

# Supplementary Information

## Photocatalytic Synthesis of Gold Nanoparticles Using TiO<sub>2</sub> Nanorods: A Mechanistic Investigation

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## Experimental Section

**Chemicals:** Tetrabutylorthotitanate (TBOT) was obtained from Fluka. Oleylamine, oleic acid, octadecene were purchased from Aldrich Chemical Co. Hydrogen tetrachloroaurate (III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.9+%) was purchased from Acros Organics. Ethyl alcohol (denatured) and toluene (99.8%) were obtained from Fisher Scientific. All chemicals were used as received without further treatment.

**Synthesis of  $\text{TiO}_2$  nanorods (NRs):**  $\text{TiO}_2$  NRs were synthesized using a high-temperature pyrolysis reaction. To an oleic acid (22 mL) solution pre-heated at 150 °C under vacuum for 1 hour and cooled down to room temperature, TBOT (3.5 mL) was injected under  $\text{N}_2$  flow. The mixture was then heated to 270 °C and kept at this temperature for 3 hours. Ethanol (40 mL) was added after the solution was cooled down to 80 °C. The resulting white precipitate was collected by centrifugation and washed with a toluene/ethanol mixture several times. The final product was re-dispersed in 20 mL of toluene to form a ~6 mg/mL dispersion.

**Photochemical Synthesis of Au Nanoparticles (NPs):** A stock solution of the gold source was prepared. 0.25 mM  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was mixed with 1ml oleylamine under vigorously stirred at room temperature in air for 1 hour. And then 2 mL toluene was added into the solution under vigorously stirred for another 1 hour formed the stock solution. In a typical synthetic approach, the total volume of the reaction solution is fixed at 3.00 mL. Typically, a 3.00 mL solution containing gold stock solution (1.50 mL),  $\text{TiO}_2$  NRs (6 mg/ml, 0.30 mL) and toluene (1.00 mL). The reaction vial was sealed by a Teflon faced rubber cap and the mixture was subsequently deaerated by gently purging with nitrogen for 15 min. Photochemical reduction was carried out by using a 6-W UV lamp (BLE-480B, Spectronics Corp.) positioned 10 cm from the reaction vial at 60 °C. Irradiation was typically performed for 30–300

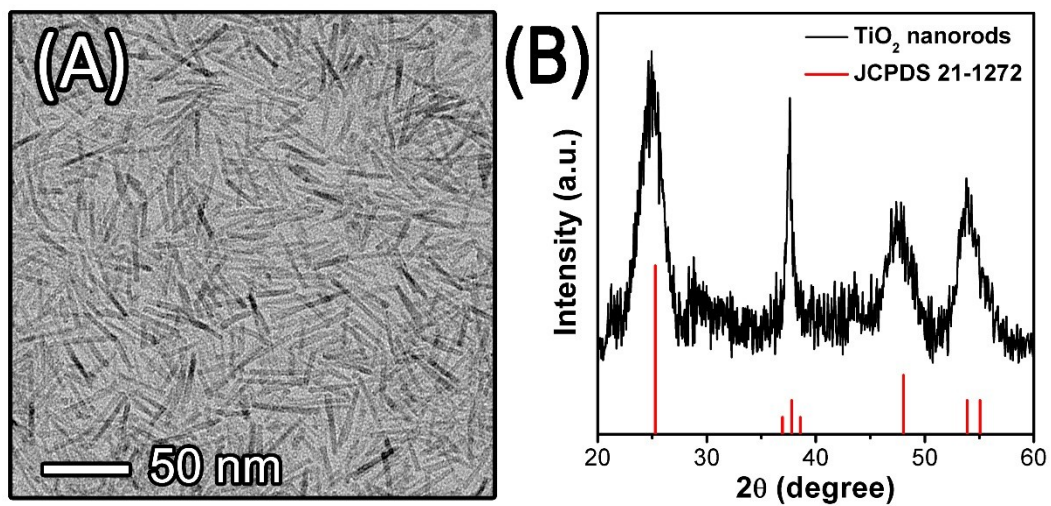
min. After the reaction completed, a red solution was obtained. The red product was precipitated by adding ethanol followed by centrifugation at 11,000 r.p.m. for 3 min. The precipitate was washed several times with ethanol and re-dispersed in toluene.

