

Facile Synthesis of Carboxylic Functionalized MFe_2O_4 (M = Mn, Co, Zn) Nanospheres

Ruimin Xing¹, Li Lu¹, Haiping Huang², Shanhu Liu^{1,*}, and Jingyang Niu^{1,*}

¹Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China

²Center for Analysis and Testing, Institute of Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

A facile one-pot solvothermal method was developed for the synthesis of carboxylic functionalized MFe_2O_4 (M = Mn, Co, Zn) nanospheres. Field-emission scanning electron microscopy, X-ray powder diffraction, Fourier transform infrared spectrometer, and a superconducting quantum interference device magnetometer were used to characterize the morphologies, compositions and properties of the functionalized materials. Results show that all of the products were cubic spinel structures and exhibited hierarchical sphere-like morphologies, which were composed of primary nanocrystals. The MFe_2O_4 present advantageous functionality and good water dispersibility due to the preferential exposure of uncoordinated carboxylate groups on their respective surfaces. These properties make them ideal candidates for various important applications such as drug delivery, bioseparation, and magnetic resonance imaging.

Keywords: MFe_2O_4 , Carboxylic, Magnetic, Solvothermal.

1. INTRODUCTION

In recent years, magnetic materials have enabled tremendous advances in the development of powerful tools for separating, detecting and loading targets of various interests in scientific research and technological applications.^{1–13} In particular, iron oxide-based magnetic materials have been extensively pursued in bio-field due to their magnetic and low toxicity properties.^{14–22} As we all know, these biomedical applications require the functionalization of magnetic nanomaterials with biocompatible molecules to stabilize them and make them dispersible in aqueous solutions.^{21, 23–26} One of the strategies is the use of bifunctional ligands in ligand exchange reactions, where one functional group (i.e., carboxylic groups) is bonded to the surface of the materials while the other stabilizes the materials by electrostatic interaction (i.e., phosphate-, thiol-, or amine-functional groups).^{27–29} Another is coating technology, which fabricate a biocompatible layer at the surface of magnetic materials.^{19, 20, 30–37} These processes were usually effective but often involved sophisticated multi-steps and tend to be time consuming, which poses a hindrance for practical application. Thus there is an urgent

need to develop efficient and facile routes for the fabrication of functionalized magnetic materials.^{38–40}

In this work, a facile solvothermal method was developed for the rapid synthesis of the carboxylic-functionalized MFe_2O_4 (M = Mn, Co, Zn) nanospheres. Various technologies were used to characterize the morphologies, compositions and properties of the functionalized MFe_2O_4 . The robust surface modification, high water dispersibility, and good magnetic properties make these nanospheres ideal candidates for various applications such as drug delivery, bio-separation, and magnetic resonance imaging. Based on this strategy, magnetic materials decorated with other functional groups (e.g., sulfhydryl) can be easily obtained by replacing functional agents.

2. MATERIALS AND METHODS

2.1. Materials

Poly acrylic acid (PAA, 35%, w/w in water, MW = 100,000) were purchased from Sigma-Aldrich. $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, anhydrous sodium acetate (NaAc), ethylene glycol (EG) and other chemical reagents were obtained from Nanjing Chemical Reagent Co., Ltd. All chemicals were directly used as received without further purification.

*Authors to whom correspondence should be addressed.

2.2. Fabrication of the Carboxylic Functionalized MFe₂O₄

1.67 mmol Mn²⁺ (or Co²⁺, or Zn²⁺) and 3.33 mmol Fe³⁺ were dissolved in 39 mL of EG solution with stirring to form a clear solution, followed by the addition of 1 ml of PAA and 40 mmol of anhydrous NaAc. The mixture was ultrasonic vigorously to give a homogeneous solution. Then the solution was sealed in autoclaves and for treatment at 200 °C for 12 hours. The solid products were collected by magnetic separation and washed at least three times with water and ethanol, then dried under vacuum at room temperature.

