Electronic Supplementary Information

Photovoltaic performance enhancement of Cu_2O photocathode by electrostatic adsorption of polyoxometalate on Cu_2O crystal faces

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Preparation details

Preparation of $[(CH_3)_4N]_5PW_{10}Mo_2O_{40}\cdot 4H_2O]$ ($PW_{10}Mo_2$)

Synthesis of solution A

$Na_2MoO_4\cdot 2H_2O$ (5.0 g, 20 mmol) was dissolved in 50 mL of 4 mol/L HCl, and $N_2H_4\cdot H_2O$ (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 $H_2C_2O_4$ (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.

$[(CH_3)_4N]_5PW_{10}Mo_2O_{40}\cdot 4H_2O]$

$Na_9PW_9O_{34}\cdot 19H_2O$ (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_2O 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 $[(CH_3)_4N]_5PW_{10}Mo_2O_{40}\cdot 4H_2O$ were filtered, washed with deionized water and ethanol, and dried in air.

Electronic Supplementary Material (ESI) for RSC Advances

Preparation of pristine Cu_2O particles and $PW_{10}Mo_2/Cu_2O$ composite particles

Pristine Cu_2O particles

139mL of deionized water was added to a beaker, and then the beaker was placed in a water bath set at 32-34 ℃. Then 10 mL of 0.1M $CuCl_2$ solution and 1.74g 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 $NH_2OH^{\cdot}$ 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.

$PW_{10}Mo_2/Cu_2O$ composite particles

0.4g of pristine Cu_2O particles and 9ml deionized water were added in 1ml saturated $PW_{10}Mo_2$ solution in vial. The mixture was stirred for 15min and homogenized in an ultrasonic bath for 30min. Then, keep the Cu_2O particles immersing in the solution for 5 days to make the polyanion ($[PW_{10}Mo_2O_{40}]^{5-}$) aborsbed on the Cu_2O active faces fundamently. 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 $PW_{10}Mo_2/Cu_2O$ films and pristine Cu_2O films

Preparation of the $PW_{10}Mo_2/Cu_2O$ films

The fluorine-doped tin oxide (FTO) glass was immersing in hot KOH saturated solution of isopropanol for 24h and then ultrasonically cleaned in distilled water and ethanol, and it was finally washed by distilled water again. The $PW_{10}Mo_2$ /Cu_2O paste was prepared with 0.2 g of the $PW_{10}Mo_2/Cu_2O$ composite particles in 2mL of N, N-Dimethylformamide (DMF), and then the mixture was homogenized in an ultrasonic bath for 30min to make sure that the $PW_{10}Mo_2/Cu_2O$ composite particles were uniformly dispersed in the DMF. In order to obtain uniform thickness films, 20μL 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 $PW_{10}Mo_2/Cu_2O$ films were annealed at 423 K for 60 min to remove the DMF and cooled in air for analysis.

Preparation of the pristine Cu_2O films

In order to highlight the role of polyoxometalate in photovoltaic performance of $PW_{10}Mo_2/Cu_2O$ films, the preparation method of the Cu_2O film was same as that of $PW_{10}Mo_2/Cu_2O$ 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-IIB 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 filmassembled FTO glass 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 $\leq \lambda \leq$ 780 nm) was used as a light source, and the average intensity reaching the composite films was measured to be ca. 25 $mW{\cdot}cm^{-2}$. 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 Na_2SO_4 electrolyte to maintain the stability of the Cu_2O 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 Cu_2O films acted as the sample. We put the Cu_2O 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

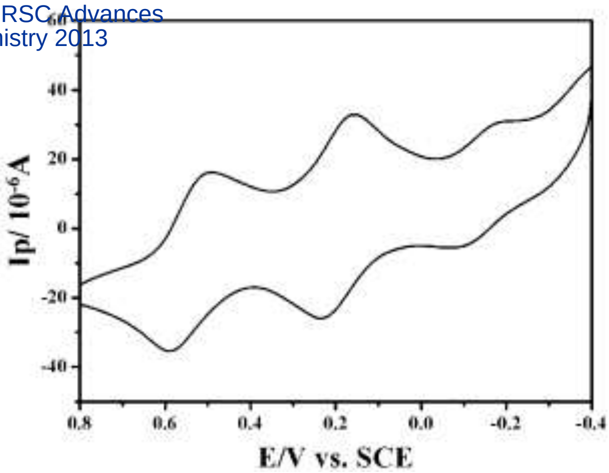

Fig. S1 Cyclic voltammogram of $PW_{10}Mo_2$ in a pH=5.0 H_2SO_4–Na_2SO_4 (0.1 M) buffer solution.

According to the cyclic voltammogram curve and electrochemical calculations, the conductive bond (CB) of $PW_{10}Mo_2$ was 0.1V (vs. NHE).

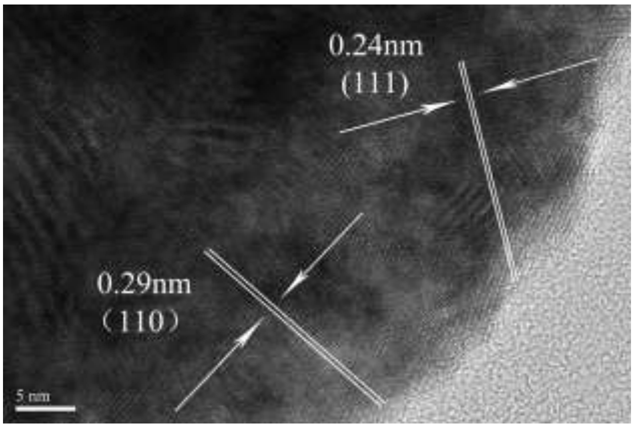

Fig. S2 HRTEM of Cu_2O particles also demonstrates the {111} and {110} orientations

