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# Enhanced photoelectrochemical hydrogen production *via* linked BiVO<sub>4</sub> nanoparticles on anodic WO<sub>3</sub> nanocoral structures†

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Morphological properties of photoanodes are crucial for improving their photoelectrochemical (PEC) performance. In this study, we fabricated bismuth vanadate (BiVO<sub>4</sub>) nanoparticles (NPs) with an optimal size of ~10 nm, as well as nanowires composed of NPs on anodized tungsten trioxide (WO<sub>3</sub>) nanocoral structures. The linked BiVO<sub>4</sub> NPs were decorated by spin-coating, with the amount of the BiVO<sub>4</sub> precursor being controlled. Subsequently, the concentrations of Bi and V in the BiVO<sub>4</sub> precursor were determined. An optimized concentration of 0.3 M Bi and V for the linked BiVO<sub>4</sub> NPs/WO<sub>3</sub> nanocoral heterostructure led to enhanced photocurrent density and hydrogen gas-production compared to those of the pristine WO<sub>3</sub> nanocorals, yielding results that were 2.4 times higher. In particular, the incident photon-to-current conversion efficiency value at 410 nm improved by 8.3 times, as the linked BiVO<sub>4</sub> NPs attained efficient absorbance of visible light and a sufficient electron transfer pathway.

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## 1. Introduction

Numerous efforts to produce hydrogen energy have been made using renewable energy from solar fuels to address the global energy crisis.<sup>1–3</sup> In particular, photoelectrochemical water splitting (PEC-WS) has emerged as a promising green engineering approach for generating hydrogen through direct utilization of sunlight.<sup>4,5</sup> For PEC-WS, metal oxide semiconductors are mostly used as photoelectrodes because of their beneficial bandgap and band positions for photoreactions.<sup>6</sup> However, metal oxide semiconductor photoanodes face several critical issues, such as reduced solar-to-hydrogen efficiency of PEC-WS, slow surface water oxidation, poor visible light absorption, and fast electron–hole recombination.<sup>7,8</sup>

Bismuth vanadate (BiVO<sub>4</sub>), the most promising metal oxide photoanode material for PEC-WS, has been investigated owing to its intrinsic properties such as abundance, nontoxicity, and low cost.<sup>9–11</sup> BiVO<sub>4</sub> also satisfies the requirements for an efficient photoanode by providing a narrow bandgap of 2.4 eV with a relatively negative conduction band edge of ~0 V *vs.* the reversible hydrogen electrode (RHE), and having a high optical absorption coefficient (~10<sup>4</sup>–10<sup>5</sup> cm<sup>-1</sup> at *hν* = 2.5–3.5 eV).<sup>12–14</sup> Despite these advantages, BiVO<sub>4</sub> still suffers from fast recombination of photogenerated electrons and holes because of its

low carrier mobility (~4.4 × 10<sup>-2</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and short hole diffusion length (~70 nm).<sup>15,16</sup>

To overcome these drawbacks and enhance the photo efficiency of PEC-WS, BiVO<sub>4</sub> often adopts a type-II heterojunction configuration with two or more n-type semiconductors. At the heterojunction interface between two semiconductors, a wide bandgap material offers a more negative conduction band (CB) edge, allowing electrons to move from the narrow bandgap material to the wide bandgap material.<sup>17</sup> In this context, tungsten trioxide (WO<sub>3</sub>) (~2.8 eV) has been considered the most suitable matching material for forming a type II heterojunction with BiVO<sub>4</sub>. This is because WO<sub>3</sub> has a superior electron mobility (~12 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), relatively long hole diffusion length (~150 nm), and lower CB edge of +0.41 V *vs.* RHE compared to BiVO<sub>4</sub>.<sup>18–20</sup> To fabricate WO<sub>3</sub> for the configuration of the BiVO<sub>4</sub>/WO<sub>3</sub> heterostructure, several simple approaches have been reported such as a hydrothermal method,<sup>17,21</sup> dip-coating,<sup>22</sup> spin-coating,<sup>23</sup> and anodization.<sup>24</sup> Among the various methods, the anodization method is an advantageous because W metal as a substrate can provide direct back contact under the WO<sub>3</sub> layer and can form various nanostructures with a high specific surface area by adjusting the anodization conditions (*e.g.*, electrolyte, temperature, applied potential, *etc.*). There is only one reported research study that used anodic WO<sub>3</sub> for fabricating a BiVO<sub>4</sub>/WO<sub>3</sub> heterostructure. However, the BiVO<sub>4</sub>/WO<sub>3</sub> heterostructure of anodized WO<sub>3</sub> structures and spin-coated BiVO<sub>4</sub> layers has not fulfilled the role of a photoanode for PEC-WS, because the thick BiVO<sub>4</sub> layer (~850 nm) interrupts the mobility of photogenerated electrons from BiVO<sub>4</sub> to WO<sub>3</sub>.<sup>25</sup> Thus, it is obvious that rapid electron movement is allowed only when BiVO<sub>4</sub> is as thin as a nanolayer or a nanoparticle (NP).<sup>10</sup> In

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particular, metal oxide NPs have attracted attention in photoelectrochemical reactions as they provide a large reaction area, leading to improved photoreaction efficiency.

In this study, we have investigated how to fabricate BiVO<sub>4</sub> NPs on anodic WO<sub>3</sub>. In addition, we developed BiVO<sub>4</sub> NPs linked as nanowires to a WO<sub>3</sub> nanocoral structure. This is the first study on the heterojunction of BiVO<sub>4</sub> NPs and anodic WO<sub>3</sub> nanocorals. The WO<sub>3</sub> nanocoral structures on W metal were fabricated by the anodization method, as previously reported.<sup>22</sup> The linked BiVO<sub>4</sub> NPs were formed on the WO<sub>3</sub> nanocorals by the spin-coating method where, instead of deionized water, we employed an ethylene glycol-based solvent as a BiVO<sub>4</sub> precursor for the spin-coating process, since the utilization of the ethylene glycol-based BiVO<sub>4</sub> precursor allows BiVO<sub>4</sub> nanoparticles to form with sizes below 100 nm as supporting particle agglomeration on WO<sub>3</sub> layers during spin-coating. The use of ethylene glycol as the solvent for the BiVO<sub>4</sub> precursor has not been previously reported. Furthermore, we focus on the amount of the BiVO<sub>4</sub> precursor used during spin-coating to construct linked BiVO<sub>4</sub> NPs on WO<sub>3</sub> nanocorals and determine their morphologies, crystal structures, and PEC performances with different precursor amounts. We then optimized the concentration of vanadium (V) in the BiVO<sub>4</sub> precursor and investigated the morphologies, compositional properties, and PEC performance of the heterostructure of the BiVO<sub>4</sub> NPs/WO<sub>3</sub> nanocorals.