2.3. Characterization

Field emission scanning electron microscopy (FE-SEM) images were obtained using Hitachi S-4800 field emission electron microscope at an accelerating voltage of 5 kV. X-ray powder diffraction (XRD) measurements were performed on a Japan Shimadzu XRD-6000 diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm); A scanning

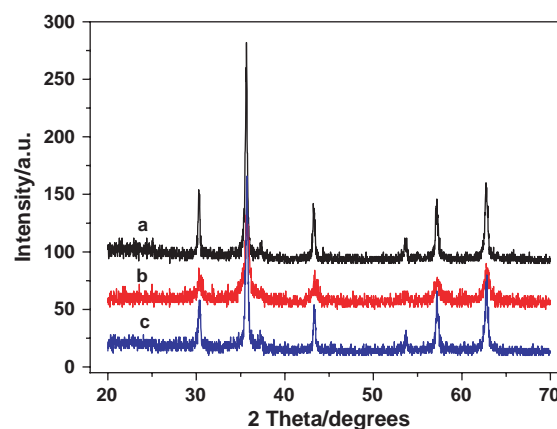


Figure 2. XRD patterns of the obtained MFe₂O₄ (M = Mn, Co, Zn) nanospheres: MnFe₂O₄ (a); CoFe₂O₄ (b); and ZnFe₂O₄ (c).

rate of 0.05 deg s⁻¹ was applied to record the patterns in the 2 θ range of 20–70°. The FTIR spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrograph in the wavenumber range of 4000–400 cm⁻¹.

