

Article

Enhanced Photoelectrochemical Water Oxidation on BiVO₄ Photoanodes Functionalized by Bimetallic Dicyanamide Molecular Catalysts

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Abstract: A novel hybrid structure of bimetallic dicyanamide decorated BiVO₄ is developed via a simple method to accelerate interfacial water oxidation kinetics. Two types of bimetallic dicyanamides, CoNi(dca)₂ and CoFe(dca)₂, are coated on BiVO₄ photoanodes and are found to exhibit far more enhanced PEC performance than Co(dca)₂ or Ni(dca)₂ as cocatalysts. The successful deposition of metal dicyanamides on BiVO₄ photoanodes is confirmed by physical characterizations including X-ray photoelectron spectroscopy (XPS). The optimized Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄ photoanode exhibits the highest photocurrent density of 2.58 mA/cm² at 1.23 V vs. RHE under 100 mW/cm² AM 1.5 G irradiation, which is 2.5 times that of bare BiVO₄. The substantial enhancement of PEC performance can be ascribed to the advantageous interfacial charge transfer and improved charge injection efficiencies. This work presents a feasible strategy using different types of bimetallic dicyanamides to design a modified BiVO₄-based photoanode system for enhanced water oxidation efficiency.

Keywords: photoelectrochemical; BiVO₄; water oxidation catalyst; bimetallic; cocatalysis



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1. Introduction

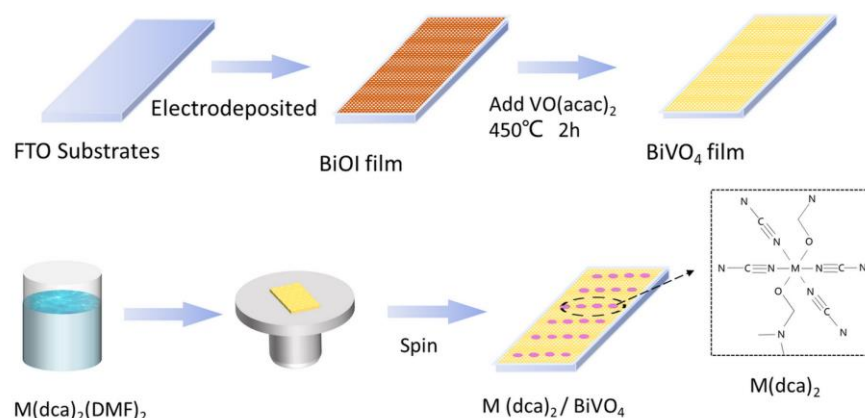
Photoelectrochemical (PEC) and photocatalytic water splitting for producing hydrogen using semiconductor materials provides a viable route to achieve the conversion and storage of solar energy in an environmentally friendly manner [1–3]. Among the promising semiconductor candidates, BiVO₄ is seen as a highly efficient photo-active visible-light-driven photocatalyst owing to a band gap of 2.4 eV, which provides sufficient overpotential for photogenerated holes to oxidize water [4] and favorable chemical stability in neutral and weak alkaline electrolyte [5]. However, its efficiency and stability are still not satisfying, and the technology bottleneck lies in slow surface kinetics for water oxidation, which hinder effective transfer and separation for photogenerated charge carriers [6,7]. Thus, it is critical to develop more suitable cost-effective cocatalysts to enhance the water oxidation kinetics and photo-reactivity of BiVO₄ [8].

Rapid developments in various modification strategies of surface loading have elevated BiVO₄ to its position as one of the most promising metal oxide photoanode materials [9–12]. Jian et al. used phenolic hydroxyl groups as anchoring groups to graft laser-generated carbon dots on Mo-doped BiVO₄ followed by the deposition of FeNiOOH to reach the excellent photocurrent density of 6.08 mA/cm² at 1.23 V_{RHE} and up to 120 h stability [13]. Zhang et al. developed a modified electron density redistribution and electronic coupling BiVO₄ system decorated with P-O-bonded FeNi catalysts to achieve a record-high photocurrent density of 6.73 mA/cm² at 1.23 V_{RHE} [14]. Metal-organic frameworks (MOFs) have also been newly used as oxygen evolution cocatalysts for BiVO₄ photoanode

modification in PEC water splitting [15]. Kim et al. prepared Bi-based MOF nanoparticles on the surface of BiVO_4 via multi-step immersion to demonstrate a higher photocurrent density of $2.35 \text{ mA}/\text{cm}^2$ at 1.23 VRHE under AM 1.5G illumination and improved operation stability [16]. Pan et al. utilized caffeic acid as a bridging agent and successfully fabricated the core-shell structure of $\text{Ov-BiVO}_4/\text{NiFe-MOFs}$ to tailor the coordination and electronic structure of active sites for enhanced water oxidation performance [17].

Based on previous studies, the selection and rational connection between cocatalysts and photoanodes is concluded to be one of the crucial factors for efficient PEC water splitting. The molecular catalysts, especially non-noble metal-based molecular catalyst hybrid photoanodes, have thus drawn much attention due to the favorable tunability of anchoring groups and active centers. It is reported that carboxylate [18], phosphate [19,20], and hydroxyl [21,22] can be used as effective surface anchoring groups for the immobilization of molecular catalysts [23] on the surface of BiVO_4 semiconductors to effectively accelerate the interface kinetics of water oxidation and thus greatly improve PEC performance [24,25]. Recently, heterogeneous systems based on cyanide [26] and cyanamide bridging groups [27] have been recently reported not only because of their prominent stabilities in both acidic and basic electrolyte but also their high catalytic activities [28–30]. Shang et al. reported a hybrid system consisting of M(dca)_2 (where M is a non-noble metal ion and dca is dicyanamide) as a water oxidation catalyst and BiVO_4 as the photosensitizer for photocatalytic oxygen evolution in aqueous solution [31]. However, systematic and comparative studies remain insufficient for better understanding the effects of metal centers on the catalytic performance and charge transfer kinetics of the composites. It is necessary to expand the types of metal center ions surrounded by N donor atoms. Moreover, the synergetic effect should be clarified on bimetallic molecular catalyst modified BiVO_4 photoanodes in electrochemical water oxidation catalysis.

In this study, we demonstrate that non-noble metal-doped bimetallic dicyanamides can be used as cocatalysts on BiVO_4 photoanodes for efficient photoelectrochemical water oxidation (Scheme 1). A series of doped and undoped metal dicyanamides are coated with composition tuning on BiVO_4 photoanodes and are found to exhibit far more enhanced performance than bare BiVO_4 . Bimetallic dicyanamides exhibit a far superior co-catalytic effect for PEC water oxidation than that of undoped metal dicyanamides. Among the bimetallic dicyanamide modified hybrid photoanodes, $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ displays the lowest electrochemical impedance, the fastest interfacial water oxidation kinetics, and the highest activity. The impact of the bimetallic dicyanamides on water oxidation kinetics is analyzed based on PEC efficiency performance tests and physical property characterization. The obtained photoanode shows favorable stability in a water oxidation reaction under AM 1.5 G light irradiation, achieving a photocurrent density of $2.58 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE. In addition, a mechanism for the excellent efficiency performance of bimetallic dicyanamide hybrid photoanodes is proposed.



Scheme 1. Schematic illustration of M(dca)_2 deposition on BiVO_4 photoanodes for PEC water oxidation.

