Electronic Supplementary Information

Effects of a SnO_2 hole blocking layer in a $BiVO_4$-based photoanode for photoelectrocatalytic water oxidation

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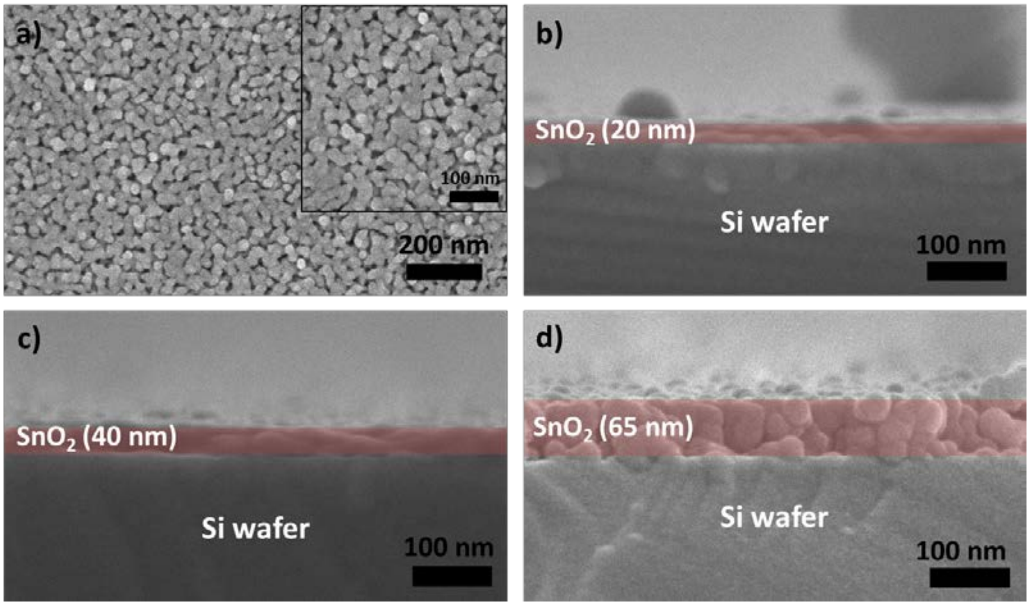

Fig. S1 SEM images of various SnO_2 layers on Si wafer. (a) Surface image of a SnO_2 layer with 65 nm thick. Inset of the figure was a magnified image. Cross-sectional SEM images of (b) 20 nm, (c) 40 nm, and (d) 65 nm thick SnO_2 layers.

Due to the rough surface of FTO substrate, it was hard to measure the exact thickness of SnO_2 buffer layers on FTO; typical surface roughness is around 44 nm RMS as seen in Fig. S2a. Therefore, SnO_2 layers were fabricated on Si wafer and their thickness were measured by using cross-sectional SEM images of each sample. (Fig. S1b–d)

