Multifunctional CNTs nanohybrids decorated with magnetic and fluorescent nanoparticles layer-by-layer

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Abstract. $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites, which were prepared by polyol-medium *in situ* high-temperature decomposition of $\text{Fe}(\text{acac})_3$ using PVP as stabilizing agent and modified with SDS, were further decorated with high-quality ZnS nanocrystal via a wet technique in glycol solution. The obtained $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ nanohybrids were characterized by XRD, FT-IR, Raman microscope, TEM, EDS, XPS, VSM and fluorophotometers. Results indicated that magnetic Fe_3O_4 nanoparticles and fluorescent ZnS nanocrystal were uniformly dispersed on the surface of CNTs layer-by-layer with PVP and SDS as stabilizing agent and ion-capture agent, respectively. The novel multi-functional nanohybrids exhibit super-paramagnetic properties with a saturation magnetization about 6.795 emu g^{-1} at room temperature and show a strong emission band at 367 nm with a broad shoulder around 342–483 nm due to the interactions and/or background emissions of Fe_3O_4 and CNTs. The superparamagnetic and fluorescent properties of obtained products are promising for potential applications in magnetically guided and fluorescence tracing drug delivery systems.

Keywords. Magnetic materials; multilayers; luminescence; magnetic properties.

1. Introduction

Carbon nanotubes (CNTs), discovered by Iijima (1991) and Robertson (1970), have attracted a great deal of attention in the last decade due to their various interesting properties such as small dimensions, high anisotropy and their fascinating one-dimensional (1D) tubular structures (Gao *et al* 2006). The combining of nanocomponents with different natures into novel hybrid systems opens wide possibilities for the design and creation of new nanosystems and nanomaterials with advanced or even novel properties and functional advantages that are important for real-world applications (Khomutov 2008). Therefore, over the years, considerable effort has been devoted to decorate carbon nanotubes with inorganic nanoparticles such as magnetic nanoparticles (Wu *et al* 2008; Liu *et al* 2009a), quantum dots (Zhou *et al* 2003; Shan and Gao 2006; Guo *et al* 2008; Shubayev *et al* 2009), nanoscale metal elements (Lafdi *et al* 1996; Peng and Wong 2009), etc. The obtained nanocomposites can improve or impart new optical, electrochemical, magnetic and mechanical properties of CNTs (Morales-Cid *et al* 2010). Especially, CNTs nanocomposites combined with magnetic and fluorescent nanoparticles permit magnetic manipulation with simultaneous fluorescent observations (Chen *et al* 2010; Ruan *et al* 2010), which will contribute for rapid development of new therapeutic and diagnostic concepts in all the areas of

medicine (Whitesides 2003; Shi 2009; Shi *et al* 2009; Chen *et al* 2010; Ruan *et al* 2010), such as advanced magnetic resonance imaging (MRI), guided drug, gene delivery (Ruan *et al* 2010), magnetic hyperthermia, cancer therapy (Wang *et al* 2005; Hergt *et al* 2006), biosensors (Qu *et al* 2007; Hu *et al* 2008), cell tracking and bioseparation (Shubayev *et al* 2009) and the therapy for oncology and infectious diseases (Prato *et al* 2008), etc. Moreover, it still remains a tremendous challenge to find a simple and effective approach for the manufacture of magnetic-fluorescent nanohybrids.

Various chemistry-based processing routes have been developed to synthesize $\text{Fe}_3\text{O}_4/\text{CNTs}$ magnetic nanocomposite. Stoffelbach *et al* (2005) achieved magnetic functionalization of CNTs by adding a solution of positively charged Fe_3O_4 nanoparticles to the negatively charged carboxylate-grafted CNTs. Korneva *et al* (2005) produced magnetic tubes by filling CNTs with paramagnetic-iron oxide particles, in which the CNTs were made via chemical vapour deposition onto alumina membranes with an average outer diameter of 300 nm. There are also some methods developed to decorate CNTs with quantum dot. Feng *et al* (2008) manufactured CNTs attached with ZnS nanocrystals by a reaction between $\text{Zn}(\text{NO}_3)_2$ and Na_2S in an aqueous suspension of CNTs. Shan and Gao (2006) developed a new wet-chemical method to coat multi-walled carbon nanotubes (MWNTs) with wurtzite ZnS nanocrystals and modify them with polyethylenethiamine or sodium dodecyl sulfate. Chen *et al* (2010) used a simple and novel layer-by-layer (LBL) assembly in combination with covalent connection strategy

