


 Cite this: *RSC Adv.*, 2021, 11, 13269

Efficient charge separation and transfer of a TaON/BiVO₄ heterojunction for photoelectrochemical water splitting†

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The separation and transfer of photogenerated electron–hole pairs in semiconductors is the key point for photoelectrochemical (PEC) water splitting. Here, an ideal TaON/BiVO₄ heterojunction electrode was fabricated *via* a simple hydrothermal method. As BiVO₄ and TaON were in well contact with each other, high performance TaON/BiVO₄ heterojunction photoanodes were constructed. The photocurrent of the 2-TaON/BiVO₄ electrode reached 2.6 mA cm⁻² at 1.23 V vs. RHE, which is 1.75 times as that of the bare BiVO₄. TaON improves the PEC performance by simultaneously promoting the photo-generated charge separation and surface reaction transfer. When a Co-Pi co-catalyst was integrated onto the surface of the 2-TaON/BiVO₄ electrode, the surface water oxidation kinetics further improved, and a highly efficient photocurrent density of 3.6 mA cm⁻² was achieved at 1.23 V vs. RHE. The largest half-cell solar energy conversion efficiency for Co-Pi/TaON/BiVO₄ was 1.19% at 0.69 V vs. RHE, corresponding to 6 times that of bare BiVO₄ (0.19% at 0.95 V vs. RHE). This study provides an available strategy to develop photoelectrochemical water splitting of BiVO₄-based photoanodes.

Received 5th February 2021

Accepted 14th March 2021

DOI: 10.1039/d1ra00974e

rsc.li/rsc-advances

Introduction

At present, the shortage of fossil fuels and increase of global warming have become very serious social and environmental problems. As a green energy source, solar energy is widely distributed. Hydrogen is also a type of clean energy with a high heating value. Therefore, the use of solar energy to produce hydrogen has attracted widespread attention.¹ Building a photoelectrochemical (PEC) cell to mimic the photosynthesis system is an effective method to realize the conversion of solar energy into hydrogen energy.^{2–6} However, in a PEC system, the water oxidation reaction half reaction occurring in the photoanode involves light capture, charge separation, and complex surface reaction with multiple electron and proton transfer. Therefore, designing an efficient photoanode to accelerate the water oxidation process becomes the key to the development of PEC cells.

In recent years, semiconductors based on metal oxides, such as BiVO₄, TiO₂, and WO₃, have been widely used as photoanode materials.^{7–11} BiVO₄, an n-type semiconductor with a band gap of 2.4 eV, is considered as one of the most promising alternative

materials.¹² Under the irradiation of a sunlight AM 1.5 G, the solar-to-hydrogen efficiency (STH) can reach 9.2%,¹³ which is close to the solar-powered water decomposition technology target (STH efficiency 10%).¹⁴ However, the severe recombination of the electron–hole pair of BiVO₄ limits its development. Different strategies were adopted to enhance the PEC performance of BiVO₄,^{15,16} such as elemental doping, nanostructure modification, loading cocatalysts and heterojunction construction. Among them, the construction of semiconductor heterojunctions with different materials is an effective approach to improve the PEC performance by enhancing the separation efficiency of photo-generated charges. Although there were numerous reports on heterojunction systems for BiVO₄-based semiconductors, such as CaFe₂O₄/BiVO₄,¹⁷ V₂O₅/BiVO₄,¹⁸ WO₃/BiVO₄^{19–21} and TiO₂/BiVO₄,^{22,23} the construction of a high-efficiency heterojunction photoanode still faces great challenges.

Here, TaON/BiVO₄ heterojunction photoanodes were constructed, which exhibited a greatly improved PEC water oxidation activity compared to the bare BiVO₄ photoanode. The photocurrent of the 2-TaON/BiVO₄ photoanode reached 2.6 mA cm⁻² at 1.23 V vs. RHE, which was 1.75-times that of BiVO₄. In order to enhance the surface water oxidation kinetics of the photoanode, the Co-Pi water oxidation catalyst was immobilized on the photoanode, and the PEC performance was further promoted. A high photocurrent density of 3.6 mA cm⁻² was obtained for Co-Pi/TaON/BiVO₄ at 1.23 V vs. RHE.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ra00974e



