Nanolayered CuWO_4 Decoration on Fluorine-Doped SnO_2 Inverse Opals for Solar Water Oxidation

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ABSTRACT

The pristine fluorine-doped SnO_2 (abbreviated as FTO) inverse opal (IO) was developed using a 410 nm polystyrene bead template. The nanolayered copper tungsten oxide (CuWO_4) was decorated on the FTO IO film using a facile electrochemical deposition, subsequently followed by annealing at 500°C for 90 min. The morphologies, crystalline structure, optical properties and photoelectrochemical characteristics of the FTO and CuWO_4 -decorated FTO (briefly denoted as FTO/ CuWO_4) IO film were investigated by field emission scanning electron microscopy, X-ray diffraction, UV-vis spectroscopy and electrochemical impedance spectroscopy, showing FTO IO in the hexagonally closed-pack arrangement with a pore diameter and wall thickness of about 300 nm and 20 nm, respectively. Above this film, the CuWO_4 was electrodeposited by controlling the cycling number in cyclic voltammetry, suggesting that the CuWO_4 formed during 4 cycles (abbreviated as CuWO_4 (4 cycles)) on FTO IO film exhibited partial distribution of CuWO_4 nanoparticles. Additional distribution of CuWO_4 nanoparticles was observed in the case of FTO/ CuWO_4 (8 cycles) IO film. The CuWO_4 layer exhibits triclinic structure with an indirect band gap of approximately 2.5 eV and shows the enhanced visible light absorption. The photoelectrochemical (PEC) behavior was evaluated in the 0.5 M Na_2SO_4 solution under solar illumination, suggesting that the FTO/ CuWO_4 (4 cycles) IO films exhibit a photocurrent density (J_{sc}) of 0.42 mA/cm^2 at 1.23 V vs. reversible hydrogen electrode (RHE, denoted as V_{RHE}), while the FTO IO and FTO/ CuWO_4 (8 cycles) IO films exhibited a J_{sc} of 0.14 and 0.24 mA/cm^2 at 1.23 V_{RHE} , respectively. This difference can be explained by the increased visible light absorption by the CuWO_4 layer and the favorable charge separation/transfer event in the cascading band alignment between FTO and CuWO_4 layer, enhancing the overall PEC performance.

Keywords : Photoelectrochemical water splitting, CuWO_4 , Heterojunction, Inverse opal

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1. Introduction

Photoelectrochemical (PEC) water splitting is regarded as an ideal way to generate H_2 energy in an aqueous solution without any external bias using an eco-friendly method. PEC mainly consists of two

processes: (1) the hydrogen-evolution reaction (HER) is a relatively rapid process to generate H_2 molecules in a reversible anodic reaction with only two electrons, and (2) the oxygen-evolution reaction (OER), which is a rate-limiting step in which four protons and four electrons from two water molecules participate in bond formation ($\sigma + \pi$ of O_2) [1]. Accordingly, the rate control to catalyze the O-O bond formation is a crucial determinant of the photo-

