

Essential Supporting Information

Bismuth-based mixed-anion compounds for anode materials in rechargeable batteries

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Experimental section

Materials and methods

We used bismuth triiodide as molecular precursor for bismuth and iodine, while thiourea was used as sulfur source. Excess of sulfur was used for Bi₁₃S₁₈I₂ while for BiSI, equimolar concentration of Bi and S were used.

For the synthesis of Bi₁₃S₁₈I₂, 304.48 mg (4 mmol) of thiourea ((NH₂CSNH₂, 99%, Sigma Aldrich)) was mixed well with 589.6 mg (10 mmol) of bismuth triiodide (BiI₃, 99.999% metal basis, Alfa Aesar) in 60 ml ethanol in an 82 ml autoclave at 60 °C for 7 hours under continuous stirring and then, this autoclave was heated at 120 °C for 24 hours in a thermal oven (Thermoscientific, Heratherm). After the reaction, black color solution was separated by centrifuge at 2000 rpm in Eppendorf centrifuge 5702R and then washed multiple times with ethanol and isopropyl alcohol (IPA) repeatedly. The separated sample was dried at 60 °C for 1 hour and used for further characterization and application. For the synthesis of BiSI, 76.12 mg (1

mmol) of thiourea ((NH₂CSNH₂, 99%, Sigma Aldrich)) was mixed well with 589.6 mg (10 mmol) of bismuth triiodide (BiI₃, 99.999% metal basis, Alfa Aesar) reacted under similar conditions as mentioned above. The electrochemical performances of the materials were evaluated with 2032-type half-cells lithium battery system. To prepare the electrode, the synthesized materials were dispersed in dimethylformamide (DMF), and then drop cast onto 13 mm diameter carbon clothes, followed by drying at 60 °C in vacuum. The use of carbon cloth instead of the conventional copper current collector was aimed to provide a better electronic conductivity because we didn't mix the materials with other carbon. Lithium metal was used as the counter electrode, the electrolyte was the commercial 1.0 M LiPF₆ ethylene carbonate-dimethyl carbonate solution, and the separator was glass fiber filter paper. The open-circuit voltage (OCV), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) analysis were carried out using VMP3 potentiostat (Bio-Logic). CV measurement was performed at a potential sweep of 0.01- 3.0 V with a constant scan rate of 0.2 mV s⁻¹. EIS measurement was performed with a frequency range between 100.0 KHz and 10.0 mHz. Cycle performance of the cells were evaluated using a multichannel battery cycler (Neware) at a potential window of 0.01 - 3.0 V and a current density of 100 mA g⁻¹. The specific capacity of the cells was calculated based on the mass of active materials of the anode (1 mg cm⁻²). The cells were assembled in the argon-filled glovebox. XRD analysis of the electrodes was performed after the first discharge and charge cycle, the samples were prepared in the glovebox.

Characterization

The morphologies of the as-prepared membrane was examined by field emission scanning electron microscope (FEI Quanta 200). Elemental distribution and quantitative analysis was carried out using Energy dispersive X-ray spectroscopy (EDS) combined with SEM. Phase purity and identification of the synthesized compounds were carried out using powder X-ray diffraction (Bruker D8 Advance) with Cu K_α radiation ($\lambda = 1.5406$ nm), step size 0.02° 2 θ , and scan speed 1° min⁻¹. Absorbance of the synthesized powder compounds were recorded on Perkin Elmer Lambda 950 instrument in reflectance mode. Thermogravimetric analysis (TGA) was carried out using thermal analyzer Discovery TGA under N₂ atmosphere with a heating rate of 10 °C min⁻¹. All the crystallographic projections were regenerated using Diamond 4.0. Rietveld refinement was carried out using Topas-5 academic program, while Le Bail fitting was carried out using GSAS-II program.

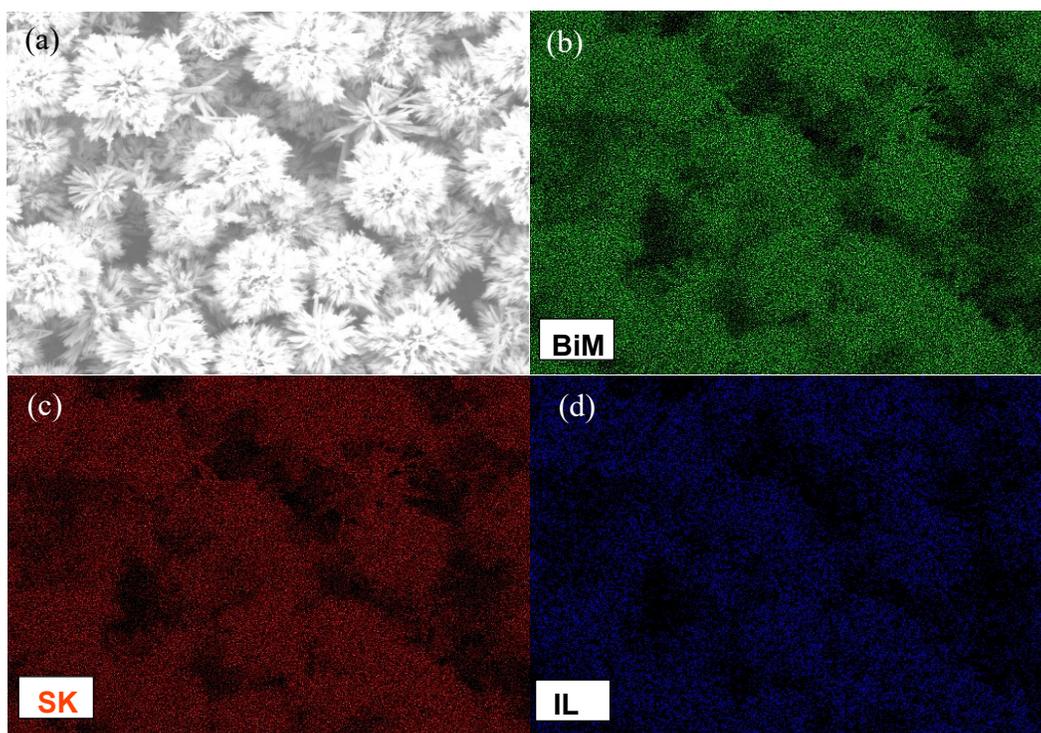


Fig. S1. (a) SEM image of the synthesized $\text{Bi}_{13}\text{S}_{18}\text{I}_2$ and corresponding elemental mapping for (b) Bi-M line (c) S-K line and (d) I-L line