## 2. Experimental

### 2.1 Materials

The following materials were used as received: ammonium fluoride (NH<sub>4</sub>F, ≥ 98%, Sigma Aldrich), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, ≥ 99.9%, Sigma Aldrich), bismuth(III) nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, ≥ 98%, Sigma Aldrich), nitric acid (HNO<sub>3</sub>, 60%, Samchun Chemicals), ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH, 99.5%, Samchun Chemicals), and ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>, 99%, Daejung Chemicals & Metals).

### 2.2 Preparation of the BiVO<sub>4</sub>/WO<sub>3</sub> photoanodes

Tungsten (W) metal (thickness: 0.1 mm, 99.95% purity, Alfa Aesar) was cut into 1.5 × 1.5 cm<sup>2</sup> and mechanically ground using a 1200 grit soft sandpaper. Next, the W metal was cleaned successively with acetone, ethanol, and deionized (DI) water using an ultrasonicator, and then dried with nitrogen (N<sub>2</sub>) gas. W metal was anodized in a 1 M Na<sub>2</sub>SO<sub>4</sub> solution containing 0.5 wt% NH<sub>4</sub>F at 15 °C. The thickness of WO<sub>3</sub> nanocorals was increased with increase in anodization time from 1 h to 5 h, to approximately 460, 540, 610, 660 and 690 nm, respectively. Among them, WO<sub>3</sub> anodized for 3 h was used as the substrate. During anodization, a constant voltage of 40 V was applied to W using a DC power source (ODA-EX300-4), and current density *versus* time curves were recorded using a Keithley 2000. After anodization, the anodic WO<sub>3</sub> nanocorals were rinsed with DI water and dried with N<sub>2</sub> gas. Heat-treatment was performed in a tubular furnace at 500 °C under an argon (Ar) atmosphere for 2 h to crystallize the anodized WO<sub>3</sub> nanocoral film. Then, the BiVO<sub>4</sub> NPs were decorated onto the WO<sub>3</sub> nanocoral films by spin-coating. The BiVO<sub>4</sub>

precursor solution for spin-coating was prepared by dissolving 0.15 (0.3), 0.23 (0.44), 0.3 (0.59), and 0.6 M (1.18) NH<sub>4</sub>VO<sub>3</sub> in a mixture of 10 mL HNO<sub>3</sub> and 20 mL ethylene glycol. After complete dissolution, 0.3 M (2.25) Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added and then the solution was stirred for 30 min. After dropping 5, 10, and 30 μL of the precursor onto the WO<sub>3</sub> substrate, the samples were rested for 1 min so that the precursor penetrates to the bottom of the nanocoral structures. The spin-coating process was performed at 500 rpm for 60 s, 1000 rpm for 30 s, and 3000 rpm for 3 s for the precursor mixture solution and was repeated 3 times. Between each cycle, the BiVO<sub>4</sub>/WO<sub>3</sub> samples were heat-treated in a box furnace at 100 °C for 5 min. After the spin-coating process, the samples were annealed at 550 °C under an air atmosphere using the box furnace for 1 h.

### 2.3 Characterization

The morphologies of the WO<sub>3</sub> and BiVO<sub>4</sub>/WO<sub>3</sub> photoanodes were observed using a field-emission scanning electron microscope (FE-SEM, S-4300, Hitachi). To characterize the crystalline structures of the photoanodes, X-ray diffraction (XRD, X'Pert PRO MRD, Phillips) with a Cu-Kα radiation source and field emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL) were used. Raman scattering measurements (LabRAM HR Evolution, HORIBA) were obtained using 532 nm lasers. The analysis was conducted at the Inha University Core Facility Center for Sustainable Energy.

### 2.4 Photoelectrochemical measurements

0.5 M Na<sub>2</sub>SO<sub>4</sub> solution, silver/silver chloride (Ag/AgCl, 3 M KCl), a Pt mesh, and BiVO<sub>4</sub>/WO<sub>3</sub> photoanodes were used as the electrolyte, and reference, counter, and working electrodes, respectively. Photocurrent density, electrochemical impedance spectroscopy (EIS), and hydrogen (H<sub>2</sub>) gas production were measured using a potentiostat (VSP, Bio-Logics) and a solar simulator (LCS-100, Oriel Instruments) with a 100 W xenon (Xe) arc lamp (100 mW cm<sup>-2</sup>). To record the photocurrent density, linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s<sup>-1</sup>. The obtained potential was converted into a RHE potential using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.0591 \times \text{pH}) + E_{\text{Ag/AgCl}}^{\circ}$$

and

$$E_{\text{Ag/AgCl}} (3 \text{ M KCl}) = 0.1976 \text{ V at } 25 \text{ }^{\circ}\text{C}$$

EIS was performed in the range of 30 kHz–10 MHz at 1.23 V *vs.* RHE. To evaluate PEC H<sub>2</sub>-gas production at 1.23 V *vs.* RHE, 200 μL gas was taken from the sealed quartz tube reactor every half hour and injected into a gas chromatograph with a TCD detector (GC/MSD 5975C, Agilent Technologies). The incident photon-to-current conversion efficiency (IPCE) was measured at 1.23 V *vs.* RHE using a monochromator (MonoRa200, DONG-WOO OPTRON) and various bandpass filters with a Xe lamp (300 W, OMA). The IPCE was calculated using the following equation:



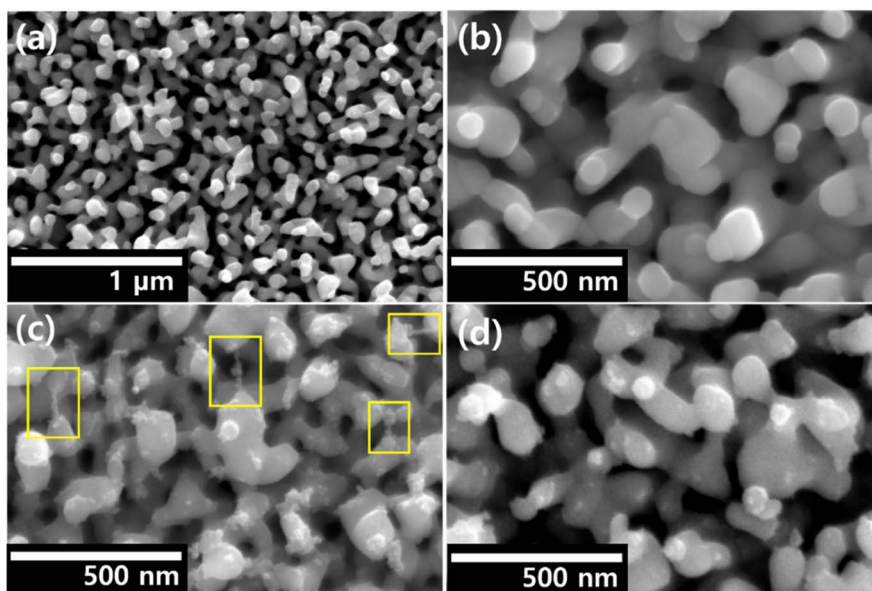


Fig. 1 FE-SEM image of (a)  $\text{WO}_3$  nanocorals, (b) 5-BW, (c) 10-BW, and (d) 30-BW.

$$\text{IPCE}(\%) = \frac{hc \times J_{\text{ph}}}{\lambda \times P} \times 100,$$

where  $h$  is Planck constant,  $c$  is the velocity of light,  $J_{\text{ph}}$  is the photocurrent density,  $\lambda$  is the incident wavelength, and  $P$  is power density of each wavelength.

### 3. Results and discussion

#### 3.1 Formation of linked $\text{BiVO}_4$ NPs on $\text{WO}_3$ nanocorals

Fig. 1a shows the morphology of  $\text{WO}_3$  nanocoral anodized W metal described in our previous report.<sup>24</sup> The  $\text{WO}_3$  nanocorals have thick branches and round edges with a high surface area, which can support the formation of NPs, and the length of the nanocoral structures is  $\sim 550$ – $600$  nm (Fig. S1†). All the  $\text{BiVO}_4/\text{WO}_3$  (BW) heterostructures formed by the anodization and spin-coating processes contained  $\text{BiVO}_4$  NPs on the  $\text{WO}_3$  nanocorals as presented in Fig. 1b–d. During the spin-coating process, the precursor amounts were controlled to be 5, 10, and 30  $\mu\text{L}$ , and the heterostructural  $\text{BiVO}_4$  NPs/ $\text{WO}_3$  nanocorals

fabricated with these precursor amounts were labelled as 5-BW, 10-BW, and 30-BW, respectively. Following heat treatment in air, a 5–10 nm size of the well-spread  $\text{BiVO}_4$  NPs was observed on the  $\text{WO}_3$  nanocorals. The formation of  $\text{BiVO}_4$  NPs on the nanocorals was related to the hydrophilicity of the anodic  $\text{WO}_3$  nanocorals. After anodization, normally the metal oxide has hydrophilicity.<sup>26</sup> The anodic metal oxide is hydrophilic, but the rest of the metal surface is relatively hydrophobic; thus, the precursor prefers to remain on the anodized surface, where it forms a droplet, as shown in Fig. S2.† As the 5  $\mu\text{L}$  precursor amount is a small quantity, it was not sufficient to form numerous  $\text{BiVO}_4$  NPs compared to a 10  $\mu\text{L}$  amount, and thus the NPs were rarely located as shown in Fig. 1b. However, a 10  $\mu\text{L}$  precursor droplet can withstand speeds up to 3000 rpm, allowing for a larger quantity of the precursor to remain on the  $\text{WO}_3$  nanocoral surface, resulting in a large amount of  $\text{BiVO}_4$  NPs being coated on the  $\text{WO}_3$  nanocorals for 10-BW. In particular, the NPs are linked as nanowires from one  $\text{WO}_3$  nanocoral branch to another, as shown in Fig. 1c. We expected 30-BW to contain more NPs than 10-BW; however, 30-BW displayed only

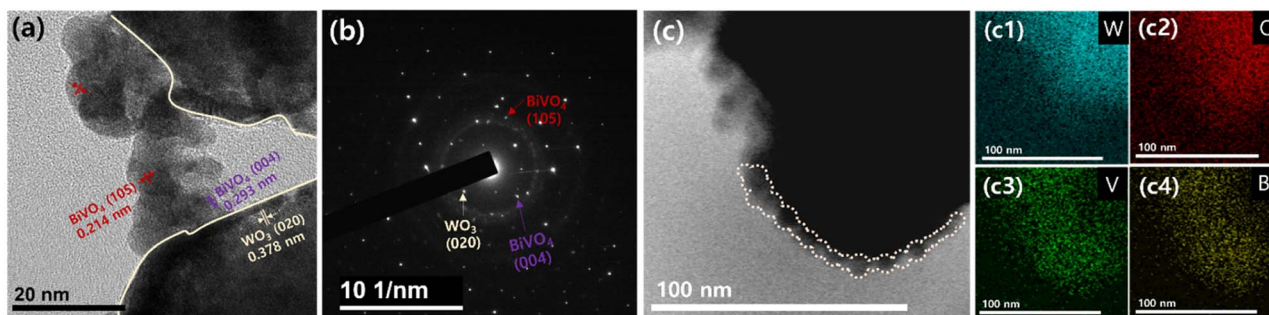


Fig. 2 (a) FE-TEM image of 10-BW, (b) corresponding SAED pattern of (a), (c) TEM image obtained in the HADDF mode of 10-BW, and (c1–c4) corresponding elemental analysis by EDS mapping of W, O, V, and Bi.



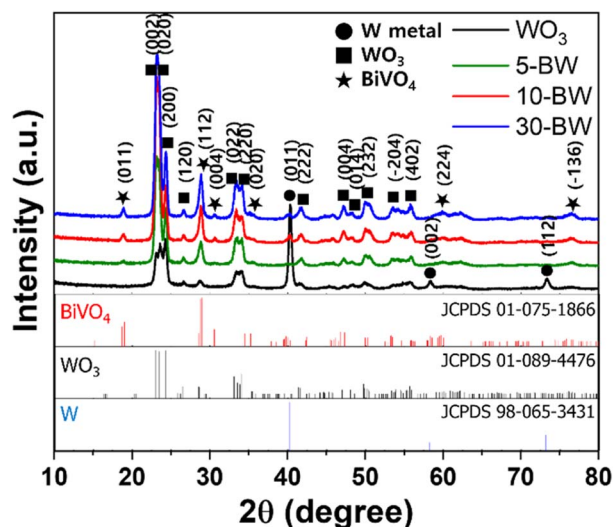


Fig. 3 XRD patterns of  $\text{WO}_3$  nanocrystals and  $\text{BiVO}_4/\text{WO}_3$  heterostructures of 5-BW, 10-BW, and 30-BW.

well-perched NPs on the  $\text{WO}_3$  nanocrystals without linking (Fig. 1d). This is because 30  $\mu\text{L}$  of the precursor is comparatively easy to disperse to the outer area than 10  $\mu\text{L}$  of the precursor when the centrifugal force interacts with the droplet during spin-coating (Fig. S2<sup>†</sup>). In the case where some part of the droplet dispersed to the non-anodized metal surface and the droplet suddenly flattened, the droplet flowed off the substrate, reducing the precursor amount.