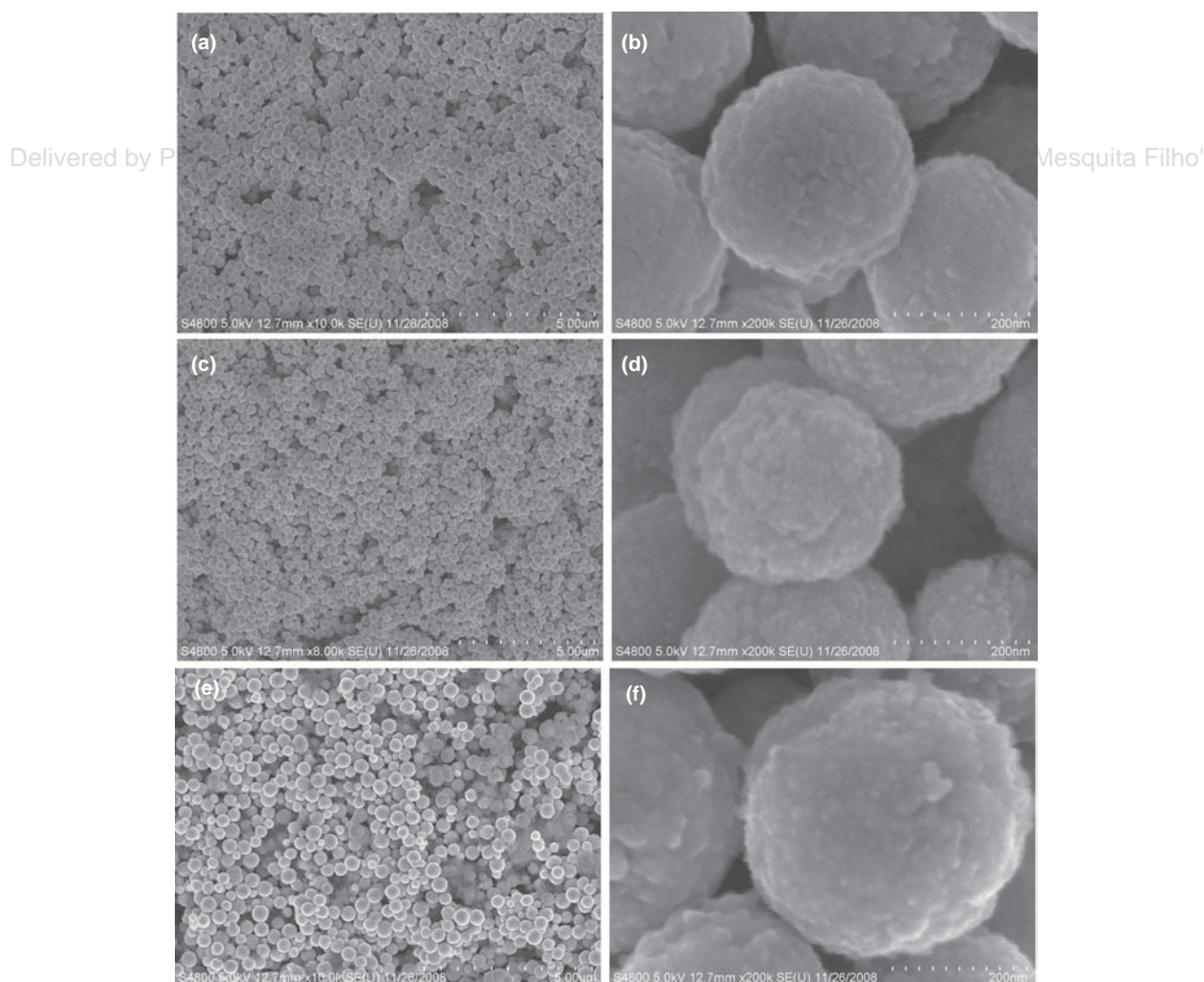


Figure 1. Typical SEM images of the obtained MFe₂O₄ nanospheres: MnFe₂O₄ (a), (b); CoFe₂O₄ (c), (d) and ZnFe₂O₄ (e), (f).

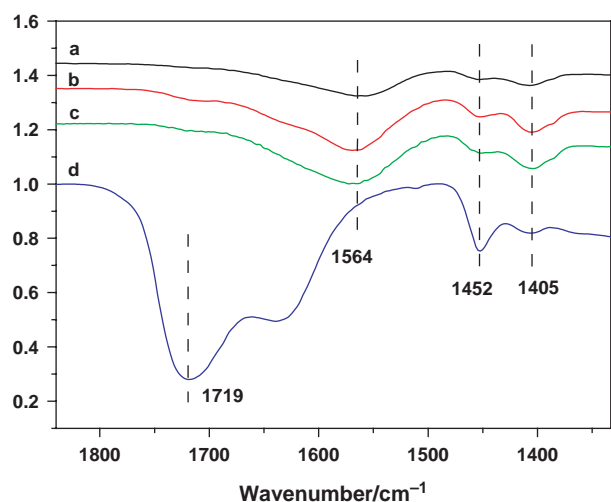


Figure 3. FTIR spectra of pure PAA (d) and obtained MFe_2O_4 ($\text{M} = \text{Mn, Co, Zn}$) nanospheres: MnFe_2O_4 (a); CoFe_2O_4 (b); and ZnFe_2O_4 (c).

Table I. Zeta potential data of the MFe_2O_4 .

MFe_2O_4	MnFe_2O_4	CoFe_2O_4	ZnFe_2O_4
ξ potential/mV	-35.3	-33.6	-33.7

Superconducting quantum interference device (SQUID, Quantum Design) magnetometer was used in the magnetic measurement at 300 K.

3. RESULTS AND DISCUSSION

The size and morphology of the as-prepared product were determined by SEM. As shown in Figure 1, all of the three products show an excellent monodispersity and a well-defined uniform spherical shape on a large scale. Statistical analyses indicate that the particles have an average diameter of about 300 nm. The high-resolution SEM images demonstrate that these nanospheres exhibit a hierarchical structure and consist of many primary nanoparticles.

The crystal structures of these products were studied by XRD analysis. As shown in Figure 2, all diffraction

peaks and positions match well with their respective standard cubic spinel structures of MnFe_2O_4 (No. 74-2403), CoFe_2O_4 (No. 22-1068), and ZnFe_2O_4 (No. 22-1012), respectively.

FTIR spectra were applied to detect the species on the surface of the hierarchical nanospheres. The FTIR spectrum of pure PAA (curve (d) in Fig. 3) present a strong peak at 1719 cm^{-1} , which was assigned to the carbonyl stretching mode for the protonated carboxyl groups (COOH); but this peak is negligible in the spectra of the MFe_2O_4 (other curves in Fig. 3). The IR peaks at 1564 , 1452 and 1405 cm^{-1} could be assigned to the vibration of symmetric $\text{C}=\text{O}$ stretching, CH_2 bending, and asymmetric $\text{C}=\text{O}$ stretching, respectively; all of which are characteristic bands of carboxylate (COO^-) groups. With these evidences, it could be concluded that the surfaces of the MFe_2O_4 nanospheres were mostly carboxylate groups (COO^-) rather than protonated carboxyl groups (COOH).^{39,41} The conclusion was further confirmed by the measurements of zeta potential. All of the products display abundant negative surface charges (Table I). The relatively high charge densities ensure them high dispersion in aqueous solutions for several days at appropriate concentration.