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conversion efficiency of water splitting. As a result, the study has been focused on the development and discovery of new photoelectrodes. Usually, metal oxides have been extensively used for photocatalytic and photoelectrochemical hydrogen evolution due to their chemical stability, nontoxicity and relatively low cost [2,3]. In particular, since the discovery of catalytic water splitting on TiO_2 photoelectrodes by Fujishima and Honda [4], considerable efforts have been devoted to developing high efficiency metal oxides in the reaction. However, the large band gap (E_g) of TiO_2 (> 3.0 eV) limits its light absorption to only 5% of solar light similar to ZnO , Nb_2O_5 and SnO_2 . Considering the intimate relationship with photocurrent density and incident solar light absorption in PEC system, the exploration of narrower bandgap materials (e.g., WO_3 , $\alpha\text{-Fe}_2\text{O}_3$, BiVO_4) as photoelectrodes is a reasonable approach to enhanced visible light capture [5-7]. More recently, copper tungstate (CuWO_4 , $E_g = 2.25$ eV), which is another material showing visible light absorption to have n -type behavior, has been actively investigated because of its narrower bandgap relative to that of WO_3 ($E_g = 2.8$ eV), the high chemical stability resulting from strong covalency associated with the copper oxygen bonds, inhibition of dissolution to form soluble tungstates by the known acid-base reaction in WO_3 at $\text{pH} > 5$, and high chemoselectivity even in the Cl^- solution [8]. Furthermore, the edge potential of conduction band is similar to that of WO_3 , but the edge potential of valence band is lower than that of WO_3 to approximately 0.5 V [9]. However, CuWO_4 with poor charge separation efficiency and slow kinetics in the electrolyte interfacial region still exhibits low photoconversion efficiency for OER. Therefore, approaches such as the introduction of effective OER electrocatalyst to minimize the energy penalty associated with water oxidation improved the catalytic efficiency and lowered the excessive potential closely related to the interfacial charge transfer. Specifically, nonprecious and abundant electrocatalysts including Mn-phosphate (MnPO), Co-phosphate, and Ni-based electrocatalysts, have been widely used to reveal the remarkable increase in electrocatalytic properties [10]. Bartlett's group reported that the MnPO -based CuWO_4 photoelectrode exhibited improved PEC performance, corresponding to the cathodic shift of the onset potential for water oxidation by ~ 100 mV and a mild increase in photocurrent density, particularly at low applied bias

[11]. In addition, iron doping or hydrogen treatment of the CuWO_4 film increased the bulk electronic conductivity [12]. Another strategy involved formation of heterojunctions between CuWO_4 and a second semiconductor, such as WO_3 , BiVO_4 , and Ag_2NCN with synergetic enhancement in photocurrent density. Adam's group used Ag_2NCN to functionalize the CuWO_4 surface resulting in 3-fold increase in photocurrent density, attributed to more efficient charge separation and hole collection efficiencies under circumstances where the higher position of conduction band edge of Ag_2NCN favored charge carrier separation at the interface [13]. Similarly, the $\text{WO}_3/\text{CuWO}_4$ photo-anodes show effective band alignment for charge separation from the conduction band edge of WO_3 to CuWO_4 resulting in higher photocurrent.

Recently, we reported the photoelectrochemical behavior based on a WO_3 -coated fluorine-doped SnO_2 (FTO) inverse opal (IO) nanostructure [14]. An electrodeposited WO_3 film was uniformly coated on the FTO inverse opal template using electrodeposition, contributing to enhanced visible-light absorption resulting in the best photocurrent of 2.9 mA/cm^2 . FTO takes part in a good electronic conducting skeleton to show semi-metallic property, enabling favorable charge transport in a non-conductive semiconductor photoanode. Further, the 3-dimensional (3D) inverse opal provides sufficient surface area for the PEC reaction, intensifying the light absorption by the photonic crystal effect. Therefore, in the present study, the CuWO_4 showing narrower band gap and strong chemical stability relative to that of WO_3 was deposited on the FTO inverse opal, directly mediating the PEC reaction, using a facile electrodeposition. According to the number of cycles in the cyclic voltammetry of a specific potential range, the electrodeposited CuWO_4 thickness was modulated, suggesting that 4 cycles yielded the optimum photocurrent density. The CuWO_4 nanoparticles covered the entire FTO IO film sparsely, contributing to enhanced visible light absorption as well as retardation in charge recombination and dramatic reduction in interfacial resistance. The development and related characterization based on the FTO/ CuWO_4 IO films are discussed.

