Synthesis and characteristics of multifunctional Fe_3O_4–SiO_2–CdS magnetic-fluorescent nanocomposites*

Zhang Ri-Chen(张日晨), Liu Ling(刘 玲), and Xu Xiao-Liang(许小亮)†

Department of Physics, University of Science and Technology of China, Hefei 230026, *China*

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A luminescent superparamagnetic nanocomposite with an Fe_3O_4–SiO_2–CdS structure is synthesized. Coated with a silica shell, Fe_3O_4 nanoparticles and CdS quantum dots (QDs) are successfully assembled together. Analysed from the test results of X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), hysteresis loop, and photoluminescence (PL) spectrum, these nanocomposites exhibit superparamagnetic and photoluminescent properties.

Keywords: superparamagnetic nanoparticles, CdS quantum dots

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1. Introduction

Magnetic nanoparticles, such as iron oxide (IO, magnetite, Fe_3O_4) and carbon-coated Fe, Co, or other ferromagnetic metals, are very attractive for biological medical treatments because they can penetrate body tissues advantageously owing to their special quality of interacting with induced electromagnetic fields of various frequencies.[1] The magnetic nanoparticles can demonstrate superparamagnetic behaviour[2] when they are small enough (10 nm–20 nm), i.e., these magnetic nanoparticles can immediately react to a magnetic field without the effect of coercive force and remnant magnetization. This property allows these nanoparticles to be manipulated, tracked and remotely heated. These unique properties have already been used in the development of medical technology, such as magnetic separation and hyperthermia technologies.[3−5]

On the other hand, a series of special photoluminescent properties of the semiconductor quantum dots (QDs), such as narrow size-tunable emission, broad absorption, limited photobleaching, and high brightness,[6] makes them attractive alternatives to conventional organic fluorophores (such as the commercially available dyes) for life sciences research.[7−9] Compared with dyes, semiconductor QDs are more stable and present reduced optical quenching. These characteristics of the QDs have opened up their medical application as a fluorescent probe. The new generations of QDs have far-reaching potential for the study of intracellular processes at the single-molecule level, high-resolution cellular imaging, long-term *in vivo* observation of cell trafficking, tumor targeting, and diagnostics.[10]

Magnetic nanoparticles and fluorescent QDs have been utilized in medical treatment. Here, we introduce a way of synthesising a kind of nanocomposite containing magnetic nanoparticles and fluorescent QDs with a coating of silica shell. These composites are bifunctional, having the advantages of both QDs and magnetic nanoparticles. The chances are that they will have more significant prospects in medical treatment because they can be used not only in biological molecular and cellular labelling and imaging, but also in separating labelled tissue or cells magnetically, and treating tumours at the same time.

2. Experiment

2.1. Materials

Tetraethylorthosilicate (TEOS) (28.4% SiO_2, AR), ferrous sulfate ($FeSO_4{\cdot}7H_2O$, 99%–100%), ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 98.5%), polyethylene glycol (PEG, Mw = 1000, AR), absolute ethanol (99.7%), ammonia (25%–28% $NH_3\cdot H_2O$, AR), hydrochloric acid (36% HCl, AR), acetone (99.5%), nitrogen (99.99%), deionized water (18.25 $M\Omega\cdot cm^{-1}$),

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†Corresponding author. E-mail: xlxu@ustc.edu.cn

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and CdS quantum dots (1 mol/L) were all purchased from Aldrich Co.

2.2. Preparation of iron-oxide magnetic nanoparticles

Iron-oxide (IO, Fe_3O_4) nanoparticles were synthesized as described below.

Briefly, 16.2 g ferric nitrate $Fe(NO_3)_3{\cdot}9H_2O$ and 5.7 g ferrous sulfate $FeSO_4 \cdot 7H_2O$ were added to 150 mL water to form a solution. 30 mL of 4 g PEG solution was dropped into the previous solution. After 10 min of magnetic stirring under nitrogen protection, a black liquid with ferro magnetofluid was obtained when the pH value was adjusted to 12 using ammonia. The black precipitate was isolated using a magnet and was washed with deionized water several times. Finally, the ferro magnetofluid was made up to a volume of 200 mL with deionized water in order to preserve, namely, NF.

2.3. Prepolymerization of TEOS

5 mL of TEOS was dissolved in 10 mL of acetone. 0.15 mL of 36% hydrochloric acid and 0.4 mL of deionized water were added to the solution, separately. After that, the products were left to stir in a 58-°C water bath until the volume dropped off to 2.5 mL, which was caused by the evaporation of the acetone. The resulting products were diluted to a volume of 10 mL using alcohol (95%), forming a transparent solution, namely PTEOS.

