

## An ultrathin surface-nitrided porous titanium sheet as a current collector-free sulfur host for high-gravimetric-capacity lithium–sulfur batteries

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### Experimental section

**Preparation of SOPT and SNPT sheets.** Customized PT sheet (thickness = 0.2 mm, porosity = 65%) was punched into discs to serve directly as cathodes for 2025 coin cells. The SOPT was synthesized by heating the discs to 750 °C in air, at a rate of 200 °C h<sup>-1</sup> and maintaining for 1 h. Under a flow of ammonia gas, the SNPT was synthesized by heating SOPT to 900 °C at a rate of 100 °C h<sup>-1</sup> and maintaining for 1 h.<sup>1</sup>

**Preparation of PT–S, SOPT–S and SNPT–S cathodes.** The PT–S, SOPT–S and SNPT–S composites were synthesized by the same way — chemical liquid deposition (CLD). Specifically, 230 mg Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (99.99%, Aladdin) was dissolved in 50 mL deionized (DI) water, and several discs were spread on the bottom of the beaker. Next, the solution was stirred by a stirring paddle, followed by slowly adding drops of 30 mL HCl (0.1 M). After deposition for 2 h, nano-sized sulfur particles were dispersed uniformly onto these discs at a mass ratio of 40% approximately. The composites were cleaned by anhydrous ethanol and dried at 80 °C for 2 h, then they were heated at 155 °C for 12 h in sealed reaction kettles to incorporate completely.<sup>2</sup>

**Preparation of SNPT–Li<sub>2</sub>S<sub>4</sub> composite.** Inside an Ar-filled glovebox, an appropriate amount of Sulfur (99.95%, Aladdin) and Li<sub>2</sub>S (99.9%, Alfa) at a molar ratio of 3:1 were mixed together in tetrahydrofuran (THF) for 12 h at 60°C. The SNPT sheet was added into the resulting solution, then it was dried under vacuum to obtain SNPT–Li<sub>2</sub>S<sub>4</sub> composite.

**Preparation of Li<sub>2</sub>S<sub>6</sub> solution and the absorption test.** Inside an Ar-filled glovebox, an appropriate amount of Sulfur (99.95%, Aladdin) and Li<sub>2</sub>S (99.9%, Alfa) at a molar ratio of 5:1 were added into the electrolyte (1,3-dioxolane: 1,2-dimethoxyethane = 1: 1, by volume), and the mixture was stirred at 55 °C for 12 h. Four glass vials were all filled with 2 mL Li<sub>2</sub>S<sub>6</sub> solution (equal to 19.2 mg of sulfur), 30 mg of PT, SOPT and SNPT were added into three of the vials separately, and the blank one was left as a comparison.<sup>3</sup>

**Materials characterization.** Thermogravimetric-differential scanning calorimetry analysis (TGA) was performed with a NETZSCH STA 449 F3 differential scanning calorimeter under N<sub>2</sub> atmosphere under a ramp rate of 5 °C min<sup>-1</sup>. X-ray diffraction (XRD) patterns were obtained on a Philips X-ray diffractometer (APD 3520) equipped with Cu K $\alpha$  radiation in the 2-Theta range of 10° to 80°. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Scientific ESCALAB 2201XL instrument using Al K $\alpha$  X-ray radiation. UV–vis absorption spectra were collected on a

LAMBDA 950 UV/Vis Spectrophotometer (PerkinElmer, USA). The surface microstructures were characterized by Field-emission Scanning Electron Microscopy (FE-SEM) with a S-4800 scanning electron microscope operating on 5 kV instruments with an energy dispersive X-ray spectrometry (EDS).

