

Titanium Silicalite as a Radical-Redox Mediator for High-Energy-Density Lithium-Sulfur Batteries

*Dan Chan^{+a}, Zhubing Xiao^{+b}, Zeqing Guo, Yuchong Lai, Yonggui Zhang, Suyu Zhou, Xingwei Ding, Huagui Nie, Zhi Yang^{*a}*

^aKey Laboratory of Carbon Materials of Zhejiang Province, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, 325035, PR China

Email: yang201079@126.com

^bHenan Key Laboratory of Photovoltaic Materials, Henan University, Kaifeng, 475004, China.

[⁺] These authors contributed equally to this work.

Experimental Section

Synthesis of CNTs-S Electrodes

The CNTs-S composites were prepared via a conventional melt-diffusion strategy. In a typical procedure, the CNTs and sulfur (high purity sulfur, 99.999% metal basis, Aladdin) were mixed according to the designment of target composite. Then the powder were ground and heated in an oven at 160 °C for 12 h. The electrode for CNTs-S electrodes were prepared by mixing 80 wt% CNT-S composite materials, 6 wt% polyvinylidene fluoride (PVDF) and 14 wt% conductive agent in NMP to form slurry. After stirring for 1 h, the slurry was pasted onto Al foil and dried at 55 °C overnight.

Synthesis of CNTs-S/TS-1 Electrodes

The electrode for Li-S batteries was prepared by mixing 80 wt% CNTs-S composite materials, 6 wt% PVDF, 14 wt% conductive agent and TS-1 powder (the conductive agent and TS-1 with a percentage ratio of 83:17) to form slurry. Subsequently, after stirring for 1 h, the slurry was pasted onto Al foil and dried at 55 °C overnight. The low areal sulfur loading in this study is about 0.8-1 mg cm⁻² and a high sulfur loading is 4.9 mg cm⁻².

Electrochemical Characterization

Electrochemical experiments were performed via CR2025 coin-type test cells assembled in anargon-filled glovebox with lithium metal as the counter and reference electrodes at room temperature. Celgard 2400 membrane was used as the separator to isolate electrons. The electrolyte was 1 M bis (trifluoromethane) sulfonimide lithium

salt (LiTFSI) with 1% LiNO₃ dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume). The electrolyte/sulfur ratio in this study is about 20:1 (uL/mg). The discharge/charge measurements were conducted using a Neware battery tests system (Neware Technology Co.). Before testing, the cells were aged for 24 h. CV and EIS measurements were performed on CHI660D electrochemical workstation. The scan rate for CV measurements was set as to be 0.1 mV s⁻¹, and the DC voltage was kept at open-circuit voltage and an AC voltage of 5 mV in amplitude was applied with a frequency of 200 kHz-20 mHz in EIS measurements.

Structure Characterization

X-ray diffraction patterns (XRD) were obtained with a D/MAX-2400 diffractometer using Cu K α radiation (40 kV, 100 mA, $\lambda = 1.54056 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultrahigh-vacuum setup, equipped with a monochromatic Al K α X-ray source and a high-resolution Gammatdata-Scienta SES 2002 analyzer. Scanning electron microscope (SEM) images were obtained with a JSM-6700F field-emission scan electron microscope. TEM images were obtained on TECNAI G2F20. The samples were degassed at 200 °C under vacuum for 3 h prior to the measurement. Pore size distribution (PSD) was derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. Total pore volumes were calculated from the amount adsorbed at a relative pressure (P/P₀) of 0.99. Thermo gravimetric analysis (TGA) was measured with a STA449 F3 Jupiter Thermo Gravimetric analyzer (NETZSCH), at a heating

rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere. UV-vis absorption spectroscopy was used to characterize the polysulfide species and their contents in the electrolyte after CV tests.

