

Electronic Supplementary Information

TiO₂ coated Au/Ag nanorods with enhanced photocatalytic activity under visible light irradiation

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Experimental Section

Chemicals and Materials

Hexadecyltrimethylammoniumbromide (CTAB) (98%), cetyltrimethylammonium chloride solution (CTAC) (25%), sodium borohydride (99%) and titanium-(triethanolaminato) isopropoxide ($\text{N}((\text{CH}_2)_2\text{O})_3\text{TiOCH}(\text{CH}_3)_2$, TTEAIP) in isopropanol (80%) were purchased from Sigma-Aldrich. Silver nitrate (AgNO_3) and L- (+) -ascorbic acid was purchased from Alfa Aesar. De-ionized water was used in all the experiments.

Synthesis of Gold nanorods (Au NRs):

Au NRs were prepared by using a previously reported seed-mediated growth method.¹⁻² The seed solution was first prepared by adding 250 μL of 0.01 M HAuCl_4 to 10 mL of 0.1M CTAB solution in a plastic tube. 0.6 mL of freshly prepared ice-cold 0.01 M NaBH_4 solution was quickly added and stirred for 2 min. The resulting brownish yellow solution was kept at room temperature for at least 2 h to be used as the seed solution. For seed-mediated growth, 2.0 mL of 0.01M HAuCl_4 and 0.4 mL of 0.01 M AgNO_3 were added into 40 mL of 0.1 M CTAB solution and mixed by gentle shaking. 0.32 mL of 0.1 M freshly prepared L- (+) -ascorbic acid solution,

0.8 mL of 1.0 M HCl, and 96 μ L of seed solution were then added into the mixture sequentially. The reaction mixture was left undisturbed at least 6 h for longitudinal overgrowth. Finally, CTAB capped Au NRs with longitudinal plasmon resonance band at 840 nm were obtained. The shorter Au NRs with longitudinal plasmon resonance band at 655nm also prepared following the same procedure by just changing the amount of 0.01 M AgNO₃ to 0.12 mL.

Synthesis of Au/Ag core-shell Nanorods (Au/Ag NRs):

Au/Ag core-shell NRs were prepared by using anisotropic silver shell formation on Au NRs in CTAC solution.³ The excess CTAB present the above prepared 840 nm Au NRs was first replaced with CTAC. Au NRs solution (2 mL) was centrifuged at 8000 rpm for 10 min and the obtained precipitate was re-dispersed in 2 mL of CTAC solution (80 mM). This procedure was repeated three times. 2 mL of the obtained solution was then diluted to 10 mL of CTAC (80 mM). 0.5 mL of L- (+) -ascorbic acid solution (100 mM) and 170 μ L of 0.01 M AgNO₃ were then added. The resultant mixture solution was placed in an oven at 60 °C for 3 h. The solution was subsequently cooled down to room temperature and centrifuged at 9000 rpm for 10 min. Finally the obtained Au/Ag core-shell NRs were re-dispersed in 2 mL of de-ionized water.

Characterization

The UV-visible extinction spectra were measured by using a Shimadzu UV 2550 spectrometer. Transmission electron micrograph (TEM) images were taken by using a JEOL 2010 electron microscope and high resolution TEM images were recorded using a Philips CM 300 FEGTEM. Scanning electron microscopy (SEM) images were taken on a JEOL_JSM6701F Scanning Electron Microscope.

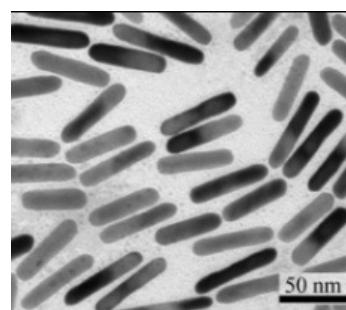


Fig. S1 TEM images of Au NRs with the averaged length and diameter of 60 and 15 nm, and aspect ratio of 4.

