

One Step Method to Encapsulate Nanocatalysts within Fe₃O₄ Nanoreactors

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Experimental Section:

Materials: Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), sodium citrate, urea, polyacrylamide (PAM), potassium chloropalladite (K_2PdCl_4), silver nitrate (AgNO_3), potassium tetrachloroaurate(III) hydrate (KAuCl_4), sodium borohydride (NaBH_4), and 4-nitrophenol (4-NP) are of analytical grade and purchased from Sinopharm Chemical Reagent Co, Ltd. All reagents were used as received without further purification. Deionized water was used for all experiments.

Synthesis of $\text{Pd}@\text{Fe}_3\text{O}_4$ microspheres with rattle type nanostructure: In a typical synthesis, 0.75 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 2 mmol sodium citrate, 3 mmol urea, 0.15 g PAM were dissolved in 20 mL distilled water. Then, a certain amount of K_2PdCl_4 was added under vigorous stirring until it was totally dissolved. After an hour, the solution was transferred to a Teflon-lined stainless-steel autoclave (25 mL volume) and then sealed to heat at 200 °C. After a 12 h reaction period, the autoclave was cooled to room temperature. The obtained spheres were washed with water and ethanol, and then dried under vacuum to form a black powder. In this synthesis, the final products which are synthesized under different K_2PdCl_4 concentration of 0 , 5×10^{-4} M, 2×10^{-3} M, 4×10^{-3} M, and 6×10^{-3} M are defined as $\text{Pd}@\text{Fe}_3\text{O}_4$ -0, $\text{Pd}@\text{Fe}_3\text{O}_4$ -1, $\text{Pd}@\text{Fe}_3\text{O}_4$ -2, $\text{Pd}@\text{Fe}_3\text{O}_4$ -3, and $\text{Pd}@\text{Fe}_3\text{O}_4$ -4, respectively. Moreover, the synthetic procedure of the $\text{Au}/\text{Fe}_3\text{O}_4$ hollow spheres is similar to the $\text{Pd}@\text{Fe}_3\text{O}_4$ except for substituting the K_2PdCl_4 with KAuCl_4 (5×10^{-3} M).

Synthesis of Ag@Fe₃O₄ microspheres with rattle type nanostructure: In a typical synthesis, 0.75 mmol Fe(NO₃)₃·6H₂O, 3 mmol sodium citrate, 3 mmol urea, 0.15 g PAM were dissolved in 15 mL distilled water. Then, an aqueous solution of AgNO₃ (5 mL) was added under vigorous stirring. After an hour, the solution was transferred to a Teflon-lined stainless-steel autoclave (25 mL volume) and then sealed to heat at 200 °C. After a 12 h reaction period, the autoclave was cooled to room temperature. The obtained spheres were washed with water and ethanol, and then dried under vacuum for 12 h. In this synthesis, the final products which are synthesized under different AgNO₃ concentrations of 5×10^{-3} M and 2.5×10^{-2} are defined as Ag@Fe₃O₄-1 and Ag@Fe₃O₄-2, respectively.

Synthesis of Cu@Cu_xFe_{3-x}O₄ rattle particles and Cu_xFe_{3-x}O₄ hollow microspheres: In a typical synthesis, 0.75 mmol Fe(NO₃)₃·6H₂O, 0.1 mmol Cu(NO₃)₂, 2 mmol sodium citrate, 3 mmol urea, 0.15 g PAM were dissolved in 20 mL distilled water under vigorous stirring. After an hour, the solution was transferred to a Teflon-lined stainless-steel autoclave (25 mL volume) and then sealed to heat at 200 °C. After a 12 h reaction period, the autoclave was cooled to room temperature. The obtained spheres were washed with water and ethanol, and then dried under vacuum for 12 h. In this synthesis, the final products which are synthesized under different Cu(NO₃)₂ concentrations of 5×10^{-3} M, 1.5×10^{-2} M, 2×10^{-2} M, 2.5×10^{-2} M, and 3.75×10^{-2} are defined as Cu@Cu_xFe_{3-x}O₄-1, Cu@Cu_xFe_{3-x}O₄-2, Cu@Cu_xFe_{3-x}O₄-3,

$\text{Cu}@\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ -4, and $\text{Cu}@\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ -5, respectively. For the synthesis of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ hollow microspheres, the $\text{Cu}@\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ -1 particles were dispersed in the ammonium aqueous under sonication. Then, the dispersion was magnetically stirred. After 12 h, the particles were separated from the solution by a magnet and rinsed by water and ethanol for 5 times. After drying under vacuum for 12 h, $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ hollow microspheres were obtained.

