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ABSTRACT
Spray pyrolysis is a convenient method for fabricating BiVO\textsubscript{4} photoanodes from a precursor solution. As the precursor solution of spray pyrolysis can significantly influence the nanostructure and the amount of oxygen vacancies of the final films, modifying the precursor solution is an efficient strategy for improving the photoelectrochemical (PEC) performance of BiVO\textsubscript{4} photoanodes. Herein, an ultraviolet and ultrasonic treatment for modifying a vanadium precursor solution of spray pyrolysis was developed to produce efficient nanoporous BiVO\textsubscript{4} photoanodes. By the simple treatment, the AM 1.5 photocurrent density of the photoanode reached 1.76 mA/cm\textsuperscript{2} at 1.23 V vs the reversible hydrogen electrode (RHE) for water oxidation, which is 12.3 times higher than the untreated BiVO\textsubscript{4} photoanode. The good PEC performance was mainly attributed to the excellent charge separation that reached approximately 94.2% at 1.23 V vs RHE. Systematic studies revealed that the treatment for the precursor solution could tune the nanoporous structure and increase the amount of oxygen vacancies in the final films. This finding offers a facile and effective approach for fabricating efficient photoelectrodes for PEC water splitting.

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I. INTRODUCTION
Photoelectrochemical (PEC) water splitting is a promising method to convert solar energy to chemical fuels.\textsuperscript{1-10} Monoclinic BiVO\textsubscript{4} was shown as a fascinating photoanode material for water splitting, owing to the suitable bandgap energy (~2.4 eV) and appropriate band edge positions.\textsuperscript{8-10} The theoretical solar-to-hydrogen (STH) efficiency of BiVO\textsubscript{4} is about 9.2% (maximum photocurrent density is about 7.5 mA/cm\textsuperscript{2}).\textsuperscript{1,3,4,10} However, most reported STH efficiencies of BiVO\textsubscript{4} photoanodes are far below the expected value because the material suffers from severe charge recombination.\textsuperscript{9,10,12} The total photocurrent densities (J\textsubscript{ph}) of the BiVO\textsubscript{4} photoanodes are mainly determined by light absorption efficiency (\(\eta_{\text{abs}}\)), charge separation efficiency (\(\eta_{\text{sep}}\)), and charge transfer efficiency (\(\eta_{\text{transfer}}\)), that is, J\textsubscript{ph} = J\textsubscript{max} \times \eta_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{transfer}}.\textsuperscript{13} Charge separation efficiency is limited by the charge recombination in the bulk. Charge transfer efficiency (\(\eta_{\text{transfer}}\)) is limited by the surface carrier recombination, which is determined by water oxidation kinetics.\textsuperscript{14,17} Since the light absorption is determined with the bandgap of the semiconductor and sluggish water oxidation kinetics can be eliminated significantly by loading proper oxygen evolution cocatalysts (OECs), enhancing the charge separation efficiency (\(\eta_{\text{sep}}\)) by suppressing the bulk carrier recombination is an important aspect for improving the PEC performance of BiVO\textsubscript{4} photoanodes.
The nanoporous structure was considered as one of the promising strategies for producing high charge separation BiVO₄ photoanodes. The introduction of the nanoporous structure to BiVO₄ photoanodes can reduce the bulk carrier recombination by increasing the volume of depletion and shortening the carrier transport distance. Notably, Choi et al. reported that nanoporous BiVO₄ photoanodes produced by an electrochemical synthesis route manifested a high charge separation efficiency, which was over 90% at 1.23 V vs reversible hydrogen electrode (RHE). However, the strategy of the electrochemical synthesis route requires complex fabrication techniques and is hard to produce on a large scale. Since the spray synthesis route is convenient and has potential to scale up, fabricating nanoporous BiVO₄ photoanodes by spray pyrolysis is particularly attractive and still needs to be explored. Moreover, increasing the density of oxygen vacancies in nanoporous BiVO₄ electrodes is an effective strategy to further enhance the charge separation efficiency. Oxygen vacancies act as n-type donors without introducing foreign elements, which effectively increase the carrier density and enhance the charge transport property. The density of oxygen vacancies can be increased by the reduction of BiVO₄ via hydrogenation, chemical reduction, and electrochemical treatment. However, the methods of creating oxygen vacancies by the reduction of BiVO₄ would produce V⁴⁺, which is harmful to the PEC performance of BiVO₄ photoanodes, because V⁴⁺ with larger radius acts as a scattering center and reduces the diffusion length of holes. Thus, creating oxygen vacancies without V⁴⁺ in nanoporous BiVO₄ photoanodes remains a challenge.

