Electronic Supplementary Information

Two Dimensional Graphene/SnS_2 Hybrids with Superior Rate Capability for Lithium ion Storage

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Experimental details:

Material Synthesis**:** Graphene oxide (GO) was synthesized from natural graphite (300 μm, Qingdao Graphite Company) by a modified Hummers method [1]. Graphene supported SnO_2 nanoparticles (G-SnO_2) were prepared by a controllable hydrolyzation process of tin salts in a GO containing ethylene glycol (EG)-water solution. In a typical experiment, as-synthesized graphene oxide (50 mg) was firstly suspended in a 100 mL of mixture of EG and water (10 mL of water contained) that was hosted in a round-bottom flask, and then ultrasonically treated for 1 h, forming a brown dispersion. Then 0.5 g of $SnCl_2 \cdot 2H_2O$ (dissolved in 10 mL of EG) was added to the obtained GO solution. After magnetic stirring for 20 min, the solution was heated to 120 ℃ and refluxed for 2 h with constant stirring under atmospheric pressure. After filtration and desiccation, the resultant black solid product was placed in a horizontal quartz tubular reactor, and heated to 500 ℃ at 10 ℃ min^{-1} in Ar (99.999 %) atmosphere with a flow rate of 200 sccm. To improve the crystallinity of SnO_2 in G-SnO_2, the product was firstly annealed at 500 ℃ for 2 h in Ar atmosphere. Subsequently, gas mixture of H_2S and Ar (Volume ratio: 1:19) were introduced in turn with a flow rate of 200 sccm when the furnace was cooled down to 300 ℃, and kept these conditions for 2 hours. Finally the system was cooled down to room temperature in Ar atmosphere. To investigate the effect of the pre-annealing treatment and flow rate of H_2S/Ar gas on the morphologies of SnS_2, the same process was used except adjusting the corresponding parameters. For comparison, bare SnS_2 was prepared by the same procedure but without the presence of GO in the first step.

Material Characterization**:** X-ray diffraction (XRD) with Cu Kα radiation (Rigaku D/max-2500B2+/PCX system) was used to determine the phase composition and the crystallinity. The morphology and microstructure of the samples were investigated by FE-SEM (Hitachi S4800), FE-TEM (FEI Tecnai G2 20 ST), and TGA (Perkin Elmer, Diamond TG) measurements. Nitrogen sorption isotherms and BET surface area were measured at 77 K with a ASAP 2020 physisorption analyzer (USA). The Raman spectra were obtained on a Renishaw Micro-Raman Spectroscopy System with excitation from an argon ion laser (514 nm). Fourier-trans-form infrared (FT-IR) spectra were recorded by a Perkin-Elmer Spectrum One FTIR Spectrometer.

Electrochemical cycling tests were performed with coin-type half-cells (2032 size). The working electrode was made from the G-SnS_2 active material, super P carbon black, and a polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10 on a copper foil. The mass of the active material in each half-cell is about 2-3 mg. The electrolyte was 1M $LiPF_6$ with 1:1 ethylene carbonate: diethylene carbonate (EC: DEC), and the counter and reference electrodes were made from lithium foil. The cycle-life of the cells was tested at different rates within a fixed voltage window of 1.3 V-5 mV. The rate capability was evaluated by varying the discharge rate from 100 mA g^{-1} to 6400 mA g^{-1}. Cyclic voltammetry was performed to examine the cathodic reaction (reduction) and the anodic reaction (oxidation) in the voltage range of 2.5-0 V (versus Li/Li^+), at a sweep rate of 0.1 mV s^{-1}.

