

Gold-plasmon enhanced solar-to-hydrogen conversion on the {001} facets of anatase TiO₂ nanosheets

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EXPERIMENTAL

Catalyst preparation. The synthesis of anatase TiO₂ nanosheets with dominated {001} facets was performed by a solvothermal method reported in literature¹. In a typical experimental procedure, 25 mL of Ti(OBu)₄ and 3.525 mL of hydrofluoric acid solution (40 wt%) were mixed in a 100 mL beaker by magnetic stirring for 1 h, and then transferred into a dried Teflon-liner stainless steel autoclave with a volume of 100 mL. The autoclave was kept at 180 °C for 24 h in an electric oven. After reaction and being cooled to room temperature, the white powder was harvested by high-speed centrifugation and washed with ethanol and distilled water for several times. The resulting solid was checked by XRD and TEM to be anatase TiO₂ single-crystal nanosheets.

The Au/anatase TiO₂ nanosheet photocatalysts were synthesized by a simple oleylamine (OLA) reduction method. 1.0 g of as-prepared anatase TiO₂ nanosheets were firstly dispersed in 50 mL of distilled water, and then mixed with 1.0 mL of OLA and 10 mg/mL of HAuCl₄ aqueous solution by magnetic stirring for 2 h at 50 °C. The suspension was finally filtered and dried at 70-100 °C overnight. The as-synthesized solid samples were denoted as Au/TiO₂-x (x represents Au loading). The Au loading is inductively coupled plasma optical emission spectroscopy (ICP-OES).

Catalyst Characterization. XRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. HRTEM images were obtained by a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. EPR spectra were recorded by a Bruker A-300-EPR X-band spectrometer. Photocurrent was measured using the conventional three-electrode electrochemical cell with a working electrode, a platinum foil counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was immersed in a sodium sulfate electrolyte solution (0.2 M) and irradiated with different lights. The light/dark short circuit photocurrent response was recorded with a BAS Epsilon workstation.

Electrochemical characterization. The Au/TiO₂ particulate film electrodes were prepared by

applying 50 μL of Au/TiO₂ slurry to the surface of an optically transparent electrode and covering approximately 0.25 cm². The Au/TiO₂ slurry was prepared by mixing 0.1 g Au/TiO₂ powder and 1 g ethanol. The electrode was then dried on a warm plate. Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and Ag/AgCl electrode (3 M KCl) as the reference electrode. The working electrode was prepared by spreading the slurries over 0.25 cm² of indium tin oxide (ITO) glass substrate. Then the film was dried in air. The electrochemical measurement was carried out in a Na₂SO₄ (0.2 M) electrolyte, which was purged with nitrogen gas for 2 h prior to the measurements. A 500 W xenon lamp (Beijin Changtuo, CHF-XM500) fitted with a (420 nm) cut-off filter and several bypass filters was used as the light source. All electrochemical potentials are reported vs. NHE.

Photocatalytic Activity Testing. The photocatalytic activities for hydrogen evolution under visible light irradiation were performed in a closed gas-recirculation system equipped with a top-irradiation Pyrex reaction vessel. 0.1 g of the catalyst was suspended in 80 ml of water containing 0.5 g of ethylenediaminetetraacetic acid disodium salt (EDTA) by a magnetic stirrer in Pyrex reaction vessel. The above suspension was evacuated 30 min to remove air prior to irradiation under a 300 W xenon lamp with a cut-off filter ($\lambda \geq 420$ nm). The evolved hydrogen gas was circulated with a gas pump and quantified by gas chromatography (Shimadzu GC-8A, TCD, Ar carrier).