2. Materials and Methods

2.1. Chemicals and Materials

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), vanadyl acetylacetonate ($(\text{VO}(\text{acac})_2)$, dimethylsulfoxide (DMSO), sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3), potassium iodide (KI), p-benzoquinone, acetone (AR), ethanol (AR), nitric acid (HNO_3 , 26–28 wt%), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium dicyanamide ($\text{NaN}(\text{CN})_2$), and dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the chemicals were used as received without further purification and deionized (DI) water (resistance $\approx 18.2 \text{ M}\Omega$) was used throughout the experiments. FTO substrates (F:SnO_2 , 14Ω per square) were ultrasonically cleaned before use for 30 min each in detergent solution, acetone, and ethanol, successively.

2.2. Fabrication of Bismuth Vanadate Nanoporous Films

The nanoporous BiVO_4 films on FTO substrates were synthesized according to the previously reported method [32]. Generally, 20 mmol of KI and 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved into 50 mL of DI water, its pH was adjusted to 1.4 by adding 1 M of HNO_3 , and it was stirred for 30 min. This solution was mixed with 20 mL of ethanol containing 4.6 mmol (0.5 g) of p-benzoquinone and vigorously stirred for a few minutes. Electrodeposition in the prepared solution was carried out potentiostatically in a typical 3-electrode system using an FTO substrate ($2 \times 2 \text{ cm}^2$) as the working electrode (WE), a platinum foil as the counter electrode (CE), and a saturated Ag/AgCl electrode as the reference electrode (RE). As an optimized condition, electrodeposition was conducted at -0.1 V vs. Ag/AgCl for 5 min. Afterwards, the resulting BiOI on FTO substrate was rinsed with deionized water and dried in ambient air.

BiVO_4 electrodes were prepared by placing 0.2 mL of DMSO solution containing 0.2 M of $\text{VO}(\text{acac})_2$ on the electrodeposited BiOI electrodes followed by heating in a muffle furnace at 450°C (ramping rate $5^\circ\text{C}/\text{min}$) for 2 h. After cooling to room temperature, the electrodes were soaked in 1 M NaOH solution for 30 min to remove the excess surface V_2O_5 present in the BiVO_4 films.

2.3. Fabrication of $\text{M}(\text{dca})_2$ Catalysts

For a typical synthesis, 5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was slowly added into 20 mL DI water under constant stirring conditions. Meanwhile, 10 mmol of $\text{NaN}(\text{CN})_2$ was dissolved into 20 mL of DMF and stirred for 30 min at room temperature. The mixed suspension was left under stirring conditions overnight followed by filtration using suction and was washed with ethanol for 10 min. Finally, the collected precipitate was dried overnight in a vacuum oven at 60°C . The preparation processes of $\text{Ni}(\text{dca})_2(\text{DMF})_2$, $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2(\text{DMF})_2$, and $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2(\text{DMF})_2$ are similar to the above steps with different ratios of metal nitrates. The as-prepared samples were defined as $\text{M}(\text{dca})_2$ (M represents different metal ions, $\text{M} = \text{Co}, \text{Ni}, \text{Co}_{0.9}\text{Ni}_{0.1}, \text{Co}_{0.9}\text{Fe}_{0.1}$, dca: dicyanamide).

2.4. Deposition of $\text{M}(\text{dca})_2$ on BiVO_4 and FTO

An $\text{M}(\text{dca})_2$ precursor solution was prepared by dissolving 2, 5, and 8 mg of $\text{M}(\text{dca})_2$ catalyst in 1 mL DI water followed by sonication for 30 min. The solution was then spin-coated onto the BiVO_4 film ($2 \text{ cm} \times 1.5 \text{ cm}$) at 1500 rpm for 60 s repeatedly. The optimal quantity of $\text{M}(\text{dca})_2$ was found to be 5 mg according to the LSV measurements. The resulting films were dried in an oven at 60°C for 2 h and left to desiccate until further use for bulk electrolysis studies. The $\text{BiVO}_4/\text{M}(\text{dca})_2$ electrodes were rinsed with DI water prior to use.

A drop-casting technique was used to deposit the $\text{M}(\text{dca})_2$ films on FTO. Firstly, a mixture of 5 mg $\text{M}(\text{dca})_2$, 500 μL water, 500 μL DMF, and 20 μL Nafion was sonicated for 30 min to form a uniform slurry. Then, 150 μL of $\text{M}(\text{dca})_2$ slurry was drop-casted on a piece of clean FTO electrode ($2 \text{ cm} \times 1.5 \text{ cm}$). The resulting film was dried in an oven at 80°C .

for 10 min and left to desiccate until further use for CV and bulk electrolysis studies. The $M(dca)_2/FTO$ electrodes were rinsed with DI water prior to use.

2.5. Material Characterization

The morphology of $BiVO_4$ and $M(dca)_2/BiVO_4$ films was observed by a JEOL JSM-7800FE scanning electron microscope. X-ray diffraction (XRD) patterns were recorded to investigate the crystal structures of the samples using a PANalytical X'pert Pro MPD diffractometer operated at 40 kV and 40 mA using Ni-filtered $Cu-K\alpha$ irradiation (wavelength 1.5406 Å). The chemical compositions and elemental valence states of the samples were obtained via X-ray photoelectron spectroscopy (XPS) (Axis UltraDLD, Kratos, Manchester, UK) with monochromatic aluminum Ka radiation. FTIR spectra were measured using Fourier transform infrared spectrometer with a Nicolet AVATAR 330 instrument in the wave number range of 4000–400 cm^{-1} .

2.6. Photoelectrochemical Measurements

The electrochemical and photoelectrochemical (PEC) measurements were carried out in a conventional three-electrode cell with a Pt wire as the counter electrode and a saturated Ag/AgCl as the reference electrode using a CHI 760E electrochemical workstation. Photocurrents were recorded under 100 mW/cm^2 AM 1.5 G irradiation with a 300 W xenon lamp as the white light source illuminated from backside in 0.5 M Na_2SO_4 (pH = 6.86) aqueous electrolyte at a scan rate of 0.01 V/s, and 0.1 M Na_2SO_3 electrolyte was used as the hole scavenger for the charge separation efficiency and injection efficiencies measurements. The electrochemical impedance spectroscopy measurements were performed within a frequency range of 1 Hz to 100 kHz with an AC amplitude of 10 mV under illumination at 1.23 V vs. RHE. Mott–Schottky measurements were performed in the dark in 0.5 M Na_2SO_4 aqueous solution with a frequency of 1 kHz.

The potentials versus Ag/AgCl were converted to reversible hydrogen electrode (RHE) using the following Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^{\circ}_{Ag/AgCl} \quad (1)$$

Incident photon-to-current conversion efficiencies (IPCEs) of the as-prepared film photoanodes were obtained at 1.23 V vs. RHE in 0.5 M Na_2SO_4 solution using a 300 W xenon light source (Beijing Merry Change Technology Co., Ltd., Beijing, China) coupled with a monochromator from 320 to 600 nm. The IPCE at each wavelength was calculated by the following equation:

$$IPCE(\%) = (1240 \times J_{ph})/(\lambda \times P) \times 100\% \quad (2)$$

where J_{ph} (mA/cm^2) is the photocurrent density at a specific wavelength, P (mW/cm^2) is the measured light power density, and λ (nm) is the wavelength of incident light.