The magnetic properties of as-prepared ferrites microspheres were investigated with a SQUID magnetometer. Figure 4 presents the magnetization curves measured at 300 K for the obtained MFe_2O_4 nanospheres. The saturation values are 66.9 , 66.1 and 64.5 emu g^{-1} for MnFe_2O_4 , CoFe_2O_4 and ZnFe_2O_4 , respectively. It is worth mentioning that remanence and coercivity were almost undetectable in the enlarged curves for MnFe_2O_4 and ZnFe_2O_4 (Fig. 4(b)), indicating that the MnFe_2O_4 and ZnFe_2O_4 products possess superparamagnetic properties at room temperature. It is believed that the threshold size of the ferrites is about 15 nm for the transition from superparamagnetism to ferromagnetism.⁴² The superparamagnetic properties further confirmed that the MnFe_2O_4 and ZnFe_2O_4 spheres were made up of smaller primary nanocrystals. Whereas the primary nanocrystals of the CoFe_2O_4 product were larger than the critical size, and thus CoFe_2O_4 presents a ferromagnetism behavior with a

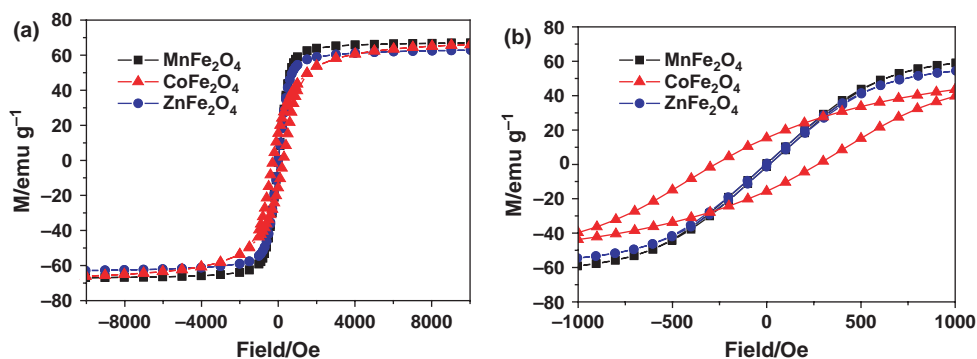


Figure 4. Magnetization curves of the obtained MFe_2O_4 nanospheres (a), the data around zero field with an expanded scale ranging from -1000 to 1000 Oe (b).

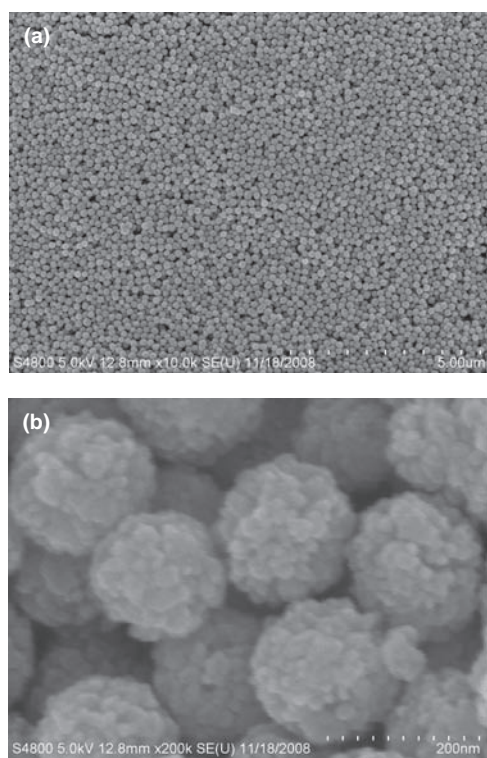


Figure 5. SEM images of the MnFe_2O_4 obtained in the absence of PAA. (a) $\times 10,000$; and (b) $\times 200,000$.

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typical hysteresis loop with the remanence of 15.4 emu g^{-1} and the coercivity of 267 Oe.

To investigate the effect of PAA, the MnFe_2O_4 product was synthesized in the absence of PAA as an example. Results show that their morphology did not change so much in the reaction system (Fig. 5), but the crystal size of the primary units were larger than those in the typical experiment. It could be presumed that PAA, not only as the functional agent but also as the stabilizing agent, regulated the size of the primary unit via coordination interaction. Based on this strategy, the demonstrated benign approach could be extended to the fabrication of other hierarchical magnetic materials functionalized with desired groups (e.g., sulfhydryls, amines), which would find widespread technological and biological applications.

