

Support information

Experimental section

Preparation of carbon-sulfur electrode

Commercial carbon black was mixed with sulfur powder and dried at 80 °C for 12 h to remove moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and then 300 °C for 3 h. The obtained sulfur-carbon black composites maintained 65 wt% sulfur loading. The electrodes were prepared by slurry casting onto aluminum foil. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluoride (PVDF) is 70:20:10. The as-prepared electrodes were finally dried at 80 °C over 12 h under vacuum.

Preparation of alucone coating on C/S electrode by MLD

Molecular layer deposition of alucone was conducted in a **Gemstar-8 ALD system (Arradiance, USA)**. Alucone was directly deposited on the C/S electrode at 100 °C by alternatively introducing trimethylaluminium (TMA) and Ethylene Glycol (EG). The sulfur loading of the C/S electrode dropped by 5 wt% after alucone coating.

Physical and electrochemical characterization

The morphologies of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operated at 5 KeV. CR-2032 type coin cells were assembled in an argon-filled glove box. The coin-type cells consisted of Li metal as the anode, Celgard 2400 as separator, and the C/S electrode prepared above as the cathode. The electrolyte was composed of 1M LiTFSI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio. Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) under a scanning rate of 0.1 mV s⁻¹ between 1.0 V - 3.0 V (vs. Li/Li⁺). Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V - 3.0 V (vs. Li/Li⁺) at room temperature using an Arbin BT-2000 Battery Test equipment. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 °C/min on the SDT Q600 (TA Instruments).

Result and discussion

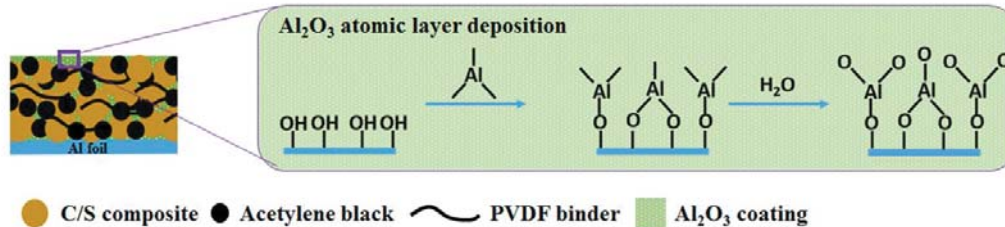


Fig. S1. Schematic of atomic layer deposition Al₂O₃ coating on carbon-sulfur cathode. A typical Al₂O₃ ALD chemical reaction is conducted using H₂O and TMA as precursors.

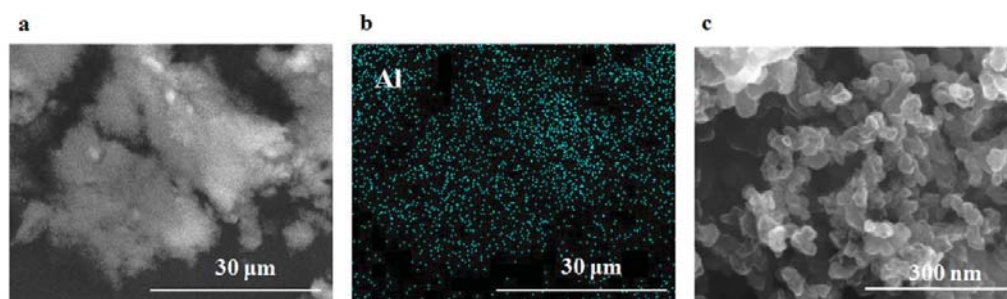


Fig. S2. FE-SEM and Al elemental mapping of 5-cycle alucone coated C/S electrode. The EDX result confirms alucone coating uniformly growing on electrode under micrometer magnification.

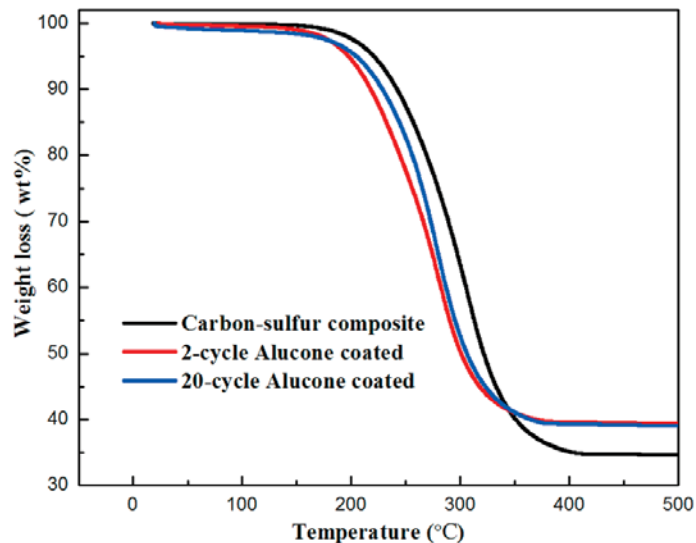


Fig. S3 TGA curves of carbon-sulfur composite with/without alucone coating.