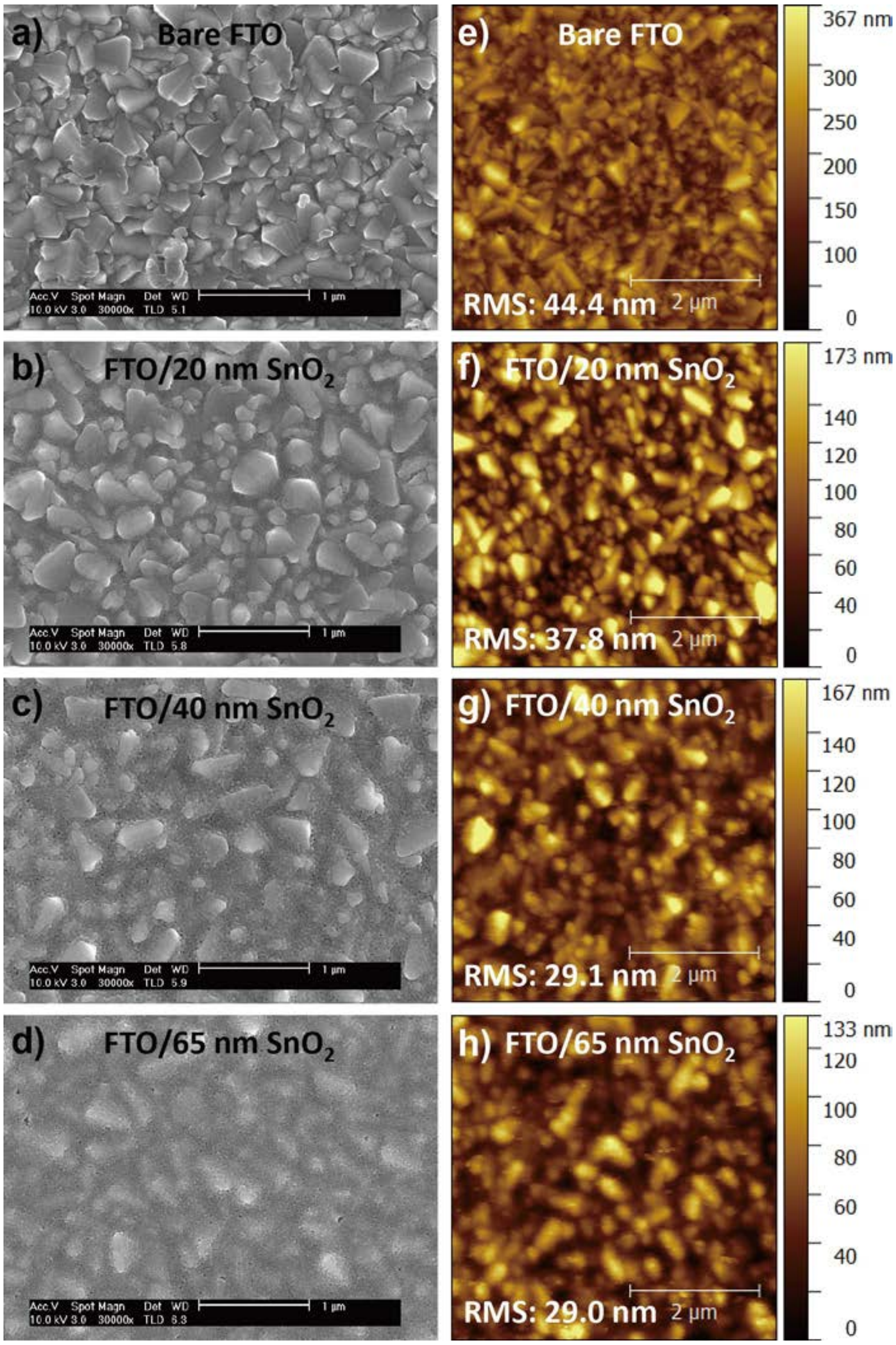

Fig. S2 (a-d) SEM and (e-h) AFM images of bare FTO and various FTO/SnO_2 substrates. As increasing SnO_2 layer thickness on FTO, RMS of FTO/SnO_2 substrate became decreased, indicating much smoother surface than bare FTO.

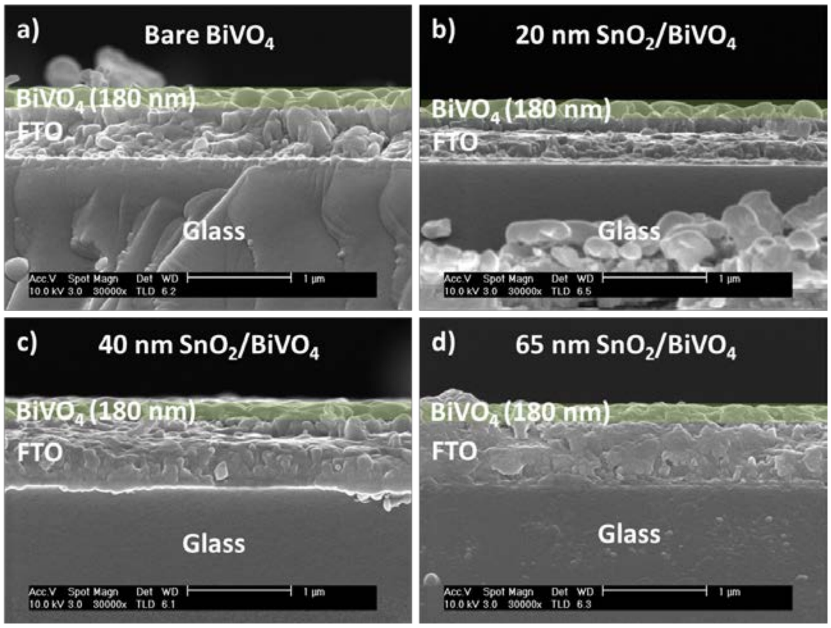

Fig. S3 SEM images of the cross-section of various $BiVO_4$ based photoanodes. (a) Bare $BiVO_4$, (b) 20 nm, (c) 40 nm, and (d) 65 nm $SnO_2/BiVO_4$. The SnO_2 buffer layers in $SnO_2/BiVO_4$ photoanodes could not be obvious in the SEM images.

