

Supporting Information

Graft of lacunary Wells-Dawson heteropoly blue on the surface of TiO₂ and its photocatalytic activity under visible light

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Experimental section

Materials and synthesis of α -K₆P₂W₁₈O₆₂·9H₂O (P₂W₁₈) and α ₂-K₁₀P₂W₁₇O₆₁·15H₂O (P₂W₁₇): Chloroplatinic acid (H₂PtCl₆·6H₂O), glycerol were of analytical grade and used without further purification. Pt was deposited on the TiO₂ surface by the photo-deposition method,^{S1} which was confirmed by TEM and XPS as shown in Fig. S1. As shown in Fig. S1a, the platinum nanoparticles, as the electron sink, are identified as small dark dots on the surface of TiO₂, which were used for acceleration of HPB formation. The size of particle is in the range of 3~8 nm. Fig. S1b shows the narrow scan of Pt (4f) core level of XPS of Pt (loaded on TiO₂) synthesized by a photo-deposition method. The spectrum shows a doublet containing a low energy band (4f_{7/2}) at 71.1 eV, and a high energy band (4f_{5/2}) centered at 74.4 eV, which is 3.3 eV higher than the low-energy

band. The lower-energy band centered at 71.1 eV ($4f_{7/2}$) agrees well with the literature values.^{S2} The results confirm that Pt exists mainly in the form of Pt(0).

α -K₆P₂W₁₈O₆₂·9H₂O (P₂W₁₈) and α ₂-K₁₀P₂W₁₇O₆₁·15H₂O (P₂W₁₇) were prepared according to literature methods^{S3} and confirmed by FT-IR spectrum (Fig. S2a and S2b). IR of P₂W₁₈ (cm⁻¹): 1091 ($\nu_{as}(P-O_a)$), 959 ($\nu_{as}(W-O_d)$), 912 ($\nu_{as}(W-O_b-W)$), 802 ($\nu_{as}(W-O_c-W)$). IR of P₂W₁₇ (cm⁻¹): 1086, 1052, 1017 ($\nu_{as}(P-O_a)$), 942, 914 ($\nu_{as}(W=O_d)$), 881 ($\nu_{as}(W-O_b-W)$), 801, 727 ($\nu_{as}(W-O_c-W)$). IR peak positions of these heteropoly acids were in agreement with those in the literature.^{S4-S6} TG: very low heating rate to avoid overflowing of the material during dehydration; water content $x = 9$ for P₂W₁₈ and 15 for P₂W₁₇ calculated according to Fig. S3a and S3b. Anal. Calcd for K₆P₂W₁₈O₆₂: K, 5.09; P, 1.35; W, 71.98. Found: K, 4.98; P, 1.43; W, 71.72. Anal. Calcd for K₁₀P₂W₁₇O₆₁: K, 8.56; P, 1.36; W, 68.64. Found: K, 8.37; P, 1.28; W, 69.01 (dried to constant weight at 400 °C. According to result of TG/DTG/DTA, decomposition temperature of P₂W₁₈ is 580 °C and P₂W₁₇ is 508 °C).

Photocatalytic experiments and photoelectrochemical measurements:

Photocatalytic experiments were performed in a Pyrex cell (ca. 140 cm³) having a flat window ca. 10.2 cm² for irradiation. The cell was sealed with a silicone rubber septum. A 250 W high pressure Hg lamp and a 300

W halogen lamp were used as the UV-light source and the visible light source for photocatalytic reaction, respectively. The visible light source was equipped with a cut-off filter (Toshiba Y 44.2, $\lambda > 420$ nm) to remove radiation below 420 nm and to ensure irradiation by visible light only. The term quantum efficiency was measured using a 450 W xenon light source with band pass filters of different wavelengths and calculated as follows: term quantum efficiency (%) = $(2 \times \text{no. of photo-generated H}_2 / \text{total no. of absorbed photons}) \times 100$.

Typically, 50 mg of 0.5 wt % Pt/TiO₂ photocatalyst and amount of HPA were suspended in 80 mL 10 (v/v) % glycerol aqueous solutions by a magnetic stirrer. Glycerol was employed as the electron donor. Argon gas was bubbled through the reaction mixture for 40 min to remove oxygen and the suspension of the catalyst was achieved by ultrasonic prior to irradiation. HPB was obtained under UV light irradiation at room temperature, then the UV light was turned off and the reaction was continued under visible light irradiation or in the dark. The H₂ evolved by reduction of water with reduced HPA have been deducted.

P₂W₁₇ or P₂W₁₈ adsorption onto TiO₂ is completed in 10 min at controlled pH value by ultrasonic mixing without template and precursor. Photoelectrochemical characterization of the samples was performed using a three-electrode configuration with P₂W₁₇-Pt/TiO₂ as the working photo-electrode, saturated calomel electrode (SCE) as a reference

electrode, and platinum foil as a counter electrode. The photocatalyst films on ITO glad slide used as the working electrode were prepared using the dip-coating method. TiO_2 suspensions were first deposited onto the surface of ITO with a microsyringe and allowed to dry under infrared lamp irradiation. Then the ITO coated with TiO_2 was immersed in P_2W_{17} solution (1 mg mL^{-1} P_2W_{17} aqueous solution, pH 8.0). Finally, the re-dried film was cut into pieces to ensure that identical films were used. The thickness of the film was controlled to $0.5\sim 0.8\ \mu\text{m}$. The surface of semiconductor working electrode exposed to the electrolyte was circular-film with a geometrical surface area of $1.6\ \text{cm}^2$. Glycerol-water solution (10 (v/v)% in $0.1\ \text{mol L}^{-1}$ Na_2SO_4) was used as the supporting electrolyte. Argon gas was bubbled through the supporting electrolyte for 40 min to remove oxygen. All photoelectrochemical measurements were carried out using a standard three-electrode system equipped with a quartz window as shown in Fig. S4. A 200 W high-pressure mercury-lamp was used as UV-light source. After HPB was generated by UV irradiation, UV light was cut off with a 420 nm cutoff filter in order to act as visible light source.

