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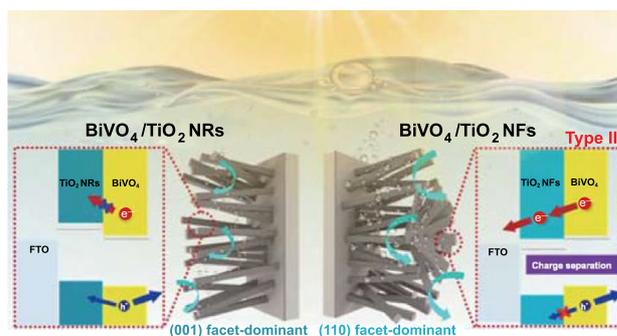
Crystal Facet Engineering of TiO₂ Nanostructures for Enhancing Photoelectrochemical Water Splitting with BiVO₄ Nanodots

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HIGHLIGHTS

- Two types of BiVO₄/TiO₂ heterostructure photoanodes comprising TiO₂ nanorods (NRs) and TiO₂ nanoflowers (NFs) with different (001) and (110) crystal facets, respectively, were designed.
- The higher photoactivity of BiVO₄/TiO₂ NFs than BiVO₄/TiO₂ NRs was attributed to the improvement of charge separation by the TiO₂ NFs.
- The formation of type II band alignment between BiVO₄ nanodots and TiO₂ NFs expedited electron transport and reduced charge recombination.

ABSTRACT Although bismuth vanadate (BiVO₄) 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 BiVO₄, titanium dioxide (TiO₂) has been considered unsuitable because of its relatively positive valence band edge and low electrical conductivity. Herein, a crystal facet engineering of TiO₂ nanostructures is proposed to control band structures for the hole blocking layer of BiVO₄ nanodots. We design two types of TiO₂ nanostructures, which are nanorods (NRs) and nanoflowers (NFs) with different (001) and (110) crystal facets, respectively, and fabricate BiVO₄/TiO₂ heterostructure photoanodes. The BiVO₄/TiO₂ NFs showed 4.8 times higher photocurrent density than the BiVO₄/TiO₂ 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 BiVO₄ nanodots and TiO₂ 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

Mi Gyoung Lee and Jin Wook Yang have contributed equally to this work.

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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 TiO_2 , Fe_2O_3 , WO_3 , and 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], BiVO_4 -based heterostructure photoanodes have been widely studied since short charge diffusion lengths and lifetimes of BiVO_4 cause severe charge recombination. In a representative $\text{BiVO}_4/\text{WO}_3$ heterostructure, WO_3 enhances the charge separation as a hole blocking layer of 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 WO_3 to the BiVO_4 , limiting the photovoltage of the combined system [5–7]. Also, the oxidation of surface hydroxyl groups of WO_3 causes the formation of peroxy-species, which reduces the stability of heterostructure photoanodes [13].

Compared to the WO_3 , rutile 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 BiVO_4 [14–16]. However, TiO_2 has an intrinsic limitation of low electrical conductivity to be used as the hole blocking layer for 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 TiO_2 NRs and increased their carrier concentration

and electrical conductivity [18]. The second problem is a mismatched band structure between BiVO_4 and TiO_2 . A relatively positive valence band edge of TiO_2 makes it difficult to form the type II heterostructure suitable for charge separation. In order to utilize TiO_2 as the hole blocking layer for 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 Cu_2O , with a lower work function than the (100) facet, is unfavorable for the migration of holes from the Cu_2O 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 TiO_2 , which are NRs and NFs, respectively. After BiVO_4 nanodots are conformally electrodeposited on the surface of the 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 TiO_2 . The ultraviolet photoemission spectroscopy (UPS) represents band edge positions of TiO_2 nanostructures are significantly dependent on their crystal facet. Since TiO_2 NFs with (110) facets have relatively negative band edges, as a hole blocking layer they form type II heterojunction with BiVO_4 nanodots. In addition, the initial facet of 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 BiVO_4 electrodeposition on the nanostructured 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 TiO_2 NRs and TiO_2 NFs

TiO_2 NRs and 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 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 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 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 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 TiO_2 nanostructures, which are TiO_2 NRs and 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 TiO_2 nanostructures were changed into NRs and NFs, as illustrated in Fig. 1a, b. 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 TiO_2 NRs, TiO_2 preferentially grew to the (001) direction and it makes the vertically aligned 1D structures, as shown in Fig. 1d, whereas 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 TiO_2 NFs formed on the TiO_2 NRs was implemented. Also, in the hydrothermal synthesis of 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 TiO_2 NFs, we enable to construct well-maintained rectangular shape of TiO_2 NFs without additional process [28, 29].

