Wrapping BiVO₄ with chlorophyll for greatly improved photoelectrochemical performance and stability

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ABSTRACT Dull surface oxygen evolution reaction (OER) dynamics seriously hinders the application of BiVO₄ (BVO) photoanodes in photoelectron-chemical (PEC) water splitting. In this study, we built an inorganic/organic hybrid photoanode to improve the PEC performance of BVO by covering a multifunctional film. The film contains modified chlorophyll (Chl) organic compounds and Co and Si ions with a gradient distribution. The Co ions present at the interface between BVO and Chl promote the transport of photogenerated holes, and the Si ions on the surface of the photoanode enhance the hydrophilicity of PEC cells. This modified Chl film not only reduces the OER barrier and promotes carrier transfer but also inhibits loss of vanadium and increases the stability of the BVO photoanode. Finally, the modified BVO photoanode exhibits a photocurrent density of 5.1 mA cm⁻² at 1.23 V_{RHE} (RHE: reversible hydrogen electrode), and the onset potential moves 350 mV negatively in 0.5 mol L⁻¹ Na₂SO₄. This article provides a general and simple surface hybrid inorganic/organic solution to improve the catalytic ability of photoanodes.

Keywords: photoanode, BiVO₄, chlorophyll, water splitting

INTRODUCTION

Photoelectron-chemical (PEC) water splitting can directly convert solar energy to hydrogen [1]. As the core of PEC cells, photoanode materials play an important role in light absorption and the separation and transfer of photogenerated carriers. Compared with other wide-bandgap photoanodes (TiO₂, WO₃, SnO₂, In₂O₃, etc.) [2–6], BiVO₄ (BVO) is a prominent photoanode material with a narrower bandgap (2.4 eV), excellent stability, and nontoxicity [7]. Nevertheless, a large amount of photogenerated carrier recombination and dull oxygen evolution reaction (OER) dynamics seriously hinder its application in PEC water splitting [8]. To resolve the current problems of BVO-based photoanodes, various solutions (heterojunction strategies [9], cocatalyst loading [10], defect engineering [11], doping [12], etc. [13]) have been proposed and applied. Among these strategies, the most common materials introduced are inorganic materials, including transition metal ions with d0 or d10 electronic structures [14], metal oxides [15,16], metal sulfides [17], and others [18]. However, adjusting and controlling the electronic properties of inorganic materials is still challenging. Moreover, the combination of two inorganic materials will

cause lattice mismatch owing to different polycrystalline facets and grain boundaries [19]. Additionally, the narrow optical response and high recombination rate of inorganic semiconductors restrict their exploitation in photocatalysts [20]. In contrast, organic species can be diversified by adjusting the molecular chemical structure [21,22], bringing special properties with multiplicity and maneuverability, which can meet different application requirements with low-cost inputs [23,24]. Furthermore, unlike combining inorganic semiconductors, combining surface hybrid photoanodes with organic materials to form an interface results in materials with more unique advantages, such as fewer intrinsic defects, better absorption characteristics, and excellent electrical properties [25–27]. In recent years, many organic compounds (e.g., polyanilines [28], porphyrins [29], benzaldehyde [30], Zn-Pt-porphyrin conjugated polymers [21], and others [31]) have been applied in PEC water splitting.

Among the many developed organic materials, chlorophyll (Chl) molecules consisting of a porphyrin ring and aliphatic hydrocarbons containing an ester group have been popularly researched in recent years [32,33]. Chl with a unique molecular structure can turn solar energy into O₂ and organic sugar through plant photosynthesis, occupying an important position in fixing and utilizing solar energy [34]. As Chl has poor conductivity and worse hydrophilicity, it is not an ideal photoanode. Recently, Zhang's group [35] used Chl and its derivative sodium copper chlorophyllin (ChlCuNa) to modify BVO and demonstrated the applications of Chl in photocatalysts, solving the hydrophobicity problem of Chl. In this study, ChlCuNa was used as a sensitizer, improving the surface hydrophilicity and light utilization capability of the BVO photoanode. Although ChlCuNa can be used to remove the ester to increase hydrophilicity, Chl loses its conformal covering film properties, which is critical to the performance of PEC water splitting. BVO materials without film coverage are susceptible to the loss of vanadium, resulting in a reduction in stability [36]. Therefore, achieving conformal coverage of the photoanode to improve the catalytic ability of Chl is the key to solving the above problems.

For this study, we use Cu²⁺ to replace Mg²⁺ in the porphyrin ring, which increases the stability of Chl (named Chu) [37]. Then, we combine Chu with Co and Si ions to obtain a multifunctional thin film (named the Chu/CoSi film) through the colloid copolymerization sink, which improves hydrophilicity while ensuring film formation. This two-step modified Chl

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ensures conformal film coverage on the BVO photoanode with higher hydrophilicity and stability than pure Chl. Furthermore, benefitting from the copolymerization sink [38] and different contents of Co and Si, a thin film is formed with a gradient distribution of Co^{2+} and Si^{4+} ions, promoting the OER dynamics, decreasing the surface impedance, and effectively reducing bulk recombination. The photocurrent density (J) of BVO coated with a Chu/CoSi film was 5.1 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ (RHE: reversible hydrogen electrode), the onset potential (V_{on}) negatively shifted 350 mV in the Na_2SO_4 solution, and the Chu/CoSi film-coated BVO exhibited excellent stability, making it comparable or even superior to most reported BVO photoanodes (Table S1).

