Supporting Information

Elucidating the regulation mechanism of photoelectrochemical effect of photocathodes on battery discharge voltages: a case study of aqueous zinc-iodine batteries

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Experimental Procedures

***Photoelectrodes preparation**:* BiOI photoelectrode was prepared via a modified hydrothermal method.[1] The $Bi(NO_3)_3 \cdot 5H_2O$ (Wako Chemicals) and KI (Wako Chemicals) were used as the bismuth source and iodine source, respectively. Detailly, 4 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 30 mL ethylene glycol (EG) (99%, Wako Chemicals) (solution A). Meanwhile, 4 mmol KI was dissolved into another 30 mL EG (solution B). The solution A was added dropwise into the solution B under continuous magnetic stirring. Subsequently, the cleaned FTO glasses were put into a hydrothermal reaction autoclave angled against the vessel wall, and the solution was transferred into the 100 mL hydrothermal autoclave and was positioned in an oven at 120 °C for 12 h. Upon naturally cooling down to room temperature, orange products were obtained after cleaning with deionized water. The mass loading of BiOI is 1.67 mg cm^{-2} on the FTO side.

TiO_2 nanorods were grown on the FTO via the hydrothermal method.[2] Briefly, 38 mL deionized water was mixed with 2 mL glycerol (99%, Wako Chemicals), 0.45 mL TTIP (98+%, Acros Organics) and 893 mg Na_2EDTA (Alfa Aesar), followed with constant magnetic stirring to produce a transparent solution. Afterward, the above solution transferred into 80 mL Teflon-lined autoclave, which was hydrothermally conducted at 200 °C for 5 h. The obtained samples were sintered at 450 °C for 2 h in a muffle furnace.

Materials Characterization: The XRD patterns were acquired using Cu K_a radiation on a Rigaku diffractometer (Panalytical Co., Netherlands). Raman scattering experiments were conducted using a He-Ne laser excitation with an excitation wavelength of 532 nm (Labram HR-800). The top and cross-sectional SEM images were characterized by using Nova NanoSEM 430 (FEI Co., Netherlands.). Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (DRS) measurements were determined using an UV-vis spectrometer (JASCO-550).

Photoelectrochemical measurements of the photoelectrodes: The Mott-Schottky plots were gained at an AC frequency of 1 kHz with 25 mV s^{-1} amplitude in 0.2 M Na_2SO_4 solution under dark environment to determine the flat-band potential in a three-electrode mode using the SP-300 electrochemical station (Bio-

Logic Co., France).

The photoelectrochemical performances of the photoelectrodes were measured in a three-electrode system using BiOI or TiO_2 as the working electrode, the saturated Ag/AgCl as the reference electrode, Pt foil as counter electrode with a SP-300 electrochemical workstation. The electrolyte contained 10 mM ZnI_2 (Aladdin) and 1.6 mM I_2 (Alfa Aesar). Light irradiation was provided by a 300 W Xe lamp (PLS-SXE300D) and the photo intensity of the excitation source was calibrated to 220 mW cm^{-2} by a standard silicon cell detector. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency of 7 MHz-100 mHz at 10 mV amplitude in dark and light conditions. The current-time curve of BiOI photoelectrode was performed under illumination at 0.64 V vs. NHE. Liner sweep voltammetry (LSV) curves were conducted with a scan rate of 10 mV s^{-1}.

Photoassisted zinc-iodine batteries assembly and Electrochemical characterizations: The light-promoted rechargeable zinc-iodine battery was built by the home-made reactor with quartz windows containing a zinc foil (0.25 mm thickness, Alfa Aesar), a Nafion 117 (0.18 mm thickness, Alfa Aesar) separator and the semiconductor photoelectrode (BiOI or TiO_2). The electrolyte was the same as the photoelectrochemical performances of the photoelectrodes. The discharge performances were tested by Land CT2001A battery tester (Wuhan LAND Electronics Co., Ltd.) upon the dark and illumination.

