

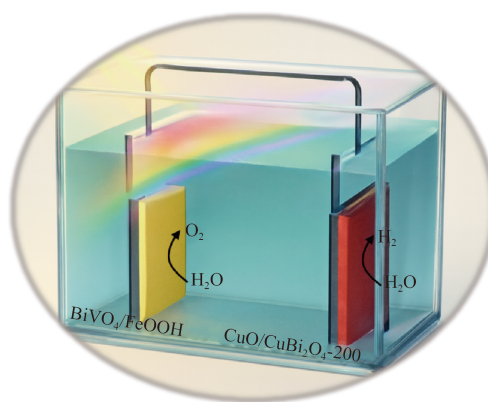
Interface regulation for enhanced photoelectrochemical performance of CuBi_2O_4 photocathodes

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Abstract: Photoelectrochemical (PEC) water splitting is an effective approach to directly convert solar energy into clean hydrogen fuel. As a visible-light-responsive *p*-type semiconductor, CuBi_2O_4 possesses a suitable bandgap and good stability. However, its performance is inhibited by high interfacial resistance and severe charge carrier recombination. In this study, a CuO interlayer was introduced between fluorine-doped tin oxide (FTO) and CuBi_2O_4 to construct $\text{CuO}/\text{CuBi}_2\text{O}_4$ photocathodes, aiming to improve interfacial charge transfer. The results showed that $\text{CuO}/\text{CuBi}_2\text{O}_4$ -200 exhibited a photocurrent density of $-1.71 \text{ mA}/\text{cm}^2$ at 0 V vs. RHE, which was more than 3.5 times higher than that of bare CuBi_2O_4 . The incident photon-to-current efficiency (IPCE) at 365 nm was enhanced to $\sim 13\%$ and the maximum applied bias photon-to-current efficiency (ABPE) reached 0.17%. Water splitting experiments revealed a hydrogen yield of $2.05 \mu\text{mol}/\text{cm}^2$, significantly surpassing that of the unmodified photoelectrode. The enhanced PEC performance indicated that the CuO layer established a favorable band alignment, promoted hole transport toward the FTO substrate and effectively suppressed interfacial carrier recombination. This work demonstrated a simple and efficient interfacial engineering strategy, offering new insights and guidance for the design and development of high-performance semiconductor-based PEC photoelectrodes.

Key words: photoelectrochemistry; CuBi_2O_4 photocathode; interface; water splitting



The global transition toward carbon-neutral energy systems has intensified the search for clean and sustainable technologies to replace fossil fuels^[1–2]. Among the emerging energy carriers, hydrogen (H_2), with its high gravimetric energy density and low environmental impact, is widely regarded as an ideal clean energy carrier^[3–4]. To enable large-scale hydrogen production in an environmentally benign manner, solar-driven PEC water splitting has gained significant attention as a promising and scalable route for converting abundant solar energy directly into green hydrogen^[5–7].

In a PEC system, the photocathode plays a crucial role in driving the hydrogen evolution reaction, which directly determines the overall PEC conversion efficiency^[8–10]. Among various materials, *p*-type CuBi_2O_4 semiconductors,

with a narrow band gap (1.5–1.8 eV), strong visible-light absorption and good chemical stability, have emerged as a highly attractive photocathode candidate^[11–12]. Compared with conventional photocathode materials such as Cu_2O ^[13] and Si ^[14], CuBi_2O_4 exhibits superior resistance to photocorrosion and more favorable band-edge alignment for solar-driven water splitting^[15–16]. Despite these advantages, the practical application of CuBi_2O_4 remains hindered by severe photogenerated carrier recombination, limited charge-transport efficiency, and high interfacial resistance at the interface of electrode and substrate^[17]. Therefore, some strategies are urgently needed to regulate carrier dynamics and accelerate interfacial charge-transfer, thereby exploiting the potential of CuBi_2O_4 photocathodes for efficient solar driven H_2 production.

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Various strategies have been developed to enhance the PEC performance of CuBi_2O_4 photocathodes, including elemental doping, surface catalyst loading, heterostructure construction, and band-structure engineering^[18–20]. For example, Hu et al.^[21] improved the carrier concentration of CuBi_2O_4 photocathodes by introducing strontium dopants. The surface-enriched SrCO_3 effectively passivated surface trap states, inhibited interfacial recombination and enhanced band bending within the bulk material. Most previous efforts have primarily focused on modifying the photoactive layer or the electrode surface, less research has paid attention to the interface charge transfer between the photoelectrode and the conductive substrate^[22]. However, the interface remains a key factor limiting the overall device efficiency^[23]. Therefore, improving interface charge-transport between CuBi_2O_4 and FTO substrate is a potential strategy for boosting PEC efficiency.

In this study, a CuO interlayer was introduced between the FTO conductive glass and the CuBi_2O_4 photocathode *via* an electrochemical deposition method. As a *p*-type semiconductor, CuO exhibits excellent hole-transport properties and a suitable band structure that is well matched with that of CuBi_2O_4 . Additionally, the CuO interlayer alleviated interfacial defects between CuBi_2O_4 and FTO, reduced the interfacial resistance and improved charge-transport kinetics. As a result, the CuO/ CuBi_2O_4 photocathode exhibited notable improvements in both photocurrent response and stability. Furthermore, the optimized CuO/ CuBi_2O_4 -200 photocathode can be successfully coupled with a BiVO_4 photoanode to construct a tandem device that enables overall water splitting under bias-free conditions, demonstrating its excellent potential for practical PEC device integration.