The TEM image of 10-BW in Fig. 2a showed  $\sim 10$  nm  $\text{BiVO}_4$  NPs with lattice spacings of 0.214 and 0.293 nm representing the planes of (1 0 5) and (0 0 4), respectively, and the  $\text{WO}_3$  nanocrystals with a lattice spacing of 0.378 nm, corresponding to the (0 2 0) plane. The selected-area electron diffraction (SAED) pattern (Fig. 2b) confirms a polycrystalline structure; the (0 2 0) plane corresponds to monoclinic  $\text{WO}_3$  and the (1 0 5) and (0 0 4) planes correspond to monoclinic  $\text{BiVO}_4$ . High-angle annular dark-field (HAADF)-scanning TEM reveals well configured  $\text{BiVO}_4$  NPs and  $\text{WO}_3$  (Fig. 2c). The NPs were linked to the surface of  $\text{WO}_3$ , and energy-dispersive X-ray spectroscopy (EDS) elemental mapping revealed that the  $\text{BiVO}_4$  NPs were uniformly distributed on the  $\text{WO}_3$  surface.

The crystalline phases of the  $\text{WO}_3$  nanocrystals (5-BW, 10-BW, and 30-BW) were examined using XRD, as illustrated in Fig. 3. Peaks corresponding to W metal were observed at  $40.2^\circ$ ,  $58.2^\circ$ , and  $73.2^\circ$  for the  $\text{WO}_3$  nanocrystals, whereas only the  $40.2^\circ$  peak was observed for the BW samples. The XRD patterns of the  $\text{WO}_3$  nanocrystal layer show peaks at  $23.0^\circ$ ,  $23.5^\circ$ ,  $24.2^\circ$ ,  $26.5^\circ$ ,  $33.1^\circ$ ,  $34.0^\circ$ ,  $41.6^\circ$ ,  $49.9^\circ$ , and  $55.7^\circ$  indexed to the (0 0 2), (0 2 0), (2 0 0), (1 2 0), (0 2 2), (2 2 0), (2 2 2), (2 3 2), and (4 0 2) planes, respectively. The  $\text{WO}_3$  nanocrystals exhibited well-crystallized monoclinic  $\text{WO}_3$  phases (JCPDS #089-4476).<sup>27,28</sup> The XRD patterns of all the BW samples exhibited peaks at  $18.9^\circ$ ,  $28.9^\circ$ ,  $30.5^\circ$ ,  $40.2^\circ$ ,  $60.0^\circ$ , and  $76.5^\circ$  corresponding to the (0 1 1), (1 1 2), (0 0 4), (0 2 0), (1 2 1), (2 2 4), and  $(-1\ 3\ 6)$  planes, respectively, which are the monoclinic phases of  $\text{BiVO}_4$  (JCPDS #075-1866).<sup>29,30</sup> Although 5-BW showed lower  $\text{BiVO}_4$  peak intensities

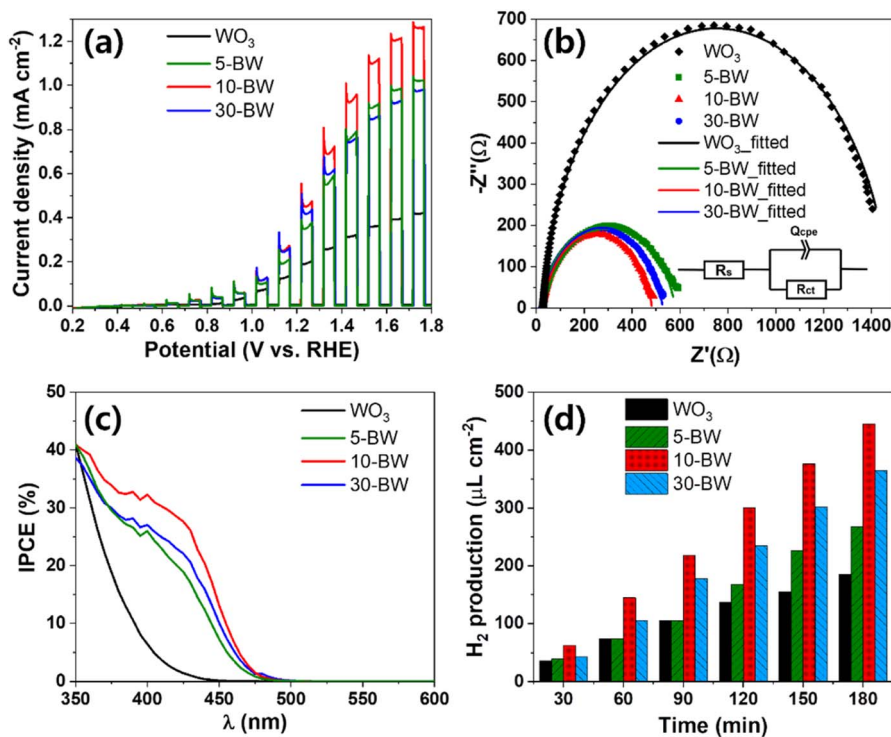


Fig. 4 Photoelectrochemical performances of the  $\text{WO}_3$  nanocrystals and  $\text{BiVO}_4/\text{WO}_3$  photoanodes of 5-BW, 10-BW, and 30-BW: (a) photocurrent densities by linear sweep voltammetry, (b) Nyquist plots and equivalent circuits, (c) PEC  $\text{H}_2$  production diagram as a function of time, and (d) IPCE spectra.