The charge injection efficiency and charge separation efficiency could be determined as follows:

$$\eta_{inj} = J_{PEC}/J_{sep} \quad (3)$$

$$\eta_{sep} = J_{sep}/J_{abs} \quad (4)$$

where J_{PEC} and J_{sep} are the photocurrent densities for PEC water oxidation and sulfite oxidation, respectively. J_{sep} is measured in a 0.1 M Na_2SO_3 electrolyte solution. J_{abs} is the photocurrent density when completely converting the absorbed photons into current (APCE = 100%). J_{abs} is calculated by integrating the UV–Vis absorbance and divided by the integration of the standard solar spectrum (AM 1.5 G).

The following equation was used to calculate the applied bias photon-to-current efficiency (ABPE) from the LSV curve.

$$ABPE(\%) = J_{PEC} \times (1.23 - V_{bias})/P \times 100\% \quad (5)$$

where J_{PEC} (mA/cm^2) refers to the photocurrent density obtained from the electrochemical workstation. V_{bias} represents the applied bias versus RHE (V) used on work electrode, and P is the incident illumination power density (AM 1.5 G, $100 \text{ mW}/\text{cm}^2$).

Cyclic voltammogram of M(dca)_2 catalyst deposited FTO electrodes were recorded in phosphate buffer solution with 1 M KNO_3 as electrolyte at pH = 7.0 at 0–1.5 V vs. Ag/AgCl at a scan rate of 0.05 V/s.

3. Results

3.1. The Physical Characterization of Samples

The morphologies of metal dicyanamide modified BiVO_4 ($\text{M(dca)}_2/\text{BiVO}_4$) samples were characterized by SEM photography. As shown in Figure 1, it can be observed that BiVO_4 presents a regular worm-like nanoporous structure. Clearly, the nanoporous characteristic of BiVO_4 film provides abundant space for M(dca)_2 nanoparticles coupling to form $\text{M(dca)}_2/\text{BiVO}_4$ heterojunction films. Due to the nature of the spin-coating method, a minuscule amount of M(dca)_2 was successfully deposited on the film surface. The morphology and particle size of BiVO_4 were not significantly changed after metal dicyanamides deposition. Moreover, the morphologies of the samples after the PEC tests showed no evident change compared with the fresh samples, indicating that the hybrid catalysts were relatively stable during PEC water oxidation.

Figure 2 presents the FTIR spectra of the M(dca)_2 , BiVO_4 , and $\text{M(dca)}_2/\text{BiVO}_4$ composite catalysts. The FTIR spectra of M(dca)_2 show several peaks at around 2360, 1380, and 940 cm^{-1} , which can be attributed to the asymmetric and symmetric stretching vibrations of $\text{C}\equiv\text{N}$, asymmetric vibrations of $\text{C}-\text{N}$, and symmetric stretching vibrations of the $\text{C}-\text{N}$ of cyanide groups in dicyanamide fragments. These results agree well with those reported previously [28,31]. No obvious change could be observed after the incorporation of the Fe and Ni component in the FTIR spectra of bimetallic dicyanamides, indicating the relatively high stability of the organic anchoring groups. In comparison with bare BiVO_4 , the FTIR spectra of $\text{M(dca)}_2/\text{BiVO}_4$ showed negligible difference after hybridization, which can be ascribed to the minimum amount of M(dca)_2 attached to the surface of BiVO_4 by physical adsorption. The crystal structures of the as-prepared metal dicyanamides before deposition on BiVO_4 were detected by X-ray diffraction (XRD) patterns as shown in Figure S1. The patterns match well with those that the literature reports [31], which confirms the successful synthesis of the molecular catalysts. After the incorporation of Fe and Ni into Co(dca)_2 , the XRD patterns showed no obvious change due to the low doping content.

Since the SEM images and XRD patterns were insufficient to detect the surface attached molecular catalysts clearly, XPS measurements were performed to further confirm the successful deposition and valence states of the hybrid photoanodes. The existence of the elements and detailed information can be inferred from the Co 2p, Ni 2p, Fe 2p, N 1s, and O 1s signals from the XPS spectra (Figures S2 and 3). The photoanodes after PEC measurements were also examined by XPS for comparison to verify the existence and possible changes of the molecular catalysts throughout the water oxidation reaction. Firstly, we took $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ as an example for XPS analysis. The peaks at around 780.5 eV and 796.5 eV in the Co 2p region were assigned to the Co 2p_{1/2} and Co 2p_{3/2} core levels. The intensities of the Co 2p signals after illumination were slightly lower than the peaks before illumination, indicating the possible loss of the molecular catalyst at the surface. The broad peaks at around 399.5 eV were assigned to N 1s configurations, which originated from organic nitrogen in the dicyanamide groups [33]. After PEC tests, the XPS peak intensity of N 1s also showed only a slight decrement, indicating the relatively good stability of M(dca)_2 on BiVO_4 surface. On the other hand, the XPS peak positions of N 1s shift to higher binding energies, which can be ascribed to the inevitable change during PEC water oxidation reactions [34]. The Fe 2p spectra from $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2/\text{BiVO}_4$ show peaks at 715.8 eV and 726.4 eV corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively [35]. After PEC tests, the peaks also show a decrement of intensity and the peak positions shift to higher binding energies, which can be attributed to the water oxidation reactions. Additionally,

similar results can also be found in other types of $M(dca)_2/BiVO_4$ photoanodes. For XPS Ni 2p signals of $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$, no obvious change except a slight decrement in intensity can be found after PEC tests, indicating the good stability of the hybrid photoanode. Notably, the Ni 2p signals in the $Ni(dca)_2/BiVO_4$ sample almost disappeared after the PEC tests. This indicates the poor combination of nickel dicyanamide at the $BiVO_4$ surface and might have contributed to adverse effects on PEC efficiency and stability.

