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Immobilization of Metal Sulfide Nanocrystals on Multiwalled Carbon Nanotubes Facilitated by Infrared Irradiation

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Abstract

Uniformly distributed metal sulfide nanocrystals are immobilized on the surface of oxygenated multiwalled carbon nanotubes (MWCNTs) by reacting metal ions (Cu^{2+}/ Zn^{2+}/Cd^{2+}) anchored to MWCNTs with hydrogen sulfide while irradiating with infrared (IR) radiation. The IR irradiation is the key step in the effective immobilization of metal sulfide nanocrystals on MWCNTs. The photoabsorption and photothermal properties of MWCNTs in the presence of IR irradiation raises the temperature of the CNTs in solution, facilitating the interaction between the acidic groups on CNTs and the metal ions, which results in effective immobilization of the nanocrystals. The metal sulfide-MWCNT hybrids are characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, scanning and transmission electron microscopy.

Keywords: Multiwalled carbon nanotubes, IR irradiation, immobilization of metal sulfide nanocrystals and CNT hybrids

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1. Introduction

Among many allotropes of carbon, carbon nanotubes (CNTs) are unique due to their mechanical, magnetic, optical and thermal properties [1-3]. The observation of tubular structure of CNTs by Ijima in 1991 [4] resulted in the explosive growth of the research activities in the field of CNTs. Owing to their tubular and anisotropic structure, CNTs are used in the fields of catalysis and composite reinforcement materials [5,6]. CNTs are also projected as future materials in the areas of field emission displays, energy storage and energy conversion, sensors, nanometer-sized semiconductor devices and more [7,8]. However the properties of CNTs are highly dependent on the diameter, helicity and the surface modification of the tubes. There have been several efforts to modify the surface of the CNTs with organic, inorganic and biological species in order to change their properties according to applications [9]. The interactions between CNT host and the guest species determine the final properties of the composite/hybrid material.

Semiconductor nanoparticles or quantum dots (QDs) are interesting guest species due to their size dependent properties. The internal electronic structure of QDs, which in turn is responsible for their optical properties, depends on particle size, medium of dispersion, interaction with the host material etc. [10]. Several approaches have been adopted for changing the band gap of QDs, however compositing with a suitable host exhibiting specific properties is promising [11-13], since they not only may show combined properties of both the host and the guest but also sometimes may possess new properties due to synergism [11,14]. QDs such as CdS [15], CdSe [16], ZnO [17], CdTe [18] and TiO_2 [19] have been immobilized on the surface of CNTs. The preparative method, the host guest interaction and the morphology of the nanoparticles are the key factors in determining the properties of the hybrids. Controlled hydrolysis and condensation of titanium bis-ammonium lactate dihydroxide in water was carried out to prepare TiO2 nanoparticles on CNTs by Lee et al [20]. In another approach Si et al [21] reports the preparation of CdSe-CNT nanohybrids facilitated by the electrostatic interaction between negatively charged mercaptocarboxylic acid capped CdSe QDs and positively charged organic molecules functionalized CNTs. Liu et al [17] reported the growth of aligned ZnO-CNT heterojunction arrays by water assisted chemical vapor deposition of carbon on zinc foil.

For the preparation of metal sulfide-CNT hybrids, the general approach is by treating functionalized CNTs with the metal ion followed by a suitable post treatment. Several preparative approaches and the different sulfur sources have been utilized. Zhao et al [14] employed thermal decomposition of thioacetamide as the sulfide source for the preparation of CdS-CNT hybrid heterostructures. A lyophilization process was adopted by Capobianchi et al [22] for controlled filling of multi walled carbon nanotubes (MWCNTs) with CdS crystals. In a different strategy Huang et al [23] synthesized CdS-MWCNTs heterojunctions by solvothermal approach using dimethyl sulfoxide both as medium and sulfur source. In some other reports sulfide ions were obtained from sources such as aqueous solutions of sodium sulfide/thioacetamide, sulfur powder in organic media [14, 24]. In most of the reported cases byproducts formed during the hybrid preparation can stick to the surface of the CNTs, necessitating its complete removal.

