Electronic Supplementary Information

A novel high efficiency composite catalyst: single crystal triangle Au nanoplates supported by functional reduced graphene oxide

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Experimental Details

1. Materials

Graphite powder (99.99995%, 100 mesh), N-propylethane-1,2-diamine and 4-nitrophenol (4-NP) were obtained from Alfa Aesar. $NaBH_4$, and $HAuCl_4.3H_2O$ were obtained from Shanghai Chemical Co. (China). H_2O_2 (30%) and N, N-dimethylformamide (DMF) were analytically pure and obtained from Sinopharm Chemical Reagent Co., Ltd. P_2O_5, $K_2S_2O_8$, $KMnO_4$, H_2SO_4, and hydrazine hydrate were analytically pure and obtained from Nanjing Chemical Reagent Co., Ltd. All these reagents were used as received. Water was obtained from a Sartorius arium 611DI water purification system.

2. Experimental Section

GO was firstly prepared by modified Hummers method[1]. The synthesized GO was purified by washing with deionized water and centrifuged successively three times, and suspended in deionized water by ultrasonication. The GO suspension was frozen dried to obtain the GO powders. 0.1 g of GO powders was dispersed in 200 mL of DMF via ultrasonication for 0.5 h. 0.2 g of N-propylethane-1,2-diamine was then added to the GO dispersion and the mixture was stirred at 80 ℃ for 10 h. The resultant was filtrated and washed by DMF successively three times to remove the excess N-propylethane-1,2-diamine. N-propylethane-1,2-diamine-GO suspension was obtained after washing and dispersed in 200 mL of DMF by ultrasonication for another 30 min. 0.2 g of hydrazine hydrate was then added into the dispersion to reduce N-propylethane-1,2-diamine-GO at 90 ℃ for 24 h. Finally the mixture was filtrated and washed by DMF successively three times. The product was dispersed in DMF by ultrasonication with the concentration of 0.3 mg.mL^{-1}. As compared, rGO was also prepared.

The as-synthesized FRGO (1mL, 0.3 mg/mL) and a DMF solution of $HAuCl_4$ (30μL, 0.01M) were mixed at 0℃ by an external ice bath under magnetic stirring. After stirring for 30 min, a DMF solution of $NaBH_4$ (30μL, 0.1M) was added. The product was washed with ethanol for three times and dried. The FRGO-Au was then dispersed in water by ultrasonication with the concentration of 0.15 mg.mL^{-1}

Samples FRGO-Au1, FRGO-Au10 and FRGO-Au100 were prepared in the same way except with the addition of $HAuCl_4$ and $NaBH_4$ in different amounts.

Table 1 Materials Used in the Preparations of FRGO-Au

Sample	Addition of $HAuCl_4$	Addition of $NaBH_4$
FRGO-Au1	3μL, 0.01M	3μL, 0.1M
FRGO-Au10	30μL, 0.01M	30μL, 0.1M
FRGO-Au100	300μL, 0. 1M	300μL, 0.1M

Control experiments were carried out to confirm the function of N-propyl ethylene diamine and rGO for the shape control of Au nanoplates. In the control experiments with N-propyl ethylene diamine, $HAuCl_4$ and $NaBH_4$, 1mL DMF solution of N-propyl ethylene diamine(0.1 mg/mL) and 30μL DMF $HAuCl_4$ (0.01M) were mixed at 0℃ by an external ice bath under magnetic stirring. After stirring for 30 min, a DMF solution of $NaBH_4$ (30μL, 0.1M) was added. In the control experiments with rGO, $HAuCl_4$ and $NaBH_4$, 1mL rGO DMF dispersion (0.3 mg/mL) and 30μL DMF solution of $HAuCl_4$ (0.01M) were mixed at 0℃ by an external ice bath under magnetic stirring. After stirring for 30 min, a DMF solution of $NaBH_4$ (30μL, 0.1M) was added.

Control experiment was carried out to compare the the catalytic activity of FRGO-Au and dot-like Au nanoparticles. The dot-like Au nanoparticles were prepared using Mathias Brust's method[2]. The nanoparticles were separated by centrifugation, washed and dispersed for catalysis.

The reduction of 4-NP was carried out in a quartz cuvette at room temperature. 30μL 4-NP solution (0.01 M) and 300μL freshly prepared $NaBH_4$ solution (0.1 M) was added to 2.57 mL water. 100 μL aqueous dispersion of FRGO-Au10 (0.15 mg/mL) were added to the mixture under sonication. For FRGO-Au1 and FRGO-Au100, the additions were 100 μL 1.28 mg/mL and 100 μL 0.04 mg/mL. UV-vis spectra of filtered sample were recorded in kinetic analysis model, the scanning wavelength was 400 nm, and the scanning interval was 1 s. As the reaction proceeded, the solution color changed from yellow to colorless. In the cycle experiment, FRGO-Au1 was used as catalyst. After the reduction was completed, the catalyst was separated by centrifugation, washed and dispersed for the next round of catalysis.

