

# Ultra-small Gold Nanoparticles Immobilized on Mesoporous Silica/Graphene Oxide as Highly Active and Stable Heterogeneous Catalysts

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## 1. Materials and Experimental

**Materials.** CO<sub>2</sub> (>99.95%) was provided by Beijing Analysis Instrument Factory. Graphene flakes were purchased from Qingdao Chenyang Graphite Company Limited. Poly(oxyethylene)iso-octylphenyl ether (TX-100) with a purity of 99%, was purchased from Sigma. H<sub>2</sub>AuCl<sub>4</sub>·4H<sub>2</sub>O was produced by Shenyang Jinke Reagent Factory. Styrene (99%), triethanolamine (98%), NaOH (98%) and NaBH<sub>4</sub> (98%) were obtained from Alfa Aesar. K<sub>2</sub>PdCl<sub>4</sub> was produced by Acros. *t*-Butyl hydroperoxide (70 wt % in water), aluminum sec-butoxide (96% purity), cetyltrimethyl ammonium bromide (99%) and urea (>99%) were purchased from J&K scientific Co., Ltd. 4-Nitrophenol (A. R.), tetraethyl orthosilicate (TEOS, A. R.), H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, KMnO<sub>4</sub>, 30% H<sub>2</sub>O<sub>2</sub> and ethyl acetate (A. R.) were produced by Beijing Chemical Reagent Company. All chemicals were used as received without any further purification. Water used in all experiments was deionized.

**Synthesis of graphene oxide (GO).** GO was synthesized from graphite powder by a modified Hummers method.<sup>1</sup> In a typical method, 1.5 g of graphite powder was dispersed in 100 mL of concentrated H<sub>2</sub>SO<sub>4</sub> and then 15 mL of concentrated H<sub>3</sub>PO<sub>4</sub> was added and the mixture was kept in ice-water bath. Next, 6 g of KMnO<sub>4</sub> was slowly added to this mixture so that the temperature was kept lower than 20°C during

these  $\text{KMnO}_4$  addition steps. Then the solution was mixed well and transferred to a 35 °C water bath and stirred for 24 h. A brownish-gray paste was formed. At room temperature 160 mL of water was added and then 10 mL of 30%  $\text{H}_2\text{O}_2$  was added slowly, which reduced the residual permanganate. The solution was stirred for further three hours. Then the solution was centrifugated and washed thoroughly with water for several times. Finally, centrifuged viscous GO was obtained.

**Synthesis of Au/SiO<sub>2</sub>/GO composite.** For the synthesis of Au/SiO<sub>2</sub>/GO composite, 2 mL GO solution was added into water (4 g), which was loaded in a stainless-steel autoclave (50 mL). Then TEOS (0.3 mL), TX-100 (0.15 g) and  $\text{HAuCl}_4$  (10 mM) were added into the autoclave.  $\text{CO}_2$  was charged into the cell under stirring until the desired pressure was reached. After the mixture was stirred at room temperature (25 °C) for 7 hours, the stirrer was stopped and  $\text{CO}_2$  was released. The product was obtained after washing with water and freeze drying for 48 hours.

**Synthesis of Au/SiO<sub>2</sub> composite.** In a typical experiment, TEOS (0.3 mL), TX-100 (0.15 g) and a desired amount of  $\text{HAuCl}_4$  (10 mM) were added into an autoclave with 6 mL water. Then  $\text{CO}_2$  was charged into the cell under stirring until the desired pressure was reached. After the mixture was stirred at room temperature for 7 hours, the stirrer was stopped and  $\text{CO}_2$  was released. The product was obtained after washing with water.

**Synthesis of Au/GO composite.** In a typical experiment, 2 mL as-synthesized GO solution was added into water (4 g), which was loaded in a stainless-steel autoclave (50 mL). Then TX-100 (0.15 g) and a desired amount of  $\text{HAuCl}_4$  (10 mM) were added into the autoclave.  $\text{CO}_2$  was charged into the cell under stirring until the desired pressure was reached. After the mixture was stirred at room temperature for 7 hours, the stirrer was stopped and  $\text{CO}_2$  was released. The product was obtained after washing with water.

