

Electronic Supplementary Information – Dynamics of photogenerated holes in undoped BiVO₄ photoanodes for solar water oxidation

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1. SEM images

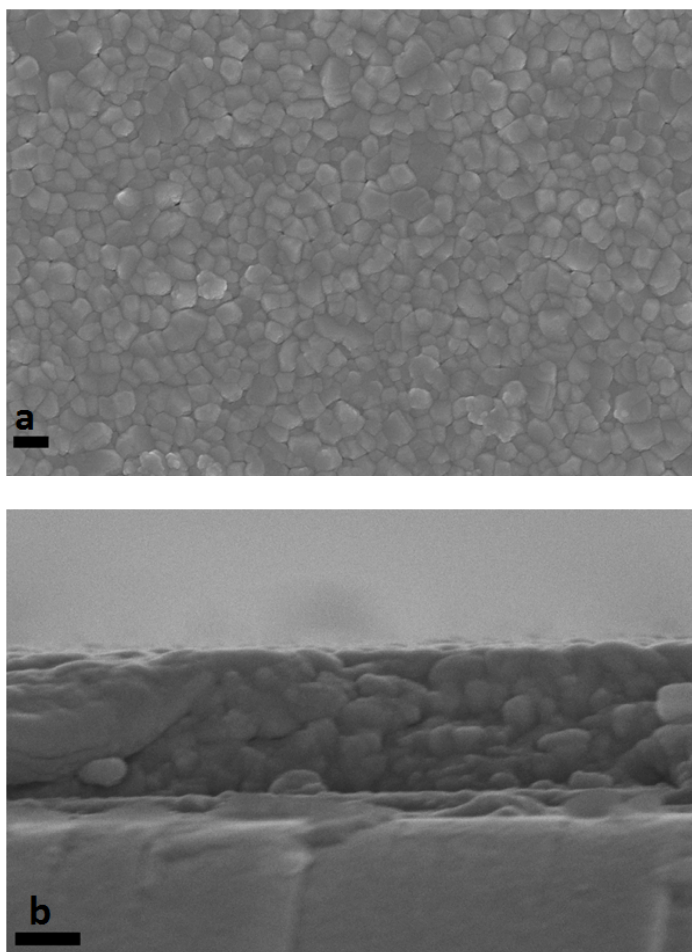


Fig. S1 (a) Top view of the BiVO₄ photoanode. (b) Cross-sectional view of the BiVO₄ photoanode. The scale bars in (a) and (b) indicate 200 nm in length.

2. XRD characterisation

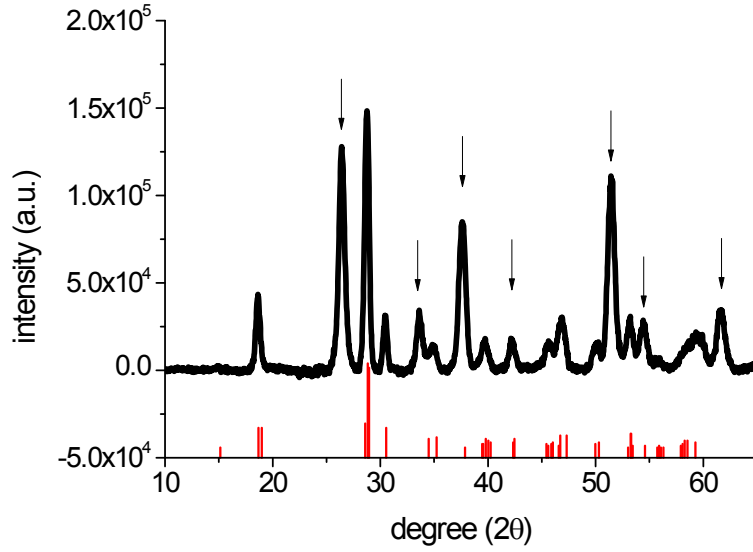


Fig. S2 XRD pattern of BiVO₄ fabricated using the MOD method. Arrows are indications of SnO₂ peaks in FTO substrates. BiVO₄ reference (red bars): 00-014-0688.

