

## Electronic Supplementary Information (ESI)

### A Novel Structural Fenton-Like Nanocatalyst with Highly Improved Catalytic Performance for Generalized Preparation of Iron Oxides@Organic Dye Polymer Core-Shell Nanospheres

Guanghui Zhao,\* Xiaomen Peng, Hongping Li, Jianzhi Wang, Lincheng Zhou, Tianqi Zhao, Zhihao Huang and Haifei Jiang

*State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China*

*\* To whom correspondence should be addressed. E-mail: zhaogh@lzu.edu.cn*

## Table of contents

### ESI-I

Experimental Details

### ESI-II

Fabrication and Characterization of  $\text{Fe}_x\text{O}_y$ @ $\text{Fe}_x\text{O}_y$ /C Nanoparticles Obtained under Different Conditions (*For determining the optimal conditions for the preparation of*

*Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C nanoparticles)*

### **ESI-III**

Characterization and Catalytic Performance of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/chitosan, Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C-PEG and Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C Nanoparticles (*For investigating the influence of nanostructure and composition of nanoparticles on the catalytic activity*)

### **ESI-IV**

Assembly of Various Dye Molecules on the Surface of Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C Nanoparticles (*For investigating the formation conditions of iron oxides@Organic Dye Polymer Core-Shell Nanospheres*)

## **ESI-I**

### **Experimental Details**

**Materials:** All the chemicals used were analytical grade without any further purification. Deionized water was used throughout this study.

**Characterization:** FT-IR spectra were obtained in transmission mode on a Fourier-transform infrared spectrophotometer (American Nicolet Corp. Model 170-SX) using the KBr pellet technique. Transmission electron microscopy (TEM, FEI Tecnai G20) images were obtained to elucidate the dimensions and the structural details of the nanoparticles. TEM specimens were prepared by placing a drop of the nanoparticle suspension on a carbon-coated copper grid. The N<sub>2</sub> adsorption/desorption isotherm was measured at liquid nitrogen temperature (77 K) using a Micrometrics ASAP

2010M instrument. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distribution was obtained using the Barret–Joner–Halenda (BJH) method. Magnetization measurements were performed on a vibrating sample magnetometer (VSM, LAKESHORE-7304, USA) at room temperature. X-ray photoelectron spectroscopy (XPS) spectra were obtained with an ESCALab220i-XL electron spectrometer (VG Scientific) using 300 W Al K $\alpha$  radiation. All fluorescence spectra were recorded using a F97Pro spectrofluorophotometer (LengGuang Industrial Co., Ltd., Shanghai, China). Thermogravimetric analysis (TGA) were performed on a STA PT1600 system in nitrogen atmosphere with a heating rate of 20 °C min<sup>-1</sup>. Mössbauer (MS) studies were performed using a conventional constant-acceleration drive and a 50 m Ci <sup>57</sup>Co:Rh source. The velocity calibration at room temperature (RT) was performed using an  $\alpha$ -Fe absorber, and the isomer shift (IS) values 181 reported are relative to  $\alpha$ -Fe.

**Preparation of Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C nanoparticles.** The mesoporous Fe<sub>3</sub>O<sub>4</sub>/chitosan nanoparticles were prepared through a modified solvothermal reaction,<sup>1</sup> where 1.35 g FeCl<sub>3</sub>·6H<sub>2</sub>O was dissolved in 70 mL ethylene glycol to form a clear solution. After that, a mixture of 3.85 g NH<sub>4</sub>Ac and chitosan (various feeding amount of chitosan: 0.1, 0.3 and 0.7g) was ultrasonically dispersed in the resulting dispersion for 1 h to form a homogeneous brownish solution which was then transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated to 200 °C and maintained at this temperature for 12 h. The mixture was then cooled to ambient temperature, and the resulting black magnetite particles were washed with ethanol and deionized water in sequence before drying in a vacuum at 60 °C for 24 h. Fe<sub>3</sub>O<sub>4</sub>/chitosan nanoparticles annealed at 300 °C for 1 h under nitrogen atmosphere, then annealed at various temperature for various time in nitrogen atmosphere with a heating rate of 5 °C min<sup>-1</sup> to synthesize a series of Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C nanoparticles.

#### **Dye Decoloration through a Heterogeneous Fenton Reaction.**

A decoloration experiment was carried out by which the nanocatalyst was added

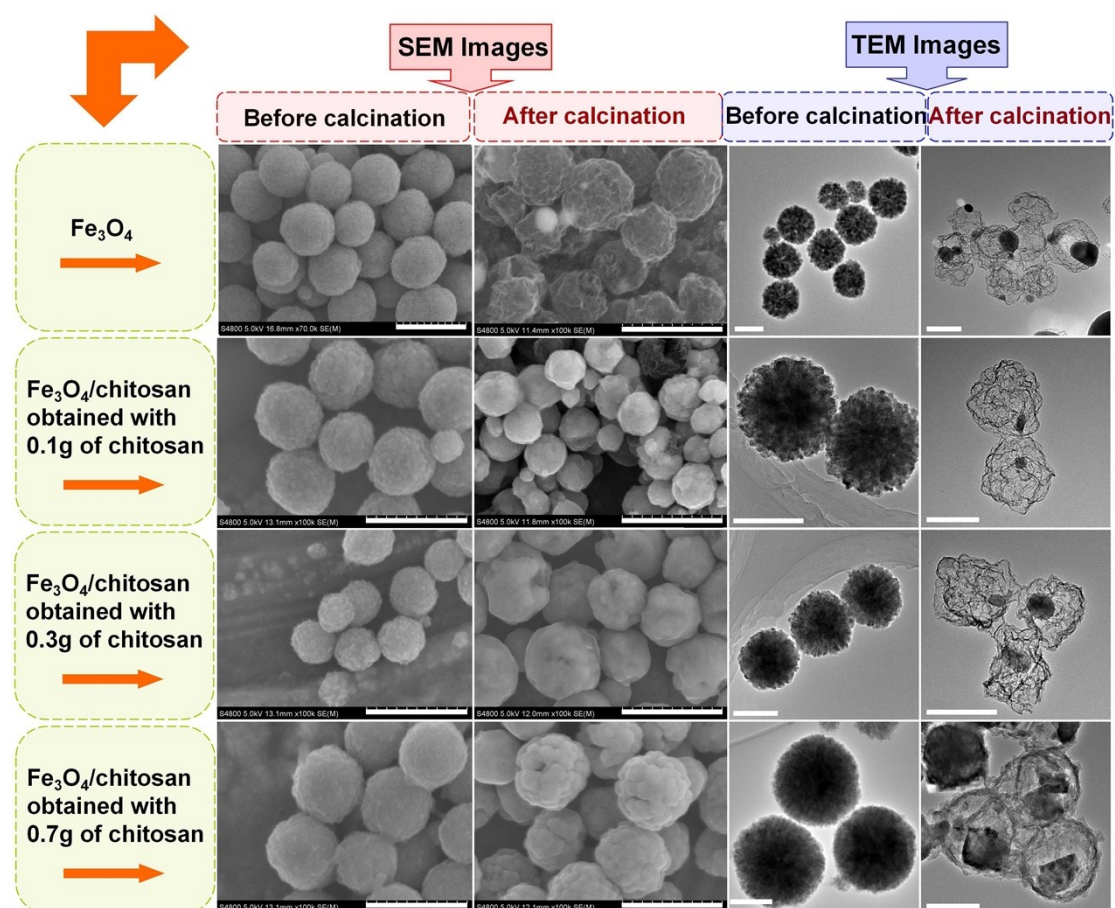
into 20 mL of a 100 mg L<sup>-1</sup> MB solution in the presence of H<sub>2</sub>O<sub>2</sub> and NH<sub>2</sub>OH, and the suspension was shaken in a thermostated shaker at 120 rpm at 30 °C. After the reaction, the nanocatalyst were separated using an external magnetic field, and the concentration of MB was determined using a UV-vis spectrometer, with a maximum absorbance wavelength for MB at 664 nm.