2. Experimental

2.1 Preparation of FTO/ CuWO_4 Inverse Opal Film

FTO (Pilkington TEC GlassTM, sheet resistance

$8 \Omega \text{ sq}^{-1}$) was cleaned with deionized (DI) water, ethanol, and acetone for 20 min each to minimize the organic contamination and dust partially for use as a template. FTO/CuWO₄ IO films were prepared using a modified procedure [15]. Briefly, an aqueous solution containing 10 wt % polystyrene (PS) beads with an average diameter of 410 (± 10) nm was spread on the surface of the FTO substrate and subsequently spin-coated at 1000 rpm for 10 s. Subsequently, the precursor solution consisting of tin tetrachloride (SnCl₄·5H₂O, 30 μL , 0.5 M) containing 10 mol % NH₄F as the F⁻ source and absolute ethanol as the solvent was dropped on the multilayered PS bead template on a spin-coating, after which the sample was spun at 1,000 rpm for 10 s. After the sample was dried briefly, high-temperature annealing was performed at 500°C for 2 h under ambient air to slowly remove the PS bead template.

In order to deposit a CuWO₄ layer on the FTO IO film, we carried out direct electrodeposition in a three-electrode cell with saturated (sat.) Ag/AgCl (0.11 V versus NHE, briefly designated as 0.11 V_{NHE}), platinum, and the FTO IO film as the reference, counter, and working electrodes, respectively. The composition of the bath solution used was the same as reported previously [16]. The CuWO₄ films were electrodeposited on FTO IO film from a 50 mM bath composed of 50 mM Cu(NO₃)₂·nH₂O, 50 mM H₂W₂O₁₁ and 5 wt% sodium dodecyl sulphate (SDS). The acidic peroxotungstate precursor was prepared by adding concentrated 30% H₂O₂ to an appropriate amount of Na₂WO₄·2H₂O in DI water. The acidity of the final solution was adjusted to pH 1.1 by adding 3 mL of concentrated HNO₃. The electrodeposition of CuWO₄ film was conducted using cyclic voltammetry under potential sweeping between -0.4 V and +0.4 V vs. homemade Ag/AgCl for 4 to 8 cycles at a scan rate 50 mV/s using an Autolab potentiostat (PGSTAT302N.FRA2). After completion of the electrodeposition, the as-deposited films were rinsed with DI water and subsequently annealed at 500°C for 900 min in air.

2.2 Characterization

The surface and cross-sectional morphology of the FTO/CuWO₄ inverse opal films were investigated using a JEOL 7500 field-emission scanning electron microscope operating at 10 kV and 10 mA. To further investigate the morphology and crystalline proper-

ties of samples, the high-resolution transmission electron microscopy (HR-TEM) using a JEOL-2010 instrument at an operating voltage of 300 kV. The crystalline properties of the FTO/CuWO₄ inverse opal films were examined using high-power X-ray diffraction (HP-XRD, X'Pert PRO Multi Purpose X-Ray Diffractometer) with Cu K α radiation operating at 60 kV and 55 mA. The PEC performance under dark and illumination conditions were assessed using a potentiostat (CHI Instruments, USA) with a homemade Ag/AgCl reference electrode (0.11 V vs normal hydrogen electrode), a Pt mesh counter electrode, and FTO/CuWO₄ inverse opal film (electroactive area of 0.2 cm²). The Ag/AgCl electrode can be converted to the reversible hydrogen electrode (RHE = NHE at pH 0) using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \text{ V} \cdot \text{pH} + 0.11 \text{ V}$$

A 150-W Xe-lamp (100 mW/cm², AM 1.5 filter) light source and a 0.5 M Na₂SO₄ solution (pH 6.5) after nitrogen bubbling to remove dissolved oxygen were used to evaluate the PEC performance. The incident photon-to-current efficiency (IPCE) was measured using a homemade system composed of a 150-W xenon light source and a monochromator (HS Technologies, Korea). Moreover, electrochemical impedance spectroscopy (EIS) on the FTO and the FTO/CuWO₄ inverse opal films was used to measure the cell resistance of each component in the PEC working condition under one-sun illumination at the open-circuit voltage (OCV) in the frequency range from 0.1 Hz to 10 kHz with amplitude of ± 10 mV. To compare with the decay lifetime of FTO and the FTO/CuWO₄ inverse opal films, the photovoltage decay measurement was performed as soon as the illumination was blocked. The transmittances of FTO and FTO/CuWO₄ IO films were evaluated with UV-vis spectroscopy (PerkinElmer LAMBDA-900 UV/VB/IR spectrometer) at room temperature.