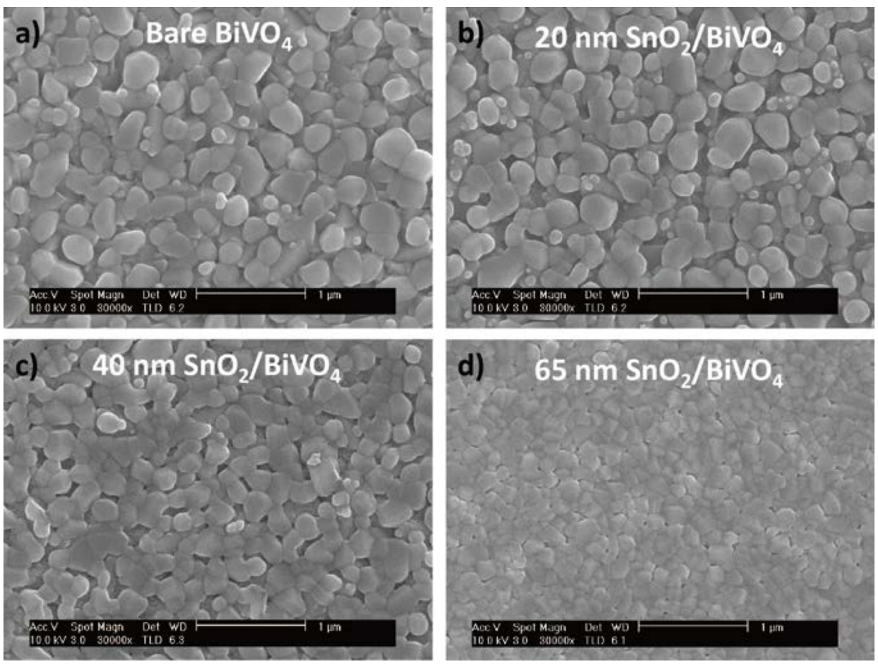

Fig. S4 SEM images of the surface of $BiVO_4$ based photoanodes. (a) Bare $BiVO_4$, (b) 20 nm and (c) 40 nm, and (d) 65 nm $SnO_2/BiVO_4$ photoanodes.

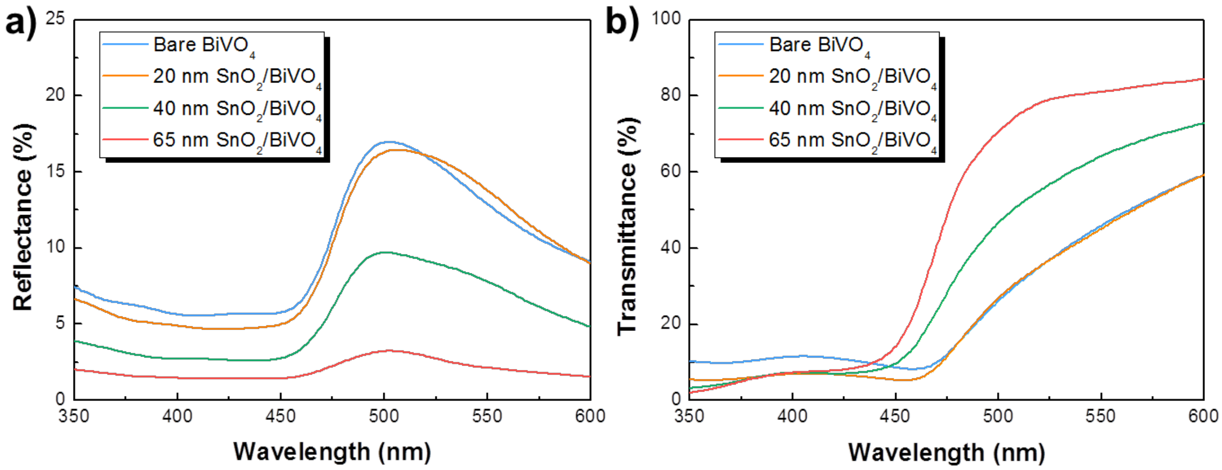

Fig. S5 UV/Vis spectra of $BiVO_4$ based photoanodes. a) Reflectance and b) Transmittance spectra.