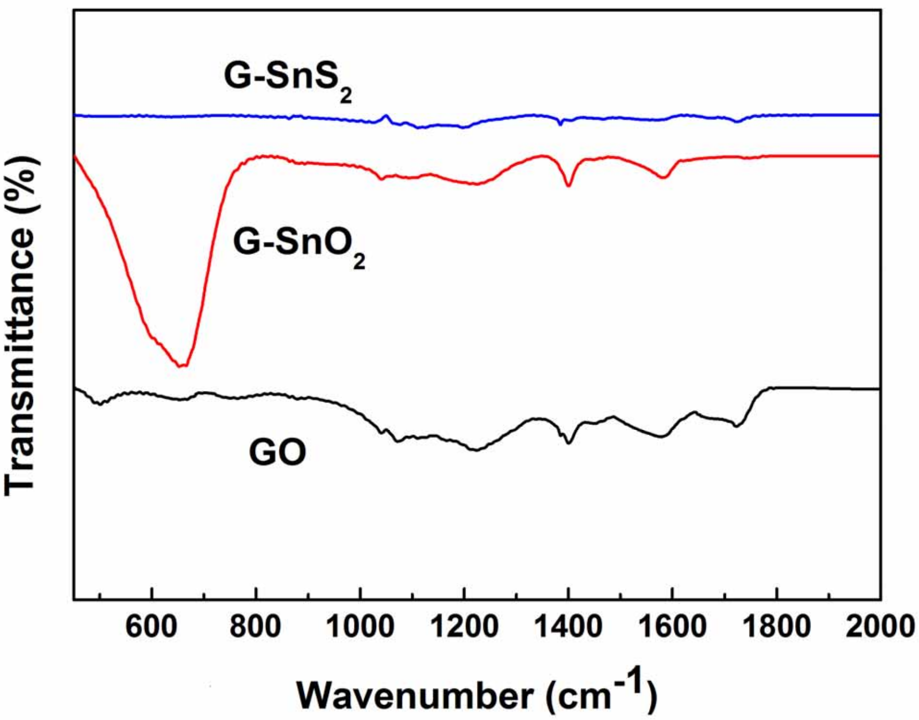

Figure S1. FT-IR spectra for graphene oxide (GO), graphene supported SnO_2 nanoparticles (G-SnO_2) and graphene supported SnS_2 nanoplates (G-SnS_2).

Figure S1 shows FT-IR spectra of graphene oxide (GO), graphene supported SnO_2 nanoparticles (G-SnO_2) and graphene supported SnS_2 nanoplates (G-SnS_2). The two bands of GO appearing at 1050 cm^{-1} and 1720 cm^{-1} are due to the epoxide and carboxyl functional moieties, respectively. This result clearly reveals that functional groups are introduced into carbon frameworks upon oxidation. However, in case of G-SnO_2, epoxide and carboxylate functional groups almost disappear, indicating that GO has been reduced by the solution process. The broad band around 670 cm^{-1} is associated with the anti-symmetric O-Sn-O stretching mode, clarifying that SnO_2 particles exist within the graphene-based matrices. After the heat treatment in H_2S/Ar, disappearing of the broad band around 670 cm^{-1} confirmed the totally conversion of SnO_2 nanoparticles to SnS_2 nanoplates.