**Synthesis of Au NPs with size ~7.5 nm:** Briefly, 0.1 mM of  $\text{HAuCl}_4$  were dissolved in 1.5 ml oleylamine and 5 ml octadecene under vigorous magnetic stirring in  $\text{N}_2$  for 15 min, referred to as Solution A. After 6 mL of oleylamine, 6 mL of oleic acid and 20 ml octadecene were injected into a 50 mL Schlenk tube under magnetic stirring at 120 °C,  $\text{N}_2$  gas was introduced into the tube for 20 min to get rid of excess air. Subsequently, the Solution A was added into the aforementioned solution under vigorous magnetic stirring, and the mixed solution appeared to be transparent and red, indicating the formation of Au NPs. The resulting solution was kept steady at 120 °C for 30 min. After the reaction completed, a red solution was obtained. The red product was precipitated by adding ethanol followed by centrifugation at 11,000 r.p.m. for 3 min. The precipitate was washed several times with ethanol and re-dispersed in toluene.

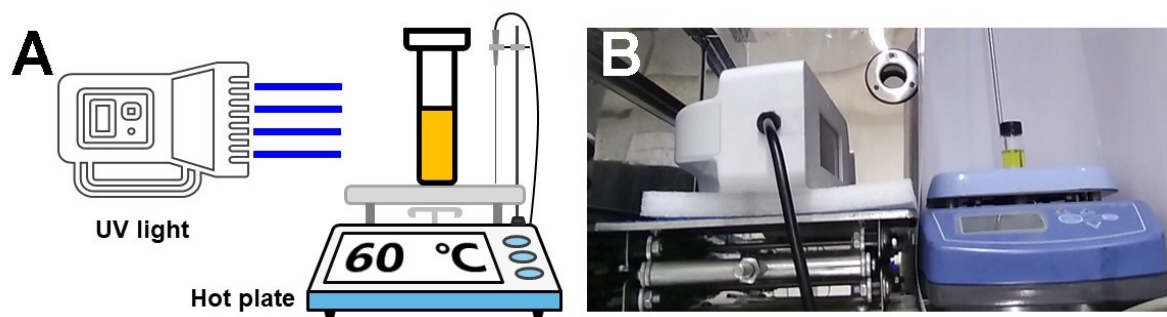
**Seeded growth of Au NPs:** A stock solution of the gold source was prepared. 0.25 mM  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was mixed with 1ml oleylamine under vigorously stirred at room temperature in air for 1 hour. And then 2 mL toluene was added into the solution under vigorously stirred for another 1 hour formed the stock solution. For the seeded growth of Au NPs, a 3.00 mL solution was prepared, containing gold stock solution (0.5 mL), Au seeds (~7.5 nm, 4 mg/ml, 0.1 mL), and 2.4 ml toluene. For photocatalytic assisted seeded growth, 0.3 ml  $\text{TiO}_2$  NRs in toluene (6 ml/ml) was added into the reaction system. For blank one, 0.5 ml pure toluene was added for comparison. The reaction vial was sealed by a Teflon faced rubber cap and the mixture was subsequently deaerated by gently purging with nitrogen for 15 min. Photochemical reduction was carried out by using a 6-W UV lamp positioned 10 cm from the

reaction vial at 60 °C. Irradiation was typically performed for 30–300 min. After the reaction completed, a red solution was obtained. The red product was precipitated by adding ethanol followed by centrifugation at 11,000 r.p.m. for 3 min. The precipitate was washed several times with ethanol and re-dispersed in toluene.

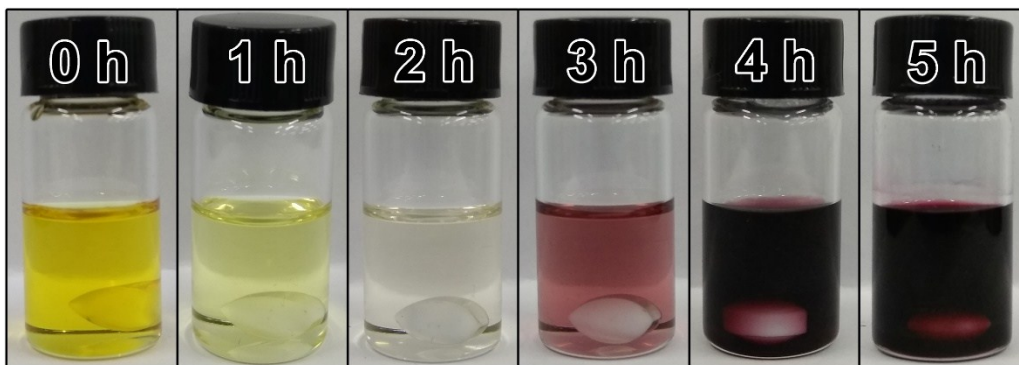
**Characterization:** The morphology of TiO<sub>2</sub> NRs and Au NPs were characterized by using a Tecnai T12 transmission electron microscope (TEM). HRTEM imaging was carried out on a FEI Tecnai G2 F30 transmission electron microscope. Powder X-ray diffraction (XRD) patterns were recorded with a Shimadzu XRD-6000 powder X-ray diffractometer, using Cu K $\alpha$  radiation ( $\lambda= 1.5406 \text{ \AA}$ ). A probe-type Ocean Optics HR2000CG-UV-NIR spectrometer was used to measure the UV-vis spectra of the reaction system to obtain the real-time spectra change during the formation of Au NPs.