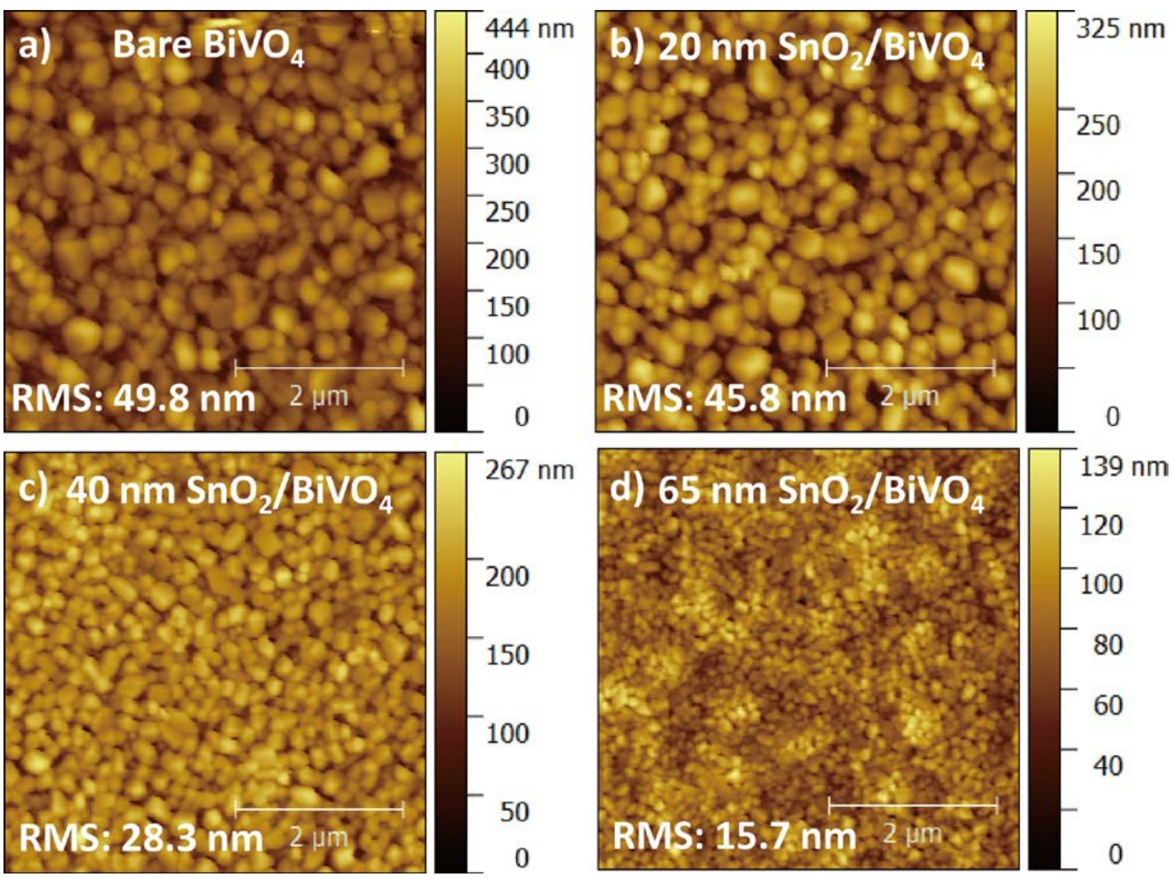

Fig. S6 AFM images of the surface of various $BiVO_4$-based photoanodes. (a) bare $BiVO_4$, (b) 20 nm, (c) 40 nm, and (d) 65 nm $SnO_2/BiVO_4$.

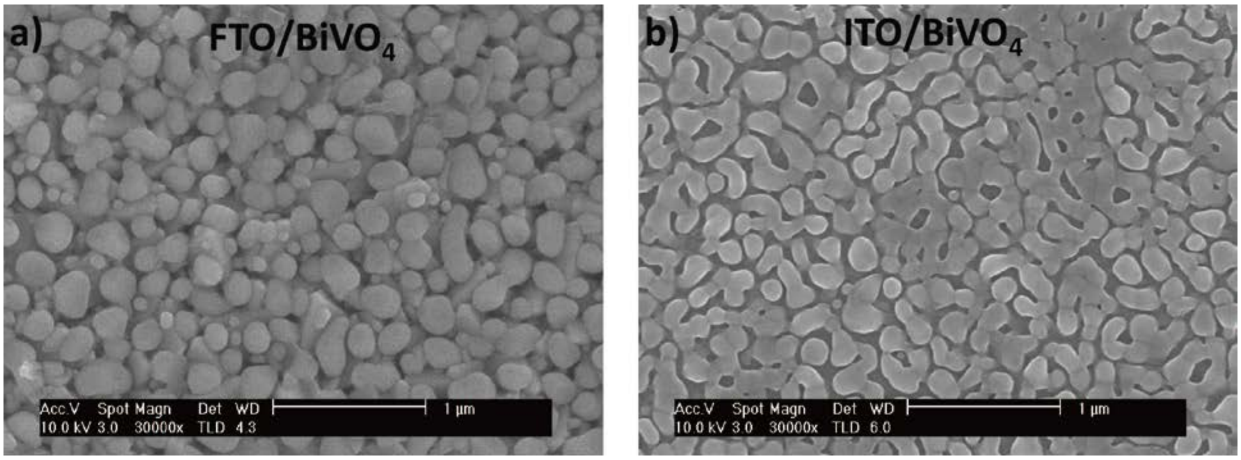

Fig. S7 $BiVO_4$ film on (a) bare FTO and (b) ITO substrates.