EXPERIMENTAL SECTION

Reagents

Potassium iodide (KI), bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), sodium hydroxide (NaOH) and cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Aladdin. Nitric acid (HNO_3), copper sulfate (CuSO_4), absolute ethanol and sodium silicate (Na_2SiO_3) were purchased from Sinopharm. Sodium copper chlorophyll salt (ChlCuNa) and chlorophyll (Chl A and Chl B mixture) were produced by Shanghaiyuan Bio-Technology Co., Ltd. Benzoquinone was produced by Macklin.

Synthesis of photoanodes

Synthesis of BVO photoanodes

BVO photoanodes were prepared on cleaned fluorine-doped tin oxide (FTO) glass according to a modified electrodeposition method [1]. The electrolyte was a mixture prepared as follows. First, 23.904 g of KI and 7.056 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dispersed in 360 mL deionized water (named A), and then, the pH was adjusted to 1.7 by adding HNO_3 . Another solution, solution B, was obtained by dissolving 3.577 g of benzoquinone in 144 mL of absolute ethanol. After stirring for 2 h, FTO was used as the working electrode (WE), and cathodic deposition was performed under $-0.1 \text{ V vs. Ag/AgCl}$ for 180 s to obtain an iodine bismuth oxide (BiOI) film. Second, 0.2 mol L^{-1} vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) with dimethyl sulfoxide (DMSO) solution was prepared, and then, 200 μL of the above solution was placed on the as-fabricated BiOI film and heated at 450°C for 2 h in a muffle furnace. Finally, excess vanadium pentoxide (V_2O_5) present in the BVO film was removed by soaking in 1 mol L^{-1} NaOH solution for 30 min. Then, the film was washed with distilled water to obtain a nanoworm-like BVO photoanode.

Preparation of chlorophyll-Cu (Chu)

Chl (0.050 g) was mixed with 15 mL of ethanol solution. The Chl used in this work is a mixture of Chl A and Chl B. Then, 250 μL of acetic acid solution was added to adjust the pH to 4.5, and then, 30 μL of 0.5 mol L^{-1} CuSO_4 solution was dropped to obtain Chu.

Synthesis of a BVO photoanode modified by Chu and cobalt silicate (BVO/Chu/CoSi)

Two kinds of colloidal solutions were used. The first solution was a violet cobalt silicate colloidal solution in which 1.421 g of Na_2SiO_3 and 0.047 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 40 mL

of deionized water. The second colloidal solution was a 15 mL ethanol solution with 0.050 g of the mixture of Chl A and Chl B. Then, two solutions with a volume ratio of 3:1 were mixed and dropped onto the surface of the BVO photoanode, which was washed with distilled water after static treatment for 15 to 20 min. This procedure was repeated twice.

Synthesis of a BVO photoanode modified by ChlCuNa and cobalt silicate (BVO/ChlCuNa/CoSi)

A total of 0.050 g of the mixture of Chl A and Chl B was replaced with 0.060 g of ChlCuNa solution in the synthesis process of the BVO/Chu/CoSi photoanode, and the other steps remained unchanged.

Synthesis of a BVO photoanode modified by Chu and cobalt ions (BVO/Chu/Co), cobalt silicate (BVO/CoSi) and Chu (BVO/Chu)

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was put into 40 mL of deionized water and then mixed with Chu solution in accordance with the above-mentioned method. After full mixing, 50 μL of liquid was dropped onto the BVO surface. BVO/Chu/Co was formed after waiting for half an hour. A total of 1.421 g of Na_2SiO_3 and 0.0472 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 40 mL of deionized water, which was allowed to stand for 20 min, rinsed with water, and dried under natural conditions to obtain BVO/CoSi. The mixture of Chl A and Chl B (0.050 g) was dissolved in 15 mL of ethanol solution. Copper ions were introduced in the same way. In addition, 50 μL of this solution was dropped onto the surface of BVO. The mixture was allowed to stand for 20 min, rinsed with water and dried under natural conditions, and then, BVO/Chu was obtained.

Characterization of materials

Microstructure observation was performed using field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 STWIN TMP). X-ray diffraction (XRD, D/MAX-III-B-40 KV, Cu K α radiation, $\lambda = 0.15418 \text{ nm}$, Panalytical, Holland) was used to characterize the phase and crystal structure of the materials. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was used to describe the changes in chemical elements. A ultraviolet-visible (UV-vis) spectrophotometer (Shimadzu UV 3600) was used to test the absorption of solar light by the photoanode. Ultraviolet photoelectron spectroscopy (UPS) spectra were obtained by a Physical Instruments 5600 photoelectron spectrometer, which was performed using He plasma discharge to generate 21.22 eV UV light. Time-resolved transient photoluminescence (TRPL) spectra were obtained on a LifeSpec II spectrometer (Edinburgh Instruments) with a 375-nm laser (FLS980). Fourier transform infrared (FTIR) spectroscopy was performed with a Fourier transform infrared spectrometer (Nicolet 6700, Bruker).