2.4. Synthesis of magnetic/fluorescent nanocomposites

The CdS quantum dots were synthesized according to the published literature.[11−13]

The purpose of this process is to coat the magnetic nanocomposites and the quantum dots together with a silica shell, and in order to realize the above purpose, four methods have been tried according to different sequences of adding the NF, PTEOS, CdS quantum dots and ammonia. Two of the methods proved successful, which will be discussed explicitly later. Table 1 shows the consequences of adding the materials in each sample-producing process (three or four steps). For example, to obtain sample 1 as shown in Table 1, first 2 mL of the NF underlayer containing ferro magnetofluid and 0.5 mL of 1 mol/L CdS QDs were mixed together under ultrasonic wave stirring, 2 mL PTEOS was then added to the previous mixture, and finally 5 mL ammonia was added.

These four samples were separately put into four little tubes and then were dried at 80 °C for 15 h. A kind of powder product was obtained after it had been ground in an agate mortar.

Table 1. Fabrication sequences of each sample.

Fabrication order	1	2	3	4
Sample 1	mixture of NF and QDs (ultrasonic wave stirring)	PTEOS	ammonia	
Sample 2	NF (ultrasonic wave stirring)	PTEOS	QDs	ammonia
Sample 3	NF (ultrasonic wave stirring)	PTEOS	mixture of QDs and ammonia	
Sample 4	NF (ultrasonic wave stirring)	mixture of PTEOS and QDs	ammonia	

2.5. Measurements

The XRD analysis was carried out with Cu Kα (0.154 nm) serving as the incident radiation. The patterns were recorded over $10° < 2\theta < 70°$. The high resolution transmission electron microscope (HRTEM) images of the magnetic/fluorescent nanocomposites were captured using a JEOL 2000 FX microscope with an acceleration voltage of 200 kV and the TEM images were taken using a JEM-1400 microscope with an acceleration voltage of 120 kV. The magnetic hysteresis loop was measured using a vibrating sample magnetometer (VSM; Quantum Design) at room temperature. PL spectra of CdS QDs were measured using a Shimadzu RF-5301 fluorescence spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction analysis of magnetic/fluorescent nanocomposites

The XRD pattern of sample 1 in Fig. 1 matches the same pattern for the magnetite (Fe_3O_4) phase and

silica (SiO_2) phase compared with standard XRD patterns reported elsewhere.[14,15] The sharp peaks that appear approximately at $2\theta = 30.33°$, 35.65°, 43.2°, 53.6°, 57.23°, and 62.96° belong to the Fe_3O_4 face-centred structure, with a board peak around $2\theta = 25°$ corresponding to the amorphous phase of SiO_2. The CdS peaks cannot definitely be identified due to the slight quantity of CdS QDs used here; the concentration of 0.5 mL 1 mol/L CdS is much smaller than that of Fe_3O_4 in the NF underlayer. In addition, the XRD results of the four samples show almost no difference.

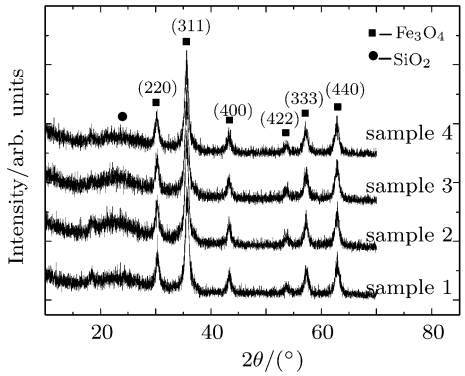


Fig. 1. X-ray powder diffraction patterns of the magnetic-fluorescent nanoparticles.

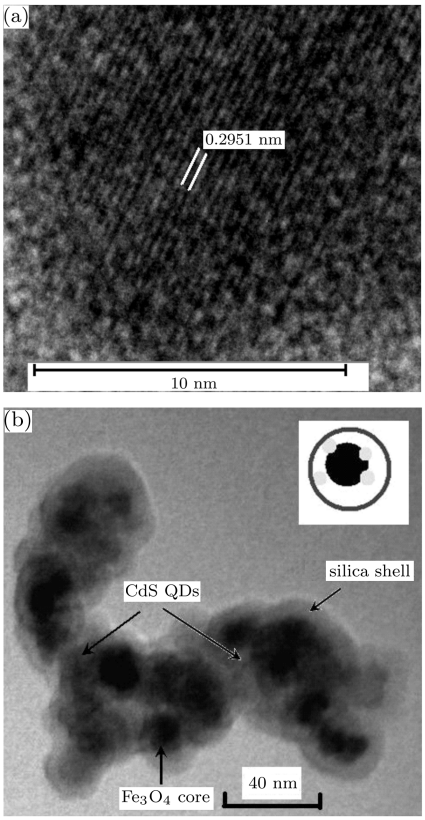


Fig. 2. HRTEM image of the Fe_3O_4 core (a) and TEM image of sample 1 (b).

