

Supplementary Information

Multi-Stacked Electrodes Employing Aluminum Coated Tissue Papers and Non-Oxidized Graphene Nanoflakes for High Performance Lithium-Sulfur Batteries

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Experimental Section

Preparation of GNFs and dispersed solution: The graphite intercalation compound (GIC) was manufactured by following the method previously reported in ref.[33]. Briefly, a ternary eutectic system (KCl, NaCl, and ZnCl₂) was used for GIC at 350 °C and the prepared GIC was exfoliated in a pyridine solution. For the functionalized GNFs, 1-pyrenebutyric acid (20 mg) was added to GNFs (20 mg) dispersed in pyridine (40 ml) and then these mixtures were mildly sonicated for 12 h. The mixtures were subsequently stored at 70 °C for 24 h. The mixture was filtered and washed with de-ionized water using a 0.1 micron Anodisc filter to remove the salts and residual pyridine. The product was dried under 100 °C in a furnace. The GNFs (10 mg) were dispersed in 10 ml of ethanol with sonication for 3 h.

Preparation of conductive Kimwipes saturated with densely structured Al films and aggregates: A chemical preparation of densely structured Al films and aggregates is achieved by the decomposition of AlH₃{O(C₄H₉)₂} into Al{O(C₄H₉)₂} and 1.5H₂ and the subsequent decomposition of Al{O(C₄H₉)₂} into Al and O(C₄H₉)₂.²⁹ This decomposition reaction commonly occurs at 165 °C; therefore, the chemical preparation of Al cannot be performed at room temperature without a catalyst to accelerate the decomposition rate. Thus, the catalytic treatment of the Kimwipes is an important step for fabrication of an Al film and aggregates on a substrate at room temperature. To prepare highly conductive Kimwipes with excellent

mechanical endurance against external deformation, we undertook a simple catalytic treatment that involves exposing the Kimwipes to a catalytic atmosphere of $\text{Ti}(\text{O-}i\text{-Pr})_4$ and subsequently immersing the catalytically treated Kimwipes into the Al precursor solution of $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$. After about 2h, the immersed Kimwipes was removed from Al precursor solution and dried. Herein, Al precursor solution of $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$ was prepared by an ethereal reaction of AlCl_3 with LiAlH_4 , and detailed schematic illustration for the catalytic treatment and $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$ preparation is described in Fig. S1†.

- **Catalytic treatment of Kimwipes:** the Kimwipes was preheated at 100 °C, and about 10 μL of catalyst $\text{Ti}(\text{O-}i\text{-Pr})_4$ was dropped on the surface of the heated plate together with Kimwipes. The Kimwipes exposed to fumed catalyst was covered by glass chamber for 10 min. This process was performed at Ar surroundings to prevent oxidation of catalyst to titanium oxide.

- **Preparation of Al precursor solution $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$:** Aluminum chloride (AlCl_3), lithium aluminum hydride (LiAlH_4 ; LAH), and dibutylether ($\text{O}(\text{C}_4\text{H}_9)_2$) were purchased from Aldrich Chemical and used as received. AlCl_3 was used as a precursor for preparing the Al precursor composite solution, while LAH was used as both a precursor and a reducing agent. Dibutylether was used as the solvent for the reaction of both chemicals. 20 mmol of AlCl_3 and 60 mmol of LAH were added to 50 mL of dibutylether. The mixed solution was heated at 75°C under magnetic stirring for 1 h. To remove any by-products of LiCl and not fully reacted precursors, the resulting gray slurry was filtered and discarded. The filtered clear solution was used as an Al precursor composite solution of $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$.

