

Article

Hydrothermal Synthesized CoS₂ as Efficient Co-Catalyst to Improve the Interfacial Charge Transfer Efficiency in BiVO₄

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Abstract: The bare surface of BiVO₄ photoanode usually suffers from extremely low interfacial charge transfer efficiency which leads to a significantly suppressed photoelectrochemical water splitting performance. Various strategies, including surface modification and the loading of co-catalysts, facilitate the interface charge transfer process in BiVO₄. In this study, we demonstrate that CoS₂ synthesized from the hydrothermal method can be used as a high-efficient co-catalyst to sufficiently improve the interface charge transfer efficiency in BiVO₄. The photoelectrochemical water splitting performance of BiVO₄ was significantly improved after CoS₂ surface modification. The BiVO₄/CoS₂ photoanode achieved an excellent photocurrent density of 5.2 mA/cm² at 1.23 V versus RHE under AM 1.5 G illumination, corresponding to a 3.7 times enhancement in photocurrent compared with bare BiVO₄. The onset potential of the BiVO₄/CoS₂ photoanode was also negatively shifted by 210 mV. The followed systematic combined optical and electrochemical characterization results reveal that the interfacial charge transfer efficiency of BiVO₄ was largely improved from less than 20% to more than 70% due to CoS₂ surface modification. The further surface carrier dynamics study performed using an intensity modulated photocurrent spectroscopy displayed a 6–10 times suppression in surface recombination rate constants for CoS₂ modified BiVO₄, which suggests that the key reason for the improved interfacial charge transfer efficiency possibly originates from the passivated surface states due to the coating of CoS₂.

Keywords: BiVO₄; CoS₂; photoelectrochemical water splitting; intensity modulated photocurrent spectroscopy; surface recombination



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1. Introduction

Hydrogen (H₂) is considered a perfect energy carrier to solve the challenge of the energy crisis [1–4]. Driven by solar energy, photoelectrochemical (PEC) water splitting can produce H₂ fuel from water to achieve a promising, sustainable, and low-cost H₂ supply. Metal oxide based high efficient photoelectrocatalysts, such as WO₃ [5–7], TiO₂ [8–11], Fe₂O₃ [12–15], ZnO [16–18], and BiVO₄ [19–24], have attracted extensive research efforts over the past few decades, among which bismuth vanadate (BiVO₄) is regarded as a promising photoanode material for practical PEC water splitting.

As a typical n-type semiconductor, BiVO₄ has a relatively narrow band gap of 2.4 eV which enables it to convert ~11% of solar energy to hydrogen to reach a theoretical solar-to-hydrogen (STH) conversion efficiency of 9% [25–28]. However, the reported PEC water splitting performance of BiVO₄ is extremely unsatisfied, and the reason is supposed to be caused by its short hole diffusion length, limited charge transportation, low charge separation efficiency, or sluggish water oxidation kinetics [29–34]. To address these issues, various approaches have been developed to promote the PEC performance of BiVO₄ [35–42]. However, only a small portion of photogenerated holes can directly participate in the water oxidation process as they are limited by the low charge transfer efficiency presented at the electrode/electrolyte interface caused by either the charge trapping effect of surface states

or poor water oxidation kinetics. Therefore, improving the charge transfer efficiency at the BiVO_4 /electrolyte interface is crucial to achieve satisfied PEC water splitting performance.

Inspired by the excellent electrochemical properties of the recent reported transition metal sulfides, such as NiS [43], CoS [44], and CoS_2 [45,46], we modified porous BiVO_4 photoanode with hydrothermal synthesized CoS_2 to address the issue of low charge transfer efficiency at the BiVO_4 /electrolyte interface. The PEC performance of BiVO_4 was significantly enhanced after surface modification by CoS_2 , which suggests that CoS_2 can be adopted as a suitable co-catalyst for BiVO_4 . Combined optical and electrochemical characterization results show that CoS_2 surface modification leads to a highly enhanced charge transfer efficiency at the solid/electrolyte interface. A further study on the surface carrier dynamics with IMPS reveals that enhanced charge transfer efficiency mainly originates from the suppressed surface recombination of charge carriers, which indicates a surface passivation effect of CoS_2 in promoting the PEC performance of BiVO_4 .

2. Materials and Methods

2.1. Materials

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AR) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Dimethyl sulfoxide (DMSO , $\text{C}_2\text{H}_6\text{SO}$), p-benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$, AR), and sodium iodide dihydrate ($\text{NaI} \cdot 2\text{H}_2\text{O}$, AR) were obtained from Tianjin Guangfu Fine Chemical Research Institute. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, AR) was purchased from Shandong Xiya Reagent Co., Ltd. (Shandong, China). Vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$, 98%), thiourea ($\text{CH}_4\text{N}_2\text{S}$, AR), and ethylene imine polymer (PEI, $(\text{CH}_2\text{CH}_2\text{NH})_n$, N.W. 7000, 50% aqueous solution) were purchased from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). F-doped tin oxide (FTO) coated glasses were purchased from Guluo Glass Co., Ltd. (Luoyang, China). Deionized water (resistivity $> 18.0 \text{ M}\Omega \cdot \text{cm}$) was used to prepare the aqueous solutions. All chemicals were used directly without purification.

2.2. Preparation of BiVO_4 Photoanode

The bismuth vanadate photoanode was synthesized according to the method reported previously [47]. Twenty mm $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was ultrasonically dissolved in 100 mL HNO_3 ($\text{pH} = 1.2$), and then 40 mm $\text{NaI} \cdot 2\text{H}_2\text{O}$ was added to obtain solution A. Another solution was prepared by dissolving 300 mM p-benzoquinone in 45 mL anhydrous ethanol, which was named as solution B. Solution B was added into solution A after the two solutions were uniformly dispersed, and then the solutions were slowly stirred for 30 min to prepare the deposition solution. BiOI film was electrodeposited on FTO glass substrate with the three-electrode system in which FTO substrate, a platinum plate, and a saturated Ag/AgCl electrode were used as working electrode (WE), counter electrode (CE), and reference electrode (RE), respectively. A two-step electrodeposition step was adopted for BiOI deposition at room temperature. First, the FTO substrate was biased at -0.3 V versus Ag/AgCl for 5 s, and then the FTO substrate was biased at -0.1 V versus Ag/AgCl for 360 s. After electrodeposition, the BiOI coated the FTO substrate and was washed using deionized water followed by drying in air. The following procedure was applied to convert BiOI film into BiVO_4 . Seventy μL dimethyl sulfoxide (DMSO) solution with 0.2 M vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) dissolved into it was drop casted onto the prepared BiOI film ($1 \times 1 \text{ cm}$), and then the sample was put into a muffle furnace which was preheated to 120°C and annealed at 450°C (with $2^\circ\text{C}/\text{min}$ ramping rate) for 2 h. The sample was then taken out after the muffle furnace was naturally cooled to room temperature. After that, the sample was stirred in a 1 M NaOH solution for 30 min to remove the excess V_2O_5 formed on the surface, and then the sample was washed with deionized water and naturally dried in air.