To compare the photoactivity according to the major facet of TiO_2 nanostructures, photocurrent density and IPCE of the TiO_2 NRs and NFs are measured, as shown in Figs. 1f and S1. Both photocurrent density and IPCE of the TiO_2 NRs were higher than those of the 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 TiO_2 was more reactive than the other facets such as (110) and (101) [30]. And vertically aligned 1D 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 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° -tilted, and 50° -tilted 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 TiO_2 NRs compared to the (110)-facet-dominant 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 TiO_2 NFs showed a similar tendency with a piece of TiO_2 . These FDTD simulation results are closely related to the photoactivity of facet-controlled TiO_2 nanostructures in linear sweep voltammetry (LSV) (Fig. 1f).

3.2 Characterization and PEC performances of TiO_2 NRs and $\text{BiVO}_4/\text{TiO}_2$ NRs

Controlled facets affect not only the photocurrent density of TiO_2 nanostructures but also the electrodeposition trend of BiVO_4 on the TiO_2 . First, we constructed heterostructure

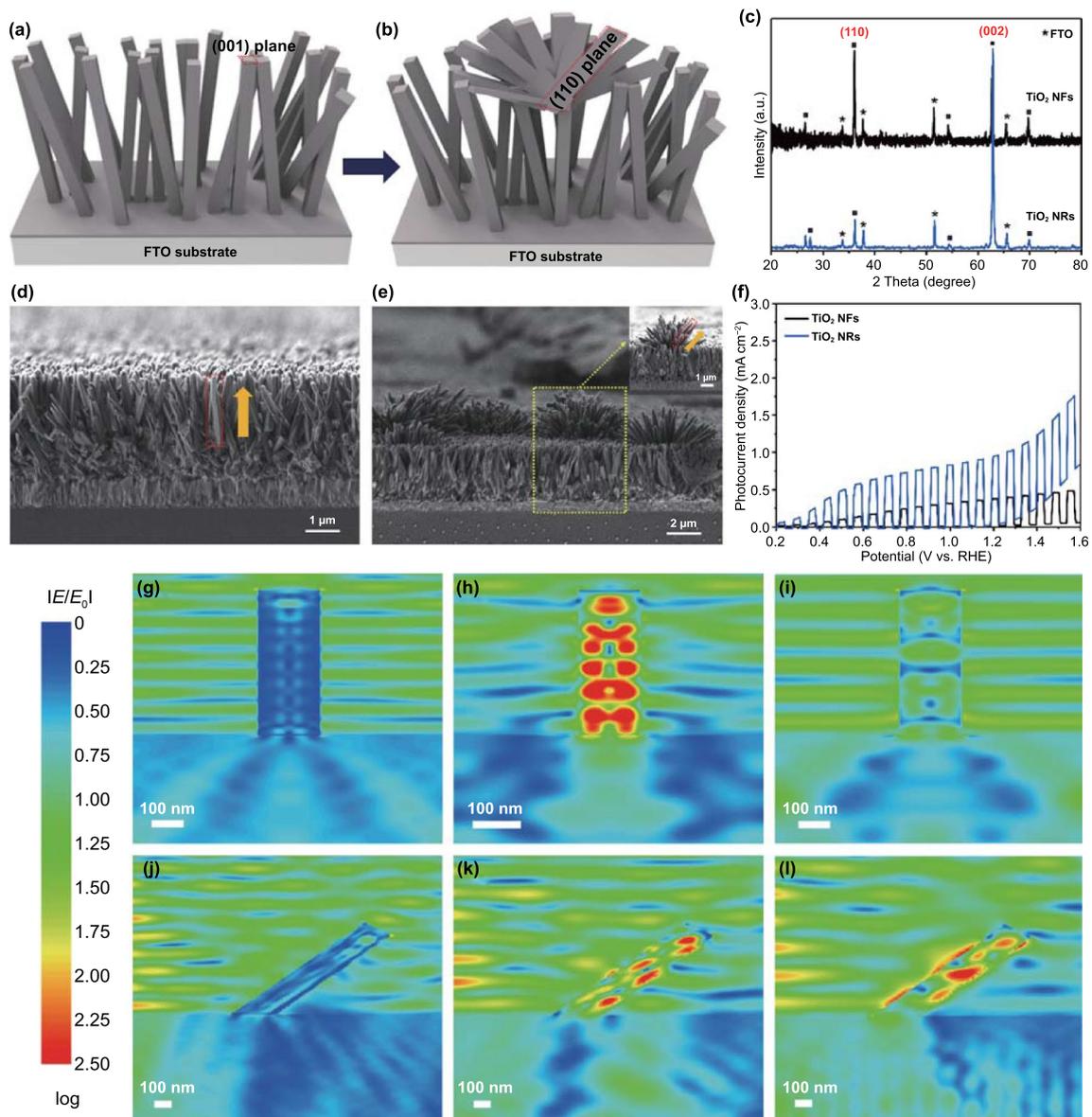


Fig. 1 Schematic illustration of **a** TiO₂ NRs and **b** TiO₂ NFs growth via hydrothermal synthesis. **c** XRD patterns of TiO₂ NRs and TiO₂ NFs. Cross-sectional SEM images of **d** TiO₂ NRs and **e** TiO₂ NFs. **f** *J*-*V* curves of TiO₂ NRs and TiO₂ NFs in 0.5M potassium phosphate (K-P₁) buffer with 1M Na₂SO₃. FDTD simulations of near field enhancement of TiO₂ NRs on FTO under **g** 350 nm, **h** 450 nm, and **i** 550 nm photons. FDTD simulations of near field enhancement of TiO₂ NFs on FTO under **j** 350 nm, **k** 450 nm, and **l** 550 nm photons