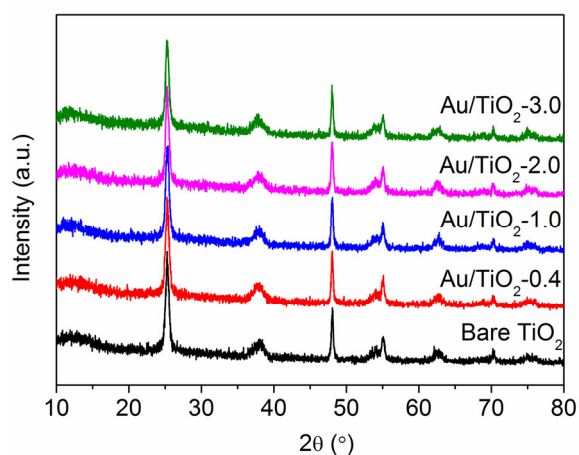


Fig. S1 XRD patterns of bare TiO₂ and Au/TiO₂-x (x denoted as percentage content of gold).

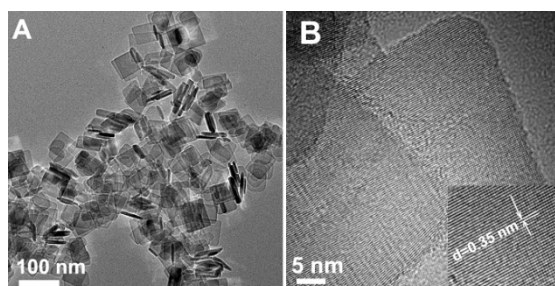


Fig. S2 TEM (A) and HRTEM (B) images of the as-synthesized anatase TiO₂ nanosheets.

TEM analysis in Fig. S2A indicates the synthesized anatase TiO₂ possess well-defined sheet-shaped structures with rectangular outline, a side length of 50-80 nm, and a thickness of 5-8 nm. HRTEM image in Fig. S2B shows the established interplanar space of about 0.35 nm, agrees with the d_{101} spacing in the XRD pattern (Fig. S1). According to the symmetry of anatase TiO₂¹⁻³, the top and bottom planes of the nanosheets are corresponding to the {001} facets. Based on the TEM results, the percentage of exposed {001} facets on the TiO₂ nanosheets is ca. 75%, in consistence with literature¹.

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(3) Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. *Nature*, **2008**, *453*, 638-641.

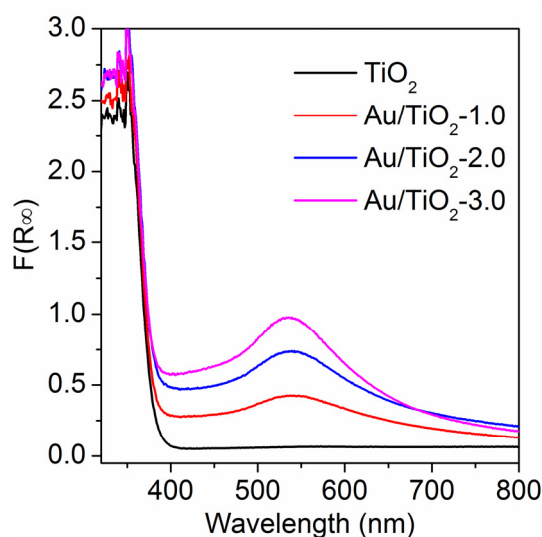


Fig. S3 UV-Vis DRS spectra of gold-supported anatase TiO₂ nanosheets.