4. CONCLUSIONS

In summary, A facile and robust strategy was developed for controlling synthesis of the carboxylic functionalized MFe_2O_4 ($\text{M} = \text{Mn}, \text{Co}, \text{Zn}$) nanospheres via one-pot solvothermal method. They exhibited hierarchical sphere-like structures, which were composed of primary nanocrystals. They present advantageous functionality and good water dispensability due to the preferential exposure of uncoordinated carboxylate groups on their respective surfaces. This work provides a new insight into the preparation of the functionalized ferrites, which would have great

potential not only in advanced optical-electronic materials and ferrofluids, but also in biomedicine and biotechnology.

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References and Notes

- S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science* 287, 1989 (2000).
- C. Xu, K. Xu, H. Gu, R. Zheng, H. Liu, X. Zhang, Z. Guo, and B. Xu, *J. Am. Chem. Soc.* 126, 9938 (2004).
- F. Wang, C. Ma, X. Zeng, C. Li, and N. Y. He, *J. Biomed. Nanotechnol.* 8, 786 (2012).
- S. Li, H. Liu, Y. Jia, Y. Deng, L. Zhang, Z. Lu, and N. Y. He, *Theranostics* 2, 967 (2012).
- M. J. Hu, Y. Lu, S. Zhang, S. R. Guo, B. Lin, M. Zhang, and S. H. Yu, *J. Am. Chem. Soc.* 130, 11606 (2008).
- C. H. Yang, K. S. Huang, Y. S. Lin, K. Lu, C. C. Tzeng, E. C. Wang, C. H. Lin, W. Y. Hsu, and J. Y. Chang, *Lab Chip* 9, 961 (2009).
- F. Ansari and M. Kavosh, *J. Bionanosci.* 6, 39 (2012).
- S. G. Mitra, D. R. Diercks, N. C. Mills, Di Anna L. Hynds, and S. Ghosh, *J. Nanosci. Nanotechnol.* 13, 8290 (2013).
- C. Ma, C. Li, F. Wang, N. Ma, Z. Li, Z. Xi, X. L. Li, and N. Y. He, *J. Biomed. Nanotechnol.* 9, 703 (2013).
- S. Li, H. Liu, Y. Jia, X. B. Mou, Y. Deng, L. Lin, and N. Y. He, *J. Biomed. Nanotechnol.* 9, 689 (2013).
- S. H. Liu, F. Lu, X. Jia, F. Cheng, L. P. Jiang, and J. J. Zhu, *Crystrngcomm* 13, 2425 (2011).
- H. H. P. Yiu, S. C. McBain, Z. A. D. Lethbridge, M. R. Lees, I. Palona, C. I. Olariu, and J. Dobson, *J. Nanosci. Nanotechnol.* 11, 3586 (2011).
- K. X. Liu, F. Lan, W. Jiang, X. B. Zeng, H. Hu, Y. Wu, and Z. W. Gu, *J. Nanosci. Nanotechnol.* 12, 8437 (2012).
- S. H. Liu, R. M. Xing, F. Lu, R. K. Rana, and J. J. Zhu, *J. Phys. Chem. C* 113, 21042 (2009).
- N. Y. He, F. Wang, C. Ma, C. Li, X. Zeng, Y. Deng, L. Zhang, and Z. Li, *J. Biomed. Nanotechnol.* 9, 267 (2013).
- B. Liu, Y. Jia, M. Ma, Z. Li, H. Liu, S. Li, Y. Deng, L. Zhang, Z. Lu, W. Wang, and N. Y. He, *J. Biomed. Nanotechnol.* 9, 247 (2013).
- Y. Tang, J. Zou, C. Ma, Z. Ali, Z. Li, X. Li, N. Ma, X. Mou, Y. Deng, L. Zhang, K. Li, G. Lu, H. Yang, and N. Y. He, *Theranostics* 3, 85 (2013).
- S. Li, H. Liu, Y. Deng, L. Lin, and N. Y. He, *J. Biomed. Nanotechnol.* 9, 1254 (2013).
- S. H. Liu, F. Lu, Y. Liu, L. P. Jiang, and J. J. Zhu, *J. Nanopart. Res.* 15, Article Number: 1331 (2013).
- L. He, Z. Y. Li, J. Fu, F. Wang, C. Ma, Y. Deng, Z. Y. Shi, H. Wang, and N. Y. He, *J. Nanosci. Nanotechnol.* 11, 2256 (2011).
- S. I. Park, B. J. Kwon, J. H. Park, H. Jung, and K. H. Yu, *J. Nanosci. Nanotechnol.* 11, 1818 (2011).
- R. Krishna, E. Titus, S. Chandra, N. K. Bardhan, D. Bahadur, and J. Gracio, *J. Nanosci. Nanotechnol.* 12, 6631 (2012).
- Z. J. Zhao, H. L. Zhao, R. H. Yu, H. H. Yuan, X. Zhu, and M. B. Lan, *J. Nanosci. Nanotechnol.* 12, 1946 (2012).
- B. Liu, Z. Li, H. Chen, Y. Deng, N. Y. He, S. Elingarami, and J. Huang, *J. Biomed. Nanotechnol.* 8, 938 (2012).
- Z. Li, H. Yang, N. Y. He, W. Liang, C. Ma, M. Ali A. Shah, Y. Tang, S. Li, H. Liu, H. Jiang, and Y. Guo, *J. Biomed. Nanotechnol.* 9, 1945 (2013).
- D. Stamopoulos, E. Manios, V. Gogola, D. Niarchos, and M. Pissas, *J. Nanosci. Nanotechnol.* 10, 6110 (2010).
- L. I. Cabrera, A. Somoza, J. F. Marco, C. J. Serna, and M. P. Morales, *J. Nanopart. Res.* 14, 14 (2012).