PEC measurements

PEC measurements were performed on the photoanode in a three-electrode configuration with the BVO photoanode or other modified samples as the WE, saturated Ag/AgCl as the reference electrode, and platinum foil ($1.0 \text{ cm} \times 1.2 \text{ cm}$) as the counter electrode with an Autolab electrochemical workstation (PGSTA 302N). A neutral solution of 0.5 mol L^{-1} Na_2SO_4 was used as the electrolyte. Using the above configuration, photocurrent-voltage (J - V) curves and current-time (i - t) curves were

obtained under AM 1.5 G illumination (100 mW cm^{-2} ; Newport, Model 94043A). Electrochemical impedance spectroscopy (EIS) was performed at the open-circuit potential (V_{OC}) and frequencies of 0.1 to 10^5 Hz with a 5-mV amplitude.

The measured potential *versus* Ag/AgCl was converted with respect to the RHE, and the conversion formula is shown below:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.1976, \quad (1)$$

where E_{RHE} is the converted potential *versus* RHE and $E_{\text{Ag/AgCl}}$ is the experimentally measured potential *versus* the Ag/AgCl reference.

Mott-Schottky (M-S) curves were measured by the workstation at an alternating current frequency of 1.0 kHz with an amplitude of 0.01 V in the dark. Cyclic voltammetry (CV) was carried out in the potential range of 0–0.1 V_{Ag/AgCl} with a scan rate from 30 to 150 mV s⁻¹. The electrochemical surface area (ECSA), estimated as half of the slope [2], was obtained by CV at different scan rates.

The incident photon-to-electron conversion efficiency (IPCE) was determined using a full solar simulator and an Autolab electrochemical workstation (PGSTA 302N). The IPCE was measured at 1.23 V_{RHE} in 0.5 mol L⁻¹ Na₂SO₄ solution using the same three-electrode setup described above for photocurrent measurements. The IPCE was calculated as follows:

$$\text{IPCE} = 1240 \times I / (P_{\text{light}} \times \lambda), \quad (2)$$

where I (mA cm⁻²) is the measured photocurrent density at a specific wavelength, λ (nm) is the wavelength of incident light, and P_{light} (mW cm⁻²) is the measured light power density at that wavelength.

The applied bias photon-to-current efficiency (ABPE) was calculated by the following equation:

$$\text{ABPE} = J \times (1.23 - V_{\text{bias}}) / P_{\text{light}}, \quad (3)$$

where J (mA cm⁻²) is the photocurrent density, V_{bias} (V) is the applied potential, and P_{light} is the incident illumination power density (100 mW cm^{-2}).

The unity converted photocurrent density ($J_{\text{abs.}}$) was calculated by absorptivity over the standard solar spectrum:

$$J_{\text{abs.}} = \int_{300}^{\lambda_{\text{max}}} \frac{\lambda \times J_{\text{abs.}}(\lambda) \times E(\lambda)}{1240} d(\lambda), \quad (4)$$

where λ_{max} is the maximum light absorption edge of a photo-electrode, λ (nm) is the light wavelength, and $E(\lambda)$ is the power density (mW cm⁻²) at a specific wavelength (λ) of the standard solar spectrum.

The charge injection efficiency (η_{inj}) and charge separation efficiency (η_{sep}) were calculated using the following equations:

$$\eta_{\text{inj}} = J / J_{\text{sulfite}}, \quad (5)$$

$$\eta_{\text{sep}} = J_{\text{sulfite}} / J_{\text{abs.}}, \quad (6)$$

where J_{sulfite} is the current density tested in 0.5 mol L⁻¹ Na₂SO₃ and 0.5 mol L⁻¹ Na₂SO₄ solutions, and J is the current density tested in 0.5 mol L⁻¹ Na₂SO₄ solution.

The formula used to calculate the photogenerated carrier lifetime τ from the V_{OC} measurements is as follows:

$$\tau = -\frac{k_{\text{B}}T}{e} \left(\frac{dV_{\text{OC}}}{dt} \right)^{-1}, \quad (7)$$

where k_{B} , T , e and dV_{OC}/dt are the Boltzmann's constant, temperature (K), charge of single electron and the V_{OC} transient decay, respectively.

RESULTS AND DISCUSSION

The specific preparation process is shown in Scheme 1. Owing to the instability of Chl, referring to previous work [37], we dissolved Chl into an alcohol solution with acetic acid and copper ions to obtain Chu to improve its stability. Fig. S1 shows that Chu does not precipitate after a week, demonstrating that this process enhances the stability of Chl. In this process, Mg²⁺ is extracted, and Cu²⁺ enters the acidic environment [39,40]. To confirm the increased stability of Chu after treatment, UV-vis

Scheme 1 Preparation process of the BVO/Chu/CoSi photoanode and the structure of some materials.

absorption spectra were measured. As shown in Fig. S2, the absorbing ability of Chl solution decreases significantly after storage for one week, while Chu solution still displays obvious absorption peaks after being stored for ten days. We found that the EIS and CV test results of the newly prepared photoelectrode did not show much difference from those of the samples after treatment (Fig. S3). The improvement in chlorophyll after copper ion replacement is reflected in the improvement in long-term stability. The SEM images display a worm-like BVO photoanode (Fig. 1a). Once the mixed solution consisting of Chu and cobalt silicate gel was drop-coated, a film tightly covered the surface of BVO (Fig. 1b). The cross-sectional SEM images (Fig. S4) indicate that the film achieves conformal coverage on the entire BVO surface. To explore the reason for film formation, another method of modifying Chl was applied. Referring to previous work, the ester groups were cut off to obtain the derivative ChlCuNa and improve its stability [35]. Fig. S5 shows that the conformal cover film disappears. Hence, the formation of the conformal cover film is due mainly to the existence of esters. In addition, unlike the Chu film, the Chu/CoSi film displays significantly enhanced hydrophilicity without destroying the existence of the film (Fig. S6). Furthermore, Si-modified Chu exhibits better hydrophilicity than Co-modified Chu and Chu/CoSi films (Fig. S7), indicating that the existence of Si ions

greatly improves the hydrophilicity of the film. Therefore, through the two-step method-modified Chl based on the presence of Chu, Si and Co ions, the hydrophilicity and stability of Chl were improved while ensuring its film-forming properties.

