Electronic Supplementary Information (ESI)

Electrical conductivity in p-type BiOCl nanosheets

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Experimental

The BiOCI nanosheets were synthesized by a chemical hydrolysis method. All the reagents were purchased from Sigma-Aldrich® (ACS quality), and were used as received without further purification. In a typical synthesis, Bi(NO₃)₃·5H₂O was added slowly into an deionized water (DI water) containing HCl, with the Bi/Cl molar ratio of 1:10. The mixture was stirred for 60 min at room temperature and in air. Then, additional DI water was added under vigorous stirring till the solution color turned white. This white solution was rinsed with distilled water and isolated by centrifugation at 8000 rpm, 20 min. The surface morphology were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL-7001LVF) and field-emission transmission electron microscopy (FE-TEM, JEOL-2100F). X-ray diffraction (XRD) was performed on a Rigaku Geigerflex D-MAX/A diffractometer. Raman spectra of the samples were obtained using a Renishaw® In Via Raman Microscope with a spot size < 1 μ m². The objective of the microscope was 50× with a numerical aperture (N.A.) of 0.75. The wavelength of the laser was 514 nm. A UV-Vis spectrophotometer (Varian, Cary 1000) was used to measure the optical properties.

The electrochemical analysis of BiOCl was performed using a standard three electrode cell in combination with the Biologic® potentiostat (SP-200). A glassy carbon disk was used as the working electrode with a diameter of 3 mm, a Pt foil auxiliary electrode as the counter electrode and a Ag/0.01 M AgNO₃ + 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) acetonitrile reference electrode (Basi Inc.) completed the three electrode set-up. The conduction band (CB) energy was calculated by performing cyclic voltammetry (CV) measurements. The reduction potential (E_{red}) values were calculated assuming the energy level of ferrocene/ferrocenium (Fc/Fc⁺) to be -4.8 eV below the vacuum level. The formal potential of Fc/Fc⁺ was measured to be 0.075 V against an Ag/Ag⁺ reference electrode. Therefore, E_{CB} (E_{LUMO}) = -(E_{red} + 4.725) eV, where the onset potential values are relative to the Ag/Ag⁺ reference electrode. The valence band (VB) energy, E_{VB} (E_{HOMO}) was calculated with band-gap information from UV-Vis spectra, where E_{VB} (E_{HOMO}) = E_{CB}-E_g(indirect).

Photolithography was used to pattern a two electrode structure consisting of thermally evaporated metallic Al on a SiO₂ substrate. The gap distance between the two electrodes was 20 μ m. A drop of 20 mg BiOCl nanosheets dispersed in 1 mL isopropanol solution was placed on the Al patterned electrode and the solvent was evaporated to form a uniform film covering the electrode. All electronic transport property measurements were carried out in a commercial probe station (Janis ST500-1-2CX) with Cu-Be probe tips, 50 μ m in tip diameter. Temperature dependent current-voltage (I-V) tests were done with temperature varying from 300 K to 425 K, with a step of 5 K. The average pressure in the chamber was maintained 1000 mbar or below 3 mbar. IV measurements were made using the Keithley 2400 Source Measure Unit. The

applied voltage was increased from 0 to 30 V, at a rate of 0.05 V per step. Steady state oxygen sensing measurement was performed at a constant bias of 30 V.

Fig. SI1. Schematic diagram of the BiOCl electrode with SEM image of the surface.



Fig. SI2 Resistance change ($\Delta R/R_0$) of the BiOCl nanosheet electrode upon its exposure to oxygen under 425 K, 30 V (left) and, the oxygen partial pressure dependent response (right).