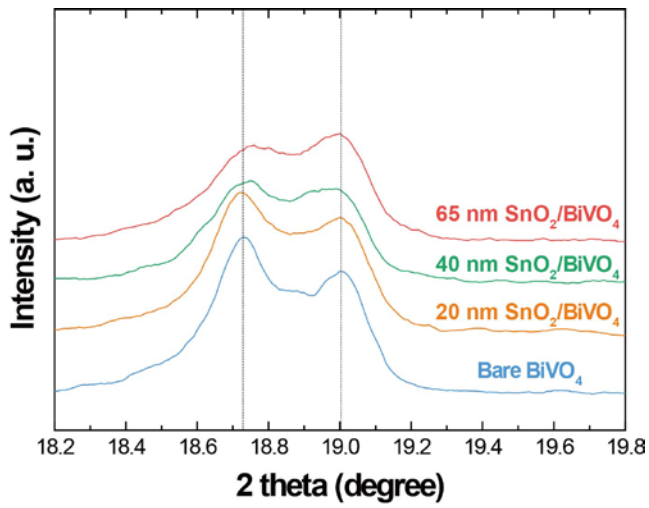

Fig. S8 Magnified region of XRD spectra of the $BiVO_4$ based photoanodes.

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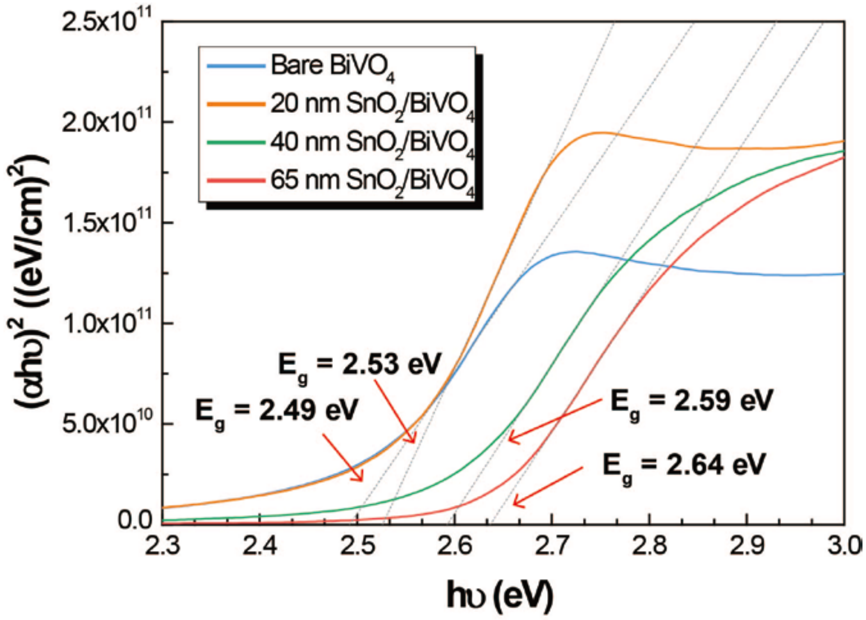


Fig. S9 Tauc plots for all $BiVO_4$ based photoanodes.

