

Electronic Supplementary Information (ESI)

Inhibition of Sn(II) oxidation in Z-scheme BiVO₄-

QD@Sn₃O₄ for overall water splitting

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Experimental Section

All reagents were analytical grade without further purification and deionized (DI) water was used in this work.

Synthesis of materials: The preparation of Sn_3O_4 was as following. Firstly, 7 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dispersed into 120 mL of DI water and the pH of the solution was adjusted to 13 with 0.1 M NaOH. The resultant mixture was stirred for 30 min and then sonicated for 5 min. Afterwards, the solution was carried out the hydrothermal reaction at 180 °C for 16 h. Sn_3O_4 was obtained after being washed by deionized water and absolute ethanol several times.

BiVO_4 -QDs was prepared by a sodium oleate modified hydrothermal method.^{1, 2} In a typical process, 1.6 mmol of sodium oleate and 0.8 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were added to a beaker with 40 mL of DI water and kept stirring. Meanwhile, 0.8 mmol of NH_4VO_3 with 40 mL of DI water was added to the above solution. Then the mixed solutions were stirred for 1 h and transferred to a Teflon-lined autoclave to kept at 100 °C for 12 h. Finally, BiVO_4 -QDs were obtained by washing the yellow powders with absolute ethanol and n-hexane repeatedly.

The Z-scheme BiVO_4 -QD@ Sn_3O_4 heterostructure was prepared by hydrothermal method. 0.1 g of Sn_3O_4 were dissolved in 10 mL DI water and a certain amount of BiVO_4 -QDs were added with ultrasonic condition. The mixture was placed in an oven to carry out the hydrothermal reaction at 100 °C for 4 h. Z-scheme BiVO_4 -QD@ Sn_3O_4 heterostructure samples were obtained after washing by DI water and absolute ethanol. In addition, the amount of BiVO_4 -QDs with mass fraction of 10%, 15%, 20% and 25% were added to regulate the optimal photocatalytic performance, and named as 10BQD@ Sn_3O_4 , 15BQD@ Sn_3O_4 , 20BQD@ Sn_3O_4 and 25BQD@ Sn_3O_4 , respectively. In order to the PEC measurements, the samples were ground and thin-films electrode

with a working area of 0.25 cm² were prepared with FTO as a substrate by a doctor blade method.

Characterization: The morphologies of samples were observed by scanning electron microscope (FE-SEM, Hitachi S-4800) and transmission electron microscope (HR-TEM, FEI Tecnai G2, 200 kV). The crystal structures were analyzed by X-ray Powder Diffraction (XRD, Philips X'pert pro, Cu K-alpha) and micro-Raman spectrometer (JY-HR800, 532 nm laser). The surface chemical compositions were studied by XPS (Kratos-AXIS ULTRA DLD) and the optical absorption performance was obtained by a UV-Vis spectrometer (TU-1901). The band structure was determined by ultraviolet photoelectron spectroscopy (UPS, ESCA-LAB210). The photogenerated charge properties were recorded by PL spectra (ZLX-PL-I, 305 nm). The photoelectrochemical (PEC) characteristics were investigated by an electrochemical workstation (CHI660E).

During the PEC measurements, the as-prepared sample, Pt plate and saturated Ag/AgCl electrode were served as the working electrodes, counter electrode and reference electrode, respectively. A 500 W Xenon lamp was used as illumination source and 0.5 M of Na₂SO₄ aqueous solution was used as the electrolyte. The amplitude and applied bias during electrochemical impedance measurements were 10 mV and 1V vs. Ag/AgCl, and the frequency was 5 k Hz in Mott-Schottky measurements.

Photocatalytic activity evaluation: The hydrogen evolution rate was estimated in a LabSolar-III-AG inline hydrogen production system equipped with a gas chromatograph. The system was completely degassed to remove O₂ and CO₂ before reactions. For the photocatalytic H₂ production, 0.1 g of samples were placed into 80 mL of DI water and 20 mL methanol as a hole scavenger with 8 h reaction. Overall water splitting of samples were carried out 8 h reaction in 100 mL of DI water at room temperature. A 500W Xenon lamp was used as the light source.