The Au content in FRGO-Au1, FRGO-Au10 and FRGO-Au100 can be calculated by the following formula:

$$\text{Au content (mass percentage)}=\frac{0.01M*V_{HAuCl_4}*196.97g/mol*1000mg/g}{0.3mg+0.01M*3.0*10^{-5}L*196.97g/mol*1000mg/g}*100\%$$

In which V_{HAuCl4} is the volume of $HAuCl_4$ solution added in the preparation of FRGO-Au.

The concentration of Au in the reduction can be calculated by the following formula:

$$\text{Au concentration}=\frac{\text{Au content (mass percentage)}*\rho_{FRGO-Au}*0.1mL}{196.97g/mol*3.0*10^{-3}L}$$

In which $\rho_{FRGO-Au}$ is the concentration of FRGO-Au solution using in reduction of 4-NP.

The reduction of p-nitrophenol ($5*10^{-4}$ M) was carried out in the same way using FRGO-Au1 as catalyst (Au $2.07*10^{-6}$ M).

The reduction of 2,4-dinitrotoluene (2,4-DNT) was carried out using FRGO-Au1 as catalyst. We referred to the experimental methods in Behzad Zeynizadeh's work[3]. 4mmol of $NaBH_4$, 1 mmol of 2,4-DNT was added into a mixture of H_2O-THF (1mL:0.5 mL, 15mL) at room temperature. Then 1mg of FRGO-Au1 was added to the system. Since the position of the absorption peak of 2,4-DNT is close to that of the product, we used TLC to monitor the reduction. The reaction was completed in 10 minutes. The melting point of the product was 96-99 ℃, which was consistent with the reported melting point of 2,4-diaminotoluene.

3. Instrumentation

Transmission electron microscopy (TEM) was conducted on a JEM-1005 instrument (JEOL Co.) at 80 kV. High resolution transmission electron microscopy (HRTEM) was conducted on a JEM-2100 instrument (JEOL Co.) at 200 kV. Energy-dispersive X-ray (EDX) detector type: SUTW-Sapphire, KV: 200.00, Azimuth: 45.00, Elevation: 22.50, AMPT: 102.4. Ultraviolet–visible (UV–vis) spectra were recorded with a UV1800PC UV–vis spectrophotometer operating at 1 nm resolution. The width of sample cuvette was 10 mm.X-ray photoelectron spectroscopy (XPS) (VG Microtech 2000 ESCA) was performed using a monochromatized Al Kα X-ray source (1486.6 eV). Wide-angle X-ray diffraction (WAXD) patterns were recorded in transmission with a Bruker D8 Advance X-ray diffractometer. The wavelength used was Cu Kα ($\lambda = 0.154$ nm), and spectra were recorded in the 2θ range of 4–80° (step size 0.01°). The Fourier transform infrared spectra (FTIR) were recorded on a NICOLET NEXUS 870 spectrophotometer.Atomic force microscopy (AFM) was characterized in tapping mode using mica tips with Olympus OMCL-AC160TS and controller from Veeco Corporation. Sample was spin-coated on mica surfaces.

4. Supporting Figures

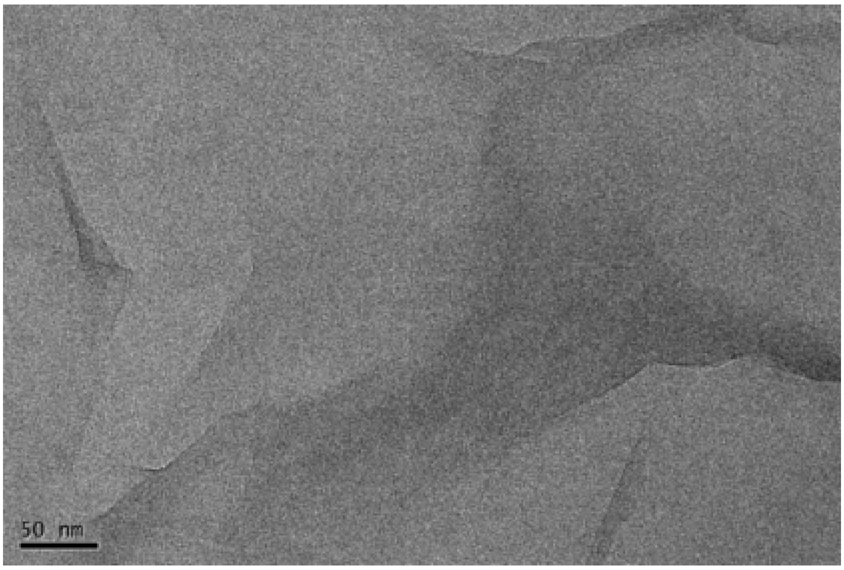


Figure S1. HRTEM image of FRGO.