## ESI-II

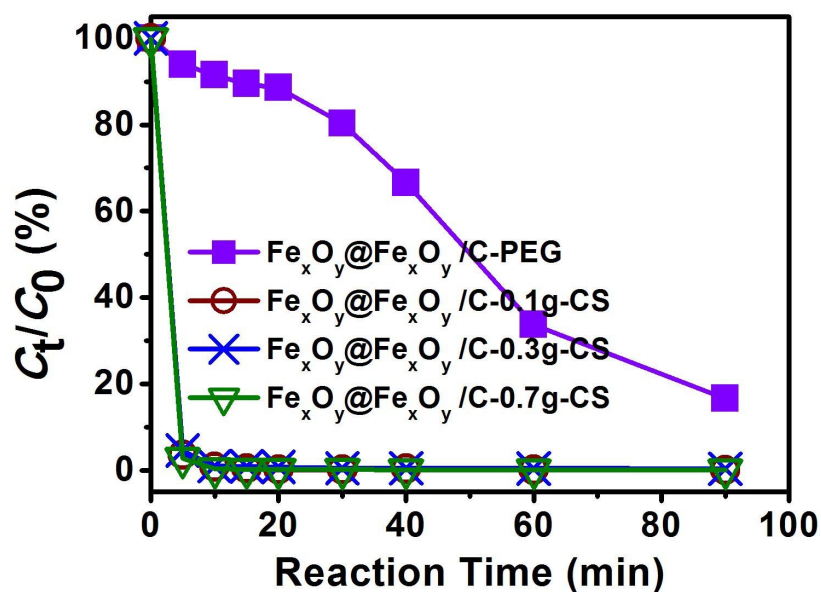
### Fabrication and Characterization of $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$ Nanoparticles Obtained under Different Conditions

#### 1. Fabrication and Characterization of $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$ Nanoparticles Obtained with $\text{Fe}_3\text{O}_4/\text{chitosan}$ (various feeding amount of chitosan) via Calcination

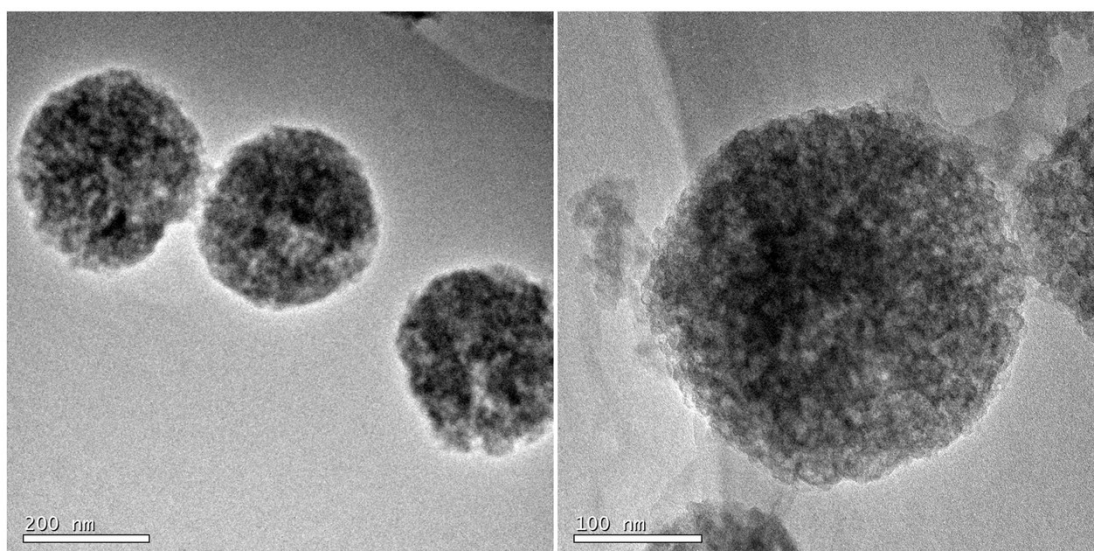
As shown in Fig. S1,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (various feeding amount of chitosan) all could be converted into core-shell nanoparticles with soap-bubble-like structured shell via calcination. This structure is beneficial to the Fenton catalysis.<sup>2</sup> Through a comprehensive analysis of the results in Fig. S1 and Fig. S2,  $\text{Fe}_3\text{O}_4/\text{chitosan}$  nanoparticles obtained with 0.1g chitosan annealed at 300 °C for 1 h under nitrogen atmosphere, then annealed at 700 °C for 2 h in nitrogen atmosphere with a heating rate of 5 °C min<sup>-1</sup> to synthesize  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$  nanoparticles, which were selected for the following study.



**Fig. S1** SEM images and TEM images of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{chitosan}$  obtained with different amount of chitosan before and after calcination. The mesoporous  $\text{Fe}_3\text{O}_4/\text{chitosan}$  nanoparticles were prepared through a modified solvothermal reaction, where 1.35 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 70 mL ethylene glycol to form a clear solution. After that, a mixture of 3.85 g  $\text{NH}_4\text{Ac}$  and chitosan (with various feeding amount of chitosan: 0.1, 0.3 and 0.7g) was ultrasonically dispersed in the resulting dispersion for 1 h to form a homogeneous brownish solution which was then transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated to 200 °C and maintained at this temperature for 12 h.  $\text{Fe}_3\text{O}_4$  prepared by a solvothermal reaction using PEG as a stabilizer instead of chitosan.  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{chitosan}$  nanoparticles annealed at 300 °C for 1 h under nitrogen atmosphere, then annealed at 700 °C for 2 h in nitrogen atmosphere with a heating rate of 5 °C  $\text{min}^{-1}$  to synthesize  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$ -PEG and  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$  nanoparticles. Scale bars in the SEM images are 500 nm, and in the TEM images are 200 nm.



**Fig. S2** Removal efficiency of MB using different Fenton catalysts. ( $Fe_3O_4$  and  $Fe_3O_4$ /chitosan nanoparticles obtained with different amount of chitosan annealed at 300 °C for 1 h under nitrogen atmosphere, then annealed at 700 °C for 2 h in nitrogen atmosphere with a heating rate of 5 °C min<sup>-1</sup> to synthesize  $Fe_xO_y@Fe_xO_y/C\text{-PEG}$  and various  $Fe_xO_y@Fe_xO_y/C$  nanoparticles.) Reaction conditions: initial MB concentration, 100 mg L<sup>-1</sup>; initial H<sub>2</sub>O<sub>2</sub> concentration, 5 mmol L<sup>-1</sup>; NH<sub>2</sub>OH concentration, 5 mmol L<sup>-1</sup>; catalyst load, 0.5 g L<sup>-1</sup>; T = 303 K.



**Fig. S3** TEM images of porous carbon spheres obtained with  $Fe_xO_y@Fe_xO_y/C$  nanoparticles via hydrochloric acid etching to remove iron oxide in  $Fe_xO_y@Fe_xO_y/C$

## 2. Fabrication and Characterization of $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C}$ Nanoparticles Obtained with $\text{Fe}_3\text{O}_4/\text{chitosan}$ (the feeding amount of chitosan: 0.1g) via Calcination at 700 °C for various time