The XRD patterns (Fig. S8) were measured to evaluate the phase. BVO and BVO/Chu/CoSi display the same diffraction peaks, and the peaks at 28.95° , 30.53° , and 35.21° are ascribed to the (112), (004), and (020) planes of monoclinic crystalline BiVO_4 (JCPDS: 83-1699), respectively. FTIR spectra (Fig. S9) were selected to determine the functional groups. Compared with the BVO spectrum, BVO/Chu/CoSi shows that the extra peaks at 1463.6 , 2810.6 , and 1697.3 cm^{-1} are attributed to the functional groups of $-\text{CH}_3$, $\text{C}=\text{C}$, and $\text{C}-\text{O}$, proving that Chu exists in the film [41,42]. TEM shows that BVO is covered by a thin film (Fig. 1c). The high-resolution TEM (HRTEM) image of BVO/Chu/CoSi reveals a crystal lattice spacing of 0.325 nm (Fig. 1d), corresponding to the (224) plane of BVO. BVO is surrounded by an amorphous Chu/CoSi film. The energy dispersive spectroscopy (EDS) elemental mappings of BVO/Chu/CoSi in Fig. 1f–m reveal that Bi, V, O, C, Cu, and N are distributed uniformly, while Si gathers on the surface and Co presents the opposite state, which correspond to the area of Fig. 1e. This phenomenon proves that BVO is conformably covered by the Chu film with a gradient distribution of Si and

Figure 1 Top-view SEM images of (a) BVO, and (b) BVO/Chu/CoSi. (c) TEM image, (d) HRTEM image, (e) high-angle annular dark field (HADF)-TEM image and (f–m) corresponding elemental mappings of BVO/Chu/CoSi.

Co. EDS line scanning was performed from the outside to the inside of BVO/Chu/CoSi (Fig. S10), clearly indicating the gradient distribution of Si and Co along with the Chu/CoSi film. To determine the reason for this distribution state, we performed an EDS test on the solution mixed with Chu alcohol and cobalt silicate colloidal solution. After standing for a period of time, this mixed solution was stratified owing to the copolymerization sink, which was a colloidal solid with different electrical properties. Fig. S11 shows fewer Co atoms in the upper part of solution and more in the lower part, while a large amount of Si appears in the upper part. Due to the different masses of Co and Si combined with Chu, after two kinds of colloidal solutions were mixed, Co ions and Si ions appeared in different areas of the mixed solution. All the above results prove the successful construction of BVO coated with an amorphous Chu/CoSi film accompanied by a gradient distribution of Si and Co.

The surface chemical states were checked by XPS, as shown in Fig. 2. The peaks at 164.30 and 158.99 eV are attributed to the

$4f_{5/2}$ and $4f_{7/2}$ levels of Bi^{3+} in BVO (Fig. 2a), while these peaks shift to 164.04 and 158.73 eV upon addition of the Chu/CoSi film. Fig. 2b indicates that the main peaks after covering with this film are located at 515.96 and 523.20 eV in the V 2p spectrum, which differ from the 524.08 and 516.59 eV peaks observed for BVO [10]. The peak of the lattice oxygen (O_L , 529.20 eV) of BVO/Chu/CoSi also shifts toward a lower binding energy compared with that of BVO (529.52 eV) (Fig. 2c). This shifting phenomenon is due to the electron transformation from the Chu/CoSi film to BVO, causing the increased electronic cloud density of Bi and V in BVO. The peak at 531.03 eV represents the surface-adsorbed oxygen (O-H), while the peaks at 532.15 and 533.23 eV correspond to C=O and C-O, respectively, which is a typical feature of Chu. In addition, the intensity of Bi and V in BVO/Chu/CoSi is significantly lower than that in BVO, while the COOR (Fig. 2d), Si 2p (Fig. 2e), and Co 2p (Fig. 2f) peaks show the conformal coating of the Chu/CoSi film on the BVO photoanode.

Figure 2 XPS spectra of (a) Bi 4f, (b) V 2p, (c) O 1s, (d) C 1s, and (e) Si 2p and (f) Co 2p for BVO and BVO/Chu/CoSi.