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in order to synthesize multifunctional carbon nanotubes (CNTs)-based magnetic-fluorescent nanohybrids. However, they first prepared superparamagnetic iron oxide nanoparticles (SPIO) and near-infrared fluorescent CdTe quantum dots, respectively and then both SPIO and CdTe were covalently coupled on the surface of CNTs in sequence via LBL assembly.

The main purpose of our present work is to demonstrate a simple and convenient procedure for the synthesis of ZnS/Fe₃O₄/CNTs nanohybrids. Herein, first, CNT-based magnetic (Fe₃O₄/CNTs) were synthesized by polyol-medium *in situ* high-temperature decomposition and then the modified Fe₃O₄/CNTs nanocomposites were further decorated with ZnS nanocrystal by a wet technique in glycol solution. In our work, the main advantage is that both Fe₃O₄ and ZnS can be uniformly dispersed on the surface of the CNTs. Furthermore, our method makes it possible to fabricate multifunctional CNTs hybrids with other magnetic particles and quantum dots layer-by-layer.

2. Experimental

2.1 Chemicals

The raw CNTs (multi-wall CNTs, diameter: 40–60 nm, purity: 95–98%) were kindly provided by Shenzhen Nanotechnologies Co. Ltd., China. Poly(−sodium 4-styrenesulfonate) (PSS, Mw = 70,000 g mol^{−1}) was purchased from Aldrich. Other reagents such as iron(III) acetylacetonate (Fe(acac)₃), ferric trichloride hexahydrate (FeCl₃ · 6H₂O), zinc chloride (ZnCl₂), triethylene glycol (TREG), ethylene glycol (EG), thiourea, polyvinyl pyrrolidone (PVP-30), ethylene diamine tetraacetic acid (EDTA), L-sodium tartrate and sodium lauryl sulfate (SDS), used in this work were of AR grade and purchased from Sinopharm Chemical Reagent Co. Ltd. without further purification.

2.2 Purification of CNTs

Purification of CNTs was reported in our initial work (Liu *et al* 2009b). The CNTs were purified by refluxing the commercial CNTs in mixed solution of concentrated sulfuric and nitric acids (1:3 by volume) at 80 °C with constant stirring for 6 h. Then, the mixture was filtered and rinsed with distilled water several times until pH value reached neutral, and filtered and dried in vacuum at 60 °C for further use.

2.3 Preparation of Fe₃O₄/CNTs nanocomposites

Fe₃O₄/CNTs nanocomposites were prepared by polyol-medium *in situ* high-temperature decomposition. 0.1 g purified CNTs were dispersed in 50 mL TREG by sonication for 30 min, and then 0.353 g iron(III)acetylacetonate (Fe(acac)₃) and 0.5 g polyvinyl pyrrolidone (PVP-30) were added to the mixture to form a clear solution. First, the mixture was slowly heated to 180 °C for 30 min in an oil bath, then fast

heated to 280 °C and kept refluxing for 2 h. The mixture was under vigorous stirring and protected by N₂ during the process. After cooling down to room temperature, the solution was washed with ethanol and ethyl acetate (Cai and Wan 2007). Subsequently, a black magnetic powder was obtained by further drying and grinding.

2.4 Preparation of ZnS/Fe₃O₄/CNTs nanohybrids

The obtained Fe₃O₄/CNTs nanocomposites were further decorated with high-quality ZnS nanocrystal via modified wet technique in glycol solution. The samples prepared were dissolved in the solution of 5 wt% SDS, after sonication for 20 min and stirring for 2 h, the products were centrifuged for three times, washed with distilled water and dried in vacuum at 60 °C for further use (Shan and Gao 2006).

