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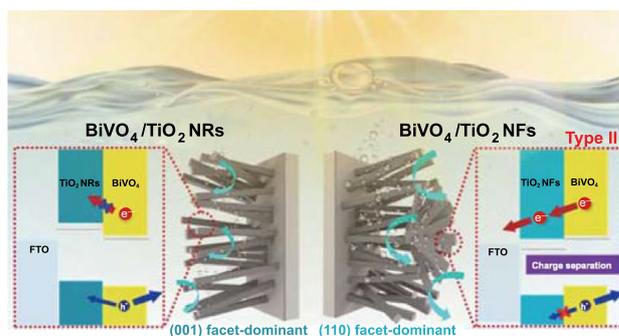
# Crystal Facet Engineering of TiO<sub>2</sub> Nanostructures for Enhancing Photoelectrochemical Water Splitting with BiVO<sub>4</sub> Nanodots

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## HIGHLIGHTS

- Two types of BiVO<sub>4</sub>/TiO<sub>2</sub> heterostructure photoanodes comprising TiO<sub>2</sub> nanorods (NRs) and TiO<sub>2</sub> nanoflowers (NFs) with different (001) and (110) crystal facets, respectively, were designed.
- The higher photoactivity of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs than BiVO<sub>4</sub>/TiO<sub>2</sub> NRs was attributed to the improvement of charge separation by the TiO<sub>2</sub> NFs.
- The formation of type II band alignment between BiVO<sub>4</sub> nanodots and TiO<sub>2</sub> NFs expedited electron transport and reduced charge recombination.

**ABSTRACT** Although bismuth vanadate (BiVO<sub>4</sub>) has been promising as photoanode material for photoelectrochemical water splitting, its charge recombination issue by short charge diffusion length has led to various studies about heterostructure photoanodes. As a hole blocking layer of BiVO<sub>4</sub>, titanium dioxide (TiO<sub>2</sub>) has been considered unsuitable because of its relatively positive valence band edge and low electrical conductivity. Herein, a crystal facet engineering of TiO<sub>2</sub> nanostructures is proposed to control band structures for the hole blocking layer of BiVO<sub>4</sub> nanodots. We design two types of TiO<sub>2</sub> nanostructures, which are nanorods (NRs) and nanoflowers (NFs) with different (001) and (110) crystal facets, respectively, and fabricate BiVO<sub>4</sub>/TiO<sub>2</sub> heterostructure photoanodes. The BiVO<sub>4</sub>/TiO<sub>2</sub> NFs showed 4.8 times higher photocurrent density than the BiVO<sub>4</sub>/TiO<sub>2</sub> NRs. Transient decay time analysis and time-resolved photoluminescence reveal the enhancement is attributed to the reduced charge recombination, which is originated from the formation of type II band alignment between BiVO<sub>4</sub> nanodots and TiO<sub>2</sub> NFs. This work provides not only new insights into the interplay between crystal facets and band structures but also important steps for the design of highly efficient photoelectrodes.

**KEYWORDS** Crystal facet control; Bismuth vanadate; Titanium dioxide; Heterojunction; Water splitting

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## 1 Introduction

Solar-driven photoelectrochemical (PEC) water splitting is considered a major breakthrough to settle an energy crisis. Despite its promise, the commercialization of PEC water splitting has been limited because of the relatively low efficiency and stability [1]. Although metal oxide-based photoelectrodes such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$ , and  $\text{BiVO}_4$  can be easily synthesized, major limitations such as charge recombination and short carrier lifetimes of from picosecond ( $ps$ ) to nanosecond ( $ns$ ) restrict their photoactivity.

The construction of heterostructure photoelectrodes is an effective approach to improve light absorption, carrier separation, and charge transfer efficiencies [2, 3]. Since it relies on the appropriate band alignment like type II heterojunction, the combination of photoelectrode materials having proper band edge positions is a key for determining their functionality in PEC water splitting. Among various heterostructures such as  $\text{Fe}_2\text{O}_3/\text{WO}_3$  [4],  $\text{BiVO}_4/\text{WO}_3$  [5–7],  $\text{Fe}_2\text{O}_3/\text{SnO}_2$  [8–10],  $\text{In}_2\text{S}_3/\text{In}_2\text{O}_3$  [11], and  $\text{BiVO}_4/\text{SnO}_2$  [12, 13],  $\text{BiVO}_4$ -based heterostructure photoanodes have been widely studied since short charge diffusion lengths and lifetimes of  $\text{BiVO}_4$  cause severe charge recombination. In a representative  $\text{BiVO}_4/\text{WO}_3$  heterostructure,  $\text{WO}_3$  enhances the charge separation as a hole blocking layer of  $\text{BiVO}_4$ , forming the type II band alignment. However, it has a relatively positive flat band potential of about 0.4 V versus (vs.) a reversible hydrogen electrode (RHE), which results in potential energy losses for electrons as they are transferred from the  $\text{WO}_3$  to the  $\text{BiVO}_4$ , limiting the photovoltage of the combined system [5–7]. Also, the oxidation of surface hydroxyl groups of  $\text{WO}_3$  causes the formation of peroxo-species, which reduces the stability of heterostructure photoanodes [13].

Compared to the  $\text{WO}_3$ , rutile  $\text{TiO}_2$  is highly stable in a wide range of pH and has a relatively negative flat band potential of about 0.2 V versus RHE, which does not significantly limit the photovoltage obtainable from  $\text{BiVO}_4$  [14–16]. However,  $\text{TiO}_2$  has an intrinsic limitation of low electrical conductivity to be used as the hole blocking layer for  $\text{BiVO}_4$  [17]. To resolve the problem, the increment of carrier concentration through doping and nanostructuring is required. In particular, both high surface area and electrical conductivity can be obtained by designing one-dimensional (1D) nanostructures such as nanorods (NRs), nanowires, and nanoflowers (NFs). Andoshe et al. developed S, N co-doped  $\text{TiO}_2$  NRs and increased their carrier concentration

and electrical conductivity [18]. The second problem is a mismatched band structure between  $\text{BiVO}_4$  and  $\text{TiO}_2$ . A relatively positive valence band edge of  $\text{TiO}_2$  makes it difficult to form the type II heterostructure suitable for charge separation. In order to utilize  $\text{TiO}_2$  as the hole blocking layer for  $\text{BiVO}_4$ , the control of band edge position is necessary, and crystal facet engineering has emerged as an emerging strategy. According to the previous works, metal oxides provided various band edge positions depending on their crystal facets [19–21]. For instance, Wang et al. demonstrated that the (111) facet of  $\text{Cu}_2\text{O}$ , with a lower work function than the (100) facet, is unfavorable for the migration of holes from the  $\text{Cu}_2\text{O}$  surface to Pd through a semiconductor–metal junction [22]. It is reasonable to select and control the contact facet for the heterostructure to achieve suitable band structures and efficient charge separation.

In this work, we compare two types of  $\text{BiVO}_4/\text{TiO}_2$  heterostructure photoanodes with different (001) and (110) crystal facets of  $\text{TiO}_2$ , which are NRs and NFs, respectively. After  $\text{BiVO}_4$  nanodots are conformally electrodeposited on the surface of the  $\text{TiO}_2$  nanostructures, the photocurrent density of  $\text{BiVO}_4/\text{TiO}_2$  NFs increases by about 4.7 times, while that of  $\text{BiVO}_4/\text{TiO}_2$  NRs decreases. Based on the analysis of charge carrier dynamics, it is revealed that the difference is derived by the charge separation ability of crystal facet-engineered  $\text{TiO}_2$ . The ultraviolet photoemission spectroscopy (UPS) represents band edge positions of  $\text{TiO}_2$  nanostructures are significantly dependent on their crystal facet. Since  $\text{TiO}_2$  NFs with (110) facets have relatively negative band edges, as a hole blocking layer they form type II heterojunction with  $\text{BiVO}_4$  nanodots. In addition, the initial facet of  $\text{TiO}_2$  has a decisive effect on the final architecture of the  $\text{BiVO}_4/\text{TiO}_2$  due to the difference in the tendency of the  $\text{BiVO}_4$  electrodeposition on the nanostructured  $\text{TiO}_2$ . In a word, crystal facet engineering plays a key role in affecting charge separation and in determining photoactivity. These findings provide a feasible avenue to adjust diverse metal oxides for use as photoelectrodes for desirable solar water splitting.

