Electronic Supplementary Information

Co_3S_4 porous nanosheets embedded in graphene sheets as high-performance anode materials for lithium and sodium storage

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Experimental section

Preparation of Co_3S_4 porous nanosheets: Co_3S_4 porous nanosheets were synthesized from $Co(OH)_2$ nanosheets by slightly modifying a previously reported process.[1] 0.4364 g of $Co(NO_3)_2·6H_2O$ was added into 60 mL of deionized (DI) water to produce a pink solution. Then, 1.5 mL of trimethylamine was gradually dropped into the above solution under continuous stirring, and the solution turned dark blue immediately. Afterward, 58.5 mL of DI water was added again to achieve a total volume of 120 mL. The resultant solution was poured into four 40 mL Teflon-lined autoclave and maintained at 180 ^{o}C for 24 h. Then, 112.5 mL of the obtained $Co(OH)_2$ stock solution was mixed with 187.5 mL of aqueous solution containing thioacetamide (1.0575 g) under vigorous stirring. After 30 min, the suspension was transferred into five 100 mL Teflon-lined autoclave and kept at 120 ^{o}C for 6 h. The black product was collected and washed repeatedly with water and ethanol, and then dried at 70 ^{o}C under vacuum for 12 h to achieve Co_3S_4 porous nanosheets.

Preparation of Co_3S_4 porous nanosheets/graphene sheets (Co_3S_4-PNS/GS) Composite: Graphene oxide (GO) was first fabricated according to a modified Hummer's method.[2] In a typical synthesis of Co_3S_4-PNS/GS, 5 mL of GO aqueous suspension (10.0 mg mL^{-1}) was dispersed in DI water (45 mL) and then sonicated for 10 min. Another suspension was prepared by dispersing 100 mg of Co_3S_4-PNS in 100 mL of DI water under sonication. Then, the later suspension was mixed with the formed one under sonication. The resultant mixture was swiftly frozen with liquid nitrogen and freeze-dried for a few days. 150 mg of the freeze-dried powder (Co_3S_4-PNS/graphene oxide composite) was loaded into a small glass beaker, which was further transferred into a glass bottle containing 3 mL of hydrazine monohydrate (Alfa Aesar, 99%), without direct contact between the hydrazine monohydrate and the powder. After sealing, the glass bottle was kept at 120 °C for 2 h to in situ reduce the graphene oxide. After cooling to room temperature naturally, the samples were collected and washed three times with DI water and ethanol, respectively, and then dried at 120 °C under vacuum for 24 h to afford the final product Co_3S_4-PNS/GS. For comparison, GS was synthesized using the same procedure without adding any Co_3S_4-PNS.

Materials characterization: X-ray diffraction (XRD) pattern was taken on a Rigaku D/max 2500/PC diffractometer using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurement was recorded on an ESCALab250Xi electron spectrometer from VG Scientific using 300 W Al Kα radiation. Scanning electron microscopy (SEM) analysis was carried out on a JEOL JSM-7600F scanning electron microscope operated at 10 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations were conducted on a JEOL JEM-2100F transmission electron microscope operated at 200 kV. Scanning transmission electron microscopy (STEM) as well as elemental mapping analysis were carried out on the JEOL JEM-2100F transmission electron microscope equipped with a Thermo Fisher Scientific energy-dispersive X-ray spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449 F3 under air flow with a heating rate of 10 ^{o}C min^{-1} from room temperature to 950 ^{o}C. Assuming complete combustion of GS and the final products of Co_3S_4-PNS/GS and Co_3S_4-PNS are the same cobalt oxide, the content of Co_3S_4 in the Co_3S_4-PNS/GS composite can be calculated based on the following equation:

$$\mathrm{Co_3S_4\,(wt\,\%)} = \frac{\text{final weight of } \mathrm{Co_3S_4}\text{-PNS}}{\text{final weight of } \mathrm{Co_3S_4}\text{-PNS/GS}} \times 100$$

Electrochemical measurements: Electrochemical experiments were carried out by using CR2032 coin cells. To make working electrodes, Co_3S_4-PNS/GS was mixed with Super-P carbon black and poly(vinylidene fluoride) with a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone using mortar and pestle. The resulting homogeneous slurry was pasted onto pure Cu foil (99.9%, Goodfellow) and then dried in a vacuum oven at 80 °C for 12 h. The typical mass loading of active material was 1.0−1.5 mg cm^{-2}. 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate/vinylene carbonate (1:1:0.04 v/v/v) was used as the electrolyte for lithium-ion batteries, and 1M $NaClO_4$ in ethylene carbonate/diethyl carbonate/fluoroethylene carbonate (1:1:0.1 v/v/v) was utilized as the electrolyte for sodium-ion batteries. Glass fibers (GF/D) from Whatman and pure lithium metal foil (sodium metal for sodium-ion batteries) were used as separators and counter electrode, respectively. The coin cells were assembled in an argon-filled glovebox (H_2O, $O_2 < 0.1$ ppm, MBraun, Germany). The charge and discharge measurements of the batteries were galvanostatically performed on a Land CT2001A multichannel battery testing system in the fixed voltage range of 0.005−3 V at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured by a PARSTAT 4000 electrochemical workstation. CV was tested at a scan rate of 0.1 mV s^{-1} while EIS was achieved by applying a sine wave with amplitude of 10.0 mV over the frequency range from 100 kHz to 100 mHz.