CNTs are known to absorb near infrared (IR) radiation, rapidly transferring electronic excitations into molecular vibration energies which induce heat [25]. This remarkable photo-absorption and photothermal property of CNTs has been made use of for remote thermal reactions [26], phase transitions of polymer gel hybrids [27], cancer therapies [28], and so forth. In the present contribution, we investigate the effect of IR irradiation in facilitating the immobilization of metal sulfide nanocrystals on oxidized MWCNTs. This is based on the premises that the induced heat is likely to facilitate interactions between the metal ions and the acidic functionalities on the CNTs and eventually promote the immobilization of metal sulfide nanocrystals. Three different metal sulfides such as CuS, ZnS and CdS are immobilized on functionalized MWCNTs. We also use hydrogen sulfide (H_2S) as the sulfur source, to avoid formation of any major byproducts which can stick or interact with the final hybrids. To the best of our knowledge, this is the first report on the immobilization of metal sulfide nanocrystals on functionalized MWCNTs facilitated by IR irradiation.

2. Experimental section

All the chemicals used were of analytical grade and used without further purification. The thin pristine MWCNTs (P-MWCNTs) obtained from Nanocyl S.A., were synthesized by the decomposition of ethylene using the combustion chemical vapor deposition method. The P-MWCNTs have an average diameter of 10 nm and length of several (0.1-10) micrometers. The purity of the P-MWCNTs was more than 95 %. $Cu(NO_3)_2.3H_2O$ was obtained from Acros Organics with the product purity of 99 % and $Zn(NO_3)_2.6H_2O$ (98 %) from Aldrich chemicals. $Cd(NO_3)_2.4H_2O$ (99.3 %) was procured from J. T. Baker Chemicals, and the hydrogen sulfide gas with 99.5 % purity from Sigma Aldrich.

2.1. Oxidation of P-MWCNTs

The surface of the P-MWCNTs were oxygen functionalized by treating them with the mixture of concentrated H_2SO_4 and HNO_3 with a molar ratio of 3:1 following the method reported in the literature [29,30]. In a typical experiment, 75 ml of conc. H2SO4 (97 %) and 25 ml of conc. HNO_3 (65 %) were carefully mixed together and added to 1 g of P-MWCNTs in a round bottomed flask. The above suspension was then heated under constant agitation at 50 oC for 8 hours. The suspension was allowed to cool down to room temperature, added to equal quantity of deionized water, filtered and the residue was washed several times with deionized water until neutral pH was attained. The residue obtained was filtered and freeze-dried. The oxidized MWCNTs thus obtained will be hereafter referred to as O-MWCNT.

2.2. Preparation of metal sulfide – MWCNT hybrids

2.2.1. Metal sulfide – MWCNT hybrids under IR irradiation

Three different metal sulfides i.e., CuS, ZnS and CdS were in-situ generated on the surface of O-MWCNTs and referred to as CuS-MWCNT, ZnS-MWCNT and CdS-MWCNT respectively, hereafter. In a typical experiment, 100 mg of O-MWCNTs were dispersed in

100 ml of deionized water containing 20 weight % of $M(NO_3)_2$ [M = Cu/Zn/Cd] by sonicating for 30 minutes. The dispersion was then IR irradiated under magnetic stirring until a constant temperature (67˚C) was reached and continued stirring for 1 hour. While dispersion was still stirring under IR irradiation, hydrogen sulfide (H2S) gas was passed for 30 minutes. The suspension was cooled to room temperature, filtered and the residue was washed with excess of water and acetone. The hybrid was dried at 60°C overnight.

2.2.2. Metal sulfide – MWCNT hybrids without IR irradiation

In another set of experiments, the above procedure was repeated except that the dispersion was not exposed to IR irradiation, to ascertain the specific effect of irradiation on the hybrid formation. The suspensions obtained were treated as mentioned above to get the final products.

2.3. Preparation of free metal sulfide nanocrystals

Free metal sulfide nanocrystals were prepared by passing H2S gas through 100 ml solution of 0.05 M $M(NO_3)_2$ [M = Cu/Zn/Cd] for 30 minutes. The solids obtained were treated as mentioned above.