photoanodes of BiVO₄/TiO₂ NRs to demonstrate the effect of major facets of TiO₂ on the final architecture of BiVO₄/TiO₂ nanostructures and the following photoactivities. On the TiO₂ NRs, electrodeposited BiVO₄ nanodots agglomerate, and thus the tops of the BiVO₄/TiO₂ 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 TiO₂ NRs due to high conductivity. Agglomerated BiVO₄ nanodots block the gaps between the TiO₂ 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 mA cm^{-2} at 1.23 V vs. RHE) was significantly less than that of pristine TiO_2 NRs (0.91 mA cm^{-2} at 1.23 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 nm at 1.23 V versus RHE, which means there are lots of charge recombination after the introduction of BiVO_4 on TiO_2 NRs.

We also analyzed the EIS to compare the charge transfer kinetics between the $\text{BiVO}_4/\text{TiO}_2$ NRs and 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_{se} 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 BiVO_4 nanodots, the charge transfer resistance across the electrode/electrolyte interface increased from 259.89 to 1948.06Ω

cm^2 , showing the larger semicircles of $\text{BiVO}_4/\text{TiO}_2$ NRs compared to that of TiO_2 NRs. As shown in SEM images of $\text{BiVO}_4/\text{TiO}_2$ NRs (Fig. 2b, c), the agglomerated BiVO_4 reduced the porosity of the TiO_2 NRs, which is a structure interfering with the electrolyte permeation. Therefore, bulky BiVO_4 and reduced porosity of 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 TiO_2 NRs (Fig. 2f), which led to the deterioration of the PEC performances.

3.3 Characterization and PEC Performances of 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 TiO_2 NFs with (110) facets as a bottom layer for BiVO_4 nanodots. Unlike on the TiO_2 NRs, the conformal coating of extremely thin BiVO_4 nanodots across the entire surface of the 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 TiO_2 NFs were totally covered with BiVO_4 nanodots by increasing the pulse cycles of BiVO_4 . A cross-sectional SEM image in

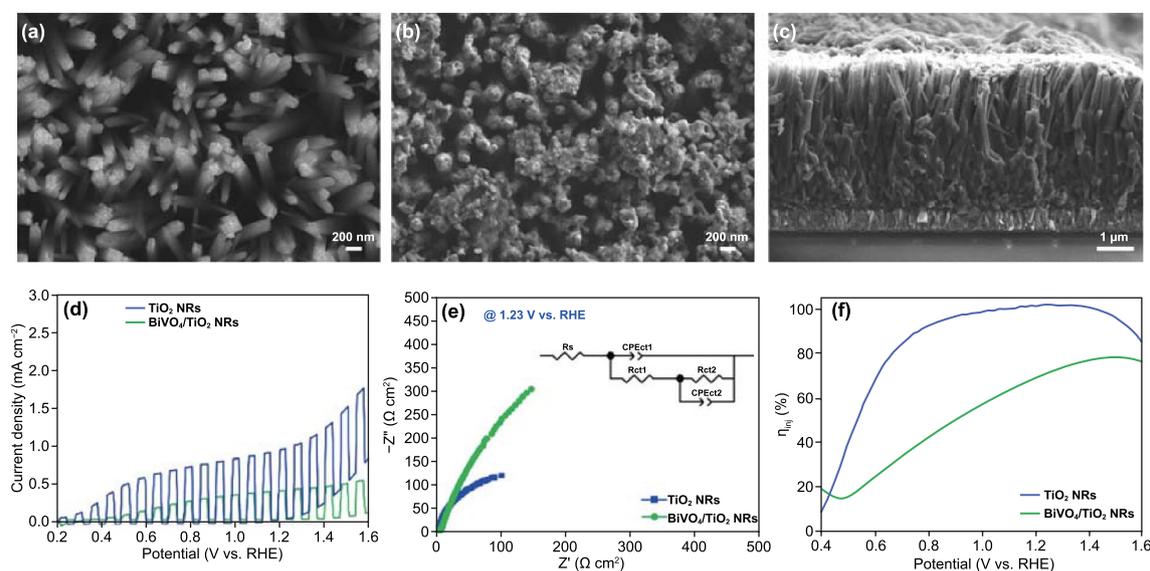


Fig. 2 Top SEM images of **a** TiO_2 NRs and **b** $\text{BiVO}_4/\text{TiO}_2$ NRs. **c** Cross-sectional SEM image of $\text{BiVO}_4/\text{TiO}_2$ NRs. **d** LSV for TiO_2 NRs and $\text{BiVO}_4/\text{TiO}_2$ NRs in 0.5M K–Pi buffer with 1M Na_2SO_3 . **e** Electrochemical impedance spectra (EIS) of TiO_2 NRs and $\text{BiVO}_4/\text{TiO}_2$ NRs at 1.23 V (vs. RHE) in 0.5M K–Pi buffer with 1M Na_2SO_3 . Inset shows equivalent circuit. **f** Charge injection efficiency of TiO_2 NRs and $\text{BiVO}_4/\text{TiO}_2$ NRs

