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Engineering TiO_2 nanosheets with exposed (001) facet via the incorporation of Au clusters for boosted photocatalytic hydrogen production

Xiaobin Liu,[a] Huaqiang Zhuang,*[b] Jiale Huang,[c] Wentao Xu,[b] Liqin Lin,[b] Yanmei Zheng,*[c] Qingbiao Li*[a,c]

[a]College of the Environment & Ecology, Xiamen University, Xiamen 361005, P. R. China

[b]College of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, P. R. China

[c]Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

E-mail: huaqiangz@163.com, zym@xmu.edu.cn, kelqb@xmu.edu.cn

Experimental

1. Catalyst preparation

TiO_2 nanosheets with exposed (001) facets: The TiO_2 nanosheets were prepared via our previous report.[1] In a typical preparation process, 25 mL $Ti(OBu)_4$ and 3.525 mL hydrofluoric acid solution (40 wt%) were mixed under vigorously stirring for 1h，then the mixture was transferred into 100 mL Teflon-lined stainless steel autoclave and was kept at 180 °C for 24 h in an electric oven. After reaction process, Teflon-lined stainless steel autoclave was cooled to room temperature, white product was washed by ethanol and deionized water for several times.

Au clusters: Au-GSH nanoclusters were prepared as following steps, 2.32 mL $HAuCl_4$ aqueous solution (the concentration of Au was 10 mg/ml) and 4.6 mL glutathione (GSH) aqueous solution (10 mg/ml) were added into 43.08 mL deionized water. The mixed solution was kept stirring for 1h at room temperature until the solution became colorless. Subsequently, the solution was continuously stirred for 24 h at 70℃ in a water bath. The as-obtained Au-GSH was purified by adding acetonitrile into Au-GSH solution (3:1, volume ratio) to recrystallize the clusters. Finally, the Au-GSH was re-dispersed in deionized water to prepare the 1 mg/mL Au-GSH aqueous solution, and stored in a refrigerator at 4 °C for further use.

Au-clusters/TiO_2 nanosheets: The 1 mg/mL Au-GSH aqueous solution was prepared by the above method. 0.7 g TiO_2 nanosheets mixed with 70 mL deionized water in a beaker were constantly stirred for 1h. Subsequently, 7 mL Au-GSH aqueous solution was added into the above suspension solution and continuously stirred for another 24 hours. After that, the as-prepared Au-clusters/TiO_2 nanosheets (denoted as Au/TiO_2-001) were washed with distilled water, and then dried in a vacuum oven at 60 °C for 12 hours. In addition, the TiO_2-101 sample using the commercial anatase TiO_2

(99%, 5 nm APS powder) is regarded as a reference sample. The Au/TiO_2-101 sample following the above steps was prepared, the only difference is that the TiO_2 nanosheets were replaced by the commercial anatase TiO_2. Au particles/TiO_2-001 nanosheets were prepared via a typtical photodeposition strategy. The 1 mL of $HAuCl_4$ (10 mg/mL) and 1 g of TiO_2-001 sample were added into 100 mL mixed solution with 5 mL of methanol and 95 mL of deionized water. Then, the system was slowly evacuated of the air by a vacuum pump until the solution of the glass reaction cell basically kept stable. Subsequently, the suspension was then irradiated for 3 hours under simulated solar light. Finally, the as-obtained Au particles/TiO_2-001 nanosheets was dried at 60 °C for 24 h in an electric oven.

2. Characterization of samples

XRD plots were measured on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å), using a voltage of 40 kV, a current of 40 mA, and a scanning rate of 0.02°/s from 10° to 80° (2θ). HRTEM images were obtained by a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The morphologies of as-prepared samples were examined by field emission scanning electron microscopy (FE-SEM, S4800, Hitachi, Japan). UV-vis DRS spectra were taken on a Varian Cary 500 Scan UV-vis-NIR spectrometer with $BaSO_4$ as the reference. X-ray photoelectron spectroscopy (XPS) was also performed using a Thermo VG ESCALAB 250 instrument equipped with a micro-focused, monochromatic A1 Kα X-ray source and a magnetic lens. The X-ray spot size was 500 μm (15 kV, 200 W). The spectra were acquired in the constant analyzer energy mode with pass energy of 20 eV for the general survey and the narrow scans. All binding energies were referenced to the C 1s peak at 284.6 eV of surface adventitious carbon.

