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## A Cobalt-Based Metal–Organic Framework as Cocatalyst on BiVO<sub>4</sub> Photoanode for Enhanced Photoelectrochemical Water Oxidation

Wang Zhang, Rui Li, Xin Zhao, Zhong Chen, Adrian Wing-Keung Law, and Kun Zhou\*

Dedication ((optional))

Abstract: A metal-organic framework (MOF)-modified bismuth vanadate (BiVO<sub>4</sub>) photoanode is fabricated by an ultrathin sheetinduced growth strategy, where ultrathin cobalt oxide sheets act as metal source for the in-situ synthesis of Co-based MOF (Co<sub>2</sub>(bim)<sub>4</sub>) nanoparticles on the surface of BiVO<sub>4</sub>. Co<sub>2</sub>(bim)<sub>4</sub> with small particle size and high dispersion can serve as a promising cocatalyst to accept holes transferred from BiVO4 and boost surface reaction kinetics for photoelectrochemical (PEC) water oxidation. The photocurrent density of a Co<sub>2</sub>(bim)<sub>4</sub>-modified BiVO<sub>4</sub> photoanode can achieve 3.1 mA/cm<sup>2</sup> under AM 1.5 G illumination at 1.23 V versus the reversible hydrogen electrode (RHE), which is better than those of pristine and cobalt-based inorganic materials-modified BiVO4 photoanodes.  $\text{Co}_2(\text{bim})_4$  with porosity and abundant metal sites exhibits a high surface charge separation efficiency (83 % at 1.2 V versus RHE), leading to the enhanced PEC activity. This work will bring new insight into the development of MOF materials as competent cocatalysts for PEC water splitting applications.

Photoelectrolysis of water by solar energy has attracted wide research interest for the production of sustainable hydrogen fuel.<sup>[1]</sup> Many inorganic semiconductors acting as photoelectrodes have been involved in the photoelectrocatalysis field.<sup>[2]</sup> In this respect, bismuth vanadate (BiVO<sub>4</sub>) is one of the most promising semiconductors for photoelectrochemical (PEC) water oxidation owing to its suitable conduction band edge position and narrow band gap.<sup>[3]</sup> Although the theoretical photocurrent densities of BiVO<sub>4</sub> can reach ~7.6 mA/cm<sup>2</sup> under AM 1.5G illumination, the reported experimental results of pure BiVO<sub>4</sub> are much smaller than the expected value.<sup>[3a]</sup> It is due to the fact that the BiVO<sub>4</sub> photoanode suffers from poor charge mobility and sluggish surface reaction kinetics in the PEC water oxidation process.<sup>[4]</sup>

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To date, intensive efforts are devoted to the improvement of PEC activity of BiVO<sub>4</sub>, such as foreign atom doping,<sup>[5]</sup> cocatalyst loading,<sup>[6]</sup> crystal facet controlling,<sup>[7]</sup> as well as morphology and nanostructure constructing.<sup>[8]</sup>

Recently, oxygen evolution catalysts (OECs) have been identified as cocatalysts for the improved PEC water oxidation performance of BiVO<sub>4</sub>.<sup>[9]</sup> Various electrochemical OECs have been loaded on the surface of BiVO<sub>4</sub> and their enhanced PEC activities have been intensively studied. For instance, Kim and Choi demonstrated the effect of two metal (oxy)hydroxides, (FeOOH and NiOOH), which can be alternately coated on the surface of BiVO<sub>4</sub> and enable an efficient decrease of surface charge recombination.<sup>[9a]</sup>

Metal-organic frameworks (MOFs) are a fascinating class of inorganic-organic hybrid porous solid, which can be rationally designed to satisfy wide applications.<sup>[10]</sup> Very recently, MOFs and their derivatives have been explored as electrocatalysts or electrode materials for energy storage and conversion.[11] Particularly, Fe, Co, Ni-based MOFs have been synthesized as OECs for efficient electrochemical water oxidation.<sup>[12]</sup> Therefore, it is expected that these MOF-based OECs can act as cocatalysts and accelerate surface reaction kinetics for PEC water oxidation. Indeed, doped BiVO<sub>4</sub> photoanodes loaded with Fe-based MOF microcrystals were reported for the enhanced PEC water oxidation performance and the results confirmed that the MOF material can act as a type of cocatalyst to accept holes transferred from BiVO<sub>4</sub> and facilitate the separation of charge carriers.<sup>[13]</sup> However, such MOF microcrystals cannot effectively enhance the final PEC activity due to their oversized volume and the low contact surface between these microcrystals and BiVO<sub>4</sub> particles.

