

Fabrication of Luminescent Superparamagnetic CdSe-QDs/SiO₂/Fe₃O₄ nanocomposite particles

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Abstract: A new kind of water-soluble luminescent superparamagnetic nanocomposite particles had been synthesized using a modified Stöber method combined with an electrostatic assembly process. Size uniform SiO₂/Fe₃O₄ core-shell nanoparticles was synthesized by Stöber method, and then the silica surface was terminated with amino groups using 3-aminopropyltrimethoxysilane (APTS). CdSe Quantum Dots was then located on the surface of APTS treated nanoparticles. Transmission electron microscopy (TEM), microelectrophoresis, UV-vis absorption and emission spectroscopy and magnetometry tests showed that dense CdSe QDs were immobilized on the silica surface and the particles exhibited favorable superparamagnetic and photoluminescent properties. These nanocomposite particles are expected to serve as luminescent markers and are capable of being driven by a magnetic field to a specific target.

1. Introduction

Semiconductor Quantum Dots (QDs) have been extensively studied in multiplexed biological analysis for their unique size-dependent optoelectronic properties, narrow emission band with broad excitation, and strong resistance to photobleaching [1]. Another class of inorganic materials, magnetic nanoparticles (MNPs), is an additional important kind of materials due to their remarkable magnetic properties, and has attracted great interest for applications in biomedical areas, such as immunoassay [2], targeted drug

delivery [3] and hyperthermia [4]. Recently, the research on luminescent magnetic nanocomposite (LMNC) particles, which contain QDs and MNPs, has attracted growing attention and this new kind of nanocomposites offers highly potential applications [5,6], including rapid bioseparation, biolabeling and targeted drug delivery.

In general, two major methods were adopted for fabricating LMNC particles. In the first method, QDs and MNPs are simultaneously embedded into a matrix based on reverse microemulsion [7,8]. However, the distances of QDs and MNPs usually are too close to be controlled, thereby leading to the strong interactions between QDs and MNPs, which may diminish the Photoluminescence (PL) dramatically [9]. In the second method, layer-by-layer technique is adopted to locate QDs on the surface of a solid magnetic core [9,10] or to construct magnetic luminescent microcapsules [11]. However, laborious and time-consuming steps were required to remove the excess polyelectrolyte in this process.

In this paper, the synthesis of a new kind of CdSe-QDs/SiO₂/Fe₃O₄ luminescent superparamagnetic nanocomposite particles (LSNPs) was reported. A surface-active agent, 3-aminopropyltrimethoxysilane (APTS) was employed as a binder between SiO₂/Fe₃O₄ MNPs and CdSe QDs. The core-shell SiO₂/Fe₃O₄ particles became positively charged after APTS treatment. Driven by electrostatic interactions, the negatively charged CdSe QDs were immobilized on the silica surface, resulting in strong luminescent effect.

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2. Experimental

2.1 Materials

CdCl₂ (99%) and thioglycolic acid (TGA) (98%) were purchased from Acros. Selenium powder (99.8%) and APTS was obtained from Aldrich. Ammonia aqueous (25 wt.%), citric acid, ethanol and tetraethyl orthosilicate (TEOS) were analytical grade and commercially available products. All chemicals were used as received.

2.2 Preparation of CdSe Quantum Dots

CdSe QDs were prepared through a hydrothermal route [12]. In brief, fresh NaHSe solution was added to a N₂-saturated CdCl₂ solution in the presence of TGA at pH 11.0 in an ice-water bath. The molar ratio of [CdCl₂]:[TGA]:[NaHSe] was fixed at 1:1.5:0.5. Then 50 ml CdSe precursor was sealed in a autoclave and maintained at 200 °C for 120 min. After a hydrocooling process, the product was precipitated with acetone, and redispersed in 10 ml deionized water.

2.3 Preparation of colloidal Fe₃O₄ nanoparticles

Fe₃O₄ nanoparticles were prepared using the method already described based on the chemical coprecipitation of Fe²⁺ and Fe³⁺ by adding a concentrated NH₃ aqueous (25 wt.%) [13]. Then 0.5 g Fe₃O₄ nanoparticles were dispersed in 100 ml citric acid solution (0.05 M) under magnetic stirring, and the pH was adjusted to 5.5 by NH₃ aqueous (25 wt.%). After 4 h, the Fe₃O₄ nanoparticles were precipitated and washed with water 3 times by magnetic decantation to remove the redundant citric acid. Subsequently, 50 ml water was added to redisperse the ultrafine magnetic particles.

