

The fabrication of 3D current collector with bitter melon-like TiO₂-NCNFs for high-stable lithium-sulfur batteries

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Experimental section

Synthesis of N-doped TiO₂-NCNFs

8 wt% solution was obtained by dissolving 1.48 g Polyacrylonitrile (PAN, Mw=150000) in 18 ml N, N-Dimethylformamide (DMF) under magnetic stirring overnight. Then 2.5 ml titanium butoxide (TBOT) was dropped into this clear solution and continued to stirring for 10 min to obtain homogeneous white emulsion. TiO₂-NCNFs was synthesized by electrospinning at 60 °C and calcination. The distance between the needle and aluminum foil was 15 cm and the voltage was maintained at 25 KV. Then the precursor nanofibers was stabilized at 280 °C for 2h with a heating rate of 5 °C min⁻¹ and carbonized at 700 °C, 800 °C and 900 °C for 2h under argon atmosphere, 1 °C min⁻¹.

Characterization for TiO₂-NCNFs

XRD patterns were analyzed by Bruker D8 Advance with Cu K α radiation at 40 kV and 40 mA. The morphologies and size of the TiO₂-NCNFs were characterized by scanning electron microscopy (ZEISS Ultra 55) and transmission electron microscopy (JEM-2100HR). EDS mapping was also carried out by EDAX analysis system of JEM-2100HR. The content of TiO₂ was detected using thermal gravity analysis (Netzsch STA449) with a heating rate of 10 °C min⁻¹ under air atmosphere. X-ray photoelectron spectroscopy was gained from ESCALAB 250Xi with Al K α radiation of 30 eV

Preparation of Li₂S₆ and sulfur cathode

3.6 M Li₂S₆ was prepared by dissolving 1.656g Li₂S (Sigma-Aldrich) and 5.76g S (Macklin) in 10ml electrolyte (1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) with volume ratio of 1:1 with the addition of 0.2 M LiNO₃). Then the mixture was heated at 80 °C for 12h under magnetic stirring. All this procedure above was required no water and no oxygen. 10 μ L 1 M Li₂S₆ (equivalent to 1.92 mg of sulfur loading) as the active material was dropping on the freestanding TiO₂-NCNFs current collector to obtain the

S composite cathode. Different mass S loading was to change the volume of Li_2S_6 for comparison. In addition, TiO_2 -NCNFs needed to be activated with small current to diffuse the active material.

Electrochemical tests

Li-S batteries were assembled in CR2016 coin cells with lithium metal as the reference electrode and Celgard 2500 polypropylene membrane as the separator. The as-prepared S- TiO_2 -NCNFs was served as the cathode. The above procedures were carried out in an Ar filled glove box ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) results were obtained from an electrochemical workstation (CHI660E, Shanghai Chen Hua Instruments Ltd) at a scan rate of 0.1 mV s^{-1} from 1.8 to 2.8 V. In addition, the galvanostatic discharge-charge experiments were tested in a NEWARE battery testing system. The specific capacity was calculated with sulfur.

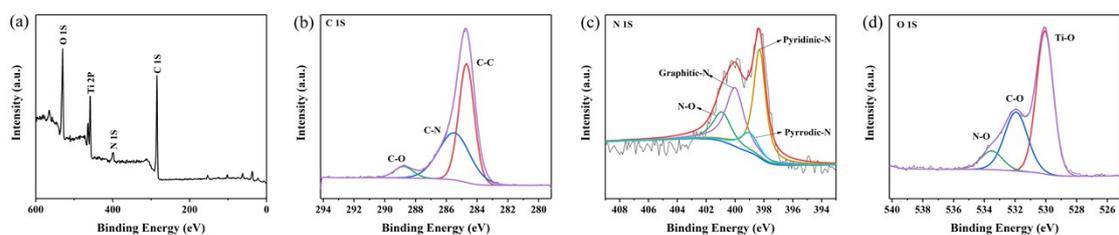


Fig. S1 (a) Wide spectrum and high-resolution XPS of $\text{TiO}_2\text{-NCNFs}$. C 1S spectra (b), N 1S spectra (c) and O 1S spectra (d) of $\text{TiO}_2\text{-NCNFs}$ without Li_2S_6 .

