Electronic Supplementary Information

Incorporation of heterostructured Sn/SnO nanoparticles in crumpled nitrogen-doped graphene nanosheets as anode for lithium-ion batteries

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Experimental Section

***Synthesis*:** For the preparation of NGNSs, graphene oxide (GO) was first prepared through the oxidative treatment of purified natural graphite using a modified Hummers method.[1,2] Then, 10 mL of 50% cyanamide solution (Aladdin) was added into 100 mL graphene oxide solution (about 1.2 mg/mL) under stirring. The GO/cyanamide was dried by heating at 90 ºC and then heated in a tube furnace at 400 ºC for 1 h in an Ar atmosphere to form C_3N_4 polymer film on the surface of the GO. With further annealing at 900 ºC for 2 h and cooling down, the resulting products were carefully collected.

Sn/SnO/NGNSs composite was prepared by a melting diffusion method. Sn nanoparticles (0.3 g) (Shanghai Chaowei company) and NGNSs (0.2 g) were mixed and ground for 10 min. Then the mixture was subsequently heated in a tube furnace at 250 ºC for 6 h in an Ar atmosphere. Strong capillary forces drove the molten Sn into the pores of the crumpled NGNSs, leading to the formation of Sn/SnO/NGNSs composite.

***Characterization*:** The N_2 adsorption/desorption isotherms were collected on a NOVA2200e analyzer (Quantachrome, USA). The X-ray diffraction (XRD) patterns were recorded on a D/max 2550VL/PC X-ray diffractometer (Rigaku, Japan) equipped with Cu Kα radiation (λ = 1.5418 Å, 40 kV, 30 mA). X-ray photoelectron spectroscopy (XPS) was performed on an AXIS Ultra DLD spectrometer (Kratos, Japan) with Al Ka radiation (hv = 1486.6 eV). The Raman spectra were acquired on an inVia-reflex micro-Raman spectrometer (Renishaw, UK) with a 532 nm wavelength incident laser. The morphology and structure of the samples was observed on a NOVA NanoSEM 230 field-emission scanning electron microscope (FESEM, FEI, USA) and a JEM-2100F transmission electron microscope (TEM, JEOL, Japan) operating at 200 kV. The thermogravimetric (TG) analysis was performed on an SDT Q600 thermoanalyzer (DSC-TGA, TA, USA) in air.

***Electrochemical measurements*:** The Sn/SnO/NGNSs composite (80 wt%), Super-P carbon black (5 wt%, Timcal), and sodium carboxymethyl cellulose (CMC, 15 wt%) were mixed in water solution to form a slurry. The slurry was spread onto a Cu foil by a doctor blade method, followed by drying in a vacuum at 70 ºC for 10 h. CR2016 coin cells were assembled in a glove box filled with ultra-high purity argon using polypropylene membrane (UBE Industries Ltd.) as the separator, Li metal as the anode, and 1 M $LiPF_6$ in ethyl carbonate/dimethyl carbonate (EC/DEC) (1:1 v/v) as the electrolyte. The galvanostatic charge and discharge experiment was performed with a battery tester LAND-CT2001A in the potential range of 0.01-3.0 V at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660B electrochemical workstation. Cyclicvoltammetry (CV) was conducted on the workstation at a scanning rate of 0.1 mV s^{-1} in a potential range of 0.01 V to 3.0 V (*vs.* Li/Li^+).