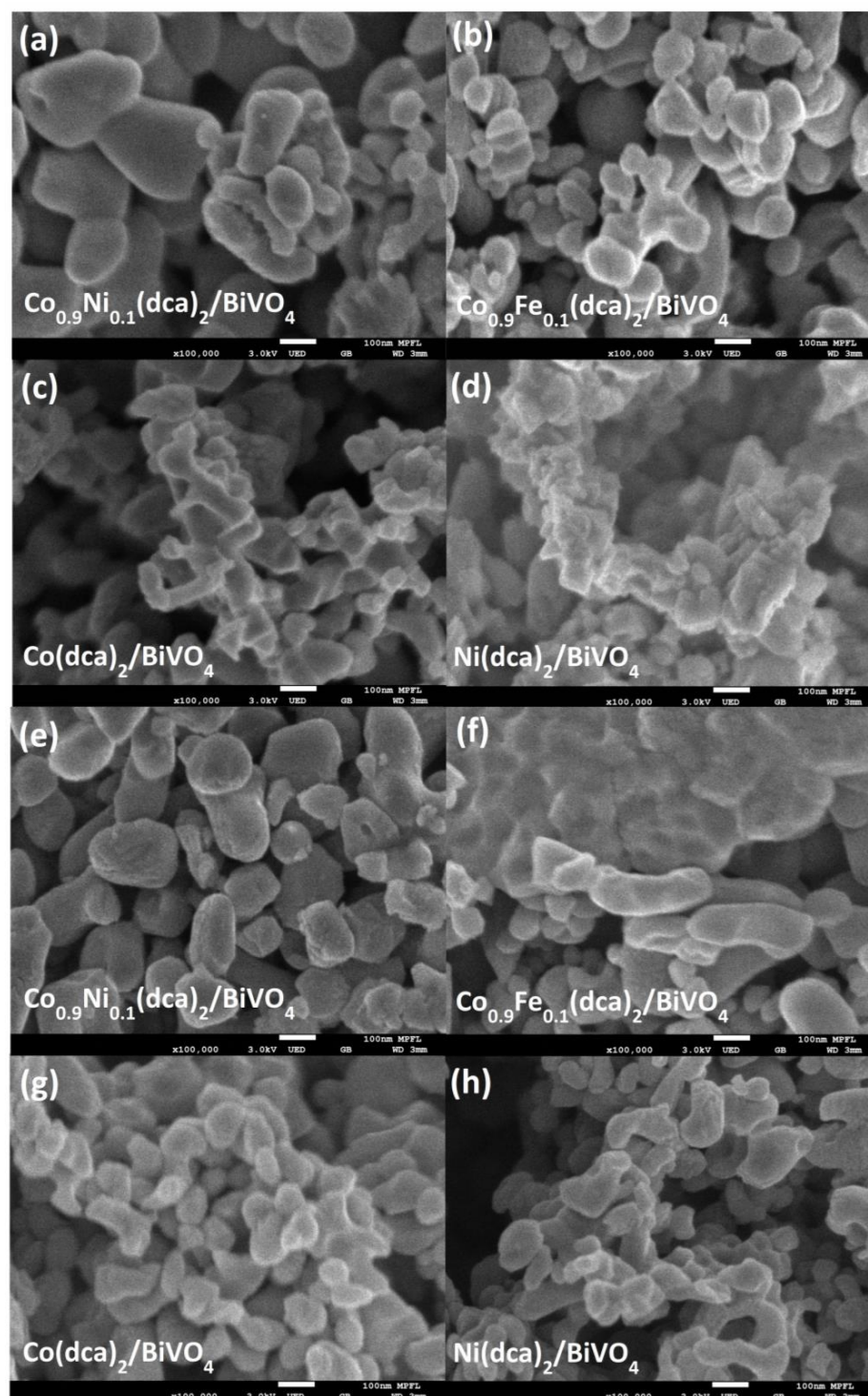


Figure 1. SEM images of $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$, $Co_{0.9}Fe_{0.1}(dca)_2/BiVO_4$, $Co(dca)_2/BiVO_4$, and $Ni(dca)_2/BiVO_4$ photoanodes before (a–d) and after (e–h) PEC measurements in 0.5 M Na_2SO_4 solution.

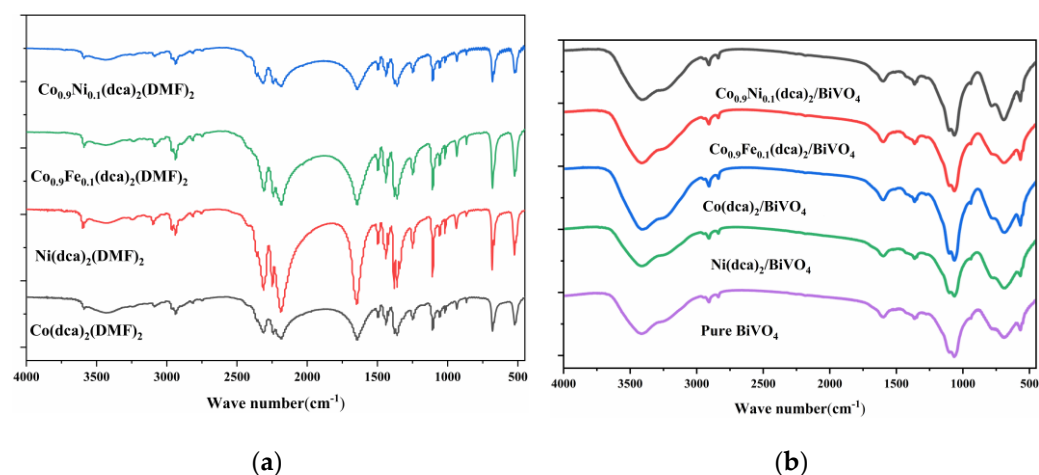


Figure 2. FTIR spectra of (a) the as-prepared molecular catalysts and (b) modified BiVO₄ photoanodes (M(dca)₂/BiVO₄).

