

Supporting Information

p-n heterogeneous Sb₂S₃/SnO₂ quantum dots anchored reduced graphene oxide nanosheets for high-performance lithium-ion batteries

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Experimental section

Materials

All chemical reagents used are commercially available and have been used without further purification. Flake graphite (C, CP) was purchased from Qingdao Chenyang Graphite Co., Ltd. (QingDao, China). Potassium permanganate (KMnO_4 , AR) was purchased from Guangzhou Jinzhisheng Chemical Co., Ltd. (Guangzhou, China). Phosphoric acid (H_3PO_4 , 85%) Sulphuric Acid (H_2SO_4 , AR) and Hydrochloric acid (HCl , 0.1 M) were purchased from Adamas Reagent Co., Ltd. (Shanghai, China), Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and Xinnake Trading Co., Ltd., respectively. Hydrogen peroxide (H_2O_2 , 30 %) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Thiourea ($\text{CH}_4\text{N}_2\text{S}$, AR) was purchased from Tianjin Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). Antimony trichloride (SbCl_3 , CP) was purchased from Adamas Reagent Co., Ltd. (Shanghai, China). Zinc chloride (ZnCl_2 , 98%) was purchased from Shanghai Titan Technology Co., Ltd. (Shanghai, China). 1-Pentyl-2,3-dimethylimidazolium chloride ($[\text{C}_5\text{MMim}]\text{Cl}$, 99%) was purchased from Lanzhou Institute of Chemical Physics. (Lanzhou, China). Tin(IV) Chloride Pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, AG) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Conductive carbon black (Super-P) and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ were purchased from Guangdong Canrd New Energy Technology Co., Ltd. (Guangdong, China). Polyvinylidene fluoride (PVDF, 99%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Lithium ion battery electrolyte (LiPF_6 , 1.0M) was purchased from Suzhou Qianmin Chemical Reagent Co., Ltd. (Suzhou, China).

Synthesis of $[\text{C}_5\text{MMIm}]_2[\text{SbCl}_5]/[\text{C}_5\text{MMIm}]_2[\text{SnCl}_6]$

4 mL of ethanol, 4 mmol of $[\text{C}_5\text{MMim}]\text{Cl}$, 1 mmol of SbCl_3 , 1 mmol of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ($[\text{C}_5\text{MMim}]\text{Cl}$ = 1-pentyl-2,3-dimethylimidazolium chloride) were added to a 50 mL of flask and mixed evenly. Subsequently, the mixture was stirred in an oil bath at 100 °C for 30 min. After natural cooling to room temperature in the oil bath, white crystals were precipitated. The obtained white crystals were dried in a vacuum oven at 60 °C for 12 h to obtain $[\text{C}_5\text{MMIm}]_2[\text{SbCl}_5]/[\text{C}_5\text{MMIm}]_2[\text{SnCl}_6]$.

Synthesis of $\text{Sb}_2\text{S}_3/\text{SnO}_2@\text{rGO}$, $\text{Sb}_2\text{S}_3@\text{rGO}$ composites

422.5 mg of $[\text{C}_5\text{MMIm}]_2[\text{SbCl}_5]/[\text{C}_5\text{MMIm}]_2[\text{SnCl}_6]$ and 50 mL of graphene oxide (GO) ethanol solution (1 mg mL^{-1} , prepared by Hummers method) were added into a 100 mL of beaker, and then were heated and stirred until all of the solid material was dissolved. Subsequently, the solution was stirred at room temperature for 2 h. After that, 6 mmol of thiourea was added with a continuous stirring of 1 h, then the solution was transferred to a 100 mL of PTFE-lined autoclave and heated in an oven at $180 \text{ }^\circ\text{C}$ for 20 h. After cooling to room temperature, the product was precipitated by centrifugation and washed by distilled water and ethanol for three times. The collected products were dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for 12 h. The dried samples were further annealed at $350 \text{ }^\circ\text{C}$ for 2 h in a mixed atmosphere of H_2 and N_2 (H_2 content of 10 vol%). As a contrast, $\text{Sb}_2\text{S}_3@\text{rGO}$ was also prepared under the same conditions by increasing the amount of SbCl_3 to 2 mmol without adding $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