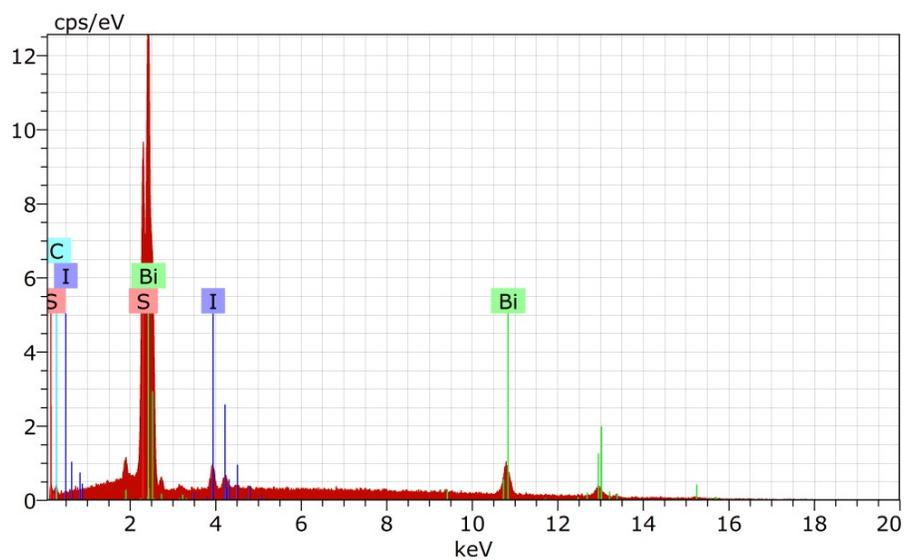


Fig. S2. EDS spectrum for synthesized $\text{Bi}_{13}\text{S}_{18}\text{I}_2$

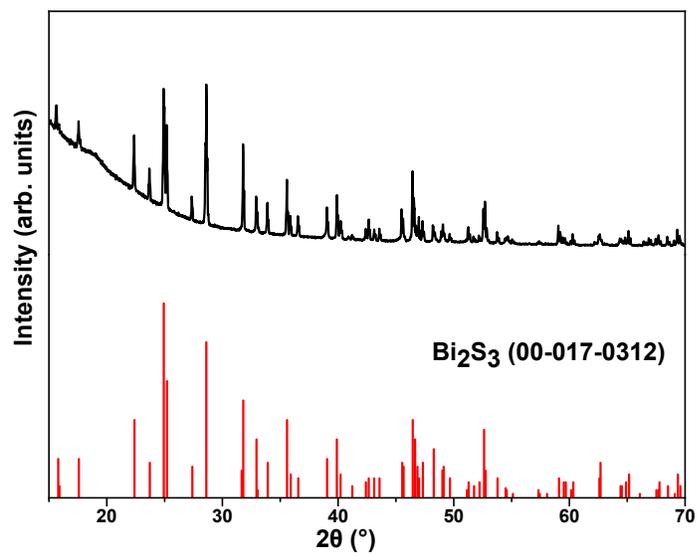


Fig. S3. Powder X-ray diffraction pattern of Bi₂S₃ obtained after the thermal dissociation of Bi₁₃S₁₈I₂ at 600 °C.

