

Synthesis and characterization of MWCNT/CdS nanocomposite

M R Khanlary and M Keshavarz

Department of Physics, Imam Khomeini International University, Qazvin, Iran

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Abstract

In this work we report the synthesis and characterization of hybrid nanostructures of multiwall carbon nanotubes (MWCNT) and cadmium sulphide (CdS) nanoparticles. In a solution of thioacetamide and cadmium sulphide, purified MWCNT are added to prepare the CNT/CdS heterostructure. XRD diagrams, SEM images, and also photoluminescence spectra of the prepared samples are analyzed. SEM images show the CdS nanoparticles of 17nm size coated on the CNTs. Visible photoluminescence with peaks at 435 nm and 535 nm, obtained from the prepared CNT/CdS, is discussed. The synthesis technique can be simply extended to other luminescent dopants, and the possibility of making optoelectronic devices based on the CNTs is confirmed by this method.

Keywords: CVD, nanocomposite, carbon nanotubes, cadmium Sulphide, photoluminescence

1. Introduction

In recent years, carbon nanotubes have been intensively studied due to their unique structure dependent mechanical, chemical and electronic properties [1, 2]. Carbon nanotubes can be envisaged as a graphite sheet rolled-up into a seamless cylinder. The surface area of each nanotube is relatively high and allows attaching of many other molecules, including those capable of emitting light. In general, surface modification of multiwall and single walled carbon nanotubes (SWNT) by organic, inorganic or biological compounds can significantly alter their physical properties and yield novel materials for special applications [3]. Recent progress in carbon nanotubes based nanocomposites, and nanostructures development and fabrication make them attractive to direct the flow of photo generated electrons to the collecting electrode surface in a dye-sensitized solar cells. In order to optimize the properties of CNTs, it is necessary to attach functional groups or other nanostructures to their surfaces. Varieties of semiconductor nanoparticles such as CdTe [4], ZnS [5], CdS [6], and ZnO [7] have been tried to functionalize the surface of CNTs. Cadmium sulfide (CdS) is an important visible-light-sensitive semiconductor with a direct band gap energy of 2.42 eV, which makes it possible to utilize solar energy efficiently. Moreover CdS has a good capability to be used as a photo catalyst for H₂ evolution under visible light [8]. However, the problem of poor quantum efficiency of CdS as photocatalyst remains

unsolved. So far a few studies of the method for decorating CnTs with CdS nanoparticles and nanowires have been reported [9, 10]. The transfer of electron between CdS, CNTs including single walled carbon nanotubes, MWNTs and functional MWNTs has been detected [11, 12] as well. Hybridizing semiconductor nanoparticles on CNT surface can modify their optical characteristic and luminescence properties. Luminescent materials including CdS can be combined with nanoscale cavities for drug storage and delivery. The hollow center of the nanotube can be filled with a cancer treatment drugs. Semiconductor CNTs have a very narrow band gap and their PL emission is in IR region of spectra [13]. Therefore, intense emissions and tunable wavelength can be provided by luminescent materials such as CdS quantum dots QDs. Due to the chemical inertness of carbon nanotubes, their surface modification must be completed in order to attach the QDs. For instance, the acid oxidation of carbon nanotubes, resulting in the carboxyl groups at the tips and other high defect density sites has been of the effective approaches [14].

Carbon nanotubes are generally processed by laser ablation of carbon rods and arc discharge or by chemical vapor deposition (CVD). The CVD method is considered to be the most advantageous because, in addition to the high yield of CNTs, synthetic parameters such as carbon source and catalytic metal which control the physical structure of CNTs are adjustable. In this study, by a simple method of functionalizing MWNTs (prepared by

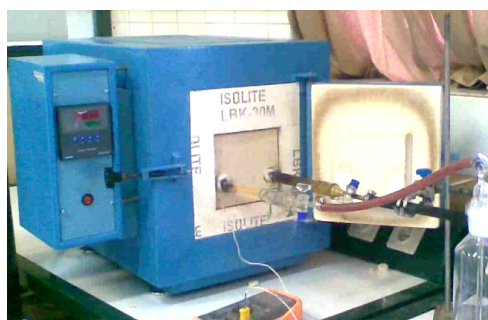


Figure 1. Image of the furnace and quartz tube.

CVD method), and decorating them by CdS nanoparticles we were able to find pronounced PL intensity spectra of CNT/CdS hybrid structure with emission, in visible region, at 435 and 532 nm which is the emissions favorite for optoelectronic and many other optical applications.