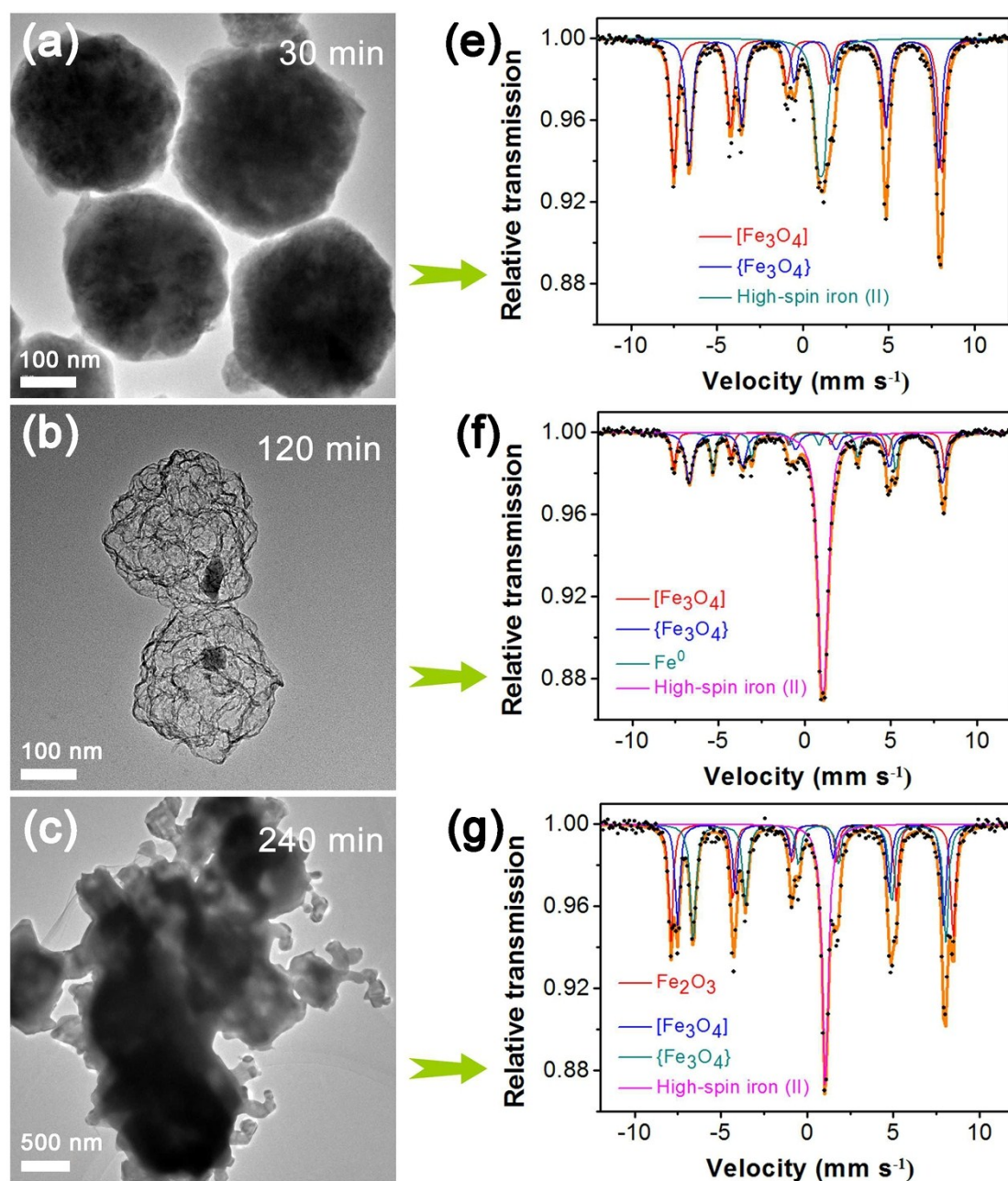
Through a comprehensive analysis of the results in Table S1, Table S2, Fig. S4, Fig. S5 and Fig. S6, the combination of  $\text{Fe}^0$  with  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C}$  nanoparticles with soap-bubble-like structured shell is efficient for enhanced Fenton-like catalysis. **The optimal conditions for the preparation of  $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C}$  nanoparticles are determined as followings:** Uniform  $\text{Fe}_3\text{O}_4/\text{chitosan}$  nanoparticles prepared by a solvothermal reaction (the feeding amount of chitosan: 0.1g) are employed as the precursor. An annealing treatment (at 300 ° C for 1 h and then at 700 ° C for 2 h in nitrogen atmosphere with a heating rate of 5 ° C min<sup>-1</sup>) is utilized to convert the  $\text{Fe}_3\text{O}_4/\text{chitosan}$  into core-shell  $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C}$  nanoparticles with soap-bubble-like structured shell.

**Table S1.** Fitted room temperature Mössbauer parameters for limonites ( $\delta$  = isomer shift relative to  $\alpha\text{-Fe}$ ,  $\Delta$  = quadruple splitting,  $H_{\text{eff}}$  = hyperfine field, RA = relative sub-spectral area, [ ] tetrahedral site, { } octahedral site.)

Sample	Mössbauer parameters			Assignment	RA (%)
	IS ( $\delta$ )	QS ( $\Delta$ )	$H_{\text{eff}}$ (H)		
	mm/s	mm/s	T		



Fe <sub>3</sub> O <sub>4</sub> /chitosan	0.299	-0.267	48.6	[Fe <sub>3</sub> O <sub>4</sub> ]	36.7
	0.611	0.005	45.2	{Fe <sub>3</sub> O <sub>4</sub> }	63.7
Fe <sub>3</sub> O <sub>4</sub> /chitosan was annealed at 700 °C for 30 min	0.292	-0.020	48.4	[Fe <sub>3</sub> O <sub>4</sub> ]	41.8
	0.648	-0.004	45.1	{Fe <sub>3</sub> O <sub>4</sub> }	39.0
	1.047	0.335	–	High-spin iron (II)	19.2
Fe <sub>3</sub> O <sub>4</sub> /chitosan was annealed at 700 °C for 120 min	0.273	-0.023	48.8	[Fe <sub>3</sub> O <sub>4</sub> ]	11.6
	0.651	-0.003	45.6	{Fe <sub>3</sub> O <sub>4</sub> }	28.6
	-0.003	-0.022	33.0	α-Fe <sup>0</sup>	13.2
	1.062	0.260	–	High-spin iron (II)	46.5
Fe <sub>3</sub> O <sub>4</sub> /chitosan was annealed at 700 °C for 240 min	0.356	-0.143	50.9	γ-Fe <sub>2</sub> O <sub>3</sub>	25.4
	0.241	-0.085	48.0	[Fe <sub>3</sub> O <sub>4</sub> ]	23.4
	0.690	0.051	45.5	{Fe <sub>3</sub> O <sub>4</sub> }	31.3
	1.050	–	–	High-spin iron (II)	20.0



**Fig. S4** (a-c) TEM images and (e-g) Mössbauer spectra at RT of  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$  nanospheres obtained with  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (feeding amount of chitosan: 0.1g) via calcination for various time. Reaction conditions:  $\text{Fe}_3\text{O}_4/\text{chitosan}$  nanoparticles obtained with 0.1g chitosan annealed at 300 °C for 1 h under nitrogen atmosphere, then annealed at 700 °C for 30, 120 and 240 min in nitrogen atmosphere with a heating rate of 5 °C min<sup>-1</sup> to synthesize  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$  nanoparticles.

### 3. Fabrication and Characterization of $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$ Nanoparticles Obtained with $\text{Fe}_3\text{O}_4/\text{chitosan}$ (the feeding amount of chitosan: 0.1g) via Calcination at various temperature for 120 min