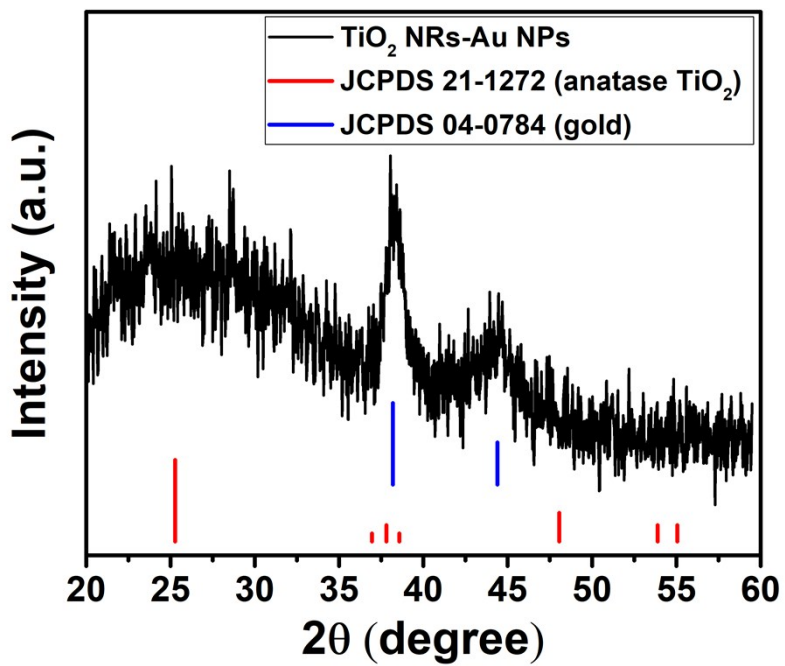
**Figure S1. Characterization of as-synthesized TiO<sub>2</sub> NRs.** (A) Low-magnification TEM image of TiO<sub>2</sub> NRs. (B) XRD pattern of TiO<sub>2</sub> NRs. The standard diffraction pattern of anatase TiO<sub>2</sub> (JCPDS No. 21-1272) is used as reference.



**Figure S2.** (a) Scheme and (b) real image of the experimental setup.



**Figure S3.** Images of the photocatalytic synthesis of Au NPs using TiO<sub>2</sub> NRs with reaction time from 0 hour to 5 hours.



**Figure S4.** XRD pattern of synthesized Au NPs using TiO<sub>2</sub> NRs as the photocatalyst. The standard diffraction patterns of anatase TiO<sub>2</sub> (JCPDS No. 21-1272) and *fcc* Au (JCPDS No. 04-0784) are used as reference.



**Table S1.** Reaction conditions for all samples mentioned in the main text.

	TiO <sub>2</sub> NRs	Temperature	UV light	Reaction time	Gold seeds
Sample 1	1.8 mg	60 °C	365 nm	1-5 hours	-
Sample 2	1.8 mg	25 °C	365 nm	1-5 hours	-
Sample 3	1.8 mg	60 °C	-	1-5 hours	-
Sample 4	0.5 mg	60 °C	365 nm	0.5-5 hours	-
Sample 5	2.4 mg	60 °C	365 nm	0.5-5 hours	-
Sample 6	12.0 mg	60 °C	365 nm	0.5-5 hours	-
Sample 7	1.8 mg	55 °C	365 nm	1-6 hours	-
Sample 8	1.8 mg	60 °C	365 nm	1-5 hours	-
Sample 9	1.8 mg	65 °C	365 nm	1-3 hours	-
Sample 10	-	60 °C	365 nm	0-6 hours	0.4 mg
Sample 11	1.8 mg	60 °C	365 nm	0-6 hours	0.4 mg