The apparent quantum yields (AQE) were calculated from the incident light intensity and generation rate of hydrogen according the equation: $AQE = 2 \times \text{number of evolved H}_2 \text{ molecules} / \text{number of incident photons} = 2RN_Ahc/AP\lambda$, in which R and N_A is the generation rate of hydrogen and Avogadro constant; h and c are the Planck constant and light speed; P and λ are the intensity and the wavelength of incident light, respectively. The used light source is a 500 W Xenon lamp equipped with a bandpass filter, and 0.3 g of powder sample is used as photocatalyst. The area of incident light (A) is 1.62 cm², which is determined by the size of filter. The light intensity was determined by means of standard silicon solar cell. The detailed information about intensity of incident light and corresponding generation amount of hydrogen are shown in Tab. S1.

Figures

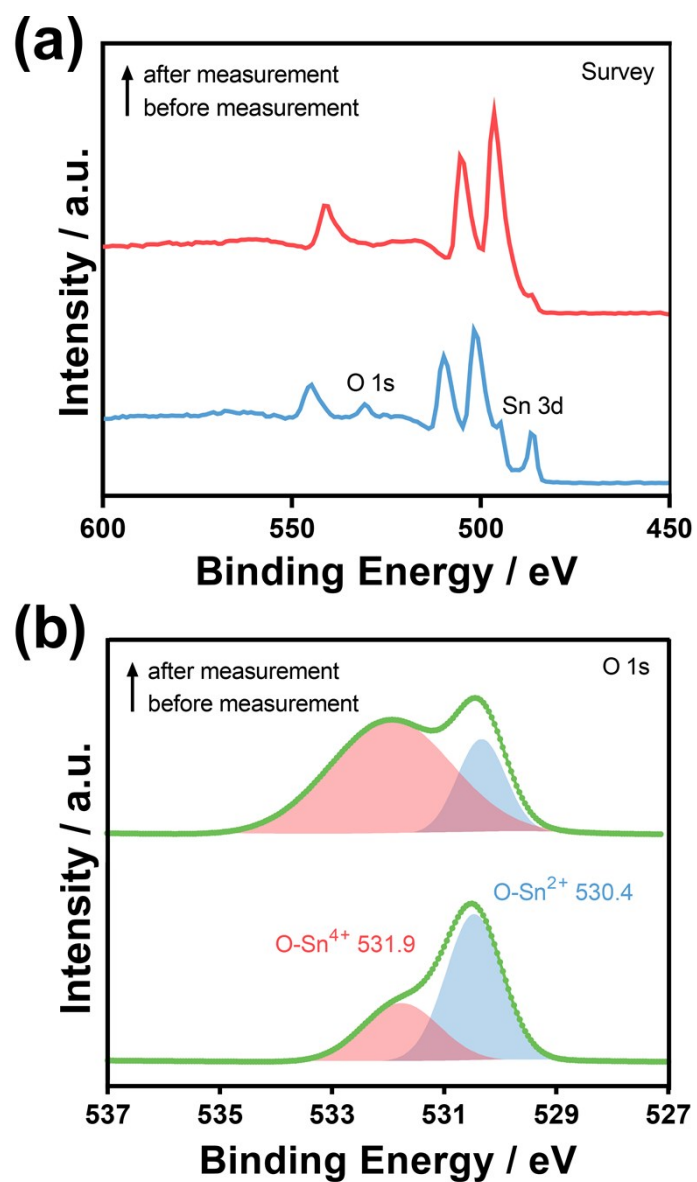


Fig. S1. Surface chemical compositions. The XPS survey spectrum (a) and high resolution XPS spectra of O 1s (b) of Sn₃O₄ before and after the *I-t* measurement.