Herein, we developed a facile spray pyrolysis synthesis route to produce nanoporous BiVO₄ photoanodes with high charge efficiency by adding an ultraviolet and ultrasonic treatment to the vanadium precursor solution. As a result, the BiVO₄ photoanodes fabricated with our method exhibited 94.2% charge separation efficiency. The AM 1.5 photocurrent densities of the photoanode were 1.76 mA/cm² for water oxidation and 4.16 mA/cm² for sulfite oxidation at 1.23 V vs RHE. The ultrasonic treatment well tuned the nanoporous structure of the final films and effectively increased the density of oxygen vacancies without producing V⁴⁺. The strategy of increasing oxygen vacancies in nanoporous BiVO₄ photoanodes can significantly enhance the charge separation by reducing bulk carrier recombination. The nanoporous BiVO₄ photoanodes with high charge separation efficiency can be achieved by the simple spray pyrolysis synthesis route.

II. EXPERIMENTAL SECTION

A. Preparation

The nanoporous BiVO₄ thin films were prepared by spray pyrolysis. The bismuth solution was prepared by dissolving an equimolar amount of vanadium in the form of VO(acac)₂ (98%, Aladdin) in 100 ml dimethyl sulfoxide (DMSO) (99.9%, Alfa Aesar). Before mixing bismuth and vanadium solution, the vanadium solution was subjected to ultraviolet (365 nm, 2 mW/cm²) and ultrasonic treatment (500 W) for 4 h by using an XH-300UL ultrasonic synthesis machine (Xianghu Science and Technology Development Limited Company, Beijing). The BiVO₄ films (named UV–US BiVO₄) were synthesized via the spray pyrolysis method on FTO substrates with the mixed precursor solution of bismuth and vanadium solution that was subjected to ultraviolet and ultrasonic treatment. The substrate temperature was maintained at 425 °C, and the nozzle–substrate distance was kept at 20 cm. Each spray cycle consisted of 10 s spray time and 3 s delay time. 2 ml precursor solution was used for preparing one film. The BiVO₄ photoanodes were obtained after calcination at 450 °C for 2 h. Meanwhile, the UV BiVO₄ photoanode (fabricated with the precursor solution only subjected to ultraviolet treatment), the US BiVO₄ photoanode (fabricated with the precursor solution only subjected to ultrasonic treatment), and the pristine BiVO₄ photoanode (fabricated with the precursor without any treatment) were also prepared via the same method.

B. Characterizations

The morphology of the BiVO₄ thin films was examined by using a field-emission scanning electron microscope (FE-SEM, FEI Quanta 250 FEG). X-ray photoelectron spectroscopy (XPS) was performed by using a VG ESCA-LAB MKII instrument with an Mg Kα ADES (hv = 1253.6 eV) source. The UV–vis absorption was measured by using a Perkin Elmer UV WinLab spectrophotometer with integrating sphere. X-ray diffraction (XRD) patterns were measured by using a Rigaku D/max-2500 diffractometer. Raman spectra measurement was conducted by using a Jobin Yvon HR 800 Raman microscope.

C. Photoelectrochemical measurements

The photoelectrochemical performance of the BiVO₄ photoanodes was characterized by using a PARSTAT 2273 electrochemical system with a typical three-electrode configuration, a Pt counter electrode, and a Ag/AgCl (3.5M KCl) reference electrode. 0.5M Na₂SO₄ aqueous solution and 0.5M Na₂SO₃ aqueous solution were used as the electrolyte. A solar simulator (Newport 370-RC) was used as the light source. An optical meter (PM 100D, Thorlabs) was used to adjust the light intensity. J–V curves were recorded with a scan rate of 10 mV/s. The Mott–Schottky analysis of BiVO₄ electrodes was measured at a frequency of 1 KHz in dark with a scan rate of 20 mV/s.

