

**Water-dispersible and Magnetic Separable Gold
Nanoparticles Supported on Magnetite/S-Graphene
nanocomposite and their Catalytic Application in Ullmann
coupling of aryl iodides in Aqueous Media**

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Preparation of GO

The graphite powder (2.5 g) was first treated with a mixture of 12.5 ml of concentrated H_2SO_4 with 2.5 g $\text{K}_2\text{S}_2\text{O}_8$ and 2.5 g P_2O_5 . The mixture was kept at 80 °C for 6 h. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL de-ionized (DI) water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pre-oxidized graphite was then subjected to oxidation by Hummers's method. The pretreated graphite powder was put into cold (0 °C) concentrated H_2SO_4 (125 ml). Then KMnO_4 (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 °C by cooling. The mixture was then stirred at 35 °C for 4 h and then diluted with DI water (250 ml). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below 50 °C. After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30% H_2O_2 was added to the mixture and the color of the mixture changed into brilliant yellow and began bubbling. The mixture was filtered and washed with 0.1 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid, and then was dialyzed against DI water. The resulting GO solid was dried in air.^{s1}

Preparation of sulfonated graphene (s-G)

GO (150 mg) was dispersed in 150 ml DI water. NaBH_4 (1.20 g) in 30 ml DI water was added into the dispersion of GO after its pH was adjusted to 9-10 with 5%wt Na_2CO_3 solution. The mixture was then kept at 80°C for 1h under constant stirring. During reduction, the dispersion turned from dark brown to black accompanied by out-gassing. After centrifuging and

rinsing with water several times, the partially reduced graphene oxide can be redispersed in 150 ml water via mild sonication. The aryl diazonium salt used for sulfonation was prepared from the reaction of sulfanilic acid (92 mg) and sodium nitrite (36 mg) in water 20 (ml) and 1M HCl solution (1 ml) in an ice bath. The diazonium salt solution was added to the dispersion of partially reduced graphene oxide in an ice bath under stirring, and was kept in ice bath for 2 h. Bubbles were expelled from the reaction mixture and aggregation was observed on the addition of the diazonium salt solution. After centrifuging and rinsing with water several times, sulfonated graphene oxide is redispersed in DI water (150 ml). Hydrazine (4 g) in water (10 ml) is added into the dispersion and the reaction mixture was kept at 100 °C for 24 h under constant stirring. A few drops of 5%wt Na₂CO₃ solution were then added into the mixture in order to precipitate the lightly sulfonated graphene. After rinsing with DI water thoroughly, the graphene thus prepared can be readily dispersed in DI water via a few minutes sonication.^{S2} The loading of Sulfur was determined to be 0.58 mmol.g⁻¹ from elementary analysis (CHNS).

Preparation of Fe₃O₄/s-G nanocomposite

An aqua solution of FeSO₄.7H₂O (26.4 mg) and FeCl₃.6H₂O (51.3 mg) with a mole ratio of 1 : 2 in 5 mL distilled water was prepared and then was added to a s-G solution (25 mg s-G in 25 mL DI water) with constant stirring under nitrogen. After several minutes, ammonia solution (0.3 mL, 25%) was added. Then the mix was kept under constant stirring at 90 °C for 4 h. The product named as Fe₃O₄/s-G was rinsed several times with DI water.^{S3} The loading of iron was measured to be 2.72 mmol.g⁻¹ by inductively coupled plasma-optical emission spectrometry (ICP-OES).

Preparation of Au/Fe₃O₄/s-G nanocomposite

The obtained Fe₃O₄/s-G (140 mg) in 120 ml DI water was mixed with a solution of 3.540 g SDS in 60 mL water. After sonication of the mixture for several minutes, HAuCl₄ (100 mg) was added and then the mixture was refluxed for 5 h.^{s4} The obtained composite, designated as Au/Fe₃O₄/s-G nanocomposite, was then rinsed several times with DI water to remove excess surfactant. The loading of gold was measured to be 0.34 mmol.g⁻¹ by inductively coupled plasma-optical emission spectrometry (ICP-OES).