Herein, we demonstrate an ultrathin sheet-induced method to prepare MOF nanoparticles uniformly loaded on the surface of BiVO<sub>4</sub> photoanode to validate the effectiveness of MOF-based cocatalysts for the enhanced PEC water oxidation performance. А Co-based MOF, poly[Co<sub>2</sub>(benzimidazole)<sub>4</sub>] (denoted Co<sub>2</sub>(bim)<sub>4</sub>),<sup>[14]</sup> was chosen as a cocatalyst because of its potential electrocatalytic water oxidation activity and stability in the neutral and alkaline aqueous system. Initially, we employed ultrathin cobalt oxide (CoO) sheets as metal source for the insitu synthesis of small-sized Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles on BiVO<sub>4</sub> surface. After being loaded with Co<sub>2</sub>(bim)<sub>4</sub>, the modified BiVO<sub>4</sub> photoanode could achieve the highest photocurrent density of 3.1 mA/cm<sup>2</sup> at 1.23 V versus the reversible hydrogen electrode (RHE) under AM 1.5G illumination. The results confirmed that Co<sub>2</sub>(bim)<sub>4</sub> could accept photogenerated holes transferred from BiVO<sub>4</sub> to catalyze water oxidation reaction and accelerate surface reaction kinetics, leading to the enhanced PEC performance.

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**Figure 1.** (a) Schematic illustration of the fabrication process of  $Co_2(bim)_4$ modified BiVO<sub>4</sub> photoanode; (b) XRD patterns of BiVO<sub>4</sub>, Cobim/BVO-20, Cobim/BVO-40, Cobim/BVO-100 and simulated  $Co_2(bim)_4$ , with the symbols asterisk, dot and triangle correspond to the peaks from FTO, BiVO<sub>4</sub> and  $Co_2(bim)_4$ , respectively; (c) crystalline structure of  $Co_2(bim)_4$ , with the gray, blue and red balls representing carbon, nitrogen and cobalt, respectively.

A nanoporous BiVO<sub>4</sub> film with the plate-like array morphology has been employed in this work because its nanostructure is capable of efficiently improving electron-hole separation yield without further doping.<sup>[9a]</sup> The fabrication process of Co<sub>2</sub>(bim)<sub>4</sub>modified BiVO<sub>4</sub> photoanode (Cobim/BVO) is illustrated in Figure 1a. The BiVO<sub>4</sub> nanoarray was prepared first by the electrodeposition of the bismuth oxyiodide (BiOI) nanoplate array onto a fluorine-doped tin oxide (FTO) glass substrate and subsequent heat treatment in the presence of vanadium source under air atmosphere at 450 °C for 2 h.<sup>[9a]</sup> Pure BiVO<sub>4</sub> can be obtained after removal of the excessive vanadium oxide. Then, a certain volume of CoO solution was dropped on the surface of BiVO<sub>4</sub> by the drop-casting technology for the formation of CoOcoated BiVO<sub>4</sub> (CoO/BVO), which was further soaked into an aqueous solution of benzimidazole at room temperature for 18 h to obtain the final Cobim/BVO photoanode. To investigate the morphology, size and final PEC performance of the Cobim/BVO photoanodes, we controlled the loading of CoO through adjusting the volume of its dispersed solution, resulting in the formation of a series of Cobim/BVO-x (x represents the volume of the used CoO

solution, with the unit of  $\mu$ L).

