

## Supporting Information for

**Very simple method for preparation of Au/TiO<sub>2</sub> plasmonic photocatalysts working under irradiation of visible light in the range of 600-700 nm**

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## **Experimental Section**

**Au colloid particles:** Colloidal Au nanoparticles were prepared using the method reported by Frens.<sup>1</sup> To 750 cm<sup>3</sup> of an aqueous tetrachloroauric acid (HAuCl<sub>4</sub>) solution (0.49 mmol dm<sup>-3</sup>), 100 cm<sup>3</sup> of an aqueous solution containing sodium citrate (39 mmol dm<sup>-3</sup>) 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 cm<sup>3</sup>) was added to remove excess sodium citrate. After 1-h treatment, MB-1 was removed from the solution using a glass filter.

**Colloid photodeposition with a hole scavenger (CPH)<sup>2</sup>:** TiO<sub>2</sub> powder (Degussa P25) calcined at 1273 K was used in most of the experiments as a supporting material for Au particles and is shown hereafter simply as TiO<sub>2</sub>. TiO<sub>2</sub> powder was suspended in 20 cm<sup>3</sup> of an aqueous solution of colloidal Au nanoparticles in a test tube, and the test tube was sealed with a rubber septum under argon (Ar). An aqueous solution (20 cm<sup>3</sup>) 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 (Eiko-sha, Osaka, Japan) 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. The content of Au was fixed at 1.0 wt%. The amounts of Au loaded on TiO<sub>2</sub> were determined by atomic absorption spectrometry after dissolving Au fixed on TiO<sub>2</sub> with aqua regia. Colloidal Au nanoparticles were almost quantitatively loaded on TiO<sub>2</sub> when CPH was used. The morphology of Au particles and Au/TiO<sub>2</sub> was observed under a JEOL JEM-3010 transmission electron microscope (TEM) operated at 300 kV in the Joint Research Center of Kindai University.

**Post-Calcination process:** Dried Au/TiO<sub>2</sub> powder was calcined at various temperatures (473, 773, 973 K) for 1 h in a box furnace. When the Au/TiO<sub>2</sub> samples obtained by calcination at various temperatures (X) were used, the temperature is shown in parentheses after Au/TiO<sub>2</sub>; for example, Au/TiO<sub>2</sub> calcined at 973 K and uncalcined Au/TiO<sub>2</sub> are designated as Au/TiO<sub>2</sub>(973) and Au/TiO<sub>2</sub>(uncal.), respectively. No change in the TiO<sub>2</sub> phase was observed (Figure S1).

**Photocatalytic reaction:** Dried Au/TiO<sub>2</sub> powder (50 mg) was suspended in distilled water (5 cm<sup>3</sup>) in a test tube. The aqueous mixture was bubbled with oxygen (O<sub>2</sub>) and the test tube was sealed with a rubber septum. Benzyl alcohol was injected into the suspension and then the suspension was irradiated with visible light from a Xe lamp with Y46 and R60 cut-off filters at 298 K. Spectra and light intensity of the Xe lamp with cut-off filters were determined by using a USR-45D spectroradiometer (Ushio, Tokyo). The amounts of benzyl alcohol and benzaldehyde 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 reaction solution (1 cm<sup>3</sup>) was added to diethyl ether/water (2/1 v/v, 3 cm<sup>3</sup>). Toluene was used as

internal standard (injection amount: 100  $\mu$ L; toluene/2-propanol, 50  $\mu$ L/5 mL). After the mixture had been stirred for 10 min, benzyl alcohol and benzaldehyde in the ethereal phase were analyzed. The amounts of benzyl alcohol and benzaldehyde were determined from the ratios of the peak areas of alcohol and aldehyde to the peak area of toluene.

### **References**

- 1) Frens, G. *Nat. Phys. Sci.* **1973**, *241*, 20-22.
- 2) Tanaka, A.; Ogino, A.; Iwaki, M.; Hashimoto, K.; Ohnuma, A.; Amano, F.; Ohtani, B.; Kominami, H. *Langmuir* **2012**, *28*, 13105-13111.

**Table S1** Photocatalyst systems for various reactions under irradiation of visible light.

Type	Photocatalyst	Working mechanism	Working wavelength	Ref. <sup>2)</sup>
1	N-TiO <sub>2</sub> , S-TiO <sub>2</sub>	anion doping	$\lambda < 500$ nm	2
	SrTiO <sub>3</sub> :Rh	cation doping	$\lambda < 540$ nm	
2	WO <sub>3</sub>	band-gap	$\lambda < 450$ nm	3
	BiVO <sub>4</sub>		$\lambda < 500$ nm	
	(Ga <sub>1-x</sub> Zn <sub>x</sub> )(N <sub>1-x</sub> O <sub>x</sub> )		$\lambda < 500$ nm	
	(CuGa) <sub>1-x</sub> ZnS <sub>2</sub>		$\lambda < 550$ nm	
3	C <sub>3</sub> N <sub>4</sub>	band-gap	$\lambda < 540$ nm	4
4	Cu <sup>2+</sup> /TiO <sub>2</sub>	IFCT <sup>1)</sup>	$\lambda < 450$ nm	5a
5	Rh <sup>3+</sup> /TiO <sub>2</sub>	sensitization	$\lambda < 450$ nm	5b
	organically modified TiO <sub>2</sub>		$\lambda < 500$ nm	6
6	Au/TiO <sub>2</sub>	Au plasmonic	$450 < \lambda < 600$ nm	7-13