3. Photoelectrochemical measurement

Photocurrent was measured using the conventional three-electrode electrochemical cell with a working electrode, a platinum foil counter electrode and an Ag/AgCl electrode as reference electrode. The working electrode was fabricated on the FTO glass: 10 mg of sample was mixed with 0.5 ml ethanol with continuous stirring for 3 h to get slurry. Then, 20 μL of slurry was spreading onto FTO glass, which side part was previously protected by Scotch tape, and the electrode was dried at room temperature for 24 h. In the experiment, the three electrodes were immersed in a sodium sulfate electrolyte solution (0.5 M) and the working electrode was irradiated by the visible light irradiation ($\lambda \geq 420$ nm). The light/dark short circuit photocurrent response and electrochemical impedance spectroscopy (EIS) experiment were recorded with the electrochemical workstation (CHI 660E).

4. Photocatalytic activity measurement

The photocatalytic hydrogen evolution experiments were performed in a relatively vacuum system allocated an external glass reaction cell. In this typical experiment, 0.1 g photocatalyst and 0.2 g EDTA-2Na used as the sacrificial reagent was suspended in 100 mL of aqueous solution by magnetic stirring and the temperature of the glass reaction cell was sustained at about 5 ℃ by circulating water. Prior to the reaction procedure, the whole system was slowly evacuated of the air by a vacuum pump until the solution of the glass reaction cell basically kept stable. In order to completely remove the system air, the evacuation was sustained 10 min and finally the blank sample was injected into the gas chromatograph to define whether the air was completely removed. The suspension was then irradiated under simulated solar light or visible light irradiation ($\lambda \geq 420$ nm). The evolved hydrogen gas was circulated with a micro diffusion pump in this system and its amount was determined by an online gas chromatograph (SHIMADZU GC-8A, TCD, Ar carrier).

Table S1. The Energy Dispersive Spectrometer (EDS) parameters of Au/TiO_2-001 sample.

Element	Weight %	Atomic %	Uncertainty %	Detector Correction	k-Factor
C(K)	10.643	26.879	0.225	0.173	6.279
O(K)	18.886	35.806	0.152	0.514	1.980
Si(K)	0.709	0.766	0.024	0.977	1.000
Ti(K)	25.039	15.856	0.129	0.985	1.299
Cu(K)	42.690	20.377	0.199	0.997	1.757
Au(L)	2.030	0.312	0.088	0.753	5.950

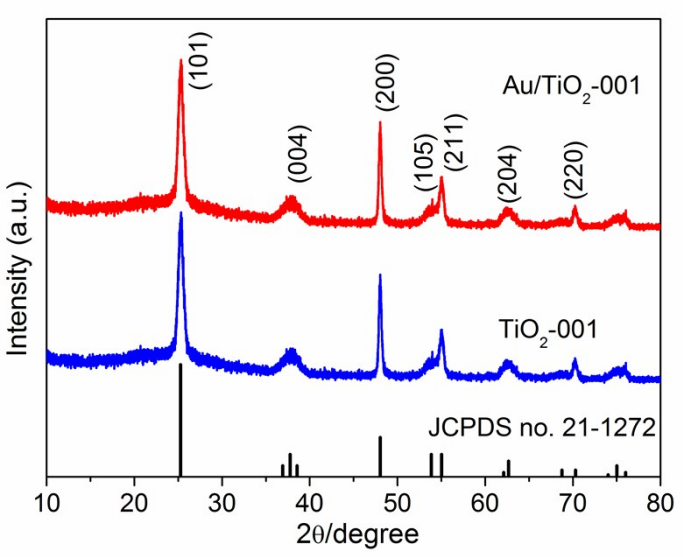

Figure S1 The XRD pattern of TiO_2-001 and Au/TiO_2-001 nanosheets.

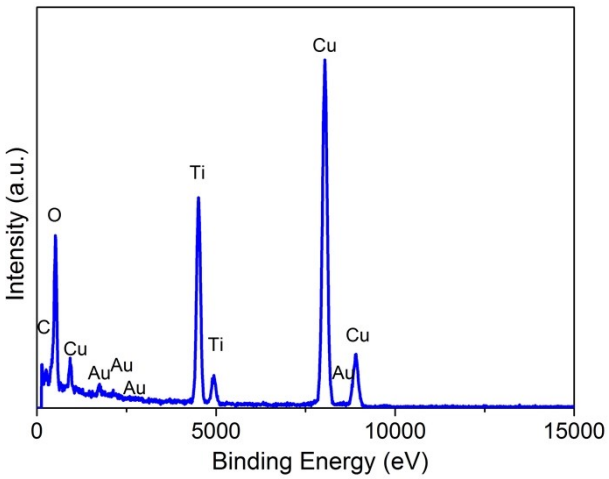

Figure S2 EDS pattern of Au/TiO_2-001 nanosheets.

