

## Supplementary Information

### **BiOBr<sub>x</sub>I(Cl)<sub>1-x</sub> based spectral tunable photodetectors fabricated by a facile interfacial self-assembly strategy**

*Zhikun Xu,<sup>a</sup> Lei Han,<sup>a,b</sup> Baohua Lou,<sup>a,b</sup> Xiaowei Zhang,<sup>a,b</sup> and Shaojun Dong\*<sup>a,b</sup>*

#### **Experimental Details:**

**Material Preparation and Characterization:** All the chemical reagents were of analytical grade and used as received without further purification. In a typical synthesis, 1 mmol Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were dissolved in 15 mL glacial acetic acid. Then the solution was added into a 12 mL aqueous solution containing 2 mmol CH<sub>3</sub>COONa and 1 mmol potassium halides mixture (composed of two kinds of potassium halides with different molar ratio, BiOI, BiOBr<sub>0.25</sub>I<sub>0.75</sub>, BiOBr<sub>0.5</sub>I<sub>0.5</sub>, BiOBr<sub>0.75</sub>I<sub>0.25</sub>, BiOBr<sub>0.95</sub>I<sub>0.05</sub>, BiOBr<sub>0.5</sub>Cl<sub>0.5</sub> and BiOCl). The mixture was stirred for 24 h at 70°C.

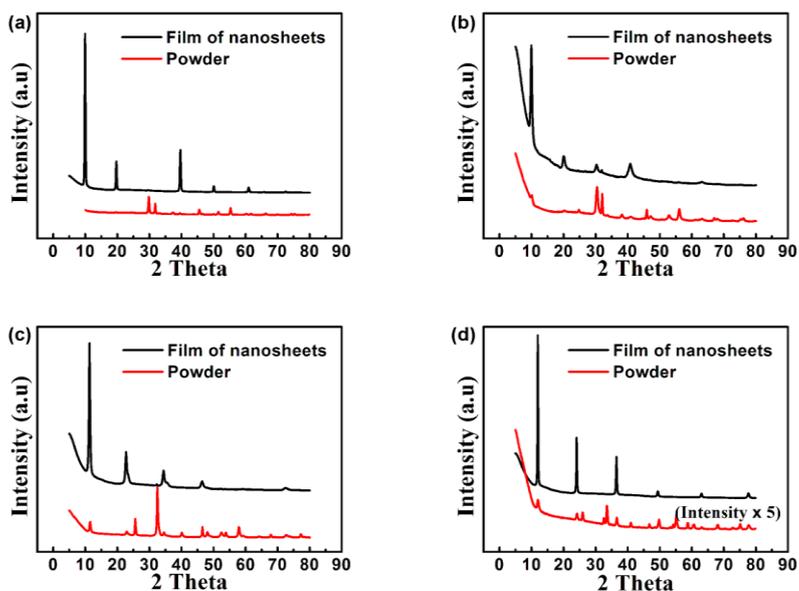
Then the as-prepared BiOBr<sub>x</sub>I(Cl)<sub>1-x</sub> NSs were self-assembled at water-air interface via the following procedures: As the synthesis of BiOBr<sub>x</sub>I(Cl)<sub>1-x</sub> NSs was completed, all the precipitates of BiOBr<sub>x</sub>I(Cl)<sub>1-x</sub> NSs were on the bottom of beaker after keeping stationary for a short period and most of the solution at the top of the beaker was carefully removed by a syringe. Afterwards certain amount of deionized water was injected into the beaker, and then a smooth and condensed film was formed very rapidly at the water-air interface.

Scanning electron microscope (SEM) images and energy-dispersive X-ray spectra (EDS) were taken with a XL30 field-emission scanning electron microscope at an

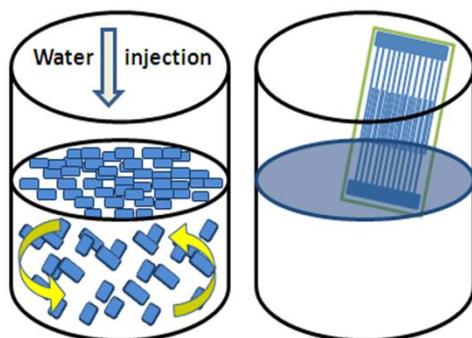
accelerating voltage of 15 kV. X-ray diffraction (XRD) patterns were collected by a Bruker D8 ADVANCE (Germany) with Cu-K $\alpha$  radiation ( $\lambda = 0.154056$  nm). TEM and HRTEM images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. Absorption spectra of the BiOBr $_x$ I(Cl) $_{1-x}$  samples were obtained with a Hitachi U-4100 spectrophotometer.