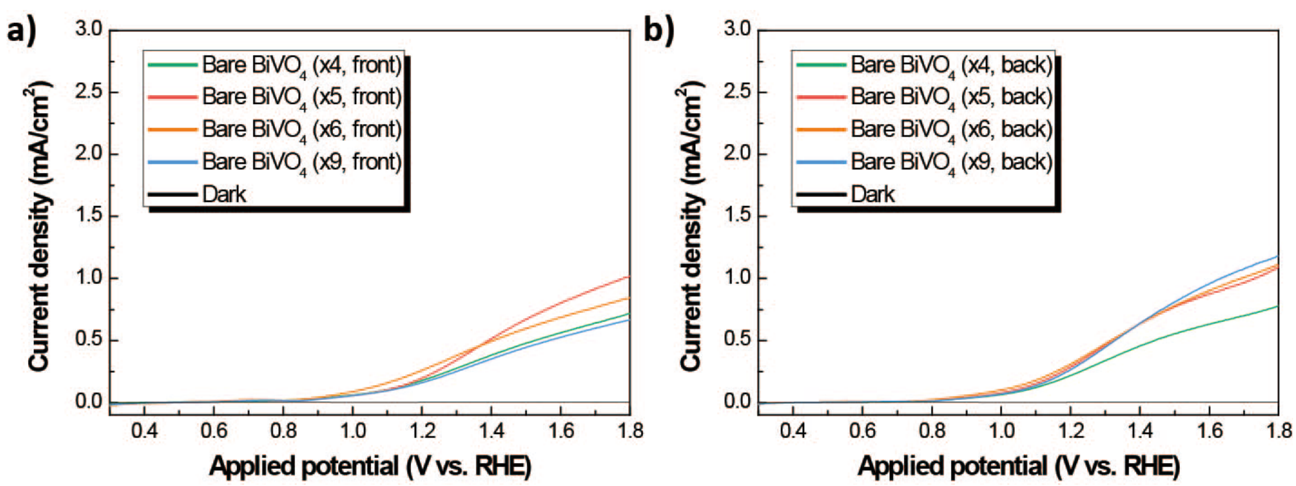


Fig. S10 Thickness optimization of $BiVO_4$ film created by the modified metal-organic decomposition (MOD) method. LSV curves for bare $BiVO_4$ with different thickness that measured under (a) front-side and (b) back-side illumination. The repeated deposition number is described as ×number. The optimum thickness of $BiVO_4$ for best PEC performance was around 180 nm thick (5 times deposition). All LSV measurement was conducted in 0.5 M Na_2SO_4 + KPi buffer solution at the scan rate of 20 mV s^{-1} under 1 sun illumination.

In order to produce our $BiVO_4$ film with a comparable PEC performance to other types of $BiVO_4$

films, bare $BiVO_4$ photoanodes with various film thicknesses were fabricated on pristine FTO substrates by the repeated MOD process. In Fig. S10, LSV curves for bare $BiVO_4$ films with different layer thickness revealed that the optimum thickness of our $BiVO_4$ film was around 180 nm, which was a similar value than an optimum thickness (200 nm) of other $BiVO_4$ films.[3, 31, 50]

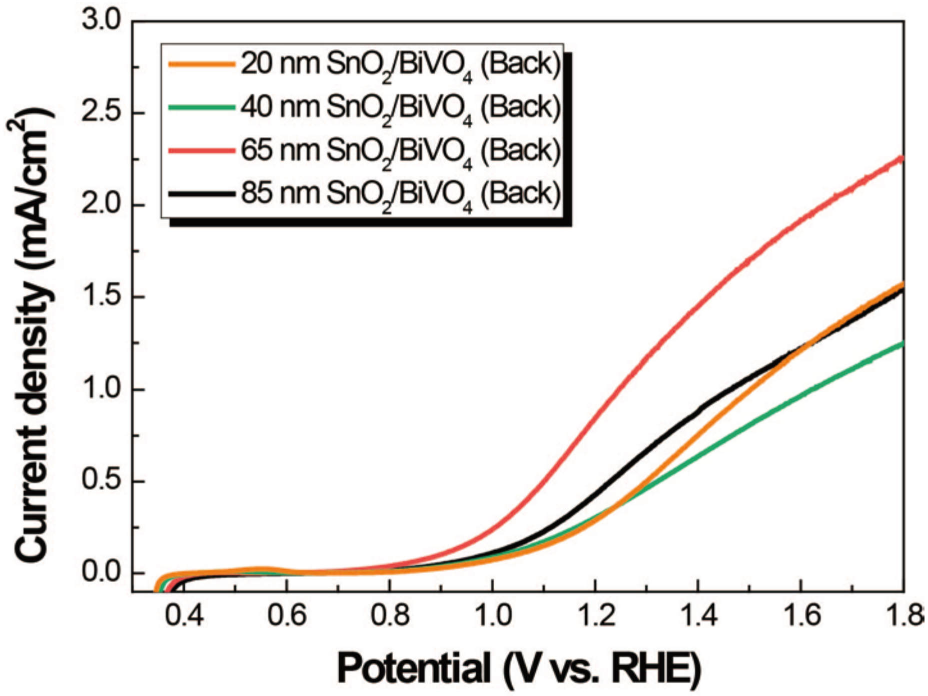


Fig. S11 LSV curves of various $SnO_2/BiVO_4$ photoanodes. For 85 nm $SnO_2/BiVO_4$, 85 nm SnO_2 layer was fabricated on a FTO substrate by two times deposition process with 50 mM and 200 mM Sn precursor solutions.

Our SnO_2 buffer layers were fabricated via a one-step method with a highly concentrated $SnCl_2$ precursor solution, and therefore, their layer thickness was hard to be increased and limited to around 65 nm thick, due to the limited solubility of $SnCl_2$ in isopropyl alcohol. In order to optimize SnO_2 layer thickness, a thick SnO_2 layer more than 65 nm was fabricated on FTO substrate through a two-step growth method using $SnCl_2$ precursor solutions used for growing 20 nm and 65 nm SnO_2

layers, which defined as 85 nm SnO_2. Although another issue such as interface defects of adjacent SnO_2 layers during the fabrication process would be happened, based on the result, as increasing a SnO_2 layer thickness more than 65, the photocurrent density became decreased. Therefore, it could be thought that the optimum thickness of SnO_2 in $SnO_2/BiVO_4$ photoanode was around 65 nm.