The structure of all as-prepared samples was characterized by X-ray diffraction (XRD) as shown in Figure 1b and S1. The XRD patterns of the as-prepared BiVO<sub>4</sub> and Cobim/BVO clearly showed several characteristic peaks with  $2\theta$  at  $18.9^{\circ}$ ,  $28.9^{\circ}$ , 30.7°, 36.7°, 39.8°, 42.5° and 47.2°, indicating a monoclinic crystalline structure of BiVO4 (JCPDS No.14-0688) and the structural integrity of BiVO<sub>4</sub> after loading Co<sub>2</sub>(bim)<sub>4</sub>. Meanwhile, a weak diffraction peak with  $2\theta$  at  $9.2^{\circ}$  was observed in the XRD pattern of Cobim/BVO-40, implying the presence of MOF. To verify the structure of the obtained MOF, Cobim/BVO-100 was prepared from CoO/BVO with a high loading of CoO sheets. The XRD patterns of Cobim/BVO-100 showed five diffraction peaks with  $2\theta$  at  $9.2^\circ$ ,  $16.6^\circ$ ,  $17.5^\circ$ ,  $20.0^\circ$  and  $21.7^\circ$ , suggesting that the as-prepared Co<sub>2</sub>(bim)<sub>4</sub> was isostructural to the previously reported Zn<sub>2</sub>(bim)<sub>4</sub>.<sup>[14]</sup> Figure 1c shows the crystalline structure of Co<sub>2</sub>(bim)<sub>4</sub>.



**Figure 2.** FESEM images and photographs (insets): (a) BiVO<sub>4</sub>, (b) CoO/BVO-20 and (c) Cobim/BVO-20; (d) elemental mappings of vanadium, cobalt, carbon and nitrogen in (c). TEM images: (e) CoO/BVO and (f) Cobim/BVO-20.

The morphology of samples was monitored by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) during the fabrication process of Cobim/BiVO<sub>4</sub>. It was confirmed that the electrodeposited BiOI was of a two-dimensional array architecture consisting of uniform nanoplate crystals with an average thickness of ~25 nm (Figure S2a-b). The pure BiVO<sub>4</sub> showed a well-retained array structure and high porosity (Figure S2c). The average thickness of the BiVO<sub>4</sub> film on the FTO substrate was ~750 nm according to the cross-sectional view (Figure S2d). Figure 2a presents a high-magnification FESEM image of BiVO<sub>4</sub>, manifesting that the plate-like structure is made up of irregular BiVO4 nanoparticles with the size of 50-100 nm. On the other hand, ultrathin CoO sheets were synthesized by a previously reported method.<sup>[15]</sup> The ultrathin two-dimensional sheet-like morphology of the asprepared CoO was verified by TEM (Figure S3a). The CoO sheets were added into absolute ethanol and then ultrasonicated to form a homogeneously dispersed solution for later use.

In a typical preparation process, 20  $\mu$ L solution containing 40  $\mu$ g CoO sheets was deposited dropwise onto the surface of pristine BiVO<sub>4</sub> for the formation of CoO/BVO-20. After being dried naturally, a uniform coverage of ultrathin CoO sheets on the surface of BiVO<sub>4</sub> was achieved (Figure 2b and S3b-c). The high-magnification TEM image of CoO/BVO-20 shows that a BiVO<sub>4</sub> particle is coated by a very thin layer of CoO (Figure 2e).

Furthermore, CoO/BVO-20 was soaked in 6 mL aqueous solution containing 30 mg benzimidazole at room temperature for 18 h to form Cobim/BVO-20. The cobalt, carbon and nitrogen were detected by energy-dispersive elements X-rav spectroscopy (EDS), implying the presence of Co<sub>2</sub>(bim)<sub>4</sub> (Figure S4). As numerous Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles were generated on the BiVO<sub>4</sub> surface, Cobim/BVO-20 exhibited coarse surface (Figure 2c), compared with the smooth surface of pristine BiVO<sub>4</sub> (Figure 2a). The element mappings of vanadium, cobalt, carbon and nitrogen further confirmed that the Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles were uniformly dispersed on the surface of BiVO<sub>4</sub> (Figure 2d), which was in agreement with the XRD result of Cobim/BVO-20 without any characteristic peak (Figure 1b). The highmagnification TEM image clearly shows that the Co<sub>2</sub>(bim)<sub>4</sub> layer was composed of nanoparticles with the average thickness of ~15 nm on a BiVO<sub>4</sub> particle (Figure 2f). Meanwhile, CoO with a sheet-like morphology was rarely observed in the TEM image of COMMUNICATION

