A, B, and C. This fact shows that the density of SnO_2 nanocrystals is a good detector for the functional group site of the carbon nanotubes. The nanotube in Fig.2 (c) is deposited with SnO_2 nanocrystals continuously and uniformly, which reveals that this nanotube is not well crystallized and functional groups cover the nanotube surface completely. At the opened sites A, B, C in Fig.2(a), (b) and Fig.2(c), SnO_2 nanocrystals are also observed in the inner cavities of the nanotubes. When the nanotubes are dispersed in Sn^{4+} solution, the Sn^{4+} ions are driven into the tube by capillary forces, and form SnO_2 nanocrystals when tertiarybutyl alcohol is added and heat treated. These particles are comparatively smaller than the SnO_2 nanocrystals on the outer surface of the nanotubes, which is ascribed to the restriction of the size of the inner cavity. In other words, these cavities act as microreactors and retard the growth of the SnO_2 nanocrystals under the size of nanotube cross-section inner diameter. Theoretical studies suggest that filling the MWNTs with foreign materials can enhance the properties of the resulting composite materials.

Heterogeneous nucleation is comparatively easier than homogeneous nucleation for particle crystallization from solution. But in our two experiments, for the same nitric acid treated MWNTs, heterogeneous nucleation and homogeneous nucleation of the SnO_2 nanocrystals are all observed. This difference can be explained by ion migration velocity of the free Sn^{4+} . In the sol-gel method, the Sn^{4+} ions are released in a very slow manner when tertiarybutyl alcohol is added to dissociate the Sn^{4+} -CA complexes, therefore, the free Sn^{4+} ions have enough time to migrate to the surface of the $\text{Sn}(\text{OH})_4$ nuclei, which leads to the growth of the SnO_2 nanocrystals at the sites of carboxyl functional groups. This ion migration in a slowly controllable manner also explains the interesting phenomenon happened at the site C in Fig.2(b). The free Sn^{4+} ions prefer to migrate to the preexisting $\text{Sn}(\text{OH})_4$ continuously rather than adsorb on the inert nanotube surface or hydrolysis to $\text{Sn}(\text{OH})_4$ by homogeneous nucleation mechanism in the solution. The free Sn^{4+} ion migrates one by one, hydrolyzing to form $\text{Sn}(\text{OH})_4$ nanocrystals, which serve as blocks for the construction of SnO_2 nanochain and extend into the mother liquor until all Sn^{4+} ions are consumed. In the precipitation experiment, the concentration of free Sn^{4+} ions is high and hydrolysis of these ions is suppressed due to the strong acidic condition. When $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution is added to the solution, the concentration of $\text{Sn}(\text{OH})_4$ is higher than the critical value for supersaturation in a very short time. Hence, the Sn^{4+} ions adsorb on the functional sites hydrolysis and form $\text{Sn}(\text{OH})_4$ nanocrystals by heterogeneous nucleation. At the same time, the Sn^{4+} ions in the mother liquor do not have enough time to migrate to the $\text{Sn}(\text{OH})_4$ nanocrystals adsorbed on the nanotube surfaces and hydrolyze to $\text{Sn}(\text{OH})_4$ nanocrystals by homogeneous nucleation despite its energy disadvantage.

Fig.4 shows micrographs of the SnO_2 nanocrystals obtained by the sol-gel method without addition of MWNTs. The nanocrystals are in size of 9 ~15 nm, larger than the SnO_2 nanocrystals coated on the surfaces and filled in the inner cavities of the nanotubes. These nanocrystals show low degree of agglomeration, which may be ascribed to the low surface tension of

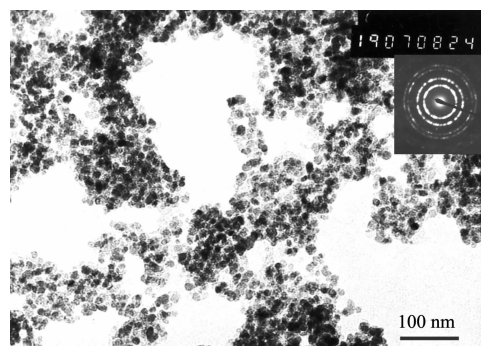


Fig.4 TEM photograph of SnO_2 nanocrystals obtained by the sol-gel method

Tertiarybutyl alcohol and free from chlorine contamination. The inset in Fig.4 is the ED patterns of the obtained particles, indicating the cassiterite structure of the nanoparticles.

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