1 Experimental

1.1 Preparation of CuO photocathode

CuO layers were fabricated on FTO substrates *via* electrodeposition, following a method similar to previously reported protocols^[24]. A solution of 0.43 g of copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and 0.15 g of potassium chloride (KCl) was dissolved in 50 mL of distilled water, followed by 20 min of magnetic stirring to form the electrodeposition electrolyte. The CuO films were prepared using a three-electrode system, where FTO conductive glass served as the working electrode, a platinum sheet as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference. Electrodeposition was performed at a constant potential of -0.5 V (vs. Ag/AgCl) for durations of 150, 200, 250 and 300 s. After deposition, the FTO electrode was rinsed with deionized water and air-dried to obtain a red copper film. The samples were then annealed in a muffle furnace at 450°C for 2 h, transforming the copper film into a CuO film.

1.2 Preparation of CuO/ CuBi_2O_4 photocathode

CuO/ CuBi_2O_4 photocathodes were fabricated on FTO/CuO substrates *via* electrodeposition. To prepare the copper precursor solution, 0.02 g of copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was dissolved in 20 mL of distilled water and magnetically stirred for 20 min. Subsequently, 0.08 g of bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was dissolved in 20 mL of distilled water and stirred for an additional 20 min. To promote the dissolution of the bismuth salt, 10 mL of a 10% nitric acid (HNO_3) solution was added to the mixture, yielding the bismuth precursor solution. The combined solution was then sonicated for 30 min to ensure uniform dispersion, resulting in the electrodeposition precursor solution. The electrodeposition of the Bi-Cu film followed the same procedure as for the Cu film, using a three-electrode system with FTO/CuO as the working electrode, a platinum sheet as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference. Electrodeposition was conducted at a constant potential of -0.4 V (vs. Ag/AgCl) for 10 min, resulting in a co-deposited Bi-Cu film. After electrodeposition, the sample was removed, dried at room temperature, and then calcined in a muffle furnace at 550°C for 2 h to obtain the CuO/ CuBi_2O_4 photocathode. The composite photoanodes prepared with different CuO electrodeposition durations (100, 150, 200 and 250 s) were denoted as CuO/ CuBi_2O_4 -100, CuO/ CuBi_2O_4 -150, CuO/ CuBi_2O_4 -200 and CuO/ CuBi_2O_4 -250, respectively. For comparison, the CuBi_2O_4 sample was prepared using the same method, except without the CuO interlayer step.

The experimental reagents, material characterization, PEC testing, and designed formulas involved in this study can be found in the supplementary materials.

2 Results and discussion

2.1 Morphology and structure characterization

The phase structure of the samples was characterized by X-ray diffraction (XRD). As shown in Figure 1, for CuBi_2O_4 , diffraction peaks appeared at 20.92° , 28.09° , 33.36° and 46.80° can be indexed to the (200), (211), (310) and (411) planes, respectively, in good agreement with the standard JCPDS No. 79-1810^[25]. For CuO, the peaks located at 32.52° , 35.57° , 37.53° and 38.77° correspond to the (022), (311), (-222) and (440) planes, respectively, matching well with the standard JCPDS No. 80-1268^[26]. Furthermore, the XRD patterns of CuO/ CuBi_2O_4 -150, CuO/ CuBi_2O_4 -200, CuO/ CuBi_2O_4 -250 and CuO/ CuBi_2O_4 -300 clearly showed an increase in the intensity of CuO-related peaks with increasing CuO content, which is consistent with the experimental expectations. These results confirmed the successful introduction of CuO layer.

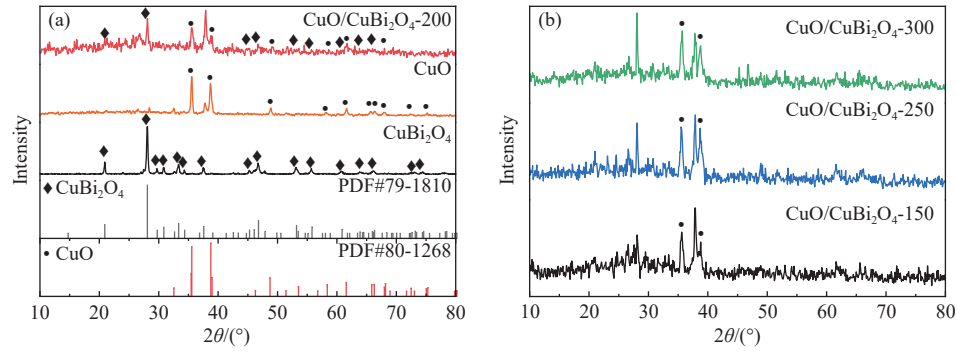


Fig. 1 (a) XRD patterns of CuO, CuBi₂O₄ and CuO/CuBi₂O₄-200; (b) XRD patterns of CuO/CuBi₂O₄-150, CuO/CuBi₂O₄-250 and CuO/CuBi₂O₄-300 photocathodes

The surface and cross-sectional morphologies of the films were characterized using scanning electron microscopy (SEM). As shown in Figure 2(a), the CuO film electrodeposited onto the FTO substrate exhibited an irregular, block-like structure. In contrast, the CuBi₂O₄ film (Figure 2(b)) presented a uniformly distributed, worm-like morphology. Upon deposition of CuBi₂O₄ onto the

FTO/CuO substrate, a dense and homogeneous CuBi₂O₄ layer is formed that uniformly covers the CuO surface, confirming the successful construction of the CuO/CuBi₂O₄ photocathode (Figure 2(c)). Cross-sectional SEM images further revealed that the CuO layer is completely covered by CuBi₂O₄, resulting in a compact and well-integrated composite structure (Figure 2(d)–(f)).