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Cobim/BVO-20 (Figure S3d), indicating that the CoO sheets were fully converted into  $Co_2(bim)_4$  nanoparticles. The results of the control experiments revealed that the loading of CoO sheets was a key parameter that influenced the size and number of the resulting  $Co_2(bim)_4$  nanoparticles (Figures S5-6).

In the conversion process of CoO into a Co-based MOF, imidazole-based linkers reacted with CoO species and was deprotonated to produce H<sup>+</sup> ions used for the dissolution of CoO to Co<sup>2+</sup> ions.<sup>[16]</sup> When the CoO coating layer on the BiVO<sub>4</sub> surface was dissolved, the Co<sub>2</sub>(bim)<sub>4</sub> seeds were in-situ generated in the presence of benzimidazole. For excessive CoO sheets, Co<sup>2+</sup> ions were released into solution, leading to the further growth of these seeds to form larger nanoparticles (Figures S6-S7).

These Cobim/BVO samples acting as photoanodes were characterized and tested to understand the effect of MOF-based cocatalyst for the enhanced PEC water oxidation performance. The light absorption properties of these photoanodes could reflect their PEC activities. The ultraviolet (UV)-visible absorptance spectra are shown in Figure 3a. A broad absorption band was observed at the wavelengths from 500 to 650 nm for pure  $Co_2(bim)_4$ , implying that the loading of  $Co_2(bim)_4$  had a negligible influence on the light absorption of BiVO<sub>4</sub>. The bandgap energy (Eg) for pristine BiVO<sub>4</sub>, Cobim/BVO-10, Cobim/BVO-20 and Cobim/BVO-40 were estimated to be 2.48, 2.45, 2.44 and 2.42 eV according to the Tauc plots, respectively (Figure S8).

PEC measurements were performed in a three-electrode system under AM 1.5G solar light illumination in the 0.5 M sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) aqueous solution as electrolyte. The current-potential (J-V) curves reveal that the BiVO<sub>4</sub> photoanode showed a very small photocurrent density of 1.2 mA/cm<sup>2</sup> at 1.23 V versus RHE (Figure 3b). After being loaded with Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles, the photoanode (Cobim/BVO-10) exhibited an improved photocurrent density of 2.2 mA/cm<sup>2</sup>. The PEC water activities of Cobim/BVO photoanodes could be optimized based on the different loadings of Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles (Figure S9a). Significantly, Cobim/BVO-20 showed the highest photocurrent density of 3.1 mA/cm<sup>2</sup>, which was much higher than those of pristine and cobalt-phosphate (Co-Pi)-modified **BiVO**<sub>4</sub> photoanodes (Figure 3b and S9b). Meanwhile, the PEC water oxidation performance of CoO/BVO-20 was tested under the same condition for comparison (Figure S9c), further confirming the effect of Co<sub>2</sub>(bim)<sub>4</sub> as a cocatalyst. Compared with other Cobased inorganic cocatalysts,<sup>[6b,9b,17]</sup> Co<sub>2</sub>(bim)<sub>4</sub> with the same metal sites showed a better catalytic performance. It is conjectured that the water molecules could penetrate the pores to be in contact with the metal sites of the MOF-based cocatalyst, leading to the improved active surface. The dark current curve of Cobim/BVO-20 exhibited a significant cathodic shift of the onset potential in contrast to that of pure BiVO<sub>4</sub> for electrochemical water oxidation, suggesting the activity of Co<sub>2</sub>(bim)<sub>4</sub> as OEC (Figure S9d).

