

Electronic Supplementary Information

Simple one-pot synthesis of Rh-Fe₃O₄ heterodimer nanocrystals and their applications to magnetically recyclable catalyst for efficient and selective reduction of nitroarenes and alkenes†

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Experimental Section

Materials. Oleic acid and oleylamine were purchased from Aldrich Chemical Co. Fe(acac)₃ and Rh(acac)₃ were purchased from Acros and Strem, respectively. These chemicals were used without further purification.

Synthesis of Rh-Fe₃O₄ heterodimer nanocrystals. The synthesis was performed by two-step thermal decomposition of a mixture solution composed of iron acetylacetonate, rhodium acetylacetonate, oleylamine, and oleic acid. In a typical synthesis, 27 mg of Rh(acac)₃ (0.066 mmol) and 0.7 g of Fe(acac)₃ (2 mmol) was added into a solution containing 6 mL of oleylamine (17.5 mmol) and 4mL of oleic acid (12.5 mmol) and the mixture was heated to 120 °C in a vacuum with vigorous stirring for 2 h. Under Ar atmosphere, the dark brown mixture solution was heated to 200 °C at a heating rate of 2 °C/min and kept at this temperature for 30 min, and then it was further heated to 300 °C at the same heating rate and aged at 300 °C for 30 min. After cooling, the mixture solution

was precipitated by adding EtOH and the powdery nanocrystals were retrieved by centrifugation. The nanocrystals were dispersible in many organic solvents such as hexane and chloroform.

General procedure for nitro and double bond reductions. Substrate (1.0 mmol) and anisole (internal standard, 1.0 mmol) were injected to a suspension of Rh-Fe₃O₄ (94 mg, 0.01 mmol) in ethanol (8.0 mL). After the addition of hydrazine monohydrate, the reaction mixture was stirred at 80 °C under argon atmosphere until the reaction was completed. After magnetic separation of the catalyst, organic layer was decanted. The remaining catalyst was extracted with dichloromethane for 2 times. The combined organic solutions were directly analyzed with gas chromatography.

General procedure for the catalyst recycling. Nitrobenzene (103 μL, 1.0 mmol) and anisole (internal standard, 1.0 mmol) were injected to a suspension of Rh-Fe₃O₄ (94 mg, 0.01 mmol) in ethanol (8.0 mL). After the addition of hydrazine monohydrate (100 μL, 2.0 equiv.), the reaction mixture was stirred at 80 °C under argon atmosphere until the reaction was completed. After magnetic separation of the catalyst, organic layer was decanted. The remaining catalyst was extracted with dichloromethane for 2 times, then washed with water (5 mL), acetone (5 mL), and dried under vacuum. Before running a new reaction cycle, 8.0 mL of ethanol was added to the catalyst-charged round bottom flask, sonicated for 5 min. Then a nitrobenzene (1.0 mmol), hydrazine hydrate (2.0 equiv.), anisole (1.0 mmol) were added, and the reaction mixture was stirred until the reaction was completed as the second run of the reaction. The extracted residue was directly analyzed with gas chromatography or purified by flash column chromatography to yield the desired product.

Characterization. All Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a JEOL EM-2010 microscope at an accelerating voltage of 200 kV. The powder X-ray diffraction (XRD) measurement was performed using a Rigaku D/Max-3C diffractometer (Cu K α radiation, $\lambda = 0.15418$ nm). The magnetic properties were characterized using a magnetic property measurement system (MPMS) 5XL Quantum design SQUID (superconducting quantum interference device) magnetometer at 5 K and 300 K. The X-ray photoelectron spectroscopy (XPS) experiments were performed in an UHV multipurpose surface analysis system (SIGMA PROBE, Thermo, UK) operating at base pressures $<10^{-10}$ mbar. The photoelectron spectra were excited by an Al K α (1486.6 eV) anode operating at constant power of 100 W (15 KV and 6.7 mA). During the spectra acquisition, the constant analyser energy (CAE) mode was employed at a pass energy of 30 eV and a step of 0.1 eV. The binding energy (BE) scale was calibrated using the C 1s peak at 284.6 eV. Elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using ICPS-7500 spectrometer (Shimadzu). Temperature-programmed reduction (TPR) measurements were carried out in a conventional flow system with a moisture trap connected to a thermal conductivity detector (TCD) at temperatures ranging from room temperature to 1,000 °C with a ramping rate of 5 °C/min. For the TPR measurements, a mixed stream of H $_2$ (2 mL/min) and Ar (20 mL/min) was used for 0.1 g of catalyst sample.