Suzuki Cross-coupling Reaction: $\text{Pd}@\text{Fe}_3\text{O}_4$ rattle particles, phenylboronic acid (1.5 mmol), sodium carbonate (2.0 mmol) were placed in an oven-dried 20 ml Schlenk-tube. The reaction vessel was evacuated and filled with argon for three times. Then iodobenzene (1 mmol) and DMF:H₂O (20:1, 5 mL) were added with a syringe under a counter flow of argon. The vessel was sealed and stirred at 80 °C for 8 h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). Gas chromatography yields were determined with the use of 1,3-dimethoxybenzene (1 mmol) as an internal standard. The nanocatalysts were magnetically separated and washed by ethyl acetate and ethanol three times for the recycling experiments. In order to compare the catalytic activity of the $\text{Pd}@\text{Fe}_3\text{O}_4$ -3 and $\text{Pd}@\text{Fe}_3\text{O}_4$ -2, the Suzuki cross-coupling reactions were conducted under the same amount of Pd species.

The Catalytic Reduction of 4-nitrophenol: $\text{Ag}@\text{Fe}_3\text{O}_4$ -2 (1 mg) were added into a solution with 4-NP (5×10^{-5} mol/L) and incubated with 30 min. After that, an aqueous

solution of NaBH₄ (3.2×10^{-2} mol/L) was rapidly injected at room temperature with stirring. The color of the mixture gradually faded, indicating the reduction of the 4-NP dye. Changes in the concentration of 4-NP were monitored by examining the variations in the maximal UV/vis absorption at 400 nm. After the catalytic reaction was completed, the nanocatalysts were separated by magnetic field and rinsed by water and ethanol for 3 times for the following recycling reaction.

Characterization: X-ray powder diffraction patterns (XRD) of the products were obtained on a Bruker D8 Advance diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.5406$ Å). Transmission electron microscopy (TEM) photographs were taken on a FEI CM120 microscope and at an accelerating voltage of 120 kV and a high-resolution transmission electron microscope (HRTEM, Tecnai Model JEOL-2100 and JEOL-2010) at an accelerating voltage of 200 kV. The field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM. Their magnetic properties (*M-H* curve) were measured at room temperature on a MPMS XL magnetometer made by Quantum Design Corp. The nitrogen (N₂) adsorption/desorption isotherms at about 77 K were studied dispending Micromeritics, ASAP 2020M system.

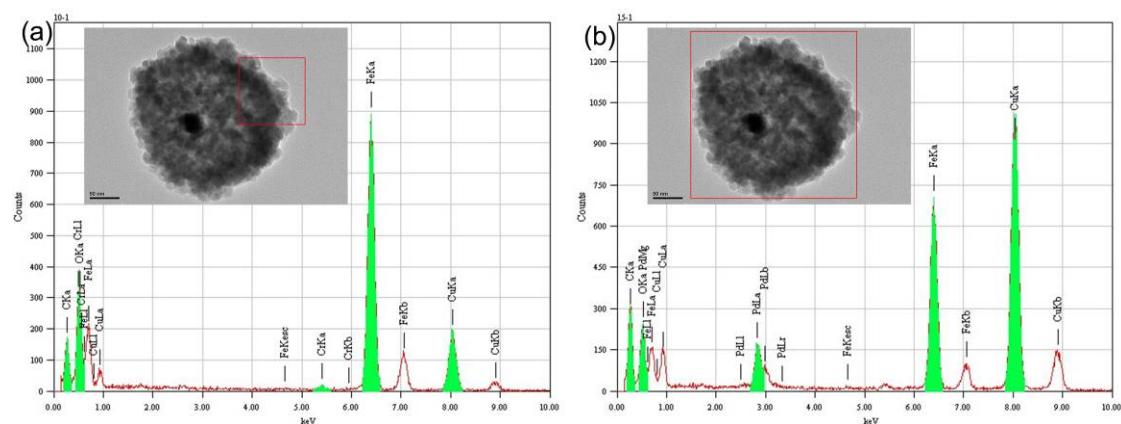


Figure SI 1. The TEM image and EDX spectra of the Pd@Fe₃O₄ nanocomposite which is taken from the shell (a) and the whole microsphere (b).

