Facile morphology control strategy to enhance charge separation efficiency of Mo:BiVO$_4$ photoanodes for efficient photoelectrochemical water splitting

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**ABSTRACT**

Bismuth vanadate (BiVO$_4$) is one of the promising earth-abundant semiconducting materials for photoelectrochemical (PEC) water splitting. However, BiVO$_4$ suffers from poor charge separation efficiency due to its low carrier mobility and short minority carrier diffusion length. Nanostructured BiVO$_4$ photoanodes provide a simple way to improve charge separation efficiency. Here, we propose a facile nanostructuring strategy for enhancing the PEC performance of molybdenum-doped BiVO$_4$ (Mo:BiVO$_4$) photoanodes by varying the molecular weight of poly(ethylene glycol) (PEG) as a pore former. It was demonstrated that the grain and pore sizes of Mo:BiVO$_4$ could be controlled by changing the molecular weight of PEG. Nanoporous Mo:BiVO$_4$ photoanodes with optimized grain and pore sizes revealed an effective charge separation efficiency of 72% and showed the highest photocurrent density of 2.2 mA cm$^{-2}$ at 1.23 V versus the reversible hydrogen electrode (V$_{RHE}$). After hydrogen treatment and decoration of nickel iron (oxy)hydroxide (NiFeOOH) as an oxygen evolution catalyst, a stable photocurrent density of 4.5 mA cm$^{-2}$ with a 10-h duration was achieved at 1.23 V$_{RHE}$ under standard 1-sun illumination. Our findings clearly suggest new insights on a simple strategy to improve the PEC performance of nanostructured Mo:BiVO$_4$ photoanodes.

1. Introduction

Photoelectrochemical (PEC) water splitting, which generates hydrogen using sunlight, has been suggested as an eco-friendly and renewable fuel production strategy to replace fossil fuels [1]. In a typical PEC cell, a semiconductor produces electron–hole pairs by absorbing photons of energy equal to or higher than its band gap that carry out the water reduction–oxidation process on the surface of the photoelectrode. Because the water oxidation involving a four-hole transfer process is considered to be the rate-determining step in PEC water splitting, many PEC research studies have aimed to develop highly efficient photoanodes. Generally, metal oxides are considered attractive photoanode materials due to their low-cost synthesis and higher stability than other semiconductors [2]. Among them, bismuth vanadate (BiVO$_4$) exhibits great promise owing to its high photocurrent density around 4–6 mA cm$^{-2}$, which is close to its theoretical photocurrent density of 7.5 mA cm$^{-2}$ (based on the band gap of 2.4 eV); high photovoltage of ~ 1 V; and photochemical stability in near-neutral aqueous medium [3]. However, the PEC performance of BiVO$_4$ photoelectrodes is limited due to their poor charge separation efficiency caused by their low carrier mobility (<1 cm$^2$ V$^{-1}$ s$^{-1}$) and short hole diffusion length [4]. In this regard, a viable strategy to enhance the charge separation efficiency is required to achieve high-performance BiVO$_4$ photoelectrodes.

Previous reports have suggested that either the substitutional doping of V$^5+$ with metal ions such as Mo$^6+$ and W$^6+$ or the creation of oxygen vacancies via H$_2$ or N$_2$ posttreatment could enhance the charge separation efficiency because of the improved electrical conductivity of doped BiVO$_4$ [5]. Other studies have suggested that the built-in electric field induced by band bending through the formation of heterojunctions (e.g., BiVO$_4$/WO$_3$) [6,7] or coating of oxygen evolution reaction (OER) catalysts (e.g., nickel iron oxide (NiFeO$_x$) [8], Co-Pi [9], and MnO$_x$ [10]) could promote charge separation. However, the heterogeneous interface formation and aliovalent doping might cause charge recombination due to the increased trap sites. The simplest way to improve the charge separation efficiency is to nanostructure BiVO$_4$ photoanodes, shortening the carrier travel distance so that more photogenerated holes can...
participate in the OER without the detrimental recombination. Various researchers have engineered the dimensional morphology, porosity and crystallographic orientation of film, while these nanostructured photoanodes have additional advantages of desirable optoelectronic properties including large specific surface area and efficient light absorption [11–16]. However, how the grain size of BIVO affects the charge separation efficiency is hardly investigated. Indeed, the grain size of a photoelectrode can play an important role in achieving high PEC performance, as the charge transport and surface band bending may vary depending on the grain size. [11,17–19].

A variety of nanostructured BIVO photoanodes such as nanorods and nanoporous structures have been fabricated by the hydrothermal technique, microwave-assisted synthesis, and electrodeposition [20–22]. However, the hydrothermal method is generally time-consuming and microwave-assisted synthesis requires complex equipment, while electrodeposition inevitably involves secondary phase formation, deteriorating the phase purity of BIVO [22,23]. Therefore, there is a need for a strategy enabling the nanostructuring of BIVO photoanodes without complicated processes and equipment. One possible method, metal organic decomposition (MOD), involves using a precursor solution of Bi and V in the presence of poly(ethylene glycol) (PEG) [24–27]. PEG is considered a suitable morphology-directing agent due to its non-toxicity, high solubility in many organic solvents, and easy decomposability without residue. The role of PEG as a pore former has been investigated by varying the amount of PEG. For example, Feng et al. demonstrated pore size-controlled nanoporous BIVO photoanodes by adjusting the amount of commercial PEG product (i.e., PEG 600, whose average molecular mass is 570–630). The optimized nanoporous BIVO photoanodes showed 3.5 mA cm−2 at 0.7 VvsRHE during sulfite oxidation. The enhanced PEC performance of nanoporous BIVO originated from the enhanced charge separation efficiency due to the enlarged surface area and multiple light scattering induced by nanostructuring [26]. Furthermore, PEG is capable of not only increasing the surface area but also controlling the grain size of the photoelectrode [28,29]. Meda et al. demonstrated grain size-controlled WO3 photoanodes by varying the molecular weight of various disper- sants, including PEG, while they were unable to fully elucidate its role in altering grain size [30].