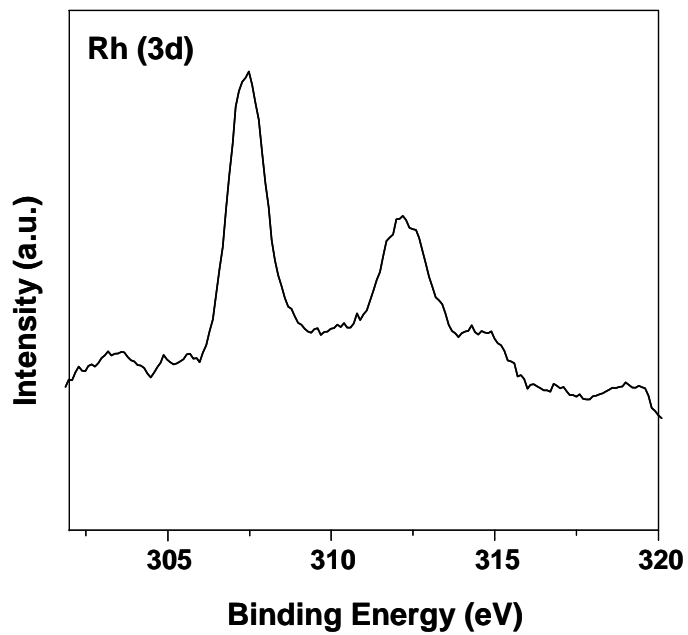


Figure S1. XPS spectrum of Rh-Fe₃O₄ heterodimer nanocrystals.

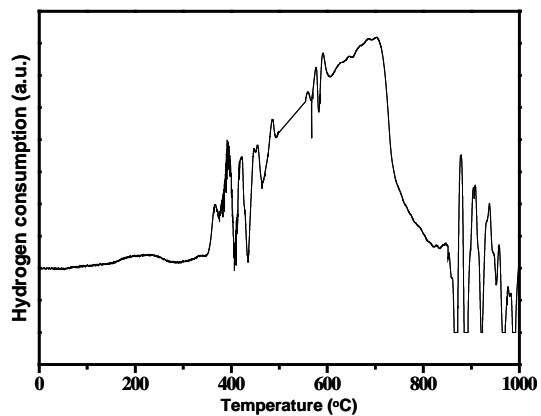


Figure S2. TPR spectrum of Rh-Fe₃O₄ heterodimer nanocrystals.

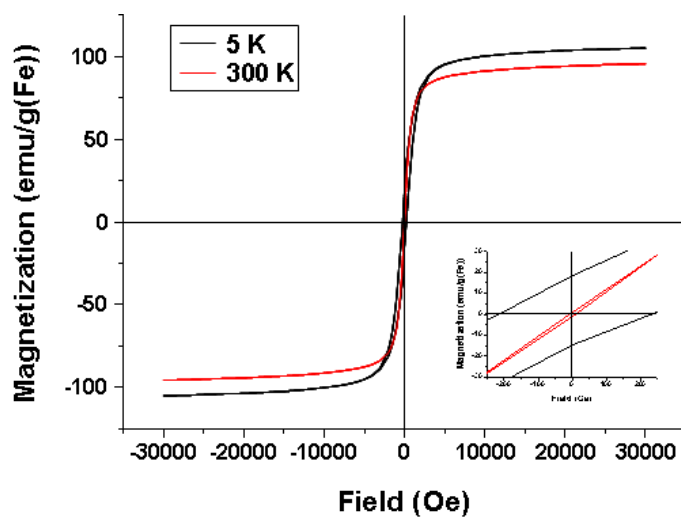


Figure S3. Magnetization curves of Rh-Fe₃O₄ heterodimer nanocrystals measured at 5 K and 300 K.



Figure S4. Photographs showing the magnetic separation of the catalysts in the mixture solution after the catalytic reaction.

