



Synthesis of Cu_2O - BiVO_4 catalysts used as high-performance photoanodes for photoelectrochemical water splitting

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ABSTRACT

Herein, Cu_2O and BiVO_4 were synthesized using different methods. The structure, morphology, light absorption ability of synthesized materials were examined by XRD, SEM, DRS UV-Vis, PL and photoelectrochemical performance. was determined by LSV and EIS methods. BiVO_4 synthesized by the electrodeposition exhibits lower crystallinity and smaller particle sizes, leading to higher photocurrent density ($0.55 \text{ mA}\cdot\text{cm}^{-2}$ at 1.23 V versus RHE). The combination of Cu_2O and BiVO_4 improves charge transfer ability and photocatalytic performance, with a current density of $1.23 \text{ mA}\cdot\text{cm}^{-2}$ at 1.23 V vs RHE, demonstrating the material's potential as a photoanode in photoelectrochemical water splitting.

Introduction

In recent years, global energy demand has surged due to industrialization and population growth. The depletion and environmental harm of fossil fuels raises concerns about energy sustainability and pollution. Producing clean, renewable energy is critical, and hydrogen stands out as a promising solution due to its high energy density, emission-free nature, and long-term storage ability [1, 2]. However, current hydrogen production, primarily via steam methane reforming, generates significant greenhouse gases. Efforts are focused on developing green technologies for water splitting, including photoelectrochemical (PEC) methods, first introduced in 1972 by Fujishima and Honda using TiO_2 under UV light. PEC water splitting uses solar energy to generate hydrogen and oxygen, with efficiency limited by the slow kinetics of the oxygen evolution reaction (OER). The efficiency of OER largely relies on employed catalytic materials, highlighting the need to enhance photocatalyst performance. Therefore, the development of high-performance photoanode materials is essential for improving PEC efficiency [3, 4]. Among potential

photoanode materials, BiVO_4 has garnered attention for its ability to absorb visible light (bandgap $\sim 2.4 \text{ eV}$), long-term stability, and appropriate band edges alignment with oxygen evolution and hydrogen evolution potentials. BiVO_4 is also composed of non-toxic, abundant elements and remains stable in near-neutral solutions, making it suitable for PEC applications. Nonetheless, inherent limitations like inefficient transfer of photogenerated charges, and rapid recombination of electron-hole pairs hinder the photocatalytic performance of BiVO_4 . To address these challenges, various approaches have been proposed, including formation of heterojunctions [5, 6], doping with metals or non-metals [7, 8], and surface modifications [9, 10]. Among these methods, heterojunction construction stands out as a particularly effective strategy. Majumder *et al.* demonstrated that a $\text{BiVO}_4/\text{Fe}_2\text{TiO}_5/\text{Co}_3\text{O}_4$ heterojunction achieved a 5.3-fold increase in photocurrent density along with a significant cathodic shift compared to bare BiVO_4 photoanodes [11]. Liu *et al.* observed that a $\text{Fe}_3\text{CoPPc-BiVO}_4$ hybrid produced an exceptional oxygen evolution rate of $4557 \mu\text{mol g}^{-1} \text{ h}^{-1}$ in the presence of iodate under visible light, nearly two orders of magnitude

higher than pristine BiVO_4 [12]. Among well-studied semiconductors, Cu_2O is characterized by its narrow direct band gap (2.1–2.3 eV), high absorption coefficient, non-toxic nature and excellent carrier mobility [13, 14]. Heterojunction between Cu_2O , a p-type semiconductor, and BiVO_4 , an n-type semiconductor, can enhance charge separation and reduce recombination of photogenerated electron-hole pairs, improving PEC performance. This synergy also broadens light absorption range and increases the efficiency of solar energy utilization. This study focuses on the effect of heterojunction of Cu_2O - BiVO_4 photoanode on its activity for photoelectrochemical water splitting.