Herein, we propose a facile nanostructuring strategy of molybdenum-doped BIVO (Mo:BIVO) photoanodes with the aid of PEG. Particle-like morphology with controlled grain and pore sizes for Mo:BIVO was obtained by varying the molecular weights of PEG in the precursor solution. Microstructural analysis revealed that the PEG can affect the grain growth rate, thereby determining the grain size and pore structure. In addition, the bulk charge separation efficiency of nanostructured Mo:BIVO was changed depending upon the grain size, in turn affecting the PEC performance. The nanostructured Mo:BIVO with large grain size not only induced large surface band bending but also retained low bulk transport resistance so that the charge carriers were easily separated and injected into the electrolyte without bulk recombination. Owing to the improved optoelectronic properties of nanostructured Mo:BIVO, the bulk charge separation efficiency increased up to 89% at 1.23 VvsRHE after the modification with hydrogen treatment. Finally, the optimized Mo:BIVO photoanodes demonstrated the photocurrent density of 4.5 mA cm−2 at 1.23 VvsRHE as well as stable operation for 10 h after decoration with a NiFeOOH co-catalyst.

Briefly, 50 mmol of SnCl2·2H2O (Sigma-Aldrich, 98%, USA) was dissolved in 5 ml of IPA. The precursor solution was spin coated on the FTO substrate at 2000 rpm for 30 s followed by annealing at 500 °C for 1 h on a hot plate under ambient conditions.

### 2.2. Fabrication of Mo:BIVO4 PEG photoanodes

First, 0.5 mol of Bi(NO3)3·5H2O (Sigma-Aldrich, 98%) was dissolved in 5 ml of glacial acetic acid (Duksan Pure Chemicals, Korea), and 0.075 mol of VO(acac)2 (Sigma-Aldrich, 98%) solution was prepared with 5 ml of methanol (Duksan Pure Chemicals, Korea). For the Mo solution, 0.075 mol of MoO2(acac)2 (Sigma-Aldrich, 98%) was dissolved in 5 ml of methanol. Each precursor was mixed with the stoichiometric molar ratio of Bi:(V + Mo) = 1:1 where the Mo doping concentration was 1 at% for Mo:BIVO4 photoanodes. For Mo:BIVO4 PEG precursor solutions, PEG 200 (molecular mass 190–210), PEG 300 (molecular mass 285–310), or PEG 400 (molecular mass 380–420) (Sigma-Aldrich) was added to Mo:BIVO4 precursor solutions after 20 min of ultrasonification. The amount of PEG added was fixed as the volume ratio between vanadium (V) precursor solution : PEG = 1 : 0.2 regardless of PEG molecular weight. The Mo:BIVO4 PEG solutions were then spin coated on the FTO/SnO2 substrate at 1500 rpm for 20 s. After the spin coating, the substrates were immediately annealed on a hot plate at 400 °C for 7 min under ambient air conditions. The repeated spin-coating and annealing processes were performed seven times to obtain a desired and followed by annealing at 480 °C for 30 min in a box furnace with a ramping rate of 10 °C per min. Finally, copper wire and silver paste were employed to form a contact with the electrode. Epoxy resin (Hysol 9642, Henkel, Düsseldorf, Germany) was selectively applied for covering the electrode excluding an active area (~0.1 cm2) exposed to the electrolyte.

### 2.3. Hydrogen treatment of Mo:BIVO4 PEG film

For hydrogen treatment, the Mo:BIVO4 films were annealed under a 5% H2/95% Ar atmosphere in a tube furnace. The flow rate was kept constant at 200 sccm, and the heating rate was 10 °C per min. Annealing temperatures of 200–300 °C were used with a fixed duration of 20 min.

### 2.4. NiFeOOH deposition on surface of Mo:BIVO4 PEG film

The NiFeOOH co-catalysts were deposited by photo-assisted electrodeposition (PED) under AM 1.5 G illumination according to the reported procedure [8]. Briefly, 60 mg of FeSO4·7H2O (>99%; Sigma-Aldrich) and 20 mg of NiSO4·6H2O (99%; Sigma-Aldrich) were dissolved in 200 ml of 0.5 M potassium hydrogen carbonate (KHCO3) aqueous solution. The solution was purged with Ar gas before and during the deposition. For deposition, under standard 1-sun illumination, linear sweep voltammetry (LSV) was conducted with a bias from −0.3 V to 0.5 V against the reference electrode (Ag/AgCl/KCl (4 M)) 18–22 times with pretreatment of −0.3 V for 5 s. The scan rate was 50 mV s−1. After deposition, the photoelectrode was washed with copious amounts of DI water and dried at 100 °C for 1 h under ambient air conditions on a hot plate.

### 2.5. Characterization of optical and structural properties

The surface and cross-sectional microstructures of the Mo:BIVO4 photoanodes were examined using a field emission scanning electron microscope (SEM, JSM-IT500HR, JEOL, Japan). The mean grain size and pore size of the Mo:BIVO4 photoanodes were obtained by measuring the diameters of 100 randomly selected grains as shown in the SEM images. To estimate the porosity and pore size, the SEM images were analyzed using ImageJ software (Wayne Rasband, National Institutes of Health, USA). A UV−vis spectrophotometer equipped with an integrating sphere (V-670, JASCO, Easton, MD, USA) was employed for determining the optical properties of the Mo:BIVO4 photoanodes. The
crystal phase was determined using X-ray diffraction (XRD) (MiniFlex 600, Rigaku, Japan) with Cu Kα radiation (λ = 0.15406 nm). The 0-20 scan mode was used for the XRD analysis. The surface chemical information of Mo:BiVO₄ before and after the H₂ treatment was analyzed via X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific Inc., UK). All XPS spectra were calibrated using the C 1 s peak, which has a binding energy of 284.6 eV, and the background was fitted using the Shirley method; fitting curves for the deconvolution of O 1 s peak were determined using a Gaussian peak function. Transmission electron microscopy (TEM) and elemental mapping were performed using a JEM-200F (JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS) at an acceleration voltage of 200 kV.

