Improved water-splitting performances of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes synthesized by spray pyrolysis

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ABSTRACT $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ solid solution of CuWO_4 and CuMoO_4 , which is a copper-based multi-component oxide semiconductor, possesses much narrower band gap than CuWO_4 . In theory, it can absorb a larger part of the visible spectrum, widening the use of solar spectroscopy and obtaining a higher photo-to-chemical conversion efficiency. In this study, $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film photoanodes on conducting glass were prepared using a simple and low-cost spray pyrolysis method. The resulting $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes perform higher photocurrent than CuWO_4 photoanodes under AM 1.5G simulated sunlight illumination (100 mW cm^{-2}) in 0.1 mol L^{-1} phosphate buffer at pH 7. Combined with IPCE and Mott-Schottky analysis, the enhancement of the photocurrent is due to the improvement of photon utilization and the increase of carrier concentration with the incorporation of Mo atoms. Moreover, with the optimal Mo/W atomic ratio, the photocurrent density increases obviously from 0.07 to 0.46 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ bias. In addition, compared with particle-assembled thin-film photoanodes prepared by solid-phase reaction and drop-necking treatment, the photoanodes prepared by spray pyrolysis have obvious advantages in terms of reducing resistance and facilitating charge transport.

Keywords: CuWO_4 , $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$, photoelectrochemical water splitting, photoanode

INTRODUCTION

Photoelectrochemical (PEC) water splitting, as a method of storing and utilizing solar energy to produce O_2 and H_2 , can be used to address energy and pollution problems [1–3]. Nevertheless, photoanodes are an important constraint on the development of this system because of low

efficiency and poor stability of the photoanodes [4]. Thus, developing inexpensive, efficient and stable photoanodes is a necessary choice to promote the practical application of PEC water splitting. In terms of the selection of materials, oxide semiconductor materials gain considerable attention because of their relatively favorable stability [5–8]. Among them, tungsten trioxide (WO_3) [9–11], hematite ($\alpha\text{-Fe}_2\text{O}_3$) [12–15] and bismuth vanadate (BiVO_4) [16–19], as photoanodes to produce O_2 , have been widely researched these decades. Nevertheless, the essential features of these semiconductor materials can restrict their further development to a certain extent. For WO_3 , the relative large band gap ($E_g = 2.7 \text{ eV}$) would limit its utilization of the solar spectrum, further influencing the PEC properties [11,20]. Hematite has a more suitable band gap ($E_g = 2.1 \text{ eV}$), but its poor charge carrier mobility and short hole diffusion length are two factors severely limiting its PEC performance [13,14]. As for BiVO_4 , its band gap ($E_g = 2.4 \text{ eV}$) and diffusion length are both proper, but the separation and migration of electron-hole pairs cannot be satisfactory [16,19]. In recent years, kinds of strategies, such as, preparing samples by various synthetic methods [21–24], designing heterojunction [25–27], and doping [28–32], have been attempted to overcome these limitations.

$\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ (i.e., solid solution of CuWO_4 and CuMoO_4) is a copper-based oxide semiconductor with a smaller band gap than CuWO_4 ($E_g = 2.2\text{--}2.4 \text{ eV}$) [33,34]. By changing Mo/W atomic ratio, the band gap of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ can be reduced to 2.0 eV and the theoretical solar-to-hydrogen conversion efficiency can be close to 20% [2,35]. CuWO_4 has been studied as a useful n-type

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semiconductor material for PEC water splitting by several research groups [36–40]. However, the relevant research and literatures about $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ are limited, especially in the field of PEC water splitting. The use of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film photoanodes in PEC cells was reported in 2013 by Choi *et al.* [35]. They have prepared $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes by an electrochemical deposition method and PEC measurements in 0.1 mol L⁻¹ phosphate buffer (pH 7) showed a solar photocurrent density of approximately 0.18 mA cm⁻² at 1.23 V_{RHE} (vs. reversible hydrogen electrode) bias under AM 1.5G sunlight illumination (100 mW cm⁻²) [35]. It is required to explore other simple and low-cost methods to prepare $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film photoanodes. Spray pyrolysis method is not only a simple and inexpensive synthetic method, but also is suitable to extend to rapid and mass production. Moreover, this method has also been extensively applied to deposit oxide materials [41–43].