2. Experimental work on MWNTs

MWNTs were synthesized by floating catalyst method. Methane gas (CH_4) was used as a carbon source and vaporized ferrocene ($\text{FeC}_{10}\text{H}_{10}$) was used as a catalyst. The reactor, shown in figure 1 is heated up by a resistive furnace. Two ends of the "quartz" tube are brought to outside of the furnace. By heating the system to 800°C , when CH_4 was flowing through the tube (with flow rate of 150 ml/min), and diluted with argon (with flow rate of 350 ml/min), MWNTs was grown and deposited on the inner surface of the quartz tube. In that case, temperature of the ferrocene rose to 250°C (well above the sublimation temperature of ferrocene), and flowed to the reactor after ~3 minutes from the beginning.

Prepared MWNTs was functionalized as follows: 100 mg of MWNTs powder was added to 40 ml of hydrochloric acid (1% Molar). The solution was stirred for 5 hours to remove residual catalyst. Purified MWNTs was added to a solution of nitric acid and sulfuric acid with the ratio of 3:1 and stirred for 24 hours. The solution was then filtered by polytetrafluoroethylene with $0.45\mu\text{m}$ holes and dried in an oven. At this point, carboxyl groups were slicked to MWNTs and were able to absorb CdS nanoparticles (see figure 2).

100 mg of the carboxylic MWCNTs powder is dispersed in 250 ml of H_2O by an ultrasonic device. 82 mg of tioacetamide (TAA) in 10 ml of H_2O and also 25 mg of cadmium sulfide (CdSO_4) in 10 ml of H_2O are separately solved. Suspension of MWNTs and the two mentioned solutions were mixed and stirred at 80°C for 6 hours and then dried at 80°C for 10 hours. Figure 2 shows the route of MWNTs/CdS composite formation. Electron microscopic images were obtained from a SEM system from Hitachi (S-4160). X-ray diffraction plots were obtained from X'pert XRD: Philips with wavelength of 1.54 \AA . Room temperature photoluminescence (PL) was measured by a fluorescence spectrometer (Cary Eclipse) under excitation wavelength of 390 nm.

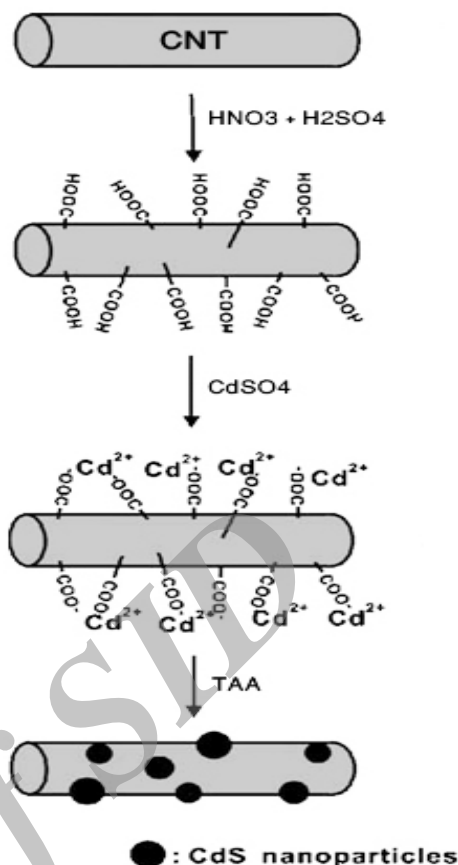


Figure 2. Scheme of CNT/CdS formation [15].

3. Result and discussion

(i) Figure 3 shows the image of an untreated MWNT sample with an average diameter of up to 30 nm. SEM of the functionalized MWNT is shown in (b) with some small white particles stuck to the CNTs' walls or at top of them. The final synthesized of MWNTs/CdS composite is shown in figure 3 (c).

(ii) From figure 4 curve (b), the (111), (200), (220), (311) and (222) planes of CdS are observed at $2\theta \approx 26.5, 30, 44, 52$ and 54° respectively. It can be seen that the diffraction peaks at $2\theta \approx 26, 43$ and 53° are assigned to (002), (110), and (004) planes of MWNTs in figure 4 (a). These three diffraction peaks are attributed to the graphitic structure of MWNTs [16]. The graphitic structure of MWNTs isn't destroyed after MWNTs were coated with CdS nanoparticles as we can observe that the the characteristic peaks of MWNTs still exist in figure 4 (b). However, the main peak of MWNTs assigned to (002) plane and also their two other peaks are overlapped by that of CdS. These features of XRD from the MWCNTs composite are reported by others (eg. [17]).