2.4. Characterization

The hybrids and the free metal sulfides were characterized by various analytical techniques. The powder X-ray powder diffraction (PXRD) analysis was carried out using PHILIPS-7602EA diffractometer operating with 40 kV of voltage and 30 mA of tube current with Cu Kα radiation (λ = 1.5418 Å) in the 2θ range of 10 to 70°. X-ray photoelectron spectroscopy (XPS) spectra were recorded at 35o take-off angle (relative to the surface normal) with an SSX-100 spectrometer using monochromatized Al Kα radiation (1486.6 eV). The analyzed core-level lines were calibrated with respect to the component C 1s of binding energy set at 284.6 eV. Fourier Transform Infra Red (FTIR) spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR Spectrometer. Trace amount of the sample was added to prepare the KBr pellets, which was then employed for the characterization. The surface morphology of the materials were studied by field-emission scanning electron microscopy (FE-SEM) using JEOL JSM-7500F microscope operating at 20 kV at a working distance of 8 mm and equipped with energy dispersive X-ray (EDX) analysis facility. The particle size and distribution of metal sulfide nanocrystals on MWCNTs were studied by low resolution transmission electron microscopy (TEM) using a TECNAI 10 PHILIPS microscope. Prior to the analysis, the samples were dispersed in ethanol and a drop of the suspension was deposited on a holey carbon-coated copper grid. The IR irradiation experiments were carried out using a Petra IR 11 lamp (capacity: 150 W, voltage: 230 V, 50/60 Hz).

3. Results and discussion

The steps involved in the immobilization of metal sulfides on MWCNTs are illustrated in Figure 1. First the P-MWCNTs were treated with acid mixture to generate hydroxyl, carboxylic and other acidic functional groups on the surface of CNTs (O-MWCNTs). In the second step O-MWCNTs were dispersed in metal nitrate solution, while stirring in presence of IR irradiation, to facilitate the interaction between the metal ions and the acidic functional groups on CNTs.

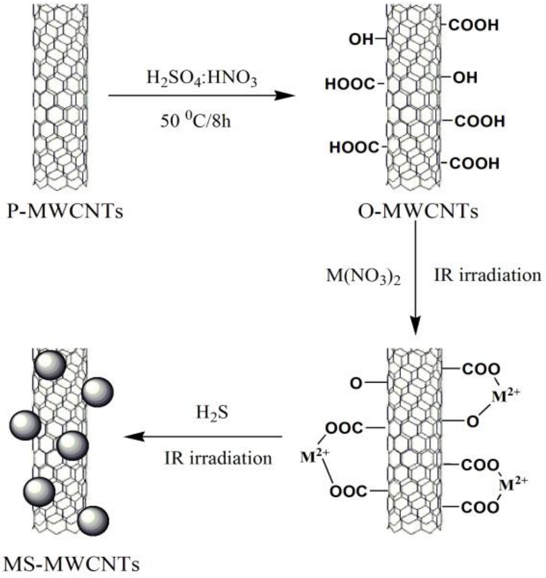

Fig 1: Schematic of various steps involved in the immobilization of metal sulfides on O-MWCNT (M = Cu/Zn/Cd)

Finally the bound metal ions were reacted with hydrogen sulfide to immobilize the metal sulfide nanocrystals on O-MWCNTs.

The PXRD patterns of the hybrids and O-MWCNTs are shown in Figure 2. In all the cases, the diffraction peaks at 2θ = 25.3o and 43.1o are due to (002) and (100) hkl reflections of the graphitic structure of MWCNTs. The peaks at 2θ = 32.9o and 48.1o in the PXRD pattern of CuS-MWCNT (Figure 2b) indicates the formation of pure hexagonal covellite phase (JCPDS no. 06-0464) of CuS in the hybrid.