The products obtained were dispersed in 50 mL 1 M ZnCl₂ glycol solution in 250 mL flask by stirring for 30 min and heated to 100 °C, then 50 mL 1 M thiourea glycol solution was rapidly added, while the mixture was heated to 150 °C. The mixture was kept at a reflux for 2 h under vigorous stirring (Wang *et al* 2006). Finally products were washed with ethanol several times and dried in vacuum at 60 °C.

2.5 Characterization

The magnetic ZnS/Fe₃O₄/CNTs nanohybrids were characterized by Fourier transform infrared (FT-IR, MB154S, Bomen, Canada), Raman microscope (Renishaw inVia), X-ray diffractometer (XRD, D/max 18 kV, Bruker D8 Super Speed) with CuK α radiation, transmission electron microscopy (TEM, accelerating voltage/120 kV, Philips Tecnai 12), energy-dispersive X-ray spectrometry (EDS, Philips XL-30), X-ray photoelectron spectra (XPS) (VG ESCALAB MK II electron energy spectrometer using Mg KR (1253.6 eV) as the X-ray excitation source), vibrating sample magnetometer (VSM, EV7, ADE, USA) and fluorophotometer (LS-50B, Perkin-Elmer), respectively.

3. Results and discussion

Figure 1 shows scheme of coating of carbon nanotubes (CNTs) with Fe₃O₄ and ZnS nanoparticles layer-by-layer. Commercial CNTs were purified with the mixtures of concentrated H₂SO₄/HNO₃ to remove the amorphous carbon, carbon nanoparticles and metal catalyzer. Preferentially nitric/sulfuric acid treatments have been proved to be effective for the creation of oxygen-containing surface groups on CNTs which become negatively charged. Fe₃O₄ nanoparticles were obtained by a polyol process on the surface of purified CNTs. During the polyol process, first, the iron salt Fe(acac)₃ was decomposed at 180 °C, and then the positively charged nuclei adsorbed on the negatively charged surface of purified CNTs and grew under fast-rising temperature of 280 °C to form Fe₃O₄ nanocrystals. SDS was used

Figure 1. Schematic illustration of coating of carbon nanotubes (CNTs) with Fe_3O_4 and ZnS nanoparticles layer-by-layer.

Figure 2. XRD patterns of $\text{Fe}_3\text{O}_4/\text{CNTs}$ (a) and $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ (b: 2 h, c: 3 h). Symbols ($\diamond$), ($\circ$) and (∇) represent peaks of CNTs, Fe_3O_4 and ZnS, respectively.

as an anion surfactant to modify $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites due to the strong electrostatic attraction with metal ions. So Zn^{2+} ions in the ethylene glycol solution are beforehand adsorbed on the negatively charged surface of modified $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites, and *in situ* formed ZnS as seen in the following discussion.

Figure 2 illustrates XRD patterns of $\text{Fe}_3\text{O}_4/\text{CNTs}$ and $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites (modified with SDS). In figure 2(a), we can see that the diffraction peak at $2\theta = 26.4^\circ$ (labelled with $\diamond$) is the typical Bragg peak of CNTs. The diffraction peaks (labelled with $\circ$) located at 30.66° , 35.64° , 43.18° , 53.5° , 57.24° and 62.74° matched well with the JCPDS

cards no. 88-315 of cubic Fe_3O_4 . Figure 2(b and c) is the XRD patterns of $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ with different reaction times of 2 and 3 h, the diffraction peaks (labelled with ∇) matched well with the JCPDS cards no. 01-0677 of Wurtzite and no. 12-0688 of Wurtzite-10H, respectively. It can be seen that the crystal structure of ZnS has changed slightly because of the extended reaction time. The diffractive peaks of ZnS are broadened, implying that the crystalline size of ZnS particles is quite small.

The structures and morphologies of the raw CNTs, purified CNTs and their corresponding magnetic $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites are determined by TEM shown in figure 3,

Figure 3. TEM images of (a) raw-CNTs and (b) purified-CNTs; TEM images of (c) Fe_3O_4 /raw-CNTs and (d) Fe_3O_4 /purified-CNTs (1 mmol $\text{Fe}(\text{acac})_3$, 0.5 g PVP); ED pattern of Fe_3O_4 /CNTs. The bar of (d) is 100 nm.