Fig. S9 also showed conformally decorated BiVO_4 on 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 BiVO_4 nanodots conformally covered on the surface of the TiO_2 NFs. The inset shows an enlarged TEM image of 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 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 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 BiVO_4 were performed using a standard three-electrode cell with an electrolyte of 0.5M potassium phosphate (K-P_i) buffer and 1M sodium sulfite (Na_2SO_3) at a scan rate of 10 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 BiVO_4 from 0 to 36 (i.e., $n \text{ BiVO}_4 = n \text{ cycles electrodeposited BiVO}_4$), and

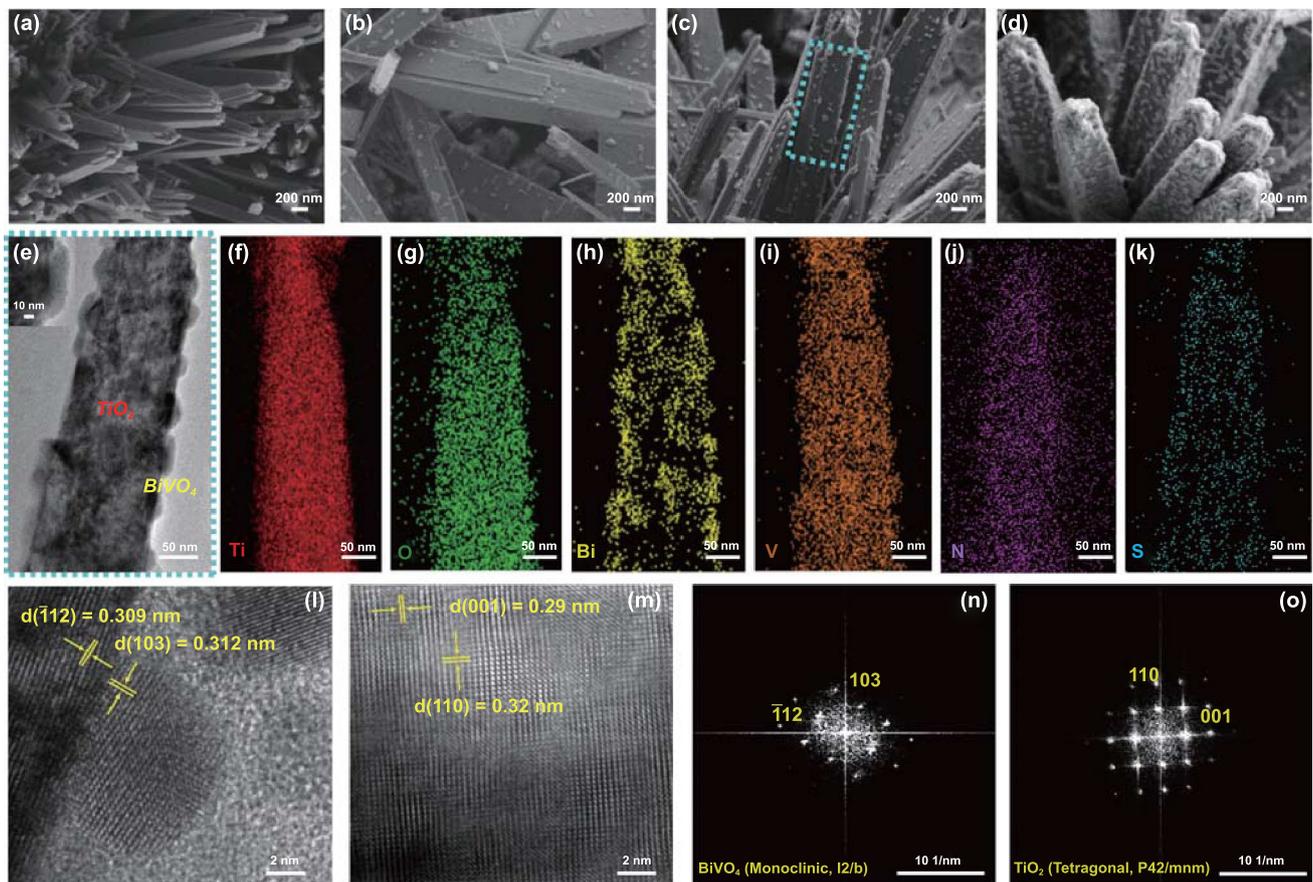


Fig. 3 SEM images of **a** TiO_2 NFs and $\text{BiVO}_4/\text{TiO}_2$ NFs with different deposition cycles of BiVO_4 : **b** 6 cycles, **c** 18 cycles, and **d** 36 cycles. **e** TEM image of $\text{BiVO}_4/\text{TiO}_2$ NFs deposited by 18 cycles. Inset shows HR-TEM image of $\text{BiVO}_4/\text{TiO}_2$ 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 BiVO_4 , **m** Crystalline planes of (001) and (110) of TiO_2 NFs. FFT patterns of **n** BiVO_4 and **o** 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 BiVO₄/TiO₂ 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 BiVO₄, the density of BiVO₄ nanodots covering the TiO₂ NFs increases (Fig. S8b–d), adding the charge transfer sites. However, after the optimized cycles (18 cycles), the agglomeration of BiVO₄ nanodots is observed at the tip of TiO₂ NFs (Fig. S8e–f), interfering with the charge transfer. The highest photocurrent density of 1.7 mA cm⁻² was obtained at 1.23 V versus RHE for the 18 BiVO₄/TiO₂ NFs. This value corresponds to 4.7 and 4.8 times that of the TiO₂ NFs and BiVO₄/TiO₂ 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 BiVO₄/TiO₂ NFs. The electron–hole recombination is structurally reduced because the conformally coated BiVO₄ nanodots on TiO₂ NFs enlarge the depletion layer and shorten the charge diffusion length to the interface [14,

33]. The small size of the BiVO₄ nanodots allows for a high collection efficiency of electrons by the TiO₂ 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_{b} is the applied bias (vs. RHE), J_{ph} is the photocurrent density at the measured potential, and P_{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 BiVO₄/TiO₂ NFs at 0.61 V versus RHE, which was 8.1

