# A New Cathode Material Synthesized by Thiol-modificatory Metal-organic Framework (MOF) Covalently Connecting Sulfur for Superior Long-cycling Stability Lithium-sulfur Batteries

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## Experimental Section

### Materials

The CNTs (2-10 nm, purity > 95%) were purchased from Shanghai Aladdin Reagent Co., Ltd. (China). N,N-dimethylformamide (DMF; AR), concentrated sulfuric acid [$H_2SO_4$; 98%, chemical pure (CP)], hydrochloric acid (HCl; 36%, CP), nitric acid (65-68%) and absolute ethyl alcohol were supplied by Beijing Chemical Works (China) and used as received directly. Zirconium chloride (98%, Aladdin), 2-aminoterephthalic acid (99%, Aldrich), Dicyclohexylcarbodiimide (DCC, 99%, Aladdin) and thioglycollic acid (TGA, 99%, Aladdin) were used directly without other processing.

### Synthesis of CNT@UiO66-$NH_2$.

The CNTs were first treated by $H_2SO_4$ and $HNO_3$ (volume ratio 3:1) at 60 ℃ for 2 h to produce acidification of carbon nanotubes (CNT-COOH). For the preparation of Nanosized CNT@UiO66-$NH_2$ particles, 200 mg of CNT-COOH was first dispersed in 65 mL of DMF under sonication for 0.5 h; then, $ZrCl_4$ (predissolved in a HCl/DMF mixture with v(HCl) : v(DMF) 1 : 5) and 2-amino-4,4 ‘ -dicarboxylic acid (predissolved in DMF) at a molar ratio of 1 : 1.4 were mixed and heated at 80 ℃ overnight. The obtained sample was segregated by centrifugation. DMF and absolute ethyl alcohol were successively used to wash the sample 3 times. Finally, the product was dried at 100 ℃ for 24 h in a vacuum.

### Synthesis of CNT@UiO66-SH

CNT@UiO66-$NH_2$ (0.5 g) and DCC (0.5 g) were added to a round bottom flask

containing 10 ml of DMF. To obtain a homogeneous mixture, the mixture was mixed for 3 min through sonication. TGA (0.6 ml) was added dropwise to the mixture and stirred at 25 ℃ for 24 h. The obtained product was isolated through centrifugation. Deionized water and absolute ethyl alcohol were successively used to wash the sample 3 times. Finally, the product was dried at 40 ℃ for 24 h in a vacuum oven.

**Shuttle currents tests:**

Shuttle current tests were performed based on the Narayanan method. In brief, CNT@UIO66-S and CNT@UIO66-$NH_2$/S electrodes were prepared with the aforementioned methods. However, the electrolyte was changed to $LiNO_3$-free electrolyte, aiming to prevent the passivation of lithium anode with $LiNO_3$. For the measurement of shuttle currents, the cells were firstly charged and discharged three times at C/20 rate. Following this, the voltage of the cells was charged to 2.7 V and the cells stayed with an open-circuit state for 10 minutes. Then, the cells were switched to a potentiostatic mode to offset the drop voltage at different stages (2.70, 2.60, 2.5, 2.4, 2.35, 2.3, and 2.25 V) for 2 hour before reaching a steady-state value. The steady-state current was the shuttle current because the voltage would continue to drop if there was no external current to compromise the shuttle effect.