Materials and Characterization

The reagents used are all commercially available products and can be used without further purification. The phase composition and content of the composites were analyzed using an X-ray powder diffractometer (PXRD Rigaku Xray Miniflex II, Cu $K\alpha$ radiation source, $\lambda = 1.5418 \text{ \AA}$). The crystallographic dimensions and morphological structural features of the composites were measured by field emission scanning electron microscopy (FESEM SU8010) and transmission electron microscopy (TEM, FEI Tecnai F20). Thermogravimetric spectra were obtained on a thermal analyzer (TGA NETZSCH STA449F3). Raman spectra were analyzed on a Raman spectrometer (Horiba Labram HR800 Evolution). X-ray photoelectron spectra were measured on an X-ray photoelectron spectrometer (XPS ESCALAB 250Xi Al $K\alpha$, $\lambda = 8 \text{ \AA}$, $h\nu = 1486.6 \text{ eV}$). The specific surface area (BET) was calculated by automatic static chemical adsorption instrument (ASAP 2020).

Electrochemical Measurements

The electrochemical performance test was performed using CR2032 button battery. The working electrode was uniformly mixed with 80 % active material, 20 % conductive carbon black, 10 % polyvinylidene fluoride (PVDF) and an appropriate

amount of 1-N-methyl-2- pyrrolidone (NMP). The slurry was evenly coated on the copper foil and dried in a blast oven at 80 °C for 6 h, and then placed in a vacuum oven at 120 °C for 12 h. The dried copper foil was pressed into 1.2 cm wafer on a 10 MPa tablet press, and the mass of active material was about 1.0 mg/cm². The storage properties of lithium were studied with the prepared materials. Lithium foil was used as the reference electrode, Celgard 2325 as the separator, and 1.0 M LiPF₆ was dissolved in ethylene carbonate/dimethyl carbonate/diethyl carbonate (volume ratio is 1 : 1 : 1; containing 5 vol% vinyl fluoride carbonate). The Constant current discharge/charge cycles and rate performance tests are performed on LAND 2001A software. Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) were performed on an electrochemical workstation of CHI660E.

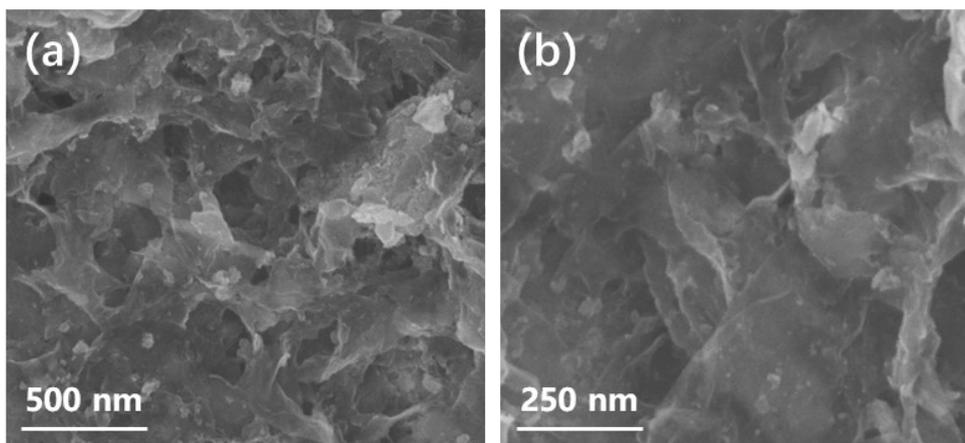


Fig. S1 SEM images of $\text{Sb}_2\text{S}_3@\text{rGO}$.