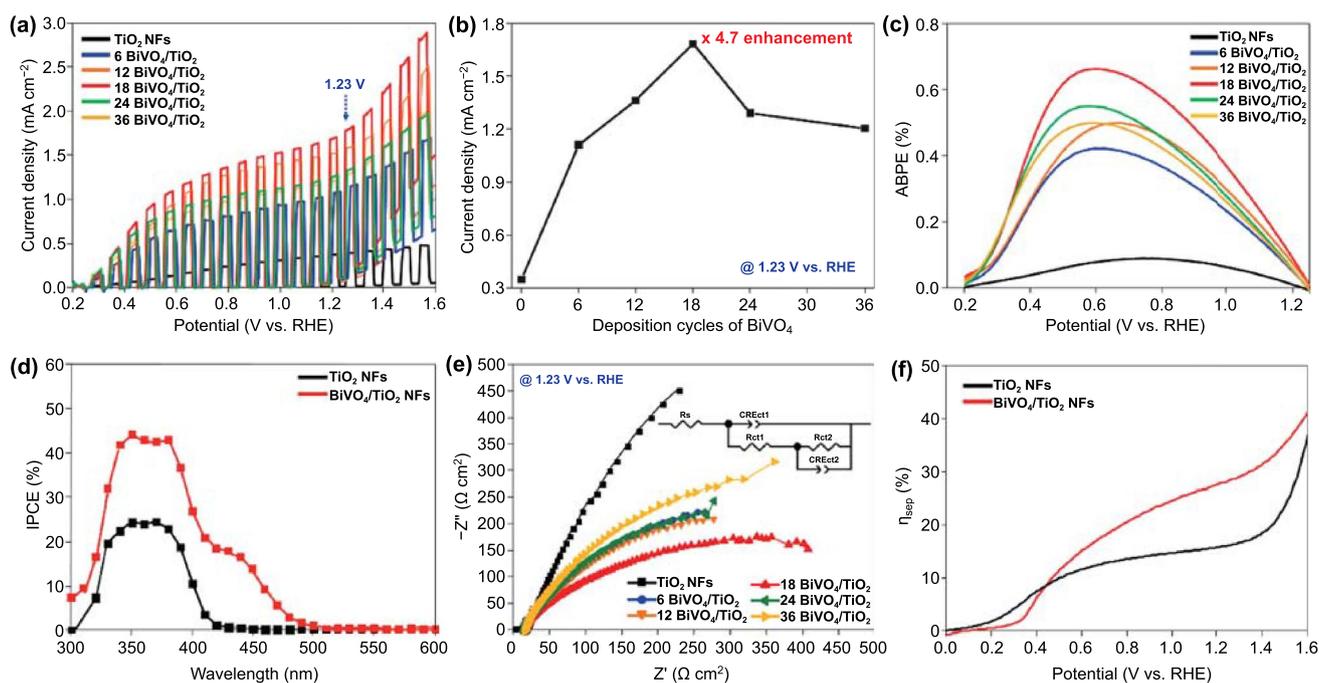


Fig. 4 **a** LSV of TiO₂ NFs and BiVO₄/TiO₂ NFs with different deposition cycles of BiVO₄ in 0.5M K–P_i buffer with 1M Na₂SO₃. **b** Photocurrent density of BiVO₄/TiO₂ NFs with different deposition cycles of BiVO₄ at 1.23 V (vs. RHE). **c** ABPE of TiO₂ NFs and BiVO₄/TiO₂ NFs with different deposition cycles of BiVO₄. **d** IPCE at 1.23 V (vs. RHE) of TiO₂ NFs and 18 BiVO₄/TiO₂ NFs. **e** EIS of TiO₂ NFs and BiVO₄/TiO₂ NFs with different deposition cycles of BiVO₄ at 1.23 V (vs. RHE) in 0.5M K–P_i buffer with 1M Na₂SO₃. Inset shows equivalent circuit. **f** Charge separation efficiency of TiO₂ NFs and 18 BiVO₄/TiO₂ NFs

times higher than that of the pristine TiO₂ NFs. Also, the maximum photoconversion efficiencies for all BiVO₄/TiO₂ NFs were obtained at a lower applied potential than the pristine TiO₂ NFs. These are associated with the reduction of the hole injection barrier at the interface between the TiO₂ NFs and electrolyte by introduction of the BiVO₄ 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 BiVO₄. 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 BiVO₄/TiO₂ 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 BiVO₄/TiO₂ NFs, and the measured data were fitted to the equivalent circuit, as shown in Fig. 4e [23]. Unlike BiVO₄/TiO₂ NRs, the charge transfer resistance of all BiVO₄/TiO₂ NFs was drastically decreased compared to pristine TiO₂ 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 BiVO₄/TiO₂ 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 ($1.602 \times 10^{-19} \text{ C}$), ϵ is the dielectric constant, ϵ_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 TiO₂ NFs is more cathodically shifted about 100 mV than the TiO₂ 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

BiVO₄ onto the TiO₂ NFs and TiO₂ NRs. As shown in Fig. S11a, the donor density of BiVO₄/TiO₂ NFs was increased, which means the internal resistance of BiVO₄/TiO₂ NFs is reduced, allowing the carrier to transport much faster than the pristine TiO₂ NFs. On the other hand, as shown in Fig. S11b, the carrier concentration of the BiVO₄/TiO₂ 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 (η_{sep}) in the potential from 0 V to 1.6 V versus RHE. As shown in Fig. 4e, the BiVO₄/TiO₂ NFs exhibited 2.5 times higher η_{sep} than the pristine TiO₂ NFs at 1.23 V versus RHE. It directly reveals that the enhanced