2.3. Preparation of CoS₂ and BiVO₄/CoS₂ Photoanode

A slightly modified hydrothermal method was adopted to prepare the CoS₂ and BiVO₄/CoS₂ sample. First, 0.1 g polyethyleneimine was dissolved in 20 mL deionized water. Next, 140 mM CoCl₂·6H₂O and 140 mM thiourea were added into the solution. The prepared solution was then stirred for 30 min at room temperature. After that, the mixed solution was transferred into a 30 mL Teflon autoclave, and FTO glass substrate and BiVO₄ coated FTO substrate were put at the bottom of the autoclave with the sample surface face up. Afterward, the autoclave was sealed and heated at 170 °C in an oven for 30 min. Finally, the prepared CoS₂ and BiVO₄/CoS₂ samples were washed with deionized water and ethanol and dried at 80 °C in vacuum oven for 12 h.

2.4. Structure and Morphology Characterizations

A Bruker D8 Advance X-ray diffractometer (Bruker Corporation) with Cu K α radiation ($k = 1.5406 \text{ \AA}$) was used to perform the X-ray diffraction (XRD) measurement, and the scan range was set to 10–70°, while the scan rate was set to 6°/min. UV–Vis diffuse reflectance characterizations were carried out using a UV–Vis spectrophotometer (TU-1901, Beijing Persee General Instrument Co. Ltd., Beijing, China) with an additional integration sphere. BaSO₄ was used as the total reflection reference during the measurement. The morphology of the sample was characterized using a HITACHI SU8010 (Hitachi Ltd., Tokyo, Japan) scanning electron microscope (SEM) at an accelerating voltage of 5 kV. High resolution transmission electron microscope (HRTEM) characterization was performed using JEOL JEM-2100 (JEOL Ltd., Tokyo, Japan) operated at an acceleration voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were determined using a PHI 5300 ESCA system (PerkinElmer Inc., Waltham, MA, USA), and C 1s peak (284.8 eV) was used as a reference to calibrate the collected spectra.

2.5. Electrochemical and Photoelectrochemical Characterization

A standard three-electrode system connected to a CHI 760e electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China) was used to perform the photoelectrochemical performance characterization. Saturated Ag/AgCl electrode, a platinum plate, and the characterized sample were used as a reference electrode (RE), a counter electrode (CE), and a working electrode (WE), respectively. A 500 W Xe arc lamp (Perfect Light) and an AM 1.5G filter were assembled to simulate the sunlight spectrum, and a thermopile detector (Photoelectric Instrument Factory of Beijing Normal University, Beijing, China) was used to calibrate the power density of the light source to 100 mW/cm². The applied potential was converted to the reversible hydrogen electrode (RHE) using the Nernst equation $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.0592 \text{ V} \times \text{pH} + 0.197 \text{ V}$ [48]. The current–voltage (J–V) curve was obtained via linear sweep voltammetry (LSV), and the scan rate was set to 0.02 V/s. The sulfite solution was 0.25 M K₂B₄O₇ solution (pH = 9.5) which contained 0.2 M sodium sulfite, and 0.5 M KPi buffer solution (pH = 7.0) was used as the electrolyte for water oxidation. The electrolyte solution was deaerated by pumping N₂ for 15 min before each test. Photoelectrochemical impedance spectroscopy (PEIS) characterizations were performed on the same electrochemical workstation working at the open circuit potential of the sample, and an AM 1.5G illumination light source was adopted during the measurement. The test frequency range was 100 kHz to 0.1 Hz with a sinusoidal AC amplitude of 10 mV.

2.6. Intensity Modulated Photocurrent Spectroscopy (IMPS) Characterization

Intensity modulated photocurrent spectroscopy (IMPS) spectra were recorded using a Zahner CIMPS setup (Zahner-Elektrik GmbH & Co. KG, Gundersdorf, Germany). The characterized sample, Ag/AgCl electrode, and Pt electrode were connected to construct a standard three-electrode setup and function as working electrode, reference electrode, and counter electrode, respectively. A 0.1 M Na₂SO₄ solution (pH = 7) was used as the electrolyte during the measurement. The frequency scan range of IMPS characterization was

set to 10 kHz–50 mHz. A light emitting diode (LED) lamp with an intensity of 1.8 mW/cm^2 at 428 nm was used as the light source to generate the modulated light illumination.

2.7. Surface Photovoltage Spectroscopy (SPV) Characterization

The surface photovoltage (SPV) spectroscopy characterization was carried out on a surface photovoltage spectrometer (PL-SPS/IPCE1000 Beijing Perfect Light Technology Company, Beijing, China). The SPV test was performed under atmosphere pressure and at 25 degrees Celsius. The SPV instrument consisted of a monochromatic light source, a lock-in amplifier (SR830-DSP, Stanford, Made in U.S.A), a light chopper (SR540, Stanford, Made in U.S.A), and a sample chamber. The details of the SPV measurement setup can be found elsewhere [49].

3. Results and Discussion

3.1. Material and Chemical Characterization

3.1.1. XRD Analysis

The crystal structure and crystallinity of the prepared samples were characterized by X-ray diffraction, and the results are shown in Figure 1a. Both the bare BiVO_4 (Figure S1 in the Supplementary Materials) and pure CoS_2 samples show clear diffraction peaks. All the diffraction peaks of BiVO_4 are consistent with the standard diffraction pattern of monoclinic BiVO_4 (JCPDS card No. 14–0688), and the diffraction peaks of CoS_2 are in accordance with the cubic cattierite structured CoS_2 (JCPDS card No. 41-1471), which indicates that the samples were prepared with high purity and good crystallinity. After CoS_2 surface modification, the XRD pattern of $\text{BiVO}_4/\text{CoS}_2$ is similar to the bare BiVO_4 sample, which indicates that the crystal structure of BiVO_4 stays the same after loading CoS_2 . However, no characteristic diffraction peaks of CoS_2 can be distinguished in the XRD pattern of $\text{BiVO}_4/\text{CoS}_2$, which may be attributed to the little loading amount of CoS_2 .

