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Supporting Information

Hydrogen Evolution Based on the Electrons/Protons Stored on Amorphous TiO₂

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Section S1. Experimental Section

Materials. All chemicals were of analytical purity and received from Shanghai Chemical Company without further purification and were used as received without further purification. The chemicals used for the mobile phase of HPLC–MS detection included HPLC grade methanol and acetonitrile from Dikma Chemical (China) and Mill-Q ultrapure water.

Preparation of Ti(OCH₂CH₂O)₂(TG). The TG precursor was prepared by the following procedures reported previously. Typically, titanium n-butoxide (3 mL) as the titanium source was added to ethylene glycol (30 mL) and the mixture was heated at 160 °C for 2 h. After cooling down to room temperature, the white TG precipitate was washed several times with ethanol and dried naturally at room temperature.

Synthesis of Amorphous TiO₂. The prepared TG (0.5 g) was dispersed in water (100 mL) in a water-cooled quartz cylindrical cell and the solution was exhausted by using nitrogen for 30min, then subject to the simulated sunlight (a 500 W Xe lamp) irradiation for 5h. During the irradiation process, the color of solid sample turned from white (TG) to intense blue (reduced porous TiO₂). After irradiation, the solid product was separated from the mixture and dried in vacuum for further characterization.

Synthesis of MoS₂. 7 mmol sodium molybdate dihydrate (Na₂MoO₄·2H₂O) and 35 mmol thiourea (Mo:S ratio =1:5) were dissolved in 40 mL distilled water under vigorous stirring, then the pH was adjusted to 3 with 2 M HCl. After being stirred for 30 min, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, maintained at 200 °C for 24 h and allowed to cool down to room temperature naturally. The obtained products were collected by centrifugation, wash with distilled water and ethanol, and dried at 60 °C for 12 h.

Synthesis of TiO₂/MoS₂. The prepared TiO₂ (0.1 g) was dispersed in water (35 mL), then 5.0 mg sodium molybdate dihydrate (Na₂MoO₄·2H₂O) and 10.0 mg thiourea was added the suspension, After being stirred for 30 min, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, maintained at 200 °C for 24 h and allowed to cool down to room temperature naturally.

Storing of Electrons. The prepared amorphous TiO_2 was dispersed in ethylene glycol water (10:90 v/v %) solution and the solution was exhausted with nitrogen for 30 min, then subject to the simulated sunlight (a 500 W Xe lamp) irradiation for 1h. During the irradiation, we observed the same phenomenon that color of solution changed, as **Synthesis of Amorphous TiO**₂ described, meaning that electrons were stored on the surface of amorphous TiO₂.

Titration of the stored electrons. Quantitative analysis of the electron accumulation was performed through titration, in which the 1 mM orange-yellow potassium dichromate ($K_2Cr_2O_7$) acted as the titrating solution. When $K_2Cr_2O_7$ was added in the solution that included stored electrons, the stored electrons reacted with $K_2Cr_2O_7$ and consumed absolutely when the blue fade away. Thus, the number of the stored electrons (n(e)) and $K_2Cr_2O_7(n(K_2Cr_2O_7)))$ would satisfy the following relationship: n(e) =1/6n($K_2Cr_2O_7$), according to the chemical equation (eq1).

$$Cr_2O_7^{2-} + 6e^- + 7H_2O \rightarrow 2Cr^{3+} + 140H^-$$

The transfer of electron and proton. The MoS_2 was dispersed in the reaction vessel and the solution was exhausted with nitrogen for 30 min, then the MoS_2 was injected into the solution which included the stored electrons. At last, the H₂ was detected after the stir of mixture for 1 h. As for different amorphous TiO₂, the mass ratio of MoS_2 and amorphous TiO₂ was still kept at 3.0%.

Section S2. Characterization Section

Characterization methods. Powder XRD patterns were collected on a Rigaku D/MAX-2550V diffractometer at 30 kV and 15 mA (Co K α radiation). TEM analysis was performed using a JEOL 2100F electron microscope operated at 200 kV. The UV-vis absorption spectras were measured on a UV-vis spectrophotometer (Hitachi U-3010). The H₂ produced in the reactor was analyzed by a GC (Tianmei 7890II) equipped with a thermal conductivity detector (TCD).



Figure S1. Powder X-ray diffraction patterns of TG (red line) and TiO_2 (black line).



Figure S2. Powder X-ray diffraction patterns of MoS₂.



Figure S3. (a)TEM and (b) HRTEM images of MoS_2 .



Raman Shift (cm⁻¹)

Figure S4. Raman spectra showing the characteristic E_{2g}^1 and A_{1g} vibrational modes of MoS₂. Inset: the atomic vibration manners of the E_{2g}^1 and A_{1g} vibrational modes.



Figure S5. TEM of (a) TiO_2 +MoS₂ and (b) TiO_2 /MoS₂.



Figure S6. The light absorbance of TiO_2/MoS_2 (black line) and TiO_2+MoS_2 (red line).



Figure S7. Time courses of H_2 evolution from ethylene glycol solution (10 vol%, 100 mL) on TiO₂ + MoS₂ with different MoS₂:TiO₂ ratio. 20 mg catalyst in the reaction system, and 500 W Xe lamp as the light source.



Figure S8. Powder X-ray diffraction patterns of TiO₂+3%MoS₂ (a) before the H₂ production and (b) after PCET cycle and HER process.



Figure S9. The light absorbance of $TiO_2+3\%MoS_2$ (a) before the H_2 production and (b) after PCET cycle and HER process.