Supporting Information

Tuning the Size of Photo-deposited Metal Nanoparticles via

Manipulating Surface Defect Structures of TiO₂ Nanocrystals

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Experimental Section

1. Catalyst Preparation

1.1 Synthesis of Anatase $TiO_2\{001\}^1$ and $TiO_2\{100\}^2$ Nanocrystals.

Anatase TiO₂{001} nanocrystals were prepared by a hydrothermal procedure. Typically, 25 mL Ti(OBu)₄ and 3 mL HF aqueous solution (40 wt.%) were mixed under stirring at RT. (Caution: Hydrofluoric acid (HF) is extremely corrosive and a contact poison, and it should be handled with extreme care! Hydrofluoric acid solution is stored in Teflon containers in use.) The solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180°C for 24 h. The resulted white precipitate was collected by centrifugation, washed repeatedly with ethanol and water, and dried at 70°C for 12 h. The acquired powder was dispersed in 1000 mL NaOH aqueous solution (0.1 mol/L), stirred for 24 h at RT, centrifuged, and washed repeatedly with water until the pH value of aqueous solution was 7-8.

Anatase TiO₂{100} nanocrystals were prepared following Liu et al.'s procedure. Typically, 6.6 mL TiCl₄ was added dropwise into 20 mL HCl aqueous solution (0.43 mol/L) at 0°C. After being stirred for an additional 0.5 h, the solution was added dropwise into 50 mL NH₃ aqueous solution (5.5 wt.%)under stirring at RT. Then the pH value of the solution was adjusted to between 6 and 7 using 4 wt.% NH₃ aqueous solution, after which the system was stirred at RT for 2 h. The resulted precipitate was filtered, washed repeatedly with water until no residual Cl⁻ could be detected, and then dried at 70°C for 12 h to acquire Ti(OH)₄ precursor. 2.0 g Ti(OH)₄ and 0.5 g $(NH_4)_2SO_4$ were dispersed in a mixture of 15 mL H₂O and 15 mL isopropanol under stirring at RT; then the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 24 h. The obtained white precipitate was collected and washed repeatedly with water.

1.2 Photodeposition for preparing Au/TiO₂, Ag/TiO₂ and Pt/TiO₂ Catalysts.³

In the PD method, 200mg TiO₂ powder and desired amounts of (Au content of 0.2%, 0.5%, 1% and 3%) Au precursor(HAuCl₄) were dispersed in a 150 mL aqueous solution of 3% v/v methanol in a flask, with subsequent irradiation under a 300W Xenon (Xe) lamp in Ar atmospher with stirring for 0.5 h. The suspension was centrifuged, dried at 333 K for 12 h. The acquired catalysts are signed as 0.2%-3% Au/TiO₂{100} and 0.2%-3% Au/TiO₂{001}.

For Ag and Pt photodeposition, 200mg TiO₂ powder and precursor (AgNO₃ and H₂PtCl₆, metal content was 1%) were dispersed in a 150 mL aqueous solution of 3% v/v methanol in a flask, with subsequent irradiation under a 300W Xenon (Xe) lamp in Ar atmospher with stirring for 0.5 h. The suspension was centrifuged, dried at 333 K for 12 h. The acquired catalysts are signed as 1% Ag/TiO₂{100} and 1% Ag/TiO₂{001}, 1% Pt/TiO₂{100} and 1% Pt/TiO₂{001}.

1.3 Lighting treatment for TiO₂.

200mg TiO₂ powder were dispersed in a 150 mL aqueous solution of 3% v/v methanol in a flask, with subsequent irradiation under a 300W Xenon (Xe) lamp in Ar

atmospher with stirring for 0.5 h. The suspension was centrifuged, dried at 333 K for 12 h. The acquired catalysts are signed as $TiO_2\{100\}$ -light and $TiO_2\{001\}$ -light.

1.4 High-temperature calcination treatments.

High-temperature calcination treatments of anatase TiO_2 nanocrystals were carried out by heating the TiO_2 nanocrystals in a quartz tube to the desired temperature at a rate of 2°C/min under a Ar gas flow (30 mL/min) or a H₂ gas flow (30 mL/min) at atmospheric pressure and then continuing the reduction process for 2h. The acquired catalysts are signed as $TiO_2\{100\}$ -400Ar, and $TiO_2\{001\}$ -300Ar.

2. Sample Characterizations

The loadings of Au on the catalysts were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). BET specific surface areas were measured using a Micromeritics Tristar II 3020M system and the sample was degassed at 180 °C under nitrogen before the measurement. Powder X-ray diffraction (XRD) patterns were recorded in the 2 θ at range 20°-80° on a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) operating at 40 kV and 50 mA. Transmission electron microscopy (TEM) and HADDF were performed with a JEOL JEM-2100F instrument at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high-performance electron spectrometer using monochromatized Al K α (h = 1486.7 eV) as the excitation source, and the likely charging of samples was corrected by setting the C 1s binding energy of the adventitious carbon to 284.8 eV. Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL JES-FA200 EPR spectrometer(9.063 GHz, X-band) at 130 K with employed microwave power, modulation frequency, and modulation amplitude of 0.998 mW, 100 kHz, and 0.35 mT, respectively. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained on a Shimadzu DUV-3700 spectrophotometer equipped with an integrating sphere attachment. The zeta potential was measured using a Zetasizer Nano ZS instrument (Malvern, U. K.). The positron annihilation lifetime spectroscopy (PALS) experiments were carried out with a fast-fast coincidence ORTEC system with a time resolution of ~200 ps. A 30 μ Ci source of ²²Na was sandwiched between two identical samples, and the total count was 3 million. All the spectra were analyzed by the LIFETIME9 program.