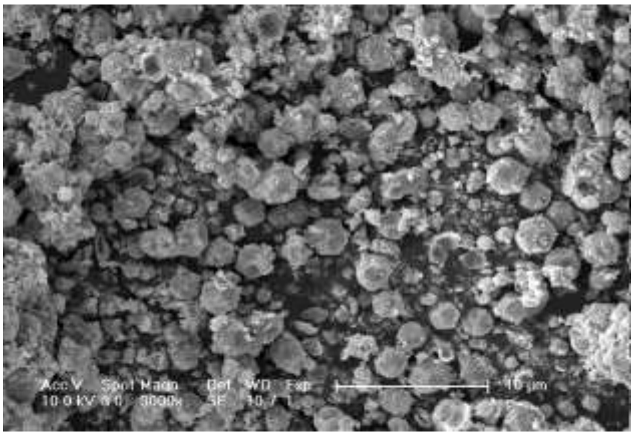

Fig. S3 SEM of $PW_{10}Mo_2/Cu_2O$ particles in a large scale

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).

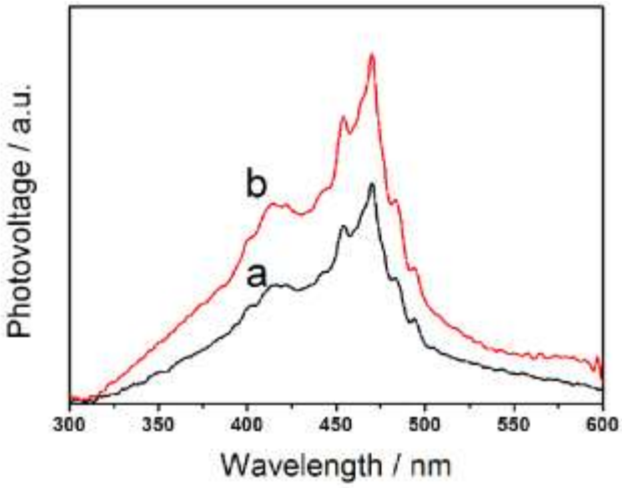

Fig. S5 The SPS of the Cu_2O film (a) and the $PW_{10}Mo_2$-Cu_2O film (b).

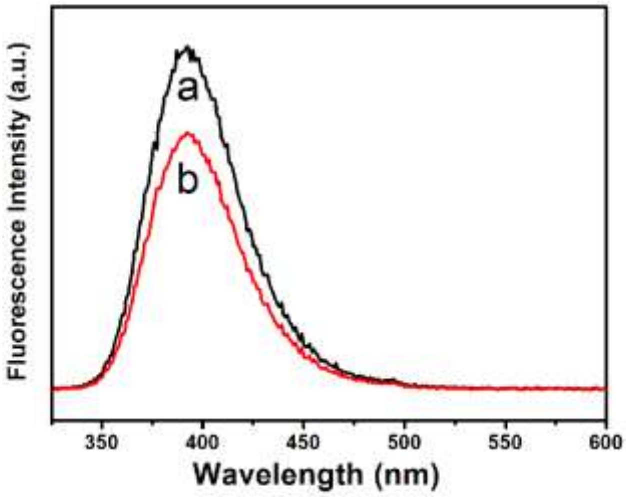

Fig. S6 The Fluorescence emission spectra of Cu_2O film (a) and the $PW_{10}Mo_2/Cu_2O$ film (b).

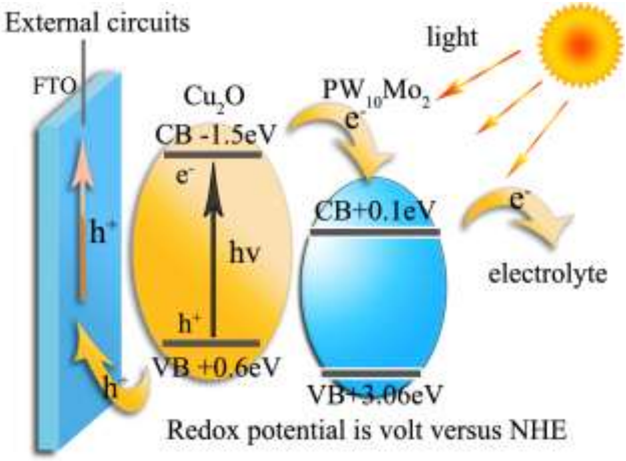

Fig. S7 The proposed mechanism of the photocurrent generation

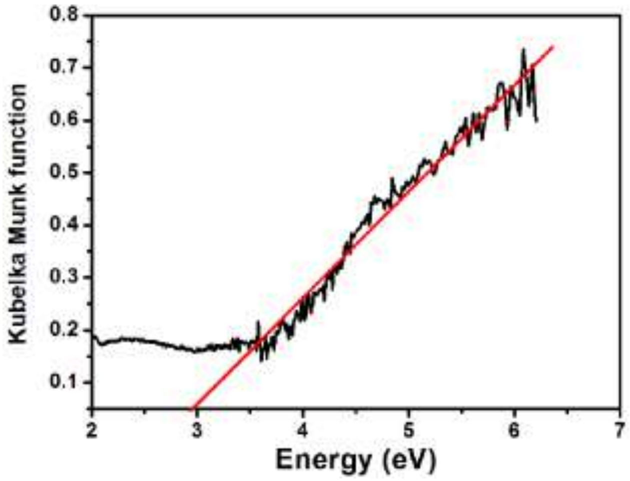

Fig. S8 The optical band gap of $PW_{10}Mo_2$

From the plot of the transformed Kubelka-Munk function versus the energy of light absorbed above it can be observed that the band gap (Eg) 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.