



Magnetic and Fluorescent Properties of Fe₃O₄/SiO₂/ZnSe Nanocomposites Based on Stabilized Non-Toxic ZnSe Quantum Dots

DONGZHI WANG^{1,2}, QUN WANG¹, FUTIAN LIU^{1,*}, QINGHUI JIANG¹ and SUEJIAO SUN¹

¹School of Materials Science and Engineering, University of Jinan, Jinan, P.R. China

²School of Materials Science and Engineering, Shandong University, Jinan, P.R. China

*Corresponding author: Fax: +86 531 87974453; Tel: +86 531 89736671; E-mail: mse_liuft@ujn.edu.cn

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Non-toxic magnetic-fluorescent Fe₃O₄/SiO₂/ZnSe multifunctional nanoparticles were synthesized by a facile chemical route. The non-toxic fluorescent ZnSe quantum dots with -COOH on the surface were assembled around the silica-coated superparamagnetic Fe₃O₄, which were modified with -NH₂ via the chemical bond formed by 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride and *N*-hydroxysuccinimide between -COOH and -NH₂. The obtained Fe₃O₄/SiO₂/ZnSe nanocomposites exhibited superparamagnetic behaviour and the saturation magnetization value was 10.76 emu/g from the magnetic spectroscopy. Fluorescent spectroscopy measurements showed that the obtained relative intensity of Fe₃O₄/SiO₂/ZnSe nanocomposites at 400 nm became lower than that of the ZnSe quantum dots.

Key Words: Nanocomposites, Luminescence, Magnetic properties, Fe₃O₄/SiO₂/ZnSe.

INTRODUCTION

Recently, magnetic nanoparticles (*e.g.* Fe₃O₄) have been investigated extensively because of their interesting magnetic properties and the applications in drug delivery, cell tracking, sorting and bioseparation¹⁻³. Quantum dots (QDs) are semi-conductive nanocrystals with unique physical, chemical and optical properties due to their small sizes and components. Compared with the organic dyes, they have the following advantages: broad excitation wavelength ranges, narrow and symmetric emission with tunable colours, large Stokes shift and excellent photochemical stability. The quantum dots are becoming more widely used in the fields of chemistry, biology, medical sciences and biotechnology⁴⁻⁸. Besides, the combination of the magnetism and quantum dots makes it possible to realize labeling and separation simultaneously.

Wang *et al.*⁹ described the formation of the luminescent and magnetic nanocomposite particles that consist of superparamagnetic core particles (γ -Fe₂O₃) and a surface layer of the luminescent CdSe/ZnS quantum dots. The anticycline E labeled particles, attached to the luminescent/magnetic particles, were successfully used to separate and detected the breast cancer cells in serum. However, it was found that the emission quantum yield of the nanocomposite particles was three times lower than that of the CdSe/ZnS quantum dots due to quenching interaction between the magnetic nano-

particles and the luminescent quantum dots. Then, silica as a coating for magnetic particles in the fabrication of fluorescent/magnetic nanocomposites is considered. First, the silica coating provides an effective barrier to quenching of any fluorophores by the magnetic cores, in fact quenching can be controlled by the thickness of the silica shell; second, the silica surface can be easily functionalized, enabling chemical bonding of various fluorescent and biological species to surface¹. Sun *et al.*¹⁰ prepared a new kind of magnetic fluorescent multifunctional nanocomposite by chemically conjugating individual thiol-functionalized silica-coated Fe₃O₄ nanoparticles with multiple TGA-modified CdTe quantum dots. Liu *et al.*¹¹ also investigated the Fe₃O₄/SiO₂/CdSe magnetic luminescent nanocomposite particles by a combined process of sol-gel and electrostatic self-assembly technique. The immobilized CdSe quantum dots in the particles provide chemically active sites for further functionalization. The cadmium chalcogenide extensively studied in the multifunctional nanomaterials are fatal to human health.