References

1 W. Zhao, C. Zhang, F. Geng, S. Zhuo and B. Zhang, *ACS Nano*, 2014, **8**, 10909.

2 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

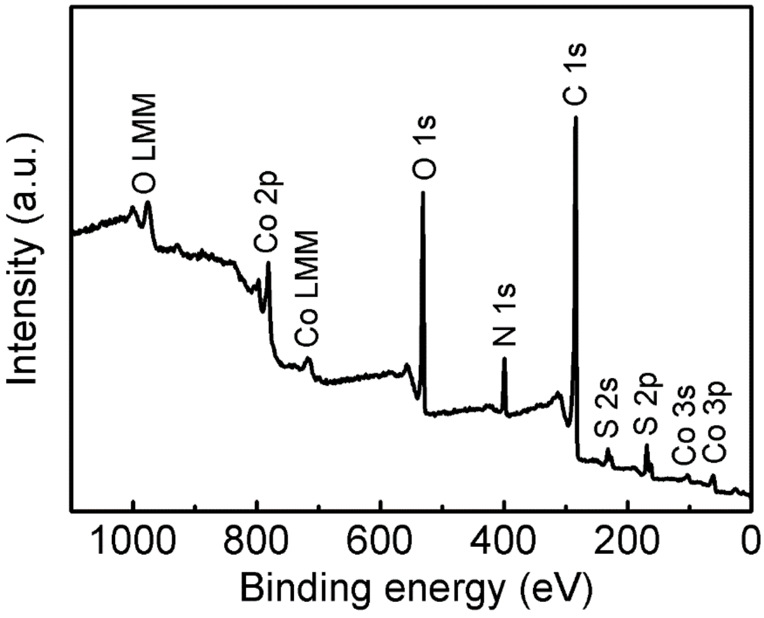

Fig. S1. XPS survey scan of the Co_3S_4-PNS/GS composite.

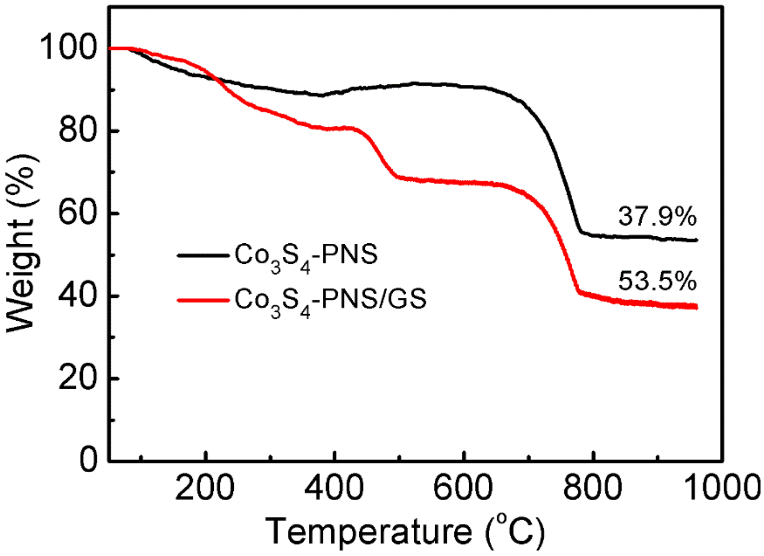

Fig. S2. TGA curves of Co_3S_4-PNS and Co_3S_4-PNS/GS under air atmosphere with a heating rate of 10 °C min^{-1}.