3. Results and Discussion

Fig. 1 represents the high resolution FE-SEM images of the hexagonally aligned FTO, FTO/CuWO₄(4 cycles), and FTO/CuWO₄(8 cycles) films. Generally, the IO films exhibit honeycomb-shaped hexagonal close-packed array, dense coverage and

Fig. 1. Surface FE-SEM images of (a) FTO, (b) FTO/CuWO₄(4cycles) and (c) FTO/CuWO₄(8 cycles) IO films.

crack-free structure. Compared with the diameter 410 (± 5) nm of the pristine multilayered PS template arranged in a regular array of close-packed and layered colloids, the pore diameter of IOs was decreased to approximately 300 nm and the pore shrinkage of about 27% probably due to the loss of liquid volume from the precursor and the densification of FTO during the phase transformation from the amorphous to the rutile phase. This shrinkage was similar to the previous case (25-30%) captured from the sol-gel based structure [17]. The wall thickness between each micropore was ~ 20 nm (± 5) nm with thicker walls at the contact area and the length of the prepared FTO IO was approximately 3.7 μ m. A thin CuWO₄ layer was coated on the FTO IO films by facile electrodeposition using cyclic voltammetry, altering the number of cycles from 4 cycles (Fig. 1(b)) to 8 cycles (Fig. 1(c)). Both FTO/CuWO₄ IO films showed distribution of partially agglomerated CuWO₄ nanoparticles through the entire FTO IO surface with a higher density in the FTO/CuWO₄(8 cycles) IO film. This result indicates that the increased cycling induced further deposition of CuWO₄ layer, although the relation was not directly linear. Hence, it is apparent that the pore diameter was slightly reduced to approximately 10 nm and the wall thickness was irregularly decreased or increased depending on the presence of CuWO₄ nanoparticles in well-ordered hexagonal-close packed arrangement of the FTO IO skeleton. To confirm the uniformity of the electrodeposited CuWO₄ layer and thickness in the FTO IO films, the cross-sectional images of FTO and FTO/CuWO₄(4 cycles) IOs films were measured, as illustrated in the inset of Fig. 1(b). Both samples exhibit a similar thickness of 3.1 μ m, disclosing the partial coating of CuWO₄ layer into the interior FTO IO films.

To further survey the morphology and crystalline properties of the IO films, the TEM measurements were performed, as presented in Fig. 2. Herein, the FTO and FTO/CuWO₄ IO films were prepared for a comparison. In the case of FTO IO film, an assembly of the extremely small crystallites of FTO with an average size of ~ 5 nm was comprised of 3D ordered macroporous IO structure because the FTO IO film was prepared by the sol-gel assisted spin coating method. The pore size of FTO IO film exists in ~ 300 nm to be identical to the image captured from FE-SEM (Fig. 1). Furthermore, to certify the crystallinity of the FTO IO film, the TEM image measured in HR-mode was shown in Fig. 2(d), revealing an inter-planar lattice spacing of 3.35 Å with clear lattice fringes which conforms to the rutile (110) plane of the SnO₂ crystal system. In the case of FTO/CuWO₄(4cycles) IO film in Fig. 2(b), the less porous IO structure was observed and partially agglomerated owing to the thick CuWO₄ coating, attributed from the electrodeposition in the repetitively cycling of potential in which the CuWO₄ nanoparticles on the vicinity of the initial seed layer formed on the surface of FTO IO can grow quite fast and the uneven coverage via the surface of FTO IO film happened. Also, the crystalline (110) and (0-11) planes from FTO and CuWO₄ phase (Fig. 2(e)) were clearly observed from an inter-planar lattice spacing of 3.35 Å and 3.77 Å with clear lattice fringes, respectively, which complies with the rutile and triclinic plane of SnO₂ and CuWO₄ crystal system [18]. Fortunately, the FTO as well as the CuWO₄ phases were concurrently found to confirm the crystallinity of the FTO/CuWO₄(4cycles) IO films. In the case of FTO/CuWO₄(8cycles) IO film in Fig. 2(c and f), the more agglomerated CuWO₄ layer on FTO IO film was observed due to the more cycling in the same potential range, further disclosing