**Electrochemical measurements.** The electrochemical performances were evaluated with standard CR2025 coin cells. Lithium foils and microporous polypropylene separators (Celgard 2400) were used as the anodes and the separators separately, and the electrolyte was composed of 1M lithium bis(trifluoromethanesulfonyl)imide in a mixture of 1,3-dioxolane and 1,2-dimethoxyethane (v/v = 1:1) with 2 wt.% LiNO<sub>3</sub>. The electrolyte volume was 45 μL for each cell, and the cells were assembled in an Ar-filled glove box. Galvanostatic charge/discharge cycles were tested by LAND CT 2001A multichannel battery testers at different current rates of 0.1 C, 0.2 C, 0.5 C, 1.0 C and 2.0 C (1 C = 1000 mA g<sup>-1</sup>) within a potential window between 1.6 V and 2.8 V. Cyclic voltammetry (CV) was conducted on an electrochemical workstation (CHI 760E, Chenghua Corp., Shanghai, China) at a scanning rate of 0.1 mV s<sup>-1</sup> between 1.6 V and 2.8 V, and electrochemical impedance spectroscopy (EIS) was conducted on the same workstation at a frequency range between 100 kHz and 0.01 Hz.

## Supplementary Figures

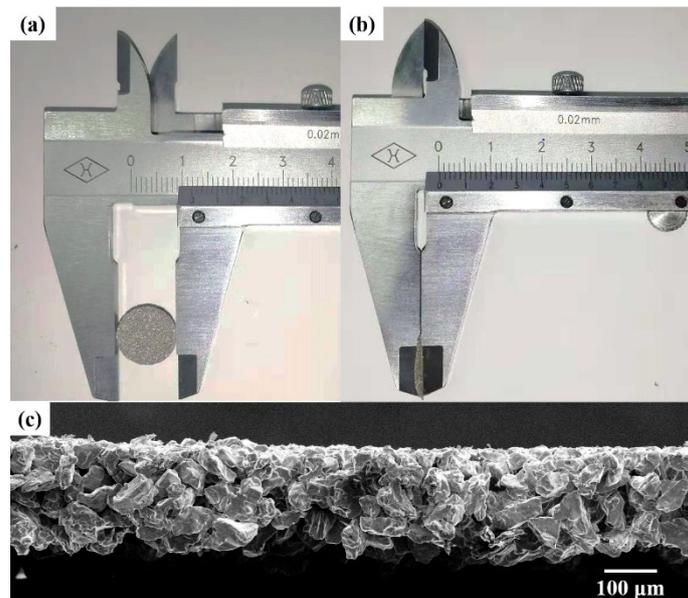


Fig. S1 (a), (b) Real pictures and (c) SEM image of a porous titanium disc.

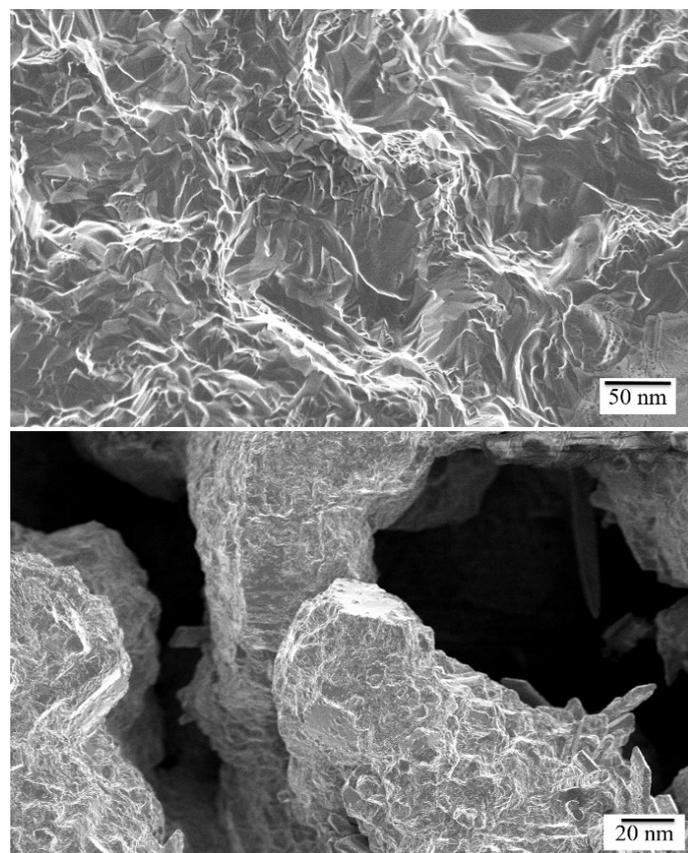


Fig S2 SEM images of the macropores in SNPT sheet.

