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A Review of Photocatalytic Effects for the Novel Metal Sulfides Combined Multi-walled Carbon Nanotubes

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Abstract: Multi-walled carbon nanotubes (MWNTs) were coated with metal sulfide such as CdS, Ag_2S and HgS by an in situ synthetic method via non-covalent functionalization of MWNTs with sodium dodecyl sulfate (SDS), which were characterized by X-ray powder diffraction (XRD), transmission electron microscope (TEM) and photoluminescence spectroscopy. The coating layer was composed of metal sulfide nanoparticles with size of less than 30 nm. This method offers MWNTs/metal sulfide composites without significantly affecting the energy states of the MWNTs.

Keywords: CNT, CdS, Ag_2S, HgS, XRD, TEM, Photocatalytic.

1. Introduction

Carbon nanotubes (CNTs) have been continuously attracting wide interests in many areas of science and technology due to their unique structure-dependent electronic, optical and mechanical properties [1] since their discovery. To optimize the use of carbon nanotubes in various applications, it is necessary to attach functional groups or other nanostructures to their surface. The combination of carbon nanotubes with other nanocrystals are expected to be useful for applications in catalysts, sensors, nanoelectronic devices, data storage/processing devices, field emission displays, and polymer or ceramic reinforcement. Different interactions between metals and CNTs have been investigated such as carbon–metal bonding as well as electronic and magnetic roperties from metal–CNT interfaces, catalytic action of metals in the growth of CNTs and , CNT-reinforced metals, and , metals inside a CNT. The formation of metal clusters inside the CNTs is an interesting way to obtain metal nanowires when filling the CNTs with a liquid metal. With such materials it is possible to make, for example, "nanothermometers" to measure the temperature in a very confined place (gallium into a CNT). However, the presence of encapsulated nanoparticles into CNTs modifies the electric and magnetic properties of metal particles as well as those of the CNTs. It has been reported that the interactions between an encapsulated metal particle and CNT are affected by the nature of the CNT (number of walls and diameter) and also by the nature of the metal. Different mechanisms may explain the encapsulation of metal

particles in a CNT (For all these reasons it is important to widen our understanding of the metal–CNT interactions.

Several semiconductor nanoparticles such as SnO_2 [2], CdS [3], CdSe [4–6], CdTe [7], ZnO[8–10], ZnS [11,12],TiO_2 [13–17], SiO2 [18,19] and Eu_2O_3[20,21] have been bound to the surfaces of CNTs. Because of their unique size-tunable chemical and physical properties, semiconductor nanoparticles have attracted much attention [22]. Metal sulfides, as important semiconductors [23–28], have been used in many new application areas, such as quantum size effect, non-linear optical properties, laser communication and light-emitting diodes [29]. For example, Ag2S has been used in photovoltaic cells, electrochemical storage cells, IR detectors, photoconductors and so on[30,31]. HgS is a promising material for catalyst and infrared detector when coated with Rh or used alone [32]. CdS is an attractive material in photo conducting cells and optic electronic device. In this paper, we report the first synthesis of multi-walled carbon nanotubes (MWNTs)/Ag_2S (HgS) nanocomposites, the metal sulfide nanoparticles could be in situ bound to multi-walled carbon nanotubes through a simple and efficient synthetic route without causing a significant modification of the energy states of the MWNTs.