## 2 Experimental Section

### 2.1 Synthesis of $\text{TiO}_2$ NRs and $\text{TiO}_2$ NFs

$\text{TiO}_2$  NRs and  $\text{TiO}_2$  NFs were grown on fluorine doped tin oxide (FTO) glass substrates using hydrothermal synthesis

similar to those in a previously reported paper [18]. Briefly, the precursor solution was prepared with 0.8 mL of titanium (IV) butoxide ( $C_{16}H_{36}O_4Ti$ , 97%, Aldrich), 5 mg of sulfamic acid ( $NH_2SO_3H$ , 99.3%, Aldrich), 25 mL of HCl (38%, Daejung), and 25 mL of deionized water ( $dH_2O$ ) under magnetic stirring. After vigorous magnetic stirring for another 10 min, the solution was poured into Teflon vessel. The Teflon vessel, which contained the precursor solution and the FTO glass, was inserted into the autoclave and heated for 4 h at 180 °C in an oven and kept inside until the temperature reached room temperature. The synthesized  $TiO_2$  NRs were removed from the Teflon vessel and rinsed repeatedly using  $dH_2O$ . After sufficient rinsing, the  $TiO_2$  NRs were annealed at 500 °C for 3 h with 5%  $H_2/95\%$   $N_2$  gas. For the synthesis of the  $TiO_2$  NFs, a larger amount of sulfamic acid was added to the precursor solution, and the reaction time was increased over that of the  $TiO_2$  NRs. A precursor solution for the growth of  $TiO_2$  NFs was prepared with 100 mg of sulfamic acid ( $NH_2SO_3H$ , 99.3%, Aldrich), 0.8 mL of titanium butoxide ( $C_{16}H_{36}O_4Ti$ , 97%, Aldrich), and 50 mL of HCl solution (25 mL of  $dH_2O$  and 25 mL of concentrated HCl (38%, Daejung)). After vigorous stirring until the solution became completely clear, the solution was transferred to the Teflon vessel and moved into an autoclave. The autoclave was sealed and heated to the reaction temperature (180 °C) in an oven for 12 h and maintained until the autoclave was cooled to room temperature. The synthesized  $TiO_2$  NFs were washed with  $dH_2O$  and annealed at 500 °C for 3 h under 5%  $H_2/95\%$   $N_2$  gas.

## 2.2 Fabrication of $BiVO_4/TiO_2$ Heterostructure Photoanodes

$BiVO_4$  was electrodeposited onto the two types of  $TiO_2$  nanostructures using previously reported methods [5, 23]. A precursor was prepared by dissolving bismuth nitrate pentahydrate ( $BiN_3O_9$ , 98%, Junsei) in a solution of vanadium oxide sulfate hydrate ( $VOSO_4$ , 99.99%, Aldrich) at  $pH < 0.5$  with nitric acid ( $HNO_3$ , 67%, Junsei). Then, sodium acetate ( $CH_3COONa$ , 99%, Aldrich) was added, raising the  $pH$  to ~5.1, which was then adjusted to  $pH$  4.7 using a few drops of concentrated  $HNO_3$ . This mildly acidic  $pH$  condition is necessary because, at  $pH$  values  $> 5$ , vanadium (IV) precipitates form in the solution. Pulsed anodic electrodeposition was conducted in a standard three-electrode system

with a working electrode of nanostructured  $TiO_2$ , an Ag/AgCl reference electrode, and a platinum counter electrode. The electrodeposition was potentiostatically carried out at 1.95 V versus Ag/AgCl at 80 °C and annealed at 500 °C for 6 h in air at a heating rate of 2 °C per minute to crystallize.

## 2.3 PEC Measurements

The photocurrent versus potential curves with a scan rate of  $10\text{ mV s}^{-1}$  and photocurrent versus time curves were recorded with a solar simulator with an AM 1.5 G filter. The light intensity of the solar simulator was calibrated to 1 sun ( $100\text{ mW cm}^{-2}$ ). The incident photon-to-current conversion efficiency (IPCE) was measured at 1.23 V versus RHE. The electrochemical impedance spectroscopy (EIS) was conducted by applying 1.23 V versus RHE. The sweeping frequency ranged from 100 to 0.1 kHz, with an AC amplitude of 10 mV. The measured spectra were fitted using ZSimpWin software. The Mott-Schottky (M-S) plots were plotted by potential scan in AC condition with a frequency of 1 kHz with the light off. The Faradaic efficiency and gas evolution were calculated by the gas chromatography system (7890B, Agilent Technologies) in an air-tight cell at 1.23 V versus RHE.

## 2.4 Characterization

The morphologies of all photoanodes were characterized by field-emission scanning electron microscopy (FESEM, MERLIN Compact, ZEISS). High-resolution transmission electron microscopic (HR-TEM) images and elemental distributions were obtained with TEM (JEM-2100F, JEOL) equipped energy-dispersive spectroscope (EDS). X-ray diffraction (XRD, D8-Advance, Bruker) characterization was performed to confirm the crystalline phase of the  $TiO_2$  NRs,  $TiO_2$  NFs, and  $BiVO_4/TiO_2$  NFs. The absorption spectra of the  $TiO_2$  NRs,  $TiO_2$  NFs, and  $BiVO_4$  were measured by UV-Visible spectroscopy (V-770, JASCO). The band structures of the  $BiVO_4/TiO_2$  NFs and  $BiVO_4/TiO_2$  NRs were determined by analyzing the UPS (Ultra DLD) in advanced in-situ surface analysis system (AiSAS)). The time-resolved photoluminescence of  $TiO_2$  NFs,  $TiO_2$  NRs,  $BiVO_4/TiO_2$  NFs, and  $BiVO_4/TiO_2$  NRs was measured using

photoluminescence (PL, FlouTime 300, PicoQuant) with an excitation laser having a wavelength of 405 nm.

## 2.5 FDTD Simulation

The simulations were performed on the FDTD solutions program (Lumerical Solutions). The dielectric function of rutile  $\text{TiO}_2$  was adopted from a prominent report [24], and FTO was considered as a perfect dielectric with a constant refractive index of 2.2 based on the analysis of previous literature [25]. The detailed simulation condition is displayed in Fig. S2. The mesh size was  $5 \times 5 \text{ nm}^2$ .

## 3 Results and Discussion

### 3.1 Synthesis and FDTD Simulations of $\text{TiO}_2$ Nanostructures

To synthesize  $\text{BiVO}_4/\text{TiO}_2$  nanostructures, we introduced an all-solution process comprising hydrothermal synthesis and electrodeposition, which is cost-effective and eco-friendly fabrication method for photoelectrode [26]. First, two types of  $\text{TiO}_2$  nanostructures, which are  $\text{TiO}_2$  NRs and  $\text{TiO}_2$  NFs, were prepared by the one-step hydrothermal synthesis method. By controlling the reaction time, precursor concentration, and pH, the morphology and alignment of  $\text{TiO}_2$  nanostructures were changed into NRs and NFs, as illustrated in Fig. 1a, b.  $\text{TiO}_2$  NRs and NFs have rutile structures with different lattice plane intensities, i.e., (001) and (110), as shown in XRD analysis (Fig. 1c). In the case of  $\text{TiO}_2$  NRs,  $\text{TiO}_2$  preferentially grew to the (001) direction and it makes the vertically aligned 1D structures, as shown in Fig. 1d, whereas  $\text{TiO}_2$  NFs showing the increased (110) direction peak in XRD have a tendency to grow laterally, as shown in Fig. 1e. The long reaction time of 10 h not only caused new heterogeneous nucleation at the tip of the nanorods, but also led to the growth of nanoflowers. As a result, the morphology of  $\text{TiO}_2$  NFs formed on the  $\text{TiO}_2$  NRs was implemented. Also, in the hydrothermal synthesis of  $\text{TiO}_2$ , acids, such as hydrochloric acid, sulfuric acid, sulfonic acid, and sulfamic acid, play highly important roles for the preferential growth as well as stabilization of the rutile phases [27]. We made a more acidic environment by adding sufficient sulfamic acid in order to induce the specific facet growth of nanoflowers. Based on the long reaction time and acidic environment,