Figure 4. FT-IR spectra of CNTs (a) before and (b) after purification and Raman spectrum of purified CNTs (c).

respectively. Comparing with the original CNTs shown in figure 3(a and b) reveals that the purified CNTs, with a diameter of 40–60 nm, present well graphitized walls, well dispersity and basically have no extra materials. The raw CNTs were decorated with Fe_3O_4 nanoparticles first shown in figure 3(c) and Fe_3O_4 nanoparticles unevenly diffused around the raw CNTs. In contrast, purified CNTs were uniformly coated with a dense layer of Fe_3O_4 nanoparticles,

indicating that our method is of high efficiency. The uniform Fe_3O_4 nanoparticles on the surface of CNTs are spherical and about 7–8 nm in diameter can be seen in figure 3(d). As can be seen from figure 3(e), the obtained Fe_3O_4 nanoparticles are polycrystalline structures.

FT-IR and Raman spectra were introduced to study the surface properties of raw CNTs and purified CNTs as shown in figure 4 which may reveal the mechanism of coating

the CNTs with Fe_3O_4 nanoparticles. No characteristic peak appeared in FT-IR spectrum of raw CNTs shown in figure 4(a). In such a case of commercial CNT, it has to be noticed that such a material does not possess high amount of functional groups on its surface and mainly surface defects can be considered as anchoring sites for metals (Philippe *et al* 2003). Concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ treatment is the most common method and it has been shown that surface oxygenic-functional groups like carboxylic groups can be introduced on the outer and possibly inner walls of the CNTs. Compared

to the raw CNTs, FT-IR spectrum of the CNTs purified with concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ is shown in figure 4(b). The peaks at 1635 cm^{-1} and 1385 cm^{-1} are the characteristic absorption peaks of $\text{C}=\text{O}$ and $-\text{OSO}_3\text{H}$, respectively and the peak at $3300\text{--}3500\text{ cm}^{-1}$ is the characteristic absorption peak of $-\text{OH}$, illuminating that there are abundant hydrophilic groups on the surface of purified CNTs. The functional groups provide feasibility for electrostatic reaction for the coating of CNTs. The purified CNTs were further studied via Raman spectrum shown in figure 4(c). The first-order

Figure 5. TEM images of (a) Fe_3O_4 nanoparticles prepared by polyol process; (b) $\text{Fe}_3\text{O}_4/\text{CNTs}$ using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as iron salt; (c) $\text{Fe}_3\text{O}_4/\text{CNTs}$ at initial reaction stage; (d) $\text{Fe}_3\text{O}_4/\text{CNTs}$ ($0.1\text{ mmol Fe}(\text{acac})_3$); (e) $\text{Fe}_3\text{O}_4/\text{CNTs}$ ($10\text{ mmol Fe}(\text{acac})_3$) and (f) $\text{Fe}_3\text{O}_4/\text{CNTs}$ ($1\text{ mmol Fe}(\text{acac})_3$, 1 g PVP). Bars of (a, d–f) are 100 nm and (b, c) are 50 nm .

Raman spectrum of purified CNTs shows strong sharp peak at 1580 cm^{-1} (G line), The G band is a double degenerated phonon mode (E_{2g} symmetry) at the Brillouin zone centre that is Raman active for sp^2 -carbon networks (Pimenta *et al* 2007). One of the most unusual properties of CNTs is that the Raman spectrum shows an additional band at 1342 cm^{-1} (D line) and a weak band at around 1611 cm^{-1} (D' line) in figure 4(c). The origins of the D and D' lines in other forms of carbon materials have been explained as disorder-induced features due to the finite particle size effect or lattice distortion. In other words, the relative intensity of 1342 cm^{-1}

mode with respect to 1580 cm^{-1} mode depends on the crystal planar domain size of graphite (Li *et al* 1997). The strong peak located at 2689 cm^{-1} (2D line), which corresponds to the overtone of the D band, originated from a double resonance (DR) Raman process (Saito *et al* 2003). The weak peak at 2900 cm^{-1} is owing to the import of hydrogen impurity in the purification process. The results of Raman spectrum agrees well with the conclusion of FT-IR spectra, which eventually bear out that there are a great deal of active sites on the surface of CNTs purified with concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$.