Fig. 2. Low magnification TEM images of (a) FTO, (b) FTO/CuWO₄(4cycles) and (c) FTO/CuWO₄(8 cycles) IO films. High-magnification TEM images of (c) FTO, (d) FTO/CuWO₄(4cycles) and (f) FTO/CuWO₄(8 cycles) IO films.

an inter-planar lattice spacing of 3.35 Å and 3.88 Å with clear lattice fringes which are consistent with the rutile (110) plane and triclinic (110) plane of SnO₂ and CuWO₄ crystal system. To verify the crystalline properties of FTO, FTO/CuWO₄(4 cycles), and FTO/CuWO₄(8 cycles) IO films, XRD analysis was performed and the results are shown in Fig. 3. All the diffraction peaks in the FTO IO-based samples were indexed to the tetragonal phase of SnO₂ (JCPDS no. 41-1445; $a = 4.7$ Å, $c = 3.2$ Å) corresponding to (110), (101), (200) and (211) reflections at 26.5°, 33.8°, 37.8° and 51.7°, respectively, even though the 10 wt % F⁻ ions were doped in the main SnO₂ material. In the case of FTO/CuWO₄ IO films, additional triclinic CuWO₄ peaks (JCPDF no: 73-1823) with the representative (110), (0-10), (100) and (021) planes at 23.01°, 23.57°, 24.24° and 33.21° were remarkably obtained with a lattice parameter of $a = 4.71$ Å, $b = 4.88$ Å and $c = 5.84$ Å, which was consistent with the preceding literature [18], together with the rutile FTO peaks. In addition, no additional peaks, establishing the absence of other crystallites or

Fig. 3. Typical XRD patterns of (a) FTO, (b) FTO/CuWO₄(4cycles) and (c) FTO/CuWO₄(8 cycles) IO films.

impurities such as SnO_x and WO_x were observed. Furthermore, based on Scherrer's equation, the average crystallite size of each sample was calculated using the main (100) plane from CuWO₄ phase to yield an average grain size of 21.57 nm in 4 and 8

Fig. 4. (a) UV-vis transmittance spectra and (b) Tauc plot of FTO, FTO/CuWO₄(4cycles) and FTO/CuWO₄(8 cycles) IO films.

cycles of FTO/CuWO₄ IO films, reflecting the absence of further growth of CuWO₄ nanoparticles during the cycling of potential.

Fig. 4 depicts the UV-vis transmittance spectra of the FTO, FTO/CuWO₄(4 cycles) and FTO/CuWO₄(8 cycles) IO films developed on the FTO substrate. The absorption onset for FTO IO was ~ 360 nm, suggesting a UV-active material. On the other hand, it was well known that the CuWO₄ shows an indirect band gap due to the absence of sharp absorption, in that the absorptivity coefficient, α , was 6600 cm^{-1} at 400 nm , which sharply decreased to 1715 cm^{-1} at 500 nm [16]. Although the CuWO₄ exhibited an indirect band gap, it may still result in high photoactivity with nanowire or nanoplatelet morphologies as well as modified charge transport pathways following introduction of other materials. In this study, the absorption onset of FTO/CuWO₄ IO film was $\sim 470 \text{ nm}$ with enhanced light absorption toward visible wavelength. The high transmittance in FTO/CuWO₄(4 cycles) IO film indirectly reflects the contribution of increased light absorption corresponding to a little scattering and reflection, compared with that of FTO/CuWO₄(8 cycles) IO film in the identical structure. A minor fluctuating absorption band above 500 nm may result from the photonic crystal effect in the 3D inverse opal structure. The precise optical bandgap (E_g) of all samples was calculated by extrapolating the linear portion of the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot, known as Tauc plot, displayed in Fig. 4(b), where α represents absorption coefficient and $h\nu$ is the incident photon energy. The estimated E_g of FTO, FTO/CuWO₄(4 cycles) and