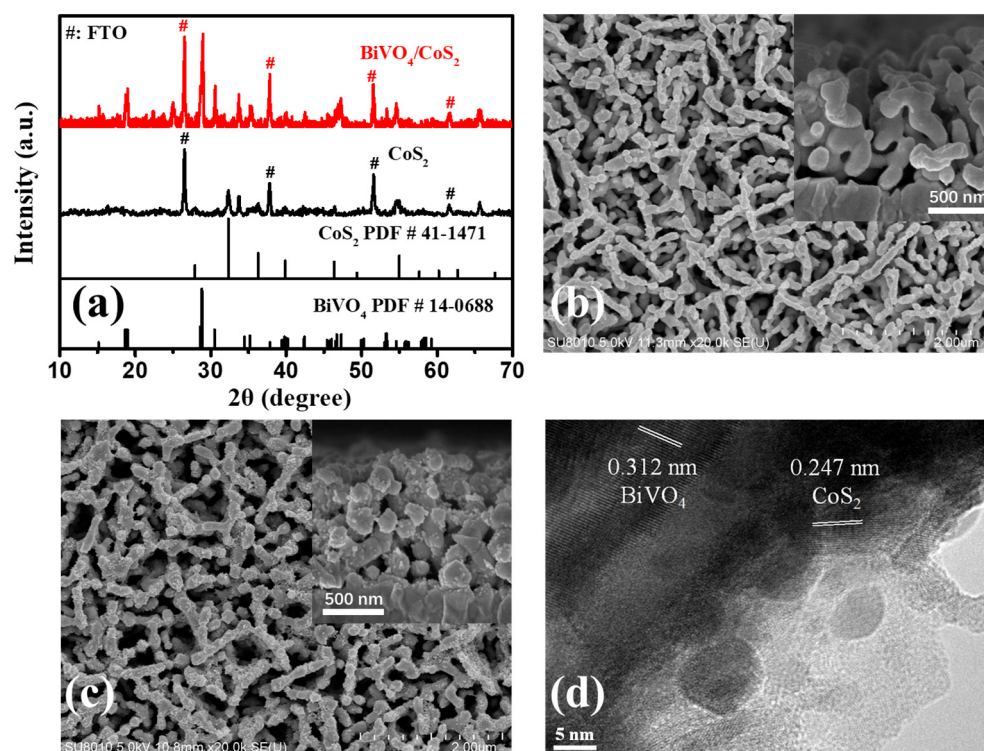


Figure 1. (a) XRD of CoS_2 and $\text{BiVO}_4/\text{CoS}_2$. (b) SEM image of bare BiVO_4 , inset: cross-section image of bare BiVO_4 . (c) $\text{BiVO}_4/\text{CoS}_2$, inset: cross-section image of $\text{BiVO}_4/\text{CoS}_2$. (d) HRTEM image of $\text{BiVO}_4/\text{CoS}_2$.

3.1.2. SEM and HRTEM Analysis

The microstructural morphology of BiVO_4 and the $\text{BiVO}_4/\text{CoS}_2$ composite sample were characterized by scanning an electron microscope (SEM) and high-resolution transmission electron microscopy (HRTEM). The SEM images of BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ are shown in Figure 1b,c. The bare BiVO_4 sample shows a nano worm morphology with a nanoporous structure which is uniformly distributed on the whole substrate. Many tiny, nanosized particles appear on the nano worm surface after the surface of BiVO_4 is modified by CoS_2 , which should be assigned to CoS_2 nanoparticles. Figure 1d presents the HRTEM image of the $\text{BiVO}_4/\text{CoS}_2$ sample. It can be seen that nanoparticles with a size of ~ 10 nm are distributed on the bulk surface, which is consistent with the SEM characterization result. Moreover, both lattice fringes corresponding to CoS_2 and BiVO_4 can be clearly observed in the HRTEM image. The lattice space of 0.247 nm observed in the surface distributed nanoparticles could be indexed to the (210) plane of CoS_2 , and the lattice space of 0.312 nm observed in the bulk matrix aligns with the ($\bar{1}21$) plane of BiVO_4 . The HRTEM characterization result demonstrates that CoS_2 is successfully attached on the surface of BiVO_4 .

3.1.3. XPS Analysis

The electronic structure and the element chemical valence states in the $\text{BiVO}_4/\text{CoS}_2$ sample were further investigated using X-ray photoelectron spectroscopy (XPS), and the results are shown in Figure 2. The survey XPS spectra are shown in Figure S2 in the Supplementary Materials, from which the presence of Co, S in the sample of $\text{BiVO}_4/\text{CoS}_2$ is verified by the signature signals of Co 2p and S 2p. As shown in Figure 2a, the high-resolution spectra of Co 2p are deconvoluted into Co 2p_{1/2} and Co 2p_{3/2} spin-orbit doublets with two shake-up satellites. The two peaks positioned at 778.6 and 793.6 eV can be ascribed to the existence of the Co–S bond, and the two peaks located at 780.7 eV and 795.8 eV are assigned to the Co–O bond [50–52]. The presence of a Co–O bond suggests the superficial surface of CoS_2 may be oxidized during air contact, while the two satellite peaks located at 783.6 eV and 802.7 eV further verify the oxidation state of Co on the surface of CoS_2 [53]. The peak positions of Co 2p_{3/2} exhibit a slight shift to higher binding energies compared with pure CoS_2 , which indicates that the change in the local chemical environment of Co in the $\text{BiVO}_4/\text{CoS}_2$ sample is weak. Furthermore, the peak intensities for the Co–O bond are more pronounced after CoS_2 surface modification, which suggests an enhanced oxidation degree of Co in the $\text{BiVO}_4/\text{CoS}_2$ sample which may be caused by the formation of a Co–O bond at the $\text{BiVO}_4/\text{CoS}_2$ interface. In Figure 2b, the two peaks that appear at 162.6 and 163.8 eV shown in the high-resolution S 2p spectra coincide with the binding energies of bridging S_2^{2-} [54], which highlights the presence of CoS_2 in the sample. The weak peak positioned at 161.6 eV indicates the existence of a small amount of divalent sulfide ions which may be attributed to surface adsorbed sulfide species. There is large overlap between the S 2p and Bi 4f spectra; therefore, the chemical state of S cannot be clearly revealed in $\text{BiVO}_4/\text{CoS}_2$, but the shakeup at 168 eV for S 2p is consistent with an oxidation state of CoS_2 in $\text{BiVO}_4/\text{CoS}_2$ [50]. The two peaks positioned at 516.5 eV and 524.5 eV shown in the V 2p XPS spectra (Figure S3 in the Supplementary Materials) are standard binding energies for V^{5+} in BiVO_4 [55]. The two binding energies of Bi 4f_{5/2} at 159 eV and Bi 4f_{7/2} at 164.3 eV indicate the chemical valence state of Bi is +3 (Figure 2c) [56]. The high-resolution spectra of V 2p and Bi 4f in $\text{BiVO}_4/\text{CoS}_2$ exhibit a visible peak shift toward lower binding energy, and considering the positive peak shift for Co 2p_{3/2}, these results indicate that a possible charge transfer process occurred between BiVO_4 and CoS_2 . Figure 2d shows the spectra of O 1s in CoS_2 , BiVO_4 , and $\text{BiVO}_4/\text{CoS}_2$. The O 1s spectra of CoS_2 have two main peaks positioned at 530.8 eV and 531.8 eV which correspond to metal oxide and metal hydroxides formed on the surface of CoS_2 [57]. The spectra of O 1s in BiVO_4 can fit into three peaks with binding energies of 529.6 eV, 531.3 eV, and 532.2 eV, which are assigned to the O^{2-} species in the lattice (O_L), surface adsorbed hydroxyl groups in the oxygen deficient region (O_V), and surface chemisorbed oxygen species dissociated from the water molecule (O_C) [58]. The