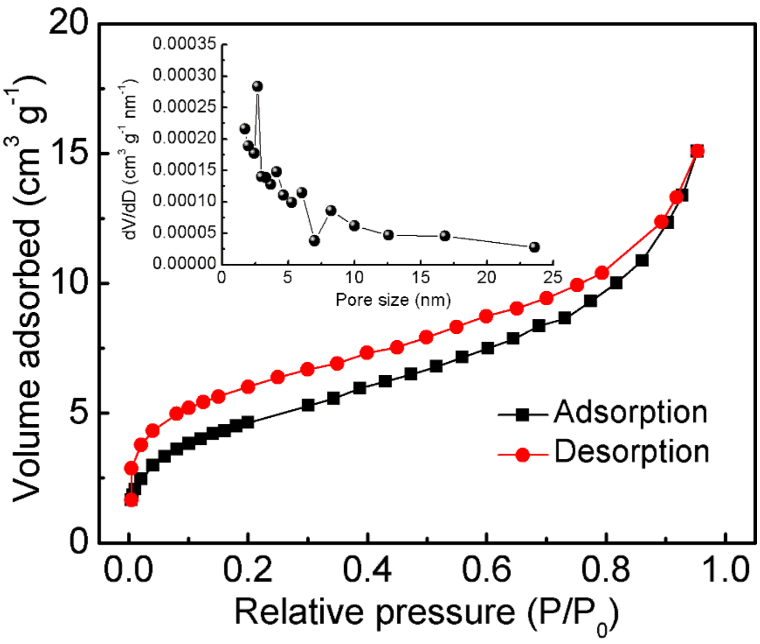

Fig. S3. N_2 adsorption–desorption isotherms of the the Co_3S_4-PNS/GS composite. The inset displays the pore-size distribution calculated from the adsorption branch.

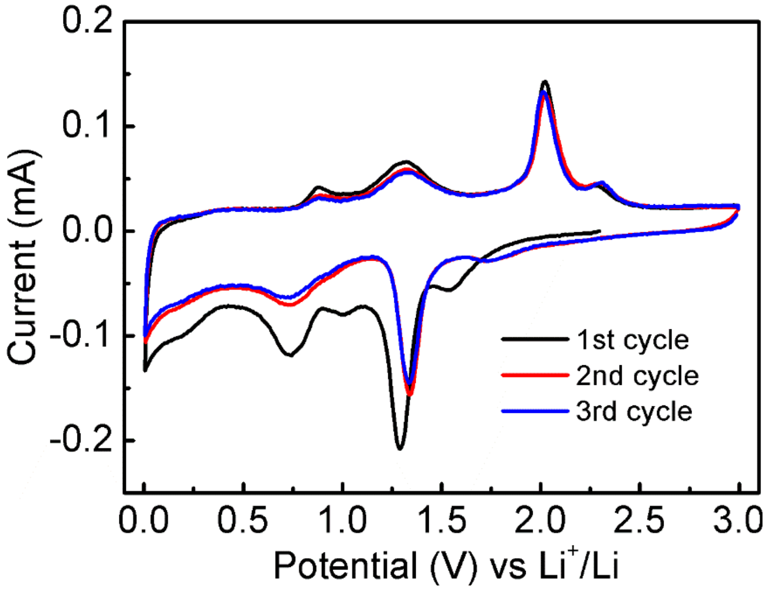

Fig. S4. Cyclic voltammetry curves of Co_3S_4-PNS/GS at a scanning rate of 0.1 mV s^{-1}.

Fig. S4 shows the cyclic voltammetry (CV) curves of the Co_3S_4-PNS/GS composite for the first three cycles in the voltage range from 0.005 to 3 V vs Li^+/Li at s scan rate of 0.1 mV s^{-1}. In the first cycle, three cathodic peaks at 1.54, 1.29 and 1.01 V are observed, which can be attributed the lithium insertion into Co_3S_4 to form $Li_xCo_3S_4$. The following broad peak at 0.73 V can be ascribed to subsequent conversion of Li with Co_3S_4 and the formation of solid electrolyte interphase (SEI). The large peak in the potential range from 0.005 to 0.39 corresponds the insertion of Li into GS, which is electroactive for lithium storage as well. During the anodic scan, four oxidation peaks at 0.88, 1.32, 2.02, and 2.30 V are observed, which are assigned to reverse extraction of Li from GS and $Li_xCo_3S_4$ host, respectively. From the second cycle onward, the cathodic peak at 1.01 V disappears while the original cathodic peaks at 1.54 and 1.29 V shift to 1.75 and 1.34 V, suggesting enhanced reversibility of lithiation and delithiation upon cycling (R. Chen, et al. *Nano Lett.*, 2014, **14**, 5899.). Moreover, no other obvious change is observed for the redox peaks, indicating that the Co_3S_4-PNS/GS electrode shows excellent electrochemical stability.