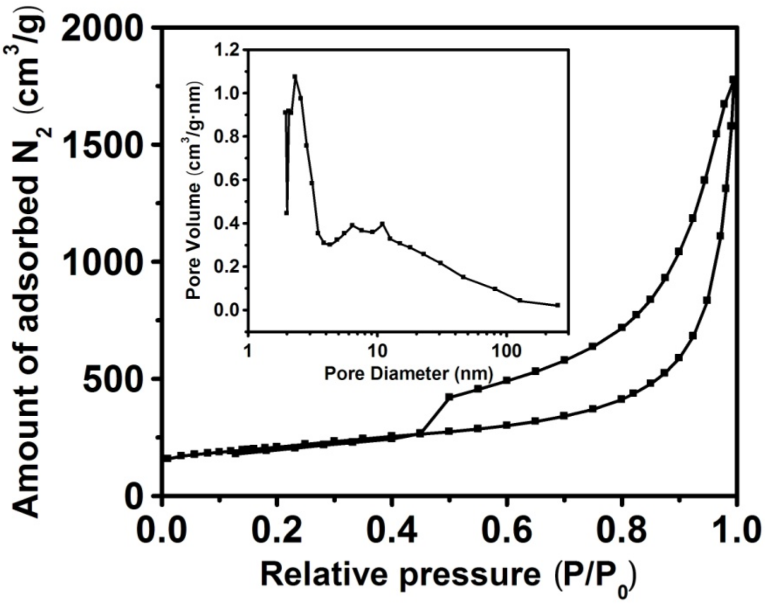

Fig. S1 Nitrogen adsorption-desorption isotherm and pore size distribution curve (inset) of the NGNSs. The Barrett-Joyner-Halenda (BJH) pore size distribution is about 18.8 nm in diameter.

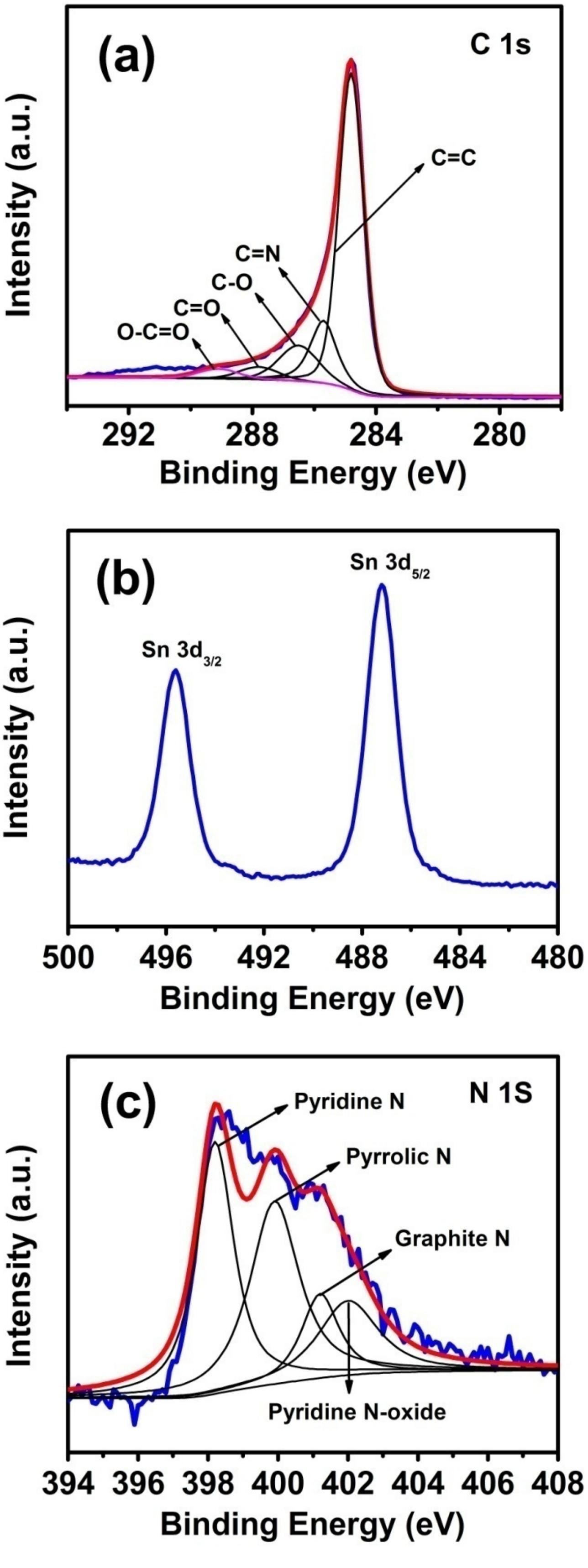

Fig. S2 (a) XPS C 1s spectrum of the NGNSs. (b) XPS Sn 3d spectrum of the Sn/SnO/NGNSs composite. (c) XPS N 1s spectrum of the Sn/SnO/NGNSs composite.