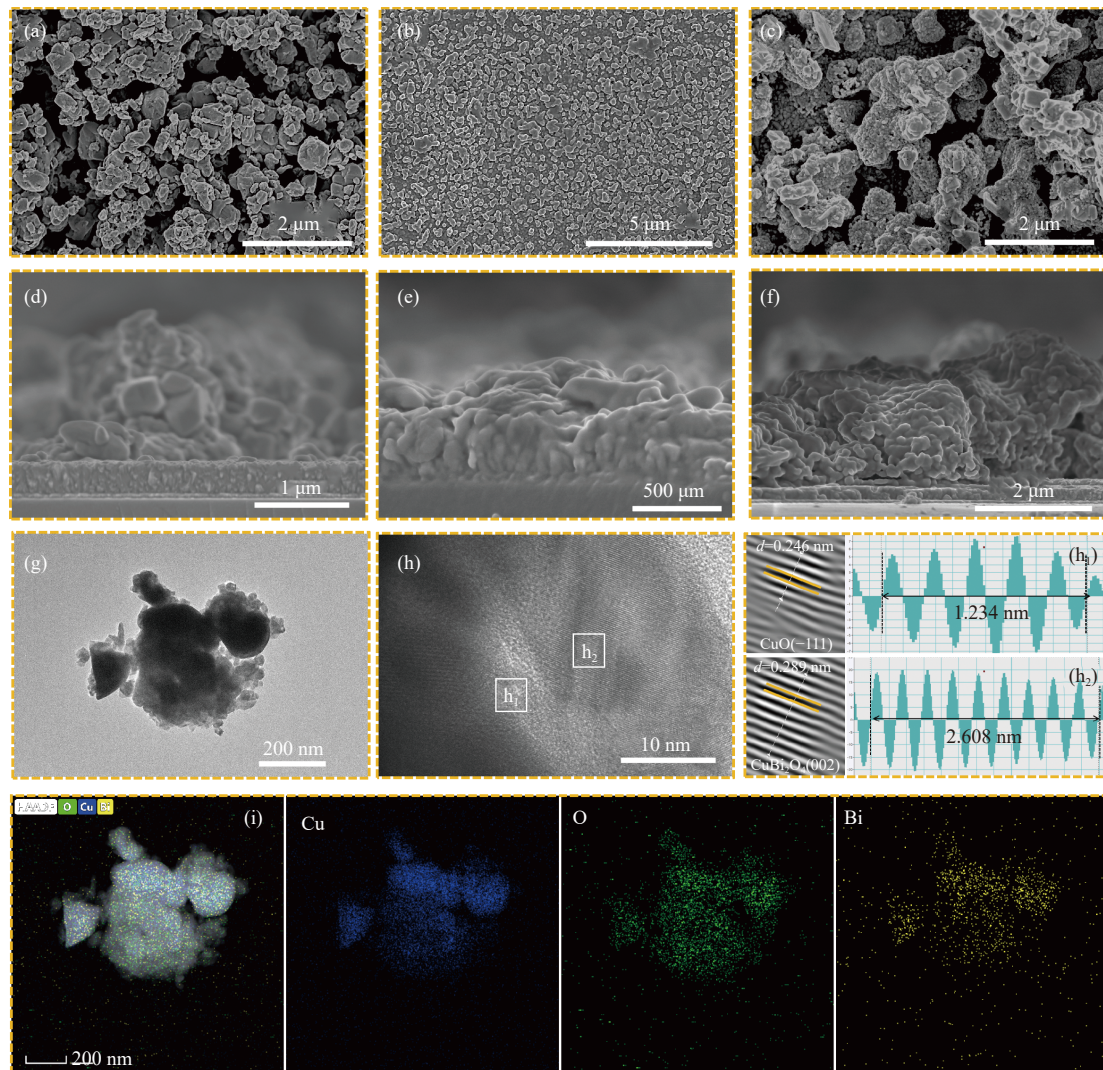


Fig. 2 SEM images of (a) CuO, (b) CuBi₂O₄, (c) CuO/CuBi₂O₄, (d) cross-sectional CuO, (e) cross-sectional CuBi₂O₄ and (f) cross-sectional CuO/CuBi₂O₄ films; (g) TEM, (h) HRTEM and (i) EDX surface spectra of CuO/CuBi₂O₄ thin films

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were employed to examine the interfacial structure between CuO and CuBi₂O₄. The TEM images revealed a distinct and well-defined junction between the two phases (Figure 2(g)). Clear lattice fringes with spacings of 0.246 and 0.289 nm are observed, corresponding to the (−111) plane of CuO and the (002) plane of CuBi₂O₄, respectively, consistent with the standard PDF cards for CuO (#80-1268) and CuBi₂O₄ (#79-1810) (Figure 2(h)). The presence of locally disordered lattice fringes at the interface further confirmed the good contact between CuO and CuBi₂O₄. Moreover, energy-dispersive X-ray spectroscopy (EDS) analysis verifies the coexistence of Cu, O and Bi within the CuO/CuBi₂O₄ film, indicating the successful synthesis of the heterostructured photocathode (Figure 2(i)).

