

Research Article

One-Step Route to Synthesize Multiwalled Carbon Nanotubes Filled with MgO Nanorods

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Multiwalled carbon nanotubes filled with MgO nanorods were synthesized through the reaction of ethanol and Mg powder in the presence of TiO₂ at 400°C. X-ray powder diffraction indicated that the sample was composed of graphite and cubic MgO. Transmission electron microscopy studies showed that multi-walled CNTs with the outer diameters of 70–130 nm were filled with discontinuous MgO nanorods whose diameter was in the range of 25–40 nm. The ratios of the band intensities ($I_D/I_G = 0.67$) in Raman spectrum implied that carbon nanotubes had good crystallinity. The influence of correlative reaction factors on the morphology of the sample and the possible formation mechanism were discussed.

1. Introduction

Filling foreign materials into the hollow cavities of carbon nanotubes (CNTs) has been of widespread interest due to their special properties [1–3]. And they have broader application compared to pure CNTs or second phases, such as Fe₂O₃-filled CNTs as a negative electrode for an Fe-air battery [4] and spherical Ni(OH)₂/CNTs as the electrode in asymmetric supercapacitor [5]. SnO₂/multi-walled CNT has a high reversible discharge capacity compared to pure nano-SnO₂ [6]. MnO₂/CNT hybrid coaxial nanotubes have also enhanced reversible capacity more than pure MnO₂ nanotubes [7].

MgO has gained extensive application in catalyst [8, 9], refractory materials [10] and optically transparent ceramic windows [11, 12]. Recently the studies indicate that MgO can make ammoniated electrons stable [13] and has weak ferromagnetism [14]. Maybe the MgO/CNTs have potential applications in electrode. And carbon-coated MgO nanoparticles had been prepared by various methods. Motiei et al. [15] had prepared hollow carbon cubes and carbon-coated MgO cubes through the reaction between Mg and Mo(CO)₆ at 900°C. Bedilo et al. [16] had synthesized carbon-coated MgO nanoparticles by the decomposition of dry

magnesium methoxide or resorcinol modified magnesium methoxide. Luo et al. [17] had synthesized MgO/C core-shell nanospheres with the diameters of 300–500 nm at 600°C by reducing ethyl ether with metallic magnesium. Zhou et al. [18] had fabricated carbon-coated MgO by the coprecipitation magnesium nitrate with sucrose. However, there are few reports about the synthesis of CNT-coated MgO nanostructures.

In this study, we report the preparation and characterization of MgO-filled multi-walled CNTs which were obtained by the reaction of ethanol and Mg powder in the presence of TiO₂ at 400°C. Transmission electron microscopy (TEM) showed that multi-walled CNTs filled with discontinuous MgO nanorods are open at the both ends, whose outer diameters were between 70 and 130 nm. A possible mechanism for MgO nanorods encapsulated in multi-walled CNTs is discussed in this study and the research of electrochemical properties of MgO/CNTs is still underway.

2. Experimental Section

All reagents used in this work were analysis-grade reagents from the Shanghai Chemical Factory, China, and were

directly used without further treatment. MgO nanorods encapsulated in multi-walled CNTs were prepared as follows: magnesium powder (1 g), ethanol (10 mL), and TiO₂ (0.5 g) were mixed in a 20 mL stainless autoclave and heated in an electric oven at 400°C for 10 hours, then cooled to room temperature. The wet black powder was collected and washed with dilute hydrochloric and hydrofluoric. The final products were washed with distilled water and absolute ethyl alcohol, and then dried under vacuum at 50°C for 4 hours.

X-ray powder diffraction (XRD) measurements were carried out using a Bruker D8 advanced X-ray diffractometer equipped with graphite-monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Field-emission scanning electron microscopy (FESEM) images were taken by a JSM-6700F scanning electron microscope. TEM images were obtained by a Hitachi model H-7000 TEM with an accelerating voltage of 100 kV. The high-resolution (HRTEM) images and energy-dispersive X-ray spectroscopy (EDS) were recorded on a JEOL 2100 HRTEM microscope. Raman spectra were obtained using a Horiba Jobin Yvon Raman microscope system. The spectrometer was operated in continuous scanning mode in the range of 500–1700 cm⁻¹ using argon-ion laser of wavelength $\lambda = 514.5 \text{ nm}$.