Experimental section

Fabrication of the BiVO₄ photoanode

A BiVO₄ electrode was prepared according to the electrodeposition method reported in literature.²⁴ 150 mL of deionized water was taken in a small beaker, and nitric acid was added to adjust the pH to 1.7. Then, 2.91 g of bismuth nitrate and 9.96 g of potassium iodide were added to the above mixture, and sonicated for about 30 min to fully dissolve. The above solution was mixed with an ethanol solution containing 0.23 M of *p*-benzoquinone, and sufficiently stirred to prepare an electrodeposition solution. An appropriate amount of the above-mentioned deposition solution was placed in a small beaker, and a three-electrode cell was used for electrodeposition (FTO was used as a working electrode, Pt was used as a counter electrode, and Ag/AgCl was used a reference electrode). At room temperature, after depositing for about 300 s at an applied bias of -0.1 V vs. Ag/AgCl, we obtained a BiOI film, which was washed with deionized water and blown with nitrogen. Then, a DMSO solution-containing 0.2 M acetylacetone was added dropwise to the deposited layer, and calcined at 450 °C for 2 h (2 °C min⁻¹) to convert BiOI into BiVO₄. Finally, it was immersed in a 1 M aqueous solution of sodium hydroxide for about 10 min in order to remove excess V₂O₅, rinsed with deionized water, and blown dry with nitrogen for use.

Fabrication of the TaON/BiVO₄ photoanode

TaON nanoparticles were prepared by heating Ta₂O₅ particles at 1123 K for 15 h under NH₃ flow (20 mL min⁻¹).²⁵ A certain amount of TaON (1, 0.02 g; 2, 0.04 g; 3, 0.06 g) was added to 100 mL of deionized water, sonicated to make a sol, and the BiVO₄ photoanodes were separately immersed in different concentrations TaON sol at 60 °C for 1 h, and calcined at 500 °C for 2 h under N₂ flow.

Fabrication of the Co-Pi/TaON/BiVO₄ photoanode

The Co-Pi cocatalyst was loaded by photoelectron deposition according to literature.²⁶ The 2-TaON/BiVO₄ photoanode was immersed in a phosphate buffer solution-containing a certain concentration of Co(NO₃)₂·6H₂O. Deposition was carried out at an applied bias of 0.1 V vs. Ag/AgCl and the sun illumination (100 mA cm⁻²) for 300 s.

Characterization of photoanodes

The XRD pattern was measured used a Bruker D8 QUEST. The SEM images were recorded on a SU8000 Schottky field emission scanning electron microscope (SFE-SEM) equipped with a Rontec EDX system. The UV-Vis absorbance spectra were recorded on a Lambda 35 UV-Vis spectrophotometer. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific ESCALAB 250 instrument (150 W, spot size of 500 μm and Al Kα radiation at 1486.6 eV) to obtain the surface elements. Photoluminescence (PL) spectroscopy measurement was performed on a Cary Eclipse spectrophotometer.

Photoelectrochemical measurements

The PEC performance tests of the electrodes were carried out using a standard three-electrode cell using an Ag/AgCl (3.5 M KCl) as the reference electrode, a platinum wire as the counter electrode and samples as the working electrode. The electrolyte used was a 0.1 M potassium buffer solution (pH 7.0) that was a mixture of mono- and dibasic hydrophosphates KH₂PO₄ and K₂HPO₄. The light intensity of the solar simulator (AM 1.5 G) was calibrated to 100 mW cm⁻². The effective surface area of the electrodes was 1 cm². The electrochemical impedance spectroscopy (EIS) was measured with the range from 0.1 Hz to 100 000 Hz. The Mott-Schottky curves were obtained under dark conditions, and the potential range was from -0.6 V to $+1.0$ V vs. Ag/AgCl.

The incident photon-to-current efficiency (IPCE) at each wavelength was determined at 1.23 V vs. RHE using monochromatic light illumination from a 300 W Xe arc lamp and neutral density filters simulating sunlight. The IPCE values have been calculated as follows:

$$\text{IPCE} = \frac{J \times \lambda}{P_{\text{light}}} \times 100\%$$

where J is the photocurrent density, λ is the incident light wavelength and P is the measured irradiance.

The applied bias photon-to-current efficiency (ABPE) was calculated from a J - V curve using the following equation:

$$\text{ABPE} = \frac{J \times (1.23 - V_{\text{bias}})}{P_{\text{in}}} \times 100\%$$

where J is the photocurrent density, V_{bias} is the applied bias and P_{in} is the incident illumination power density (AM 1.5 G, 100 mW cm⁻²).