3. UV-Vis, IPCE spectra and light penetration depth

3.1 Determination of light penetration depth

The absorption coefficient was obtained from Beer-Lambert law, shown in Equation S1:

$$\alpha(\lambda) = \frac{abs(\lambda)}{l} \quad (S1)$$

Where $\alpha(\lambda)$ is the absorption coefficient (m⁻¹), $abs(\lambda)$ is the absorbance measured by UV-vis spectroscopy and l is the film thickness (m).

The light penetration depth is then determined by Equation S2:

$$D_p = 1/\alpha(\lambda) \quad (S2)$$

Where D_p (m) is the light penetration depth.

3.2 Calculation of the theoretical photocurrent in BiVO₄ photoanodes

The single photon energy is calculated from Equation S3

$$E(\lambda) = h \times \frac{C}{\lambda} \quad (S3)$$

Where $E(\lambda)$ is the photon energy (J), h is Planck's constant (6.626×10^{-34} J s), C is the speed of light (3×10^8 m s⁻¹) and λ is the photon wavelength (m).

The solar photon flux is then calculated according to Equation S4

$$Flux(\lambda) = \frac{P(\lambda)}{E(\lambda)}$$

(S4)

Where $Flux(\lambda)$ is the solar photon flux ($\text{m}^{-2} \text{s}^{-1} \text{nm}^{-1}$), and $P(\lambda)$ is the solar power flux ($\text{W m}^{-2} \text{nm}^{-1}$).¹

The theoretical maximum photocurrent density under solar illumination, J_{max} (A m^{-2}), is then calculated by integrating the solar photon flux, shown in Equation S5:

$$J_{max} = e \times \int_{\lambda_2}^{\lambda_1} Flux(\lambda) d\lambda$$

(S5)

Where λ_1 is the absorption edge of BiVO_4 , 500 nm (2.5 eV band gap) in this study, λ_2 is the lower limit of the measured solar spectrum, and e is the elementary charge ($1.602 \times 10^{-19} \text{ C}$). The theoretical photocurrent of such BiVO_4 photoanodes is accordingly calculated to be 64.5 A m^{-2} (6.45 mA cm^{-2}).

The integration of the photon flux converted in chemical energy by BiVO_4 photoanodes (i.e. $IPCE \times \text{AM1.5G}$ spectrum), measured at $1.2 \text{ V}_{\text{RHE}}$ and $1.7 \text{ V}_{\text{RHE}}$, gives photocurrent densities of 0.58 and 1.38 mA cm^{-2} , respectively, according to Equation S6, taking into account that we neglected the photons absorbed below 360 nm in the IPCE measurement.

$$J(V) = e \times \int_{\lambda_2}^{\lambda_1} Flux(\lambda) \times IPCE(\lambda, V) d\lambda$$

(S6)