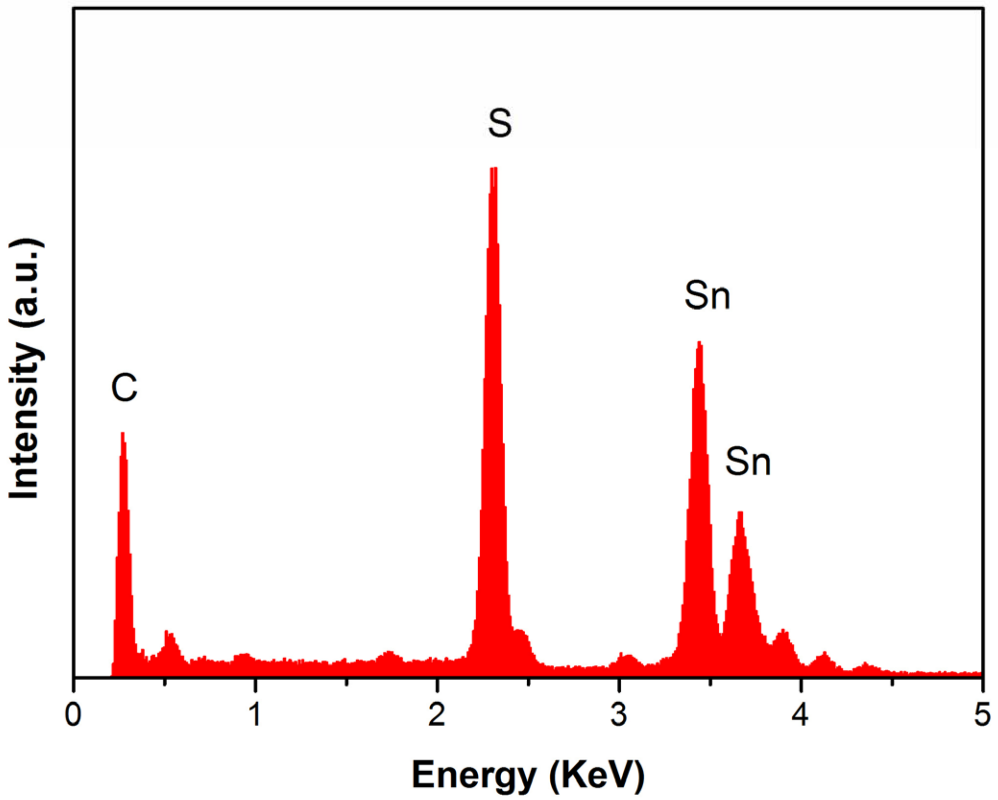

Figure S2. Energy-dispersive X-ray (EDX) spectrum of G-SnS_2.

