Effects of Al₂O₃ Coating on BiVO₄ and Mo-doped BiVO₄ Film for Solar Water Oxidation

Maheswari Arunachalam¹, Gun Yun², Hyo Seok Lee³, Kwang-Soon Ahn⁴, Jaeyeong Heo³, and Soon Hyung Kang^{2,*}

¹Department of Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, South of Korea

²Department of Chemistry Education and Optoelectronic Convergence Research Center, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, South of Korea

³School of Materials Science and Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, South of Korea

⁴School of Chemical Engineering, Yeungnam University, 280 Daehak-Ro, Gyeongsan, Gyeongsangbuk-do 38541, South of Korea

ABSTRACT

Planar BiVO₄ and 3 wt% Mo-doped BiVO₄ (abbreviated as Mo:BiVO₄) film were prepared by the facile spin-coating method on fluorine doped SnO₂(FTO) substrate in the same precursor solution including the Mo precursor in Mo:BiVO₄ film. After annealing at a high temperature of 450°C for 30 min to improve crystallinity, the films exhibited the monoclinic crystalline phase and nanoporous architecture. Both films showed no remarkably discrepancy in crystalline or morphological properties. To investigate the effect of surface passivation exploring the Al₂O₃ layer, the ultra-thin Al₂O₃ layer with a thickness of approximately 2 nm was deposited on BiVO₄ film using the atomic layer deposition (ALD) method. No distinct morphological modification was observed for all prepared BiVO₄ and Mo:BiVO₄ films. Only slightly reduced nanopores were observed. Although both samples showed some reduction of light absorption in the visible wavelength after coating of Al₂O₃ layer, the Al₂O₃ coated BiVO₄ (Al₂O₃/BiVO₄) film exhibited enhanced photoelectrochemical performance in 0.5 M Na₂SO₄ solution (pH 6.5), having higher photocurrent density (0.91 mA/cm² at 1.23 V vs. reversible hydrogen electrode (RHE), briefly abbreviated as V_{RHE}) than BiVO₄ film (0.12 mA/cm² at 1.23 V_{RHE}). Moreover, Al₂O₃ coating on the Mo:BiVO₄ film exhibited more enhanced photocurrent density (1.5 mA/cm² at 1.23 V_{RHE}) than the Mo:BiVO₄ film (0.86 mA/cm² at 1.23 V_{RHE}). To examine the reasons, capacitance measurement and Mott-Schottky analysis were conducted, revealing that the significant degradation of capacitance value was observed in both BiVO₄ film and Al₂O₃/Mo:BiVO₄ film, probably due to degraded capacitance by surface passivation. Furthermore, the flat-band potential (V_{FB}) was negatively shifted to about 200 mV while the electronic conductivities were enhanced by Al₂O₃ coating in both samples, contributing to the advancement of PEC performance by ultra-thin Al₂O₃ layer.

Keywords : Photoelectrochemical Water Splitting, Surface Passivation, Al₂O₃, Blocking Layer, Charge Recombination

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1. Introduction

Photoelectrochemical (PEC) water splitting using solar light source and proper semiconductor photoelectrode has been considered a sustainable hydrogen production method. To develop a high-

performance photoanode for water oxidation, half reaction under visible light, a semiconductor with a suitable band gap ($1.9 \text{ eV} < E_g < 3.1 \text{ eV}$), and a proper position of band gap decorated with a thin layer of water oxidation cocatalyst are required [1,2]. As a representative, BiVO₄ ($E_g = 2.4 \text{ eV}$) has emerged as one of the most promising photoanode materials to absorb more visible light with proper band position to evolve the hydrogen and oxygen from water photoelectrolysis and excellent stability of the liquid-solid interface [3,4]. Based on band gap

*E-mail address: skang@jnu.ac.kr (S.H.K)

