Supporting Information for

Lithium Nitrate Assisted Hydrothermal Synthesis of Ultrathin Bi_2O_2Se Nanosheets and their Photoelectrochemical Performance

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Experimental section

Materials Preparation: Firstly, Se precursor was prepared by dissolving 0.25 mmol Se powder with $NaBH_4$ in deionized water under ultrasonication, and the excess $NaBH_4$ was eliminated by adding 3 M HNO_3 until pH<3. Then, 1.0 g NaOH was added into the mixture and an orange solution was obtained. The synthesis of Bi_2O_2Se nanosheets was conducted under the protection of argon. Typically, 0.5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 10 g $LiNO_3$ were mixed with 3 mL water in a three-necked flask. The flask is sealed, vacuumized and filled with argon gas flow. After that, 2 mL orange solution containing 0.25 mmol Se^{2-} and 1.0 g NaOH was injected into the flask. The mixture was heated to ~98 ℃ and kept stirring for 30 min. Finally, the solution was cooled down to room temperature and the dark-brown products were separated by centrifugation. The products were washed with water for several times and dried at 70 °C for 6 hours. For synthesis of Bi_2O_2Se nanosheets with smaller sizes, only the amounts of $LiNO_3$ were changed into 0, 3 and 6 g, respectively.

Characterization: TEM images were obtained from a Hitachi 7700. The HRTEM, dark field TEM image and corresponding EDX mapping analyses were obtained using a JEOL JEM-F200 TEM/STEM instrument. XRD patterns for the products were performed on a Philips X'pert PRO X-ray diffractometer, Cu Kα, λ = 1.54182 Å). AFM

observations were taken on Dimension ICON. SEM images were obtained with a high-resolution scanning electron microscope (FEI APREO S, Thermo Scientific), and HAADF-STEM image was obtained on a transmission electron microscope with spherical aberration correction (Titan Cubed Themis G201). XPS spectra were acquired on an ESCALAB MK II with Mg Kα as the excitation source. The specific surface area was measured with the BET (Brunauer-Emmet-Teller) method using an automatic specific surface area and porosity analyzer (ASAP 2460, USA). Raman spectrum was recorded using a Confocal Raman Microscope (Alpha300 R, Germany) equipped with a 532 nm laser. UV-Vis-NIR diffuse reflectance spectra were obtained on a UV-Vis-NIR spectrophotometer (SOLID3700, Shimadzu).

Photoelectrochemical Measurements: The photoelectrochemical performance was measured in a three-electrode system, with a platinum wire as the counter electrode, a saturated Ag/AgCl as the reference electrode, the Bi_2O_2Se nanosheets loaded on a FTO glass as the working electrode, and 1.0 M Na_2SO_4 as the electrolyte. The Bi_2O_2Se-FTO electrodes were prepared by drop-casting Bi_2O_2Se nanosheets slurry (in ethanol) onto FTO glass (1 mg/cm^2) and followed by annealed at 250 °C for 2 hours. All the electrochemical tests were recorded by a CHI760E (Chenhua, Shanghai, China) electrochemical workstation. The linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV/s, and the electrochemical impedance spectra were measured at 1.0 V in the frequency range of 10^6 to 1 Hz with an amplitude of 5 mV. The visible light illumination was simulated with light from a 300 W xenon arc lamp equipped with a 420 nm cut-off filter, and the power intensity of the incident light was

fixed at 50 mW/cm^2.