The applied bias photon-to-current efficiency (ABPE) calculated by the corresponding J-V curve could reach 0.9% for Cobim/BVO-20 and 0.13% for BiVO<sub>4</sub> at 0.7 V versus RHE (Figure 3c). Furthermore, the transient photocurrent response measurements showed that the photocurrent density of Cobim/BVO-20 was significantly higher than that of pristine

BiVO<sub>4</sub>, suggesting an enhanced efficiency in the separation of electron-hole pairs (Figure S9e). The enhanced charge separation efficiency could be further verified by incident photon-to-current conversion efficiency (IPCE). The IPCE curves of pristine and modified BiVO<sub>4</sub> photoanodes are shown in Figure 3d. Cobim/BVO-10 and Cobim/BVO-20 both demonstrated largely enhanced IPCE compared with pristine BiVO<sub>4</sub> over the entire wavelength range. The IPCE for Cobim/BVO-20 reached 50% at 420 nm.



**Figure 3.** (a) UV-visible absorptance spectra for pristine BiVO<sub>4</sub> and Cobim/BVO photoanodes as well as Co<sub>2</sub>(bim)<sub>4</sub>; (b) *J*-*V* curves for pristine BiVO<sub>4</sub> and Cobim/BVO photoanodes measured under an AM 1.5G solar simulator in 0.5 M Na<sub>2</sub>SO<sub>4</sub>; (c) ABPE for BiVO<sub>4</sub> and Cobim/BVO-20; (d) IPCE for pristine BiVO<sub>4</sub> and Cobim/BVO photoanodes measured at 1.23 versus RHE in 0.5 M Na<sub>2</sub>SO<sub>4</sub>; (e) charge separation efficiency on the surface ( $\eta_{surface}$ ) for BiVO<sub>4</sub> and Cobim/BVO-20; (f) EIS spectra for pristine BiVO<sub>4</sub> and Cobim/BVO-20; (f) EIS spectra for pristine BiVO<sub>4</sub> and Cobim/BVO-20; (g) and Cobim/BVO-20; (h) EIS spectra for pristine BiVO<sub>4</sub> and Cobim/BVO photoanodes measured under 0.7 versus RHE and AM 1.5G illumination in 0.5 M Na<sub>2</sub>SO<sub>4</sub>.

PEC sulfite oxidation was investigated to understand the role of Co<sub>2</sub>(bim)<sub>4</sub> in the PEC catalytic process. BiVO<sub>4</sub> and Cobim/BVO-20 showed comparable *J*-*V* curves for sulfite oxidation in the presence of 0.2 M sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) as the hole scavenger (Figure S9f), indicating a negligible influence on bulk carrier recombination after the loading of Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles in the Cobim/BVO-20 photoanode. Based on the *J*-*V* curves of BiVO<sub>4</sub> and Cobim/BVO-20 for sulfite and water oxidation (Figure 3b and S9f), a high surface charge separation efficiency ( $\eta_{surface}$ , 83% at 1.2 V versus RHE) was achieved for Cobim/BVO-20, which was much better than that for BiVO<sub>4</sub> (30% at 1.2 V versus RHE), confirming the formation of a favorable

interface at the  $Co_2(bim)_4/BiVO_4$  junction and the fast water oxidation reaction kinetics of  $Co_2(bim)_4$  (Figure 3e).