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of 2.4 eV, the theoretical maximum photocurrent of $\sim 7.5 \text{ mA/cm}^2$ at one sun irradiation can be achieved [5]. However, most of BiVO_4 films still exhibit quite low PEC performance. The main reasons can be explained by an inefficient charge separation at the interface and unfavorable charge transportation through the photoelectrode, leading to the low photocurrent density in PEC working condition [6]. Thus, the heterojunction composed of the core and shell layer showing good band alignment could potentially cope with these weak points of BiVO_4 material. As a recent representative example, 1D cobalt-phosphate (Co-Pi) modified BiVO_4/ZnO junction showing cascading band alignment has exhibited a photocurrent of $\sim 3 \text{ mA/cm}^2$ at the highest photocurrent density [7]. This is probably due to enhanced visible light absorption and fast electron transport along 1D ZnO nanorods. Also, controlled growth of BiVO_4 layer on the inverse opal WO_3 photoanodes has been fabricated by a template-assisted route to form the heterojunction of the $\text{WO}_3/\text{BiVO}_4$ layer [8]. In the similar viewpoint, ultra-thin passivation layers have also been introduced on BiVO_4 photoanode as the blocking layer against charge recombination reaction and the photocorrosion [9]. Several materials have been already investigated, including TiO_2 , NiO_x , CoO_x , and Al_2O_3 [10-13]. Lewis et al. have reported that ultra-thin amorphous TiO_2 layers with a thickness of $\sim 1 \text{ nm}$ can suppress the photocorrosion, revealing a stable photocurrent of $\sim 1.4 \text{ mA/cm}^2$ at $1.23 \text{ V}_{\text{RHE}}$ under one sun irradiation during the testing of several hours [14]. Domen *et al.* have found that ultra-thin NiO_x layers with a thickness of $\sim 6 \text{ nm}$ can enhance PEC performance as well as photostability in CoO_x -coated BiVO_4 film, achieving solar-to-hydrogen efficiency of $\sim 1.5\%$ [15]. Kafizas et al. have investigated the effect of ultra-thin Al_2O_3 layer with an optimum thickness of approximately 0.33 nm , displaying a remarkable increase in theoretical solar photocurrent from $\sim 0.47 \text{ mA/cm}^2$ (uncoated BiVO_4 film) to $\sim 3.0 \text{ mA/cm}^2$ ($\text{Al}_2\text{O}_3/\text{BiVO}_4$ film), due to suppression of charge recombination reaction [16]. However, in this paper, there is no report on the doped BiVO_4 film which shows the more efficient PEC performance. Even though the surface state of pristine and doped BiVO_4 film is somewhat different, it can be expected that the introduction of ultra-thin Al_2O_3 layer on the doped

BiVO_4 film can contribute to the efficient photoelectrochemical activity.

Accordingly, we investigated the role of ultra-thin Al_2O_3 layer on the undoped and Mo-doped BiVO_4 (briefly abbreviated as Mo: BiVO_4) film and their PEC behavior was studied in detail. The Al_2O_3 layer with a thickness of approximately 2 nm was prepared on the BiVO_4 and Mo: BiVO_4 films by the atomic layer deposition (ALD) process and the effectiveness of surface passivation on undoped and doped BiVO_4 films was compared using several analyses tools. $\text{Al}_2\text{O}_3/\text{Mo}:\text{BiVO}_4$ films exhibited enhanced PEC performance, having a photocurrent of 1.5 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ compared to Mo: BiVO_4 film (0.91 mA/cm^2). Similarly, the $\text{Al}_2\text{O}_3/\text{BiVO}_4$ film exhibited improved photocurrent density of 0.86 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$, relative to BiVO_4 film (0.12 mA/cm^2). This may be due to the favorable charge transfer/transportation in the Mo: BiVO_4 film as well as the degraded charge recombination. Above different films, when cobalt-phosphate (Co-Pi) as a cocatalyst was covered on the top of the film, the maximum photocurrent density of 1.85 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ was obtained.