photocurrent density of BiVO₄/TiO₂ NFs was mainly originated from the improved charge separation between BiVO₄ nanodots and TiO₂ NFs. To support this result, we also measured PEC water oxidation performances of TiO₂ NFs and 18 BiVO₄/TiO₂ NFs in 0.5M K-Pi buffer without hole scavenger. As shown in Fig. S12a, BiVO₄/TiO₂ NFs showed more efficient water oxidation and higher photocurrent density compared to TiO₂ NFs at 1.23 V versus RHE. The lower photocurrent density of BiVO₄/TiO₂ NFs in the lower potential region than that of TiO₂ NFs was derived from the sluggish hole transfer of BiVO₄. To expedite the hole transfer at the low potential, an additional introduction of oxygen evolution catalyst to BiVO₄ is necessary [13]. Also, BiVO₄/TiO₂ NFs showed a 29% higher maximum IPCE and wider absorption wavelength range than TiO₂ NFs as shown in Fig. S12b. We also measured the EIS of TiO₂ NFs and 18 BiVO₄/TiO₂ NFs at 1.23 V versus RHE in K-Pi buffer electrolyte. As shown in Fig. S12c, BiVO₄/TiO₂ NFs showed a smaller semicircle compared to TiO₂ 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 BiVO₄/TiO₂ 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 BiVO₄/TiO₂ NFs at 1.23 V versus RHE. As shown in Fig. S12e, the 18 BiVO₄/TiO₂ 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 TiO₂ 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 BiVO₄/TiO₂ NFs and BiVO₄/TiO₂ 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 TiO₂ NFs, BiVO₄/

TiO₂ NFs, TiO₂ NRs, and BiVO₄/TiO₂ NRs is displayed in Fig. 5b. As shown in Table S2, the transient decay time for the BiVO₄/TiO₂ NFs was 26.35 s, which is approximately 4.15 times longer than that of the TiO₂ NFs at about 6.36 s. It represents a lower charge recombination rate of BiVO₄/TiO₂ NFs compared to the TiO₂ NFs. Otherwise, the BiVO₄/TiO₂ NRs showed a decay time of 1.57 s, which is shorter than that of the TiO₂ NRs at about 2.58 s. It is also related to the poor charge separation between BiVO₄ nanodots and TiO₂ NRs. These results indicate that TiO₂ 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 TiO₂ 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 (τ_1) and radiative recombination lifetimes (τ_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 BiVO₄ that is the part in contact with the electrolyte on the band structures, they have similar τ_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

