Electronic Supplementary Information

Carbon-protected Au Nanoparticles Supported on Mesoporous TiO_2 for Catalytic Reduction of *p*-nitrophenol

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1. Experiments

1.1 Support preparation

Mesoporous TiO_2 was prepared from soft-chemistry and template-free method, the experimental details refer to our previous work[26]. Briefly, $K_2Ti_2O_5$ was ion-exchanged with HCl aqueous solution (0.1 $mol\cdot L^{-1}$) until K^+ ion was completely exchanged (residual of $K^+ < 0.3$ wt %, detected by X-ray fluorescence spectrometry (XRF, ARL- 9800, USA)). Then, products ($H_2Ti_2O_5$) were filtered and washed with de-ion water and dried in a desiccator at 60 ºC under vacuum. At last, calcination of $H_2Ti_2O_5$ was performed in a muffle oven at 500 ºC in air for 2 h. After air cooling, mesoporous TiO_2 support has been synthesized.

1.2 Synthesis of Au/TiO_2 catalyst.

The deposition of gold on supports was prepared by the typical deposition-precipitation(DP) with urea as a precipitator[27]. Excess of urea (1.287 g) was dissolved in 50 mL of an aqueous solution of $HAuCl_4$ (1.04 $mmol\cdot L^{-1}$). 1 g of support was added to the yellow solution, and the resulting mixture was then heated at 80 ºC for 2 h under vigorous stirring and in the absence of light. The solids were gathered by filtration and washing several times to remove the Cl^- ions, which were detected by $AgNO_3$ solution. The solid product was oven-dried at 65 ºC for 24 h. Then the sample was calcinated at 500 ºC for 2 h in the tube furnace under air atmosphere. Finally the sample was stored away from light in a refrigerator at 4 ºC(fig. 1(d)).

1.3 Synthesis of C/Au/TiO_2 catalyst

Firstly, 0.3 g of Au/TiO_2 catalysts were added into the flask under vacuum for 8 hours (fig. 1(a)). Then injected 10 mL glucose aqueous solution (4.4 $mmol\cdot L^{-1}$) into the flask. After 4 h of vacuum stirring, the productions were filtered and then oven-dried at 120 ºC for 1 h (fig. 1(b)). The dried solid was heated at 500 ºC for 2 h in the tube furnace under argon. As the samples were cooled to room temperature, C/Au/TiO_2 was prepared (fig. 1(c)).

1.4 Catalyst evaluation

The *p*-nitrophenol reduction to *p*-aminophenol by $NaBH_4$ (liquid phase) was investigated in a batch mode. The aqueous solution of PNP (6 mmol·L^{-1}, 50 mL) was mixed with $NaBH_4$ (0.1 mol·L^{-1}, 50mL) as a reducing agent only for PNP and then the C/Au/TiO_2 or Au/TiO_2 was added to the solution. In each case, the amount of Au catalyst was set at 0.1g. The reaction was carried out at 25 ºC with continuous stirring. At a given time, the reaction solution (1.0 mL) was sampled, and was filtered through a 0.2 µm membrane filter (Chromatodisk, GL Sciences, Ltd.). UV–vis spectra of the reaction solutions (1.0 mL) was recorded using a spectrophotometer (UNICO UV-2802S). According to Concentrate-Absorption standard curve, the rate constants of the reduction process were calculated by measuring the change in absorbance at 400 nm per 3 min.

1.5 Characterization

Raman spectra was obtained using a Horiba HR 800 spectrometer, equipped with a CCD camera detector. As a source of excitation the 514 nm line of a Spectra Physics 2018 Argon/Krypton Ion Laser system were focused through an Olympus BX41 microscope equipped with a 50 magnification objective. The laser power never exceeded 5 mW for each sample. Thermo-gravimetric (TG) analysis was performed on a Model SDT 2960 (TA, America) instrument. The measure was conducted with the temperature of 40~600 ºC at a rate of 10 ºC·min^{-1} under air atmosphere. The crystal phase of the raw material and products was determined by powder X-ray diffraction (XRD, Bruker D8, Cu Ka radiation). Structural properties of samples were determined by N_2 adsorption-desorption (at -196 ºC) in a Micromeritics TristarII 3020M apparatus. Surface area was calculated by Brunauer-Emmett-Teller (BET) method. Pore volume was determined by nitrogen adsorption at a relative pressure of 0.99. The morphology of the gold nanoparticles was characterized by high-resolution transmission electron microscopy conducted on a JEM-2010 UHR (JEOL Co., Japan) at 200 kV. The catalysts to be measured were ultrasonically dispersed in ethanol and testing samples were prepared by dropping the dispersed suspensions on carbon-coated copper grids. An ultraviolet-visible (UV-vis) spectrometer (Perkin-Elmer Lambda 900) was used to identify the spectral properties of the samples.