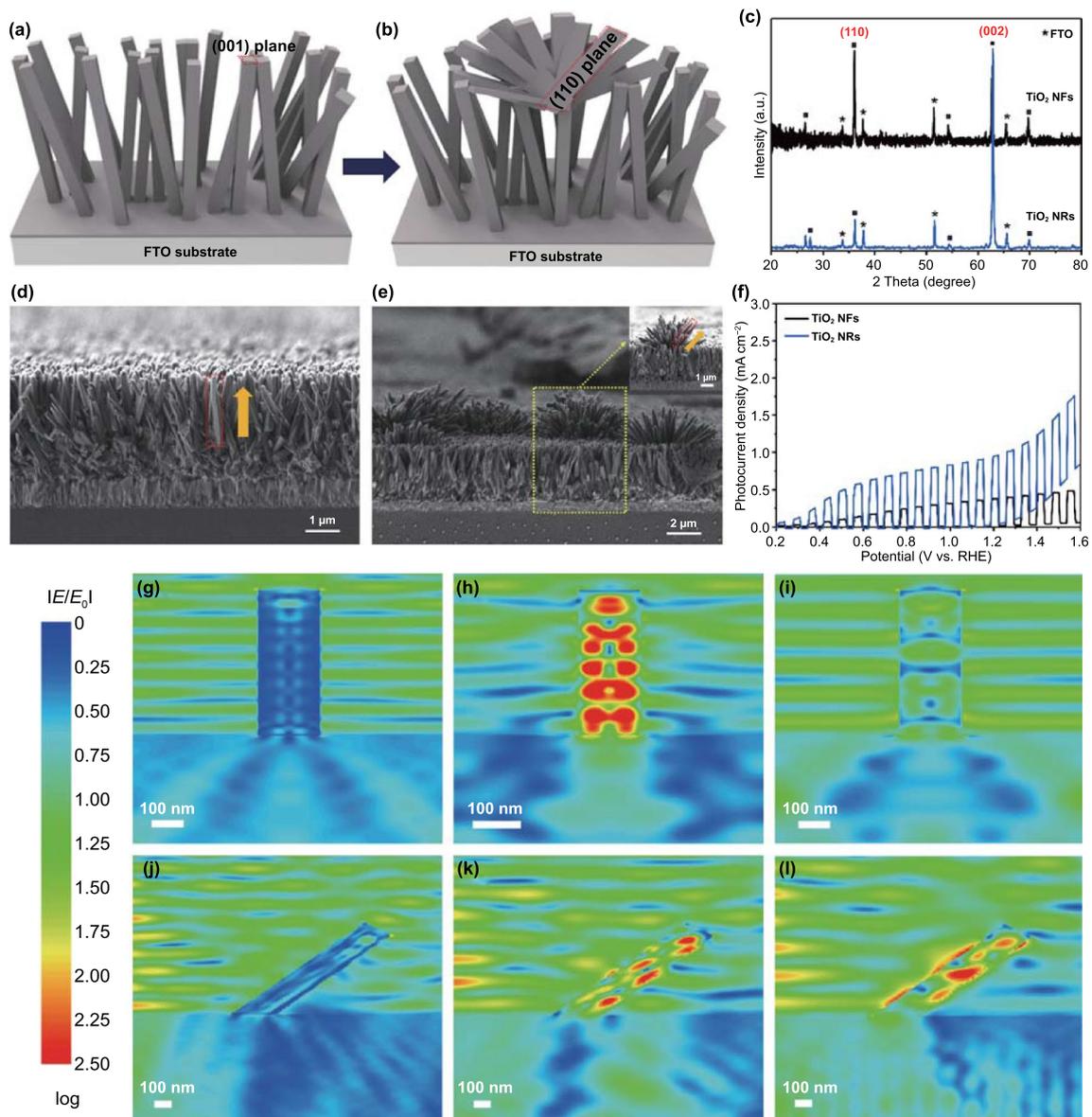
unlike previous reports for synthesizing the  $\text{TiO}_2$  NFs, we enable to construct well-maintained rectangular shape of  $\text{TiO}_2$  NFs without additional process [28, 29].

To compare the photoactivity according to the major facet of  $\text{TiO}_2$  nanostructures, photocurrent density and IPCE of the  $\text{TiO}_2$  NRs and NFs are measured, as shown in Figs. 1f and S1. Both photocurrent density and IPCE of the  $\text{TiO}_2$  NRs were higher than those of the  $\text{TiO}_2$  NFs. Since the (001) facet possesses the highest surface energy due to the coordinately unsaturated Ti and O atoms on (001) and very large Ti–O–Ti bond angles, the (001) facet of  $\text{TiO}_2$  was more reactive than the other facets such as (110) and (101) [30]. And vertically aligned 1D  $\text{TiO}_2$  NRs can make direct and ordered channels for electron transport and enhance light absorption. Furthermore, minority charge diffusion paths can be decoupled to different directions to enhance the photocharge collection efficiency [31].

To clearly understand light-harvesting capacity according to the  $\text{TiO}_2$  crystal facets, we performed a finite-domain time-difference (FDTD) simulation, as shown in Fig. 1g–i. The electric field ( $|E|$ ) distribution was calculated and visualized using the FDTD method to assist in understanding the light absorption mechanism. The model for the FDTD simulation is shown in Fig. S2. We considered vertical-,  $30^\circ$ -tilted, and  $50^\circ$ -tilted  $\text{TiO}_2$  NRs by reflecting the SEM images (Fig. 1d, e). The results of the simulated absorption distribution along the z-axis acquired at light wavelengths of 350, 450, and 550 nm. The FDTD results clearly show strong absorption enhancement in the (001)-facet-dominant  $\text{TiO}_2$  NRs compared to the (110)-facet-dominant  $\text{TiO}_2$  NFs, especially at the wavelength of 450 nm, indicating that the (001) facet traps the incident light efficiently. As shown in Figs. S3, S4, the real configuration of  $\text{TiO}_2$  NFs showed a similar tendency with a piece of  $\text{TiO}_2$ . These FDTD simulation results are closely related to the photoactivity of facet-controlled  $\text{TiO}_2$  nanostructures in linear sweep voltammetry (LSV) (Fig. 1f).

### 3.2 Characterization and PEC performances of $\text{TiO}_2$ NRs and $\text{BiVO}_4/\text{TiO}_2$ NRs

Controlled facets affect not only the photocurrent density of  $\text{TiO}_2$  nanostructures but also the electrodeposition trend of  $\text{BiVO}_4$  on the  $\text{TiO}_2$ . First, we constructed heterostructure



**Fig. 1** Schematic illustration of **a** TiO<sub>2</sub> NRs and **b** TiO<sub>2</sub> NFs growth via hydrothermal synthesis. **c** XRD patterns of TiO<sub>2</sub> NRs and TiO<sub>2</sub> NFs. Cross-sectional SEM images of **d** TiO<sub>2</sub> NRs and **e** TiO<sub>2</sub> NFs. **f** *J*-*V* curves of TiO<sub>2</sub> NRs and TiO<sub>2</sub> NFs in 0.5M potassium phosphate (K-P<sub>1</sub>) buffer with 1M Na<sub>2</sub>SO<sub>3</sub>. FDTD simulations of near field enhancement of TiO<sub>2</sub> NRs on FTO under **g** 350 nm, **h** 450 nm, and **i** 550 nm photons. FDTD simulations of near field enhancement of TiO<sub>2</sub> NFs on FTO under **j** 350 nm, **k** 450 nm, and **l** 550 nm photons

photoanodes of BiVO<sub>4</sub>/TiO<sub>2</sub> NRs to demonstrate the effect of major facets of TiO<sub>2</sub> on the final architecture of BiVO<sub>4</sub>/TiO<sub>2</sub> nanostructures and the following photoactivities. On the TiO<sub>2</sub> NRs, electrodeposited BiVO<sub>4</sub> nanodots agglomerate, and thus the tops of the BiVO<sub>4</sub>/TiO<sub>2</sub> NRs are close to each other, as shown in Figs. 2a–c and S5. It is related to the

concentration gradient in the solution under the electrodeposition process since ions tend to converge toward the vertex of TiO<sub>2</sub> NRs due to high conductivity. Agglomerated BiVO<sub>4</sub> nanodots block the gaps between the TiO<sub>2</sub> NRs, which might be deteriorating the light absorption and electrolyte permeation for PEC water splitting. As a result, the photocurrent