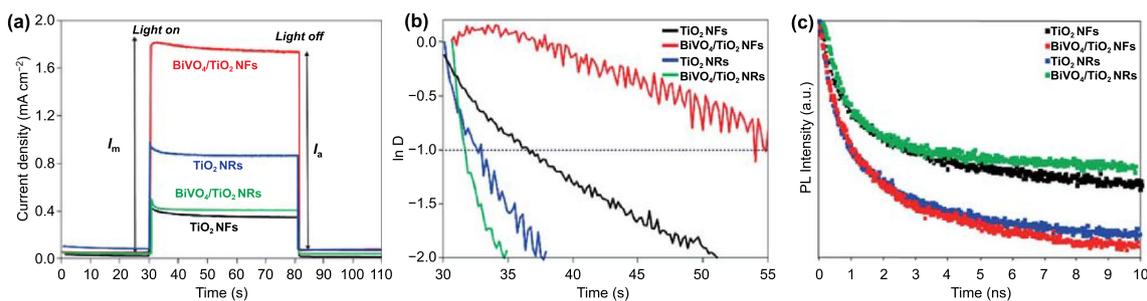


Fig. 5 **a** The transient photocurrent decay that occurs immediately upon illumination at 1.23 V (vs. RHE). **b** Transient decay times for TiO₂ NFs, TiO₂ NRs, BiVO₄/TiO₂ NFs, and BiVO₄/TiO₂ NRs. **c** TRPL of TiO₂ NFs, TiO₂ NRs, BiVO₄/TiO₂ NFs and BiVO₄/TiO₂ NRs

into the neighboring layers, the radiative recombination lifetime of the heterostructured photoelectrode decreases. In this regard, the smaller τ_2 value of BiVO₄/TiO₂ NFs (5.20 ns) than that of BiVO₄/TiO₂ NRs (6.10 ns) denotes the efficient extraction of photoexcited electrons by TiO₂ 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 TiO₂ nanostructures is a powerful tool to allow TiO₂ to be utilized as the hole blocking layer for BiVO₄ by boosting charge separation efficiency.

To investigate the reason for the charge separation difference of TiO₂ NRs with (001) facets and TiO₂ NFs with (110) facets, we compared the band structures of BiVO₄/TiO₂ NRs and BiVO₄/TiO₂ 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 α , 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 TiO₂ NFs and TiO₂ 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 TiO₂, diminishing the band gap of TiO₂ nanostructures [18]. And, a smaller band gap of TiO₂ NRs compared to that of TiO₂ NFs caused the absorption of the larger wavelength of visible light. Thus, as shown in Fig. 5a, the TiO₂ NRs generated a higher photocurrent density at 1.23 V versus RHE than TiO₂ NFs. According to Fig. 6b, the band gap of BiVO₄ was 2.4 eV, which is similar to the values in previous studies.

The secondary electron emission (SEE) spectra of the TiO₂ NFs, TiO₂ NRs, BiVO₄, BiVO₄/TiO₂ NFs, and BiVO₄/TiO₂ NRs were given by the high-binding-energy region in UPS, as shown in Fig. 6c. The work functions of TiO₂ NFs (4.46 eV), TiO₂ NRs (3.58 eV), BiVO₄/TiO₂ NFs (4.18 eV), and BiVO₄/TiO₂ 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 TiO₂ NFs (2.62 eV), TiO₂ NRs (2.67 eV), BiVO₄/TiO₂ NFs (2.39 eV), and BiVO₄/TiO₂ 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 TiO₂ NRs and TiO₂ 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 TiO₂ NFs have a more negative CBM than the (001) facet-dominant TiO₂ NRs. Based on these results, the energy band diagrams for the BiVO₄/TiO₂ NRs and BiVO₄/TiO₂ NFs are illustrated in Fig. 6e, f, respectively. In the case of BiVO₄/TiO₂ NRs, the CBM of the TiO₂ NRs significantly move upward, making the transport of photogenerated electrons from BiVO₄ difficult [38, 40, 44, 45]. Also, due to the relatively positive VBM of the TiO₂ NRs, photogenerated holes from BiVO₄ cannot be effectively blocked, causing the charge recombination, whereas TiO₂ NFs having a relatively negative CBM and VBM can be effective electron transport layer and hole-blocking layer for BiVO₄. As a result, the BiVO₄/TiO₂ NFs clearly form the type II band alignment, which is energetically favorable to separate the photogenerated electrons and holes from BiVO₄. In the final analysis, it was found that the enhanced photoactivity of BiVO₄/TiO₂ NFs was originated from the improvement of charge separation according to the band structure of crystal facet-engineered TiO₂.