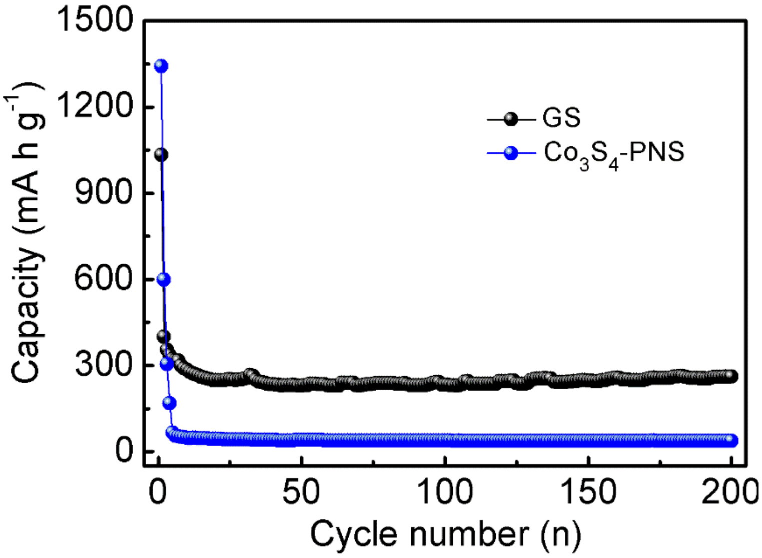

Fig. S5. Cycling performances of GS and Co_3S_4-PNS at a current density of 0.5 A g^{-1} between 0.005 and 3 V vs Li^+/Li.

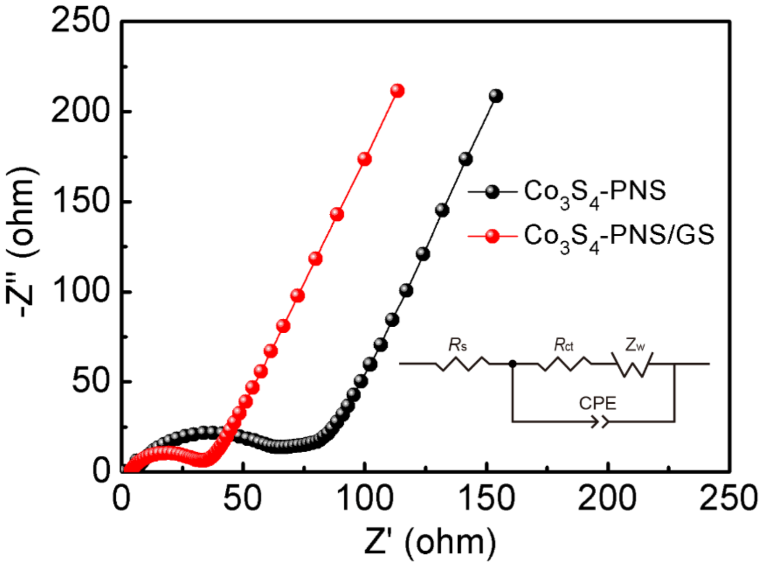

Fig. S6. Nyquist plots and modified Randles equivalent circuit (inset) of the Co_3S_4-PNS and Co_3S_4-PNS/GS electrodes at open potential before cycling.

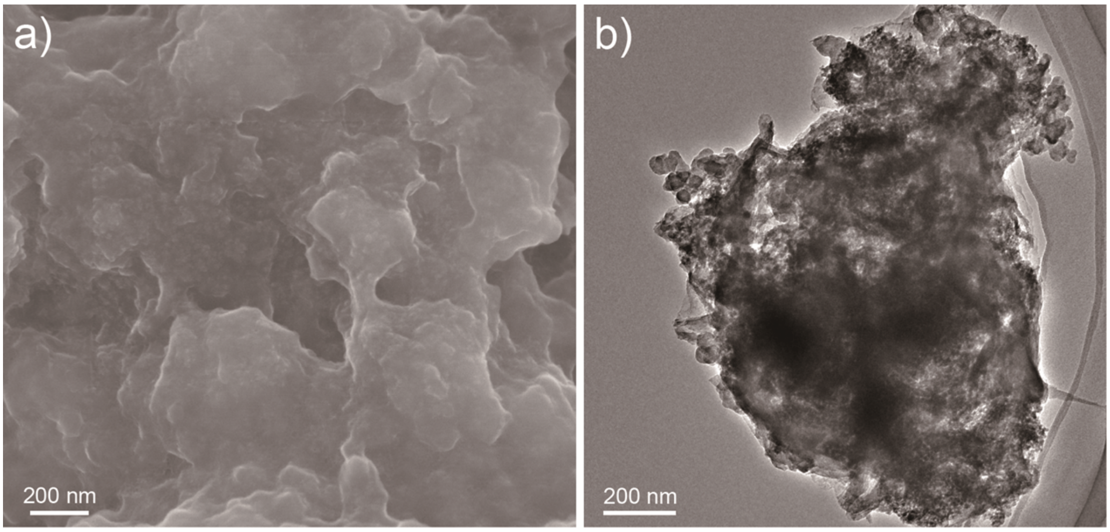

Fig. S7. (a) SEM and (b) TEM images of the Co_3S_4-PNS/GS electrode material after discharging to 1.0 V after 50 cycles.