Preparation of sulfur cathode and GNFs layer (1st interlayer) coating: The pristine sulfur cathode was prepared by mixing sulfur powder (100 mesh powder, purified by sublimation, Sigma-Aldrich Co., Ltd., USA) with Super P carbon black and polyvinylidene fluoride (PVDF) at weight ratios of 80 : 10 : 10. A small amount of n-methyl-2-pyrrolidone (NMP) was added in the course of mechanical mixing until the active materials show the proper

viscosity. The mixed slurry was casted on Al foil and subsequently dried at 50 °C overnight in a convection oven, followed by punching out circular electrodes of a 14 mm diameter (loading mass of sulfur was 1.3 mg cm⁻²). The surface morphology and the cross-section SEM images of the sulfur cathode are shown in Fig. S11a† and S11b†, respectively. The circular electrodes were loaded onto the suitable cylindrical bath (> 14 mm diameter), and the bath was filled with the graphene nanoflakes solution with 0.5, 1 and 1.4 ml (2.5, 5 and 7 wt.% (0.03, 0.068 and 0.097 mg cm⁻²) vs. sulfur mass, respectively). The filled solution bath was subsequently dried at 50 °C for 3 h in a flat state convection oven.

Microstructural Characterization: The microstructural evolutions of the sulfur cathode, the GNFs, and the Al-coated Kimwipes interlayer electrodes were investigated by field-emission scanning electron microscope (Field Emission SEM, Magellan400, FEI) and with a transmission electron microscope (TEM, tecnai F30 S-Twin, 300 kV, FEI). The investigation of the multilayer-/monolayer-graphene nanoflakes and the lattice fringe of Al metal was carried out by a high-resolution TEM (HR-TEM). The crystalline phase of the Al of the Al-coated Kimwipes was confirmed by X-ray diffraction pattern (XRD, RIGAKU, D/MAX-2500). The elemental analysis of the GNFs and the Al-coated Kimwipes interlayers was conducted by means of energy-dispersive X-ray spectroscopy (EDS) equipped in SEM and TEM devices. Raman spectroscopy was carried out to investigate the nature of the GNFs using Dispersive-Raman/ARAMS by Horiba Jobin Yvon of France. Thickness of the Al-coated Kimwipes interlayer was measured by micrometer (Mitutoyo, 0 – 25 mm, 0.001 mm, Japan).

Measurement for the electrolyte uptake of the Al-coated Kimwipes: The electrolyte uptake was determined by using Equation (1) with the weights of the Kimwipes tissue paper before and after infiltrating liquid electrolyte for 2 hours under an argon filled glove box.

$$\text{Electrolyte uptake (\%)} = ((W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}) \times 100 \dots \text{Eq. (1)}$$

(W_{dry} and W_{wet} are the weights of the Kimwipes tissue paper before and after electrolyte uptake, respectively)

Electrochemical characterization: The GNFs and the Al-coated Kimwipes interlayer electrodes were placed between the separator and the sulfur cathode during the cell assembly, and electrochemical performances of the sulfur cathode, the GNFs, and the Al-coated Kimwipes interlayer electrodes were evaluated using coin half-cells (2032, Hohsen). A Li-metal foil was used as the counter electrode and 1 M LiTFSI in a 1:1 mixture (v/v) of TEGDME : DIOX (Soulbrain Co., Ltd., Korea) with 0.2 M LiNO₃ (20 μ l in 2032 cell) was used as the electrolyte. The separator was Celgard 2325 (25 μ m thick). The weight of the one sheet Al-coated Kimwipes interlayer is 1.93 mg cm⁻², compared with that of bare Kimwipes (1.92 mg cm⁻²). The cells were galvanostatically charged and discharged between 1.5 and 3.0 V at various current densities with a battery testing system (WBCS3000 device by WonATech). The electrochemical impedance spectroscopy (Si 1260, Solatron) of the pristine sulfur cathode and the interlayer electrodes were measured in a frequency range from 100 kHz to 10 mHz with AC voltage amplitude of 5 mV.