2. Experimental

Multi-walled carbon nanotubes with an average outer diameter between 20 and 50 nm and length up to a dozen micrometers were prepared by the thermal catalytic decomposition of hydrocarbon and the purity is more than 90%. The procedure employed by us for preparing MWNTs and metal sulfide composites is as follows. In a typical synthesis, MWNTs were first dispersed in a 1 wt.% sodium dodecyl sulfate (SDS) aqueous solution by ultrasonication for 3 h, in order to make SDS adsorb on the surface of MWNTs After rinsing repeatedly and drying, 100 mg SDS adsorbed MWNTs was sonicated in 20 ml 0.1 mol/l metal salt (such as $CdCl_2$, or $AgNO_3$, or $Hg(NO_3)_2$) solution for 5 min. Then 20 ml 0.1 mol/l Na_2S solution was added slowly into the above mixed solutions with vigorous stirring. After 30 h reaction, the final products was rinsed with water further and then dried at 80 °C for 10 h. TEM images were taken using a Hitachi Model H-800 transmission electron microscope, with an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) was carried out on a Shimadzu (Japan) XRD-6000 X-ray diffractometer with Cu Kradiation (λ = 0.15406 nm, U=40kV,I=30mA) at a scanning rate of 0.02 °/s in the 2èrange from 10 °to 80°. The photoluminescence spectra were recorded on Hitachi F-4500 fluorescence spectrometer.

3. Results and Discussion

3.1. Characterization

Fig. 1 shows the X-ray powder diffraction (XRD) patterns of MWNTs/metal sulfide samples obtained, the shoulder peak at 26.00–26.50° in all of the figures is estimated to be the characteristic peak of MWNTs. In Fig. 1(a), the peaks at 2θvalues of 26.3°, 43.68° and 51.93°, correspond to the crystal planes of (1 1 1), (2 2 0) and (3 1 1), respectively, of the

crystalline cubic CdS (JCPDS75-1546). The width of the peaks harmonizes to the small particle size. The mean nanocrystal size calculated from the half-width of the (2 2 0) diffraction peak using the Scherrer formula is 3.4 nm. In Fig. 1(b), the diffraction angles at 2θ = 22.52°, 26.0°, 29.07°, 31.61°, 33.72°, 34.51°, 37.83°, 40.85°, 43.51°, can be assigned to (1 0 2), (1 1 2), (1 1 0), (1 1 3), (1 2 1), (1 2 2),(120), (0 3 1), (2 0 2) planes of the monoclinic structures of Ag_2S (JCPDS 75-1061). The mean nanocrystal size obtained from the half-width of the (1 1 0) diffraction peak using the Scherrer formula is 34.7 nm. In Fig. 1(c), the diffraction angles at 2θ = 26.42°, 28.14°, 43.85°, 51.82°, can be assigned to (1 1 1), (2 0 0), (2 2 0), (3 1 1) planes of the cubic structure of HgS (JCPDS 75-1538). The mean nanocrystal size obtained from the half-width of the (3 1 1) diffraction peak using the Scherrer formula is 10.4 nm.

The direct evidence of the formation of metal sulfides nanoparticles on the surface of MWNTs was given by TEM shown in Fig. 2. The surface of MWNTs was uniformly covered with a certain amount of metal sulfides. The coating layer is composed of CdS, Ag_2S, HgS nanoparticles with size of less than (a) 5 nm, (b) 30 nm and (c) 10 nm, respectively, which are consisted with the results calculated using the Scherrer equation. The selected-area electron diffraction (SAED) patterns of the CdS, Ag_2S and HgS coated on MWNTs are shown in Fig. 3, which can also be indexed to the reflection of MWNTs, cubic CdS, monoclinic Ag2S and cubic HgS structures.

No charge-transfer bands in the UV–vis spectrum were observed for the composites, which suggest that the fabrication methods here would preserve the electronic properties of MWNTs. Without adversely affecting the energy states of the MWNTs, MWNTs were coated with CdS, Ag_2S, and HgS layers, respectively. Because of hydrophobic interactions through the CH_3groups, the non-covalent interaction between MWNTs and SDS is effective for imparting a negative charge, which attaches positive ions to the MWNTs surface. The positive ions (Cd^{2+}, Ag^{+} or Hg^{2+}) can beadsorbed onto the surface of MWNTs due to the electrostatic attraction, then negative ions (S^{2-}) can react in situ with the positive ions to form metal sulfides precipitates via electrovalent bonds.

