Lanthanide-Functionalized Hydrophilic Magnetic Hybrid Nanoparticles: Assembly, Magnetic Behaviour, and Photophysical Properties

Shuai Han1,3*, Yu Tang2, Haijun Guo1, Shenjun Qin1,3 and Jiang Wu2

Abstract

The lanthanide-functionalized multifunctional hybrid nanoparticles combining the superparamagnetic core and the luminescent europium complex were successfully designed and assembled via layer-by-layer strategy in this work. It is noted that the hybrid nanoparticles were modified by a hydrophilic polymer polyethyleneimine (PEI) through hydrogen bonding which bestowed excellent hydrophilicity and biocompatibility on this material. A bright-red luminescence was observed by fluorescence microscopy, revealing that these magnetic-luminescent nanoparticles were both colloidal and chemically stable in PBS solution. Therefore, the nanocomposite with magnetic resonance response and fluorescence probe property is considered to be of great potential in multi-modal bioimaging and diagnostic applications.

Keywords: Magnetite, Luminescent europium complex, Polyethyleneimine, Multifunctional

Background

The past decade has witnessed an explosion of interest in combining optically active components with magnetic nanoparticles (NPs) in one entity [1]. This new class of hybrid nanocomposite has been successfully employed for biomedical imaging [2], drug delivery [3], sensing [4], etc. Owing to their superparamagnetic behaviours, Fe3O4 NPs could be manipulated by external magnetic field which makes it easier to separate from solution in further modifications.

Therefore, fluorescent compounds such as semiconducting quantum dots [5], fluorescent organic dyes [6], and metal complexes [7] were commonly incorporated with Fe3O4 NPs to achieve multifunctional capabilities. Compared with these fluorochromes, lanthanide-based complexes are of particular attractiveness for their large Stokes shift and sharp line-like emission bands [8].

Moreover, their long luminescence lifetimes, typically in the millisecond range, make lanthanide complexes become the most fascinating and useful candidates as time-gated probes in biological systems for the reason that they can typically diminish the background fluorescence of other organic substances [9]. It can be anticipated that the combination of superparamagnetic Fe3O4 with a lanthanide-based complex would open up the opportunity to provide potential applications in highly sensitive bio-applications.

Although the progress in combination lanthanides and magnetic NPs within one hybrid nanomaterial has advanced rapidly, there are still some challenges for these novel functional materials. One of the most important challenges is the risk of fluorescence quenched by magnetic cores. Therefore, it is of great importance to make sure that both optically active components and magnetic properties were conveyed without compromising by each other. In our synthetic strategy, SiO2 was chosen as the coating spacer between the lumophore and the magnetic NPs which could effectively diminish the fluorescence quenching by magnetic cores and prevent Fe3O4 NPs from aggregation in the solution. Meanwhile the...
SiO$_2$ shell can be easily surface-functionalized and is more biocompatible for further application in biomedical uses [10]. In order to introduce the luminescent centre, we grafted lanthanide complexes directly on the SiO$_2$ shell through the covalent bonding. As a strong interaction, covalent bonding can successfully overcome the leaching of fluorescent compounds and enhance the thermal and chemical stabilities of the hybrid nanomaterial.

Polymers are one of the best candidates in modifying the nanostructures for that they can afford controllable functional groups on the surface of nanomaterials. Polyethyleneimine (PEI) is a kind of cationic polyamine owing to the protonation of primary amines on its macromolecular chains. It can be attracted on the surfaces of different materials by hydrogen bonding and can be further functioned for various applications such as removal of heavy metal ions from blood [11], efficient gene delivery in cells [12], nano-drug delivery systems [13], and so on [14]. PEI coating not only offers opportunities to render the Fe$_3$O$_4$ NPs with excellent hydrophilicity and biocompatibility but also can overcome the fluorescence disturbed by the environment.