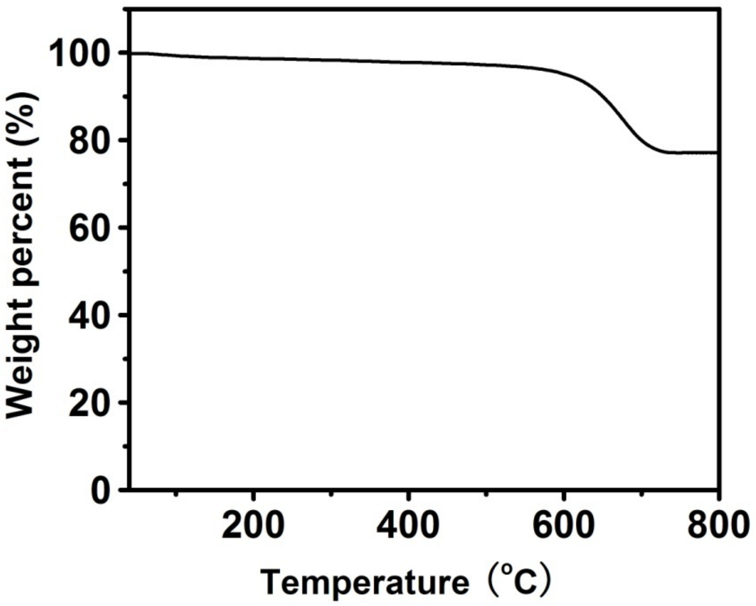

Fig. S3 TG analysis curve of the Sn/SnO/NGNSs composite in air at a heating rate of 20 ºC min^{-1}. The weight loss for the composite is 22.8%, which is attributed to both the decomposition of NGNSs and the oxidation of Sn and SnO to SnO_2. As determined by semi-quantitative XRD analysis, the mass ratio of SnO and Sn in the composite is approximately 14: 86. Combined with TG and semi-quantitative XRD analyses, the contents of Sn, SnO and NGNSs in the composite are approximately 53, 9, and 38 wt%, respectively.

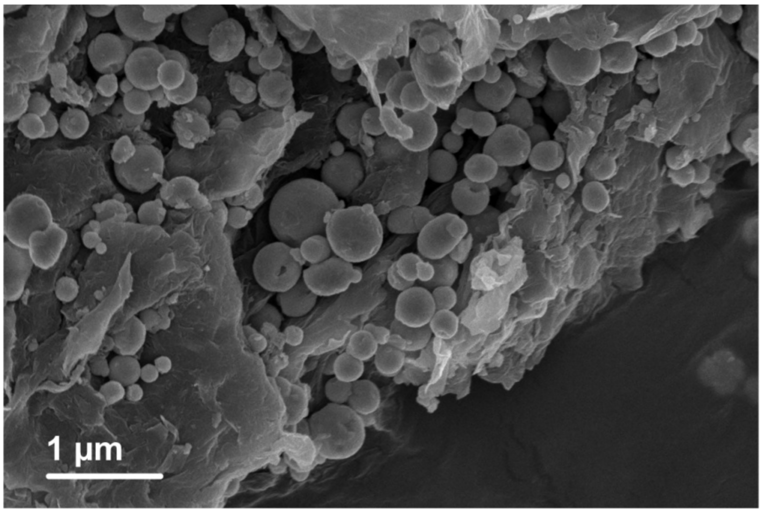

Fig. S4 SEM image of the initial mechanical mixture of NGNSs and commercial Sn nanoparticles.