Since the P_2W_{17} is stable at higher pH range (6.0~8.4) while P_2W_{18} is stable at lower pH range (1.0~5.0),^{S7,S8} the experiments were performed at pH 8.0 and pH 3.0 for P_2W_{17} and P_2W_{18} , respectively.

Instruments and apparatus: Fourier transform infrared (FT-IR) spectra

were recorded on an IFS120 HRFTIR spectrophotometer using KBr pellets. The thermogravimetry (TG/DTG/DTA) measurements were made with a PE Pyris Diamond thermal analyzer. The transmission electron microscopy (TEM) images were obtained in a JEM-1200EX TEM. The X-ray photoelectron spectroscopy (XPS) spectra were recorded in a VG ESCALAB 210 electron spectrometer using Mg K α radiation, and binding energies were calculated with respect to C(1s) at 285.00 eV. The pH measurements were performed using a Markson 6200 model pH meter. Ultraviolet-visible spectra were recorded using a HP 8453 spectrophotometer. The produced hydrogen was analyzed on a GC8800-model gas chromatography (TCD, Ar as the carrier, a zeolite 13X column). The incident photon flux was determined with a Ray virtual radiation actinometer (FU 100, sensitivity: 10~50 μV $\mu\text{mol}^{-1}\text{m}^{-2}\text{s}^{-1}$). A CHI 660A electrochemistry workstation (CH Instruments, Shanghai, China) and a standard three-electrode system were employed for photoelectrochemical measurements.

References:

- S1 R. Abe, K. Sayama and H. Arakawa, *Chem. Phys. Lett.*, 2002, **362**, 441-444.
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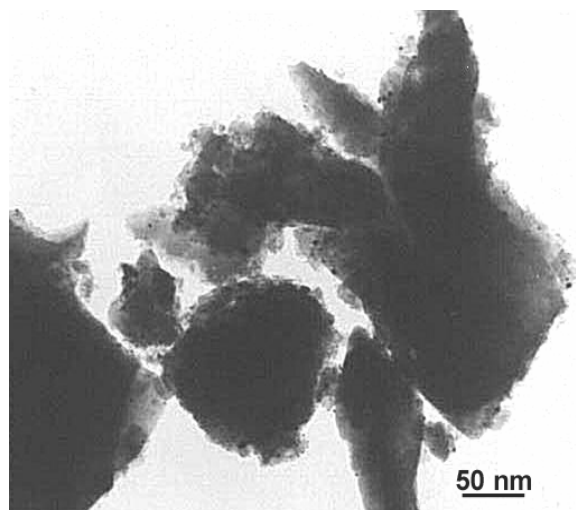


Figure S1a.

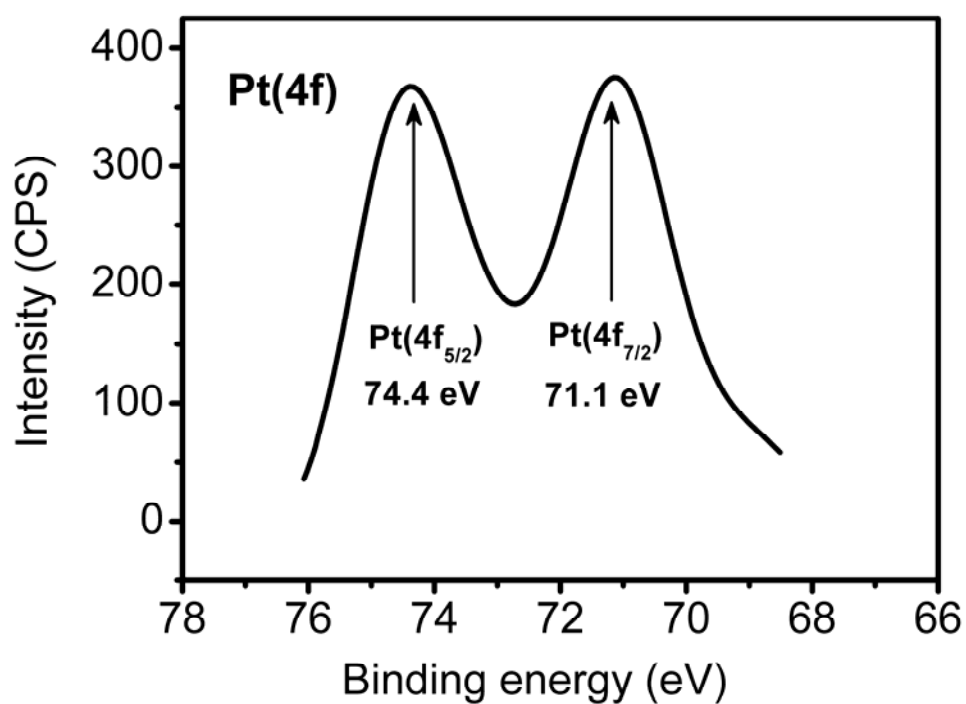


Figure S1b.