Herein, a kind of novel magnetic-luminescent NP has been assembled by the coupling of a europium(III) complex with dibenzoylmethanate (DBM) and 2-(4-hydroxy-phenyl)imidazo[4,5-f]1,10-phenanthroline (L$_p$) onto Fe$_3$O$_4$@SiO$_2$ NPs. The obtained NPs which have the imidazo structure and many oxygen and nitrogen atoms on the surface could conjugate with PEI by hydrogen bonding to fabricate a four-component nano-composite Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_p$]@PEI (Fig. 1). Moreover, it is worth mentioning that this nanocomposite could be effectively sensitized by visible light ($\lambda > 385$ nm), thus to reduce the effect of UV damage on living biological samples [15], making it of great potential in multimodal biomedical imaging and diagnostic applications.

Methods

Materials and Reagents
1,10-Phenanthroline-5,6-dione and ammonium acetate were obtained from Shanxi Xinhua Co. FeCl$_3$·6H$_2$O, sodium acrylate, and NaOAc were purchased from Tianjin Guangfu Chemical. 3-(Triethoxysilyl)propyl isocyanate was purchased from Jinan Xinning Medicine Science and Technology Co. Other chemicals and solvents were obtained from Aladdin Chemicals Company and were of analytical grade.

Analysis

NMR spectra were recorded on a Varian Mercury-300B spectrometer. CHN elemental analyses were measured on an Elementar Vario EL analyser; the contents of Eu(III) ions were obtained by inductively coupled plasma-atomic emission spectroscopy (ICP) using an IRIS Advantage ER/S spectrophotometer. The solid-state absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. Fourier transform infrared (FTIR) spectra were conducted within the 4000–400 cm$^{-1}$ wave number range using a Nicolet 360 FTIR spectrometer with the KBr pellet technique. Transmission electron microscope (TEM) images were taken on a JEM-100CX II apparatus, and the fluorescence images were taken on an Olympus FluoView 500 laser scanning confocal microscope (FV1000, MPE). Dynamic light-scattering (DLS) measurements were performed at
25 °C using a Malvern Zetasizer Nano ZS. Magnetic measurements were carried out at room temperature with a Lake Shore-735 vibrating sample magnetometer (VSM) magnetometer. The steady-state luminescence spectra and the lifetime measurements were measured on an Edinburgh Instruments FSL.920 fluorescence spectrometer, with a 450-W Xe arc lamp as the steady-state excitation source or an Nd-pumped OPOLlette laser as the excitation source for lifetime measurements. The solid-state quantum yield was measured using a Model F-3029, Quanta-Phi 6 Integrating Sphere connected with a Horiba Jobin Yvon Fluorolog-3 spectrophotometer.

**Synthesis of the Ligand L<sub>p</sub>**

1,10-Phenanthroline-5,6-dione (0.5 g, 2.3 mmol) and ammonium acetate (2.93 g, 66.5 mmol) were dissolved in 5 mL glacial acetic acid. While the mixture was stirred, a solution of 4-hydroxybenzaldehyde (0.283 g, 2.3 mmol) in glacial acetic acid was added dropwise to the mixture. After heating for 3 h, the mixture was then poured in 200 mL water. The solution was neutralized with ammonia to pH = 7 and then was cooled to room temperature. The precipitate was filtered off and washed with large portions of water, then the crude product was purified by recrystallization from a mixture of EtOH and water solution (yield 65 %). \( \delta_1 \) (400 MHz, DMSO-d<sub>6</sub>) 7.65–7.68 (dd, \( J = 7.6, 4.4 \) Hz, 1H), 8.37–8.40 (dd, \( J = 7.6 \) Hz, 1.6 Hz, 1H), 8.98–9.00 (dd, \( J = 4.4 \) Hz, 1.6 Hz, 1H). Anal. Calcd C, 73.07; H, 3.87; N, 17.94. Found C, 73.37; H, 3.57; N, 17.82.