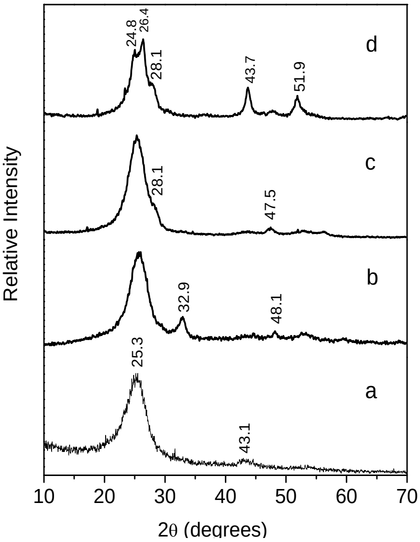

Fig 2: PXRD patterns of O-MWCNT (a), CuS-MWCNT (b), ZnS-MWCNT (c), and CdS-MWCNT (d)

The formation of the cubic sphalerite phase (JCPDS no. 05-0566) of ZnS is confirmed by the presence of peaks at 2θ = 28.1o and 47.5o in the PXRD pattern of ZnS-MWCNT hybrid (Figure 2c). Further in case of CdS-MWCNT hybrid (Figure 2d), hexagonal greenockite phase (JCPDS no. 41-1049) of CdS is formed, which is evident from the presence of peaks at 2θ = 24.8o, 26.4o, 28.1o, 43.7o and 51.9o. The formation of only the pure phases of metal sulfide nanocrystals without any impurities in the hybrids indicates that the method employed here is general and very efficient for the preparation of CNT based hybrids.

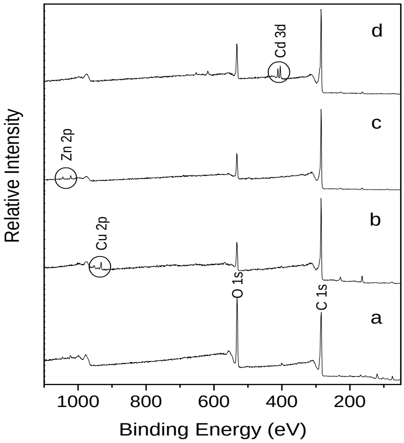

Fig 3: General survey XPS spectra of O-MWCNT (a), CuS-MWCNT (b), ZnS-MWCNT (c), and CdS-MWCNT (d)

The chemical composition and the electronic state of the metals in the hybrids were determined by XPS analysis. The XPS general survey spectra of O-MWCNTs and the hybrids are shown in Figure 3, while high resolution XPS spectra of the hybrids are shown in Figure 4. The oxidation of CNTs is confirmed by the presence of the O 1s peak in the XPS spectrum of O-MWCNTs [30] (Figure 3a).

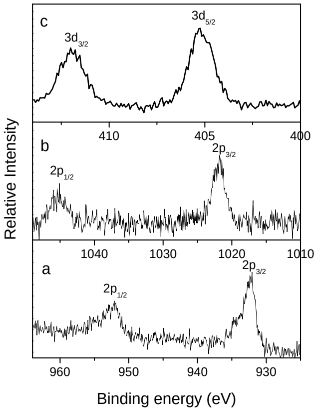

Fig 4: High resolution XPS spectra of CuS-MWCNT (a), ZnS-MWCNT (b), and CdS-MWCNT (c)

It was calculated from the XPS spectrum (Figure 3a) and found that there was about 26 % of oxygen in comparison to 74 % carbon in O-MWCNTs. The peaks with the binding energy of 164 eV in the hybrids (Figures 3b to 3d, very low intense peaks) is due to the S 2p3/2 from the corresponding metal sulfides indicating that sulfur is in -2 oxidation state [31].

The well resolved peaks in the high resolution spectrum of CuS-MWCNT (Figure 4a) with the binding energies of 932.5 and 953 eV corresponds to Cu 2p3/2 and Cu 2p1/2, respectively, and indicate that copper is present in +2 oxidation state [31]. Further the electronic state of zinc is found to be +2 as can be seen from the presence of peaks due to Zn 2p3/2 and Zn 2p1/2 with the binding energies of 1021.8 and 1045 eV in XPS spectrum of ZnS-MWCNT hybrid (Figure 4b) [31]. The oxidation state of cadmium in the CdS-MWCNT hybrid is determined from the high resolution XPS spectrum (Figure 4c) which shows the peaks due to Cd 3d5/2 and Cd 3d3/2 with the binding energies of 405.1 and 412 eV respectively, and found that cadmium is in +2 oxidation state [31].

