

Surfactant-free hydrothermal synthesis of sub-10 nm γ -Fe₂O₃/polymer porous composite for catalytic reduction of nitroarenes

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Experimental section

Iron (III) acetylacetonate, γ -Fe₂O₃ (nanopowder, 20-40 nm particle size) and α -Fe₂O₃ (>99%) were purchased from Afla Aesar; Acetylacetonate and Fe₃O₄ (nanopowder, <50 nm particle size, >98%) were provided by Sigma-Aldrich; other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd, China. All chemicals were of analytical grade and were used as received without further purification.

Synthesis of γ -Fe₂O₃/polymer composite: In a typical synthesis, 0.4 mL of 0.05M Iron (III) acetylacetonate (Fe(acac)₃) in acetonitrile solution and 50 μ L of 37% formaldehyde were added into 10 ml deionized water. Then, 350 μ L of 1M sodium hydroxide solution was added. After stirring mildly for about five minutes, the solution was transferred into a Teflon-lined autoclave of 25 mL and heated to 160°C for 4hrs. A solution with brown color finally obtained from the hydrothermal treatment was washed with water twice by centrifugation at 8000 rpm for 10 min and then dried at 60°C for about 12 hrs, the solid powder was obtained.

Characterization: The XRD patterns of the products were obtained using a

D/MAX-2500 PC X-ray diffractometer with monochromatized Cu K α radiation ($\lambda=1.54 \text{ \AA}$). The Morphology of samples was characterized under scanning electron microscope (Nova Nano SEM 450) and transmission electron microscope (JEM-2100 and FEI-F30). The fourier-transform infrared (FTIR) spectra were obtained on a Thermo Nicolet iS10 infrared spectroscope from 4000 to 400 cm^{-1} by KBr method at room temperature. Thermogravimetric/differential scanning calorimetry (TG/DSC) was performed on NETZSCH STA 449 F3 under a flow of air (50 ml/min) with a heating rate of $10^\circ\text{C min}^{-1}$ from 35 to 1000 $^\circ\text{C}$. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption-desorption isotherms on a Micrometrics ASAP 2020 system, and the pore size distribution was obtained from the Horvath-Kawazoe Differential Pore Volume Plot. The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) ESCALAB 250 set-up equipped with a monochromatic Al K α X-ray source (1486.6eV; anode operating at 15kV and 20mA). ^{57}Fe Mössbauer spectra of $\gamma\text{-Fe}_2\text{O}_3$ /polymer composite were taken on a Topologic 500 A spectrometer and a proportional counter at room temperature.

Catalysis test: The nitrobenzene (0.5 mL) was dissolved in 5mL ethanol in two-neck flask. Then, hydrazine hydrate (1 mL), catalyst (20 mg), and ethylbenzene (0.5 mL) as internal standard were added. The reaction mixture was stirred for 20 min at 85°C . After cooling the reaction mixture to room temperature, the catalyst was retrieved by centrifugation, and the sample of the mixture was directly subjected to GC analysis. The yields were determined by GC-FID (HP7890 with FID detector, column HP-5 30 m length, 0.32 mm internal diameter, 0.25 μm film thickness) and compared with authentic samples.

Table S1 The optimization synthesis parameters of the composites.

Sample	H ₂ O (ml)	0.05M Fe(acac) ₃ (μl)	37% HCHO (μl)	1M NaOH (μl)
1	10	400	0	350
2	10	400	30	350
3	10	400	50	350
4	10	400	50	0
5	10	400	50	50
6	10	400	50	100
7	10	400	50	350
8	10	0.02 mmol FeCl ₃ , 0.06 mmol acetylacetone	50	350

Table S2 Catalytic activity of various iron oxide samples for the reduction of nitrobenzene.