Figure 6. TEM images of $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ with or without stabilizer. $\text{Fe}_3\text{O}_4/\text{CNTs}$ were modified with (a) no surfactant; (b) PVP; (c) EDTA; (d) L-sodium tartrate and (e, f) SDS. Difference of (e) and (f) is: (e) add zinc source firstly and (f) add sulfur source. Bars of (a, c, d), (b, e) and (f) are 100, 200 and 20 nm, respectively.

The polyol process, widely used to provide monodispersion of fine metal or metal-oxide nanoparticles, is used to control the nucleation and growth steps of the particles. Their nanometer scale and narrow-size distribution can be explained by a fast nucleation along with a growth step controlled by the rate of hydrolysis reaction and/or diffusion of the dissolved species towards the surface of the particles (Ammar *et al* 2001). In the previous work, the author prepared Fe_3O_4 nanoparticles by polyol process using $\text{Fe}(\text{acac})_3$ as iron salt and TREG as high boiling point solvent and reductant as shown in figure 5(a). Fe_3O_4 nanoparticles are spherical with 12.5 nm in diameter and gather together slightly. Our group have prepared $\text{Fe}_3\text{O}_4/\text{CNTs}$ successfully by using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as iron salt and the TEM image is shown in figure 5(b) in which CNTs were incompletely coated with a spot of quadrate- Fe_3O_4 nanocrystals. Here, we used the purified CNTs as the inhibition templates and/or substrates for the growth of Fe_3O_4 nanoparticles on their surface. As a well known method of purification of CNTs, the use of mixtures of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ has been proved effective in introducing various functional groups such as carboxyl, carbonyl and phenolic groups onto the surface of CNTs which become negatively charged (Yu *et al* 1998; Gregory *et al* 2006). As the conclusion of FT-IR and Raman spectra in figure 4, there are hydrophilic groups such as $\text{C}=\text{O}$ and $-\text{OSO}_3\text{H}$ on the surface of CNTs purified with concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$. The negative functional groups provide active points for interaction with metal ions and the oxidants effectively opened the nanotubes, but the essential structural features were still present at the end of the treatment as can be seen from figure 3(b) (Satishkumar *et al* 1996). In our case, as shown in figure 5(c), upon introduction of iron salts into the system, some of the ion (III) acetylacetonate would be *in situ* decomposed to be small soluble Fe_3O_4 nuclei and the surface functional groups could catch and strongly bond with positive Fe_3O_4 nuclei through electrostatic attraction and serve as nucleation centres (Wang *et al* 2006). At the same time, the polyol solution (TREG), which acts as reducing agent and stabilizer, reduce iron (III) salt to magnetite and prevent further gathering to give a monodispersity of Fe_3O_4 on the surface of CNTs due to great viscosity. In the following heating process, Fe_3O_4 nuclei crystallized into ferrite nanocrystallites. When the amount of $\text{Fe}(\text{acac})_3$ changed from 0.1 mmol to 10 mmol, density of the coated layer became more dense. Comparing with 1 mmol $\text{Fe}(\text{acac})_3$ used in figure 3(d), a few of Fe_3O_4 nanoparticles was attached to the surface of CNTs and most of the CNTs were bare in figure 5(d) (0.1 mmol $\text{Fe}(\text{acac})_3$). When an excess of $\text{Fe}(\text{acac})_3$ (10 mmol) were used, the CNTs were compactly coated with a mass of Fe_3O_4 nanoparticles in figure 5(e). However, some free Fe_3O_4 nanoparticles gathered around CNTs indicating that excess Fe_3O_4 nanoparticles cannot be attached completely to the negatively charged surface of CNTs. Surfactant (PVP), have well-colloid protection and film-forming ability, acted as dispersant, stabilizer and thickener in the polyol process to prevent gathering among the Fe_3O_4 nuclei. However, in figure 5(f) (CNTs

0.1 g, PVP 1.0 g), the Fe_3O_4 nanoparticles on the carbon nanotubes are less uniformly dispersed than the particles in figure 3(d) (CNTs 0.1 g, PVP 0.5 g), which can be attributed to the increased viscosity by adding excess PVP. The increased viscosity of the reaction mixture inhibit the transmission of Fe_3O_4 nuclei resulting in an increased size of Fe_3O_4 nanoparticles (10.5 nm).