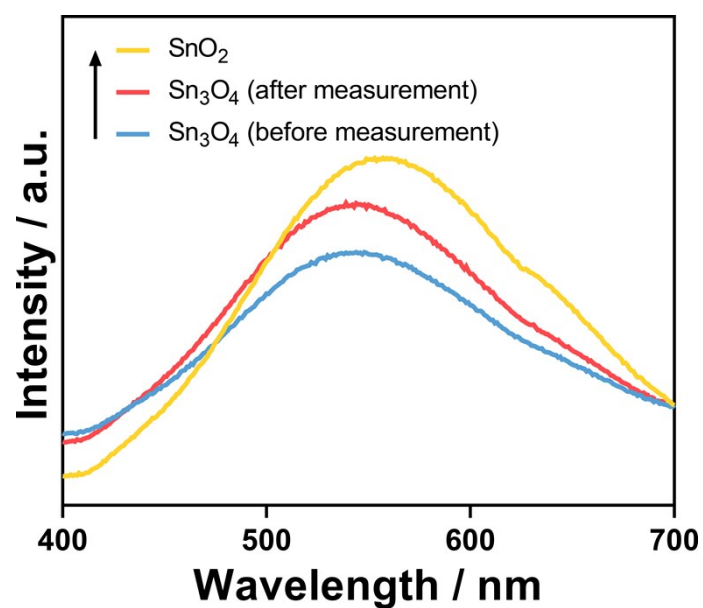


Fig. S2. Photoluminescence spectra of SnO₂ and Sn₃O₄ before and after the *I-t* measurement.

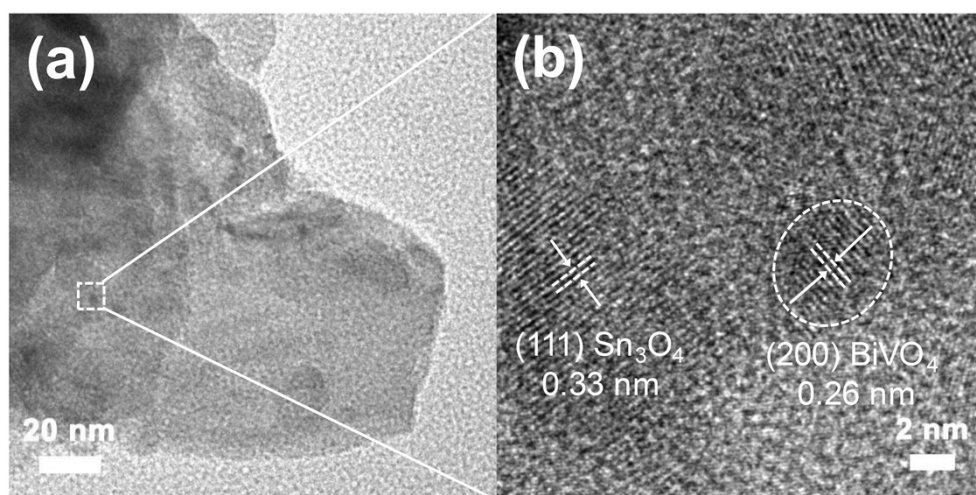


Fig. S3. Microstructures. (a) and (b) are TEM images at different magnifications of 20BQD@Sn₃O₄.