**Device fabrication and characterization:** BiOBr $_x$ I(Cl) $_{1-x}$  film photodetectors were constructed using ITO coated glass substrates as the interdigital electrodes which were fabricated through standard photolithography and etching procedure. First, the ITO substrate with a sheet resistance of 25  $\Omega$ /sq was cleaned in acetone, ethanol and deionized water for 5 min, respectively. Then, it was dried by nitrogen flow and the RZJ-390 photoresist was spin-coated on the ITO substrate. After the exposal and removing steps, the uncovered ITO film was etched by hydrochloric acid to form the ITO interdigital electrodes.

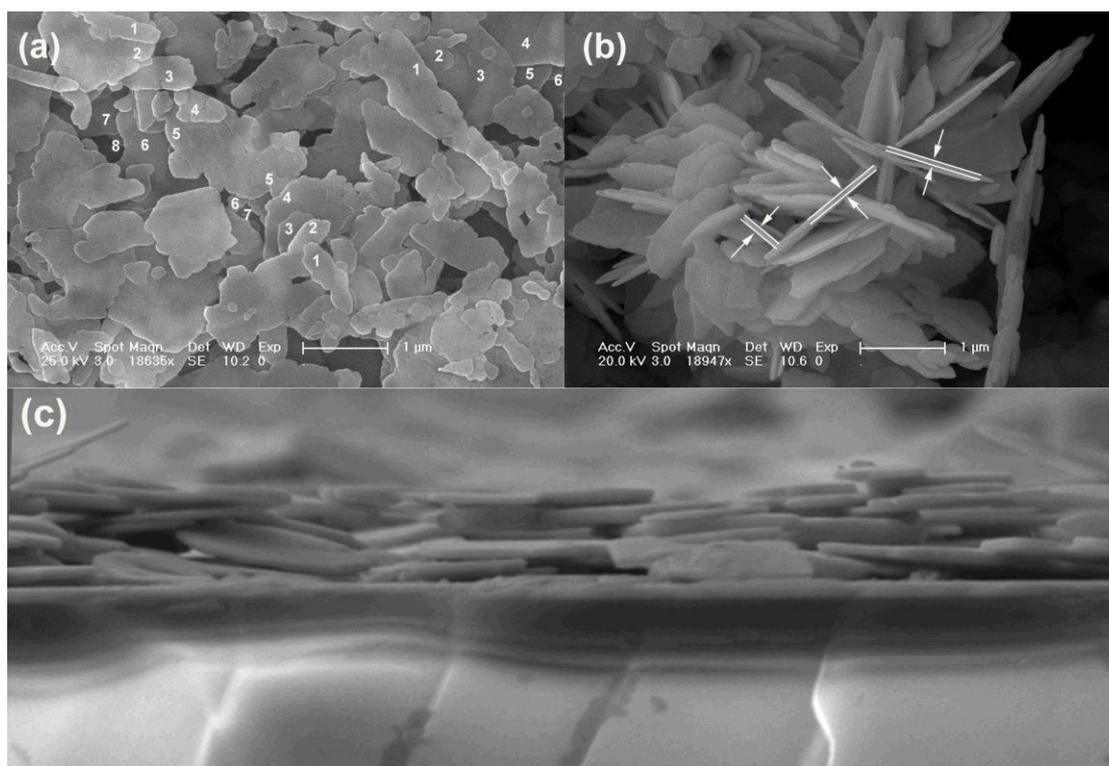
The substrates with ITO interdigital electrodes was immersed into the water and withdrawn at a certain angle using a dip coater at a constant speed. Then the BiOBr $_x$ I(Cl) $_{1-x}$  films at the water-air interface were transferred onto the surface of the ITO interdigital electrodes and the as-prepared devices were kept in air until all water was evaporated. The spectral responsivity of the BiOBr $_x$ I(Cl) $_{1-x}$  film photodetectors were measured using a standard lock-in amplifier technique at room temperature.