Figure S1a. Transmission electron microscopy (TEM) image of Pt-loaded TiO₂. **S1b.** Pt (4f) X-ray photoelectron spectroscopy (XPS) spectrum of Pt loaded on TiO₂.

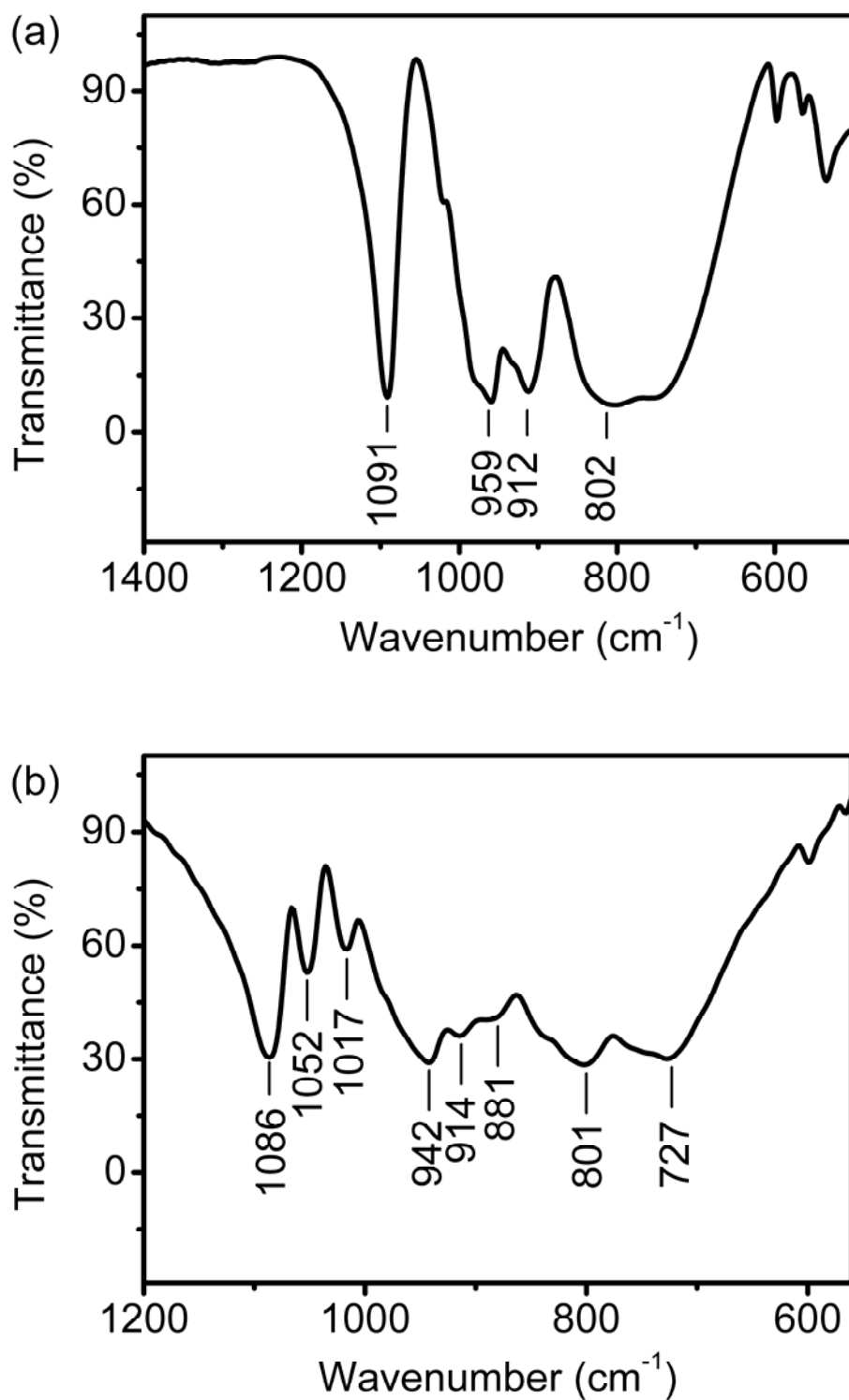


Figure S2. IR spectra of α -K₆P₂W₁₈O₆₂·9H₂O (a) and α_2 -K₁₀P₂W₁₇O₆₁·15H₂O (b).