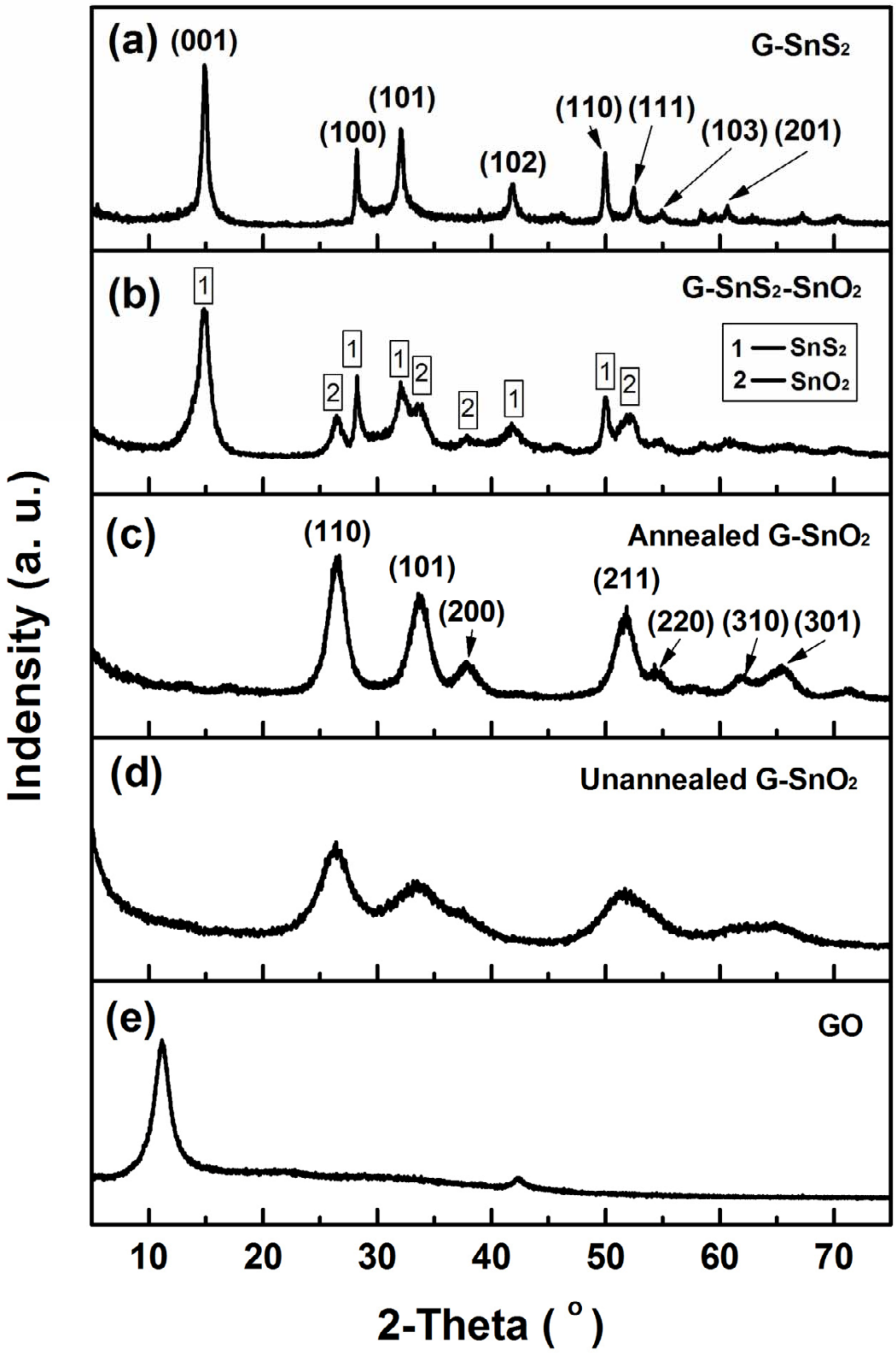

Figure S3. Comparison of XRD patterns of (a) G-SnS_2, (b) G-SnO_2-SnS_2 (sample collected during the second step), (c) Annealed G-SnO_2, (d) Unannealed G-SnO_2, and (e) GO.