The PEC water splitting performance of the photoanode was determined by measuring J - V curves in $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$. Fig. S12 shows the J - V curves of the BVO/Chu/CoSi photoanode fabricated with Chu solution:cobalt silicate colloidal solutions of different ratios, which indicates that 3:1 is the optimum reaction ratio. As the ratio of Chu alcohol solution to cobalt silicate colloidal solution changes, the film becomes uneven (Fig. S13) and reveals the best performance when the film is conformally covered. Fig. 3a shows that the performance of optimum samples is gradually improved compared with that of BVO. The J of BVO/Chu/CoSi is 5 times that of BVO, achieving 5.1 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$. The η_{ABPE} of BVO/Chu/CoSi is obviously improved (Fig. S14), reaching 2.2% at $0.5 \text{ V}_{\text{RHE}}$. The UV-vis absorption curves and corresponding Tauc plots are shown in Fig. 3b. Coating with the Chu/CoSi film narrows the bandgap (2.40 eV) and slightly enhances light absorption. The special absorption

peak at 660 nm indicates the appearance of Chu and cobalt ion complexes [32,34]. According to the UV-vis absorption curves, the unity converted photocurrent density (J_{abs} , Table S2) of the photoanode increases from 6.64 to 7.20 mA cm^{-2} , demonstrating that the Chu/CoSi film improves the light utilization efficiency of the device and contributes to the increase in J . The IPCE values are enhanced over the measured wavelength range, and their average value increases from 13.6% to 50.3% at wavelengths of 350 to 450 nm. (Fig. S15). M-S plots (Fig. S16) were measured at a frequency of 1 kHz in the dark to explore the change in carrier concentration (N_d) and flat band potential (V_{FB}). BVO and BVO/Chu/CoSi exhibit positive M-S plots, representing n-type semiconductors with electrons as majority carriers. N_d can be obtained according to the following equation: $1/C^2 = (2/\epsilon\epsilon_0 N_d A^2) \times [V - V_{\text{FB}}] - k_B T/e$, (8) where C is the specific capacity, ϵ is the dielectric constant of the

Figure 3 (a) Linear sweep voltammogram curves, (b) UV-vis absorption spectra with inserted Tauc plots, (c) V_{OC} values, (d) EIS Nyquist plots under light illumination (the inset is the fitting circuit used to extract resistances), (e) V_{OC} -derived carrier lifetime, and (f) C_{dl} of the BVO and BVO/Chu/CoSi photoanodes.

photoanode, ϵ_0 is the electric permittivity of vacuum, N_d is the carrier density, A is the area, V is the applied potential, and V_{FB} is the flat band potential. The N_d values of BVO/Chu/CoSi and BVO are calculated to be 4.99×10^{17} and $6.29 \times 10^{16} \text{ cm}^{-3}$, respectively. As expected, the BVO/Chu/CoSi film exhibits a significantly increased N_d [43]. A negatively shifted V_{FB} (intercept on the x axis) is consistent with the V_{on} change shown in the J - V curve. V_{OC} measurements were conducted to further explore the change in V_{on} (Fig. S17). The BVO/Chu/CoSi photoanode displays a significantly increased photovoltaic value (Fig. 3c), favoring the negative shift of V_{on} . These results cause the V_{on} of BVO/Chu/CoSi to shift negatively compared with that of BVO.

To confirm the improved surface hole extraction ability induced by the Chu/CoSi overlayer and further explain the reason for the change in V_{on} , EIS spectra (Fig. 3d) were obtained to determine the reaction kinetics. The Chu/CoSi overlayer-covered BVO exhibits two semicircles, indicating that an additional interface is formed. The series resistance (R_s) represents the impedance between FTO and the photoanode, and charge transfer resistances R_{p1} and R_{p2} represent the impedance at the interface between the film/BVO and the photoanode/electrolyte, respectively. The values of R_s , R_{p1} , and R_{p2} are summarized in Table S3. The OER kinetics are affected mainly by surface impedance, and BVO/Chu/CoSi displays a smaller radius of R_{p2} under light illumination than BVO, confirming the positive role of the Chu/CoSi overlayer in charge transfer [44]. Furthermore, BVO/CoSi and BVO/Chu display smaller resistances than BVO (Fig. S18), indicating that the surface impedance of the modified photoanode is reduced. The hole lifetime is calculated to be from 147 to 45 ms on the surface, as shown in Fig. 3e, showing that the covered multifunctional film promotes OER dynamics and J increases. Meanwhile, these data indicate that the negative V_{on} is attributed to the negative V_{FB} , large V_{OC} and fast OER reaction kinetics. Furthermore, cyclic voltammograms were measured in a non-Faradaic region at scan rates ranging from 30–150 mV s⁻¹ to measure the double-layer capacitance (C_{dl}), which can confirm the increased number of active sites (Fig. S19). Fig. 3f shows that the C_{dl} values are in the order of BVO/Chu/CoSi > BVO. A more positive slope implies more active reaction sites. Therefore, the Chu/CoSi amorphous overlayer provides a larger surface-active reaction area than BVO, promoting the surface OER kinetics and increasing PEC performance.

To explore the respective roles of Chu and cobalt silicate in the multifunctional film, we performed a control experiment by replacing the solution with Chu alcohol solution or cobalt silicate solution only. The lower J of BVO/Chu and BVO/CoSi (Fig. S20) means that Chu and cobalt silicate together play an important role in enhancing the PEC performance. First, the film covering the surface of BVO/CoSi disappears, while BVO/Chu has an uneven film layer (Fig. S21). This result indicates that the presence of Chu is the key to the construction of films. Secondly, according to the similar XRD patterns (Fig. S22), the solutions of different components affect only the coverage of the surface film and do not affect the phase of the photoanode. In addition, we removed Si to obtain new samples (BVO/Chu/Co) to study the effect of Si on the surface. The J of BVO/Chu/Co (Fig. S23) being lower than that of BVO/Chu/CoSi demonstrates that the surface distribution of Si can effectively promote OER dynamics and reduce the surface reaction overpotential. Silicate roots given on the surface of the photoanode as catalytic active sites have greatly improved the photocurrent in recent research

[45]. As mentioned above, Co and Si in the film show a gradient distribution phenomenon. According to previously reported literature, the existence of Co²⁺ can extract holes and suppress photon-generated carrier recombination, while SiO₂₋₃ contributes to the formation of oxidation reaction intermediates, and porphyrin rings greatly improve the hole extraction ability, reducing the OER barrier [31].