General procedure for the Ullmann homo-coupling reaction

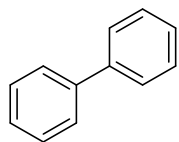
A mixture of as Au/Fe₃O₄/s-G nanocomposite (2 mol % of Au), K₃PO₄ (3 mmol), aryl halide (1.0 mmol), and H₂O 2 mL under air was stirred at 110 °C. After completion of the reaction as indicated by TLC, the heterogeneous mixture was cooled to room temperature and filtered through a pad of celite. The filtrate was concentrated and then residue was purified by thin layer chromatography (Ethyl acetate and *n*-Hexane) to yield pure product. The catalysts were recovered by simple filtration and washed extensively with acetone and DI water and drying in the air.

Characterization

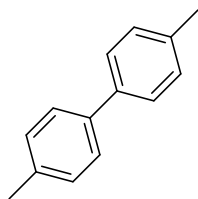
All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). XPS analysis was performed using a Gamdata-scienta ESCA 200 hemispherical analyzer equipped with an Al K α (1486.6 eV) X-ray source. Raman spectra of s-GO, Fe₃O₄/s-G and Au/Fe₃O₄/s-G nanocomposites were recorded on a Bruker SENTERR (2009) with an excitation beam wavelength at 785 nm. Scanning electron microscopy and EDX mapping characterizations of Au/Fe₃O₄/s-G nanocomposite were performed using an electron microscopy Philips XL-30

ESEM. Transmission Electron Microscopy characterization of Fe₃O₄/s-G and Au/Fe₃O₄/s-G nanocomposites were performed using a transmission microscope Philips CM-30 with an accelerating voltage of 150 kV. ¹H-NMR spectra were recorded on a BRUKERDRX-300AVANCE spectrometer. NMR spectra were obtained in DMSO-*d*₆ using TMS as internal standard. Melting points of products were measured on an Electrothermal 9100 apparatus and are uncorrected. The concentration of iron and gold were estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer and inductively coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. Elemental analysis of s-G nanocomposite was performed using an Elementar Analysensysteme GmbH VarioEL CHNS. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx[®]-1 capillary column.

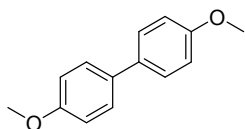
The all of products are known compounds and were reported previously.



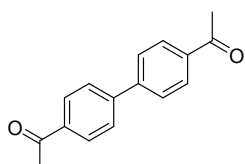
Mp. 67-69 °C (Lit.^{s5} Mp. 70-71 °C). ¹H-NMR (CDCl₃): δ 7.37 (t, 2H, *J*=7.4 Hz), 7.96-7.46 (t, 4H, *J*=7.3 Hz), 7.62 (d, 4H, *J*=7.5 Hz).



Mp. 119-120 °C (Lit.^{s6} Mp. 119-120 °C). ¹H-NMR (CDCl₃): δ 2.43 (s, 6H), 7.27 (d, 4H, *J*=7.8 Hz), 7.52 (d, 4H, *J*=8.1 Hz).



Mp. 172-174 °C (Lit.^{s6} Mp. 173-174 °C). ¹H-NMR (DMSO-*d*₆): δ 3.72 (s, 6H), 6.96 (d, 4H, *J*=8.7 Hz), 7.58 (d, 4H, *J*=8.7 Hz).



Mp. 193-194 °C (Lit.^{s6} Mp. 194-195 °C). ¹H-NMR (DMSO-*d*₆): δ 2.67 (s, 6H), 7.71 (d, 4H, *J*=7.2 Hz), 8.06 (d, 4H, *J*=8.1 Hz).