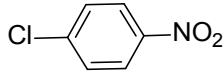
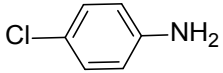
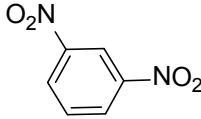
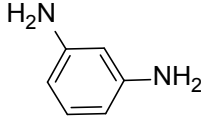
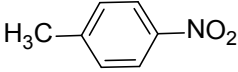
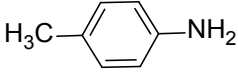
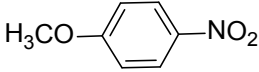
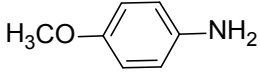
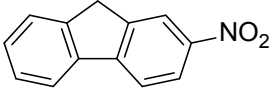
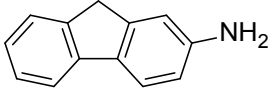
Catalyst ^[a]	TEM image	Yield (%)
Commercial γ -Fe ₂ O ₃	Fig. S9a	48.6
Commercial α -Fe ₂ O ₃	Fig. S9b	2.1
Commercial Fe ₃ O ₄	Fig. S9c	38.1
Fe ₃ O ₄ ^[b]	Fig. S9d	26.3
γ -Fe ₂ O ₃ /polymer composites ^[c]	Fig. 1	99
γ -Fe ₂ O ₃ /polymer composites after calcinations at 350 °C	Fig. S9e	78.5
γ -Fe ₂ O ₃ /polymer composites after calcinations at 500 °C	Fig.S9f	7.6

[a] Reaction condition: nitrobenzene (5 mmol), hydrazine hydrate (17.5 mmol), ethanol (5 mL), catalyst (20 mg), 85°C;

[b] Fe₃O₄ was prepared according to reference **19**;

[c] The content of Fe₂O₃ in composites was about 77.6%

Table S3 Reduction of nitroarenes over the γ -Fe₂O₃/polymer composites.^[a]

Entry	Substrate	Time (min)	Product	Yield
1		15		99%
2		25		99%
3		25		99%
4		30		99%
5		30		99%

[a] reaction condition: nitroarenes (5 mmol), hydrazine hydrate (17.5 mmol), ethanol (5 ml), catalyst (20 mg), 85°C.

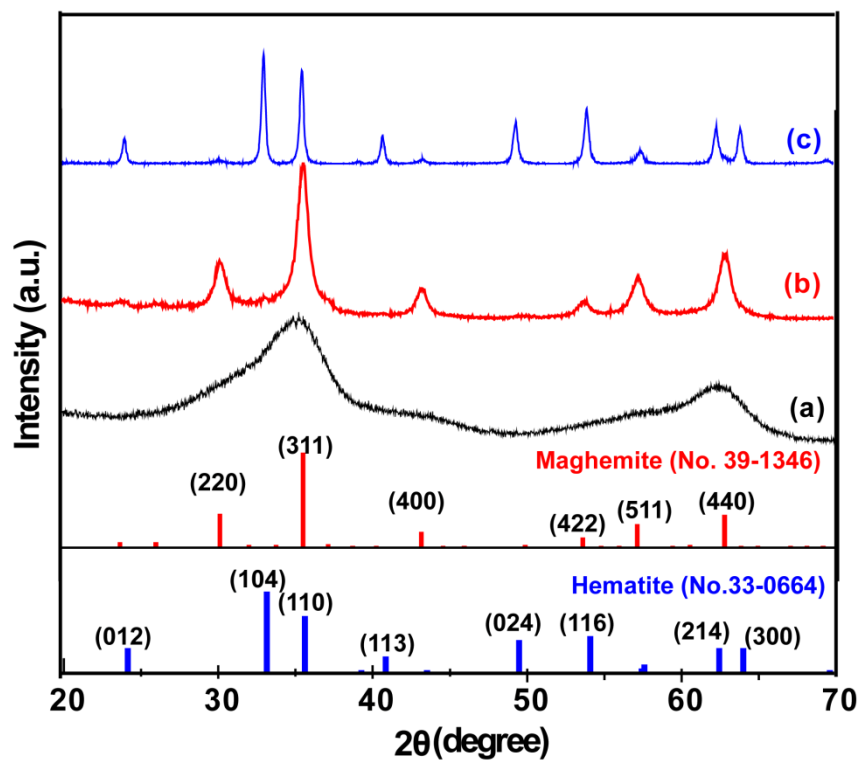


Figure S1 The XRD patterns of the γ -Fe₂O₃/polymer composites (a), the γ -Fe₂O₃/polymer composites after calcinations at 350°C (b) and 500 °C (c).