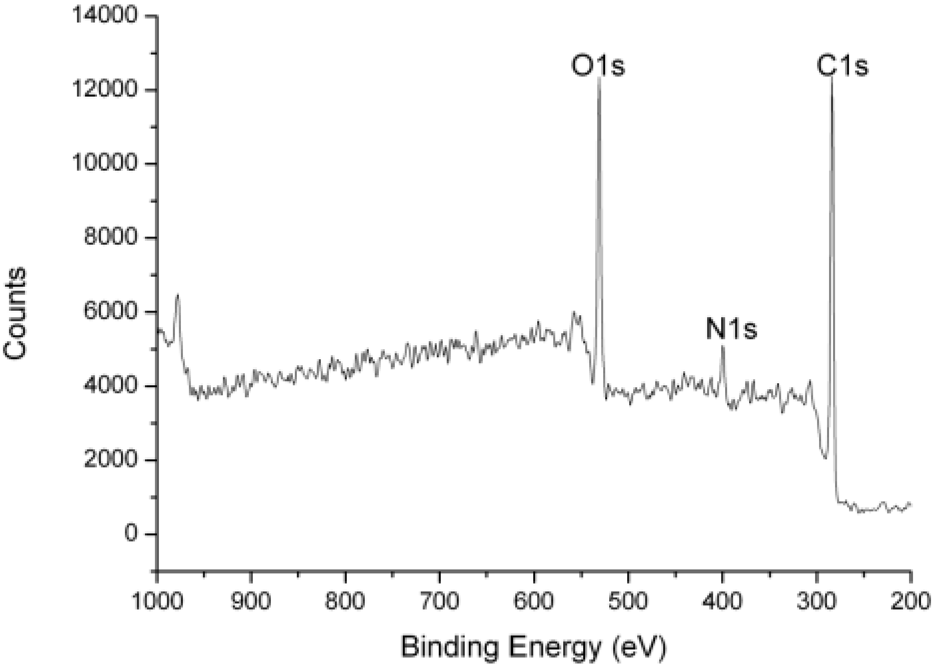


Figure S2. XPS analysis of FRGO.

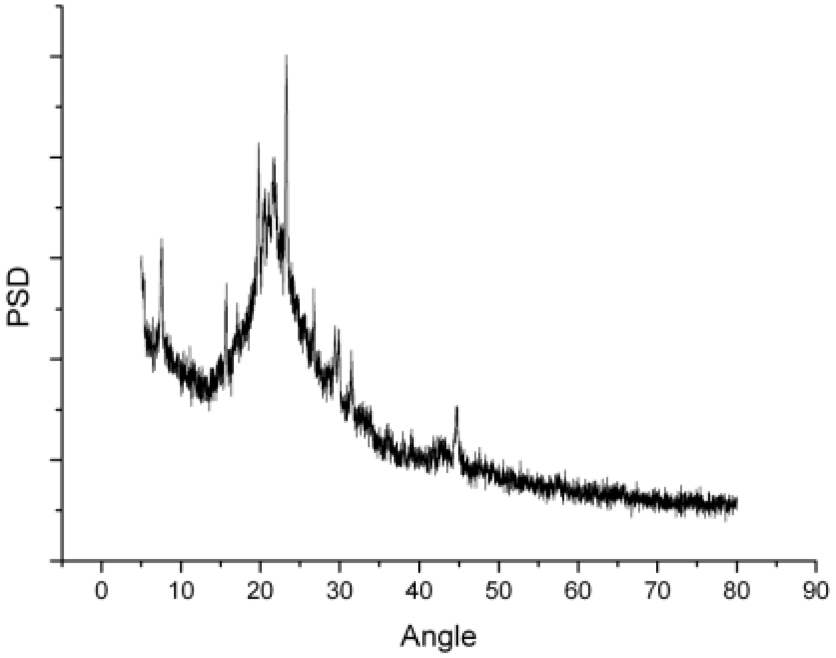


Figure S3. XRD pattern of FRGO.