III. RESULTS AND DISCUSSION

The preparation process of the UV–US BiVO₄ electrodes reported in this study was illustrated in Fig. 1. UV–US BiVO₄ films were grown on fluorine-doped SnO₂ (FTO) substrates by the spray pyrolysis method, followed by calcination in air atmosphere at 450 °C for 2 h. Before spraying, the vanadium precursor solution was subjected to ultraviolet and ultrasonic treatment (named UV–US treatment) for 4 h. The UV–US BiVO₄ photoanode with the most suitable thickness of about 600 nm was selected to serve as the working electrode. For comparison, the pristine BiVO₄ electrode with the same thickness fabricated by the precursor without UV–US treatment was also investigated. The crystal structure can be confirmed by x-ray diffraction. Along with FTO signals, the peaks of UV–US BiVO₄ and pristine BiVO₄ films were indexed to be monoclinic
FIG. 1. Schematic illustration of the process used to make nanoporous BiVO$_4$ photoanodes with abundant oxygen vacancies.

BiVO$_4$ (Fig. S1). The Raman spectra of UV–US BiVO$_4$ and pristine BiVO$_4$ also exhibited the characteristics of monoclinic BiVO$_4$ (Fig. S2).

Figure 2(a) shows the J–V curves of UV–US BiVO$_4$ and pristine BiVO$_4$ photoanodes measured in the electrolyte of 0.5M Na$_2$SO$_4$ and 0.5M Na$_2$SO$_3$ aqueous solution under AM 1.5 G illumination. In all cases, the values of dark current densities could be neglected. The AM 1.5 photocurrent density of UV–US BiVO$_4$ measured in the electrolyte of Na$_2$SO$_4$ aqueous solution was 1.76 mA/cm$^2$ at 1.23 V vs RHE, which was about 12.3 times higher than that of pristine BiVO$_4$. The photocurrent densities of UV–US BiVO$_4$ and pristine BiVO$_4$ measured in the Na$_2$SO$_3$ aqueous solution were used to calculate the charge separation efficiency ($\eta_{\text{sep}}$) and charge transfer efficiency ($\eta_{\text{transfer}}$) by using the following equation:

$$J_{\text{PEC}} = J_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{transfer}} = 100\%.$$  \hspace{1cm} (1)

$J_{\text{abs}}$ is the photon-absorption rate expressed as current density, which can be estimated by using the absorption and the value of 2.4 eV bandgap of BiVO$_4$ \cite{1,2} (Fig. S3). The $J_{\text{abs}}$ of UV–US BiVO$_4$ was calculated to be 4.42 mA/cm$^2$, and the $J_{\text{abs}}$ of pristine BiVO$_4$ was 4.44 mA/cm$^2$. As shown in Fig. 2(c), the $\eta_{\text{transfer}}$ of pristine BiVO$_4$ was only 13.2% at 1.23 V vs RHE, while the value of UV–US BiVO$_4$ was increased to 41.9% at 1.23 V vs RHE. The UV–US treatment also boosted the charge separation efficiency ($\eta_{\text{sep}}$) of UV–US BiVO$_4$ to be 94.2% at 1.23 V vs RHE, which was about 3.9-fold that of the pristine BiVO$_4$ [Fig. 2(b)].

UV–US treatment obviously changed the morphology of the final BiVO$_4$ film. The UV–US BiVO$_4$ film showed nanoporous morphology [Figs. 3(b) and 3(d)]. The pristine BiVO$_4$ was a planar film with a small quantity of pores [Figs. 3(a) and 3(c)]. Because
of different morphologies, we inferred that a combustion reaction was induced by the UV–US treatment, which could result in the nanoporous structure of the BiVO₄ film. To bring out a combustion reaction, an oxidizer and fuel are required. In our method, Bi(NO₃)₃ and VO(acac)₂ were used as feedstock to prepare the precursor solution. NO₃⁻ could act as an oxidizer, which was from Bi(NO₃)₃. The fuel might be acetylacetone generated by the decomposition of VO(acac)₂ during the process of UV–US treatment. Previous studies have shown that metal acetylacetone complexes can be decomposed under the ultraviolet irradiation. Hence, VO(acac)₂ could be decomposed and produce acetylacetone under the UV–US treatment. To confirm the inference, the BiVO₄ film was prepared by using the precursor solution with 0.5% acetylacetone added and the morphology of the BiVO₄ films was confirmed to be nanoporous (Fig. S4).

