

Supporting Information

Au nanoparticles supported on magnetically separable Fe₂O₃- graphene oxide hybrid nanosheets for the catalytic reduction of 4-nitrophenol

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Experimental Section

Instrumentation. The morphology of each sample was characterized by transmission electron microscopy (TEM) (FEI, Tecnai F30 Super-Twin, National Nanofab Center, South Korea) by placing a few drops of the corresponding colloidal solution on carbon-coated copper grids (200 mesh, F/C coated, Ted Pella Inc., Redding, CA, USA). Magnetization data were taken using a superconducting quantum interference device (SQUID) (MPMS-7, Quantum design). Dynamic force microscope (DFM) images were taken using a SPA 400 (Seiko). The elemental compositions of the hybrid catalysts were obtained using energy-dispersive x-ray spectroscopy (EDS) (550i, IXRF Systems, Inc.), while the x-ray diffractometer (XRD) patterns were recorded by a Rigaku GDX-11P3A diffractometer (Pusan National University). X-ray photoelectron spectroscopy (XPS) (Theta Probe, Thermo) were employed to measure the structural and chemical properties of the nanocomposites. The porous structure of the $\text{FeSO}_4 \cdot (\text{H}_2\text{O})$, Fe_2O_3 -GO and $\text{Au}/\text{Fe}_2\text{O}_3$ -GO nanocomposites was analyzed by acquiring nitrogen-adsorption isotherms (ASAP 2020, Micromeritics). Prior to the N_2 -adsorption measurements, the samples were degassed under a vacuum at $100\text{ }^\circ\text{C}$ for 12 h. The surface area and pore-size distribution of the samples were calculated by using the Brunauer-Emmett-Teller (BET) equation and the BJH method, respectively. Thermal gravity analyzer (TGA) was carried out using an ASAP 2020 (Micromeritics) instrument. The concentration of 4-nitrophenol was determined using a spectrophotometer at a wavelength of 400 nm using a SINCO S-3150 spectrophotometer.

Synthesis of Fe_3O_4 microspheres. Magnetite particles were synthesized using a solvothermal method.¹ The details were as follows: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.4 g, 5.2 mmol) and trisodium citrate (0.29 g, 0.96 mmol) were dissolved in ethylene glycol/ethanol (36 mL/4 mL) solution; then, sodium acetate (1.9 g, 23 mmol) was added under vigorous stirring for 5 min. The resulting mixture was then transferred to a Teflon-lined stainless-steel autoclave (with a capacity of 50 mL) for heating at $200\text{ }^\circ\text{C}$ for 10 h. Then, the autoclave was carefully taken out and allowed to cool to room temperature. The as-made black products were thoroughly washed with ethanol three times, and they were then vacuum-dried.

Synthesis of $\text{Au}/\text{Fe}_3\text{O}_4$ microspheres. Au nanoparticles were immobilized onto Fe_3O_4 microspheres according to modified procedure of Yang et al. literature.¹ Each Fe_3O_4 microspheres (100 mg) were incubated in 0.2 M NaOH aqueous solution to ionize the

carboxyl groups. The residual NaOH was removed by washing with deionized water through centrifugation. Then, the ionized Fe₃O₄ microspheres were dispersed in the solution (30 mL, 0.1 M) of HAuCl₄·3H₂O during 1 h under sonication. After this, the microspheres were harvested with the aid of the magnet and washed with deionized water three times. Then, the microspheres were redispersed in 20 mL of deionized water, and 1 mL of 50 mM NaBH₄ aqueous solution was added dropwise under the ice water bath during 5 minutes with vigorous stirring. The final product was purified through washing with ethanol three times and dried under vacuum.

Synthesis of GO nanosheets. GO was synthesized from graphite powder according to the modified Hummer's method.² The graphite powder (1 g) was added to 46 mL of cold H₂SO₄ (0 °C), then KMnO₄ (6 g) was gradually added under continuous stirring in ice-bath. After 15 min, NaNO₃ (1 g) was introduced into the mixture. The solution was further stirred at 35 °C for 1 h and DI-H₂O (80 mL) was added. After being stirred for 15 min, the reaction was terminated by addition of DI-H₂O (200 mL) and 10 mL of 30% H₂O₂. The product was washed with HCl (1:10) and then with water, and then suspended in distilled water. The brown dispersion was extensively dialyzed to remove residual metal ions and acids. After the unexploited graphite in the resulting mixture was removed by centrifugation, as-synthesized GO was dispersed into individual sheets in distilled water at a concentration of 0.47 mg/mL with the help of sonication.