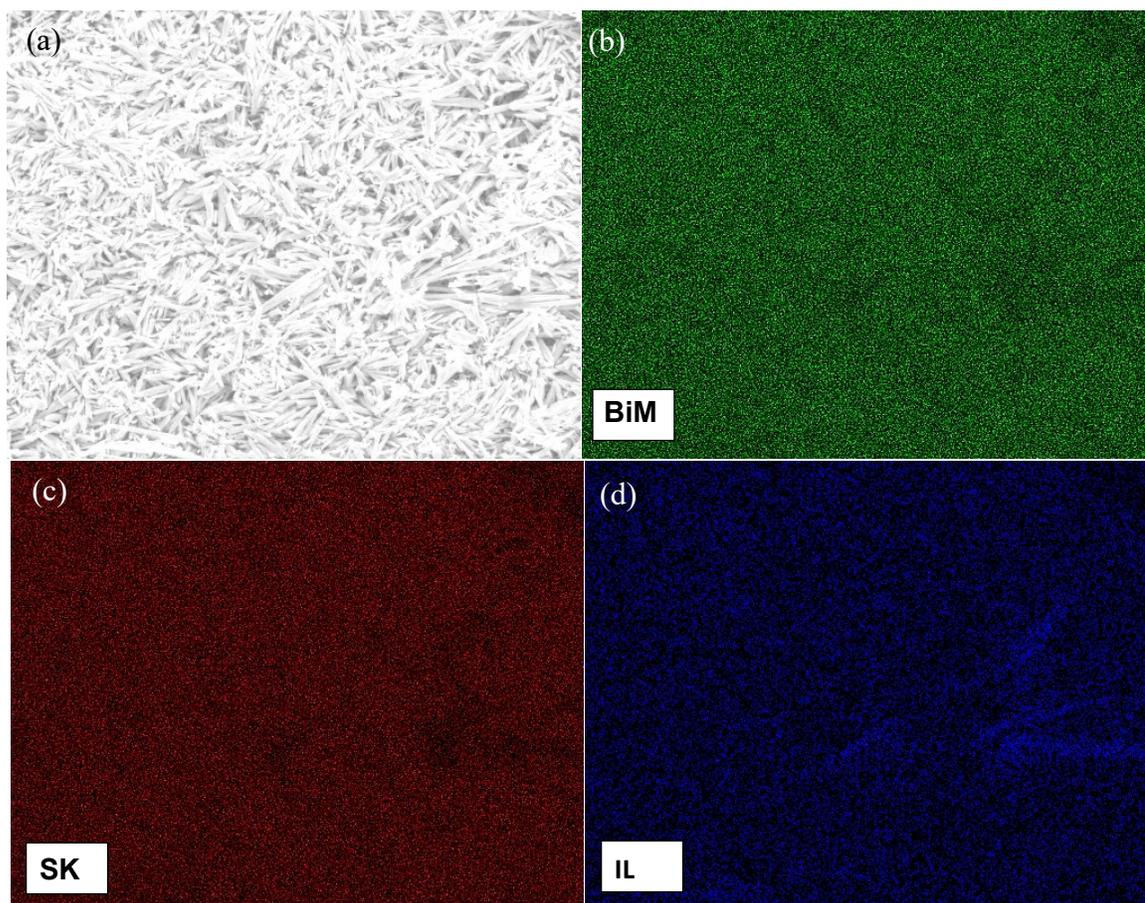


Fig. S4. (a) SEM image of the synthesized BiSI and corresponding elemental mapping for (b) Bi-M line (c) S-K line and (d) I-L line.

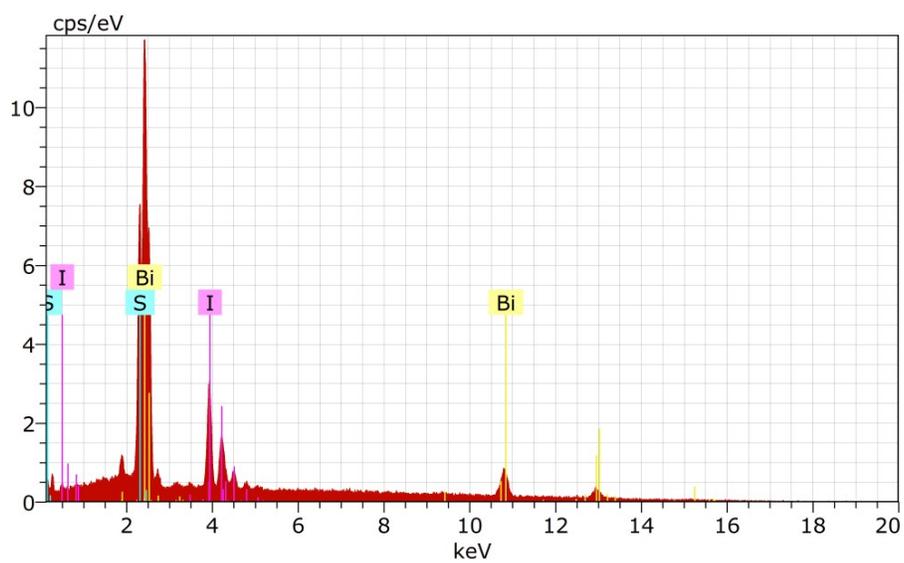


Fig. S5. EDS spectrum for synthesized BiSI.