FTO/CuWO₄(8 cycles) IO films were 3.55 eV , 2.57 eV , and 2.42 eV , respectively. It has been reported that the original CuWO₄ band gap was approximately 2.2 eV . However, increasing the cycle number in cyclic voltammetry elevated the loading amount of CuWO₄ layer. Considering that the light recognizes the combined FTO and CuWO₄ layers in 3D inverse opal structure, the E_g of FTO/CuWO₄(8 cycles) IO film was shifted to a lower band gap, relative to that of 4 cycles, to approach the original band gap of CuWO₄. Perhaps, as the loading amount of CuWO₄ on the FTO IO film increased further, the total bandgap was decided by the deposited CuWO₄ layer to reach to the bandgap of 2.2 eV .

To identify the PEC behavior of FTO and FTO/CuWO₄ IO films, the fundamental PEC properties were characterized as shown in Fig. 5. Fig. 5(a) shows a set of linear sweep voltammetry of FTO, FTO/CuWO₄(4 cycles) and FTO/CuWO₄(8 cycles) IO films under chopped illumination (AM 1.5G, 100 mW/cm^2) in $0.5 \text{ M Na}_2\text{SO}_4$ (pH 6.5). Considering that the dark current acquired under dark was in the range of $\sim 10^{-2} \text{ mA/cm}^2$, the photoresponse of all the samples was remarkably under light illumination. Furthermore, the prompt photoresponse of the samples indicates general stability of the photocurrents without photo-induced charging effects. FTO IO film exhibited a photocurrent density (J_{sc}) of 0.14 mA/cm^2 at 1.23 V_{RHE} , whilst the substantially larger photocurrent densities were achieved by the FTO/CuWO₄(4 cycles) with a J_{sc} of 0.42 mA/cm^2 , followed by the FTO/CuWO₄(8 cycles) possessing a

Fig. 5. (a) Chopped LSV under full sun on/off cycles, (b) Chopped LSV under visible sun on/off cycles (c) IPCE spectra of FTO and FTO/CuWO₄ IO films in 0.5 M Na₂SO₄ solution, and (d) EIS spectra under solar illumination in FTO and FTO/CuWO₄ IO films including the electrical equivalent circuit in the inset of (d).

J_{sc} of 0.24 mA/cm² at 1.23 V_{RHE}. Compared with the FTO IO film, the FTO/CuWO₄(4 cycles) IO films attained approximately 3-fold enhancement emphasizing the positive role of heterojunction FTO-CuWO₄ combination as a core-shell structure improving the photoactivity of FTO or CuWO₄ film under illumination. This photocurrent densities is a little bit lower than the recently reported the highest value (0.58 mA/cm² at 0.8 V V_{RHE}) and exist in the meaningful value [19]. However, increasing the amount of CuWO₄ loading reversibly, the J_{sc} was rapidly degraded, probably due to the mechanically unstable contact between FTO IO and CuWO₄ layers, resulting in rapid charge recombination. Furthermore, the modification of FTO IO structure with a CuWO₄ layer resulted in the anodic shift of the onset potential by ca. 150 mV, compared with