3. Results and Discussion

Figure 1 shows XRD pattern of the as-prepared products. The diffraction peaks at 43.0 and 62.4° were identified as the (200) and (220) reflections of MgO (JCPDS card no. 65-0476), and those at 26.5 and 44.9° were attributed to the (002) and (101) planes of CNT-related graphite (marked with “c”). There are TiC and a little stable rutile-type titanium dioxide [19] in the XRD pattern.

Figure 2(a) is a SEM image of the samples washed with HCl. A great number of CNTs with outer diameters of 70 ~ 130 nm and lengths of tens of micrometers were observed in Figure 2(a). The top of nanotube displayed in the inset of Figure 2(a) is open, which likes nanocapillary to absorb hydrogen or other gases [20]. Figure 2(b) is a TEM image of the samples. The internal structure of CNTs, inside which discontinuous nanorods were encapsulated with the diameters of 25–40 nm, was observed clearly. The inset in Figure 2(b) is the corresponding EDS of nanorods, suggesting that their chemical compositions were MgO (the Cu peaks are from the copper grid that supports the specimen and C peaks are possibly from the nanotubes). That Ti peak was not observed in EDS indicated that TiC particles were not located inside CNTs. The TEM image of the aggregated particles located outside CNTs was further confirmed (see Figure S1 in supplementary material available online at doi:10.1155/2010/671863 supporting information). A further investigation by HRTEM (Figure 2(c)) reveals that the interlayer separation of 0.34 nm corresponds to the (002) plane of the multi-walled CNTs and the fringe spacing of 0.21 nm matches the (200) reflection of MgO nanorods.

The representative Raman spectrum (Figure 3) of the sample shows the typical features of multi-walled CNTs.

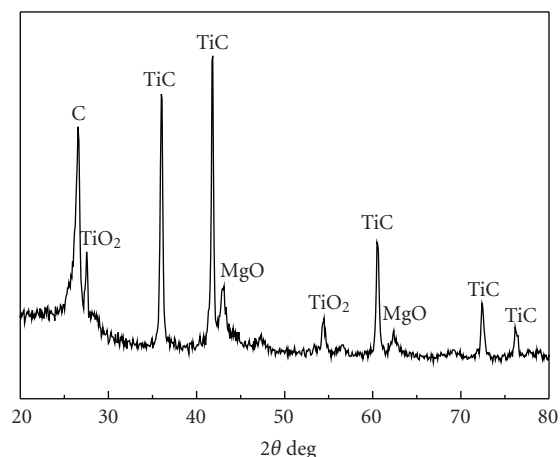
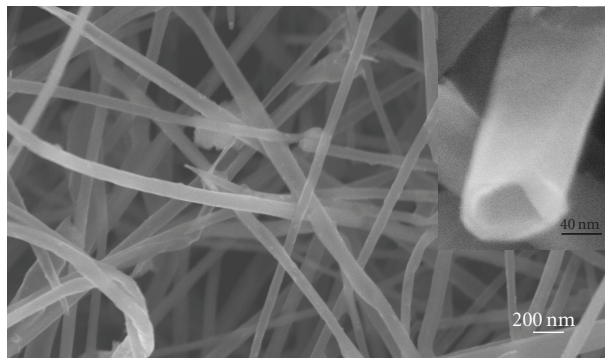


FIGURE 1: The typical XRD patterns of the products washed with dilute acid.

