Electronic Supplementary Information

Synthesis and multiple reuse of eccentric Au@TiO$_2$ nanostructures as catalysts

Zhi Wei Seh,[a,§] Shuhua Liu,[a,§] Shuang-Yuan Zhang,[a] Kwok Wei Shah,[a] and Ming-Yong Han*[a,b]

[a] Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 3 Research Link, Singapore 117602

[b] Division of Bioengineering, National University of Singapore, Singapore 117576

[§] These authors contributed equally to this work.

*To whom correspondence should be addressed. Email: my-han@imre.a-star.edu.sg

Experimental Section

Materials

$HAuCl_4 \cdot 3H_2O$ (99.9+%), sodium citrate dihydrate (99+%), hydroxypropyl cellulose (M_w = 370,000), titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol) and 4-nitrophenol (≥99%) were purchased from Aldrich. Silver nitrate (99.8+%) and sodium borohydride (99%) were purchased from Acros Organics. Isopropanol (VLSI Puranal 250) and ammonia (25 wt%) were purchased from Honeywell. Deionized water (Millipore, Milli-Q grade) was used in all experiments. All chemicals were used as received.

Characterization

UV-visible spectra were taken with a Shimadzu UV-3150 spectrophotometer. Transmission electron microscopy (TEM) images were recorded using a JEOL 1010 TEM operating at an accelerating voltage of 100 kV. High resolution TEM images were recorded using a Philips CM 300 FEGTEM operating at an accelerating voltage of 300 kV. Raman measurements were performed on a Renishaw inVia Raman microscope with an excitation wavelength of 785 nm. The maximum laser power was 135 mW and the exposure time was 10 s.

Seeded Growth of 50-nm Au Nanoparticles

First, 15-nm Au nanoparticles were prepared by injecting a sodium citrate solution (5 mL, 1 wt%) into a boiling $HAuCl_4$ solution (50 mL, 1 mM) under vigorous magnetic stirring. Heating was continued for 15 min before the mixed solution was allowed to cool to ambient temperature. The 15-nm Au nanoparticles were then filtered using a filtering unit (PTFE, 1.0 µm), and the purified Au nanoparticles were used as seeds for seeded growth of 50-nm Au nanoparticles. Experimentally, the 15-nm Au seeds (2.25 mL) together with a sodium citrate solution (1.12 mL, 1 wt%) were injected into a boiling $HAuCl_4$ solution (250 mL, 0.3 mM) under vigorous magnetic stirring. After boiling for 30 min, heat was removed and 10 mL of aqueous hydroxypropyl cellulose solution (0.5 wt%) was added followed by continuous stirring overnight. The as-synthesized 50-nm Au nanoparticles were then filtered using a filter paper prior to use for TiO_2 coating.

Growth of TiO_2 Shells onto 50-nm Au Nanoparticles

Typically, the filtered 50-nm Au nanoparticles (50 mL) was mixed with isopropanol (200 mL) and ammonia (6.25 mL, 25 wt%) using vortex. Titanium diisopropoxide bis(acetylacetonate) in isopropanol (10 mM) was then added and the solution was left to shake overnight at 200 rpm using a Heidolph Unimax 2010 Shaker. For the synthesis of Au@TiO_2 (5/25) and Au@TiO_2 (5/125) nanostructures, a total

of 12 mL and 36 mL of the titanium alkoxide precursor was added respectively, in 3 mL portions at an interval of 1 h each. After washing with isopropanol 3 times, the as-purified Au@TiO$_2$ nanostructures were redispersed into 50 mL of deionized water for characterization.

Catalytic Reduction of 4-Nitrophenol

The Au@TiO$_2$ nanostructures were used as catalysts in the reduction of 4-nitrophenol by sodium borohydride. First, the optical density of all the catalysts was standardized to 1.0, which corresponds to a concentration of $\sim 5.0 \times 10^{10}$ particles/mL. The catalysts (10 mL) were then added to sodium borohydride solution (10 mL, 1.2 M). After 10 min of magnetic stirring, 4-nitrophenol solution (10 mL, 3.4 mM) was added. At every 5 min interval, a 100 µL aliquot of the reaction mixture was extracted, diluted to 2 mL (56.7 µM 4-nitrophenol, 20 mM sodium borohydride) and analyzed using UV-visible spectroscopy. As the reaction progressed, the characteristic absorption peak of 4-nitrophenol at 400 nm decreased in intensity, indicating the conversion to 4-aminophenol.