In our previous work, we studied the preparation and properties of ZnSe quantum dots, Fe₃O₄ nanoparticles and Fe₃O₄/SiO₂ nanoparticles. This encouraged us to make an attempt to synthesize the non-toxic Fe₃O₄/SiO₂/ZnSe fluorescent/magnetic multifunctional nanoparticles. In this work, we synthesized the multifunctional nanomaterials *via* the chemical bond of -COOH and -NH₂ in aqueous solution.

EXPERIMENTAL

ZnSe quantum dots were synthesized in aqueous solution *via* a co-precipitation method as reported earlier¹². The obtained ZnSe quantum dots have an average diameter of ~2.5 nm and exhibit good fluorescence. Fe₃O₄ nanoparticles were prepared through the solvothermal method and coated with silica by the modified Stöber method. In brief, FeSO₄·7H₂O and FeCl₃·6H₂O (mol ratio Fe²⁺:Fe³⁺ = 1:1.6) were dissolved in the mixture of distilled water (30 mL) and glycol (30 mL), respectively. The solutions were mixed and pH values were adjusted to 11. After 0.5 h, the mixture was introduced into the reaction kettle and kept at 160 °C for 6 h. Then, the obtained Fe₃O₄ particles were added into absolute ethanol (150 mL), distilled water (50 mL) and concentrated ammonia solution (1.3 mL). 6.8 mL of tetraethyl orthosilicate (TEOS) was added dropwise. After the reaction of 3 h under continuous mechanical stirring, the resultant core-shell Fe₃O₄/SiO₂ products were separated and collected with a magnet, which followed by cross-washing with absolute ethyl alcohol and distilled water.

The magnetic/fluorescent nanoparticles can be obtained through the condensation of -COOH and -NH₂. Fe₃O₄/SiO₂-NH₂ were obtained by adding 50 µL of 3-aminopropyltriethoxysilane (ATPES) after reaction for 0.5 h at room temperature firstly. Meanwhile, 0.0014 g of EDC and 0.0017 g of sulfonhcs were added into the above -COOH modified ZnSe quantum dots. The solution of Fe₃O₄/SiO₂-NH₂ was added. After being stirred for 3 h at 55 °C, the magnetic/fluorescent nanocomposites were successfully collected and purified by using a permanent magnet.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of different nanoparticles. All the diffraction peaks in Fig. 1 (curve a) can be assigned to the spinel structure of Fe₃O₄ (JCPDS card: 89-691). In curve b, a strong and broad peak around 2θ = 20°-25° can be seen obviously, indicating the existence of coating silica. Other peaks in curve b can be assigned to the Fe₃O₄ phase. The results demonstrate that amorphous silica was successfully coated on the surface of Fe₃O₄¹³. Curve c is a typical XRD pattern of ZnSe quantum dots with the cubic zinc blende structure ((JCPDS card: 80-0021) and the broadening of X-ray peaks is characteristic of nano materials. The XRD pattern of the Fe₃O₄/SiO₂/ZnSe magnetic/fluorescent nanocomposites are shown in Fig. d. All peaks can be indexed as Fe₃O₄, SiO₂, or ZnSe. The peaks of Fe₃O₄ in the pattern are much weaker than those of ZnSe because of the core-shell structure of Fe₃O₄/SiO₂/ZnSe and the large proportion of ZnSe in the final nanocomposites¹⁰.

Fig. 2 shows digital photographs of the obtained solution. The as-prepared Fe₃O₄/SiO₂/ZnSe nanocomposites are well dispersed in the aqueous solution under both normal light and UV irradiation without the magnetic field (the rightmost vials in both Fig. 2a and b). In Fig. 2a and b, the Fe₃O₄/SiO₂/ZnSe nanocomposites are attracted and drawn to the magnet side of the leftmost vials by a magnetic bar, the bulk solution becomes a clear phase. If the individual particle possessed a remnant

magnetic field, each particle would act as a small dipole magnet, resulting in aggregations and precipitation of the particles¹⁴. The results suggest that the prepared nanocomposites are superparamagnetic. Upon illuminating the vial with UV light, an intense blue colour emission is observed on the magnet side, indicating that the Fe₃O₄/SiO₂/ZnSe nanocomposites are multifunctional with magnetism and fluorescence¹⁵.