H-type simulation electrolytic cell measurements

The CNTs electrodes were prepared by mixing CNTs, polyvinylidene fluoride (PVDF) in NMP to form slurry. After stirring for 1 h, the slurry was pasted onto Al foil and dried at $55\text{ }^{\circ}\text{C}$ overnight. The CNTs/TS-1 cathode were prepared by mixing CNTs, TS-1 powder and PVDF in NMP to obtain a homogeneous slurry, the slurry was then coated on an Al foil and dried at $55\text{ }^{\circ}\text{C}$ overnight. Pure electrolyte and lithium polysulfides solution were placed on the left and right sides, respectively. At a scan rate of 50 mV s^{-1} , we performed CV tests in a potential window of 1.5-3.0 V using CNTs and CNTs/TS-1 cathodes and Li foil anodes.

Synthesis of polysulfides solution

The Li_2S_x ($x=8, 6, 4$) solution with an overall stoichiometric ratio matching Li_2S_x ($x=8, 6, 4$) was synthesized according to the literature method.¹ Typically, the stoichiometric sulfur and Li_2S with a molar ratio of $n:1$ ($n=7, 5, 3$) were dissolved in dimethyl sulfoxide (DMSO) in an argon-filled glovebox, the solution was stirred at room temperature for 24 h to form a 10 mmol L^{-1} Li_2S_x ($x=8, 6, 4$) stock solution.

Electrode Preparation: The bare glassy carbon electrodes (GCE) were polished with different sizes alumina slurry on a microcloth and subsequently rinsed with ultrapure water and ethanol. The electrodes were then sonicated in ethanol, and dried under a gentle nitrogen stream. The CNTs/TS-1 cathode was prepared by mixing CNTs, TS-1

powder and PVDF in NMP 10 μ L of the resultant suspension was then dropped onto the GCE surface and dried at 55 $^{\circ}$ C. For comparison, the CNTs cathode was prepared with the same way.

***In-situ* UV-vis adsorption measurements**

To prepare *in-situ* UV-visible spectroscopy measurement, the reactive liquid was fabricated by mixing 10~30 μ L 10 M Li_2S_x solution and 2.8 mL DMSO, meanwhile the CNTs/TS-1 was recognized as working electrode and the Pt wire was used as counter and reference electrode. They were combined in the sealed electrolytic cell. For comparison, the CNTs electrode were tested with the same method.

Symmetrical cell assembly and measurements

In a typical process, each electrode material (CNTs and CNTs/TS-1) and binder with a mass ratio of 4:1 were dispersed in NMP with stirring. The resultant slurry was coated on aluminum foils. The punched electrode disks (14.0 mm) were used as working and counter electrodes. 0.5 mol L^{-1} Li_2S_6 and 1 mol L^{-1} LiTFSI in 40 μ L DOL/DME (v/v, 1/1) were used as the electrolyte. CV measurements of the symmetrical cells were performed at scan rate of 10 mV s^{-1} . EIS tests were conducted at open circuit potential. A sinusoidal voltage with an amplitude of 10 mV and a scanning frequency 0.01-200 kHz were applied.

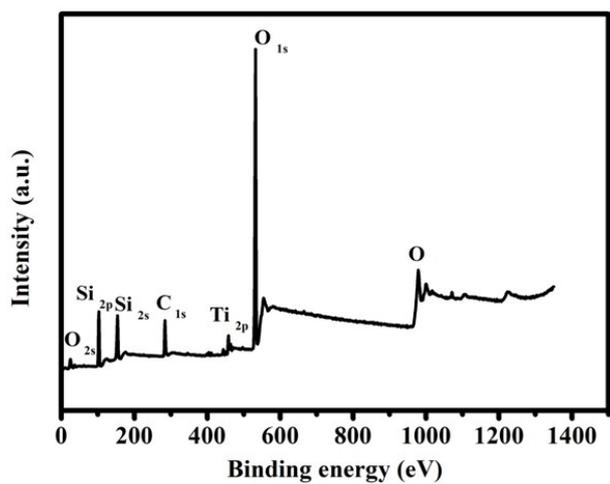


Fig. S1 XPS survey spectra of TS-1.

