

## Microwave-polyol Process for Functionalizing Carbon Nanotubes with SnO<sub>2</sub> and CeO<sub>2</sub> Coating

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Multiwalled carbon nanotubes (MWNTs) coated with CeO<sub>2</sub> and SnO<sub>2</sub> nanoparticles were successfully prepared by microwave-polyol process. The samples are characterized by XRD, TEM, HRTEM, and UV-vis analysis. SnO<sub>2</sub> and CeO<sub>2</sub> nanoparticles are homogeneously distributed on the wall of the MWNTs.

SnO<sub>2</sub> and carbon nanotubes (CNTs) are both well known as active components in molecular detection and transduction systems. Recently, it has been demonstrated that CNTs, and CNTs functionalized with ultrathin foreign species coating, represent a new type of chemical sensor capable of detecting small concentrations of molecules under ambient conditions.<sup>1</sup> And among the different materials studied for gas-sensing applications SnO<sub>2</sub> dominated over all other metal oxides and is most extensively studied. Well-known advantages of this material include its low cost and high sensitivities for different gas species.<sup>2</sup> The work function of the MWNTs is approximately equal to that of tin oxide, the Schottky barrier between them is very low. Electrons travel through the tin oxide grains into the MWNTs and then conduct in the MWNTs with low resistance while in SnO<sub>2</sub> nanobelt sensors, the conduction takes place in the SnO<sub>2</sub> nanobelt's bulk where electron mobility is very low. The applications of SnO<sub>2</sub>-functionalized CNTs for nanoscale sensor was suggested. Their composites has been proved by Liang et al.<sup>3</sup> to be a good gas sensor to detect oxidizing and reducing gases (NO, NO<sub>2</sub>, ethanol, and acetylene) down to a ppm level. Han and Zettl<sup>4</sup> have coated single-walled carbon nanotubes with a thin SnO<sub>2</sub> layer (about 4 nm) by a chemical-solution route using SnCl<sub>2</sub> as the starting materials. At the same time they coat boron nitride nanotubes with SnO<sub>2</sub> using the same method.<sup>5</sup> Zhao et al.<sup>6</sup> have reported the surface coating of MWNTs with a thick SnO<sub>2</sub> layer by a new and simple one-step wet chemical method without chlorine ions. Although CeO<sub>2</sub> (ceria) is not popularly used as a gas-sensing material, but CeO<sub>2</sub> or ceria-based sensors are currently being explored as possible candidates for oxygen sensing especially applying in sensing automotive exhaust gases.<sup>7</sup> CeO<sub>2</sub> combined with SnO<sub>2</sub> is sensitive to H<sub>2</sub>S at room temperature and is also sensitive to CO<sub>2</sub> while combined with BaCO<sub>3</sub>. By making proper thin-film depositions on silicon this material appears to be a good choice for the fabrication of integrated alcohol detector useful for industrial applications as well as for measuring the alcohol intake of an intoxicated person.<sup>2</sup>

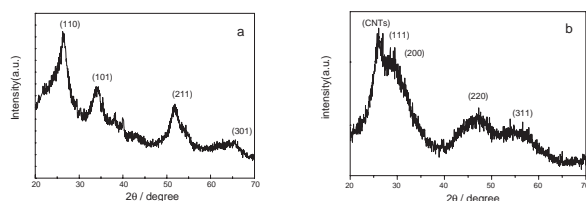
As a heating method, microwave-polyol irradiation has recently shown a very rapid growth in applying in material science because of its unique advantages such as rapid volumetric heating and the consequent dramatic increase in reaction rates. Here, we report a general method with one-step reaction for coating carbon nanotubes with monodispersed metal oxide nanoparticles