**Synthesis of Au/Al<sub>2</sub>O<sub>3</sub> composite.** The Au/Al<sub>2</sub>O<sub>3</sub> composite was synthesized according to literature.<sup>2</sup> In a typical experiment, a solution containing 0.8 g NaOH in 4 mL  $\text{H}_2\text{O}$  was added to 80mL triethanolamine and heated at 120 °C for 5 min to evaporate the water. Over this solution, 21.8 mL aluminum sec-butoxide was added

dropwise with stirring. The resulting solution was then heated at 150 °C for 10 min (solution I). (2) 14.56 g cetyltrimethyl ammonium bromide was dissolved in 240 mL H<sub>2</sub>O at 60 °C (solution II). (3) Solution I was slowly added to solution II with vigorous stirring at 60 °C, and the mixture was allowed to age for another 72 h. The precipitate was filtered, washed with ethanol, dried at 30 °C and calcined at 500 °C for 5 h in flowing air. The supported gold catalyst was prepared by the method of homogeneous deposition precipitation (HDP) using urea as a precipitation reagent. In a typical procedure, 1 g of alumina support was added to 100 mL of an aqueous solution containing HAuCl<sub>4</sub> (0.0458 M, 2.2 mL). Excess urea was added. The suspension was vigorously stirred and heated to 75 °C in order to decompose the urea. The suspension was then cooled down and filtered, washed with hot deionized water several times until no Cl<sup>-</sup> was detected. The resulting Au/Al<sub>2</sub>O<sub>3</sub> was dried overnight at 80 °C in air, followed by calcined in air at 330 °C for 1 h under a heating rate of 5 °C min<sup>-1</sup> and then calcined at 300 °C for 0.5 h in a flow of 4% (v/v) H<sub>2</sub>/He.

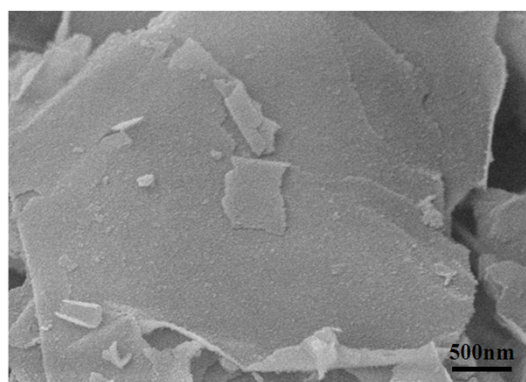
**Characterization.** The morphologies of the catalysts were characterized by high-resolution transmission electron microscopy (HRTEM) (FEI Tecnai G2 F20U-TWIN) and HITACHI S-4800 SEM. The product was characterized by XRD (Model D/MAX2500, Rigaka) with Cu K $\alpha$  radiation at a scanning rate of 5°min<sup>-1</sup>. The porosity properties were gained from nitrogen adsorption-desorption isotherms using a Micromeritics ASAP 2020M system. The loading content of Au was determined by ICP-AES (VISTA-MPX). The EXAFS experiment was carried out at Beamline 1W2B at Beijing Synchrotron Radiation Facility (BSRF). XPS measurement was performed on the VG Scientific ESCALab220i-XL spectrometer using Al K $\alpha$  radiation.

**4-NP reduction.** The reduction of 4-NP was carried out in a quartz cuvette and monitored using UV-vis spectroscopy (Shimadzu UV-2550) at room temperature. A total of 0.10 mL of aqueous 4-NP solution (0.005 M) was mixed with 1.0 mL of fresh NaBH<sub>4</sub> (0.2 M) solution. Subsequently, 0.5 mL of aqueous dispersion of the Au/SiO<sub>2</sub>/GO (5.9 ppm) and 0.5 mL water were added, and the solution was quickly subjected to UV-vis measurement. To study the reusability of the catalyst, the