2.6. PEC characterizations

The PEC measurements, including LSV and chronoamperometry, were conducted using a potentiostat (SI 1287, Solartron, UK) with a typical three-electrode system with an Ag/AgCl/KCl (4 M) reference electrode and a Pt wire as the counterelectrode. A commercial AM 1.5 G solar simulator and a Si reference cell (Newport Corporation, USA) were utilized for the simulated sunlight and 1-sun calibration, respectively. The applied potentials were based on the reversible hydrogen electrode (RHE) scale for comparison with other reports. The following equation was used to convert the potential:

\[ \text{E}_{\text{RHE}} = \text{E}_{\text{Ag/AgCl}} + 0.0591 \text{pH} + 0.197 \]  

(1)

EIS was conducted using the same potentiostat, along with a frequency analyzer (1260, Solartron, Leicester, UK). The series (Rₛ) and polarization resistance (Rₚ) of the Mo:BiVO₄ photoanodes were measured in 0.5 M potassium phosphate buffer (KPi) containing 0.5 M Na₂SO₄ (pH = 7.1) with the frequency range of 100 kHz to 1 Hz under 1-sun illumination at 0.8 V with an alternating-current amplitude of 10 mV. The M–S analysis was measured in 0.5 M KPi (pH = 7) under dark conditions with an amplitude of 10 mV at a frequency of 1 kHz. The incident photon to conversion efficiency (IPCE) measurements were conducted using an electrochemical workstation (Zennium, Zahner, Germany) and a potentiostat (PP211, Zahner, Germany) with a monochromatic light source (TLS03, Zahner) under 0.5 M KPi (pH = 7) at 1.23 V at the same three-electrode configuration.

2.7. Estimation of donor density and flat band potential

The M–S analysis was conducted in 0.5 M KPi (pH = 7) under dark conditions with a frequency of 1 kHz and an amplitude of 10 mV to obtain the donor density (Nₐ) and flat band potential (E₀). The capacitance of the space charge layer (Cₑ) can be expressed by the following equation:

\[ C_{e}^{-1} = \frac{2}{\varepsilon_{e} \varepsilon_{0} A^{2} N_{D}} (E - E_{fb} - \frac{K_{B} T}{e}) \]  

(2)

where \( \varepsilon_{e} \) is the vacuum permittivity (8.854 × 10⁻¹² F m⁻¹), \( \varepsilon_{0} \) is the relative permittivity of BiVO₄ ~ 86 [26], \( A \) is the electron charge (1.602 × 10⁻¹⁹ C), A is the surface area of the photoelectrode, E is the applied potential, \( E_{fb} \) is the flat band potential, \( k_{B} \) is the Boltzmann constant (1.381 × 10⁻²³ J K⁻¹), and \( T \) is the absolute temperature. The x-axis intercept of the tangent line in the plot indicates the flat band potential of the electrode.

Then, \( N_{D} \) can be calculated as follows:

\[ N_{D} = \frac{2}{\varepsilon_{e} \varepsilon_{0} e} \left( \frac{d(C_{e}^{-1})}{dE} \right)^{-1} \]  

(3)

2.8. Estimation of bulk charge separation efficiency and charge injection efficiency:

The measured photocurrent density from the water oxidation reaction (Jₚ) can be expressed as follows:

\[ J_{p} = J_{max} \times \eta_{abs} \times \eta_{light} \times \eta_{inj} = J_{abs} \times \eta_{light} \times \eta_{inj} \]  

(4)

where \( J_{max} \) is the maximum theoretical photocurrent density, \( \eta_{abs} \) is the light absorption efficiency, and \( J_{abs} \) is the maximum photocurrent density based on light absorption, whereas \( \eta_{light} \) and \( \eta_{inj} \) indicate the bulk charge separation efficiency and charge injection efficiency, respectively. \( J_{abs} \) can be calculated as follows:

\[ J_{abs} = \int_{\lambda_1}^{\lambda_2} \frac{\lambda}{1240} P_{abs}(\lambda) d\lambda \]  

(5)

where \( \lambda_{1} \) and \( \lambda_{2} \) are 300 nm and 515 nm, respectively, when considering the absorption edge of the BiVO₄ band gap energy (2.4 eV). \( P_{abs} \) indicates the actual power of light absorbed by the Mo:BiVO₄ photoanodes, which can be presented as follows:

\[ P_{abs}(\lambda) = P_{s} \times \text{LHE} \]  

(6)

where \( P_{s} \) is the power of light provided by the solar simulator (AM 1.5 G, 100 mW cm⁻²) and LHE represents light harvesting efficiency which can be written as follows:

\[ \text{LHE} = 1 - 10^{-\alpha_{B}} \]  

(7)

(\( \alpha_{B} \): absorbance at wavelength \( \lambda \))

Since the charge injection efficiency can be assumed to be almost 100% (i.e., \( \eta_{inj} = 1 \)) when a sacrificial agent (i.e., sulfite ion (SO₃²⁻)) is involved, the photocurrent density obtained from the SO₃²⁻ oxidation reaction (Jₚ) can be expressed as follows:

\[ J_{p} = J_{abs} \times \eta_{bulk} \]  

(8)

Then, \( \eta_{bulk} \) can be expressed as follows:

\[ \eta_{bulk} = \frac{J_{p}}{J_{abs}} \]  

(9)

and \( \eta_{inj} \) can be expressed as follows:

\[ \eta_{inj} = \frac{J_{p}}{J_{p}^{\text{max}}} \]  

(10)

2.9. Estimation of applied bias photon-to-current efficiency (ABPE) of Mo:BiVO₄ photoanodes and O₂ evolution

The ABPE efficiency of the Mo:BiVO₄ photoanodes can be calculated using the following equation:

\[ \text{ABPE} = \left( \frac{J_{p}^{\text{max}} \times (1.23 - V)}{P_{s}} \right) \]  

(11)

where \( J_{p}^{\text{max}} \) is the photocurrent density (mA cm⁻²) of water oxidation, \( V \) is the applied bias (volts), and \( P_{s} \) is the power density provided by the solar simulator (AM 1.5 G, 100 mW cm⁻²).

GC (6500GC system, YL Instrument, Anyang, Korea) was performed using a pulsed discharge detector and a molecular sieve column to analyze the O₂ evolution. All the connections of the device were completely sealed with rubber bulkheads to prevent gas leakage from the quartz tubes. The Faradaic efficiency was defined as the ratio of the rate of oxygen evolution to that of \( e/4 \). The active area of the photo-electrode for this measurement was 0.3 cm².

