A Green Desulfurization Technique: Utilization of Flue Gas SO\textsubscript{2} to Produce H\textsubscript{2} via a Photoelectrochemical Process Based on Mo-Doped BiVO\textsubscript{4}

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A green photoelectrochemical (PEC) process with simultaneous SO\textsubscript{2} removal and H\textsubscript{2} production has attracted an increasing attention. The proposed process uses flue gas SO\textsubscript{2} to improve H\textsubscript{2} production. The improvement of the efficiency of this process is necessary before it can become industrial viable. Herein, we reported a Mo modified BiVO\textsubscript{4} photocatalysts for a simultaneous SO\textsubscript{2} removal and H\textsubscript{2} production. And the PEC performance could be significantly improved with doping and flue gas removal. The evolution rate of H\textsubscript{2} and removal of SO\textsubscript{2} could be enhanced by almost three times after Mo doping as compared with pristine BiVO\textsubscript{4}. The enhanced H\textsubscript{2} production and SO\textsubscript{2} removal is attributed to the improved bulk charge carrier transportation after Mo doping, and greatly enhanced oxidation reaction kinetics on the photoanode due to the formation of SO\textsubscript{2}−\textsubscript{3} after SO\textsubscript{2} absorption by the electrolyte. Due to the utilization of SO\textsubscript{2} to improve the production of H\textsubscript{2}, the proposed PEC process may become a profitable desulfurization technique.

Keywords: hydrogen, sulfur dioxide, solar energy, Photoelectrochemical (PEC), Mo-doped BiVO\textsubscript{4}

INTRODUCTION

Sulfur dioxide (SO\textsubscript{2}), as one of the acid gases, could transform into some atmospheric products (e.g., sulfate, sulfuric acid aerosol) through the chemical process in the atmosphere. It and its atmospheric products are detrimental to human health, and cause lots of environmental problems such as smog formation, acid deposition, and degradation of visibility. As is well-known, the SO\textsubscript{2} mainly enters the atmosphere through the anthropogenic processes, e.g., combustion and release of petroleum, fossil fuel, etc. (Lelieveld and Heintzenberg, 1992; McDonald-Buller et al., 2016). Till now, to remove SO\textsubscript{2} released from the burning of fossil fuels, several effective methods has been developed (Srinivasan and Grutzeck, 1999; Bashikova et al., 2001; Xia et al., 2011; Kaplan et al., 2013; Yang et al., 2013). Among these technologies, Wet Flue Gas Desulfurization (WFGD) has been one of the state-of-the-art technologies for SO\textsubscript{2} removal with high efficiency, simple equipment and obtaining multi-useful byproducts (Yang et al., 2012; Lu et al., 2013). Unfortunately, there are some inevitable drawbacks with the WFGD process: for example, the oxidation process energy of SO\textsubscript{2}−\textsubscript{3} to final SO\textsubscript{2}−\textsubscript{4} is wasted and it is not consistent with the sustainable principles. In order to solve this problem, our group proposed a solar-to-H\textsubscript{2} energy conversion with SO\textsubscript{2} removal
simultaneously via a solar water splitting process for the first time (Han et al., 2017). Since the oxidation of SO$_2^-$ (formed during desulfurization process) needs much lower activation energy and 2 electrons than that of water, acted as a sacrificing reagent during the process, thus it could significantly improve the evolution rate of H$_2$. This method not only utilizes the waste energy during the desulfurization process, also realizes the energy production by using air pollutants, which could achieve the zero release of SO$_2$.