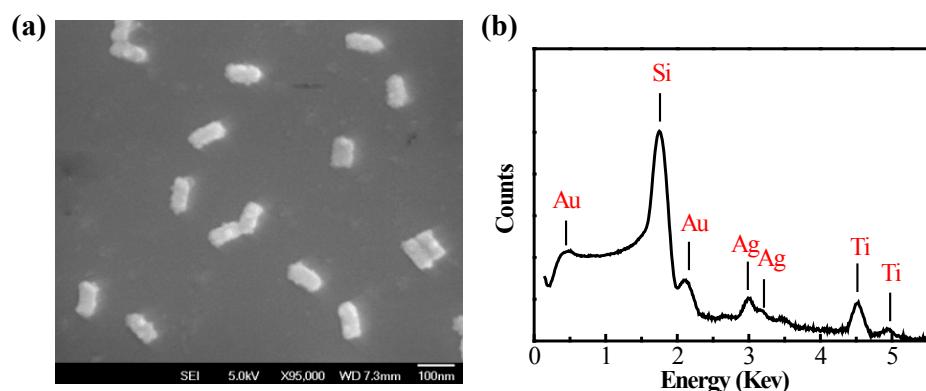


Fig. S2 SEM image (a) and EDS spectrum (b) of the Au/Ag/ TiO₂ composite nanoparticles.

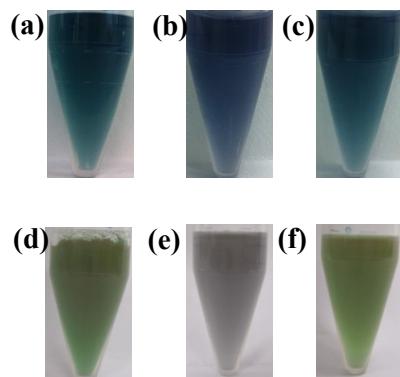


Fig. S3 Digital photographs of Au NRs in water (a) and ethanol (b), Au/TiO₂ composite nanoparticle in ethanol (c), Au/Ag core-shell NRs in water (e) and ethanol (f), and Au/Ag/TiO₂ composite nanoparticles in ethanol (g).

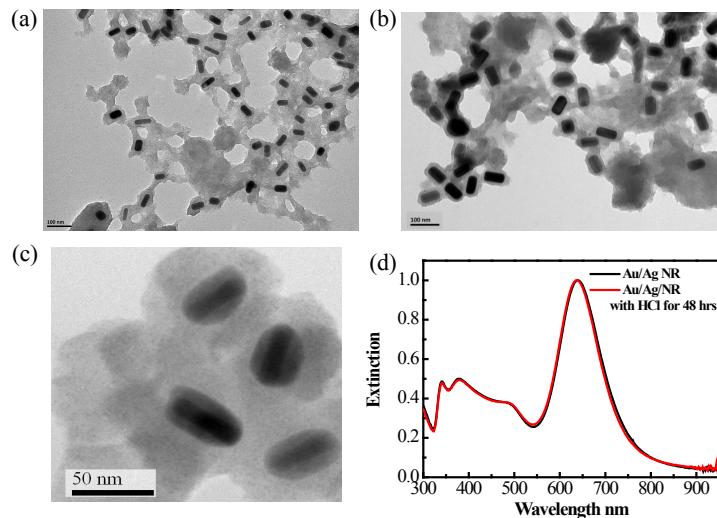


Fig. S4 (a, b) TEM images of Au/TiO₂ (a) or Au/Ag/TiO₂ (b) composite nanoparticles prepared with excess TTEAIP precursor. Addition of excess precursor led to formation of isolated TiO₂ nanoparticles instead of the increase of the TiO₂ shell. (c) A typical TEM image of Au/Ag/TiO₂ nanoparticles prepared in an ammonia environment, in which the Ag shell was partially etched by ammonia. (d) UV-vis extinction spectra of Au/Ag NRs before and after mixing with HCl under stirring for 48 hrs.

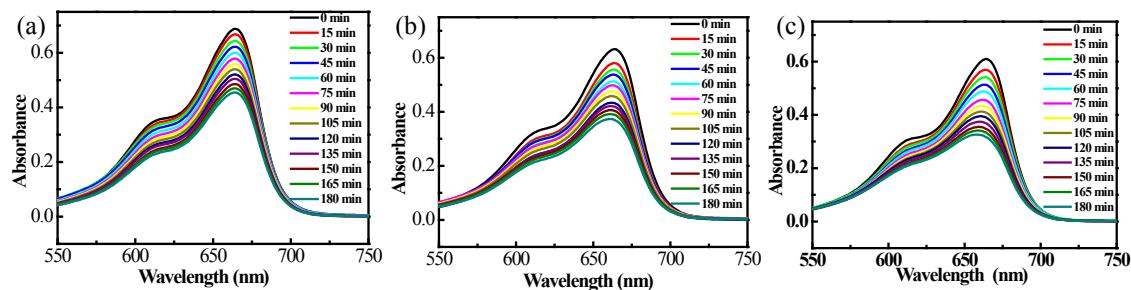


Fig. S5 UV-Vis absorption spectra of MB upon visible light (400-750 nm) irradiation for different time periods without any photocatalyst (a), in the presence of P25-TiO₂ (b) and Au/TiO₂ (c).