The total water oxidation photocurrent $J_{\text{H}_2\text{O}}$ was determined by the following expression:

$$J_{\text{H}_2\text{O}} = J_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{trans}}$$

where J_{abs} is the photocurrent density when the absorbed photons completely converted into current, η_{sep} is the charge separation efficiency, and η_{trans} is the surface charge transfer efficiency.

To obtain η_{trans} , Na₂SO₃ was added into the 0.1 M PBS electrolyte, which was an efficient hole scavenger. Therefore, the η_{trans} efficiency equal to 1, and the photocurrent could be described as $J_{\text{Na}_2\text{SO}_3} = J_{\text{abs}} \times \eta_{\text{sep}}$. So, the η_{sep} could be described as:

$$\eta_{\text{sep}} = J_{\text{Na}_2\text{SO}_3} / J_{\text{abs}}$$

The η_{trans} was calculated using the equation:

$$\eta_{\text{trans}} = J_{\text{H}_2\text{O}} / J_{\text{Na}_2\text{SO}_3}$$

where $J_{\text{H}_2\text{O}}$ is the photocurrent density of the TaON/BiVO₄ electrode in 0.1 M PBS, and $J_{\text{Na}_2\text{SO}_3}$ is the photocurrent density of the TaON/BiVO₄ electrode in 0.1 M PBS containing 0.1 M Na₂SO₃.



Results and discussion

BiVO_4 films were fabricated *via* the electrochemical-deposition method. TaON nanoparticles were loaded onto the BiVO_4 surface, as shown in Scheme 1. By controlling the amount of TaON nanoparticles, different TaON/ BiVO_4 electrodes were fabricated (denoted as 1-TaON/ BiVO_4 , 2-TaON/ BiVO_4 and 3-TaON/ BiVO_4 , respectively). The microstructure of the pristine BiVO_4 is shown in Fig. 1a. A porous structure could be seen clearly in the whole area, which guaranteed the combination with TaON nanoparticles. The SEM images of TaON/ BiVO_4 electrodes containing different amounts of TaON are shown in Fig. 1. The distribution density of TaON nanoparticles increased with the amount of TaON (Fig. 1b–d). The crystal structures of the TaON, BiVO_4 and TaON/ BiVO_4 samples were tested by X-ray diffraction (XRD) patterns, as shown in Fig. S1,[†] confirming that TaON has been successfully modified on the BiVO_4 electrode.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical states of the TaON/ BiVO_4 electrodes. Ta, O, N, Bi and V elements were detected and shown in Fig. 2. Compared to the pristine BiVO_4 , the characteristic signals of TaON can be observed in the spectrum of the TaON/ BiVO_4 electrode. The characteristic peaks of N 1s and Ta 4p are shown in Fig. 2a. The binding energies of 529.7 eV and 532.0 eV are assigned to the O 1s of BiVO_4 , and the O 1s peak of TaON appears at 530.6 eV (Fig. 2b). The binding energies of 159.1 eV and 164.4 eV were assigned to the $4f_{7/2}$ and $4f_{5/2}$ of the Bi element, confirming that the Bi element was present as Bi^{3+} (Fig. 2c).²⁷ The binding energies for the V $2p_{3/2}$ and V $2p_{1/2}$

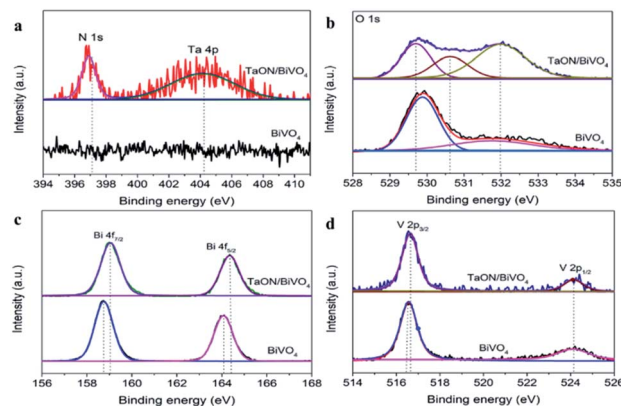


Fig. 2 XPS spectra of BiVO_4 and TaON/ BiVO_4 electrodes: (a) N 1s, Ta 4p, (b) O 1s, (c) Bi 4f, (d) V 2p.

located at 516.6 and 524.2 eV were typical values for V^{5+} (Fig. 2d).²⁸ The Bi 4f and V 2p peaks of the TaON/ BiVO_4 electrode shifted positively compared to that of the BiVO_4 electrode, indicating an interaction between TaON and BiVO_4 .