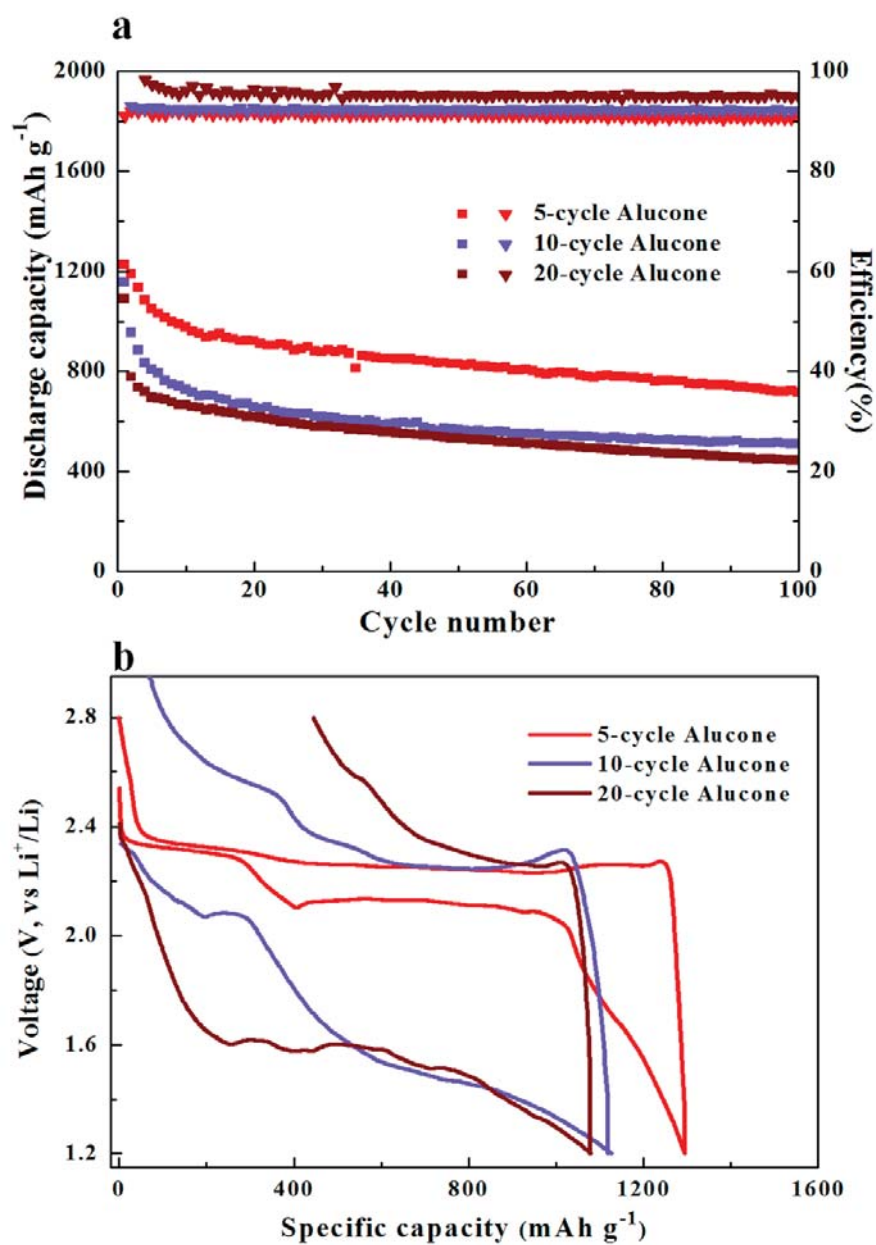


Fig. S4. (a) Cycle performance under 160 mA g⁻¹ and (b) discharge-charge profiles of 5-, 10-, and 20-cycle alucone coated C/S electrode. The 20-cycle alucone coated cathode showed lower initial discharge capacity and serious potential polarization, confirming the thick coating layer hinder the transmission of Li-ions.