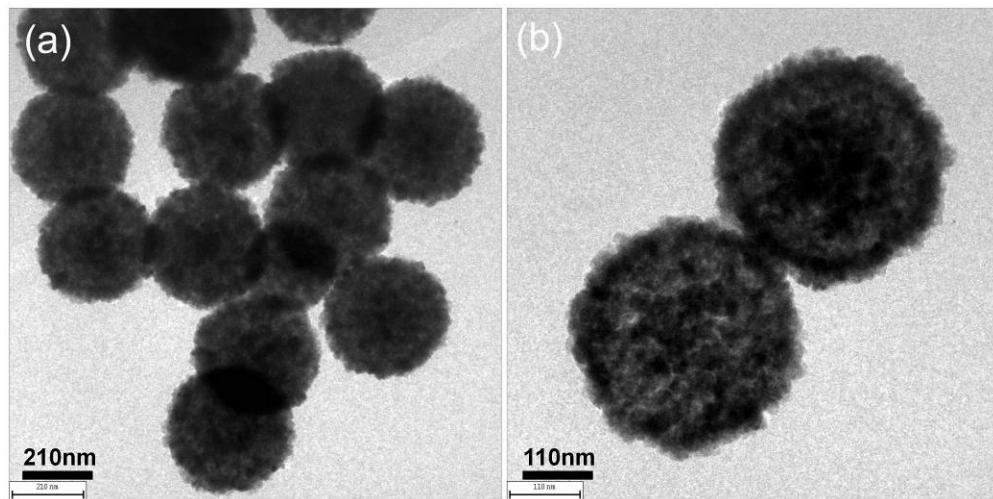


Figure SI 2. The TEM image of the Pd@Fe₃O₄-0 with different magnifications (hollow Fe₃O₄ microspheres).

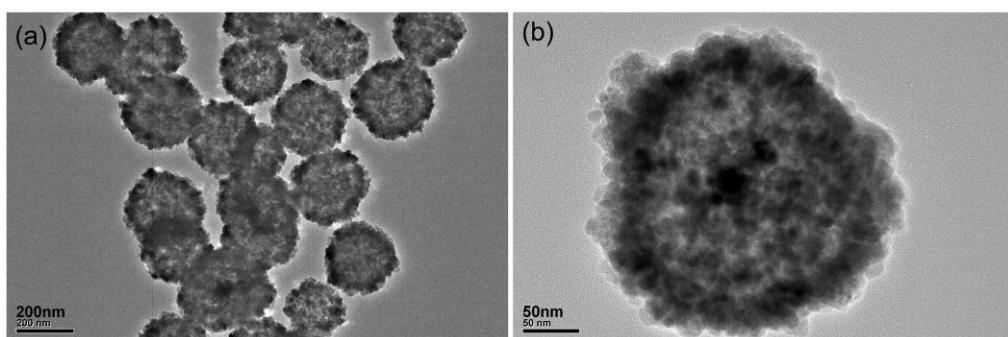


Figure SI 3. The TEM image of the Pd@Fe₃O₄-1 with different magnifications.

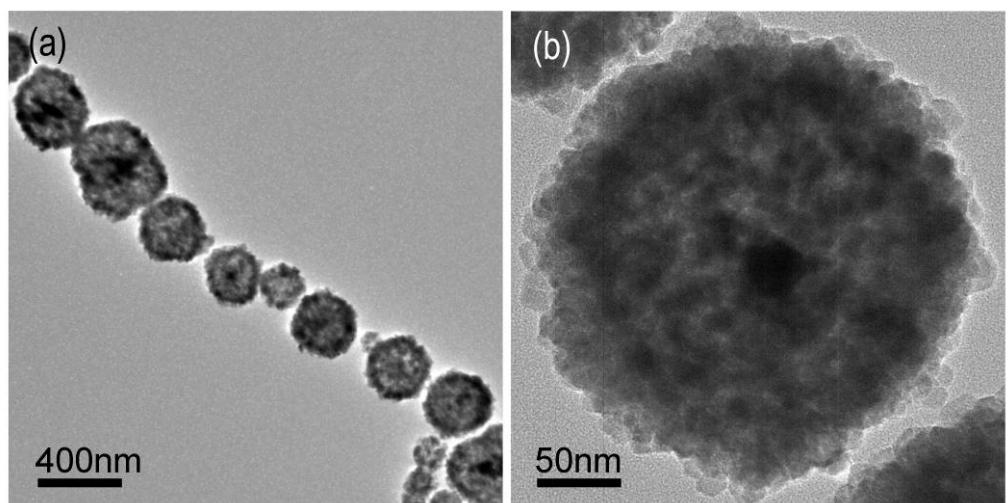


Figure SI 4. The TEM image of the Pd@Fe₃O₄-2 with different magnifications.