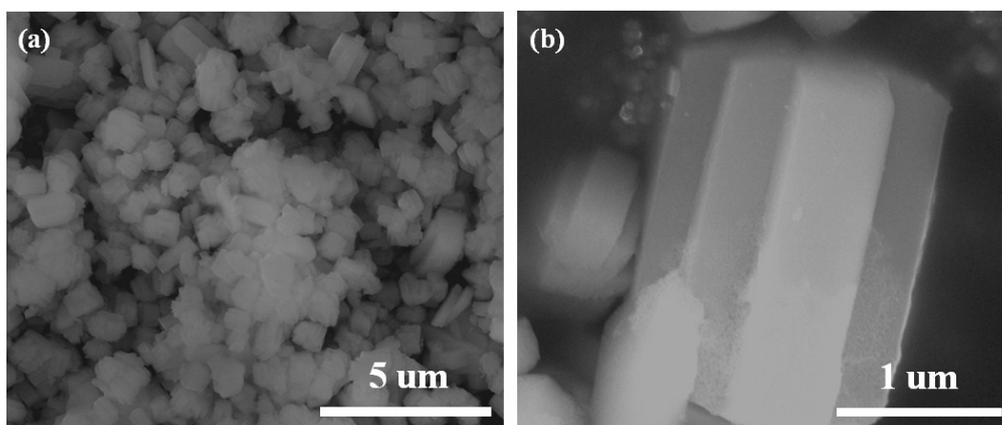


Fig. S2 SEM images of TS-1.

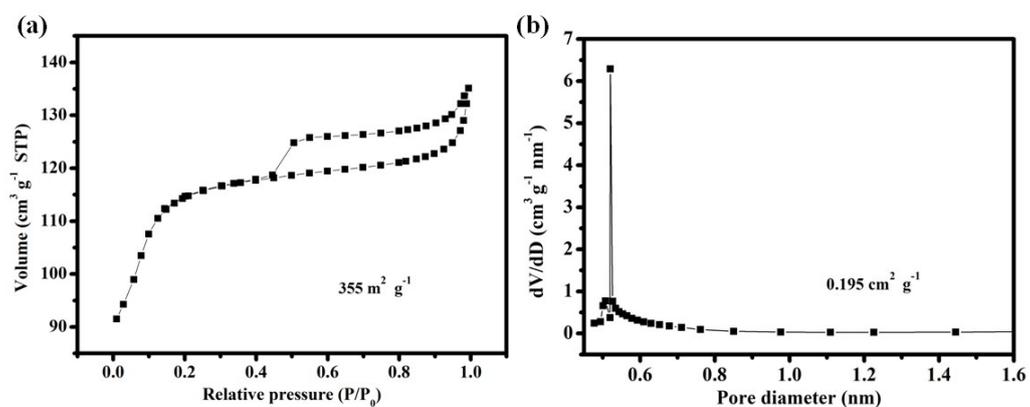


Fig. S3 (a) N₂ adsorption/desorption isotherms of TS-1. (b) Pore-size distribution of TS-1.

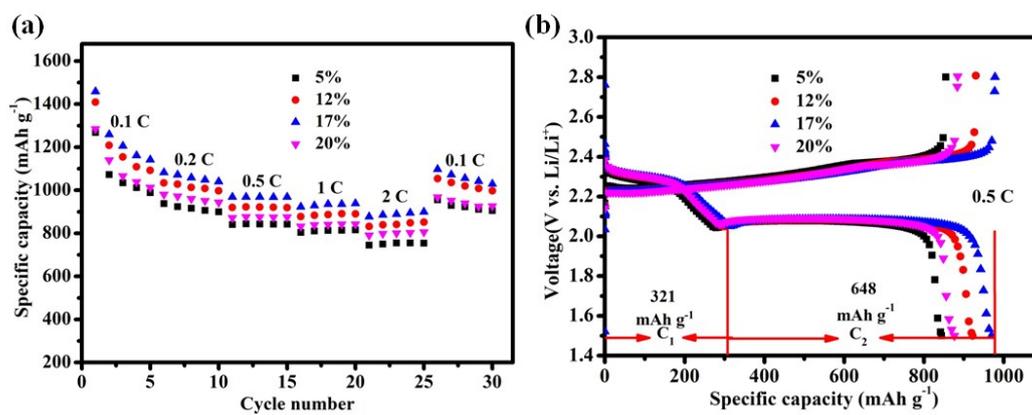


Fig. S4 (a) The rate performance of CNTs-S/TS-1 electrode with different contents of TS-1. (b) Galvanostatic charge-discharge profiles of CNTs-S/TS-1 electrode with different contents of TS-1.