Experimental

Chemicals

All chemicals, including bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), vanadyl acetylacetonate ($\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$), ammonium metavanadate (NH_4VO_3), dimethyl sulfoxide ($\text{C}_2\text{H}_6\text{OS}$), ethylenediaminetetraacetic acid (EDTA), ethylene glycol (EG), nitric acid (HNO_3), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$); sodium tartrate dihydrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$); glucose; urea and sodium hydroxide were of analytical grade and procured from China. All these chemicals were utilized without further purification. Fluorine-doped tin oxide (FTO) substrates were cut into 1.0 cm \times 2.5 cm pieces. They were cleaned using soap and subsequently sonicated in acetone, ethanol, and deionized water for 30 minutes each.

Synthesis of BiVO_4 by chemical precipitation

For the chemical precipitation method, 8.730 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 250 mL of 1M HNO_3 . Then, 2.106 g of NH_4VO_3 was added to the solution, and the mixture was stirred for 1 hour at 40°C. After adding 9.00 g of urea, the solution was kept in 80°C oil bath for 24 hours. After centrifuging, washing, and drying, the powder was collected and denoted as BiVO_4 -CP. The powder was loaded on FTO by doctor blade method, dried at 60°C for 6 hours, and calcined at 450°C for 2 hours. The final sample is denoted as BiVO_4 -CP/FTO.

Synthesis of Cu_2O by chemical reduction

8.725 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 50 mL of distilled water. Then, 2.80 g of NaOH and 6.02 g of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ were dissolved in 50 mL of distilled water. Sodium tartrate solution was mixed with copper sulfate solution to form copper tartrate alkaline solution with continuous stirring at 60 °C. Then 50 mL of 1.4 M glucose was added to copper tartrate alkaline solution, forming a red-brick Cu_2O precipitate. The pH of the solution was adjusted to 10. The obtained Cu_2O

precipitate was filtered, washed, and dried with acetone. This sample was designated as Cu_2O . Cu_2O was deposited on FTO glass using the doctor blade method, dried at 60°C for 6 hours, and calcined at 450°C for 2 hours and designated as Cu_2O /FTO.

Synthesis of BiVO_4 thin film by electrodeposition

Bi metal was deposited on FTO glass through electrochemical deposition in a solution containing 0.4852 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 100 mL EG and 50 mL water. A three-electrode setup was employed, comprising an FTO working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode, with deposition performed at -0.6 V (vs. Ag/AgCl) for 500 seconds. The Bi-coated electrode was washed, dried, and coated with 200 μL of 0.2M $\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$ solution in $\text{C}_2\text{H}_6\text{OS}$. After calcination at 450°C for 2 hours, the electrode was immersed in 1M NaOH for 30 minutes to remove residual V_2O_5 , washed, dried at 60°C, and denoted as BiVO_4 -ED/FTO.

Synthesis of Cu_2O - BiVO_4 thin film by electrodeposition

Cu_2O was electrodeposited on BiVO_4 -ED/FTO synthesized by above procedure with BiVO_4 -ED/FTO working electrode, which was immersed in an electrolyte solution containing 0.02 M $\text{Cu}(\text{CH}_3\text{COO})_2$ and 0.08 M CH_3COOH . Electrolysis was performed at -0.3 V vs Ag/AgCl for 200 seconds. At this condition, the following reaction occurs: $2\text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+$. The prepared photoanode was thoroughly rinsed and dried at 60°C. The resulting product is designated as the Cu_2O - BiVO_4 -ED/FTO

Material Characterization

The structure of synthesized samples was determined by powder X-ray diffraction (XRD) using D8 Advance-Bruker diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in 2θ range of 20–80°. Scanning electron microscopy (SEM) was examined with a JEOL JSM-5410LV microscope. UV-vis diffuse reflectance spectroscopy (DRS) evaluated optical properties using BaSO_4 as a reference in a Shimadzu UV-2600. Photoluminescence (PL) spectra were recorded with a Hitachi F-4600 spectrophotometer at a 210 nm and 520 nm excitation wavelength.

Study the Photoelectrochemical Performance

Photoelectrochemical measurements were carried out in a three-electrode system by linear sweep voltammetry (LSV) method with electrodes immersed in 0.1M phosphate buffer solution (PBS, pH 7.4). A 200W lamp was illuminated to a 1 cm² photoanode. Current-voltage curves were recorded at 20 mV/s scan rate, with potential reference converted from Ag/AgCl to the reversible hydrogen electrode (RHE) using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl \text{ vs. NHE}} + 0.059 \cdot pH$$

where $E_{Ag/AgCl \text{ vs. NHE}} = 0.1976 \text{ V}$ at 20°C

Electrochemical impedance spectroscopy (EIS) measurements spanned frequencies from 10 kHz to 100 MHz with a 5 mV AC voltage.