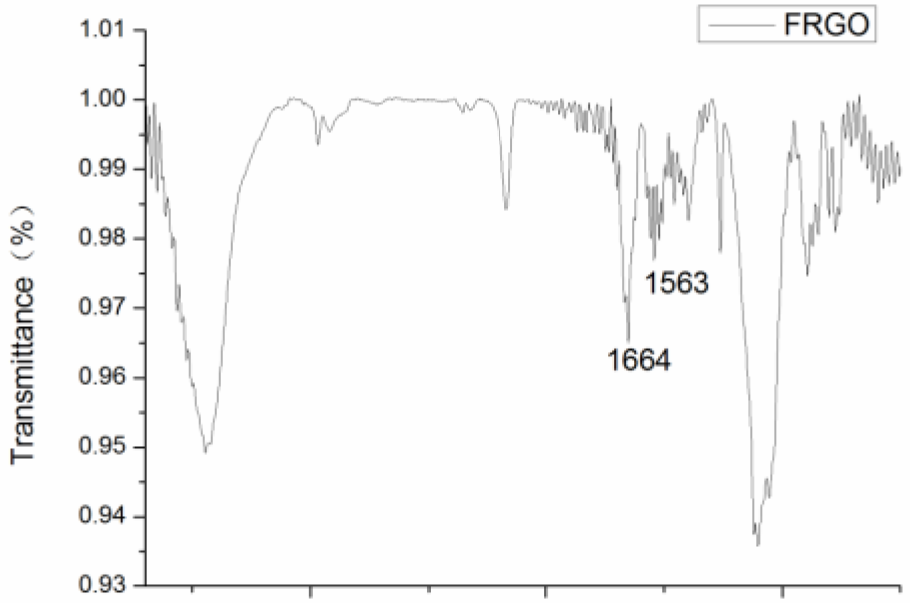
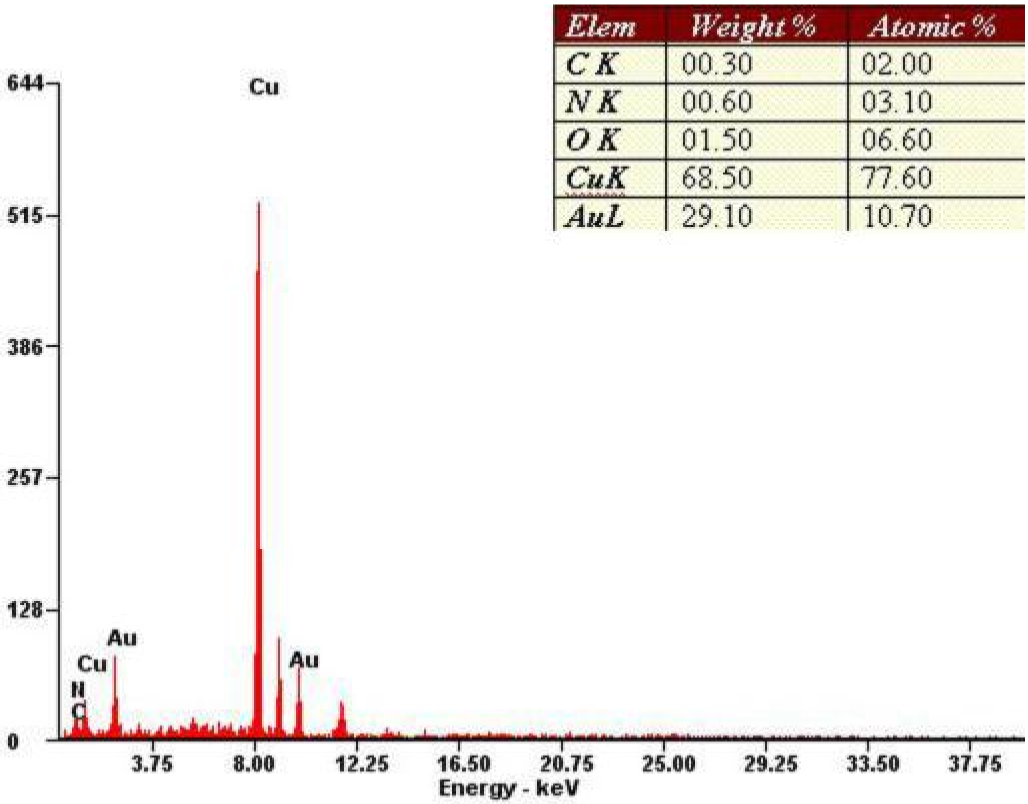


Figure S4. IR absorption spectroscopy of FRGO.



Elem	Weight %	Atomic %
C K	00.30	02.00
N K	00.60	03.10
O K	01.50	06.60
CuK	68.50	77.60
AuL	29.10	10.70

Figure S5. EDX analysis of FRGO-Au.