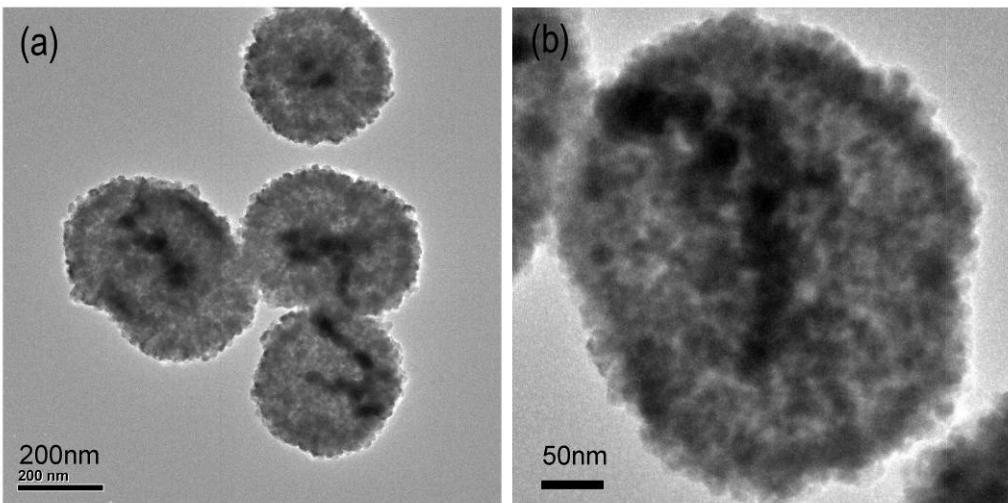


Figure SI 5. The TEM image of the Pd@Fe₃O₄-3 with different magnifications.

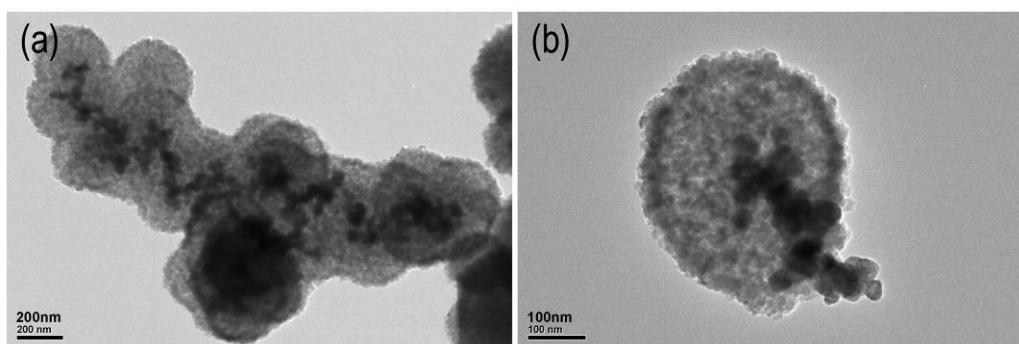


Figure SI 6. The TEM image of the Pd@Fe₃O₄-4 with different magnifications.