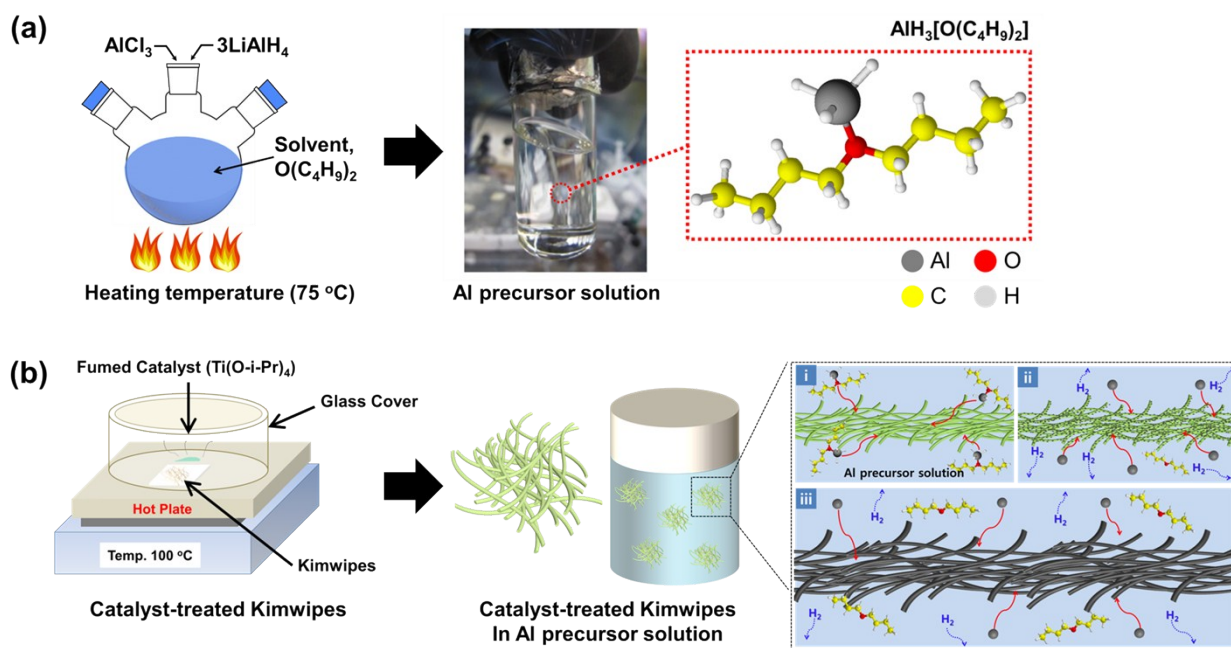


Fig. S1 Schematic illustration of (a) preparation of Al precursor solution $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$ and (b) mechanism for Al-coating.

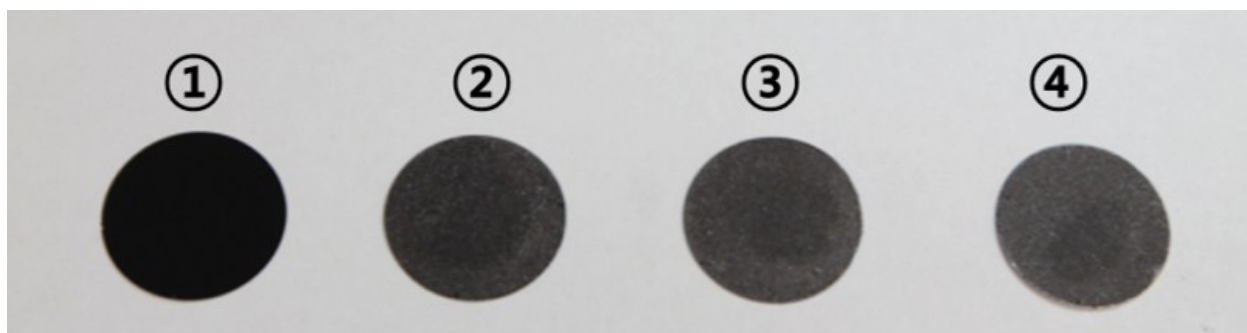


Fig. S2 Digital images of the slurry-casted pristine sulfur cathode ((4)), and the sulfur electrodes coated by the GNFs with different weight ratios of 2.5 wt% ((3)), 5 wt% ((2)) and 7 wt% ((1)) vs. mass loading of sulfur.