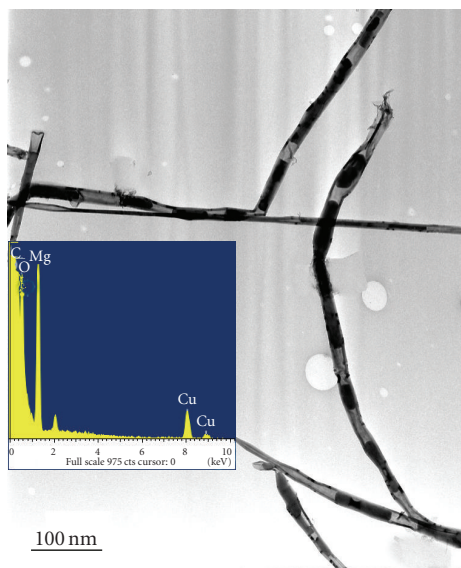
The spectrum demonstrates that the peak frequencies of the graphite (G) mode are at 1575 cm⁻¹ and contains disorder (D) modes that are at 1343 cm⁻¹. An indication of the relative graphitization of the deposited material can be expressed as the ratio of I_D/I_G [21]. The ratios of the band intensities shown in Figure 3 are $I_D/I_G = 0.67$, suggesting a higher degree of graphitization.

Several experimental factors including metal oxides, temperature, and metals were adopted to investigate the possible formation mechanism of the MgO-filled multi-walled CNTs. The introduction of metal oxides played a key role in encapsulating MgO nanorods inside multi-walled CNTs. In the absence of TiO₂, only pure multi-walled CNTs appeared in the products, which agreed with previous results [22]. If the amount of TiO₂ was less than 0.5 g in our experimental route, the encapsulations of MgO inside multi-walled CNTs were difficult to be observed by TEM. As TiO₂ was replaced by other metal oxides such as Fe₂O₃, the main morphology of as-prepared samples was different with that of TiO₂ added in the reaction system. The abovementioned experimental results suggested that the presence of TiO₂ in the reaction system could assist the formation of MgO nanorods encapsulated in multi-walled CNTs. The detail reason for the influence of metal oxides on the products was still under investigation. In addition, the influences of the temperature and metals on the MgO-filled multi-walled CNTs had also been studied. Results showed that the yield of MgO nanorods encapsulated inside multi-walled CNTs was reduced with the reaction temperature decreasing. When the reaction temperature was lower than 200°C, irregular graphite films were the major products. Furthermore, when Mg powder was substituted by Al, Fe, Zn, Co, or Ni, the reaction did not happen. A possible reason is that the activity of Mg powder was higher than that of abovementioned metals.

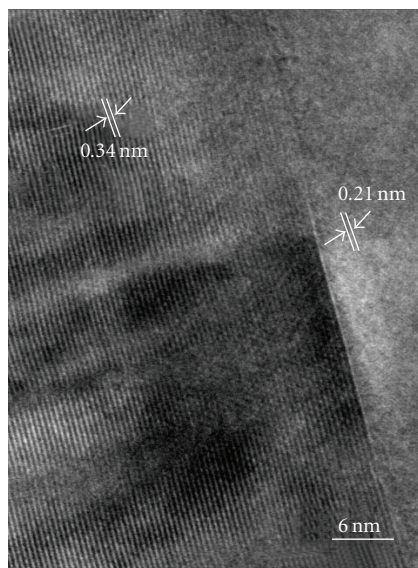
Based on the results of HRTEM and EDS, a possible growth mechanism of multi-walled CNTs filled with MgO nanorods was proposed. It is known that catalyst materials



(a)



(b)



(c)

FIGURE 2: (a) SEM image of CNTs (The inset is a high-resolution image.); (b) TEM image of CNTs filled with MgO nanorods (inset, EDS); (c) HRTEM image of multi-walled CNTs filled with MgO.