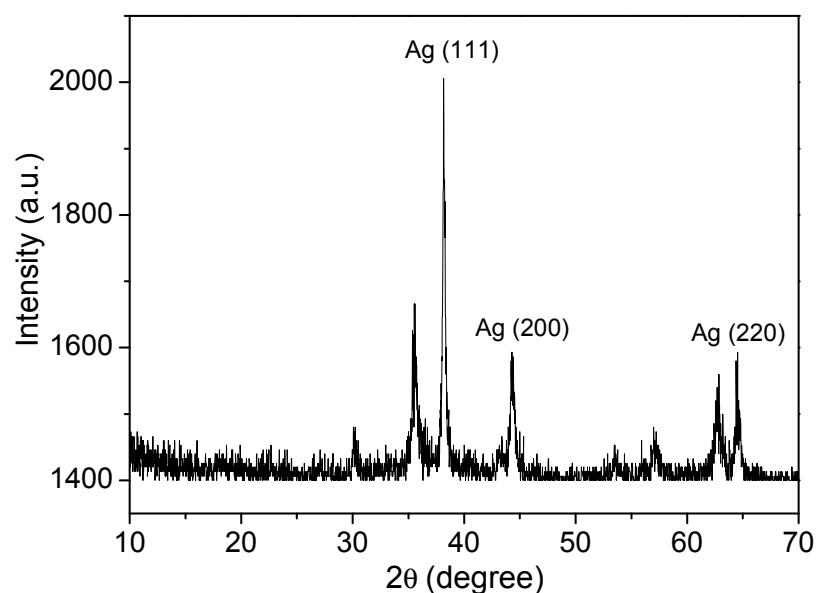


Figure SI 7. The XRD pattern of the Ag@Fe₃O₄ nanocomposite. The peaks located in 38°, 44.6°, and 64.7° are indexed to be face-centered Ag (JCPDF No. 03-0921).