Though we have reported a photosensitive semiconductor (BiVO$_4$) for H$_2$ generation with SO$_2$ removal, but it is still a challenge to facilitate the performance due to the intrinsic low mobility of photogenerated charges of BiVO$_4$. Lots of methods have been proposed to solve this problem, such as controlling the morphology (McDonald and Choi, 2012; Kim and Choi, 2014; Zhou et al., 2014), metal and nonmetal doping (Jo et al., 2012; Chen et al., 2015; Huang H. et al., 2015; Huang H. W. et al., 2015; Huang et al., 2017), forming heterojunctions (Hong et al., 2011; Luo et al., 2011; Seabold and Choi, 2012; Zhang et al., 2016). These modifications have improved the properties of BiVO$_4$ greatly by reducing the band-gap energy or improving the charge carrier transport. It has been reported that Mo$_6^{6+}$ ion substitute the V site in monoclinic sheelite BiVO$_4$ could improve the photoinduced carriers, which could facilitate the oxidation while in water splitting reaction system theoretically and experimentally (Luo et al., 2011, 2013; Parmar et al., 2012; Ding et al., 2014; Park et al., 2014; Seabold et al., 2014; Zhou et al., 2014; Jiang et al., 2015, 2017; Kuang et al., 2016; Nair et al., 2016; Pattengale and Huang, 2016). However, Mo-doped BiVO$_4$ has not been studied as photoanode for flue gas SO$_2$ removal. Here, we prepared Mo-doped BiVO$_4$ for enhancing H$_2$ generation with simultaneous SO$_2$ removal. Moreover, the importance of the amount of Mo-dopants on the performance of BiVO$_4$ with SO$_2$ removal was also studied. Besides we prepared a series of Mo-doped BiVO$_4$ films with different content. The structure characterizations of the obtained films were investigated by XRD, SEM, Raman, UV-vis. Furthermore, we studied the performance of H$_2$ generation and efficiency of SO$_2$ removal.

**EXPERIMENT**

**Synthesis of the Catalysts**

In this work, the deionized water (DI water) was used throughout the whole experiment, and all the chemical reagents are analytical grade and used without any further purification.

F-doped SnO$_2$ coated glass (FTO) were purchased from China Southern Glass Co. Ltd, and the FTO glasses were sonicated by immersing in acetone, ethanol and DI water for removing the impurities on the surface of the glass. For comparison, the pristine BiVO$_4$ was also prepared. All of the electrodes were synthesized by drop-coating method. The precursor solution was dropped onto the conducting side of FTO, followed by annealing in air. The precursor solutions were synthesized by the following procedure (Zhang et al., 2014): diethylene-triaminepentaacetic acid (DTPA) and ammonia in water (13.0 mol L$^{-1}$) were added into hot deionized water. After dissolution, the stoichiometric Bi(NO$_3$)$_3$•5H$_2$O, V$_2$O$_5$ powder and moderate ammonium molybdate tetrahydrate (H$_2$Mo$_7$N$_2$O$_{24}$•4H$_2$O) were added into sequence as listed. The resulted mixture was stirred and heated for an hour to promote the dissolution and reaction (complexation of Bi$^{3+}$, V$^{5+}$, and Mo$^{6+}$ with DTPA) until the mixture turned into a transparent solution. Here, we prepared three different samples with the content of Mo ranging from 1, 3, to 5. The amounts of doped Mo were 1 atom%, 3 atom%, 5 atom%, and were denoted as BiVO$_4$(Mo-1), BiVO$_4$(Mo-3), BiVO$_4$(Mo-5), respectively. Then, 40 µl prepared solutions were dropped onto the conducting side of FTO (1 × 2 cm) respectively. After dried at 60°C in oven, the films were annealed at 500°C for 3 h with a ramping rate of 2°C min$^{-1}$ in air. The above process was repeated by three times for the synthesis of the electrode.

