Supporting Information for

Lithium Nitrate Assisted Hydrothermal Synthesis of Ultrathin Bi$_2$O$_2$Se Nanosheets and their Photoelectrochemical Performance

Yuan Sun, Shuai Ye,* Jing Zhang, Jun Song, Feifan Zhou and Junle Qu

**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$_2$O$_2$Se nanosheets was conducted under the protection of argon. Typically, 0.5 mmol Bi(NO$_3$)$_3$·5H$_2$O 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 °C 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$_2$O$_2$Se 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, $\lambda = 1.54182$ 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$_2$O$_2$Se nanosheets loaded on a FTO glass as the working electrode, and 1.0 M Na$_2$SO$_4$ as the electrolyte. The Bi$_2$O$_2$Se-FTO electrodes were prepared by drop-casting Bi$_2$O$_2$Se 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$_2$O$_2$Se nanosheets.

Fig. S2 (a) TEM image of the Bi$_2$O$_2$Se, (b) HRTEM image of the Bi$_2$O$_2$Se, from the marked area in a, (c) HAADF-STEM image of the Bi$_2$O$_2$Se observing from the side direction, (d) side view of Bi$_2$O$_2$Se 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$_2$O$_2$Se$_{1}$, Bi$_2$O$_2$Se$_{2}$, Bi$_2$O$_2$Se$_{3}$ and Bi$_2$O$_2$Se$_{4}$. 

Fig. S4 TEM images of the Bi$_2$O$_2$Se nanosheets obtained from (a) 9 g NaNO$_3$, and (b) 10 g KNO$_3$. 
Fig. S5 TEM images of the Bi$_2$O$_2$Se 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$_2$O$_2$Se$_4$ photoelectrode at different applied potentials.
Fig. S7 A single photocurrent response curve with marked rising and decay times for the (a) Bi$_2$O$_2$Se$_1$, (b) Bi$_2$O$_2$Se$_2$, (c) Bi$_2$O$_2$Se$_3$ and (d) Bi$_2$O$_2$Se$_4$ photoelectrodes.

Fig. S8 N$_2$ adsorption/desorption isotherms of the (a) Bi$_2$O$_2$Se$_1$, (b) Bi$_2$O$_2$Se$_2$, (c) Bi$_2$O$_2$Se$_3$ and (d) Bi$_2$O$_2$Se$_4$ 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$_2$O$_2$Se$_4$ electrode with light illumination at applied voltage of 1.0 V.
Fig. S11 (a) TEM image and (b) HRTEM image of the Bi$_2$O$_2$Se$_4$ nanosheets after stability test.

<table>
<thead>
<tr>
<th>catalysts</th>
<th>$R_s$($\Omega$)</th>
<th>CPE(F)</th>
<th>$R_{ct}$($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$O$_2$Se$_1$</td>
<td>11.9</td>
<td>5.438$\times$10$^{-6}$</td>
<td>1.176$\times$10$^5$</td>
</tr>
<tr>
<td>Bi$_2$O$_2$Se$_2$</td>
<td>11.9</td>
<td>5.512$\times$10$^{-6}$</td>
<td>1.091$\times$10$^5$</td>
</tr>
<tr>
<td>Bi$_2$O$_2$Se$_3$</td>
<td>12.0</td>
<td>5.617$\times$10$^{-6}$</td>
<td>9.178$\times$10$^4$</td>
</tr>
<tr>
<td>Bi$_2$O$_2$Se$_4$</td>
<td>12.1</td>
<td>5.694$\times$10$^{-6}$</td>
<td>7.629$\times$10$^4$</td>
</tr>
<tr>
<td>In the dark</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>With light</td>
<td>12.1</td>
<td>6.112$\times$10$^{-6}$</td>
<td>5.081$\times$10$^4$</td>
</tr>
<tr>
<td>illumination</td>
<td>Bi$_2$O$_2$Se$_2$</td>
<td>11.6</td>
<td>6.335$\times$10$^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Bi$_2$O$_2$Se$_3$</td>
<td>11.7</td>
<td>6.468×10$^{-6}$</td>
<td>2.302×10$^4$</td>
</tr>
<tr>
<td>Bi$_2$O$_2$Se$_4$</td>
<td>12.2</td>
<td>6.611×10$^{-6}$</td>
<td>1.794×10$^4$</td>
</tr>
</tbody>
</table>