In this study, a simple and effective spray pyrolysis method was used to prepare $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film photoanodes. We studied the PEC water splitting activities of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes with different Mo/W atomic ratio. In addition, we also prepared particle-assembled thin-film photoanodes by solid-phase reaction and drop-necking treatment for comparison.

EXPERIMENTAL SECTION

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.5%, Strem Chemicals, Inc.), ammonium metatungstate hydrate ($(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$, Alfa Aesar Chemicals Co., Ltd.), ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 99%, Alfa Aesar Chemicals Co., Ltd.) were used in the experiment with no further purification. Fluorine-doped tin oxide (FTO) coated glass was cleaned sequentially by sonication in deionized water, acetone and ethanol before using as the substrates.

$\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film photoanodes were prepared *via* spray pyrolysis method. Taking $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ for an example, the precursor solution was prepared by dissolving 1.5 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 50 mL of ethanol solution under constant stirring. Upon complete dissolution of the copper precursor, 1.2 mL of nitric acid was added to lower the pH value of the solution. Subsequently, ammonium metatungstate hydrate and ammonium molybdate tetrahydrate with 0.65:0.35:1 molar ratio of W:Mo:Cu were added and constantly stirred until the powder was completely dissolved, forming a homogeneous blue solution. Next, the mixture solution was sprayed onto the FTO substrates whose temperature was kept at 160°C. The films were allowed to cool to room

temperature before annealing at 550°C for 2 h in air. In comparison, CuWO_4 photoanodes were prepared by a similar procedure, except that no ammonium molybdate tetrahydrate was added.

The crystal structures of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film samples were investigated by a Rigaku Ultima III X-ray diffractometer (XRD) equipped with a Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) powered at 40 kV and 40 mA. The morphologies of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ films were recorded using a scanning electron microscope (SEM; ZEISS ULTRA 55) and the accelerating voltage was set to 3 kV. The microstructure of these thin-film samples was further observed by a transmission electron microscope (TEM, JEOL JEM-200CX). UV-vis absorption spectra of these samples were acquired by a Shimadzu UV-2550 spectrophotometer. Absorption efficiency of these thin-film samples was obtained by recording reflection spectra and transmission spectra of these samples (Absorbance = 1 – Reflectance – Transmittance).

Photoelectrochemical characterization of the $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film photoanodes was measured in a three-electrode cell using an electrochemical analyzer (CHI-660E, Shanghai Chenhua, China). The prepared $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes were used as the working electrode. Pt foil and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The electrolyte in all PEC experiments was 0.1 mol L⁻¹ phosphate buffer at pH 7. Here, all potentials of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ working electrode were reported as E_{RHE} , calculated by the formula: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^0_{\text{Ag/AgCl}}$, where $E_{\text{Ag/AgCl}}$ is the measured potential reversible Ag/AgCl electrode and $E^0_{\text{Ag/AgCl}}$ is 0.197 V at 25°C. $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes were irradiated with AM 1.5G simulated sunlight which was produced by a Newport Sol3A Class AAA simulator, and the light intensity was adjusted to 100 mW cm⁻² with the calibration of a standard Newport 91150 silicon cell. For a photoanode, there was an effective area of 0.28 cm² irradiated because of a mask, and the photocurrent densities of the photoanode were eventually normalized to 1 cm². The capacitance measurements for Mott–Schottky plots were carried out at the alternating current (AC) frequency of 1 kHz. The incident photon-to-current conversion efficiency (IPCE) of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes was obtained under monochromatic light irradiation with a xenon lamp (USHIO, Optical Module X500) equipped with 330–630 nm band pass filters. The bias potential was fixed at 1.23 V_{RHE}.