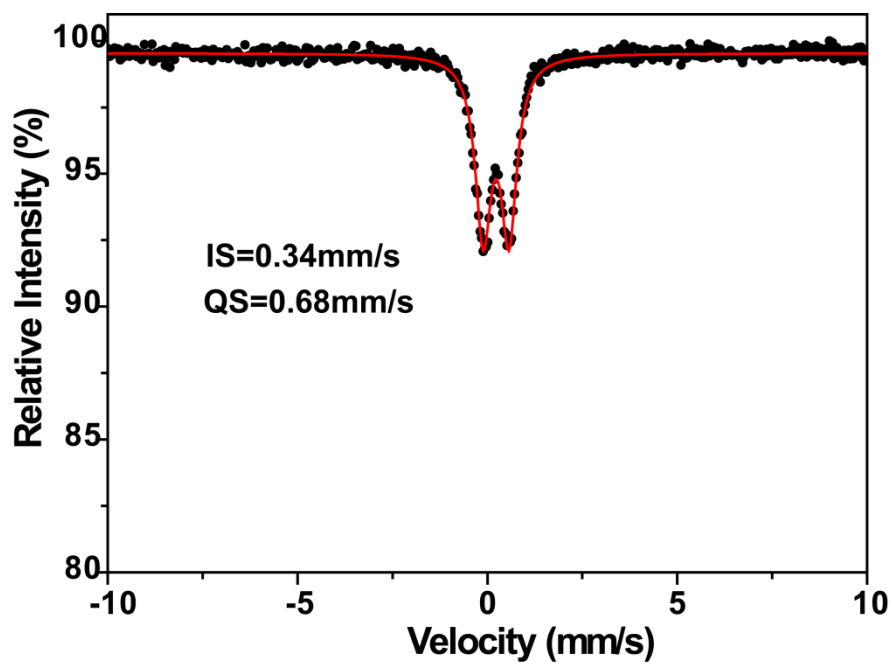


Figure S2 Room temperature Mössbauer spectrum of the γ -Fe₂O₃/polymer composites.