3. Results and discussion

3.1. Morphology of Mo:BiVO₄ films depending upon the molecular weight of PEG

Mo:BiVO₄ films were fabricated onto a fluorine-doped tin oxide (FTO)/SnO₂ substrate by spin coating using a Mo:BiVO₄ homogeneous precursor solution with 1 at% Mo concentration composed of
stoichiometric metal ions and PEG. The as-spin-coated films were immediately placed on a hot plate followed by annealing at 400 °C in air for 7 min (Fig. 1, see Experimental Section for details). Compared to conventional nanostructuring method for BiVO₄, our fabrication did not involve a complex process, expensive equipment, or time-consuming treatment to obtain nanostructured Mo:BiVO₄ photoanodes. The reference electrode without any addition of PEG in the precursor solution (denoted as Mo:BiVO₄ w/o PEG) exhibited a pinhole-free dense microstructure with a film thickness of 225.4 ± 11 nm (Fig. 2a). By adding PEG to the precursor solution, we observed particulate films with different sizes of grains and pores depending on the molecular weight of PEG (Fig. 2b-d). Each PEG-added film was denoted as Mo:BiVO₄ PEG ×, where × refers to the molecular weight of PEG which can be calculated as 44.05n × 18.02 g/mol, where n is the number of repeating monomer (i.e., ethylene glycol (EG)). The average n value of PEG 200, PEG 300, and PEG 400 is 4, 6, and 8, respectively. The Mo:BiVO₄ PEG 200 photoanodes exhibited an average grain size of 278.4 ± 44 nm with a film thickness of 234.4 ± 12 nm as determined by image analysis. With the increasing molecular weight of PEG, the Mo:BiVO₄ PEG photoanodes showed a decreasing grain size while maintaining a similar film thickness. Mo:BiVO₄ PEG 300 showed a grain size of 220.3 ± 31 nm, which was further reduced to 155.7 ± 27 nm for Mo:BiVO₄ PEG 400, whereas the film thickness remained in the range of 232.8 ± 6 nm and 225.9 ± 8 nm (see Table S1, Supplementary Information). Moreover, Mo:BiVO₄ PEG 200 exhibited the largest pore size of 199.1 ± 32 nm followed by Mo:BiVO₄ PEG 300 (164.1 ± 50 nm) and Mo:BiVO₄ PEG 400 (83.7 ± 32 nm). In the case of Mo:BiVO₄ PEG 400, a higher porosity of 53.0% was observed compared to that of Mo:BiVO₄ PEG 300 (38.9%) and Mo:BiVO₄ PEG 200 (27.7%). This is presumably due to the increased number of small pores resulting from decreasing the grain size of Mo:BiVO₄ PEG 400 (see Table S2, Supplementary Information).

To investigate the effect of PEG molecular weight on the morphology of Mo:BiVO₄, thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were conducted with Mo:BiVO₄ PEG precursor solutions. As shown in Fig. 3a, all precursor solutions similarly showed a broad endothermic peak near 250 °C due to the vaporization of residual solvents and decomposition of organic ligands. It is considered that the first exothermic peak accompanying the major weight loss observed at ~300 °C corresponds to the crystallization of Mo:BiVO₄ upon the combustion of PEG [31]. The second exothermic peak observed at 400–450 °C represented the phase transition from a tetragonal to monoclinic-scheelite crystal structure. Notably, this exothermic peak involving the crystallization was shifted to a higher temperature with the increasing molecular weight of PEG. The peak was observed at 312 °C for Mo:BiVO₄ PEG 200, whereas it shifted to 326 °C for Mo:BiVO₄ PEG 300 and 334 °C for Mo:BiVO₄ PEG 400 (Fig. 3b). This peak shift indicates that high-molecular-weight PEG could delay the crystallization of Mo:BiVO₄. Considering the fabrication procedure, after the initial spin coating and annealing at 400 °C for 7 min, a thin Mo:BiVO₄ layer (~30 nm) should be formed after complete pyrolysis of PEG and solvent evaporation (dry film). As-formed Mo:BiVO₄ grains individually play a role as a small nuclei for the following step of spin coating in which the metal-PEG complex solution covers the Mo:BiVO₄ layer (wet film). It was demonstrated that the metal-PEG complex is formed by strong interaction between ether oxygens of PEG and dissolved metal ions [32,33]. During the next annealing and crystallization process, the as-formed Mo:BiVO₄ nuclei grow by the classical nuclei growth mechanism which is the ion-by-ion addition through diffusion to the formed crystal [13,34]. However, the Mo:BiVO₄ could be interfered by surrounding PEG chains which are strongly bonded to metal ions, suppressing the crystal growth [35–37]. Moreover, the longer chain length (i.e., higher molecular weight) of PEG can severely hinder the nuclei growth from the metal ion addition during the crystallization process [38]. Therefore, it is reasonable to assume that the presence of higher-molecular-weight PEG within the wet film reduces the growth rate of nuclei, resulting in small-grain-sized Mo:BiVO₄ film.

