Electronic Supplementary Information

In situ green synthesis of Au nanostructures on graphene oxide and their application for catalytic reduction of 4-nitrophenol

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Experimental Section

Materials Graphite powder, tannic acid (TA) and 4-nitrophenol (4-NP) were purchased from Aladin Ltd. (Shanghai, China). $HAuCl_4$ were purchased from Aldrich Chemical Comp. $NaNO_3$, H_2O_2, H_2SO_4 (98%), and $KMnO_4$ were purchased from Beijing Chemical Corp. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of GO GO was prepared from natural graphite powder through a modified Hummers method. In a typical synthesis, 1 g of graphite was added into 23 mL of 98 % H_2SO_4, followed by stirring at room temperature over a period of 24 h. After that, 100 mg of $NaNO_3$ was introduced into the mixture and stirred for 30 min.

Subsequently, the mixture was kept below 5 ºC by ice bath, and 3 g of $KMnO_4$ was slowly added into the mixture. After heating to 35-40 ºC, the mixture was stirred for another 30 min. After that, 46 mL of water was added into above mixture during a period of 25 min. Finally, 140 mL of water and 10 mL of H_2O_2 were added into the mixture to stop the reaction. 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 0.5 mg/mL with the aid of ultrasound for further use.

In situ synthesis of Au nanostructures on GO In a typical experiment, 1 mL of grapheme oxide (GO) was dispersed in 2 mL of 5 mg/L TA aqueous solution under ultrasonic irradiation for 30 min. Then the excess TA was discarded by centrifugation and the as-prepared TA-functionalized GO was dissolved into 500 μL of water. Next, 30 μL of 24.3 mM $HAuCl_4$ aqueous solution was added into the above TA/GO dispersion at room temperature, followed by an obvious color change from light yellow to purplish red and accompanied by the presence of precipitates. The resulting precipitates was centrifuged and washed twice with distilled water and redispersed in water for characterization and further use. Another two experiments with the use of 60-μL and 100-μL $HAuCl_4$ were performed under otherwise identical conditions.

Preparation of Au nanoparticles (AuNPs) For comparison, AuNPs were prepared with the use of TA as a reducing agent. In brief, 50 μL of 5 mg/L TA aqueous solution was diluted to 500 μL by adding water firstly, and then 30 μL of 24.3 mM $HAuCl_4$ aqueous solution was added into the above TA aqueous solution. Next an obvious color change from light yellow to purplish red occurred, meaning TA-reduced AuNPs was obtained.

Characterization Transmission electron microscopy (TEM) measurement was made on a HITACHI H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. UV-visible spectra were obtained on a UV5800 Spectrophotometer.

$NaBH_4$ reduction of 4-nitrophenol (4-NP) catalyzed by Au nanostructures/GO nanocomposites Typically, freshly prepared aqueous solution of $NaBH_4$ (1.0 mL, 0.16 M) was mixed with 4-NP aqueous solution (1.0 mL, 7 mM) in the quartz cell (1 cm path length), leading a color change from light yellow to yellowgreen. Then, the catalysts were added into the mixture and immediately placed in the cell holder of the spectrophotometer. UV-visible absorption spectroscopy was used to monitor the progress of the conversion of 4-NP to 4-aminophenol (4-AP) in the presence of Au nanostructures/GO catalysts (containing Au: 18 mg/L) by recording the time-dependent adsorption spectra of the reaction mixture in a scanning range of 200-600 nm at ambient temperature. It should be mentioned that the amount of Au nanostructure/GO catalysts used in each catalyst solutions is estimated from the amount of $HAuCl_4$ in each preparation process, to ensure the same Au concentration of catalysts used.

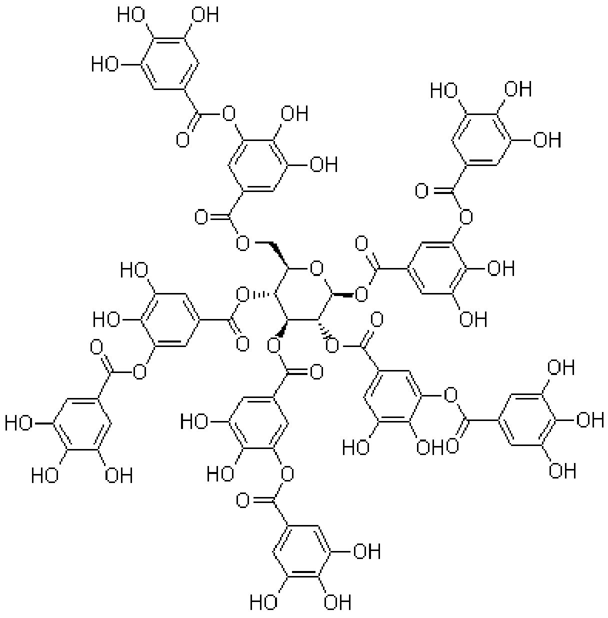

Fig. S1 Chemical structure of tannic acid (TA).

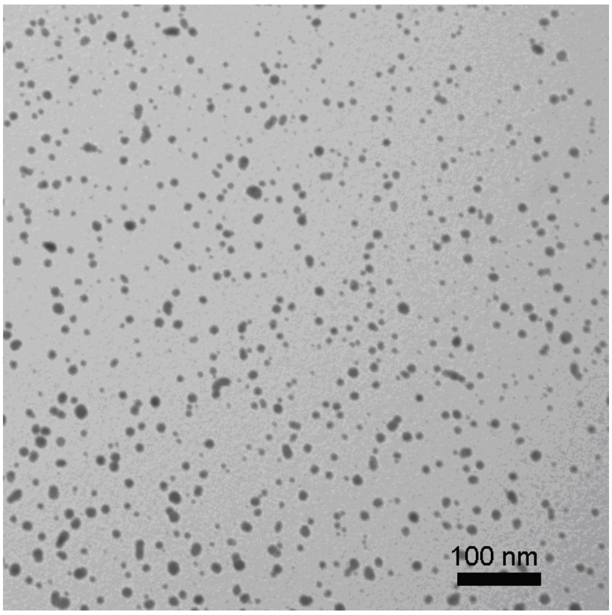

Fig. S2 TEM image of the TA-reduced Au nanoparticles.