Synthesis of FeSO₄(H₂O)-GO nanosheets.³ In a typical process, 2 mmol FeCl₃·6H₂O were dissolved in 20 mL distilled water. Then 0.315 g polyvinyl pyrrolidone as surfactant was added. After stirring for at least 20 mins, 0.4 ml 37.5% H₂SO₄ was added. After stirring for another several minutes, the precursor solution was separated by two parts (10 ml each). One part was added with 10ml GO ethylene glycol solution (20g L⁻¹) and was treated by ultrasonic for 30 mins. Then both two mixtures were heated up to 200 °C in the Teflon-lined autoclave (50 mL in capacity) and maintained at that temperature for 12 h. The precipitates were cooled down to room temperature naturally, collected and washed with distilled water and ethanol several times. After drying at vacuum overnight, the final products were obtained.

Synthesis of Au/Fe₂O₃-GO nanosheets. Au NPs were immobilized onto Fe₂O₃-GO according to modified procedure of Yang et al. literature.¹ Each FeSO₄(H₂O)-GO (100 mg) were incubated in 0.2 M NaOH aqueous solution to ionize the hydroxyl groups. The residual NaOH was removed by washing with deionized water through

centrifugation. Then, the $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in the solution (30 mL, 0.1 M) were dispersed above mixture during 1 h under sonication. After this, the nanosheets were washed with deionized water three times. Then, the nanosheets were redispersed in 20 mL of deionized water, and 1 mL of 50 mM NaBH_4 aqueous solution was added dropwise under the ice water bath during 2 minutes with vigorous stirring. The final product was purified through washing with ethanol three times and dried under vacuum.

References

1. B. Liu, W. Zhang, F. Yang, H. Feng and X. Yang, *J. Phys. Chem. C*, 2011, **115**, 15875.
2. H. Xu, Q. Yang, F. Li, L. Tang, S. Gao, B. Jiang, X. Zhao, L. Wang and C. Fan, *Analyst*, 2013, **138**, 2678.
3. D. Su, H.-J. Ahn and G. Wang, *Chem. Commun.*, 2013, **49**, 3131.

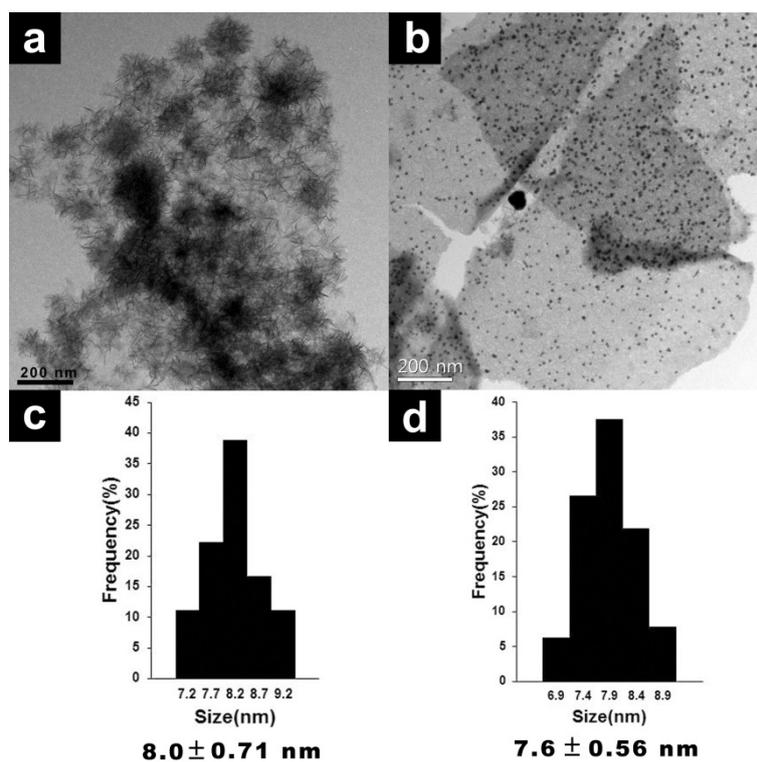


Fig. S1. Low resolution TEM images of FeSO₄(H₂O)-GO and Au/Fe₂O₃-GO (a,b). Size distributions of Au NPs of Au/Fe₃O₄ and Au/Fe₂O₃-GO (c,d).

