Fabrication of well-defined water-soluble core/shell heteronanostructures through the SiO_2 spacer†

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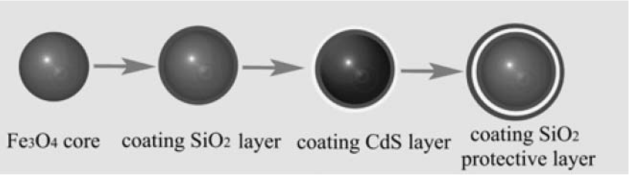
A generalized approach for the fabrication of core/shell heteronanostructures through a simple chemical bath deposition method assisted by the bridging of SiO_2 spacer has been developed and a slow heterogeneous nucleation mechanism identified as the key to the success of this method.

Recently, bifunctional or multifunctional heterogeneous nanoarchitectures (heteronanostructures) have attracted increasing attention in materials chemistry and nanotechnology due to the demand for miniaturization.[1] Among them, the core/shell heteronanostructure is one of the significant systems because of its enhanced properties from core and shell components and their synergy,[2] which are promising for potential applications, such as catalysis, drug or gene delivery, and cell separation.[3] Decomposition of organometallic complex compounds and the redox-transmetallation process have been developed as effective methods for the fabrication of core/shell heteronanostructures, such as Co@CdSe, Au@CdSe, Au@Fe_3O_4 and core/shell bimetals.[4] However, due to the mismatch of the lattice parameters and the phase transition occurring, dimers often tended to be formed.[5] Alternatively, a coating technique was utilized to construct core/shell nanostructures, in which particulate shell materials were attached or bound to the cores by electrostatic interaction or a complexing action.[6] With one time coating, however, the coverage area was not large enough to form a continuous layer. Halas *et al.* found the coverage area ratio would not exceed 25% by electrostatic interaction when they studied the Au@SiO_2 core/shell system.[6a] So, layer-by-layer and seeded growth techniques were used to increase the coverage area and the thickness of the shell, which need repetition of the coating step many times to achieve a desired thickness, such as Fe_3O_4/PE_n/CdTe and Fe_3O_4/γ-Fe_2O_3/SiO_2/PE_n/CdTe nanocomposites.[7] To avoid these problems, magnetic particles and quantum dots were also embedded in the (mesoporous) silica sphere to realize a bifunctional heteronanostructure.[8]

In the present work, we found that the CdS semiconductor layer could be uniformly coated on the magnetic Fe_3O_4 core to form a water-soluble magnetic luminescent heteronanostructure assisted by the SiO_2 spacer without tediously repeating the coating step. Through tuning the experimental parameters, such as the holding time or solution concentration, the thickness of the layer can be varied in a wide range. This water-soluble heteronanostructure successfully integrates magnetic and luminescent properties into one particle.



Scheme 1 The sketch of the fabrication procedure.

The fabrication of this magnetic luminescent core/shell heteronanostructure involved the coating of SiO_2 and CdS on Fe_3O_4 particles, respectively (Scheme 1 and ESI†).‡ Spherical Fe_3O_4 particles were firstly synthesized by a modified solvothermal method.[9] To overcome the difficulties in directly grafting active groups or bonding foreign molecules on to the surface of the Fe_3O_4 particle, a thin SiO_2 transition layer (spacer) was coated on the Fe_3O_4 core by a modified Stöber process, in isopropanol and water media, to change the surface characteristics, as well as to increase the stability and oxidation resistance. After the coating of the CdS layer, a thin protective SiO_2 layer was coated again in order to increase the structural stability. This SiO_2 layer is also indispensable to improving the biocompatibility in their prospective applications in cell separation and magnetically controlled biological labelling or other hydrophilic biological conditions.