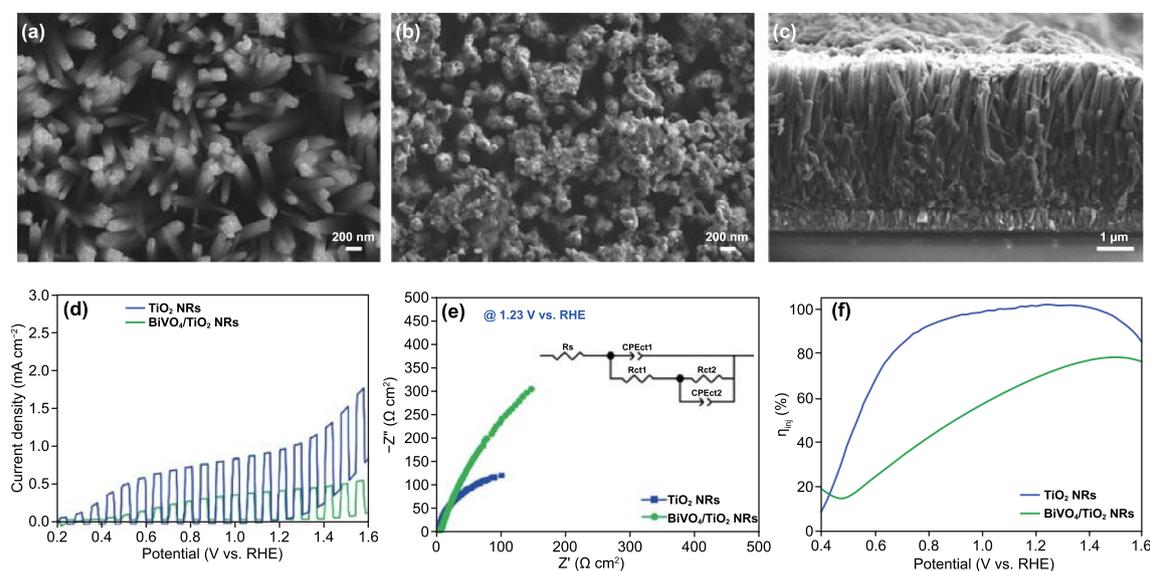
density of the  $\text{BiVO}_4/\text{TiO}_2$  NRs ( $0.35 \text{ mA cm}^{-2}$  at  $1.23 \text{ V}$  vs. RHE) was significantly less than that of pristine  $\text{TiO}_2$  NRs ( $0.91 \text{ mA cm}^{-2}$  at  $1.23 \text{ V}$  vs. RHE), as shown in Figs. 2d and S6. Also, as shown in Fig. S7, the IPCE of  $\text{BiVO}_4/\text{TiO}_2$  NRs was significantly decreased to 22% under the wavelength of  $390 \text{ nm}$  at  $1.23 \text{ V}$  versus RHE, which means there are lots of charge recombination after the introduction of  $\text{BiVO}_4$  on  $\text{TiO}_2$  NRs.

We also analyzed the EIS to compare the charge transfer kinetics between the  $\text{BiVO}_4/\text{TiO}_2$  NRs and  $\text{TiO}_2$  NRs, as shown in Fig. 2e. Considering our architecture, we used the Haman equivalent circuit composed of three resistances and two capacitances since the EIS circuit is closely related to the structure of photoelectrodes [23]. In the EIS circuit,  $R_s$  is the series resistance,  $C_{PE1}$  and  $C_{ct}$  are the constant phase elements (CPE) for the semiconductor interface and the electrolyte/electrode interface, respectively, and  $R_{ct1}$  and  $R_{ct2}$  are the charge transfer resistances across the semiconductor interface and electrode/electrolyte interface, respectively. The values of  $R_s$ ,  $R_{ct1}$ , and  $R_{ct2}$  obtained from the fittings are summarized in Table S1. The high photoactivity is represented by a small semicircle in the Nyquist plot. After the deposition of  $\text{BiVO}_4$  nanodots, the charge transfer resistance across the electrode/electrolyte interface increased from  $259.89$  to  $1948.06 \Omega$

$\text{cm}^2$ , showing the larger semicircles of  $\text{BiVO}_4/\text{TiO}_2$  NRs compared to that of  $\text{TiO}_2$  NRs. As shown in SEM images of  $\text{BiVO}_4/\text{TiO}_2$  NRs (Fig. 2b, c), the agglomerated  $\text{BiVO}_4$  reduced the porosity of the  $\text{TiO}_2$  NRs, which is a structure interfering with the electrolyte permeation. Therefore, bulky  $\text{BiVO}_4$  and reduced porosity of  $\text{TiO}_2$  NRs become the main factors that increase the charge transfer resistance of  $\text{BiVO}_4/\text{TiO}_2$  NRs photoanode. This result was also represented in that  $\text{BiVO}_4/\text{TiO}_2$  NRs have a lower charge injection efficiency than  $\text{TiO}_2$  NRs (Fig. 2f), which led to the deterioration of the PEC performances.

### 3.3 Characterization and PEC Performances of $\text{TiO}_2$ NFs and $\text{BiVO}_4/\text{TiO}_2$ NFs

In order to investigate differences in nanostructures and photoactivities according to the crystal facet, we set up  $\text{TiO}_2$  NFs with (110) facets as a bottom layer for  $\text{BiVO}_4$  nanodots. Unlike on the  $\text{TiO}_2$  NRs, the conformal coating of extremely thin  $\text{BiVO}_4$  nanodots across the entire surface of the  $\text{TiO}_2$  NFs could be possible through the control of pulse cycles during the electrodeposition, as shown in Fig. S8. According to SEM images in Fig. 3a–d, the surfaces of  $\text{TiO}_2$  NFs were totally covered with  $\text{BiVO}_4$  nanodots by increasing the pulse cycles of  $\text{BiVO}_4$ . A cross-sectional SEM image in

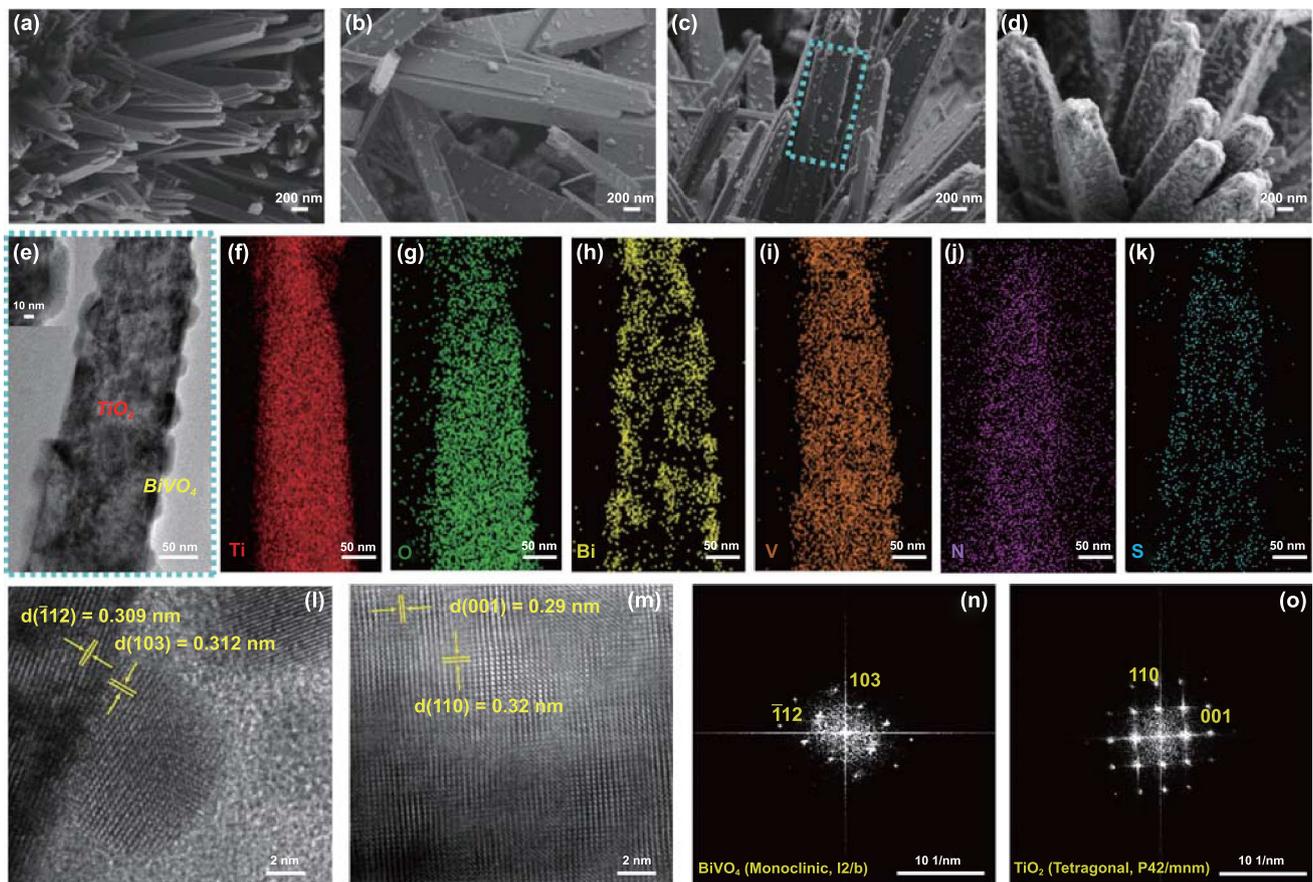


**Fig. 2** Top SEM images of **a**  $\text{TiO}_2$  NRs and **b**  $\text{BiVO}_4/\text{TiO}_2$  NRs. **c** Cross-sectional SEM image of  $\text{BiVO}_4/\text{TiO}_2$  NRs. **d** LSV for  $\text{TiO}_2$  NRs and  $\text{BiVO}_4/\text{TiO}_2$  NRs in  $0.5\text{M}$  K–Pi buffer with  $1\text{M}$   $\text{Na}_2\text{SO}_3$ . **e** Electrochemical impedance spectra (EIS) of  $\text{TiO}_2$  NRs and  $\text{BiVO}_4/\text{TiO}_2$  NRs at  $1.23 \text{ V}$  (vs. RHE) in  $0.5\text{M}$  K–Pi buffer with  $1\text{M}$   $\text{Na}_2\text{SO}_3$ . Inset shows equivalent circuit. **f** Charge injection efficiency of  $\text{TiO}_2$  NRs and  $\text{BiVO}_4/\text{TiO}_2$  NRs