X-ray photoelectron spectroscopy (XPS) was employed to analyze the composition of the films. As shown in Figure 3, the XPS spectra of the pristine CuBi₂O₄ and the CuO/CuBi₂O₄ film were compared. In the Bi 4*f* spectra (Figure 3(a)), the Bi 4*f*_{7/2} and Bi 4*f*_{5/2} peaks of the pristine CuBi₂O₄ were located at approximately 159 and 164 eV, respectively, corresponding to the typical oxidation state of Bi³⁺. In contrast, the peaks in the composite sample underwent a negative shift of about 0.10–0.20 eV, indicating an increase in the electron cloud density around Bi due to the presence of CuO and suggesting a redistribution of charge at the interface^[27]. In the Cu 2*p* spectra (Figure 3(b)), the Cu 2*p*_{3/2} peak of the pristine CuBi₂O₄ film was centered at 933–934 eV, accompanied by a pronounced satellite peak (~942 eV), which is characteristic of Cu²⁺ species. For the composite sample, the main peak shifted positively by approximately 0.20–0.30 eV, while the intensity of the satellite peak is significantly reduced. This indicated that the local electronic environment of Cu was modified upon the introduction of CuO, which was consistent with the role of CuO as a hole transport layer that facilitated interfacial charge transfer^[28]. In the O 1*s* spectra (Figure 3(c)), the main peak for the pristine CuBi₂O₄ appeared at 529.5 eV (lattice oxygen). In the composite sample, a notable increase

in peak intensity was observed at approximately 531 eV, which was attributed to surface-adsorbed hydrogen species. This suggested that the CuO interlayer promoted the surface passivation of oxygen, thereby enhancing the stability and interfacial properties^[29]. Overall, the XPS results confirmed the formation of a stable interface interaction between CuO and CuBi₂O₄, which facilitated charge redistribution and separation. Furthermore, these results provided further validation of the role of CuO as an effective hole transport layer in the FTO/CuBi₂O₄ system.

2.2 PEC properties evaluation

The PEC performance of CuBi₂O₄ and CuO/CuBi₂O₄ composite films was evaluated using a three-electrode electrochemical analysis system. As shown in Figure 4(a), the photocathodes of CuBi₂O₄, CuO/CuBi₂O₄-150, CuO/CuBi₂O₄-200, CuO/CuBi₂O₄-250 and CuO/CuBi₂O₄-300 achieved photocurrent densities of approximately −0.49, −1.12, −1.71, −1.22 and −1.01 mA/cm², respectively, at 0 V vs. RHE. Notably, CuO/CuBi₂O₄-200 exhibited the highest photocurrent density among all samples, which is ~3.5 fold higher than that of pristine CuBi₂O₄. Further analysis using transient photocurrent (*I*–*t*) curves (Figure 4 (b)) revealed that all photocathodes exhibited typical photoresponse behavior, and CuO/CuBi₂O₄-200 maintained stable output over multiple on/off cycles. These results indicated a significant reduction in interfacial charge recombination, with more efficient charge separation and transfer processes.

To evaluate the energy conversion capabilities of the photoelectrodes, IPCE and ABPE were measured. As shown in Figure 4(c), pristine CuBi₂O₄ exhibited an IPCE of only ~3.5% at 365 nm, whereas CuO/CuBi₂O₄-200 delivered a markedly enhanced value of ~13%, corresponding to a ~3.7 fold improvement. In comparison, the IPCE value of CuO/CuBi₂O₄-150, CuO/CuBi₂O₄-250 and CuO/CuBi₂O₄-300 is 4.2%, 7.1% and 4.5%, respectively.

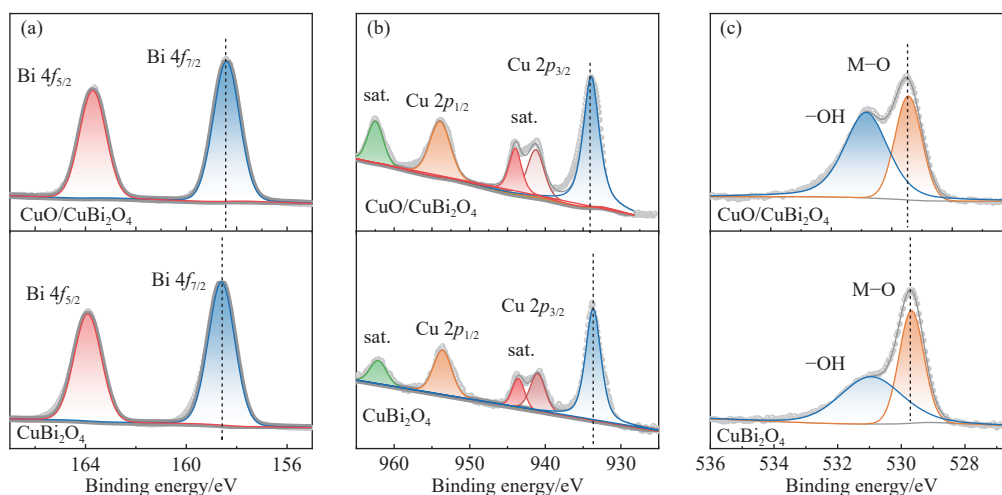


Fig. 3 XPS spectra of CuBi₂O₄ and CuO/CuBi₂O₄: (a) Bi 4*f*, (b) Cu 2*p* and (c) O 1*s*