by a simple microwave irradiation approach. In the process, diethylene glycol was used as the solvent, and common compounds such as metal nitrate or chloride and sodium hydroxide as reactants were used directly. The MWNTs in the solution heated by microwave irradiation have no notable effect on the microwave absorption.<sup>8</sup> MWNTs were prepared by catalytic chemical vapor deposition (CCVD), the synthesis details may be found elsewhere.<sup>9</sup> For better anchoring the metal oxide nanoparticles, CNTs were oxidized by refluxing in concentrated HNO<sub>3</sub> at 413 K for 6 h. The typical experimental procedure is described as follows. First, 3 mmol of SnCl<sub>2</sub>·4H<sub>2</sub>O or Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were dissolved in 20 g of diethylene glycol (DEG) in a flask. Second, 0.05 g of CNTs was uniformly dispersed in the metal nitrate solution by ultrasound for several hours. Separately, 12 mmol of NaOH was dissolved in another 40 g of DEG. The DEG solution of metal nitrate with CNTs was added to the solution of NaOH while stirring at room temperature, then treated with ultrasound for another hour. The mixture in a beaker was placed in the center of a household microwave oven (National NN-S327WF, 2450 MHz, 700 W) and heated for 20 s under microwave power of 700 W. The resulting suspension was centrifuged and washed with acetone. The solid product was dried at 353 K for 2 h in a vacuum oven. Thus, CNTs coated with small size of nanocrystalline SnO<sub>2</sub> or CeO<sub>2</sub> powders were obtained. X-ray diffraction (XRD) was performed on a Thermo X'TRA diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). TEM and HRTEM images were obtained on a JEOL-200X and JEOL-2010X electron microscope using an accelerating voltage of 100 and 200 kV. The absorption spectra (dissolved in deionized water) were recorded on a Shimadzu UV-vis 3100 spectrometer.

Powder XRD patterns of the SnO<sub>2</sub> and CeO<sub>2</sub> coated CNTs composite are shown in Figure 1. The broad peaks in the XRD patterns compared to those of bulk SnO<sub>2</sub> and CeO<sub>2</sub> indicate the nanocrystalline nature of the samples. Each diffraction features correspond to the planes of the tetragonal rutile structure of SnO<sub>2</sub> (JCPDS 41-1445) and face-centered cubic structure (JCPDS 34-0394) of CeO<sub>2</sub>. The grain sizes of SnO<sub>2</sub> and CeO<sub>2</sub> nanoparticles on the surface of CNTs are about 3 or 4 nm, respectively, estimated by the Scherrer equation. The peaks of CNTs could not be observed in the XRD pattern of SnO<sub>2</sub> composite (Figure 1a), possibly because of the broad peak of tetragonal SnO<sub>2</sub>(110) which almost overlaps over the main peaks of the CNTs C(002).

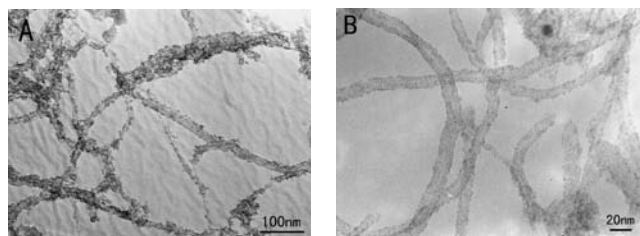
From the XRD patterns of the CeO<sub>2</sub> composite (Figure 1b), the peak of CNTs can be observed at 25.72°, which corresponds to the (002) plane of CNTs, and the main peaks of cubic center fluorite CeO<sub>2</sub>(111) is at 28.5°.

Figure 2 shows typical low-resolution TEM images of the



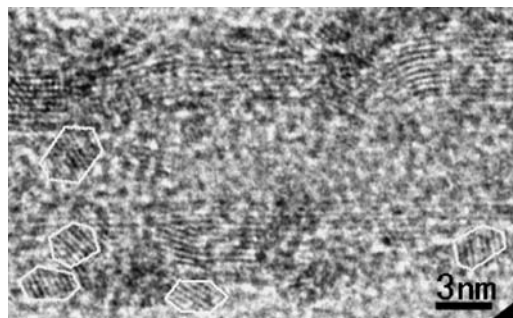
**Figure 1.** XRD pattern of the samples of CNTs coated with SnO<sub>2</sub> (a) and CeO<sub>2</sub> (b).

CNTs coated with SnO<sub>2</sub> and CeO<sub>2</sub> nanoparticles. From the images, it is observed that the CNTs are coated with many ultrafine particles with an average diameter below 5 nm, which is in well agreement with the calculated results from XRD patterns.



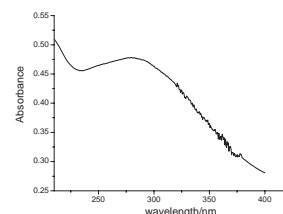
**Figure 2.** TEM images of CNTs coating with SnO<sub>2</sub> (A) and CeO<sub>2</sub> (B).