(0.36 V) observed for the base FTO IO electrode (not shown here). However, the magnitude of the photocurrent was extremely low and possibly lost in the background signal due to the high overpotential in this region. As a control sample, the CuWO₄ film on the FTO substrate was also grown under the same experimental condition, showing no photoresponse in the entire potential range (not shown here). To intimately examine the photoresponse under visible light from the CuWO₄ layer with an E_g of approximately 2.5 eV, the chopped on/off LSVs were again measured using a 400 nm cutoff filter and the results are presented in Figure 5(b). Unexpectedly, a significant J_{sc} (0.1 mA/cm² at 1.23 V_{RHE}) from the CuWO₄ layer (4 cycles) was achieved under visible light coinciding with the sequence obtained from the LSVs under full solar illumination. Further CuWO₄

layer (8 cycles) also showed the degradation of J_{sc} under visible light.

To review the generation of photocurrent density, IPCE measurements were carried out at 1.0 V vs RHE in the 0.5 M Na_2SO_4 solution, as depicted in Fig. 5(c). The FTO IO film showed the typical photoresponse of FTO material corresponding to a maximum IPCE of 3.42% at 315 nm and an onset potential of 385 nm. Furthermore, the FTO/ CuWO_4 IO films exhibit two distinct peaks from the respective FTO and CuWO_4 layers and have identical overall IPCE patterns. In the case of FTO/ CuWO_4 (4 cycles), the maximum IPCE value of 9.4% was obtained at 315 nm with a broad shoulder peak caused by the CuWO_4 layer, corresponding to an IPCE value of 7.45% at 390 nm, whereas the FTO/ CuWO_4 (8 cycles) shows the maximum IPCE value of 5.89% at 315 nm with the IPCE shoulder peak of 4.17% at 390 nm. The onset wavelength of FTO/ CuWO_4 IO films exists in the same wavelength of 475 nm due to the light absorption of the CuWO_4 layer. In general, the IPCE is obtained by the following equation [20]:

$$IPCE = \frac{1239.8(W \cdot \text{nm}/A) \cdot J(\text{mA}/\text{cm}^2)}{\lambda(\text{nm}) \cdot J_{light}(\text{mW}/\text{cm}^2)}$$

where J denotes the measured photocurrent density at a specific wavelength; λ is the wavelength of incident light; and J_{light} stands for the measured irradiance at a specific wavelength. The J_{sc} calculated by the integration of each IPCE spectrum was similar to J_{sc} at 1.0 V vs. RHE in Fig. 5(a). As a whole, the FTO/ CuWO_4 (4 cycles) film exhibits substantially enhanced photoactivity over the entire UV and near visible region, attributed to electrically conducting FTO core IO as well as the visible light absorbing CuWO_4 shell layer under the favorably cascading band alignment between the FTO and CuWO_4 materials.

To determine the electrochemical kinetics at each component and interfacial region in the PEC system,

the EIS analysis was conducted at the frequency range of 10 kHz to 0.1 Hz at OCV under solar illumination. Fig. 5(d) shows the Nyquist plots of the FTO and FTO/ CuWO_4 IO films in the 0.1 M Na_2SO_4 solution including the suggested equivalent circuit for the simulation to obtain the exact and quantitative fitted values from each component, including R_s indicating the ohmic or series resistance including the FTO substrate, the resistance associated with the ionic conductivity in the electrolyte and the external contact resistance at the high frequency. R_{ct} in the low and middle frequency is correlated with the semiconductor/electrolyte charge transfer resistance. Furthermore, the constant phase element (CPE) represents the non-ideal capacitance of the Helmholtz layer in the nanoporous semiconductor/electrolyte interface [21]. The quantitatively fitted data are summarized in Table 1. All samples exhibited a similar value of $\sim 220 \Omega$, suggesting that all samples existed in the analog environment. Meanwhile, FTO IO showed significantly high R_{ct} of approximately 18890 Ω , whereas FTO/ CuWO_4 IO films exhibited quite low R_{ct} values of 8000-10000 Ω , indicating that the photogenerated holes in the FTO IO film experience more than twice the magnitude of difficulty to reach the electrolyte compared with the FTO/ CuWO_4 (4 cycles) IO film. The introduction of CuWO_4 layer on the FTO IO film passivates the surface state or trap sites in the surface region of FTO IO film, promoting rapid charge transfer in the solid-liquid interface, which induces a low R_{ct} and finally, contributes to the enhanced PEC activity.