Fig. 1 shows the XRD patterns of solvothermally prepared bare Fe_3O_4 particles and CdS coated Fe_3O_4 composite. In the curve (a), all the diffraction peaks can be indexed to well crystallized magnetic Fe_3O_4 (JCPDS 75–1609). In the curve (b), except for the

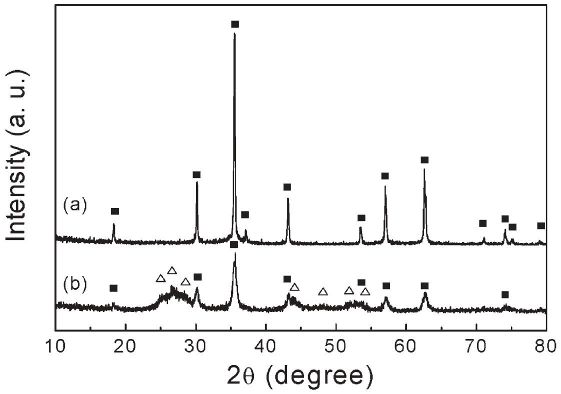


Fig. 1 XRD patterns of the samples: (a) Fe_3O_4 and (b) Fe_3O_4@SiO_2@CdS (■, Fe_3O_4; △, CdS).

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peaks from Fe_3O_4, the other peaks can be indexed to wurtzite CdS (JCPDS 41–1049). These broad peaks indicate the small size of CdS nanocrystals.

The detailed structural and morphological information on the initial SiO_2 coated Fe_3O_4 core/shell structure was characterized by TEM and SAED (Fig. S1 and S2†). The diameters of Fe_3O_4 cores can be tuned in the range of 100–500 nm by carefully controlling the solvothermal parameters, such as the holding temperature and time, concentration of reactants, and amount of surfactant. The SEM image indicates a high yield of spherical particles with rough surfaces, resulting from the coating of SiO_2. This thin SiO_2 transition layer serves as the spacer which is in favour of the coating of semiconductor materials on magnet cores. The obvious difference in contrast between the central part and fringe in the TEM image proves a core/shell structure with an average SiO_2 spacer thickness of ~12 nm.

The uniform silica intermediate spacer plays a key role in the final coating of CdS on the Fe_3O_4 core. The surfactant, PVP, added as a stabilizer, could effectively hold back the aggregation of Fe_3O_4 from the magnetic attraction, improve the thickness uniformity of the SiO_2 transition layer and help to obtain well-dispersed spherical composite particles. A CdS shell was expected to grow on the surface of the SiO_2 through slow heterogeneous nucleation instead of rapid homogeneous nucleation, which needs a low ion concentration and a slow growth speed. In the growth solution, trisodium citrate acted as the complexing agent to reduce the concentration and realize the slow release of Cd^{2+} ions through the formation of $[Cd–Citr]^-$ complex ion. Because the surface of the silica coated Fe_3O_4 particle was negatively charged in basic conditions, the released Cd^{2+} ions would be adsorbed on to the surface of a magnetic core by electrostatic interaction. Then, the slowly released S^{2-} ions from thiourea, in basic conditions with increasing holding temperature, reacted with the adsorbed Cd^{2+} ions and CdS nucleated *in-situ* at the adsorbed sites. The repeated adsorption and nucleation could finally form a dense CdS layer composed of CdS nanoparticles. As a result, the magnet–semiconductor core/shell heteronanostructure could be conveniently prepared by this chemical bath deposition growth route assisted by the SiO_2 transition spacer. The slow heterogeneous nucleation mechanism was the key to the success of this method. For the formation of a dense shell on SiO_2, an ion–ion mechanism was preferred to a cluster–cluster mechanism.[10] The reaction processes could be depicted as follows:

$$[Cd–Citr]^- \rightarrow Cd^{2+} + Citr^{3-} \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$(NH_2)_2CS + OH^- \rightarrow CH_2N_2 + H_2O + HS^- \quad (3)$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \quad (4)$$