Initially the obtained raw $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites were used as templates for the decoration of ZnS. In figure 6(a), the ZnS nanoparticles were agglomerate around CNTs with a clear dark contrast. Hence, we tried to modify $\text{Fe}_3\text{O}_4/\text{CNTs}$ with several surfactants or complexing agents such as polyvinyl pyrrolidone (PVP), ethylene diamine tetraacetic acid (EDTA), L-sodium tartrate and SDS, and the TEM images are shown in figure 6(b–e), respectively. In figure 6(b), the product was obtained by adding PVP and ZnS nanoparticles were casually dispersed away from the CNTs. Anionic-organic molecules were considered to modify the surface of CNTs. In figure 6(c), when EDTA was introduced to the reaction system, there were nearly few ZnS nanoparticles as can be seen from the TEM image and the surface of some CNTs were bare as compared with the raw $\text{Fe}_3\text{O}_4/\text{CNTs}$ in figure 3(d). Notoriously, EDTA has relatively stronger complexation of iron ion than the complexation between Fe_3O_4 and purified CNTs. Therefore, some of the Fe_3O_4 nanoparticles were captured by EDTA away from the surface of CNTs. L-sodium tartrate, a very important additive which was used to control the formation speed of silver mirror to get an uniform coating, was expected to decorate the CNTs with monodisperse ZnS nanoparticles. In contrast to dark Fe_3O_4 nanoparticles, shallow and thin layer was observed on the surface of CNTs in figure 6(d) illuminating the existence of ZnS. However, the coated effect of ZnS is not as well as SDS-modified $\text{Fe}_3\text{O}_4/\text{CNTs}$ in figure 6(e). $\text{Fe}_3\text{O}_4/\text{CNTs}$ were coated distinctly by a thicker and shallow layer of ZnS nanoparticles which was uniformly dispersed on the surface of CNTs and there were no

Figure 7. FT-IR spectra of (a) $\text{Fe}_3\text{O}_4/\text{CNTs}$ and (b) SDS-modified $\text{Fe}_3\text{O}_4/\text{CNTs}$.

diffuse particles. The successful coating of ZnS indicates that SDS-modified $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites provide negatively charged surface for the electrostatic attraction of positive Zn^{2+} (Shan and Gao 2006). The author also carried out comparative experiment by adding sulfur source first, followed by zinc source to test and verify the electrostatic attraction between negatively charged surface of CNTs and positive Zn^{2+} and TEM image was shown in figure 6(f). The weeny-ZnS particles diffused around the CNTs in contrast to figure 6(e) confirming that SDS was

successfully attached to CNTs. Thiourea decompose to S^{2-} with increasing temperature which was repulsive to the negatively charged $\text{Fe}_3\text{O}_4/\text{CNTs}$ modified by SDS. Therefore, ZnS nanocrystals were formed rapidly and diffused when Zn^{2+} sources were dropped into the flask.

FT-IR spectra were used to analyse the surface of $\text{Fe}_3\text{O}_4/\text{CNTs}$ and SDS-modified $\text{Fe}_3\text{O}_4/\text{CNTs}$ shown in figure 7. As seen from figure 7(a), the peak at 580 cm^{-1} is the stretching

Figure 8. (a) TEM images of SDS-modified $\text{Fe}_3\text{O}_4/\text{CNTs}$ (straggling Fe_3O_4 nanoparticles were labelled with red lines). TEM images of $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$, (b) Na_2S was substituted for thiourea, (c) 0.05 mol thiourea, (d) 0.1 mol thiourea and (e) 0.15 mol thiourea. (f) ED pattern of $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ (0.1 mol thiourea). Bars are 100 nm in addition to figure 8(b) which is 200 nm.

