Bifunctional Fe_3O_4/CdS Nanocomposites Synthesized by Surface-initiated Atom Transfer Radical Polymerization

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(Received February 1, 2005; CL-050140)

This paper described the fabrication of a new Fe_3O_4/CdS nanocomposite. $PCd(MA)_2$ was firstly polymerized by surface-initiated atom transfer radical polymerization (ATRP) on the surface of Fe_3O_4 nanoparticles, and then the formation of CdS nanoparticles took place in situ when S^{2-} ions were released by thioacetamide upon heating. The nanocomposites were characterized by XPS, TEM, and UV–vis. The PL and magnetic properties were also studied.

Nanoparticulate materials are currently the subject of intense research work due to their novel properties which could have promising applications.[1–5] In particular, nanoparticles with multifunctional properties have been widely investigated because of possessing several desirable properties in a single entity.[6,7] Several bifunctional nanocomposite particles consisting of magnetic particles and luminescent CdSe/ZnS quantum dots have been synthesized.[8] Gaponik et al. demonstrated the simultaneous encapsulation of both luminescent semiconductors and magnetic oxide nanoparticles in polymer microcapsules.[9] Wang and co-workers described the fabrication of luminescent/magnetic nanocomposite particles through a single layer of quantum dots bounded to the surface of thiol-modified magnetic bead.[10] Gu's group have shown that a bifunctional heterodimers of nanoparticles: a conjugate of quantum dot and magnetic nanoparticle by taking advantage of lattice mismatching and selective annealing at a low temperature.[11] Kim et al. reported that Co/CdSe core/shell nanocomposites were prepared by controlled deposition of CdSe onto preformed Co nanocrystals.[12]

Previously we reported the fabrication of cross-linked PbS or CdS nanoparticles/polymer composite thin films through the combined use of surface-initiated ATRP and gas/solid reaction, which was from the planar or silica particles surface.[13,14] A new metal salt monomer containing two C=C bonds was used in the polymerization, which provided further introduction of functional nanoparticles into the composite. The nanocomposites were covalently bonded to the planar or silica particles surface, which offered a basis for enhancing the stability of composite films. Herein, we report the fabrication of bifunctional nanoparticles with superparamagnetic Fe_3O_4 nanoparticle core and CdS nanoparticles shell by surface-initiated ATRP from Fe_3O_4 nanoparticles surface based on our previously work.

Figure 1 schematically shows the procedure used for the fabrication of the bifunctional nanocomposites. Oleic acid stabilized Fe_3O_4 nanopartices, which were synthesized by the chemical coprecipitation of ferrors and ferric chloride, were ligand exchanged with 3-chloropropionic acids as the initiator of ATRP. Firstly, polymerization of cadmium dimethacrylate $Cd(MA)_2$ was performed on the initiator modified Fe_3O_4 nanoparticles. The particles were collected with a magnet and repeatedly washed with DMF. There were two C=C bonds in each $Cd(MA)_2$ monomer, so a cross-linked poly(cadmium dimethacrylate) $PCd(MA)_2$ shell was produced in the polymerization procedure, which enhanced the mechanical strength and the thermal stability of the composite nanoparticles. The formation of CdS nanoparticles took place in situ when S^{2-} ions were released by thioacetamide upon heating. The decomposition mechanism of thioacetamide has been described before.[15]

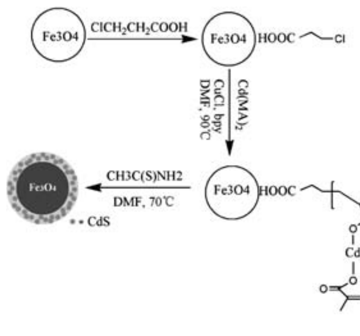

Figure 1. Schematic illustration of the fabrication of Fe_3O_4/CdS nanocomposites.

In order to further test the succeeded coating of $PCd(MA)_2$ on the surface of Fe_3O_4 nanoparticles, the process of the experiment was monitored by XPS measurement (Figure 2). The signal of Cd_{3d} of $PCd(MA)_2$ coated Fe_3O_4 nanoparticles was clearly collected. The S_{2p} peak of Fe_3O_4/CdS sample indicated that the CdS phase was present in the bifunctional nanocomposites.