3.2. Photoluminescence

Fig. 4 shows the photoluminescence spectra of metal sulfide coated on MWNTs at room temperature. Excitation spectrum of CdS/MWNTs was recorded with λem = 492 nm and emission spectrum with λex= 370 nm [29]. The PL spectrum in Fig. 4(a) shows a band at 450–525 nm with peak at 500 nm. A similar emission peak at ca. 505 nm was observed for 5–6 nm size CdS particles. The blue shift and the broader peak are also indicative of the size quantization. Emission spectrum of Ag2S/MWNTs was recorded with λex = 240 nm and excitation spectrum with λem= 398 nm. The PL spectrum in Fig. 4(b) shows a strong peak at 398 nm and a shoulder band at 300–450 nm, which arise from the Ag2S coating on the carbon nanotubes. Excitation spectrum of HgS/MWNTs was recorded with λem= 330 nm and emission spectrum with λex= 214 nm. The PL spectrum in Fig. 4(c) shows two peaks at 322 and 404 nm, which arise from the HgS coating on the carbon nanotubes. All the emission spectra are may result from the recombination of electrons and holes in the

surface state of metal sulfide, and indicated the quantum size and its distribution.

3.2. Photocatalytic Activity of the Samples

Figure 8 shows RhB degradation versus time using pure CNT, CdS-CNT, Ag_2S-CNT, and HgS-CNT under visible light. The spectra for the RhB solution after visible light irradiation showed the relative degradation yields at different irradiation time. The dye concentration continuously decreased with a gentle slope, which was due to visible light irradiation. The concentration of RhB was 5.0×10^{-5} mol/L [5], and the absorbance for RhB decreased with increasing visiblelight irradiation time. Moreover, the RhB solution increasingly lost its color as the RhB concentration continued to decrease [18]. Two steps are involved in the photocatalytic decomposition of dyes: adsorption of dye molecules and their degradation. After adsorption in the dark for 30 min with magnetic stirring, the samples were at adsorption desorption equilibrium. In the adsorption step, pure CNT, CdS-CNT, Ag_2S-CNT, and Ag_2S-CNT composites showed different adsorption capacity, with Ag_2S-CNT having the highest adsorption capacity [11-15].