**Synthesis of Eu(DBM)<sub>3</sub>L<sub>p</sub>**

Solid L<sub>p</sub> (31.2 mg, 0.10 mmol) prepared was mixed with 25 mL of 95 % ethanolic solution of Eu(DBM)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> (86.0 mg, 0.10 mmol, prepared according to the literature), and then the suspension was sonicated for 20 min. After sonication, the reaction system was stirred at room temperature overnight. The yellow precipitate formed was filtered and washed with ethanol. The solution was neutralized with ammonia to pH = 7 and was then cooled to room temperature. The precipitate was filtered off, washed, and then dissolved in ethanol. The solution was filtered, and the ethanol was removed by rotary evaporation. The obtained compound was dissolved in a small portion of dichloromethane (DCM). This DCM solution was added dropwise to 30 mL of cold hexane to reprecipitate the compound. The purified product was filtered off and dried in vacuo. Yield 60 %; \( \delta_1 \) (400 MHz, DMSO-d<sub>6</sub>) 1.08–1.15 (t, \( J = 17.0 \) Hz, 9H), 1.51–1.55 (m, 2H), 3.02–3.07 (m, 2H), 3.71–3.76 (q, \( J = 6.8 \) Hz, 6H), 7.31–7.33 (d, \( J = 8.8 \) Hz, 2H), 7.79–7.86 (m, 2H), 8.24–8.26 (d, \( J = 7.6 \) Hz, 2H), 8.91 (dd, \( J = 8.0 \) Hz, 1.6 Hz, 2H), 9.04 (dd, \( J = 4.4 \) Hz, 1.6 Hz, 2H), 13.73 (s, 1H).

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>−L<sub>p</sub>**

Two hundred milligrams Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> were refluxed for 8 h. The solid obtained was then separated by centrifugation, washed with ethanol, and dried at room temperature.

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>−Eu(DBM)<sub>3</sub>L<sub>p</sub>**

A batch of 200 mg of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>−L<sub>p</sub> was refluxed with 30 mg of Eu(DBM)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in ethanol, then the obtained magnetic-luminescent NPs were collected by centrifugation, washed with ethanol, and dried in vacuum.

it could be seen that all the diffraction peaks are indexed to the cubic structure, known for the Fe<sub>3</sub>O<sub>4</sub> crystal (JCPDS no. 88-0315) and no other peaks are detected, indicating that the products are pure-phase Fe<sub>3</sub>O<sub>4</sub>.

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs**

The core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanospheres were prepared according to a previously reported method. Typically, the Fe<sub>3</sub>O<sub>4</sub> NPs was treated with diluted HCl solution by ultrasonication for 10 min. The magnetite NPs were washed and homogeneously dispersed in a mixture of ethanol, deionized water, and concentrated ammonia aqueous solution, followed by the addition of tetraethyl orthosilicate (TEOS; 0.03 g, 0.144 mmol). After being stirred for 6 h, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanospheres were separated, washed, and then dried in vacuum.

**Synthesis of Eu(DBM)<sub>3</sub>−L<sub>p</sub>**

A batch of 200 mg (7.45 mmol) of L<sub>p</sub> was homogeneously dispersed in an excess of 3-(triethoxysilyl)propyl isocyanate (2.5 mL) under ultrasonication. Then, the mixture was stirred under argon at 80 °C for 72 h. The mixture was added slowly to 20 mL of cold hexane, and a white-yellow precipitate was formed. The precipitate was filtered off, washed, and then dissolved in ethanol. The solution was filtered, and the ethanol was removed by rotary evaporation. The obtained compound was dissolved in a small portion of dichloromethane (DCM). This DCM solution was added dropwise to 30 mL of cold hexane to reprecipitate the compound. The purified product was filtered off and dried in vacuo. Yield 60 %; \( \delta_1 \) (400 MHz, DMSO-d<sub>6</sub>) 1.08–1.15 (t, \( J = 17.0 \) Hz, 9H), 1.51–1.55 (m, 2H), 3.02–3.07 (m, 2H), 3.71–3.76 (q, \( J = 6.8 \) Hz, 6H), 7.31–7.33 (d, \( J = 8.8 \) Hz, 2H), 7.79–7.86 (m, 2H), 8.24–8.26 (d, \( J = 7.6 \) Hz, 2H), 8.91 (dd, \( J = 8.0 \) Hz, 1.6 Hz, 2H), 9.04 (dd, \( J = 4.4 \) Hz, 1.6 Hz, 2H), 13.73 (s, 1H).
Synthesis of Fe₃O₄@SiO₂-[Eu(DBM)₃]@PEI
A batch of 200 mg of Fe₃O₄@SiO₂-[Eu(DBM)₃] was homogeneously dispersed in ethanol under ultrasonication; PEI ethanol solution was then slowly added to the solution. After being fiercely stirred at room temperature for 6 h, the microspheres were separated, washed with ethanol, and then dried in vacuum at 60 °C for 6 h.