**Characterization of the Samples**

The crystal structures of the as-prepared samples were determined using an X-Ray Diffraction (XRD) with Cu Kα radiation ranging from 10 to 60º. The crystallite sizes of the samples were calculated using the Scherrer formula:

$$D = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (1)

Where D is the average crystallite size (nm), λ is the wavelength of the X-ray radiation (0.154 nm), K is the shape factor (0.9), β is the peak width at half-maximum height, corrected for instrumental broadening, and θ = 28.7º. The micromorphology and the microstructure of the samples were determined by using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan). UV-vis transmission spectra of the as-prepared catalysts were measured using a UV-Vis spectrophotometer (SHIMADZU UV-2600) with an integrating sphere attachment. BaSO$_4$ was used as a standard. Raman spectra were recorded with a Raman spectrometer (HORIBA, X-plo RA Plus), a green laser (532 nm) were used as excitation sources.

**PEC Measurement**

The apparatus for the PEC tests was a gastight photoreactor. The PEC performance were conducted with a typical three-electrode configuration by using a potentiostat (CHI 660E, Shanghai Chenhua Co. Ltd. China). The synthesized pure BiVO$_4$ or Mo-doped BiVO$_4$ electrode was used as working electrode, Pt wire was used as counter electrode and Hg/HgO electrode was used as reference electrode. The electrolyte solutions for the PEC tests were prepared by absorbing SO$_2$ gas with NaOH solutions of certain concentration (detailed in Table 1). We bubbled SO$_2$ of concentration is 1,000 ppm successively to NaOH aqueous with the flow rate of 200 ml min$^{-1}$ to form Na$_2$SO$_3$ with a specific concentration. Eventually, the obtained electrolytes for PEC tests were 0.1 M NaOH−0.025 M Na$_2$SO$_3$ [denoted as NaOH(aq)+SO$_2$(g)-1], 0.1 M NaOH-0.05 M Na$_2$SO$_3$ [denoted as NaOH(aq)+SO$_2$(g)-2], 0.1 M NaOH-0.075 M Na$_2$SO$_3$ [denoted as NaOH(aq)+SO$_2$(g)-3]. For comparison, the NaOH (aq, 0.1 M) solution was also prepared. The PEC tests were measured under illumination by using a 300 W Xe lamp solar simulator with AM 1.5 G filter (100 mW cm$^{-2}$) from the back side of the working electrode, as well as in dark conditions. Liner Sweep Voltammetry (LSV) was measured with the sweep rate of 10 mV s$^{-1}$.
The structures of prepared BiVO₄ and Mo-doped BiVO₄ bulk were optimized by using the CASTEP code (Ding et al., 2014). The primitive cell of pure monoclinic sheelite BiVO₄ was relaxed using 400 eV energy cut off for the plane-wave expansion. The structural model of Mo-doped monoclinic sheelite BiVO₄ was built by substituting one V atom in a relaxed (2 × 1 × 2) supercell of monoclinic sheelite BiVO₄ with one Mo atom.

**Hydrogen Evolution**

The reactor for hydrogen evolution experiments is identical with the apparatus used for PEC tests, which use a two-electrode configuration. The electrolyte was NaOH solution bubbled with SO₂ gas. The experiments were conducted under illumination using a 300 W Xe lamp with AM 1.5 G filter (100 mW cm⁻²) from the back side of the photoanodes in a 150 ml reactor with 100 ml electrolytes filled in and the external bias was 1.6 V. The amount of H₂ was analyzed by gas chromatography using a thermal conduction detector (TCD) once an hour. The pH values of the solution during the PEC tests were detected by Ohaus (STARTER 2100). The theoretical evolution rate of H₂ is calculated according to the following equation:

\[ \nu = \frac{I \times t}{Z \times F \times A \times 3600} \]  

Where, \( \nu \) indicates the evolution rate of H₂ (mol cm⁻² h⁻¹); \( I \) indicates the average current (A); \( t \) indicates the time (s); \( Z \) indicates the transferred electron number (1); \( F \) is the Faraday's constant (96,500 C mol⁻¹); \( A \) is the area of the film (cm²).