Electrochemical impedance spectroscopy (EIS) was conducted at 0.7 V versus RHE for all the as-prepared photoanodes to further understand the interfacial charge separation and transfer process. As shown in Figure 3f, the results could be fitted with the Randles equivalent circuit model for all samples because single semicircles were presented in their Nyquist plots. The diameter of the semicircle reflects the charge-transfer resistance at the working electrode surface: a smaller diameter means a better charge-transfer ability.<sup>[18]</sup> Cobim/BVO-10 and Cobim/BVO-20 showed a smaller impedance arc radius than BiVO<sub>4</sub>, indicating the improved conductivity and mitigated charge-transfer resistance at the Co<sub>2</sub>(bim)<sub>4</sub>/BiVO<sub>4</sub> junction. The EIS result was consistent with the enhanced current density of Co<sub>2</sub>(bim)<sub>4</sub>-modified BiVO<sub>4</sub> photoanodes for water oxidation in the J-V curves. Although the semicircular diameter of the Nyquist plots for Cobim/BVO-10 was close to that for Cobim/BVO-20, the enhancement of PEC activity of Cobim/BVO-10 was not as large as that of Cobim/BVO-20 because insufficient Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles were loaded on the surface of BiVO<sub>4</sub>. Meanwhile, the semicircular diameter of the Nyquist plots for Cobim/BVO-40 was larger than that of pristine BiVO<sub>4</sub>, revealing the high chargetransfer resistance and week charge-transfer ability of Cobim/BVO-40, which was in agreement with the results of the UV-visible absorptance PEC tests and IPCE results.

The positive and comparable slopes of the Mott-Schottky plots for all the as-prepared photoanodes indicated that the loading of  $Co_2(bim)_4$  could not influence the n-type semiconducting characteristic of BiVO<sub>4</sub> and the charge carrier density within it (Figure S10).<sup>[9a]</sup> The flat band potentials of  $Co_2(bim)_4$ -modified BiVO<sub>4</sub> photoanodes showed negative shift in contrast to that of the pristine BiVO<sub>4</sub> photoanode, implying the existence of interaction between BiVO<sub>4</sub> and  $Co_2(bim)_4$ .



Figure 4. (a) XPS spectra of  $BiVO_4$  and Cobim/BVO-20; (b-d) high-resolution XPS spectra for  $BiVO_4$  and Cobim/BVO-20: (b) Bi4f, (c) V2p and (d) O1s.

The X-ray photoelectron spectroscopy (XPS) analysis for BiVO<sub>4</sub> and Cobim/BVO-20 further confirmed the interaction between BiVO<sub>4</sub> and Co<sub>2</sub>(bim)<sub>4</sub>. The predominant peaks of Bi4f, C1s, N1s, V2p, O1s and Co2p in survey spectrum of Cobim/BVO-20 (Figure 4a), indicating the presence of both BiVO<sub>4</sub> and Co<sub>2</sub>(bim)<sub>4</sub>. In the high-resolution spectra (Figure 4bd), the binding energies of Bi4f and V2p in Cobim/BVO-20 showed obvious shift toward higher binding energies compared with those of BiVO<sub>4</sub>. The peak of O 1s at 529.9 eV assigned to O<sup>2-</sup> in the BiVO<sub>4</sub> lattice also showed a distinct shift in Cobim/BVO-20, while the peak at 532.2 eV attributed to O species from adsorbed hydroxyl groups showed a slight shift.<sup>[6c,7b]</sup> The electrochemical and XPS results both implied the formation of a favorable interface at the Co<sub>2</sub>(bim)<sub>4</sub>/BiVO<sub>4</sub> junction, enabling the photogenerated holes to be transferred from the valence states of BiVO4 to the highest occupied molecular orbitals of Co<sub>2</sub>(bim)<sub>4</sub>.

The amperometric *i-t* curve of Cobim/BVO-20 showed a stable photocurrent of ~1.62 mA/cm<sup>2</sup> for 8000 s at a potential of 0.7 V versus RHE (Figure S11). Furthermore, the SEM image and XPS spectra confirmed unchanged  $Co_2(bim)_4$  after the PEC water oxidation test (Figure S12).