Results and Discussion

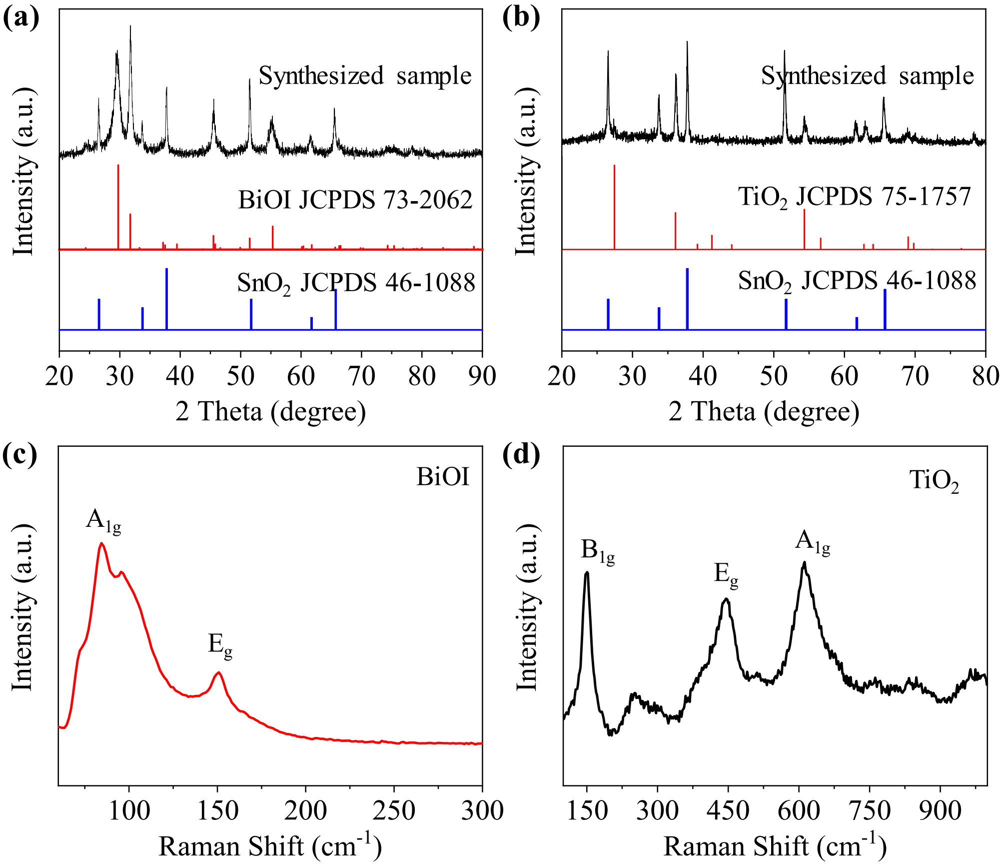

Fig. S1 XRD patterns of (a) BiOI and (b) TiO_2. Raman spectra of (c) BiOI and (d) TiO_2.

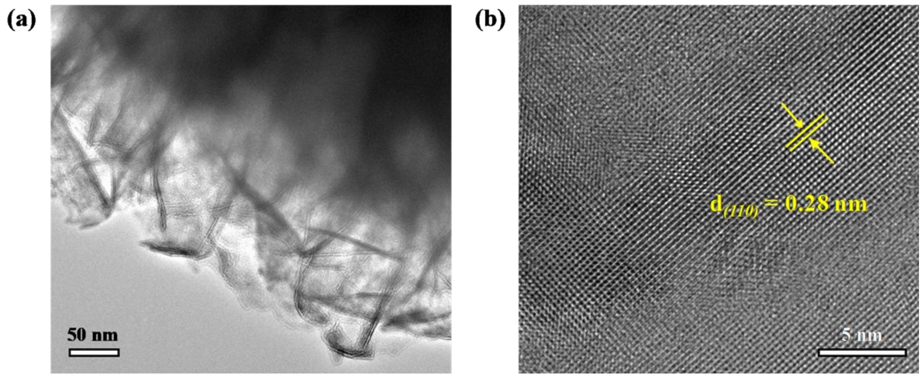

Fig. S2 (a) TEM and (b) HRTEM images of sample BiOI.

