

Charge Carrier Dynamics of Surface Back Electron/Hole Recombination in BiVO₄ and TiO₂ Photoanodes

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1 Experimental Section

1.1 Materials

Potassium phosphate monobasic (99.5%) was purchased from Aladdin. Vanadyl acetylacetonate (99%) and potassium phosphate dibasic (99%) were purchased from Energy Chemical. Acetic acid (> 99.5%) was purchased from Titan. Bismuth (III) nitrate pentahydrate and acetylacetone (99%) were purchased from Sinopharm Chemical Reagent. Titanium butoxide ($\geq 99\%$) was purchased from Macklin. Fluorine-doped tin oxide (FTO, resistance $< 15 \Omega \text{ sq}^{-1}$, transmittance $> 83\%$) substrates were purchased from Zhuhai Kaivo Optoelectronic Technology. All the chemicals were used as received without purification, and all electrolytes were prepared with deionized (DI) water (18.25 M Ω cm, YL400BU, Ereeran).

1.2 Fabrication of photoanodes

1.2.1 Fabrication of BiVO₄ photoanodes

Undoped BiVO₄ photoanodes were fabricated using a modified metal organic decomposition method, as previously reported.^{1, 2} Bismuth (III) nitrate pentahydrate (0.2 mol/L) dissolved in acetic acid (1.5 mL) and vanadyl acetylacetonate (0.2 mol/L) dissolved in acetylacetone were stirred for 30 minutes until the solution turns dark blue. The FTO (3 × 2.5 cm) was sonically cleaned (Shanghai Johnson) with solution containing deionized water glass cleaner and ethanol (95%) for 20 minutes. The FTO was then calcined at 450 °C (Nabertherm, LE 6/11/R7) for 30 minutes to remove organic impurities.

BiVO₄ films were fabricated by depositing precursor solution on the FTO. A small piece of the substrate was covered with a piece of tape to leave blank FTO for electrical connection (2.5 × 0.5 cm) and each layer needs 50 μL precursor solution. Spincoating parameters of the spincoater (Laurel, WS-650Mz-23NPPB) were set at 1000 rpm for 30 s for each layer of deposition. After each layer was deposited, the film was annealed

at 450 °C for 10 minutes. This spincoating/annealing procedure was repeated 15 times. After depositing the 15th layer, the coated glass was annealed at 500 °C for 5 hours.

1.2.2 Fabrication of TiO₂ photoanodes

Undoped TiO₂ photoanodes were fabricated using a modified metal organic decomposition method, previously reported.^{1,3} Titanium butoxide (3.91 mL) dissolved in acetic acid (1.5 mL) and acetylacetone (10 mL) were stirred for 30 minutes. The FTO (3 × 2.5 cm) was sonically cleaned (Shanghai Johnson) with solution containing deionized water, glass cleanser and ethanol (95%) for 20 minutes. The FTO was then calcined at 450 °C (Nabertherm, LE 6/11/R7) for 30 minutes to remove organic impurities.

TiO₂ films were fabricated by depositing precursor solution on the FTO. A small piece of the substrate was covered with a piece of tape to leave blank FTO for electrical connection (2.5 × 0.5 cm) and each layer needs 100 μL precursor solution. Spincoating parameters of the spincoater (Laurel, WS-650Mz-23NPPB) were set at 1000 rpm for 30 s for each layer of deposition. After each layer was deposited, the film was annealed at 580 °C for 10 minutes. This spincoating/annealing procedure was repeated 15 times. After depositing the 15th layer, the coated glass was annealed at 580 °C for 3 hours.

1.3 Characterization

The characterization of morphology of BiVO₄/FTO and TiO₂/FTO was carried out using Japan Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) at an accelerating voltage of 5 kV. Gold particles were sprayed on the electrode surface to enhance the conductivity of samples. The X-ray diffraction (XRD) data were carried out using a Bruker D8 Advance X-ray diffractometer at a tube voltage of 40 kV with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). UV-Vis spectra of BiVO₄/FTO, TiO₂/FTO and FTO were obtained using UV-Vis spectrophotometer (Shimadzu, UV-1099i) as shown in Figure S3.