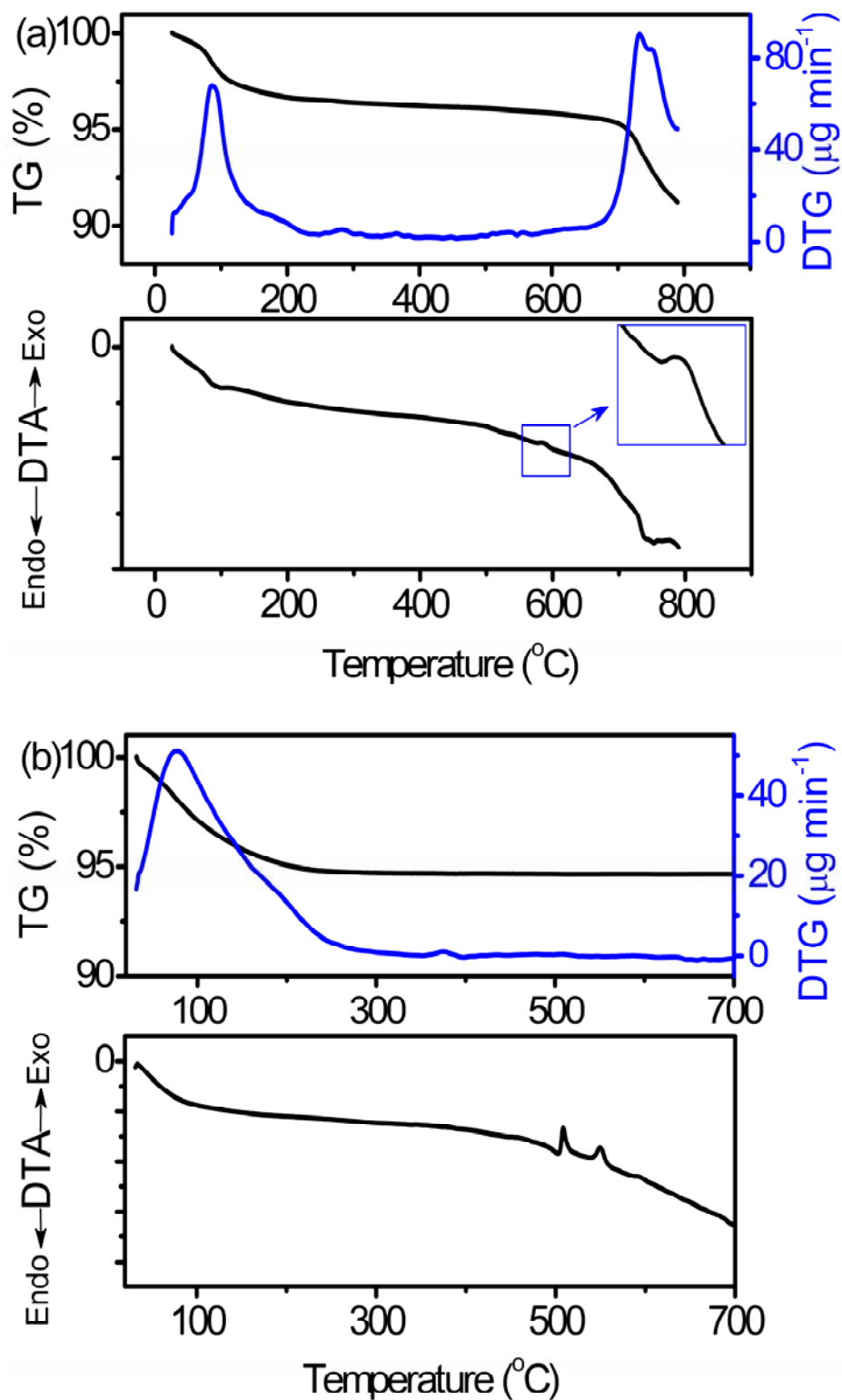


Figure S3. TG/DTG/DTA of $\alpha\text{-K}_6\text{P}_2\text{W}_{18}\text{O}_{62}\cdot 9\text{H}_2\text{O}$ (a) and $\alpha_2\text{-K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}\cdot 15\text{H}_2\text{O}$ (b).

