

## Functionalization of carbon nanotubes for nanoparticle attachment

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In this paper, multiwalled carbon nanotubes (MWNTs) have been functionalized by two methods, which are a concentrated acid treatment and a noncovalent treatment by a polyelectrolyte. The structure of the carbon nanotubes after treatment has been characterized by Raman measurements. Zeta potential analysis shows that the carbon nanotubes become obviously negatively charged after these two treatments. Inorganic nanoparticles, including  $\text{NiFe}_2\text{O}_4$ , CdS and  $\text{SnO}_2$  are homogeneously attached onto the functionalized MWCNTs using an in situ formation method utilizing the electrical attraction between the functionalized MWCNTs and the metal ions. The composites obtained have been characterized by transmission electron microscopy (TEM) and energy dispersive spectroscopic (EDS) analysis. These composites can be potentially useful for fabricating catalysts, photovoltaic cells, light-emitting diodes, etc..

**Key words:** Carbon nanotube, Functionalization, Hybrid material

### Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted considerable interest for their possible technological applications [1]. Carbon nanotube/inorganic nanoparticle hybrid materials have attracted more and more interest since they are believed to be useful as building blocks for optoelectronic devices, solar energy conversion, and photocatalysis [2, 3]. However, the effective preparation of this type of hybrid using wet chemical methods is difficult since the CNTs are insoluble in common solvents. Furthermore, the surfaces of CNTs are generally inert and have almost no functional groups. Therefore, in order to attach the nanoparticles firmly onto the nanotube, a strong interaction force needs to be introduced between CNTs and the nanoparticles. These two goals can be accomplished by the functionalization of CNTs, which are generally categorized as covalent and noncovalent methods [4].

In this paper, multiwalled carbon nanotubes (MWCNTs) are covalently functionalized by a treatment in mixed  $\text{H}_2\text{SO}_4/\text{HNO}_3$ , and nickel ferrite nanoparticles are then attached. The MWNTs are also noncovalently functionalized by sodium lignosulfonate (SLS), then CdS and  $\text{SnO}_2$  nanoparticles are attached by an in situ formation method. The structures and the surface electrokinetic properties of the functionalized MWCNTs have been analyzed. Furthermore, the morphologies of the hybrids are also characterized.

### Experimental Procedure

The pristine MWCNTs (ShenZhen Nanoport Company, China) were first ultrasonicated in concentrated  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixtures (3 : 1 v/v) for 8 h at  $10^\circ\text{C}$ , and then washed repeatedly with water. The product obtained was dried and denoted as o-MWCNTs (oxidized MWCNTs). A specific amount of the o-MWNTs was dispersed in a mixed ethanolic solution of  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Fe}(\text{NO}_3)_3$ , in which the Ni : Fe molar ratio was maintained at 1 : 2. Then the ethanolic NaOH solution was added dropwise with stirring until the pH reached 8.5. The mixture obtained was then placed in a Teflon-lined autoclave and maintained at  $110^\circ\text{C}$  for 6 h. The product was dried at  $60^\circ\text{C}$  overnight in vacuum.

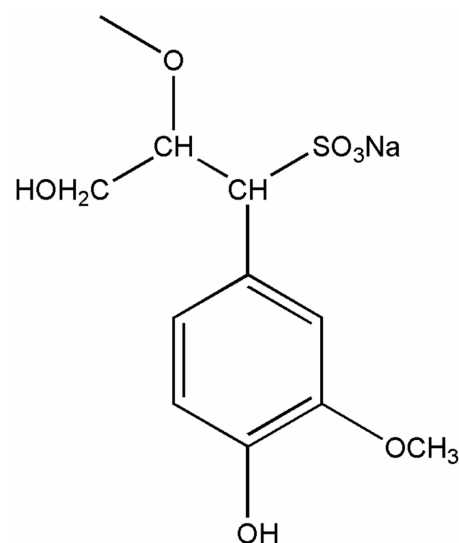


Fig. 1. Chemical structure of a typical SLS segment [5].