Figure 9. Wide XPS spectra of $\text{Fe}_3\text{O}_4/\text{CNTs}$ (a), expanded XPS spectra of Fe (b) and EDS spectrum of $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ (c).

vibration due to the interaction of $\text{Fe}-\text{O}-\text{Fe}$ in Fe_3O_4 and there is no other significant peak. In figure 7(b), the peaks at 1383, 2918 and 2850.5 cm^{-1} are attributed to the in-plane bending vibration of methyl ($-\text{CH}_3$) and the symmetric and asymmetric vibration of methylene ($-\text{CH}_2-$). The characteristic absorption peaks of the $-\text{OSO}_3$ and $-\text{SO}_3$ are located at 1215 and 1245.5 cm^{-1} , although some peaks are weak, indicating that the $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites were modified with SDS successfully. The peak at 1634.5 cm^{-1} is the characteristic absorption peak of $\text{C}=\text{O}$ due to the purification by concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$. The peak at about 3442 cm^{-1} is assigned to stretching vibration of $-\text{OH}$.

The SDS modified $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites were studied systematically with different sulfur sources and coating quantity. In the process of coating of ZnS, anionic surfactant SDS was used to modify $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites successfully, which was demonstrated by FT-IR spectrum in figure 7(b). However, few Fe_3O_4 nanoparticles, which were labelled with red line in figure 8(a), were desorbed with SDS from the surface of CNTs. Because of the adsorption of abundance of functional groups $-\text{SO}_4^{2-}$, the surface of $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites became more negatively charged and provide a lot of negative-active sites for the adsorption of Zn^{2+} ions through the electrostatic attraction between Zn^{2+} ions and $-\text{SO}_4^{2-}$ groups. Furthermore, the thickness of ZnS coating on the surface of SDS-modified $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites was controlled efficiently by adjusting the molar weight of ZnCl_2 and thiourea such as 0.05, 0.1 and 0.5 mol shown in figure 8(c-e), respectively. ZnS nanoparticles formed uniformly on the surface of $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites with the slow releasing of S^{2-} due to the decomposition of thiourea. The coating layer became thicker with the increased amount of zinc source and sulfur source. Different sulfur sources such as Na_2S was discussed in the study to further expand the mechanism of coating with ZnS and TEM image is exhibited in figure 8(b). The ZnS nanoparticles clustered along the CNTs unequally due to the fast nucleation of ZnS with the rapid ionization of S^{2-} from Na_2S . As can be seen from the ED pattern in

Figure 10. Magnetic hysteresis loops of (a) $\text{Fe}_3\text{O}_4/\text{CNTs}$ and (b) $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ nanohybrids at room temperature.

figure 8(f), the obtained ZnS nanoparticles are polycrystalline structures.

The wide and expanded XPS spectra of $\text{Fe}_3\text{O}_4/\text{CNTs}$ (1 mmol $\text{Fe}(\text{acac})_3$) nanocomposites and EDS spectrum of $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ nanohybrids (0.1 mol ZnCl_2) are shown in figure 9 which further confirmed the existence of both Fe_3O_4 and ZnS nanoparticles on the surface of CNTs. It can be seen that there are elements of C, Fe and O in $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanohybrids and C, Fe, O, Zn and S in $\text{ZnS}/\text{Fe}_3\text{O}_4/\text{CNTs}$ nanohybrids in figure 9(a-c), respectively. The photo-electron lines at binding energy of about 285, 530 and 711 eV are attributed to $\text{C}1s$, $\text{O}1s$ and $\text{Fe}2p$, respectively. As shown in figure 9(b), the peaks located at 711 and 724.9 eV correspond to $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$, respectively which further affirms that the oxide in the sample was Fe_3O_4 . The existence of ZnS can be concluded from the EDS spectrum in figure 9(c) confirming the growth of ZnS on the surface of $\text{Fe}_3\text{O}_4/\text{CNTs}$ magnetic nanocomposites.

