

Supporting information

Polyoxometalate-anatase TiO₂ composite introduced into the photoanode of the dye-sensitized solar cells to retard the recombination and increase the electron lifetime

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Experimental

Materials: N719, Degussa P25 and FTO glass ($14 \Omega/\square$, Nippon Sheet Glass) were purchased from Heptachroma (Dalian, China). Titanium tetra-isopropoxide, DMPII, LiI (99.9%), I_2 (99%), tert-butylpyridine (TBP) (97%) were purchased from Aladdin. $H_3PW_{12}O_{40} \cdot nH_2O$ and the other reagents were purchased from Beijing Chemicals Co. Ltd. are of analytical grade and used as received without further purification.

Characterization: The photovoltaic tests of the DSSCs were carried out by measuring the photocurrent–voltage (J – V) characteristics of the devices under AM 1.5 simulated solar illumination at 100 mW cm^{-2} . Open circuit voltage decay (OCVD) and EIS measurements were performed on CS350 electrochemistry station (Wuhan CorrTest[®] Instrument Corporation, China) with a Xe lamp and an AM 1.5 solar filter. A 100W Xe arc lamp (XQ-500W, Beijing Changtuo Device, P.R.China) was used under ambient conditions. IR spectra were recorded in the range of $400 - 4000 \text{ cm}^{-1}$ on an Alpha Centaur FT/IR Spectrophotometer on the Si substrate. TG analyses was performed on a Perkin–Elmer TGA7 instrument under air condition with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. X-ray diffraction pattern (XRD) was measured using a Rigaku D/max-IIB X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). High resolution transmission electron microscope (HRTEM) image was taken on a JEOL-2100F transmission electron microscope with an accelerating voltage of 200 kV.

Sol-gel method of the synthesis $PW_{12}TiO_2$: Titaniumtetraisopropoxide (TTIP, 98%, 6ml) was dissolved with 30ml of iso-propyl alcohol while stirring was used. In another container, $H_3PW_{12}O_{40}$ (0.4 g) was dissolved with water (0.8ml), and then added into the TTIP solution drop by drop. The resulting mixture was adjusted to pH 1–2 by addition of 8 mol L^{-1} HCl, and then stirred at room temperature for 1 h. Then, the mixture was heated to 50°C until homogeneous $H_3PW_{12}O_{40}/TiO_2$ hydrogel formed. This hydrogel was transferred into a 50mL autoclave, and then heated to 200°C at a heating rate of about 2°C min^{-1} . Finally, the temperature was kept at 200°C for 1 h. After cooling the hydrogel to room temperature, the hydrogel was dehydrated slowly at 50°C in a vacuum for 24 h. The dried gel was washed with hot water three times and absolute alcohol once, and then dried at room temperature. The product is white powder. Elemental Anal. for PW_{12} -anatase TiO_2 composite: P, 0.18%; W, 12.78%. The amount of $H_3PW_{12}O_{40}$ doped in TiO_2 was 16.98% calculated based on W.

The preparation of the photoanode paste and the fabrication of DSSCs: The TiO_2 powder was a mixture of the PW_{12} -anatase TiO_2 composite and pure P25 by the mass ratio of 1:3, 1:5 and 1:7. The paste for screen printing was prepared according to the literature using different TiO_2 powder. Before the screen printing process, the FTO was

immersed in 40mmol L⁻¹ TiCl₄ aqueous solution at 70°C for 30 min to form a compact layer. A layer of paste was coated on the FTO glass plates by screen-printing. The screen printing procedure was repeated (layer of 2 μm) with TiO₂ paste to obtain a transparent nanocrystalline film of thickness around 8 μm and area of 0.36 cm². The TiO₂ electrodes were gradually heated in an electric stove in an air atmosphere. The temperature gradient program has four levels at 325°C (5 min), 375°C (5min), 450°C (15min) and 500°C (15min).

The calcined photoanodes were sensitized for 24 hours in N719 dye solution. The sensitized photoanodes were washed with ethanol to remove unanchored dye molecules and subsequently dried by nitrogen at room temperature. Platinum-sputtered FTO glass was used as the counter electrode. A drop of electrolyte solution [0.6M DMPII, 0.05M I₂, 0.1M LiI and 0.5M tert-butylpyridine in a mixture of acetonitrile–valeronitrile (85: 15, v/v)] was injected into the cell.

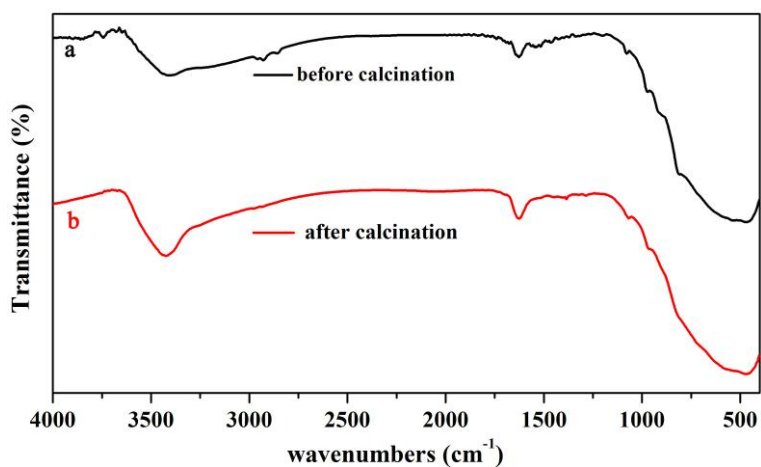


Fig. S1 the IR spectrum of the PW₁₂-anatase TiO₂ composite before calcination (a) and after calcination (b).