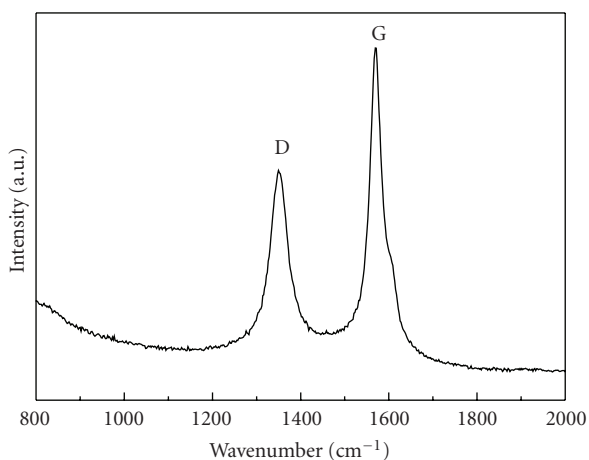
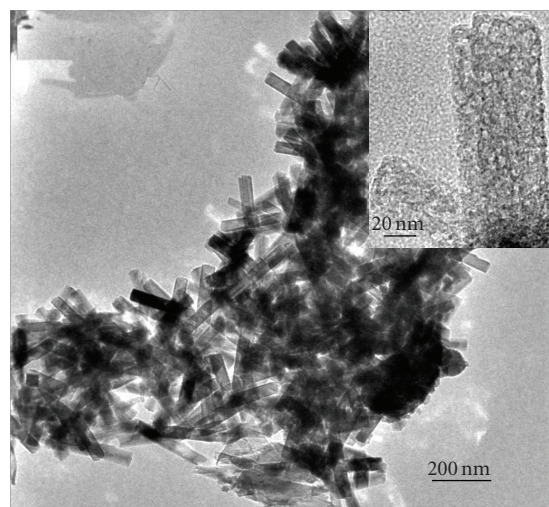


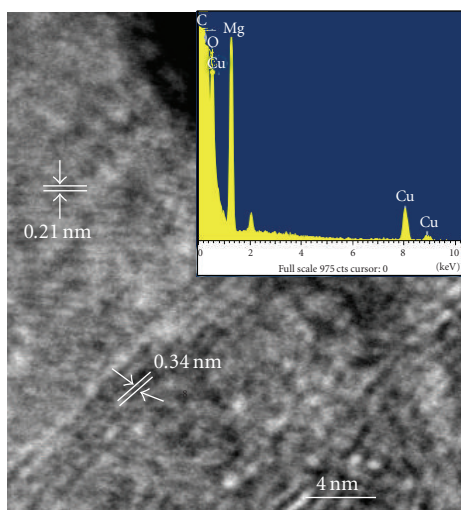
FIGURE 3: Raman spectrum of the as-prepared sample.

at the ends of CNTs were easy to be encapsulated into the CNTs [23–25]. However, in this system, there were no

magnetic catalysts to promote the encapsulation and their growth mechanism cannot be used to explain the growth of the MgO-filled multi-walled CNTs. And there are no other reports on the encapsulation of MgO nanostructures inside multi-walled CNTs. Some porous MgO nanorods with the diameters of 25–40 nm, similar in size to the MgO nanorods encapsulated by multi-walled CNTs, were observed by TEM (Figure 4(a)). The inset in Figure 4(a) is an enlarged individual porous MgO nanorod, which was characterized by HRTEM (Figure 4(b)). The formation of MgO may be ascribed to the reaction of Mg power and TiO_2 . Simultaneously TiC nanoparticles form between Ti coming from TiO_2 and carbon atoms. The inset in Figure 4(b) further proved that the porous nanorods were coated with layers of graphite. Porous structures have high specific surface area and high surface energy [26]. Therefore carbon atoms were easy to deposit on the surface of the MgO nanorods. As the reaction proceeded, the graphite layers turned into highly ordered multi-walled CNTs and finally the MgO-filled CNTs were formed.



(a)



(b)

FIGURE 4: (a) TEM image of the porous products (The inset image shows the enlarged nanorods.); (b) HRTEM analysis of the porous MgO nanorod (The inset image is the EDS spectrum.).

4. Conclusions

MgO nanorods encapsulated in multi-walled CNTs were fabricated by a one-step synthesis in a 20 mL autoclave at 400°C. TEM and HRTEM images show that MgO nanorods with diameters of 25–40 nm were encapsulated inside multi-walled CNTs with outer diameters of 70–130 nm and lengths of tens of micrometers. Raman spectrum suggested that multi-walled CNTs had excellent crystalline. The MgO nanorods are believed to be a template for the multi-walled CNTs growing. The electrochemical properties of MgO/CNTs are being studied.

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