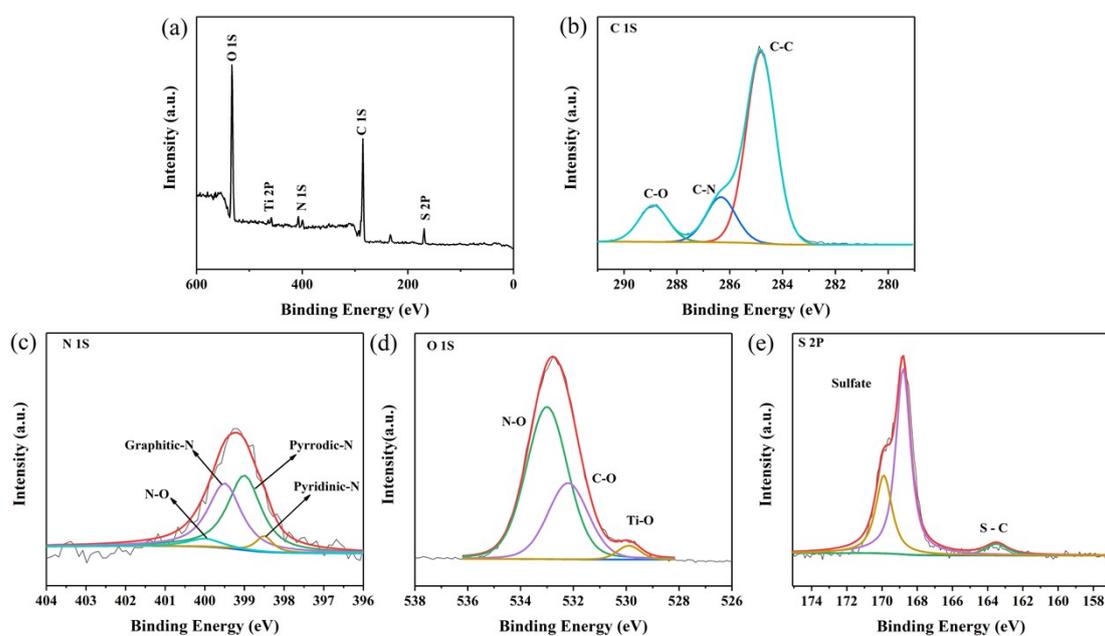


Fig. S2 (a) Wide spectrum and high-resolution XPS of $\text{TiO}_2\text{-NCNFs}$ after adding Li_2S_6 . C 1S spectra (b), N 1S spectra (c) and O 1S spectra (d) of $\text{TiO}_2\text{-NCNFs}$ with Li_2S_6 . (e) S 2p after adsorbing Li_2S_6 . (There are oxidation of Li_2S_6 to sulfate for contact with air for seconds.)

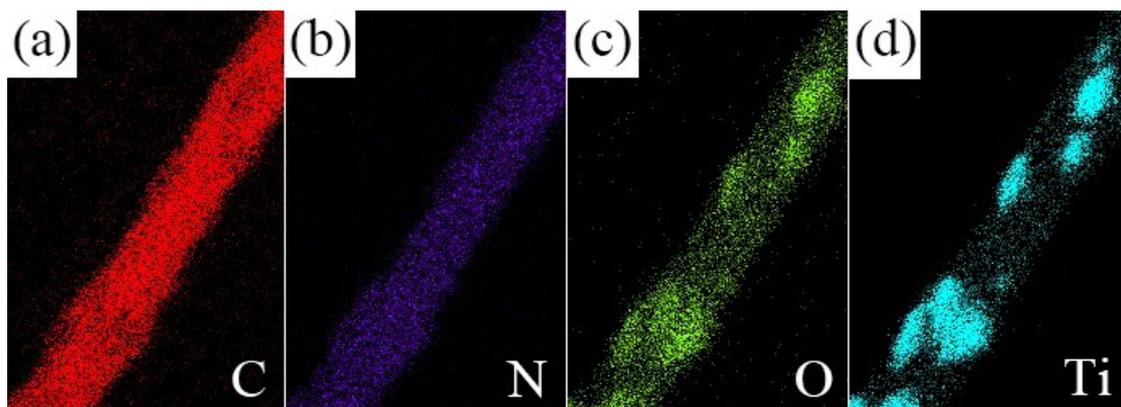


Fig. S3 EDS mapping of TiO₂-NCNFs.

