Supplementary Information for

Facile and rapid synthesis of RGO-In₂S₃ composite with enhanced cyclability and high capacity for lithium storage

Fangmin Ye¹, Gaohui Du², Zhoufeng Jiang¹, Yijun Zhong², Xiaodong Wang^{1,*}, Qingping Cao¹, J. Z. Jiang^{1,*} ¹ International Center for New-Structured Materials (ICNSM), Zhejiang University and Laboratory of New-Structured Materials, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, P.R. China. 2Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, P.R. China.

Experimental section:

Materials Synthesis: Graphene oxide sheets (GO) were prepared by a modified Hummer's method^[S1]. In a typical procedure for the synthesis of reduced graphene oxide-β-In₂S₃ (RGO-In₂S₃) composite, 15 mg GO was dispersed into 15 ml distilled water by ultrasonication for 60 min. Simultaneously, about 0.8 mmol indium (III) chloride tetrahydrate (InCl₃·4H₂O, Alfa Aesar, 97%) was added to additional 10 ml distill water and stirred for 60 min. After stirred for 60 min, both solutions were mixed together and stirred for 90 min. Finally, thioacetamide (TAA) was dissolved in above mixed solution and stirred for 10 min. The obtained solution was transferred to a round flask and refluxed at 95 °C for 80 min. After cooling, the as-synthesized yellow products were harvested after centrifuging four times and dried at 40 °C overnight. The pure β-In₂S₃ sheets were obtained in the absence of GO.

Materials Characterization: The morphology, element mapping and energy dispersive spectroscopy (EDS) of as-prepared samples were investigated by using a scanning electron microscopy (SEM) Hitachi S4800 operated at 5 kV. Structures of samples were characterized by using a transmission electron microscopy (TEM) Philips FEI 200CX operated at 160 kV, high resolution transmission electron microscopy (HRTEM) JEOL 2100F with an image-side Cs-corrector operated at 200 kV, and X-ray diffractometer PANalytical X'pert Pro using CuK α radiation (λ =1.5416 Å). Nitrogen adsorption/desorption isotherms were measured on a Beckman coulter omnisorp100cx to evaluate the specific surface area and Barretl-Joyner-Halenda (BJH) pore diameter. Raman spectra were obtained with a Renishaw in Via Raman

microscopy system with a laser wavelength of 532 nm. The RGO content in the as-fresh RGO-In₂S₃ composite was estimated by TGA (SDT Q600) measurements. X-ray photoelectron spectroscopy (XPS) analyses were performed using a Kratos Amicus XPS. Photoemission was stimulated by monochromated Mg K α radiation (12 kV) with an operating power of 180 W.

Electrochemical Measurement: The electrochemical measurements were carried out using Land CT2001A with lithium metal as the counter and reference electrodes at room temperature. The electrode consists of active material (sheet-on-sheet RGO-In₂S₃ composite or pure β -In₂S₃), conductivity agent (acetylene black), and polymer binder (polyvinylidene difluoride, PVDF, Aldrich) by a weight ratio of approximately 70:20:10, the active material loading in each electrode was typically 1~2 mg. The electrolyte was 1 M LiPF6 in a 1:1 wt/wt mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glove box. The cell was charged/discharged at a fixed voltage window between 5 mV and 3 V. Cyclic voltammogram and AC impedance spectra were carried out using an electrochemical work station (CHI660C) to investigate the electrode reaction processes. The scan range of 5 mV-3 V (vs. Li/Li⁺) was swept at the rate of 0.1 mV/s. AC impedance spectra were performed by applying a sine wave with an amplitude of 5.0 mV in the frequency range from 0.01 Hz to 100 kHz.



Fig. S1 SEM image of as-prepared pure β -In₂S₃ sheets



Fig. S2 XRD pattern of as-prepared pure β -In₂S₃ sheets



Fig. S3 Energy-disperse spectroscopy of as-prepared RGO-In₂S₃ composite.



Fig. S4 TGA curves of RGO-In₂S₃ composite and pure β -In₂S₃ sheets. The measurement was taken in air with a heating rate of 10 °C min⁻¹. The content of RGO was estimated to be about 7.1 wt.% by the difference of weight loss of RGO-In₂S₃ and pure β -In₂S₃.



Fig. S5 Adsorption–desorption isotherm and pore size distribution of the pure β -In₂S₃ sheets (a and b) and RGO-In₂S₃ composite (c and d). The RGO-In₂S₃ composite exhibits a specific surface area of 79.6 m²/g and an average pore diameter of 173 nm, whereas the pure β -In₂S₃ sheets exhibit a specific surface area of 48.4 m²/g and an average pore diameter of 120 nm.



Fig. S6 Cyclic voltammogram of the pure β -In₂S₃ (a) and RGO-In₂S₃ (b) electrodes.



Fig. S7 Coulombic efficiency of pure β -In₂S₃ electrode charged/discharged at a current density of 100 mA g⁻¹.



Fig. S8 Modified Randles equivalent circuit for RGO- In_2S_3 composite and pure β - In_2S_3 electrode/ electrolyte interface. R_{Ω} and R_{ct} are the ohmic resistance (total resistance of the electrolyte, separator and electrical contact) and charge-transfer resistance, respectively. CPE is the constant phase-angle element, involving double layer capacitance, and W (Warburg impedance) relates to the diffusion of lithium ions into the bulk electrodes.

Sample	R_{Ω}	R_{ct}	i_0
	(Ω)	(Ω)	$\mu A \text{ cm}^{-2}$
RGO-In ₂ S ₃	9.6	68	20
In_2S_3	8.8	122	11

Table S1 Kinetic parameters of RGO-In₂S₃ composite and pure β -In₂S₃ electrodes

Note: The exchange current density i_0 is calculated according to the equation of $i_0 = RT/nFR_{ct}$, *R* is the gas constant, *T* is the absolute temperature, *n* is the number of transferred electrons, *F* is the Faraday constant. According to the work in ref. [S2], n is estimated to be 4.33.

Supporting references

[S1] W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339.

[S2]W. H. Ho, C. F. Li, H. C. Liu and S. K. Yen, J. Power Sources, 2008, 175, 897.