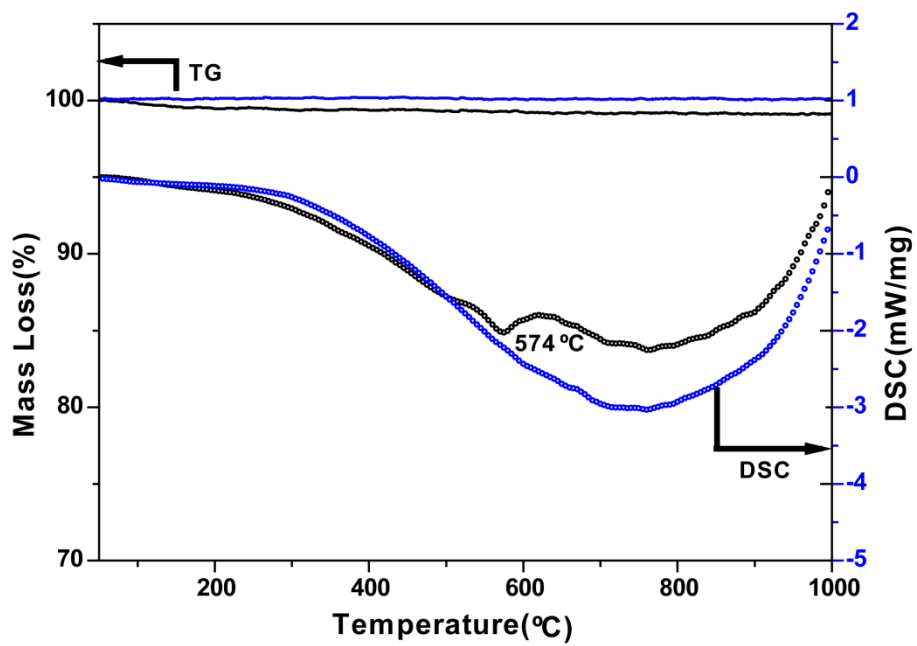


Figure S3 TG-DSC curves of the γ -Fe₂O₃/polymer composites after calcinations at 350 °C (black line) and 500 °C (blue line), respectively.

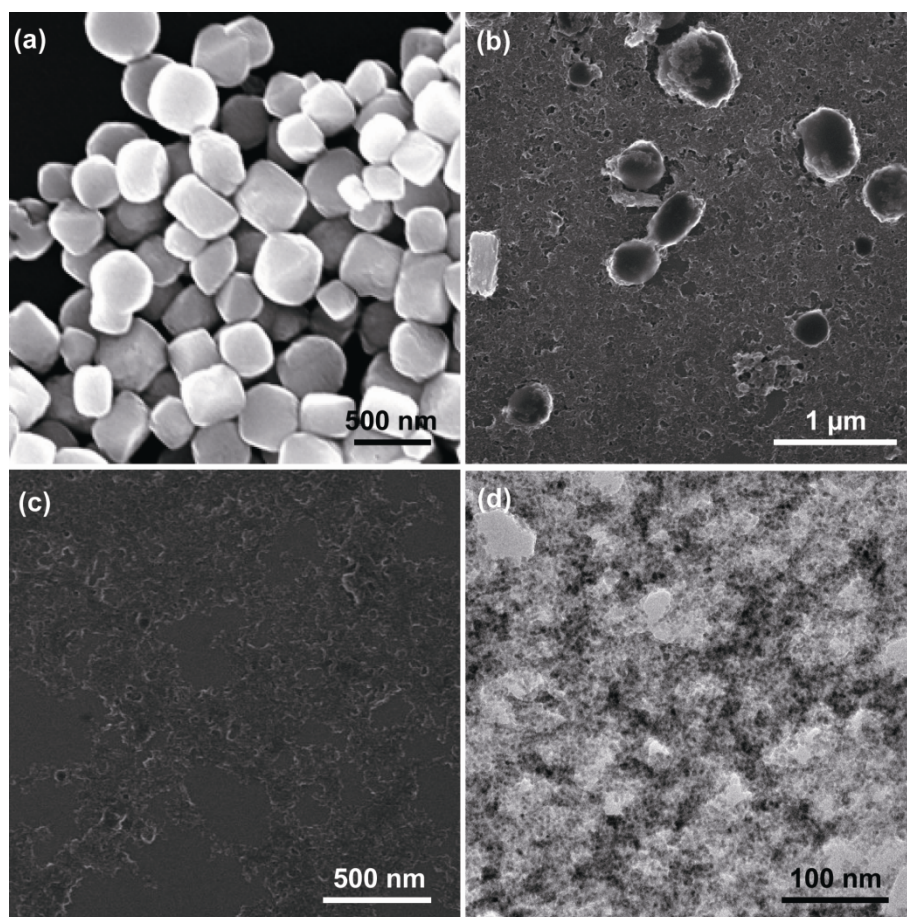


Figure S4 SEM and TEM images of the composites synthesized with varying volumes of HCHO solution: (a) 0 μl, (b) 30 μl, (c) and (d) 50 μl.