For UV-visible analysis, the concentration of 4-nitrophenol at the start of the experiments was 56.7 µM, corresponding to an absorbance value of 1.0 for experimental convenience, which lies in the linear regime of the absorbance as a function of concentration curve for 4-nitrophenol (Fig. S1). As 4-nitrophenol was degraded with time, all subsequent absorbance values were less than 1.0, which implies that the conditions of Beer-Lambert Law were fulfilled at all times. This justifies the use of the absorbance value at 400 nm as an accurate means of measuring the concentration of 4-nitrophenol as the reaction progressed. For all experiments, the percentage conversion of 4-nitrophenol was calculated at the end of 20 min.
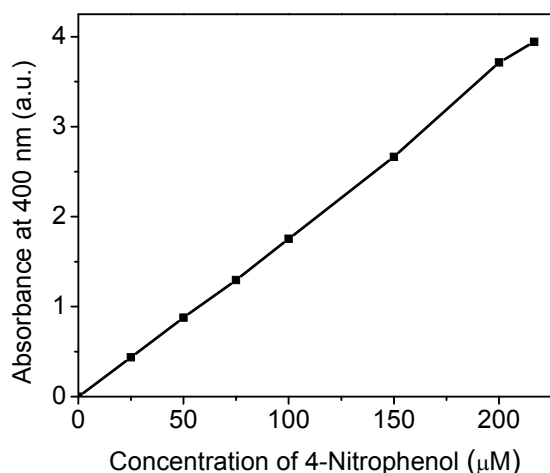

Fig. S1 The absorbance vs. concentration curve of 4-nitrophenol (in a 20 mM sodium borohydride solution), showing the region where Beer-Lambert Law is fulfilled.

Citrate Reactivation of the Catalysts

To reactivate the used catalysts, the reaction mixture (30 mL containing 10 mL of catalysts) was boiled with sodium citrate solution (30 mL, 1 wt%) for 1 h at the end of each cycle. The solution turned brown due to discoloration of the reaction product, 4-aminophenol. The catalysts were then recovered by centrifugation at 4000 rpm and redispersed into deionized water (10 mL) to prepare them for the next cycle. The Au@TiO$_2$ (5/25) and Au@TiO$_2$ (5/125) catalysts were each subject to a total of 5 cycles of reuse. 50-nm bare Au nanoparticles were also used as catalysts for comparison purposes.
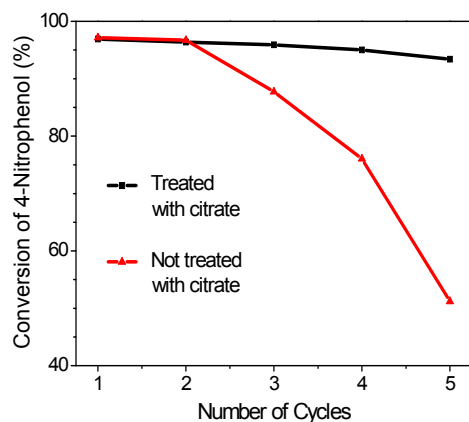