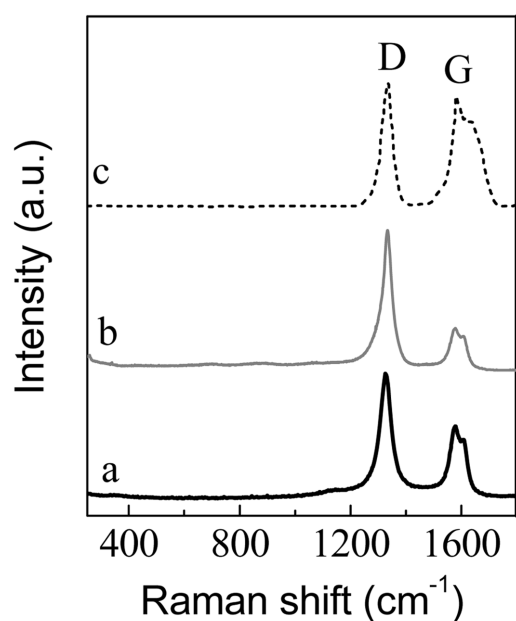
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Lignosulfonates have no regular structure, however, they are mainly composed of phenylpropane segments with sulfuric acid groups. [5] The chemical structure of a typical segment of lignosulfonate is shown in Fig. 1. The MWCNTs were mixed with SLS (Mw = 100,000) in an agate mortar by hand for 2 h, with the addition of a small amount of water. The brownish slurry obtained was diluted using water and then subjected to filtering and washing in order to remove excess SLS. The product was denoted as SLS-MWCNTs. For the preparation of a MWCNTs/SnO<sub>2</sub> hybrid, a specific amount of the SLS-MWCNTs was dispersed in 30 ml of 0.01 M SnCl<sub>4</sub> aqueous solution. Then, 30 ml of 0.04 M hydrazine solution was added dropwise with vigorous stirring. Subsequently, the mixture was hydrothermally treated at 150 °C for 24 h. After filtering and washing, a MWCNTs/SnO<sub>2</sub> hybrid was obtained. A similar process was adopted for the synthesis of MWCNTs/CdS hybrids except that 0.01 M Cd(CH<sub>3</sub>COO)<sub>2</sub> and 0.01 M Na<sub>2</sub>S solution was used as the reagent and the hydrothermal treatment was performed at 110 °C for 5 h.

Transmission electron microscopy (TEM) measurements of the hybrids were carried out in a JEOL JEM-2010 with an acceleration voltage of 200 kV. Surface properties of the samples were characterized by zeta potential measurements (Zetaplus, Brookhaven Instruments Corp., Holtsville, NY). Raman spectra of the aqueous suspensions were recorded using a Renishaw MicroRaman with an excitation length of 632.8 nm.

## Results and Discussion

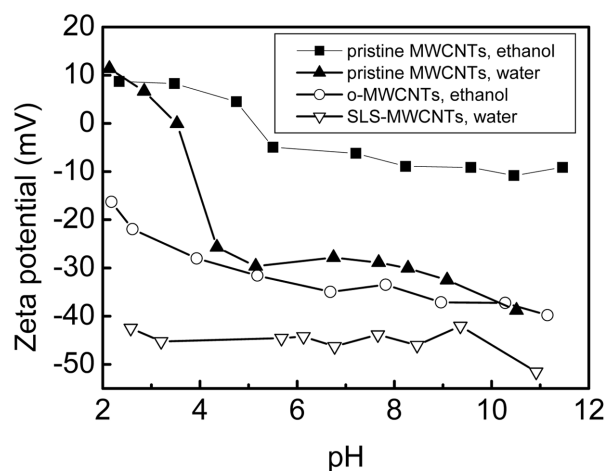
Fig. 2 shows the Raman spectroscopy results of the pristine MWCNTs, the o-MWCNTs and the SLS-MWCNTs. All these three curves exhibit two typical domains, the



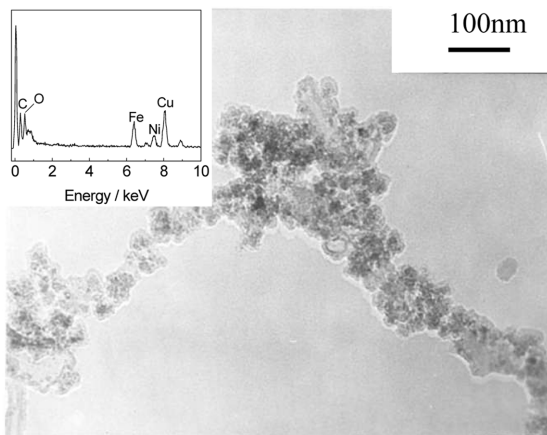
**Fig. 2.** Raman curves of (a) pristine MWCNTs, (b) o-MWCNTs and (c) SLS-MWCNTs.

tangential G-band within 1,550-1,605 cm<sup>-1</sup> and the disorder-induced D-band at ~1,350 cm<sup>-1</sup> [6]. It is generally accepted that the D band is due to defects in the hexagonal framework of CNT walls and the D/G intensity ratio is widely used to evaluate the sidewall damage of CNTs [6]. For the acid treated MWCNTs, the D/G ratio significantly increases, which is attributed to the carboxyl and hydroxyl groups caused in the treatment process, these results are consistent with those reported earlier [7]. In contrast, the D/G ratio shows no increase after SLS functionalization, indicating that no significant sidewall damage is caused. In fact, the D/G ratio slightly diminishes after the SLS functionalization, which might be attributed to the enhanced resonance processes of Raman scattering due to the exfoliation of the nanotubes. A similar behavior has been observed by other researchers [8].