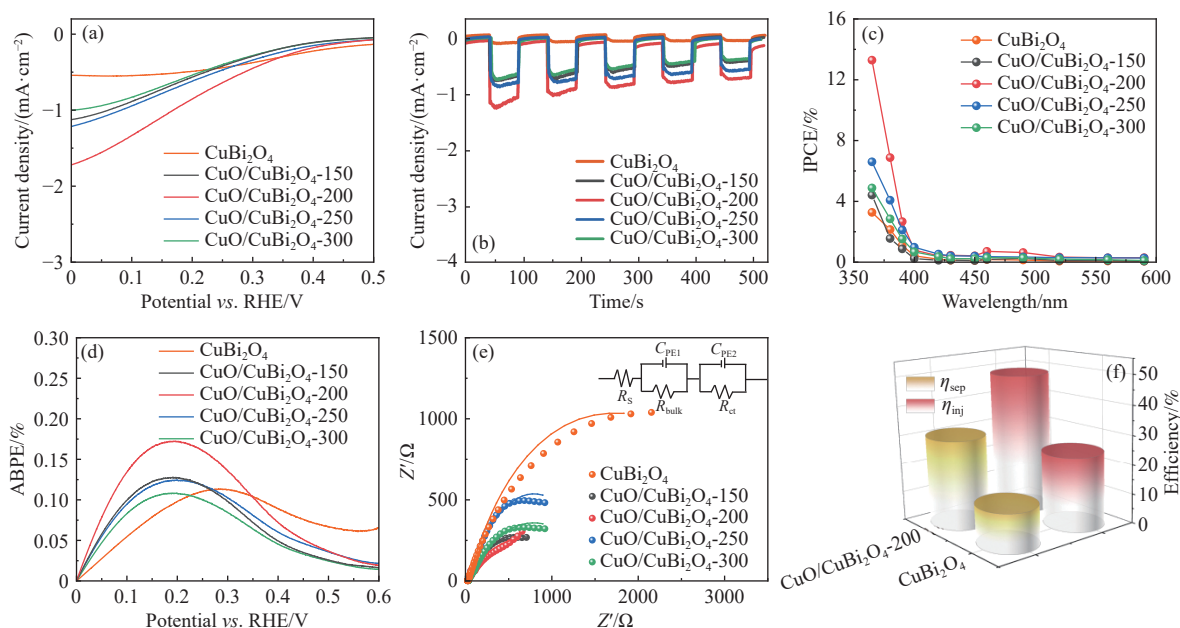


Fig. 4 (a) LSV curves, (b) $I-t$ curves, (c) IPCE spectra, (d) ABPE plots and (e) EIS spectra of CuBi_2O_4 , $\text{CuO/CuBi}_2\text{O}_4$ -150, $\text{CuO/CuBi}_2\text{O}_4$ -200, $\text{CuO/CuBi}_2\text{O}_4$ -250 and $\text{CuO/CuBi}_2\text{O}_4$ -300 photocathodes; (f) Charge separation and injection efficiency curves of CuBi_2O_4 and $\text{CuO/CuBi}_2\text{O}_4$ -200

The ABPE curves (Figure 4(d)) reveal that the maximum value of CuBi_2O_4 is 0.075%, while it increases to 0.17% for $\text{CuO/CuBi}_2\text{O}_4$ -200. These results confirm again that CuO modification layer significantly enhanced the overall energy conversion performance of CuBi_2O_4 photocathodes.

In addition, photoelectrochemical impedance spectroscopy (PEIS) was employed to probe the charge-transport kinetics within the photocathodes and across the interface between semiconductor and electrolyte (Figure 4(e)). The equivalent circuit fitting (Table S1) revealed that the optimized CuO interlayer significantly reduced the interfacial charge transfer resistance, thereby facilitating the efficient transport of photogenerated holes to the FTO substrate and effectively inhibiting bulk charge recombination in CuBi_2O_4 . Further analysis of the carrier separation (η_{sep}) and injection (η_{inj}) efficiencies (Figure 4(f)) demonstrated that the introduction of CuO as a hole transport layer substantially improved bulk carrier separation and reduced surface recombination, thereby enhancing the overall PEC performance.