**Table S2.** Summary of some reported photocatalytic syntheses of Au NPs by using TiO<sub>2</sub> nanomaterials.

TiO <sub>2</sub> nanomaterials	Gold precursor	Light source	Reaction time	Size of Au nanoparticles	Refence
TiO <sub>2</sub> film	HAuCl <sub>4</sub> in water	UV light (1 mW cm <sup>-2</sup> )	> 1 hour	5-20 nm	<i>J. Am. Chem. Soc.</i> , 2005, 127, 7632
Degussa P-25	HAuCl <sub>4</sub> in water-methanol solution	Hg lamp (400 w)	-	non-uniform nanoparticles	<i>Chem. Commun.</i> , 2009, 241-243
TiO <sub>2</sub> powder	HAuCl <sub>4</sub> in water-methanol solution	Hg lamp (400 w)	-	non-uniform nanoparticles	<i>Phys. Chem. Chem. Phys.</i> , 2010, 12, 2344
Degussa P-25	AuCl <sub>3</sub> in ethanol-water solution	W lamp (200 W)	2 hours	non-uniform nanoparticles	<i>Int. J. Hydrog. Energy</i> , 2014, 39, 3617
TiO <sub>2</sub> powder	HAuCl <sub>4</sub> ·4H <sub>2</sub> O in water-methanol solution	Xe lamp (300 W)	3 hours	non-uniform nanoparticles	<i>Appl. Catal. B</i> , 2012, 115-116, 294
TiO <sub>2</sub> powder	HAuCl <sub>4</sub> in water-isopropanol solution	Hg lamp (400 W)	6 hours	10-100 nm	<i>J. Phys. Chem. C</i> , 2009, 113, 12840
Degussa P-25	HAuCl <sub>4</sub> ·3H <sub>2</sub> O in water	UV-C lamp (Philips, TUV 4W)	5 hours	non-uniform nanoparticles	<i>J. Mol. Catal. A</i> , 2007, 263, 32
TiO <sub>2</sub> nanosheets	KAuCl <sub>4</sub> in water-ethanol solution	Xe lamp (250 W)	1 hours	8-70 nm	<i>Appl. Surf. Sci.</i> , 2015, 347, 275
TiO <sub>2</sub> nanorods	HAuCl <sub>4</sub> in water	Xe lamp (150 W)	30-180 min	3-30 nm	<i>Small</i> , 2006, 2, 413
TiO <sub>2</sub> microspheres	HAuCl <sub>4</sub> ·4H <sub>2</sub> O in water	Xe lamp (300 W)	10 min	-	<i>J. Mater. Chem.</i> , 2011, 21, 9079
Degussa P-25	HAuCl <sub>4</sub> in water	UV lamp (16 W)	10-60 min	1.3-2.4 nm	<i>Int. J. Hydrog. Energy</i> , 2009, 34, 8912
TiO <sub>2</sub> nanobelts	HAuCl <sub>4</sub> ·3H <sub>2</sub> O in water	Hg lamp (400 W)	6 hours	-	<i>Appl. Surf. Sci.</i> , 2019, 467-468, 1076
Degussa P-25	NaAuCl <sub>4</sub> ·H <sub>2</sub> O in water	Hg(Xe) lamp (200 W)	30 min	5.5-9.3 nm	<i>J. Phys. Chem. C</i> , 2015, 119, 24750
Commercial TiO <sub>2</sub> catalyst	HAuCl <sub>4</sub> ·3H <sub>2</sub> O in water	Hg lamp (400 W)	6 hours	-	<i>Appl. Catal. B</i> , 2014, 147, 439
Sulphated TiO <sub>2</sub>	HAuCl <sub>4</sub> in water	Hg lamp (400 W)	6 hours	non-uniform nanoparticles	<i>J. Photochem. Photobiol. A</i> , 2011, 217, 275
TiO <sub>2</sub> powder	HAuCl <sub>4</sub> in water-isopropanol solution	UV lamp (300 W)	15-240 min	non-uniform nanoparticles	<i>Appl. Catal. A</i> , 2011, 397, 112
Degussa P-25	HAuCl <sub>4</sub> ·4H <sub>2</sub> O in water-methanol mixed solution	Hg lamp (400 W)	30 mins	-	<i>Nanoscale</i> , 2015, 7, 13477