Results and Discussion
Microstructure Characterization of the Nanocomposite Fe₃O₄@SiO₂-[Eu(DBM)₃]@PEI
TEM images of the Fe₃O₄ magnetic NPs, the Fe₃O₄@SiO₂ composite NPs are shown in Fig. 2b, f. After being coated with a non-porous silica layer, core-shell Fe₃O₄@SiO₂ NPs with a thin silica layer ~10 nm in thickness were obtained. TEM images of the Fe₃O₄@SiO₂-[Eu(DBM)₃] NPs which are shown in Fig. 2c, g indicate that the subsequent Eu(III) complex modification process resulted in a continuous and uniform coating on the surface of Fe₃O₄@SiO₂ nanospheres. And TEM images of the PEI-modified nanocomposite are shown in Fig. 2d, h. However, the PEI molecules cannot be seen from the images for the reason that the interference of high-voltage electrons (120 kV, or 200 kV) with the light element compound (C, H, O, N) was too weak to be observed. Besides, the DLS measurements have been performed and the obtained data was shown in Additional file 1: Figure S2. While the mean diameters of the four samples were determined to be 100, 108, 122, and 125 nm which are corresponding with the TEM test results.

The above electron microscope observation results can be further confirmed by zeta potential measurements of the products, which are sensitive mainly to the outer surface of the NPs [17]. The measurements showed that after the SiO₂ coating, the value zeta potential at physiological pH of 7.4 decreased from ~12.7 mV for the starting Fe₃O₄ NPs to ~28.3 mV. The zeta potential value changed to 9.4 mV upon Eu(III) complex conjugation and increased steeply to 30.2 mV after modifying with PEI, confirming the pronounced increase in the surface amino group density. Thus, the changes in the potential value of the NPs suggested that the surface modifications of SiO₂, Eu(III) complex and PEI to the NPs were successful.

Furthermore, as a cationic dispersant, PEI could provide both electrostatic repulsion and steric hindrance effect to the nanocomposite and prevent the NPs to coming close enough together to agglomerate into larger NPs. This means that the PEI functionalization on Fe₃O₄@SiO₂-[Eu(DBM)₃] could significantly increase the water solubility and stability of the nanocomposite, which was essential for them in biological applications [18].

FTIR spectra were conducted to further verify the obtained products. As seen from Additional file 1: Figure S3, IR spectroscopy provided clear evidence for the layer-by-layer surface modification. Additional file 1: Figure S1b displays the IR spectrum of the bare magnetic NPs, and the characteristic band of Fe₃O₄ appeared at about 586 nm. The FTIR spectrum of Fe₃O₄@SiO₂ (Additional file 1: Figure S1c) indicated that the silica shell was coated on the surface of the magnetite cores, which could be confirmed by assignments of the bands Si-O-Si (1085 cm⁻¹) and Si-OH...
(945 cm\(^{-1}\)), and the characteristic Fe-O peak of Fe\(_3\)O\(_4\) NPs at 586 cm\(^{-1}\) shifted to 589 cm\(^{-1}\) in the spectrum of SiO\(_2\)-coated magnetic NPs [19]. Compared with the FTIR spectrum of Fe\(_3\)O\(_4\)@SiO\(_2\) NPs, the sharp peaks located at 1704 and 1565 cm\(^{-1}\) which appeared in the spectrum of Fe\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\) (Additional file 1: Figure S1d) corresponded to the adsorption of the SiO\(_2\)-coated magnetic NPs [19]. Compared with that of Eu(DBM)\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\) @PEI nanocomposite, the functionalized nanocomposite displayed a peak at 230 nm that was typical for PEI. More importantly, comparing with that of Fe\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\)@PEI nanocomposite at different excitation wavelengths from the UV to visible range (330, 360, 390, 405, and 420 nm). From these comparisons, one could note that both the precursor and the nanocomposite exhibited significant luminescent efficiency at different excitation