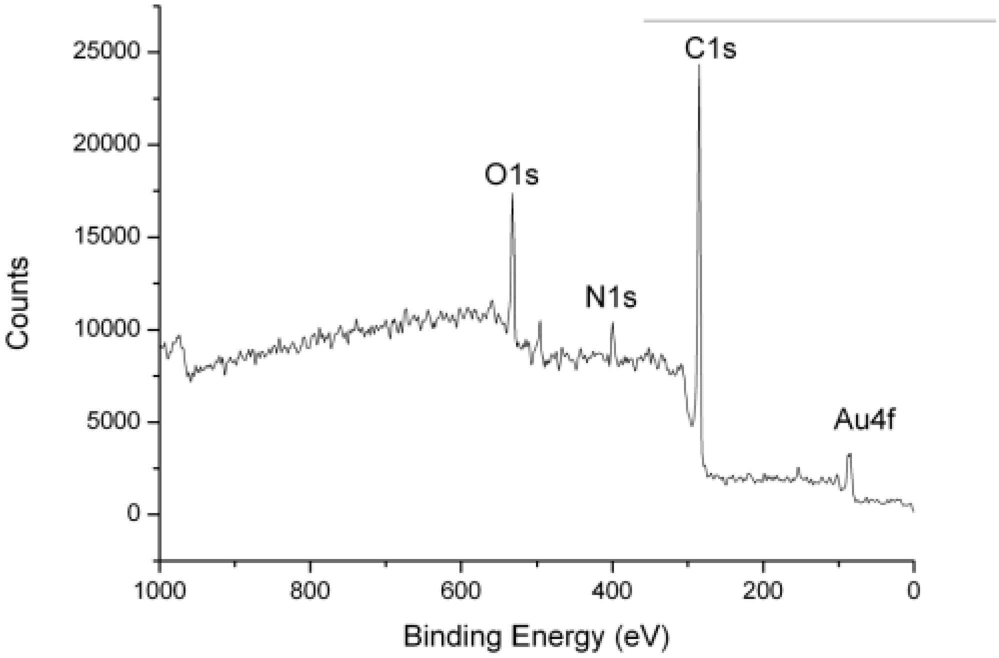


Figure S6. XPS analysis of FRGO-Au10.

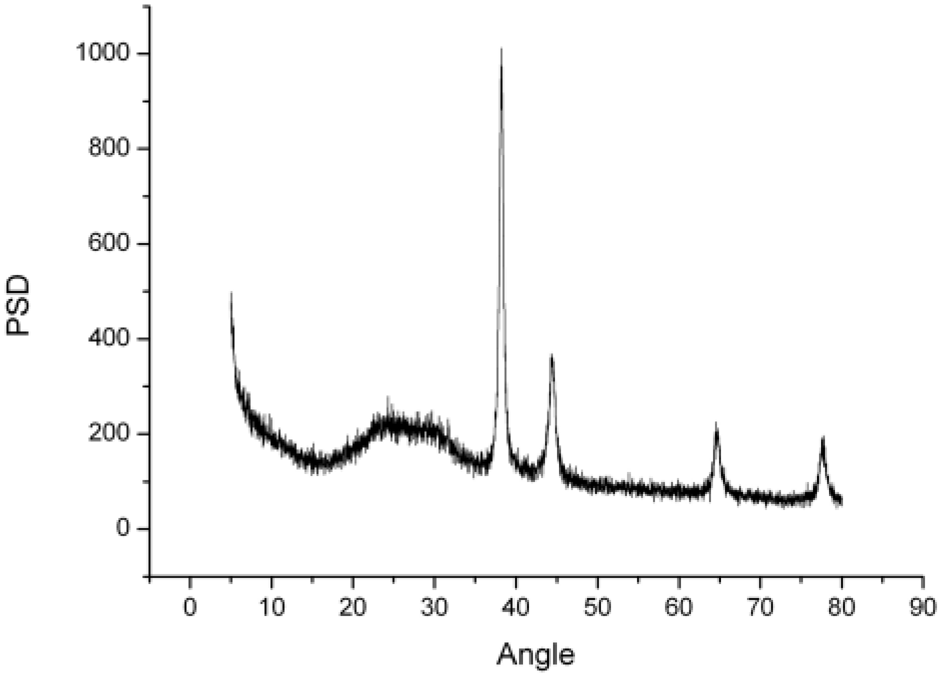


Figure S7. XRD pattern of FRGO-Au10.

