

Supplementary Information for

**Functionalization of plasmonic Au/TiO₂ photocatalyst with Ag
co-catalyst for quantitative reduction of nitrobenzene to aniline in
2-propanol suspensions under irradiation of visible light**

Experimental procedure

Loading of 0.5 wt% Ag nanoparticles on TiO₂ (preparation of TiO₂-Ag) was performed by the PH method. TiO₂ powder was suspended in 10 cm³ of an aqueous solution of methanol (50 vol%) in a test tube and the test tube was sealed with a rubber septum under argon (Ar). An aqueous solution of silver(I) sulfate (Ag₂SO₄) as a metal source was injected into the sealed test tube and then photoirradiated for 1 h at $\lambda > 300$ nm by a 400-W high-pressure mercury arc (Eiko-sha, Osaka) with magnetic stirring in a water bath continuously kept at 298 K. The Ag source was reduced by photogenerated electrons and Ag was deposited on the surface of TiO₂ particles. Analysis of the liquid phase after photodeposition revealed that the Ag source had been almost completely (>99.9%) deposited on the TiO₂ particles. The resultant powder was washed repeatedly with distilled water and then dried at 310 K overnight under air.

Colloidal Au nanoparticles were prepared using the method reported by Frens.^{S1)} To 750 cm³ of an aqueous tetrachloroauric acid (HAuCl₄) solution (0.49 mmol dm⁻³), 100 cm³ of an aqueous solution containing sodium citrate (39 mmol dm⁻³) was added. The solution was heated and boiled for 1 h. After the color of the solution had changed from deep blue to deep red, the solution was boiled for a further 30 min. After cooling the solution to room temperature, Amberlite MB-1 (ORGANO, 60 cm³) was added to remove excess sodium citrate. After 1-h treatment, MB-1 was removed from the solution using a glass filter. Loading of 2.0 wt% Au particles on

the TiO₂-Ag samples was performed by the CPH method.^{8g)} A TiO₂-Ag sample (82 mg) was suspended in 20 cm³ of an aqueous solution of colloidal Au nanoparticles (0.085 mg cm⁻³) in a test tube and the test tube was sealed with a rubber septum under Ar. An aqueous solution of oxalic acid (50 μmol) was injected into the sealed test tube. The mixture was photoirradiated at λ>300 nm by a 400-W high-pressure mercury arc under Ar with magnetic stirring in a water bath continuously kept at 298 K. The resultant powder was washed repeatedly with distilled water and then dried at 310 K overnight under air. Ag-free samples (Au/TiO₂) were also prepared by the same method using bare TiO₂ samples. Hereafter, an Au-loaded TiO₂-Ag sample is designated as Au/TiO₂-Ag. Morphology of the samples was observed under a JEOL JEM-3010 transmission electron microscope (TEM) operated at 300 kV in the Joint Research Center of Kinki University.

The dried photocatalyst powder (50 mg) was suspended in a 2-propanol solution (5 cm³), bubbled with Ar, and sealed with a rubber septum. The suspension was irradiated with visible light of a 500 W xenon (Xe) lamp (Ushio, Tokyo) filtered with a Y-48 cut filter (AGC Techno Glass) (450-600 nm: 83 mW cm⁻²) with magnetic stirring in a water bath continuously kept at 298 K (Figure S1). The amounts of H₂ and CO₂ in the gas phase were measured using a Shimadzu GC-8A gas chromatograph equipped with an MS-5A column and Porapak QS column, respectively. The amounts of nitrobenzene and aniline in the liquid phase were determined with a Shimadzu GC-14B gas chromatograph equipped with a DB-1 capillary column (30 m, 0.25 mm). The amount of acetone in the liquid phase was determined with a Shimadzu GC-14A gas chromatograph equipped with a fused silica capillary column (HiCap-CBP20, 25 m, 0.22 mm). Toluene was used as an internal standard sample. The amounts of nitrobenzene, aniline and acetone were determined from the ratios of the peak areas of nitrobenzene, aniline and acetone to the peak area of toluene.

Results

Absorption spectra of TiO_2 , $\text{TiO}_2\text{-Ag}$, Au/TiO_2 and $\text{Au/TiO}_2\text{-Ag}$ samples are shown in Figure S1. Strong photoabsorption was observed at around 550 nm for the Au-loaded samples.

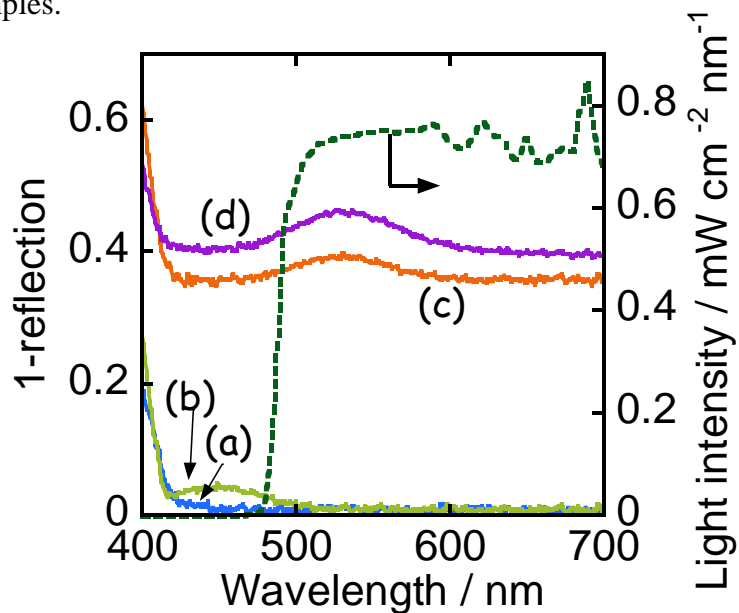


Figure S1 Absorption spectra of the (a) TiO_2 , (b) $\text{TiO}_2\text{-Ag}$, (c) Au/TiO_2 and (d) $\text{Au/TiO}_2\text{-Ag}$ samples and visible light irradiated to reaction systems from a Xe lamp with a Y-48 filter.

Results for nitrobenzene reduction under various conditions are summarized in

Table S1

Table S1 Reduction of nitrobenzene in 2-propanol suspensions of various photocatalysts under irradiation of visible light from a Xe lamp with a Y-48 cut filter in the absence of O₂^a

Entry	photocatalyst	^b Light intensity	Time	^c Conv.	^c Sel.
		/ mW cm ⁻²	/ h	/ %	/ %
1	Au/TiO ₂ -Ag	83	10	>99	>99
2	Au/TiO ₂	83	10	54	96
3	Au/TiO ₂ -Ag	0(dark)	10	trace	-
4	TiO ₂ -Ag	83	10	trace	-
5	TiO ₂	83	10	trace	-
6	non	83	10	trace	-

^aNitrobenzene: 75 μmol, photocatalyst: 50 mg, 2-propanol: 5cm³. ^bVisible light in the range of 450-600 nm. ^cDetermined by GC using the internal standard method.

References

S1) G. Frens, *Nat. Phys. Sci.* 1973, 241, 20–22.