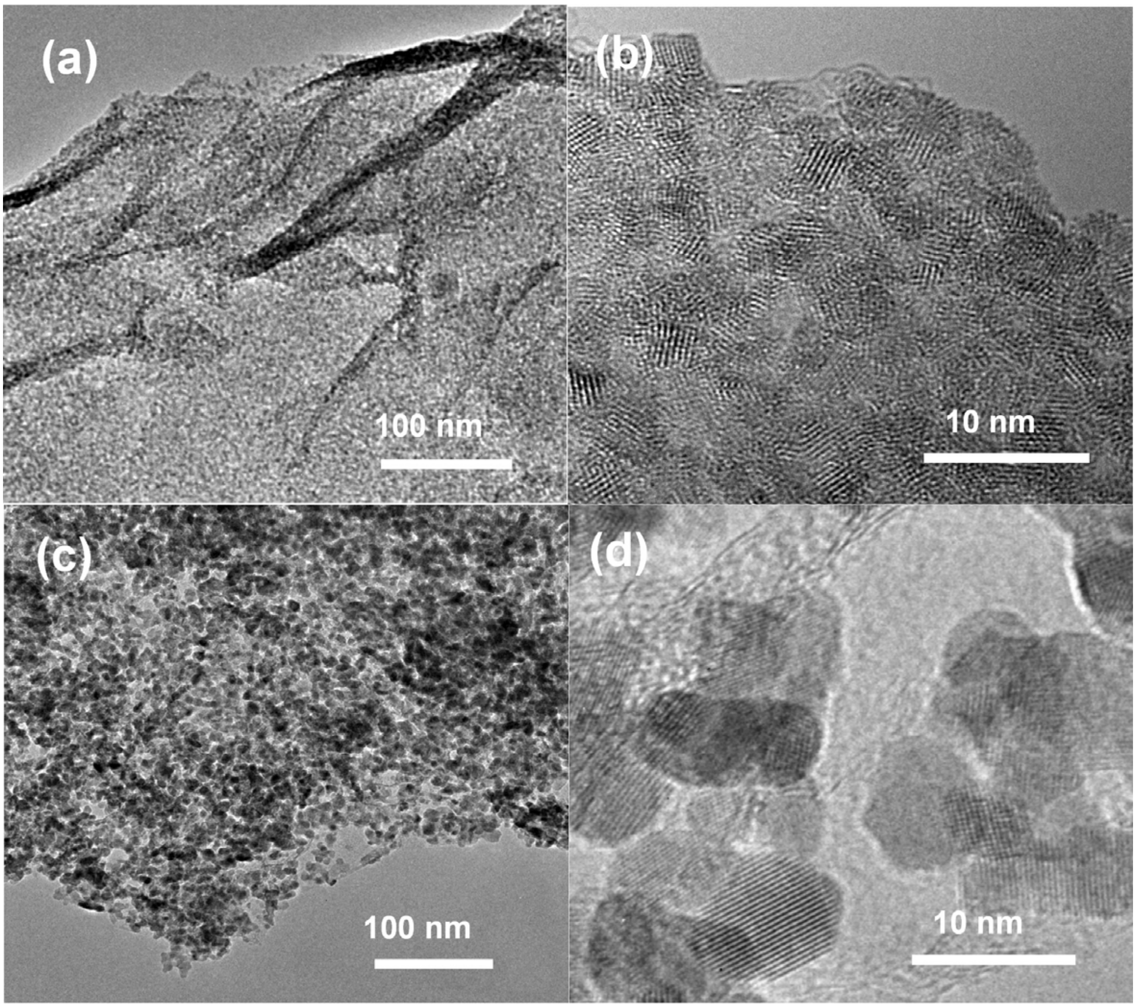

Figure S4. TEM images of (a, b) unannealed G-SnO_2, and (c, d) annealed G-SnO_2.

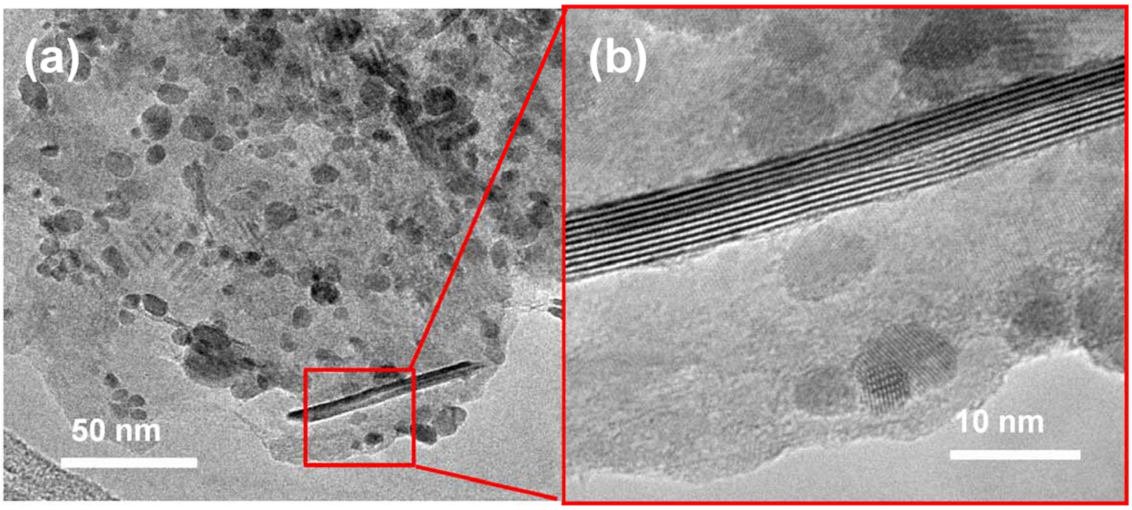

Figure S5. TEM images of G-SnS_2-SnO_2 (samples collected after heat treatment in H_2S/Ar for 1 hour)