2. Experimental

2.1 Development of undoped and Mo: BiVO_4 films

An FTO (Pilkington TEC GlassTM, sheet resistance $8 \Omega \text{ sq}^{-1}$) as a substrate was prepared by following a cleaning process in deionized (DI) water, ethanol, and acetone for 20 min in each step to remove some organic contamination and dust. For spin-coating to make undoped BiVO_4 film, precursors composed of 0.2 M ammonium metavanadate in 5 mL deionized (DI) water and 5 mL $60 \text{ wt}\%$ HNO_3 solution were mixed and stirred continuously until turning to a transparent solution. Then 0.2 M bismuth nitrate in 10 mL methanol was added to complete the BiVO_4 solution. Prior to spin coating, the prepared solution was aged for one day. The spin-coating (a volume of $50 \mu\text{L}$) was performed under 1500 rpm for 20 sec to make a BiVO_4 film. In the case of $3 \text{ wt}\%$ Mo: BiVO_4 film, the composition of the prepared solution was the same as BiVO_4 except that $3 \text{ wt}\%$ sodium molybdate as an additional source material was added into the solution. The deposition procedure to make the Mo: BiVO_4 film was the same as that for making the BiVO_4 film. Finally, to enhance the crystallinity of as-formed undoped BiVO_4 and

Mo:BiVO₄ films, a post-thermal treatment was carried out at 500°C for 2 hrs in ambient air.

Thin Al₂O₃ layer (thickness = 2 nm) was deposited in an ALD vacuum chamber using trimethylaluminum (TMA, Al(CH₃)₃, EGChem, Inc.) and DI water as sources of Al and O, respectively. The growth temperature was 250°C. ALD sequences (precursor-pulse–reactant-pulse) were set to 0.1 s - 10 s - 0.4 s - 25 s for AlO_x. Its growth per cycle (GPC) was confirmed to be 0.144 nm/cycle. The as-deposited Al₂O₃ layer exhibited an amorphous crystalline phase or a weak crystallinity. Therefore, an additional annealing process was performed at 450°C for 30 min under an air atmosphere to improve the crystallinity.

Cobalt phosphate (Co-Pi) as a cocatalyst was deposited on the top of Mo:BiVO₄ films. The precursor solution for the Co-Pi layer was composed of 0.05M cobalt nitrate and 0.1M potassium phosphate buffer solution (pH 7) [17]. Electrodeposition above the film was applied under a constant potential of 1.0 V_{Ag/AgCl} for 20 sec. Finally, the film was rinsed with DI water and dried in N₂ flow.

2.2 Characterization

To determine the morphology of the surface and cross-section of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films, JEOL 7500 field-emission scanning electron microscopy (FE-SEM, JEOL Inc.) operating at 10 kV and 10 mA was utilized. Crystalline properties of films were investigated using a high-power X-ray diffraction (HP-XRD, X'Pert PRO Multi Purpose X-Ray Diffractometer) with Cu K_α radiation operating at 60 kV and 55 mA. Ultraviolet-visible (UV-vis) spectra of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films were recorded with a PerkinElmer UV-vis Lambda 365 spectrometer equipped with a diffuse reflectance accessory. PEC measurements involving current-voltage (*J-V*) characteristics under dark and illuminated conditions were conducted with a potentiostat (CHI Instruments, USA) using an Ag/AgCl reference electrode, a Pt mesh counter electrode, and BiVO₄ electrodes. A 150 W Xe lamp (100 mW/cm², AM 1.5 filter) as a light source and 0.5 M Na₂SO₄ solution (pH 6.5) after nitrogen bubbling to remove dissolved oxygen gas were employed to evaluate PEC performance. Incident photon to current efficiency (IPCE) was measured using a 150 W xenon light source and a monochromator (HS technologies, Korea).

Electrochemical impedance spectroscopy (EIS) of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films was also performed to evaluate cell resistance of each component in the PEC working condition under 1 sun illumination at open-circuit voltage (OCV). The frequency ranged from 0.1 Hz to 10 kHz at amplitude of ±10 mV. To evaluate flat-band potential (*V*_{FB}) and donor concentration of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films, Mott-Schottky plots (AUTOLAB/PGSTAT, 128N, Nova) with a frequency of 1 kHz were achieved with the same electrochemical configuration and electrolyte.