Fig. S9 also showed conformally decorated  $\text{BiVO}_4$  on  $\text{TiO}_2$  NFs. Through the TEM equipped with EDS, we confirmed the detailed surface morphologies and elemental distributions of  $\text{BiVO}_4/\text{TiO}_2$  NFs. The TEM image in NFs region (Fig. 3e) also indicated that  $\text{BiVO}_4$  nanodots conformally covered on the surface of the  $\text{TiO}_2$  NFs. The inset shows an enlarged TEM image of  $\text{BiVO}_4$  nanodots. As shown in EDS mappings (Fig. 3f–k), all the constituent elements were well represented. High-resolution TEM (HR-TEM) images and a fast Fourier transform (FFT) pattern are shown in Fig. 3l–o. According to high-resolution TEM (HR-TEM) images and fast Fourier transform (FFT) patterns, electron diffraction patterns of the selected area showed  $d$ -spacing of 0.309 and 0.312 nm (Fig. 3l), corresponding to the  $(-112)$  and  $(103)$  planes of monoclinic  $\text{BiVO}_4$ , respectively (Fig. 3n), and  $d$ -spacing of 0.29 and 0.32 nm (Fig. 3m), which can be

assigned to the  $(001)$  and  $(110)$  planes of rutile  $\text{TiO}_2$  NFs, respectively (Fig. 3o). These results are well-matched with the XRD analysis (Fig. S10).

PEC measurements of the  $\text{BiVO}_4/\text{TiO}_2$  NFs with different coverages of  $\text{BiVO}_4$  were performed using a standard three-electrode cell with an electrolyte of 0.5M potassium phosphate ( $\text{K-P}_i$ ) buffer and 1M sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) at a scan rate of  $10 \text{ mV s}^{-1}$  under a AM 1.5G solar light. Oxidation of sulfite ( $\text{SO}_3^{2-}/\text{SO}_3^-$ ,  $E^\circ = 0.73 \text{ V vs. NHE}$ ;  $\text{SO}_3^{2-}/\text{S}_2\text{O}_6^{2-}$ ,  $E^\circ = 0.026 \text{ V vs. NHE}$ ), is thermodynamically and kinetically much more favorable than water oxidation [32]. Therefore, surface recombination losses due to slow interfacial hole transfer kinetics can be assumed to be negligible for the photo-oxidation of sulfite.  $\text{BiVO}_4/\text{TiO}_2$  NFs were fabricated by adjusting the electrodeposition cycles of  $\text{BiVO}_4$  from 0 to 36 (i.e.,  $n \text{ BiVO}_4 = n \text{ cycles electrodeposited BiVO}_4$ ), and



**Fig. 3** SEM images of **a**  $\text{TiO}_2$  NFs and  $\text{BiVO}_4/\text{TiO}_2$  NFs with different deposition cycles of  $\text{BiVO}_4$ : **b** 6 cycles, **c** 18 cycles, and **d** 36 cycles. **e** TEM image of  $\text{BiVO}_4/\text{TiO}_2$  NFs deposited by 18 cycles. Inset shows HR-TEM image of  $\text{BiVO}_4/\text{TiO}_2$  NFs. EDS mapping images of **f** Ti, **g** O, **h** Bi, **i** V, **j** N, and **k** S. **l** Crystalline planes of  $(-112)$  and  $(103)$  of  $\text{BiVO}_4$ , **m** Crystalline planes of  $(001)$  and  $(110)$  of  $\text{TiO}_2$  NFs. FFT patterns of **n**  $\text{BiVO}_4$  and **o**  $\text{TiO}_2$  NFs

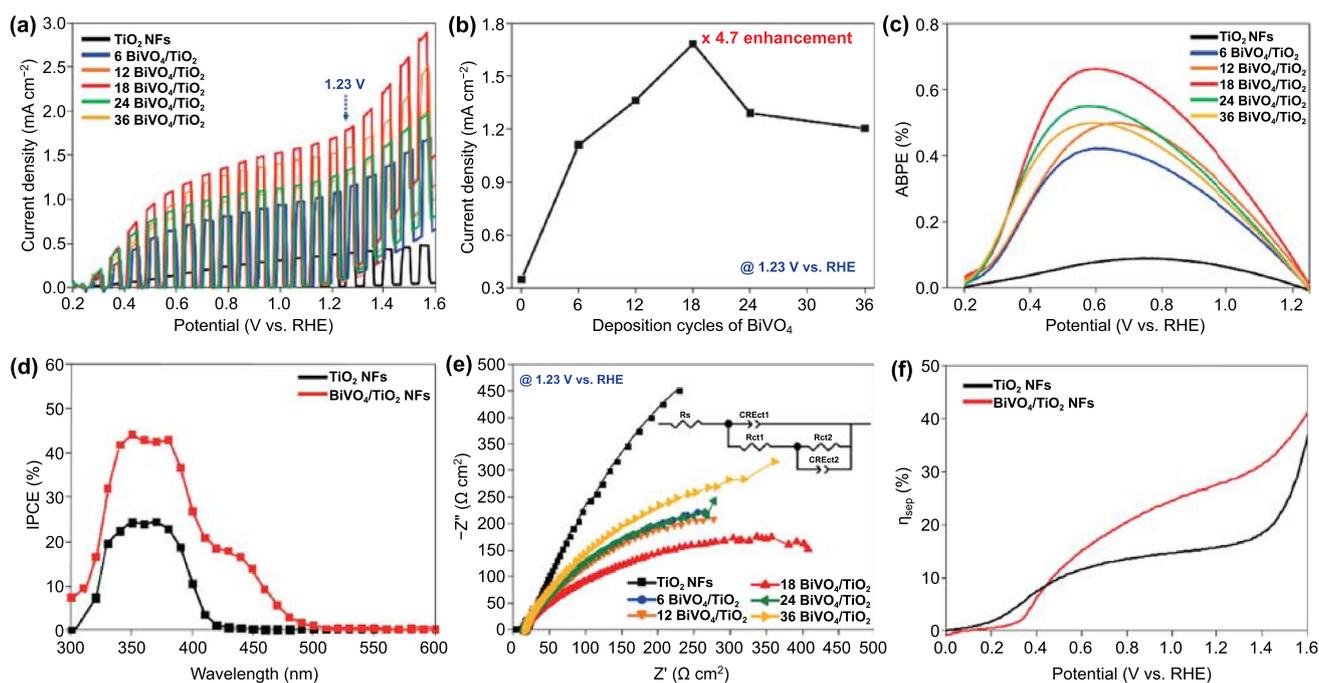
their LSV curves were recorded under the chopped (on/off) light condition. As shown in Fig. 4a, the photocurrent densities of the BiVO<sub>4</sub>/TiO<sub>2</sub> NFs gradually increase until the number of electrodeposition cycles increases to 18 cycles and then starts to decrease. As the increase in the deposition cycle of BiVO<sub>4</sub>, the density of BiVO<sub>4</sub> nanodots covering the TiO<sub>2</sub> NFs increases (Fig. S8b–d), adding the charge transfer sites. However, after the optimized cycles (18 cycles), the agglomeration of BiVO<sub>4</sub> nanodots is observed at the tip of TiO<sub>2</sub> NFs (Fig. S8e–f), interfering with the charge transfer. The highest photocurrent density of 1.7 mA cm<sup>-2</sup> was obtained at 1.23 V versus RHE for the 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs. This value corresponds to 4.7 and 4.8 times that of the TiO<sub>2</sub> NFs and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs, respectively. In addition to the enlarged absorption wavelength range from the ultraviolet (UV) to ultraviolet–visible (UV–Vis) region), improved charge separation is decisive for the cause of PEC performances of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs. The electron–hole recombination is structurally reduced because the conformally coated BiVO<sub>4</sub> nanodots on TiO<sub>2</sub> NFs enlarge the depletion layer and shorten the charge diffusion length to the interface [14,

33]. The small size of the BiVO<sub>4</sub> nanodots allows for a high collection efficiency of electrons by the TiO<sub>2</sub> NFs, and the proximity of the semiconductor liquid junction allows holes to reach the surface to perform the water splitting reaction [1, 14, 33, 34]. However, after the optimal deposition cycle, increasing the surface area also has negative effects such as the formation of surface defects and grain boundaries, which degrade PEC performances. In this respect, the design of photoanodes with appropriate active areas is crucial for photoactivity [5, 35, 36].

The PEC water splitting efficiency of photoelectrodes was also quantitatively evaluated using the applied bias photon-to-current conversion efficiency (ABPE) as follows:

$$\text{ABPE (\%)} = J_{\text{ph}}(1.23 - V_{\text{b}}) * 100/P_{\text{total}} \quad (1)$$

where  $V_{\text{b}}$  is the applied bias (vs. RHE),  $J_{\text{ph}}$  is the photocurrent density at the measured potential, and  $P_{\text{total}}$  is the power density of light. The ABPE takes applied potential into account as important factor in the conversion of solar to chemical energy [37]. As shown in Fig. 4c, maximum photoconversion efficiency of 0.65% was achieved for the 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs at 0.61 V versus RHE, which was 8.1



**Fig. 4** **a** LSV of TiO<sub>2</sub> NFs and BiVO<sub>4</sub>/TiO<sub>2</sub> NFs with different deposition cycles of BiVO<sub>4</sub> in 0.5M K–P<sub>i</sub> buffer with 1M Na<sub>2</sub>SO<sub>3</sub>. **b** Photocurrent density of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs with different deposition cycles of BiVO<sub>4</sub> at 1.23 V (vs. RHE). **c** ABPE of TiO<sub>2</sub> NFs and BiVO<sub>4</sub>/TiO<sub>2</sub> NFs with different deposition cycles of BiVO<sub>4</sub>. **d** IPCE at 1.23 V (vs. RHE) of TiO<sub>2</sub> NFs and 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs. **e** EIS of TiO<sub>2</sub> NFs and BiVO<sub>4</sub>/TiO<sub>2</sub> NFs with different deposition cycles of BiVO<sub>4</sub> at 1.23 V (vs. RHE) in 0.5M K–P<sub>i</sub> buffer with 1M Na<sub>2</sub>SO<sub>3</sub>. Inset shows equivalent circuit. **f** Charge separation efficiency of TiO<sub>2</sub> NFs and 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs

times higher than that of the pristine TiO<sub>2</sub> NFs. Also, the maximum photoconversion efficiencies for all BiVO<sub>4</sub>/TiO<sub>2</sub> NFs were obtained at a lower applied potential than the pristine TiO<sub>2</sub> NFs. These are associated with the reduction of the hole injection barrier at the interface between the TiO<sub>2</sub> NFs and electrolyte by introduction of the BiVO<sub>4</sub> nanodots [36]. According to the IPCE spectra (Fig. 4d), the absorption wavelength edge was expanded from 430 (UV region) to 512 nm (UV-Vis region) after the introduction of BiVO<sub>4</sub>. It also led to a 44% enlargement of maximum IPCE at a wavelength of 350 nm. In the chronoamperometry at 1.23 V versus RHE under 1 sun illumination, the 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs showed stable PEC performances for 6 h, as shown in Fig. S8h.

We also analyzed the EIS to figure out the charge transfer kinetics of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs, and the measured data were fitted to the equivalent circuit, as shown in Fig. 4e [23]. Unlike BiVO<sub>4</sub>/TiO<sub>2</sub> NRs, the charge transfer resistance of all BiVO<sub>4</sub>/TiO<sub>2</sub> NFs was drastically decreased compared to pristine TiO<sub>2</sub> NFs. These results represent the effective charge transfer at the interfaces of each semiconductor and the semiconductor/electrolyte by suppressing the charge recombination. Of these, the lowest value of charge transfer resistances ( $R_{ct1} = 0.84 \Omega \text{ cm}^{-2}$  and  $R_{ct2} = 475.11 \Omega \text{ cm}^{-2}$ ) were recorded for the 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs, which well corresponds to the tendency of photocurrent density (Fig. 4b).

To gain more insight into the crystal facet effect, we investigated the electronic characteristics using Mott-Schottky (M-S) analysis to grasp a flat band potential by using Eq. (2):

$$C^{-2} = (2/e\epsilon\epsilon_0N_d)[V - V_{FB} - k_B T/e] \quad (2)$$

where  $C$  is the capacitance of the space charge layer,  $e$  is the electron charge ( $1.602 \times 10^{-19} \text{ C}$ ),  $\epsilon$  is the dielectric constant,  $\epsilon_0$  is the permittivity of vacuum ( $8.854 \times 10^{-12} \text{ F m}^{-1}$ ),  $V$  (vs. RHE) is the applied potential,  $V_{FB}$  (vs. RHE) is the flat band potential,  $k_B$  is the Boltzmann constant ( $1.381 \times 10^{-23} \text{ J K}^{-1}$ ),  $T$  is the temperature (298 K),  $E$  is the applied potential, and  $N_d$  is the charge carrier (donor) density. The flat band potentials were determined from the intercepts of the  $1/C^2$  versus  $V$  curve, subtracting  $k_B T/e = 0.025 \text{ V}$  from the intercept. And the carrier concentration can be calculated from the slope of the M-S curves. As the slope of the M-S plot flattens, the carrier concentration increases. The flat band potential of the TiO<sub>2</sub> NFs is more cathodically shifted about 100 mV than the TiO<sub>2</sub> NRs, as shown in Fig. S11. It is favorable for the electrons to pass through the circuit to the counter electrode [5]. We analyzed the M-S plot after electrodeposition of

BiVO<sub>4</sub> onto the TiO<sub>2</sub> NFs and TiO<sub>2</sub> NRs. As shown in Fig. S11a, the donor density of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs was increased, which means the internal resistance of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs is reduced, allowing the carrier to transport much faster than the pristine TiO<sub>2</sub> NFs. On the other hand, as shown in Fig. S11b, the carrier concentration of the BiVO<sub>4</sub>/TiO<sub>2</sub> NRs was drastically reduced, which derives the decrease in photoactivity. These results indicate that the facet and morphology control of the bottom layer could be a significant factor in controlling PEC water splitting kinetics.

We also measured charge separation efficiency ( $\eta_{sep}$ ) in the potential from 0 V to 1.6 V versus RHE. As shown in Fig. 4e, the BiVO<sub>4</sub>/TiO<sub>2</sub> NFs exhibited 2.5 times higher  $\eta_{sep}$  than the pristine TiO<sub>2</sub> NFs at 1.23 V versus RHE. It directly reveals that the enhanced photocurrent density of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs was mainly originated from the improved charge separation between BiVO<sub>4</sub> nanodots and TiO<sub>2</sub> NFs. To support this result, we also measured PEC water oxidation performances of TiO<sub>2</sub> NFs and 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs in 0.5M K-Pi buffer without hole scavenger. As shown in Fig. S12a, BiVO<sub>4</sub>/TiO<sub>2</sub> NFs showed more efficient water oxidation and higher photocurrent density compared to TiO<sub>2</sub> NFs at 1.23 V versus RHE. The lower photocurrent density of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs in the lower potential region than that of TiO<sub>2</sub> NFs was derived from the sluggish hole transfer of BiVO<sub>4</sub>. To expedite the hole transfer at the low potential, an additional introduction of oxygen evolution catalyst to BiVO<sub>4</sub> is necessary [13]. Also, BiVO<sub>4</sub>/TiO<sub>2</sub> NFs showed a 29% higher maximum IPCE and wider absorption wavelength range than TiO<sub>2</sub> NFs as shown in Fig. S12b. We also measured the EIS of TiO<sub>2</sub> NFs and 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs at 1.23 V versus RHE in K-Pi buffer electrolyte. As shown in Fig. S12c, BiVO<sub>4</sub>/TiO<sub>2</sub> NFs showed a smaller semicircle compared to TiO<sub>2</sub> NFs, which represented the smaller charge transfer resistance during the water oxidation. In the chronoamperometry at 1.23 V versus RHE in K-Pi buffer electrolyte, the 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs showed stable PEC performances for 2 h, as shown in Fig. S12d. By using gas chromatography, we measured gas evolution and Faradaic efficiency of 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs at 1.23 V versus RHE. As shown in Fig. S12e, the 18 BiVO<sub>4</sub>/TiO<sub>2</sub> NFs photoanode and Pt cathode continuously generated oxygen and hydrogen gas. Near-complete Faradaic efficiency was achieved, representing that the photogenerated charge carriers were mostly used for evolving the oxygen and hydrogen gases.