Figure 11. Fluorescent emission spectrum of ZnS/Fe₃O₄/CNTs nanocomposites with a broad shoulder.

The magnetic properties of the synthesized magnetic nanohybrids are characterized by vibrating sample magnetometer (VSM) as shown in figure 10. Fe₃O₄/CNTs (1 mmol Fe(acac)₃) and ZnS/Fe₃O₄/CNTs (0.1 mol ZnCl₂) nanohybrids exhibit super-paramagnetic behaviour with a saturation magnetization of about 29.030 and 6.795 emu g⁻¹, respectively which are lower than the value of corresponding pure bulk ferrites (Fe₃O₄, 93 emu g⁻¹). In this case, the reduction of saturation magnetization may be mainly attributed to the smaller size and disfigurement of Fe₃O₄ nanoparticles on the surface (Cattaruzza *et al* 2005; Chiu *et al* 2007). Generally, the introduction of non-magnetic materials such as CNTs and ZnS decrease the saturation magnetization of the nanocomposites. The saturation magnetization of the nanocomposites can be readily tailored via adjusting the density of Fe₃O₄ and ZnS on the surface of the CNTs.

Figure 11 exhibits fluorescent spectrum of ZnS/Fe₃O₄/CNTs. As seen in this figure, emission of ZnS/Fe₃O₄/CNTs nanohybrids is centred at 367 nm with shoulders around 342, 393, 420 and 483 nm. The bands can be assigned to a band-edge emission feature at 342 nm, shallow-donor and acceptor emission peaks at 367 and 393 nm with little red shift, a weak deep-trap emission feature at 420 nm (Yu *et al* 2005) and donor acceptor pair transition (483 nm) in which the acceptor is related to the Zn²⁺ vacancy (Yu *et al* 2009). The emission wavelength of the individual ZnS is a function of size and local environment. One of the main problems is the complexity in the preparation of this nanohybrid which frequently involves a multi-step synthesis and many purification stages. Another special difficulty in the preparation of two-in-one magnetic fluorescent nanocomposites is the risk of quenching by the magnetic particles. Serena *et al* (Corr *et al* 2008) studied the problem of quenching which can be partially resolved by providing the magnetic nanoparticle with a stable shell prior to the introduction of the fluorescent molecule, or by first treating the fluorophore with

an appropriate spacer, therefore, we attached ZnS to the surface of the Fe₃O₄/CNTs in abundance to prevent the quenching by Fe₃O₄ nanoparticles. However, complex interactions between ZnS and Fe₃O₄ and CNTs should be further studied.

4. Conclusions

In conclusion, the monodisperse magnetic nanoparticles and fluorescent ZnS nanoparticles have been successfully deposited on the surface of carbon nanotubes (CNTs) by *in situ* high-temperature hydrolysis in polyol solution and wet technique, respectively. CNTs purified with concentrated H₂SO₄/HNO₃ provide negatively charged surface to anchor Fe₃O₄ nanoparticles. Fe₃O₄ nanoparticles, spherical and 7–10 nm in diameter, were uniformly dispersed on the surface of purified CNTs and the coated density can be controlled by the ratio of Fe(acac)₃ to CNTs. The as-prepared Fe₃O₄/CNTs nanocomposites were further modified with PVP, EDTA, L-sodium tartrate and SDS in which the SDS-modified Fe₃O₄/CNTs exhibit excellent anchoring of ZnS nanoparticles. As to SDS-modified Fe₃O₄/CNTs, because of the high density of the functional groups –SO₄²⁻, the CNTs became more negatively charged. Zn²⁺ ions are adsorbed on the CNTs through the electrostatic attraction between Zn²⁺ ions and –SO₄²⁻ groups, and then form ZnS on the surface of Fe₃O₄/CNTs nanocomposites. The novel multifunctional ZnS/Fe₃O₄/CNTs nanohybrids exhibit super-paramagnetic and fluorescent properties with a saturation magnetization of about 6.795 emu g⁻¹ at room temperature. The nanohybrids also show a strong emission band located at 367 nm with some weak shoulders. The obtained products can be used for potential application in magnetically guided and fluorescence tracing drug delivery systems and others.

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