The influence of an additive with a shorter chain length than PEG 200 on the morphology of Mo:BiVO₄ photoanodes was also investigated by adding to the precursor solution EG and diethylene glycol (DEG), both of which have a shorter chain length (i.e., lower molecular weight) than PEG 200 (Fig. S1a,b, Supplementary Information). The Mo:BiVO₄ EG film revealed a large grain size of 406 ± 96 nm with a thickness of 239.8 ± 6 nm, whereas Mo:BiVO₄ DEG exhibited a small grain size of 118.1 ± 30 nm with a thickness of 224.5 ± 6 nm and occasional pinholes. While the grain sizes differed significantly, both samples exhibited a dense film-like morphology rather than the nanoporous structure associated with Mo:BiVO₄ PEG films. It is considered that additives having relatively short chains do not significantly affect the metal ion
addition during the growth and that the pores resulting from the elimination of additives can be easily filled by grain growth, leading to a compact film morphology. On the other hand, the additives with longer chains (i.e., PEG 200 to PEG 400) readily hinder the nuclei growth by ion addition and surface reaction during the crystallization process, reducing the grain size and resulting in a nanoporous structure (Fig. S2, Supplementary Information). The crystallinity and phase of Mo:BiVO$_4$ photoanodes as a function of PEG molecular weight were revealed by XRD (Fig. S3a, Supplementary Information). All Mo:BiVO$_4$ photoanodes showed peak splitting at $\theta \sim 34.8^\circ$ and $35.4^\circ$ corresponding to the (200) and (020) planes, respectively. The observed peak splitting at $\sim 35^\circ$ indicates that Mo:BiVO$_4$ photoanodes have a monoclinc scheelite crystal structure (JCPDS No. 00-014-0688) without any secondary phase or impurities regardless of PEG molecular weight, implying that the Mo was successfully doped into the BiVO$_4$ lattice [39]. Moreover, the relative peak intensity of the (200) and (020) planes became broader with the increasing PEG molecular weight, indicative of the decreased crystal size for the Mo:BiVO$_4$ films, which is consistent with the tendency observed in Fig. 2.

### 3.2. Optical and PEC properties of Mo:BiVO$_4$ photoanodes

The influence of different morphologies on the light absorption properties of Mo:BiVO$_4$ photoanodes was investigated by ultraviolet–visible (UV–vis) spectroscopy (Fig. 4a). All photoanodes with PEG clearly showed enhanced light absorption with respect to the sample without PEG. Note that the light absorption spectra were obtained by subtracting the transmittance and reflectance from unity (Fig. S4, Supplementary Information), Considering the band gap of BiVO$_4$ (2.4 eV), the absorbance over 515 nm which is the light absorption edge, does not represent the actual absorption by BiVO$_4$. Assuming 100% absorbed photon-to-current conversion efficiency (APCE), the maximum achievable photocurrent from Mo:BiVO$_4$ photoanodes was calculated by integrating the LHE and photon flux of the light in the range from 300 nm to 515 nm. The calculated maximum achievable photocurrent densities were 5.19, 5.08, and 4.83 mA cm$^{-2}$ for Mo:BiVO$_4$ PEG 200, Mo:BiVO$_4$ PEG 300, and Mo:BiVO$_4$ PEG 400, respectively, higher than that of Mo:BiVO$_4$ w/o PEG (4.15 mA cm$^{-2}$) (Table S3, Supplementary Information). Furthermore, we determined the $\eta_{abs}$ for Mo:BiVO$_4$ films by dividing the maximum achievable photocurrent density by $J_{max}$ of 7.5 mA cm$^{-2}$ obtained from BiVO$_4$’s band gap of ~2.4 eV. The resulting $\eta_{abs}$ was determined to be 69.2% for Mo:BiVO$_4$ PEG 200, 67.7% for Mo:BiVO$_4$ PEG 300, 64.4% for Mo:BiVO$_4$ PEG 400, and 55.3% for Mo:BiVO$_4$ w/o PEG. Because the thickness for all Mo:BiVO$_4$ photoanodes was nearly identical, the enhanced $\eta_{abs}$ in Mo:BiVO$_4$ PEG photoanodes could be attributed to enhanced light absorption by the multiple light scattering occurring in the particulate arrays and pores within the Mo:BiVO$_4$ PEG films. It has been reported that incident light can be trapped in the pores involved in Mo:BiVO$_4$ PEG photoanodes, leading to multiple internal scattering [26,40]. Therefore, more light can be absorbed in Mo:BiVO$_4$ PEG photoanodes due to the reduced reflection in the range from 300 nm to 515 nm (Fig. S4, Supplementary Information).

To gain insight on the influence of different Mo:BiVO$_4$ morphologies on PEC performance, we performed LSV. Fig. 4b shows the photocurrent for water oxidation ($J^{\text{HER}}$) versus applied potential measured in 0.5 M
**Fig. 4.** a) Light absorption properties of Mo:BiVO₄ photoanodes investigated by UV–vis analysis. b) Photocurrent density for water oxidation ($J^{\text{abs}}$) versus applied potential for Mo:BiVO₄ w/o PEG (maroon), Mo:BiVO₄ PEG 200 (orange), Mo:BiVO₄, PEG 300 (green), and Mo:BiVO₄ PEG 400 (navy) measured in 0.5 M KPI (pH = 7) under front-side 1-sun illumination at scan rate of 20 mV s⁻¹. c) IPCE spectra of Mo:BiVO₄ photoanodes measured in 0.5 M KPI (pH = 7) at 1.23 V$_{\text{RHE}}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)


cm⁻² at 1.23 V$_{\text{RHE}}$, respectively, whereas Mo:BiVO₄ PEG 400 showed a lower $J^{\text{abs}}$ (0.9 mA cm⁻²). Moreover, the values obtained from LSV measurement for Mo:BiVO₄ photoanodes matched the calculated photocurrent achieved by integrating the IPCE over the light spectrum well (Fig. 4c). The IPCE for the Mo:BiVO₄ PEG 200 photoanodes exhibited the highest value of 46%, followed by Mo:BiVO₄ PEG 300 (36.5%), Mo:BiVO₄ w/o PEG (26%), and Mo:BiVO₄ PEG 400 (20%). The $J^{\text{abs}}$ can be theoretically expressed as $J^{\text{abs}} = J^{\text{max}} \times \eta_{\text{abs}} \times \eta_{\text{bulk}} \times \eta_{\text{inj}}$. Based on the calculated $\eta_{\text{abs}}$ values (Table S3, Supplementary Information), it can be assumed that the PCE performance of Mo:BiVO₄ PEG photoanodes with respect to Mo:BiVO₄ w/o PEG can be improved by ~1.2 times. However, despite the nearly identical $\eta_{\text{abs}}$ among the three Mo:BiVO₄ PEG photoanodes, water oxidation performance significantly differs presumably due to the microstructure-dependent $\eta_{\text{bulk}}$ and $\eta_{\text{inj}}$ values (i.e., the varying grain sizes and pore structures).