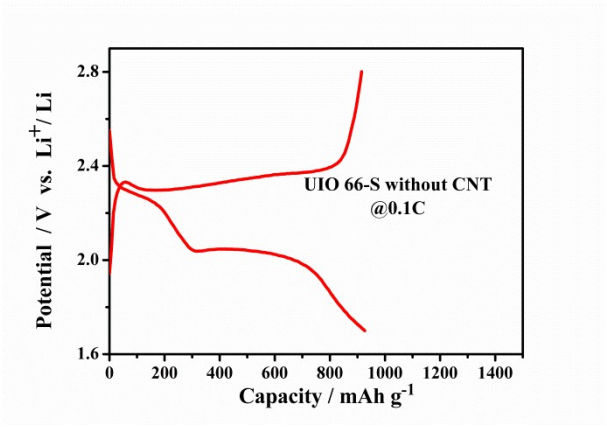


**Figure S1** The charge/discharge curve for UIO66-S/Li coin cell, Current density: 0.1C; cut off voltages: 1.7–2.8 V.

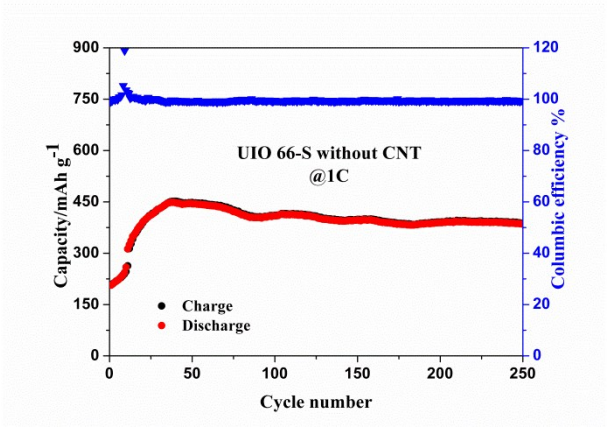


**Figure S2** Cycling performance of the UIO66-S/Li coin cells at 1C

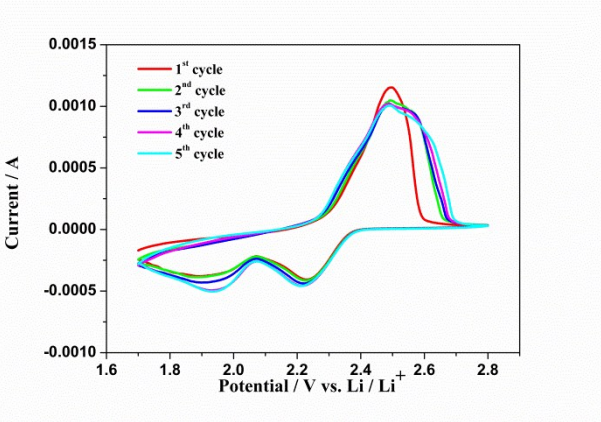


**Figure S3.** CV curves of CNT@UIO66-$NH_2$/S electrode

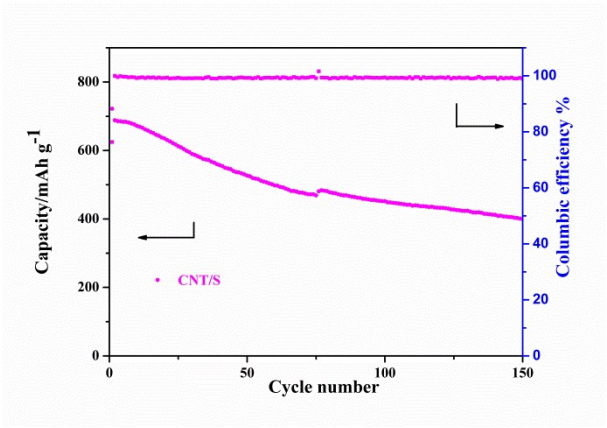


**Figure S4** Cycling performance of the CNT/S/Li coin cells at 1C

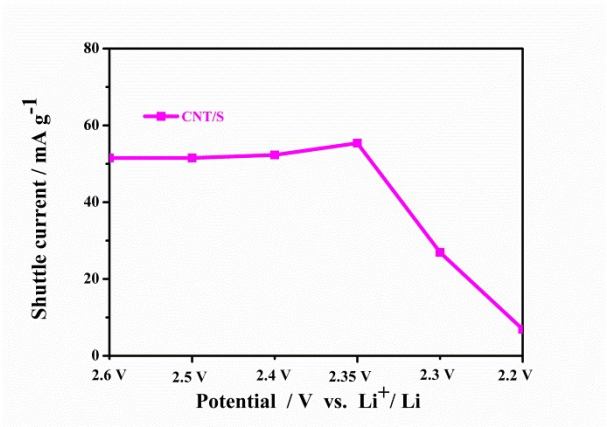


**Figure S5**The shuttling current of CNT/S/Li coin cells

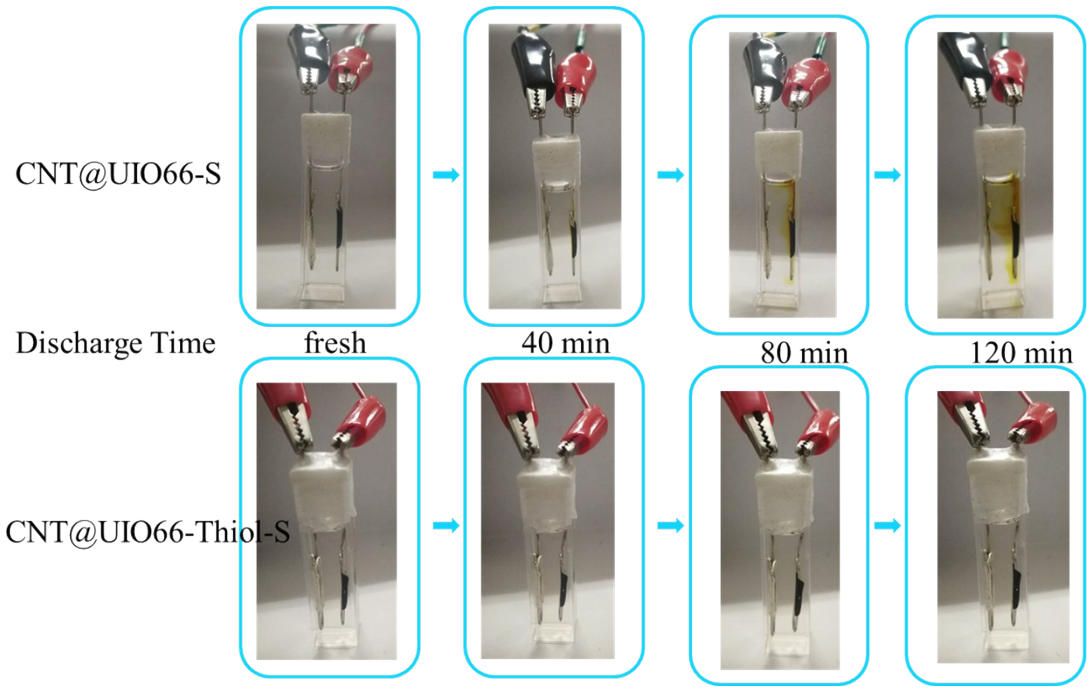


**Figure S6.** Photographs displaying the dissolution of polysulfide intermediates into electrolyte during discharge at 0.5C for CNT@UIO66-S cathode and CNT@UIO66-$NH_2$/S cathode

**Table S1** Elemental analyses data of CNT@UIO66-$NH_2$, CNT@UIO66-SH and CNT@UIO66-S

| Sample | C wt.% | N wt.% | S wt.% |
|---|---|---|---|
| CNT@UIO66-$NH_2$ | 45.5 | 4.3 | 0.1 |
| CNT@UIO66-SH | 41.9 | 3.2 | 7.5 |
