Electronic Supplementary Information (ESI) for:

One-pot synthesis of Au@TiO$_2$ core-shell nanocomposite and its catalytic properties

Lei Han, Chengzhou Zhu, Peng Hu, Shaojun Dong*

Experimental section

Reagents Poly(oxyethylene) nonylphenyl ether (Igepal CO-520) was bought from Aldrich. Titanium (III) chloride (20% in 3% hydrochloric acid) was purchased from Alfa Aesar. $HAuCl_4 \cdot 4H_2O$ and cyclohexane were obtained from Shanghai Chemical Factory (Shanghai, China) and used as-received without further purification. Water used for preparation of aqueous solutions was purified using a Millipore-Q water purification system.

Synthesis of Au@TiO$_2$ The Au@TiO$_2$ nanocomposite (Au@TiO$_2$) was synthesized by combining the reverse micelle technique with a redox reaction between Au (III) and titanium (III). Reverse micelle systems were formed by poly(oxyethylene) nonylphenyl ether, cyclohexane, and an aqueous solution of metal precursors. Reverse micelles containing the gold precursor were prepared as follows. Poly(oxyethylene) nonylphenyl ether (1.6 mL) was added to 4 mL of cyclohexane, and the mixture was stirred using a Teflon-coated magnetic stir bar. $HAuCl_4$ aqueous solution (0.4 mL, 6.25 mM) was added into a cyclohexane/poly(oxyethylene) nonylphenyl ether mixture with vigorous stirring to give a clear solution. 0.4 mL aqueous solution containing 100 μL titanium (III) chloride (20% in 3% hydrochloric acid) was added into the cyclohexane/poly(oxyethylene) nonylphenyl ether mixture to give reverse micelles containing the cerium precursor. These two reverse micelle solutions were mixed for 1 h at 60 °C, giving a red suspension indicating the occurrence of the redox reaction of Au (III) with titanium (III) to Au NPs and TiO_2 within a single micelle. After cooling to room temperature, 8 mL of ethanol was injected into the mixture to break the reverse micelles and the mixture was stirred for 0.5 h. The red precipitate was collected by centrifugation (13000 rpm), washed with ethanol and re-dispersed in ethanol.

Apparatus UV-vis detection was carried out on a Cary 50 UV–vis spectrophotometer (Varian, USA). TEM and HRTEM images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation.

Catalytic reduction toward *p*–nitrophenol The aqueous solutions of *p*-nitrophenol (10 mM) and $NaBH_4$ (3 M) were freshly prepared. 2.5 mL of an aqueous solution containing 25 μL Au@TiO_2 was added into a quartz cuvette. Then, 25 μL of the mixture containing 12.5 μL *p*–nitrophenol solution and 12.5 μL of $NaBH_4$ solution was injected into the cuvette to start the reaction, and the intensity of the absorption peak at 400 nm was monitored by UV-vis spectroscopy as a function of time. After each round of reaction, another 25 μL of mixed aqueous solution was added to the reaction solution. This step was repeated nine times to explore the stability of the catalysts. As comparison, we also investigated the catalytic activity of uncapped Au NPs and TiO_2.

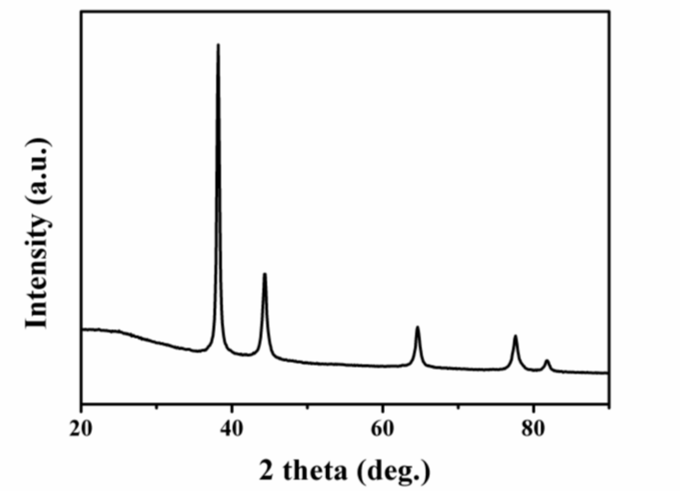

Fig. S1 The XRD pattern of the Au@TiO_2 sample.