We demonstrate a novel strategy for the in-situ synthesis of MOF nanoparticles loaded on BiVO4 photoanodes by an ultrathin sheet-induced growth method using metal oxide sheets as metal source. Ultrathin CoO sheets were coated on the surface of BiVO<sub>4</sub> and converted into Co<sub>2</sub>(bim)<sub>4</sub> nanoparticles, which were scattered on the surface of BiVO4 to form a nanoparticle layer. The Co-based MOF was employed as a potential cocatalyst combined with BiVO4 to achieve an enhanced PEC water oxidation activity. Compared with other Co-based inorganic cocatalysts, the MOF-based cocatalyst exhibited a preferable catalytic activity due to its porosity and abundant metal sites. Moreover, the structural and electrochemical studies indicated that a favorable interface which effectively mitigated the interface recombination and accelerated the surface reaction kinetics was constructed between Co<sub>2</sub>(bim)<sub>4</sub> and BiVO<sub>4</sub>.

The present work provides new opportunities for the development of MOFs as catalyst materials in the PEC water splitting field by using the ultrathin sheet-induced strategy. The great potential lies in that the PEC performance can be further optimized in terms of the rational design and selection of MOFs with ultrathin structure, high porosity, excellent conductivity and electrochemical oxygen evolution activity.

#### **Experimental Section**

*Materials:* All chemicals and solvents were purchased from Sigma-Aldrich, Singapore and used directly without further purification. FTO glass was purchased from Latech Scientific Supply, Singapore.

*Fabrication of BiVO*<sub>4</sub> *photoanodes*: BiVO<sub>4</sub> films were synthesized on FTO substrates as reported previously.<sup>[9a]</sup> Briefly, 3.32 g potassium iodide was dissolved into 50 mL deionized water and then 80  $\mu$ L concentrated nitric acid (ca. 65wt%) was added into the solution to adjust the pH value to be around 1.73. Subsequently, 0.97 g bismuth nitrate pentahydrate was added into the solution. After a vigorous magnetic stirring for 20 min, the above solution was mixed with 20 mL absolute ethanol containing 0.497 g p-benzoquinone under magnetic stirring to obtain the resulting

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electrodeposition solution. In the electrodeposition process, a threeelectrode system was performed at room temperature, with an FTO glass (1 cm × 2 cm) as the working electrode, a platinum foil as the counter electrode and an Ag/AgCI (3.5 M KCI) as the reference electrode. The bismuth oxyiodide BiOI nanosheet array was obtained through potentiostatic cathodic deposition at -100 mV vs. Ag/AgCI for 260 s. The BiOI array was rinsed several times with deionized water and dried naturally for further use. After 0.1 mL dimethyl sulfoxide containing 0.2 M vanadium acetylacetonate was dropped onto the dried BiOI, it was transferred into a muffle furnace and then heated to 450 °C for 2 h at a rate of 2 °C min<sup>-1</sup>. The product was soaked in 1 M sodium hydroxide aqueous solution with a gentle stirring for 0.5 h. The resulting BiVO<sub>4</sub> photoanode was rinsed several times with deionized water and dried naturally.

Synthesis of ultrathin CoO sheets: CoO sheets were synthesized as reported previously.<sup>[15]</sup> Typically, 70 mg cobalt (III) acetylacetonate was added into a mixed solvent of ethylene glycol (14 mL) and deionized water (2.8 mL). After a vigorous magnetic stirring for 20 min, the above mixture was transferred into a 23 mL Teflon-lined stainless-steel autoclave and maintained at 190 °C for 48 h. After being cooled down to room temperature, the product was washed using water and ethanol by centrifuging, and then was dispersed in absolute ethanol for further use. The concentration of CoO solution is 2 mg/mL.

Synthesis of Cobim/BVO photoanodes: CoO solutions with different volumes were dropwise deposited onto the surface of  $BiVO_4$ . After a natural drying, the obtained CoO/BVO was soaked in 6 mL of aqueous solution containing 30 mg benzimidazole at room temperature for 18 h. The obtained Cobim/BVO photoanodes were rinsed several times with deionized water and dried naturally.