28. A. K. Gupta and M. Gupta, *Biomaterials* 26, 3995 (2005).
29. M. A. Wang, M. L. Peng, W. Cheng, Y. L. Cui, and C. Chen, *J. Nanosci. Nanotechnol.* 11, 3688 (2011).
30. G. P. Li, B. Shen, N. Y. He, C. Ma, S. Elingarami, and Z. Y. Li, *J. Nanosci. Nanotechnol.* 11, 10295 (2012).
31. H. X. Sun, X. Zeng, M. Liu, S. Elingarami, G. P. Li, B. Shen, and N. Y. He, *J. Nanosci. Nanotechnol.* 12, 267 (2012).
32. O. D. Jayakumar, R. Ganguly, A. K. Tyagi, D. K. Chandrasekharan, and C. K. K. Nair, *J. Nanosci. Nanotechnol.* 9, 6344 (2009).
33. S. Q. Tang, S. J. Moon, K. H. Park, S. H. Paek, K. W. Chung, and S. Bae, *J. Nanosci. Nanotechnol.* 11, 82 (2011).
34. C. Ma, C. Li, N. Y. He, F. Wang, N. Ma, L. Zhang, Z. Lu, Z. Ali, Z. Xi, X. Li, G. Liang, H. Liu, Y. Deng, L. Xu, and Z. Wang, *J. Biomed. Nanotechnol.* 8, 1000 (2012).
35. H. Jiang, X. Zeng, N. Y. He, Yan Deng, G. Lu, and K. Li, *J. Nanosci. Nanotechnol.* 13, 1617 (2013).
36. Y. Tang, Z. Li, N. Y. He, L. Zhang, C. Ma, X. Li, C. Li, Z. Wang, Y. Deng, and L. He, *J. Biomed. Nanotechnol.* 9, 312 (2013).
37. H. Jiang, X. Zeng, Z. Xi, M. Liu, C. Li, Z. Li, L. Jin, Z. Wang, Y. Deng, and N. Y. He, *J. Biomed. Nanotechnol.* 9, 674 (2013).
38. X. Jia, D. Chen, X. Jiao, and S. Zhai, *Chem. Comm.* 968 (2009).
39. J. Ge, Y. Hu, M. Biasini, C. Dong, J. Guo, W. P. Beyermann, and Y. Yin, *Chem. Eur. J.* 13, 7153 (2007).
40. A. Lu, E. L. Salabas, and F. Schüth, *Angew. Chem. Int. Ed.* 46, 1222 (2007).
41. S. Si, A. Kotal, T. K. Mandal, S. Giri, H. Nakamura, and T. Kohara, *Chem. Mater.* 16, 3489 (2004).
42. S. H. Liu, F. Lu, R. M. Xing, and J. J. Zhu, *Chem. Eur. J.* 17, 620 (2011).

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