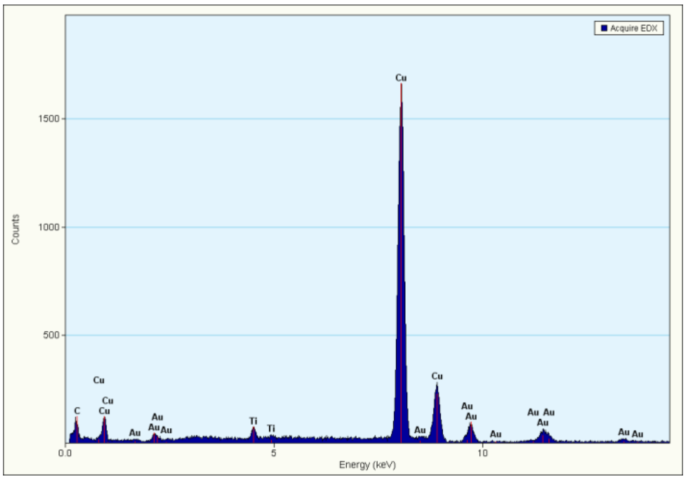

Fig. S2 Energy-dispersive X-ray image of the as-synthesized Au@TiO_2 nanocomposite.

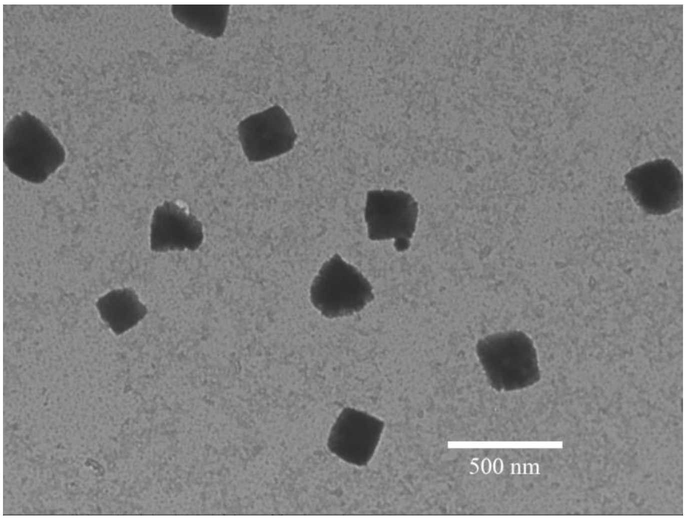

Fig. S3 The typical TEM images of the obtained sample when the reverse micelle method was not used.

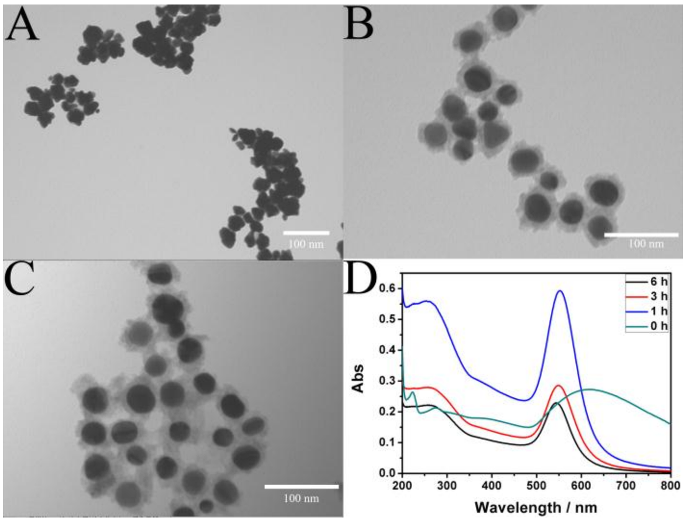

Fig. S4 (A-C) The typical TEM images and (D) The UV-visible absorption of the obtained samples with different reaction time at 60 °C: 0 h (A), 3 h (B), and 6 h (C).

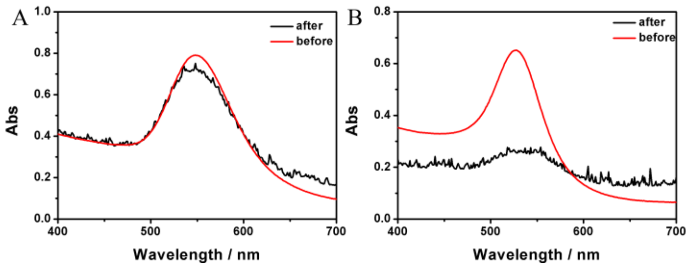

Fig. S5 UV-visible absorption spectra of (A) Au@TiO_2 and (B) Au catalysts before and after five cycles of use.