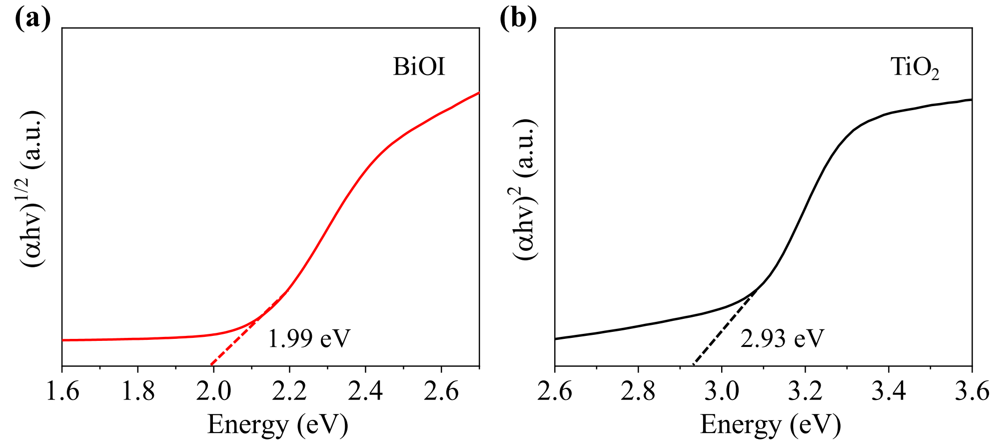

Fig. S3 Band structures of the photoelectrodes. Estimated band-gap energy of (a) BiOI and (b) TiO_2.

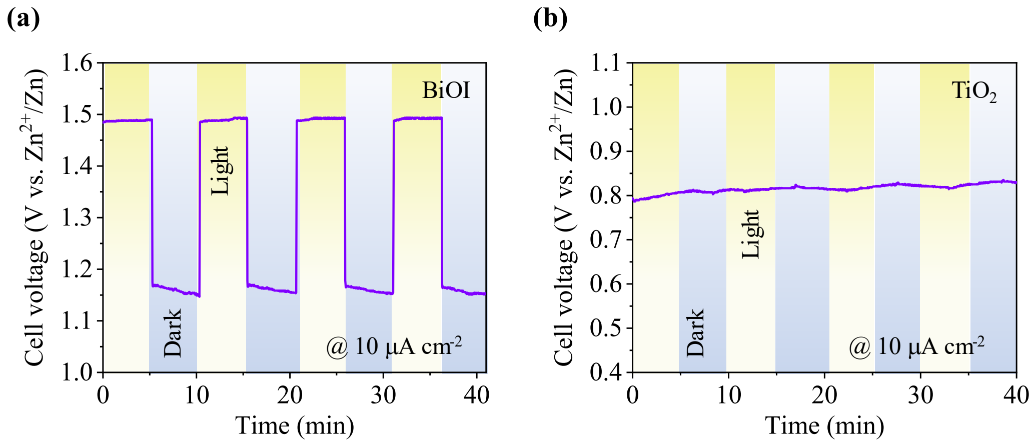

Fig. S4 Voltage response of the zinc-iodine battery based on (a) BiOI and (b) TiO_2 photoelectrodes with intermittent light on and off in the discharge process at 10 μA cm^{-2}.

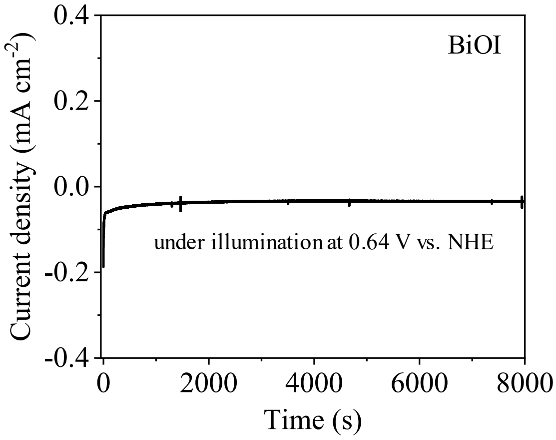

Fig. S5 Current density-time curve of the BiOI photoelectrode under illumination at 0.64 V vs. NHE.