The PEC measurements of BiVO_4 and TaON/ BiVO_4 were carried out using a three-electrode system under simulated solar light 100 mW cm^{-2} . The linear sweep voltammetry (LSV) curves of the sample electrodes are shown in Fig. 3a. The photocurrent density of TaON/ BiVO_4 electrodes was significantly higher than that of the bare BiVO_4 electrode. The 2-TaON/ BiVO_4 photoanode showed the highest photocurrent density, reaching 2.6 mA cm^{-2} at 1.23 V *vs.* RHE, which was 1.75-times that of bare BiVO_4 . However, the photocurrent density of 3-TaON/ BiVO_4 was lower than that of 2-TaON/ BiVO_4 , suggesting that excessive TaON nanospheres hindered the charge transfer. The applied bias photon-to-current efficiencies (ABPEs) of BiVO_4 and TaON/ BiVO_4 electrodes were calculated by the LSV curves (Fig. 3b). The maximum value of the 2-TaON/ BiVO_4 electrode reached 0.61% at 0.74 V, about 3-times of the BiVO_4 electrode (0.19% at 0.95 V).

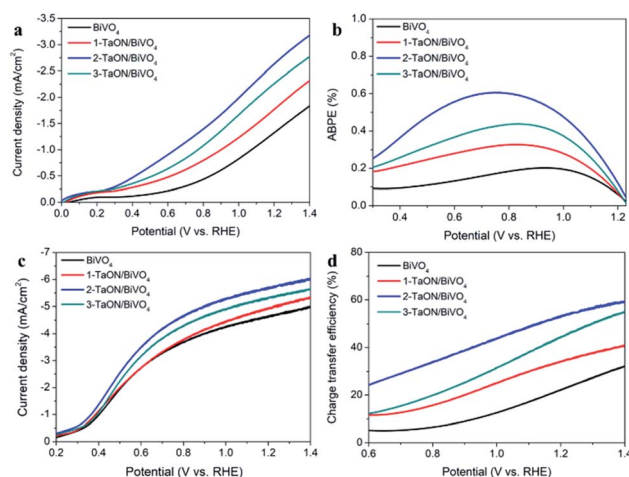
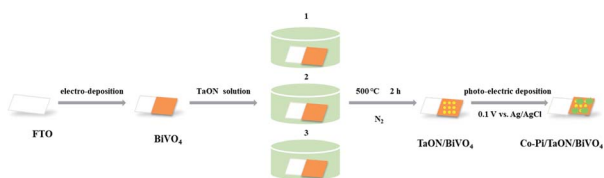


Fig. 3 (a) LSV curves in the PBS solution, (b) ABPE values, (c) LSV curves in the PBS solution containing 0.1 M Na_2SO_3 and (d) the charge transfer efficiencies of different electrodes.



Scheme 1 An illustration of the preparation of TaON/ BiVO_4 and Co-Pi/2-TaON/ BiVO_4 electrodes.

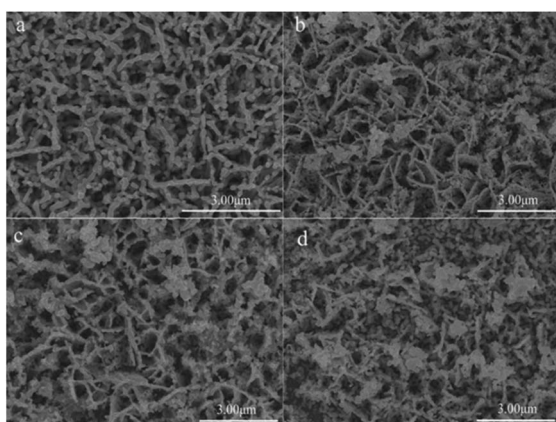


Fig. 1 SEM images of different electrodes. (a) BiVO_4 , (b) 1-TaON/ BiVO_4 , (c) 2-TaON/ BiVO_4 , (d) 3-TaON/ BiVO_4 .