| CNT@UIO66-S | 19.3 | 1.4 | 53.6 |

**Table S2** Comparison of the cycle performance of the reported electrodes material by simply blending sulfur with MOF. (1C=1675 $mA \cdot g^{-1}$)

| Cathode materials | Discharge current | Maximum Capacity (mAh $g^{-1}$) | Capacity retention ( Cycle Numbers ) | Capacity fading rate (% per cycles) | Reference |
|---|---|---|---|---|---|
| **CNT@UIO66-S** | 1 C | 660 | 92.12% (550) | 0.017 | This work |
| | 2 C | 519 | 80.19% (900) | 0.022 | |
| **S/D-CNTs@ZIF-8** | 1C | 550 | 85% (300) | 0.05 | 1 |
| **NCCNT-Co-S** | 1C | 986 | 88% (500) | 0.024 | 2 |
| **S/MOF-74-Ni/CNT** | 2C | 773 | 65.1% (400) | 0.087 | 3 |
| **CNT@CoNC/S** | 0.2C | 1174.6 | 79.8% (500) | 0.0403 | 4 |
| **S/CN-5@NSHPC** | 1C | 615 | 72.3% (500) | 0.048 | 5 |
| **CNT-GC@NC/S** | 1C | 863 | 67.2% (800) | 0.041 | 6 |
| **S/ZIF-8** | 0.5C | 738 | 75% (300) | 0.083 | 7 |
| **S@Co-N-GC (ZIF-67)** | 1C | 1150 | 54% (500) | 0.092 | 8 |

## References


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