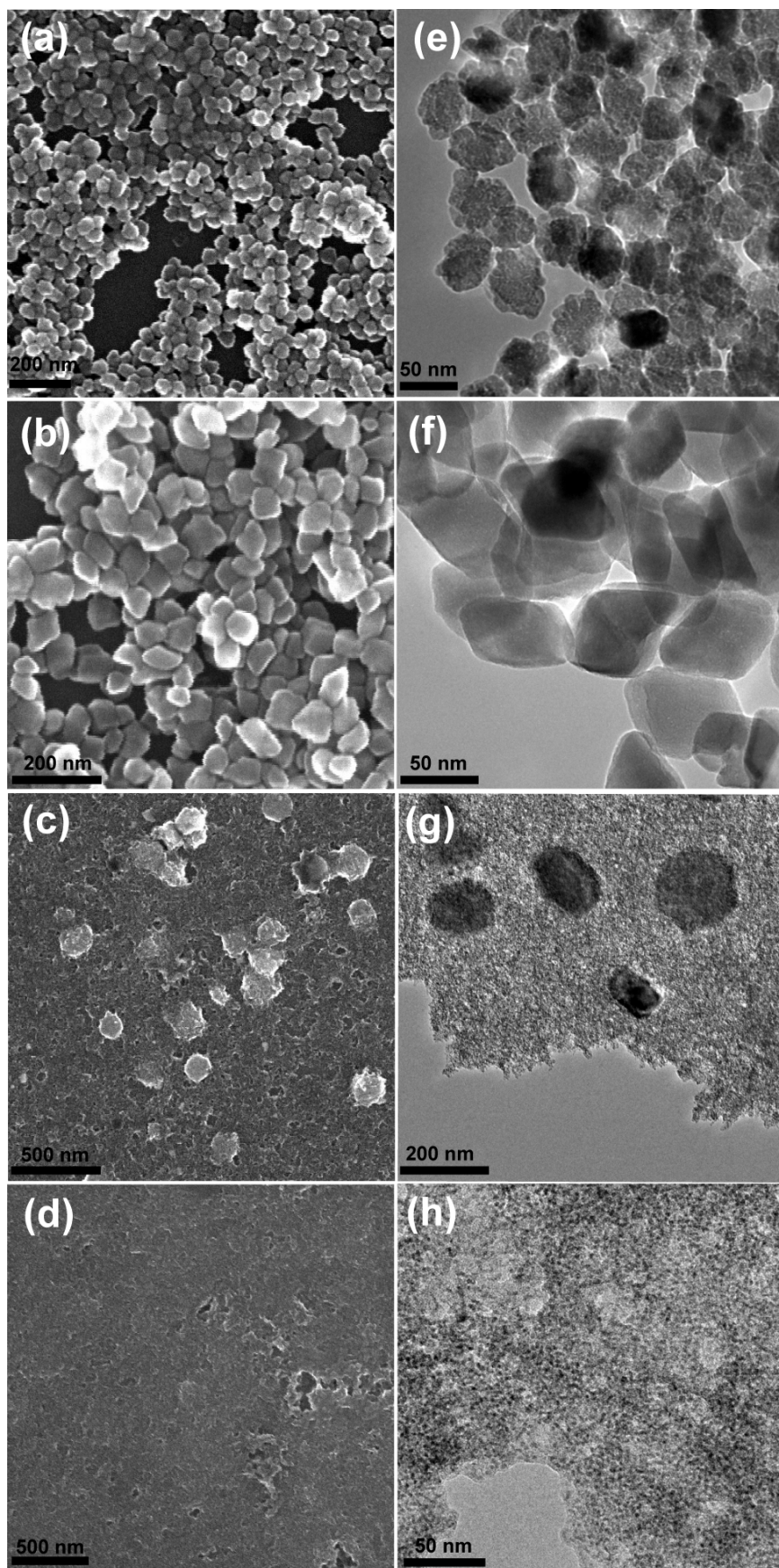


Figure S5 SEM and TEM image of the composites synthesized by using various volume of NaOH solution: (a) and (e) 0 μ l, (b) and (f) 50 μ l, (c) and (g) 100 μ l, (d) and (h) 350 μ l.