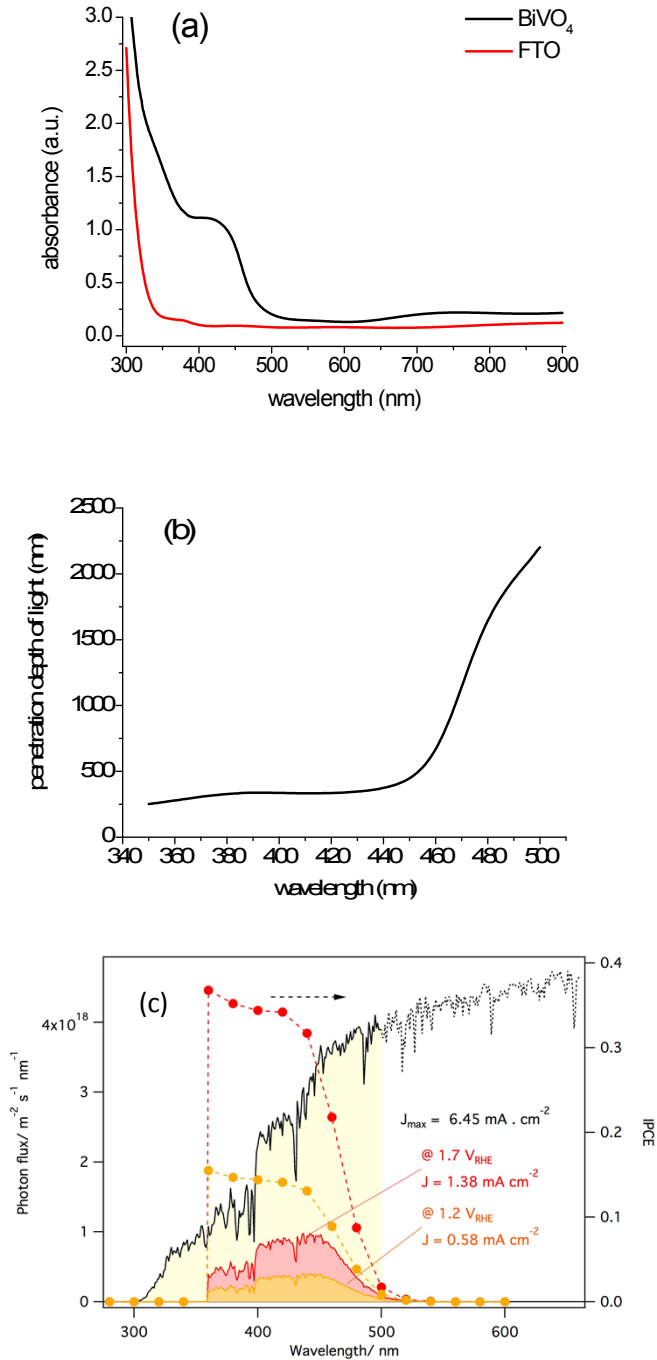


Fig. S3 (a) UV-Vis absorption spectrum of BiVO₄ (black) and the FTO substrate (red). (b) Light penetration depth as a function of excitation wavelength. (c) Absorbed photon flux converted to chemical energy by the BiVO₄ photoanode measured at 1.2 V_{RHE} (orange) and 1.7 V_{RHE} (red) compared to the solar photon flux spectrum (black) at AM1.5.¹ The BiVO₄ photon flux spectrum is calculated according to the IPCE data under 1.2 V_{RHE} (orange dots) and 1.7 V_{RHE} (red dots) conditions. Accordingly the theoretical maximum photocurrent under 1.2 and 1.7 V_{RHE} under AM1.5 illumination are shown in the inset text in (c).

4. Mott-Schottky analysis

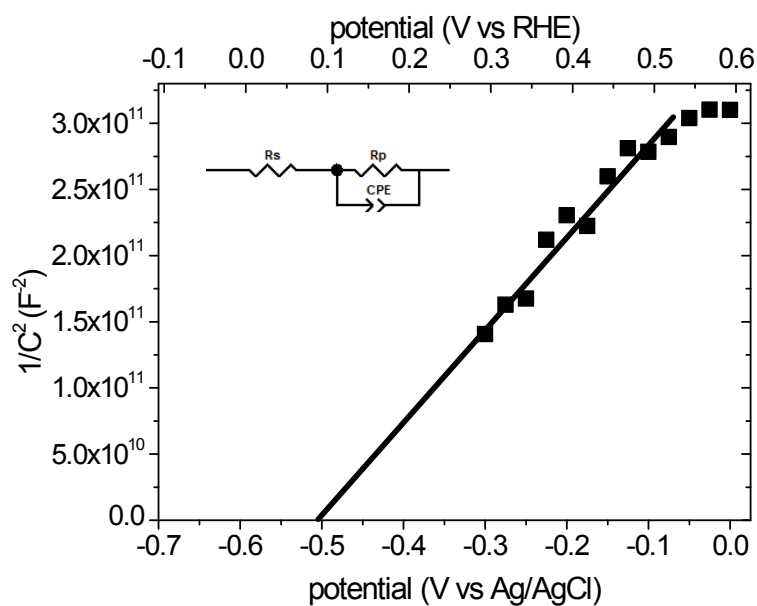


Fig. S4 Mott-Schottky plot of the BiVO₄ photoanode using the Randle model shown inset. The flat-band potential is measured as ~ 0.1 V vs RHE.