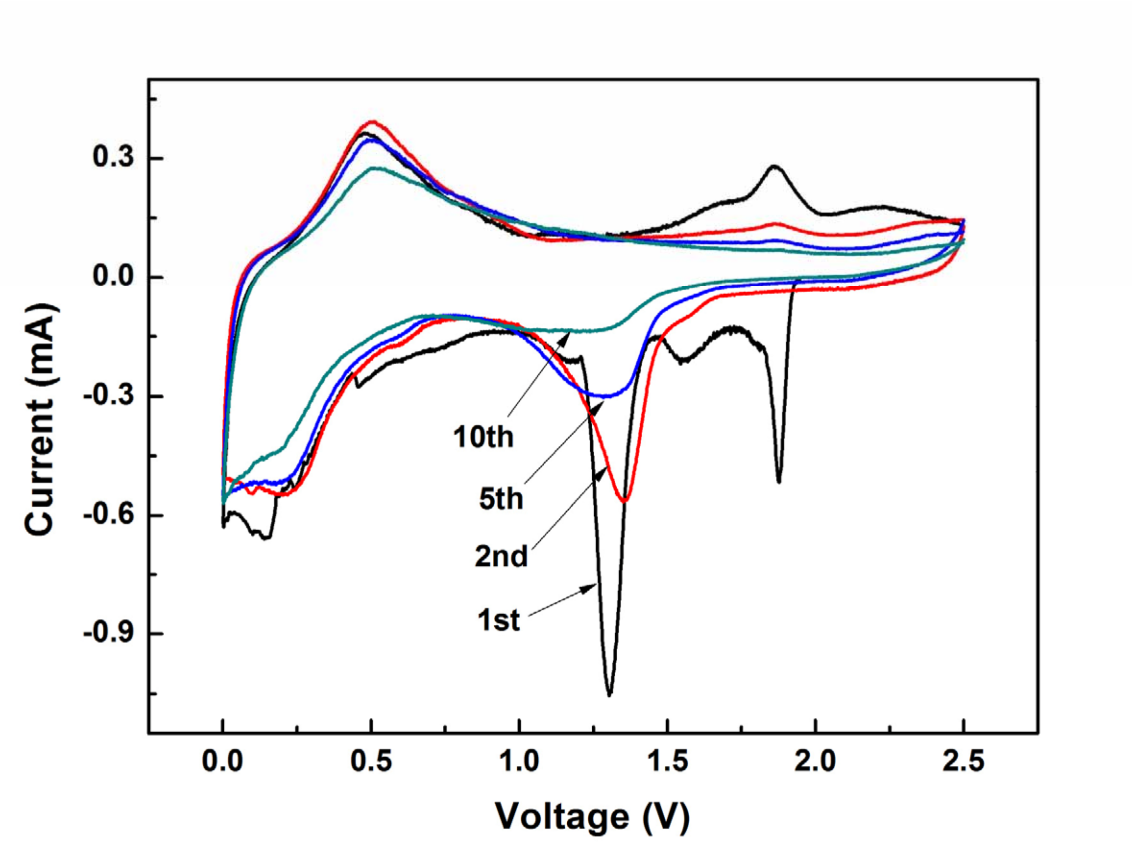

Figure S6. Cyclic voltammograms for G-SnS_2-S electrode, cycled between 0.05V and 2.5V at a scan rate of 0.01mV/s.

Figure S6 shows the Cyclic Voltammograms (CV) for the first ten cycles at a scan rate of 0.01mVs^{-1} in the potential window of 0.05V-2.5V. Specifically, several reduction peaks are observed in the first cathodic scan. Two broader peaks were present at about 1.25 V and 1.1 V in the first potential sweeping process. The cathodic peak at 1.25 V, observed during the first sweep, was assigned to the decomposition of the SnS_2 into metallic tin and Li_2S, and the formation of solid electrolyte interface (SEI), which should be responsible for the first irreversible capacity loss. The third dominant peak between 0.6 and 0 V is known to arise from the formation of Li_xSn alloys. The additional peaks at ~1.6 and ~1.9V were attributed to the lithium intercalation of the SnS_2 layers without phase decomposition, which were also partly responsible for the high initial discharge capacities.