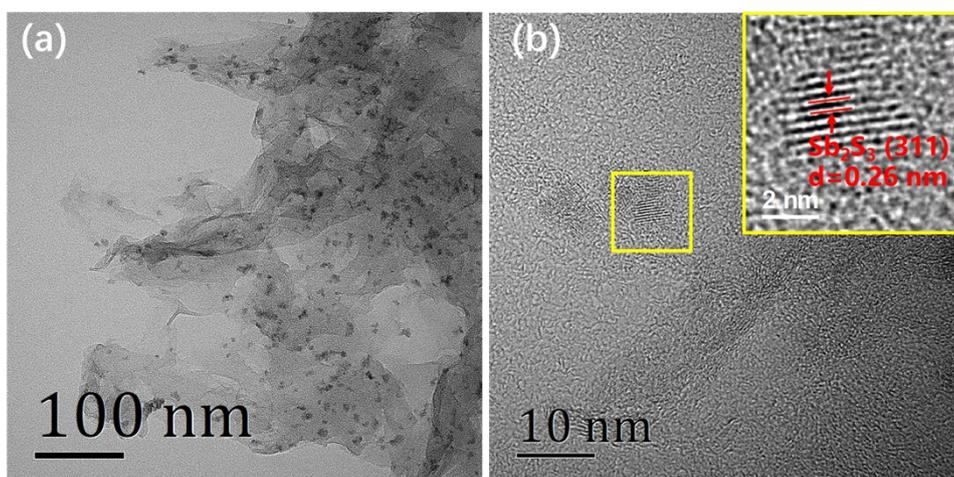


Fig. S2 (a) TEM and (b) HRTEM images of $\text{Sb}_2\text{S}_3@\text{rGO}$.

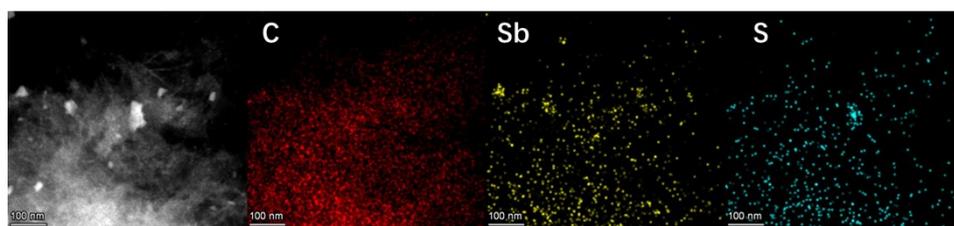


Fig. S3 HADF-TEM and elemental mapping images of $\text{Sb}_2\text{S}_3@\text{rGO}$.

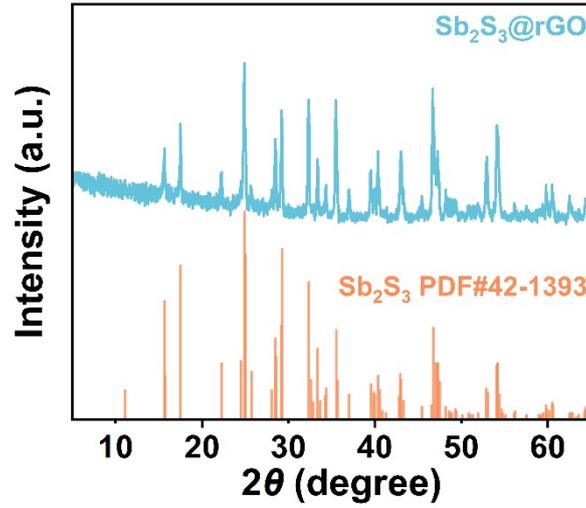


Fig. S4 XRD pattern of $\text{Sb}_2\text{S}_3@\text{rGO}$.