2.4 Preparation of CdSe-QDs/SiO₂/Fe₃O₄ LSNPs

Coating Fe₃O₄ nanoparticles with silica was carried out at room temperature by a modified Stöber method. Firstly, 2 ml Fe₃O₄ solution was ultrasonically dispersed in a mixture of 80 ml ethanol, 18 ml deionized water and 2.5 ml 25 wt.% ammonia aqueous. Then under continuous stirring, 0.4 ml TEOS was consecutively added. The sol-gel reaction lasted for 8 h and the products was obtained by magnetic separa-

tion and washed with water 4 times. Then the particles were dispersed in 100 ml ethanol solution containing 0.1 ml APTS. The solution was stirred at 60 °C for 6 h. Finally, the amino-functionalized particles were collected by magnetic separation and washed with ethanol 4 times.

The amino-terminated SiO₂/Fe₃O₄ nanoparticles were added to 10 ml aqueous solution of as-synthesized CdSe QDs. The mixture was sonicated to prevent aggregation and stirred for 6 h at room temperature to complete the assembly process. The excess CdSe QDs were subsequently removed by magnetic decantation and CdSe-QDs/SiO₂/Fe₃O₄ LSNPs were collected.

2.5 Characterization

The morphology of the products was characterized by transmission electronic microscopy (TEM) (H-800, HITACHI). Electrophoretic mobilities of particles were measured on a zeta potential analyzer (Zetasizer Nano Z, Malvern). PL spectra were obtained using a FLS920 spectrofluorimeter with an excitation wavelength of 400nm. Ultra-violet-visible (UV-vis) absorption spectra were obtained on a spectrophotometer (Shanghai 3rd Optical Analysis Instrument Co. 760CRT). A vibrating sample magnetometer (VSM) (Nanjing University Instrument Plant, LH-3) was used to measure the magnetic moment.

3. Results and discussion

As a result of anisotropic dipolar attraction, the pristine Fe₃O₄ MNPs tend to aggregate into large clusters, and thus lose the special magnetic properties associated with single-domain. Citric acid was employed as a surfactant to create an electrostatic double layer, leading the particles to avoid aggregation through electrostatic repulsion. The TEM image of the citric acid-stabilized Fe₃O₄ MNPs is shown in Fig. 1(a). No cluster was found and the average diameter of the observed Fe₃O₄ MNPs was about 12 nm.

Fe₃O₄ MNPs were coated with silica shell through a sol-gel approach involving the hydrolysis and condensation of TEOS, which relies on the well-known Stöber method. The surface of the colloidal Fe₃O₄ MNPs has a strong affinity to silica, thus silica can be directly deposited on the Fe₃O₄ MNPs without other pretreatment. Fig.1(b) shows the