The FTIR spectra shown in Figure 5 are recorded to understand the chemical state and nature of bonding in the hybrids. The broad peak observed around 3440 cm^{-1} in all the spectra is due to O-H stretching frequencies of acidic functional groups on the O-MWCNTs and possibly of water molecules, which might have adsorbed on the sample during washing and exposure to atmosphere during measurements. The peak at 1627 cm^{-1} is attributed to the bending mode of water molecules. The peak observed at 1717 cm^{-1} in O-MWCNTs (Figure 5a) is due to the C=O stretching frequency, indicating the presence of carboxylic groups created during the oxidation of P-MWCNTs.

In order to understand the interaction of M^{2+} ions of sulfides with CNTs, the FTIR spectra are enlarged in the range 1500 to 2000 cm^{-1} as shown in Figure 6. It is evident that the intensity of the peak due to C=O stretching frequency is decreased in all the hybrids (Figure 6b-d) in comparison with O-MWCNTs (Figure 6a) indicating that the metal sulfide nanocrystals are immobilized on the MWCNTs through bonding between M^{2+} ions and functional groups of the MWCNTs [32].

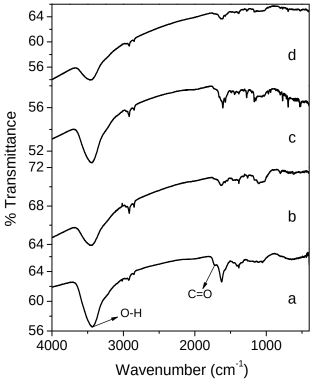

Fig 5: FTIR spectra of O-MWCNT (a), CuS-MWCNT (b), ZnS-MWCNT (c), and CdS-MWCNT (d).

Furthermore, the C=O stretching frequency of the hybrids (Figure 6b-d) has shifted from 1717 to 1735 cm^{-1} corroborating the presence of bonding between M2+ ions of sulfides and functional groups of MWCNTs [33]. In the case of the hybrids prepared in absence of IR irradiation, the intensity of the C=O stretching frequency remained almost the same in comparison with O-MWCNTs (Figure 7). This indicates that IR irradiation played an important role in facilitating the interaction between M^{2+} ions and functional groups of the MWCNTs, which in turn resulted in immobilization of uniformly distributed metal sulfide nanocrystals on O-MWCNTs.

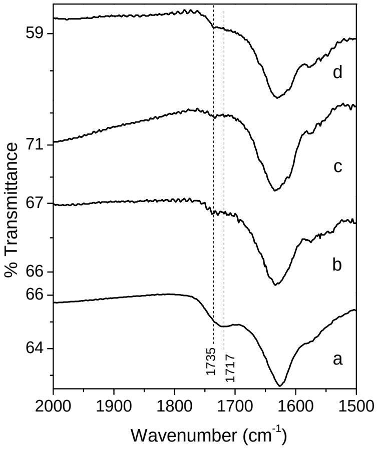

Fig 6: FTIR spectra of O-MWCNT (a), CuS-MWCNT (b), ZnS-MWCNT (c), and CdS-MWCNT (d) shown in the range 1500 to 2000 cm^{-1}.

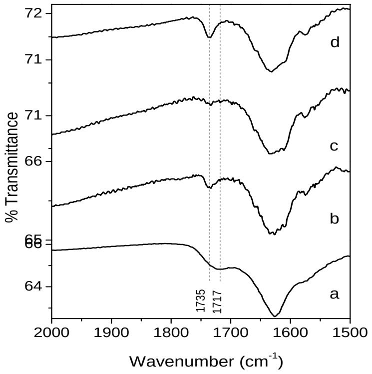

Figure 7: FTIR spectra of O-MWCNT (a), CuS-MWCNT (b), ZnS-MWCNT (c) and CdS-MWCNT (d) prepared without IR irradiation shown in the range 1500 to 2000 cm^{-1}.

The morphologies of the O-MWCNTs and the hybrids are studied by FE-SEM (Figure 8). Figure 8a shows the highly entangled nature of MWCNTs. The metal sulfide nanocrystals are uniformly distributed on the MWCNTs as can be seen from their images (Figure 8b-d). All three hybrids contain metal sulfide nanocrystals of sizes in the range of 15 to 20 nm (Figure 8b-d). The size of the CdS nanocrystals in CdS-MWCNT hybrid (Figure 8d) appear to be much bigger (around 40 nm) than the other two hybrids, however close investigation reveals that each aggregate consists of smaller aggregates of the size around 17 nm.