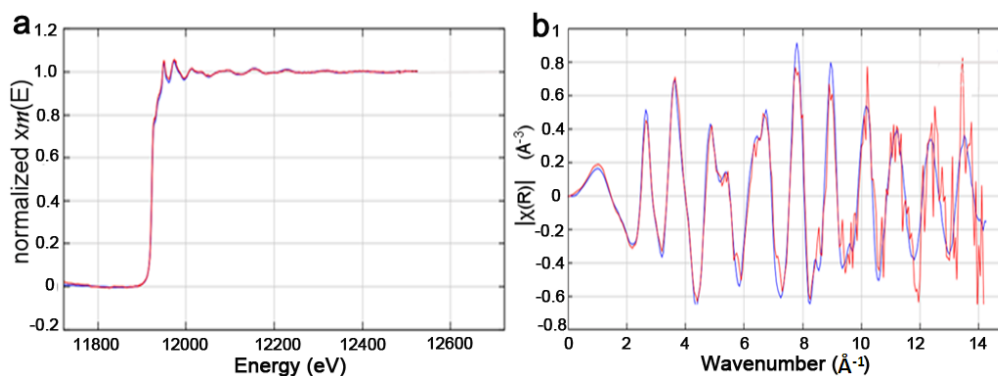
recycled catalyst was washed with deionized water 4 times. Then the catalyst was re-dispersed in 1.0 mL of deionized water and mixed with 0.1 mL of aqueous 4-NP solution (0.005 M) and 1.0 mL of fresh NaBH<sub>4</sub> solution (0.2 M). After reaction for 3 min, the solution was measured by UV-vis spectroscopy. The product 4-AP was confirmed by high performance liquid chromatography (HPLC) with a Shimadzu LC-15C pump, a Shimadzu UV-Vis SPD-15C detector at 295.0 nm, and a Hypersil ODS2 column at 35 °C.

**Styrene epoxidation.** The styrene epoxidation was carried out in a 25 mL flask. The flask was charged with catalyst (40 mg, Au: 1.02 wt%), styrene (1.2 mL, 10 mmol), acetonitrile (15 mL). N<sub>2</sub> was introduced into the flask from an N<sub>2</sub> balloon under atmospheric pressure, and the mixture was stirred for 30 min at room temperature. Then 5.0 g (38 mmol) of *t*-butyl hydroperoxide (70 wt % in water) was added to the flask and the mixture was heated to 80 °C under stirring. After reaction for a certain time, the catalyst was separated and the product was extracted with ethyl acetate and then mixed with dodecane as the internal standard. The mixture was analyzed by gas chromatograph (Agilent 6820).

## 2. Results

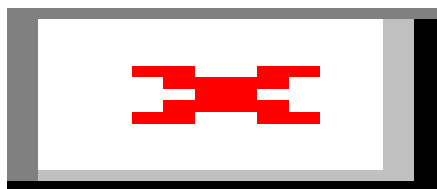


**Fig. S1** SEM image of Au/SiO<sub>2</sub>/GO catalyst synthesized at 5.03 MPa.

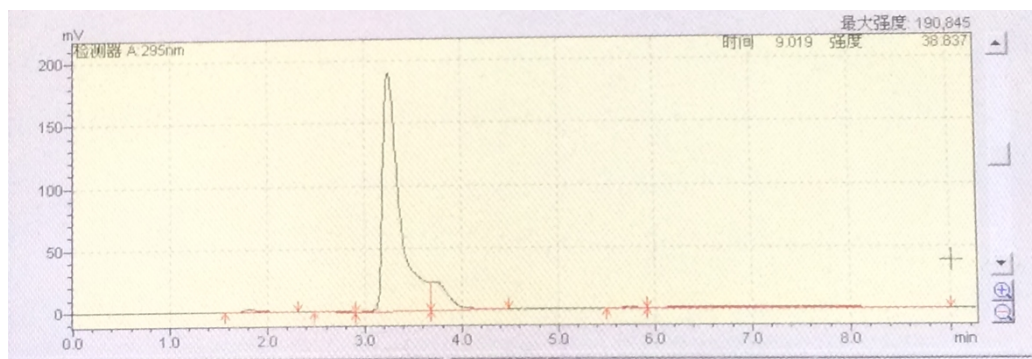


**Fig. S2** a) EXAFS spectra of Au/SiO<sub>2</sub>/GO composite (red) and Au foil (blue). b) Spectra of the Au/SiO<sub>2</sub>/GO composite (red) and Au foil (blue) presented in the  $k$ -space. For the determination of the dependence of EXAFS function ( $\chi(R)$ ) on distance ( $R$ ), mathematical analysis using IFFEFIT software of experimental spectrum was carried out. The first step of the analysis was recalculation of experimental spectrum from the energy ( $E$ ) space to wave vector ( $k$ ) space (b). Then the Fourier transform of the spectrum was followed at the adjusted transform parameters: window type, Hanning;  $k$ -weight=1,  $k$ -range=3-8 Å<sup>-1</sup>.