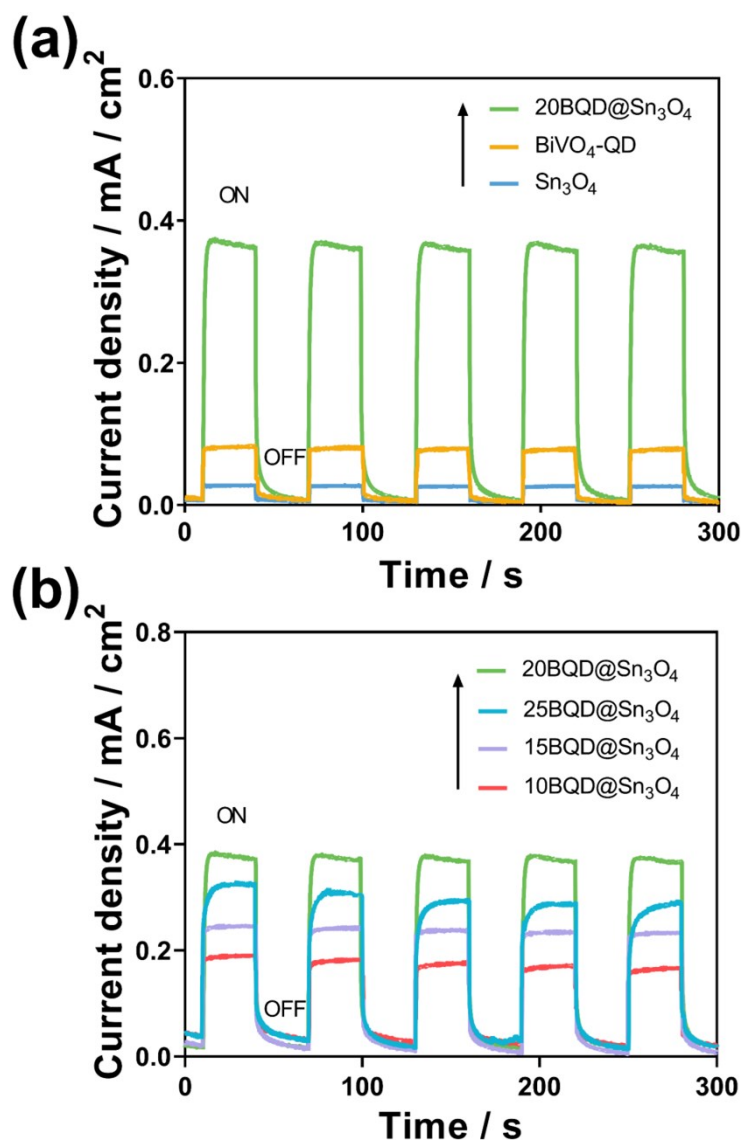


Fig. S4. $I-t$ curves under irradiation of a 500 W xenon lamp as the light source. The applied bias is 1 V vs. Ag/AgCl and the electrolyte used is 0.5 M Na₂SO₄.

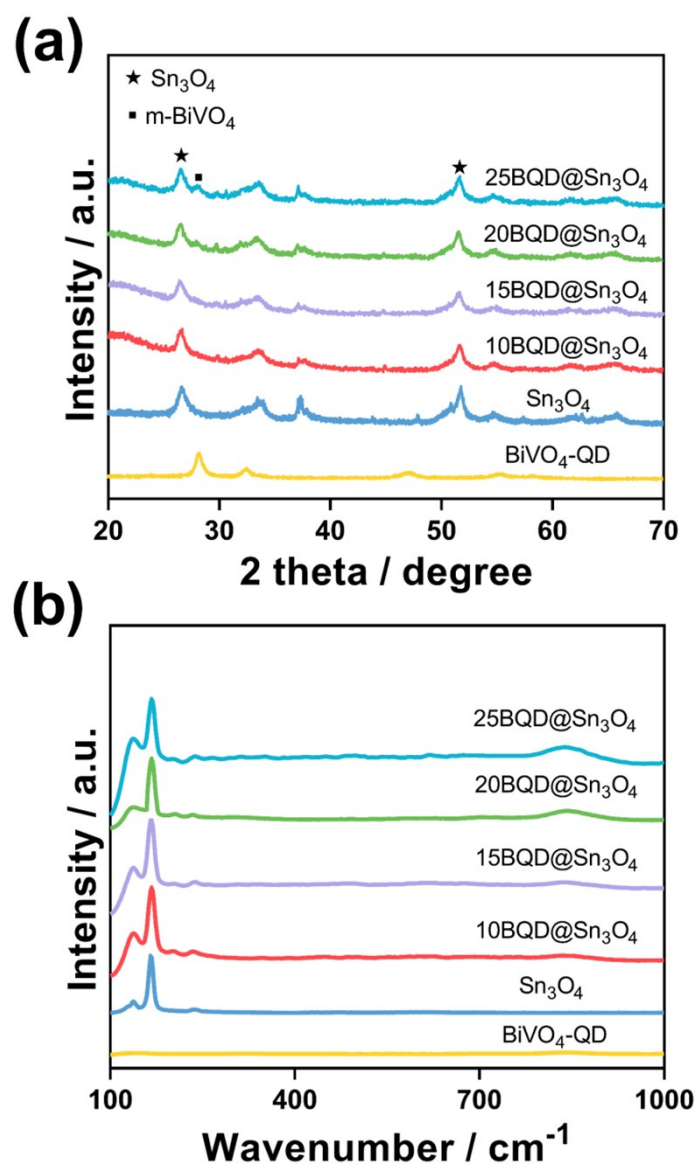


Fig. S5. XRD patterns (a) and Raman spectra (b) of samples.