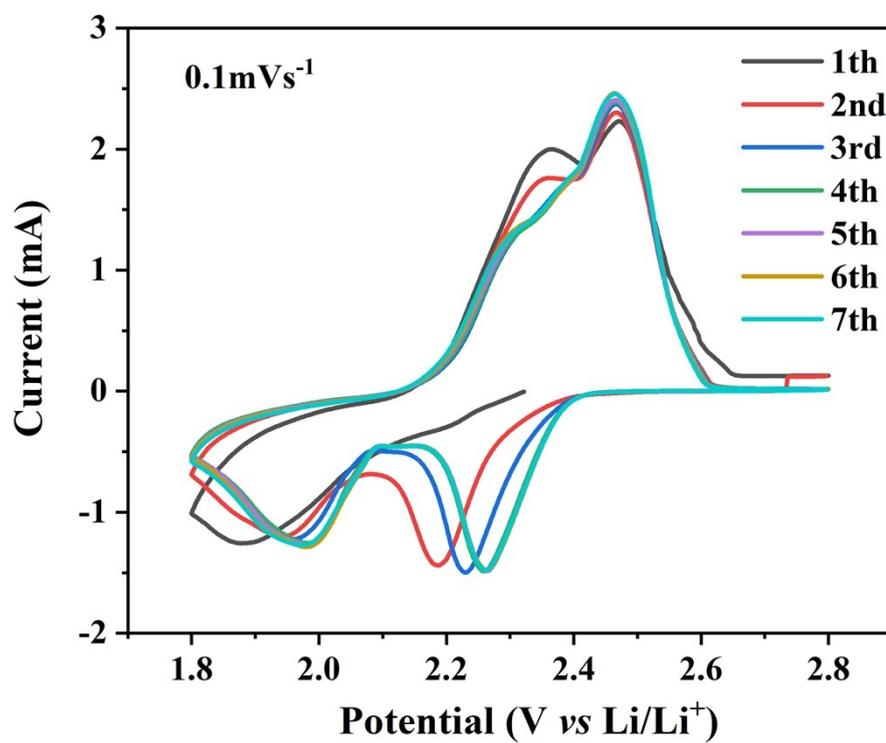


Fig. S4 CV test of TiO₂-NCNFs before activation.

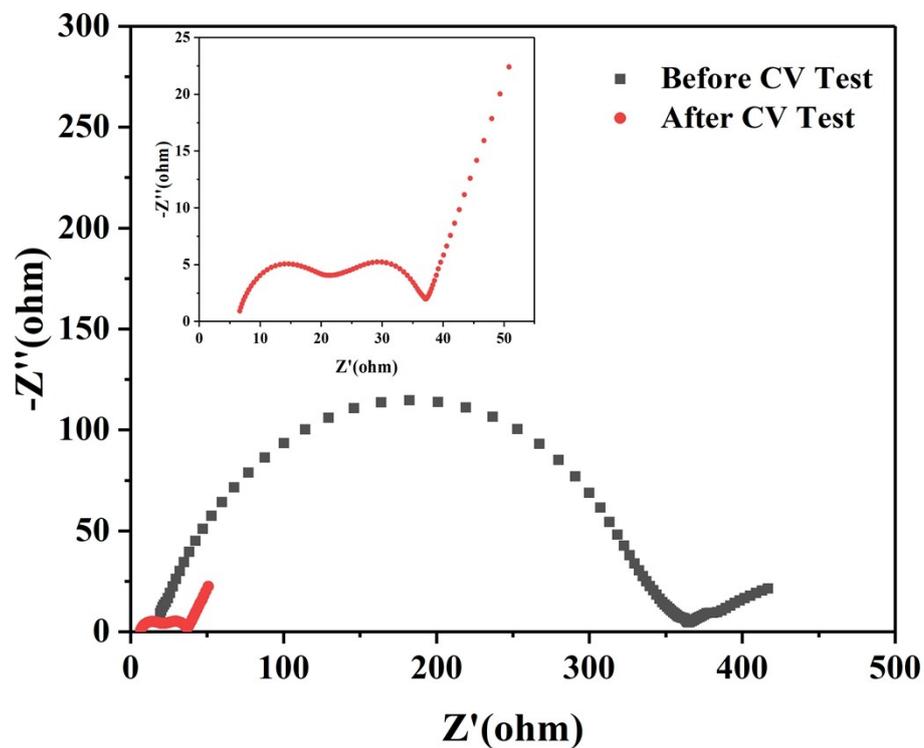


Fig. S5 EIS of TiO₂-NCNFs before and after activation.