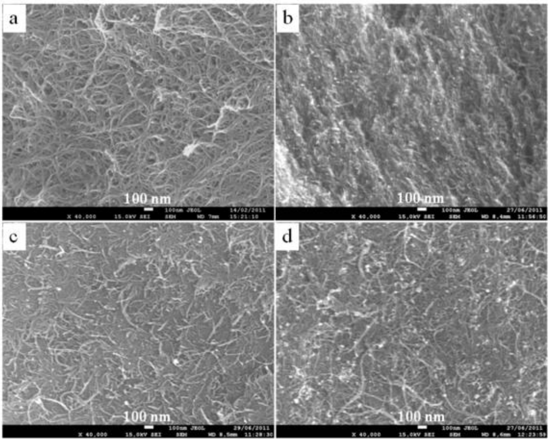

Figure 8: FE-SEM images of O-MWCNT (a), CuS-MWCNT (b), ZnS-MWCNT (c), and CdS-MWCNT (d).

The EDX spectral analysis of all the hybrids (not shown) shows that the mass percentage of the metal on MWCNTs is around 19-20 % indicating that almost all of the metal loaded initially is immobilized on the surface of O-MWCNTs.

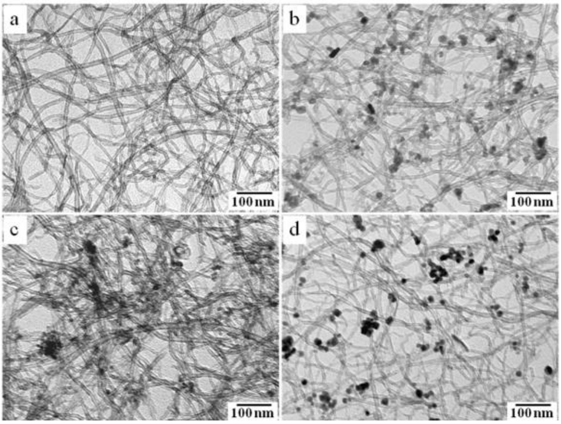

Figure 9: TEM images of O-MWCNT (a), CuS-MWCNT (b), ZnS-MWCNT (c), and CdS-MWCNT (d).

The TEM images of the O-MWCNTs and the hybrids are shown in Figure 9. The diameter of the CNTs (Figure 9a) is in the range of 10 to 12 nm. The presence of relatively continuous strands of CNTs without any fragments indicates that the CNTs are quite stable to acid treatment. The TEM images of metal sulfide immobilized hybrids indicate that the nanocrystals are largely monodispersed over CNTs. The particle sizes of CuS nanocrystals in the hybrids (Figure 9b) is around of 20 nm, while the ZnS nanocrystals (Figure 9c) are in the range of 9 to 12 nm. In case of CdS-MWCNTs hybrid (Figure 9d) the size of the nanocrystals are in the range of 17 to 20 nm. The presence of nanocrystals only on the surface of the CNTs indicates the effective interaction between nanocrystals and CNTs.

When we attempted to prepare the hybrids without IR irradiation we met with limited or no success as is evident from their TEM images (Figure 10). Owing to the poor interaction between the M^{2+} ions and functional groups of the MWCNTs in absence of IR irradiation, very few M^{2+} ions were attached to the CNTs surface. When the hydrogen sulfide gas was passed, the M^{2+} ions attached to the CNTs surface acted as nuclei for the rest of the M^{2+} ions, which are not attached to CNTs surface, resulting in formation of larger aggregates of metal sulfides. Further it can be seen that most of the nanocrystals are not attached to the CNTs surface, but grown out of the nanocrystals which are already attached to the surface (Figure 10).

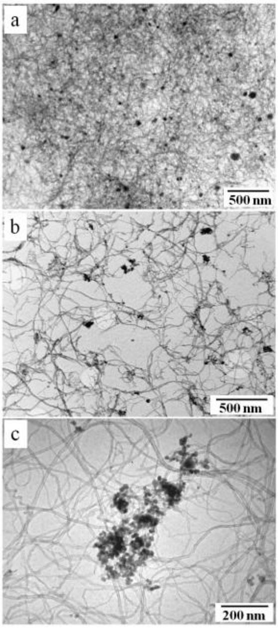

Figure 10: TEM images of CuS-MWCNT (a), ZnS-MWCNT (b), and CdS-MWCNT (c) prepared without IR irradiation.