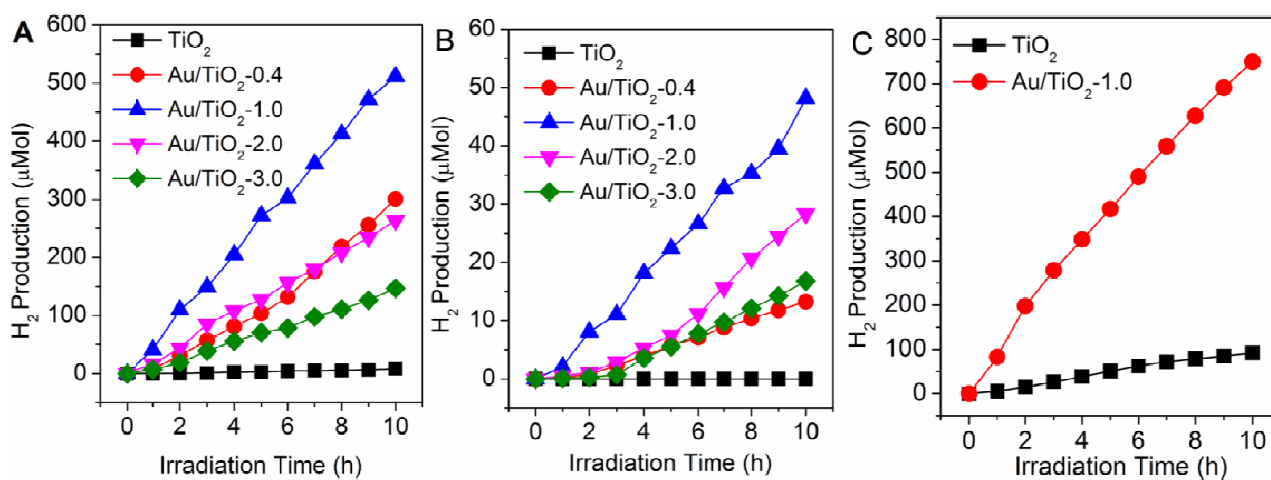


Fig. S4 H₂ production of Au/TiO₂-x (x= 0.4, 1.0, 2.0 and 3.0) as a function of irradiation time under solar light irradiation (A), >420 nm visible light irradiation (B), and 365 nm UV light irradiation (C).

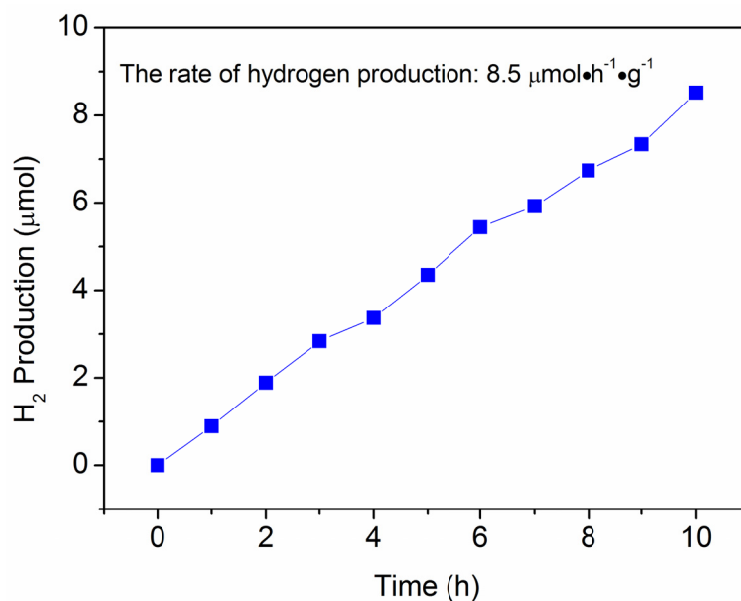


Fig. S5 H₂ production of the reference photocatalyst, P25 TiO₂ with 1.0 wt% loading of Au NPs, as a function of irradiation time under > 420 nm visible light.

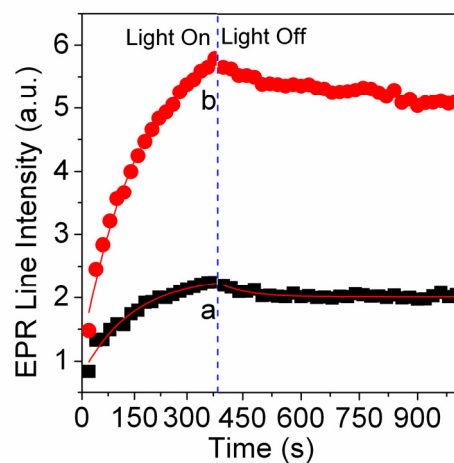


Fig. S6 Intensity decay of the ESR line at $g = 2.004$ (a) and 1.989 (b) as a function of irradiation time.