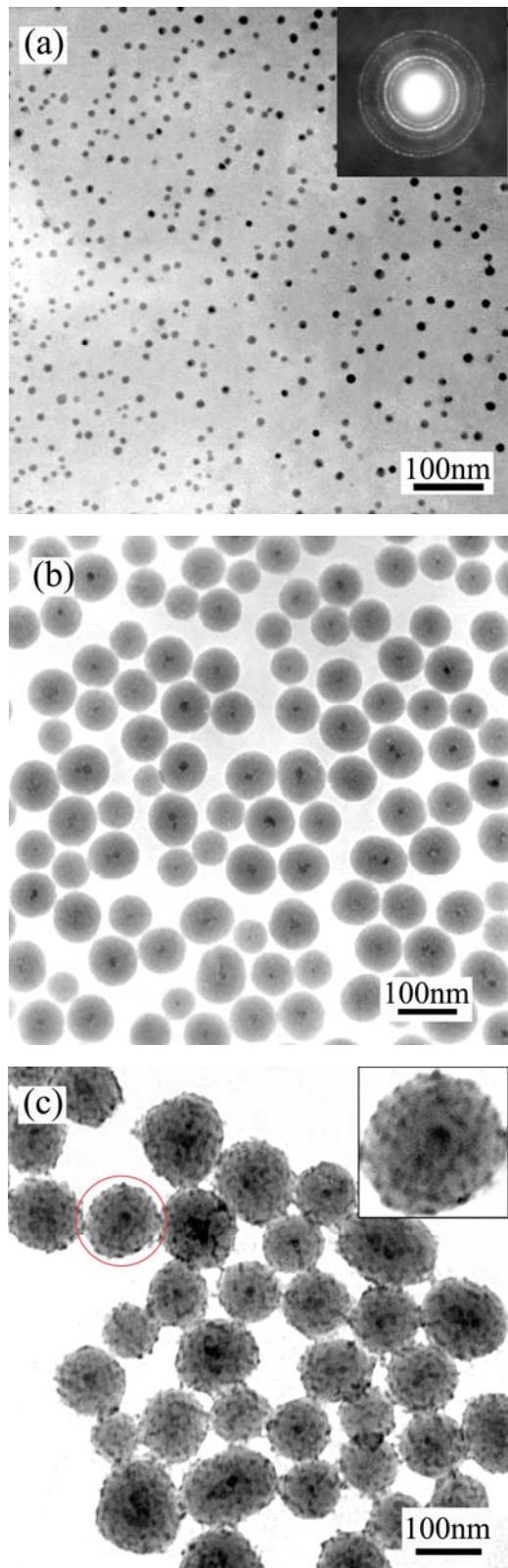


Figure 1. TEM images of Fe_3O_4 MNPs (a), $\text{SiO}_2/\text{Fe}_3\text{O}_4$ particles (b) and CdSe-QDs/ $\text{SiO}_2/\text{Fe}_3\text{O}_4$ LSNPs (c)

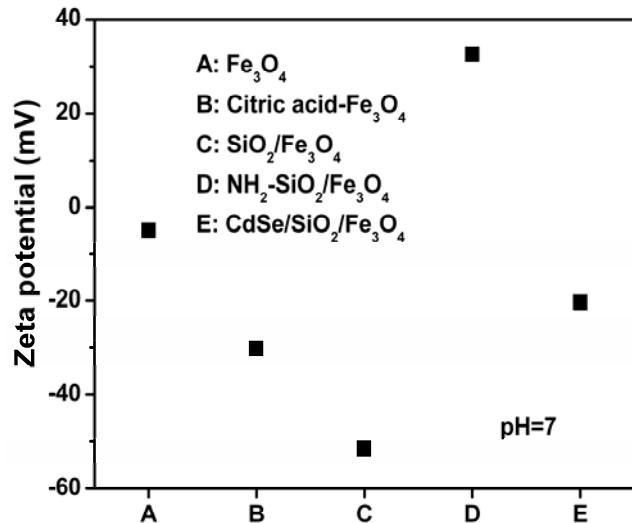


Figure 2. Variation of zeta potential at each stage of the preparation of LSNPs

TEM image of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles. The core-shell structural particles were rather spherical and uniform, even though some of them had more than one magnetic core. The thickness of silica shell can be changed from a few to several hundred nanometers simply by varying the initial amount of TEOS [14]. The nanoparticles employed here for the synthesis of SPLNC particles had a shell thickness of about 35 nm on average and the particle size was about 90 nm.

The end of thiol group in TGA can be used to protect the CdSe surface, and the other end of carboxyl group in TGA can be linked to the free amino group in APTS molecule that is already bonded to the silica surface. Driven by electrostatic interaction, the negatively charged CdSe QDs were assembled on the positively charged $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs. Fig. 1(c) shows the TEM images of the final CdSe-QDs/ $\text{SiO}_2/\text{Fe}_3\text{O}_4$ LSNPs. Small crystals were anchored on the surface of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs. Dense small crystals of CdSe QDs were anchored onto the surfaces of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles. The separation distance of magnetic cores and CdSe QDs was about 35 nm, indicating that the APTS treatment almost had no effect on the morphology of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles. The diameter of the final products was mainly in the range of 95–105 nm.

The measurement of ζ -potential confirmed each stage of the preparation of LSNPs. As shown in Fig. 2, citric acid