The charge separation efficiency (η_{sep}) and charge injection efficiency (η_{inj}) were calculated to acquire the effect of the Chu/CoSi film under simulated solar light illumination. Fig. S24 reveals the J - V curves measured in the electrolyte containing 0.5 mol L⁻¹ Na₂SO₃, which is used as the hole scavenger. The detailed calculation process is presented in the Supplementary information. The significant enhancement in the η_{inj} (Fig. 4a) of BVO/Chu/CoSi is attributed to the formation of a Chu/CoSi multifunctional gradient film. The existence of the film promotes the surface transfer of photogenerated holes and reduces the OER reaction barrier. Fig. 4b shows that the η_{sep} of BVO/Chu/CoSi is enhanced little compared with that of BVO, which is ascribed to the enrichment of Co at the interface between BVO and the film, accelerating the transfer of photogenerated holes. However, the improvement in η_{sep} may be related to the change in the energy band structure. To verify this point of view, we measured the UPS spectra (Fig. S25). Based on E_g , the positions of the conduction band (E_c), valence band (E_v), and Fermi energy level (E_f) are determined by the equation $E_c = E_v + E_g$, which is shown in Fig. 4c. The locations of E_c and E_v move upward after covering with the thin film. Therefore, a type II structure is formed, which benefits the carrier separation and reduces the bulk recombination [46,47]. Fig. 4d reveals the TRPL decay to further explore the charge carrier dynamics of the photoanode. The relevant fitted data are shown in Table S4. The lifetime of BVO/Chu/CoSi is reduced from 7.41 to 1.53 ns, indicating that the existence of the Chu/CoSi film can make the holes transfer quickly from BVO to the film and oxidize with water [44]. In addition, the existence of the multifunctional film also effectively enhances the stability of the sample due to the efficient suppression of vanadium overflow into the electrolyte. We performed inductively coupled plasma (ICP) emission spectrometry to test the content of vanadium in the electrolyte after a period of testing, and the detailed numerical results are shown in Table S5, proving that the film inhibited the loss of vanadium and improved stability. The i - t curve is shown in Fig. 4e. The J of BVO is reduced by approximately half of its initial value after 30 min. Nevertheless, BVO/Chu/CoSi presents excellent J that can reach more than 90% after testing for 3 h because the cover of the conformal film can suppress the loss of vanadium. We observed the morphology of BVO/Chu/CoSi after a 90-min test, as shown in Fig. S26. Although some leaks appear on the film surface, the overall morphology is intact. From the XRD results, there are no new peaks or peak movements (Fig. S27); thus, the BVO crystal lattice is preserved. The V–O and Bi–O peaks are still clear and distinct in the Raman spectrum (Fig. S28).

CONCLUSIONS

In this study, using a simple colloidal copolymerization sink method based on two-step modified Chl, we successfully synthesized an amorphous multifunctional film that combines Chu and cobalt silicate ions to improve the performance of a BVO photoanode. This film contains Si and Co catalyst ions with a

Figure 4 (a) Injection and (b) separation efficiencies of BVO and BVO/Chu/CoSi. (c) Energy level diagram of BVO/Chu/CoSi obtained from the UPS results. (d) TRPL decay spectra and (e) long-term photocurrent measurements of BVO and BVO/Chu/CoSi photoanodes at 1.23 V_{RHE} .

gradient distribution. The Co ions present at the interface between BVO and Chl promote the transport of photogenerated holes, and the Si ions on the surface of the photoanode enhance the hydrophilicity of PEC cells. A type-II energy band structure is formed in favor of extracting photon-generated carriers. In addition, the surface Si ions act as catalytic oxidation reaction activation centers, enhancing the overall performance. Combining the advantageous properties of the two substances, J reaches 5.1 $mA\ cm^{-2}$ at 1.23 V_{RHE} , which is approximately 5 times that of the original BVO. After covering the multifunctional film, the phenomenon of vanadium loss is effectively inhibited. This work will inspire the design of PEC systems using natural organic matter.