In order to measure the charge recombination of the TaON/ BiVO_4 electrodes, 0.1 M Na_2SO_3 was added into the electrolyte as a hole scavenger for the PEC measurement.²⁹ The introduction of Na_2SO_3 can eliminate the surface charge recombination. The PEC measurement results are shown in Fig. 3c. Compared to the bare BiVO_4 electrode, all the TaON/ BiVO_4 electrodes showed higher photocurrent, which indicated that the combination of the two semiconductors produced a better charge separation. The 2-TaON/ BiVO_4 electrode showed the highest photocurrent density of 5.6 mA cm^{-2} at 1.23 V vs. RHE. Based on the LSV curves, the separation and surface charge transfer efficiencies of the sample electrodes are calculated and shown in Fig. S4† and 3d, respectively. All the TaON/ BiVO_4 electrodes exhibited higher η_{sep} and η_{trans} than the bare BiVO_4 . 2-TaON/ BiVO_4 showed the highest values. These results indicated that the construction of TaON/ BiVO_4 could promote both charge separation and surface charge transfer.

The incident photon-to-current conversion efficiency (IPCE) values are shown in Fig. S2.† In the visible spectrum, TaON/ BiVO_4 showed a higher IPCE value than BiVO_4 . At 520 nm, the IPCE value dropped to 0, which was consistent with the absorption spectra (Fig. S3†).

In order to understand the charge transfer characteristics of TaON/ BiVO_4 and BiVO_4 electrodes, electrochemical impedance spectroscopy (EIS) tests were performed in 0.1 M PBS at 1.23 V. Smaller semicircles represent better charge transfer capabilities and faster surface reaction kinetics. As shown in Fig. 4a, the BiVO_4 electrode exhibited the largest semicircle among all electrodes, indicating the highest interface charge transfer barrier. Three sample TaON/ BiVO_4 electrodes showed smaller charge transfer resistance than the BiVO_4 electrode, further confirming that TaON was beneficial to improve the charge transfer. The interface charge transfer resistance (R_{ct}) of the sample electrodes is shown in Table S1.† 2-TaON/ BiVO_4 showed the smallest charge transfer resistance, which was in accordance with the photocurrents.

To investigate the charge transfer behavior between BiVO_4 and TaON, photoluminescence (PL) measurements were

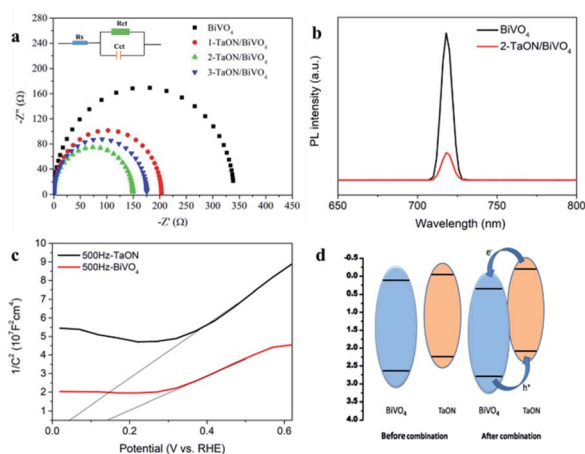


Fig. 4 (a) Electrochemical impedance spectroscopy (EIS) of different electrodes. (b) PL measurements of the BiVO_4 and 2-TaON/ BiVO_4 electrode (exciting source: 360 nm). (c) The Mott–Schottky plots of BiVO_4 and TaON. (d) The charge transfer mechanism of the TaON/ BiVO_4 electrode.

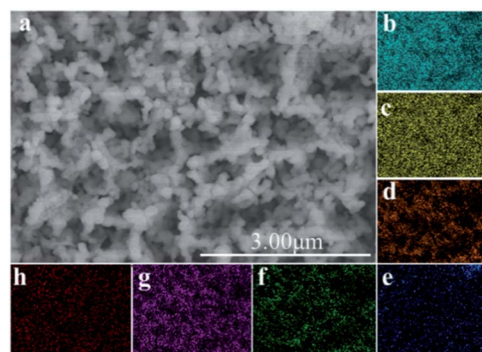


Fig. 5 SEM image of the Co-Pi/TaON/ BiVO_4 electrode (a) and the EDS-mapping element of the Co-Pi/TaON/ BiVO_4 electrode. (b) Bi, (c) V, (d) O, (e) Ta, (f) N, (g) Co, (h) P.

performed. As shown in Fig. 4b. BiVO_4 electrode exhibited a high-intensity characteristic emission, suggesting an obvious radiative charge recombination. However, the TaON/ BiVO_4 electrode exhibited much lower emission intensity. The obvious photoluminescence quenching for TaON/ BiVO_4 electrode fully proved the formation of TaON/ BiVO_4 heterojunctions.

