Electronic Supplementary Information

Photovoltaic performance enhancement of Cu$_2$O photocathode by electrostatic adsorption of polyoxometalate on Cu$_2$O crystal faces

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Preparation details

Preparation of [([CH$_3$)$_4$N]$_5$PW$_{10}$Mo$_2$O$_{40}$·4H$_2$O] (PW$_{10}$Mo$_2$)

Synthesis of solution A
Na$_2$MoO$_4$·2H$_2$O (5.0 g, 20 mmol) was dissolved in 50 mL of 4 mol/L HCl, and N$_2$H$_4$·H$_2$O (0.250 ml, 5 mmol) was added. The mixture was stirred for 1 h at 65 °C. The resulting dark orange solution was then let to cool at room temperature, and H$_2$C$_2$O$_4$ (2.7 g, 20 mmol) was added. Then, the pH was adjusted to 2 by a dropwise addition of an 8 mol/L NaOH solution.

[(CH$_3$)$_4$N]$_5$PW$_{10}$Mo$_2$O$_{40}$·4H$_2$O
Na$_9$PW$_9$O$_{34}$·19H$_2$O (0.1 g) was dissolved in 10 mL of deionized water followed by addition of 1mL solution A. The resulting solution was heated to 80 °C and maintained for 30 min. Another 10 mL of H$_2$O and 0.1 g tetramethylammonium bromide were added to the solution and then the solution was adjusted to pH 4.5–5.3 with 10% HAc aqueous solution. A dark-brown solution was obtained and the solution was heated to 80 °C and maintained for about 90 min. Within about 7 days, black crystals [([CH$_3$)$_4$N]$_5$PW$_{10}$Mo$_2$O$_{40}$·4H$_2$O were filtered, washed with deionized water and ethanol, and dried in air.
**Preparation of pristine Cu$_2$O particles and PW$_{10}$Mo$_2$/Cu$_2$O composite particles**

**Pristine Cu$_2$O particles**

139 mL of deionized water was added to a beaker, and then the beaker was placed in a water bath set at 32-34 °C. Then 10 mL of 0.1M CuCl$_2$ solution and 1.74 g of SDS powder were added to the beaker with vigorous stirring. After complete dissolution of SDS powder, 3.6 mL of 1.0 M NaOH solution was introduced. The resulting solution turned light blue immediately, indicating the formation of Cu(OH)$_2$ precipitate. Finally, 48 mL of 0.1M NH$_3$OH·HCl were quickly injected in 5 s into the beaker. The total solution volume in each vial is 200 mL. The beaker was stirred for 20 s. The solution was kept in the water bath for 1 h for nanocrystal growth and centrifuged at 5000 rpm for 3 min. After the top solution was decanted, the precipitate was washed with a 1:1 volume ratio of water and ethanol. The precipitate was centrifuged and washed again using the same water/ethanol mixture to remove unreacted chemicals and SDS surfactant.

**PW$_{10}$Mo$_2$/Cu$_2$O composite particles**

0.4 g of pristine Cu$_2$O particles and 9 mL deionized water were added in 1 mL saturated PW$_{10}$Mo$_2$ solution in vial. The mixture was stirred for 15 min and homogenized in an ultrasonic bath for 30 min. Then, keep the Cu$_2$O particles immersing in the solution for 5 days to make the polyanion ([PW$_{10}$Mo$_2$O$_{40}$]$^{5-}$) absorbed on the Cu$_2$O active faces fundamentally. Then the mixture was filtered. The precipitate was washed with deionized water and ethanol to remove unabsorbed PW$_{10}$Mo$_2$, and then the precipitate was dried in air for storage and analysis.

**Preparation of PW$_{10}$Mo$_2$/Cu$_2$O films and pristine Cu$_2$O films**

**Preparation of the PW$_{10}$Mo$_2$/Cu$_2$O films**

The fluorine-doped tin oxide (FTO) glass was immersing in hot KOH saturated solution of isopropanol for 24 h and then ultrasonically cleaned in distilled water and ethanol, and it was finally washed by distilled water again. The PW$_{10}$Mo$_2$/Cu$_2$O paste was prepared with 0.2 g of the PW$_{10}$Mo$_2$/Cu$_2$O composite particles in 2 mL of N,N-Dimethylformamide (DMF), and then the mixture was homogenized in an ultrasonic bath for 30 min to make sure that the PW$_{10}$Mo$_2$/Cu$_2$O composite particles were uniformly dispersed in the DMF. In order to obtain uniform thickness films, 20 μL of the paste was carefully dropped on the conductive surface of FTO glasses (illumination area was 0.9 × 0.6 cm$^2$) by the use of syringe for chromatography. Then the FTO glasses with the paste were placed in a horizontal position in air. After air drying, the PW$_{10}$Mo$_2$/Cu$_2$O films were annealed at 423 K for 60 min to remove the DMF and cooled in air for analysis.
**Preparation of the pristine Cu₂O films**

In order to highlight the role of polyoxometalate in photovoltaic performance of \( \text{PW}_{10}\text{Mo}_2/\text{Cu}_2\text{O} \) films, the preparation method of the \( \text{Cu}_2\text{O} \) film was same as that of \( \text{PW}_{10}\text{Mo}_2/\text{Cu}_2\text{O} \) film.