signal for lattice oxygen in BiVO_4 is largely suppressed due to the surface covered CoS_2 ; therefore, the O 1s spectra of $\text{BiVO}_4/\text{CoS}_2$ predominately consist of the oxygen signals of CoS_2 . Furthermore, both the peaks standing for lattice oxygen in BiVO_4 and surface formed metal oxide in CoS_2 are slightly shifted toward the low binding energy direction in the sample of $\text{BiVO}_4/\text{CoS}_2$, which indicates a strong correlation between CoS_2 and BiVO_4 through oxygen.

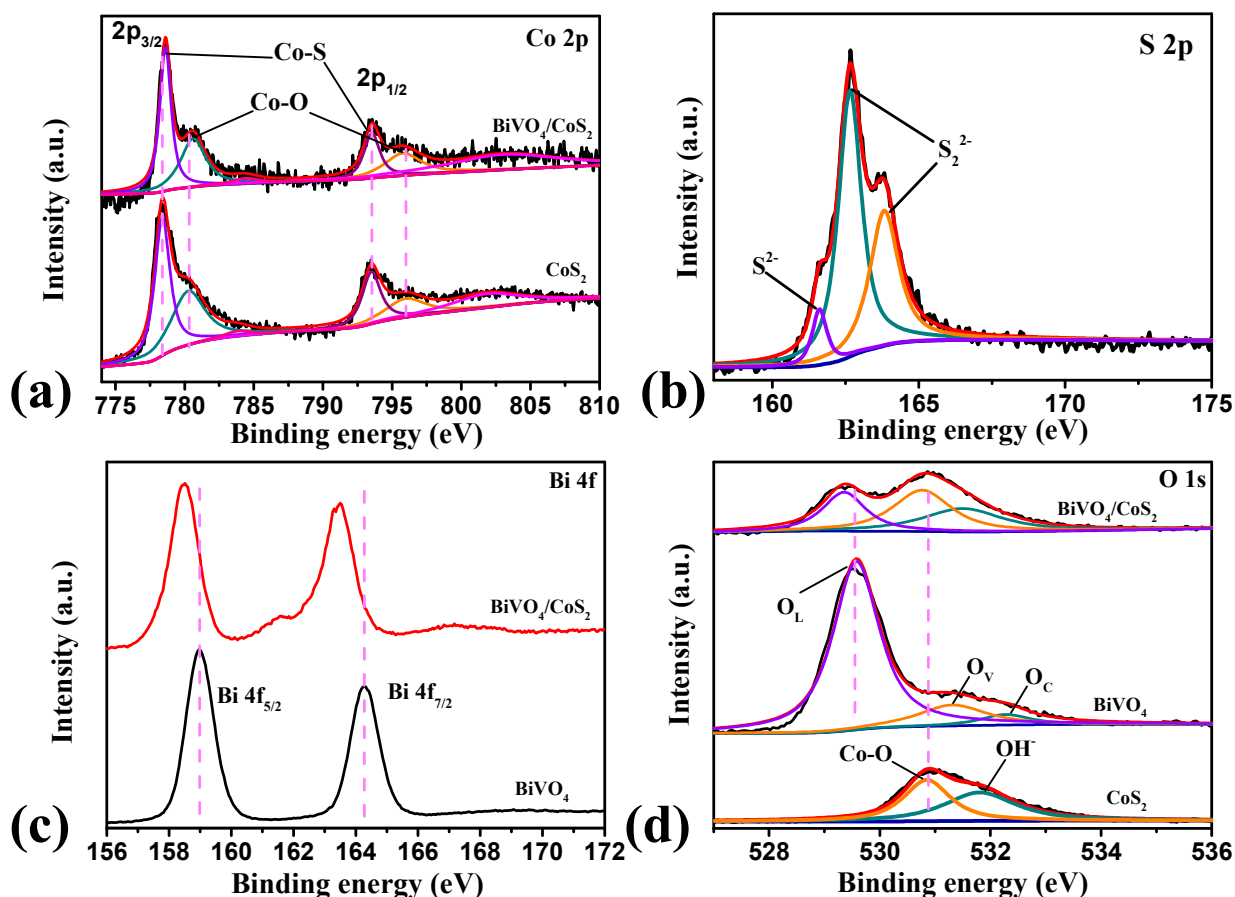


Figure 2. XPS spectra of the bare BiVO_4 , CoS_2 , and $\text{BiVO}_4/\text{CoS}_2$ samples. (a) Co 2p, (b) S 2p, (c) Bi 4f, and (d) O 1s.