3. Results and Discussion

Fig. 1 shows FE-SEM images of the BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films. All films consisted of differently sized porous areas (briefly denoted as domains) separated from each other by thin grooves. In the case of BiVO₄ film (Fig. 1a), within a domain, wormlike pores with a size of several hundreds of nanometers were wholly distributed. Furthermore, the thin groove separating porous domains was completely separated through the entire film (not shown in here) with a thickness of about 200 nm. Meanwhile, the Mo:BiVO₄ film (Fig. 1b) exhibited wormlike pores with a size of several tens of nanometers, displaying a relative small amount of pore size ascribed to grain growth of BiVO₄ film blocked by the added Mo⁶⁺ cations [18]. Above these films, ultra-thin Al₂O₃ layer was deposited by ALD process. Their images are shown in Fig.

Fig. 1. FE-SEM images of (a) BiVO₄, (b) Mo:BiVO₄, (c) Al₂O₃/BiVO₄, and (d) Al₂O₃/Mo:BiVO₄ films.

Fig. 2. (a) XRD patterns and (b) absorbance spectra of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films.

1c and 1d. Al₂O₃/BiVO₄ and Al₂O₃/Mo:BiVO₄ films exhibited overall similar morphologies, but their wormlike nanopores in a domain were steadily reduced mainly due to steady growth of BiVO₄ grains with an additional thermal annealing process under 450°C, not contributed from just 2-nm thick Al₂O₃ layer. Entirely Al₂O₃ covered nanoporous BiVO₄ films were observed.

Crystalline characteristics and optical properties of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films were surveyed using XRD measurement (Fig. 2a) and UV-VIS spectroscopy (Fig. 2b). Dotted vertical lines in Fig. 2a refer to peaks from the FTO substrate. The XRD pattern of the pristine BiVO₄ film (Fig. 2a) after calcined at 500°C under air ambient showed well crystallized monoclinic structure corresponding to (013), (004), (024) and (116) planes with lattice parameters of $a = 5.195$, $b = 5.093$ and $c = 11.704$ Å, in excellent accordance with the standard data (JCPDS NO.: 83-1699) [19]. No other peaks for impurity or other binary or ternary compounds were found anywhere, thereby showing the development of a high-quality BiVO₄ film. In the case of Mo:BiVO₄ film, the position and intensity of all peaks had similar patterns to those of the BiVO₄ film probably due to the extremely small amount of molybdate precursor. Furthermore, no modification or change of peaks after Al₂O₃ coating was found through the entire film, only showing a little bit reduction of peak intensity. In addition, the average crystalline size was calculated using Scherrer's equation, considering the main peak of (221) plane in all samples. Average crystalline sizes of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films were 19.3 nm, 19.4 nm, 19.3 nm,

and 19 nm, respectively, disclosing no significant difference in average crystalline size even after deposition of thin Al₂O₃ layer.

Fig. 2b shows optical absorbance of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films fabricated on FTO substrate. The BiVO₄ and Mo:BiVO₄ film started to absorb light at the wavelength of 525 nm. Its overall absorbance spectra showed similar tendency. Meanwhile, the ultra-thin Al₂O₃ coated film showed degraded absorbance, showing a little bit reduction of the absorbance and the shift of onset wavelength toward longer wavelength. The exact direct optical bandgap (E_g) was determined for all samples by extrapolating linear portion of the $(\alpha h\nu)^2$ vs. $h\nu$ plot as shown in the inset of Fig. 2b, where α was the absorption coefficient and $h\nu$ was the incident photon energy [20]. Estimated E_g values of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films were 2.36 eV, 2.34 eV, 2.34 eV, and 2.20 eV respectively. The slightly reduced E_g value was observed in Mo:BiVO₄ film after the ultra-thin Al₂O₃ coating, indicating the formation of sub-bandgap just below the conduction band of Mo:BiVO₄ film, resulting in the extension of visible light absorption to wavelength of 560 nm.