### 3.3. Understanding charge transport properties of nanostructured Mo:BiVO₄ photoanodes.

To determine $\eta_{\text{bulk}}$, we conducted LSV for the sulfite oxidation reaction (SOR) over Mo:BiVO₄ PEG photoanodes in 0.5 M potassium phosphate buffer solution containing 0.5 M Na₂SO₃ (pH = 7.1) under standard front-side illumination (1-sun AM 1.5 G). For SOR, the surface charge recombination is negligible due to the facile electrochemical oxidation reaction at the electrode/electrolyte interface, and hence, $\eta_{\text{inj}}$ can be assumed to be 100% [3]. Therefore, in the case of SOR, the water oxidation performance is represented as $J^{\text{SOR}} = J^{\text{max}} \times \eta_{\text{abs}} \times \eta_{\text{bulk}}$. Under this circumstance, $\eta_{\text{bulk}}$ of each photoanode can be obtained by dividing the photocurrent density value obtained from SOR ($J^{\text{SOR}}$) by the maximum achievable photocurrent density (see Experimental Section for details). In case of Mo:BiVO₄ w/o PEG with compact film morphology, we obtained the $\eta_{\text{bulk}}$ of 59% at 1.23 V$_{\text{RHE}}$ (Fig. S5, Supplementary Information). It has been reported that the compact and preferentially [001]-oriented BiVO₄ exhibited the $\eta_{\text{bulk}}$ up to ~96% at 1.23 V$_{\text{RHE}}$, but a sophisticate of fabrication technology was required compared to facile sol–gel process [16]. Hereafter, for further analyses, we mainly considered three types of Mo:BiVO₄ PEG photoanodes with similar thickness to demonstrate the variation of $\eta_{\text{bulk}}$ depending on the grain size of sol–gel reaction based nanostructured BiVO₄ photoanodes.

The observed $J^{\text{SOR}}$ showed a tendency similar to that of $J^{\text{abs}}$ (Fig. 5a). At 1.23 V$_{\text{RHE}}$, the Mo:BiVO₄ PEG 200 photoanodes exhibited the highest $J^{\text{SOR}}$ of 3.75 mA cm⁻², followed by 3.13 mA cm⁻² (Mo:BiVO₄ PEG 300), and 2.07 mA cm⁻² (Mo:BiVO₄ PEG 400). Moreover, as shown in Fig. 5b, it was found that the $\eta_{\text{bulk}}$ of Mo:BiVO₄ PEG 200 was 72% at 1.23 V$_{\text{RHE}}$, followed by 62% (Mo:BiVO₄ PEG 300), and 42% (Mo:BiVO₄ PEG 400). A previous report indicated that the small pore size of a nanostructure did not impede the electrolyte penetration, so the hole injection from the photoelectrode to the electrolyte was not limited [37]. Therefore, it can be assumed that the difference in $J^{\text{abs}}$ observed for Mo:BiVO₄ PEG photoanodes results from different $\eta_{\text{bulk}}$ among photoanodes, which originates not from the porosity-related surface area difference but from the grain size variation [41]. $\eta_{\text{bulk}}$ represents the fraction of photogenerated holes that are transferred to the electrolyte interface without bulk recombination. Therefore, the decreased $\eta_{\text{bulk}}$ indicates more charge recombination before participating in the oxidation reaction.

To gain an understanding of the $\eta_{\text{bulk}}$ for Mo:BiVO₄ PEG photoanodes, electrochemical impedance spectroscopy (EIS) was performed under the same SOR electrolyte. To prevent dark electrolysis of sulfites, EIS was conducted at the applied potential of 0.8 V$_{\text{RHE}}$ with 1-sun illumination in the frequency range of 100 kHz to 1 Hz [42]. Nyquist plots for all Mo:BiVO₄ PEG photoanodes exhibited one arc in the entire frequency range (Fig. 5c). To fit the EIS results, we employed an equivalent circuit model consisting of one $R_p$ and serially connected $R_p$ with parallel combination of constant phase element (CPE) (inset in Fig. 5c). Here, $R_p$
can be interpreted as the total resistance of charge transport and recombination in the bulk absorber layer due to negligible charge transfer resistance, as supported by the absence of the low-frequency arc (~1 Hz) in the Bode plot (Fig. 5).

The fitting results are listed in Table S4 (Supplementary Information) [43]. The Nyquist plots of Mo:BiVO₄ PEG 300 and Mo:BiVO₄ PEG 400 photoanodes showed the largest arc, and its size further decreased from the Mo:BiVO₄ PEG 300 to Mo:BiVO₄ PEG 200 photoanodes. A large arc in the Nyquist plot (i.e., high $R_{\text{arc}}$ value) indicates severe impedance of charge transport in Mo:BiVO₄ PEG 400 photoanodes having the smallest grain size. As the charge transport and charge separation behaviors in the photoelectrode are closely related to grain boundaries, the reduced $\eta_{\text{GER}}$ and $\eta_{\text{bulk}}$ for the Mo:BiVO₄ PEG 400 photoanodes are attributed to the small grain size–induced grain boundary scattering [37]. Moreover, the higher charge separation efficiency and better PEC performance associated with the Mo:BiVO₄ PEG 200 photoanodes than other Mo:BiVO₄ PEG photoanodes likely originate from the reduced grain boundary scattering owing to the larger grain size, so that more photogenerated holes are able to participate in the water oxidation reaction without bulk recombination.