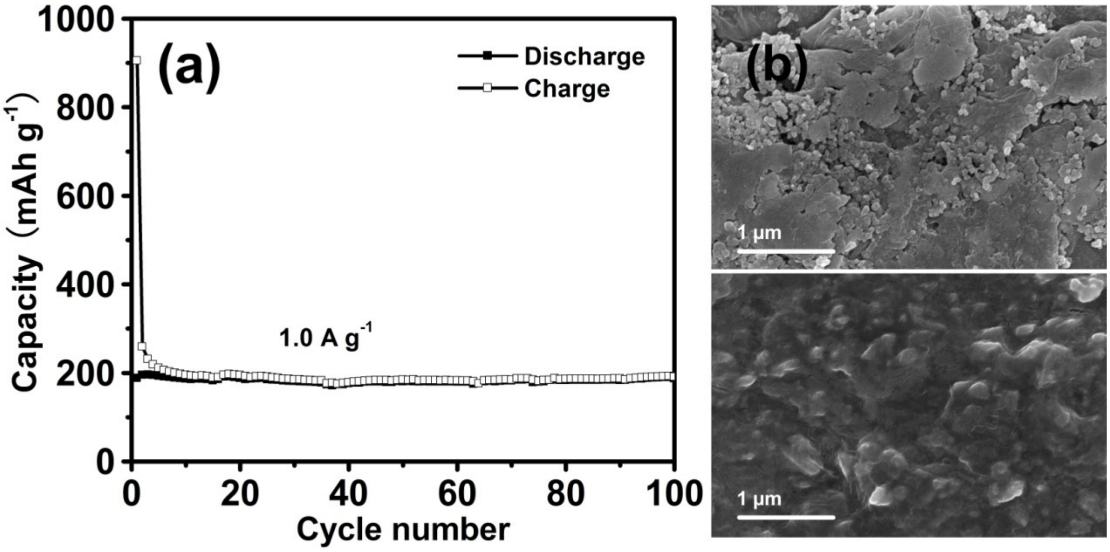

Fig. S5 (a) Cycling performance of NGNSs at a current density of 1.0 A g^{-1} between the voltage limits of 0.01-3 V *vs* Li$^+$/Li. (b) SEM images of the Sn/SnO/NGNSs electrode before (up) and after (down) 250 cycles.

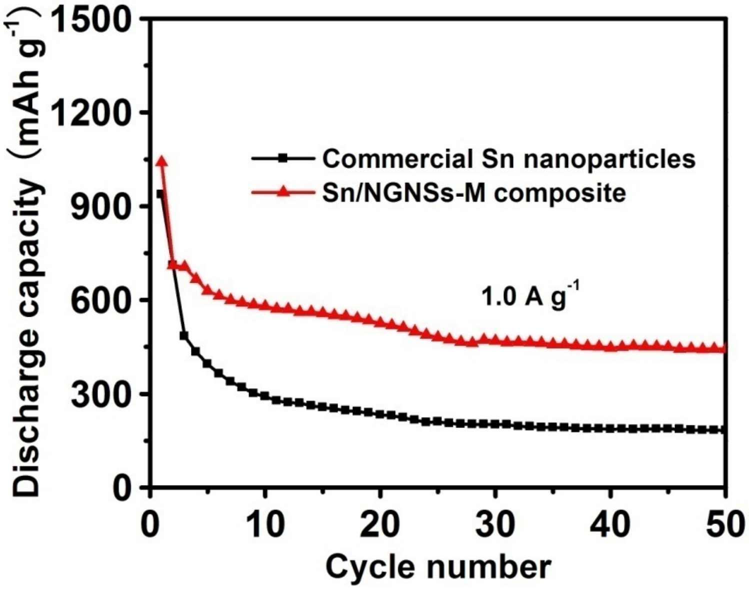

Fig. S6 Cycling performance of commercial Sn nanoparticles and Sn/NGNSs-M composite at a current density of 1.0 A g^{-1} between the voltage limits of 0.01-3 V *vs* Li$^+$/Li.

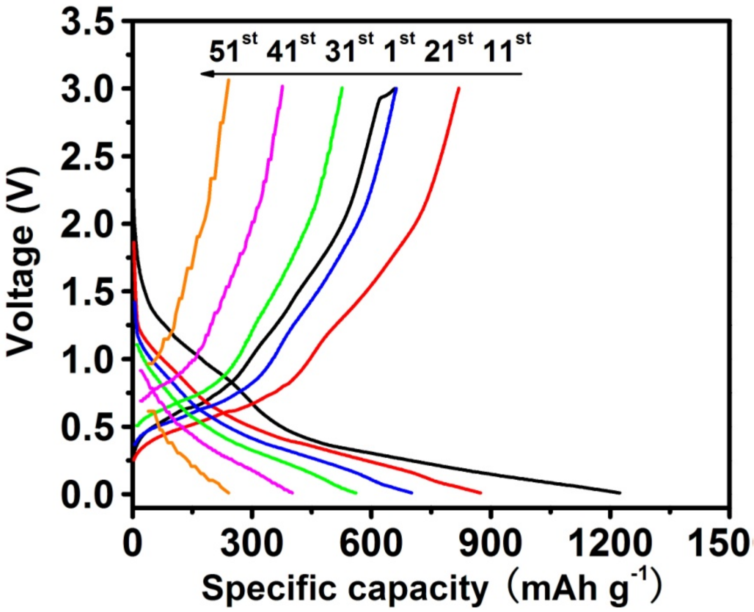

Fig. S7 Charge-discharge profiles of the Sn/SnO/NGNSs composite at various current densities from 1.0 to 16.0 A g^{-1}.

REFERENCES

1. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771.
2. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.