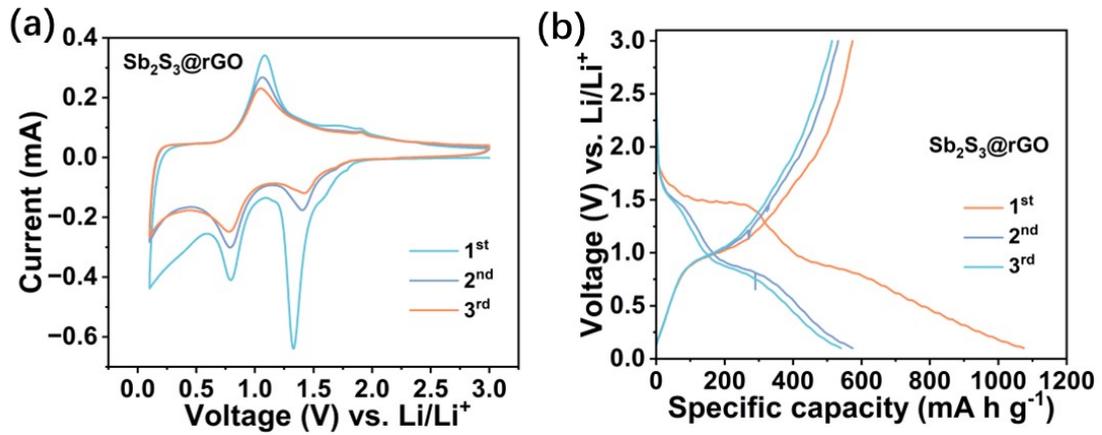


Fig. S5 (a) CV curves at 0.1 mV s^{-1} and (b) discharging/charging curves at 0.1 A g^{-1} of $\text{Sb}_2\text{S}_3@\text{rGO}$.

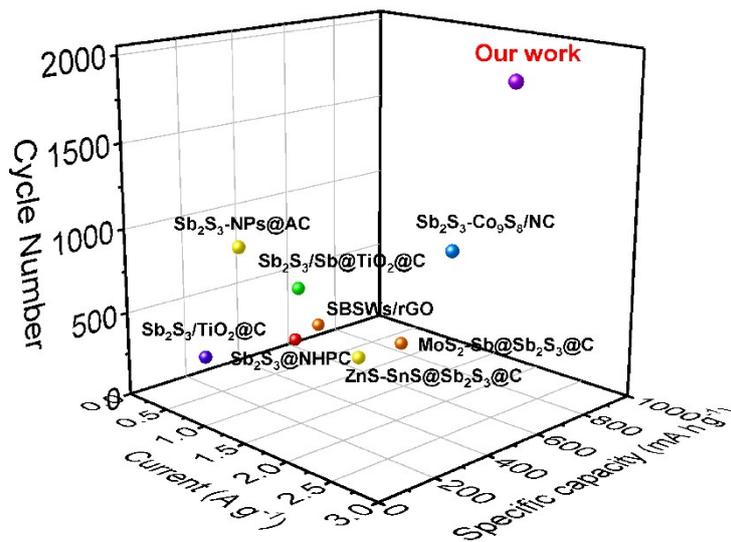


Fig. S6 Comparison of the cycling performance of $\text{Sb}_2\text{S}_3/\text{SnO}_2@\text{rGO}$ with that of previously reported Sb_2S_3 -based carbon materials.¹⁻⁸