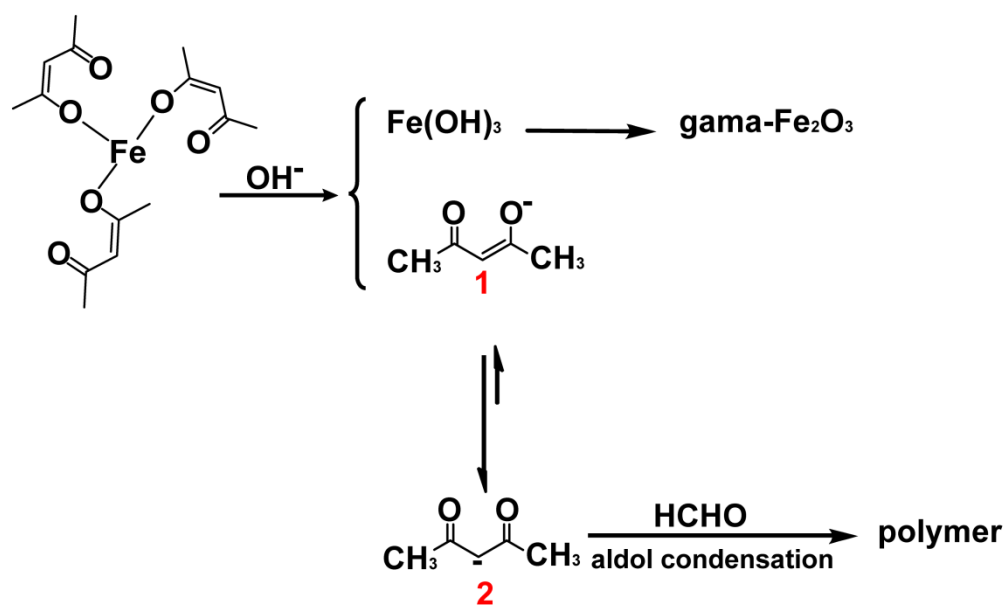


Figure S6 Possible reactions involved in the formation of the composites.