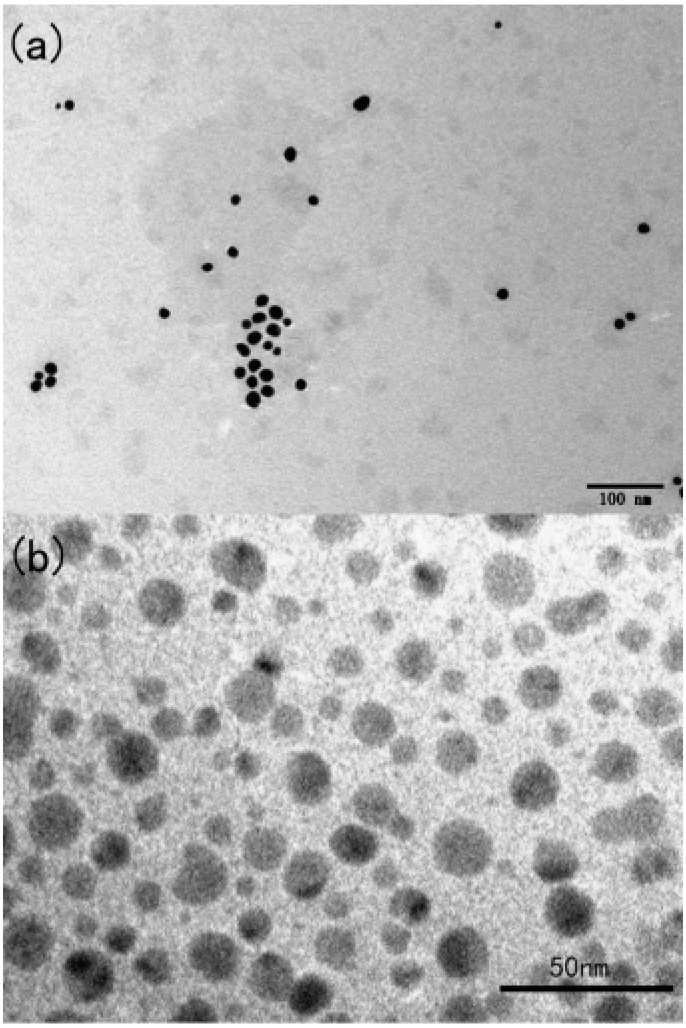


Figure S8. TEM images of two control samples, (a): Control sample with N-propyl ethylene diamine, $HAuCl_4$ and $NaBH_4$; (b): Control sample with rGO, $HAuCl_4$ and

NaBH$_4$.

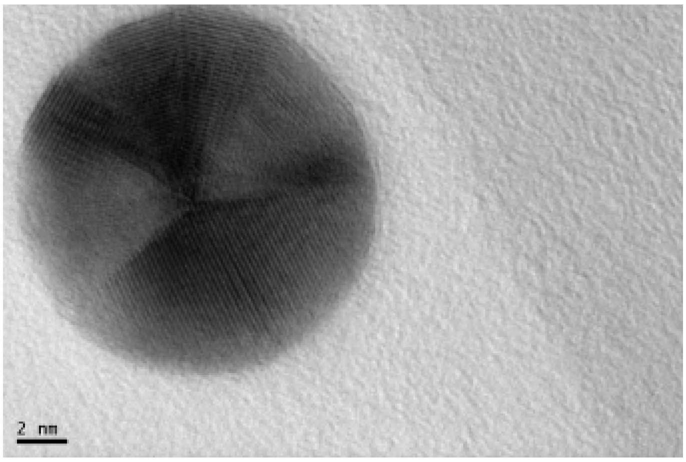


Figure S9. HRTEM images of the round structure in FRGO-Au10 (Figure 1(a)).

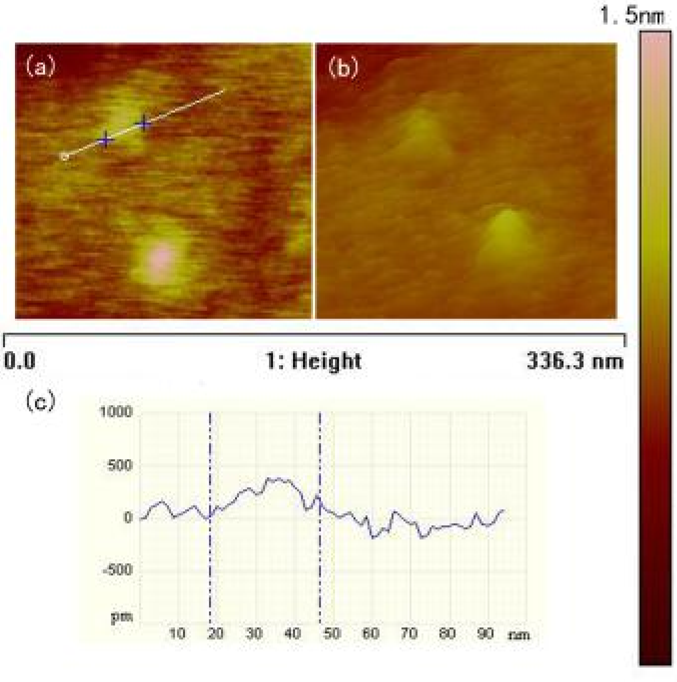


Figure S10. AFM height image (a), 3D image (b) of FRGO-Au100 and height profiles recorded along the white line(c) .