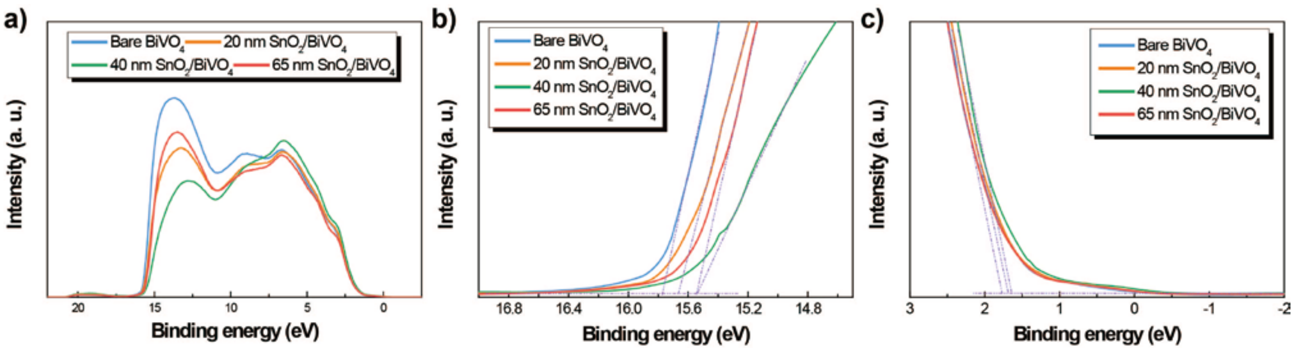


Fig. S12 UPS spectra of all $BiVO_4$-based photoanodes for their band structure. (a) Whole range, and (b–c) magnified region of UPS spectra to measure the work function and VBM, respectively.

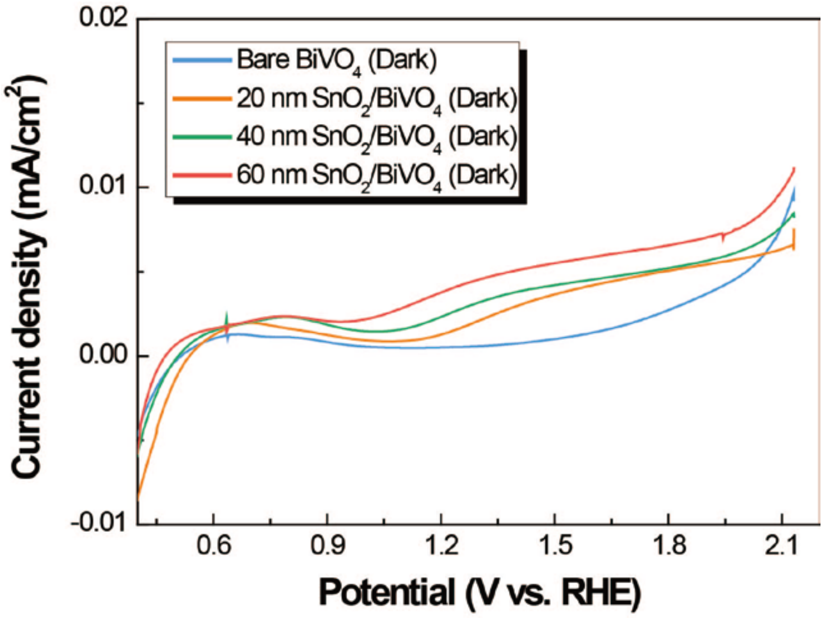


Fig. S13 LSV curves of all $BiVO_4$ based photoanodes in dark. This measurement was conducted in 0.5 M Na_2SO_4 + KPi buffer solution at the scan rate of 20 mV s^{-1}.