In order to investigate the surface chemical composition and the change in the oxidation states of BiVO₄, x-ray photoelectron spectroscopy (XPS) analysis was carried out. Figures 4(a)–4(c) show the XPS spectra of Bi 4f, V 2p, and O 1s of the pristine BiVO₄ and the UV–US BiVO₄. Apart from the Bi, V, and O peaks, the C 1s signal at about 284.6 eV was also observed and used as the binding energy reference (Fig. S5). The peaks of the signals of Bi 4f⁵/₂ and Bi 4f⁷/₂ were found at 158.7 eV and 164.0 eV, which coincided with the values reported in previous studies [Fig. 4(a)]. No obvious differences in Bi peaks were found between the pristine BiVO₄ and the UV–US BiVO₄. Hence, the UV–US treatment did not influence the chemical state of Bi. The XPS spectra of O 1s peaks indicated that two different oxygen species existed on the surface of both UV–US BiVO₄ and pristine BiVO₄ electrodes [Fig. 4(c)]. The peak at a lower binding energy (~529.5 eV) is for lattice O (Oₐₙ₉), and the peak at a higher binding energy (~531.0 eV) is for adsorbed O (Oₐₐ₉). The ratio of Oₐ₈ to Oₐ₉ on the surface of the pristine BiVO₄ electrode was calculated to be about 0.21 using the Gaussian–Lorentzian (GL) fitting method, and the ratio of Oₐ₈ to Oₐ₉ of the UV–US BiVO₄ electrode was increased to 1.27, indicating that the density of oxygen vacancies in UV–US BiVO₄ was higher than that of pristine BiVO₄. Figure 4(b) shows the peaks of V 2p of the pristine BiVO₄ electrode and UV–US BiVO₄ electrode, which coincide with the reported values of monoclinic BiVO₄. In previous reports, V⁵⁺ species appeared at a binding energy of about 0.7–1.2 eV that was higher than for V⁴⁺ species. The signal of V⁴⁺ cannot be found in the XPS spectra for both types of BiVO₄, and all peaks were attributed to V⁵⁺ species. In comparison with pristine BiVO₄, a small shift of 0.2 eV to lower energy for the V 2p peak was observed in UV–US BiVO₄. The shift of binding energy originated from the reduction of V⁵⁺ to lower oxidation states with the corresponding oxygen vacancies, indicating that the density of oxygen vacancies was increased in UV–US BiVO₄ electrodes.

By using the UV–US treatment for the vanadium solution, the density of oxygen vacancies was successfully increased. Oxygen vacancies acted as an effective n-type doping that enhanced the carrier density, which was proved by the Mott–Schottky analysis (Fig. 5). The electrochemical surface area of UV–US BiVO₄ and pristine BiVO₄ films was estimated by the electrochemical active surface area (ECSA) measurement. The results suggested that the surface area of UV–US BiVO₄ was about 2.4 times that of pristine BiVO₄ (Fig. S6). According to the Mott–Schottky equation,

$$\frac{1}{C^2} = 2(V - V_{FB} - k_BT/e)A^0\epsilon_{\text{eff}}N_d$$  \hspace{1cm} (2)

and the electrochemical surface area, the N₃ of UV–US BiVO₄, could be estimated to be about 1.4 times larger than the pristine BiVO₄, which was attributed to the increasing amount of oxygen vacancies. Moreover, the V₉ of UV–US BiVO₄ exhibited 0.06 V negative than pristine BiVO₄, reflecting that the Fermi level of UV–US BiVO₄ was closer to its conduction band (CB) edge.