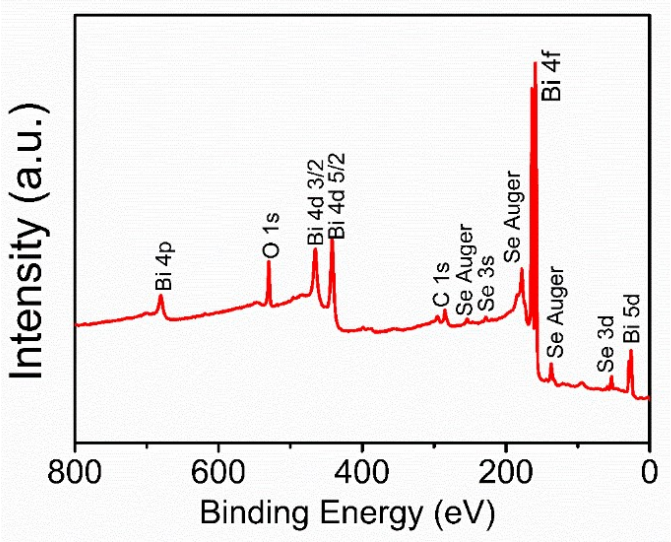

Fig. S1 XPS survey spectrum of the ultrathin Bi_2O_2Se nanosheets.

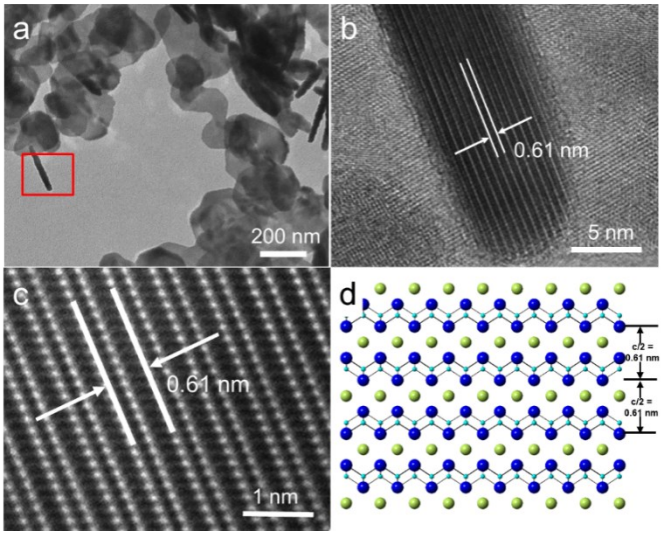

Fig. S2 (a)TEM image of the Bi_2O_2Se_2, (b) HRTEM image of the Bi_2O_2Se_2, from the marked area in a, (c) HAADF-STEM image of the Bi_2O_2Se_2 observing from the side direction, (d) side view of Bi_2O_2Se crystal structure from [100]. The atomic arrangement in c is not identical to d, due to a rotation in viewing direction.

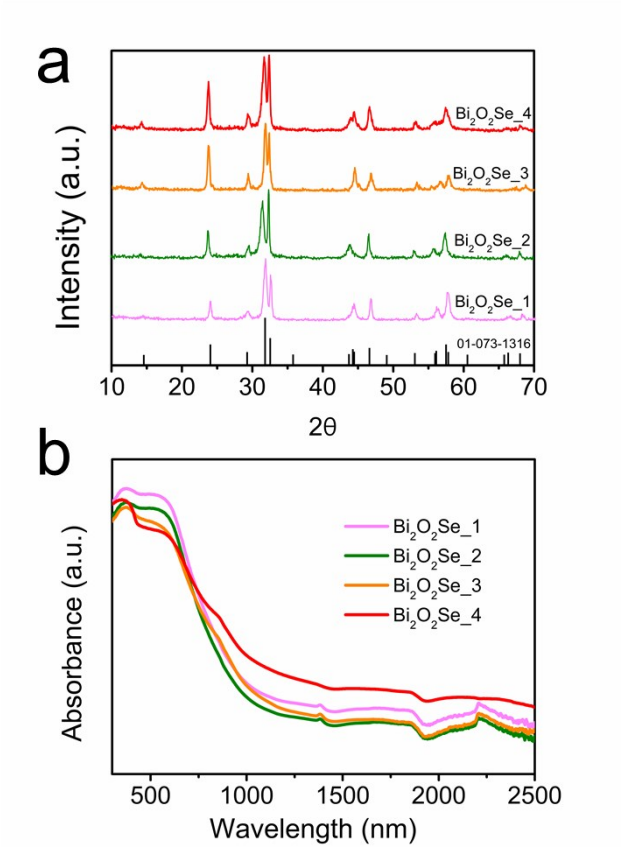

Fig. S3 (a) XRD patterns, and (b) UV-Vis-NIR diffuse reflectance spectra of the Bi_2O_2Se_1, Bi_2O_2Se_2, Bi_2O_2Se_3 and Bi_2O_2Se_4.