RESULTS AND DISCUSSION

In this experiment, all the thin-film samples of CuWO_4

Figure 1 XRD patterns of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ samples. (a) View from 10° to 70° ; (b) detail view from 29.5° to 33.5° . In the XRD patterns, the peaks from FTO substrate and $\text{Cu}_3\text{Mo}_2\text{O}_9$ are denoted by symbols * and ♦, respectively.

and $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ obtained by spraying appeared to be yellow-green, but upon annealing at 550°C for 2 h, the color changed significantly. Moreover, the higher the content of Mo was, the deeper the color of photoanodes became. CuWO_4 was yellow, while $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ and $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ were orange and $\text{CuW}_{0.35}\text{Mo}_{0.65}\text{O}_4$ was brick-red (Fig. S1).

To identify the phase purity of CuWO_4 and $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ samples, the XRD tests were performed firstly, as recorded in Fig. 1. The peaks of FTO substrates in the patterns are marked with symbol (*) and other peaks are compared with the standard peaks of wolframite CuWO_4 (PDF#72-0616). The results show that CuWO_4 and $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ are pure phase and have a wolframite structure when x was not more than 0.35. As x continues to grow, impurities start to appear in the samples in the form of $\text{Cu}_3\text{Mo}_2\text{O}_9$. It should be noted that the amount of $\text{Cu}_3\text{Mo}_2\text{O}_9$ is far less than that of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ in the samples, especially when the atomic ratio of Mo and W is not more than 1:1. For $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ prepared by spray pyrolysis, the relative intensities of the Bragg scattering are roughly consistent with those of the standard peaks. A detail view from 29.5° to 33.5° was shown in Fig. 1b. Whether the peaks shift or not depends on the indices of the specific crystallographic planes. In addition, the direction and degree of the shifts are all related to the indices. For a particular (hkl) peak, the offset increases gradually as the ratio of Mo/W increases, which obviously means that the addition of Mo changes the lattice constants.

To observe the changes in surface morphology with the change of Mo/W atomic ratio, the SEM measurement were conducted, as shown in Fig. 2. The resulting $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes are porous films composed of worm-like structures with various shapes when the

atomic ratio of Mo and W is not more than 1:1. In addition, as the ratio of Mo and W increases, the worm-like structures become finer, which further forms into more porous films. The porous structure can facilitate the diffusion of the electrolyte in the thin-film electrodes, thereby increasing the contact area between the thin-film electrodes and the electrolyte. In addition, it can reduce the transfer distance of the holes so that more holes can participate in the water oxidation reaction, thus promoting PEC performances to a certain extent [5]. The SEM images from the cross-section view shows that the thickness of CuWO_4 and $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ films is roughly same and the average thickness is ca. $3.5 \pm 0.5 \mu\text{m}$, as shown in Figs S2 and S3. The high-resolution transmission electron microscopy (HRTEM) was also conducted to further observe the microstructures of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ samples. Fig. 2d–f show lattice fringe images of CuWO_4 (011), $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ (101) and $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ (111), respectively. The results demonstrate the existence of CuWO_4 and $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$, which are consistent with the results of the XRD patterns.

UV-vis absorption spectra were investigated to analyze the light absorption properties of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ samples, as shown in Fig. 3 and Fig. S4. With the increase of the Mo/W ratio, the light absorption edge gradually becomes larger. The light absorption edge of CuWO_4 is around 550 nm (E_g is around 2.25 eV), which is consistent with the results reported in the previous literature [33,34]. The light absorption edge of $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ and $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ is around 600 nm and 615 nm, respectively, greatly widening the range of light absorption and allowing the visible light to be utilized more fully.