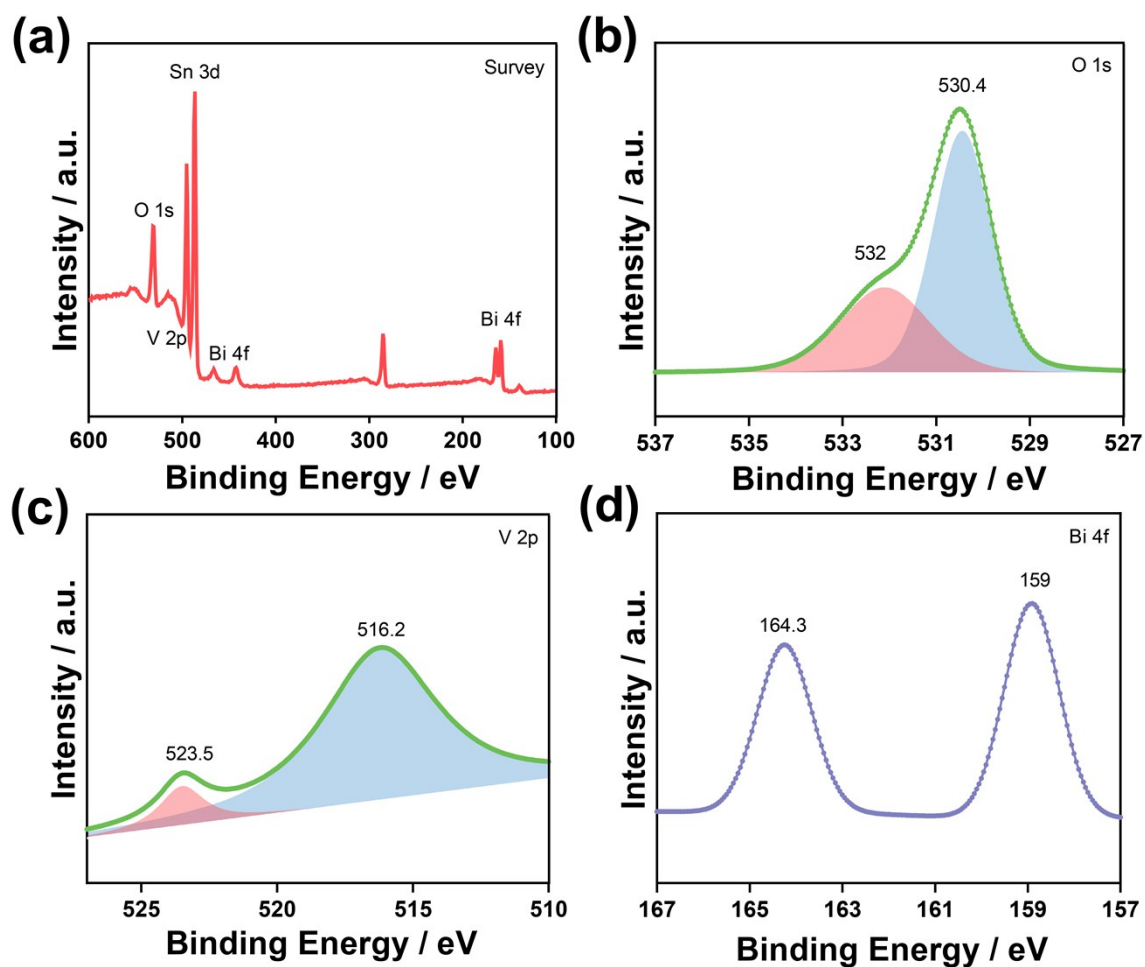


Fig. S6. Surface chemical compositions. (a) is the XPS survey spectrum; (b), (c) and (d) are the high resolution XPS spectra of O 1s, V 2p and Bi 4f, respectively. The intensities of V 2p is enlarged by 5 times for displaying properly.