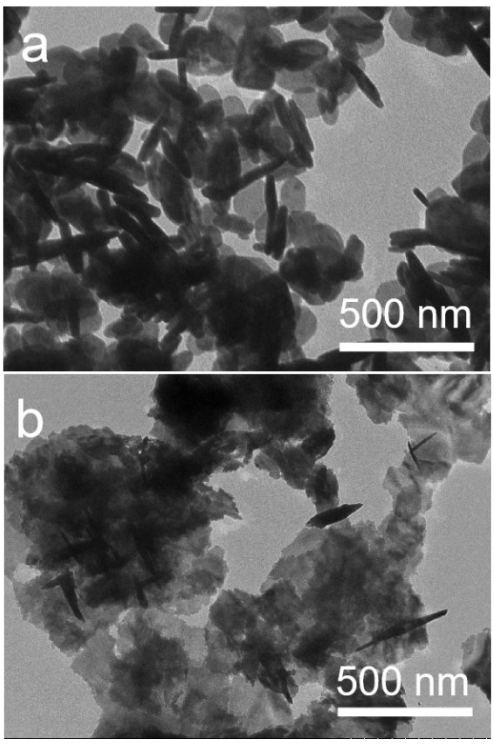

Fig. S4 TEM images of the Bi_2O_2Se nanosheets obtained from (a) 9 g $NaNO_3$, and (b) 10 g KNO_3.

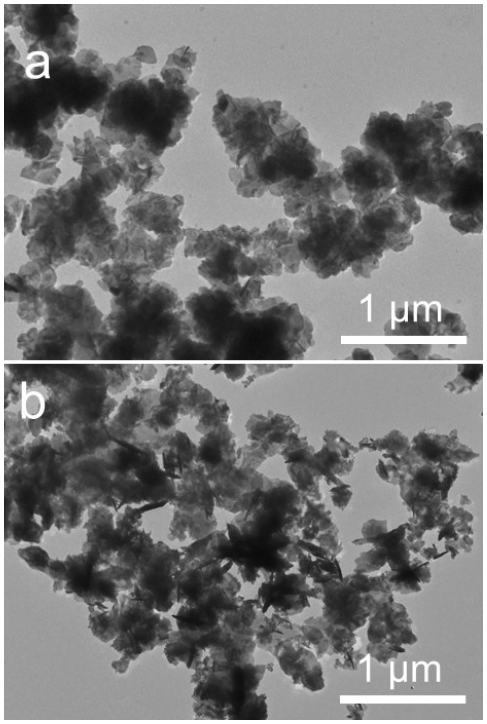

Fig. S5 TEM images of the Bi_2O_2Se nanosheets obtained from (a) 6.8 g $LiNO_3$ and (b) 10 g KNO_3.

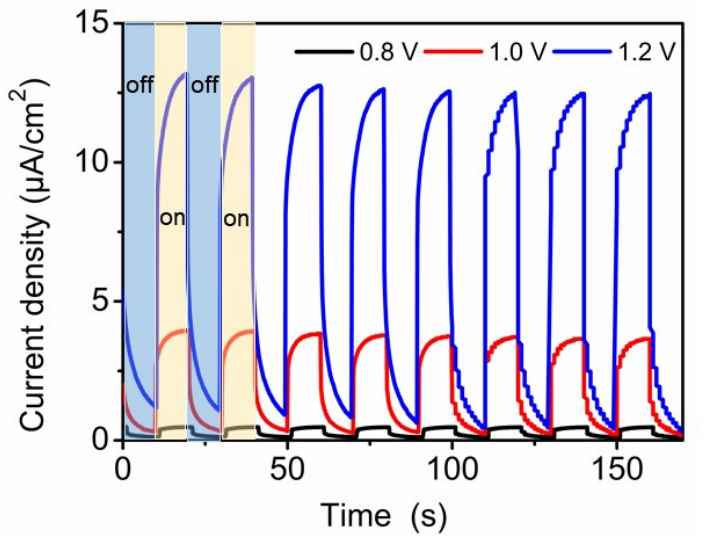

Fig. S6 Time-dependent photocurrent response curves of the Bi_2O_2Se_4 photoelectrode at different applied potentials.