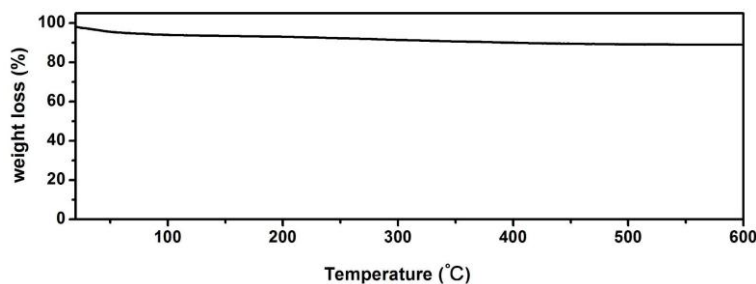


Fig. S2 the TG curves of the PW₁₂-anatase TiO₂ composite.

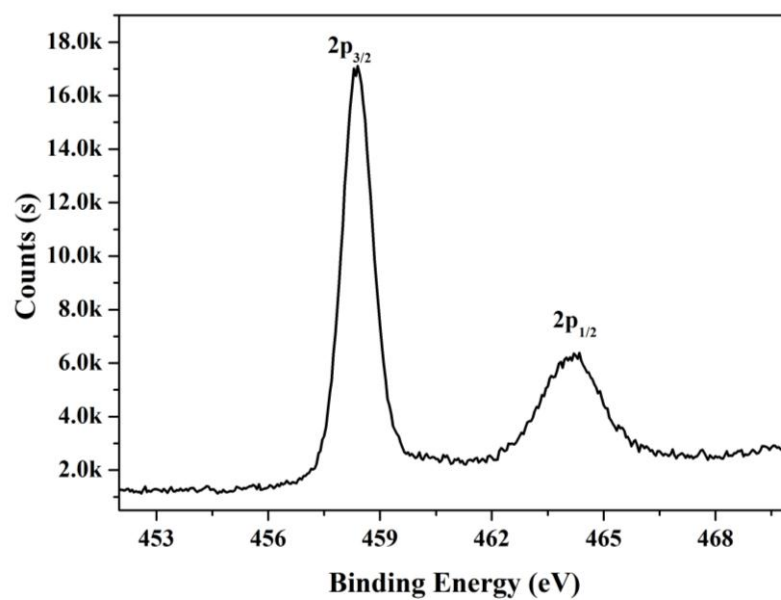


Fig. S3 The Ti2p XPS spectrum of the PW₁₂-anatase TiO₂ composite.

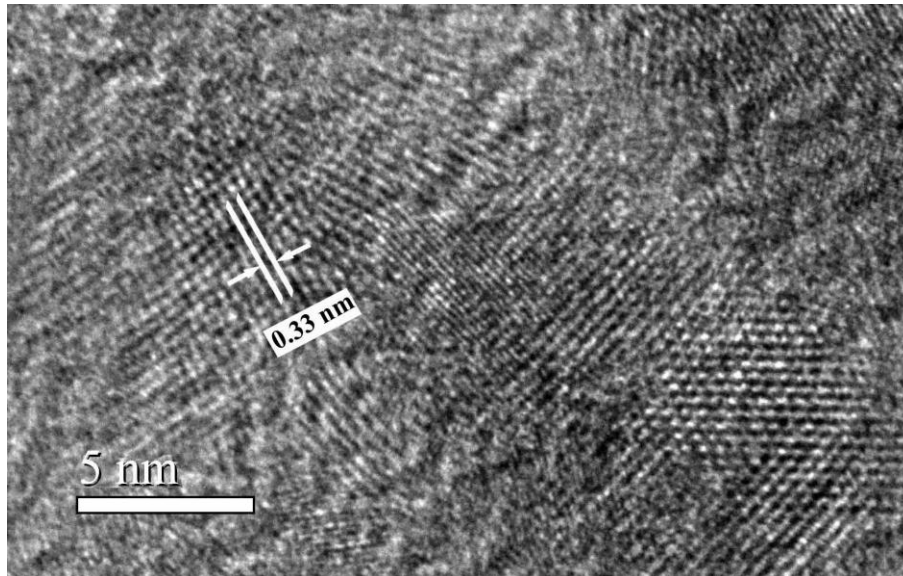


Fig. S4. HRTEM image of PW₁₂-anatase TiO₂ composite. TiO₂ is well crystallized with a lattice spacing of 0.33 nm.