Significant energy band bending can occur within large-sized photocatalysts, which in turn enhances the charge separation [17]. In this regard, the enhanced $\eta_{\text{bulk}}$ of Mo:BiVO₄ PEG photoanodes with large grain size can be ascribed not only to the reduced grain boundary scattering but also to the large surface band bending. To investigate the surface band bending tendency for Mo:BiVO₄ PEG photoanodes, we firstly calculated the space charge region width ($W_o$). If the grain size radius ($r_o$) is larger than $W_o$, the surface band bending potential ($V_{\text{BB}}$) can be expressed as $V_{\text{BB}} = \frac{eN_e\varepsilon_r}{2\varepsilon_0}$, where $e$ is the electronic charge, $\varepsilon_r$ is the vacuum permittivity, and $\varepsilon_0$ is the relative permittivity of BiVO₄ (~86) [44]. On the other hand, for the grain size in which the condition of $r_o < \sqrt{3W_o}$ is satisfied, the surface band bending potential is represented by $V_{\text{BB}} = \frac{eN_e\varepsilon_r}{2\varepsilon_0} \frac{1}{eN_d}$ [45]. From the classical solid state physics theory, $W_o$ can be expressed as follows:

$$W_o = \left( \frac{2e\varepsilon_r(E - E_{\text{fb}})}{eN_d} \right)$$  \hspace{1cm} (12)$$

where $E$ represents the applied potential, $E_{\text{fb}}$ represents the flat band potential, and $N_d$ represents the donor density. To obtain $N_d$ and $E_{\text{fb}}$ of Mo:BiVO₄ PEG photoanodes, we conducted Mott-Schottky (M–S) analysis under dark conditions with a fixed frequency of 1 kHz under 0.5 M KPi (pH = 7). As shown in Fig. 5d, all the Mo:BiVO₄ PEG photoanodes showed a positive slope, indicative of n-type semiconductor characteristics. The $E_{\text{fb}}$, determined by the extrapolation of linear region, of Mo:BiVO₄ PEG photoanodes was around 0.3 V RHE, which is consistent with the onset potentials for OER of those photoanodes. The $N_d$ values of the Mo:BiVO₄ PEG photoanodes obtained from the M–S analysis were 3.75 $\times$ 10¹⁷ cm⁻³ for Mo:BiVO₄ PEG 200, 4.61 $\times$ 10¹⁷ cm⁻³ for Mo:BiVO₄ PEG 300, and 5.54 $\times$ 10¹⁷ cm⁻³ for Mo:BiVO₄ PEG 400. In addition, the calculated $W_o$ at 1.23 V RHE was 154 nm, 141 nm and 126 nm for Mo:BiVO₄ PEG 200, Mo:BiVO₄ PEG 300 and Mo:BiVO₄ PEG 400, respectively. Assuming $r_o$ as a half of the average grain size obtained from image analysis (Table S1), it is confirmed that all Mo:BiVO₄ PEG photoanodes satisfy $r_o < \sqrt{3W_o}$, therefore $V_{\text{BB}}$ could be obtained from the equation $V_{\text{BB}} = \frac{eN_e\varepsilon_r}{2\varepsilon_0} \frac{1}{eN_d}$. The $V_{\text{BB}}$ value was determined.
as 0.25 V for Mo:BiVO$_4$ PEG 200, 0.19 V for Mo:BiVO$_4$ PEG 300, and 0.11 V for Mo:BiVO$_4$ PEG 400, respectively. As large internal electric fields such as $V_{in}$ develop at the electrode and electrolyte interface, the more photogenerated carriers can be easily separated to participate in the OER without recombination. Clearly, the higher PEC performance of the Mo:BiVO$_4$ PEG 200 photoanodes is associated with its large grain size effect, enabling not only the reduced charge recombination but also the enhanced $\eta_{\text{bulk}}$ owing to the development of a large interfacial built-in potential [46].

### 3.4. H$_2$ treatment of the Mo:BiVO$_4$ PEG 200

To further improve the PEC performance of the Mo:BiVO$_4$ PEG 200 photoanodes, we performed hydrogen (H$_2$) treatment. A previous study demonstrated that the introduction of H$_2$ into BiVO$_4$ could enhance the PEC performance by increasing the overall electrical conductivity due to the created oxygen vacancies that act as shallow donors in n-type semiconductor materials [47]. To optimize the treatment temperature, the $J_{\text{SOR}}$ values were determined by varying the H$_2$ treatment temperatures from 200 to 300 °C. At 250 °C, the highest $J_{\text{SOR}}$ value of 4.7 mA cm$^{-2}$ at 1.23 V$_{\text{RHE}}$ and an onset potential of about 0.3 V$_{\text{RHE}}$ were observed under standard 1-sun front illumination (Fig. S7a, Supplementary Information). There were no significant changes in morphology, crystal structure, or optical characteristics after H$_2$ treatment (Fig. S7b–d, Supplementary Information). Fig. 6a compares $\eta_{\text{bulk}}$ for Mo:BiVO$_4$ PEG 200 before and after H$_2$ treatment (denoted as H, Mo:BiVO$_4$ PEG 200). $\eta_{\text{bulk}}$ of H, Mo:BiVO$_4$ PEG 200 reached 89% at 1.23 V$_{\text{RHE}}$, ∼12.3% higher than Mo:BiVO$_4$ PEG 200. The relative concentration of oxygen vacancy was characterized using XPS performed on both Mo:BiVO$_4$ PEG 200 and H, Mo:BiVO$_4$ PEG 200 (Fig. S8, Supplementary Information). The O 1s peak of Mo:BiVO$_4$ can be fitted into three deconvoluted peaks at 530.0, 531.1 and 532.1 eV, corresponding to O$_2^-$ in the lattice (O$_L$), oxygen vacancy (O$_V$), and adsorbed/dissociated oxygen from water molecules (O$_o$) [48]. After H$_2$ treatment, we observed that all Bi 4f, V 2p, Mo 3d and O1s peaks shifted to lower binding energies, implying the increment of the electron density of each atom due to the formation of oxygen vacancies [49,50]. The relative O$_V$ concentration, calculated based on the portion of O$_V$ peak areas, was 9.98% and 12.05% for Mo:BiVO$_4$ PEG 200 and H, Mo:BiVO$_4$ PEG 200, respectively. Therefore, the $\eta_{\text{bulk}}$ improvement could be attributed to the improved electrical conductivity of Mo:BiVO$_4$ PEG 200 because of high oxygen vacancy concentration after H$_2$ treatment.

