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

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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 an argon-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 Kα radiation (40 kV, 100 mA, λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultrahigh-vacuum setup, equipped with a monochromatic Al KR X-ray source and a highresolution Gammadata-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 °C min⁻¹ in nitrogen atmosphere. UV-vis absorption spectroscopy was use 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 °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 °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 Li₂Sₓ (x=8, 6, 4) solution with an overall stoichiometric ratio matching Li₂Sₓ (x=8, 6, 4) was synthesized according to the literature method.¹ Typically, the stoichiometric sulfur and Li₂S 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 Li₂Sₓ (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 uL of the resultant suspension was then dropped onto
the GCE surface and dried at 55 °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 μL 10 M Li$_2$S$_x$ 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$_2$S$_6$ and 1 mol L$^{-1}$ LiTFSI in 40 uL
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) N$_2$ 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

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Collection coefficient</th>
<th>Voltage hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs-S/TS-1</td>
<td>2.82</td>
<td>0.33</td>
</tr>
<tr>
<td>CNTs-S</td>
<td>2.66</td>
<td>0.35</td>
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**Table S2.** Comparison of different CNTs-S composite materials and CNTs-S/TS-1 electrode in our work.

<table>
<thead>
<tr>
<th>Materials</th>
<th>S loading</th>
<th>Cycling performance</th>
<th>Capacity retention rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCNTs-S/3%T²</td>
<td>1.2 mg cm⁻²</td>
<td>0.5 C, 250 cycles, 802~658 mAh g⁻¹</td>
<td>82%</td>
</tr>
<tr>
<td>CC/TiO₂/S³</td>
<td>1.5~2.0 mg cm⁻²</td>
<td>0.2 C, 240 cycles, 1120~797 mAh g⁻¹</td>
<td>71.2%</td>
</tr>
<tr>
<td>CNTs-S@G/TiS₂⁴</td>
<td>2.8 mg cm⁻²</td>
<td>0.2 C, 200 cycles, 813~664 mAh g⁻¹</td>
<td>81.7%</td>
</tr>
<tr>
<td>2850CNTs–Gra–S⁵</td>
<td>3.03 mg cm⁻²</td>
<td>0.1<del>1 C, 350 cycles, 1201</del>440 mAh g⁻¹</td>
<td>80%</td>
</tr>
<tr>
<td>CNTs–Gra–S</td>
<td>3.51 mg cm⁻²</td>
<td>0.2 C, 200 cycles, 1253~984 mAh g⁻¹</td>
<td>78.5%</td>
</tr>
<tr>
<td>PCNTs–Gra/DTT⁶</td>
<td>3.5 mg cm⁻²</td>
<td>0.2 C, 150 cycles, 1012~820 mAh g⁻¹</td>
<td>81.0%</td>
</tr>
<tr>
<td>S@CNTs/Co₃S₄⁻NBs⁷</td>
<td>3.5 mg cm⁻²</td>
<td>0.2 C, 100 cycles, 1032~670 mAh g⁻¹</td>
<td>64.9%</td>
</tr>
<tr>
<td>TiC@G⁸</td>
<td>3.5 mg cm⁻²</td>
<td>0.2 C, 50 cycles, 2.0 mg cm⁻²</td>
<td></td>
</tr>
<tr>
<td>G@HMCN/S-G⁹</td>
<td>3.5 mg cm⁻²</td>
<td>1268<del>1102 mAh g⁻¹, 1130</del>972 mAh g⁻¹</td>
<td>87%</td>
</tr>
<tr>
<td>FLPT–S¹⁰</td>
<td>10.5 mg cm⁻²</td>
<td>0.3 C, 60 cycles, 957~746 mAh g⁻¹</td>
<td>78.0%</td>
</tr>
<tr>
<td>This work</td>
<td>4.9 mg cm⁻²</td>
<td>0.1 C, 198 cycles, 769~658 mAh g⁻¹</td>
<td>71.1%</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Battery</th>
<th>$R_s$ (Ω)</th>
<th>$R_{p1}$ (Ω)</th>
<th>$R_{p2}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs-S-fresh</td>
<td>2.52</td>
<td>95.2</td>
<td>/</td>
</tr>
<tr>
<td>CNTs-S-100th</td>
<td>1.62</td>
<td>53.7</td>
<td>0.979</td>
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<tr>
<td>CNTs-S-150h</td>
<td>2.15</td>
<td>49.2</td>
<td>0.898</td>
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<tr>
<td>CNTs-S-TS-1-fresh</td>
<td>1.83</td>
<td>33.5</td>
<td>8.80</td>
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<tr>
<td>CNTs-S-TS-1-100h</td>
<td>2.65</td>
<td>16.4</td>
<td>3.61</td>
</tr>
<tr>
<td>CNTs-S-TS-1-150h</td>
<td>2.58</td>
<td>12.8</td>
<td>2.00</td>
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</table>
**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 Li₂S₆-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 S$_8^{2-}$ 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.
References:


