

# Facile synthesis of magnetic-fluorescent and water-soluble $ZnS:Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$ core/shell/shell nanocomposites with pure dopant emission

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Abstract In this paper, we synthesized water-soluble ZnS:Mn<sup>2+</sup>(-SH) nanowires (NWs)/Fe<sub>3</sub>O<sub>4</sub>(-SH) quantum dots (QDs)/SiO<sub>2</sub> core/shell/shell nanocomposites with pure dopant emission, room temperature superparamagnetic and excellent photostablility. The average diameter of the Fe<sub>3</sub>O<sub>4</sub> QDs, ZnS:Mn<sup>2+</sup> NWs, ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH) and  $ZnS:Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$  nanocomposites was about 3, 7, 8.5 and 10 nm, respectively. The dopant emission intensity of the functionalized ZnS:Mn<sup>2+</sup> (-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites was much higher than that of the ZnS:Mn<sup>2+</sup>/Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanocomposites due to MPA modification. The ZnS:Mn<sup>2+</sup>(-SH)/ Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites also exhibited excellent photostability under the intense UV irradiation because of the blocking of exciton migration and retarding exciton trapping at local defects by the SiO<sub>2</sub> shell. The superparamagnetic properties of the nanocomposites were also studied at room temperature,

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and the magnetic saturation value was decreased as the  ${\rm SiO}_2$  thickness increased.

# **1** Introduction

Magnetic-fluorescent nanocomposites composed with biocompatible semiconductor nanocrystals and magnetic nanoparticles are opening up broader avenues for their applications as dual-modality imaging probes in the fields of targeted drug delivery, cell tracing, magnetic bio-separation, biological imaging, information storage, etc. [1, 2]. Among the widely studied fluorescent labeling nanomaterials, Mn<sup>2+</sup> doped ZnS nanocrystals contain no toxic elements and can give rise to the strong yellow-orange light emission located at about 580 nm (through the  ${}^{4}T_{1}$  to  ${}^{6}A_{1}$ internal transition) with a long luminescence lifetime which is about 1 ms [3-5]. Such a strong luminescence and long lifetime allows the light penetrate into and out of the tissues and distinguish the luminescence from the background autofluorescence. Besides, Mn<sup>2+</sup> doped ZnS nanocrystals are environment friendly and biocompatible [6]. Hence, the  $ZnS:Mn^{2+}$  nanocrystals with those excellent properties have been frequently used for fluorescent labeling agents [7, 8]. Herein, in order to get the dualmodality imaging probes, we need to introduce magnetic nanoparticles based on the ZnS:Mn<sup>2+</sup> nanocrystals. Magnetic nanoparticles are a kind of nanoparticles that can be controlled through an external magnetic field. Among all the magnetic nanoparticles which generally consist of magnetic elements, such as iron, nickel, cobalt and their oxides, Fe<sub>3</sub>O<sub>4</sub> nanoparticles are the most prominent class for their biocompatibility and stability by far [9–11]. Therefore, combination of Mn<sup>2+</sup> doped ZnS nanocrystals and magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles to obtain the magneticfluorescent nanocomposites has been highly desired. However, fluorescence quenching always occurs due to the energy transfer process between the  $ZnS:Mn^{2+}$  and  $Fe_3O_4$ [12]. To address the problem and achieve the purpose of further bioimaging applications, surface modification, such as silica, carbon, or polymer coating techniques has been used [13–15]. Among them, silica coating technique was used in the synthesis of the core/shell nanocomposites due to its absolutely biocompatibility, excellent chemical stability and easy further conjugation with various functional groups and biological molecules [15–17].

In the present work, water-soluble and bi-functional ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> magnetic-fluorescent nanocomposites with pure dopant emission and without using other components as the transition layers were synthesized by Stöber method. The synthesis approach is a very facile and considered to be nontoxic, low cost, low temperature and suitable for fabricating nanocomposites [18–20]. Moreover, the diameter of the synthesized nanocomposites were about 10 nm which was nearly minimal among the reported methods for the fabrication of water-soluble silica-coated nanocomposites. Remarkably, the PL intensity of the ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites was found to be stable under intense UV irradiation for 7000 s indicating their potential applications in biological labeling and light emitting devices.

## 2 Experimental section

#### 2.1 Materials

Zinc nitrate, manganese nitrate, thiourea, ethylenediamine (EN), thioglycolic acid (MPA), ferric chloride (FeCl<sub>3</sub>·  $6H_2O$ ), ferrous chloride (FeCl<sub>2</sub>· $4H_2O$ ), PEG-4000, ethylene glycol, concentrated ammonia aqueous solution (25 %), tetraethyl orthosilicate (TEOS) and ethanol were all analytical grade (Shanghai Chemical Reagents Co.), and used without further purification.

## 2.2 Preparation and chemical modification of ZnS:Mn<sup>2+</sup>(1 %) NWs

In a typical process, 0.99 mmol of zinc nitrate and 0.01 mmol of manganese nitrate were dissolved in 16 ml EN and water (1:1 in volume ratio). After stirring for 1 h, 3 mmol of thiourea was added to the resulting complex. After stirring for 2 h, the colloid solution was transferred into a 20 ml Teflon-lined autoclave and kept at 180 °C for 12 h. After the reaction, the autoclave was taken out and cooled down to room temperature. The product was washed with ethanol and deionized water for several times

and separated by centrifugation, and then dried at 80  $^{\circ}$ C for 1 h to yield a white powder.

ZnS:Mn<sup>2+</sup>(1 %) NWs was modified with MPA as follows: 9.7 mg of ZnS:Mn<sup>2+</sup> NWs were dispersed ultrasonically in deionized water (100 ml), and then 75  $\mu$ l of MPA was added to the above solution under magnetic stirring for 1 h to form the ZnS:Mn<sup>2+</sup>(–SH) water solution.

# 2.3 Preparation and chemical modification of Fe<sub>3</sub>O<sub>4</sub> QDs

Fe<sub>3</sub>O<sub>4</sub> QDs were prepared through an improved chemical co-precipitation method. FeCl<sub>3</sub>·6H<sub>2</sub>O (6 mmol), FeCl<sub>2</sub>· $4H_2O$  (10 mmol) and PEG-4000 (10 g) were dissolved in absolute ethylene glycol (250 ml). After stirring for 30 min at room temperature, 100 ml of concentrated ammonia aqueous solution (25 %) was added rapidly to the resulting complex. Then the reaction mixture was heated at 110 °C for 2 h under mechanical stirring, producing a black and homogeneous suspension. After cooling to room temperature, the precipitate was separated with a permanent magnet and washed with deionized water and ethanol for several times until the pH decreased to 7.0, followed by drying in a vacuum oven at 40 °C for 48 h.

 $Fe_3O_4$  QDs was modified with MPA as follows: 0.023 g of  $Fe_3O_4$  QDs and 0.011 g of MPA were dispersed in 250 ml of deionized water under mechanical stirring for 1 h to form the  $Fe_3O_4(-SH)$  water solution.

# 2.4 Preparation of ZnS:Mn<sup>2+</sup>(-SH) NWs/Fe<sub>3</sub>O<sub>4</sub> (-SH) QDs/SiO<sub>2</sub> core/shell/shell nanostructures

100 ml of ZnS:Mn<sup>2+</sup>(–SH) water solution and 250 ml of Fe<sub>3</sub>O<sub>4</sub>(–SH) water solution were mixed in a three-necked flask under mechanical stirring for 1 h. A mixed solution including 50 ml of absolute alcohol, 1 ml of distilled water, 1.7 ml of aqueous ammonia, and 200  $\mu$ l of TEOS was injected into the above solution. The mixture was continuously stirred for 5 h at room temperature. The product was washed with ethanol several times and separated by centrifugation, and then dried at 60 °C for 3 h to obtain a powder. To investigate the effects of the SiO<sub>2</sub> thickness on the magnetic properties of the samples, a set of samples were synthesized at different time periods (t = 3, 7 h).

## 2.5 Characterization of products

X-ray diffraction (XRD) pattern was collected on a MAC Science MXP-18 X-ray diffractometer using a Cu target radiation source. Transmission electron micrographs (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on JEM-2100 electron microscope. A quantitative compositional analysis was carried out by using an X-ray photoelectron spectroscopy (XPS) in an ultra-high vacuum chamber at a pressure lower than  $1.333 \times 10^{-7}$  Pa. Photoluminescence (PL) measurements were carried out at room temperature, using 325 nm as the excitation wavelength and a He–Cd laser as the source of excitation. Magnetic hysteresis loop was measured by a Lake Shore 7407 vibrating sample magnetometer (VSM) with the maximum field of 6 kOe.

## 3 Results and discussion

Figure 1 shows the XRD patterns of the  $Fe_3O_4$  QDs, ZnS:Mn<sup>2+</sup>(1 %) NWs and ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/ SiO<sub>2</sub> nanocrystals with different hydrolysis time of TEOS. As seen from Fig. 1a, all the diffraction peaks can be well indexed as the face-centered cubic structure of Fe<sub>3</sub>O<sub>4</sub>, which are consistent with the standard card (JCPDS No. 19-0629). The average size estimated from the FWHM using the Debye–Scherrer formula is about 3 nm [21]. In the case of the ZnS:Mn<sup>2+</sup> NWs, all the diffraction peaks can be well indexed as the hexagonal wurtzite phase structure of ZnS, which are consistent with the standard card (JCPDS No. 36-1450). There is no extra diffraction peak from the doped  $Mn^{2+}$  ions for the sample in Fig. 1b thereby suggesting that the Mn<sup>2+</sup> ions have been incorporated into the ZnS lattice. It is possible to predict the growth direction by comparing the full width at half maximum (FWHM) for different XRD peaks [22]. It is noticeable that the FWHM value of the (002) diffraction peak is stronger and narrower than the other peaks, suggesting a preferential growth direction along the c-axis [3].



Fig. 1 XRD patterns of (a)  $Fe_3O_4$  QDs, (b)  $ZnS:Mn^{2+}(1 \%)$  NWs, and  $ZnS:Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$  nanocomposites with the SiO<sub>2</sub> growth time of (c) 3 and (d) 7 h

The XRD pattern of the ZnS: $Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$ nanocomposites (Fig. 1c, d) with the SiO<sub>2</sub> growth time of 3 and 7 h, respectively, shows the characteristic peak of the amorphous SiO<sub>2</sub>, ZnS: $Mn^{2+}$  and Fe<sub>3</sub>O<sub>4</sub>, to some extent indicating that the sample is a composite material including the SiO<sub>2</sub>, ZnS: $Mn^{2+}$  NWs and Fe<sub>3</sub>O<sub>4</sub> QDs. With the increase of TEOS hydrolysis time, the relative intensity of the SiO<sub>2</sub> peak increased, which indicated that the thickness of the SiO<sub>2</sub> shell increased as the hydrolysis time of TEOS increased from 3 to 7 h.

To further prove the formation of ZnS:Mn<sup>2+</sup>(-SH)/  $Fe_3O_4(-SH)/SiO_2$  nanocomposites, we perform the TEM, SAED and HRTEM measurements. Figure 2a-d display the TEM and SAED images of the  $Fe_3O_4$  QDs and ZnS:Mn<sup>2+</sup> NWs. It can be seen that the Fe<sub>3</sub>O<sub>4</sub> QDs (Fig. 2a) and ZnS:Mn<sup>2+</sup> NWs (Fig. 2c) are well crystallized and the average diameter of Fe<sub>3</sub>O<sub>4</sub> QDs and ZnS:Mn<sup>2+</sup> NWs is about 3 and 7 nm, respectively. Figure 2b, d show the corresponding SAED image of the Fe<sub>3</sub>O<sub>4</sub> QDs and ZnS:Mn<sup>2+</sup> NWs, revealing that the Fe<sub>3</sub>O<sub>4</sub> QDs samples are the face-centered cubic structure and the ZnS:Mn<sup>2+</sup> NWs samples are the hexagonal wurtzite structure. Figure 2e, f display the HRTEM images of the  $ZnS:Mn^{2+}(-SH)/Fe_{3}O_{4}(-SH)$  and the  $ZnS:Mn^{2+}(-SH)/Pe_{3}O_{4}(-SH)$  $Fe_3O_4(-SH)/SiO_2$  samples. As the Fig. 2e shows, the average diameter of the ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH) nanocomposites is about 8.5 nm, and the QDs assemble uniformly around the surface of the NWs, which suggests the existence of the core/shell structure. Moreover, the growth direction of the  $ZnS:Mn^{2+}$  NWs is perpendicular to the lattice fringes, and the d spacing of the (002) plane is about 0.31 nm. The lattice fringes with the d spacing of 0.25 nm can be assigned to the (311) plane of the cubic Fe<sub>3</sub>O<sub>4</sub> QDs, which is consistent with the XRD results. The different lattice fringes between the Fe<sub>3</sub>O<sub>4</sub> QDs and ZnS:Mn<sup>2+</sup> NWs in Fig. 2e provides strong evidence for the composite nature of the sample [23, 24]. The HRTEM image of the ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites (Fig. 2f) shows an apparent contrast between the inner core and the outer shell, which further proves the formation of the core/shell/shell structure. The average diameter of the ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites is about 10 nm, which is not obviously enlarged, revealing that the SiO<sub>2</sub> layer is thin.

To investigate the surface information of the prepared samples, X-ray photoelectron spectrum (XPS) analysis was carried out. Figure 3 is the typical XPS spectra of the asprepared ZnS: $Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$  nanocomposites. The binding energy values obtained in the XPS analysis are corrected by referencing the C 1*s* peak to 284.60 eV. The survey XPS spectrum (Fig. 3a) of the nanocomposites shows the presence of C, Zn, S, Si, Fe, O. The presence of the carbon in the survey spectrum is due to the carbon tape used

Fig. 2 a, b TEM and SAED images of Fe<sub>3</sub>O<sub>4</sub> QDs; c, d TEM and SAED images of ZnS: $Mn^{2+}$ NWs; HRTEM images of e ZnS: $Mn^{2+}(-SH)/Fe_3O_4(-SH)$ nanocomposites and f ZnS: $Mn^{2+}(-SH)/Fe_3O_4(-SH)/$ SiO<sub>2</sub> nanocomposites



for the measurement [25]. As shown in Fig. 3b, the highresolution XPS spectrum of the Si 2p peak in ZnS:Mn<sup>2+</sup> (–SH)/Fe<sub>3</sub>O<sub>4</sub>(–SH)/SiO<sub>2</sub> nanocomposites shows the peak at 103.2 eV, corresponding to the Si 2p peak of SiO<sub>2</sub> [26]. The high-resolution binding energy spectrum of the S 2p peak (Fig. 3c) can be decomposed into two Gaussian peaks. The peak centered at 161.6 and 162.9 eV is coming from the S 2p3/2 and S 2p1/2 peak of ZnS [27]. The high-resolution XPS spectrum of the Fe 2p1/2 and Fe 2p3/2 peak (Fig. 3d) shows the peak centered at 723.5 and 711.4 eV, corresponding to the Fe 2p1/2 and Fe 2p3/2 peak of Fe<sub>3</sub>O<sub>4</sub> [28]. As Fig. 3e shows, the high-resolution XPS spectrum of the Zn 2p3/2 peak in ZnS:Mn<sup>2+</sup>(–SH)/Fe<sub>3</sub>O<sub>4</sub>(–SH)/SiO<sub>2</sub> nanocomposites shows the peak at 1022.0 eV, corresponding to the Zn 2p3/2 peak of ZnS [3]. Since XPS does not usually detect Mn in doped ZnS nanostructure, as, only 0.14 at.% Mn are detected for ZnS:Mn<sup>2+</sup>(–SH)/Fe<sub>3</sub>O<sub>4</sub>(–SH)/SiO<sub>2</sub> nanocomposites (Fig. 3f) and the the Mn peak is so weak comparable to the noise level.