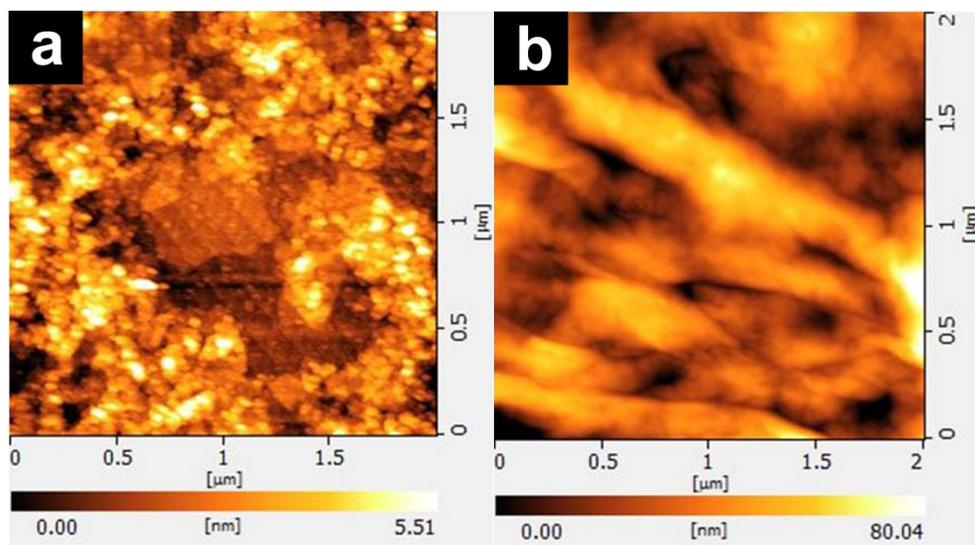


Fig. S2. DFM topology images of GO (a) and FeSO₄(H₂O)-GO (b) nanocomposites.

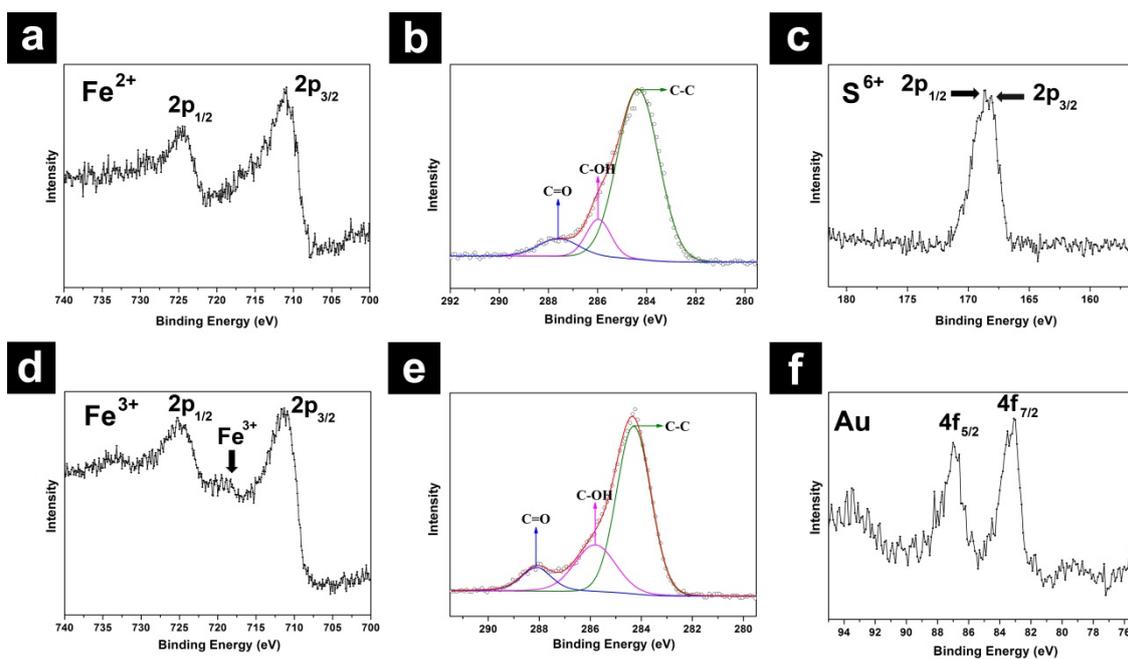


Fig. S3. The XPS spectra of Fe²⁺, C and S⁶⁺ of FeSO₄(H₂O)-GO (a-c) and Fe³⁺, C and Au of Au/Fe₂O₃-GO (d-f).