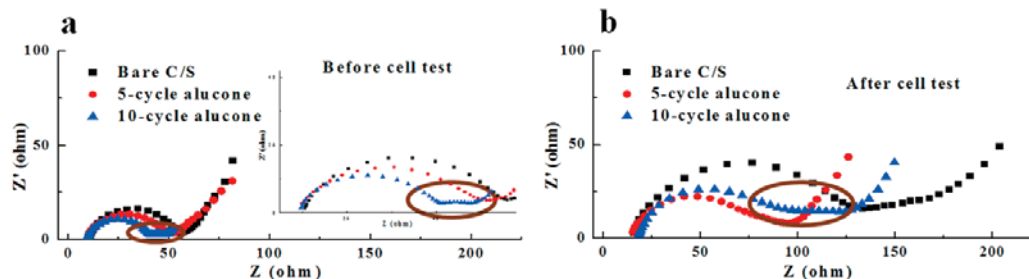


Fig. S5. EIS spectra of sulfur cathodes with and without alucone coating. (a) Before cells test, the three cells all show very small surface electron transfer resistances, confirming the alucone coating retain the conductivity of electrode. (b) After over 30-cycle discharge-charge process, the alucone coated cathodes still maintain small surface electron transfer resistances, whereas the bare C/S cathode shows a big half circle, corresponding to the low conductivity of electrode resulting from deposited discharge product on surface (shown in Figure 3b). Furthermore, it should note that the 10-cycle alucone coated electrode shows a short line between the half circle and straight line in the two spectra (brown circle). The short line can be considered as a semi-infinite diffusion derived from thick 10-cycle insulating coating layer, corresponding to reduced conductivity of thick 10-cycle alucone coated cathode.

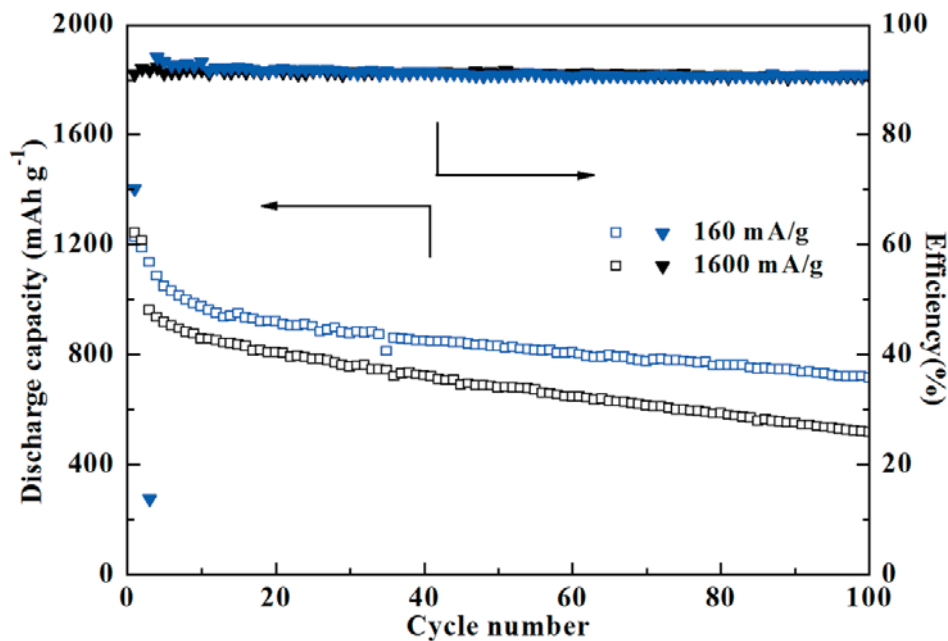


Fig. S6 Cycle performance of 5-cycle alucone coated cathode under different current densities. The coated cathode can retain over 600 mAh g⁻¹ under 1600 mA g⁻¹ over 100 cycles.