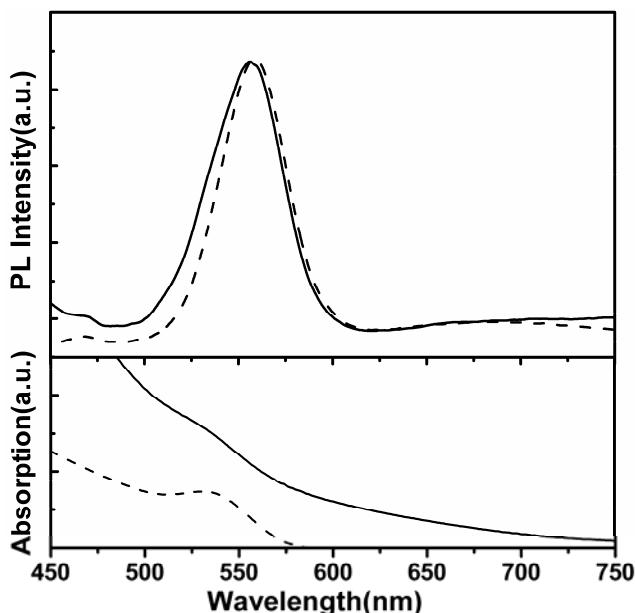


Figure 3. PL and UV-vis absorption spectra of CdSe QDs (dashed line), LSNPs (solid line)

modification shifted the ζ -potential of Fe_3O_4 from -5.2 mV to -30.1 mV and the ζ -potential was further decreased to -51.5 mV after silica coating. The particles were positively charged after amino-termination of silica surface and the ζ -potential was +32.7 mV. The potential changed to -20.3mV for the final products, indicating that CdSe QDs were successfully deposited on the silica surface.

The CdSe QDs employed in this case for the preparation of LSNPs had a fluorescent emission peak of 558 nm. Fig. 3 shows the PL and UV-vis absorption spectra of the CdSe before (dashed line) and after (solid line) deposition on the surfaces of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles. According to previous work [9], there are strong interactions between QDs and MNPs which reduce the PL intensity dramatically. This kind of interactions was sensitive to the separation distance between the two kinds of nanocrystals. The thickness-tunable silica kept the QDs away from magnetic cores and thus diminished the effect on the PL of CdSe QDs. As could be seen, the PL spectrum of LSNPs, of which the peak had a little blue shift to 556 nm, was similar to that of CdSe QDs. The Uv-vis spectrum of the LSNPs was much different from that of CdSe QDs, due to the strong absorption of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles.

The room-temperature magnetization curves of the

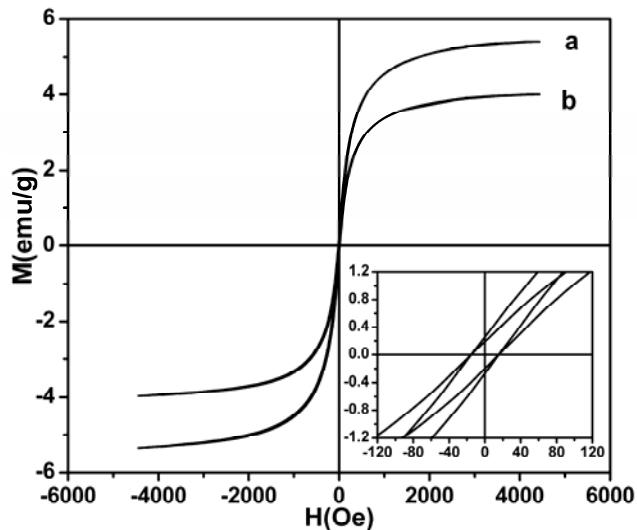


Figure 4. Magnetization curves of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles before (a) and after (b) CdSe deposition. The inset is a magnified view of the magnetization curves

$\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles before and after CdSe deposition are shown in Fig. 4. The saturation magnetization (M_s) value of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles was about 5.4 emu/g and the value reduced to 3.8 emu/g after the deposition of CdSe QDs. Both of them were far less than the initial M_s value of Fe_3O_4 (68 emu/g), which could be explained by taking into account the contributions of the thick silica shell and CdSe QDs surrounding the magnetic cores. The coercive forces were about 15 Oe and the M_r (remanence magnetization)/ M_s were about 0.04 for both the silica-coated MNPs and the final products. Because the values were very small, the particles were considered to be favorably superparamagnetic.

4. Conclusions

A new kind of luminescent superparamagnetic nanocomposite particles (LSNPs) with core-shell structure can be prepared by a facile combination process of sol-gel and electrostatic self-assembly techniques. The thickness of silica shell can be controlled to prevent the reaction between QDs and magnetic cores. The PL intensity will increase with thickness of silica shell and the LSNPs still have favorable saturation magnetization. Furthermore, the immobilized CdSe QDs in CdSe-QDs/ $\text{SiO}_2/\text{Fe}_3\text{O}_4$ LSNPs provide chemically active sites for further functionalization. These

nanocomposites are expected to serve as luminescent markers and are capable of being driven by a magnetic field to a specific target.

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