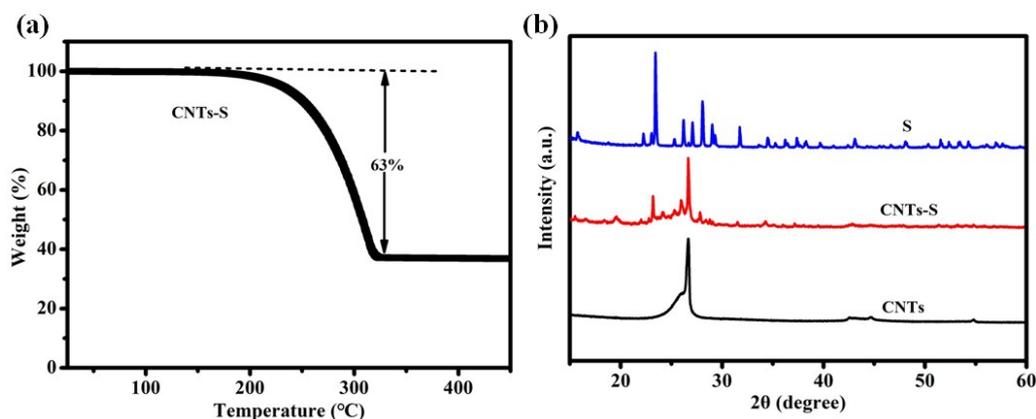


Fig. S5 (a) TGA curve of CNTs-S composite. (b) XRD patterns of pure sulfur, CNTs, CNTs-S composite.

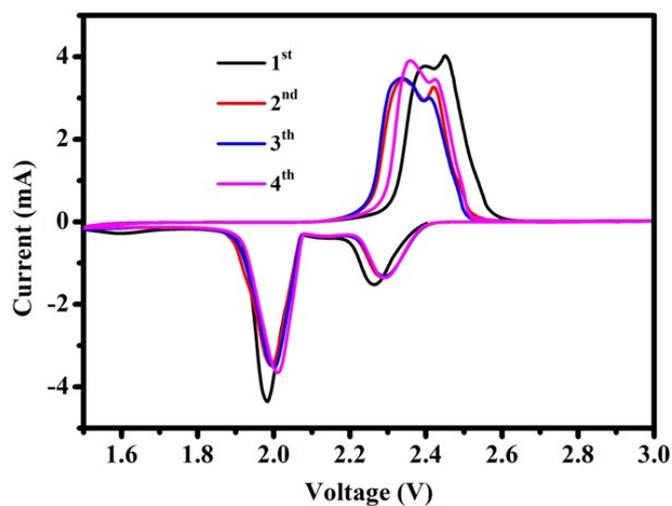


Fig. S6 CV curves for CNTs-S electrode.

Table S1. Collection coefficient and voltage hysteresis of CNTs-S and CNTs-S/TS-1 electrodes

Electrode	Collection coefficient	Voltage hysteresis
CNTs-S/TS-1	2.82	0.33
CNTs-S	2.66	0.35

Table S2. Comparison of different CNTs-S composite materials and CNTs-S/TS-1 electrode in our work.

