Design and fabrication of hollow, magnetic and fluorescent CdS–magnetite–poly(styrene-*co*-methyl methacrylate) microspheres†

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Herein, we report a facile method for fabricating multifunctional CdS–magnetite–poly(styrene-*co*-methyl methacrylate) microspheres (CMPM) which possess simultaneously magnetic, fluorescent and hollow properties under room temperature and at ambient pressure. Based on the synthesized hollow magnetite–poly(styrene-*co*-methyl methacrylate) microspheres (HMPM), CdS nanoparticles are formed at the surface of HMPM through γ-radiation. The as-obtained HMPM and CMPM were thoroughly characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron diffraction (TEM), field-emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS), which showed the formation of HMPM and CMPM. The quantum-confined effect of CMPM is confirmed by the ultraviolet-visible (UV-vis) and photoluminescent (PL) spectra. Magnetic hysteresis loop measurements revealed that CMPM displayed superparamagnetism and still showed strong magnetic induction.

Introduction

Multifunctional nanomaterials have recently become an absorbing research field. Nanomaterials with magnetic and luminescence properties have great potential in biological applications such as cell sorting, as drug delivery carriers, MRI contrast agents and for labeling.[1] A few reports have focused on the synthesis and investigation of bifunctional nanomaterials, such as hybrid[2] and core-shell nanocomposites.[3]

Hollow spheres with nanometre-to-micrometre sizes have attracted a great deal of attention because of their potential applications in various fields such as encapsulation, delivery systems, controlled storage and release, catalysis, separation and so on,[4] owing to their low density, large specific area, tailored structures, and optical and surface properties. Various hollow spheres have been synthesized employing different types of templates including polystyrene latex spheres,[5] silica sols,[6] liquid drops,[7] vesicles,[8] polymer micelles[9] and emulsion,[10] microemulsion[11] and miniemulsion[12] droplets.

If multifunctional nanocomposite microspheres possess simultaneously magnetic, fluorescent and hollow properties, they would have a great predominance in biomedical applications. However, there are currently few reports about the synthesis multifunctional nanocomposite microspheres. Kim and co-workers[13] synthesized mesoporous silica spheres embedded with monodisperse magnetic and semiconductor nanocrystals and investigated the released curve of ibuprofen. Lin and co-workers[14] prepared multifunctional composite nanoparticles that simultaneously possess magnetic, luminescent and porous properties and further measured the relaxivity and took phantom images of them in the MRI T2 mode. However, the saturation magnetization of those products is about 2 emu g^{-1}, which is so small that it is disadvantageous to biotechnology applications. Meanwhile, the reported preparation methods have many steps and are relatively complicated, for example, calcination is necessary to obtain the porous structure. Moreover, the preparation conditions are rigorous (under high temperature). Thus, the development of facile and mild methods for obtaining multifunctional nanocomposite microspheres that possess simultaneously magnetic, fluorescent and hollow properties still remains a challenge for chemists.

In our previous work, we reported the preparation of (multi)hollow superparamagnetic magnetite–polystyrene nanocomposite microspheres *via* interface polymerization,[15] inverse miniemulsion polymerization[16] and double emulsions polymerization[17] without the process of etching the template for the formation of the hollow structure. Moreover, the use of γ-rays is one of the most simple and effective methods for synthesizing inorganic–polymer nanocomposites. Our group has been interested in synthesizing inorganic–polymer nanocomposites using γ-rays in various emulsion systems, such as silver–poly(butylacrylate-*co*-styrene),[18] CdS–polyacrylamide,[19] MoO_2–poly(St-*co*-MMA-*co*-AA)[20] and CdS–polystyrene,[11c] which had been successful. Herein, combining the previous approach for the preparation of hollow magnetic nanocomposite micospheres and the simple and facile method of preparing inorganic nanoparticles using γ-rays, we develop a new strategy for the synthesis of multifunctional CdS–magnetite–poly(styrene-*co*-methyl methacrylate) microspheres, which simultaneously possess magnetic, fluorescent and hollow properties.

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Experimental

Chemicals

Ferric chloride ($FeCl_3$), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), sodium dodecyl sulfate (SDS), cetyl alcohol (CA), aqueous ammonia [25% (*w*/*w*)], oleic acid, $CdCl_2{\cdot}2.5H_2O$, $NaS_2O_3{\cdot}5H_2O$ and ethanol were all of analytical grade and used without any further treatment. Styrene (St) and Methyl methacrylate (MMA) was of reagent grade from commercial sources and distilled under a reduced pressure before use. All the chemicals were purchased from Shanghai Reagents Corporation.

Synthesis of magnetite nanoparticles surface-modified with oleic acid

MPs were synthesized by the conventional coprecipitation method with some modification as our previous work,[15] which used in this work is the same as Mag-2 listed in Table 1 mentioned in that paper.

Synthesis of hollow magnetite–poly(St-*co*-MMA) microspheres

Hollow magnetite–poly(St-co-MMA) microspheres (HMPM) were prepared by interfacial polymerization in miniemulsion according to our previous work.[15] In a typical experiment, MPs (0.25 g) and cetyl alcohol (0.31 g) were dispersed in styrene (3.5 g) and methyl methacrylate (1.5 g). The obtained stable oil–base dispersion was added to a solution of SDS (0.12 g) in water (45 ml). The mixture was stirred for 1 h, followed by ultrasonication for 10 min to obtain a stable O/W miniemulsion. During ultrasonication, the mixture was kept cold to avoid polymerization. The miniemulsion was continuously bubbled with nitrogen for 20 min to remove oxygen, then sealed to be irradiated in the field of a 1.30×10^{15} Bq ^{60}Co γ-ray source at the dose rate of 80.3 Gy min^{-1} with the absorbed dose of 38.4 kGy. At last, the HMPM were separated with the help of a magnet and washed repeatedly with distilled water and ethanol, then dried in air at ambient temperature.

Synthesis of hollow CdS–magnetite–poly(St-*co*-MMA) microspheres

In a typical procedure to prepare hollow CdS–magnetite–poly(St-*co*-MMA) microspheres (CMPM), 0.25 g $CdCl_2{\cdot}2.5H_2O$ and 0.27 g $Na_2S_2O_3{\cdot}5H_2O$ were dispersed in 20 ml deionized water, then 0.20 g HMPM and 2 ml isopropyl alcohol as a scavenger of radicals to remove oxidative hydroxyl radicals was added into the mixture. The solution was bubbled with nitrogen for 20 min to remove oxygen, then sealed to be irradiated in the field of a 1.30×10^{15} Bq ^{60}Co γ-ray source at the dose rate of 70.3 Gy min^{-1} with the absorbed dose of 71.7 kGy. At last, the CMPM were separated with the aid of a magnet and washed repeatedly with distilled water and ethanol, then dried in air at ambient temperature.

Characterization of the HMPM and CMPM

Powder XRD patterns of as-synthesized samples were recorded with a Japan Rigaku D/max γ_A X-ray diffractometer equipped with graphite monochromatized Cu-Kα irradiation (λ = 0.154178 nm), employing a scanning rate of 0.02 deg s^{-1} in the 2θ range from 20 to 80°. TEM images were observed on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV. FESEM images were obtained on a JEOL JSM-6700 field-emission scanning electron microanalyzer. XPS spectra were recorded on an ESCA Lab MKII instrument with Mg Kα radiation as the exciting source. FTIR spectra were carried out on a Bruker Vector-22 FTIR spectrometer using KBr method. TGA analysis was performed with a Shimadzu TGA-50H instrument under an atmosphere of nitrogen with a gas flow of 25 cm^3 min^{-1}. The sample was heated from 50 to 700 °C at 10 °C min^{-1}. The ultraviolet-visible (UV-vis) absorption spectrum was recorded at room temperature on a UV spectroscopy (UV-2401PC Sahimaczu Corporation, Japan). The photoluminescent (PL) spectrum was taken on a Hitachi 850 fluorescence spectrometer with a Xe lamp at room temperature (λ_{ex} = 350 nm). The magnetic properties (M–H curves) of powder samples at room temperature were evaluated on a MPMS XL magnetometer (Quantum Design Corporation). During measurement, the applied magnetic field successively varied in the sequence 0–1–0––1–0 T. Magnetic susceptibilities were not corrected for the background signal of the sample holder and for diamagnetic susceptibilities of all atoms, because they were very small ($<10^{-4}$ emu g^{-1}) and could be neglected.

Results and discussion

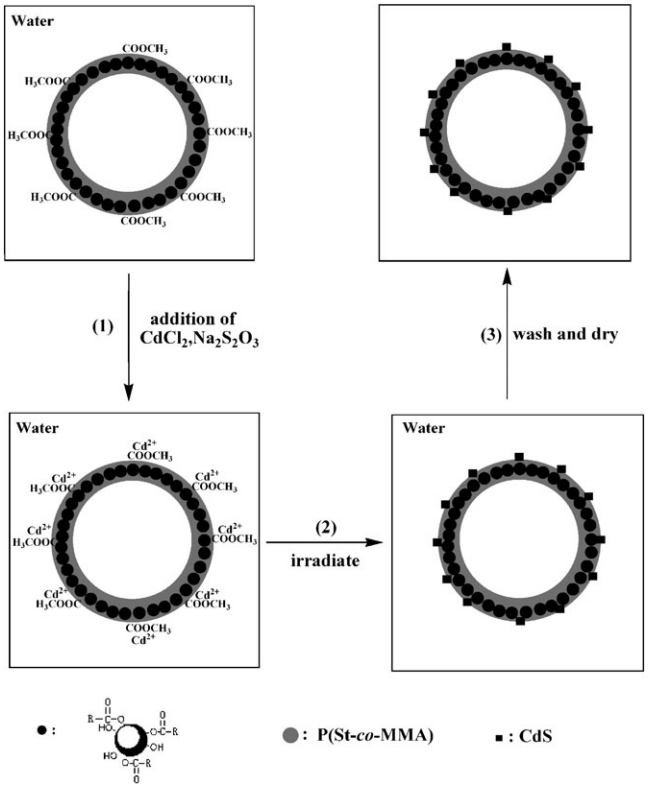
The synthesis procedure of multifunctional CdS–magnetite–poly(St-*co*-MMA) microspheres is shown in Scheme 1. HMPM is first synthesized and the formation mechanism of hollow magnetic microspheres had been studied in our previous work.[15] The methyl methacrylate is added to make Cd^{2+} ions chelated with carbonyl groups at the surface of HMPM. Because the hydrophilicity of the methyl methacrylate is better than that of the styrene, the PMMA tends to be enriched at the surface of HMPM.

Then, HMPM is added to the aqueous solution of $CdCl_2{\cdot}2.5H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$. When the aqueous dispersion is irradiated by γ-rays, many active intermediates such as e_{aq}^-, $H^\bullet$ and $^\bullet OH$ are generated owing to the radiolysis of water (see reaction 1). Among them, the reducing species e_{aq}^- could reduce $S_2O_3^{2-}$ to S^{2-} ions (reaction 2), which react with Cd^{2+} ions chelated with carbonyl groups of PMMA to generate CdS nanoparticles (reaction 3) at the surface of HMPM. After washing and drying, CMPM are formed.

Fig. 1 shows the XRD patterns of HMPM and CMPM. From Fig. 1(a), all the diffraction peaks can be indexed as the

Table 1 The concentration of various elements present in CMPM

Atomic	C1s	O1s	Cd3d	S2p	Fe2p
%	55.36	21.53	10.52	10.41	2.18



Scheme 1 Schematic illustration of the procedures for preparing multifunctional CMPM.

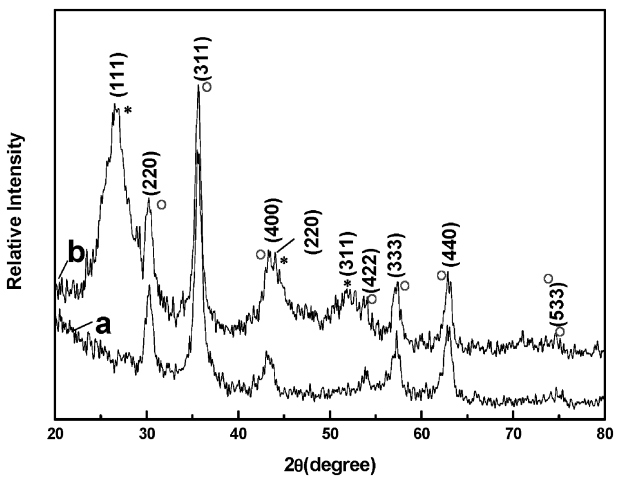


Fig. 1 The XRD patterns of (a) HMPM; (b) CMPM. Note: Marked with * for face-centered cubic CdS peaks; ○ for face-centered magnetite peaks.

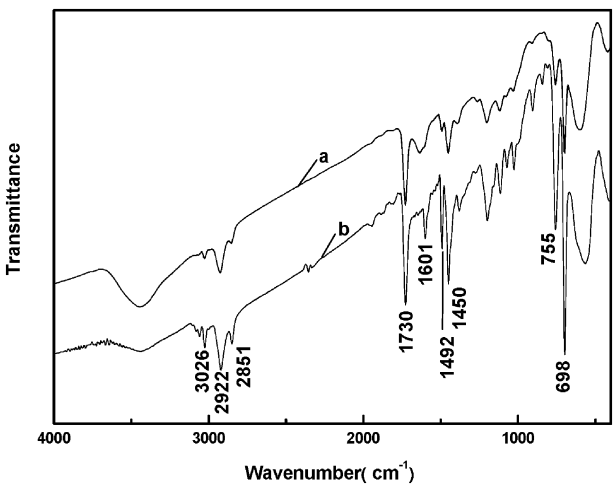


Fig. 2 FTIR spectrum of (a) HMPM; (b) CMPM.

face-centered magnetite (Fe_3O_4) crystallite by comparison with the literature (JCPDS card. File no. 74–0748). In Fig. 1(b), the diffraction peaks marked with * correspond to the face-centered cubic CdS crystallite by comparison with the literature (JCPDS card. File no. 75–0581), while the diffraction peaks signed with ○ are indexed to the face-centered magnetite (Fe_3O_4) crystallite the same as that in Fig. 1(a). According to Scherrer's equation ($d = k\lambda/\beta\cos\theta$), the average crystallite size of the CdS nanoparticles is about 4 nm.

FTIR spectra of the corresponding HMPM and CMPM are illustrated in Fig. 2, in which the bands of the two spectra are almost consistent. The bands at 698, 755 cm^{-1} can be assigned to flexural vibrations (δ_{C-H}) of benzene ring, 1450, 1492, 1601 cm^{-1} can be checked to benzene ring vibrations (ν_{C-C}) of polystyrene, and 2851, 2922 cm^{-1} can be attributed to ν_{C-H} of saturated –C–H–, while 3026 cm^{-1} can be corresponded to ν_{C-H} of the benzene ring. Moreover, the band at 1730 cm^{-1} is observed and corresponds to the stretching vibration of C═O group ($\nu_{C=O}$) of PMMA.

The XPS spectra of HMPM are shown in Fig. 3. In a typical survey spectrum of HMPM (Fig. 3(a)), it shows the presence of Fe, O and C at the surface of HMPM. The existence of C1s

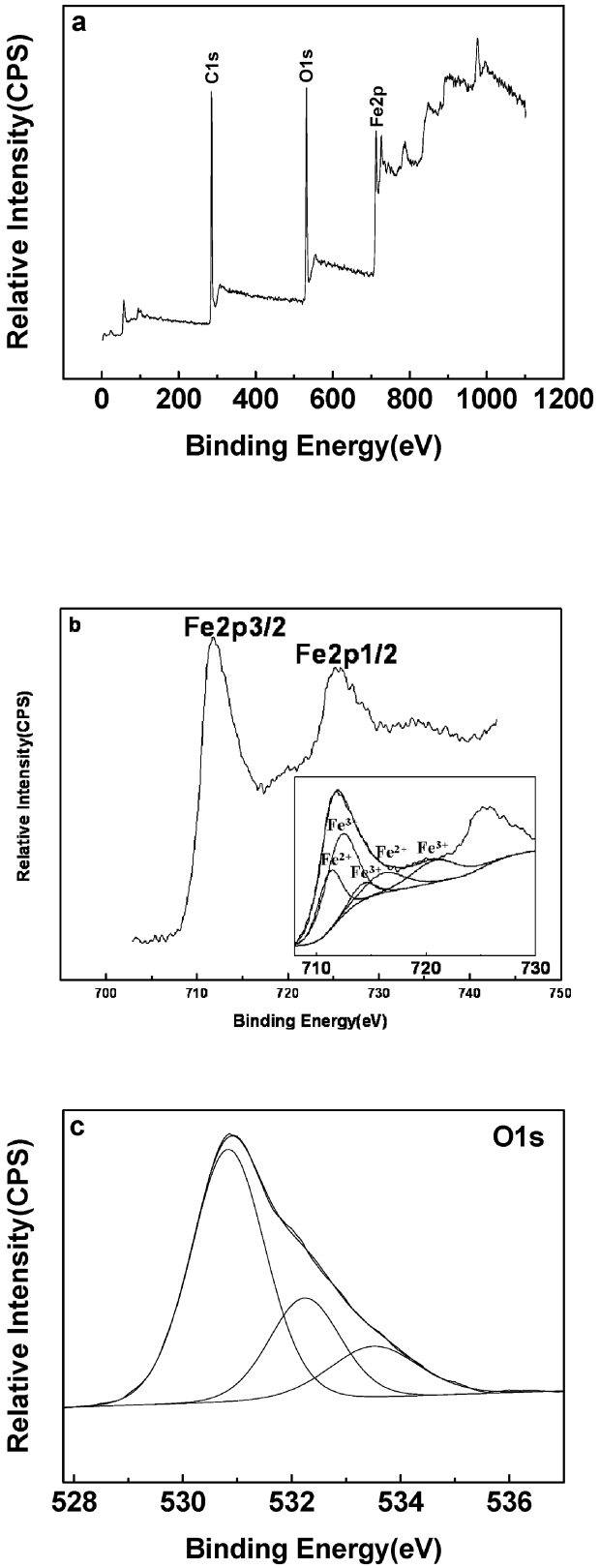


Fig. 3 XPS spectrum of HMPM: (a) the survey spectrum; (b) the higher resolution spectrum of Fe2p3 (the deconvolution of the $Fe2p_{3/2}$ peak shown in the inset); (c) the higher resolution spectrum of O1s.

peak is mainly caused by the polymers, and partly by gas molecules, for example CO_2, absorbed by the surface of the sample. The higher resolution spectrum of Fe and O regions are shown in the Fig. 3(b) and (c). From the Fig. 3(b), the photoelectron peaks at 711.8 and 725.7 eV are the characteristic doublet of Fe $2p_{3/2}$ and $2p_{1/2}$ core-level spectra of iron oxide, respectively, which is consistent with the oxidation state of Fe in Fe_3O_4.[21] Furthermore, through the deconvolution of Fe $2p_{3/2}$ peak (shown in the inset of Fig. 3(b)), the ratio of Fe(II) to Fe(III) ions can be calculated to be about 0.5, which is consistent with the ratio of Fe(II) to Fe(III) ions of magnetite. From the Fig. 3(c), we can see that the O1s region can be fit into three peaks located at 530.9, 532.3 and 533.6 eV, which is respectively due to oxygen of iron oxide, oxygen of poly(St-*co*-MMA) and water absorbed at the sample surface. The XPS spectra indicate the existence of carbonyl groups at the surface of HMPM.

Fig. 4 shows the XPS spectra of CMPM. It can be clearly seen that the elements of Cd, S, C, O, Fe exist at the surface of CMPM. The Cd3d XPS spectrum (Fig. 4(b)) has two peaks at 405.1 eV ($3d_{5/2}$) and 412.0 eV ($3d_{3/2}$).[22] Similarly, the S2p peak is observed at 161.3 eV (Fig. 4(c)), corresponding to S^{2-} of CdS nanoparticles. The peaks of Fe2p are shown in Fig. 4(d), which is consistent with Fig. 3(b). The atomic concentrations of CMPM measured by XPS are shown in Table 1. It can be seen that the Cd : S ratio is about 1. Furthermore, it is showed that the Fe_3O_4 is embedded in polymer matrix due to the small content of Fe and CdS is chelated on the surface of polymer due to the big content of Cd and S.