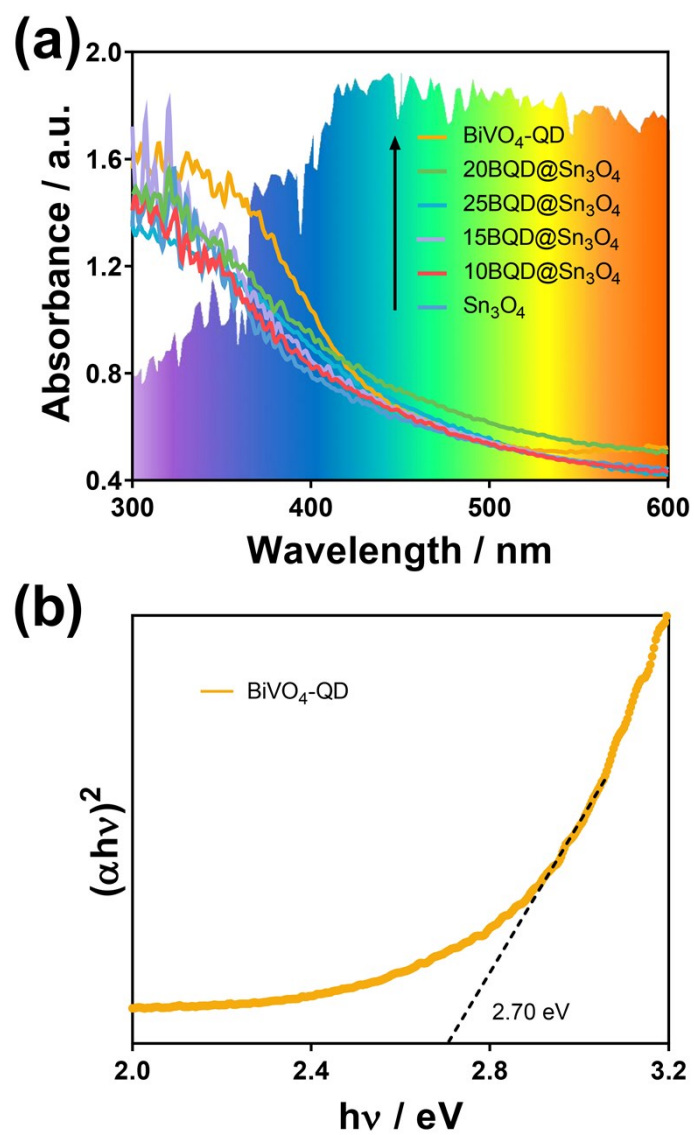


Fig. S7. Optical absorption and band-gap. (a) is the UV-vis absorption spectra and (b) is the Tauc-plot of BiVO₄-QD.

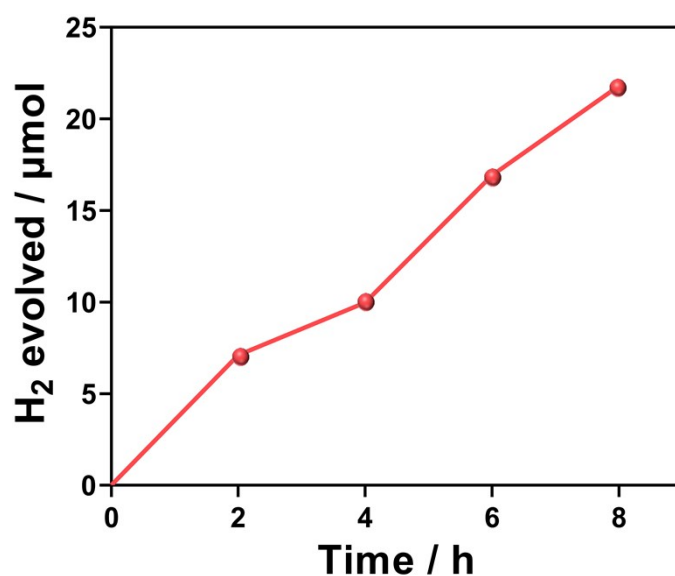


Fig. S8. Photocatalytic H₂ evolution from Sn₃O₄. 0.1 g of samples were dispersed in CH₃OH aqueous solution using a magnetic stirrer (80 mL of DI water and 20 mL of CH₃OH). A 500 W Xenon lamp was used as the light source.

Tab. S1. The incident light intensity and amount of generated H₂ in 8 h of 20BQD@Sn₃O₄ with different wavelengths.