Photoelectrochemical (PEC) water oxidation measurements were carried out in a custom-made transparent quartz reactor. The measurement uses a three-electrode configuration, with BiVO₄ and TiO₂ photoanodes as the working electrodes, a platinum mesh (1.5 cm × 1.5 cm) as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. We use a 365 nm LED (LG, XP-3535) as the excitation illumination and adjust the specified light intensity as needed. Furthermore, all PEC measurements are performed by back-side (substrate-electrode) illumination in Potassium phosphate (KPi) buffer (0.1 mol L⁻¹ K₂HPO₄ and KH₂PO₄, pH = 6.7). The chopped light current density-Voltage (*J-V*) response and chopped light transient photocurrent (TPC) of BiVO₄ and TiO₂ photoanodes were carried out using CHI 1140C potentiostat. The light on/off condition was controlled by a DDS Signal Generator/Counter (JDS6600) with a time interval of 10 s. All applied potentials reported in this paper was converted to be versus the reversible hydrogen electrode (RHE) using the Equation S1:

$$V_{RHE} = V_{Ag/AgCl} + 0.0591 \times pH + V_{Ag/AgCl}^0 \quad \text{Equation S1}$$

where V_{RHE} is the applied potential versus the reversible hydrogen electrode; $V_{Ag/AgCl}^0$ is the standard potential of the Ag/AgCl reference electrode (0.198 V_{RHE} at 25°C) and $V_{Ag/AgCl}$ is the applied potential versus Ag/AgCl.

Electrochemical impedance spectroscopy (EIS) measurements in the dark was carried out using an Autolab PGSTAT204 potentiostat. The Randle equivalent circuit diagram was constructed to analyze the data of the electrochemical impedance spectrum. The flat band potential of BiVO₄ and TiO₂ was determined using Mott-Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 A^2 e N_D} \times (V - V_{FB} - k_B T / e) \quad \text{Equation S2}$$

where C (F) is the space-charge capacitance; A (cm²) is the active geometric area; N_D (cm⁻³) is the donor density; e is the electronic charge (1.602×10^{-19} C); ε is the relative permittivity of BiVO₄; ε_0 is the vacuum permittivity (8.854×10^{-12} F m⁻¹); V (V vs.

RHE) is the applied potential; V_{FB} (V vs. RHE) is the flat-band potential; k_{B} is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$) and T is the temperature (298 K).

The photo-induced absorption spectroscopy and transient absorption spectroscopy were employed to monitor changes in photogenerated holes. The PIA measurement used a three-electrode configuration described above and a 365 nm LED was placed as the excitation illumination at an angle of 45° to the transparent quartz reactor. Transient absorption spectroscopy used a laser flash with a wavelength of 355 nm as the excitation illumination (DaWa-200, Beamtech Optronics). The frequency of the laser flash was 0.33 Hz and the laser intensity was adjusted to be $95.5 \mu\text{J cm}^{-2}$. A 150 W tungsten lamp coupled with a monochromator (TLS15-T150A, Zolix Instruments) was employed as the probe light source. The probe light has a wavelength of 550 nm. The PIA and TA data were monitored by a home-made photodetector (Hamamatsu S5973) and recorded by a data-acquisition device (USB-6361) and an oscilloscope (MDO34, Tektronix). The TPC data was recorded by the CHI 1140C potentiostat simultaneously.