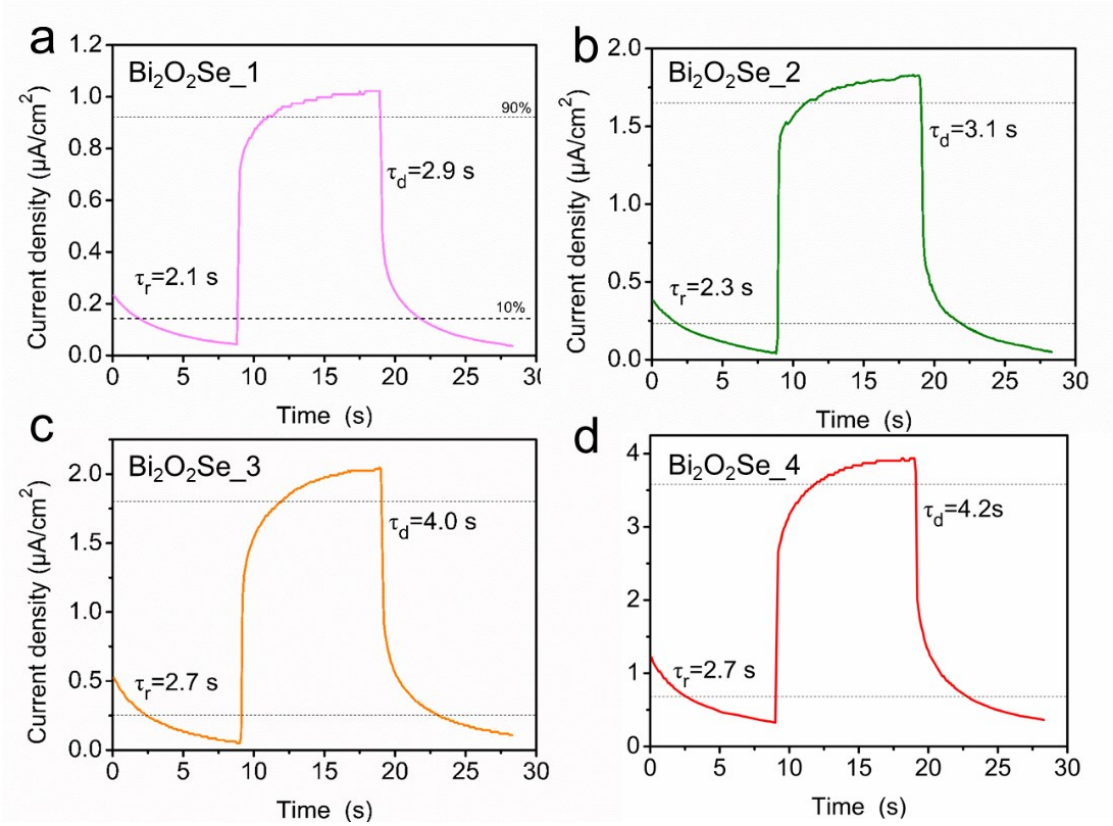

Fig. S7 A single photocurrent response curve with marked rising and decay times for the (a)Bi_2O_2Se_1, (b)Bi_2O_2Se_2, (c)Bi_2O_2Se_3 and (d)Bi_2O_2Se_4 photoelectrodes.