	$\lambda_{\pm 10}$ (nm)					
	400	440	480	520	560	600
Intensity of incident light (mW/cm ²)	0.43	0.43	0.56	0.56	0.55	0.49
Amount of generated H ₂ (μmol)	2.5	2.4	2.3	1.8	0.5	0.3

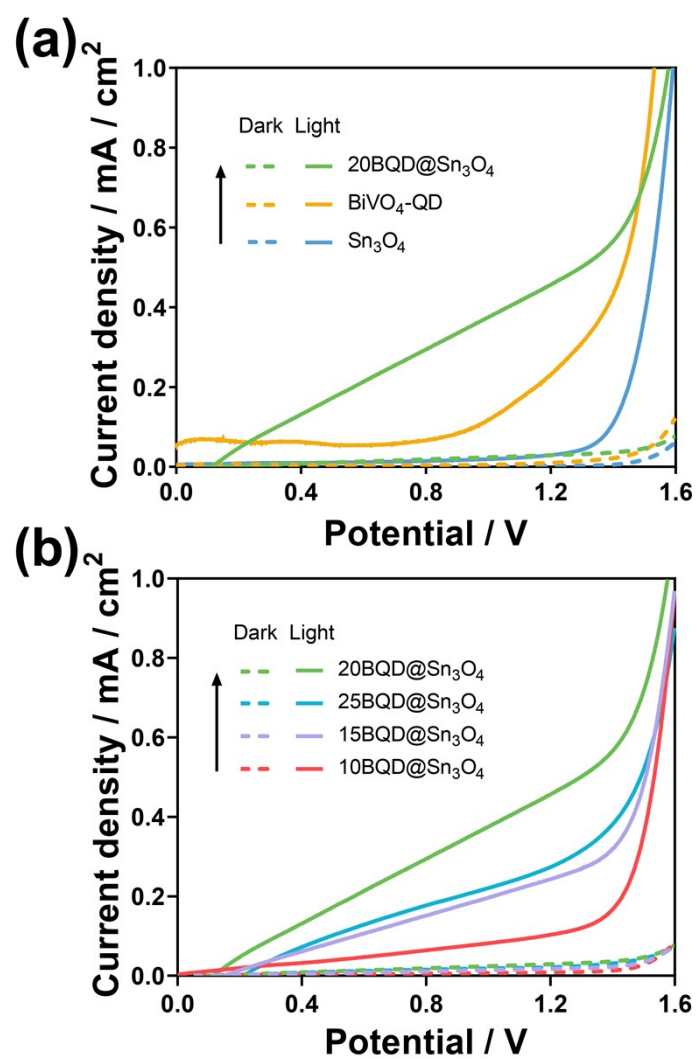


Fig. S9. I - V curves under irradiation of a 500 W xenon lamp as the light source. The electrolyte used is 0.5 M Na₂SO₄.