2 Supplementary Figures

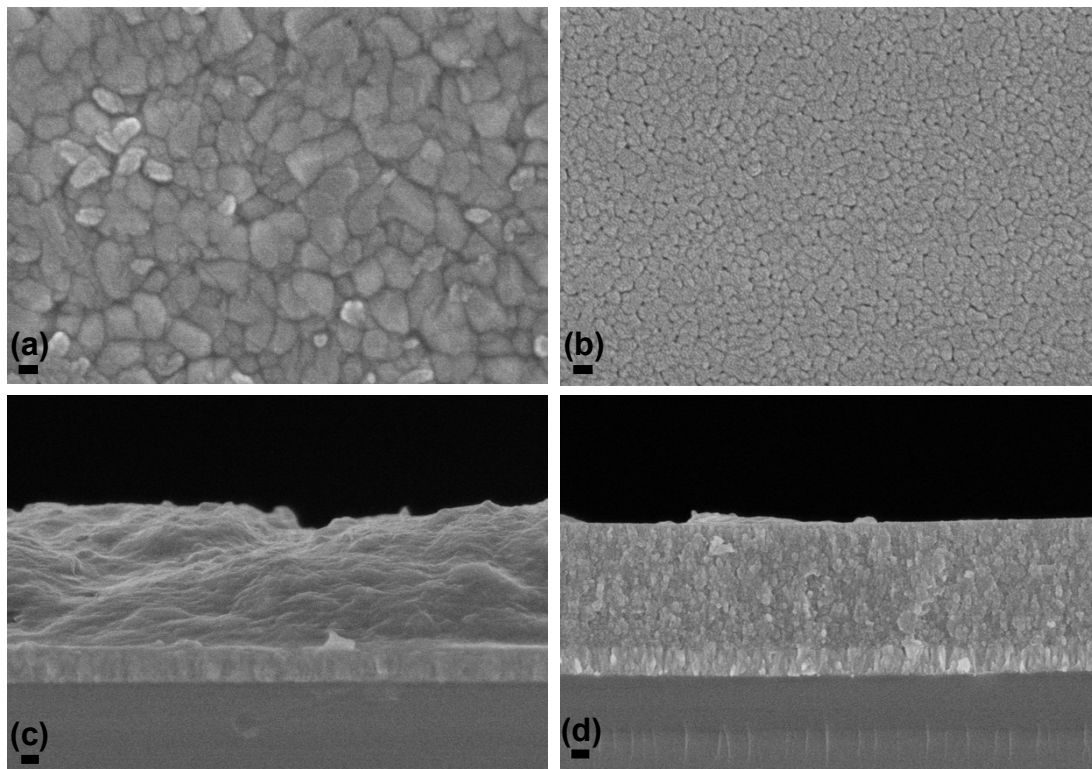


Figure S1. Top view of the (a) BiVO₄ photoanode and (b) TiO₂ photoanode. Cross-sectional view of the (c) BiVO₄ photoanode and (d) TiO₂ photoanode. The scale bars in (a) and (b) indicate 50 nm in length. The scale bars in (c) and (d) indicate 200 nm in length.

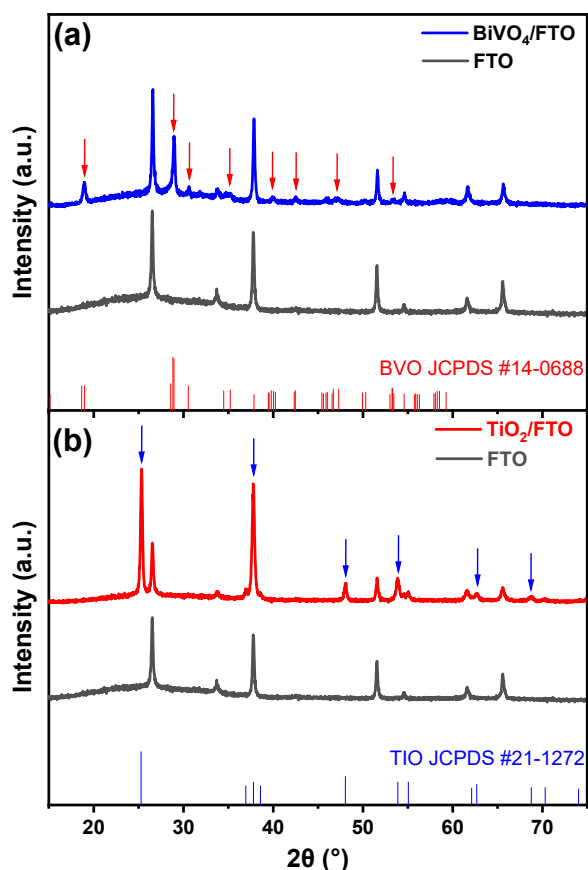


Figure S2. XRD pattern of (a) BiVO₄ and (b) TiO₂ fabricated using the MOD method. The arrows indicate the diffraction peaks of the photoanode materials in comparison with the XRD of the FTO substrate (black) used in this work.