5. Transient absorption of undoped BiVO₄ under applied bias in a PEC cell

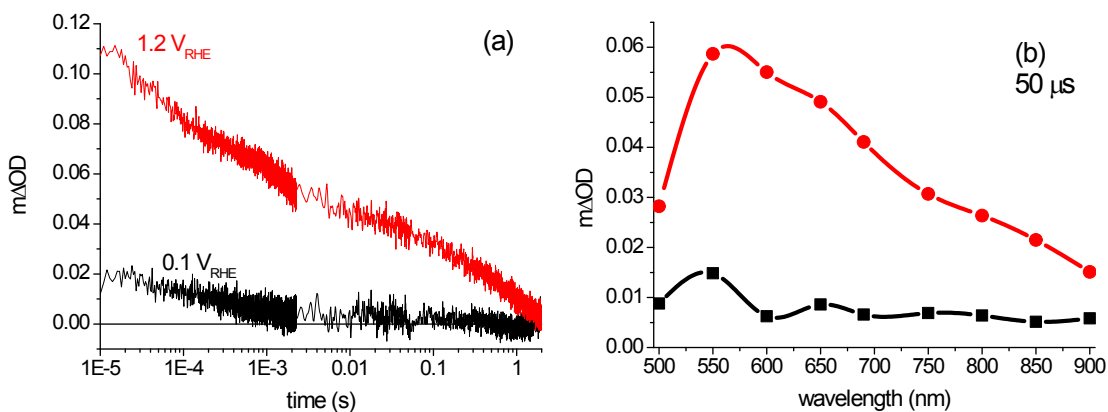


Fig. S5 (a) Transient absorption decays of a BiVO₄ photoanode measured at 1.2 V_{RHE} (red) and 0.1 V_{RHE} (black; near the flat-band potential), probing at 550 nm. (b) Transient absorption spectra of the BiVO₄ photoanode measured at 1.2 V_{RHE} and 0.1 V_{RHE} (color matches Fig. S5a) recorded at 50 μs after laser excitation (355 nm).

6. Kinetics of photogenerated holes in BiVO₄ as a function of laser excitation intensity

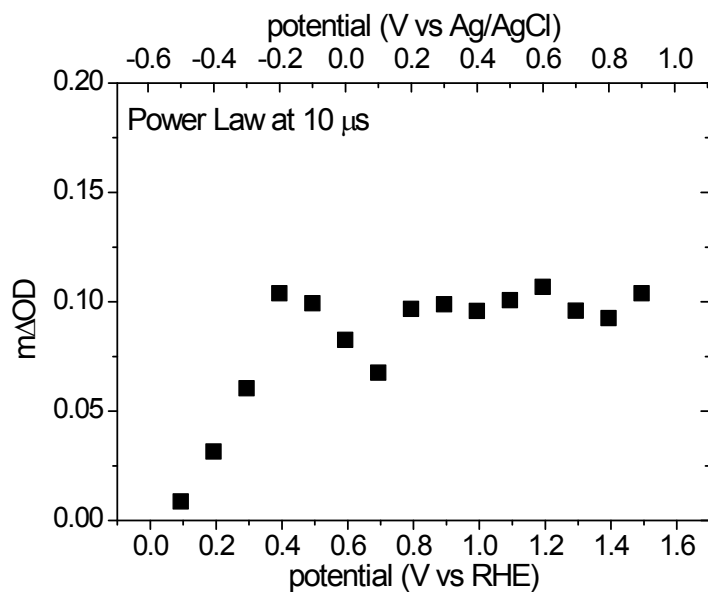


Fig. S6 The amplitude of the power law fitting (μ s transient absorption decay) at 10 μ s as a function of applied bias, corresponding to the hole amplitude for fast bimolecular recombination at 10 μ s.