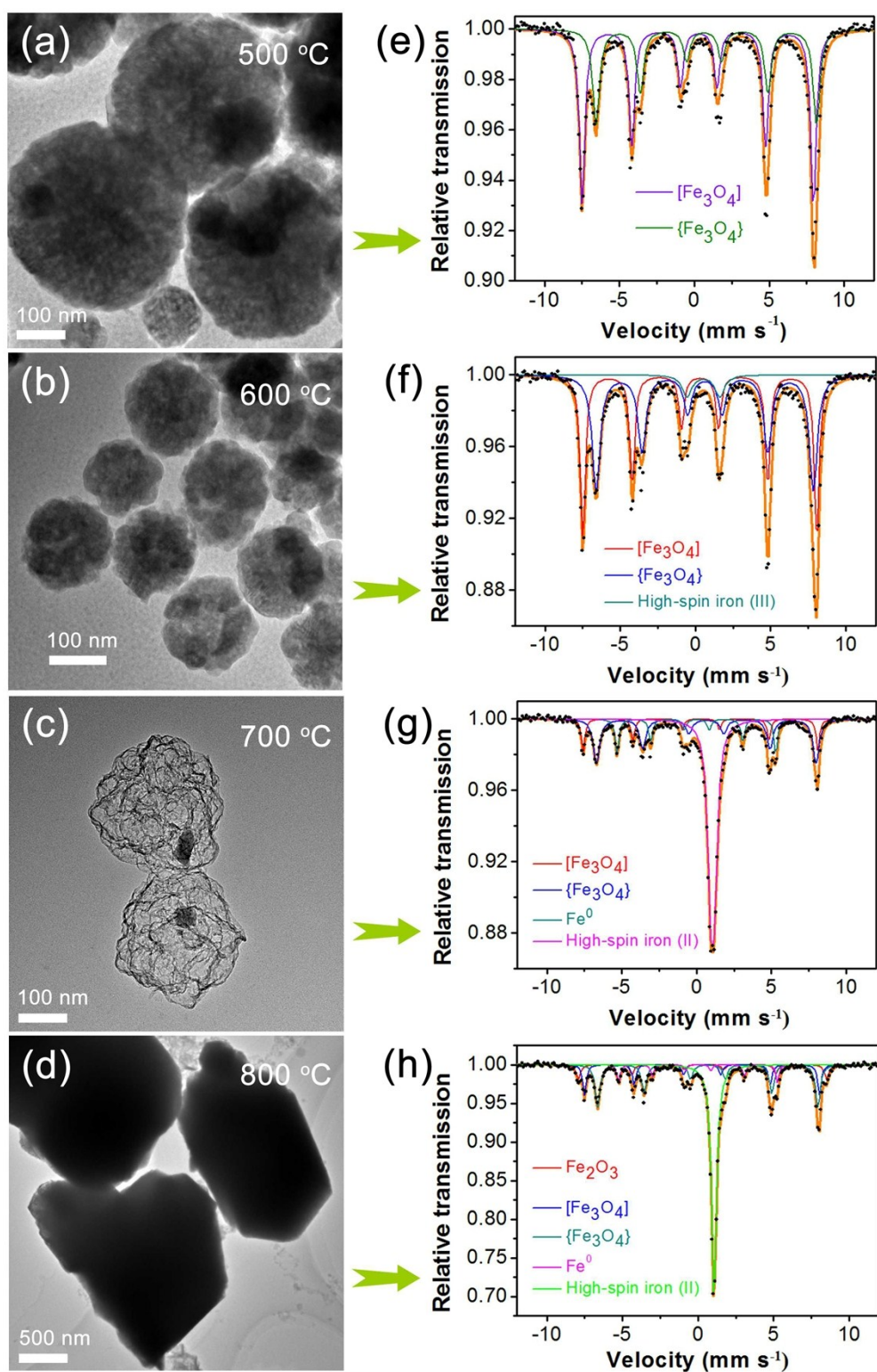
**Table S2.** Fitted room temperature Mössbauer parameters for limonites ( $\delta$  = isomer shift relative to  $\alpha$ -Fe,  $\Delta$  = quadruple splitting,  $H_{\text{eff}}$  = hyperfine field, RA = relative sub-spectral area, [ ] tetrahedral site, { } octahedral site.)

Sample	Mössbauer parameters			Assignment	RA (%)
	IS ( $\delta$ ) <sup>a</sup>	QS ( $\Delta$ )	$H_{\text{eff}}$ (H)		
	mm/s	mm/s	T		
Fe <sub>3</sub> O <sub>4</sub> /chitosan	0.299	-0.267	48.6	[Fe <sub>3</sub> O <sub>4</sub> ]	36.7
	0.611	0.005	45.2	{Fe <sub>3</sub> O <sub>4</sub> }	63.7
Fe <sub>3</sub> O <sub>4</sub> /chitosan was annealed at 500 °C for 2h	0.262	-0.069	48.0	[Fe <sub>3</sub> O <sub>4</sub> ]	60.7
	0.723	0.144	45.8	{Fe <sub>3</sub> O <sub>4</sub> }	39.3
Fe <sub>3</sub> O <sub>4</sub> /chitosan was annealed at 600 °C for 2h	0.298	-0.012	48.3	[Fe <sub>3</sub> O <sub>4</sub> ]	45.2
	0.625	-0.008	44.9	{Fe <sub>3</sub> O <sub>4</sub> }	49.3
	0.526	2.180	–	High-spin iron (III)	5.5
Fe <sub>3</sub> O <sub>4</sub> /chitosan was annealed at 700 °C for 2h	0.273	-0.023	48.8	[Fe <sub>3</sub> O <sub>4</sub> ]	11.6
	0.651	-0.003	45.6	{Fe <sub>3</sub> O <sub>4</sub> }	28.6
	-0.003	-0.022	33.0	$\alpha$ -Fe <sup>0</sup>	13.2
	1.062	0.260	–	High-spin iron (II)	46.5
Fe <sub>3</sub> O <sub>4</sub> /chitosan was annealed at 800 °C for 2h	0.345	-0.085	51.0	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	8.4
	0.270	-0.013	48.3	[Fe <sub>3</sub> O <sub>4</sub> ]	14.9
	0.648	-0.017	45.3	{Fe <sub>3</sub> O <sub>4</sub> }	27.9

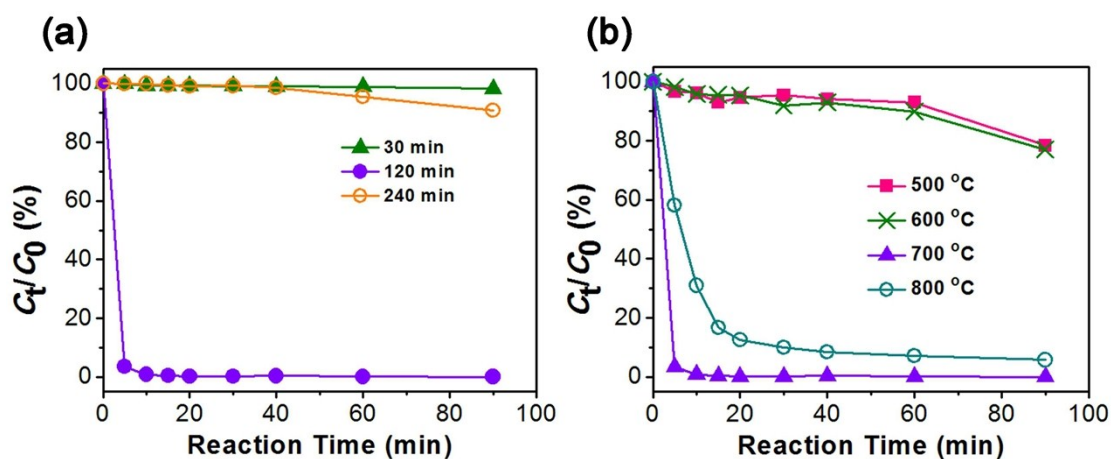
---

0.012	-0.020	32.6	$\alpha$ -Fe <sup>0</sup>	7.8
1.055	-	-	High-spin iron (II)	41.1

---



**Fig. S5** (a-d) TEM images and (e-h) Mössbauer spectra at RT of  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$  nanospheres obtained with  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (feeding amount of chitosan: 0.1g) via calcination at various temperature. Reaction conditions:  $\text{Fe}_3\text{O}_4/\text{chitosan}$  nanoparticles obtained with 0.1g chitosan annealed at 300 °C for 1 h under nitrogen atmosphere, then annealed at 500, 600, 700 and 800 °C for 120 min in nitrogen atmosphere with a heating rate of 5 °C min<sup>-1</sup> to synthesize  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$  nanoparticles.