The change of the surface properties of MWCNTs after functionalization can be clearly seen by inspecting their zeta potential curves, which are shown in Fig. 3. The isoelectric point of the pristine MWCNTs in ethanol and water is about pH ~5 and 4, respectively. Additionally, their absolute zeta potential values do not exceed 10 mV and 40 mV, respectively. In contrast, the MWCNTs after functionalization become much more negatively charged. The zeta potential of MWCNTs in ethanol decreased from -10 mV to -40 mV after the acid treatment. This change can be explained by the introduction of negatively charged groups on the o-CNTs by the acid treatment. These functional groups exist at the tip and on the outer shell of the tubes and make them more easily dispersed in polar solvents, such as water, ethanol, etc [7]. In the aqueous media, the zeta potential is decreased to about -45 mV between pH 5 and 10, after the SLS modification. It is generally known that SLS contains various anionic groups, including sulfonate groups (SO<sub>3</sub><sup>-</sup>; *pK<sub>a</sub>* = 1.5), carboxylate (COO<sup>-</sup>; *pK<sub>a</sub>* = 5.1) and phenolic hydroxyl (PhOH; *pK<sub>a</sub>* = 10.5) groups, which can increase the negative charges on the MWNTs once adsorbed. It is expected that the MWCNTs interact with the SLS through combined hydrophobic and  $\pi$ - $\pi$  stacking



**Fig. 3.** Zeta potential as a function of pH for pristine and functionalized MWCNTs.

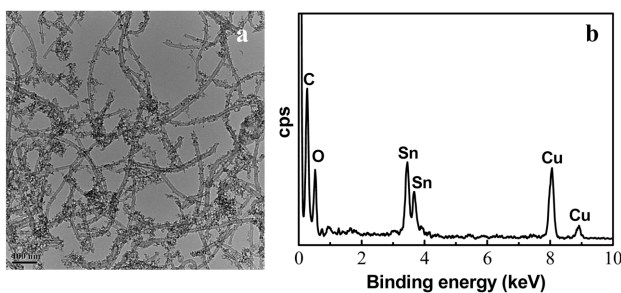


**Fig. 4.** TEM image and EDS (inset) spectra of the MWCNT-NiFe<sub>2</sub>O<sub>4</sub> hybrid.

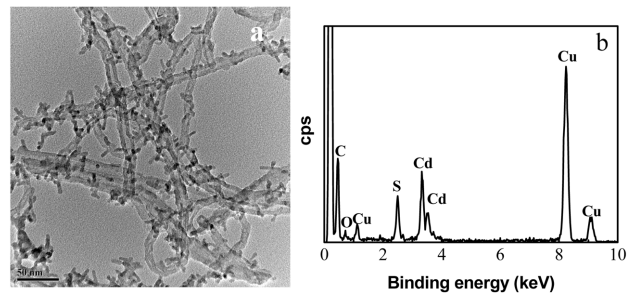
interactions [9].

The functionalized MWCNTs prepared above were further used as supports to attach nanoparticles. Fig. 4 shows the TEM images of the CNT-NiFe<sub>2</sub>O<sub>4</sub> hybrid powders obtained. It can be seen that the carbon nanotubes are densely coated with NiFe<sub>2</sub>O<sub>4</sub> nanoparticles. The EDS spectrum (inset) clearly indicates these particles consist of Ni, Fe, and O. The functional groups introduced by surface oxidation play an important role for the deposition of metal ions. These negatively charged groups provide a strong electrostatic attraction with the metal ions, thus making the in-situ formed NiFe<sub>2</sub>O<sub>4</sub> homogeneously decorated on the o-MWCNT surface.

The SLS-MWCNTs were also found to be good supports for decorating nanoparticles. Fig. 5a and Fig. 6a show the TEM images of the SnO<sub>2</sub>/MWCNTs and the CdS/MWCNTs nanoparticles, respectively. It can be seen that the decoration of CdS and SnO<sub>2</sub> nanoparticles onto MWCNTs is very uniform. The composition of the hybrids was also confirmed by the EDS results shown in Fig. 5b and Fig. 6b, respectively. The SnO<sub>2</sub> nanoparticles are mostly spherical with a size about 4-6 nm. The CdS nanoparticles have a rod shape with diameters around 5 nm and lengths about 7-10 nm. In the control experiments using pristine MWCNTs as decorating supports (data not shown), the MWCNTs are still bare and almost no SnO<sub>2</sub> or CdS nanoparticles have been decorated on the sidewall. These results suggest



**Fig. 5.** TEM image (a) and EDS spectra (b) of the MWCNTs-SnO<sub>2</sub> hybrids.



**Fig. 6.** TEM image (a) and EDS spectra (b) of the MWCNTs-CdS hybrids.

that the SLS coating plays an important role in decorating the CNTs with nanoparticles. The homogeneous decoration should be attributed to the strong interaction between the anionic groups of the SLS and the metal ions.

## Conclusions

In conclusion, two methods were taken to functionalize MWCNTs, including an oxidative acid treatment and physical grinding using SLS polyelectrolytes. The functionalized MWCNTs obtained can be easily dispersed in water. They are found to be good supports to be decorated with nanoparticles. NiFe<sub>2</sub>O<sub>4</sub>, SnO<sub>2</sub> and CdS nanoparticles were homogeneously decorated on the functionalized MWCNTs. The hybrids prepared can be potentially used as catalysts, photovoltaic cells, light-emitting diodes, and biosensors.

## Acknowledgement

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