Results and discussion

XRD results

The crystalline structure of the synthesized samples was analyzed using XRD. The XRD profiles for Cu_2O , $\text{BiVO}_4\text{-CP}$, $\text{BiVO}_4\text{-ED/FTO}$, $\text{Cu}_2\text{O-BiVO}_4\text{-ED/FTO}$ are shown in the Fig. 1.

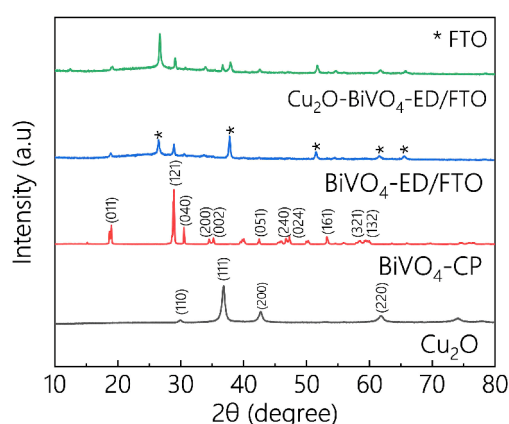


Fig. 1: XRD patterns of Cu_2O , $\text{BiVO}_4\text{-CP}$, $\text{BiVO}_4\text{-ED/FTO}$, $\text{Cu}_2\text{O-BiVO}_4\text{-ED/FTO}$

XRD pattern of Cu_2O displays diffraction peaks at $2\theta = 29.55^\circ$, 36.41° , 42.29° , and 61.34° characteristic for cubic Cu_2O single-phase. These peaks are indexed to the (110), (111), (200), and (220) facets (JCPDS: 65-3288). For $\text{BiVO}_4\text{-CP}$, the characteristic diffraction peaks observed at 2θ angles of 18.9° , 28.9° , 30.6° , 34.5° , 35.2° , 39.5° , 40.2° , 42.5° , 46.8° , 47.3° , 50.3° , 53.3° , 58.5° , and 59.5° corresponding to the crystal planes (011), (121), (040), (200), (002), (211), (112), (051), (240), (042), (202), (161), (321), and (132) of monoclinic BiVO_4 (JCPDS 14-0688). No diffraction peaks of Bi_2O_3 or tetragonal BiVO_4 were detected, confirming the formation of a pure monoclinic BiVO_4 phase. For $\text{BiVO}_4\text{-ED/FTO}$ and $\text{Cu}_2\text{O-BiVO}_4\text{-ED/FTO}$, diffraction peaks of the FTO at 26.7° , 37.9° , 51.8° , 61.9° , and 65.7° are observed. Besides, the characteristic peaks for monoclinic BiVO_4 facets (121), (040), and (200) still appear but become broader and less intense, signifying reduced crystallinity. Additionally, peaks of cubic Cu_2O at 36.41° , 42.29° , and 61.34° can be also observed in XRD pattern of $\text{Cu}_2\text{O-BiVO}_4\text{-ED/FTO}$ with significantly lower intensity. The XRD results indicate the successful deposition of BiVO_4 and Cu_2O on the surface of FTO.

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SEM results

To examine the morphology of synthesized samples, SEM analysis was conducted, and the resulting images are presented in Fig. 2. Cu_2O consists of relatively uniform spherical particles with sizes of about $1 \mu\text{m}$. $\text{BiVO}_4\text{-CP}$ consists of irregularly aggregated particles with a rhombic dodecahedral shape and varying sizes from several hundred nanometers to a few microns. These particles cluster together to form larger aggregates. Meanwhile, $\text{BiVO}_4\text{-ED}$ is composed of nanoparticles with grain sizes smaller than 200 nm. $\text{Cu}_2\text{O-BiVO}_4\text{-ED}$ forms very small, uniform particles with sizes below 100 nm on the FTO surface. The particle size of samples synthesized by electrodeposition methods reduces significantly, forming nanocrystals and creating an even surface on FTO as compared to those prepared by chemical precipitation. This is probably due to the decrease in the crystallinity of the electrodeposited samples. These results align well with analysis of the materials by the XRD method.