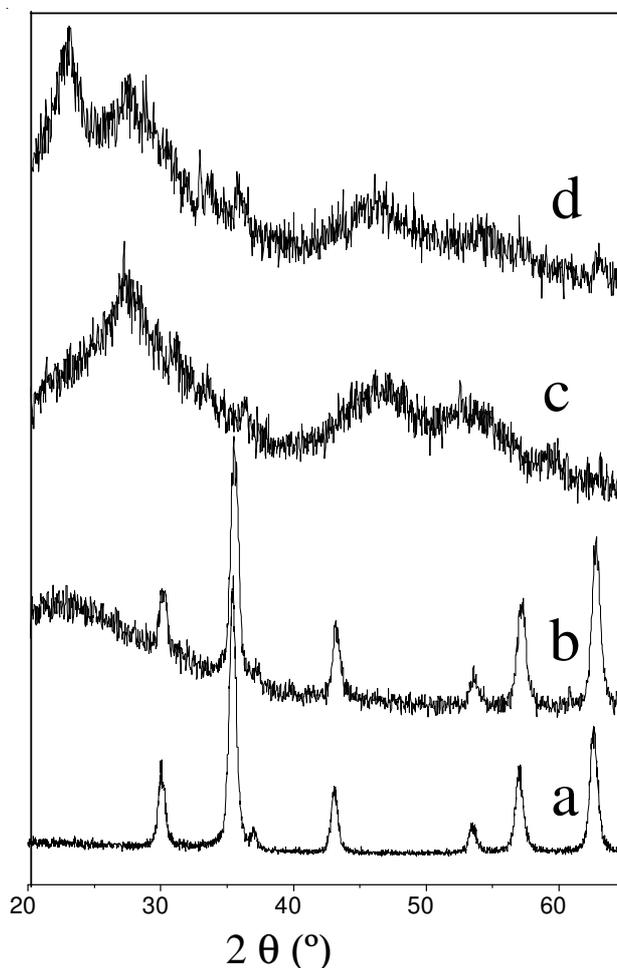


Fig. 1. XRD patterns of Fe₃O₄ nanoparticles (a), Fe₃O₄/SiO₂ nanoparticles (b), ZnSe quantum dots (c) and Fe₃O₄/SiO₂/ZnSe nanocomposites (d)

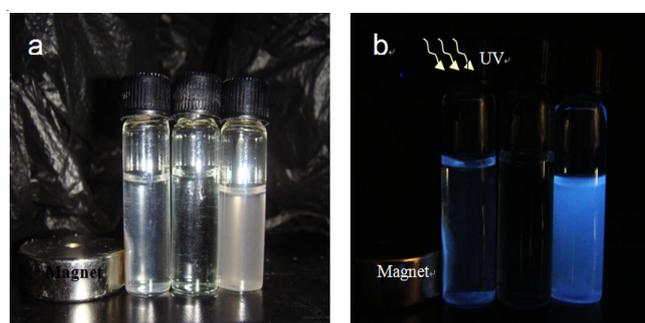


Fig. 2. Photographs of the obtained Fe₃O₄/SiO₂/ZnSe nanocomposites and distilled water before (a) and after (b) UV light irradiation. In both of the two photographs, the left one is Fe₃O₄/SiO₂/ZnSe nanocomposites under the magnetic field, the middle one is the distilled water and the right one is Fe₃O₄/SiO₂/ZnSe nanocomposites is not under magnetic field

Fig. 3 shows the hysteresis loops of the Fe₃O₄ nanoparticles (curve a), Fe₃O₄/SiO₂ (curve b) and Fe₃O₄/SiO₂/ZnSe magnetic/fluorescent nanocomposites (curve c). The Ms values of 74.09, 49.09 and 10.76 emu/g respectively. No remanence is detected for all of the samples, which confirms the superparamagnetism of the particles¹⁶. The value of saturation magnetization decreases from 74.09 to 10.76 due to the silica and ZnSe shells on the surface of Fe₃O₄¹⁷.