The equation for the calculation of Faradaic efficiency is:

\[ \text{Faradaic efficiency} \ (\%) = \frac{m \times n \times F}{I \times t} \times 100\% \]  

Where, \( m \) is the experimental value of H₂ (mol); \( n \) is the reacted electron number (1); \( F \) is the Faraday's constant (96,500 C mol⁻¹); \( I \) is the average current (A); \( t \) is the time (s).

| Items                        | NaOH(aq)-SO₂(g)-1 | NaOH(aq)-SO₂(g)-2 | NaOH(aq)-SO₂(g)-3 |
|------------------------------|-------------------|-------------------|-------------------|
| Concentration of NaOH/M      | 0.150             | 0.200             | 0.250             |
| Concentration of SO₂/ppm     | 1,000             | 1,000             | 1,000             |
| SO₂ flow rate/ml min⁻¹       | 200               | 200               | 200               |
| SO₂ inletting time/min       | 112               | 224               | 336               |
| Resulted concentration of SO₂³⁻/M | ~0.025           | ~0.050            | ~0.075            |
| SO₂ absorbing efficiency/%   | ~99               | ~98               | ~98               |

**FIGURE 1** | SEM images and particle range of (a) pure BiVO₄; (b) BiVO₄(Mo-1); (c) BiVO₄(Mo-3); (d) BiVO₄(Mo-5).
RESULTS AND DISCUSSION
Structure and Physical Properties of the Photoelectrode

The SEM (Scanning Electron Microscopy) images of pristine BiVO$_4$ and Mo-doped BiVO$_4$ films are shown in Figure 1. All of the films present nanoparticle structure while a rougher, more disordered structure can be observed in the BiVO$_4$ films. Besides, the incorporation of Mo could decrease the average size of BiVO$_4$ with decreasing aggregation of the particles. The average diameter of pure BiVO$_4$ is about 280 nm (Figure 1a), and the average diameter of Mo-doped BiVO$_4$ are ranging from 200 to 250 nm, which are smaller than that of pure BiVO$_4$ (Figures 1b–d). Besides, the smaller particle size of the as-prepared photocatalyst could provide more available active sites, which could be in favor of the PEC performance.

Figure 2A compares the XRD (X-Ray Diffraction) patterns of pure and Mo-doped BiVO$_4$ films with different concentrations of Mo dopant. All the diffraction peaks are assigned to phase-pure monoclinic sheelite BiVO$_4$ structure (JCPDS No. 14-0688). Since the films are very thin, the diffraction peaks of FTO substrate are also observed in XRD. No noticeable peaks of MoO$_3$ is detected in the Mo-doped BiVO$_4$, the results are consistent with previous study (Berglund et al., 2012; Luo et al., 2013; Chen et al., 2015; Nair et al., 2016; Thalluri et al., 2016). Additionally, the main peaks of the monoclinic BiVO$_4$ structure shift to lower intensity and higher scattering angles in the Mo-doped BiVO$_4$ films since the radius of Mo is higher than that of V. This represents a shrinkage or an enlargement of the $d$ spacing of corresponding crystal planes due to incorporation of dopant cations into V sites of BiVO$_4$ (Parmar et al., 2012). As the pure phase and modification in $d$ spacing, it can be calculated that the Mo have been effectively incorporated into the crystal lattice of BiVO$_4$ with the monoclinic phase unchanged (Parmar et al., 2012). Furthermore, the crystallite sizes calculated by using the Scherrer formula are 110, 117, 83, 85 nm for the BiVO$_4$, BiVO$_4$(Mo-1), BiVO$_4$(Mo-3), BiVO$_4$(Mo-5), respectively.

Though XRD shows some trace that Mo have been doped in the crystal of pure BiVO$_4$. However, it is too rough to identify the doping sites in the crystal lattice because of the low doping concentration. To probe the doping sites and local distortions of Mo-doped BiVO$_4$, the Raman spectra were measured and the results are shown in Figure 2B. The Raman mode located at 829 cm$^{-1}$ is assigned to the symmetric stretching mode of VO$_3^{2-}$ units. It is clear that the symmetric stretching mode in Mo-doped BiVO$_4$ shifts to a lower wave number, which suggests Mo$^{6+}$ substitutes V$^{5+}$ in the VO$_3^{2-}$ tetrahedron (Luo et al., 2013; Zhang et al., 2014).