2. Results

2.1 XRD spectrum

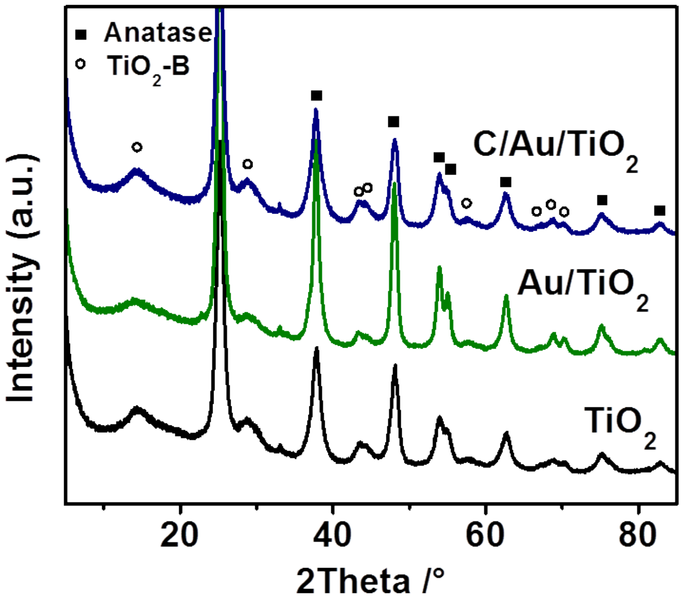

Fig.S1 XRD spectrum of TiO_2, Au/TiO_2 and $C/Au/TiO_2$. ■, anatase; ○, TiO_2 (B).

2.2 pore-size distribution

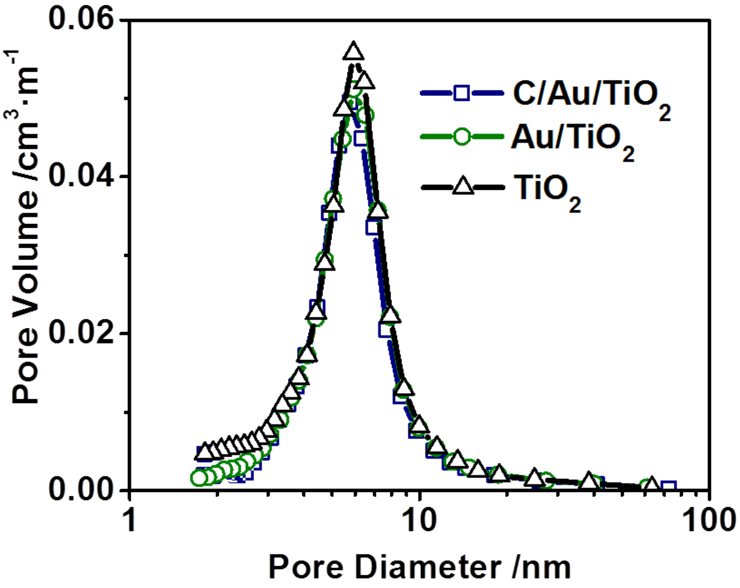

Fig.S2 pore-size distribution of TiO_2, Au/TiO_2 and $C/Au/TiO_2$

2.3 PNP adsorption curve

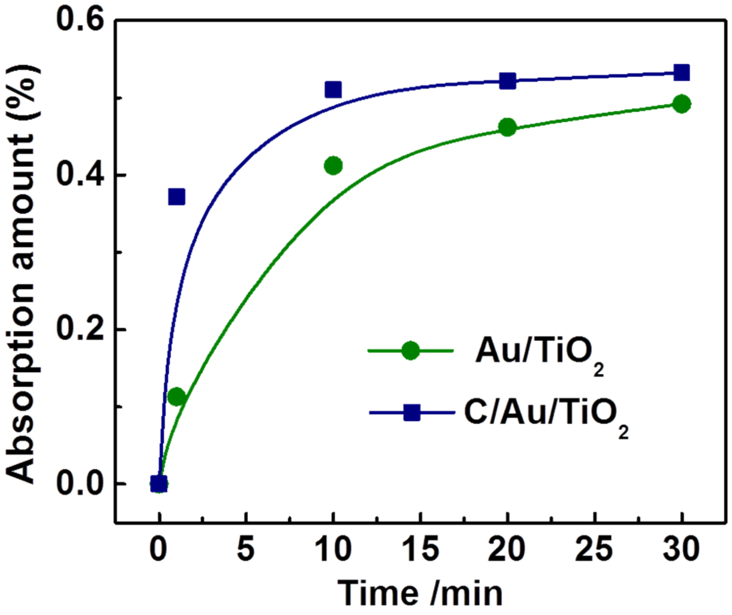

Fig.S3 PNP absorption curve on gold catalysts.