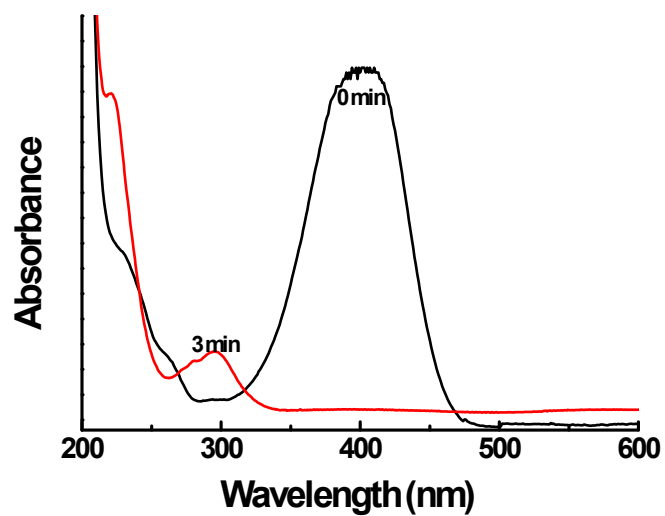
Standard sample:



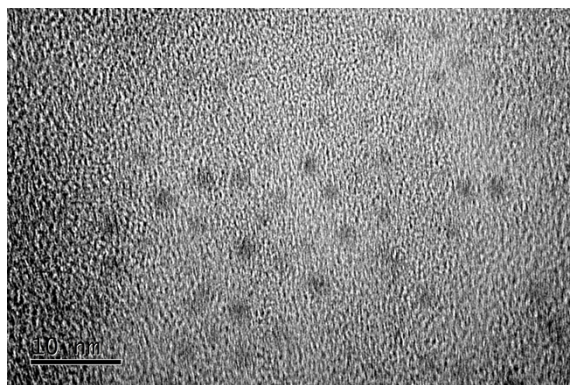
Experimental sample:



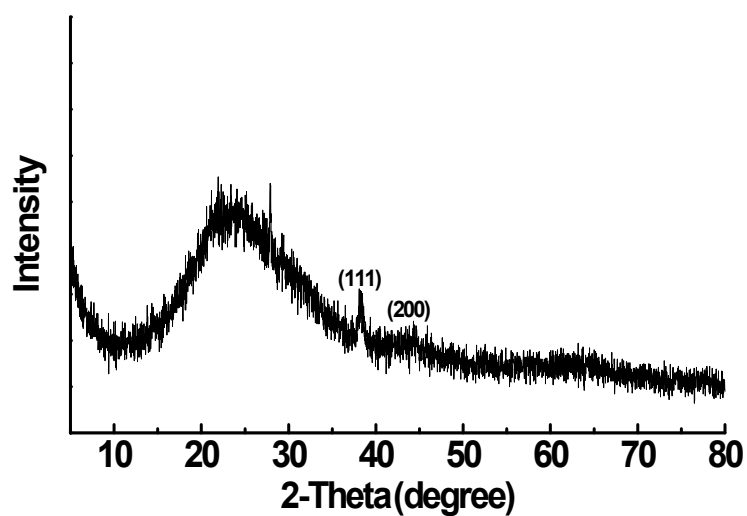
**Fig. S3** HPLC data for 4-aminophenol (4-AP).