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1 Lee DK, Choi KS. Enhancing long-term photostability of $BiVO_4$ pho-

toanodes for solar water splitting by tuning electrolyte composition. *Nat Energy*, 2018, 3: 53–60

- Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, 238: 37–38
- Sun M, Gao RT, He J, *et al.* Photo-driven oxygen vacancies extends charge carrier lifetime for efficient solar water splitting. *Angew Chem Int Ed*, 2021, 60: 17601–17607
- Pan Q, Li A, Zhang Y, *et al.* Rational design of 3D hierarchical ternary $SnO_2/TiO_2/BiVO_4$ arrays photoanode toward efficient photoelectrochemical performance. *Adv Sci*, 2020, 7: 1902235
- Chao Y, Zhou P, Li N, *et al.* Ultrathin visible-light-driven Mo incorporating In_2O_3 - $ZnIn_2Se_4$ Z-scheme nanosheet photocatalysts. *Adv Mater*, 2019, 31: 1807226
- Landman A, Dotan H, Shter GE, *et al.* Photoelectrochemical water splitting in separate oxygen and hydrogen cells. *Nat Mater*, 2017, 16: 646–651
- Kim JH, Lee JS. Elaborately modified $BiVO_4$ photoanodes for solar water splitting. *Adv Mater*, 2019, 31: 1806938
- Kim TW, Choi KS. Nanoporous $BiVO_4$ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. *Science*, 2014, 343:

- 990–994
- 9 Low J, Yu J, Jaroniec M, *et al.* Heterojunction photocatalysts. *Adv Mater*, 2017, 29: 1601694
 - 10 Hermans Y, Murcia-López S, Klein A, *et al.* BiVO₄ surface reduction upon water exposure. *ACS Energy Lett*, 2019, 4: 2522–2528
 - 11 Gao RT, Wang L. Stable cocatalyst-free BiVO₄ photoanodes with passivated surface states for photocorrosion inhibition. *Angew Chem Int Ed*, 2020, 59: 23094–23099
 - 12 Jo WJ, Jang JW, Kong K, *et al.* Phosphate doping into monoclinic BiVO₄ for enhanced photoelectrochemical water oxidation activity. *Angew Chem*, 2012, 124: 3201–3205
 - 13 Tian Z, Zhang P, Qin P, *et al.* Novel black BiVO₄/TiO_{2-x} photoanode with enhanced photon absorption and charge separation for efficient and stable solar water splitting. *Adv Energy Mater*, 2019, 9: 1901287
 - 14 Nellist MR, Qiu J, Laskowski FAL, *et al.* Potential-sensing electrochemical AFM shows CoPi as a hole collector and oxygen evolution catalyst on BiVO₄ water-splitting photoanodes. *ACS Energy Lett*, 2018, 3: 2286–2291
 - 15 Li H, Yu H, Quan X, *et al.* Improved photocatalytic performance of heterojunction by controlling the contact facet: High electron transfer capacity between TiO₂ and the {110} facet of BiVO₄ caused by suitable energy band alignment. *Adv Funct Mater*, 2015, 25: 3074–3080
 - 16 Meng L, Tian W, Wu F, *et al.* TiO₂ ALD decorated CuO/BiVO₄ p-n heterojunction for improved photoelectrochemical water splitting. *J Mater Sci Tech*, 2019, 35: 1740–1746
 - 17 Meng L, Wang S, Cao F, *et al.* Doping-induced amorphization, vacancy, and gradient energy band in SnS₂ nanosheet arrays for improved photoelectrochemical water splitting. *Angew Chem*, 2019, 131: 6833–6837
 - 18 Faraji M, Yousefi M, Yousefzadeh S, *et al.* Two-dimensional materials in semiconductor photoelectrocatalytic systems for water splitting. *Energy Environ Sci*, 2019, 12: 59–95
 - 19 Laskowski FAL, Nellist MR, Qiu J, *et al.* Metal oxide/(oxy)hydroxide overlayers as hole collectors and oxygen-evolution catalysts on water-splitting photoanodes. *J Am Chem Soc*, 2018, 141: 1394–1405
 - 20 Klahr B, Gimenez S, Fabregat-Santiago F, *et al.* Water oxidation at hematite photoelectrodes: the role of surface states. *J Am Chem Soc*, 2012, 134: 4294–4302
 - 21 Wang J, Xu L, Wang T, *et al.* Porphyrin conjugated polymer grafted onto BiVO₄ nanosheets for efficient Z-scheme overall water splitting via cascade charge transfer and single-atom catalytic sites. *Adv Energy Mater*, 2021, 11: 2003575
 - 22 He H, Liao A, Guo W, *et al.* State-of-the-art progress in the use of ternary metal oxides as photoelectrode materials for water splitting and organic synthesis. *Nano Today*, 2019, 28: 100763
 - 23 He Z, Zhong C, Su S, *et al.* Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure. *Nat Photon*, 2012, 6: 591–595
 - 24 He Z, Xiao B, Liu F, *et al.* Single-junction polymer solar cells with high efficiency and photovoltage. *Nat Photon*, 2015, 9: 174–179
 - 25 Draxl C, Nabok D, Hannewald K. Organic/inorganic hybrid materials: Challenges for *ab initio* methodology. *Acc Chem Res*, 2014, 47: 3225–3232
 - 26 Cao S, Low J, Yu J, *et al.* Polymeric photocatalysts based on graphitic carbon nitride. *Adv Mater*, 2015, 27: 2150–2176