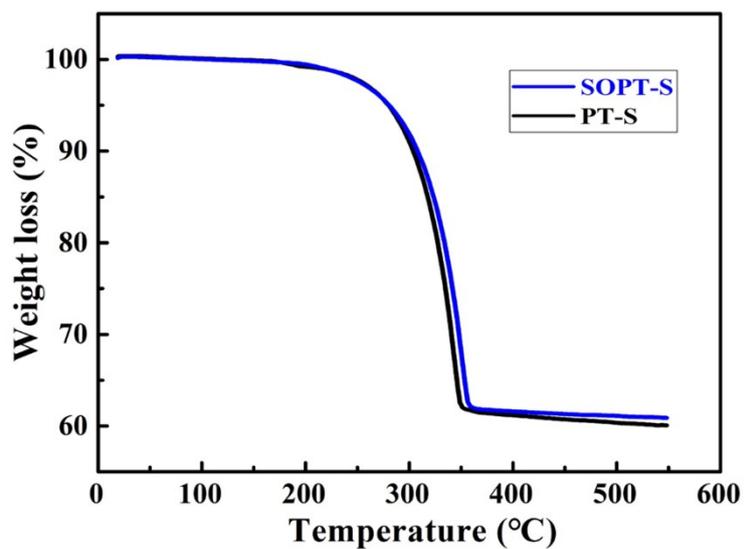


Fig. S3 TGA curve of SNPT and SNPT-S composites.

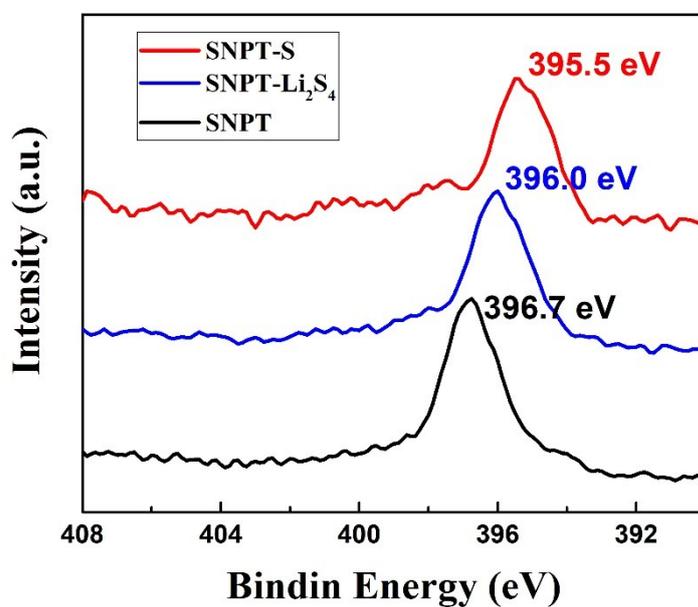


Fig. S4 N 1s spectra of SNPT, SNPT-Li<sub>2</sub>S<sub>4</sub> and SNPT-S composites.