### 3.5. Decoration of NiFeOOH catalyst on the H, Mo:BiVO$_4$ photoanode.

Despite of the $\eta_{\text{bulk}}$ enhancement after H$_2$ treatment, the $J_{\text{OER}}$ of H, Mo:BiVO$_4$ PEG 200 was still low (Fig. 6b), implying that the surface OER kinetics should be further improved for high PEC performance. To expedite the OER kinetics, NiFeOOH was deposited as an OER catalyst using the photo-assisted LSV method (see details in Experimental Section) [8]. The optimized H, Mo:BiVO$_4$ PEG 200/NiFeOOH exhibited remarkable enhancement in water oxidation performance including an onset potential of −0.4 V$_{\text{RHE}}$, $J_{\text{OER}}$ of 4.5 mA cm$^{-2}$ at 1.23 V$_{\text{RHE}}$ compared to the water oxidation performance of H, Mo:BiVO$_4$ PEG 200 photoanodes under 1-sun front-side illumination in 0.5 M KPi electrolyte containing 0.01 M vanadium oxide (V$_2$O$_5$) (pH = 7.4). The calculated ABPE was also increased to 1.64% at 0.69 V$_{\text{RHE}}$ for H, Mo:BiVO$_4$ PEG 200/NiFeOOH as compared to 0.41% at 0.91 V$_{\text{RHE}}$ (H, Mo:BiVO$_4$ PEG 200) (Fig. 6c).

For direct observation of the morphology of H, Mo:BiVO$_4$ PEG 200/NiFeOOH, we performed transmission electron microscopy (TEM) analysis (Fig. 7). The high-resolution TEM image shows that NiFeOOH exists as an amorphous states, while the lattice fringe of 0.252 nm was clearly observed which ascribed to the (020) plane of crystalline BiVO$_4$ (Fig. 7b) [51]. The high-angle annular dark field (HAADF) image and...
energy-dispersive X-ray spectroscopy (EDS) elemental mapping image clearly reveal the uniform distribution of Ni and Fe on the H, Mo:BiVO$_4$ PEG 200 photoanode (Fig. 7c).

The decoration of NiFeOOH catalyst was optimized by controlling the sweeping number and annealing. Among four candidates of Mo:BiVO$_4$ films that we fabricated (Fig. 2), it was confirmed that even after the identical processes of H$_2$ treatment and the NiFeOOH decoration, Mo:BiVO$_4$ PEG 200 exhibited the best PEC performance (Fig. S9, Supplementary Information). Moreover, the chemical states of NiFeOOH catalyst were confirmed by XPS. No peak shift was observed before and after annealing, while the Ni 2p$_{3/2}$ (855.5 eV) and Ni 2p$_{1/2}$ (873.2 eV) peaks and the Fe 2p$_{3/2}$ (711.0 eV) and Fe 2p$_{1/2}$ (724.5 eV) peaks with satellite signals were clearly observed which corresponds to Ni$^{2+}$ and Fe$^{3+}$, respectively (Fig. S10 a-c, Supplementary Information). The O 1 s peaks were observed at 529.6 eV, 531.1 eV and 531.8 eV which corresponds to O$^{2-}$, OH$^-$, and bounded water (H-O--H), respectively [52]. Moreover, the clear OH$^-$ peaks appeared in O 1 s spectra of H, Mo:BiVO$_4$ PEG 200 / NiFeOOH indicating that Ni and Fe exist as a form of NiFe (oxy)hydroxide (NiFeOOH) [53,54].

3.6. Stability of H, Mo:BiVO$_4$ PEG 200/ NiFeOOH photoanode

Finally, the photocurrent stability of H, Mo:BiVO$_4$ PEG 200/ NiFeOOH was evaluated in 0.5 M KPi + 0.01 M V$_2$O$_5$ (pH = 7.4) at 1.23 V$_{RHE}$ under 1-sun front-side illumination. The H, Mo:BiVO$_4$ PEG 200/ NiFeOOH device showed excellent photocurrent stability, retaining ~90% of its initial photocurrent after 10 h irradiation, whereas H,Mo:BiVO$_4$ PEG 200 without catalyst exhibited not only low photocurrent density but also poor stability, showing almost full degradation within 5 h (Fig. 8a). Our PEC result was comparable to or higher than other previously reported BiVO$_4$-based photoanodes (Table S5, Supplementary Information). The oxygen (O$_2$) produced during the stability test was monitored by gas chromatography (GC) (Fig. 8b). The solid line represents the theoretical value assuming 100% Faradaic efficiency. The actual Faradaic efficiency was obtained by dividing the detected O$_2$ gas with the expected amount of O$_2$ calculated by the photocurrent density. The detected O$_2$ amount matched the theoretical value well, showing Faradaic efficiency of 82–96%. This result indicates that most photogenerated holes participated in the water oxidation reaction without detrimental recombination. The slightly lower Faradaic efficiency in the middle of measurement presumably resulted from the temporal adhesion of the generated O$_2$ on the surface of the photoelectrodes.

4. Conclusions

In summary, we introduced a facile nanostructuring strategy to fabricate nanoporous Mo:BiVO$_4$ photoanodes for enhancing charge separation efficiency and the water oxidation reaction. The grain and pore sizes of Mo:BiVO$_4$ film were controlled by using PEG with different molecular weights in the precursor solution. Large-molecular-weight PEG 400 within the wet film reduced the growth rate of nuclei by hindering ion addition, resulting in small-grain-sized Mo:BiVO$_4$ film during...
the crystallization process. By contrast, small-molecular-weight PEG 200 led to large-grain-sized nanoporous Mo:BiVO₄ exhibiting the enhanced ηbulk of ~72% and ηOER of ~2.2 mA cm⁻² at 1.23 V_RHE. The improved PEC performance associated with large grain size can be understood in terms of the reduced charge recombination due to less grain boundary scattering as well as the large interfacial band bending potential. After the H₂ treatment, ηbulk increased up to 89% at 1.23 V_RHE due to passivation of the defect states, leading to the extended carrier lifetime. Finally, with deposition of NiFeOOH as an OER catalyst, the optimized H₂, Mo:BiVO₄ PEG 200/NiFeOOH exhibited remarkable enhancement in water oxidation performance including a ηOER of ~4.5 mA cm⁻² at 1.23 V_RHE and an applied bias photon-to-current efficiency of 1.64% at 0.69 V_RHE with stable operation for 10 h. Our findings clearly suggest a facile low-cost approach to fabricate Mo:BiVO₄ photoanodes for highly efficient PEC water oxidation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References