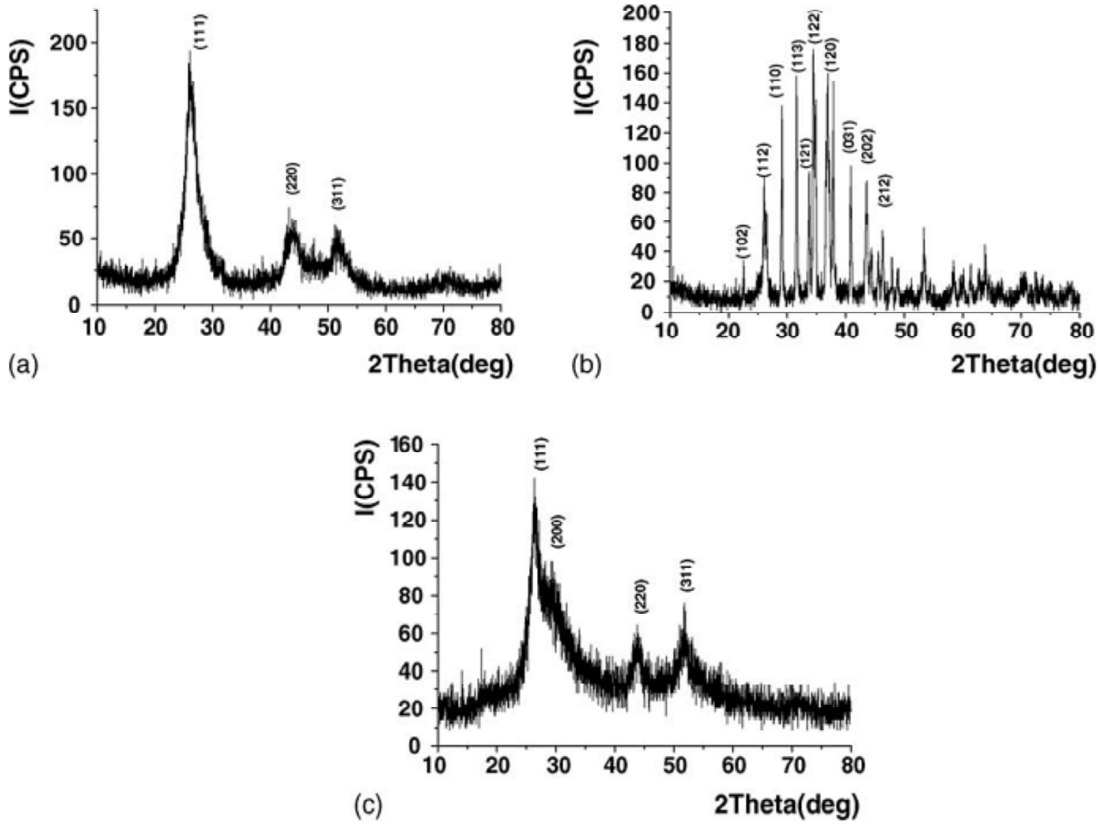

Figure 1: XRD patterns of MWNTs coated with (a) CdS, (b) Ag_2S and (c) HgS.

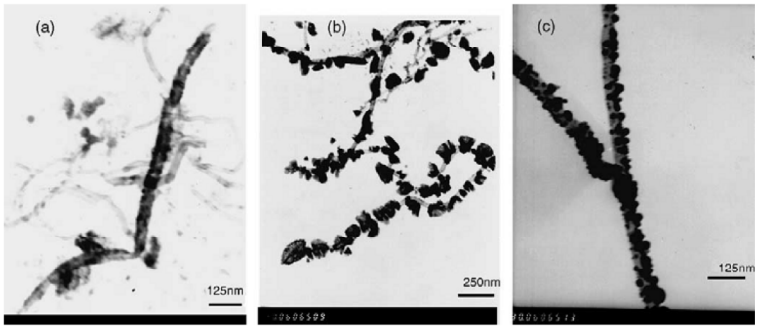

Figure 2: TEM images of MWNTs coated with (a) CdS, (b) Ag_2S and (c) HgS.

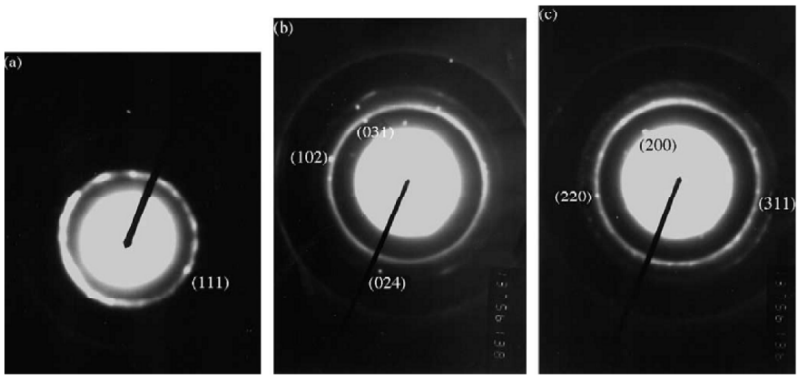

Figure 3: SAED patterns of MWNTs coated with (a) CdS, (b) Ag_2S and (c) HgS.