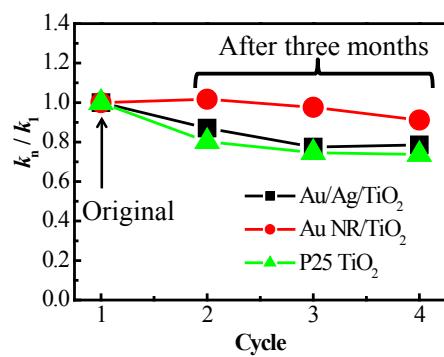


Fig. S6. The reusability test of photocatalytic activities of Au/Ag/TiO₂, Au/TiO₂ and P25-TiO₂ nanoparticles. k_n/k_1 represent the change in the photocatalytic activities of each cycle (every three hours) compared to those three months ago. The results show that the reusability of the prepared Au/Ag/TiO₂ and Au/TiO₂ nanoparticles are slightly better than the commercial P25-TiO₂.

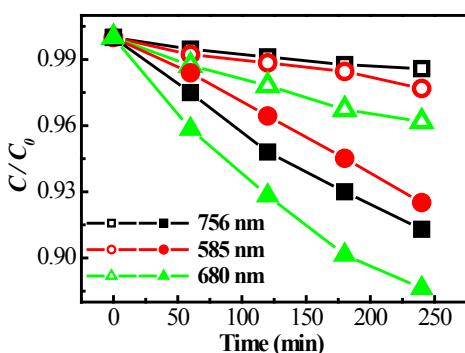


Fig. S7 Photolysis activities of MB (hollow symbols) and photo-catalytic activities of MB degradation using Au/Ag/TiO₂ composite nanoparticles as the photocatalyst (solid symbols) under light illumination of different wavelength.

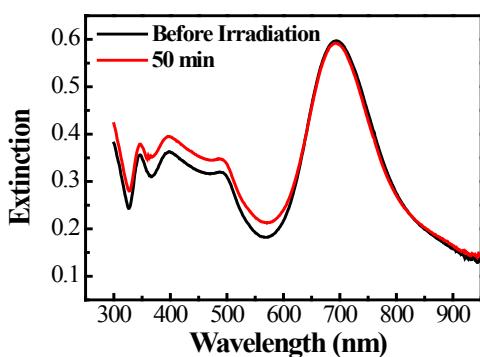


Fig. S8 UV-Vis extinction spectra of Au/Ag/TiO₂ composite nanoparticles before and after irradiation with 633 nm laser for 50 min. The increased intensity at the 350-600 nm range indicates the formation of Ag nanoparticles on the surface of Au/Ag/TiO₂ composite nanoparticles.

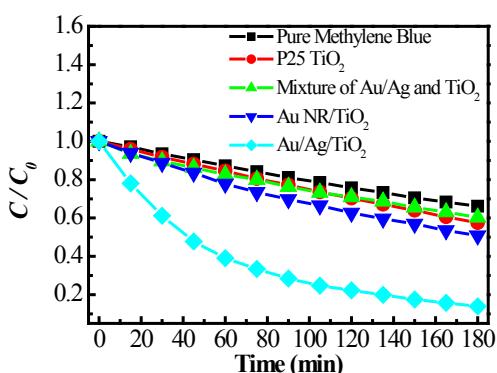


Fig. S9 Photo-degradation of MB under visible light irradiation in the absence and presence of photocatalysts (P25-TiO₂, Au/TiO₂, Au/Ag/TiO₂ or mixture of Au/Ag NRs and P25-TiO₂).

Reference:

- 1 B. Nikoobakht, M. A. El-Sayed, *Chem. Mater.* **2003**, *15*, 1957.
- 2 K. Yu, L. Polavarapu, Q.-H. Xu, *J. Phys. Chem. A* **2011**, *115*, 3820.
- 3 Y. Okuno, K. Nishioka, A. Kiya, N. Nakashima, A. Ishibashi, Y. Niidome,

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