To determine electronic characteristics of the BiVO₄ film, Mott-Schottky plots were measured in 0.5 M Na₂SO₄ solution as a function of applied potential. Results are displayed in Fig. 3. The Mott-Schottky plot (M-S plot) was involved in the capacitance (C) of the space charge region as a function of electrode potential under depletion conditions. It was based on the Mott-Schottky relationship of a semiconductor film. Accordingly, these results gave the information on carrier densi-

Fig. 3. Mott-Schottky plots of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films measured in 0.5 M Na₂SO₄ solution under dark condition.

Table 1. Flat band potential (V_{FB}) and donor densities (N_d) of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films.

Samples	Flatband potential (V_{FB} , V)	Donor density (N_d , cm ⁻³)
BiVO ₄	0.19	1.52×10^{17}
Mo:BiVO ₄	0.31	3.44×10^{18}
Al ₂ O ₃ /BiVO ₄	0.1	2.6×10^{17}
Al ₂ O ₃ /Mo:BiVO ₄	0.31	4.2×10^{18}

ties through the gradient $dV/d(1/C^2)$ of Mott-Schottky plots and flat band potential (E_{fb}) determined by extrapolating $C = 0$ [21].

$$N_d = \frac{2}{e_0 \epsilon \epsilon_0} \left[\frac{dV}{d(1/C^2)} \right] \quad (1)$$

where e_0 was electronic charge, ϵ was dielectric constant (~ 86) of BiVO₄, ϵ_0 was permittivity of the vacuum, N_d was donor density, and V was the applied voltage. All BiVO₄ films exhibited positive slopes as expected for n -type semiconductor. In particular, ultra-thin Al₂O₃ coated films showed smaller slope than pristine BiVO₄ and Mo:BiVO₄ films, manifesting increased carrier densities. Quantitatively calculated electron densities of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ were calculated to be 1.52×10^{17} , 3.44×10^{18} , 2.6×10^{17} , and 4.2×10^{18} cm⁻³, respectively. Here, Mo:BiVO₄ film showed approximately one order of magnitude higher donor densities than the pristine BiVO₄ film probably due to

Table 2. Quantitative value of ohmic resistance (R_s) and charge transfer resistance (R_{ct}) of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films fitted by using the suggested equivalent electrical circuit.

Samples	R_s (Ω)	R_{ct} (Ω)
BiVO ₄	102	72432
Mo:BiVO ₄	96	17012
Al ₂ O ₃ /BiVO ₄	94	4441
Al ₂ O ₃ /Mo:BiVO ₄	96	2904

increased carrier densities induced from Mo doping which could contribute to the improvement of electrical conductivities of Mo:BiVO₄ film [22]. In addition, the introduction of ultra-thin Al₂O₃ layer on the top surface of film improved carrier densities a little bit probably ascribed to the high probability of photo-generated charges surviving against the charge recombination reaction. The extent of high carrier densities was as follows: BiVO₄ < Al₂O₃/BiVO₄ < Mo:BiVO₄ < Al₂O₃/Mo:BiVO₄. In case of flat-band potential (V_{FB}), BiVO₄ and Mo:BiVO₄ films showed V_{FB} of 0.18 V_{RHE} and 0.28 V_{RHE}, respectively, whilst V_{FB} of 0.067 V_{RHE} and 0.16 V_{RHE} were obtained for Al₂O₃/BiVO₄ and Al₂O₃/Mo:BiVO₄ films, respectively. A little bit negative shift of V_{FB} was observed in Al₂O₃/BiVO₄ and Mo:BiVO₄ films probably due to the high-band gap Al₂O₃ ($E_g \approx 3.6$ eV) layer.