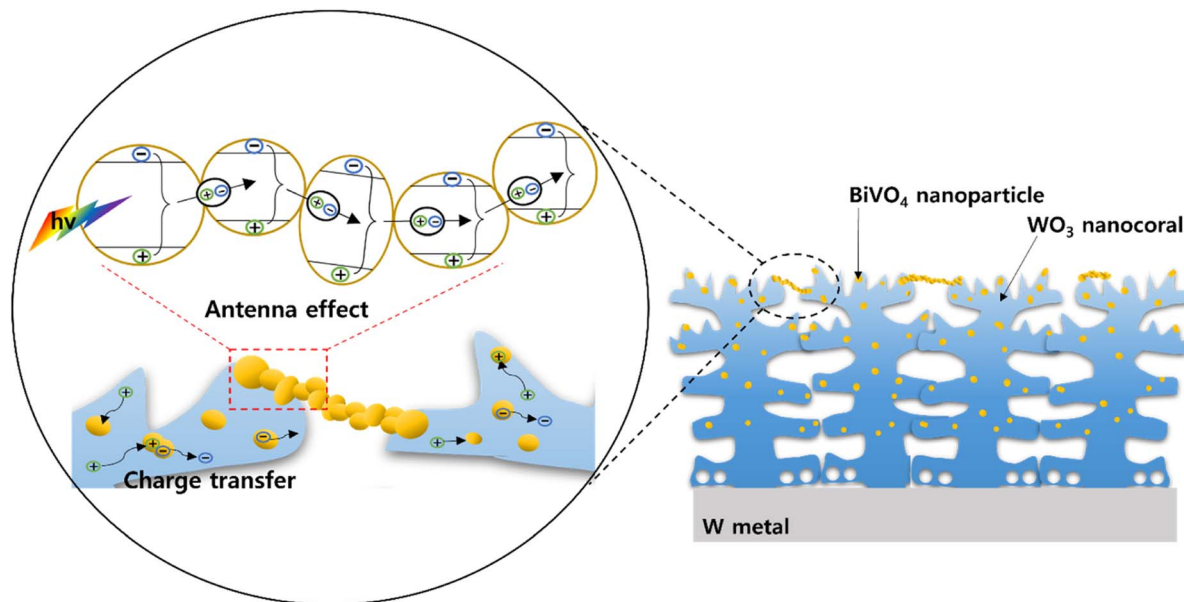


Fig. 5 Schematic illustration of 10-BW and its mechanism of charge transfer and the antenna effect.

at  $18.9^\circ$  and  $30.5^\circ$  owing to the quantity of  $\text{BiVO}_4$ , the 10-BW and 30-BW peak intensities were similar. This indicates that  $10 \mu\text{L}$  of the  $\text{BiVO}_4$  precursor is sufficient to form well-crystallized  $\text{BiVO}_4$  NPs that are to be used as photoanodes.

The chopped linear sweep voltammetry (LSV) curves with the PEC performance of 5-BW, 10-BW, and 30-BW are illustrated in Fig. 4a. Compared to the pristine  $\text{WO}_3$  nanocorals, all the BW photoanodes exhibited a higher photocurrent density, indicating that the heterostructural BW achieved an improved photocurrent density. The highest photocurrent density of  $0.45$

$\text{mA cm}^{-2}$  at  $1.23 \text{ V vs. RHE}$  was obtained with the  $10 \mu\text{L}$  spin-coated  $\text{BiVO}_4/\text{WO}_3$  photoanode, and it was 2.4 times higher than that obtained for the  $\text{WO}_3$  nanocorals ( $0.19 \text{ mA cm}^{-2}$  at  $1.23 \text{ V vs. RHE}$ ). The  $\text{BiVO}_4/\text{WO}_3$  photoanodes of 30-BW and 5-BW were followed to  $0.42$  and  $0.35 \text{ mA cm}^{-2}$  at  $1.23 \text{ V vs. RHE}$ . The 5-BW sample exhibited the lowest photocurrent density owing to the extremely small quantity of  $\text{BiVO}_4$  NPs on the  $\text{WO}_3$  layer. The fitted EIS Nyquist plots of the 5-BW, 10-BW, 30-BW, and  $\text{WO}_3$  nanocorals are depicted in Fig. 4b. In addition, the applied equivalent circuit consisting of the solution resistance

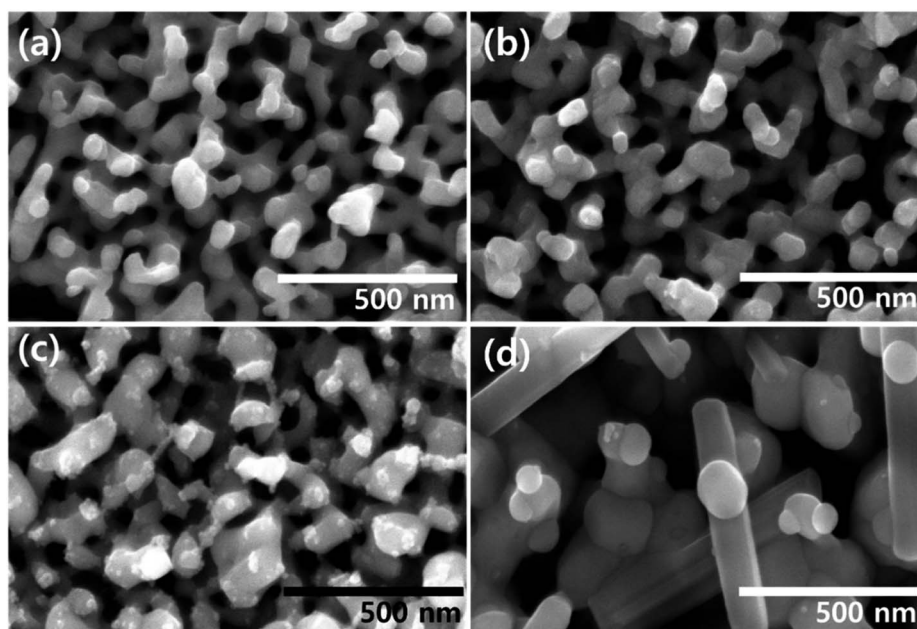


Fig. 6 FE-SEM image of  $\text{BiVO}_4/\text{WO}_3$  photoanodes depending on V concentration of the  $\text{BiVO}_4$  precursor; (a) 0.15, (b) 0.23, (c) 0.3, and (d) 0.6 M.