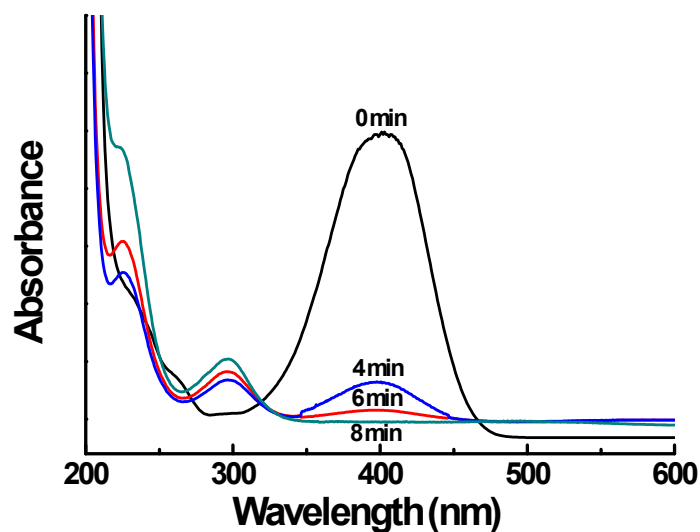
**Fig. S4** UV-vis spectra of the reduction process of 4-nitrophenol in aqueous solution using Au/SiO<sub>2</sub>/GO catalyst after running for 14 cycles.



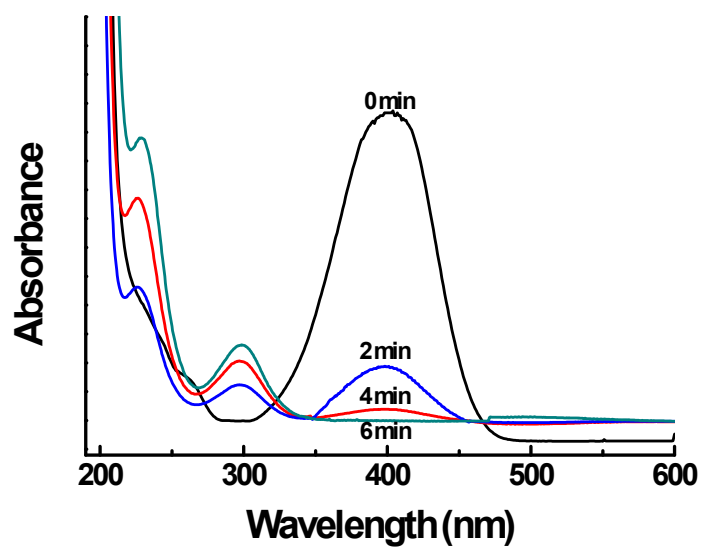
**Fig. S5** TEM image of Au/SiO<sub>2</sub>/GO catalyst after running for five runs for styrene epoxidation.



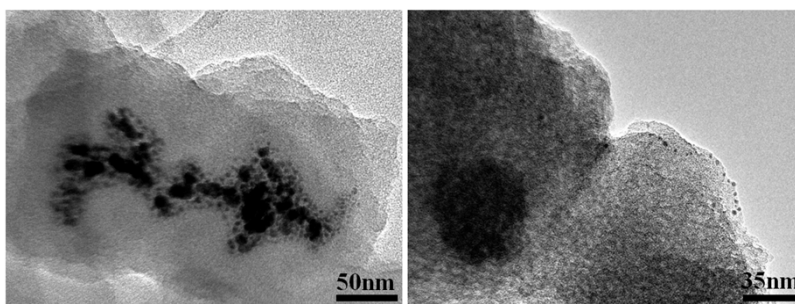
**Fig. S6** XRD pattern of Au/SiO<sub>2</sub>/GO catalyst after running for five runs for styrene epoxidation.



**Fig. S7** UV-vis spectra of the reduction process of 4-nitrophenol in aqueous solution using Au/GO composite (Au: 53  $\mu\text{mol/L}$ ). It needs 8 min to reduce the 4-NP completely. The Au/GO catalyst is much less active than the ternary Au/SiO<sub>2</sub>/GO catalyst (Au: 7.5  $\mu\text{mol/L}$ ) under the same experimental conditions.