Materials	S loading	Cycling performance	Capacity retention rate
PCNTs-S/3%T ²	1.2 mg cm ⁻²	0.5 C, 250 cycles, 802~658 mAhg ⁻¹	82%
CC/TiO ₂ /S ³	1.5~2.0 mg cm ⁻²	0.2 C, 240 cycles , 1120~797 mAh g ⁻¹	71.2%
CNTs-S@G/TiS ₂ ⁴	2.8 mg cm ⁻²	0.2 C, 200 cycles , 813~664 mAh g ⁻¹	81.7%
2850CNTs-Gra-S ⁵	3.03 mg cm ⁻²	0.1~1 C,350 cycles 1201~440 mAh g ⁻¹	80%
PCNTs-S@Gra/DTT ⁶	3.51 mg cm ⁻²	0.2 C, 200 cycles, 1253~984mAh g ⁻¹	78.5%
S@CNTs/Co ₃ S ₄ -NBs ⁷	3.5 mg cm ⁻²	0.2 C, 150 cycles 1012~820 mAh g ⁻¹	81.0%
TiC@G ⁸	3.5 mg cm ⁻²	0.2 C,100 cycles 1032~670 mAh g ⁻¹	64.9%
G@HMCN/S-G ⁹	2.0 mg cm ⁻² 3.5 mg cm ⁻² 5 mg cm ⁻²	0.2 C, 50 cycles 1268~1102 mAh g ⁻¹ 1130~972 mAh g ⁻¹ 1050~903 mAh g ⁻¹	87% 86% 86%
FLPT-S ¹⁰	10.5 mg cm ⁻²	0.3C, 60cycles 957~746 mAh g ⁻¹	78.0%
This work	4.9 mg cm⁻²	0.1 C, 198 cycles, 769~658 mAh g⁻¹	71.1%

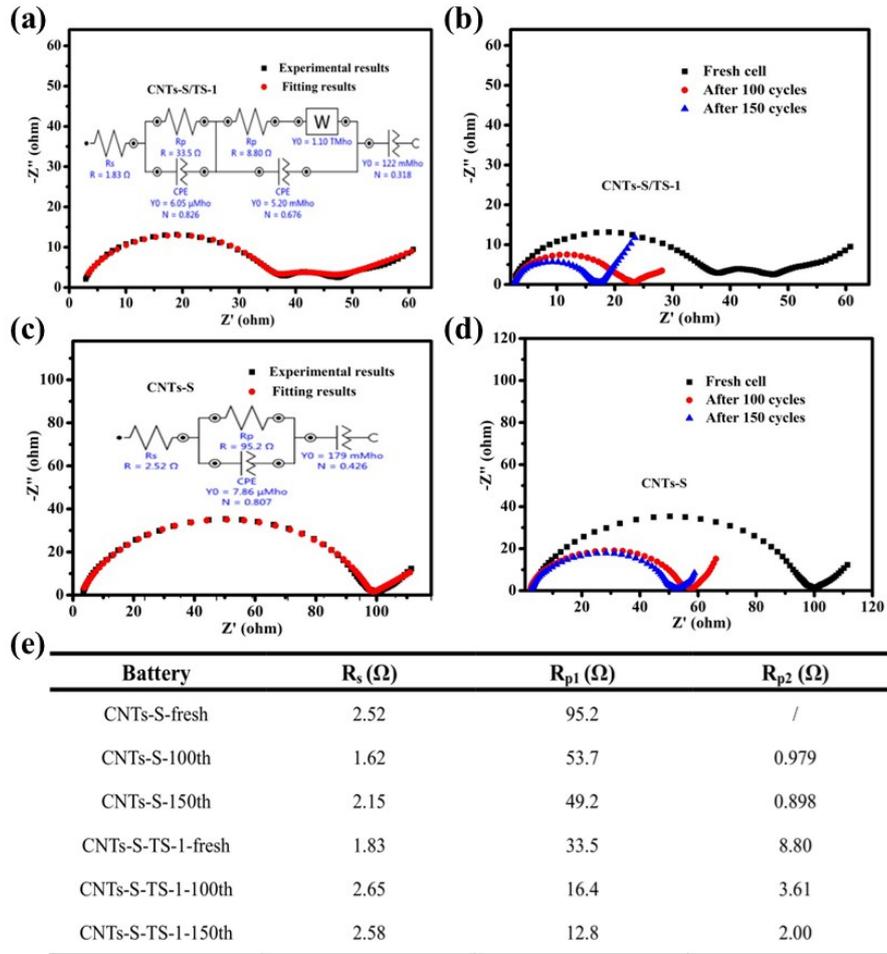


Fig. S7 (a) EIS plot and corresponding equivalent circuits of CNTs-S/TS-1. (b) EIS plots of CNTs-S/TS-1 electrode before and after cycling at 1 C. (c) EIS plot and corresponding equivalent circuits of CNTs-S. (d) EIS plots of CNTs-S electrode before and after cycling at 1 C. (e) The inherent resistance (R_s), the first (R_{p1}) and (R_{p2}) second interface resistance of two electrodes.