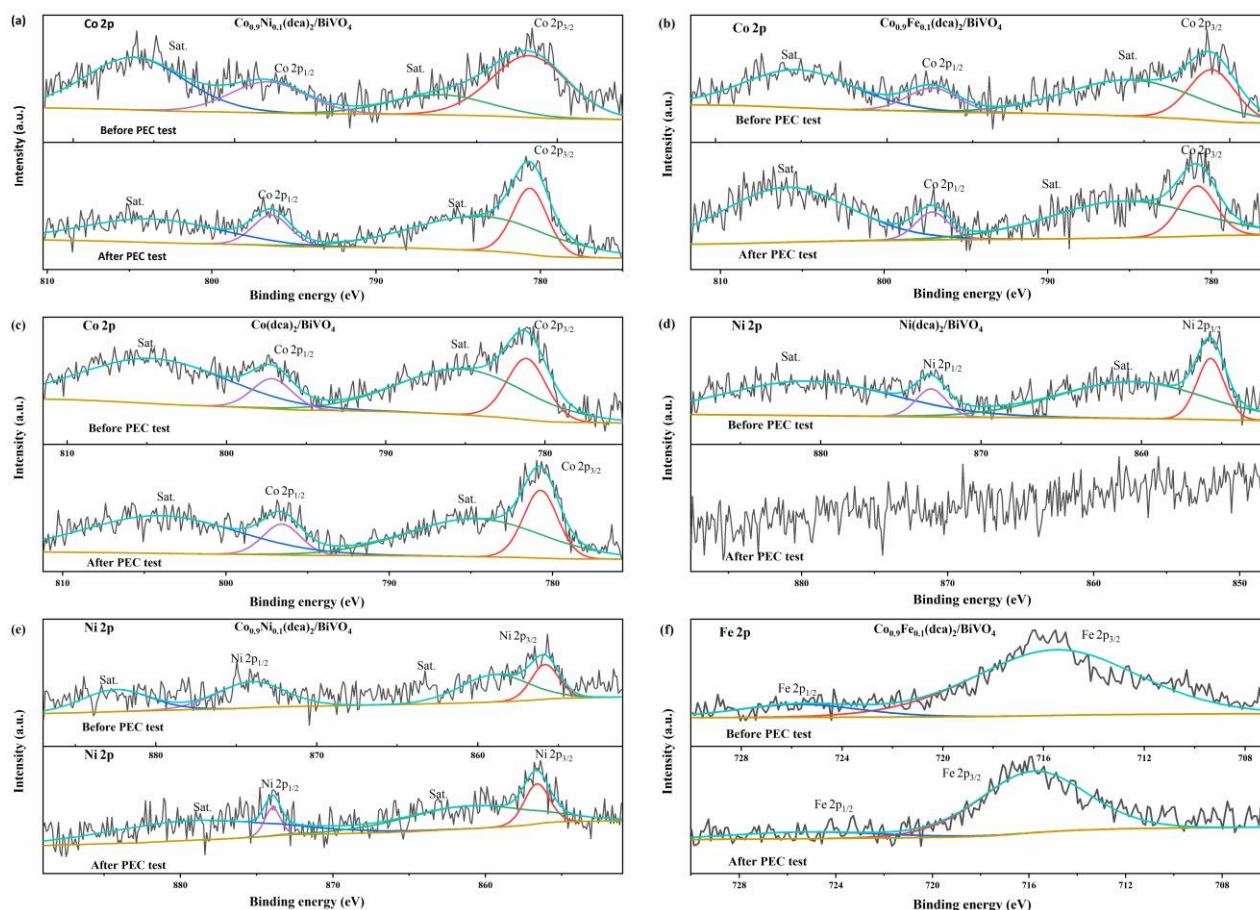


Figure 3. XPS spectra of the molecular catalyst modified BiVO₄ photoanodes (M(dca)₂/BiVO₄) before and after PEC tests, (a) Co 2p of Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄, (b) Co 2p of Co_{0.9}Fe_{0.1}(dca)₂/BiVO₄, (c) Co 2p of Co(dca)₂/BiVO₄, (d) Ni 2p of Ni(dca)₂/BiVO₄, (e) Ni 2p of Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄, and (f) Fe 2p of Co_{0.9}Fe_{0.1}(dca)₂/BiVO₄.

3.2. The PEC Measurements

The OER activities of the molecular catalyst attached FTO film photoanodes were measured in a 3-electrode system with a 0.1 M phosphate buffer neutral solution as the electrolyte without illumination. As shown in Figure 4, the cyclic voltammogram curves

(CVs) of $M(dca)_2$ showed the distinctive feature of strong increasing tendencies in anodic currents at above 1.4 V vs. RHE, which can be attributed to catalytic oxygen evolution performance. Obviously, $Co_{0.9}Ni_{0.1}(dca)_2$ exhibited a higher current density than those of other catalysts at the same potential, indicating the highest intrinsic electrocatalytic activity. Moreover, $Co_{0.9}Ni_{0.1}(dca)_2$ also shows the lowest onset potential compared with other catalysts, which can be beneficial for further PEC cocatalysis performance.

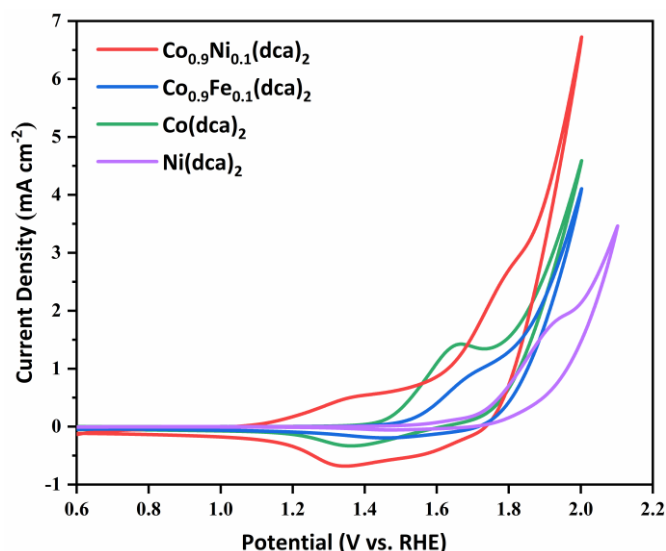


Figure 4. Cyclic voltammogram curves (CV) of the as-prepared molecular catalysts on FTO.

The molecular catalysts with different compositions were then employed on $BiVO_4$ photoanode surfaces and the PEC water splitting performance of bare $BiVO_4$ and $M(dca)_2/BiVO_4$ was measured under AM 1.5 G illumination in a 0.5 M Na_2SO_4 aqueous solution in a 3-electrode system. First, the deposition amount was optimized, as shown in Figure 5a. The coating concentration of $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$ deposition was set as 2, 5, and 8 mg. It can be clearly seen that the PEC efficiencies all increased in the hybrid photoanodes with various deposition levels. Moreover, the photoanode prepared with a 5 mg concentration showed the highest photocurrent density, while the photoanode prepared with a 2 mg concentration only showed a slight increase. For cocatalysis, excess deposition levels (8 mg) might lead to the blocking of light and surface aggregation which could hinder the light harvest and surface charge transfer. These results indicate that bimetallic dicyanamides are excellent candidates as cocatalysts for PEC water splitting and that there is an optimum hybrid photoelectrode loading content of $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$ (5 mg) for PEC efficiency enhancement. In the following study, all the catalysts with different compositions were prepared with this optimum loading content.

Both metal centers and anchoring ligands play critical roles in the catalytic performance of $M(dca)_2$. Bimetallic dicyanamides with different metal centers and compositions show totally different effects on the PEC performance of hybrid photoanodes. Figure 5b shows the chopped light LSV curves of the hybrid catalysts in comparison with bare $BiVO_4$. The $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$ photoanode showed the best photocurrent density and onset potential performance, indicating a positive synergistic effect between $Co_{0.9}Ni_{0.1}(dca)_2$ and $BiVO_4$. The photocurrent onset potential was observed at 0.25 V vs. RHE, and a photocurrent density of 2.58 mA/cm^2 was obtained at 1.23 V vs. RHE, which was 2.5, 1.8, 1.4, and 1.2 times that of bare $BiVO_4$, $Ni(dca)_2/BiVO_4$, $Co(dca)_2/BiVO_4$, and $Co_{0.9}Fe_{0.1}(dca)_2/BiVO_4$, respectively. $Co(dca)_2/BiVO_4$ showed superior efficiency over $Ni(dca)_2/BiVO_4$, which is in accordance with the cyclic voltammogram results. The difference in performance between Co and Ni in $M(dca)_2$ originated from the intrinsic water oxidation catalytic characteristics. The improved photocurrent of $Co_{0.9}Ni_{0.1}(dca)_2$ decorated $BiVO_4$ was due to accelerated interface kinetics that brought about effective charge

separation and transfer. Both Ni and Fe incorporation resulted in remarkable increases in the photocurrent densities compared with $\text{Co(dca)}_2/\text{BiVO}_4$. However, the photocurrent performance of $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2/\text{BiVO}_4$ showed no obvious enhancement compared with that of $\text{Co(dca)}_2/\text{BiVO}_4$ at a bias lower than 0.7 V vs. RHE, indicating relatively slow interface water oxidation kinetics. Moreover, the onset potential and photocurrent densities of the low applied potential range of $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2$ were far superior to that of $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2/\text{BiVO}_4$. Excepting the comparison of its favorable photocurrent density performance, the stability of $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ was compared with bare BiVO_4 , as shown in Figure S3. The bare BiVO_4 photoanode suffered from sluggish OER kinetics and severe photo-corrosion, thus exhibiting a relatively lower photocurrent density and a rapid decrease. Surprisingly, $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2$ decorated BiVO_4 showed excellent stability during PEC water oxidation under illumination during a 2 h long-term test with only a decrease of less than ~10% after 1.5 h, which demonstrates that bimetallic dicyanamides are effective cocatalysts for both efficiency and stability. These results reveal that the rational incorporation of metal centers in bimetallic dicyanamides can be a feasible and practical strategy for accelerating OER kinetics.