TEM images of HMPM and CMPM and SEM images of CMPM are shown in Fig. 5. The mean size of HMPM is 450 nm or so. The hollow structure can be clearly seen from Fig. 5(a), which shows the sphere with the obvious contrast between the pale center and the dark edge as reported for other hollow spheres. The mean size of CMPM is also 450 nm or so shown in Fig. 5(b) and (c), which is almost consistent with that of HMPM. The hollow structure of CMPM can be verified by SEM images of the broken spheres (Fig. 5(d) and (e)) and the TEM images inserted in the Fig. 5(b).

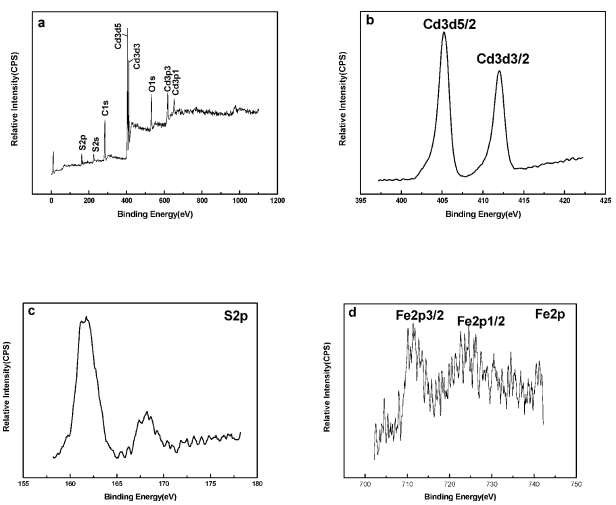


Fig. 4 XPS spectrum of CMPM: (a) the survey spectrum; (b) the higher resolution spectrum of Cd3d; (c) the higher resolution spectrum of S2p; (d) the higher resolution spectrum of Fe2p3.

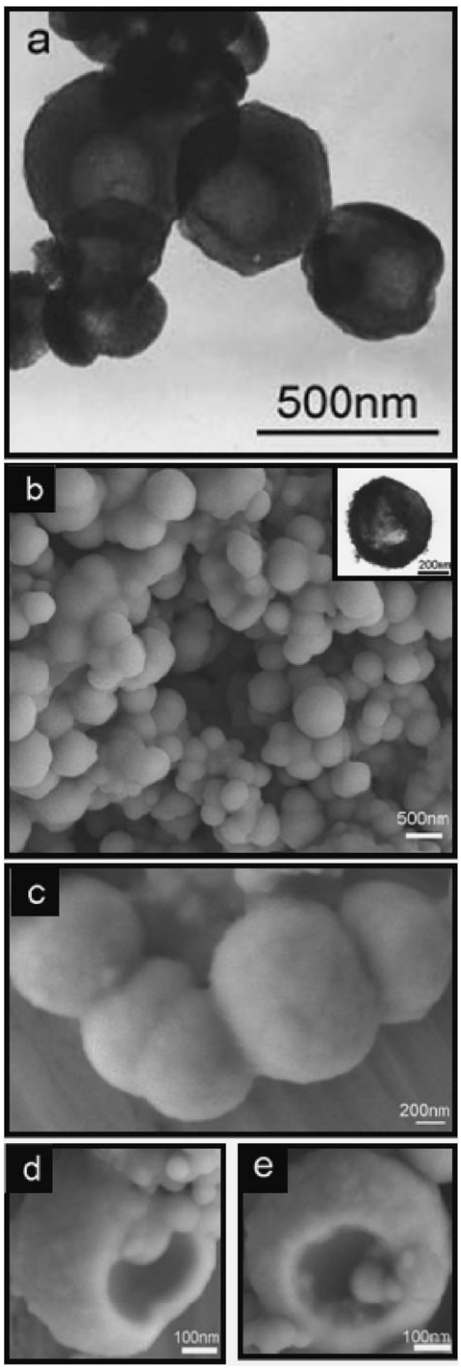


Fig. 5 TEM and SEM images of HMPM and CMPM: (a) TEM images of HMPM; (b) SEM image of CMPM (the inset picture is the TEM image of CMPM); (c) SEM image of CMPM at higher magnifications; (d) and (e) SEM images of broken CMPM.