Optical properties of the films are very important for the PEC performance. Figure 3A displays the UV-Vis DRS absorption
spectra of the four films. All of the films present a strong absorption in the UV-Vis range, and the incorporation of Mo can hardly affect the absorption edges of BiVO$_4$. Besides, there isn’t any peak shift in the UV-Vis spectra of Mo-doped films, which indicates there is not existence of the phase transfer from monoclinic to tetragonal structures with doping of Mo (Figure 3A; Pattengale and Huang, 2016). As the pure BiVO$_4$ shows a larger optical absorbance at wavelengths (>325 nm), thus the pure BiVO$_4$ are less porous than the Mo-doped BiVO$_4$ (Nair et al., 2016).

The optical band gap energy can be calculated by the following equation:

$$\alpha h\nu = A(h\nu - E_g)^n/2$$

where, $\alpha$, $h\nu$, $A$, and $E_g$ are the absorption coefficient, photo energy, constant and band gap energy, respectively. The value of $n$ depends on whether the transition is direct ($n = 1$) or indirect ($n = 4$). The bandgap of all the films are about 2.5 eV (Figure 3B), which is consistent with the reported band gap of BiVO$_4$ (Zhang et al., 2014). This result indicates that the incorporation of low amount of Mo could hardly influence the bandgap of BiVO$_4$, and it is considered to be the characteristic band gap of monoclinic phase of BiVO$_4$.

In the experiments, the SO$_2$ gas was absorbed by NaOH solutions and the concentration of SO$_3^{2-}$ was detected. Through analyzing, the removal efficiencies of SO$_2$ gas were about 98%, it indicated that the absorption method could removal SO$_2$ completely. In order to determine the PEC properties of the photoelectrodes, the Linear Sweep Voltammograms (LSV) were measured both in dark and under AM 1.5 G illumination (100 mW cm$^{-2}$; Figure 4). After analyzing the photocurrent densities of the photoanodes in different electrolyte systems after absorbing SO$_2$ (Figure 4A), it is concluded: (1) the photocurrent densities are negligible under dark conditions in different electrolyte systems; (2) the photocurrent densities could be significantly enhanced after inletting SO$_2$ into electrolyte. Since the introduction of SO$_2$ into electrolyte, the concentration of SO$_3^{2-}$ could be increased, and the oxidation reaction of SO$_3^{2-}$ needs lower activation energy and kinetically faster than that of water, thus the formed SO$_3^{2-}$ consumes the photogenerated holes instantaneously and generates a higher photocurrent density than that of water. Though the doping of Mo could decrease the light-absorbing slightly (Figure 3A), but it could
significantly enhance the bulk charge carrier transportation of BiVO$_4$. Therefore, the PEC performance of Mo-doping BiVO$_4$ is higher than that of BiVO$_4$. The photocurrent density is greatly dependent on the amount of SO$_2$ absorbed in the electrolyte. In NaOH(aq)+SO$_2$(g)-3, the photocurrent density is improved by 1.2 times, 1.6 times, and 5 times than that of NaOH(aq)+SO$_2$(g)-2, NaOH(aq)+SO$_2$(g)-1, NaOH(aq) at 0.5 V vs. Hg/HgO, respectively. The photocurrent density is significantly improved by 5 times as compared with our previous research on porous BiVO$_4$ (Han et al., 2017).