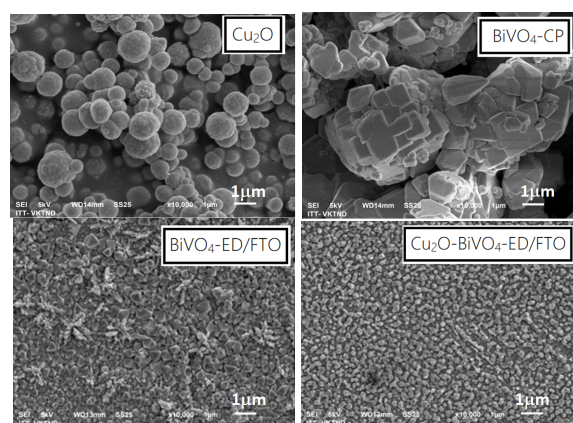


Fig. 2: SEM images of Cu_2O , $\text{BiVO}_4\text{-CP}$, $\text{BiVO}_4\text{-ED/FTO}$, $\text{Cu}_2\text{O-BiVO}_4\text{-ED/FTO}$

UV-Vis DRS results

The DRS UV-Vis results in Fig. 3a for all prepared samples indicate that all synthesized catalysts are photoactive. The UV-Vis spectra of the synthesized materials show absorption peaks in the visible light region with relatively high absorbance intensity. The absorption peaks for Cu_2O , $\text{BiVO}_4\text{-CP}$, $\text{BiVO}_4\text{-ED/FTO}$, $\text{Cu}_2\text{O-BiVO}_4\text{-ED/FTO}$ were observed at wavelengths of 490 nm, 472 nm, 437 nm, and 454 nm, respectively. The bandgap values determined using the Kubelka-Munk method and Tauc plots are presented in fig. 3b. The bandgap energies for the Cu_2O , $\text{BiVO}_4\text{-CP}$, $\text{BiVO}_4\text{-ED/FTO}$, $\text{Cu}_2\text{O-BiVO}_4\text{-ED/FTO}$ samples are 1.92 eV, 2.38 eV, 2.45 eV, and 1.82 eV, respectively. Additionally, it is evident that when Cu_2O is combined with BiVO_4 on the FTO substrate, the bandgap energy decreases. This

suggests an interaction between Cu_2O and BiVO_4 , resulting in a material with improved light absorption capabilities, particularly in the longer wavelength region.

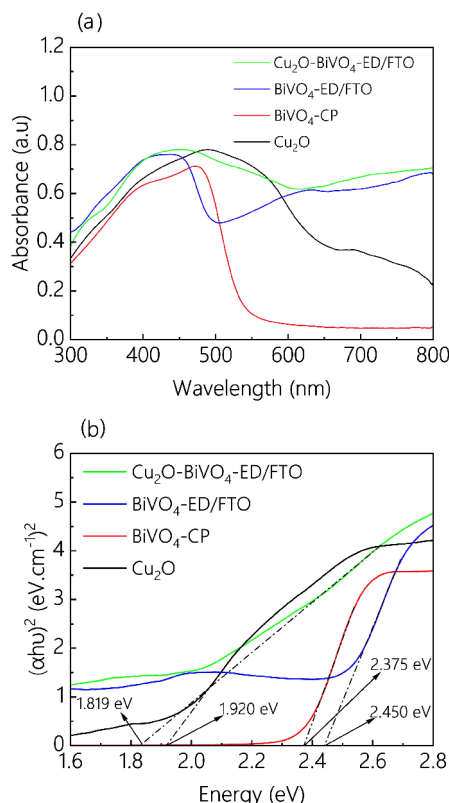


Fig. 3: DRS UV-Vis spectra (a) and Tauc plots (b) of Cu_2O , BiVO_4 -CP, BiVO_4 -ED/FTO, Cu_2O - BiVO_4 -ED/FTO