In addition, the average crystallite size of the CdS nanoparticles on the surface of MWNTs is calculated from the main diffraction peak (111) of CdS by using Deby-Scherrer equation:

$$d = \frac{0.89\lambda}{\beta \cos \theta} \quad ,$$

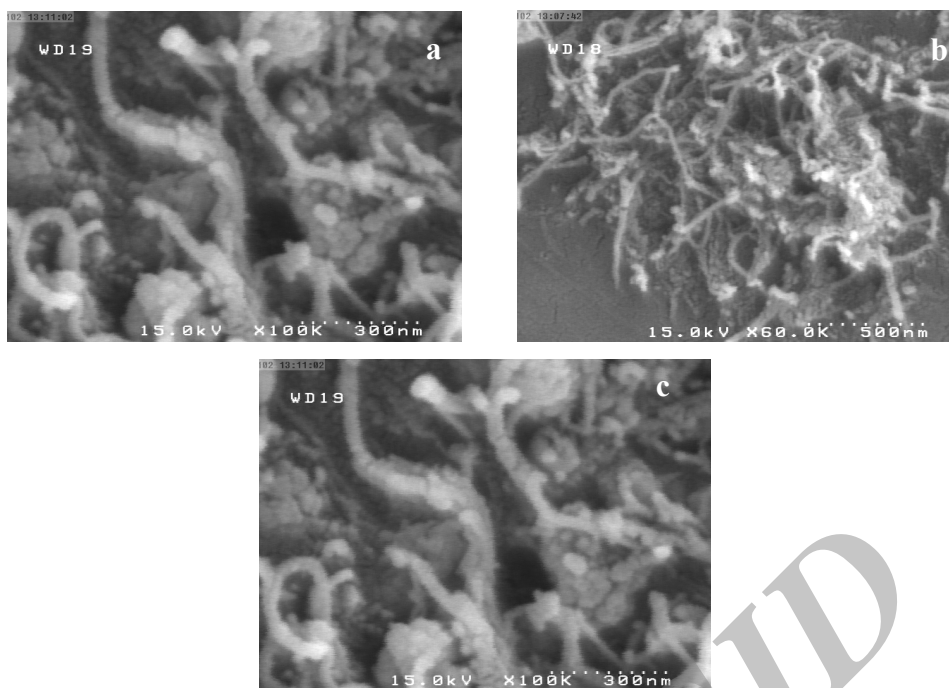


Figure 3. SEM image of; (a) untreated MWNT, (b) functionalized MWNT and (c) CNT/CdS composite.

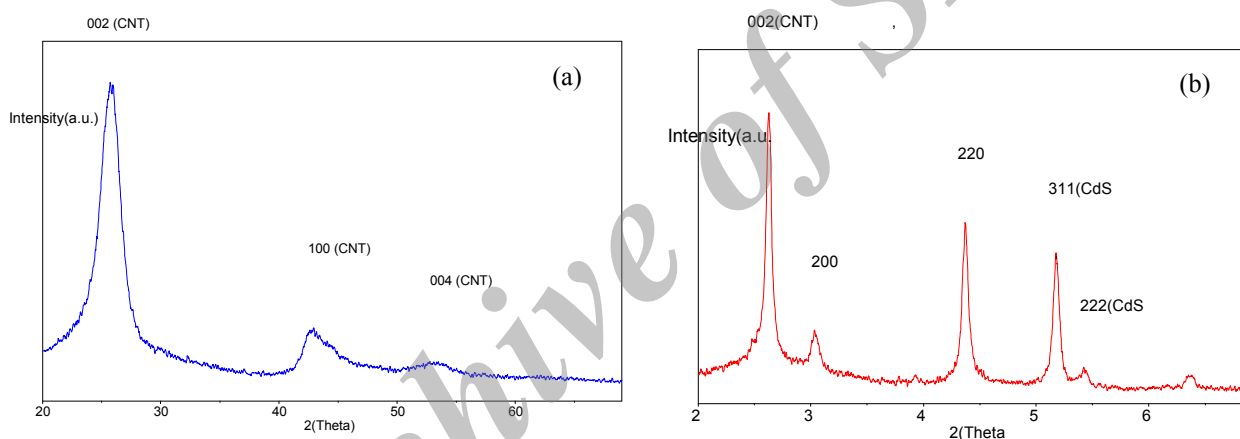


Figure 4. (color online) (a) XRD spectrum of MWCNT. (b) XRD plot of MWNTs/CdS composite.