Compared with the four different electrode films in NaOH(aq)+SO$_2$(g)-3 electrolyte, it is clear that BiVO$_4$(Mo-3) displayed an outstanding PEC performance. The photocurrent density of BiVO$_4$(Mo-3) is 1.7 times than that of BiVO$_4$(Mo-1), 2 times than that of BiVO$_4$(Mo-5), and 5 times than that of BiVO$_4$ at 0.5 V vs. Hg/HgO (Figure 4B). The current densities of BiVO$_4$(Mo-3) in NaOH(aq) with and without SO$_2$(g)-3 at 0.6 V vs. Hg/HgO are ca. 0.6 and 0.1 mA cm$^{-2}$, respectively; the current density in NaOH(aq)+SO$_2$(g)-3 is 6 times higher than that in NaOH(aq). On the other hand, the evolution rate of H$_2$ in NaOH(aq)+SO$_2$(g)-3 (39.4 µmol h$^{-1}$ cm$^{-2}$) is more than 40 times higher than that in NaOH (0.92 µmol h$^{-1}$ cm$^{-2}$) in the Table 2. The above results indicate that the amount of Mo at 3 atom% could be an optimal choice.

The experiments for H$_2$ evolution in different systems were measured with a two-electrode configuration at a bias of 1.6 V under AM 1.5G irradiation. Figure 5A shows the amount of H$_2$ evolved in different systems and Table 2 summarized the data of current densities, theoretical/experimental evolution rates of H$_2$ and the Faradaic efficiencies in the different systems. Comparing each photoanodes in different solution systems, it is clear that the SO$_2$ reduction could significantly facilitate the current density and evolution rate of H$_2$, which is in good agreement with our previous research (Han et al., 2017). Besides, the current density and evolution rates for BiVO$_4$(Mo-1, 3, 5) under light irradiation are higher than that under the dark condition. Furthermore, all of the Mo doped BiVO$_4$ photoanodes show more attractive performance than that of pure BiVO$_4$, and the BiVO$_4$(Mo-3) performed the best H$_2$ generation activities. As calculated, a highest H$_2$ evolution rate of 39.4 µmol h$^{-1}$ cm$^{-2}$ is realized in NaOH(aq)+SO$_2$(g)-3 with BiVO$_4$(Mo-3) as photoanode, and the H$_2$ evolution rate is only 0.19 µmol h$^{-1}$ cm$^{-2}$ in NaOH(aq) with the BiVO$_4$ as photoanode, suggesting the H$_2$ production can be enhanced about 200 times with the removal of SO$_2$ simultaneously with 3 atom% Mo-doped BiVO$_4$. Furthermore, the theoretical evolution rates of H$_2$ are close to theoretical rates in each system, indicating a high Faradaic efficiency of H$_2$ production (higher than 95%). Besides, the catalysts could not dissolve although the solution is a strong basic aqueous solution.

TABLE 2 | The current density, theoretical and experimental evolution rate of H$_2$, and the Faradaic efficiency in different electrolytes [A—0.1 M NaOH; B—NaOH(aq)+SO$_2$(g)-3].

| Items | BiVO$_4$ | BiVO$_4$(Mo-1) | BiVO$_4$(Mo-3) | BiVO$_4$(Mo-5) |
|-------|---------|--------------|--------------|--------------|
|       | A | B | A | B | A | B | A | B |
| Current density/mA cm$^{-2}$ | 0.01 | 0.8 | 0.005 | 0.03 | 1.85 | 0.007 | 0.05 | 2.1 | 0.004 | 0.023 | 1.6 |
| Theoretical evolution rate of H$_2$/µmol h$^{-1}$ cm$^{-2}$ | 0.19 | 14.8 | 0.092 | 0.55 | 34.2 | 0.13 | 0.92 | 39.4 | 0.075 | 0.43 | 29.6 |
| Experimental evolution rate of H$_2$/µmol h$^{-1}$ cm$^{-2}$ | 0.18 | 14.4 | 0.088 | 0.54 | 33.7 | 0.126 | 0.90 | 38.8 | 0.071 | 0.41 | 29.2 |
| Faradaic efficiency/% | 95 | 97 | 96 | 98 | 99 | 97 | 98 | 98 | 95 | 95 | 99 |
In order to better understand the structure reconstruction with/without Mo doping, the geometric structures of pristine and the Mo-doped BiVO₄ were compared in Figure 6. It is clear that the doping of Mo could increase the length of Bi-O bonds. This phenomenon indicates that the original coordinated O atoms are “shifted” toward the doped Mo sites, and introduce “oxygen vacancies.” As well-known, the oxygen vacancies could play an important role in improving the photocatalytic performance. Besides, the Mo⁶⁺ ion substitute the V site in monoclinic sheelite BiVO₄ could improve the transportation of photoinduced carriers, which could facilitate the charge carrier separation and leads to suppressed bulk recombination (Ding et al., 2014). Therefore, the photocatalytic activity is enhanced significantly after Mo-doping, as shown in Figure 4.