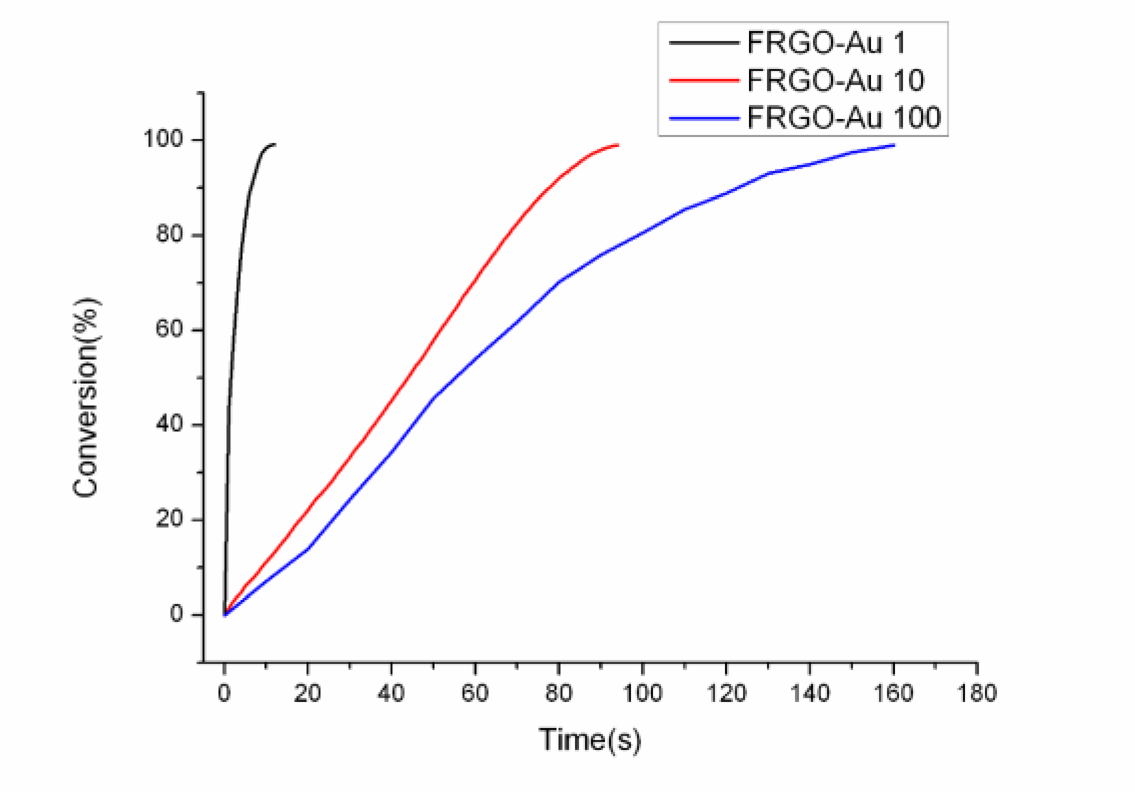


Figure S11. Time-dependent conversion of 4-NP with different catalysts.

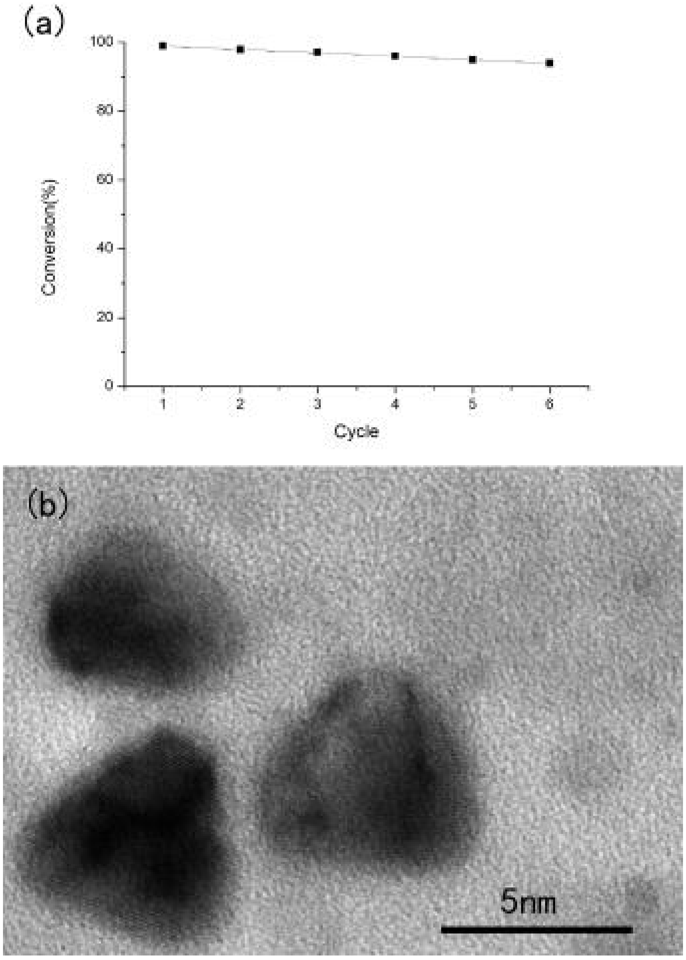


Figure S12. (a): the 4-NP conversion rate in the reduction catalyzed by FRGO-Au1 in 6 cycles, (b): HRTEM image of FRGO-Au1 after reduction .