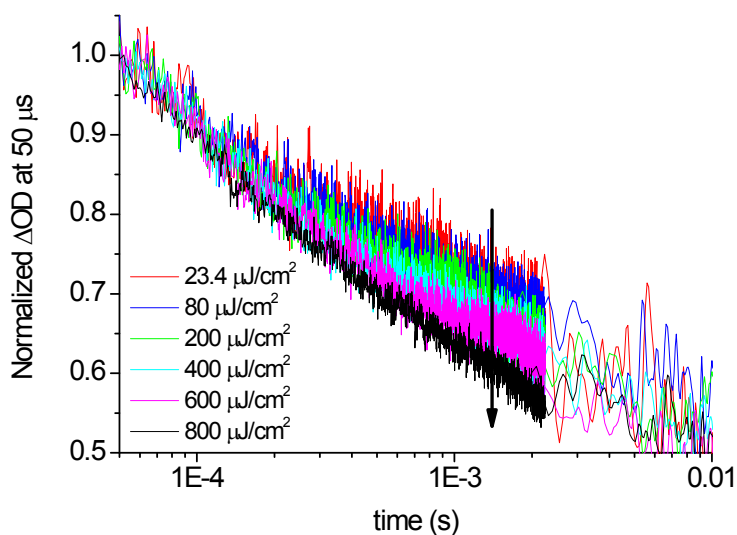


Fig. S7 Normalized TA decays of Fig. 4a in the main paper, normalized at 50 μ s. Intensity-dependent kinetics are observed from 50 μ s to 2 ms. Laser excitation intensity range: 20 μ J/cm² to 800 μ J/cm².

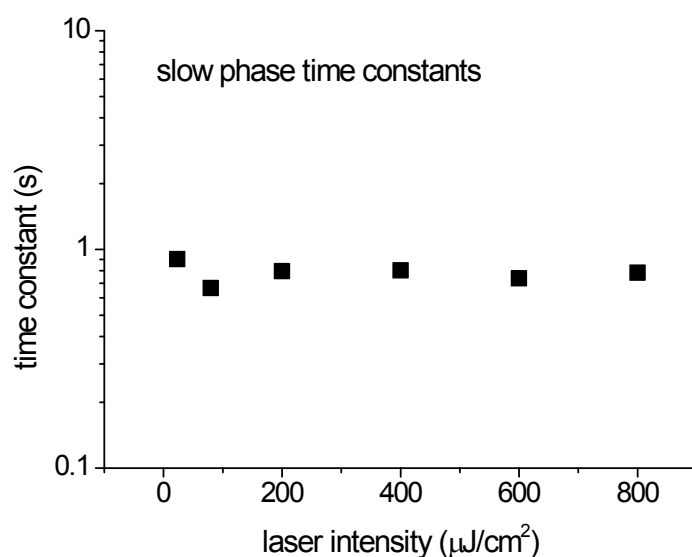


Fig. S8 Lifetime of the slow phase decay (ms-s timescale), fitted by a single exponential, as a function of laser excitation intensity under 1.2 V_{RHE} bias.

7. Time constants of water oxidation; recombination of long-lived holes in BiVO_4

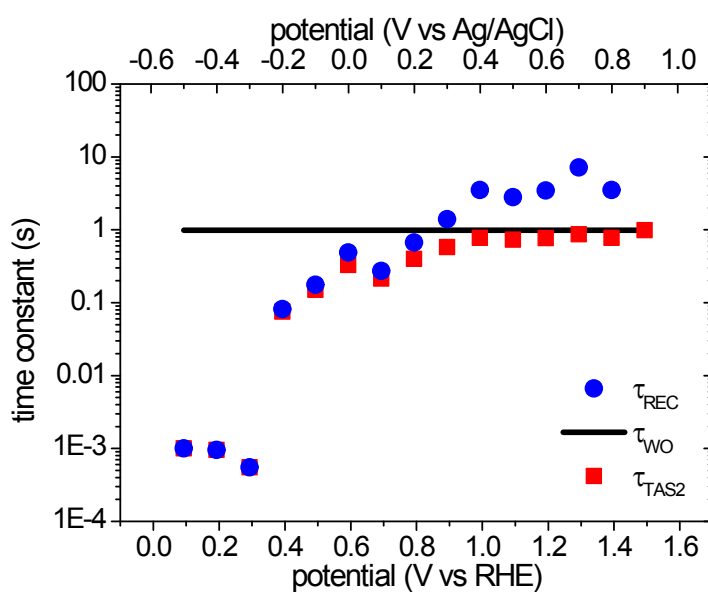


Fig. S9 Time constants of slow decay kinetics (ms-s) of long-lived holes (τ_{TAS2} , red squares) determined from the single exponential fitting to the transient decays; time constants of recombination kinetics of long-lived holes (τ_{REC} , blue dots, determined by $1/k_{\text{REC}}$) determined from Equation 6 and described in the main paper, and time constants of water oxidation kinetics of long-lived holes (τ_{WO} , black solid line) determined from the transient absorption decay time constant at 1.5 V_{RHE} .