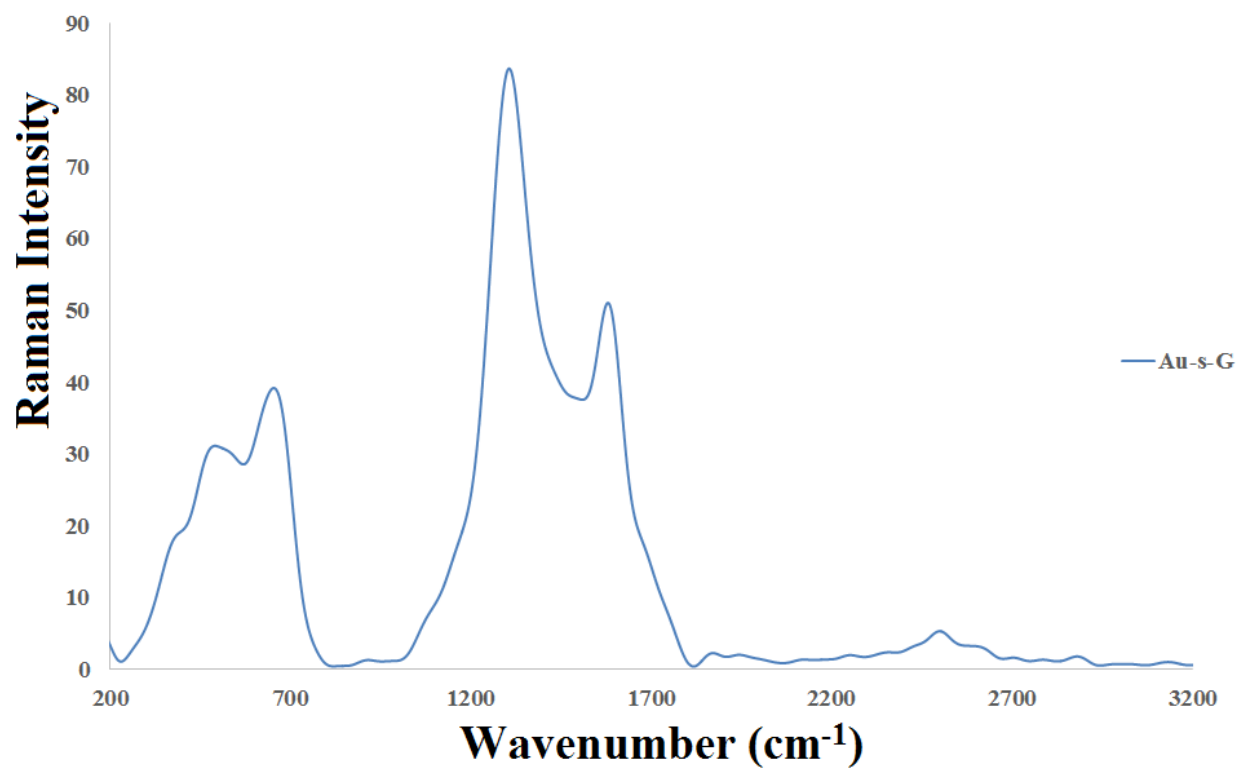


Fig. S1. Raman spectrum of Au/s-G nanocomposite

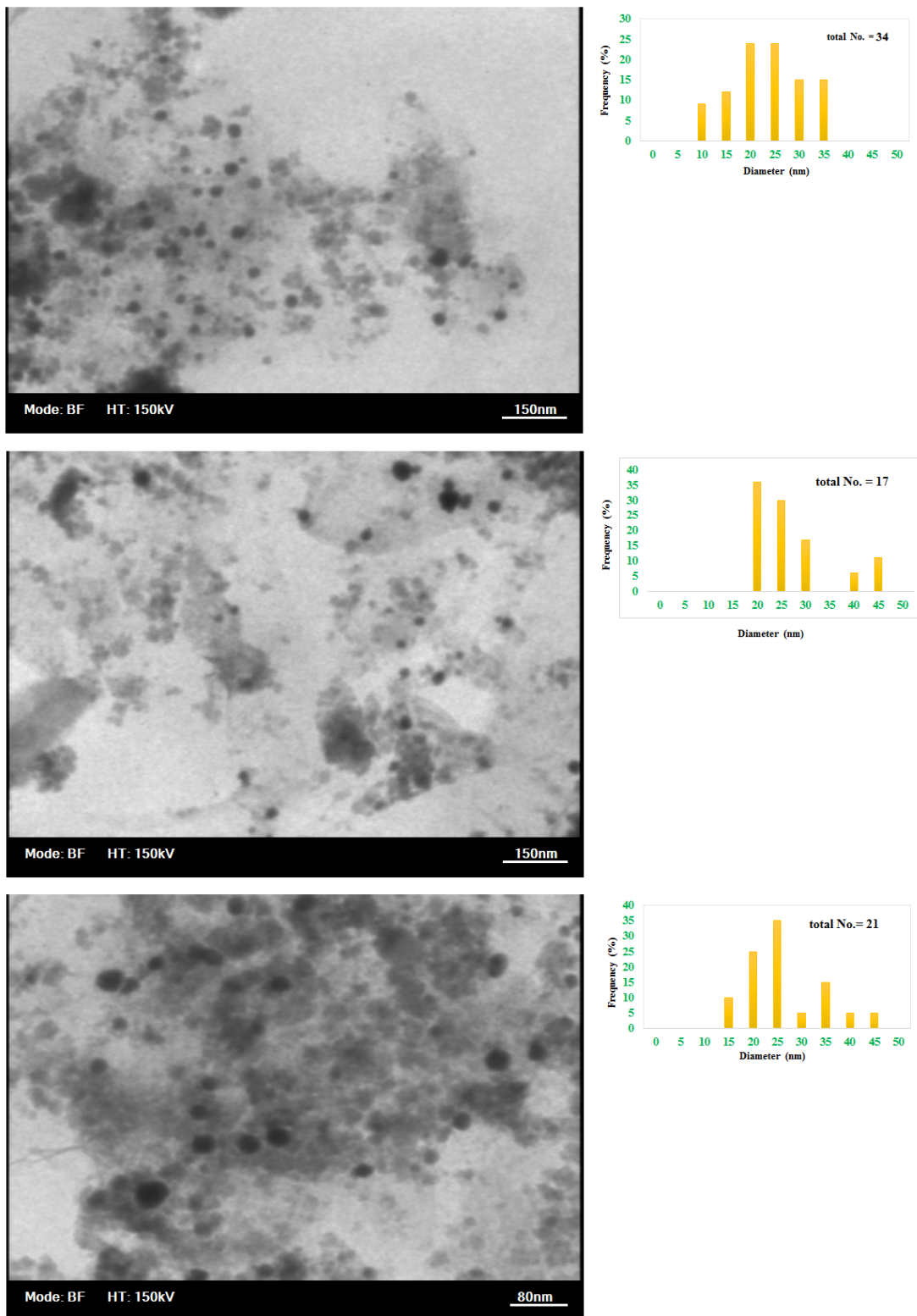


Fig. S2. TEM images of Au/Fe₃O₄/s-G nanocomposite and the corresponding size histograms of Au NPs

References

1. W.S. Hummers and R.E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339; N.I. Kovtyukhova, P.J. Olliver, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva and A.D. Gorchinsky, *Chem. Mater.*, 1999, **11**, 771.
2. Y. Si and E.T. Samulski, *Nano Lett.*, 2008, **8**, 1679.
3. J. Hu, Y. Wang, M. Han, Y. Zhou, X. Jiang and P. Sun, *Catal. Sci. Technol.*, 2012, **2**, 2332.
4. Y. Li, X. Fan, J. Qi, J. Ji, S. Wang, G. Zhang and F. Zhang, *Mater. Res. Bull.* 2010, **45**, 1413.
5. Q. Zhang, H. Su, J. Luo and Y. Wei, *Catal. Sci. Technol.*, 2013, **3**, 235.
6. N. Kirai and Y. Yamamoto, *Eur. J. Org. Chem.*, 2009, 1864.