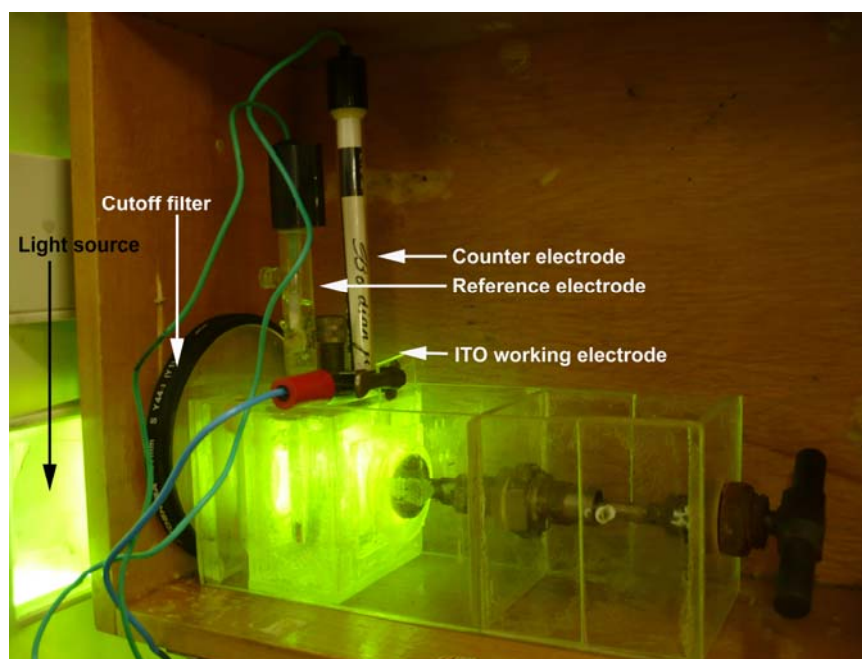


Figure S4. Picture of the photo-electrochemical cell

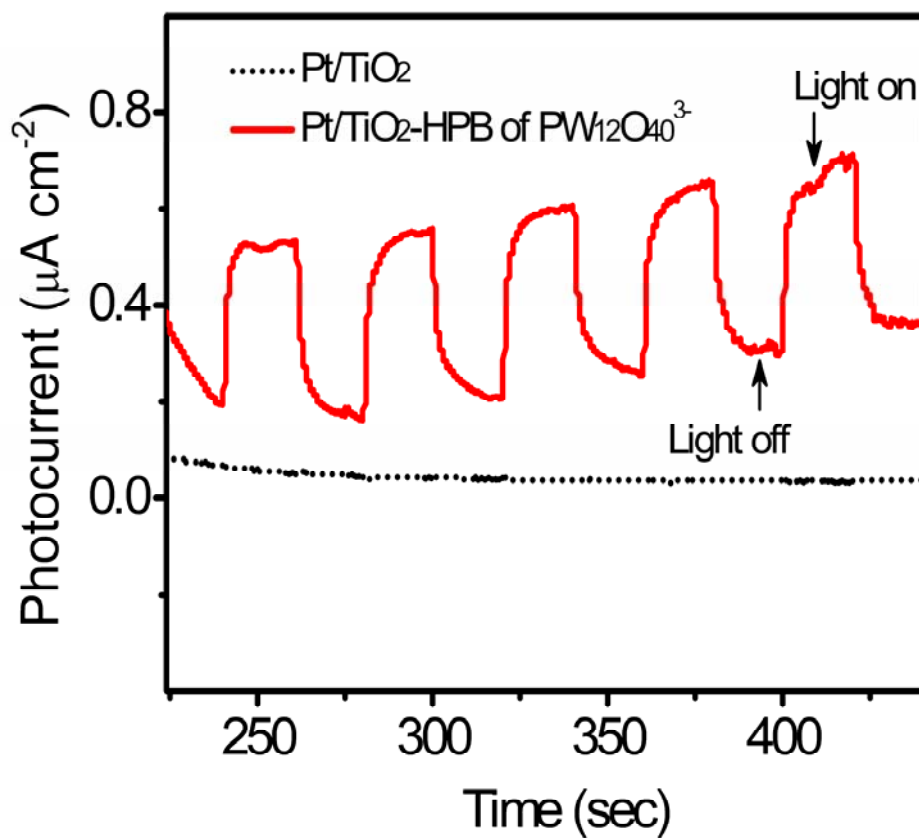


Figure S5 Unbiased potential photocurrents response of Pt/TiO₂ and Pt/TiO₂-HPB of PW₁₂O₄₀³⁻ ITO electrode under intermittent irradiation ($\lambda > 420$ nm) in 0.1 M Na₂SO₄ 10 (v/v) % glycerol aqueous solution.

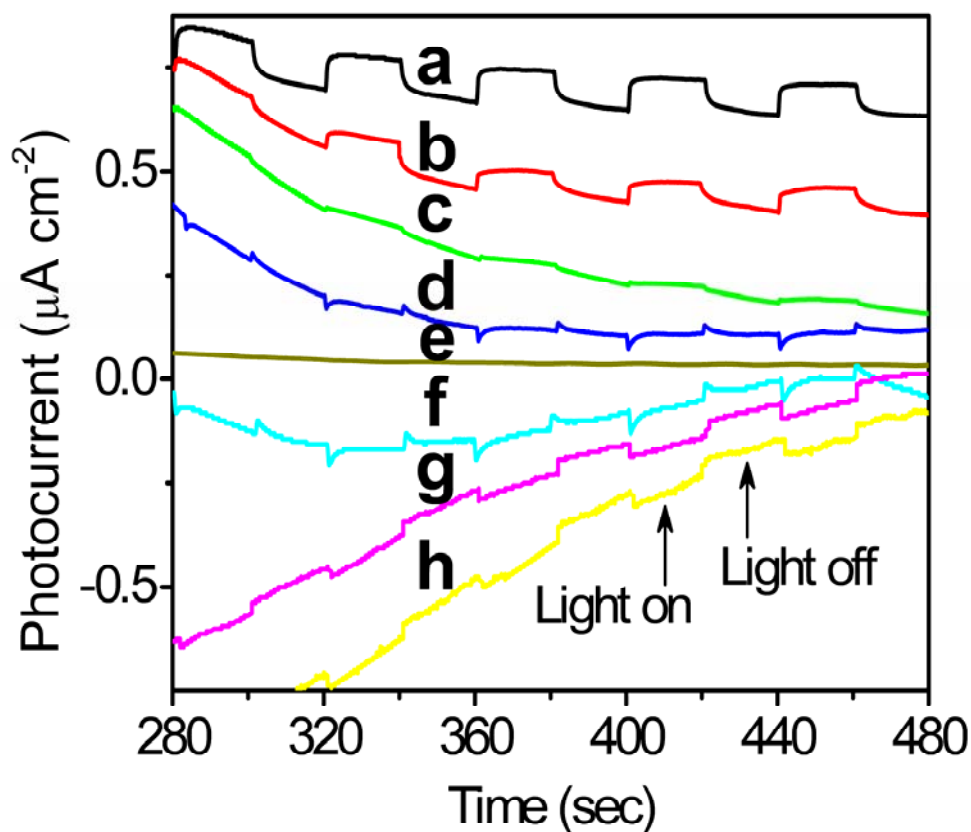


Figure S6. Photocurrent response of Pt/TiO₂-HPB-18 ITO electrode under intermittent irradiation ($\lambda > 420$ nm) with different potentials in 0.1 M Na₂SO₄ 10 (v/v) % glycerol aqueous solution. The applied bias potentials: (a) 0.5 V, (b) 0.4 V, (c) 0.2 V, (d) 0 V, (f) -0.2 V, (g) -0.4 V, (h) -0.6 V. (e) represents the photocurrent response of Pt/TiO₂ ITO electrode under unbiased potential.