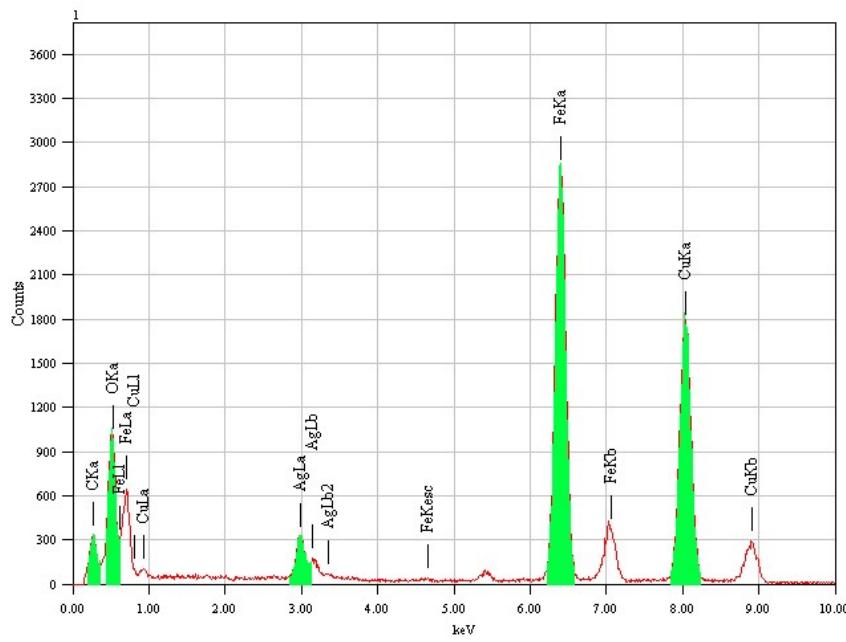


Figure SI 8. EDX spectra of the Ag@Fe₃O₄ nanocomposite

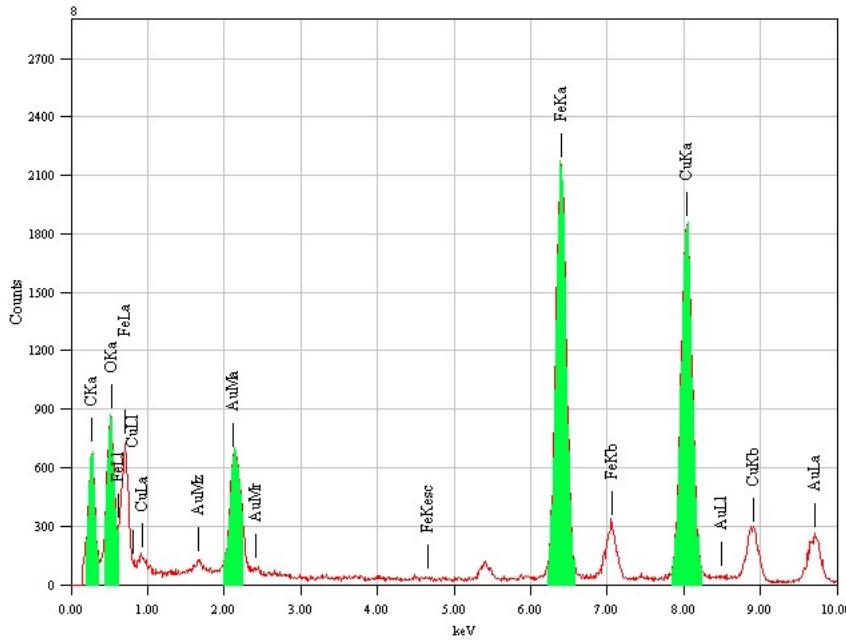


Figure SI 9. EDX spectra of the Au@Fe₃O₄ nanocomposite

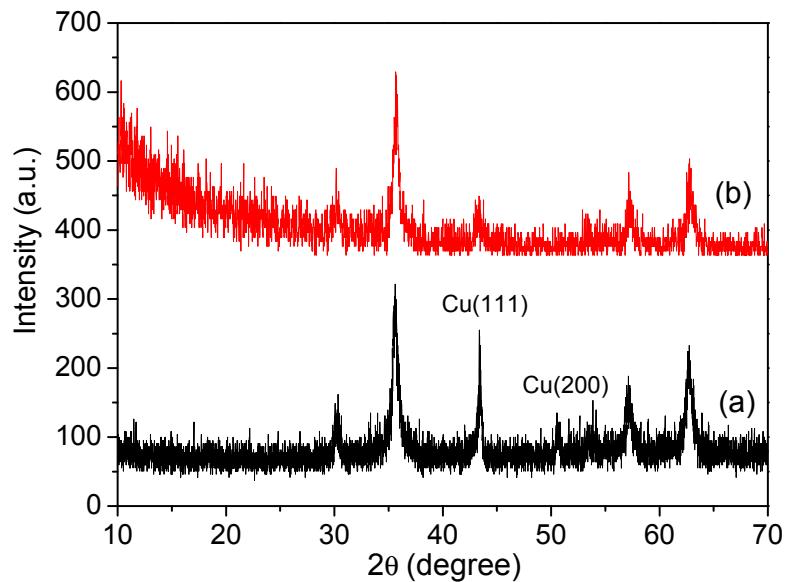


Figure SI 10. XRD patterns of the Cu/Cu_xFe_{3-x}O₄ nanocomposites (a) and Cu_xFe_{3-x}O₄ hollow spheres (b). The peaks located in 43.3°, and 50.4° are indexed to be face-centered Ag (JCPDF No. 03-1005).

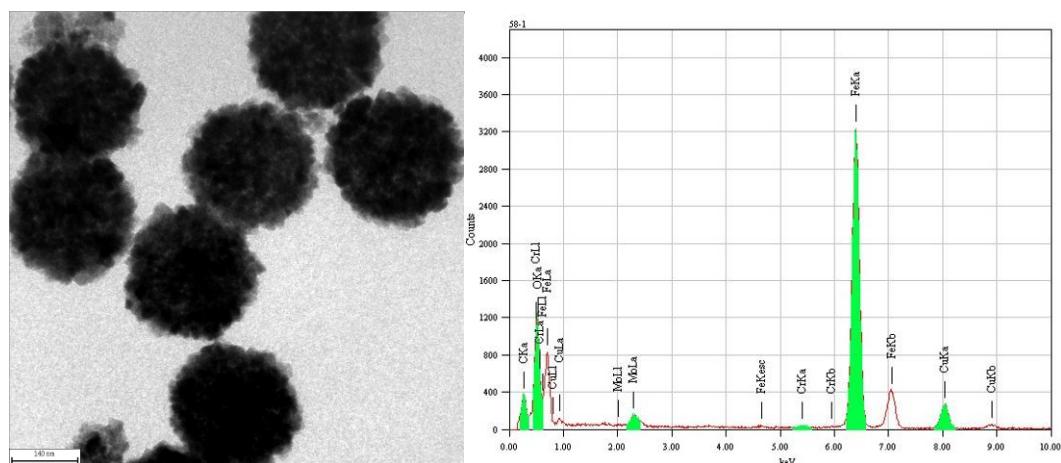


Figure SI 11. TEM image and EDX spectrum of the Cu_xFe_{3-x}O₄-1 hollow microspheres. Based on the element analysis, it is found that the as-prepared hollow spheres are Cu_{0.3}Fe_{2.7}O₄.