### 3.4 Studies of Charge Carrier Dynamics and Band Structures

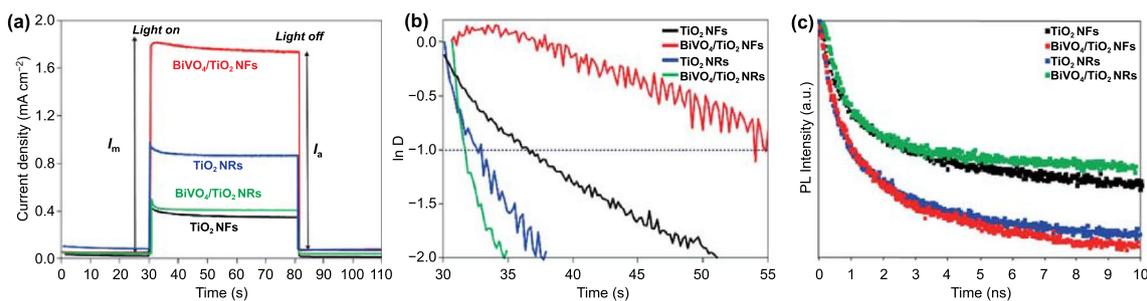
To profoundly understand the effect in the crystal facet of TiO<sub>2</sub> nanostructures to the charge transport and recombination behavior, the transient photocurrent decay occurring immediately upon illumination was evaluated. As shown in the chronoamperometry at 1.23 V versus RHE (Fig. 5a), when the light was switched on, a photocurrent spike was observed due to the rapid generation of electron and hole pairs. It would lead to severe charge recombination and cause the decrease in the photoactivity for the water splitting reaction. In general, the charge recombination can be caused by the accumulation of either electrons in the bulk or holes at the surface. The accumulation of holes would cause an equally large cathodic transient when the light is switched off, and electrons in the conduction band react with the accumulated hole. However, cathodic transients can scarcely be observed in Fig. 5a, suggesting the accumulation of holes at the surface of the films is not the main recombination process in both BiVO<sub>4</sub>/TiO<sub>2</sub> NFs and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs. Thus, it is represent that the transient decays were mainly dependent to the accumulation of electrons due to the poor electron transport in the photoanodes. The transient decay time in the photoanodes was calculated from the logarithmic plot of parameter  $D$ , given by Eq. (3):

$$D = (I_t - I_s) / (I_m - I_s) \quad (3)$$

where  $I_m$  is the photocurrent spike,  $I_t$  is the photocurrent at time  $t$ , and  $I_s$  is the steady-state photocurrent (i.e., as the recombination and charge generation reaches equilibrium). The transient decay time is defined as the time at which in  $\ln D = -1$ . Based on the photocurrent profiles measured in Fig. 5a, the transient decay time of the TiO<sub>2</sub> NFs, BiVO<sub>4</sub>/

TiO<sub>2</sub> NFs, TiO<sub>2</sub> NRs, and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs is displayed in Fig. 5b. As shown in Table S2, the transient decay time for the BiVO<sub>4</sub>/TiO<sub>2</sub> NFs was 26.35 s, which is approximately 4.15 times longer than that of the TiO<sub>2</sub> NFs at about 6.36 s. It represents a lower charge recombination rate of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs compared to the TiO<sub>2</sub> NFs. Otherwise, the BiVO<sub>4</sub>/TiO<sub>2</sub> NRs showed a decay time of 1.57 s, which is shorter than that of the TiO<sub>2</sub> NRs at about 2.58 s. It is also related to the poor charge separation between BiVO<sub>4</sub> nanodots and TiO<sub>2</sub> NRs. These results indicate that TiO<sub>2</sub> NFs can play a key role as a hole blocking layer, which expedites electron transport and reduces charge recombination.

To gain a deeper insight into charge recombination behaviors according to the TiO<sub>2</sub> facet, time-resolved photoluminescence (TRPL) analysis was carried out at a wavelength of 540 nm, as shown in Fig. 5c. TRPL is a powerful technique to gain information about dynamics of the photogenerated electron and hole pairs, reflecting the charge recombination/separation behavior and charge trapping process in defects [38–40]. The TRPL results were fitted with a biexponential decay function, and photoluminescence lifetimes were calculated as represented in Table S3. The nonradiative ( $\tau_1$ ) and radiative recombination lifetimes ( $\tau_2$ ) of the photoexcited electrons and holes can be determined by measuring the luminescence signals resulting from recombination [38, 40]. The nonradiative recombination lifetime is generally determined from the surface recombination by the trap sites. Since, in both heterostructured photoelectrodes, it is the same BiVO<sub>4</sub> that is the part in contact with the electrolyte on the band structures, they have similar  $\tau_1$  values. However, the electron injection behavior into adjacent layers can be investigated by monitoring the radiative recombination lifetime. If the photoexcited carriers can be effectively transported



**Fig. 5** **a** The transient photocurrent decay that occurs immediately upon illumination at 1.23 V (vs. RHE). **b** Transient decay times for TiO<sub>2</sub> NFs, TiO<sub>2</sub> NRs, BiVO<sub>4</sub>/TiO<sub>2</sub> NFs, and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs. **c** TRPL of TiO<sub>2</sub> NFs, TiO<sub>2</sub> NRs, BiVO<sub>4</sub>/TiO<sub>2</sub> NFs and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs

into the neighboring layers, the radiative recombination lifetime of the heterostructured photoelectrode decreases. In this regard, the smaller  $\tau_2$  value of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs (5.20 ns) than that of BiVO<sub>4</sub>/TiO<sub>2</sub> NRs (6.10 ns) denotes the efficient extraction of photoexcited electrons by TiO<sub>2</sub> NFs. It corresponds with the transient decay time analysis in Fig. 5b. Based on the analysis of charge carrier dynamics, we demonstrated that the crystal facet engineering of TiO<sub>2</sub> nanostructures is a powerful tool to allow TiO<sub>2</sub> to be utilized as the hole blocking layer for BiVO<sub>4</sub> by boosting charge separation efficiency.

To investigate the reason for the charge separation difference of TiO<sub>2</sub> NRs with (001) facets and TiO<sub>2</sub> NFs with (110) facets, we compared the band structures of BiVO<sub>4</sub>/TiO<sub>2</sub> NRs and BiVO<sub>4</sub>/TiO<sub>2</sub> NFs. The UPS measures occupied electronic states, providing information on the Fermi level and valence band maximum (VBM) energy of a material. The conduction band minimum (CBM) energy can be calculated by adding the optical band gap energy ( $E_g$ ), which is given by the UV–Vis spectroscopy, to the VBM. The band gap can be evaluated from Eq. (4):