Surface modification turns out to be essential to determine the optical properties of the nanocrystals. Figure 4 show the room temperature PL spectra of the ZnS:Mn<sup>2+</sup>/ Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanocomposites with the SiO<sub>2</sub> growth time of 3 and 7 h, ZnS:Mn<sup>2+</sup> NWs and ZnS:Mn<sup>2+</sup>(–SH)/Fe<sub>3</sub>O<sub>4</sub> (–SH)/SiO<sub>2</sub> nanocomposites with the SiO<sub>2</sub> growth time of 3 and 7 h, respectively. The PL spectrum of all the samples nearly show 100 % dopant emission at about 580 nm (corresponding to the Mn<sup>2+ 4</sup>T<sub>1</sub> to <sup>6</sup>A<sub>1</sub> transition), no band emission was observed, indicating the highly efficient energy transfer from the ZnS host to the Mn<sup>2+</sup> ions [4, 29]. The yellow-orange emission intensity of the ZnS:Mn<sup>2+</sup>/ Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanocomposites significantly reduced compared with that of the ZnS:Mn<sup>2+</sup> NWs. This mainly due to the quenching effect from the Fe<sub>3</sub>O<sub>4</sub> QDs to the ZnS:Mn<sup>2+</sup> NWs. It is worth noting that the PL intensity of the fabricated ZnS:Mn<sup>2+</sup>(–SH)/Fe<sub>3</sub>O<sub>4</sub>(–SH)/SiO<sub>2</sub> nanocomposites is much stronger than that of the ZnS:Mn<sup>2+</sup> NWs. The enhancement of the PL intensity could be attributed to the following factors: first and most importantly, the –SH groups on the surface of ZnS:Mn<sup>2+</sup> NWs and Fe<sub>3</sub>O<sub>4</sub> QDs, respectively, can serve as an barrier for preventing the energy transfer from ZnS:Mn<sup>2+</sup> NWs to Fe<sub>3</sub>O<sub>4</sub> QDs [30]; secondly, the surface of ZnS:Mn<sup>2+</sup> NWs was modified with MPA which is enough to passivate the surface defects of ZnS:Mn<sup>2+</sup> NWs and then the exciton migration quenching was decreased. So it would increase the possibility of the electrons to fall into the *d*-orbital of Mn<sup>2+</sup> ions, and subsequently enhance the dopant emission [31]. The yellow-orange emission intensity of the ZnS:Mn<sup>2+</sup>/Fe<sub>3</sub>O<sub>4</sub>/



**Fig. 4** Room temperature PL spectra of  $ZnS:Mn^{2+}/Fe_3O_4/SiO_2$  nanocomposites with the SiO<sub>2</sub> growth time of 3 and 7 h, ZnS:Mn<sup>2+</sup> NWs and ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites with the SiO<sub>2</sub> growth time of 3 and 7 h, respectively; *Left insets* are the digital pictures of corresponding (*a*) Fe<sub>3</sub>O<sub>4</sub> QDs, (*b*) ZnS:Mn<sup>2+</sup> NWs, (*c*) ZnS:Mn<sup>2+</sup>/Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanocomposites and (*d*) ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites dispersed in water under 365 nm UV lamp excitation

 $SiO_2$  and  $ZnS:Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$  nanocomposites reduced with the increase of TEOS hydrolysis time. The PL intensity of the emission is mainly determined by the degree of surface passivation. At the early stage of the hydrolysis of TEOS, only parts of  $ZnS:Mn^{2+}$  NWs and  $Fe_3O_4$  QDs were encapsulated by the silica shell, while the rest of the  $ZnS:Mn^{2+}$  NWs and  $Fe_3O_4$  QDs still remained in the solution, which can be removed in the experiment. So, the surface of the  $ZnS:Mn^{2+}$  NWs and  $Fe_3O_4$  QDs can be passivated fully by the  $Fe_3O_4$  QDs and  $SiO_2$ , respectively. With the increase in the hydrolysis time of TEOS, the silica shell became thick and more  $ZnS:Mn^{2+}$  NWs and



Fig. 5 Photostability of ZnS:Mn^2+(-SH)/Fe\_3O\_4(-SH)/SiO\_2 nanoc omposites

 $Fe_3O_4$  QDs would be encapsulated. But the thick  $Fe_3O_4$  and  $SiO_2$  coating would induce strain at the interface caused by the lattice mismatch between one another. It would result in new traps for carriers, which are thought to be the main reason for the decrease of the yellow orange emission.