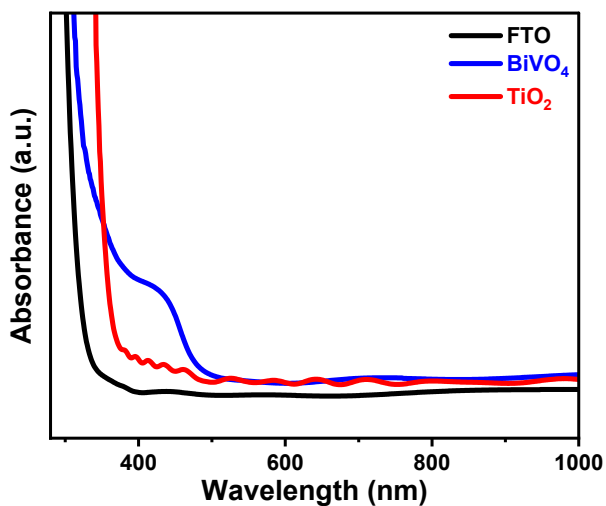


Figure S3. UV-Vis absorption spectra of BiVO₄ photoanodes (blue), TiO₂ photoanodes (red) and the FTO substrate (black).

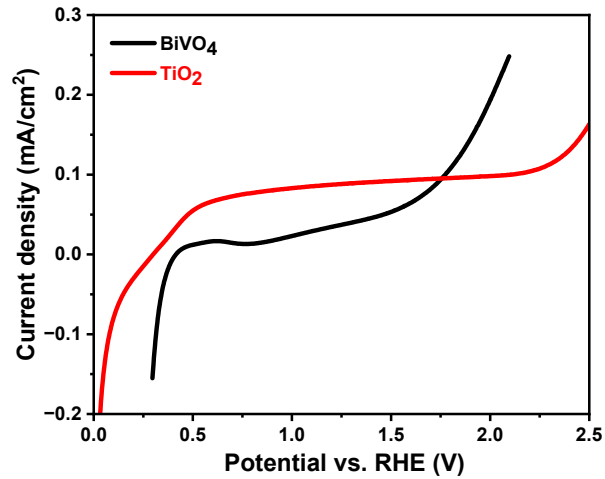


Figure S4. Current density-Voltage (J - V) response of BiVO_4 (black) and TiO_2 (red) photoanodes under the continuous illumination of a 365 nm LED measured in 0.1 M KP_i buffer (pH 6.7). Light intensity: 3.4 mW cm⁻².

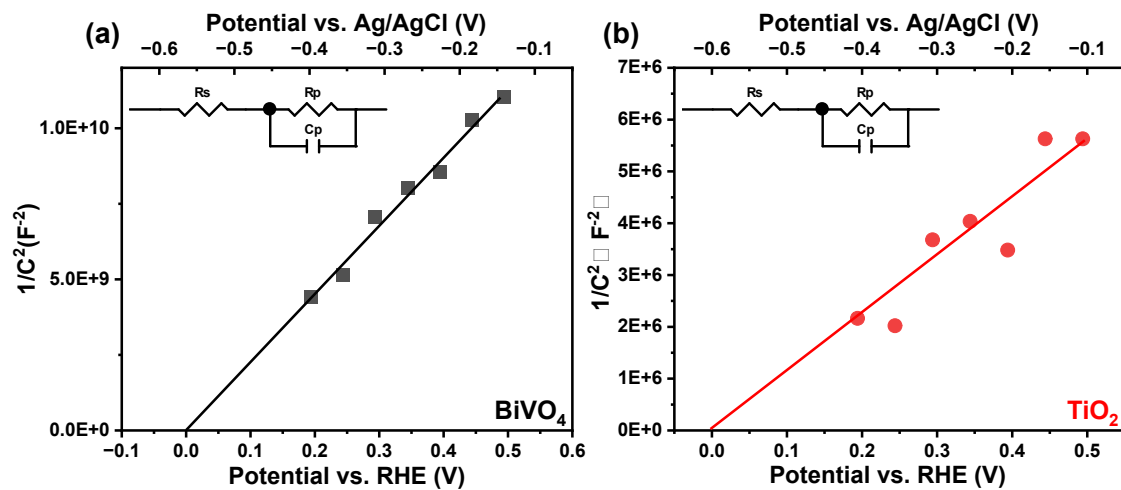


Figure S5. The Mott-Schottky analyses of (a) the BiVO_4 photoanode and (b) TiO_2 photoanode using the Randle model (inset) in 0.1 M KP_i (pH 6.7).