$$Cd^{2+} + S^{2-} \rightarrow CdS \quad (5)$$

The TEM images of the as-prepared magnet-semiconductor core/shell heteronanostructure are shown in Fig. 2 (a) and (b). From the contrast difference, three kinds of contrasts confirm a high quality sandwich-like core/shell nanostructure. A comparison of the XRD patterns and EDS spectra of $Fe_3O_4@SiO_2@CdS$ and $Fe_3O_4@SiO_2$ particles confirms that the outermost shells were composed of wurtzite CdS nanoparticles (Fig. 1 and Fig. S3†). As is marked in Fig. 2(b), the coated CdS nanoparticles have formed a continuous layer on the surface of the magnet core and the average thickness of the CdS layer is ~27 nm (also see Fig. S4†). The TEM images of the final products are shown in Fig. 2 (c) and (d), indicating that another layer of SiO_2 has been satisfactorily coated and formed as a continuous film. In the high magnification TEM image (Fig. 2(d)), distinguishing from the contrast difference, we can clearly find three layers over the magnet core. Obviously, these three layers are SiO_2, CdS and SiO_2, respectively. The thickness and structure of the CdS shell can be tailored by simply tuning the holding time and reactant concentration. The time dependent and concentration dependent experimental results indicate the feasibility of the control of the shell thickness (Fig. S5†).

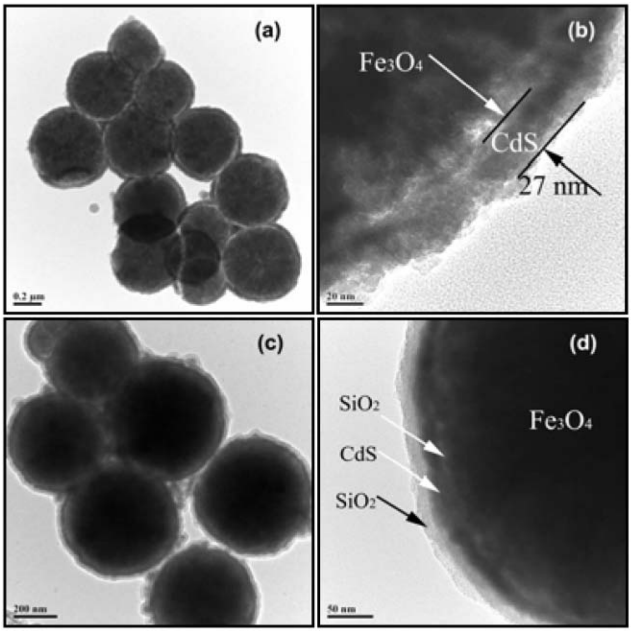

Fig. 2 TEM images of: (a, b) $Fe_3O_4@SiO_2@CdS$ heteronanostructures, indicating a layer of CdS film with a thickness of ~27 nm; (c, d) $Fe_3O_4@SiO_2@CdS@SiO_2$ heteronanostructures, indicating a sandwich-like core/shell nanostructure with three layers around the magnet core.

The optical properties of the final product were characterized by UV-Vis and PL spectra (Fig. 3 (a–c)). Fig. 3 (a) and (b) show the UV-Vis spectra of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@CdS$, respectively. In curve (a), it can be seen that Fe_3O_4 absorbs broadly in the

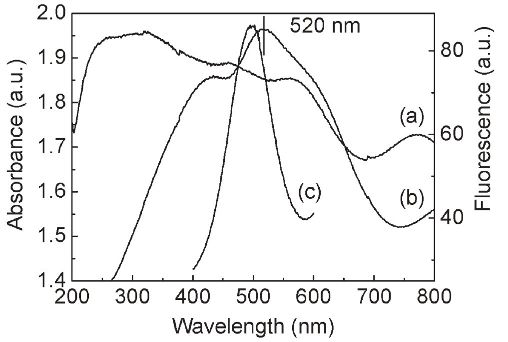

Fig. 3 UV-Vis absorption spectra of the samples: (a) $Fe_3O_4@SiO_2$; (b) $Fe_3O_4@SiO_2@CdS@SiO_2$; (c) room temperature PL spectrum of the final product, indicating a broad emission peak at ~510 nm.