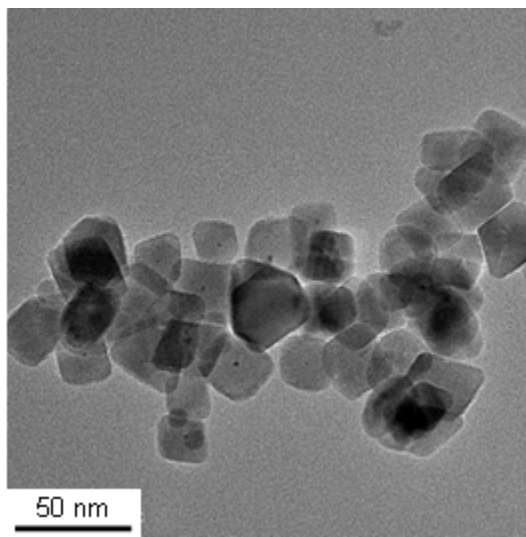


Figure S5. TEM image of the catalyst separated after 8 cycles of the catalytic reaction.

Table S1. Catalytic result on the reduction of nitrobenzene using various catalysts

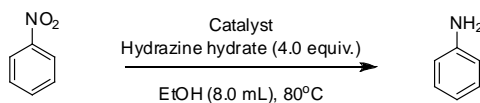
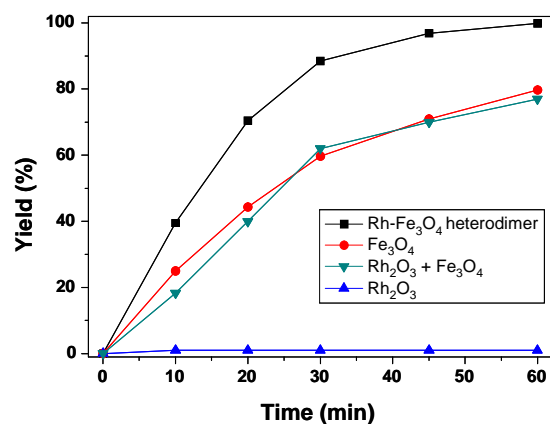


Table S2. Catalytic result on the reduction of *trans*-stilbene using various catalysts

Catalyst	Rh-Fe ₃ O ₄ heterodimer NC	Fe ₃ O ₄	Rh ₂ O ₃	Rh ₂ O ₃ + Fe ₃ O ₄
Yield (%)	99.9	68.1	38.0	66.3

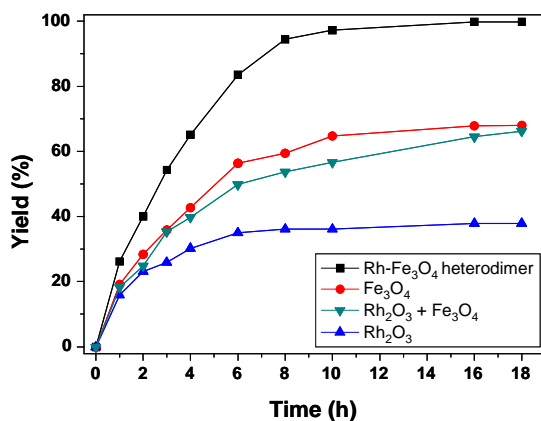
* Reaction conditions : *trans*-stilbene (1.0 mmol, 180 mg), Catalyst (1.0 mol% of Rh or 60 mg of Fe₃O₄), Hydrazine hydrate (10 equiv., 500 μ L), EtOH (8.0 mL), 80 °C, 18 h

* Experiments using Rh₂O₃ catalyst were carried out in 2.0 mmol scale.



Catalyst	Rh-Fe ₃ O ₄ heterodimer NC	Fe ₃ O ₄	Rh ₂ O ₃	Rh ₂ O ₃ +Fe ₃ O ₄
Initial rate (mM/min)	4.94	3.12	1.25	2.29

Figure S6. Reaction profiles on the reduction of nitrobenzene using various catalysts.



Catalyst	Rh-Fe ₃ O ₄ heterodimer NC	Fe ₃ O ₄	Rh ₂ O ₃	Rh ₂ O ₃ +Fe ₃ O ₄
Initial rate (mM/h)	3.29	2.41	2.00	2.29

Figure S7. Reaction profiles on the reduction of *trans*-stilbene using various catalysts.