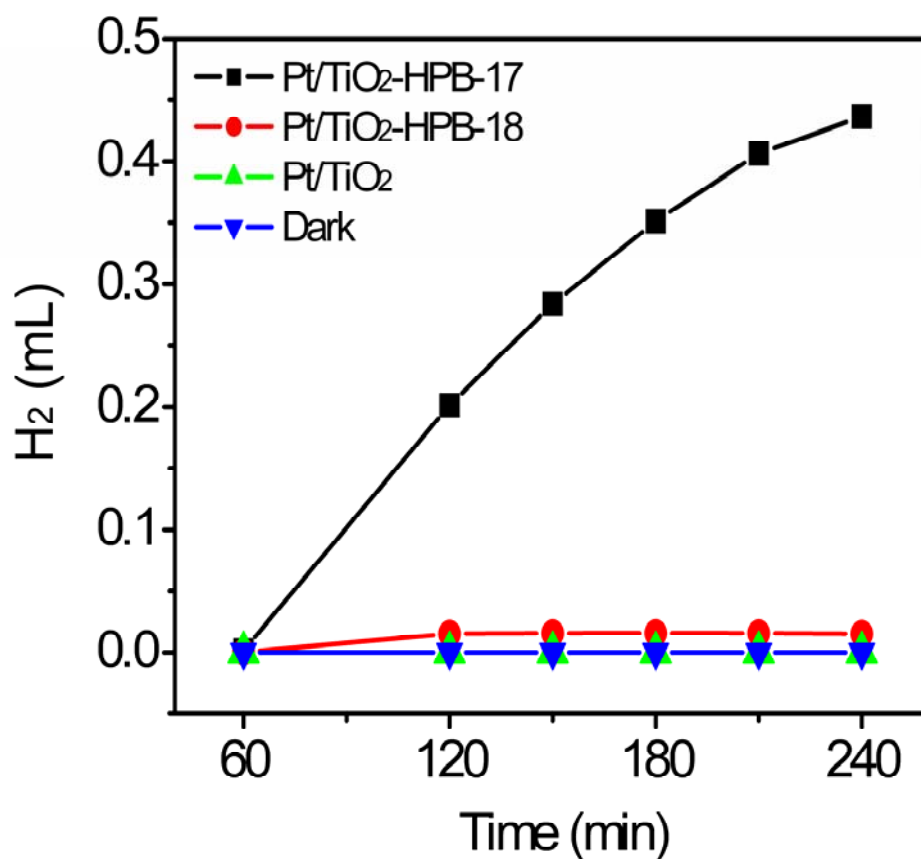


Figure S7. Time course of H₂ evolution over Pt/TiO₂-HPB-17, Pt/TiO₂-HPB-18 and Pt/TiO₂ catalysts under visible light irradiation. The “Dark” means the reactions of these catalysts were carried out in the dark. Reaction conditions: $\lambda > 420$ nm, 66 μ M P₂W₁₇ or P₂W₁₈.

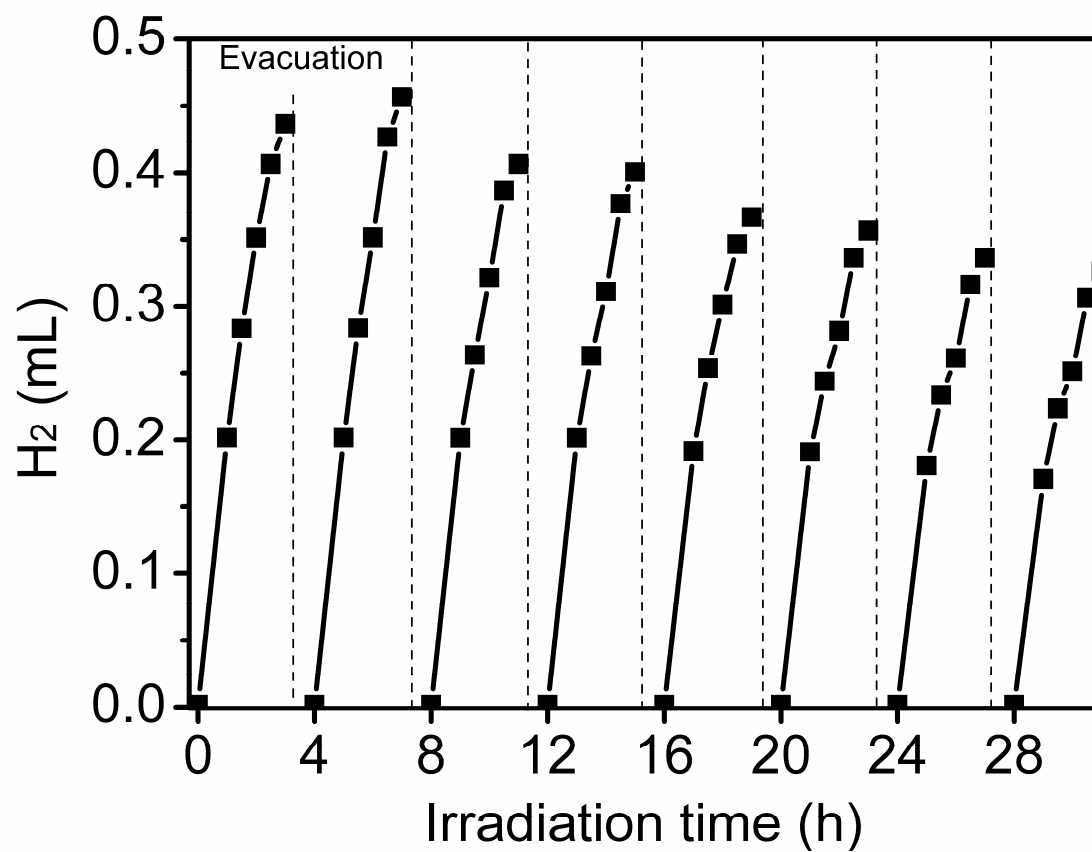


Figure S8. Stability of Pt/TiO₂-HPB-17 catalyst. Reaction conditions:

$\lambda > 420$ nm, 66 μ M P₂W₁₇.