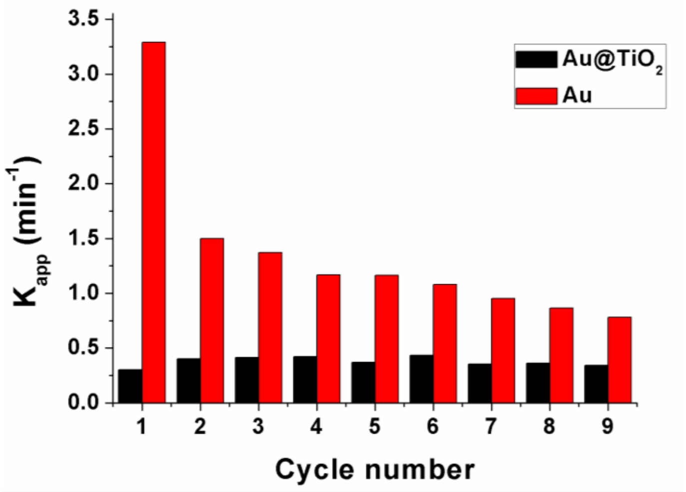

Fig. S6 Values of K_{app} for successive reactions employing Au and Au@TiO_2 as the catalyst.

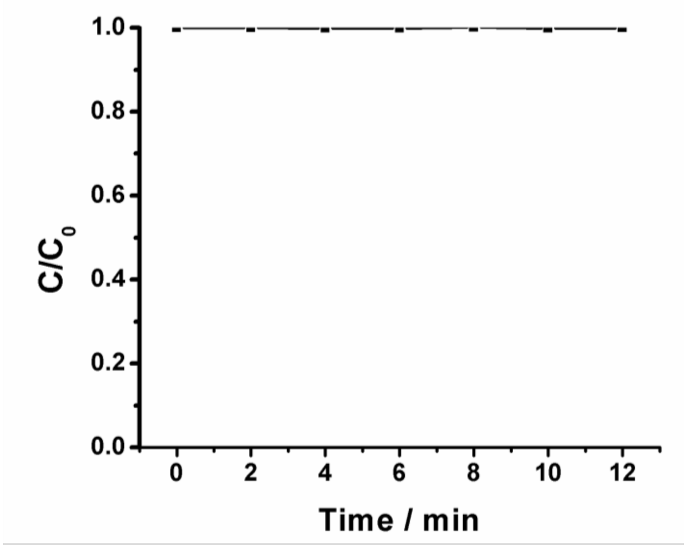

Fig. S7 C/C_0 versus reaction time for the reduction of 4-NP over TiO_2 nanocomposite. C_0 and C was the absorption peak at 400 nm initially and at time t.

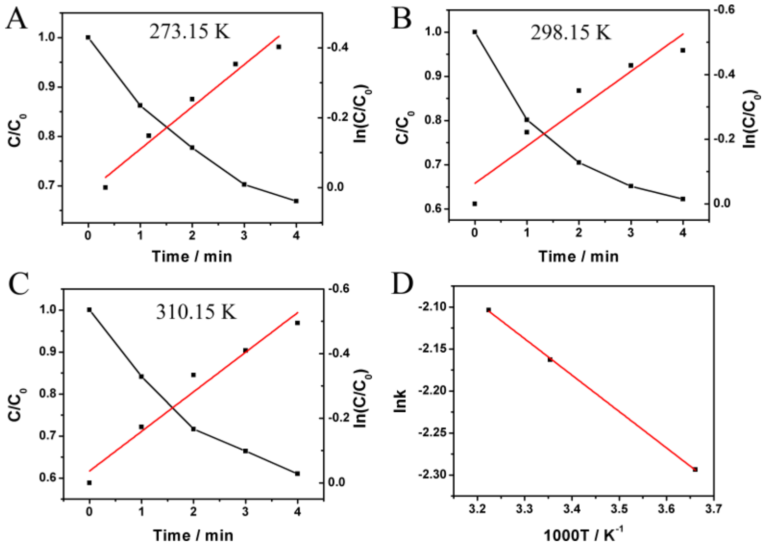

Fig. S8 (A-C) C/C_0 and $\ln(C/C_0)$ versus reaction time for the reduction of 4-NP over Au@TiO_2 nanocomposite at different reaction temperatures. C_0 and C was the absorption peak at 400 nm initially and at time t. (D) The Arrhenius plots for reactions catalyzed by Au@TiO_2 nanocomposite. The activation energy (Ea) can be calculated from the slope of the linear fitting.

Table S1. Summary of the reaction rate constant (k) at three different temperatures for the Au@TiO_2 nanocomposite.

T (K)	*273.15*	*298.15*	*310.15*
k (min)	0.1009	0.115	0.12

Note: Ea=3.6 KJ/mol, according to the Arrhenius equation ($\ln k = \ln A - Ea/RT$).