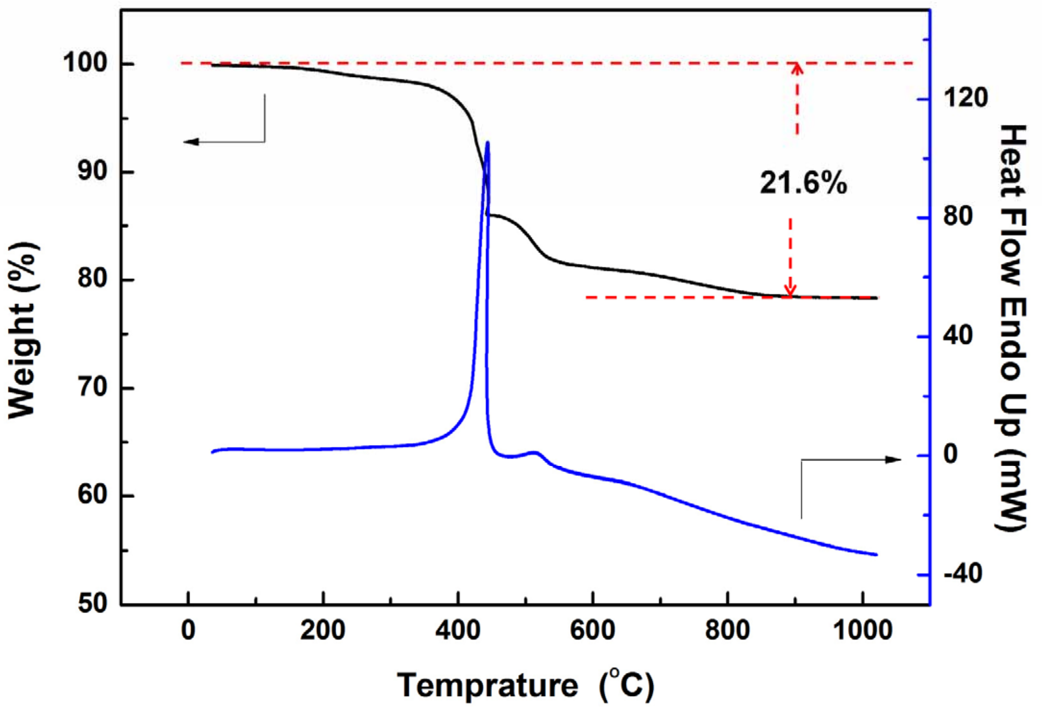

Figure S7. Thermal analysis (by TGA and DTA) of as-prepared G-SnS_2-M hybids. The SnS_2 content estimated from the thermal analysis was ca. 95.0 wt % (Note: SnS_2 had been oxidized into SnO_2). The analysis was taken in air using a heating rate of 10℃ min^{-1}. The weight loss from room temperature to 200℃ was due to the removal of physisorbed and chemisorbed water.