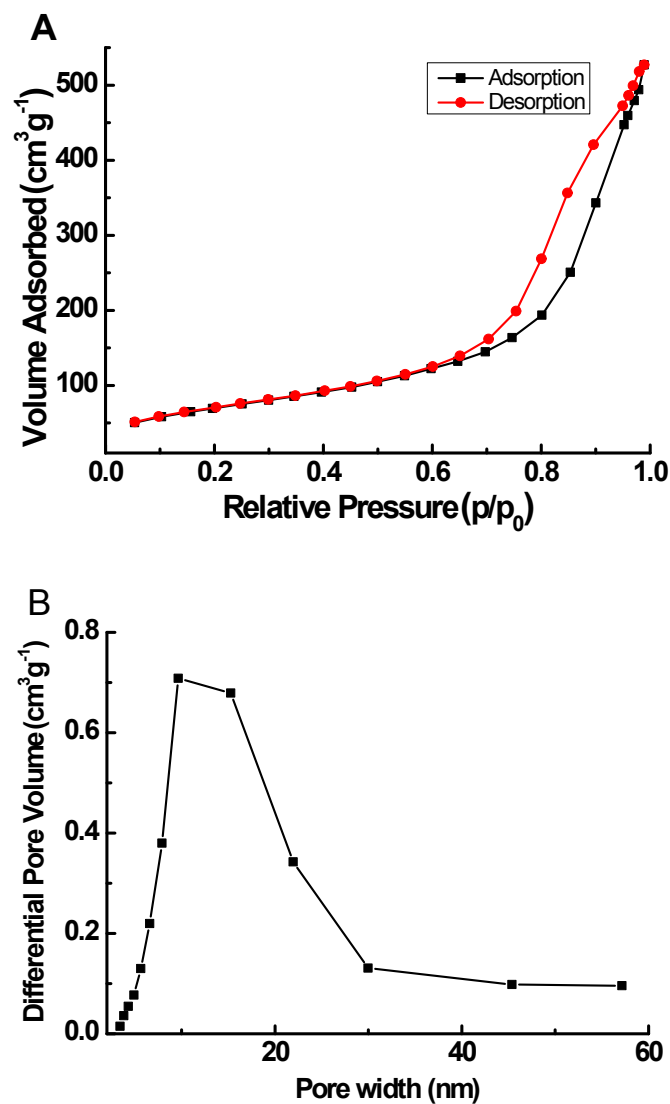


**Fig. S8** UV-vis spectra of the reduction process of 4-nitrophenol in aqueous solution using Au/SiO<sub>2</sub> composite (Au: 18.5 μmol/L). It needs 6 min to reduce the 4-NP completely. The Au/SiO<sub>2</sub> catalyst is much less active than the ternary Au/SiO<sub>2</sub>/GO catalyst (Au: 7.5 μmol/L) under the same experimental conditions.

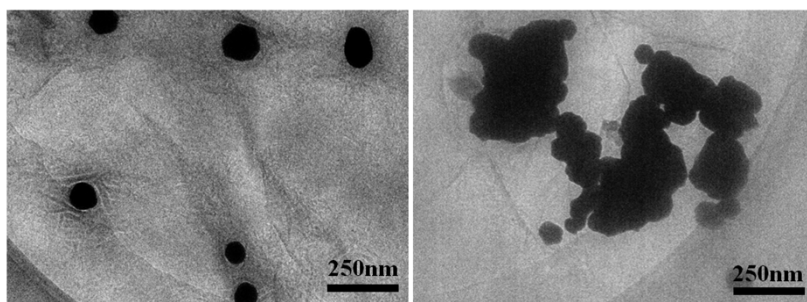


**Fig. S9** TEM images of Au/SiO<sub>2</sub> composite synthesized at 5.03 MPa. The gold content in the Au/SiO<sub>2</sub> composite was determined to be 0.66 wt% by ICP-AES analysis.