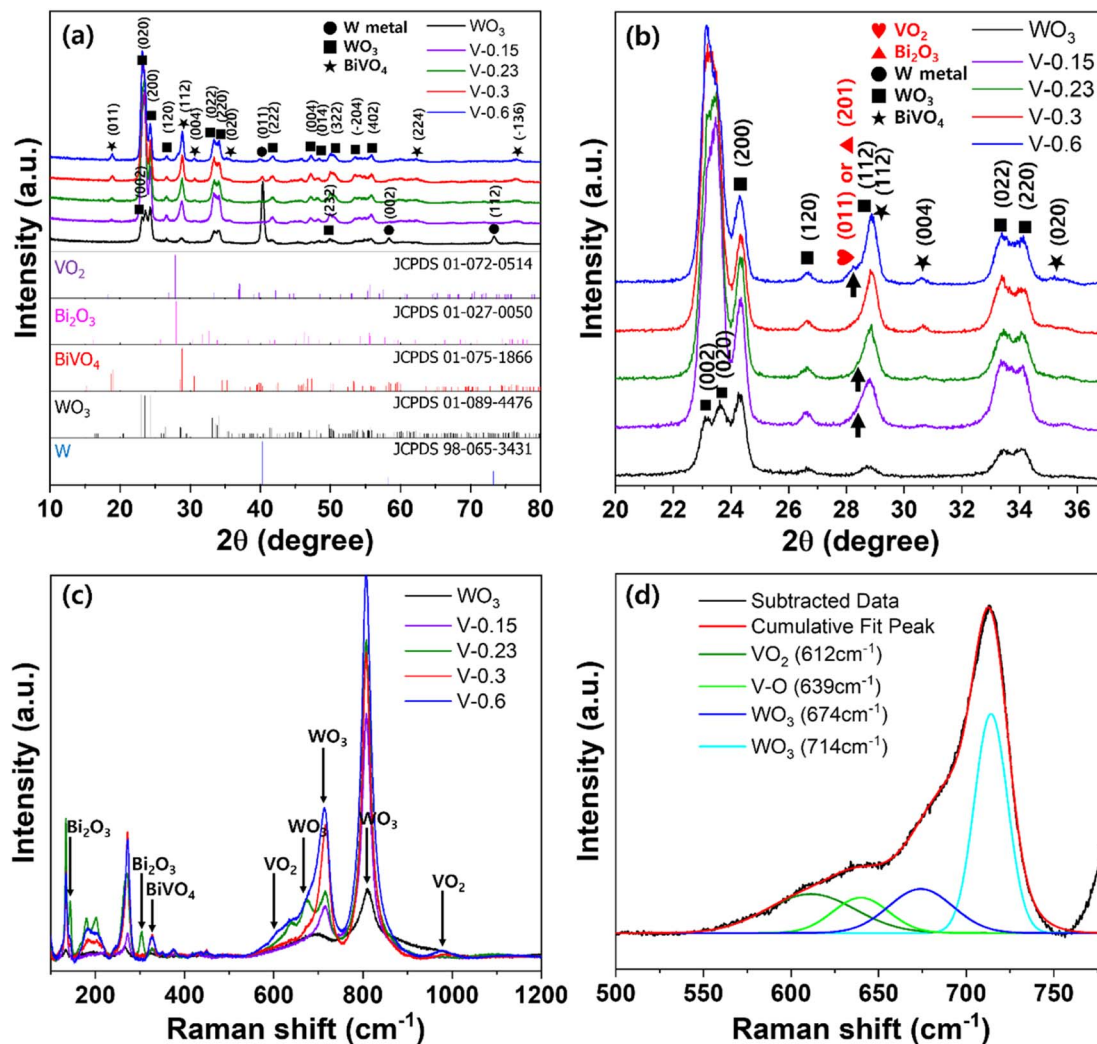
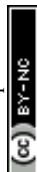


Fig. 7 (a) XRD patterns of BiVO<sub>4</sub>/WO<sub>3</sub>, (b) enlargement of (a) from 20° to 37°, (c) Raman spectra of BiVO<sub>4</sub>/WO<sub>3</sub> photoanodes depending on V concentrations of 0.15, 0.23, 0.3, and 0.6 M for the BiVO<sub>4</sub> precursor; and (d) peak separation of V-0.6 at (c) from 500 to 750 cm<sup>-1</sup>.

( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), and constant phase element ( $Q_{cpe}$ ) is shown in the inset. The sequence of charge transfer resistance values was in line with the photocurrent densities: 10-BW (457.3  $\Omega$ ) < 30-BW (506.2  $\Omega$ ) < 5-BW (561.1  $\Omega$ ) < WO<sub>3</sub> nanocorals (1450  $\Omega$ ). After the PEC measurements, 10-BW showed an identical morphology and crystal structure (Fig. S3–S4<sup>†</sup>). In addition, the chemical composition of each element, except V, displayed identical intensities as illustrated in Fig. S5.† The decreased intensity of V is due to dissolution of V<sup>5+</sup> ions, and the Bi peaks slightly shifted to higher binding energies owing to the strong influence of O bonding energy on Bi after the removal of V. However, this had negligible impact on the changes in performance. As presented in Fig. 4c, the linked BiVO<sub>4</sub> NPs of 10-BW achieved the highest IPCE values of 39% at 360 nm and 30% at 410 nm. At 350 nm, the WO<sub>3</sub> nanocorals, 5-BW, and 10-BW showed an approximate value of 40%, but 10-BW exhibited superior absorbance of light, even at a longer wavelength of 350 nm. The sequence of the IPCE values of the BW samples was 5-BW (36%), 30-BW (35%), and WO<sub>3</sub>

nanocorals (31%) at 360 nm; meanwhile, at 410 nm, the order changed to 30-BW (25%), 5-BW (23%), and WO<sub>3</sub> nanocorals (4%). The two IPCE values of 5-BW and 30-BW were reversed at 372 nm, implying that 30-BW absorbed more visible light than 5-BW. Conversely, 5-BW can absorb more UV light than 30-BW. This indicates that a higher absorbance of visible light, instead of UV light, results in an improved PEC efficiency. The bandgaps evaluated using IPCE data are shown in Fig. S6.† Even though the amounts of the precursor were significantly different, the bandgaps of the WO<sub>3</sub> nanocorals, 5-BW, 10-BW, and 30-BW were relatively similar, that is, 2.80, 2.54, 2.53, and 2.55 eV, respectively. PEC H<sub>2</sub>-production under solar light irradiation for 3 h is depicted in Fig. 4d. The H<sub>2</sub> amounts of WO<sub>3</sub> nanocorals, 5-BW, 10-BW, and 30-BW were 185.6, 267.6, 445.3, and 365.5  $\mu\text{L cm}^{-2}$ , respectively, and they linearly increased with increasing reaction time. H<sub>2</sub> production is interrelated with photocurrent density, and high photocurrent density led to a high production rate; thus 10-BW obtained a higher H<sub>2</sub> production rate of 123.0  $\mu\text{L h}^{-1} \text{cm}^{-2}$  compared to