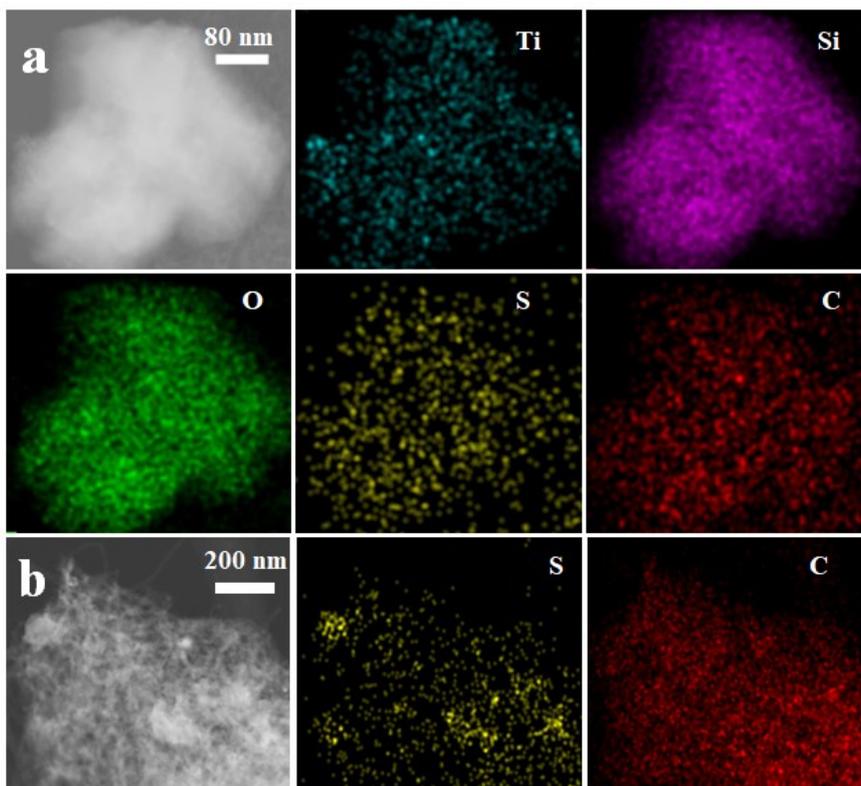


Fig. S8 STEM and corresponding elemental mapping of cycled (a) CNTs-S/TS-1 and (b) CNTs-S electrodes.

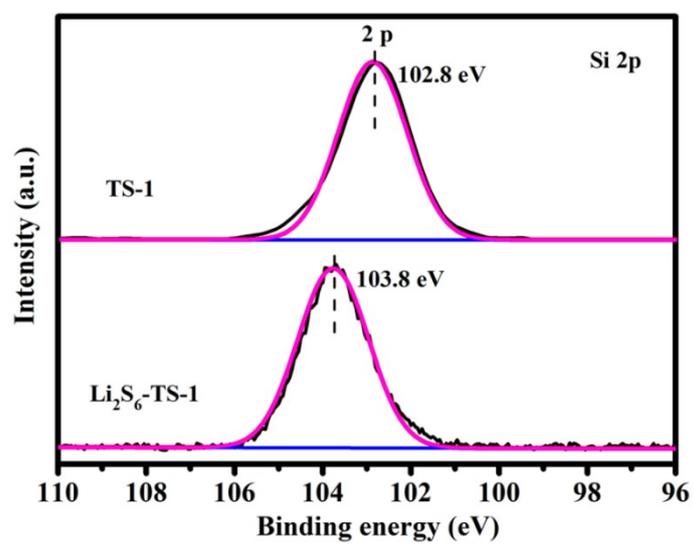


Fig. S9 Si 2p spectra of TS-1 and $\text{Li}_2\text{S}_6\text{-TS-1}$.