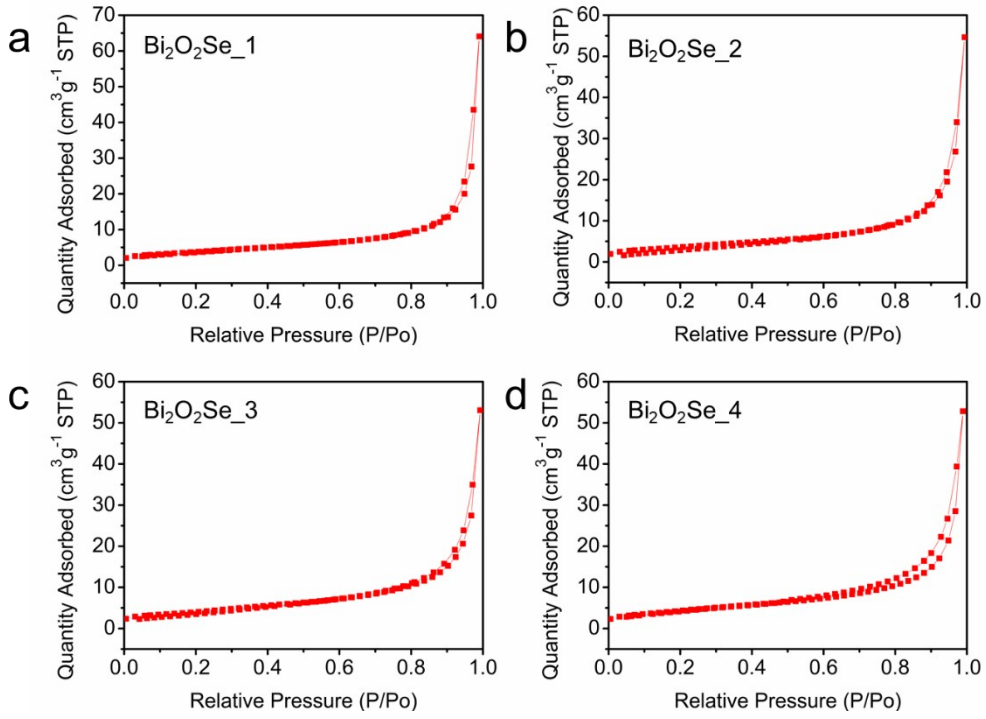

Fig. S8 N_2 adsorption/desorption isotherms of the (a) Bi_2O_2Se_1, (b) Bi_2O_2Se_2, (c) Bi_2O_2Se_3 and (d) Bi_2O_2Se_4 nanosheets. The corresponding BET surface areas are

16.7, 17.7, 18.0 and 20.8 m^2/g, respectively.

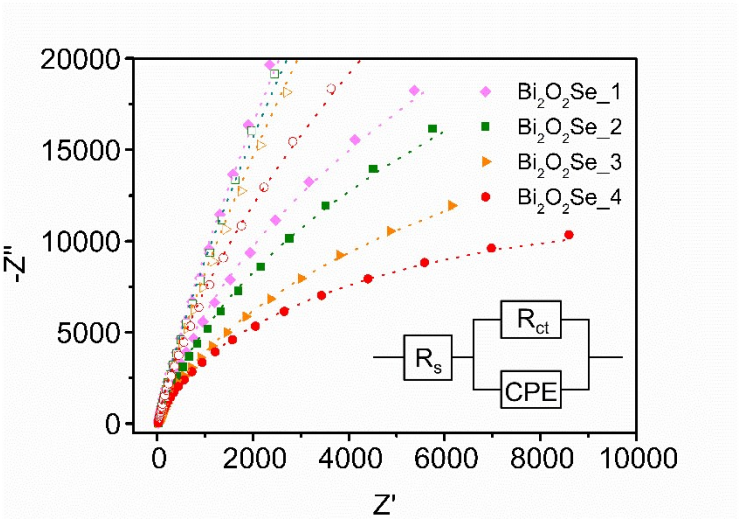

Fig. S9 The fitted plots for the EIS spectra by ZSimpWin software using the proposed equivalent circuit model.