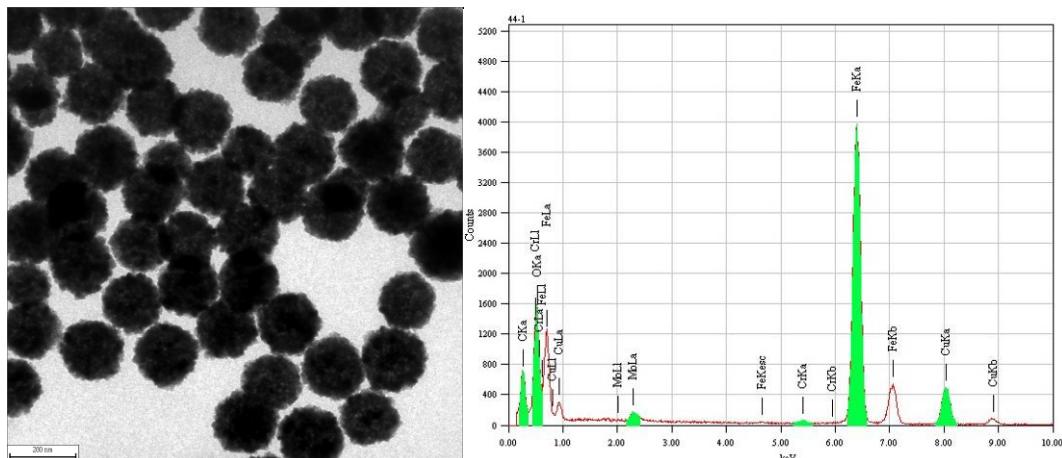


Figure SI 12. TEM image and EDX spectrum of the Cu/Cu_xFe_{3-x}O₄₋₁ nanocomposites. Based on the element analysis, it is found that the as-prepared hollow spheres are Cu_{0.1}/Cu_{0.3}Fe_{2.7}O₄.

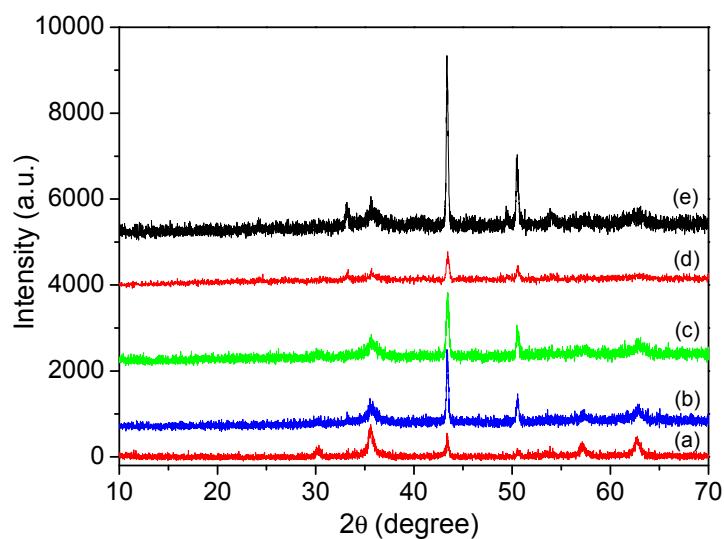


Figure SI 13. XRD patterns of the Cu@Cu_xFe_{3-x}O₄₋₁ (a), Cu@Cu_xFe_{3-x}O₄₋₂ (b), Cu@Cu_xFe_{3-x}O₄₋₃ (c), Cu@Cu_xFe_{3-x}O₄₋₄ (d), and Cu@Cu_xFe_{3-x}O₄₋₅ (e) nanocomposites