The morphology and size distribution of the nanocomposites were also investigated using TEM. Figure 3 displays the TEM photographs of the nanoparticles before (a) and after (b) reaction with S^{2-}. The individual particle showed about 10 nm core as the dark center that was surrounded by a light polymer shell (Figure 3a). There were few aggregates, which were likely owing to the interaction of magnet or the polymer chain entanglement during

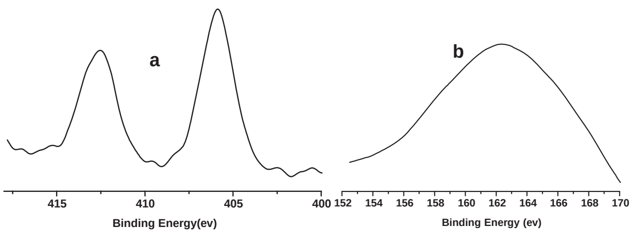

Figure 2. XPS spectra of (a) Cd of $Fe_3O_4/PCd(MA)_2$ and (b) S of Fe_3O_4/CdS.

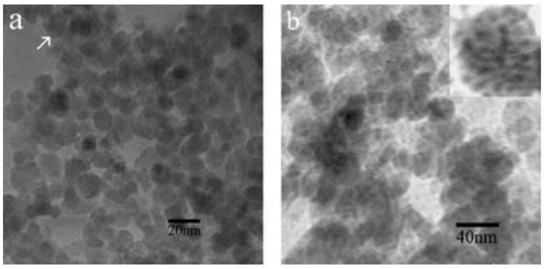

Figure 3. TEM photographs of the PCd(MA)$_2$ capped Fe$_3$O$_4$ nanoparticles before (a) and after (b) reaction with S^{2-}.

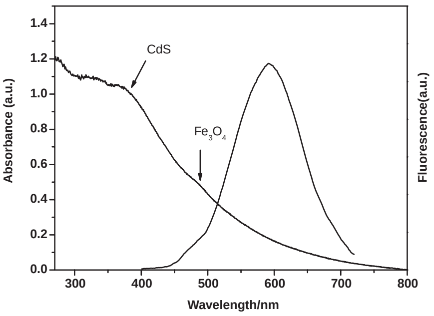

Figure 4. Absorption and emission spectra of the bifunctional nanocomposites in DMF.

solvent evaporation.[16] CdS nanoparticles were formed in polymer shell after reaction with S^{2-}, which was seen very distinctly with the insert of Figure 3b. CdS nanoparticles were uniformly spheric and the diameter was about 2–4 nm.

Absorption and emission spectra of the bifunctional nanocomposites were presented in Figure 4. The absorption of about 470 nm originated from the Fe$_3$O$_4$ part, which agreed with the previous observation.[17] The shoulder centered at 366 nm corresponded with the absorption spectra of CdS nanoparticles reported in the literature.[18] The PL properties of the composites were investigated at the fixed concentration of the coated Fe$_3$O$_4$ nanoparticles. Figure 4 displays an emission maximum at 591 nm, which was also consistent with the value in the literature of corresponding CdS nanocrystals of trap-state characteristic emission[16] and it was not existed in the emission spectrum of the Fe$_3$O$_4$ nanoparticles precursor.

Figure 5 displays the hysteresis curves of the samples at room temperature. The curves were free of any hysteresis and the zero coercivities were obvious, which were consistent with superparamagnetic behavior and the nanoscale dimensions of the particles. There was a large drop in saturation magnetization per gram in the nanocomposites due to the presence of the nonmagnetic CdS phase.

In summary, we have shown that Fe$_3$O$_4$/CdS bifunctional nanocomposites were fabricated by surface-initiated atom transfer radical polymerization approach. This method could be extended to many other systems that involved the use of different functional metal-containing monomers.

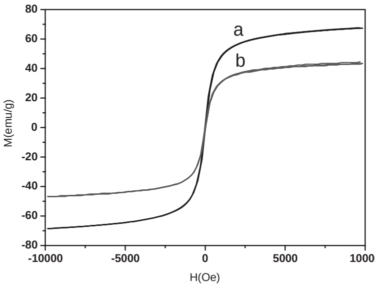

Figure 5. Hystersis curves of (a) initiator modified Fe$_3$O$_4$ nanoparticles and (b) the Fe$_3$O$_4$/CdS composites at room temperature.

The financial supports from the National Natural Science Foundation of China (Project No. 20374024), the Special Funds for Major State Basis Research Projects (No. 2002CB613401) and PCSIRT are gratefully acknowledged.

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