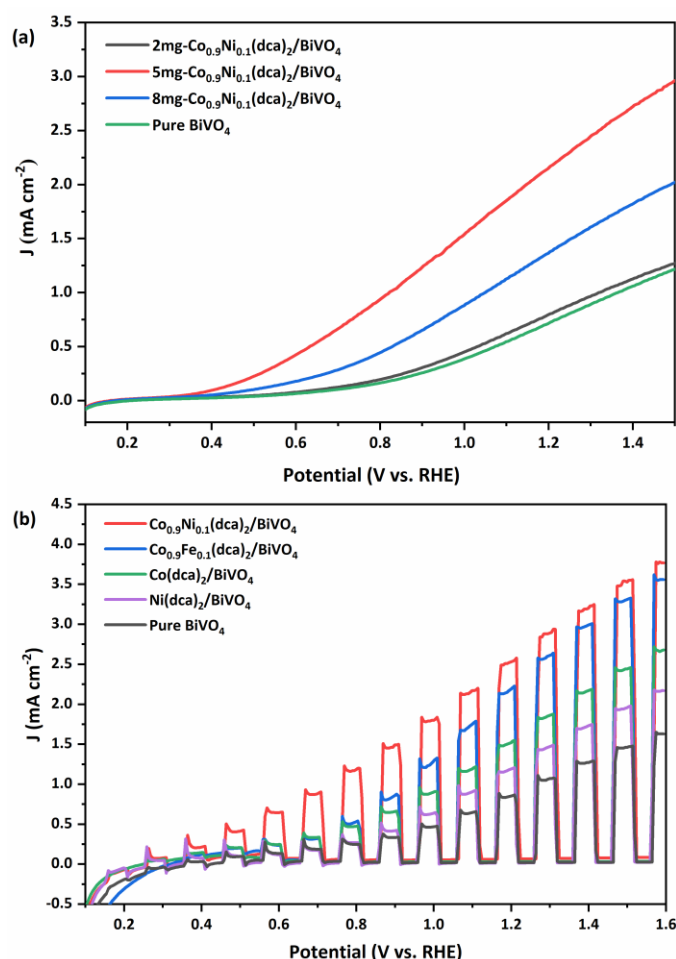


Figure 5. (a) Linear sweep voltammetry curves (LSV) with different deposition ratios and (b) PEC chopped light linear sweep voltammetry curves of metal dicyanamide modified BiVO_4 and bare BiVO_4 in 0.5 M Na_2SO_4 aqueous solution under AM 1.5 G illumination.

In a typical photoelectrochemical water splitting system, solar light absorption, photoexcited charge separation and surface charge injection are the three crucial processes for high efficiency. Modifications to the photoanodes are usually based on the mentioned processes to which the photocurrent density efficiencies are closely related. To investigate the effect of the surface deposition of M(dca)_2 on BiVO_4 photoanodes, the charge

separation efficiencies and charge injection efficiencies were measured with Na_2SO_3 as the hole scavenger (Figure S4). As shown in Figure 6a, the curves of the charge separation efficiencies (η_{sep}) of BiVO_4 and $\text{M(dca)}_2/\text{BiVO}_4$ hybrid photoanodes were close, indicating that the deposition of M(dca)_2 did not obviously improve bulk charge separation in the photoanodes. On the other hand, the hole injection efficiency (η_{inj}) value of $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ was up to 55.5% at 1.23 V vs RHE (Figure 6b), which was much larger than those of bare BiVO_4 (17.6%), $\text{Ni(dca)}_2/\text{BiVO}_4$ (20.8%), $\text{Co(dca)}_2/\text{BiVO}_4$ (33.7%), and $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2/\text{BiVO}_4$ (47.1%). These results demonstrate that molecular catalysts play a vital role as typical cocatalysts in the surface charge injection process. The single metal molecular catalyst-loaded photoanodes $\text{Ni(dca)}_2/\text{BiVO}_4$ and $\text{Co(dca)}_2/\text{BiVO}_4$ showed only slight increases in their hole injection efficiencies. By contrast, bimetallic catalyst-loaded photoanodes $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ and $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2/\text{BiVO}_4$ showed far higher hole injection efficiencies. Moreover, the hole injection efficiencies of the samples displayed similar tendencies with respect to photocurrent density. These results demonstrate that the introduction of a bimetallic catalyst with optimal loading content can significantly accelerate the surface oxygen evolution reaction and thus suppress the surface charge recombination, resulting in greatly enhanced PEC water splitting activity.

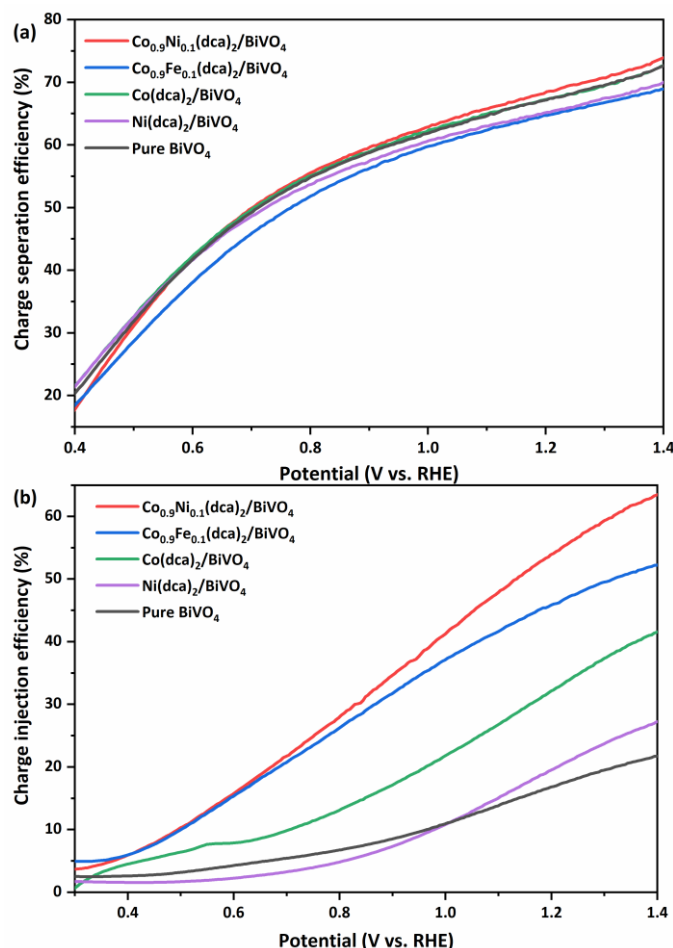


Figure 6. PEC (a) charge separation efficiencies and (b) charge injection efficiencies for BiVO_4 and $\text{M(dca)}_2/\text{BiVO}_4$ photoanodes in 0.5 M Na_2SO_3 aqueous solution under AM 1.5 G illumination.