 - 27 Nürnberg DJ, Morton J, Santabarbara S, *et al.* Photochemistry beyond the red limit in chlorophyll f-containing photosystems. *Science*, 2018, 360: 1210–1213
 - 28 Zhao M, Chen T, He B, *et al.* Photothermal effect-enhanced photoelectrochemical water splitting of a BiVO₄ photoanode modified with dual-functional polyaniline. *J Mater Chem A*, 2020, 8: 15976–15983
 - 29 Kang SH, Jeong MJ, Eom YK, *et al.* Porphyrin sensitizers with donor structural engineering for superior performance dye-sensitized solar cells and tandem solar cells for water splitting applications. *Adv Energy Mater*, 2017, 7: 1602117
 - 30 Luo L, Wang Z, Xiang X, *et al.* Selective activation of benzyl alcohol coupled with photoelectrochemical water oxidation via a radical relay strategy. *ACS Catal*, 2020, 10: 4906–4913
 - 31 Ning X, Lu B, Zhang Z, *et al.* An efficient strategy for boosting photogenerated charge separation by using porphyrins as interfacial charge mediators. *Angew Chem Int Ed*, 2019, 58: 16800–16805
 - 32 Yang B, Lu Y, Jiang D, *et al.* Bioinspired multifunctional organic transistors based on natural chlorophyll/organic semiconductors. *Adv Mater*, 2020, 32: 2001227
 - 33 Ye S, Ding C, Chen R, *et al.* Mimicking the key functions of photosystem II in artificial photosynthesis for photoelectrocatalytic water splitting. *J Am Chem Soc*, 2018, 140: 3250–3256
 - 34 Vishniac W, Rose IA. Mechanism of chlorophyll action in photosynthesis. *Nature*, 1958, 182: 1089–1090
 - 35 Feng Y, Cheng H, Han J, *et al.* Chlorophyll sensitized BiVO₄ as photoanode for solar water splitting and CO₂ conversion. *Chin Chem Lett*, 2017, 28: 2254–2258
 - 36 Kuang Y, Jia Q, Ma G, *et al.* Ultrastable low-bias water splitting photoanodes via photocorrosion inhibition and *in situ* catalyst regeneration. *Nat Energy*, 2017, 2: 16191
 - 37 Kim WS. Copper replacement of magnesium in the chlorophylls and bacteriochlorophyll. *Z für Naturforschung B*, 1967, 22: 1054–1061
 - 38 Li M, Wang X, Luo Y, *et al.* A second-coordination-sphere strategy to modulate nickel- and palladium-catalyzed olefin polymerization and copolymerization. *Angew Chem*, 2017, 129: 11762–11767
 - 39 Bols PS, Anderson HL. Shadow mask templates for site-selective metal exchange in magnesium porphyrin nanorings. *Angew Chem*, 2018, 130: 8000–8003
 - 40 Ding Y, Zhu WH, Xie Y. Development of ion chemosensors based on porphyrin analogues. *Chem Rev*, 2017, 117: 2203–2256
 - 41 Li X, Zhou R, Xu K, *et al.* Rapid determination of chlorophyll and pheophytin in green tea using fourier transform infrared spectroscopy. *Molecules*, 2018, 23: 1010
 - 42 Sun J, Li X, Zhao Q, *et al.* Construction of p-n heterojunction β-Bi₂O₃/BiVO₄ nanocomposite with improved photoinduced charge transfer property and enhanced activity in degradation of ortho-dichlorobenzene. *Appl Catal B-Environ*, 2017, 219: 259–268
 - 43 Gao RT, He D, Wu L, *et al.* Towards long-term photostability of nickel hydroxide/BiVO₄ photoanodes for oxygen evolution catalysts via *in situ* catalyst tuning. *Angew Chem*, 2020, 132: 6272–6277
 - 44 Wang S, He T, Chen P, *et al.* *In situ* formation of oxygen vacancies achieving near-complete charge separation in planar BiVO₄ photoanodes. *Adv Mater*, 2020, 32: 2001385
 - 45 Kim JS, Park I, Jeong ES, *et al.* Amorphous cobalt phyllosilicate with layered crystalline motifs as water oxidation catalyst. *Adv Mater*, 2017, 29: 1606893
 - 46 He W, Wang R, Zhang L, *et al.* Enhanced photoelectrochemical water oxidation on a BiVO₄ photoanode modified with multi-functional layered double hydroxide nanowalls. *J Mater Chem A*, 2015, 3: 17977–17982
 - 47 Tang Y, Wang R, Yang Y, *et al.* Highly enhanced photoelectrochemical water oxidation efficiency based on triadic quantum dot/layered double hydroxide/BiVO₄ photoanodes. *ACS Appl Mater Interfaces*, 2016, 8: 19446–19455

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

Supplementary information Supporting data are available in the online version of the paper.

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叶绿素修饰的钨酸铋对光电化学水分解性能和稳定性的提升

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摘要 钨酸铋表面缓慢的催化反应动力学严重阻碍了其在光电化学水分解领域的应用。基于此, 我们通过覆盖多功能薄膜成功构建出无机/有机杂化光阳极以改善钨酸铋的光电化学性能。该薄膜包含梯度分布的钴离子和硅离子以及经过改性的叶绿素有机化合物。其中, 存在于钨酸铋和叶绿素界面处的钴离子促进了光生空穴的传输, 而光阳极表面的硅离子提升了器件的亲水性。进一步, 该薄膜的存在有效降低了氧化反应的势垒, 促进了光生载流子转移, 同时能够抑制钨的流失并提高钨酸铋光阳极的稳定性。总的来说, 经过修饰后的钨酸铋光阳极, 测试中光电流密度在1.23 V_{RHE}下达到5.1 mA cm⁻², 起始电位负向移动350 mV。本文提供了一种通用且简便的无机/有机杂化电极的制备方案以提高器件的光电催化能力。