2.3 PEC water splitting test

To further assess the hydrogen-production capability of the photocathodes, the H_2 and O_2 evolution rates of CuBi_2O_4 and $\text{CuO/CuBi}_2\text{O}_4$ -200 photocathodes under AM 1.5 G (100 mW/cm²) illumination were quantitatively analyzed. As shown in Figure 5(a) and (c), both photocathodes exhibited a stable increase in H_2 and O_2 production over time. Within 1 h, the CuBi_2O_4 photocathode produced

0.93 $\mu\text{mol}/\text{cm}^2$ of H_2 and 0.45 $\mu\text{mol}/\text{cm}^2$ of O_2 , whereas the $\text{CuO/CuBi}_2\text{O}_4$ -200 photocathode achieved significantly higher yields of 2.05 and 0.96 $\mu\text{mol}/\text{cm}^2$, respectively (Figure 5(b) and (d)). Additionally, the $\text{CuO/CuBi}_2\text{O}_4$ -150, $\text{CuO/CuBi}_2\text{O}_4$ -250 and $\text{CuO/CuBi}_2\text{O}_4$ -300 photocathodes also exhibited enhanced water-splitting activity relative to bare CuBi_2O_4 (Figure S1). These results were in agreement with the photocurrent and efficiency measurements, further indicating that the introduction of an optimized CuO interlayer between the FTO substrate and CuBi_2O_4 significantly enhanced interfacial charge separation and transfer, thereby effectively promoting the utilization of photogenerated carriers and improving PEC water-splitting performance.

Given its high H_2 evolution capability, the $\text{CuO/CuBi}_2\text{O}_4$ -200 photocathode was further integrated in series with a BiVO_4 photoanode to construct a bias-free tandem water-splitting device (Figure 6(a)). The preparation method and structural characterization of the BiVO_4 photoanode were provided in the Supporting Information (Figure S2 and S3). The BiVO_4 photoanode supplied photogenerated carriers, while FeOOH used as a co-catalyst improved charge separation and transfer efficiency. In addition, FeOOH promoted the oxygen evolution reaction, enhancing the catalytic efficiency of the photoanode. When combined with the $\text{CuO/CuBi}_2\text{O}_4$ -200 photocathode, the tandem system delivered a maximum photocurrent density of 0.56 mA/cm² under solar illumination (Figure 6(b)), demonstrating its capability to drive overall water splitting under completely bias-free conditions.