30-BW ( $86.3 \mu\text{L h}^{-1} \text{cm}^{-2}$ ) and 5-BW ( $33.6 \mu\text{L h}^{-1} \text{cm}^{-2}$ ), as shown in Fig. S7.† The faradaic efficiency for PEC  $\text{H}_2$ -production using the optimal 10-BW was calculated to be 86%. In addition, the mixed structures of  $\text{BiVO}_4$  NPs and linked chains of NPs of 10-BW significantly improved the PEC efficiency by providing a charge-transfer pathway for electrons or holes to move easily toward  $\text{WO}_3$  or  $\text{BiVO}_4$  (Fig. 5). Moreover, the linked  $\text{BiVO}_4$  NPs can transfer photon energy from one NP to another, which is called the antenna effect<sup>31</sup> resulting in high PEC activities. The linked  $\text{BiVO}_4$  NPs also connected one  $\text{WO}_3$  nanocoral to another during the migration of electron-hole pairs (excitons). Once the exciton is transferred to the  $\text{WO}_3$  nanocoral, the exciton is separated into both electron and hole, and the electron/hole transfer is activated.<sup>32</sup> Then, each transferred electron migrates to the  $\text{WO}_3$  nanocoral, and the holes are transferred to the  $\text{BiVO}_4$  NPs. Furthermore, numerous generated excitons increase solar-to-hydrogen conversion efficiency,<sup>33</sup> resulting in the generation of a high amount of  $\text{H}_2$ .

### 3.2 Optimization of the $\text{BiVO}_4$ precursor

To improve the quality of  $\text{BiVO}_4$ , V concentrations in the  $\text{BiVO}_4$  precursor were controlled to be 0.15, 0.23, 0.3, and 0.6 M, and samples with these concentrations were labelled as V-0.15, V-0.23, V-0.3, and V-0.6, respectively, while the bismuth (Bi) concentration was fixed at 0.3 M. Each precursor was spin-coated on  $\text{WO}_3$  nanocorals with 10  $\mu\text{L}$  optimized for PEC performance. Fig. 6 presents the different morphologies of the

BW samples obtained with different V concentrations in the  $\text{BiVO}_4$  precursors. In the SEM image of V-0.15 (Fig. 6a),  $\text{BiVO}_4$  NPs were not observed, and the morphology was identical to that of the pristine  $\text{WO}_3$  nanocorals.  $\text{BiVO}_4$  NPs were rarely present in the SEM images of V-0.23, as illustrated in Fig. 6b. Linked  $\text{BiVO}_4$  NPs were observed only for V-0.3, as shown in Fig. 6c. The quantity of  $\text{BiVO}_4$  NPs increased with an increase in the V concentration from 0.23 M to 0.3 M. However, when the V concentration was increased to 0.6 M, some nanorods are suddenly obtained along with  $\text{BiVO}_4$  NPs as shown in Fig. 6d. The nanorods were composed of V and oxygen (O), as shown in Fig. S8.† Vanadium oxide nanorods were formed because of the high concentration of V.

The XRD patterns of the V-controlled  $\text{BiVO}_4/\text{WO}_3$  photoanodes are shown in Fig. 7a. The monoclinic phases of  $\text{WO}_3$  and  $\text{BiVO}_4$  exhibit the same patterns as those shown in Fig. 3. However, all the samples, except V-0.3, demonstrated a broad peak with a strong shoulder peak at approximately  $28^\circ$ , particularly V-0.6 (Fig. 7b). As shown in Fig. 6d, V-0.6 has vanadium oxide nanorods at the surface; thus, the peak at  $27.89^\circ$  was predicted to be of  $\text{VO}_2$  (JCPDS #072-0514),<sup>34</sup> whereas the lack of V in the V-0.15 or V-0.23 samples could lead to the formation of bismuth oxides, which are responsible for the peak at  $27.94^\circ$  (JCPDS #027-0050).<sup>35</sup> As the other peaks of  $\text{VO}_2$  or  $\text{Bi}_2\text{O}_3$  overlapped with the  $\text{WO}_3$  or  $\text{BiVO}_4$  peaks, additional peaks were not investigated.

Raman scattering measurements were conducted to precisely characterize the V-controlled  $\text{BiVO}_4$  (Fig. 7c). The