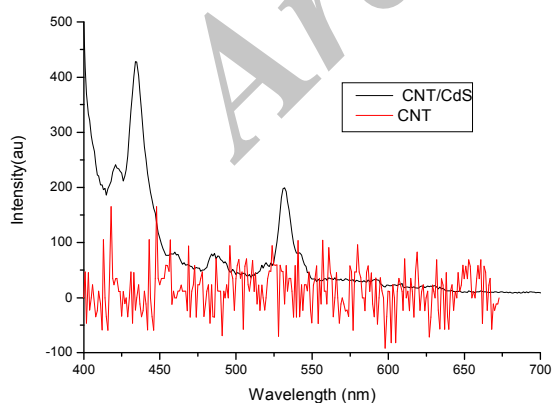


Figure 5. (color online) PL spectra of CNT/CdS composite.

is about 17 nm. Here, β as the full width of half maximum (FWHM) for the preferential plane of (220) is

$\sim 0.5^\circ$.

(iii) Although carbon nanotubes are known to have near-infrared emissions, the luminescence intensities are generally too weak to be detected in many applications and, untreated MWCNTs have essentially no PL peaks in the visible region of spectra. However, some authors eg. C Elizabeth *et al.* and P Rima Paul, *et al.* reported visible PL emission from CNTs doped with the oxide or metallic dopants [18].

Here, from the PL data of prepared MWNTs/CdS, we can see some features in the visible region of spectra. Figure 5 shows, PL spectra from MWNTs and also MWNTs/CdS, there are two predominant peaks at 435 and 532 nm for the composite CNT. The second one at 532 nm is directly related to CdS nanoparticles and is previously reported by PL studies of CdS nanoparticles. However, the blue peak at 435 nm is attributed to the MWNT/CdS and it appears just from the composite sample. It is believed that the excitation of CNT/CdS

causes the electrons from the valance band of CdS nanoparticles to be excited and move towards the conduction band forming electron-hole pair. Excited electrons of CdS migrate to conduction band of CNTs and finally experience a transition from energy trapping sites with a strong light emission. Two other weak bands with peak at 421 and 486 are also clearly observable from figure 5. These two peaks are also attributed to the CNT/CdS composite and are not previously reported for CdS alone [19].

4. Conclusion

MWCNT/CdS composite is simply synthesized by

thermal analysis of CdSO₄ and CNT contained in a hydrated solution. Interaction between S⁻² and Cd⁺² ions during the thermal analysis process occurring in the surface of CNTs causes the deposition of CdS nanoparticle on CNT walls. Surface deformation of CNTs and sulfur ions source has a significant role in deposition, morphology, and structure of CdS nanoparticles. XRD and PL studies of CNT/CdS showed that (a) the surface of CNTs are coated with zinc blende structure of CdS nanoparticles, and (b) the prepared composite is able to emit in the visible region of the spectra. This method can simply be used to functionalize carbon nanotubes for optical applications.

References

1. M S Dresselhaus, G Dresselhaus, R saito, and A Jorio, *Phys. Rep.* **409** (2005) 47.
2. M Yu and M Dyer, *Appl. Phys.* **89** (2001) 4554.
3. S Banerjee, M J C Khan, and S S Wong, *Chem. Eur. J.* **9** (2003) 1898.
4. S Banerjee and S S Wong, *Adv. Mater.* **16** (2004) 34.
5. H Kim and W Sigmund, *J. Cryst. Growth* **255** (2003) 114.
6. Y Liu and L Gao, *Mater. Chem. Phys.* **91** (2005) 365.
7. Y Zhu *et al.*, *Adv. Mater.* **18** (2006) 587.
8. M Matsumura, Y Sato and H Tsubomura, *J. Phys. Chem.* **87** (1983) 3807.
9. J Cao, J Sun, J Hong, H LiH Chen, and M Wang, *Adv. Mater.* **16** (2004) 84.
10. C Li, Y Tang, K Yao, F Zhou, Q Ma, H lin, and M Tao, *Carbon* **44** (2006) 2021.
11. I Robel, B Bunker, and P. Kamart, *Adv. Mater.* **17** (2005) 2458.
12. Z Cai and X Yan, *Nanotechnology* **17** (2006) 4212.
13. S Lebedkin, F Hennrich, T Skipa, and M M Kappes: *J. Phys. Chem. B* **107** (2003) 1949.
14. A Rinzler *et al.*, *Appl. Phys. A* **67** (1998) 29.
15. J. Shiet *et al.* *Carbon* **42** (2004) 423.
16. W Chen, J Tu, L Wang, H Gran, Z Xu, and X Zhang, *Carbon* **41** (2003) 215.
17. Y Zhao, H Liu, F Wang, J Liu, K Ch Park, and M Endo, *J. Solid State Chem.* **182** (2009) 875.
18. E C Dickey, C A Gramies, and M K Jain, *Appl. Phys. Lett.* **79**, 24, 10 (2001) 4022.
19. R Paul, P Kumbhakar, and A K Mitra, *Mater. Sci. Eng. B* **167** (2010) 97.