The Mott–Schottky plots of BiVO_4 and TaON were also measured. As shown in Fig. 4c, it can be seen that the CB positions of BiVO_4 and TaON are 0.15 eV and 0.05 eV. The band gap width of BiVO_4 and TaON obtained from the absorption spectrum were 2.41 eV and 2.16 eV, respectively (Fig. S5†). The valence band positions of BiVO_4 and TaON can be calculated by the formula using $E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}}$, which were 2.56 eV and 2.21 eV. The CB edge potential of TaON was more negative than that of BiVO_4 . Thus, a difference of band potentials existed between the two materials, and a contact electric field was built at the interface of the TaON and BiVO_4 . When electrons and holes were photogenerated, as shown in Fig. 4d, driven by the contact electric field, electrons transferred from TaON to BiVO_4 and holes transferred from BiVO_4 to TaON, thereby leading to an enhancement both in photo-generated charge separation and transfer.

In order to further enhance the PEC performance, Co-Pi, which is well-used as highly efficient catalyst in PEC water oxidation, was equipped onto the TaON/ BiVO_4 electrode. The SEM image of the Co-Pi/TaON/ BiVO_4 electrode showed that Co-Pi appeared to be discontinuous particles (Fig. 5a). The EDS-mapping (Fig. 5b–h) suggested the existence of Bi, V, O, Ta, N, Co, and P elements, indicating the successful fabrication of the Co-Pi/TaON/ BiVO_4 electrode. According to the LSV curves shown in Fig. 6a, an obviously increased photocurrent density was obtained for the Co-Pi/TaON/ BiVO_4 photoanode, achieving 3.6 mA cm^{-2} at 1.23 V vs. RHE, which was about 3-times higher than that of the BiVO_4 electrode. During a potentiostatic electrolysis at 0.8 V vs. RHE, the bare BiVO_4 electrode always exhibited very low photocurrent density. For Co-Pi/TaON/ BiVO_4 high activity and stability was observed for more than 6000 s (Fig. S6†). The half-cell photoconversion efficiency of the Co-Pi/TaON/ BiVO_4 electrode achieved 1.19% at 0.69 V (Fig. 6a), approximately 6-times compared to that of BiVO_4 electrode.



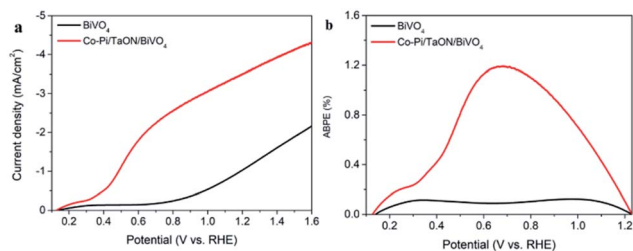


Fig. 6 LSV curves (a) and ABPE values (b) of BiVO_4 and Co-Pi/TaON/ BiVO_4 electrodes.

Conclusions

In summary, we have successfully fabricated TaON/ BiVO_4 heterojunction electrodes by integrating TaON nanoparticles onto BiVO_4 electrodes. The as-prepared TaON/ BiVO_4 electrodes exhibited significantly higher performances for PEC water oxidation. The 2-TaON/ BiVO_4 electrode showed the highest photocurrent, reaching 2.6 mA cm^{-2} at 1.23 V vs. RHE , 1.75 times that of the bare BiVO_4 electrode. In order to further increase the photocurrent, a Co-Pi water oxidation catalyst was attached onto the TaON/ BiVO_4 electrode. A high photocurrent density as high as 3.6 mA cm^{-2} (1.23 V vs. RHE) was obtained, and the half-cell photoconversion efficiency achieved 1.19% at 0.69 V, approximately 6-times that of the BiVO_4 photoanode. This study provides a promising route to achieve highly efficient PEC water splitting in designing solar-to-fuel conversion devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21671089), the Liaoning Revitalization Talents Program (XLYC1807210), the Natural Science Foundation of Liaoning Province of China (2020-YKLH-22) and the Scientific Research Fund of Liaoning Provincial Education Department (L2020002).

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