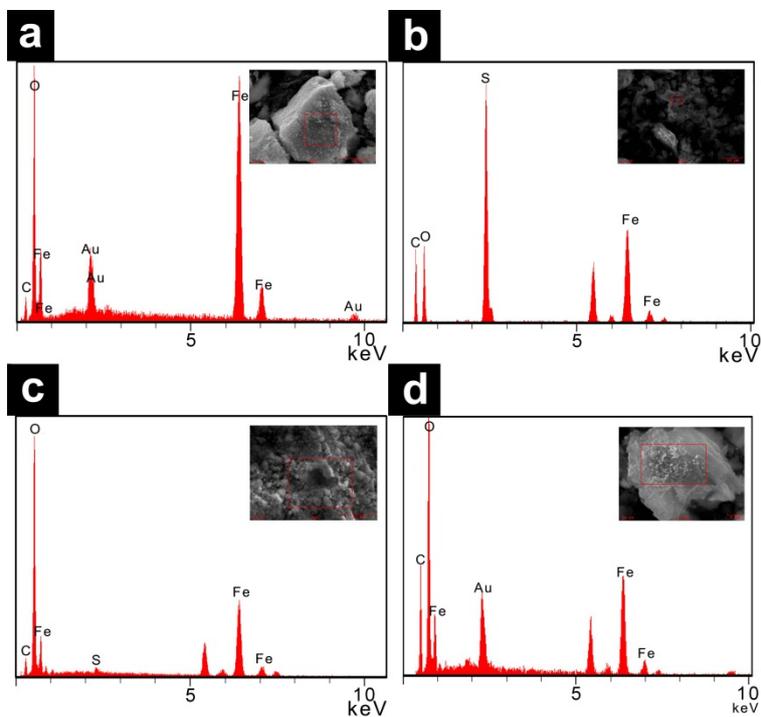


Fig. S4. EDS spectrum of (a) Au/Fe₃O₄, (b) FeSO₄(H₂O)-GO, (c) Fe₂O₃-GO and (d) Au/Fe₂O₃-GO nanocomposites.

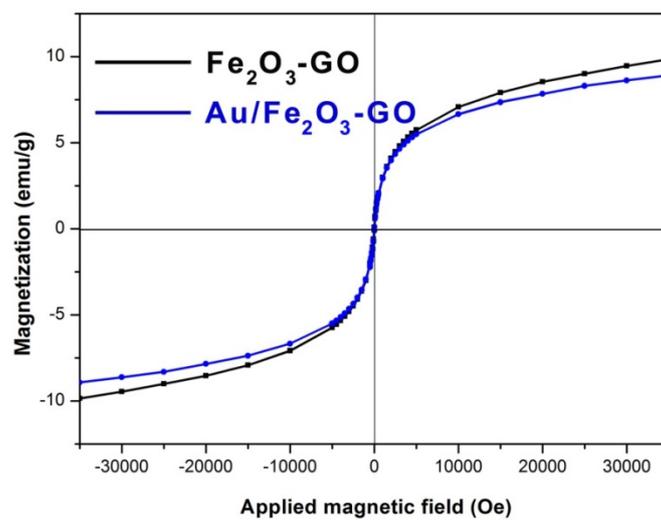


Fig. S5. SQUID data of Fe₂O₃-GO and Au/Fe₂O₃-GO nanocomposites.

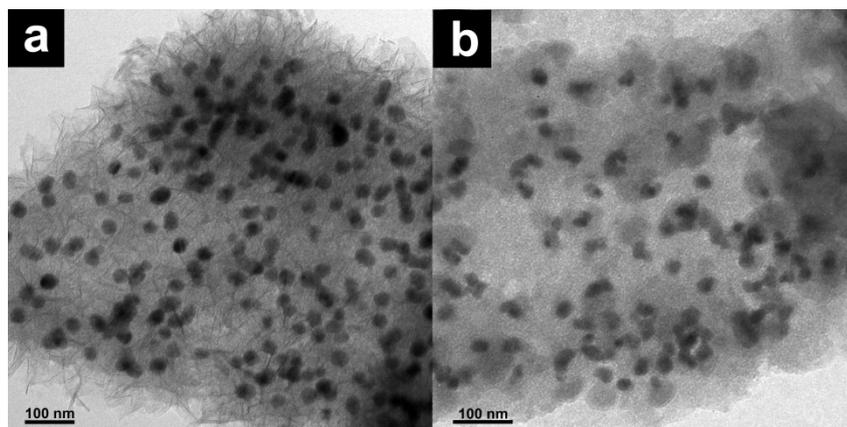


Fig. S6. TEM images of Au/Fe₂O₃-GO catalyst before reaction (a) and after reuse 7 times (b).

Table S1. Surface areas, pore volumes and pore diameters of FeSO₄(H₂O)-GO, Fe₂O₃-GO and Au/Fe₂O₃-GO.

Sample	BET surface area (m ² g ⁻¹)	Langmuir surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
FeSO ₄ (H ₂ O)-GO	18.62	25.75	0.0342	11.5
Fe ₂ O ₃ -GO	213.0	291.8	0.233	4.48
Au/Fe ₂ O ₃ -GO	212.4	292.3	0.231	4.43