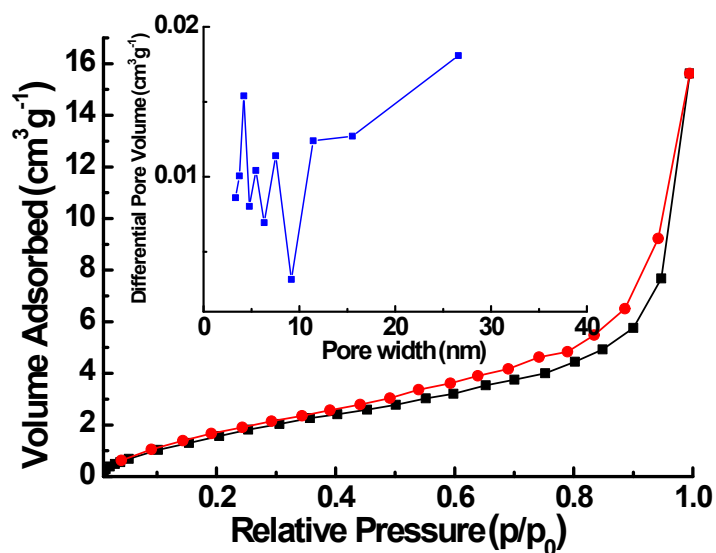


**Fig. S10** N<sub>2</sub> adsorption-desorption isotherms (A) and mesopore size distribution curve (B) of Au/SiO<sub>2</sub>. The BET surface area and total pore volume are 228 m<sup>2</sup>/g and 0.72 cm<sup>3</sup>/g, respectively.

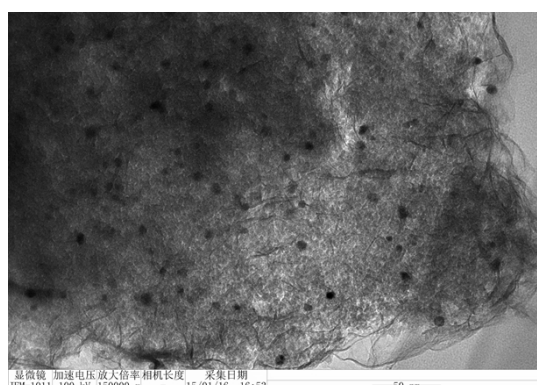


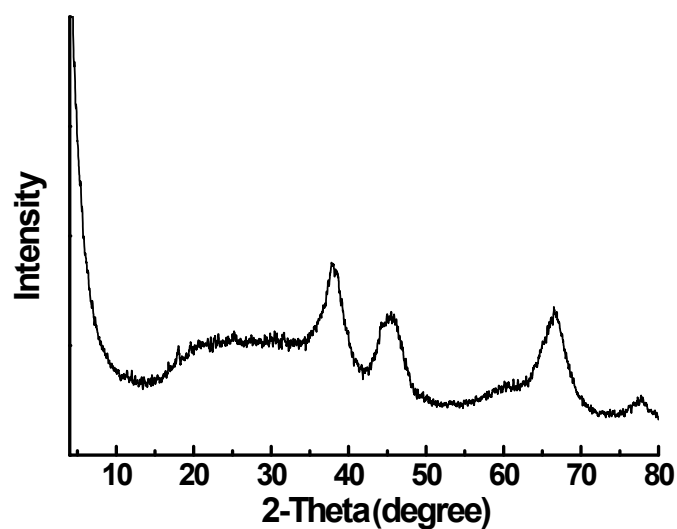
**Fig. S11** TEM images of Au/GO composite synthesized at 5.03 MPa. The gold

content in the Au/ GO composite was determined to be 1.98 wt% by ICP-AES analysis.