Increasing the density of oxygen vacancies is an efficient strategy for enhancing the PEC performance of the nanoporous BiVO₄ electrode. The traditional methods such as hydrogenation, chemical reduction, and electrochemical treatment were conducted to create oxygen vacancies via reducing BiVO₄. However, these traditional methods would produce V⁴⁺, which is harmful to charge transport. V⁴⁺ acted as scattering centers and reduced the effective diffusion length of holes because the radius of V⁴⁺ is larger. Recent investigations demonstrated that the density of oxygen vacancies in BiVO₄ films could be increased by optimizing the process of fabrication. In our study, a simple UV–US treatment for the precursor solution was used for increasing the density of oxygen vacancies in the final film. By comparing the previous study and our UV–vis absorbance spectra of vanadium precursor solutions (Fig. S7), we inferred that an oxidation reaction occurred and incomplete oxidation of V⁴⁺ to V⁵⁺ occurred during the process of the UV–US treatment. It is known that gaseous oxygen is consumed to convert V⁴⁺ into V⁵⁺ in the final BiVO₄ photoanode during the process of annealing. Incomplete oxidation of
$V^{4+}$ to $V^{5+}$ could lead to the formation of oxygen vacancies to meet the charge balance in the final BiVO$_4$. In addition, the combustion reaction induced by the UV–US treatment can cause local higher temperature, which can also lead to the generation of oxygen vacancies in the nanoporous UV–US BiVO$_4$. XPS demonstrated that the density of oxygen vacancies was increased and no $V^{4+}$ species existed on the surface of the final BiVO$_4$ film. Hence, by the simple solution route, an increase in the density of oxygen vacancies without excess $V^{4+}$ was achieved in the nanoporous BiVO$_4$ photoanode, which can significantly enhance the charge separation efficiency.

The UV BiVO$_4$ photoanode and the US BiVO$_4$ photoanode were prepared for comparative investigation. Both UV BiVO$_4$ and US BiVO$_4$ exhibited significantly enhanced photocurrent densities compared with pristine BiVO$_4$ (Fig. S8). The porosity of the final films can be enhanced by both the single ultraviolet treatment and the single ultrasonic treatment (Fig. S9). The US BiVO$_4$ film shows higher porosity than the UV BiVO$_4$ film (Figs. S9(c) and S9(d)), indicating that the US treatment played a more significant role in generating the structure of nanoporous photoanodes. According to the Mott–Schottky analysis, the $V_{FB}$ of UV BiVO$_4$ is more negative than that of US BiVO$_4$, indicating that the electronic density of UV BiVO$_4$ is higher, which is attributed to the larger amount of oxygen vacancies (Fig. S10). (Although the electronic density of UV BiVO$_4$ is higher, it is reasonable that the Mott–Schottky plot of UV BiVO$_4$ is steeper as the surface area of the US BiVO$_4$ film is larger.) Hence, the ultraviolet treatment played a more significant role in generating oxygen vacancies. Combining the ultraviolet treatment and ultrasonic treatment, the UV–US BiVO$_4$ photoanode with the nanoporous structure and rich oxygen vacancies exhibited a more significantly enhanced photocurrent density.

IV. CONCLUSION

In summary, we demonstrated a facile UV–US treatment for the vanadium precursor solution of spray pyrolysis to prepare highly efficient BiVO$_4$ photoanodes for photoelectrochemical water splitting. The UV–US treatment for the precursor solution controlled the nanostructure of the films and created oxygen vacancies without producing $V^{4+}$. By combining the strategies of nanoporous morphology and increasing the amount of oxygen vacancies, the photoanode showed good PEC performance, which exhibited an AM 1.5 photocurrent density of 1.76 mA/cm$^2$ in Na$_2$SO$_4$ and 4.16 mA/cm$^2$ in Na$_2$SO$_3$ at 1.23 V vs RHE. The charge separation of the BiVO$_4$ photoanode was dramatically enhanced, which reached 94.2% at 1.23 V vs RHE. Modifying the precursor solution with the UV–US treatment is an efficient strategy for preparing highly efficient BiVO$_4$ photoanodes. Moreover, we believed that the spray synthesis route can be applied to the synthesis of other metal oxides and provide a new opportunity in the development of solar water splitting.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional figures, analysis, and discussion.

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