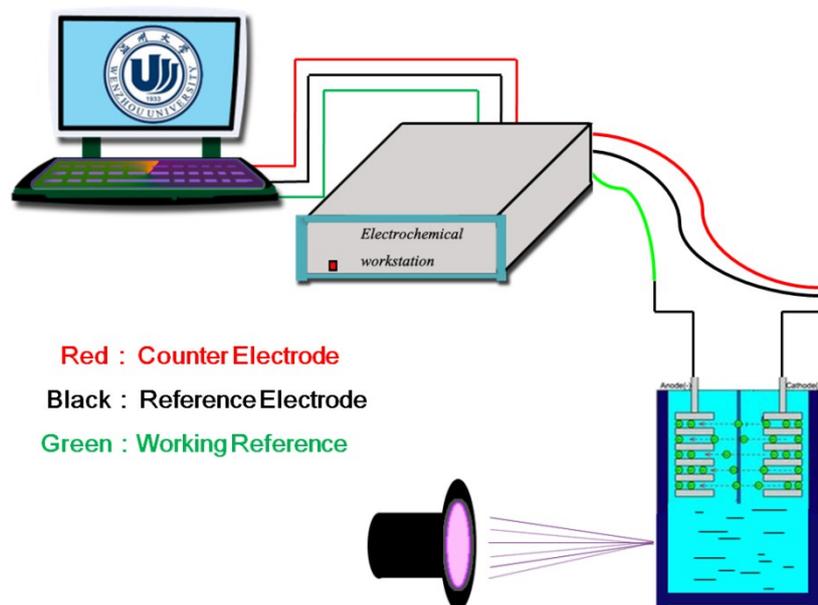


Fig. S10 Schematic illustration of *in-situ* UV-vis measurement.

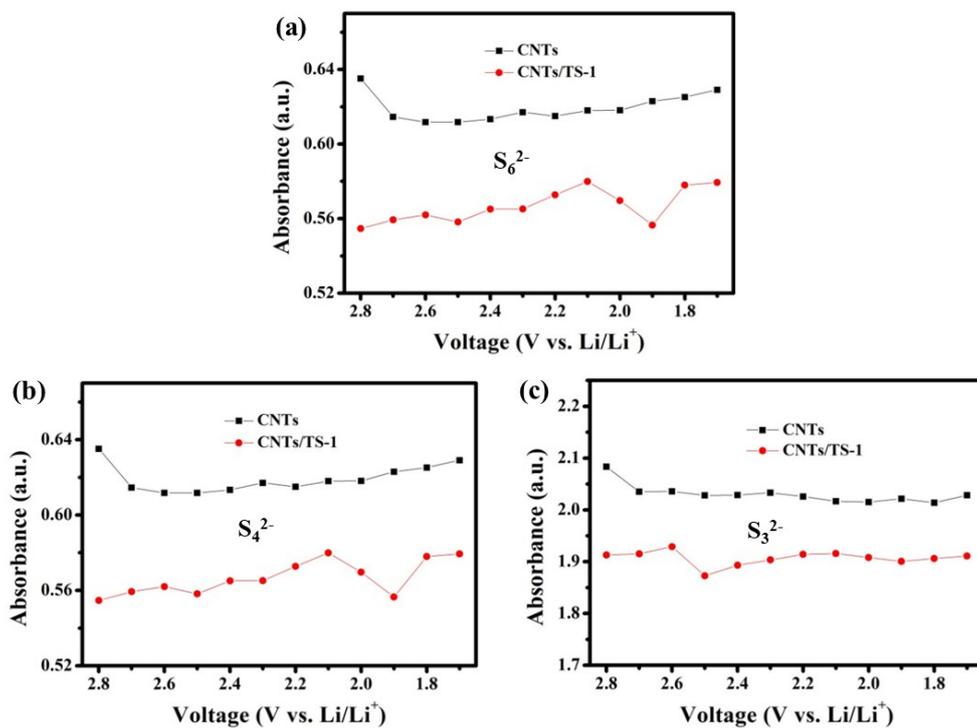


Fig. S11 (a)-(c) Evolution of the UV-vis absorbance at 350, 325 and 270 nm at various stages of the CV scanning in nominal S₈²⁻ solution.