The current-potential characteristics of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes with different ratio of Mo and W were measured in 0.1 mol L^{-1} phosphate buffer (pH 7), as

Figure 2 SEM images of as-prepared samples: (a) CuWO_4 , (b) $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ and (c) $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$. HRTEM images of (d) CuWO_4 , (e) $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ and (f) $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$. The inset images are the fast Fourier transform patterns of the corresponding images.

Figure 3 UV-vis absorption spectra of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ thin-film samples.

Figure 4 J - V curves of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes measured in darkness and under AM 1.5G sunlight illumination (100 mW cm^{-2}) in 0.1 mol L^{-1} phosphate buffer (pH 7). The short dash is dark response.

shown in Fig. 4 and Fig. S5. The dark response of all $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes is almost negligible up to $1.8 V_{\text{RHE}}$. The photocurrent density of CuWO_4 photoanode is 0.07 mA cm^{-2} at $1.23 V_{\text{RHE}}$ and 0.12 mA cm^{-2} at $1.6 V_{\text{RHE}}$. When Mo atoms are incorporated, the photocurrent density of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes begins to grow significantly with the increase of the ratio of Mo and W. When the atomic ratio of Mo and W reaches 1:1, the thin-film photoanodes gain the best PEC performance with the photocurrent density of 0.46 mA cm^{-2} at $1.23 V_{\text{RHE}}$ and 0.81 mA cm^{-2} at $1.6 V_{\text{RHE}}$, which are six times larger than that of CuWO_4 photoanodes. As mentioned above, $\text{Cu}_3\text{Mo}_2\text{O}_9$ impurity existed in the $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ ($x > 0.35$). In order to exclude the influence of $\text{Cu}_3\text{Mo}_2\text{O}_9$, $\text{Cu}_3\text{Mo}_2\text{O}_9$ electrodes were prepared by solid-phase reaction and electrophoretic deposition (Figs S6, S7). The J - V curves show that $\text{Cu}_3\text{Mo}_2\text{O}_9$ electrode has

almost negligible photocurrent under the same testing conditions (Fig. S8), which indicates that the photocurrent of the sample photoanodes may originate from $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$, rather than $\text{Cu}_3\text{Mo}_2\text{O}_9$.

In order to investigate the response of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ to light irradiation of different wavelengths, we tested the IPCEs of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes as a function of photon wavelengths. Fig. 5a shows the IPCE plots of different $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes measured at $1.23 V_{\text{RHE}}$ in 0.1 mol L^{-1} phosphate buffer (pH 7). The results indicate that $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ and $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ not only significantly increase the value of IPCE in the range of 320 to 530 nm, but also greatly broaden the utilization range of light wavelength. In addition, the IPCEs of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ and $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ photo-

Figure 5 (a) IPCE plots of CuW_{1-x}Mo_xO₄ photoanodes measured at 1.23 V_{RHE} applied bias in 0.1 mol L⁻¹ phosphate buffer (pH 7). (b) IPCE of CuW_{1-x}Mo_xO₄ photoanodes at +1.23 V_{RHE} bias and the AM 1.5G solar spectrum (100 mW cm⁻²) are multiplied together to give the number of photons stored in the form of hydrogen (shaded area). (c) Mott-Schottky plots of CuW_{1-x}Mo_xO₄ photoanodes measured with the frequency of 1,000 Hz in darkness in 0.1 mol L⁻¹ phosphate buffer (pH 7). (d) J-V curves of CuW_{1-x}Mo_xO₄ photoanodes measured under AM 1.5G sunlight illumination (100 mW cm⁻²) in 0.1 mol L⁻¹ phosphate buffer (pH 7) containing hole scavenger of 0.1 mol L⁻¹ H₂O₂.

anodes present a proportionally larger enhancement at longer wavelengths, indicating that CuW_{0.5}Mo_{0.5}O₄ and CuW_{0.65}Mo_{0.35}O₄ photoanodes have greater ability to harvest longer wavelength photons to promote PEC water splitting [44]. Thus the increase in photon utilization may be one of the reasons for the increase in the photocurrent. We also integrate the IPCE data of CuW_{1-x}Mo_xO₄ photoanodes with the standard solar spectrum to obtain calculated photocurrents, as shown in Fig. 5b. The difference between the calculated and the experimental values of CuW_{1-x}Mo_xO₄ photoanodes is almost negligible, confirming that both the light source used in the measurement and the measured photocurrents are all reliable.