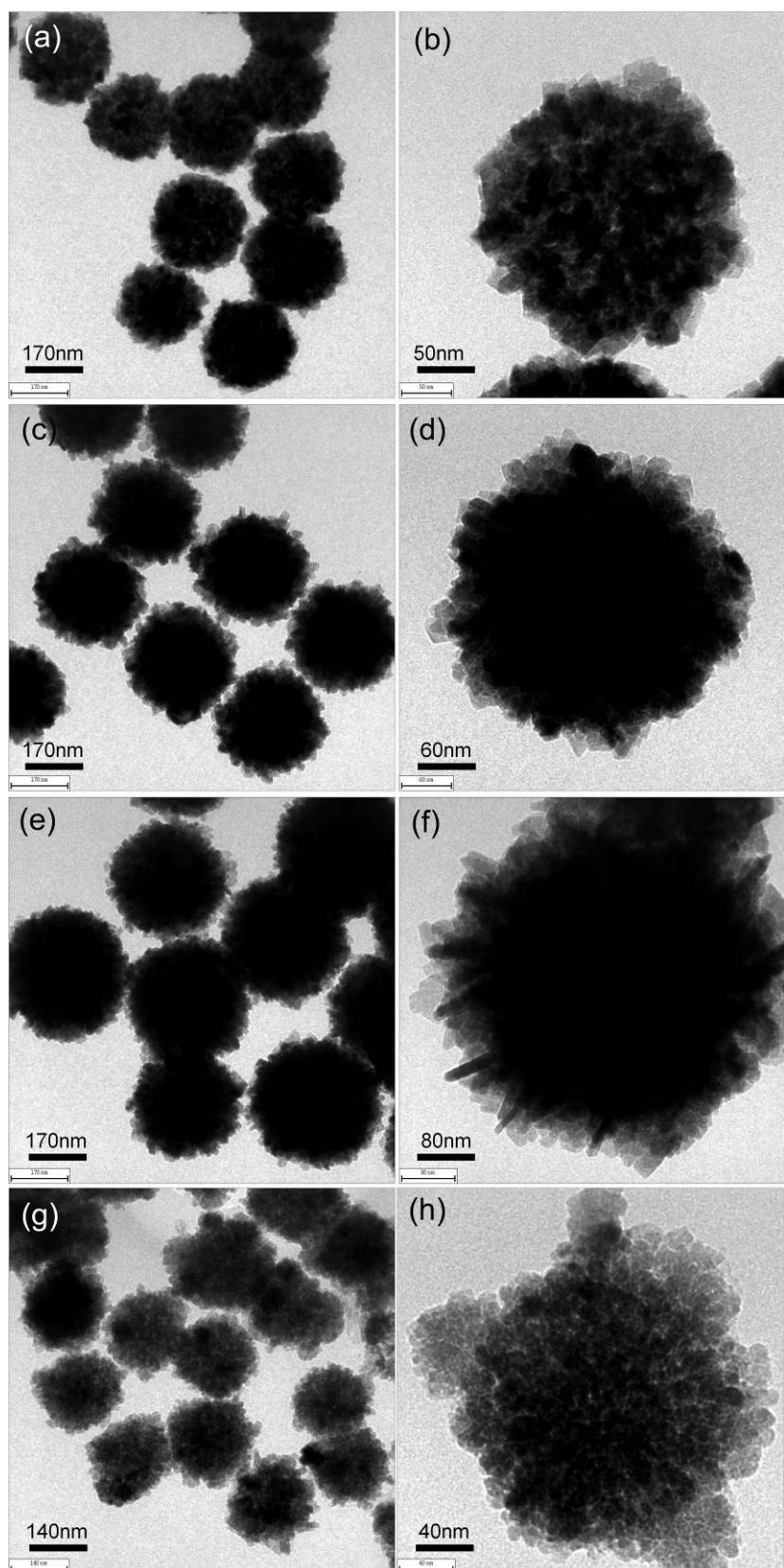


Figure SI 14. TEM images of the $\text{Cu}@\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ -1 (a,b), $\text{Cu}@\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ -2 (c,d), $\text{Cu}@\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ -3 (e,f), and $\text{Cu}@\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ -5 (g,h).

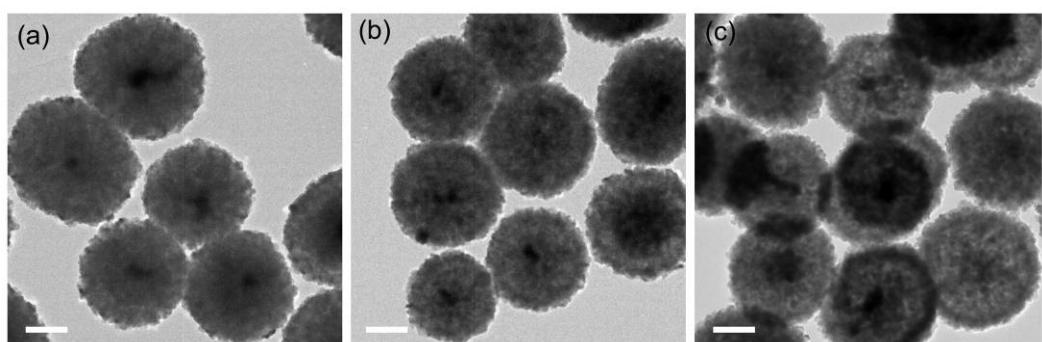


Figure SI 15. The TEM images of the Pd@Fe₃O₄ nanorattles synthesized under different reaction times: 4 h (a), 8 h (b), 12 h (c); the scale bar is 100 nm.

Table SI1. Suzuki cross-coupling in the presence of Pd@Fe₃O₄ nanorattles

Catalyst	Temperature	Time	Yield
Pd@Fe ₃ O ₄ -2	80 °C	8h	>98%
Pd@Fe ₃ O ₄ -3	80 °C	8h	82%