Figure 3 shows a HRTEM image of a CNTs coated with CeO<sub>2</sub> nanoparticles, which reveals that the surface of such composite is composed of monodisperse CeO<sub>2</sub> nanoparticles with approximately 3 nm in size, as demonstrated by the presence of the lattice fringes of such randomly oriented crystallites. Several ceria nanoparticles are indicated by linear cycles in Figure 3.



**Figure 3.** Typical HRTEM image of CNTs coated with CeO<sub>2</sub> nanoparticles.

When SnCl<sub>2</sub>·4H<sub>2</sub>O or Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved into sodium hydroxide solutions, hydrate complexes with positively charged ions were obtained and formed as major species. While the surfaces of the MWNTs possessed a great deal of functional carboxyl groups and became negatively charged, after oxidation by nitric acid, the positively charged complexes ions were easily absorbed onto the surface of the acid-treated MWNTs through the electrostatic attraction and later formed SnO<sub>2</sub> and CeO<sub>2</sub> nanoparticles by heating. Compared with conventional heating methods, microwave heating presents a more rapid and simultaneous nucleation due to the fast and homogeneous heating



**Figure 4.** UV-vis spectra of CNTs coated with CeO<sub>2</sub> nanoparticles.

effects of microwaves, moreover, uniform small particles can be synthesized owing to the simultaneous nucleation and homogeneous heating. The diethyl glycol is commonly used as the solvent because of its high dielectric constant and dielectric loss; hence, rapid heating occurs easily under microwave irradiation. In absence of CNTs, the metal ion solution reacted with sodium hydroxide solution (with a ratio of Me:OH<sup>-</sup> = 1:4) under the microwave irradiation to form a transparent brown colloid solution, which means that the metal ion and hydroxyl can produce very small particles in DEG. When adding CNTs into the solution, these metal oxide nanoparticles can easily separated from DEG solution and nucleated on the surface of CNTs to form the coated composite. The UV-vis optical absorption spectra of CNTs coated with CeO<sub>2</sub> nanoparticles are shown in Figure 4. The spectra distinctly exhibited a strong absorption band at the UV region due to the charge-transfer transitions from O<sub>2p</sub> to Ce<sub>4f</sub>, and there have no absorption detected above 500 nm in wavelength.

In summary, a microwave-assisted heating hydrolysis method has successfully established for the preparation of multiwalled CNTs coated with nanocrystalline metal oxide. This method is found to be convenient, mild, efficient, and environmentally friendly. Metal oxides such as SnO<sub>2</sub> and CeO<sub>2</sub> are well known as active components in many applications, meanwhile CNTs can also be seen as promising functional materials. CNTs coated with nanocrystalline metal oxide prepared by using this simple method are expected to exhibit more interesting properties.

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## References

- 1 J. Li, Y. J. Lu, Q. Ye, M. Cinke, J. Han, M. Meyyappan, *Nano Lett.* **2003**, 3, 929.
- 2 G. Eranna, B. C. Joshi, D. P. Runthala, R. P. Gupta, *A Comprehensive Review: Critical Reviews in Solid State and Materials Sciences*, **2004**, Vol. 29, p. 11.
- 3 Y. X. Liang, Y. J. Chen, T. H. Wang, *Appl. Phys. Lett.* **2004**, 85, 666.
- 4 W.-Q. Han, A. Zettl, *Nano Lett.* **2003**, 3, 681.
- 5 W. Q. Han, A. Zettl, *J. Am. Chem. Soc.* **2003**, 125, 2062.
- 6 L. Zhao, L. Gao, *Carbon* **2004**, 42, 1858.
- 7 P. Fornasiero, G. Balducci, R. Di Monte, J. Kapar, V. Sergo, G. Gubitosa, A. Ferrero, M. Graziani, *J. Catal.* **1996**, 164, 173.
- 8 F. H. Ko, C. Y. Lee, C. J. Ko, T. C. Chu, *Carbon* **2005**, 43, 727.
- 9 P. Chen, H. B. Zhang, G. D. Lin, Q. Hong, K. R. Tsai, *Carbon* **1997**, 35, 1495.