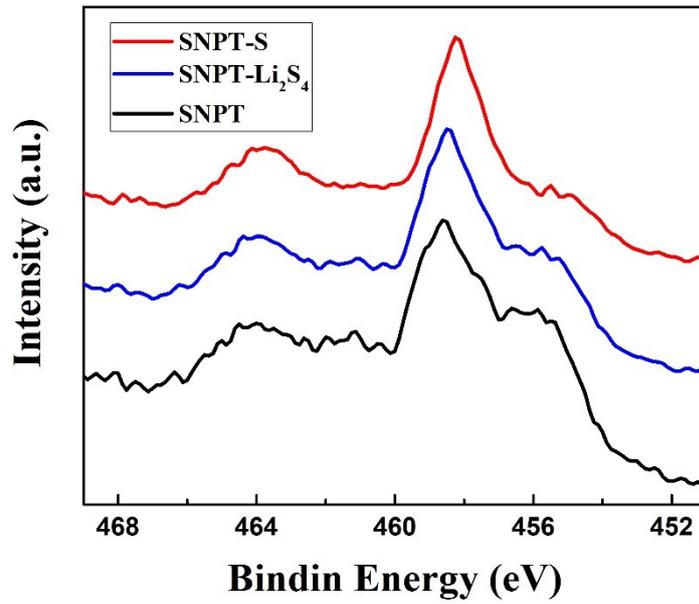


Fig. S5 Ti 2p spectra of SNPT, SNPT-Li<sub>2</sub>S<sub>4</sub> and SNPT-S composites.

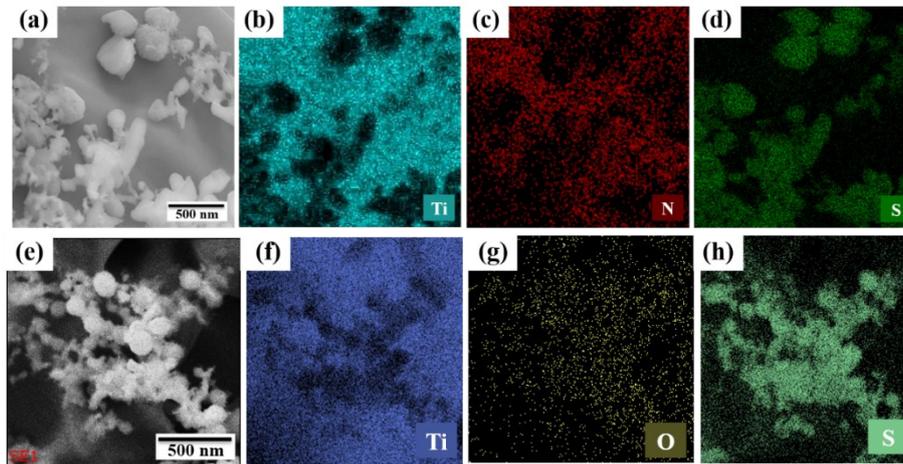


Fig. S6 (a) SEM image of SNPT-S composite and the corresponding elemental maps of (b) Ti, (c) N and (d) S. (e) SEM image of SOPT-S composite and the corresponding elemental maps of (f) Ti, (g) O and (h) S.

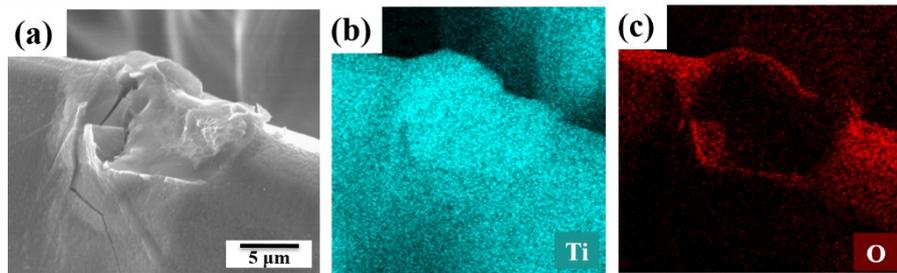


Fig. S7 (a) Cross section SEM image of SOPT sheet and the corresponding elemental maps of (b) Ti, (c) O.