To further elucidate the change of PEC performance, Mott-Schottky analysis was performed. The Mott-Schottky plots of CuW_{1-x}Mo_xO₄ photoanodes measured in 0.1 mol L⁻¹ phosphate buffer (pH 7) with the frequency of 1,000 Hz are shown in Fig. 5c. All the three samples show a positive slope, meaning that they are all n-type semiconductors and electrons are the majority carrier in these thin films. The fitting of the line region of the Mott-

Schottky plots can generate two important parameters of CuW_{1-x}Mo_xO₄ photoanodes: the flat-band potential and the carrier concentration [17,37]. The flat-band potential of CuW_{1-x}Mo_xO₄ can be obtained by extrapolating the linear region to the x-axis in Fig. 5c. Accordingly, the flat-band potentials of CuWO₄, CuW_{0.65}Mo_{0.35}O₄ and CuW_{0.5}Mo_{0.5}O₄ are 0.53 V_{RHE}, 0.65 V_{RHE} and 0.65 V_{RHE}, respectively. The carrier concentrations of CuW_{1-x}Mo_xO₄ photoanodes can be calculated from the slopes of the linear region, which are 4.04×10¹⁹, 1.38×10²⁰, and 2.35×10²⁰ cm⁻³ for the three photoanodes, respectively. The carrier concentrations of CuW_{0.65}Mo_{0.35}O₄ and CuW_{0.5}Mo_{0.5}O₄ photoanodes are about three times and five times as high as that of CuWO₄ photoanodes, respectively. It may improve the conductivity and reduce the recombination of electron-hole pairs, motivating more holes to participate in water oxidation reaction and achieving the improvement of PEC performance. The carrier concentrations may be overestimated because Mott-Schottky analysis is based on a flat model, but CuW_{1-x}Mo_xO₄ thin-film photoanodes in the experiment

are porous structure.

To study the effect of electron-hole separation efficiency of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes on PEC performance, the photocurrents were measured in the 0.1 mol L^{-1} phosphate buffer containing hole scavenger of $0.1 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ (Fig. 5d). The onset potentials of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes measured with hole scavenger show a cathode shift of 80–90 mV compared to the onset potentials of water oxidation. This shift is caused by the accelerated reaction kinetics and reduced surface recombination rates. Moreover, the photocurrents measured with H_2O_2 show a significant improvement under all potential bias. The curves about the electron-hole separation efficiency at different potential bias are shown in Fig. S9. As the applied potential bias becomes larger, the separation efficiency of all $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes shows an obvious increase. In addition, compared to CuWO_4 , $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ and $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ have a higher separation efficiency at all potential bias, which is useful to promote PEC performance.

The photochemical stability is also one of the important criteria. The photocurrent-time (I - t) curves of CuWO_4 and $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoanodes measured at $+1.23 \text{ V}_{\text{RHE}}$ applied bias and under AM 1.5G sunlight illumination are shown in Fig. S10. The I - t curves show an initial spike in current density followed by a multi-exponential decrease to a relatively steady photocurrent. The photocurrent of CuWO_4 photoanodes is quite low and is reduced slightly from 0.070 to 0.067 mA cm^{-2} after exposure for 1,000 s. During the process of exposure, the photocurrent of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoanodes exhibits a fluctuation due to the adsorption and desorption of bubbles. After exposure for 1,000 s, the photocurrent is reduced by 10%. On one hand, it is possible that the catalyst on the photoanode surface peeled off; on the other hand, the excess bubbles adsorbed on the surface of the photoanode may prevent the contact between the electrolyte and the photoanode, thus hindering water oxidation reaction to some extent. These problems can be alleviated by applying protective layers or supporting cocatalysts in subsequent experiments.