In order to investigate PEC activities of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films, linear sweep voltammograms (LSVs) were measured under AM1.5 illumination. Results are presented in Fig. 4a. The dark current of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films collected in the potential range between 0.0 and 1.5 V_{RHE} under the dark condition exists in the region of $\sim 10^{-3}$ mA/cm², showing no meaningful current values (not shown here). At first, onset potentials of BiVO₄ and Mo:BiVO₄ were near 0.33 and 0.19 V_{RHE}, respectively while Al₂O₃/BiVO₄ and Al₂O₃/Mo:BiVO₄ films exhibited onset potentials of 0.05 and 0.1 V_{RHE}, respectively, displaying a little bit negative shift of onset potential. These results were similar to those evoked from Mott-Schottky plot probably due to surface passivation from the ultra-thin Al₂O₃ layer. Herein, the photocurrent density (J) of 0.12 mA/cm² at 1.23 V_{RHE} was achieved for the pristine BiVO₄ film. On the other hand, the

Fig. 4. (a) J - V curves of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, Al₂O₃/Mo:BiVO₄, and Co-Pi/ Al₂O₃/Mo:BiVO₄ films under solar light (100 mW/cm² with AM 1.5) in 0.5 M Na₂SO₄ solution and (b) IPCE spectra of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, Al₂O₃/Mo:BiVO₄, and Co-Pi/ Al₂O₃/Mo:BiVO₄ films measured with applied potential of 1.23 V_{RHE} in 0.5 M Na₂SO₄ solution.

Mo:BiVO₄ film had a quite high J value of 0.86 mA/cm² at 1.23 V_{RHE}. On the contrary, Al₂O₃/BiVO₄ and Al₂O₃/Mo:BiVO₄ films showed J values of 0.91 mA/cm² and 1.5 mA/cm² at 1.23 V_{RHE}, respectively. These results indicated that the ultra-thin Al₂O₃ layer promoted J values of intrinsic BiVO₄ and Mo:BiVO₄ films. Furthermore, the Co-Pi cocatalyst was deposited on the top surface of Al₂O₃/Mo:BiVO₄ films, showing the most enhanced J value of 1.85 mA/cm² at 1.23 V_{RHE} due to favorably hole transfer to the electrolyte under the cascading hole transferring phenomenon.

To determine photoactivities as a function of the illuminated wavelength of BiVO₄, Mo:BiVO₄, and Al₂O₃ deposited films, we quantitatively investigated the photoactivity as a function of wavelength of incident light referred to as incident photon-to-current conversion efficiency (IPCE). IPCE measurements were performed for BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films using an applied potential of 1.23 V_{RHE} (Fig. 4b). IPCE can be generally expressed by the following equation [23];

$$\text{IPCE} = (1240J)/(\lambda \cdot J_{\text{light}}) \quad (2)$$

where J is the measured photocurrent density at a specific wavelength, λ is the wavelength of incident light, and J_{light} is the measured irradiance at a specific wavelength. In comparison with the pristine BiVO₄ film, Mo:BiVO₄ films exhibited significantly enhanced IPCE over the entire UV and visible light region. Particularly, the onset wavelength to start to give a meaningful photo-response was tremendously shifted from 510 nm to 530 nm, further going to

550 nm (Al₂O₃/Mo:BiVO₄) and 570 nm (Co-Pi/Al₂O₃/Mo:BiVO₄). These results provide direct evidence showing increased visible light photoresponse of Mo:BiVO₄ film by Mo doping thanks to more survived photogenerated charges from the deposition of ultra-thin Al₂O₃ layer against the charge recombination process. In addition, the Mo:BiVO₄ film exhibited IPCE of 15.6% (@486 nm) whereas the BiVO₄ film had an IPCE of 5.7% (@486 nm). Al₂O₃ coated samples exhibited IPCE of 22% (Al₂O₃/Mo:BiVO₄) and 7% (Al₂O₃/BiVO₄) at the same wavelength, indicating that charge transfer/transportation events were very efficient in these Mo-doped and Al₂O₃-coated samples. Moreover, the Co-Pi deposited Al₂O₃/Mo:BiVO₄ film showed remarkably red-shifted IPCE curve, containing a shift of λ_{max} toward 500 nm having an IPCE value of 22.5% promoted by the more contribution of visible light-induced charges. Therefore, both Mo-doping and Al₂O₃ coating contributed to the improvement of PEC performance mainly coming from the more charges photogenerated from visible light.