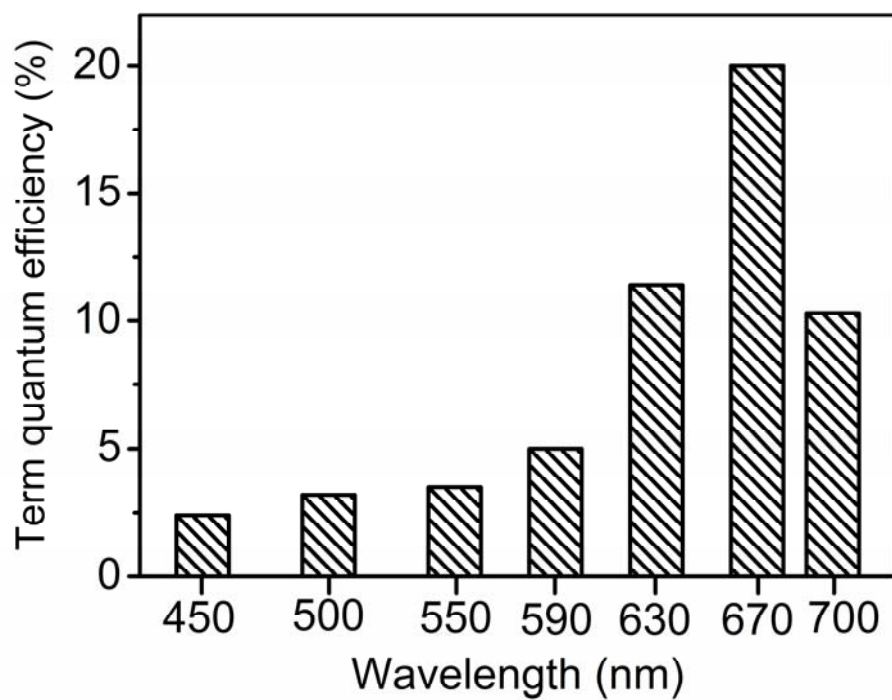


Figure S9. Term quantum efficiency of Pt/TiO₂-HPB-17 in 10 (v/v)% glycerol aqueous solution upon visible light irradiation at different wavelengths. Reaction conditions: 66 μ M P₂W₁₇.