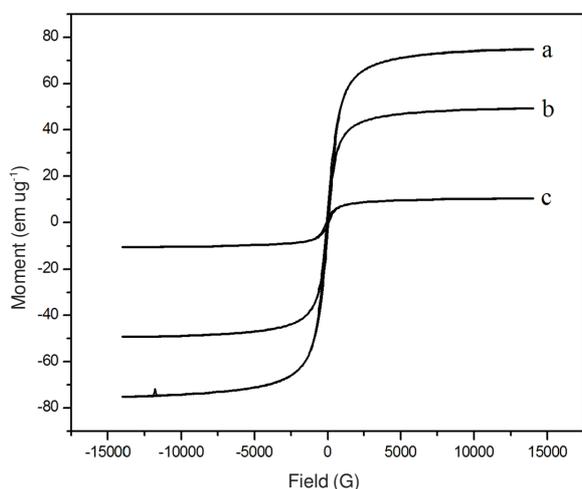


Fig. 3. Hysteresis loops for the Fe₃O₄ nanoparticles (a), Fe₃O₄/SiO₂ nanoparticles (b) and Fe₃O₄/SiO₂/ZnSe nanocomposites (c)

The fluorescence of the obtained nanoparticles in water under 365 nm are shown in Fig. 4. There is a peak at 400 nm which is the characteristic of ZnSe quantum dots¹⁸. Compared with the curve 'a', the intensity of the peak in curve b at 400 nm is lower because of the quenching of the fluorescent entity by the magnetic core. Crystal defects on the surface of ZnSe crystals lead to the appearance of the peak between 450 nm and 500 nm. However, there is no any obvious peak but a little peak in curve b between 425 nm and 475 nm, because the SiO₂ shell over the Fe₃O₄ reduces the structural and the crystal defects on the surface of ZnSe crystals¹⁹.

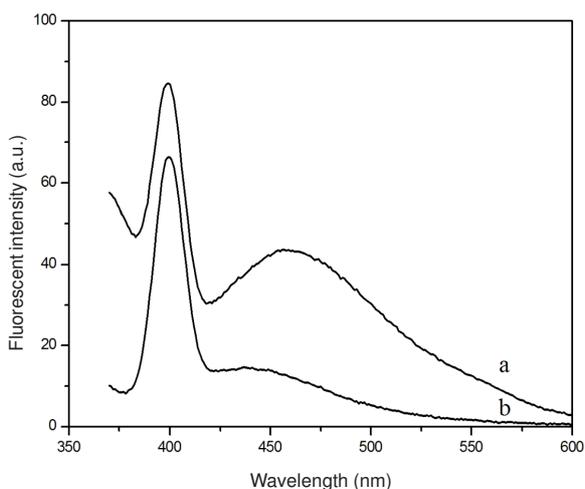


Fig. 4. Photoluminescence emission spectra of ZnSe QDs (a) and Fe₃O₄/SiO₂/ZnSe (b) nanocomposites

Conclusion

Multifunctional magnetic/fluorescent Fe₃O₄/SiO₂/ZnSe nanocomposites were prepared by chemical conjugation of the condensation of -COOH and -NH₂, which exhibited favourable magnetic and fluorescent properties. These nanocomposites are stable because of the chemical covalent bond and they are nontoxic in comparison to cadmium chalcogenide. The Fe₃O₄/SiO₂/ZnSe magnetic/fluorescent nanoparticles have great potentials abilities to serve in bio-applications.

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