Synthesis of Co-Pi/BVO photoanodes: Co-Pi cocatalyst was photoassisted electrodeposited on BiVO<sub>4</sub> in 0.1 M potassium phosphate buffer (pH = 7) with 0.15 mM cobalt nitrate under AM 1.5G illumination at 0.3 V versus Ag/AgCl for 600s.<sup>[6a]</sup>

*Characterization:* The morphology measurements were carried out on FESEM, JEOL7600F, at 2 kV and TEM, JEOL JEM-1400Plus, at 80 kV. Elemental analysis was performed by EDS equipped on the FESEM at 5 kV. The crystalline structures of the samples were identified by XRD patterns (Shimadzu 6000 X-ray diffractometer) with Cu K $\alpha$  radiation ( $\lambda$  = 0.154 nm). XPS measurements were conducted on a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with monochromatic Mg K $\alpha$  X-ray (1283.3 eV). The optical absorptance of the samples was obtained using a UV-visible spectrophotometer equipped with an integrating sphere (Lambda 950, PerkinElmer).

PEC measurements: All PEC measurements were conducted at room temperature by using a three-electrode system, in which the as-prepared photoanodes, platinum foil and Ag/AgCl (3.5 M KCl) served as the working electrode, the counter electrode and the reference electrode, respectively. The simulated light source was obtained by a solar simulator (HAL-320, Asahi Spectra Co., Ltd.) with a power intensity of 100 mW/cm<sup>2</sup>. Back-side illumination through the FTO side was used and the illuminated areas were 0.28 cm<sup>2</sup>. Photocurrent tests were conducted on a PCI/300TM potentiostat (Gamry Electronic Instruments, Inc.) in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as the electrolyte at a scanning rate of 30 mV/s for water oxidation and a 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution with 0.2 M Na<sub>2</sub>SO<sub>3</sub> for sulfite oxidation. Chopped-light amperometric J-t measurements were performed at an applied potential of 0.7 V versus RHE under chopped light irradiation (light on or off cycles: 20s). EIS results were recorded with an AC voltage amplitude of 10 mV within the frequency range from 10000 to 0.1 Hz at a DC bias of 0.7 V versus RHE under AM 1.5 G illumination. IPCE was measured on a DC power meter (Newport 2936-R) and a 300-W full-spectrum solar simulator (Newport 66984), coupled with a filter (Newport 74010) and an aligned monochromator (Newport 74125). The Mott-Schottky plots were obtained on a CHI 660D potentiostat at a frequency of 1000 Hz and amplitude of 10 mV under the dark condition. The measured potentials versus Ag/AgCl were converted against RHE using the Nernst equation:  $E_{RHE} =$   $E_{\text{Ag/AgCl}}$  + 0.059 pH + 0.2046. ABPE was calculated by ABPE(%) =  $Jx(1.23\text{-}V_{\text{bias}})/P_{\text{light}}$ , where J is the photocurrent density (mA/cm<sup>2</sup>),  $V_{\text{bias}}$  is the applied potential versus RHE (V), and  $P_{\text{light}}$  is the illumination power density (100 mW/cm<sup>2</sup>). The  $\eta_{\text{surface}}$  was calculated by  $\eta_{\text{surface}} = J_{\text{water}}/J_{\text{sulfite}}$ , where  $J_{\text{water}}$  and  $J_{\text{sulfite}}$  refer the photocurrent density (mA/cm<sup>2</sup>) for water and sulfite oxidation, respectively.

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**Keywords:** metal–organic framework • ultrathin sheet-induced strategy • cocatalyst • BiVO<sub>4</sub> • PEC water oxidation

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Cobalt-based metal-organic framework (MOF) nanoparticles were uniformly loaded on the surface of bismuth vanadate (BiVO<sub>4</sub>) by an ultrathin sheet-induced growth strategy. Such Co-based MOF with small particle size and high dispersion can act as a promising cocatalyst to boost surface reaction kinetics, leading to the enhanced water oxidation performance of MOFmodified BiVO<sub>4</sub> photoanodes.



Wang Zhang, Rui Li, Xin Zhao, Zhong Chen, Adrian Wing-Keung Law, and Kun Zhou\*

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A Cobalt-Based Metal–Organic Framework as Cocatalyst on BiVO<sub>4</sub> Photoanode for Enhanced Photoelectrochemical Water Oxidation

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## COMMUNICATION

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