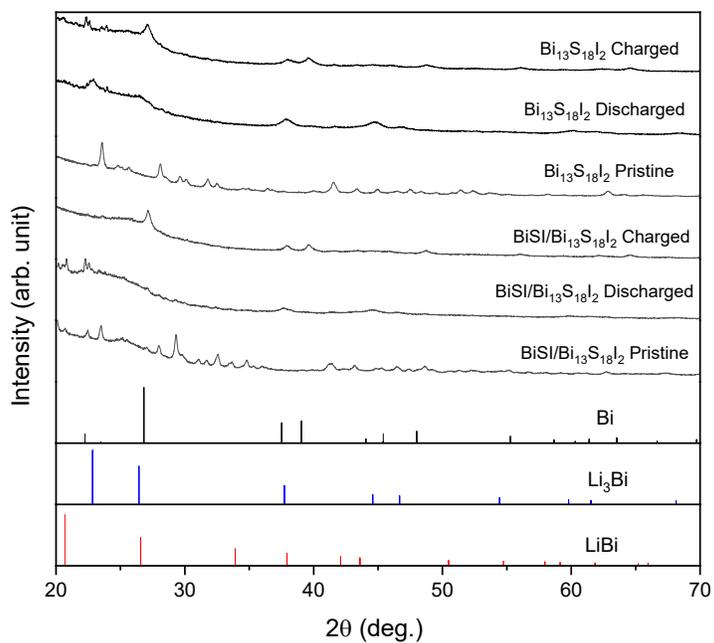


Fig. S6. Ex-situ XRD patterns of $\text{Bi}_{13}\text{S}_{18}\text{I}_2$, and BiSI/ $\text{Bi}_{13}\text{S}_{18}\text{I}_2$ electrodes after the first discharge and charge processes. Planes corresponding to LiBi , Li_3Bi and Bi are shown by red, blue and black colors vertical lines.

Table S1. Comparison of bismuth-based electrode performances in lithium (LIB), sodium (SIB), and potassium (PIB) battery systems.

Reference	Materials	1 st Cycle (mAh g ⁻¹)	15 th Cycle (mAh g ⁻¹)	Battery System
This work	BiSI Bi ₁₃ S ₁₈ I ₂	1087 at 100 mA g ⁻¹ 807 at 100 mA g ⁻¹	800 630	LIB
Ref. ¹ <i>ACS Appl. Mater. Interfaces</i> , 2020, 12 , 42902-42910	Bi ₂ S ₃ /MoS ₂	500 at 500 mA g ⁻¹	500	SIB
		410 at 1 A g ⁻¹	380	PIB
Ref. ² <i>Dalton Trans.</i> , 2019, 48 , 10448-10454	BiSbS ₃ -Carbon	900 at 100 mA g ⁻¹	~700	SIB
Ref. ³ <i>ACS Nano</i> , 2018, 12 , 12597-12611	Bi ₂ S ₃ yolk shell	800 at 100 mA g ⁻¹	600	LIB
Ref. ⁴ <i>Nano Res.</i> , 2018, 11 , 4614-4626	Bi ₂ S ₃ -graphene	600 at 312.5 mA g ⁻¹	400	SIB
Ref. ⁵ <i>Nano Energy</i> , 2017, 33 , 213-220	Bi ₂ S ₃ yolk shell	580 at 312.5 mA g ⁻¹	550	LIB
		500 at 312.5 mA g ⁻¹	470	SIB
Ref. ⁶ <i>J. Power Sources</i> , 2016, 309 , 135-140	Bi ₂ S ₃ nanorod	620 at 100 mA g ⁻¹	500	SIB
Ref. ⁷ <i>Chem. Commun.</i> , 2015, 51 , 2798-2801	BiOI	700 at 30 mA g ⁻¹	-	LIB
Ref. ⁸ <i>J. Mater. Chem. A</i> , 2014, 2 , 13854-13858	Bi ₂ S ₃ -CNT	700 at 100 mA g ⁻¹	~680	LIB
Ref. ⁹ <i>Adv. Energy Mater.</i> , 2014, 4 , 1400798	Bi ₂ S ₃ -CNT	510 at 200 mA g ⁻¹	490	LIB
Ref. ¹⁰ <i>J. Alloys Compd.</i> , 2013, 579 , 18-26	BiPO ₄	250 at 26.45 mA g ⁻¹	100	LIB

Supporting References

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