PL results

The fluorescence spectra of BiVO_4 -CP, BiVO_4 -ED/FTO, Cu_2O - BiVO_4 -ED/FTO at 210 nm excitation wavelength are shown in Fig. 4a. It emits fluorescence at approximately 421 nm. This emission peak is characteristic of the fluorescence ability of BiVO_4 . When BiVO_4 is electrodeposited on FTO surface, the fluorescence intensity at 421 nm decreases. This result may indicate that the recombination of electron-hole pairs in BiVO_4 -ED is lower than that in BiVO_4 -CP. Notably, when Cu_2O is combined with BiVO_4 , fluorescence emission intensity at 421 nm decreases significantly. This is likely due to the interaction between Cu_2O and BiVO_4 , facilitating electron-hole separation. Similarly, when Cu_2O -containing materials are excited at 520 nm, a fluorescence emission peak is observed at around 780 nm, which is characteristic of Cu_2O fluorescence. It is evident that the incorporation of Cu_2O with BiVO_4 also significantly reduces the fluorescence intensity, suggesting lower recombination of photogenerated electron-hole pairs in the Cu_2O component and, therefore, creating materials with better expected photocatalytic performance.

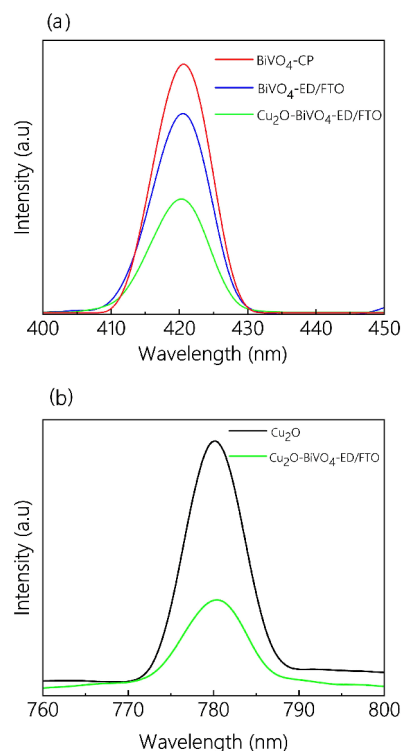


Fig. 4: PL spectra of BiVO_4 -CP, BiVO_4 -ED/FTO, Cu_2O - BiVO_4 -ED/FTO at 210 nm excitation wavelength (a) and of Cu_2O , Cu_2O - BiVO_4 -ED/FTO at 520 nm excitation wavelength (b)

Results of OER photoelectrochemical performance

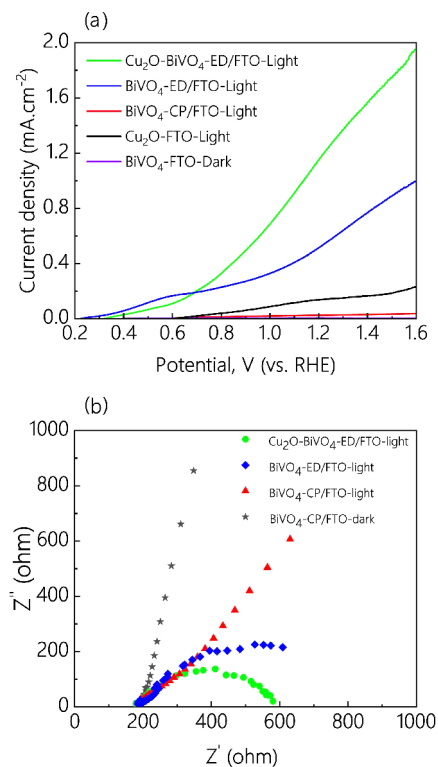


Fig. 5: Linear sweep voltammetry diagrams in the dark and under illumination (a) and Nyquist plot (b) of BiVO_4 -CP, BiVO_4 -ED/FTO, Cu_2O - BiVO_4 -ED/FTO