3.2. Photoelectrochemical Water Splitting Performance of the $\text{BiVO}_4/\text{CoS}_2$ Photoanode

The photocurrent density-potential (J-V) curves of BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ photoanodes were obtained using linear sweep voltammetry measurements. As shown in Figure 3a, the bare BiVO_4 photoanode gives a photocurrent density of $1.4 \text{ mA}/\text{cm}^2$ at 1.23 V versus RHE, along with an onset photocurrent at 0.45 V versus RHE, which gives a J-V curve in a concave shape. Obviously, the PEC performance of bare BiVO_4 is much less than the theoretical value expected from its decent bandgap structure. In comparison, the PEC performance is significantly enhanced in the $\text{BiVO}_4/\text{CoS}_2$ photoanode. After CoS_2 surface modification, the photocurrent density of $\text{BiVO}_4/\text{CoS}_2$ at 1.23 V versus RHE is enhanced by 3.7 times, which reaches $5.2 \text{ mA}/\text{cm}^2$. Furthermore, a 210 mV cathodic shift in onset potential is observed along with the enhanced photocurrent, so the shape of the J-V curve changes from concave to convex, which usually stands for an improved photoconversion process. The J-V curves obtained under chopped light illumination (Figure 3b) show clearly that CoS_2 surface modification has an insignificant effect on the dark current of the photoanode. Therefore, the improved photocurrent in the $\text{BiVO}_4/\text{CoS}_2$ photoanode should be attributed to an enhanced photoconversion process.

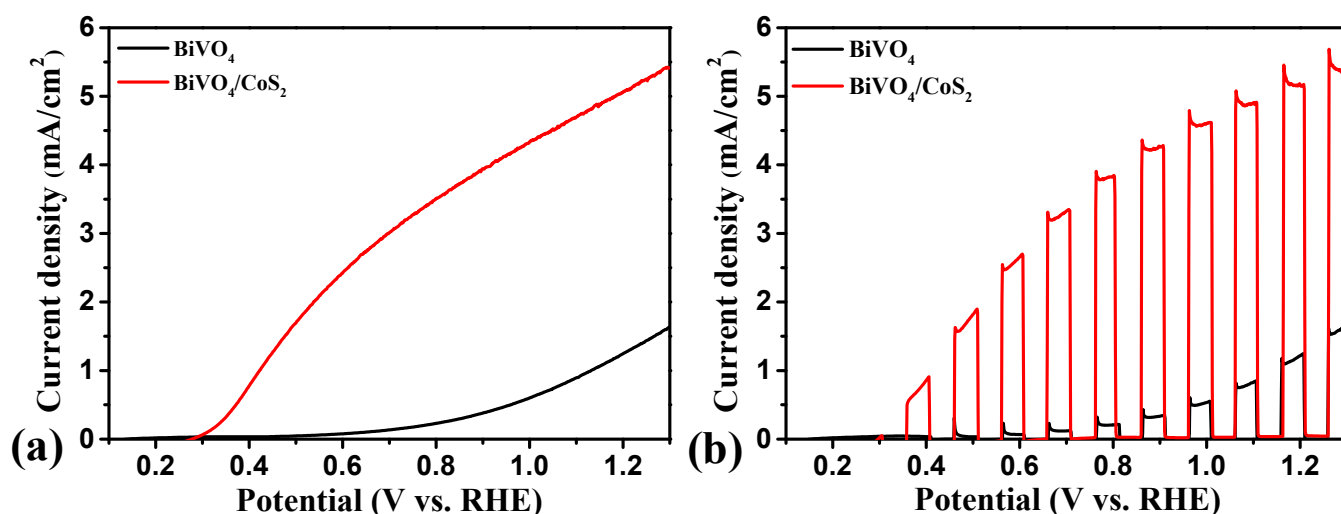


Figure 3. J–V curves of the bare BiVO₄ and BiVO₄/CoS₂ photoanodes measured under (a) continuous and (b) chopped AM 1.5G illumination; 0.5 M KPi buffer solution (pH = 7) was used as the electrolyte.

3.3. Mechanism Study for the Enhanced Photoelectrochemical Water Splitting Performance

3.3.1. Optical Absorption Characterization

A series of systematic combined optical and electrochemical characterizations were performed to explore the reason for the improved PEC performance in the BiVO₄/CoS₂ photoanode. First, UV-Vis spectroscopy was adopted to study the influence of CoS₂ on the light absorption of BiVO₄. Figure 4a presents the UV-Vis spectra of BiVO₄ and BiVO₄/CoS₂. The absorbance of BiVO₄/CoS₂ is similar to BiVO₄ in the range of 300–480 nm, but it exhibits a significantly enhanced light absorption in the range of 480–800 nm, which results in a dark color for BiVO₄/CoS₂ in contrast with the yellowish color shown in BiVO₄. The optical bandgap of BiVO₄ is estimated to be 2.57 eV based on the Tauc plot, which is similar to reported values in the literature [47]. CoS₂ surface modification only results in a 0.2 eV decrease in the optical bandgap of BiVO₄, which means the enhanced light absorption in the range of 480–800 nm is mainly caused by the light absorption of CoS₂. In general, if the photons absorbed by CoS₂ contribute to form free charge carriers while there is no change in the charge separation efficiency of BiVO₄, an improved PEC performance would be obtained due to the enhanced light absorption as more free charge carriers are available to drive the water splitting process.

3.3.2. Bulk Charge Separation Efficiency Analysis

J–V curves of the bare BiVO₄ and BiVO₄/CoS₂ photoanodes in a 0.25 M K₂B₄O₇ buffer solution (pH = 9.5) with 0.2 M sodium sulfite as a hole scavenger were measured under AM 1.5G illumination to check whether the presence of CoS₂ would affect the charge separation efficiency in BiVO₄ (Figure 4b). Contrary to our expectation, the photocurrent density of the BiVO₄/CoS₂ photoanode characterized in the sulfite solution is slightly lower than the bare BiVO₄ in the whole potential range. Compared with the four-electron transfer process involved in water oxidation, sulfite oxidation only requires a charge transfer of two electrons so the free charge carriers generated by BiVO₄ can be consumed extremely fast once when they arrive at the surface; therefore, the surface recombination of charge carriers is significantly suppressed in the presence of sulfite ions, and the interfacial charge transfer efficiency is regarded as 100% [47]. In this regard, the photocurrent characterized in the sulfite solution stands for the quantity of free charge carriers that arrive at the photoelectrode/electrolyte interface. However, if all the photo excited electron-hole pairs generated in BiVO₄ are separated as free charge carriers and drift onto the surface—which means a 100% bulk charge separation efficiency—the quantity of theoretical photogenerated charge carriers can be obtained by combining the light absorption properties of the BiVO₄

photoanode with the photon flux spectra of AM 1.5 G illumination. Consequently, the bulk charge separation efficiency of BiVO_4 can be obtained by dividing the experimental derived quantity of charge carriers by the theoretical value derived from light absorption. Following the same procedure, the bulk charge separation efficiencies of the $\text{BiVO}_4/\text{CoS}_2$ photoanode are also obtained, and the summarized results are shown in Figure 4c. Clearly, the bulk charge separation efficiency of $\text{BiVO}_4/\text{CoS}_2$ is slightly lower than that of bare BiVO_4 in almost the whole potential range, which is not a surprising result as a lower sulfite oxidation current is observed for $\text{BiVO}_4/\text{CoS}_2$. Therefore, CoS_2 surface modification should not work to form heterojunction or Schottky junction with BiVO_4 , which helps enhance the bulk charge separation efficiency, and the enhanced optical absorption raised from CoS_2 should not contribute to the enhanced PEC water splitting performance.