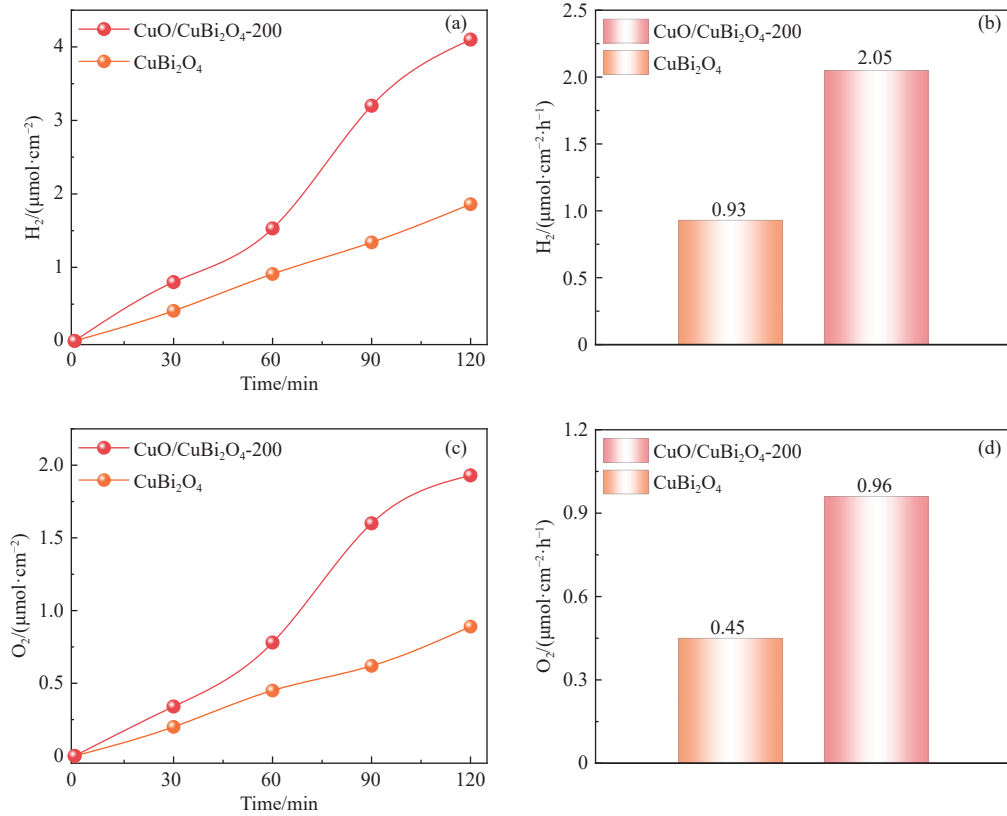


Fig. 5 PEC water-splitting tests of CuBi₂O₄ and CuO/CuBi₂O₄-200 films

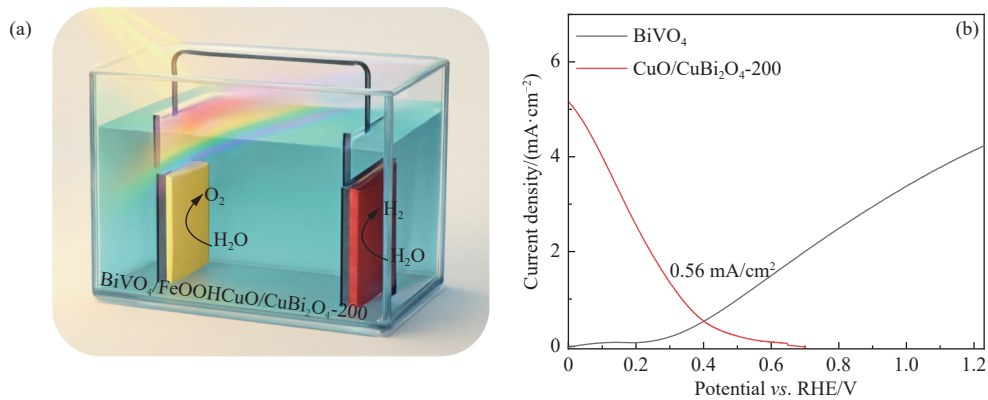


Fig. 6 Performance of the *p-n* tandem cell: (a) schematic illustration of the BiVO₄/FeOOH|CuO/CuBi₂O₄-200 tandem device; (b) *J-V* curves of the individual BiVO₄/FeOOH photoanode and CuO/CuBi₂O₄-200 photocathode

2.4 Optical characteristics

Figure 7 presents the optical absorption characteristics and corresponding bandgap calculations for CuBi₂O₄ and CuO/CuBi₂O₄-200 photocathodes. As shown in the UV-vis diffuse reflectance spectra (UV-vis DRS) (Figure 7(a)), all electrodes exhibited prominent absorption features in the visible light range (300–900 nm). Notably, CuO/CuBi₂O₄-200 shows significantly higher absorption intensity compared to CuBi₂O₄, indicating that the CuO layer effectively enhances light-harvesting capability. Further analysis of the Tauc plot (Figure 7(b)) was performed to

determine the optical bandgap. CuBi₂O₄ exhibited a bandgap of approximately 1.79 eV, while that of CuO/CuBi₂O₄-200 showed a slightly reduced value of 1.76 eV. This reduction of the bandgap facilitated light absorption in the visible region, thereby enhancing the excitation efficiency of photogenerated carriers.

2.5 Charge transfer mechanism

To further elucidate the role of the CuO interlayer in the charge transfer process, the band structure of the composite photocathodes was analyzed using UV-vis and Mott-

Schottky (M-S) testing. The UV-vis results indicated that the bandgap of CuBi_2O_4 was approximately 1.79 eV, while that of CuO is 1.81 eV (Figure S4). Additionally, the flat-band potential from the Mott-Schottky curves was used to estimate the Fermi levels (E_f) of CuBi_2O_4 and CuO (Figure 8(a) and (b)). Based on these results, the band structure diagram for the $\text{CuO}/\text{CuBi}_2\text{O}_4$ photocathode was constructed (Figure 8(c)). Based on the band structure, a mechanism for photogenerated charge carrier separation and transmission was proposed. Under illumination, CuBi_2O_4 generated photogenerated electrons and holes. However, its intrinsic band structure led to significant bulk and interfacial recombination, limiting the PEC efficiency. The introduction of the CuO interlayer provided a favorable energy-level alignment that facilitated the rapid extraction

of photogenerated holes from CuBi_2O_4 into CuO , effectively inhibiting the recombination at the CuBi_2O_4 interface. These holes were subsequently transported through the FTO substrate to the counter electrode, where they participated in oxidation reactions. Simultaneously, the reduced recombination within the CuBi_2O_4 bulk allowed a greater number of electrons to migrate to the electrode surface and drive the hydrogen-evolution reaction. Thus, in the $\text{CuO}/\text{CuBi}_2\text{O}_4$ photocathode, CuO served as an efficient interfacial “bridge,” lowering the charge-transfer barrier and inhibiting electron-hole recombination. This synergistic interfacial modulation significantly improved carrier separation efficiency and enhanced the overall PEC performance of the photocathode.

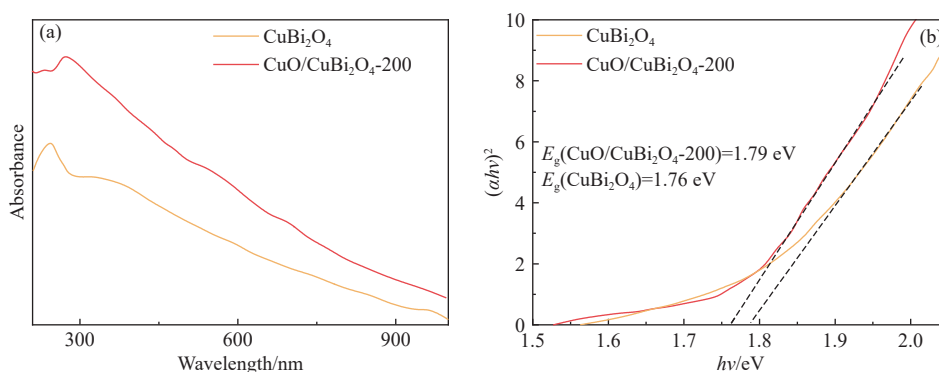


Fig. 7 (a) UV-vis absorption spectra and (b) Tauc plots of CuBi_2O_4 and $\text{CuO}/\text{CuBi}_2\text{O}_4$ samples