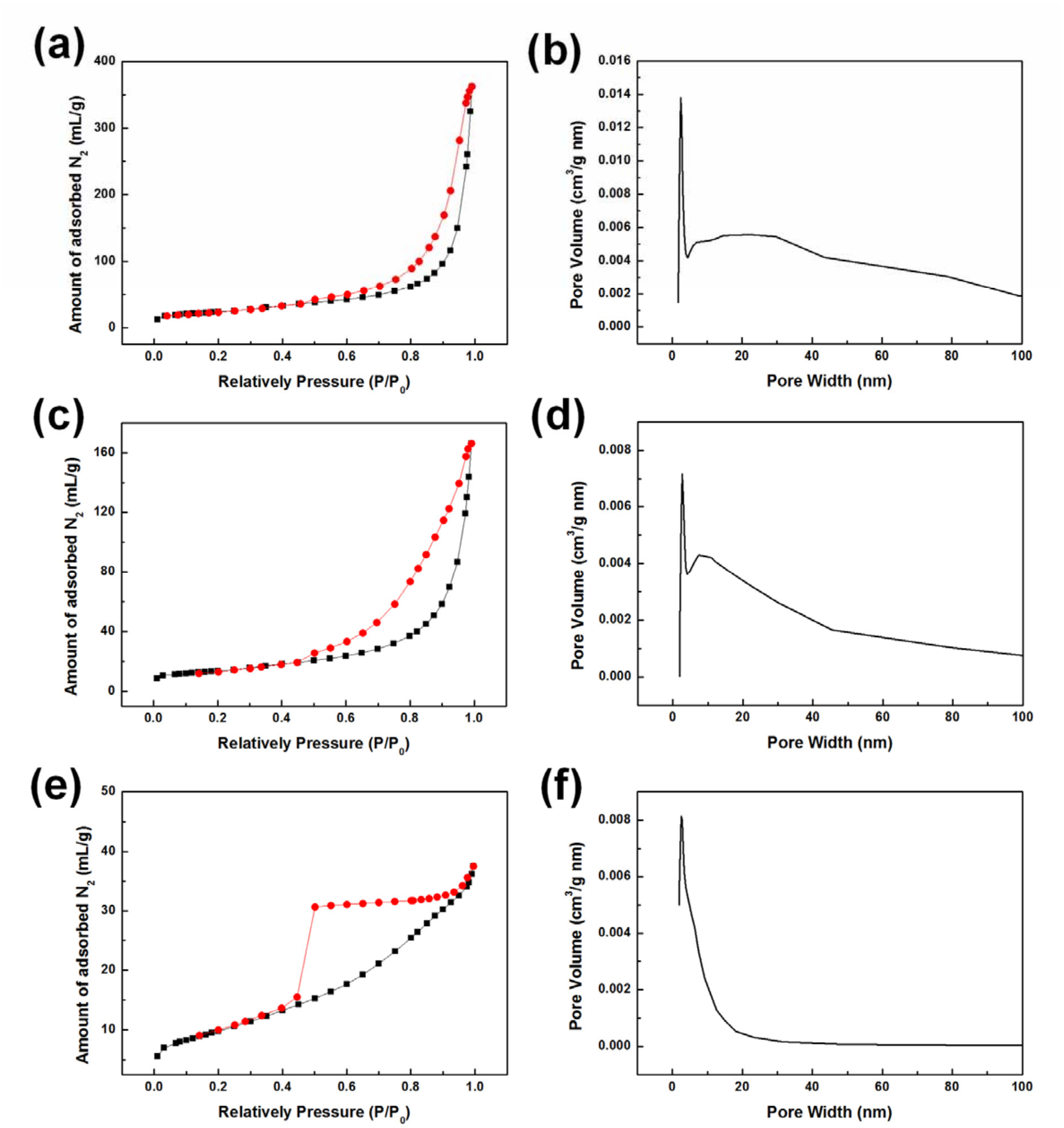

Figure S8. Nitrogen adsorption-desorption isotherms and pore-size distribution of as-prepared G-SnS_2-L (a, b), G-SnS_2-M (c, d) and G-SnS_2-S (e, f), respectively.

Table S1. Size distribution of SnS_2 nanoplates of three typical G-SnS_2 samples obtained at different Experimental conditions.

Samples	Experimental conditions		Size distribution of SnS_2 nanoplates	
	Pre-annealing treatment of G-SnO_2	Flow rate of H_2S/Ar gas mixture	Diameter	Calculated thickness
G-SnS_2-S	with	400sccm	~100nm	~3.7nm
G-SnS_2-M	with	200sccm	~200nm	~6.9nm
G-SnS_2-L	without	200sccm	~500nm	~11.4nm

Table S2. BET surface area, BJH adsorption cumulative volume of pores, and BJH adsorption average pore width of as-prepared G-SnS_2 samples.

Samples	BET surface area $m^2\ g^{-1}$	BJH adsorption cumulative volume of pores $cm^3\ g^{-1}$	BJH adsorption average pore width nm
G-SnS_2-S	35.3	0.060	6.1
G-SnS_2-M	47.2	0.259	18.6
G-SnS_2-L	84.1	0.562	22.5

The isotherm for G-SnS_2-L and G-SnS_2-M is characteristic of a type IV with a type H3 hysteresis loop, revealing that the material is composed of aggregates (loose assemblages) of sheet-like particles forming slit-like pores. Meanwhile, the isotherm for G-SnS_2-S with a Type H4 loops feature can be attributed to adsorption-desorption in narrow slit-like pores, which is in corresponding with our microscopy findings.

Supporting references

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