Magnetic and Photophysical Properties of the Nanocomposite Fe\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\)@PEI

Magnetic characterization at 300 K with a VSM showed that the saturation magnetization values of Fe\(_3\)O\(_4\) NPs, Fe\(_3\)O\(_4\)@SiO\(_2\), Fe\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\), and the PEI-modified nanocomposite were 68.7, 51.0, 32.3, and 27.4 emu g\(^{-1}\) (Fig. 4), respectively, and the magnified hysteresis loops further confirmed the superparamagnetism of these NPs. Though the saturation magnetization of the Fe\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\)@PEI nanocomposite is less than the magnetite NPs as magnetic core, it may be believed to possess enough strong magnetic attraction for effectively magnetic targeting and separation.

Figure 5 illustrates the corrected excitation (left) and emission (right) spectra of the isolated Eu\(^{3+}\) complex [Eu(DBM)]\(_3\)L\(_p\) and the Fe\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\)@PEI nanocomposite as solid at room temperature. The excitation spectra which were both obtained by monitoring at 612 nm exhibited a broad excitation band (BEB) between 250 and 450 nm. In the emission spectra, only characteristic emission of Eu(III) arising from the transition \(^{5}D_{0} \rightarrow \ ^{7}F_{j} (j = 0, 1, 2, 3, 4)\) was detected with the transition \(^{5}D_{0} \rightarrow \ ^{7}F_{2}\) (red emission) as the dominant group, which indicated that an efficient energy transfer from the ligands to Eu(III) could take place not only in the Eu(III) complex but also in the complex incorporated in the matrix [23]. Figure 6 shows the comparison of luminescence intensities of the Eu(III) complex [Eu(DBM)]\(_3\)L\(_p\) with the Fe\(_3\)O\(_4\)@SiO\(_2\)-[Eu(DBM)]\(_3\)L\(_p\)@PEI nanocomposite at different excitation wavelengths from the UV to visible range (330, 360, 390, 405, and 420 nm). From these comparisons, one could note that the precursor and the nanocomposite exhibited significant luminescent efficiency at different excitation
wavelengths, which demonstrated the potential utility of this novel material in bioimaging [24].

The quantum yield ($\Phi$) of the Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$]@PEI nanocomposite was measured to be 2.70 % lower than that of the free Eu(DBM)$_3$L$_{lp}$ (14 %), which might be due to the absorption of the matrix. The excited-state lifetime of the Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$]@PEI NPs is 0.32 ms, which was close to that of the free Eu(DBM)$_3$L$_{lp}$ (0.48 ms), indicating that the assembled nanocomposite was capable of eliminating background emission from a biological background for sensitive optical-imaging applications. The shortened lifetime might have given rise to the quenching of O-H oscillators on the matrix surfaces and the non-radiative dissipation of energy on the high-energy N-H vibrations from the modified PEI molecule, which also made the quantum yield of Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$]@PEI nanocomposite be lower than that of Eu(DBM)$_3$L$_{lp}$ [25].

Direct proof of magnetic-luminescent properties of the final product could be found in the following designed experiments. Upon UV light irradiation, the well-dispersed aqueous Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$]@PEI nanocomposite emitted bright-red light originating from the characteristic emission of Eu(III) as shown in the digital photographs of Fig. 7b. When a handheld magnet was placed close to the glass vial, the nanocomposite particles were attracted to the magnet very quickly (Fig. 7c). Meanwhile, corresponding bright-red light emissions could be observed at these positions under UV light irradiation (Fig. 7d). After removal of the external magnet and sonication, the magnetic microspheres could be rapidly redispersed again. These results showed that the Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$]@PEI nanocomposite possessed excellent magnetic responsiveness, luminescent property, and water solubility, which were important in terms of the practical manipulation.