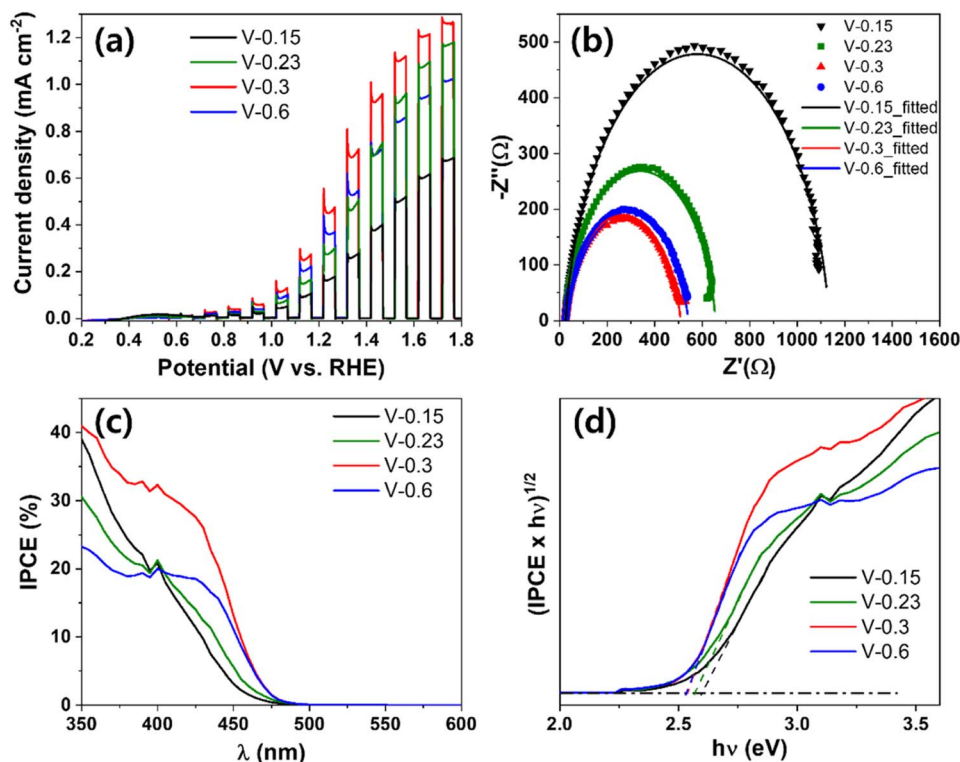


Fig. 8 Photoelectrochemical performances of  $\text{BiVO}_4/\text{WO}_3$  photoanodes depending on V concentrations of 0.15, 0.23, 0.3, and 0.6 M of the  $\text{BiVO}_4$  precursor; (a) photocurrent densities by linear sweep voltammetry, (b) Nyquist plots, (c) IPCE spectra, and (d) bandgap evaluated by IPCE measurement.



O–W–O stretching bands at 714 and 806  $\text{cm}^{-1}$  allowed for the identification of monoclinic  $\text{WO}_3$ .<sup>36</sup> The peaks for V-0.15 were comparable to those of pristine  $\text{WO}_3$ , as the  $\text{BiVO}_4$  NPs were rarely present on the surface of the  $\text{WO}_3$  nanocorals. After the formation of  $\text{BiVO}_4$ , the remaining Bi in the  $\text{BiVO}_4$  precursor with V-0.23 formed bismuth oxide. Thus, the peak of Bi–O stretching mode of  $\text{Bi}_2\text{O}_3$  at 304  $\text{cm}^{-1}$  was only observed for V-0.23.<sup>37</sup> Similarly, the residue of V in the  $\text{BiVO}_4$  precursor with V-0.6 formed vanadium oxide,  $\text{VO}_2$ ; thus, the corresponding peaks appeared at 612 and 988  $\text{cm}^{-1}$ , as shown in Fig. 6d.<sup>38,39</sup> As a result, V-0.3 showed  $\text{BiVO}_4$  peaks at 326 and 374  $\text{cm}^{-1}$  without any by-products, which were attributed to the asymmetric and symmetric deformation of  $\text{VO}_4^{3-}$ .<sup>40</sup> Therefore, 0.3 M of Bi and V is an optimal concentration as a  $\text{BiVO}_4$  precursor for fabrication of high-quality  $\text{BiVO}_4$  NPs.

The PEC performances of different V-controlled  $\text{BiVO}_4/\text{WO}_3$  photoanodes are shown in Fig. 8a. The optimal BW photoanode with V-0.3 showed the highest photocurrent density value of 0.45  $\text{mA cm}^{-2}$  at 1.23 V vs. RHE. The V-0.6 and V-0.23 samples then followed with photocurrent densities of 0.36 and 0.27  $\text{mA cm}^{-2}$  at 1.23 V vs. RHE, and 0.15 M showed an even lower photocurrent density of 0.16  $\text{mA cm}^{-2}$  at 1.23 V vs. RHE compared to pristine  $\text{WO}_3$  nanocorals. Based on the photocurrent results, the sequence of charge transfer resistance should exhibit an opposite trend: the optimal BW photoanode of V-0.3 had the lowest resistance of 486.9  $\Omega$  followed by V-0.9 (518.1  $\Omega$ ), V-0.44 (633.0  $\Omega$ ), and V-0.3 (1110  $\Omega$ ) as shown in Fig. 8b. The equivalent circuit and its components are the same as those shown in Fig. 4b. In Fig. 8c, the optimal BW photoanode (V-0.3) also shows the highest IPCE value of 29% at 420 nm. The order of the IPCE values for V-0.9 (19%), V-0.44 (15%), and V-0.3 (13%) at 420 nm is in line with the PEC results, proving that absorbing a high proportion of visible light remarkably enhances the PEC efficiency. For the evaluated bandgap from the IPCE values in Fig. 8d, the V-0.3 and V-0.44 samples showed bandgap values of 2.60 and 2.57 eV, and the V-0.3 and V-0.9 samples showed the same bandgap value of 2.53 eV. Nevertheless, V-0.9 showed a lower PEC performance than V-0.3 due to low IPCE efficiency in the range of 350 to 450 nm.

## 4. Conclusions

In summary, this study addressed the formation of heterostructured  $\text{BiVO}_4$  and  $\text{WO}_3$  with a mixed structure of NPs and linked  $\text{BiVO}_4$  NPs on  $\text{WO}_3$  nanocoral structures to enhance PEC performance. The linked  $\text{BiVO}_4$  NPs were simply constructed on anodic  $\text{WO}_3$  nanocorals by controlling the amount of the  $\text{BiVO}_4$  precursor to be 10  $\mu\text{L}$  during spin-coating. This phenomenon was related to the hydrophilicity of the  $\text{WO}_3$  nanocorals, as the precursor amount on the  $\text{WO}_3$  nanocorals that could withstand a high speed rpm during spin-coating was important. Furthermore, the linked  $\text{BiVO}_4$  NPs/ $\text{WO}_3$  nanocoral heterostructure showed improved PEC performance, including photocurrent density, PEC  $\text{H}_2$  production, and IPCE, compared to the  $\text{BiVO}_4$  NPs/ $\text{WO}_3$  nanocoral heterostructure. The linked NPs on the  $\text{WO}_3$  nanocorals provided photogenerated electrons to move to the  $\text{WO}_3$  substrate and improved the charge carrier and charge separation *via* the antenna effect. Moreover, the NPs did not

fully cover the  $\text{WO}_3$  nanocorals, and the nanocoral structures could harvest more light, which allowed for multiple light scattering. The optimized  $\text{BiVO}_4$  precursor concentration was 0.3 M of V and Bi, which formed the purest  $\text{BiVO}_4$  on the  $\text{WO}_3$  nanocorals without any by-product. When the V concentration was lower or higher than the Bi concentration,  $\text{Bi}_2\text{O}_3$  or  $\text{VO}_2$  was formed along with  $\text{BiVO}_4$ . Thus, the BW photoanode of the purist V-0.3 allowed realization of the highest photocurrent density and IPCE values of 0.45  $\text{mA cm}^{-2}$  (at 1.23 V vs. RHE) and 29% (at 420 nm), respectively, and accordingly the lowest charge transfer resistance of 486.9  $\Omega$ .

## Conflicts of interest

There are no conflicts to declare.

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