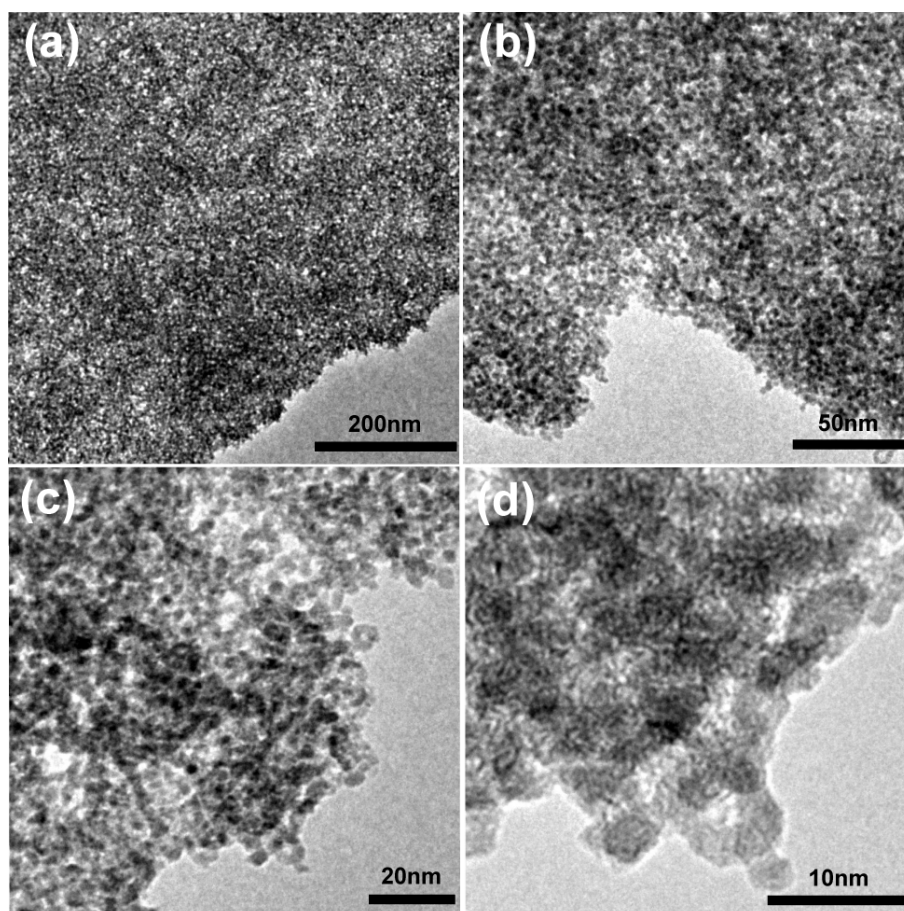


Figure S7 TEM image of composite synthesized by using FeCl₃ as Fe source.

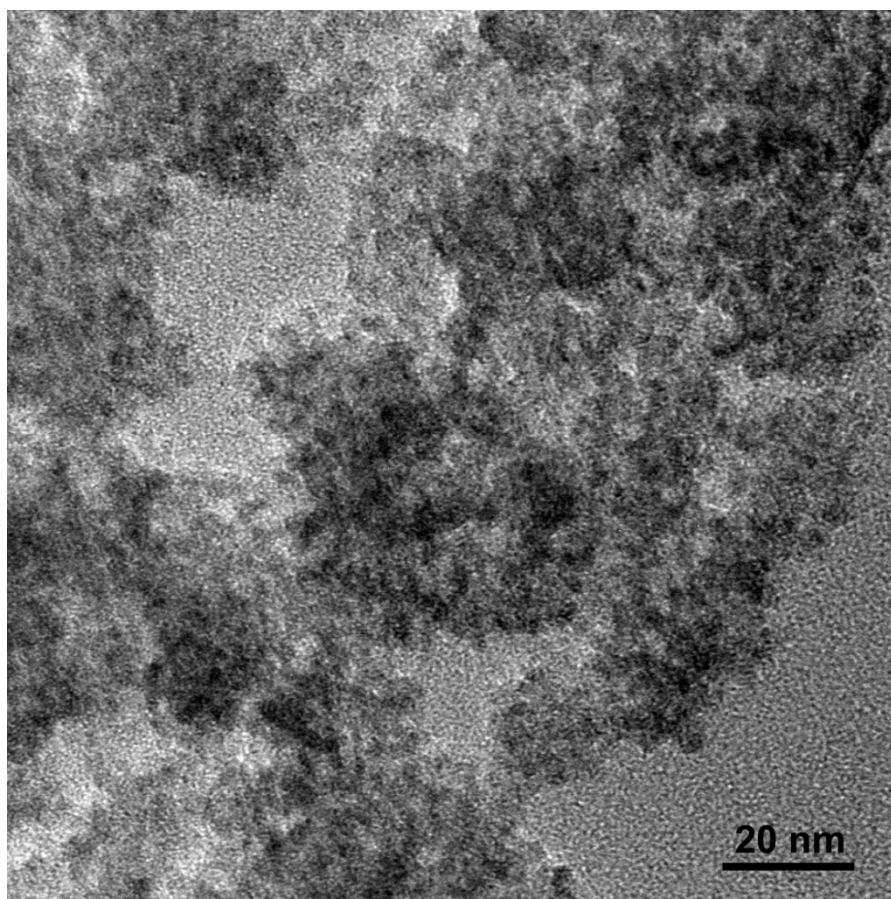


Figure S8 TEM image of the γ -Fe₂O₃/polymer composite after reaction.