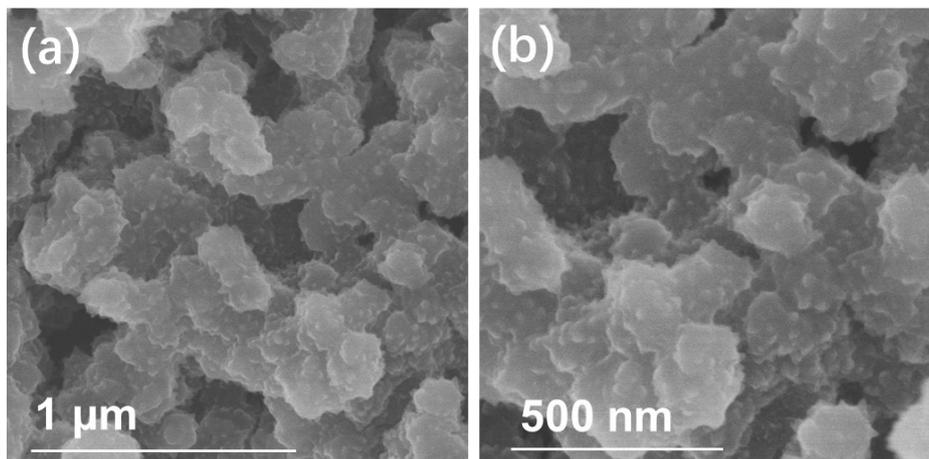


Fig. S7 (a-b) Different magnifications of SEM images for $\text{Sb}_2\text{S}_3/\text{SnO}_2@\text{rGO}$ electrode after 2000 cycles at 3 A g^{-1} .

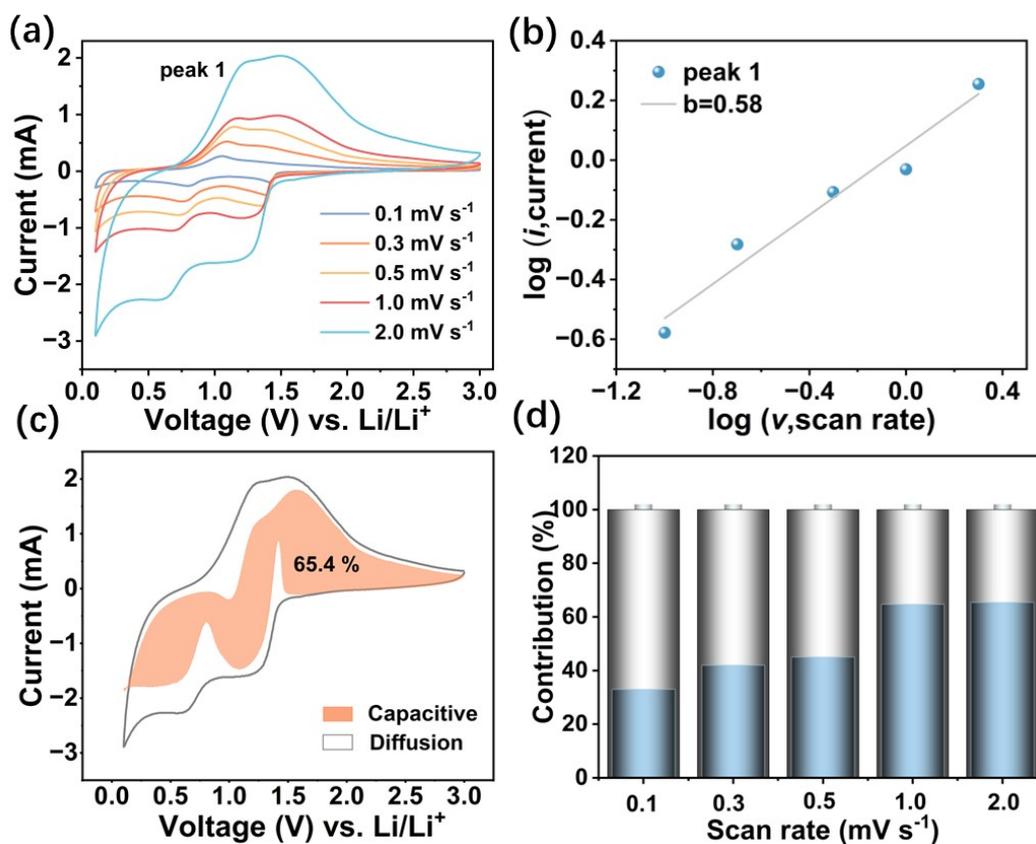


Fig. S8 $\text{Sb}_2\text{S}_3@\text{rGO}$: (a) CV curves at scan rates from 0.1 to 2.0 mV s^{-1} , (b) the fitting plots of $\log(i)$ and $\log(v)$, (c) pseudocapacitive contribution (shaded area) at scan rates of 2.0 mV s^{-1} , (d) pseudocapacitive contribution of LIBs at different scan rates.

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