Supporting information

Reduced TiO₂ rutile nanorods with defined facet and their visible-light photocatalytic activity

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Chemicals and Materials.
TiCl₃ (15%~20%), chloroplatinic aci, zinc powder and rutile TiO₂ nanoparticles with ~ 30 nm in diameter (Rutile NPs) were purchased from Aladdin Reagent Company. Isopropanol and Methanol were purchased from Beijing Chemical Reagent Company. All chemicals were used without further purification.

Synthesis of Reduced TiO₂.
In a typical synthesis, 1 mL of TiCl₃ (15%~20%) and Zn powder (0.5-2.5mmol) were mixed with isopropanol (30 mL). The resulting solution was stirred about 30 min, and then transferred into a 50 mL Teflon-lined stainless-steel autoclave. Subsequently, the autoclave was sealed and heated at 180 °C for 6 h. After being naturally cooled to room temperature, the precipitate was collected, washed with 4M HCl aqueous solution for several times, and dried at 75°C.

Non-reduced TiO₂ rutile nanorods (rutile NRs) were prepared from the reduced TiO₂ rutile nanorod via calcination at 450 °C for 30min in air.

Photocatalytic Activity Measurements.
The photocatalytic activities of samples were evaluated by photocatalytic H₂ generation. A photocatalyst (0.1 g) loaded 1 wt.% Pt was added into aqueous methanol solution (30 vol%, 120 mL) in the cell and then magnetically stirred during the whole photocatalytic testing. The light source was a 300-W Xe lamp (Beijing Perfectlight Technology Co. Ltd). An optical filter, (UV-400, Newport Corp.; or UV-420, CE Aulight. Inc.) was used to cut off the short wavelength part (< 400 or
420 nm). The evolved gases were detected in situ by using an online gas chromatograph (GC-2014C, Shimadzu) equipped with a thermal conductivity detector (TCD).

**Characterization.** The crystalline structure was recorded by using an X-ray diffractometer (XRD) (Bruker AXS D8 Focus), using Cu Kα radiation (λ = 1.54056 Å). Transmission electron microscope (TEM) images were taken using an FEI Tecnai G2 operated at 200 kV. Scanning electron microscope (SEM) images were measured on a JEOL JSM 4800F. The UV–Vis absorption spectra were recorded on a UV-3600 UV–vis–NIR scanning spectrophotometer (Shimadzu). X-Ray photoelectron spectra were obtained on a Thermo Scientific ESCALAB 250 Multitechnique Surface Analysis. The electron paramagnetic resonance (EPR) spectra were recorded at 100K on a Bruker A-200 EPR spectrometer. The Brunauer–Emmett–Teller (BET) specific surface area was measured using a Micromeritics Gemini V Surface Area and Pore Size Analyzer.

![Label A: Clorite (Oxidation levels: 38.86, 78.86, 34.83, 1.14, 3.84, 0.72)](image)

**Fig. S1.** The EDAX results of reduced TiO₂.
Fig. S2 TiO$_2$ obtained from hydrothermal reaction

Fig. S3. X-ray diffraction (XRD) pattern of TiO$_2$ prepared by solvothermal reaction without Zn powder.
Fig. S4. The plot of transformed Kubelka-Munk function vs the energy of reduced TiO$_2$ obtained with 1.5 mmol Zinc powder and pure rutile TiO$_2$. 
Fig. S5. The full XPS spectrum of reduced TiO$_2$. 
Fig. S6. The SEM images of reduced TiO\textsubscript{2} obtained with different amount of Zn powder. (A 0.5mmol, B 1.0mmol, C 1.5mmol, D 2.0mmol).
Fig. S7. The N\textsubscript{2} adsorption-desorption isotherms and BET surface area of reduced TiO\textsubscript{2} obtained with different amount of Zn powder.
Fig. S8 Time courses of H$_2$ production from reduced TiO$_2$ loaded with 0.5% Pt in 20% methanol/ water under Xeon lamp (300W) without (A) and with (B) UV-400 cut-off filter illumination. (C) H$_2$ production rate for reduced TiO$_2$ prepared from different amount of Zn powder under visible light ($\lambda > 400$ nm). (D) Cycling tests of photocatalytic activity of reduced TiO$_2$ prepared from 1.5 mmol Zn powder under visible light ($\lambda > 400$ nm).
Fig. S9 The possible mechanism of reduced TiO₂ for H₂ production.