3.2. HRTEM image of uncoated Fe_3O_4 nanoparticles and TEM image of magnetic/fluorescent nanocomposites

In the HRTEM image of the final nanocomposites in sample 1, the structure of the Fe_3O_4 core in the TEM image can be seen clearly (as shown in Fig. 2). After simple calculation according to the scale, the stripe spacing is about 0.2951 nm, which equals the standard interplanar crystal spacing[16] of the $(2, 2, 0)$ planes in an Fe_3O_4 face-centred structure in a range of allowable error. In the TEM image of sample 1, a semi-transparent silica shell with a thickness of 8 nm was coated on the dark black Fe_3O_4 core. Between the shell and the core, some little globubar half dark products can be seen, which are CdS QDs. The inset shows a model of the structure of these nanocomposites. In addition, the Fe_3O_4 core, with a diameter of 15 nm or so, is small enough to meet the requirement for superparamagnetism, which will be demonstrated later.

3.3. Analysis of PL spectrum of the magnetic/fluorescent nanocomposites

This process aims to test the photoluminescence (PL) property of the nanocomposites and to see whether the CdS quantum dots were successfully packed into the SiO_2 shell.

In Fig. 3, compared with the spectrum of the pure QDs,[17] the PL spectra of samples 1 and 4 have 110 nm and 120 nm red shift (from 440 nm to 550 nm and 560 nm), respectively, demonstrating that the

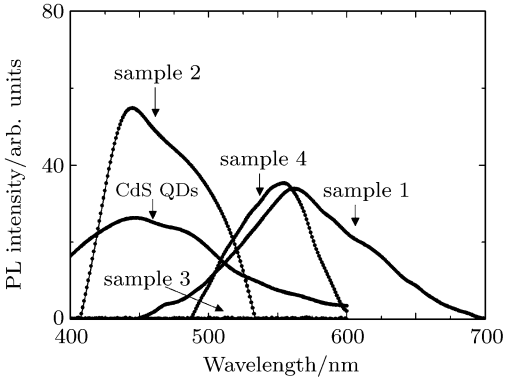


Fig. 3. PL spectra of four samples and pure CdS QDs.

CdS QDs have been embedded in the SiO_2 shell with the Fe_3O_4 core.[18] The red shift of the emission peak

may originate from partial exciton leakage into the shell.[19,20] Sample 3 actually did not emit an intensity of light at all, which is probably because the QDs had been ruined by some chemical reaction with the ammonia when they were mixed before the SiO_2 shell formed. Sample 2 peaks at the same wavelength as the pure QDs do, implying that the QDs were left out of the SiO_2 shell, which is not the result we hope to see.

3.4. Analysis of nanocomposite response to the magnetic field

The magnetic/fluorescent nanocomposites show a very good quality of superparamagnetism.[14,21] The hysteresis loop of the nanocomposites in Fig. 4 indicates that the magnetic moment of the nanoparticles

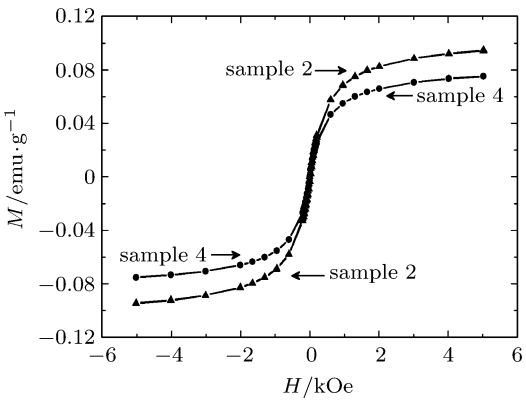


Fig. 4. Hysteresis loops of samples 2 and 4, 1 Oe = 79.5775 A/m.

increases considerably with the magnetic field increasing near the origin, without the effect of coercive force and remanent magnetism. In addition, SiO_2/Fe_3O_4 particles show greater magnetization in comparison with SiO_2/Fe_3O_4–CdS, which is consistent with the result reported in similar materials to CdSe quantum dots.[22,23] This test result paved the way for the application of these materials in the area of magnetic target therapy.

4. Conclusion

We have synthesized novel bifunctionalized nanocomposites by coating two unique types of nanomaterials in semiconductor QDs and iron oxide with a silica shell. Tested by various measurements, the products obtain both photoluminescence and superparamagnetic qualities, enabling them to have a new application in medicine.

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