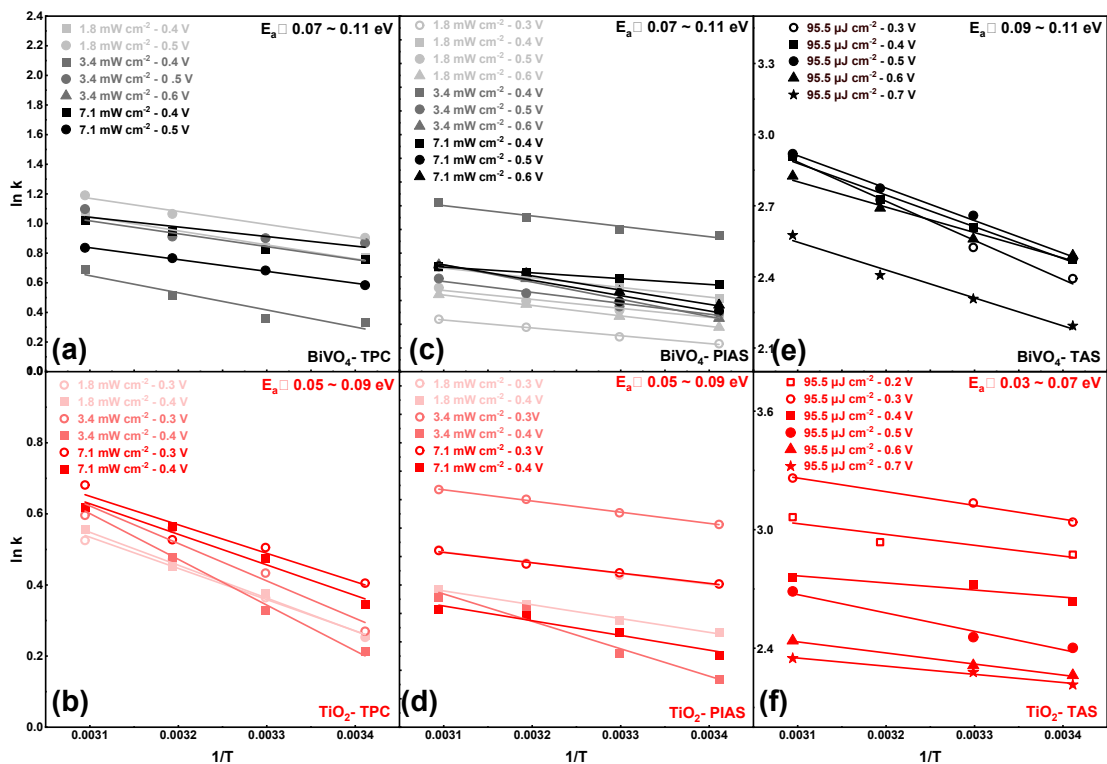


Figure S6. Arrhenius analyses of the BER determined using TPC for (a) BiVO₄ and (b) TiO₂. (c) PIA spectroscopy for BiVO₄ and (d) TiO₂. TA spectroscopy for (e) BiVO₄ and (f) TiO₂.

References

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2. K. Sayama, A. Nomura, T. Arai, T. Sugita, R. Abe, M. Yanagida, T. Oi, Y. Iwasaki, Y. Abe and H. Sugihara, *J Phys Chem B*, 2006, **110**, 11352-11360.
3. X. Guo, Z. Ma, Y. Yuan, Y. Kang, H. Xu, Z. Mao and Y. Ma, *Adv. Sci.*, 2023, **10**, 2206685.