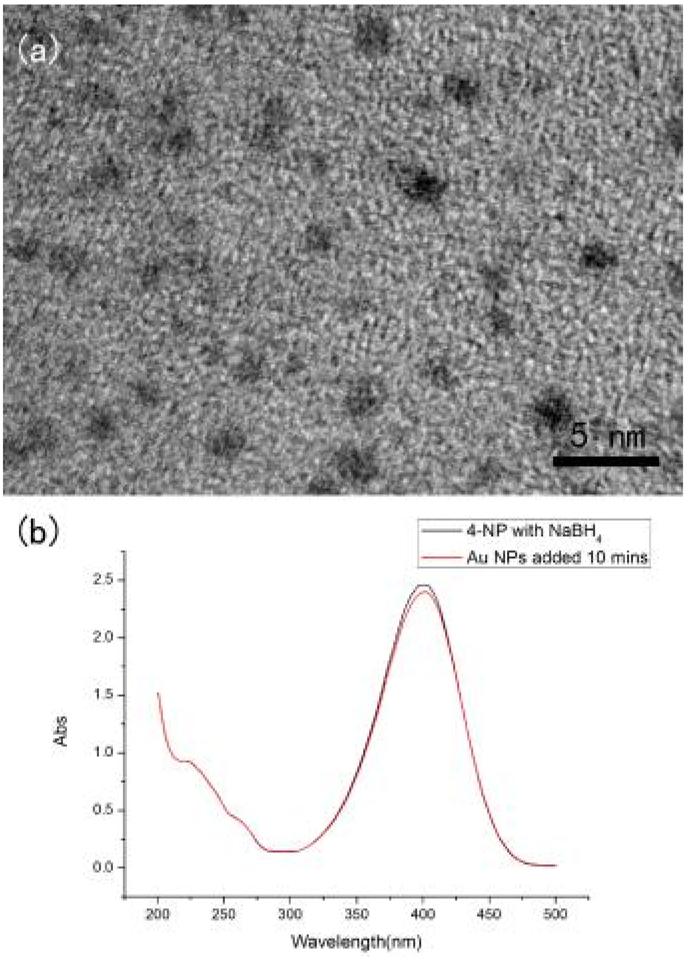


Figure S13. (a): HRTEM image of Au nanoparticles, (b): time-dependent UV-vis absorption spectroscopies of 4-NP solution catalyzed by Au NPs.

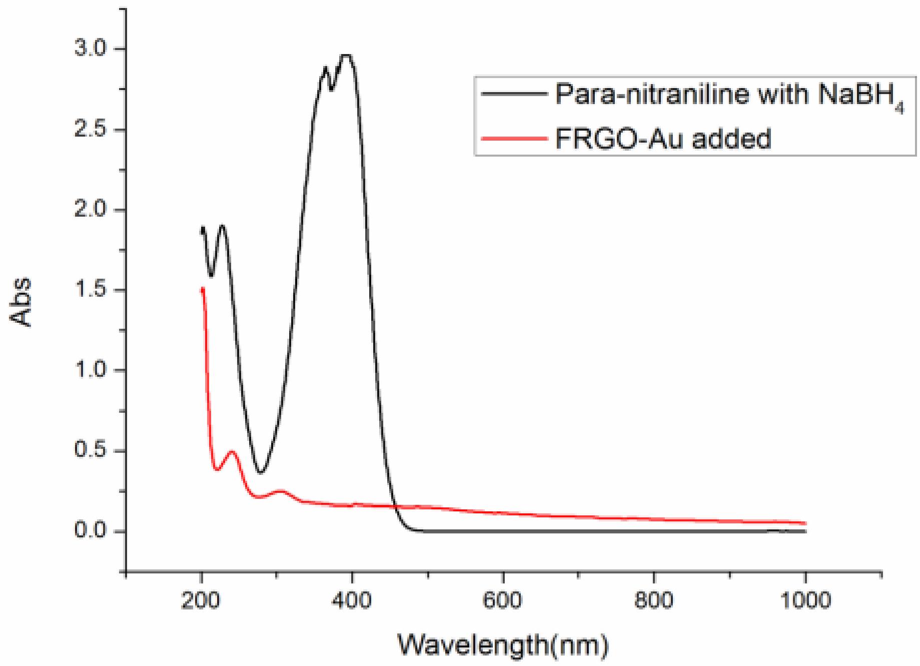


Figure S14. UV-vis absorption spectroscopies of para-nitroaniline solution before and after catalyzed by FRGO-Au1.

Reference

1. W. S. Hummers Jr and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339-1339.
2. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801-802.
3. B. Zeynizadeh and D. Setamdideh, *Synthetic communications*, 2006, **36**, 2699-2704.