4 Conclusions

In summary, we have demonstrated the effect of crystal facet-controlled TiO₂ nanostructures on band structures and charge separation. Two types of BiVO₄/TiO₂ heterostructure photoanodes having TiO₂ NRs with (001) facets and TiO₂ NFs with (110) were systematically studied to reveal the role of facets for facile PEC water splitting. We revealed that the improved photoelectrochemical

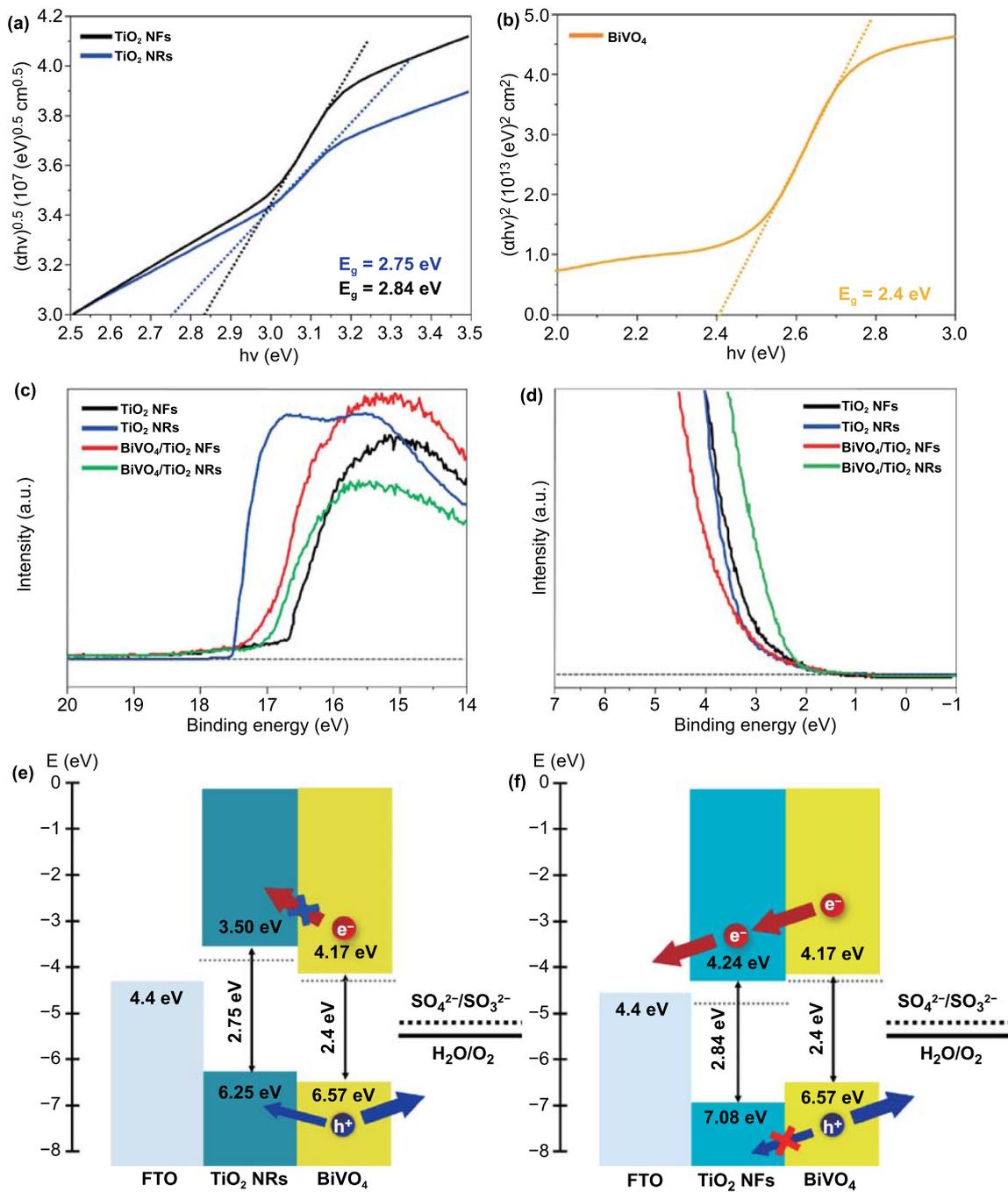


Fig. 6 UV-Vis Tauc plots of **a** TiO₂ NFs, TiO₂ NRs, and **b** BiVO₄. **c** Secondary electron emission spectra and **d** valence band spectra of TiO₂ NFs, TiO₂ NRs, BiVO₄/TiO₂ NFs, and BiVO₄/TiO₂ NRs. Flat band structures of **e** BiVO₄/TiO₂ NRs and **f** BiVO₄/TiO₂ NFs

performances of BiVO₄/TiO₂ NFs compared with BiVO₄/TiO₂ 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 TiO₂. 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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