In summary, the electrodeposition of thin CuWO_4 layer on the FTO IO film was successfully developed using cyclic voltammetry by varying the cycling number from 4 to 8 cycles. FTO/ CuWO_4 (4 cycles) IO film exhibited the highest J_{sc} (0.42 mA/cm^2 at 1.23 V_{RHE}), while FTO IO film showed a J_{sc} of 0.14 mA/cm^2 at 1.23 V_{RHE} . The FTO/ CuWO_4 (8 cycles) IO film displays a J_{sc} of 0.24 mA/cm^2 at 1.23 V_{RHE} . An approximately 3-fold enhancement of J_{sc}

Table 1. Quantitative values of ohmic resistance (R_s) and charge-transfer resistance (R_{ct}) of FTO and FTO/ CuWO_4 IO films fitted using the suggested equivalent electrical circuit.

	$R_s(\Omega\text{cm}^2)$	$R_{ct}(\Omega\text{cm}^2)$	CPE-T(μFcm^{-2})	CPE-P(μFcm^{-2})
FTO IO	234.8	18890	0.00015	0.75
FTO IO/ CuWO_4 (4 cycles)	210	7866	0.0002	0.84
FTO IO/ CuWO_4 (8 cycles)	322.6	10220	0.00027	0.78

Fig. 6. Schematic cascade of band alignment between FTO and CuWO_4 materials to show the beneficial charge transfer events.

was attained in the deposition of the optimum CuWO_4 layer on FTO IO film, attributed to improved visible light absorption and favorable band alignment between CuWO_4 and FTO materials (Fig. 6), accelerating the charge separation and charge transfer rate in the solid/liquid junction. On the other hand, the thick and denser CuWO_4 loading on the FTO IO film induced mechanically brittle connection, reversibly increasing the charge recombination reaction, resulting in the degradation of PEC performance.

4. Conclusions

Facile FTO and FTO/ CuWO_4 IO films were developed via polystyrene opal template-based method and electrochemical deposition using cyclic voltammetry, exhibiting similar morphology and crystalline properties. The PEC behavior of the films was tested in 0.5 M Na_2SO_4 solution under solar illumination, revealing that the high J_{sc} of 0.42 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ was achieved in the FTO/ CuWO_4 (4 cycles) IO film, followed by the FTO/ CuWO_4 (8 cycles) possessing a J_{sc} of 0.24 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ and FTO IO film with a J_{sc} of 0.14 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$. The primary enhancement factor resulted from visible light absorption by the CuWO_4 layer and the cascading band alignment between CuWO_4 and FTO layer promoted favorable charge separation and transfer, suppressing the charge recombination rate. Further-

more, from the Nyquist of EIS analysis, a substantially reduced R_{ct} was attained in the FTO/ CuWO_4 (4 cycles) IO film, establishing the surface passivation effect of nanolayer CuWO_4 and the beneficial hole transfer to the electrolyte, compared with that of FTO and FTO/ CuWO_4 (8 cycles) IO films. The original CuWO_4 showing intrinsically low electrical conductivity was not effective for a photoelectrode indicated for solar water oxidation. The thin CuWO_4 layer was combined with a highly conductive FTO IO structure as a skeleton resulting in synergistic effects to capture light in the visible wavelength as well provide enhanced electrical conductivity. Therefore, the heterojunction formed by the combination of appropriate materials represents a challenging and promising approach for advanced PEC device.

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