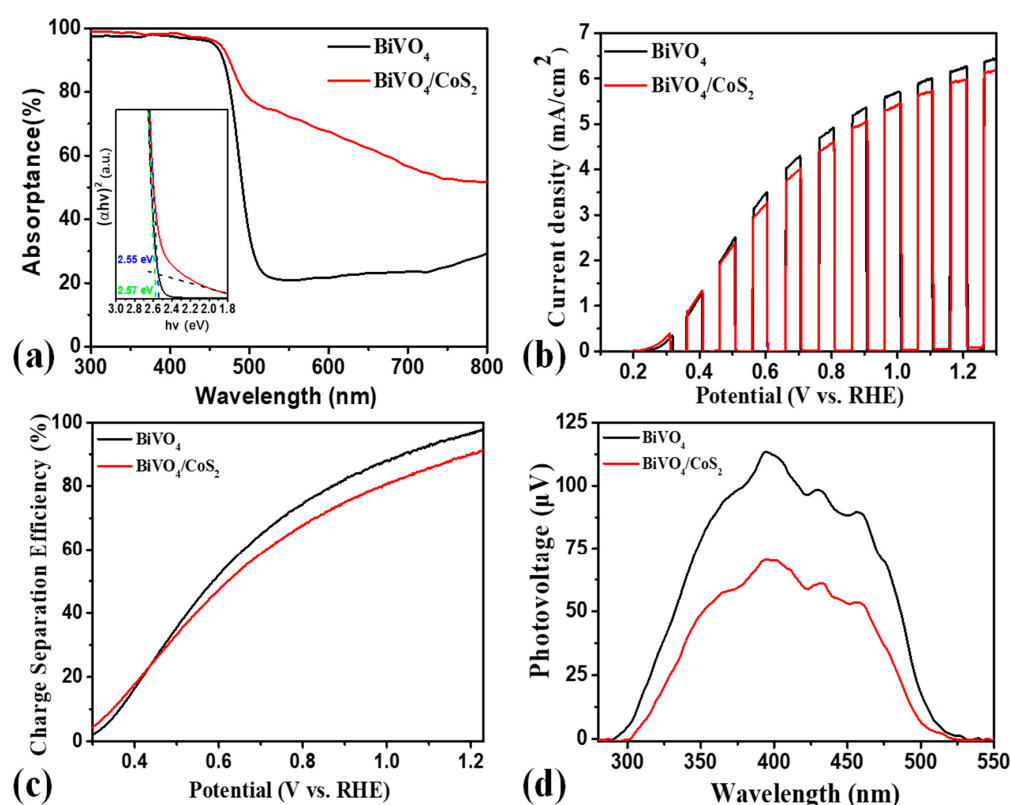


Figure 4. (a) UV-Vis spectra of the bare BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ photoanodes. (b) J-V curves of the bare BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ photoanodes measured under chopped AM 1.5G illumination. A 0.25 M $\text{K}_2\text{B}_4\text{O}_7$ buffer solution (pH = 9.5) with the addition of 0.2 M sodium sulfite was used as the electrolyte. (c) Derived bulk charge separation efficiencies of BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$. (d) Surface photovoltage spectroscopy of the bare BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ photoanodes.

The decreased bulk charge separation efficiency after CoS_2 surface modification can be further confirmed via surface photovoltage spectroscopy (SPV) characterization. The characterized sample is positioned at an open circuit during the measurement. Therefore, the SPV signal reflects the state of quasi-Fermi level splitting achieved under alternative illumination and dark conditions; or, in other words, the bulk charge separation efficiency at different wavelengths can be evaluated by comparing the intensity of the SPV signal. The SPV characterization results for BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ are shown in Figure 4d. Both photovoltage signals of the two samples have an onset positioned at ~ 525 nm, which corresponds to the bandgap light absorption of BiVO_4 . The surface photovoltage apparently decreases after the BiVO_4 is modified with CoS_2 , which is consistent with the decreased bulk charge separation efficiency observed in $\text{BiVO}_4/\text{CoS}_2$.

3.3.3. Interfacial Charge Transfer Efficiency Analysis

No enhanced bulk charge separation efficiency was observed; therefore, the significantly enhanced water splitting performance can only be explained as an improved charge transfer process at the electrode/electrolyte interface. The photocurrent acquired in the sulfite solution represents the quantity of free charge carriers arrived at the photoelectrode/electrolyte interface, and the photocurrent obtained in the phosphate buffer solution stands for the quantity of free charge carriers involved in the water oxidation process. Therefore, the interfacial charge transfer efficiencies for BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ can be simply evaluated through the ratio between the photocurrents obtained in the phosphate buffer solution and in the sulfite solution [47], and the summarized results are presented in Figure 5a. Less than 20% interfacial charge transfer efficiency is derived at the whole potential range for bare BiVO_4 photoanode. In contrast, the interfacial charge transfer efficiency at all potentials is greatly improved after the bare BiVO_4 photoanode is modified by CoS_2 , which stays higher than 70% before the applied bias is reduced to 0.45 V. Photoelectrochemical impedance spectroscopy (PEIS) is applied to confirm the enhanced interfacial charge transfer process, and the PEIS characterization results measured at open circuit potential irradiated by AM 1.5 G illumination are shown in Figure 5b. The PEIS spectra were fitted by an equivalent Randles circuit shown in the inset of Figure 5b to evaluate the charge transfer resistance presented at the electrode/electrolyte interface. R_s stands for all the series resistance in the system; C_{bulk} represents the capacitance of the bulk; $R_{\text{ct,bulk}}$ is the resistance of the hole trapping rate due to the presence of surface states; C_{ss} stands for the capacitance of the surface states; and $R_{\text{ct,ss}}$ is the resistance of the transferring holes to the donor species dispersed in the electrolyte [59]. The derived $R_{\text{ct,ss}}$ for $\text{BiVO}_4/\text{CoS}_2$ is 20.11 Ω , which is much smaller than the 452.9 Ω derived for bare BiVO_4 .