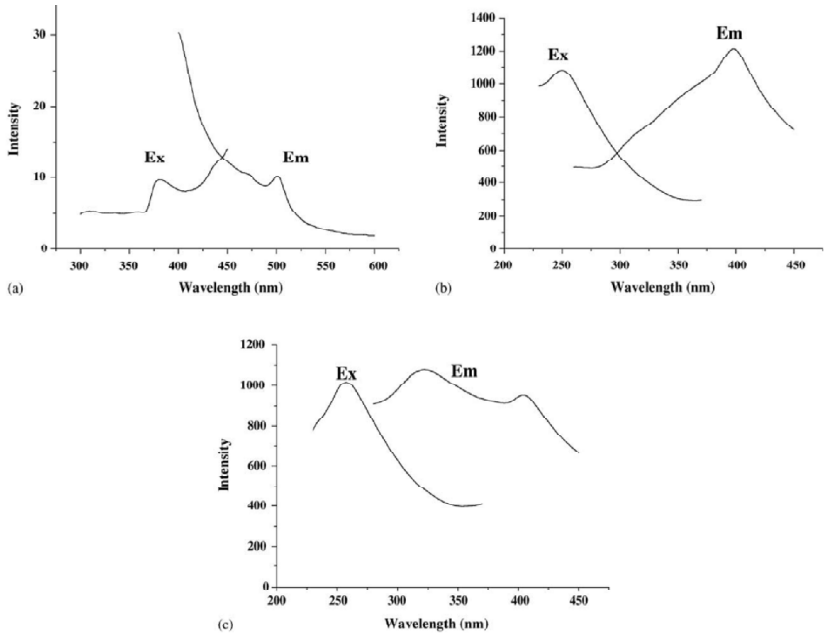

Figure 4: Emission and excitation spectra of (a) CdS/MWNTs, (b) Ag_2S/MWNTs and (c) HgS/MWNTs.

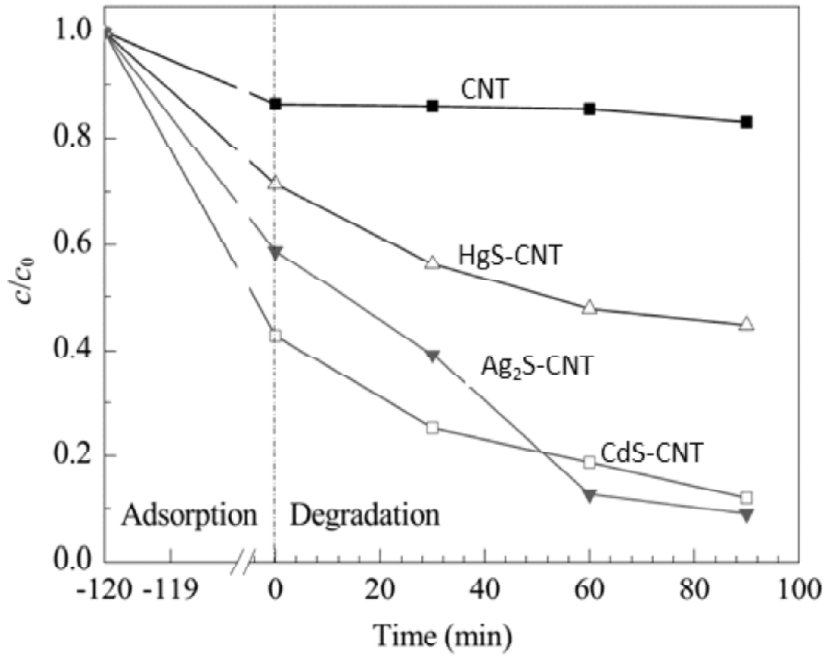

Figure 5: Degradation of RhB under visible light irradiation with magnetic stirring over pure CNT, HgS-CNT, CdS-CNT, and Ag_2S-CNT. c is the concentration of RhB solution, and c_0 is the initial concentration.

4. Conclusions

Metal sulfides CdS, Ag_2S and HgS nanoparticles with size of less than 30 nm were coated on MWNTs successfully by a simple and effective in situ synthetic method without severely affecting the energy states of the MWNTs. The versatility of this method could be extended to other transition metal compound nanostructures. It should be further noted that this new type of hybrid carbon nanotubes with coated metal sulfides nanoparticles on the sidewall may have more interesting potential applications in field emitters, or nanometer-scale optoelectronic devices.

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