It is well known that the photostability was very important in numerous applications. Thus, we investigated the photostability of the as-prepared ZnS:Mn<sup>2+</sup>(–SH)/Fe<sub>3</sub>O<sub>4</sub>(–SH)/SiO<sub>2</sub> nanocomposites, which was uninterruptedly irradiated by a 450W xenon lamp under 365 nm and monitored by the PL emission spectrum. As Fig. 5 shows, the PL intensity of the ZnS:Mn<sup>2+</sup>(–SH)/Fe<sub>3</sub>O<sub>4</sub> (–SH)/SiO<sub>2</sub> nanocomposites only decreased slightly, preserving about 70 % of the initial intensity under even 7000 s intense UV irradiation, which exhibited the excellent photostability. The dominant mechanism for the



**Fig. 6** a Magnetic hysteresis loops of ZnS: $Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$  nanocomposites with the SiO<sub>2</sub> growth time of (*I*) 3 and (*II*) 7 h; b Magnetic hysteresis loops of (*I*) ZnS: $Mn^{2+}/Fe_3O_4/SiO_2$  and (*II*) ZnS: $Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$  nanocomposites with the SiO<sub>2</sub> growth time of 3 h

photostability could be the blocking of exciton migration and retarding exciton trapping at local defects by the  $SiO_2$  shell [32, 33].

Figure 6a shows the magnetization curve pattern of the ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub> (-SH)/SiO<sub>2</sub> nanocomposites with different SiO<sub>2</sub> thickness and Fig. 6b shows the magnetization curve pattern of the ZnS:Mn<sup>2+</sup>/Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and  $ZnS:Mn^{2+}(-SH)/Fe_3O_4(-SH)/SiO_2$  nanocomposites with the  $SiO_2$  growth time of 3 h. It can be seen that the all the nanocomposites show the superparamagnetic properties at the room temperature. As can be seen from Fig. 6a, the Ms value of the ZnS:Mn<sup>2+</sup>(-SH)/Fe<sub>3</sub>O<sub>4</sub>(-SH)/SiO<sub>2</sub> nanocomposites is decreased as the thickness of the SiO<sub>2</sub> increased, which is mainly due to the lower mass content of Fe<sub>3</sub>O<sub>4</sub> in the nanocomposites as the mass of the  $SiO_2$  increased [34]. In Fig. 6b, the Ms value of the  $ZnS:Mn^{2+}(-SH)/Fe_3O_4$ (-SH)/SiO<sub>2</sub> nanocomposites is slightly lower than that of the ZnS:Mn<sup>2+</sup>/Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanocomposites. Usually, the decrease in Ms can be ascribed to the change of the size or the surface states on the  $Fe_3O_4$  QDs [35]. Here, the slightly decrease of Ms can be attributed to the surface modifications by MPA [12].

## 4 Conclusions

In summary, the small-sized and water-soluble ZnS:Mn<sup>2+</sup> (–SH)/Fe<sub>3</sub>O<sub>4</sub>(–SH)/SiO<sub>2</sub> core/shell/shell nanocomposites were fabricated successfully by assembling the MPA-coated Fe<sub>3</sub>O<sub>4</sub> QDs on MPA-coated ZnS:Mn<sup>2+</sup> NWs by the Stöber method. Compared to the traditional synthesis methods, our method used the low-cost and nontoxic chemicals under mild conditions. The synthetic water-soluble core/shell/shell nanocomposites exhibited excellent pure dopant emission at about 580 nm and retain the superparamagnetic properties of the Fe<sub>3</sub>O<sub>4</sub> QDs. Therefore, the water-soluble, fluorescent and superparamagnetic properties of the ZnS:Mn<sup>2+</sup>(–SH)/Fe<sub>3</sub>O<sub>4</sub>(–SH)/SiO<sub>2</sub> nanocomposites would allow them to find applications in biolabeling, bioseparation and diagnostic analysis.

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