**Figure S1.** XRD patterns of the as-prepared  $\text{BiOBr}_x\text{I}(\text{Cl})_{1-x}$  films and powders. (a) BiOI, (b)  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ , (c)  $\text{BiOBr}_{0.5}\text{Cl}_{0.5}$  and (d) BiOCl.

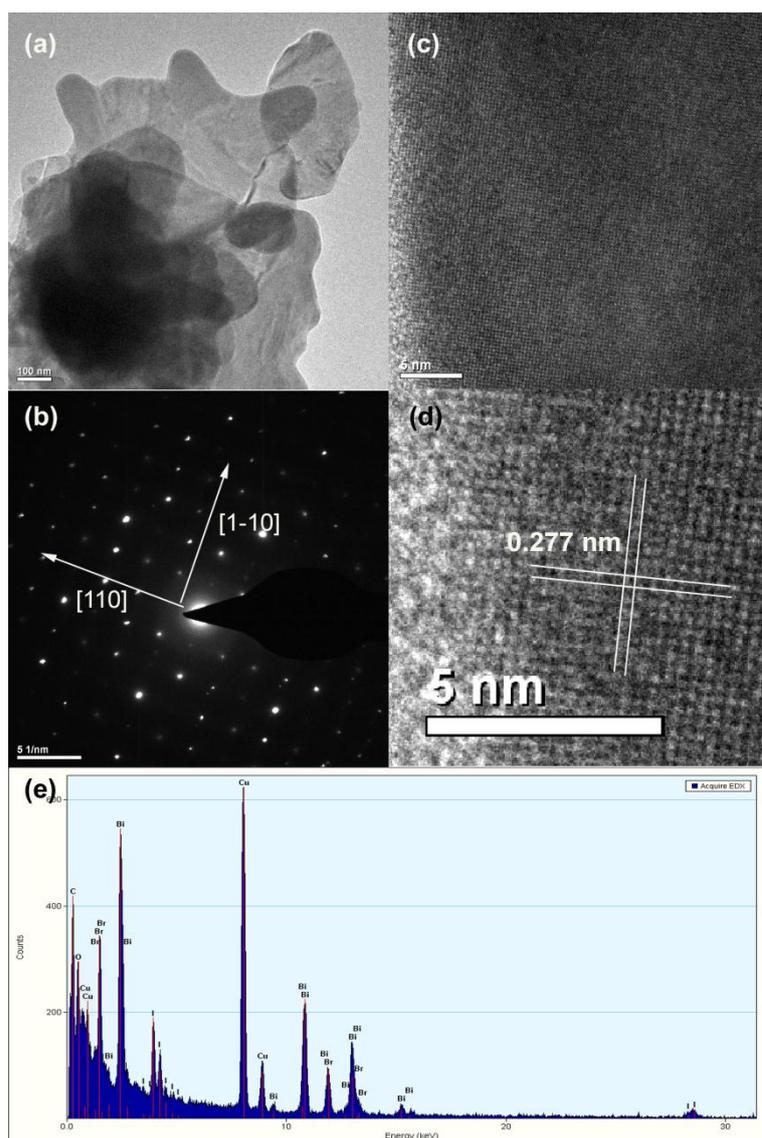


**Figure S2.** Schematic of a proposed self-assembly process of the  $\text{BiOBr}_x\text{I}(\text{Cl})_{1-x}$  films at water-air interface.