The intense luminescent character of the Eu(III) complexes enables us to directly capture the Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$]@PEI by using a fluorescence microscope. One of the advantages of using a fluorescence microscope as a tool is that the dispersive and luminescent properties at a micro level can be monitored. In the current study, observations using a fluorescence microscope were carried out on the Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$]@PEI nanocomposite dispersed in PBS solution. When the nanocomposite was sonicated with a concentration of 0.1 wt. %, a stable dispersion was formed. Inside this dispersion, shining red spots were observed as shown in Additional file 1: Figure S4, indicating the luminescent character of the composite. For comparison, Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)$_3$L$_{lp}$] were dispersed in PBS solution at the same condition; however, great agglomeration could be seen from the photographs (Additional file 1: Figure S5). The most obvious reason for this
phenomenon was that PEI modification significantly increased the water solubility of the nanocomposite.

Conclusions
In summary, a simple and versatile strategy has been developed to transform Fe$_3$O$_4$ NPs into hydrophilic and biocompatible magnetic-luminescent dual-functional nanocomposites. The silica shells formed via the sol-gel method played significant roles in terms of trapping Fe$_3$O$_4$ NPs; the Eu(III) complex grafted made the NPs potential in a time-resolved imaging, and the PEI surface layer endowed the final material with hydrophilic and modifiable properties. The nanocomposite obtained was characterized by various techniques, and the results showed the desired properties as designed. Furthermore, this approach of functionalizing magnetic-luminescent nanocomposite via hydrogen-bonding method may be applied to fabricate other nanocomposites in order to obtain broader optical properties and potential applications.

Additional File

**Additional file 1**: Figure S1. DLS results of the samples. (a) Eu(DBM)$_3$ complex; (b) Fe$_3$O$_4$@SiO$_2$; (c) Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)]$_L$ and (d) Fe$_3$O$_4$@SiO$_2$-[Eu(DBM)]$_L$@PEI. Figure S2. FTIR spectra and images obtained under a fluorescence microscope for Fe$_3$O$_4$-[Eu(DBM)]$_L$@PEI nanocomposite. Figure S3. A typical image obtained under a fluorescence microscope for Fe$_3$O$_4$-[Eu(DBM)]$_L$@PEI nanocomposite dispersed in PBS solution. Images a, b, c were taken at different regions of the same sample. Figure S4. A typical image obtained under a fluorescence microscope for Fe$_3$O$_4$-[Eu(DBM)]$_L$@PEI nanocomposite dispersed in PBS solution. Images a, b, and c were taken at different regions of the same sample. Figure S5. The PXRD analysis of the Fe$_3$O$_4$ NPs. (DOC 2084 kb)

Competing Interests
The authors declare that they have no competing interests.

Authors’ Contributions
SH fabricated all the nanostructures and drafted the manuscript. SJQ performed the fluorescence microscope tests on the composite nanostructures. YT and JW planned the whole work and revised the manuscript. HG performed the PXRD tests of the Fe$_3$O$_4$ and the DLS analysis on the composite nanostructures. All authors read and approved the final manuscript.

Authors’ Information
SH worked as a docent in the College of Science, Hebei University of Engineering. His research interests are nanochemistry, nanotechnology, and coordination chemistry. YT worked as a professor in the College of Chemistry and Chemical Engineering, Lanzhou University. Her research interests are nanochemistry, coordination chemistry, and biochemistry. SJQ worked as the dean of the College of Science, Hebei University of Engineering. His research interests are nanobiotechnology and mineral chemistry. JW worked as a technician in the College of Science, Hebei University of Engineering. His research interests are nanochemistry and nanotechnology. JW worked as an docent in the College of Chemistry and Chemical Engineering, Lanzhou University. His research interests are nanomaterials and biochemistry.

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Author details
1College of Science, Hebei University of Engineering, Handan, 056000, People’s Republic of China. 2Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People’s Republic of China. 3Hebei Collaborative Innovation Center of Coal Exploitation, Hebei University of Engineering, Handan, Hebei 056038, People’s Republic of China.

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