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2} \quad (4)$$

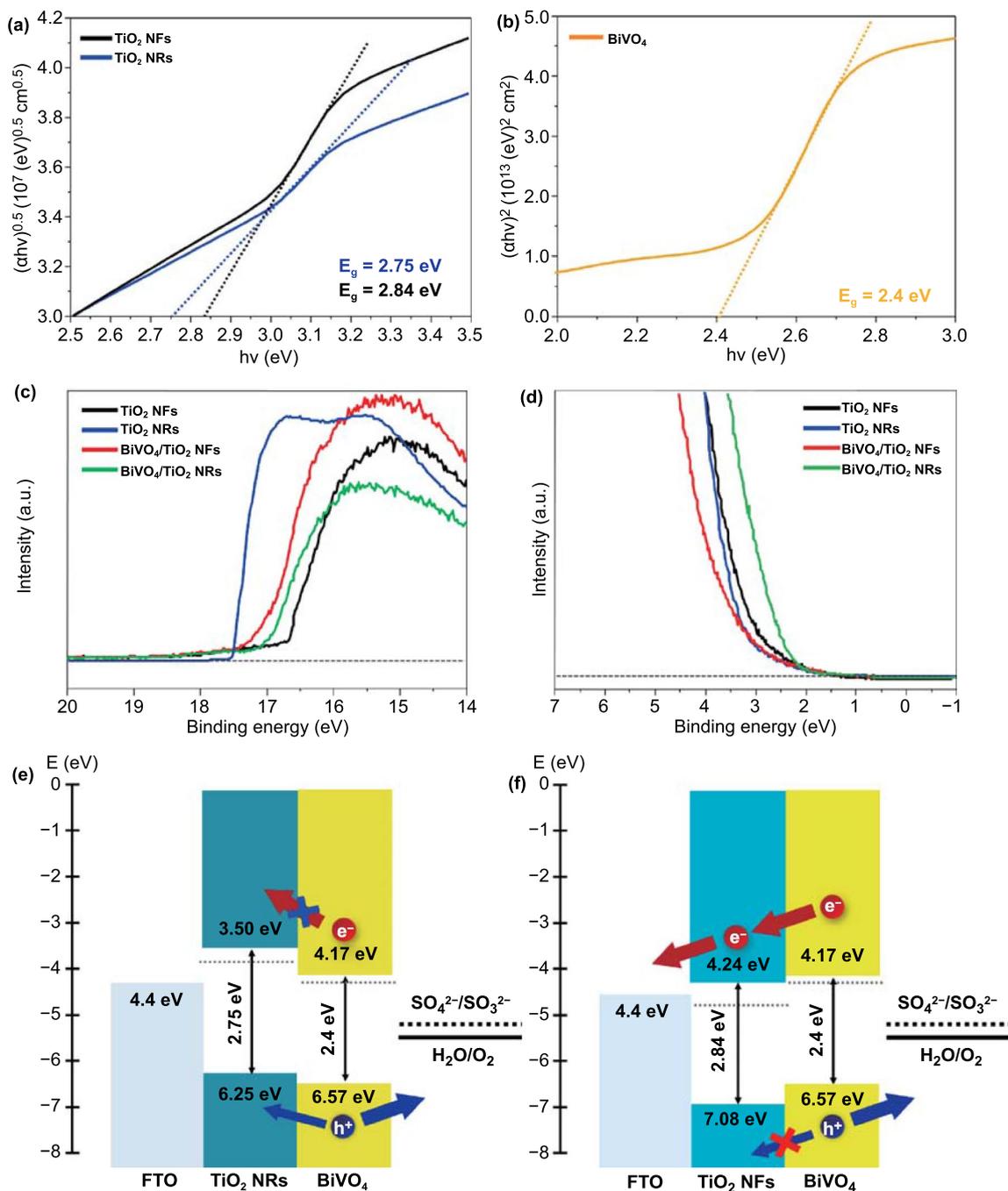
where  $\alpha$ ,  $E_g$ , and  $A$  are the absorption coefficient, band gap energy, and a constant, respectively. Based on the UV–Vis spectra (Fig. S13) and Tauc plots, the optical band gap of the TiO<sub>2</sub> NFs and TiO<sub>2</sub> NRs was 2.84 and 2.75 eV, respectively (Fig. 6a). These are the smaller values than the band gap in previous reports (~3.2 eV). Because co-doped sulfur and nitrogen from the sulfamic acid form S 3p and N 2p state between the conduction band and valence band of TiO<sub>2</sub>, diminishing the band gap of TiO<sub>2</sub> nanostructures [18]. And, a smaller band gap of TiO<sub>2</sub> NRs compared to that of TiO<sub>2</sub> NFs caused the absorption of the larger wavelength of visible light. Thus, as shown in Fig. 5a, the TiO<sub>2</sub> NRs generated a higher photocurrent density at 1.23 V versus RHE than TiO<sub>2</sub> NFs. According to Fig. 6b, the band gap of BiVO<sub>4</sub> was 2.4 eV, which is similar to the values in previous studies.

The secondary electron emission (SEE) spectra of the TiO<sub>2</sub> NFs, TiO<sub>2</sub> NRs, BiVO<sub>4</sub>, BiVO<sub>4</sub>/TiO<sub>2</sub> NFs, and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs were given by the high-binding-energy region in UPS, as shown in Fig. 6c. The work functions of TiO<sub>2</sub> NFs (4.46 eV), TiO<sub>2</sub> NRs (3.58 eV), BiVO<sub>4</sub>/TiO<sub>2</sub> NFs (4.18 eV), and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs (4.18 eV) could be estimated from the differences between SEE spectra cutoffs and He I photon source energy (21.22 eV), as shown in Fig. S14. According to the valence band (VB) spectra given by

the low-binding-energy region in UPS, the energy difference between the Fermi level and the valence band maximum ( $E_F - E_{VBM}$ ) could be calculated, as shown in Fig. 6d. The values of  $E_F - E_{VBM}$  for the TiO<sub>2</sub> NFs (2.62 eV), TiO<sub>2</sub> NRs (2.67 eV), BiVO<sub>4</sub>/TiO<sub>2</sub> NFs (2.39 eV), and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs (2.39 eV) were calculated by the VB spectra cutoffs, as shown in Fig. S15. The values measured by UPS are summarized in Table S4. Since the band edge positions are highly dependent on the change of electrostatic potential in near-surface atoms, the VBM and CBM shifts between TiO<sub>2</sub> NRs and TiO<sub>2</sub> NFs is derived from the preferential crystal facet [41–43]. The titanium atoms on the (001) surface are tetrahedral-coordinated, and thus their environment is relatively close to the bulk. It causes the splitting of the occupied and unoccupied levels to be large, which leads to the highest CBM value [36, 37, 41]. Therefore, the (110) facet-dominant TiO<sub>2</sub> NFs have a more negative CBM than the (001) facet-dominant TiO<sub>2</sub> NRs. Based on these results, the energy band diagrams for the BiVO<sub>4</sub>/TiO<sub>2</sub> NRs and BiVO<sub>4</sub>/TiO<sub>2</sub> NFs are illustrated in Fig. 6e, f, respectively. In the case of BiVO<sub>4</sub>/TiO<sub>2</sub> NRs, the CBM of the TiO<sub>2</sub> NRs significantly move upward, making the transport of photogenerated electrons from BiVO<sub>4</sub> difficult [38, 40, 44, 45]. Also, due to the relatively positive VBM of the TiO<sub>2</sub> NRs, photogenerated holes from BiVO<sub>4</sub> cannot be effectively blocked, causing the charge recombination, whereas TiO<sub>2</sub> NFs having a relatively negative CBM and VBM can be effective electron transport layer and hole-blocking layer for BiVO<sub>4</sub>. As a result, the BiVO<sub>4</sub>/TiO<sub>2</sub> NFs clearly form the type II band alignment, which is energetically favorable to separate the photogenerated electrons and holes from BiVO<sub>4</sub>. In the final analysis, it was found that the enhanced photoactivity of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs was originated from the improvement of charge separation according to the band structure of crystal facet-engineered TiO<sub>2</sub>.

## 4 Conclusions

In summary, we have demonstrated the effect of crystal facet-controlled TiO<sub>2</sub> nanostructures on band structures and charge separation. Two types of BiVO<sub>4</sub>/TiO<sub>2</sub> heterostructure photoanodes having TiO<sub>2</sub> NRs with (001) facets and TiO<sub>2</sub> NFs with (110) were systematically studied to reveal the role of facets for facile PEC water splitting. We revealed that the improved photoelectrochemical



**Fig. 6** UV-Vis Tauc plots of **a** TiO<sub>2</sub> NFs, TiO<sub>2</sub> NRs, and **b** BiVO<sub>4</sub>. **c** Secondary electron emission spectra and **d** valence band spectra of TiO<sub>2</sub> NFs, TiO<sub>2</sub> NRs, BiVO<sub>4</sub>/TiO<sub>2</sub> NFs, and BiVO<sub>4</sub>/TiO<sub>2</sub> NRs. Flat band structures of **e** BiVO<sub>4</sub>/TiO<sub>2</sub> NRs and **f** BiVO<sub>4</sub>/TiO<sub>2</sub> NFs

performances of BiVO<sub>4</sub>/TiO<sub>2</sub> NFs compared with BiVO<sub>4</sub>/TiO<sub>2</sub> NRs were attributed to the prohibition of charge recombination through interface and morphology control. According to the analysis of charge carrier dynamics such as transient decay time and time-resolved

photoluminescence, the charge separation effect was supported. Based on the UPS, it was represented that crystal facet engineering affects the band edge position of TiO<sub>2</sub>. In conclusion, this study not only provides new perspectives in band structure engineering but also opens a promising

avenue in designing heterostructure photoelectrodes for efficient PEC water splitting.

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