Fig. S2 Conversion of 4-nitrophenol as a function of cycles using Au@TiO$_2$ (5/25) catalysts, showing the effect of citrate treatment after every cycle.
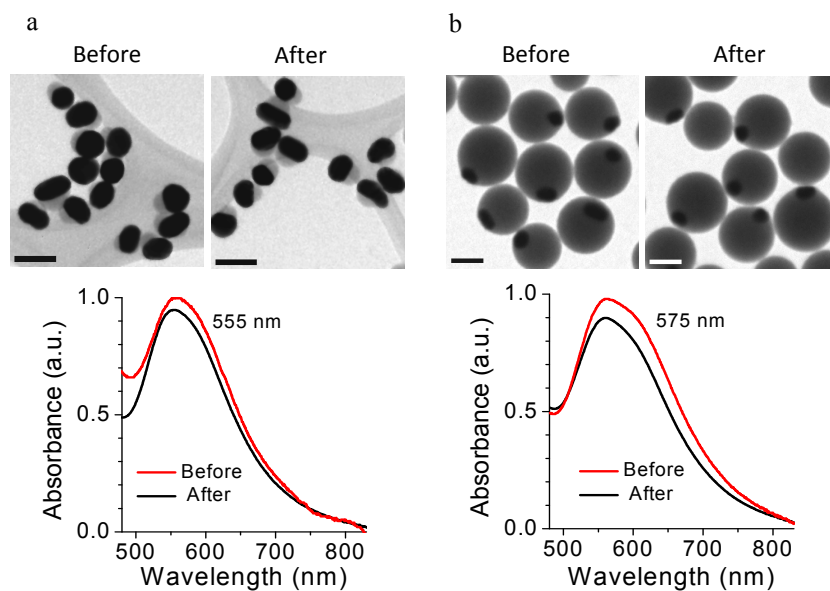