**Characterization details**

Infrared spectra (IR) were recorded with a Nicolet Magna 560 FT-IR Spectrometer. X-ray diffraction patterns (XRD) of the particles were measured by a Rigaku D/max-IIIB using Cu Ka radiation. Field-emission scanning electron microscopy (Hitachi S-4800FEG-SEM) was used to investigate the surface morphology. TEM was performed on a JEOLFETEM-2100 transmission electron microscope under 200 kV accelerating voltage. All photoelectrochemical experiments were performed on a CHI660C Electrochemical Workstation (Shanghai Chenhua Instrument Corp., China) at room temperature. Linear sweep voltammetry was used to obtain current–voltage (I–V) curves. A three-electrode system (Fig. S4) was employed in a quartz cell with a saturated calomel electrode (SCE) as the reference electrode, a platinum foil as the counter electrode, and the composite film as the working electrode. All photocurrent transient experiments were carried out at a constant bias of 0 V. A 500 W xenon lamp (CHFXQ500 W, Global Xenon Lamp Power, 320 nm ≤ \( \lambda \) ≤ 780 nm) was used as a light source, and the average intensity reaching the composite films was measured to be ca. 25 mW·cm\(^{-2}\). Films were deposited on the conductive side and the conductive side was oriented facing the light. The illumination area of the working electrode was set constant at 0.9 × 0.6 cm\(^2\). All photoelectrochemical measurements were done in a 0.1 M \( \text{Na}_2\text{SO}_4 \) electrolyte to maintain the stability of the \( \text{Cu}_2\text{O} \) particles. The surface photovoltage (SPV) measurement system included a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltaic cell, and a computer. A 500 W xenon lamp (CHFXQ500 W, Global Xenon Lamp Power) and a double-prism monochromator (Zolix SBP500) provided monochromatic light as the source light. The construction of the SPS photovoltaic cell is a sandwich like structure of ITO-sample-ITO. The FTO with the \( \text{Cu}_2\text{O} \) films acted as the sample. We put the \( \text{Cu}_2\text{O} \) film electrode sample on the ITO electrode and press it with another ITO electrode to obtain a circuit. The fluorescence spectra were recorded on the FL900/FS920 steady-state fluorescence spectrometer. The UV–vis diffuse reflectance spectroscopy (DRS) was recorded with a UV-Vis-NIR Spectrophotometer (Varian).

**Figures**
Fig. S1 Cyclic voltammogram of PW\textsubscript{10}Mo\textsubscript{2} in a pH=5.0 H\textsubscript{2}SO\textsubscript{4}–Na\textsubscript{2}SO\textsubscript{4} (0.1 M) buffer solution.

According to the cyclic voltammogram curve and electrochemical calculations, the conductive bond (CB) of PW\textsubscript{10}Mo\textsubscript{2} was 0.1V (vs. NHE).

Fig. S2 HRTEM of Cu\textsubscript{2}O particles also demonstrates the \{111\} and \{110\} orientations

Fig. S3 SEM of PW\textsubscript{10}Mo\textsubscript{2}/Cu\textsubscript{2}O particles in a large scale
**Fig. S4. The three-electrode system.**
A three-electrode system was employed in a quartz cell with a saturated calomel electrode (SCE) as the reference electrode (the white electrode), a platinum foil as the counter electrode (the red electrode), and the FTO glass as the working electrode (the green electrode).

**Fig. S5 The SPS of the Cu$_2$O film (a) and the PW$_{10}$Mo$_2$-Cu$_2$O film (b).**

**Fig. S6 The Fluorescence emission spectra of Cu$_2$O film (a) and the PW$_{10}$Mo$_2$/Cu$_2$O film (b).**
The proposed mechanism of the photocurrent generation

![Proposed mechanism diagram]

**Fig. S7** The proposed mechanism of the photocurrent generation

The optical band gap of PW$_{10}$Mo$_2$

From the plot of the transformed Kubelka-Munk function versus the energy of light absorbed above it can be observed that the band gap ($E_g$) of PW$_{10}$Mo$_2$ is 2.96eV. Because of the CB of PW$_{10}$Mo$_2$ is 0.1eV, the VB of PW$_{10}$Mo$_2$ is 3.06eV.

**Fig. S8** The optical band gap of PW$_{10}$Mo$_2$