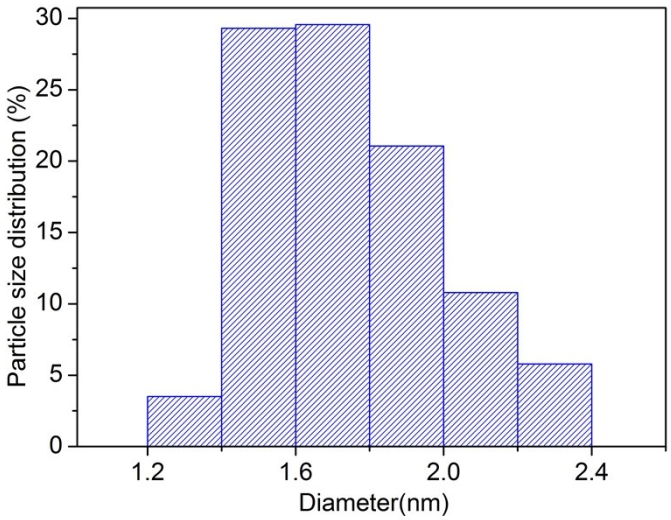

Figure S3 Particle size distrubution of Au on the surface of TiO_2 nanosheets.

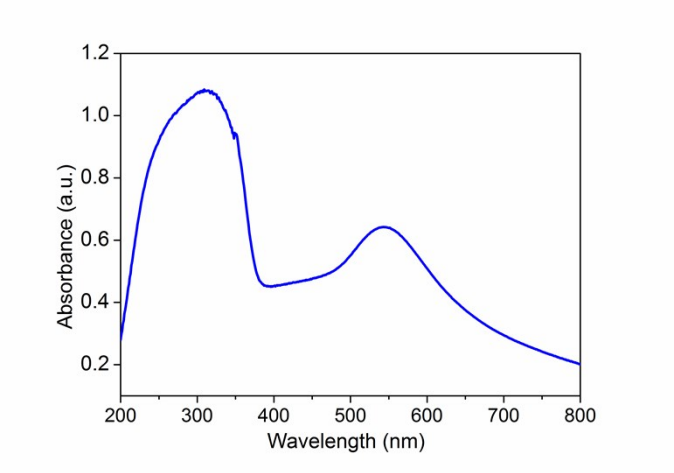

Figure S4 DRS measurement of Au particles/TiO_2-001 nanosheets.

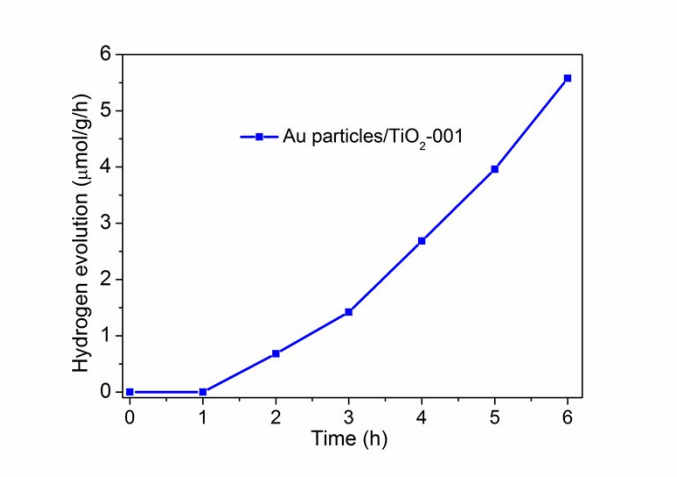

Figure S5 Hydrogen production rate of Au particles/TiO_2-001 nanosheets under visible light irradiation.

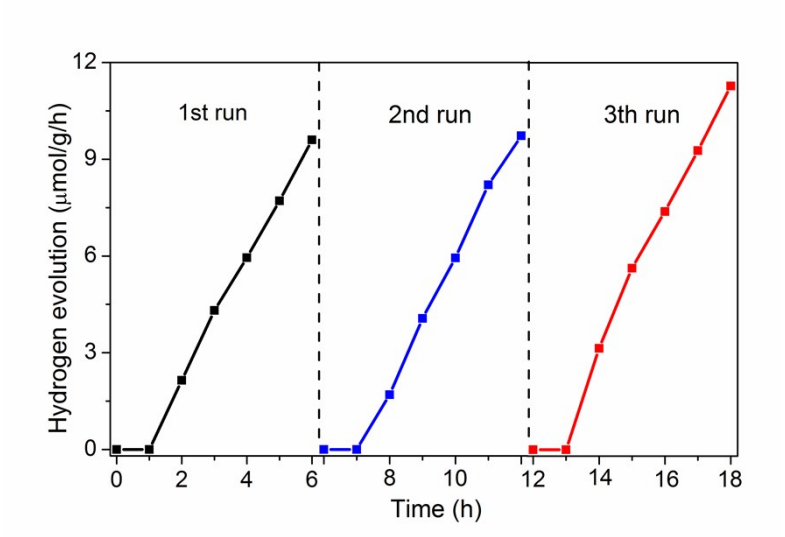

Figure S6 Long-term stability test of hydrogen evolution rate over Au/TiO_2-001 nanosheets under visible light irradiation.