8. Correlation of back electron/hole recombination amplitudes measured by TAS and chopped light TPC

8.1 Calculation of transient absorption amplitude of slow charge recombination in the slow phase.

The transient absorption amplitude of slow recombination (ms-s) can be calculated using Equation S7 shown below,

$$\phi_{rec}(V) \propto \phi(V) \times \frac{k_{rec}(V)}{k_{rec}(V) + k_{WO}} \quad (S7)$$

where $\phi_{rec}(V)$ is the yield of holes which recombine in the slow phase; $\phi(V)$ is the total yield of holes (slow phase amplitude of the exponential function, A_{TAS} , in Equation 5) from decay fittings of Fig. 3, the same as Equation 6 in the main paper; k_{WO} and $k_{rec}(V)$ correspond to the rate constants for water oxidation (k_{WO}) and back electron/hole recombination, respectively.

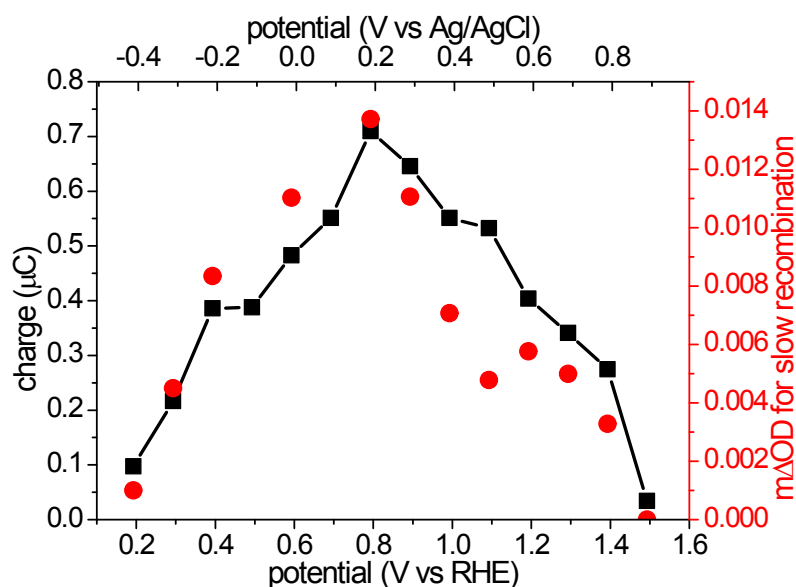


Fig S10. Comparison of slow charge recombination measured with two techniques (transient absorption spectroscopy and chopped light transient photocurrent). Black squares: accumulated charges (holes) that undergo back recombination determined from chopped light TPC measurements, obtained by integrating the negative transient current with time. Red dots: transient absorption amplitude of holes that undergo slow charge recombination, calculated from the fit amplitude of the exponential function and Equation S1.

9. Fit results of transient absorption decays as a function of applied bias

Table S1. Fit parameters of transient absorption decays in Fig. 3a in the main paper, using a combination of power law and single exponential function, shown in Equation 5 in the main paper.

potential / V vs RHE	power law		single exponential function	
	a	b	A_{TAS2}	$\tau(TAS2)/s$
1.5	4.0E-6	-0.28	3.1E-5	0.99
1.4	4.6E-6	-0.26	3.0E-5	0.77
1.3	5.9E-6	-0.24	2.7E-5	0.86
1.2	5.4E-6	-0.26	2.2E-5	0.76
1.1	5.1E-6	-0.26	2.2E-5	0.73
1	5.6E-6	-0.25	2.2E-5	0.77
0.9	6.0E-6	-0.24	1.7E-5	0.57
0.8	4.8E-6	-0.26	1.9E-5	0.40
0.7	3.4E-6	-0.26	1.8E-5	0.21
0.6	3.7E-6	-0.27	1.4E-5	0.19
0.5	4.9E-6	-0.26	1.3E-5	0.15
0.4	2.5E-6	-0.32	1.4E-5	0.075
0.3	2.7E-6	-0.27	8.4E-6	5.5E-4
0.2	1.6E-6	-0.26	4.5E-6	9.5E-4
0.1	4.3E-7	-0.26	1.0E-6	1.0E-3

References

1. Reference Solar Spectral Irradiance: Air Mass 1.5. NREL. ASTM G-173 package. <http://rredc.nrel.gov/solar/spectra/am1.5/>