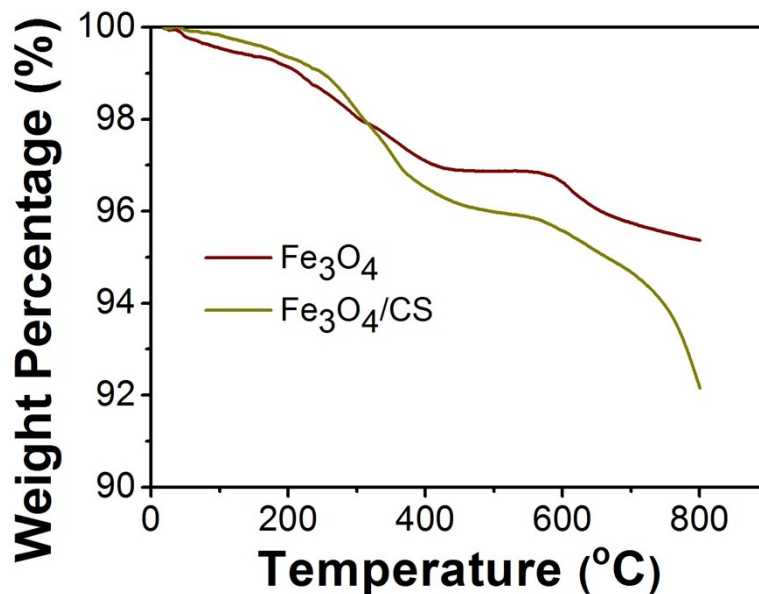


**Fig. S6** (a) Removal efficiency of MB using different  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$  catalysts obtained with  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (feeding amount of chitosan: 0.1g) via calcination at 700 °C for various time. (b) Removal efficiency of MB using different  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$  catalysts obtained with  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (feeding amount of chitosan: 0.1g) via calcination at various temperature for 120 min. Reaction conditions: initial MB concentration, 100 mg L<sup>-1</sup>; initial H<sub>2</sub>O<sub>2</sub> concentration, 5 mmol L<sup>-1</sup>; NH<sub>2</sub>OH concentration, 5 mmol L<sup>-1</sup>; catalyst load, 0.5 g L<sup>-1</sup>; T = 303 K.

## ESI-III

### Characterization and Catalytic Performance of $\text{Fe}_3\text{O}_4$ , $\text{Fe}_3\text{O}_4/\text{chitosan}$ , $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C-PEG}$ and $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C}$ Nanoparticles

In order to further verify the influence of nanostructure and composition of nanoparticles on the catalytic activity,  $\text{Fe}_3\text{O}_4$  nanoparticles reported by the precursor,<sup>3</sup> were prepared by a solvothermal reaction using PEG as a stabilizer instead of chitosan. This is because the  $\text{Fe}_3\text{O}_4$  nanoparticles show a similar organic matter content (Fig. S7) and nanostructure (Fig. S1) compared with  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (feeding amount of chitosan: 0.1g) nanoparticles. Furthermore, a similar nanostructure has unfolded regarding  $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C-PEG}$  with  $\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C}$  (Fig. S1), which are individually obtained with  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (feeding amount of chitosan: 0.1g) via calcination at 700 °C for 2h. **The results are summarized in Table S5.**



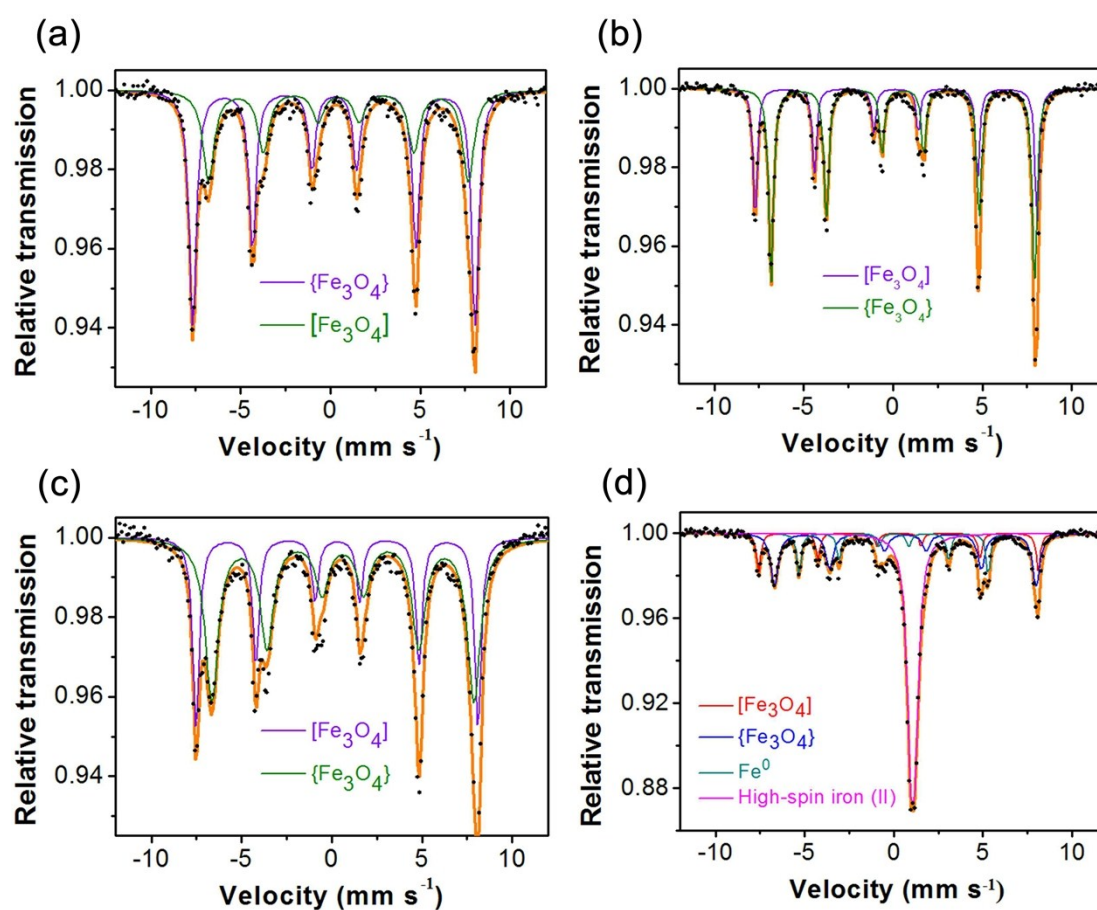
**Fig. S7** TG curves of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/chitosan obtained with 0.1g chitosan.

**Table S3.** Fitted room temperature Mössbauer parameters for limonites ( $\delta$  = isomer shift relative to  $\alpha$ -Fe,  $\Delta$  = quadruple splitting,  $H_{\text{eff}}$  = hyperfine field, RA = relative sub-spectral area, [ ] tetrahedral site, { } octahedral site.)

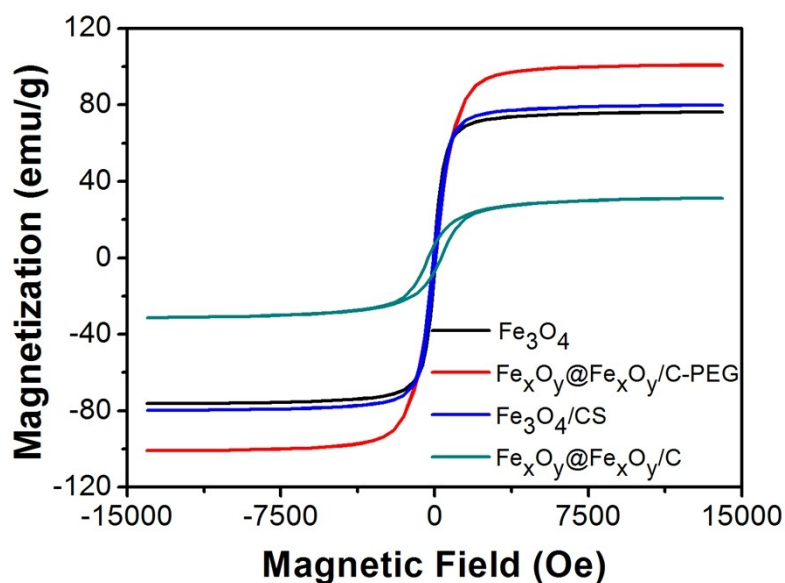
Sample	Mössbauer parameters			Assignment	RA (%)
	IS ( $\delta$ ) <sup>a</sup>	QS ( $\Delta$ )	$H_{\text{eff}}$ (H)		
	mm/s	mm/s	T		
Fe <sub>3</sub> O <sub>4</sub>	0.203	-0.021	48.9	[Fe <sub>3</sub> O <sub>4</sub> ]	62.5
	0.452	-0.013	45.0	{Fe <sub>3</sub> O <sub>4</sub> }	37.5
Fe <sub>x</sub> O <sub>y</sub> @Fe <sub>x</sub> O <sub>y</sub> /C-PEG	0.166	0.003	49.1	[Fe <sub>3</sub> O <sub>4</sub> ]	36.8
	0.547	0.002	45.9	{Fe <sub>3</sub> O <sub>4</sub> }	63.2
Fe <sub>3</sub> O <sub>4</sub> /chitosan	0.299	-0.267	48.6	[Fe <sub>3</sub> O <sub>4</sub> ]	36.7
	0.611	0.005	45.2	{Fe <sub>3</sub> O <sub>4</sub> }	63.7