With the existence of flue gas SO₂ removal, SO₃²⁻ was formed in electrolyte solution. Then the photo-generated holes could be more quickly consumed by the formed SO₃²⁻ than that without SO₃²⁻ (pure NaOH solution), because oxidation of SO₃²⁻ has a much lower activation energy and kinetically much faster than water oxidation or OH⁻ oxidation (McDonald and Choi, 2012; Seabold and Choi, 2012). The oxidation of SO₂ is thus proposed to replace the oxygen evolution reaction in water splitting, which can improve the water splitting efficiency and reduce the cost of H₂ production. The whole process for SO₂ removal with simultaneous production of H₂ is thus summarized and illustrated in Figure 7. Mo-doped BiVO₄ is first excited to generate e⁻ in conduction band (CB) and create hole (h⁺) in the valence band (VB) at the same time. With the assistance of space charge layer and extra bias, the e⁻ transfer to the cathode and participate in cathode reaction for H₂ production. While the formed of SO₃²⁻ after flue gas SO₂ absorption is oxidized by the holes on the photoanode. As the Mo incorporated in BiVO₄ could improve the electronic conductivity of pure BiVO₄ (Luo et al., 2011; Pilli et al., 2011), therefore, the e⁻ produced in Mo doped...
BiVO₄ moves faster than that produced in BiVO₄, and shows a significantly increased photocurrent density (Figure 4) and rate of H₂ production (Figure 5). The reactions are summarized as following:

\[
\text{SO}_2(g) + \text{OH}^- \rightarrow \text{HSO}_3^- \quad (5)
\]

\[
\text{HSO}_3^- + \text{OH}^- \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O} \quad (6)
\]

Reaction on photoanode (Mo-doped BiVO₄ film):

\[
\text{SO}_3^{2-} + 2\text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + 2e^- \quad (7)
\]

Reaction on cathode (Pt wire):

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \quad (8)
\]

The total reaction:

\[
\text{SO}_2(g) + 2\text{OH}^- \rightarrow \text{H}_2(g) + \text{SO}_4^{2-} \quad (9)
\]

CONCLUSIONS

In summary, the effect of Mo doping on BiVO₄ used as photoanode for H₂ production with simultaneously flue gas SO₂ removal is investigated. The 3 atom% Mo-doped BiVO₄ (BiVO₄(Mo-3)) possessed the best PEC activity due to its better charge carrier transportation. With the help of Mo, the H₂ evolution rate and SO₂ removal rate of Mo-doped BiVO₄ almost 3 times higher than pristine BiVO₄. Through this process, the SO₂ in flue gas is removed and collected to produce H₂, which could greatly reduce the cost of desulphurization process, and even make it profitable.

AUTHOR CONTRIBUTIONS

JH: assisted in design of the experiments and wrote the manuscript; KL: performed the experiments and wrote the manuscript; HC: assisted in the analysis and interpretation of the data; LZ: planned the project, designed the experiments, and also wrote the manuscript.

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