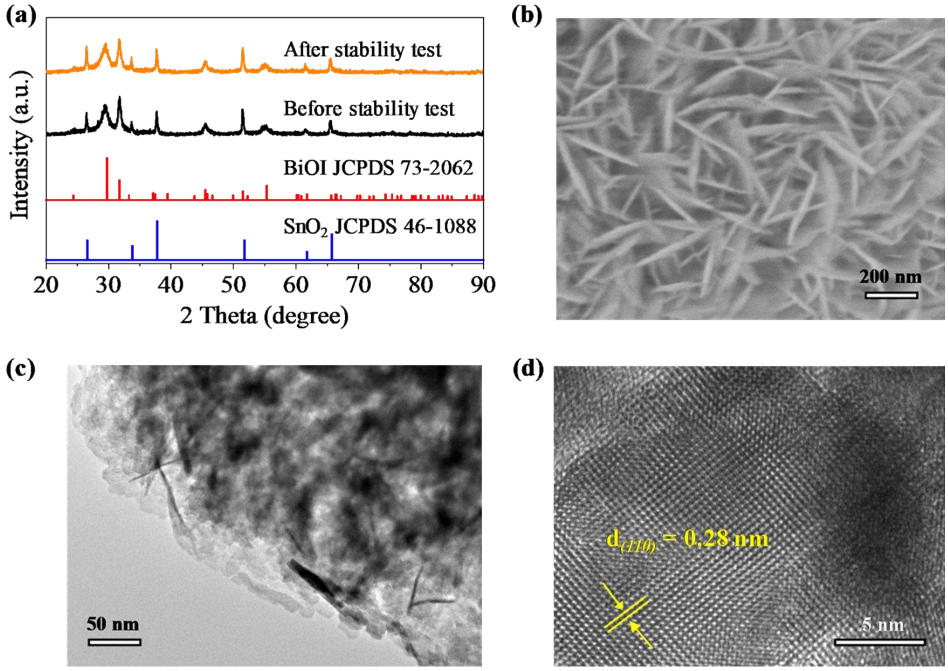

Fig. S6 (a) XRD pattern of BiOI photoelectrode before and after current density-time stability test. (b) SEM, (c) TEM and (d) HRTEM images of BiOI photoelectrode after current density-time stability test.

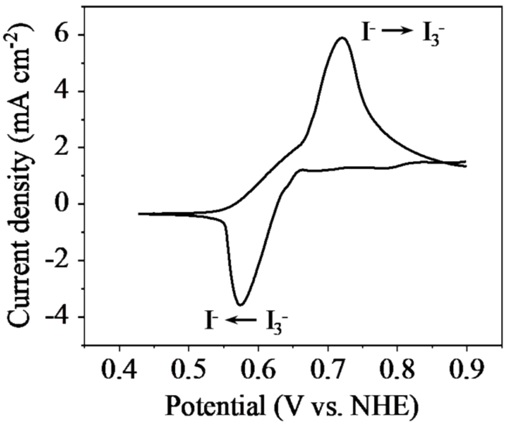

Fig. S7 CV of 10 mM ZnI_2 and 1.6 mM I_2 in 0.5 M KCl at 0.1 mV s^{-1} on a carbon paper electrode.

Table S1 EIS fitting results at 0.64 V vs. NHE (Fig. 4d) using an aqueous electrolyte containing 10 mM ZnI_2 and 1.6 mM I_2.

Equivalent Circuit		R_1(Ohm)	R_2(Ohm)	R_3(Ohm)
BiOI	dark	115.2	607.3	921
	light	88.93	308.6	579.3

References

1 X. Su, J. Yang, X. Yu, Y. Zhu and Y. Zhang, *Appl. Surf. Sci.*, 2018, **433**, 502-512.

2 Y. Man, Q. Hao, F. Chen, X. Chen, Y. Wang, T. Liu, F. Liu and N. Li, *ChemElectroChem*, 2019, **6**, 5872-5875.