For comparison, we also prepared particle-assembled thin-film photoanodes of $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ using solid-phase reaction combined with drop-necking treatment (Fig. S11, S12). The detailed experimental procedure can be found in the Supplementary information. The current-potential characteristics of $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ photoanodes prepared by two different methods were compared under AM 1.5G simulated sunlight illumination in 0.1 mol L^{-1} phosphate buffer (pH 7), as shown in Fig. S13. Compared

with $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ photoanodes prepared by spray pyrolysis, the saturation photocurrent density of $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ photoanodes prepared by drop-necking treatment is almost halved. We also carried out electrochemical impedance spectroscopy (EIS) measurements to evaluate the resistance of two photoanodes, as shown in Fig. S14 in darkness and under $1.21 \text{ V}_{\text{RHE}}$ bias. The semicircle is attributed to the charge-transfer process. The photoanodes prepared by drop-necking treatment has a larger semicircle diameter, indicating a high charge transfer resistance in the particle-assembled thin film. However, for $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$ photoanodes prepared by spray pyrolysis, the semicircle diameter becomes relatively small, indicating good charge transport characteristics and reduced resistance, which is in accordance with J - V curves.

CONCLUSIONS

$\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes were prepared *via* spray pyrolysis, followed by annealing at 550°C for 2 h. Compared to CuWO_4 photoanodes, the photocurrent of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes produce a significant increase because of the improvement of photon utilization as well as the increase of carrier concentration. The photocurrent density at $1.23 \text{ V}_{\text{RHE}}$ increases six times higher with the optimal Mo/W atoms ratio. In addition, compared with particle-assembled thin-film photoanodes prepared by solid-phase reaction combined with drop-necking treatment, the photoanodes prepared by spray pyrolysis have obvious advantages in terms of reducing resistance and facilitating charge transport.

Of course, more efforts can be made to improve the performances. The highest IPCE value of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes is quite small, suggesting that both light absorption and charge collection can be further improved. Hence, we will design favorable host-guest structures to improve the performances. Besides, to improve the stability of the photoanodes and enhance the collection efficiency of the hole to promote the PEC properties of $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes, it is necessary to explore the appropriate protective layers and cocatalysts, which will be further studied in subsequent experiments.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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通过喷雾热裂解法合成而改进的 $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ 光阳极的分解水性能

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摘要 CuWO_4 和 CuMoO_4 的固溶体 $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ 是一种铜基多组氧化物半导体, 拥有比 CuWO_4 更窄的带隙. 理论上, 它可以拓宽对太阳光谱的响应范围, 吸收更大部分的可见光, 获得更高的太阳能-化学能转换效率. 本研究通过简单、低成本的喷雾热裂解法在导电玻璃上制备了 $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ 薄膜光阳极. 在AM 1.5G模拟太阳光(100 mW cm^{-2})照射下, 制备出的 $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ 光阳极在pH 7的 0.1 mol L^{-1} 磷酸缓冲液中产生了比 CuWO_4 光阳极更高的光电流. 结合IPCE和莫特-肖特基分析可知, 光电流的增长来源于Mo原子的加入所造成的光子利用率提高以及载流子浓度的增加. 而且, 在最优的Mo/W原子比例下, $1.23 \text{ V}_{\text{RHE}}$ 偏压时的光电流从 0.07 mA cm^{-2} 显著地增加到 0.46 mA cm^{-2} . 与对应的颗粒组装薄膜光阳极(通过固相反应结合涂覆-粘结后处理得以制备)相比较, 喷雾热裂解法所制备的光阳极有利于降低电阻和促进电荷传输.