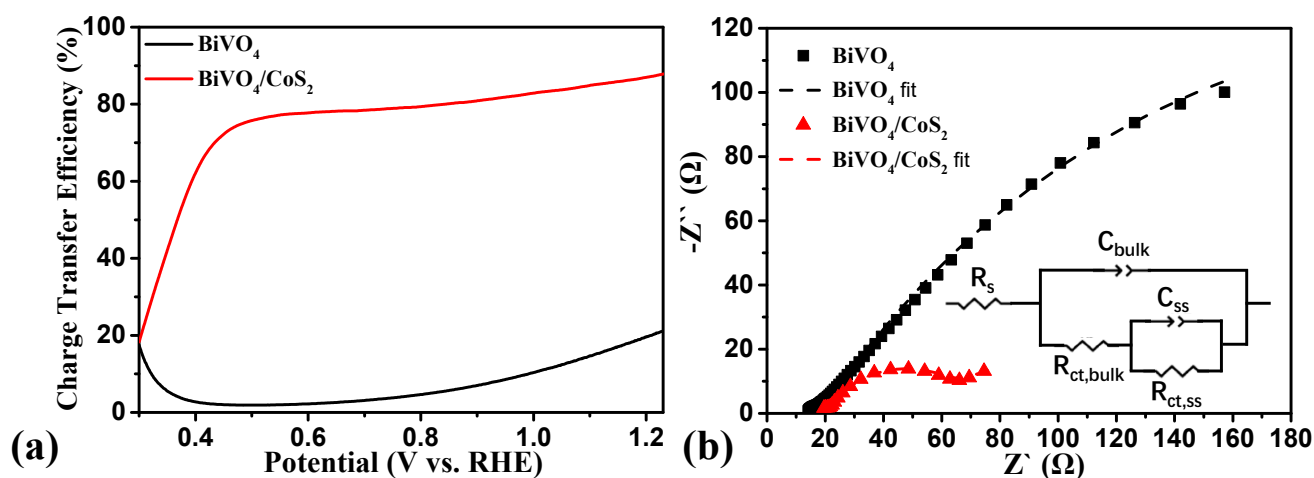


Figure 5. (a) Charge transfer efficiencies of BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$. (b) The Nyquist plots of the BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ photoanodes.

3.3.4. Surface Charge Dynamics Study with Intensity Modulated Photocurrent Spectroscopy

The observed interfacial charge transfer efficiency enhancement in $\text{BiVO}_4/\text{CoS}_2$ can be caused by accelerated water oxidation kinetics or a suppressed surface recombination process or both [60]. The rate constants of charge transfer (k_{tr}) and surface recombination (K_{roc}) at the electrode/electrolyte interface were characterized using intensity modulated photocurrent spectroscopy (IMPS) in order to explore which is the key reason for the significantly improved interfacial charge transfer efficiency [60–62].

The IMPS plots characterized in the potential range of 0.6–1.1 V versus RHE for bare BiVO_4 and $\text{BiVO}_4/\text{CoS}_2$ are shown in Figure 6a,b, respectively. All the IMPS plots are composed of two connected semicircles, and the small semicircles in the upper quadrant shown in the IMPS plots of $\text{BiVO}_4/\text{CoS}_2$ suggest a relatively enhanced charge transfer process at all potentials, which is consistent with the combined optical and electrochemical

characterization results. The semicircle positioned in the upper quadrant of the complex plane was analyzed to derive the pseudo-first-order rate constants of k_{tr} and k_{rec} , and the results are summarized in Figure 6c,d. In contrast to what one would intuitively expect for BiVO₄ modified by CoS₂ with excellent electrocatalytic properties, the charge transfer rate constant is reduced instead of enhanced. This observation suggests that the excellent electrocatalytic property of CoS₂ is not the main reason for the enhanced charge transfer efficiency in the BiVO₄/CoS₂ system. Alternatively, the introduction of CoS₂ deteriorates the slow water oxidation kinetics in bare BiVO₄ into an even worse case. Considering the excellent electrocatalytic property possessed by CoS₂, the observed reduced charge transfer rate constant may be caused by the sluggish charge transfer at the BiVO₄/CoS₂ interface. Interestingly, the surface recombination rate constants are suppressed by 6–10 times in the sample of BiVO₄/CoS₂ at all biased potentials, which indicates that the largely suppressed surface recombination should be the main contributing factor to the improved charge transfer efficiency observed in the BiVO₄/CoS₂ system, in which much more photogenerated charge carriers arrived at the surface that have an increased chance to oxidize the surface adsorbed water molecules. Therefore, the main function of CoS₂ in the BiVO₄/CoS₂ system is supposed to passivate the surface states in BiVO₄, which may be achieved by reducing the dangling bonds on the surface of BiVO₄ with the formation of the Co–O bond at the BiVO₄/CoS₂ interface.