The PEC activities of M(dca)_2 -deposited BiVO_4 photoanodes were further confirmed by their incident photon-to-current conversion efficiencies (IPCE) and applied bias photocurrent efficiencies (ABPE). The UV–Vis light absorption properties of the $\text{M(dca)}_2/\text{BiVO}_4$ hybrid photoanodes were first determined at 300–700 nm (Figure S5). The bare BiVO_4 showed an absorbance edge of around 515 nm, while the absorbance edges of $\text{M(dca)}_2/\text{BiVO}_4$ photoan-

odes showed slight red shifts to around 520–525 nm. The light absorbance intensities of $M(dca)_2/BiVO_4$ also increased compared with bare $BiVO_4$. As shown in Figure 7a, in the whole absorption wavelength range, the IPCE values of the $M(dca)_2$ -deposited samples showed significant increases. The $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$ catalyst obviously exhibited the best IPCE value with an efficiency value of about 30% at 450 nm. The IPCE values of the as-prepared photoanodes exhibited the same order as the photocurrent densities: $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4 > Co_{0.9}Fe_{0.1}(dca)_2/BiVO_4 > Co(dca)_2/BiVO_4 > Ni(dca)_2/BiVO_4 > bare BiVO_4$. The applied bias photocurrent efficiencies (ABPE) of these photoanodes were calculated from the LSV curves. As shown in Figure 7b, the photoconversion efficiencies showed the same trend as the photocurrent densities for the molecular catalyst hybrid photoanodes. The $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$ photoanode had the most enhanced ABPE value in most regions, indicating that this hybrid photoanode had greatly improved solar energy utilization capacity. Moreover, the photoconversion efficiency of the $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$ photoanode reached a maximum of 0.65% at 0.82 V vs. RHE, which was about 13 times as high as that of the $BiVO_4$ photoanode (0.05% at 1.02 V vs. RHE). In addition, it can be clearly seen that the applied potentials of the maximum photoconversion efficiencies also decreased dramatically after $M(dca)_2$ deposition. These results indicate that better PEC efficiencies can be reached with lower applied bias after the combination of efficient molecular catalysts on photoanodes.

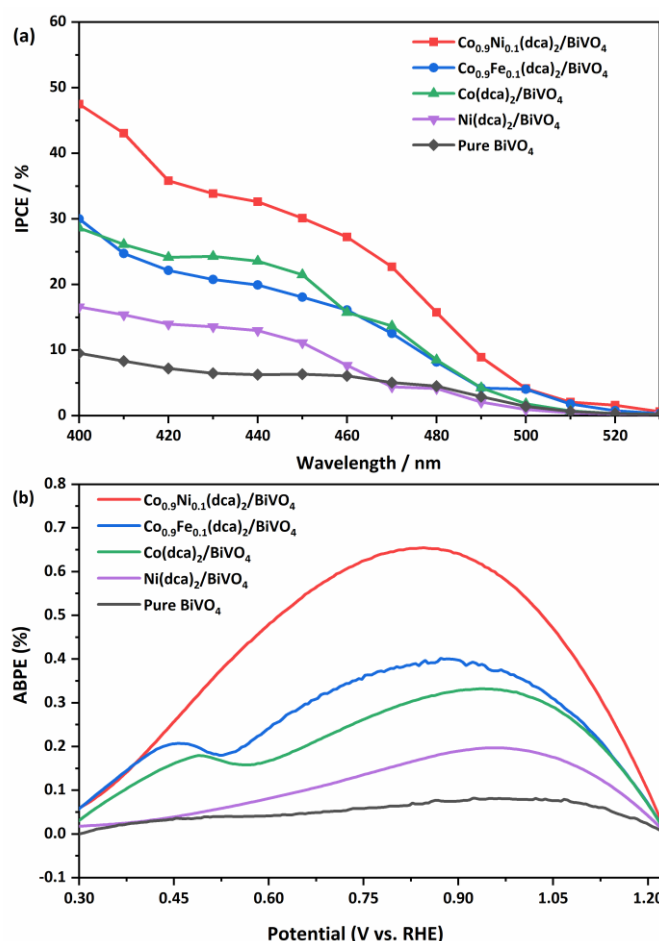


Figure 7. (a) Incident photon-to-current conversion efficiency (IPCE) plots at 1.23 V vs. RHE of $BiVO_4$ and $M(dca)_2/BiVO_4$ photoanodes; (b) applied bias photon-to-current efficiencies (ABPEs) of $BiVO_4$ and $M(dca)_2/BiVO_4$ photoanodes in 0.5 M Na_2SO_4 aqueous solution under AM 1.5 G illumination.

In order to further analyze the key influence of the molecular catalysts on the interface water oxidation reaction, electrochemical impedance spectroscopy (EIS) measurements were conducted under illumination. Nyquist plots of all the samples were recorded and

then fitted with Zsimpwin software based on an equivalent circuit consisting of two RQ components in series as shown in Figure 8a. The Nyquist plots of the BiVO₄ and M(dca)₂/BiVO₄ photoanodes in the dark were also tested for comparison (Figure S6). In the equivalent circuit, R_S represents the electrolyte resistance; Q is the constant phase element (CPE); and the two RQ elements account for the semiconductor bulk and surface processes. Although the fitted data from the software were not sufficiently accurate for the practical PEC water oxidation process, the reasonable comparison of the relative values qualitatively was instructive for analysis. The radii of the Nyquist plots under illumination were far smaller than those in the dark, indicating the lower charge transfer resistances. The fitted values of charge transfer resistance (R_{CT}) for Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄, Co_{0.9}Fe_{0.1}(dca)₂/BiVO₄, Co(dca)₂/BiVO₄, Ni(dca)₂/BiVO₄, and bare BiVO₄ were 96.02, 135.7, 180.2, 216.6, and 269.2 Ω/cm², respectively, while the fitted values of bulk resistance (R_{SC}) for the corresponding hybrid photoanodes were 14.29, 17.55, 19.98, 16.35, and 21.4 Ω/cm², respectively (Table S1). Moreover, the Q_H values for charge transfer behavior and Q_{SC} for space charge region were also fitted and are shown in Table S1. The deposition of bimetallic dicyanamides generally leads to a slight increase in Q_H and a significant increase in Q_{SC}, which may be the result of interface modification to charge distribution. These results indicate that the Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄ photoanode had the smallest charge transfer resistance and thus had the highest charge transfer efficiency, which explains its efficiencies in the PEC tests. The decrease in charge transfer resistance was more remarkable when the bulk resistance decreased slowly, elucidating that molecular catalyst deposition mainly accelerates interface charge transfer and the correlated water oxidation reaction. This result agrees well with the charge separation and charge injection efficiency results.

Mott–Schottky measurements were further employed to provide detailed information on the flat-band potentials and charge carrier densities. According to the Mott–Schottky equation [33], flat-band potentials are inferred from the x-intercept of tangent lines and carrier densities are calculated from the slopes of the linear parts of curves. As shown in Figure 8b, the flat-band potentials for Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄, Co_{0.9}Fe_{0.1}(dca)₂/BiVO₄, Co(dca)₂/BiVO₄, Ni(dca)₂/BiVO₄, and bare BiVO₄ were 5.16, 18.8, 39.8, 42.5, and 46.9 mV vs. RHE, respectively. A negative shift of 41.7 mV in flat-band potential could be achieved after Co_{0.9}Ni_{0.1}(dca)₂ deposition compared with the bare BiVO₄ photoanode, which provided a stronger driving force for favorable interface charge transfer. On the other hand, the charge carrier densities inferred from the slopes of the linear parts also decreased with cocatalyst loading, indicating that the donor densities in the photoanodes increased accordingly. Hence, the metal dicyanamide modified BiVO₄ photoanodes enhanced the band bending, increased the donor density, and thus provided the stronger charge transfer driving forces needed for faster water oxidation reaction.