PL spectrum of CMPM (as shown in Fig. 6) indicates a 440 nm absorption peak. Compared with the emission of bulk CdS (520 nm), 80 nm of blue shift is observed. These features indicate the quantum-confined effect of CMPM.[23] A small shoulder peak observed at around 410 nm could be assigned to the effect of the dispersant ethanol(see Fig. S3 in ESI†).[24] Furthermore, for studying whether the magnetite affects on the CdS fluorescence indirectly, the UV-vis absorption spectrum of magnetite nanoparticles (see Fig. S4 in ESI†) is

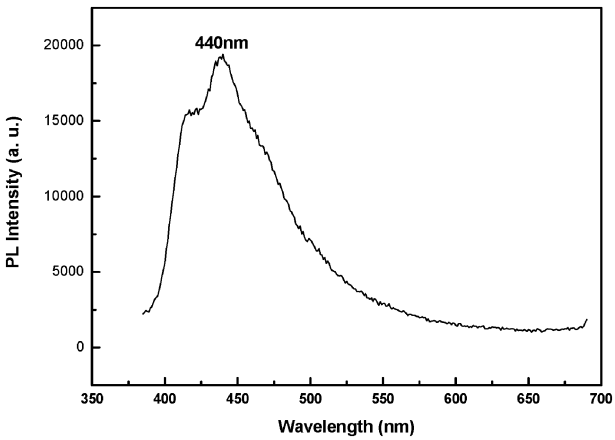


Fig. 6 PL spectrum of CMPM (λ_{ex} = 350 nm).

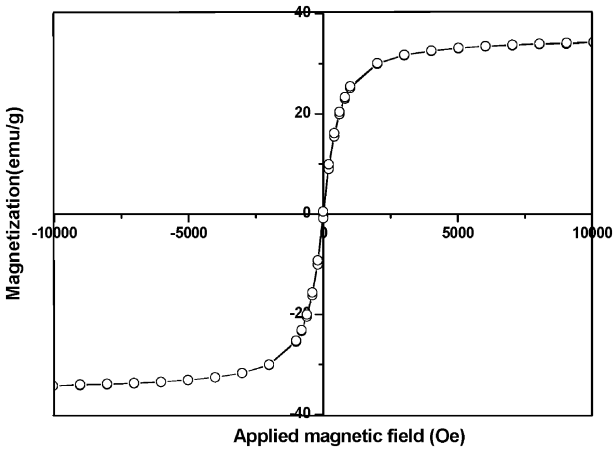


Fig. 7 Hysteresis loop measurement of CMPM measured at 300 K.

obtained, from which magnetite nanoparticles have a strong absorption peak at 275 nm. But the excitation wavelength is 350 nm and the emission wavelength is 440 nm in PL spectrum of CMPM. Therefore the effect of magnetite nanoparticles on the CdS fluorescence may be little.

Magnetic characterization of CMPM measured at 300 K is shown in Fig. 7. It can be seen that it has no specific saturation magnetization and its coercivities approach to 0 Oe, indicating its superparamagnetic property. The saturation magnetization (Ms) for CMPM is close to 34.43 emu g^{-1}, which is much bigger than that of the results reported by the literatures,[13,14] for which the saturation magnetization do not exceed 2 emu g^{-1}. Furthermore, the CMPM have strong magnetic induction due to their high magnetite content, which will make them being promising for the bio-applications.

Conclusion

In summary, we have described a facile free-template route for the fabrication of CMPM under ambient pressure and at room temperature. CMPM simultaneously possess magnetic, fluorescent and hollow properties. Compared to other methods for the formation of multifunctional structures, our method is simply, mild and facile. We believe that these

CMPM will have important applications in biotechnology such as cell tracking and drug delivery.

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