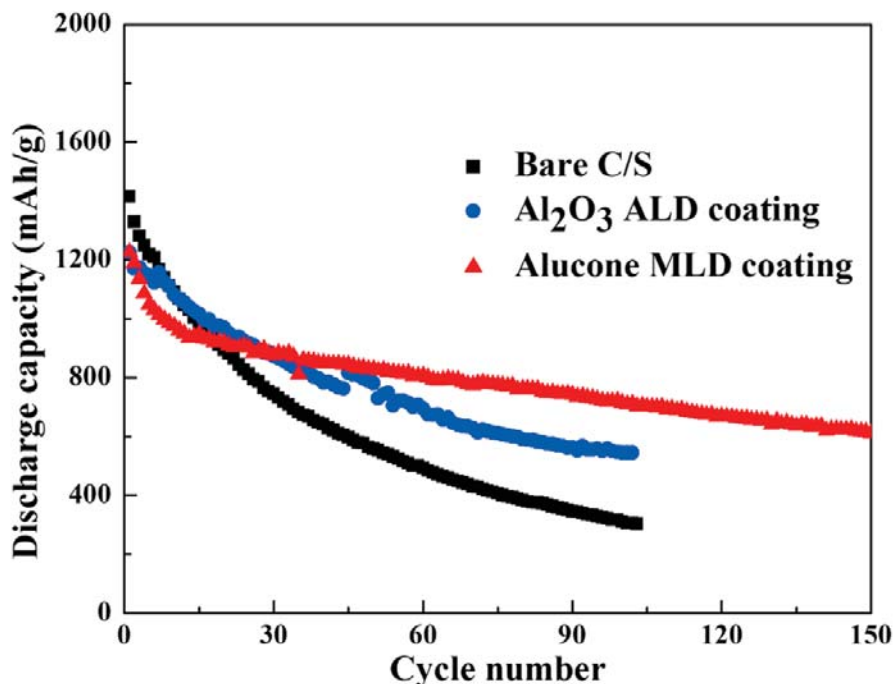


Fig. S7. Cycle performances of bare, ALD- Al_2O_3 coated, and MLD-alucone coated C/S cathodes at a current density of 160 mA g^{-1} . It should be noted that the conductivity of the alucone coating layer is limited, and may cause a drop in capacity during cycling. Compared with ALD Al_2O_3 coating, it is demonstrated that the hybrid inorganic-organic MLD alucone layer improves thermal stability and flexibility. Lee *et al* reported a similar flexible Al-GC coating to accommodate the huge volume expansion of Si to achieve the high reversibility of Si anode (*Adv Mater*, 2014, **26**, 1596). These advanced properties of MLD coating are proposed to improve the performance of sulfur cathodes better than that of ALD coating in long cycle life.

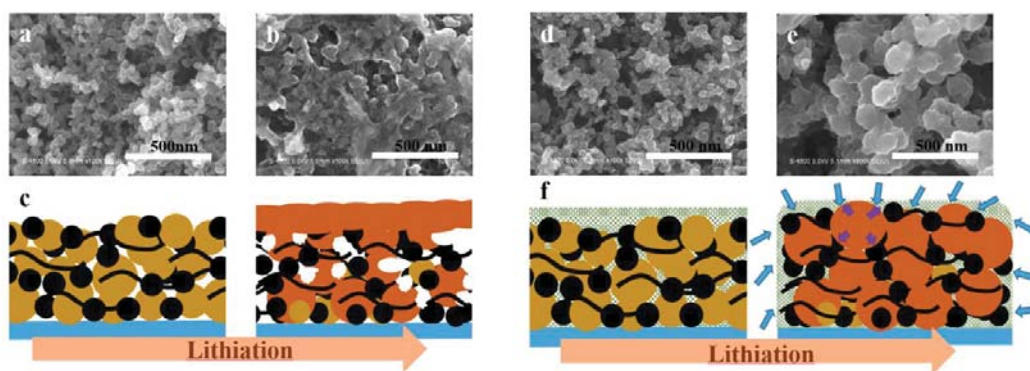


Fig. S8. A proposed mechanism of alucone coating effect during lithiation process. The bare C/S electrode after cycling is covered by discharge product (Fig. S8b), which is due to the polysulfides dissolution and finally formed insulated discharge product covered on the surface, as shown in Fig. S8c. On the other hand, the alucone coated electrode after cycling shows an increased particle size, which can be proposed that

the dissolved polysulfides are trapped by alucone coating, as shown in Fig.S8f.

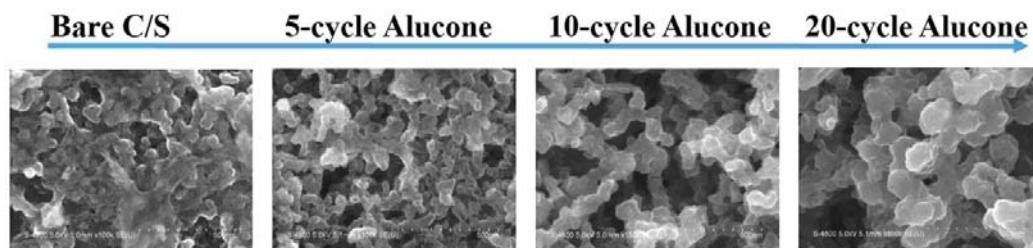


Fig. S9. FE-SEM images of bare C/S, 5-cycle, 10-cycle, 20-cycle alucone coated C/S electrodes after battery test. The alucone coated electrodes obviously show fewer discharge product depositing on surface, which confirms the coating layer prevent the dissolution of polysulfides. Interestingly, the particle size of electrodes is increased with the increasing MLD coating cycles. This may due to the particle with thicker coating layer show more obvious expansion than that of the particle with thin coating layer during the lithiation process. The mechanism of expanded particle with alucone coating is proposed that alucone coating layer is flexible to accommodate the volume expansion of sulfur cathode during cycling, which improve the performance of sulfur cathode in long cycle life (*Adv Mater*, 2014, **26**, 1596). Further study with detailed MLD coating effect and other MLD coating materials will be underwent in our future work.