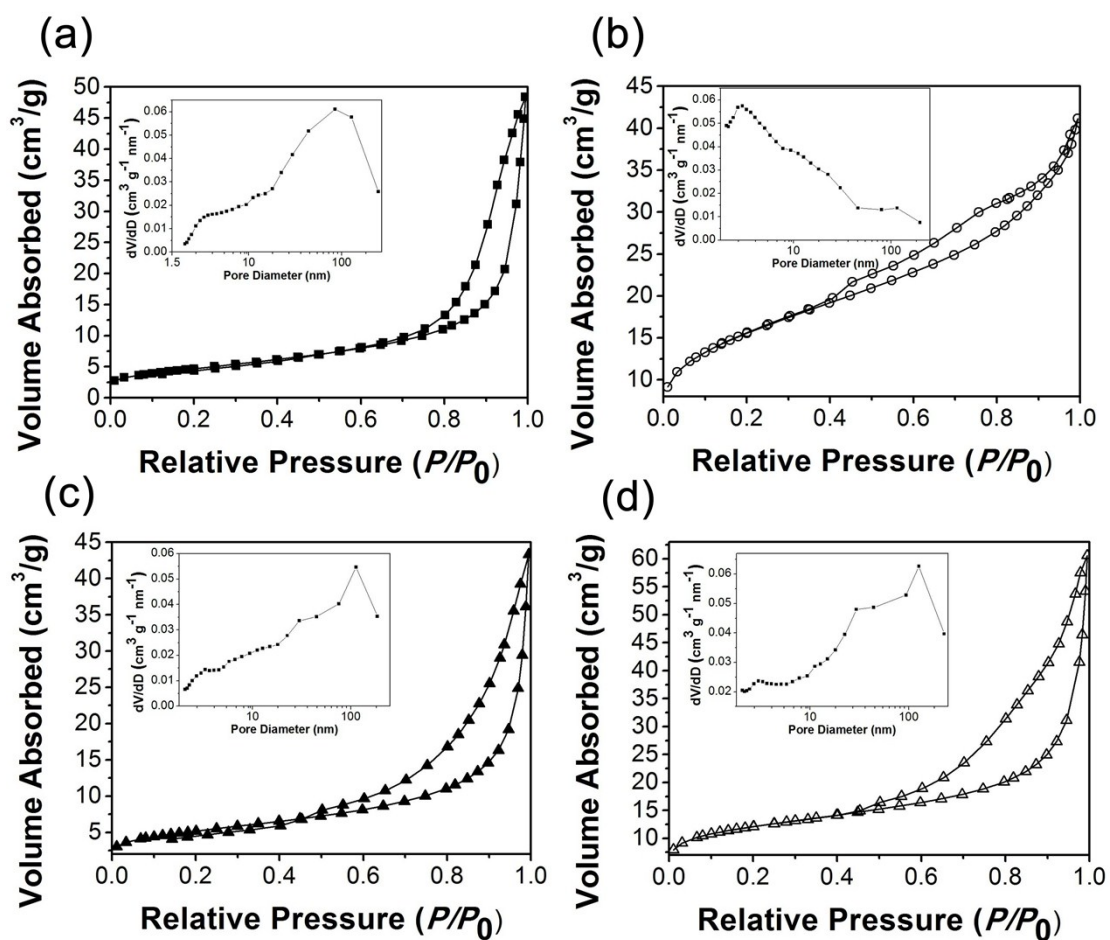
$\text{Fe}_x\text{O}_y@\text{Fe}_x\text{O}_y/\text{C}$	0.273	-0.023	48.8	$[\text{Fe}_3\text{O}_4]$	11.6
	0.651	-0.003	45.6	$\{\text{Fe}_3\text{O}_4\}$	28.6
	-0.003	-0.022	33.0	$\alpha\text{-Fe}^0$	13.2
	1.062	0.260	–	High-spin iron (II)	46.5



**Fig. S8** Mössbauer spectra at RT of Fe<sub>3</sub>O<sub>4</sub> (a) before and (b) after calcination at 700 °C for 120 min. Mössbauer spectra at RT of Fe<sub>3</sub>O<sub>4</sub>/chitosan obtained with 0.1g chitosan (c) before and (d) after calcination at 700 °C for 120 min.



**Fig. S9** Magnetic hysteresis loops of Fe<sub>3</sub>O<sub>4</sub> before and after calcination at 700 °C for 120 min (Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C-PEG), Fe<sub>3</sub>O<sub>4</sub>/chitosan obtained with 0.1g chitosan before and after calcination at 700 °C for 120 min (Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C).