To evaluate the photoelectrochemical catalytic ability of the materials for OER, LSV measurements were performed on the samples with results shown in Fig 5a. Obviously, in the absence of light, no current is observed on the FTO surface across the potential range of 0.2V to 1.6V versus RHE. However, under xenon lamp illumination, the photocurrent density on both BiVO₄ and Cu₂O electrodes increases with rising potential. Comparing samples synthesized by precipitation, BiVO₄-CP/FTO, and electrodeposition methods, BiVO₄-ED/FTO, it is evident that the photocurrent density of electrochemically synthesized samples is far superior to that of samples synthesized through conventional chemical methods. At E=1.23V vs RHE, current density reaches 0.025 mA cm⁻² for BiVO₄-CP/FTO, and is 0.55 mA cm⁻² for BiVO₄-ED/FTO. The value of current density of BiVO₄-ED/FTO is comparable to that of BiVO₄ reported by Majumder et al. [12]. The enhancement in photocurrent density of BiVO₄-ED/FTO as compared to that of BiVO₄-CP/FTO is likely because the electrochemical synthesis method enables BiVO₄ to adhere strongly to the FTO surface, forming a uniform layer with smaller particle sizes and better interaction between the components in electrode. This facilitates easier movement of electrons and holes, enhancing their participation in electrode processes. The combination of Cu₂O and BiVO₄ significantly enhances photocurrent density. While current density of Cu₂O/FTO and BiVO₄-ED/FTO samples are 0.142 mA cm⁻² and 0.55 mA cm⁻², respectively, the current density of Cu₂O-BiVO₄-ED/FTO reaches 1.23 mA cm⁻². These results suggest that heterojunction between Cu₂O and BiVO₄ probably promotes separation of electrons and holes leading to better photocatalytic activity of the electrode material.

To evaluate the resistance to charge transfer at the interface between the electrode surface and the electrolyte during the OER, EIS measurements were conducted and the Nyquist plots were shown in Fig.5b. Typically, diameter of the semicircle in the high-frequency region reflects charge transfer resistance, R_{ct} . A smaller diameter indicates lower charge transfer resistance. Obviously, the semicircle diameter in the high-frequency region of BiVO₄-CP/FTO-dark is much larger than that of BiVO₄-CP-light, indicating the influence of illumination, which enhances the charge transfer at the interface between the electrode surface and the electrolyte. For the synthesized electrodes, the semicircle diameter decreases in the following order: BiVO₄-CP > BiVO₄-ED/FTO > Cu₂O-BiVO₄-ED/FTO. The charge transfer resistance of BiVO₄-CP, BiVO₄-ED/FTO and Cu₂O-BiVO₄-ED/FTO are determined to be 1728 Ω , 647 Ω and 401 Ω . The significantly lower value of charge transfer resistance for electrodeposited materials, BiVO₄-ED/FTO and Cu₂O-BiVO₄-ED/FTO as

compared to BiVO₄-CP is likely attributed to the smaller particle size and the tighter adhesion of the deposited layer to the FTO surface, which may play a crucial role in the superior photoelectrochemical performance of the electrodeposited samples. Besides, the combined Cu₂O-BiVO₄-ED/FTO suggests the best efficient charge transfer and improved electron mobility at the interface between the electrolyte and the electrode with the lowest R_{ct} . Thus, the combination of Cu₂O with BiVO₄ enhances the charge transfer ability of the materials. This improvement could be one of the factors contributing to the improvement of photoelectrocatalytic activity of the Cu₂O-BiVO₄-ED/FTO.

Conclusion

In this study, Cu₂O and BiVO₄ samples were successfully synthesized using different methods. The synthesis technique significantly influences crystallinity, morphology, particle size, ability of light absorption and photoelectrochemical performance of the electrode materials. BiVO₄ synthesized by electrochemical method (BiVO₄-ED) has lower crystallinity and significantly smaller particle sizes, therefore, exhibits higher photocurrent density (0.55 mA·cm⁻² at 1.23 V versus RHE) as compared to the materials synthesized by precipitation methods (BiVO₄-CP). When Cu₂O and BiVO₄ are combined, the interaction between these two components in the material possibly reduces the recombination of electron-hole pairs, resulting in the higher charge transfer ability, R_{ct} =401 Ω , and better photocatalytic performance, with current density at 1,23 V vs RHE equal 1.23 mA cm⁻², showing its great potential for use as a photoanode material in photoelectrochemical water splitting.

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