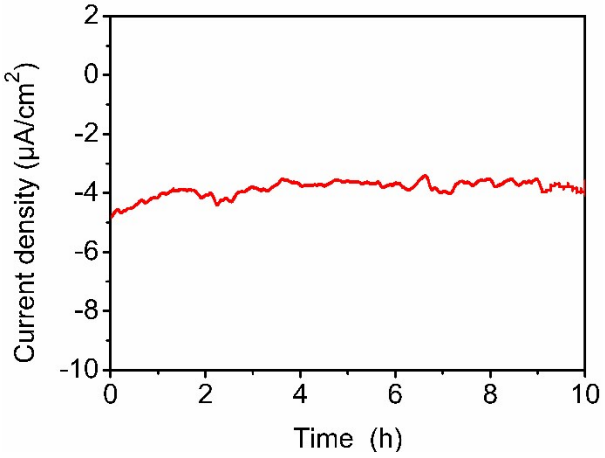

Fig. S10 The amperometric i–t curve of the Bi_2O_2Se_4 electrode with light illumination at applied voltage of 1.0 V.

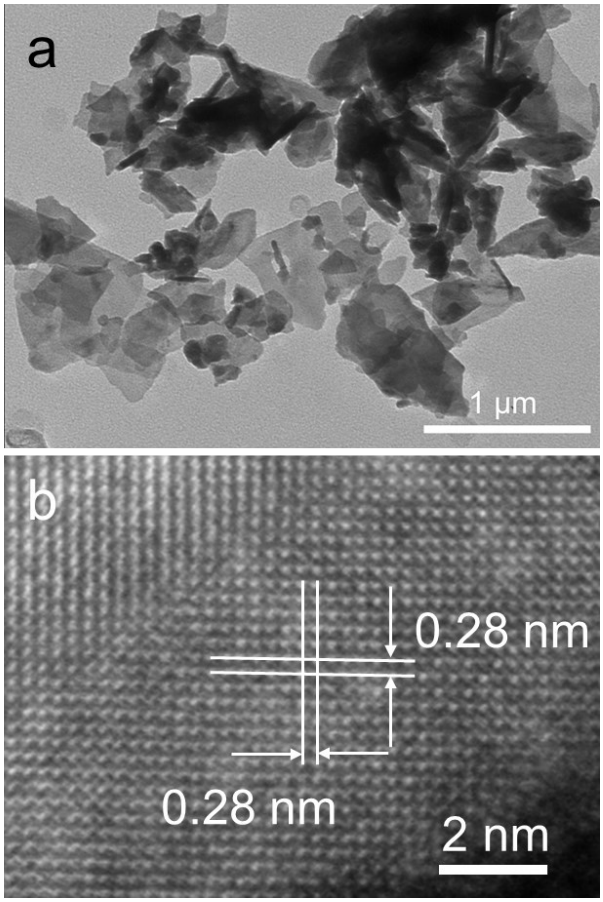

Fig. S11 (a) TEM image and (b) HRTEM image of the Bi_2O_2Se_4 nanosheets after stability test.

Tab. S1 Values of circuit elements obtained by fitting the impedance spectra in the equivalent circuit.

	catalysts	$R_s(\Omega)$	CPE(F)	$R_{ct}(\Omega)$
In the dark	Bi_2O_2Se_1	11.9	5.438×10^{-6}	1.176×10^{5}
	Bi_2O_2Se_2	11.9	5.512×10^{-6}	1.091×10^{5}
	Bi_2O_2Se_3	12.0	5.617×10^{-6}	9.178×10^{4}
	Bi_2O_2Se_4	12.1	5.694×10^{-6}	7.629×10^{4}
With light illumination	Bi_2O_2Se_1	12.1	6.112×10^{-6}	5.081×10^{4}
	Bi_2O_2Se_2	11.6	6.335×10^{-6}	3.879×10^{4}

	Bi_2O_2Se_3	11.7	6.468×10^{-6}	2.302×10^{4}
	Bi_2O_2Se_4	12.2	6.611×10^{-6}	1.794×10^{4}