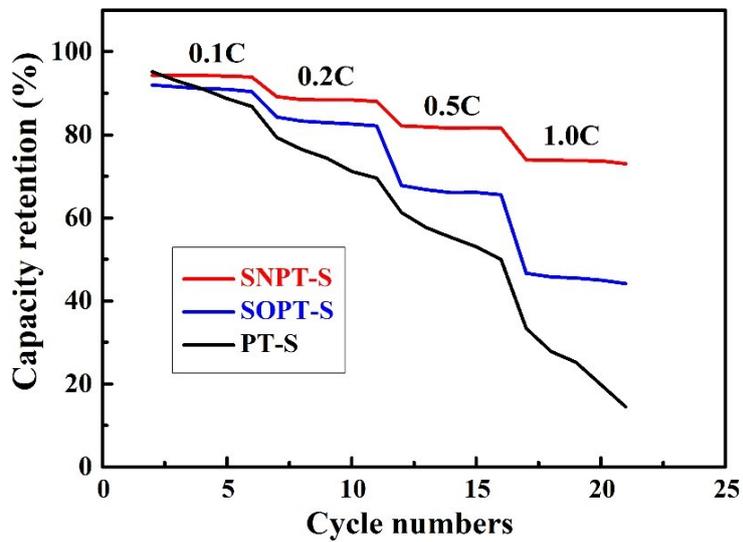


Fig. S8 Capacity retentions upon rate cycling of PT-S, SOPT-S and SNPT-S cathodes.

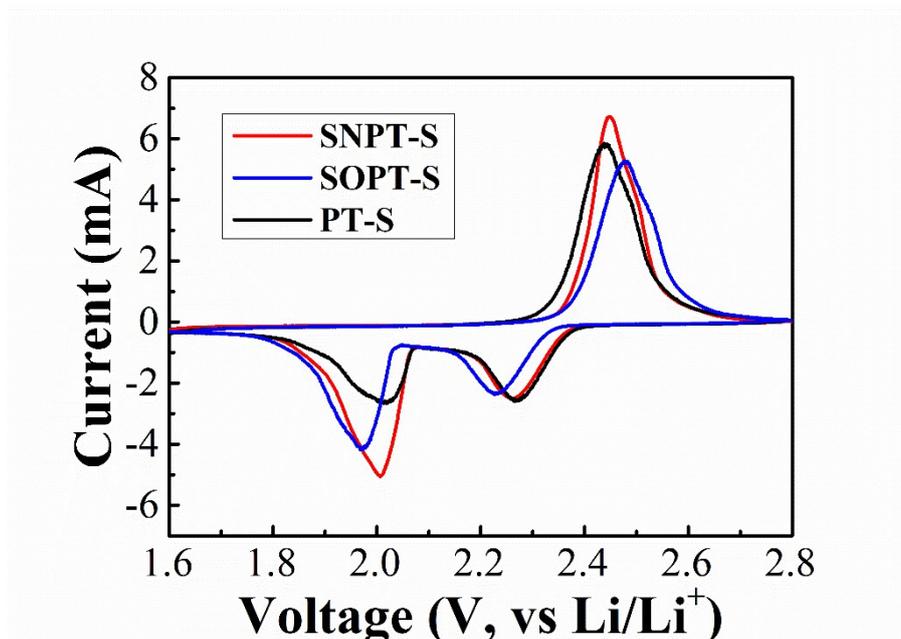


Fig. S9 CV profiles of PT-S, SOPT-S and SNPT-S cathodes during the first scan.

## References

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- 2 H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li, A. Jackson, Y. Cui and H. Dai, *Nano Lett.*, 2011, **11**, 2644–2647.
- 3 (a) T. Chen, Z.W. Zhang, B.R. Cheng, R.P. Chen, Y. Hu, L.b. Ma and Z. Jin, *J. Am. Chem. Soc.*, 2017, **139**, 12710–12715; (b) Z.H. Sun, J.Q. Zhang, L.C. Yin, G.J. Hu, R.P. Fang, H.-M. Cheng and F. Li, *Nat. Commun.*, 2017, **8**, 14627.