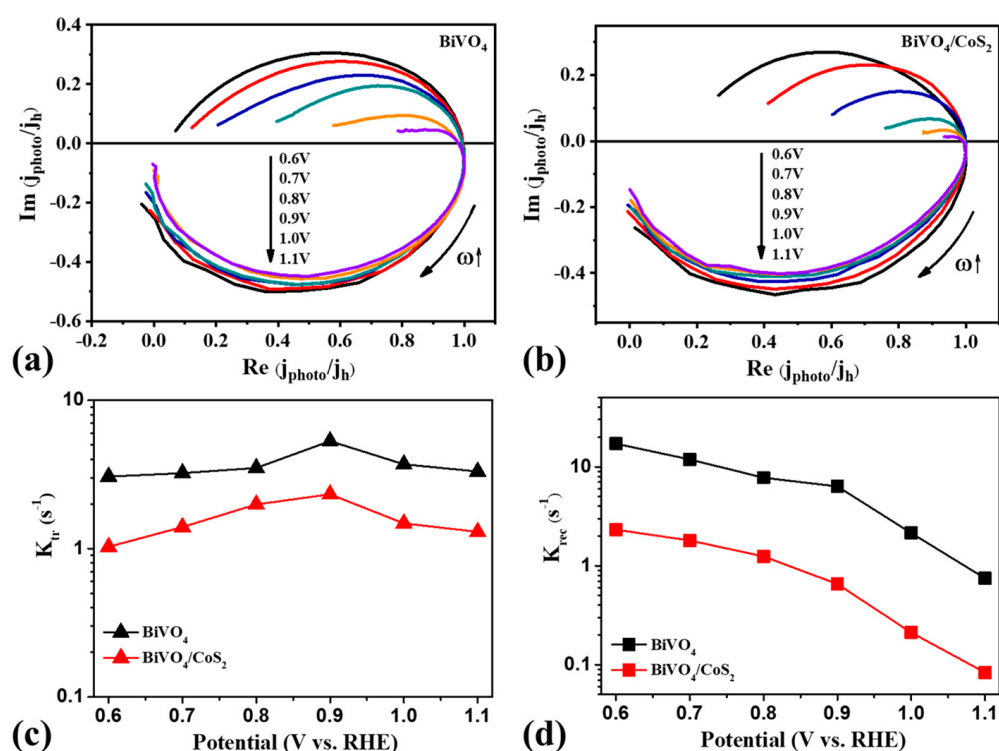


Figure 6. (a) IMPS spectra of BiVO₄. (b) IMPS spectra of BiVO₄/CoS₂. (c) Derived charge transfer rate constant. (d) Recombination rate constant for BiVO₄ and BiVO₄/CoS₂.

3.3.5. Proposed Mechanism for Enhanced Photoelectrochemical Water Splitting Performance

Based on the characterization results mentioned above, a supposed mechanism for the enhanced PEC performance in the BiVO₄/CoS₂ photoanode is proposed and illustrated in Figure 7. In bare BiVO₄, the electron-hole pairs generated by optical absorption can be separated into free charge carries in a decent efficiency. However, when the photogenerated holes arrive at the surface, they are predominately trapped by the high density of surface states present on the surface of bare BiVO₄, and a further attraction of photoelectrons generated in the bulk phase is followed, which results in a sever surface recombination. Therefore, much less photogenerated holes are involved in the water oxidation process,

and the obtained photocurrent is much lower than the value expected in theory. After the surface of bare BiVO_4 is modified by CoS_2 , the formation of the Co-O bond at the $\text{BiVO}_4/\text{CoS}_2$ interface possibly reduces the density of dangling bonds on the surface of BiVO_4 , which passivates the surface states of BiVO_4 to a decent level. Furthermore, the presence of the $\text{BiVO}_4/\text{CoS}_2$ interface may also act as a barrier for the recombination of charge carriers once the photogenerated holes are transferred to CoS_2 . In this way, the surface recombination of charge carriers is largely suppressed, and more photogenerated holes arrived at the surface have a large chance to be involved in the water oxidation process, which then achieves an enhanced PEC performance.

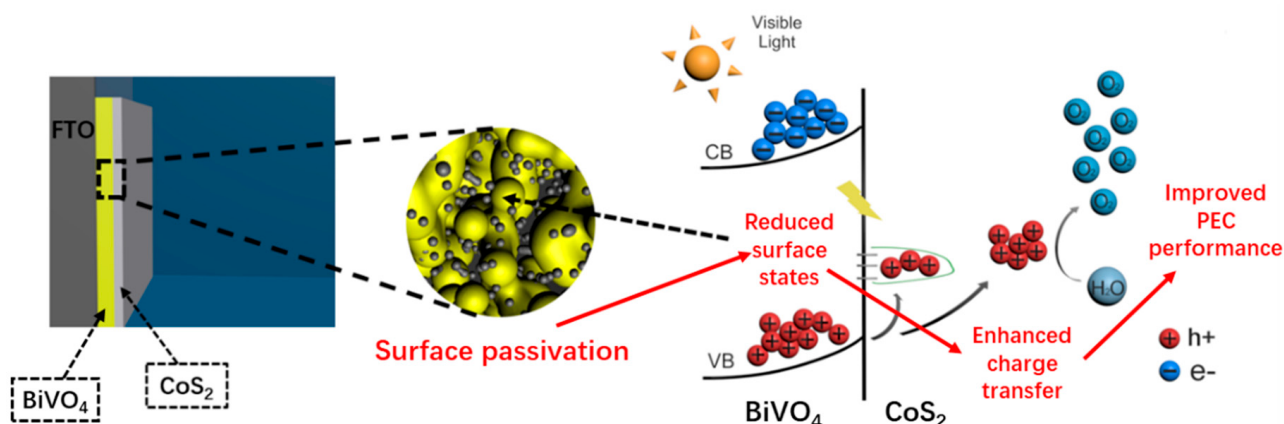


Figure 7. Schematic illustration for the proposed function of CoS_2 to improve the PEC performance of BiVO_4 .

4. Conclusions

In summary, the surface of bare BiVO_4 is modified by CoS_2 via a simple hydrothermal method to form composited $\text{BiVO}_4/\text{CoS}_2$ photoanode. After CoS_2 surface modification, the J–V curve of the $\text{BiVO}_4/\text{CoS}_2$ photoanode shows a 210 mV cathodic shift in onset potential and 3.7 times enhancement in photocurrent, which exhibits a photocurrent density of 5.2 mA cm^{-2} at 1.23 V versus RHE. Combined optical and electrochemical characterization results show that the bulk charge separation efficiency is not enhanced in the composite photoanode. Instead, a significantly enhanced interfacial charge transfer efficiency is observed. IMPS was adopted to characterize the rate constants of charge carriers related to the interface charge transfer process in order to explore the reason for the enhanced interfacial charge transfer efficiency by CoS_2 surface modification. Unexpectedly, a reduced charge transfer rate constant is observed at all the characterization potentials for $\text{BiVO}_4/\text{CoS}_2$ compared to bare BiVO_4 , which indicates that the electrocatalytic properties of CoS_2 make little positive contribution to the enhanced charge transfer process. In contrast, the surface recombination rate constants in BiVO_4 are observed to be suppressed by 6–10 times after CoS_2 surface modification at all biased potentials. Therefore, the main function of CoS_2 is supposed to passivate the surface states presented on the surface of BiVO_4 , which results in more photogenerated holes involved in the water oxidation process. Our work shows that the excellent electrocatalytic properties of co-catalyst may not be responsible for the enhanced PEC performance in composite photoelectrodes, but the influence of co-catalyst on the surface states and surface recombination of the photoelectrode should also be considered when designing highly efficient photoelectrodes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics10120264/s1>, Figure S1: XRD pattern of BiVO_4 ; Figure S2: XPS survey spectra; Figure S3: High-resolution XPS spectra of V 2p.

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