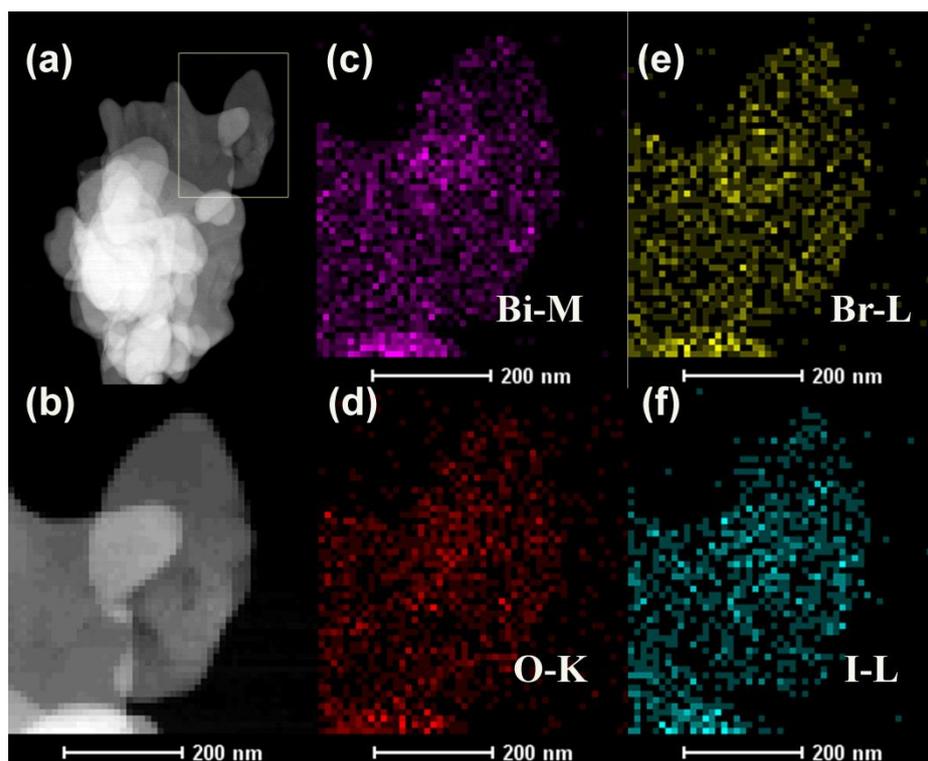


**Figure S3.** (a) SEM image of self-assembled BiOCl nanosheets film; (b) SEM image of the powder of disordered BiOCl nanosheets; (c) cross-sectional image of self-assembled BiOCl nanosheets film.

We select the BiOCl nanosheets as the typical sample. It can be observed from the figure that the thickness of a single nanosheet is between 37 and 65 nm, and the film is consisted of about 8-10 layers of nanosheets and therefore the thickness of the film is about 300 - 650 nm.



**Figure S4.** (a) TEM image of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ ; (b) SAED pattern of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ ; (c, d) HRTEM images of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ ; (e) Energy-dispersive X-ray image of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ , the ratio of Br and I is about 0.56 : 0.44.



**Figure S5.** HAADF-STEM (a, b) and elemental mapping images (c–f) of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ .

**Table S1.** The EDS analysis of the  $\text{BiOBr}_x\text{I}(\text{Cl})_{1-x}$  samples.

	$\text{BiOBr}_{0.25}\text{I}_{0.75}$	$\text{BiOBr}_{0.5}\text{I}_{0.5}$	$\text{BiOBr}_{0.75}\text{I}_{0.25}$	$\text{BiOBr}_{0.95}\text{I}_{0.05}$	$\text{BiOBr}_{0.5}\text{Cl}_{0.5}$
<b>Element</b>	<b>At %</b>	<b>At %</b>	<b>At %</b>	<b>At %</b>	<b>At %</b>
<b>Br</b>	<b>12.43</b>	<b>26.53</b>	<b>38.8</b>	<b>48.65</b>	<b>24.04</b>
<b>Bi</b>	<b>51.02</b>	<b>50.65</b>	<b>50.19</b>	<b>50.25</b>	<b>50.27</b>
<b>I</b>	<b>36.55</b>	<b>22.82</b>	<b>11.01</b>	<b>1.1</b>	
<b>Cl</b>					<b>25.68</b>
<b>Total</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>

**Table S2.** The maximum photocurrents for corresponding photodetectors.

	<b>BiOI</b>	<b><math>\text{BiOBr}_{0.25}\text{I}_{0.75}</math></b>	<b><math>\text{BiOBr}_{0.5}\text{I}_{0.5}</math></b>	<b><math>\text{BiOBr}_{0.75}\text{I}_{0.25}</math></b>	<b><math>\text{BiOBr}_{0.95}\text{I}_{0.05}</math></b>	<b><math>\text{BiOBr}_{0.5}\text{Cl}_{0.5}</math></b>	<b>BiOCl</b>
<b>Photocurrent</b>	<b>23 nA</b>	<b>14 nA</b>	<b>17 nA</b>	<b>11 nA</b>	<b>30 nA</b>	<b>21 nA</b>	<b>16 nA</b>