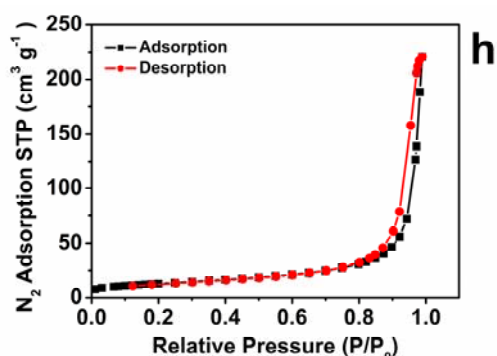
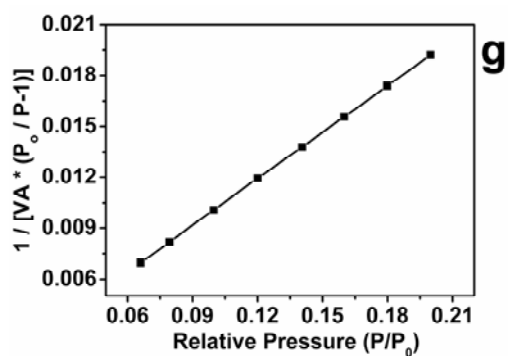
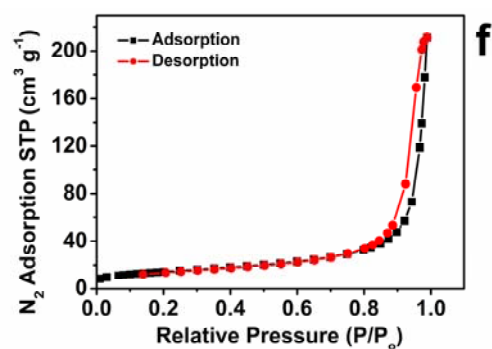
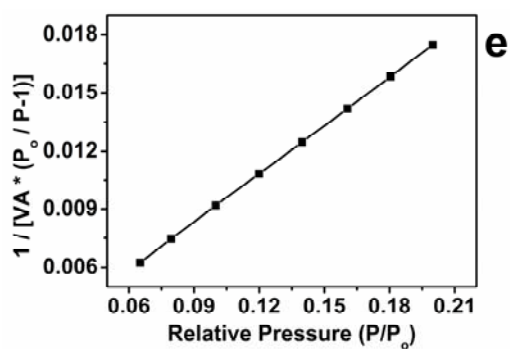
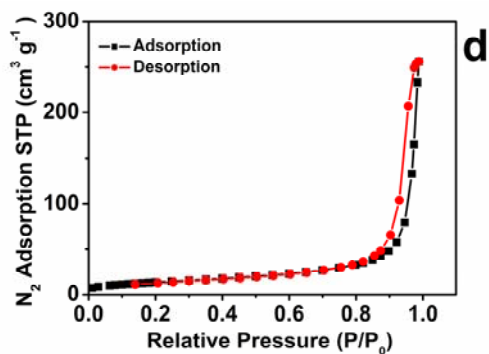
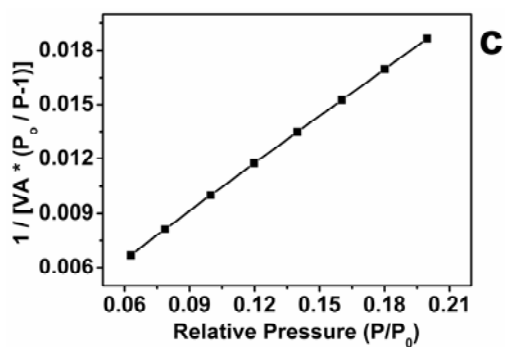
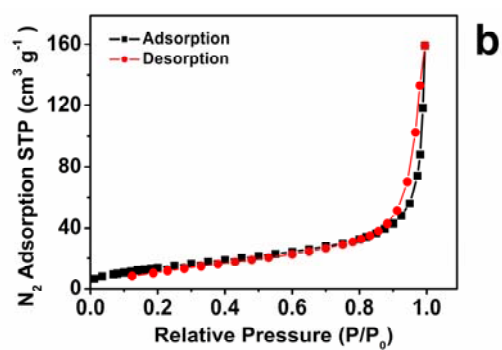
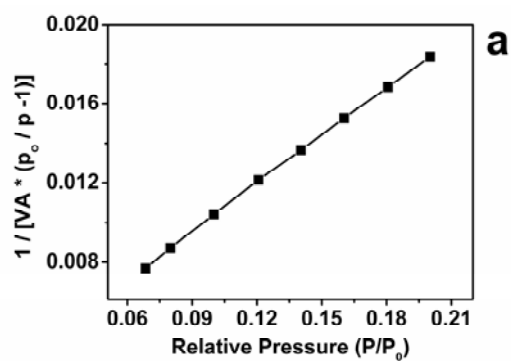
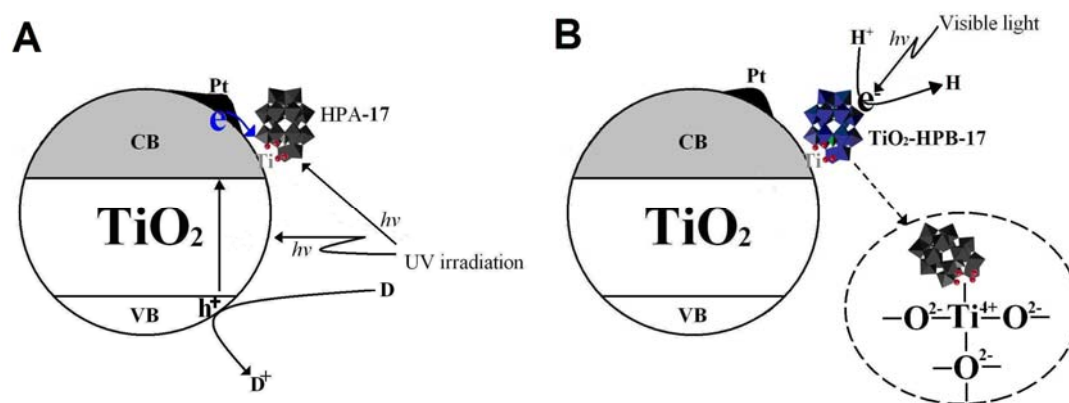


Figure S10. BET surface area plot and N₂ adsorption/desorption isotherms of P25 (a, b); Pt/TiO₂ (c, d); Pt/TiO₂-HPB-17(e, f); Pt/TiO₂-HPB-18 (g, h).

Photocatalyst	Surface area (m ² /g)
P25 TiO ₂	60
Pt/TiO ₂	49
Pt/TiO ₂ -HPB-17	52
Pt/TiO ₂ -HPB-18	47

The BET results show that surface area of catalysts is not the main role for the difference between photocatalytic activity of Pt/TiO₂-HPB-17 and Pt/TiO₂-HPB-18.



Scheme S1. Schematic diagrams of hydrogen evolution.

A and B are schematic diagrams of the current report, in which the HPB-17 was connected with surface of TiO_2 by coordinate bond due to its lacunary structure and formed “surface complex”. In scheme D, Pt/ TiO_2 -HPB-17 can reduce H^+ directly under the visible-light irradiation without electron transfer from excited HPB to CB of TiO_2 , and Pt/ TiO_2 -HPB-17 returns to the ground-state Pt/ TiO_2 -HPA-17 after reduction of H^+ .

Table S1: Peak-Fitting results of W4f XP spectra of samples

Catalyst	Emission source	Binding energy (eV)	Percentage (%)
P₂W₁₈	W4f_{5/2} (W^{VI})	38.3	38
	W4f_{7/2} (W^{VI})	36.2	62
TiO₂-P₂W₁₈	W4f_{5/2} (W^{VI})	38.1	44
	W4f_{5/2} (W^V)	37.3	15
	W4f_{7/2} (W^{VI})	36.1	24
	W4f_{7/2} (W^V)	35.3	17
P₂W₁₇	W4f_{5/2} (W^{VI})	38.0	42
	W4f_{7/2} (W^{VI})	35.9	58
TiO₂-P₂W₁₇	W4f_{5/2} (W^{VI})	38.1	30
	W4f_{5/2} (W^V)	37.3	19
	W4f_{7/2} (W^{VI})	36.0	23
	W4f_{7/2} (W^V)	35.3	28