Even though there are several reports of the preparation of the CNT-metal sulfide hybrids, this is the first time the application of IR irradiation is reported for preparing such hybrids using hydrogen sulfide as the source of sulfide ion. We have made use the photoabsorption and photothermal properties of CNTs in presence of the IR irradiation for the immobilization of metal sulfide nanocrystals on the surface of oxygenated MWCNTs. We have earlier shown that controlled decoration of MWCNTs with copper/copper oxide nanocrystals could be achieved through the application of IR irradiation [34]. In general IR irradiation raises the temperature of the MWCNTs in solution due to the photothermal conversion of the radiation by CNTs, which facilitates the interaction between the metal ions and the acidic functionalities on the CNTs. On reacting metal bound MWCNTs with hydrogen sulfide, uniformly distributed metal sulfide nanocrystals immobilized on MWCNTs could be achieved. The effectiveness of the application of IR irradiation is further proved by the fact that no such uniform immobilization could be realised when IR irradiation was not employed.

4. Summary

A simple and efficient wet chemical method is reported for the immobilization of metal sulfide nanocrystals on the surface of oxygenated MWCNTs. The photothermal property of the CNTs, facilitated by the IR irradiation is the key step in the effective immobilization of nanocrystals on CNTs. The use of the hydrogen sulfide as the sulfide source makes this method quick and convenient. The method employed here is general for the preparation of metal sulfide nanocrystals immobilized CNT hybrids, which might have applications in the field of photocatalysis, electronic and optical devices. As future perspectives, it would be interesting to study the effect of IR irradiation on CNT based hybrids with varieties of guest species, varying the loading of guest species and extent of oxidation of CNTs.

References

[1] P. J. F. Harris, *Carbon nanotube science: synthesis, properties and applications*, Cambridge University Press, 2009, pp. 146-199.

[2] E. T. Thostenson, Z. Renb, T. S. Choua, “Advances in the science and technology of carbon nanotubes and their composites: a review”, *Composites Science and Technology* 2001, 61(13):1899–912.

[3] T. W. Odom, J. L. Huang, P. Kim, C. M. Lieber, “Structure and Electronic Properties of Carbon Nanotubes”, *J. Phys Chem B,* 104(13), pp. 2794-809, 2000.

[4] S. Iijima, “Helical microtubules of graphitic carbon”, *Nature,* vol 354, pp. 56-58, 1991.

[5] G. G. Wildgoose, C. E. Banks, R. G. Compton, “Metal nanoparticles and related materials supported on carbon nanotubes: methods and applications”. *Small,* 2(2), 182-193, 2006.

[6] M. Cadek et al., “Reinforcement of polymers with carbon nanotubes: The role of nanotube surface area”, *Nano Lett,* 4(2), 353-6, 2004.

[7] N. S. Lee et al., “Application of carbon nanotubes to field emission displays”, *Diamond and Related Materials,* 10(2), 265-70, 2001.

[8] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, “Carbon nanotubes- the route toward applications”. *Science,* 297, 787-92, 2002.

[9] S. Banerjee, M. G. C. Kahn, S. S. Wong, “Rational chemical strategies for carbon nanotube functionalization:, *Chem Eur J.,* 9(9), 1898-908, 2003.

[10] D. Bera et al., “Quantum dots and their multimodal applications: a review”, *Materials,* 3, 2260-345, 2010.

[11] B. R. Venugopal et al., “Layered double hydroxide-CdSe quantum dot composites through colloidal processing: effect of host matrix-nanoparticle interaction on optical behaviour”, *J Phys Chem B,* 110(2), 772-6, 2006.

[12] C. Nethravathi, “Graphene–nanocrystalline metal sulphide composites produced by a one-pot reaction starting from graphite oxide”. *Carbon,* 47(8), 2054-9, 2009.