Based on the previous analysis of the hybrid photoanodes, the enhanced PEC water oxidation activities of M(dca)₂/BiVO₄ were proposed and are illustrated in Scheme 2. The bimetallic dicyanamides acted as efficient cocatalysts at the electrode/electrolyte interface for water oxidation. Photoexcited electron and hole transfer and transportation at the interface were accelerated for enhanced charge separation and injection efficiencies. The improved interfacial energetics inferred from the energy band structure also promoted the interface charge transfer. Among the hybrid photoanodes, Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄ showed the most favorable intrinsic activity, donor density, and charge transfer properties for PEC water oxidation.

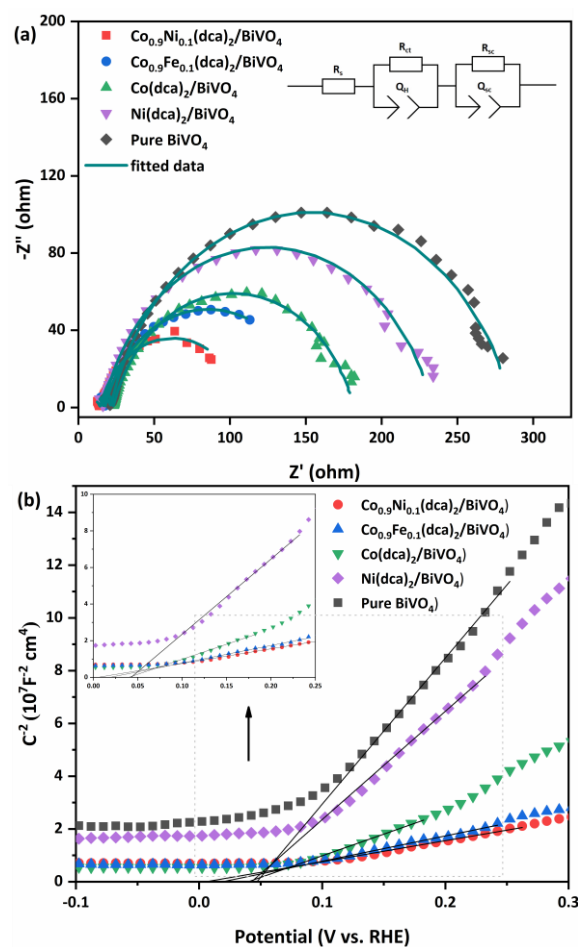
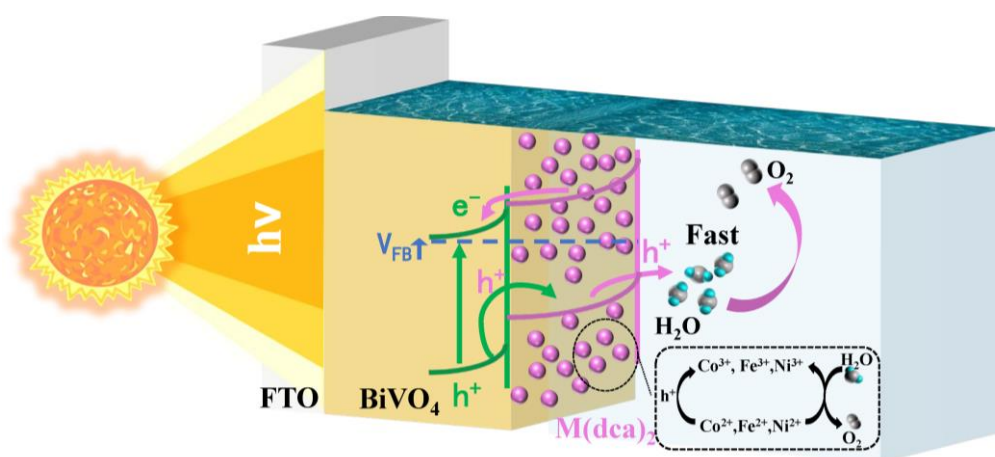


Figure 8. (a) Tested (scatter) and simulated (line) results of electrochemical impedance spectroscopy (EIS) of BiVO_4 and $\text{M(dca)}_2/\text{BiVO}_4$ photoanodes; (b) Mott-Schottky plots for BiVO_4 and $\text{M(dca)}_2/\text{BiVO}_4$ photoanodes in 0.5 M Na_2SO_4 aqueous solution. Inset: the magnified view of Mott-Schottky plots.



Scheme 2. Schematic of mechanism for photoelectrochemical water oxidation process on $\text{M(dca)}_2/\text{BiVO}_4$.

4. Conclusions

In summary, we showed that bimetallic dicyanamides can be utilized as efficient co-catalysts deposited on BiVO_4 nanoporous photoanodes for enhanced photoelectrochemical water oxidation. The surface decorated bimetallic dicyanamides suppressed charge recom-

bination and accelerated interface charge transport and transfer, thus improving PEC water oxidation performance. $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ showed the most improved PEC efficiency among the investigated molecular catalyst hybrid photoanodes with rational composition tuning. $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ achieved a photocurrent density of $2.58 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE with excellent stability. Most notably, the enhanced efficiencies with bimetallic dicyanamide decoration were mainly attributed to improved charge injection efficiencies rather than charge separation efficiencies. Electrochemical impedance spectra analysis confirmed the enhanced surface charge transfer, improved donor densities, and favorable interface energetics. This work demonstrated the advantageous tunability of molecular catalysts via a facile and effective strategy for the improvement of OER kinetics in PEC water oxidation and provided new insights for further studies on heterogeneous molecular catalysts utilized as cocatalysts for renewable energy utilization.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/su15043129/s1>, Figure S1: XRD patterns of the as-prepared metal dicyanamides; Figure S2: (a) XPS survey spectra of $\text{M}(\text{dca})_2/\text{BiVO}_4$ photoanodes, (b) XPS N 1s spectra of $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$, (c) XPS Fe 2p spectra of $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2/\text{BiVO}_4$, (d) XPS N 1s spectra of $\text{Co}_{0.9}\text{Fe}_{0.1}(\text{dca})_2/\text{BiVO}_4$, (e) XPS N 1s spectra of $\text{Co}(\text{dca})_2/\text{BiVO}_4$, (f) XPS N 1s spectra of $\text{Ni}(\text{dca})_2/\text{BiVO}_4$ before and after PEC tests; Figure S3: stability I-t curves of $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ and bare BiVO_4 photoanodes measured at 1.23 V vs. RHE in 0.5 M Na_2SO_4 aqueous solution under AM 1.5 G illumination; Figure S4: photocurrent densities for BiVO_4 and $\text{M}(\text{dca})_2/\text{BiVO}_4$ photoanodes in 0.1 M Na_2SO_3 aqueous solution under AM 1.5 G illumination; Figure S5: UV-Vis spectra of BiVO_4 and $\text{M}(\text{dca})_2/\text{BiVO}_4$ photoanodes; Figure S6: comparative EIS of (a) BiVO_4 and (b) $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ photoanodes in the dark and under illumination.; Table S1: EIS-fitted values and flat-band potentials of BiVO_4 and $\text{M}(\text{dca})_2/\text{BiVO}_4$ photoanodes in the equivalent circuit for PEC water oxidation.

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