S4

Fig. S3 TEM images and UV-visible absorption spectra of (a) Au@TiO$_2$ (5/25) and (b) Au@TiO$_2$ (5/125) catalysts before and after five cycles of use. Scale bars = 100 nm.
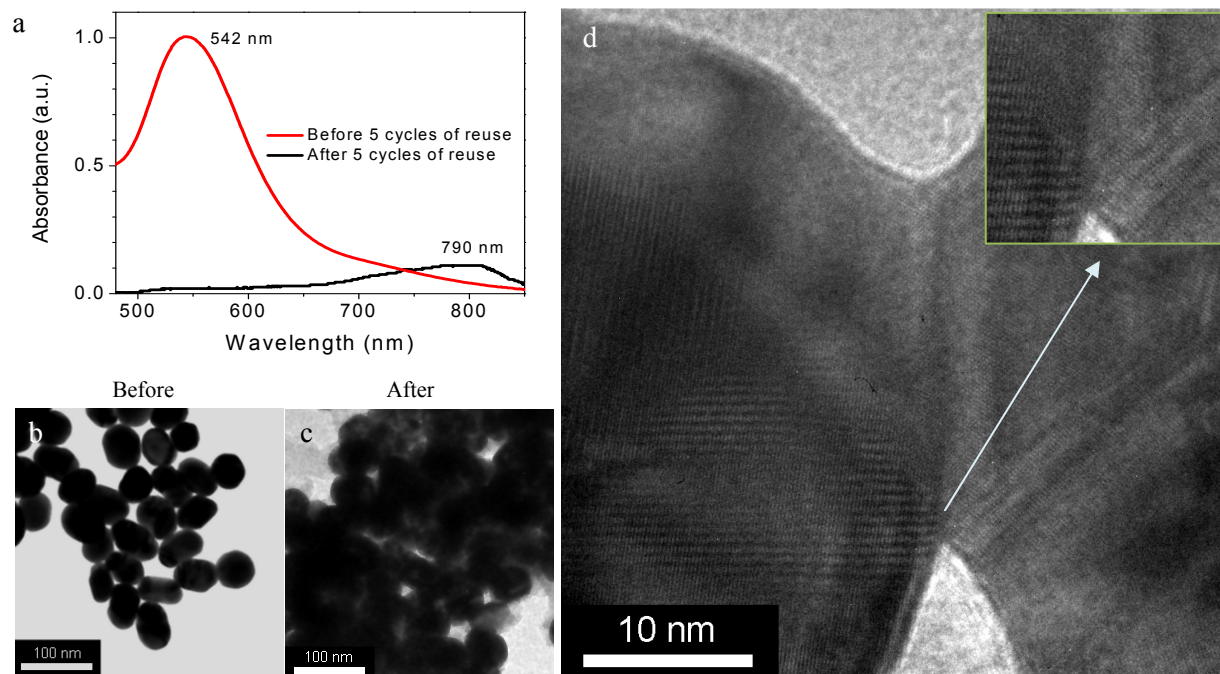
Fig. S4 The 50-nm bare Au nanoparticles subject to five cycles of reuse: (a) UV-visible spectra changes before and after five cycles of reuse, showing the drastic drop in the plasmon resonance peak of Au at 542 nm and the appearance of a broad peak at 790 nm, indicating aggregation of the Au nanoparticles. (b-c) TEM images of Au nanoparticles (b) before and (c) after five cycles of reuse, showing aggregation of the nanoparticles. (d) HRTEM image of Au nanoparticles after five cycles of reuse. The image shows linking of the lattices of aggregated nanoparticles, indicating irreversible aggregation.
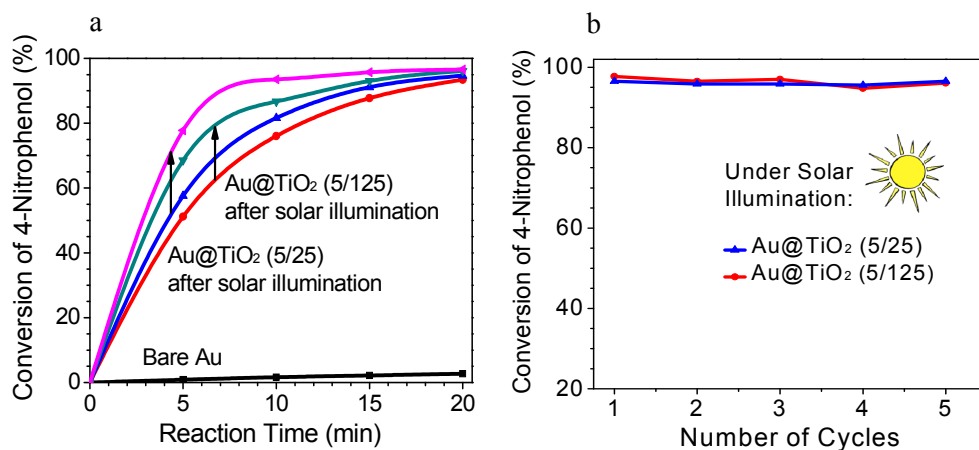
Fig. S5 Au@TiO$_2$ catalysts under solar illumination (as a source of UV radiation). (a) The conversion of 4-nitrophenol as a function of reaction time, showing the increase in conversion rate using Au@TiO$_2$ catalysts under solar illumination. This can be ascribed to the photogeneration of excited electrons in TiO$_2$ which helps in the reduction process. The fifth cycle of use is shown. (b) The conversion of 4-nitrophenol as a function of cycles using the catalysts under solar illumination, showing that the catalysts can be reactivated and reused with no obvious loss of catalytic activity after five cycles. A Newport 96000 150 W Solar Simulator was used at a power of 150 W for solar illumination and the experiments were carried out in a constant temperature water bath kept at ambient temperature of 24 °C to avoid any heating effect.
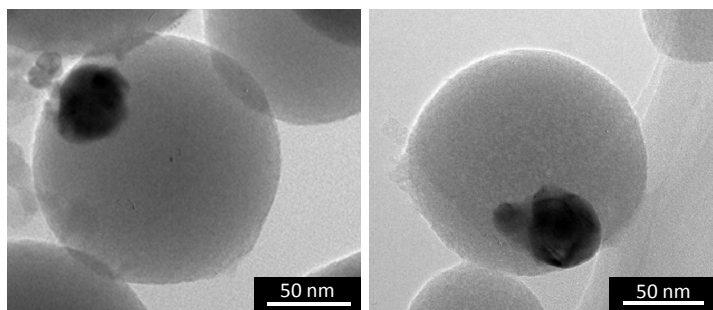

Fig. S6 TEM images of 40-nm Ag nanoparticles coated with TiO$_2$ shells. The Ag nanoparticles were synthesized following the method of Liu et al.[1] and the procedure for TiO$_2$ coating was the same as that of Au nanoparticles as described above. The growth of TiO$_2$ on the Ag cores was found to be anisotropic as well, forming eccentric Ag@TiO$_2$ nanostructures.

Reference

1. S. H. Liu, Z. H. Zhang and M. Y. Han, *Anal. Chem.*, 2005, **77**, 2595-2600.