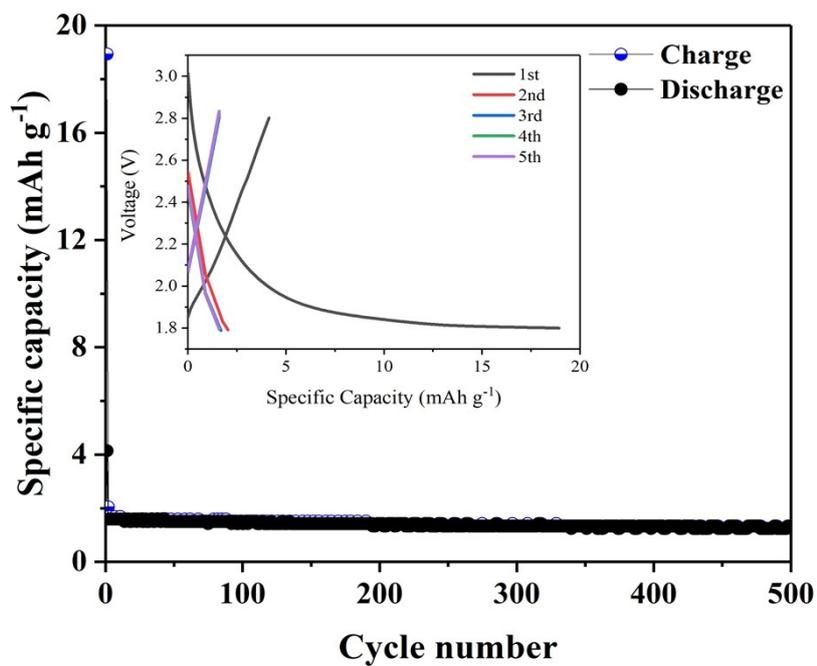


Fig. S6 Cycling performance of TiO₂-NCNFs-700°C without Li₂S₆.

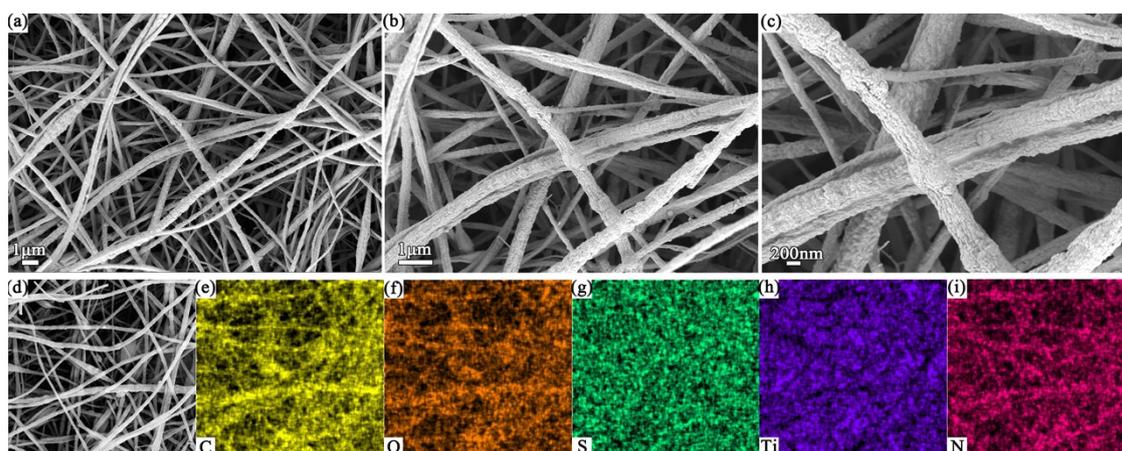


Fig. S7 SEM image of TiO₂-NCNFs after galvanostatic charge/discharge for 200 cycles.

Table. S1 Comparison of cycling performance in Li-S batteries with different Ti-based materials.

Reference	Sulfur loading	Initial capacity (mAh g ⁻¹)	Capacity Retention (after cycles)	Materials
1	-	1328	39.2% (0.2C after 500 cycles)	CNF-TiO ₂ interlayer
2	3.2 mg cm ⁻²	915	77% (0.2 C after 100 cycles)	TiO ₂ -ACF/S hybrid electrode
3	0.18 mg cm ⁻²	667.7	64% (1 C after 300 cycles)	Rutile TiO ₂ mesocrystals
4	67.8 wt%	1040	62.5% (0.5 C after 200 cycles)	HCNF@TiO ₂
5	-	1002	71.06% (1 C after 500 cycles)	TiO ₂ @NC interlayer
This work	1.5	865	91% (0.2C after 200 cycles)	TiO₂-NCNFs Current collector

Reference:

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