[13] M. Moffitt, H. Vali, A. Eisenberg, “Spherical assemblies of semiconductor nanoparticles in water-soluble block copolymer aggregates”. *Chem Mater,* 10(4), 1021-8, 1998.

[14] Y. Zhao et al., “A simple route to synthesize carbon-nanotube/cadmium-sulfide hybrid heterostructures and their optical properties”, *J Solid State Chem,* 182(4), 875–80, 2009.

[15] C. Li et al, “Decoration of multiwall nanotubes with cadmium sulfide nanoparticles”, *Carbon,* 44(10), 2021-6, 2006.

[16] Z. Lei et al., “Preparation and characterization of carbon nanotubes-polymer/CdSe hybrid nanocomposites through combining electrostatic adsorption and ATRP technique”. *Colloid Surface A,* 324(1-3), 131-6, 2008.

[17] J. Liu, X. Li, L. Dai, “Water-assisted growth of aligned carbon nanotube–ZnO heterojunction arrays”, *Adv Mater,* 18(13), 1740-4, 2006.

[18] S. Banerjee, S. S. Wong, “In-situ growth of ‘fused’, ozonized single-walled carbon nanotubes—CdTe quantum dot junctions”, *Adv Mater,* 16(1), 34-7, 2004.

[19] S. Banerjee, S. S. Wong, “Synthesis and characterization of carbon nanotube-nanocrystal heterostructures”, “*Nano Lett,* 2(3), 195-200, 2002.

[20] S. W. Lee, W. M. Sigmund, “Formation of anatase TiO2 nanoparticles on carbon nanotubes”, *Chem Commun,* 780-1, 2003.

[21] H. Y. Si et al., “Shell-controlled photoluminescence in CdSe/CNT nanohybrids”, *Nanoscale Res Lett,* 4, 1146-52, 2009.

[22] A. Capobianchi et al., “Controlled filling and external cleaning of multi-wall carbon nanotubes using a wet chemical method”, *Carbon,* 45(11), 2205-8, 2007.

[23] Q. Huang, L. Gao, “Synthesis and characterization of CdS/multiwalled carbon nanotube heterojunctions”, *Nanothechnolgy,* 15, 1855-60., 2004

[24] J. Cao et al., “Carbon nanotube/CdS core–shell nanowires prepared by a simple room-temperature chemical reduction method”, *Adv Mater,* 16(1), 84-87, 2004.

[25] E. Miyako et al., "Carbon nanotube–polymer composite for light-driven microthermal control", *Angew Chem Int Ed,* 47(19), 3610-3, 2008.

[26] S. J. Pastine, et al., "Chemicals on demand with phototriggerable microcapsules", *J Amer Chem Soc,* 131(38), 13586-87, 2009.

[27] T. Fujigaya et al., "NIR laser-driven reversible volume phase transition of single-walled carbon nanotube/poly(N-isopropylacrylamide) composite gels", *Adv Mater,* 20(19), 3610-4, 2008.

[28] S. Ghosh et al., "Increased heating efficiency and selective thermal ablation of malignant tissue with DNA-encased multiwalled carbon nanotubes", *ACS Nano,* 3(9), 2667-73, 2009.

[29] V. Datsyuk et al. "Chemical oxidation of multiwalled carbon nanotubes". *Carbon,* 46(6), 833-40, 2008.

[30] G. Zhang et al., "The surface analytical characterization of carbon fibers functionalized by H2SO4/HNO3 treatment", *Carbon,* 46(2), 196-205, 2008.

[31] J. F. Moulder et al., *Handbook of X-Ray photoelectron spectroscopy*, Eden, Paris: Perkin-Elmer, 1992.

[32] Q. Huang, L. Gao, "Synthesis and characterization of CdS/multiwalled carbon nanotube heterojuntions:, *Nanotechnology,* 15, 1855-60, 2004.

[33] Q. Huang, L. Gao, "Immobilization of rutile TiO2 on multiwalled carbon nanotubes:, *J Mater Chem,* 7, 1517-9, 2003.

[34] P. Martis, "Infrared irradiation controlled decoration of multiwalled carbon nanotubes with copper/copper oxide nanocrystals", *Acta Materialia,* 59(12), 5040-7, 2011.