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) study measurements of CO adsorption were performed on a Nicolet 6700 FTIR spectrometer equipped with an in situ low-temperature and vacuum DRIFTS reaction cell (Harrick Scientific Products, Inc.) to enhance the chemisorption with minimum interference of gas-phase molecules. The DRIFTS spectra were measured with 256 scans and a resolution of 4 cm⁻¹ using an MCT/A detector. A 50 mg amount of catalyst was loaded on the sample stage of the reaction cell. Prior to adsorption experiments, the samples were degassed at a base pressure of 0.01 Pa and cooled to the desirable temperature, whose spectra were taken as the background spectra. CO was then admitted into the reaction cell to desirable pressures via a leak valve, and the DRIFTS spectra were recorded after the chemisorption reaches the steady state.

3. Photocatalytic Reaction Test

Photocatalytic hydrogen production experiments (Experiments in photocatalytic water reduction to produce hydrogen) were performed in a top-irradiation Pyrex flask. A 300 W simulated solar light (full wavelength 300-1100 nm) (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the light source. Typically, 50 mg photocatalysts were dispersed in 120 mL 20% volume methanol aqueous solution under magnetic stirring. Prior to the irradiation, the reaction mixture was deaerated repeatedly with Ar gas for 45 min to thoroughly remove air and dissolved oxygen. A cooling-water jacket was used to keep the photocatalytic reaction temperature at 25°C. To evaluate the photocatalytic hydrogen production, the gas-phase composition of the photocatalytic reactor was analyzed every hour by extracting 0.5 mL gas into a GC-14C gas chromatograph equipped with a column of 5 Å molecular sieves and employing the Ar carrying gas.



Figure S1. Zeta potentials of $TiO_2\{100\}$ and $TiO_2\{001\}$ as a function of pH values of aqueous solution.



Figure S2. UV-vis DRS spectra of TiO₂ nanocrystals.



Figure S3. The plots of modified Kubelka-Munk function versus the photon energy of $TiO_2\{100\}$ and $TiO_2\{001\}$.



Figure S4. XRD patterns of various TiO₂ and Au/TiO₂ catalysts.



Figure S5. Positron annihilation lifetime spectra of various TiO_2 and Au/TiO_2 catalysts. The channel width is 10.4 ps.



Figure S6. Ti 2p and O 1s XPS spectra of various Au/TiO₂ catalysts: (A and C) $TiO_2\{100\}$ and Au/TiO₂ $\{100\}$; (B and D) $TiO_2\{001\}$ and Au/TiO₂ $\{001\}$.



Figure S7. *In-situ* DRIFTS spectra of CO chemisorption on various Au/TiO₂ catalysts and TiO₂-light nanocrystals at 123 K and $P_{CO} = 200$ Pa. (A) TiO₂{100}-light and 0.2%, 0.5% Au/TiO₂{100}; (B) TiO₂{001}-light and 0.2%, 0.5% Au/TiO₂{001}.



Figure S8. HAADF-STEM images of (A) 1 % Au/TiO₂{100} and (B) 1% Au/TiO₂{100}-400Ar, (C) 1 % Au/TiO₂{001} and (D) 1% Au/TiO₂{001}-300Ar.



Figure S9. HAADF-STEM images of (A) 1% Ag/TiO₂{100} and (B) 1%Ag/TiO₂{001}, (D) 1% Pt/TiO₂{100} and (E) 1% Pt/TiO₂{001}. Metal nanoparticles size distributions of (C) 1% Ag/TiO₂{100} and 1% Ag/TiO₂{001}, (F) 1%Pt/TiO₂{100} and 1% Pt/TiO₂{001}.



Figure S10. TEM images of (A) 1% Ag/TiO₂{100} and (B) 1% Ag/TiO₂{001}; (C) 1% Pt/TiO₂{100} and (D) 1% Pt/TiO₂{001}.



Figure S11. Photocatalytic H₂ evolution profiles of $TiO_2\{100\}$, $TiO_2\{001\}$, 1% Au/TiO₂{100}, 1% Au/TiO₂{100}-400Ar and 1% Au/TiO₂{001}.



Figure S12. (A) S 2p XPS spectra of TiO₂{100}, (B) F 1s XPS spectra of TiO₂{001}, (C and D) Cl 2p XPS spectra of various Au/TiO₂ catalysts.

TiO ₂ nanocrystals	BET (m^2/g)	Surface isoelectric points	Bandgap energy (eV)
TiO ₂ {100}	99	5.2	3.02
$TiO_{2}\{001\}$	102	4.7	3.09

Table S1. BET, isoelectric points and bandgap energy of TiO₂ nanocrystals.

Au/TiO ₂ catalysts	Size Distributions (nm)	Au content (wt.%)
0.2% Au/TiO ₂ {100}	4.7±1.4	0.25
0.5% Au/TiO ₂ {100}	4.8±2.9	0.55
1% Au/TiO ₂ {100}	25.5±9.7	1.3
3% Au/TiO ₂ {100}	186.7±123.2	3.5
0.2% Au/TiO ₂ {001}	2.9±1.4	0.13
0.5% Au/TiO ₂ {001}	4.1±1.4	0.45
$1\sqrt[6]{6}$ Au/TiO ₂ {001}	6.6±1.9	0.9
3% Au/TiO ₂ {001}	18.5±7.5	2.8

Table S2. Au particle-size distributions and Au content.

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