To definitely examine the interfacial issues, electrolyte interface capacitance as a function of the applied potential under dark condition was measured using the electrochemical capacitive current scan method [24]. Results are presented in Fig. 5a. Both BiVO₄ and Mo:BiVO₄ films exhibit a peak centered at about +0.75 V_{RHE} previously characterized as evidence for a surface state by Bard et al [25]. However, these peaks disappeared after the deposition of ultra-thin Al₂O₃ layer, proving the role of surface passivation. Overall, capacitance values of BiVO₄ and Mo:BiVO₄ films were significantly decreased, mani-

Fig. 5. (a) Capacitance value as a function of the applied potential for BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films under dark condition and (b) Nyquist plots of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ film containing fitted data using the suggested equivalent circuit in the inset of (b).

festing that the insulating Al₂O₃ layer as an outermost layer could dramatically reduce charge storage in the BiVO₄ film, enabling fast charge transfer or blocking nearby films or electrolyte.

To investigate minutely the interfacial working condition according to Mo-doping and Al₂O₃ coating in the BiVO₄ film, EIS measurements under dark condition were conducted. Results are shown in Fig. 5b. Fig. 5b compares the Nyquist plots for BiVO₄, Mo:BiVO₄ and Al₂O₃ coated films including the fitting data using the equivalent circuit in which R_s indicates the series resistance which includes FTO substrate, the resistance associated with the ionic conductivity in the electrolyte, and the external contact resistance. R_{ct} is related to the semiconductor/electrolyte charge transfer resistance at the low-frequency arc [26]. In our system, similar R_s of about 98 (± 4) Ω was achieved in the similar working condition. R_{ct} of the intrinsic BiVO₄ film was about 10⁴ value, existing a quite high value. The Mo:BiVO₄ film exhibited abruptly reduced R_{ct} of about 17000 Ω further showing decreased R_{ct} values after Al₂O₃ coating. This may be explained by the beneficial charge transfer at the interfacial region in the Mo:BiVO₄ film that was further improved by the introduction of ultra-thin Al₂O₃ layer to the scale of 10³. This dedicates that the Al₂O₃ layer can promote photogenerated hole transfer from the electrode to electrolyte as well as passivate the surface defect or traps sites, leading to more survived photogenerated charges to enhance PEC performance. To clearly confirm the extent of charge recombination, the open-circuit photovoltage was measured, presented

Fig. 6. Open-circuit voltage decay curve of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films as a function of time after turning off the light.

in Fig. 6. The photovoltage-time (*V*-*t*) profile of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films and the decay lifetimes of each *V*-*t* spectra by fitting to a biexponential function with two-time constants were calculated [27].

$$y(t) = A_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (3)$$

$$\tau_m = (\tau_1 \tau_2) / (\tau_1 + \tau_2) \quad (4)$$

where τ_m is the harmonic mean of the lifetime, and the total half-life is $\log(2 \times \tau_m)$. The total half-life of BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films was estimated to be 2.58s, 1.10s, 1.31 and 0.89s respectively. This result indicates that the Al₂O₃/BiVO₄ film shows shorter decay lifetime

Fig. 7. Photocurrent density as a function of time for BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films in 0.5 M Na₂SO₄ solution.

than that of BiVO₄ and Mo:BiVO₄ films. This was resulted from the modification of BiVO₄ to form the ultra-thin Al₂O₃ layer as well as the Mo doping, which favored good electron transporting paths by the Mo doping and suppressed recombination of photoinduced carriers from the ultra-thin Al₂O₃ layer.