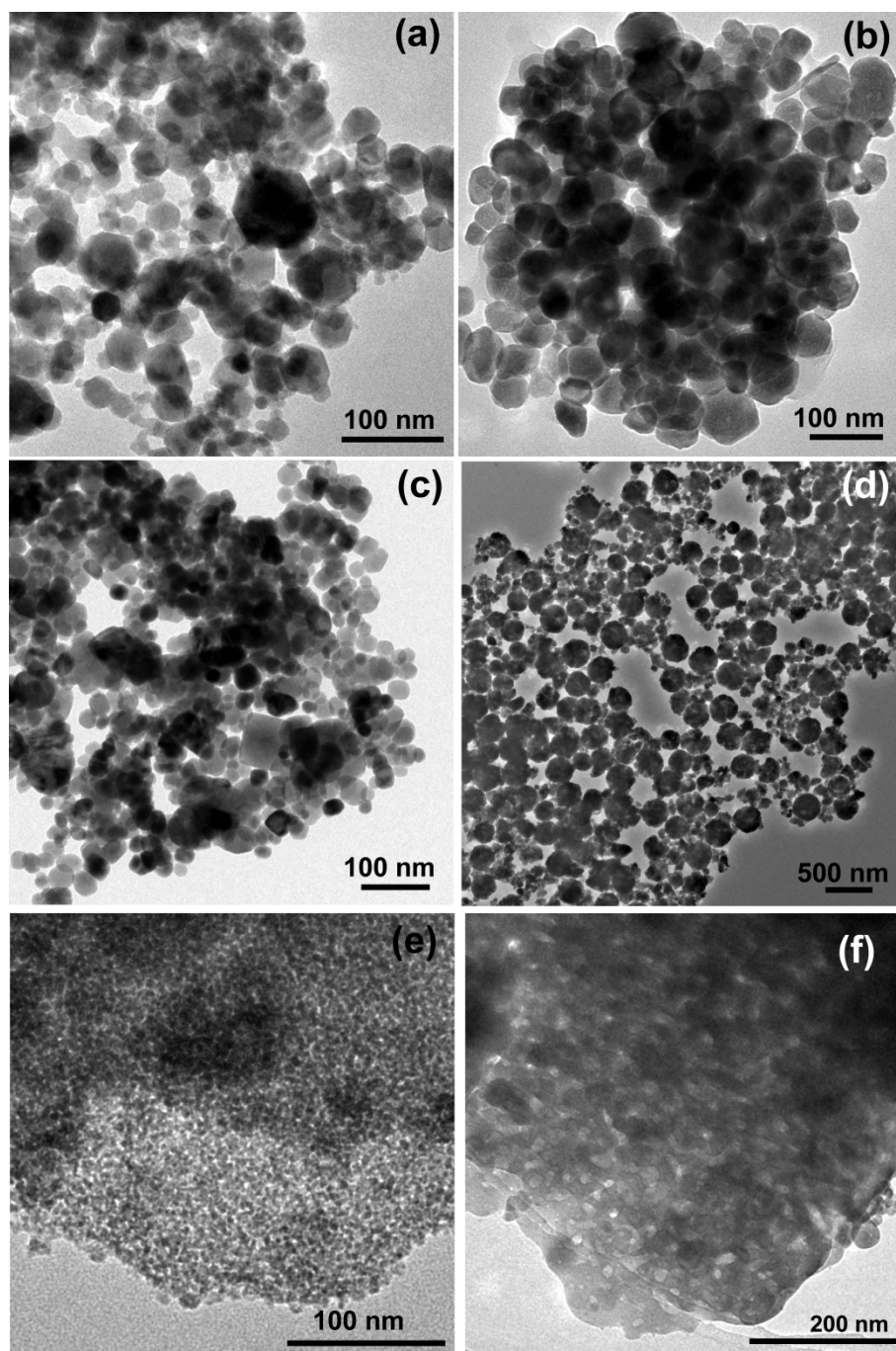


Figure S9 TEM images of different catalysts: (a) commercial γ - Fe_2O_3 , (b) commercial α - Fe_2O_3 , (c) commercial Fe_3O_4 , (d) Fe_3O_4 nanoparticles prepared according to reference 19, and γ - Fe_2O_3 /polymer composites after calcinations at 350 °C (e) and 500 °C (f), respectively.

Reference

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