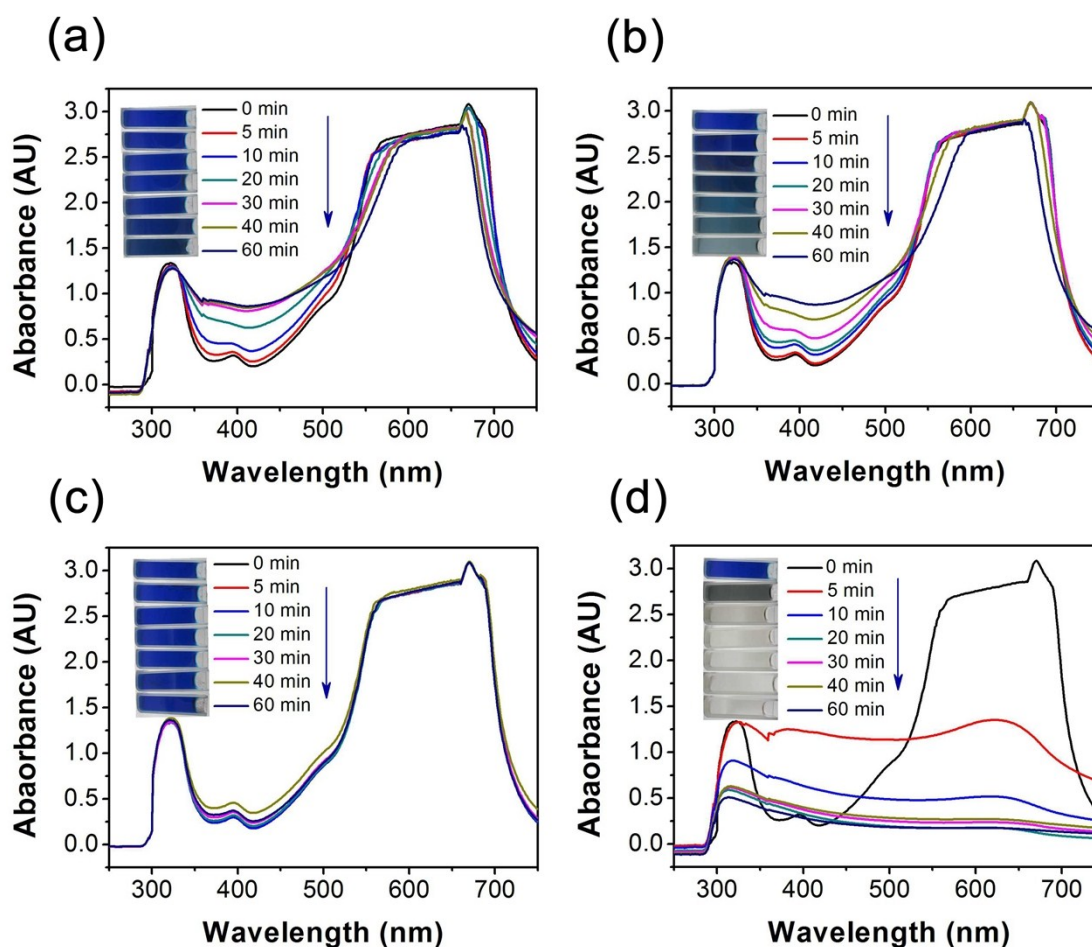


**Fig. S10** Nitrogen adsorption-desorption isotherms of Fe<sub>3</sub>O<sub>4</sub> (a) before and (b) after calcination at 700 °C for 120 min (Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C-PEG),

Fe<sub>3</sub>O<sub>4</sub>/chitosan obtained with 0.1g chitosan (c) before and (d) after calcination at 700 °C for 120 min (Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C). The inset shows the pore size distribution curve obtained from the adsorption data.

**Table S4.** Porous characteristics of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/chitosan, Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C-PEG and Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C nanoparticles

Sample	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
Fe <sub>3</sub> O <sub>4</sub>	16.9	0.075	17.7
Fe <sub>x</sub> O <sub>y</sub> @Fe <sub>x</sub> O <sub>y</sub> /C-PEG	54.4	0.061	4.7
Fe <sub>3</sub> O <sub>4</sub> /chitosan	17.8	0.067	14.7
Fe <sub>x</sub> O <sub>y</sub> @Fe <sub>x</sub> O <sub>y</sub> /C	40.3	0.086	9.3



**Fig. S11** UV-vis spectral changes of the 100 mg L<sup>-1</sup> MB solution in the removal process as a function of the reaction time using different Fenton catalysts: Fe<sub>3</sub>O<sub>4</sub> (a) before and (b) after calcination at 700 °C for 120 min (Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C-PEG), Fe<sub>3</sub>O<sub>4</sub>/chitosan obtained with 0.1g chitosan (c) before and (d) after calcination at 700 °C for 120 min (Fe<sub>x</sub>O<sub>y</sub>@Fe<sub>x</sub>O<sub>y</sub>/C). Reaction conditions: initial H<sub>2</sub>O<sub>2</sub> concentration, 5 mmol L<sup>-1</sup>; NH<sub>2</sub>OH concentration, 5 mmol L<sup>-1</sup>; catalyst load, 0.5 g L<sup>-1</sup>; T = 303 K.

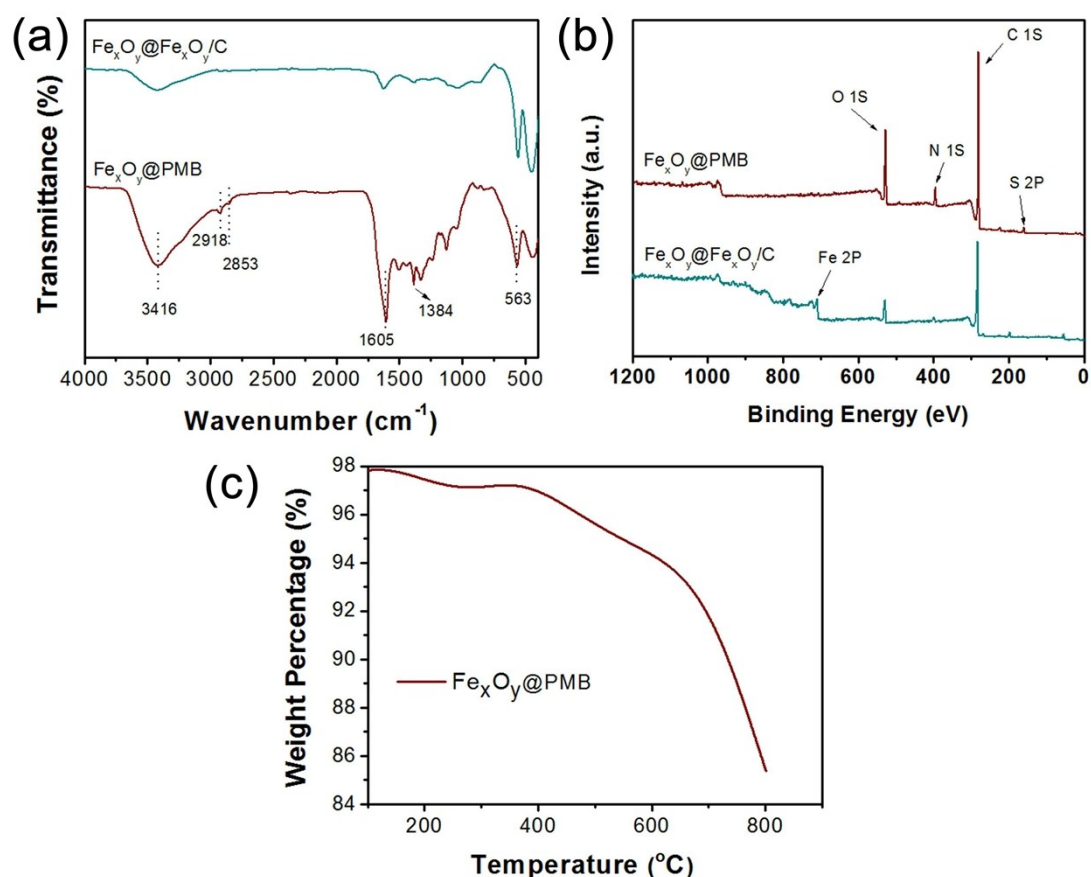
**Table S5.** The influence of nanostructure and composition of nanoparticles on the catalytic activity

Sample	$\alpha$ -Fe <sup>0</sup>	Nanostructure	BET surface area	Removal of MB
	(Table S3)	(Fig. S1)	(Table S4)	(Fig. 2e)
Fe <sub>3</sub> O <sub>4</sub>	×	Solid nanosphere	16.9 m <sup>2</sup> /g	3.92%

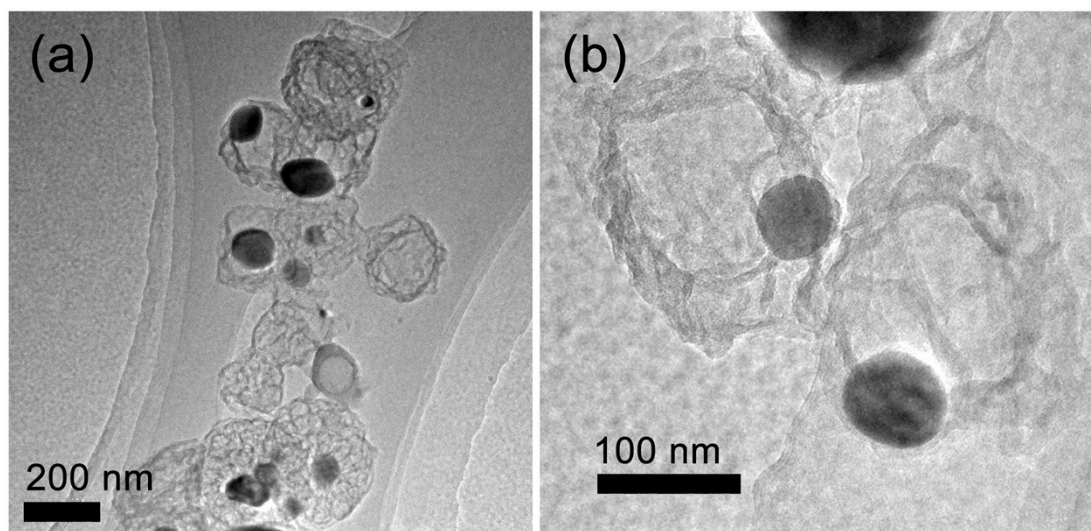
$\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C-PEG}$	×	Soap-bubble-like shell structure	54.4 $\text{m}^2/\text{g}$	83.4%
$\text{Fe}_3\text{O}_4/\text{chitosan}$	×	Solid nanosphere	17.8 $\text{m}^2/\text{g}$	5.84%
$\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$	✓	Soap-bubble-like shell structure	40.3 $\text{m}^2/\text{g}$	99.96%