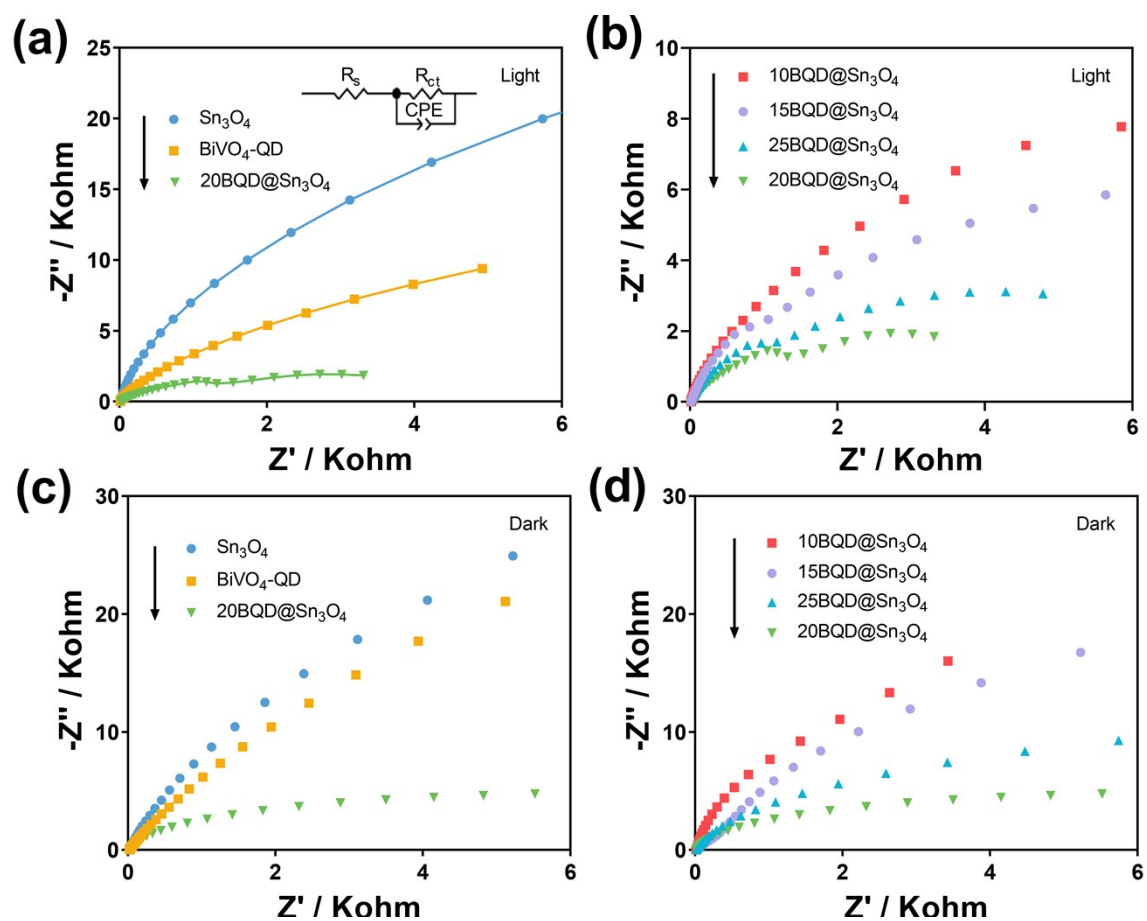


Fig. S10. Nyquist plots under the irradiation of a 500 W xenon lamp (a, b) and in dark (c, d). Inset of (a) is the fitted equivalent circuit. The electrolyte used is 0.5 M Na_2SO_4 . The applied bias, frequency and amplitude are 1 V vs. Ag/AgCl, 5 kHz and 10 mV, respectively.

Tab. S2. The values of R_{ct} and R_s of Sn_3O_4 , $\text{BiVO}_4\text{-QD}$ and $20\text{BQD@Sn}_3\text{O}_4$ samples.

Samples	Sn_3O_4	$\text{BiVO}_4\text{-QD}$	$20\text{BQD@Sn}_3\text{O}_4$
R_{ct} (Ω)	88125	27368	4629
R_s (Ω)	15.57	11.15	16.05

The R_{ct} and R_s values represent the charge transfer resistance in the semiconducting layer and series resistance in the interface of the photoanode material and the FTO substrate, respectively.⁴

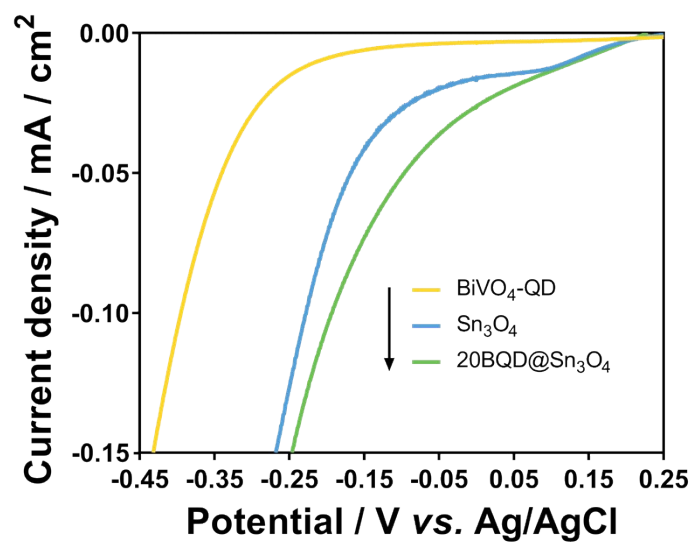


Fig. S11. PEC oxygen reduction curves of Sn_3O_4 , $\text{BiVO}_4\text{-QDs}$ and $20\text{BQD@Sn}_3\text{O}_4$.

References

1. Y. F. Sun, Y. Xie, C. Z. Wu, S. D. Zhang and S. S. Jiang, *Nano Res.*, 2010, **3**, 620-631.
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