It is well known that the ultra-thin Al₂O₃ layer can block photocorrosion of BiVO₄ layer under illumination. To confirm the photostability of Al₂O₃ coated films in our system, changes of photocurrent densities as a function of time were detected for BiVO₄, Mo:BiVO₄, Al₂O₃/BiVO₄, and Al₂O₃/Mo:BiVO₄ films at a constant potential of 1.23 V_{RHE} for 30 min. Results are displayed in Fig. 7. Both pristine and Mo:BiVO₄ films exhibited steadily decrease of *J* value as time went by. Reversely, ultra-thin Al₂O₃ coated films maintained almost the same *J* value compared to their initial *J* values. These results indicate that the ultra-thin Al₂O₃ layer can also suppress the corrosion of photoelectrode under illumination in our system.

In summary, uniform coating of thin Al₂O₃ layer having a thickness of approximately 2 nm on BiVO₄ and Mo:BiVO₄ films was successfully developed. Based on these well-made Al₂O₃/BiVO₄ and Al₂O₃/Mo:BiVO₄ films, the PEC performance of Al₂O₃/Mo:BiVO₄ film was found to be the highest, showing photocurrent density of 1.5 mA/cm² at 1.23 V_{RHE} attributable to the improved electronic conductivity deduced from Mo doping and surface passivation on the defect or trap sites from ultra-thin Al₂O₃ layer as

well as to favorably transfer of photogenerated holes to electrolyte. In particular, the interfacial resistance (*R*_{ct}) was sharply reduced in the Mo-doped and Al₂O₃ coated BiVO₄ film. This demonstrates that deposition of ultra-thin Al₂O₃ layer on the top of BiVO₄ film can grant a favorable environment for charge transport/transfer in the film irrelevant to the presence or absence of doping.

4. Conclusions

BiVO₄ and Mo:BiVO₄ films were prepared by the facile sol-gel assisted spin-coating method. Ultra-thin Al₂O₃ layer with a thickness of 2 nm was uniformly coated by the ALD process. All films were composed of differently sized porous area, separated from each other by thin grooves. Above these films, ultra-thin Al₂O₃ layer steadily reduced wormlike nanopores, showing uniformly coated nanoporous layer through the entire surface of BiVO₄ film. Overall, Al₂O₃/Mo:BiVO₄ film exhibited the highest photocurrent density (1.5 mA/cm² at 1.23 V_{RHE}), followed by Al₂O₃/BiVO₄ film (0.91 mA/cm²), Mo:BiVO₄ film (0.86 mA/cm²), and BiVO₄ film (0.12 mA/cm²). This is from the enhanced electronic conductivity of Mo doping in the BiVO₄ film and coating of ultra-thin Al₂O₃ layer to retard the charge recombination reaction as well as the beneficial hole transfer to the electrolyte. Herein, the Co-Pi layer as a cocatalyst was deposited on the Al₂O₃/Mo:BiVO₄ film, displaying a photocurrent density of 1.85 mA/cm² at 1.23 V_{RHE} due to low interfacial resistance to promote favorable hole transfer to the electrolyte. The IPCE curve also showed the highest value of about 22.5% at 500 nm for Co-Pi/Al₂O₃/Mo:BiVO₄, followed by 22% for Al₂O₃/Mo:BiVO₄, 7% for Al₂O₃/BiVO₄, and 5.7 % for BiVO₄ at wavelength of 486 nm. From Mott-Schottky plot, Al₂O₃/Mo:BiVO₄ film showed the highest electronic conductivity probably due to Mo doping and surface passivation of ultra-thin Al₂O₃ layer at the defect or trap sites, leading to reduced electron-hole recombination. These results were similar to the trend of interfacial resistance (*R*_{ct}) in the Nyquist plot obtained from EIS measurement, showing that Mo doping and the coating of Al₂O₃ layer together induced the abrupt decrease of *R*_{ct}, overall influencing the advancement of PEC activity. Taken together, these results indicate that coating or deposition of proper materials in the thin film can

modify or alternate thin film to enhance its PEC performance.

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