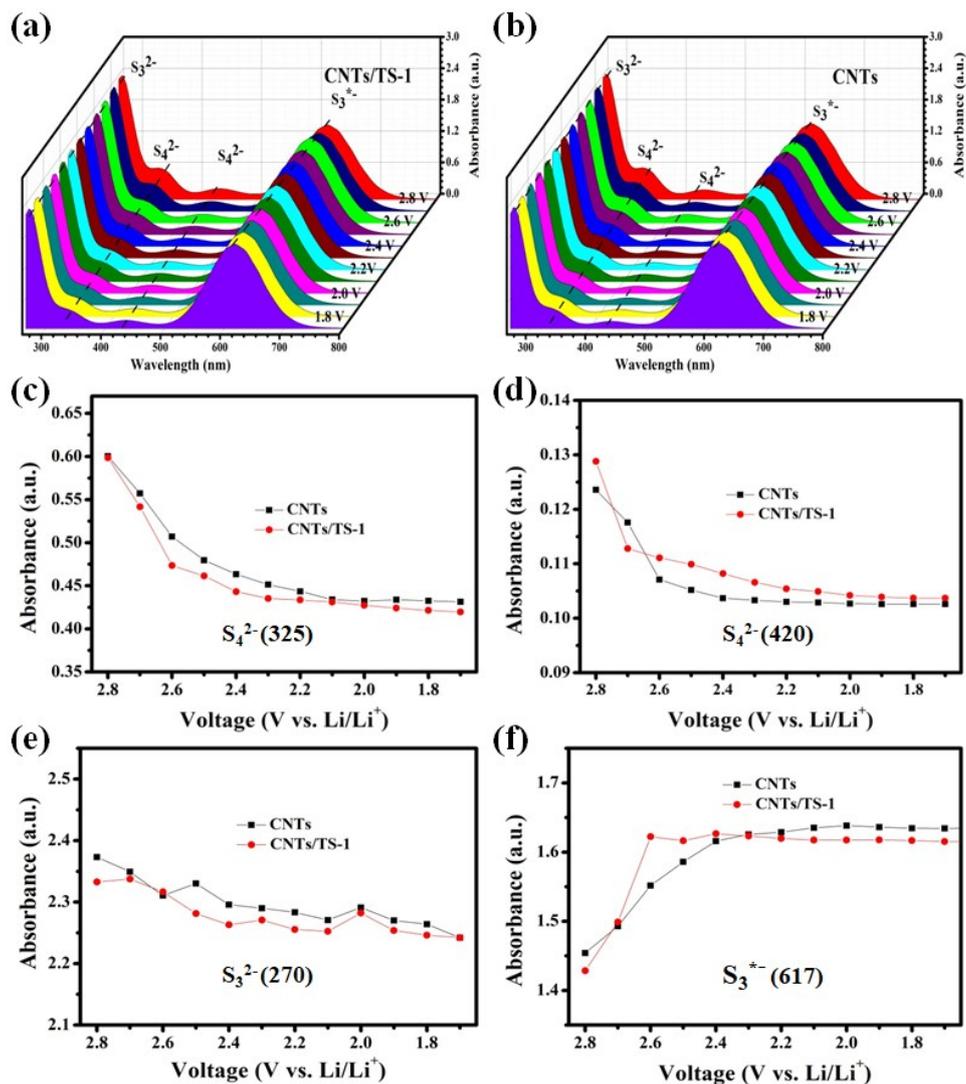


Fig. S12 The *in-situ* UV-vis spectra of sulfur species during discharge process. (a) CNTs and (b) CNTs/TS-1 cell at various voltages in nominal S_4^{2-} solution (UV band attribution: S_4^{2-} at 420 and 325 nm, S_3^{2-} at 270 nm, S_3^{*-} at 617 nm). (c) - (f) Evolution of the UV-vis absorbance at 325, 420, 270 and 617 nm at various stages of the CV scanning in nominal S_4^{2-} solution.

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