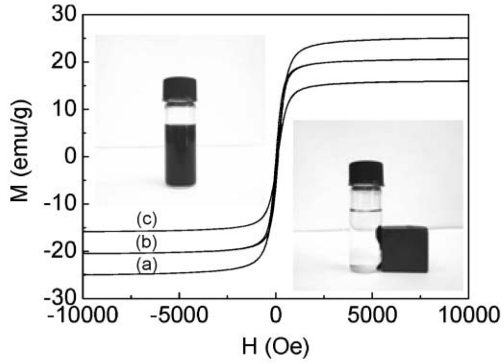

Fig. 4 The magnetization curves of the samples measured at 300 K for (a) Fe_3O_4; (b) Fe_3O_4@SiO_2; (c) Fe_3O_4@SiO_2@CdS@SiO_2. The inserted digital pictures show the strong magnetic response to an exterior magnetic field.

visible spectrum, which could weaken the excitation light and the emitted fluorescence of CdS in the final core/shell structure.[11] In curve (b), the peak centered at ~520 nm can be attributed to the absorbance of CdS, which is close to the band edge of the free-standing CdS particles (Fig. S6†). The room temperature PL spectrum of the final product is shown in Fig. 3(c), indicating an emission peak at ~510 nm when excited by 350 nm Xe light. The magnetization curves of the various products measured at 300 K are shown in Fig. 4 (a–c). The decrease in magnetic saturation values for the coating of SiO_2 and CdS on the surfaces of magnets is consistent with the decrease of Fe_3O_4 ratio in the composites. The magnetic saturation value is 16 emu g^{-1} for the final magnetic luminescent heteronanostructures. As is shown in the digital picture, the final magnet–semiconductor composite possesses strong magnetism and the well dispersed particles in ethanol can be rapidly collected by an exterior magnetic field.

In summary, a generalized approach to the fabrication of core/shell heteronanostructures through a simple chemical bath deposition method by the bridging of SiO_2 spacer has been developed. A slow heterogeneous nucleation mechanism has been identified as the key to the success of this method. The present magnetic luminescent heteronanostructure based on bifunctional core/shell Fe_3O_4@CdS endows it with prospective applications in magnetic field controlled biological labelling, cell separation, medical imaging and portable magnetic biosensors. Furthermore, simply changing the shape, size and composition of the core materials and combining them with the shell materials can result in novel bi- or multi-functional heteronanostructures, such as those with oxide cores, *e.g.*, ZnO, SnO_2, TiO_2, and sulfide (selenide) shells, *e.g.*, CdS, CdSe, CdTe, PbS, ZnS.

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Notes and references

‡ Brief experimental procedures: (1) Fe_3O_4 spheres were firstly synthesized by a polyol medium solvothermal method with some modifications.[9] (2) For the coating of silica spacer on the Fe_3O_4 core, a certain amount of synthesized Fe_3O_4 spheres were dispersed in a mixture of 70 mL isopropanol, 3.8 mL water and 2.1 mL of aqueous ammonia in a round bottomed flask by ultrasonic agitation for 15 min. Then 0.3 g of PVP was added with gentle stirring using an oil bath to hold the temperature at 40 °C. Finally, 0.2 mL of TEOS was added to the mixture and it was kept at 40 °C for 15 h. (3) For the coating of magnetic cores with CdS, a certain amount of silica coated Fe_3O_4 spheres were dispersed in 300 mL of distilled water by ultrasonic agitation, and then 0.5 mL of triethanolamine (TEA), 20 mL of trisodium citrate solution (0.1 M), 10 mL of $CdCl_2$ solution (0.1 M) and 20 mL of thiourea solution (0.1 M) were added. The pH value was adjusted to 11 by use of aqueous ammonia. After 15 min, the mixture was heated and kept at 60 °C under vigorous stirring for 2 h. The Fe_3O_4@CdS nanocomposite was magnetically collected and washed with distilled water and alcohol repeatedly to remove the excess CdS nanoparticles. Another thin silica layer was also coated on the Fe_3O_4@CdS core/shell nanostructure by repeating the second step with 0.1 mL of TEOS added in order to gain a protective layer over CdS.

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