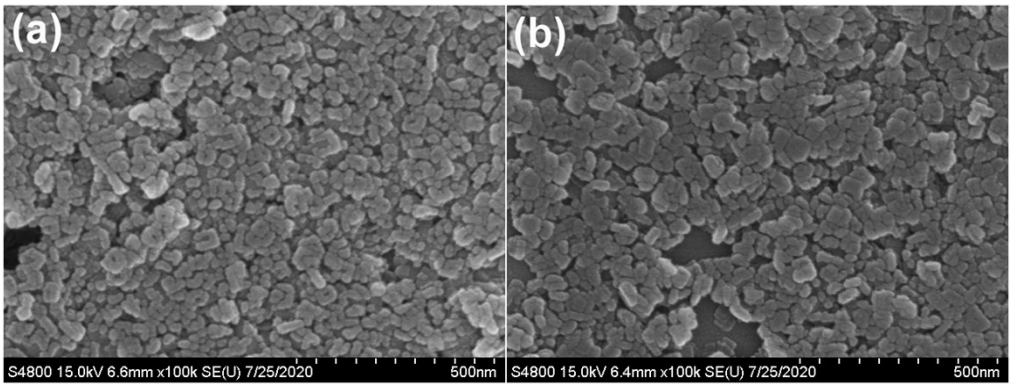

Figure S7 SEM images of Au/TiO_2-001nanosheets before (a) and after (b) photocatalytic reaction.

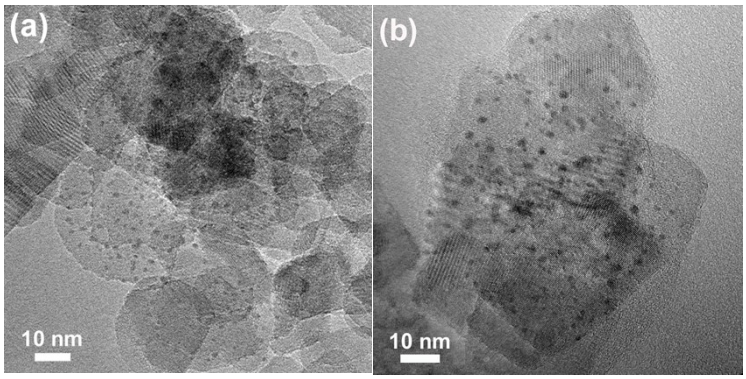

Figure S8 TEM images of Au/TiO_2-001 nanosheets before (a) and after (b) photocatalytic reaction.

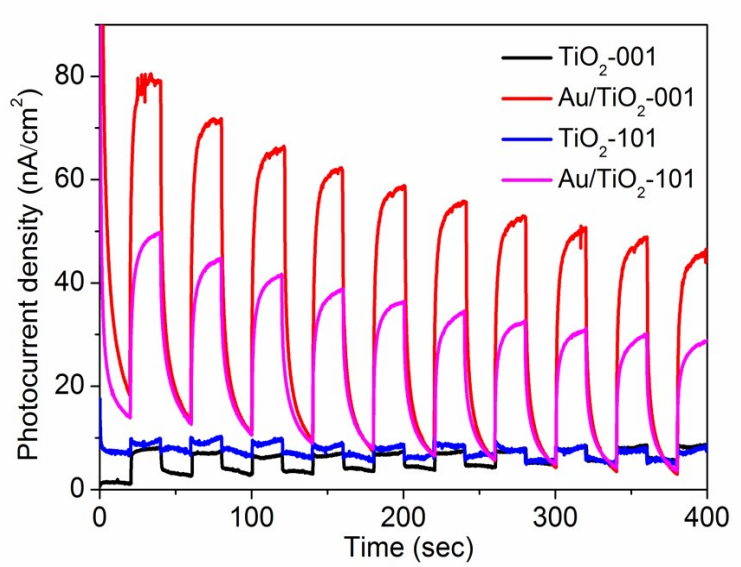

Figure S9 Transient photocurrent responses of TiO_2-101, Au/TiO_2-101, TiO_2-001 and Au/TiO_2-001 samples conducted under visible light irradiation.

[1] Zhuang H, Chen W, Xu W, Liu X (2020) Facile synthesis of MoS_2 QDs/TiO_2 nanosheets via a self-assembly strategy for enhanced photocatalytic hydrogen production. Int J Energy Res 44:3224-3230