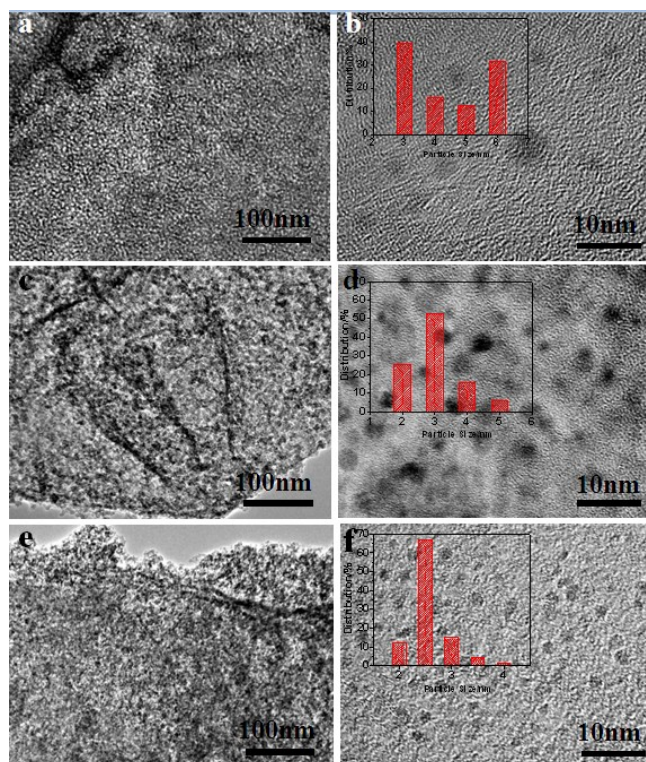


**Fig. S12** N<sub>2</sub> adsorption-desorption isotherms and mesopore size distribution curve of Au/GO composite. The BET surface area and total pore volume are 7.5 m<sup>2</sup>/g and 0.024 cm<sup>3</sup>/g, respectively. By combination with Fig. S10, it can be deduced that the pore size distribution obtained from N<sub>2</sub> adsorption-desorption isotherm of the Au/SiO<sub>2</sub>/GO composite shown in Fig. 3 mainly belongs to SiO<sub>2</sub>.

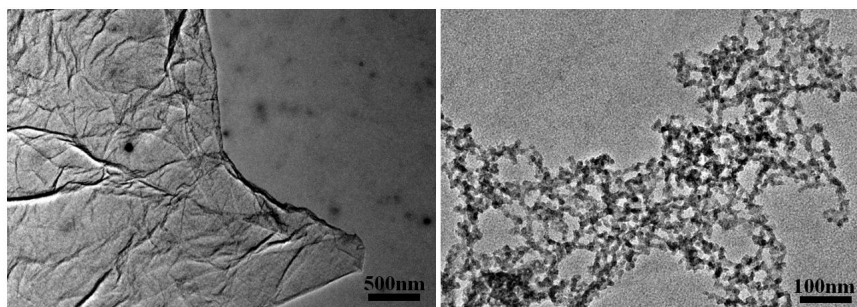




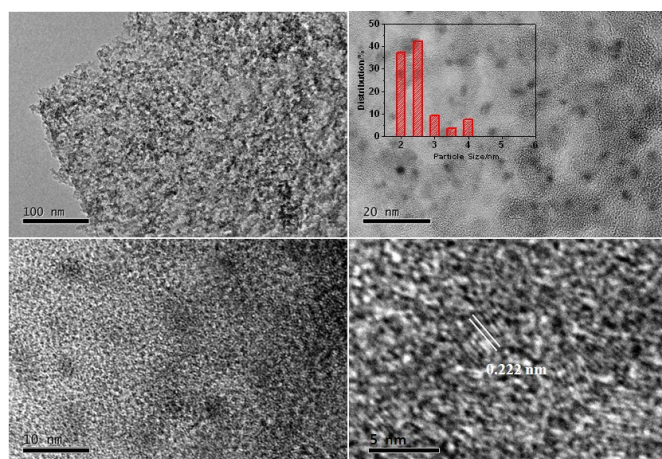
**Fig. S13.** TEM image and XRD pattern of the Au/Al<sub>2</sub>O<sub>3</sub> synthesized as the literature report. The gold content in the Au/Al<sub>2</sub>O<sub>3</sub> composite was determined to be 1.19 wt% by ICP-AES analysis.



**Fig. S14** TEM images of the Au/SiO<sub>2</sub>/GO composite synthesized at 1.14 MPa (a, b), 3.02 MPa (c, d) and 4.02 MPa (e, f). The inset shows the particle size distribution.



**Fig. S15** TEM images of Au/SiO<sub>2</sub>/GO composite synthesized without CO<sub>2</sub>.



**Fig. S16** TEM images of the Pd/SiO<sub>2</sub>/GO composite synthesized at 5.08 MPa.

## Reference

- 1 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806–4814.
- 2 D. Yin, L. Qin, J. Liu, C. Li and Y. Jin, *J. Mol. Catal. A*, 2005, **40**, 40–48.