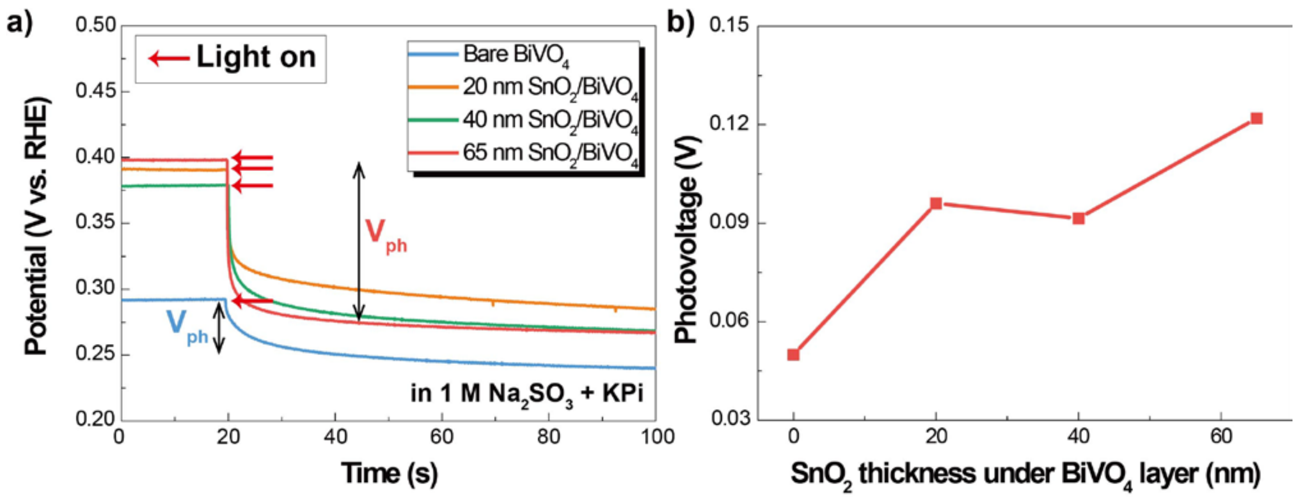
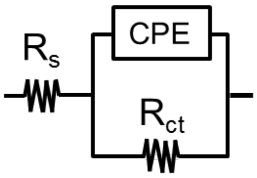


Fig. S14 Photovoltage (V_{ph}) measurement of all $BiVO_4$ based photoanodes. (a) Open-circuit potential (OCP) measurement versus time in the dark and illumination conditions, and (b) the calculated V_{ph} values as a function of the SnO_2 layer thickness.

a)



b)

Sample	R_s (ohm)	R_{ct} (ohm)
Bare $BiVO_4$	11.94	11858
20 nm $SnO_2/BiVO_4$	12.86	2160
40 nm $SnO_2/BiVO_4$	14.03	2489
65 nm $SnO_2/BiVO_4$	29.19	1597

Fig. S15 (a) A simple equivalent circuit model for the Nyquist plot fitting (Fig. 4b), and (b) the corresponding fitting results. R_s: series resistance, R_{ct}: charge-transfer resistance, and CPE: constant phase element.

Table S1. PEC performance comparisons among unmodified $BiVO_4$ based photoanodes.

Year	Photoelectrode	Electrolyte	Current density at 1.23 V vs. RHE	Growth method	Ref.
2006	Bare $BiVO_4$	0.5 M Na_2SO_4 (pH 5.8)	0.9 mA cm^{-2}	MOD	35
2008	$SnO_2/BiVO_4$	0.5 M Na_2SO_4 (pH 5.8)	0.01 mA cm^{-2}	MOD	30
2012	Bare $BiVO_4$	0.1 M Na_2SO_4 (pH 5.8)	0.45 mA cm^{-2}	MOD	23
2013	$WO_3/BiVO_4$	0.5 M Na_2SO_4 + 0.1 M K_2HPO_4 (pH 7.0)	0.8 mA cm^{-2}	Sputtering	51
2011	Bare $BiVO_4$ $WO_3/BiVO_4$	0.5 M Na_2SO_4 (pH 6.6)	0.63 and 2.78 mA cm^{-2}	Polymer assisted deposition	4
2016	Bare $BiVO_4$, photocharged $BiVO_4$	0.1 M KPi (pH 7.2)	0.8 and 3.3 mA cm^{-2}	Modified MOD	43
2016	Bare $BiVO_4$, UV cured $BiVO_4$	0.5 M KPi (pH 7.0)	0.6 and 1.2 mA cm^{-2}	MOD	16
2016	$WO_3/BiVO_4$	1 M Na_2SO_3+ 0.5 M KPi (pH 7.0)	4.55 mA cm^{-2}	Pulsed electrodeposition	31
2012	$WO_3/SnO_2/BiVO_4$	0.1 M Na_2SO_4	1.2 mA cm^{-2}	Wet coating	32
2016	$SnO_2/BiVO_4$, $SnO_2/WO_3/BiVO_4$	0.5 M Na_2SO_4 + 0.1 M NaPi (pH 7.0)	1.2 and 1.5 mA cm^{-2}	Pursed laser deposition	52
This work	$SnO_2/BiVO_4$	0.5 M Na_2SO_4 + 0.1 M KPi (pH 7.0), 1 M Na_2SO_3+ 0.5 M KPi (pH 7.0)	0.95 and 3.76 mA cm^{-2}	Modified MOD	This work