## ESI-IV

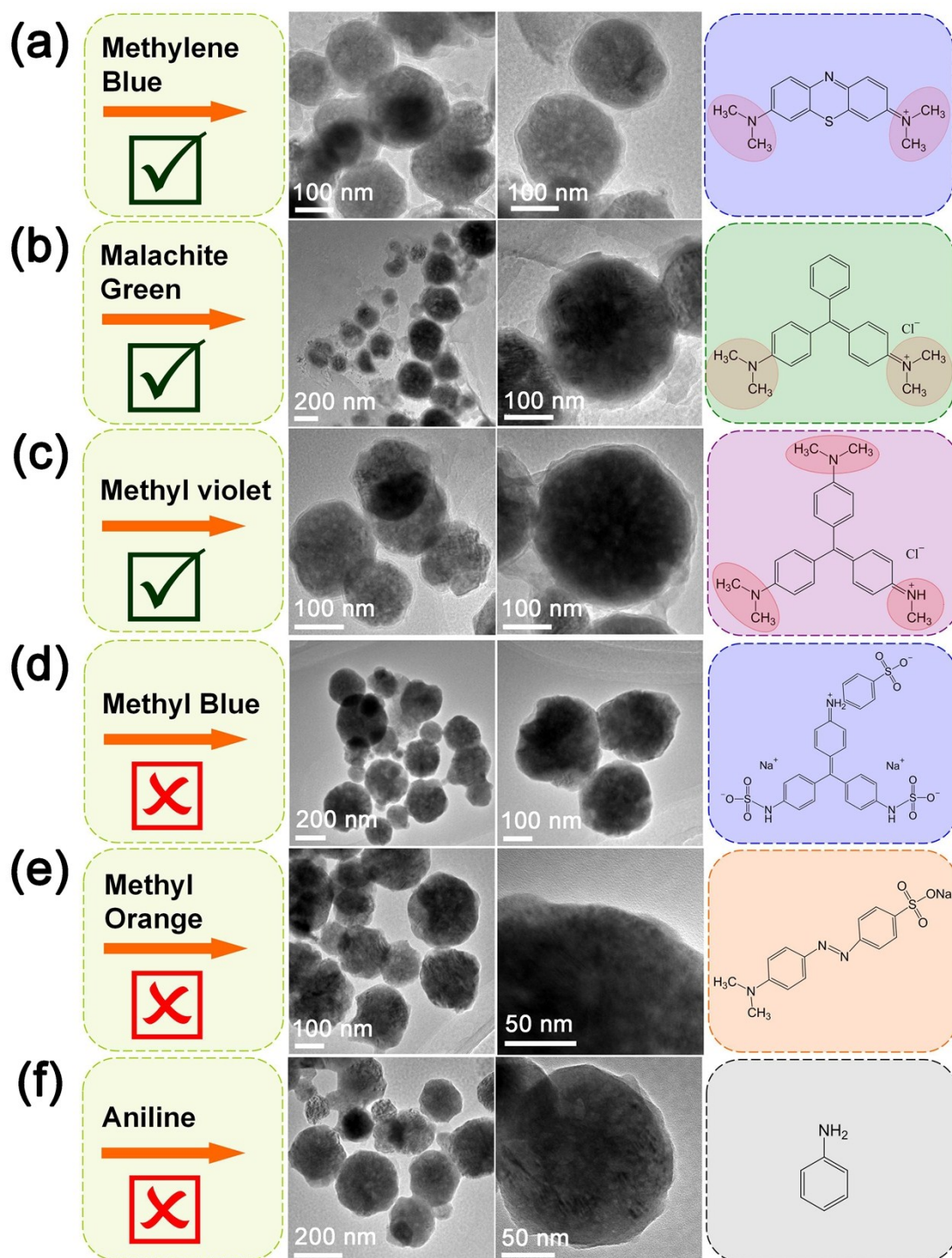
### Assembly of Various Dye Molecules on the Surface of $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$ Nanoparticles



**Fig. S12** (a) FTIR and (b) XPS of  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$  and  $\text{Fe}_x\text{O}_y@PMB$  obtained by conducting ten cycles of the catalytic process using  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C}$  as Fenton catalyst. (c) TG curves of  $\text{Fe}_x\text{O}_y@PMB$  obtained by conducting ten cycles.



**Fig. S13** TEM images of (a)  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C-PEG}$  and (b)  $\text{Fe}_x\text{O}_y@Fe_x\text{O}_y/\text{C-PEG}$  after ten cycles of the catalytic process as Fenton catalyst. Reaction conditions: initial MB concentration,  $100 \text{ mg L}^{-1}$ ; initial  $\text{H}_2\text{O}_2$  concentration,  $5 \text{ mmol L}^{-1}$ ;  $\text{NH}_2\text{OH}$  concentration,  $5 \text{ mmol L}^{-1}$ ; catalyst load,  $0.5 \text{ g L}^{-1}$ ; reaction time, 60min;  $T = 303 \text{ K}$ .



**Fig. S14** TEM images of  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$  as Fenton catalyst after five cycles of the catalytic process using various dyes as substrate.  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$  catalysts obtained with  $\text{Fe}_3\text{O}_4/\text{chitosan}$  (feeding amount of chitosan: 0.1g) via calcination at 700 °C for 120 min. Reaction conditions: initial dyes concentration, 0.27 mmol L<sup>-1</sup>; initial  $\text{H}_2\text{O}_2$  concentration, 5 mmol L<sup>-1</sup>;  $\text{NH}_2\text{OH}$  concentration, 5 mmol L<sup>-1</sup>; catalyst load, 0.5 g L<sup>-1</sup>; reaction time, 60min; T = 303 K. ✓: Dye molecule could be coated on the surface of  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$ ; ×: Dye molecule could not be coated on the surface of  $\text{Fe}_x\text{O}_y@/\text{Fe}_x\text{O}_y/\text{C}$ .

## References

1 (a) S. Hong, Y. Chang and I. Rhee, *J. Korean Phys. Soc.* 2010, **56**, 868; (b) Y. Ge, Y. Zhang, S. He, F. Nie, G. Teng and N. Gu, *Nanoscale Res. Lett.* 2009, **4**, 287; (c) H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen and Y. D. Li, *Angew. Chem. Int. Ed.*, 2005, **44**, 2782; (d) G. Zhao, J. Wang, X. Peng, Y. Li, X. Yuan and Y. Ma, *Chem.-Asian J.*, 2014, **9**, 546.

2 (a) X. Fang, Z. Liu, M.-F. Hsieh, M. Chen, P. Liu, C. Chen and N. Zheng, *ACS Nano*, 2012, **6**, 4434; (b) W. Li, Y. Deng, Z. Wu, X. Qian, J. Yang, Y. Wang, D. Gu, F. Zhang, B. Tu and D. Zhao, *J. Am. Chem. Soc.* 2011, **133**, 15830; (c) T. Zeng, X. Zhang, S. Wang, Y. Ma, H. Niu and Y. Cai, *Chem. Eur. J.*, 2014, **20**, 6474.

3 H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, and Y. Li, *Angew. Chem. Int. Ed.*, 2005, **44**, 2782.