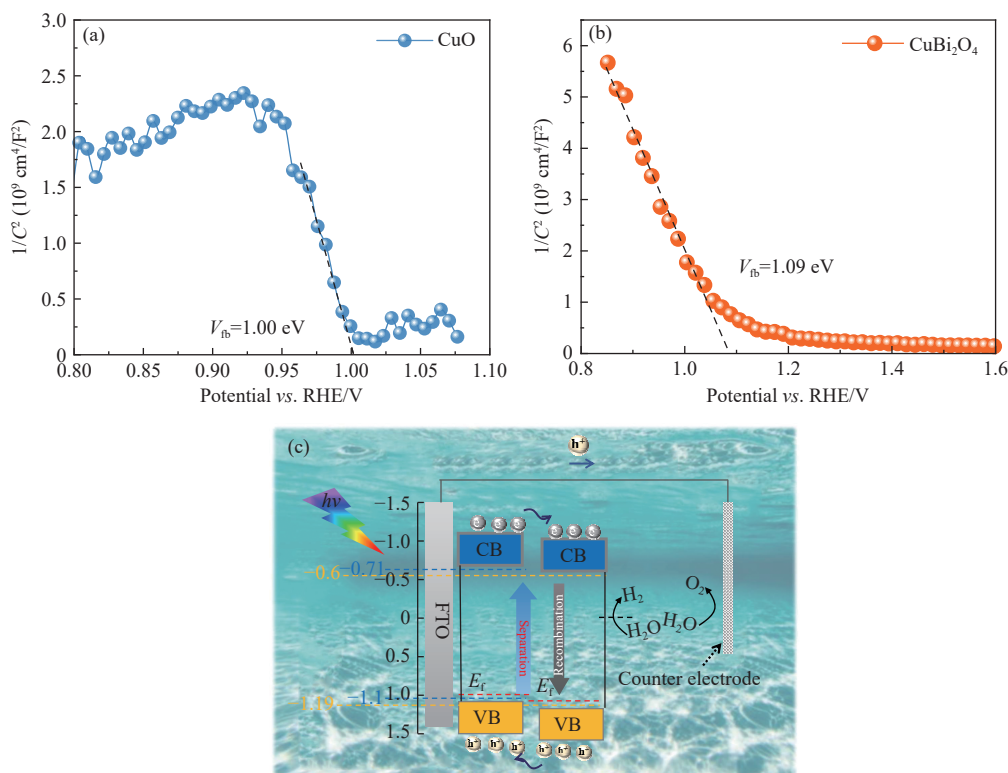


Fig. 8 (a) M-S plots of CuO and (b) CuBi_2O_4 films; (c) Schematic illustration of the electron-hole transfer pathway in $\text{CuO}/\text{CuBi}_2\text{O}_4$ films during PEC water splitting

3 Conclusion

In this study, a high-performance CuO/CuBi₂O₄ photocathode was successfully constructed by introducing a CuO interlayer between the FTO substrate and CuBi₂O₄. Systematic structural characterization revealed that the CuO layer not only improved the surface morphology and interfacial adhesion of CuBi₂O₄ but also established favorable band alignment. As a result, the optimized CuO/CuBi₂O₄-200 photocathode delivered a photocurrent density of -1.71 mA/cm^2 at 0 V vs. RHE, more than 3.5 times that of the pristine CuBi₂O₄, along with an enhanced IPCE of $\sim 13\%$ at 365 nm and a maximum ABPE of 0.17%. Furthermore, when coupled with a classical BiVO₄ photoanode, the CuO/CuBi₂O₄-200 photocathode successfully enabled bias-free overall water splitting, demonstrating strong potential for practical PEC applications. Mechanistic investigations further verified that the CuO interlayer functioned as an effective hole-transport layer, reducing interfacial resistance and improving charge separation and injection efficiencies, thereby enhancing both PEC activity and operational stability. This work provided a simple yet effective interface-engineering strategy and offered valuable insights for the rational design of high-performance PEC photocathodes.

Declaration of Competing Interest

The authors declare no conflict of interest.

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界面调控提升 CuBi₂O₄ 光阴极光电化学性能

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摘要: 光电化学 (PEC) 水分解是一种将太阳能直接转化为清洁氢燃料的有效途径。铋酸铜 (CuBi₂O₄) 作为可见光响应的 *p* 型半导体, 具有合适的带隙与稳定性。然而, 其性能受限于较高的界面电阻以及严重的载流子复合。本研究在 FTO 与 CuBi₂O₄ 之间引入 CuO 中间层, 构筑 CuO/CuBi₂O₄ 光阴极, 以改善界面电荷转移。结果表明, CuO/CuBi₂O₄-200 在 0 V vs. RHE 下的光电流密度达 -1.71 mA/cm², 是 CuBi₂O₄ 的 3.5 倍以上; 在 365 nm 处的 IPCE 提升至 ~13%, 最大 ABPE 达 0.17%。水分解实验显示其氢气产量为 2.05 μmol/cm², 显著优于未修饰电极。性能提升表明, CuO 层构建了有利的能带匹配, 促进了空穴向 FTO 的传输, 并有效抑制了界面载流子复合。本研究提出了一种简便高效的界面调控工程策略, 为高性能半导体 PEC 光电极的设计与开发提供了新的思路与指导。

关键词: 光电化学; CuBi₂O₄ 光阴极; 界面; 分解水

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