<sup>1)</sup> IFCT: interfacial charge transfer

<sup>2)</sup> Reference of manuscript

**Table S2** Oxidation of benzyl alcohol in aqueous suspensions of various samples under irradiation from the Xe lamp with Y46 and R60 cut-off filters in the presence of O<sub>2</sub>

Entry	Photocatalyst	Cut filter	Time / h	Conv. / %	Sel. / %
1	Au/TiO <sub>2</sub> (uncal.)	Y46	5	76	> 99
2	Au/TiO <sub>2</sub> (uncal.)	Y46	10	> 99	> 99
3	Au/TiO <sub>2</sub> (uncal.)	R60	5	12	> 99
4	Au/TiO <sub>2</sub> (uncal.)	R60	10	25	> 99
5	Au/TiO <sub>2</sub> (973)	Y46	5	75	> 99
6	Au/TiO <sub>2</sub> (973)	Y46	10	> 99	> 99
7	Au/TiO <sub>2</sub> (973)	R60	5	46	> 99
8	Au/TiO <sub>2</sub> (973)	R60	10	91	> 99
9	Au/TiO <sub>2</sub> (uncal.)	dark	10	trace	-
10	Au/TiO <sub>2</sub> (973)	dark	10	trace	-
11	TiO <sub>2</sub>	Y46	10	trace	-
12	TiO <sub>2</sub>	R60	10	trace	-
13	non	Y46	10	trace	-
14	non	R60	10	trace	-

Benzyl alcohol: 50 μmol, Photocatalyst: 50 mg, Water: 5 cm<sup>3</sup>, O<sub>2</sub>: 1 atm

[Method for calculation of the material balance]

$$\text{Material balance} = \frac{\text{summation of benzyl alcohol and benzaldehyde}}{\text{Initial amount of benzyl alcohol}}$$

[Method for calculation of the rate of incident photons]

Light intensity: A [ $\text{W cm}^{-2}$ ] ( $W = \text{J s}^{-1}$ ), ( $1.0 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ )

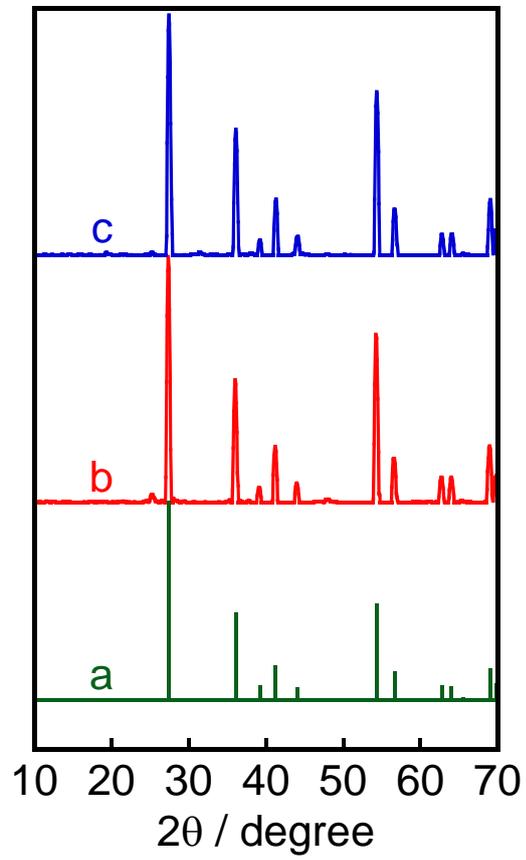
Irradiation area: B [ $\text{cm}^2$ ]

Center wavelength: C [nm] ( $1240/C \text{ [eV]}$ )

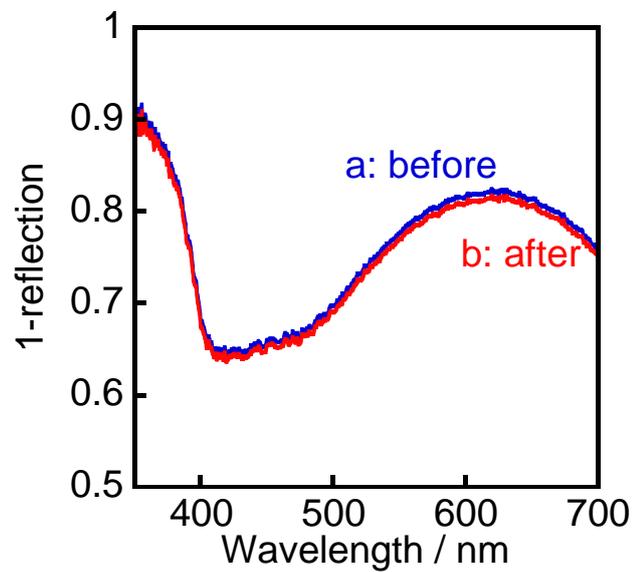
Avogadro's constant:  $6.022 \times 10^{23} \text{ [mol}^{-1}\text{]}$

**The rate of incident photons [ $\text{mol s}^{-1}$ ]**

$$= A \text{ [J s}^{-1} \text{ cm}^{-2}\text{]} \times B \text{ [cm}^2\text{]} \times \{(1240/C) \times 1.602 \times 10^{-19}\}^{-1} \text{ [J}^{-1}\text{]} \times (6.022 \times 10^{23})^{-1} \text{ [mol]}$$



**Figure S1** XRD patterns of various samples. (a) JCPDS No. 76-0317, (b) Au/TiO<sub>2</sub>(uncal.) and (c) Au/TiO<sub>2</sub>(973).



**Figure S2** Absorption spectra of Au/TiO<sub>2</sub>(973) (a) before and (b) after photocatalytic reaction.