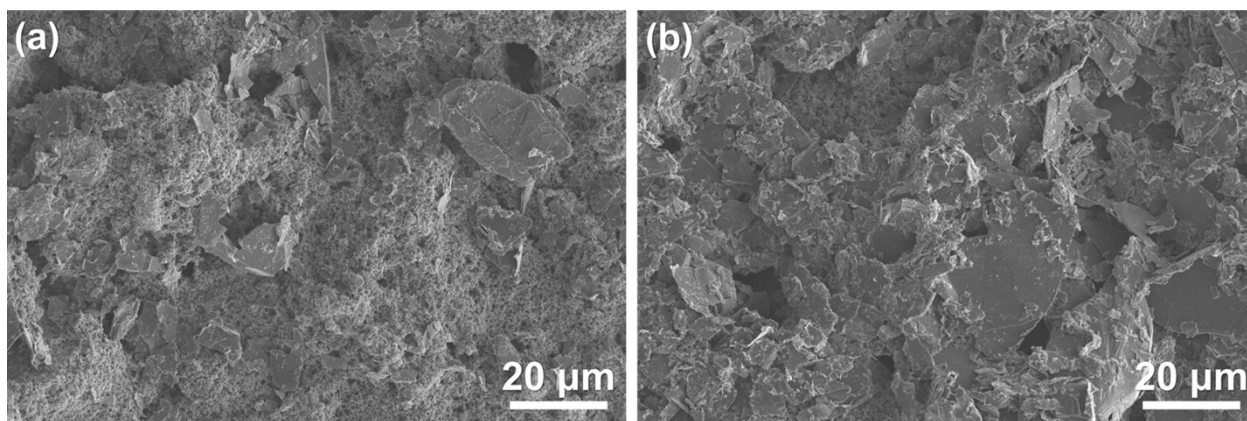


Fig. S3 Surface morphologies of sulfur cathode after electrodes are coated with (a) 2.5 wt%, and (b) 5 wt% GNFs.

Discussion of Fig. S3:

To entirely cover the slurry-casted sulfur cathode, we controlled the concentration of GNFs in the dispersed solution with weight ratios of 2.5, 5, and 7 wt% vs. mass loading of sulfur. For the 2.5 and 5 wt.% GNFs, the surface of sulfur cathodes were not fully covered, which indicates insufficient passivating layer against penetration of the dissolved polysulfide through the interlayer and poor electrical connection with Al current collector in the edge part. For 7 wt.% GNFs, on the other hand, the sulfur electrode could be entirely coated by the GNFs, which means that the low amount of the GNFs effectively makes the sulfur electrode a direct interlayer. The weight of the GNFs was limited to 7 wt.% because original synergetic properties of the Al-coated Kimwipes included electrode cannot be identified for the samples including large amount of the GNFs.

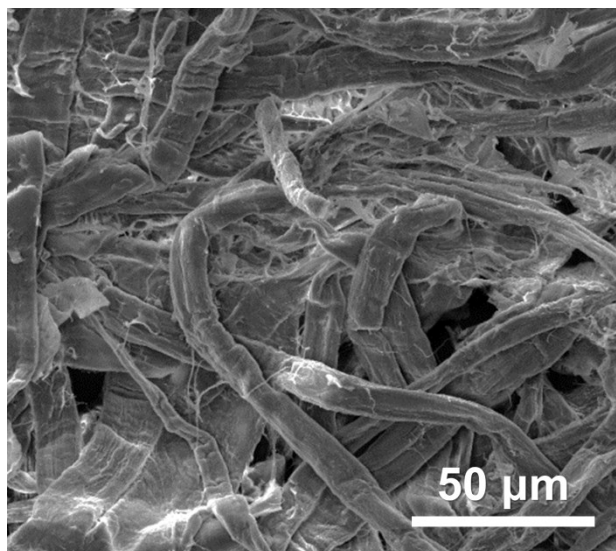


Fig. S4 SEM image of the pristine Kimwipes.

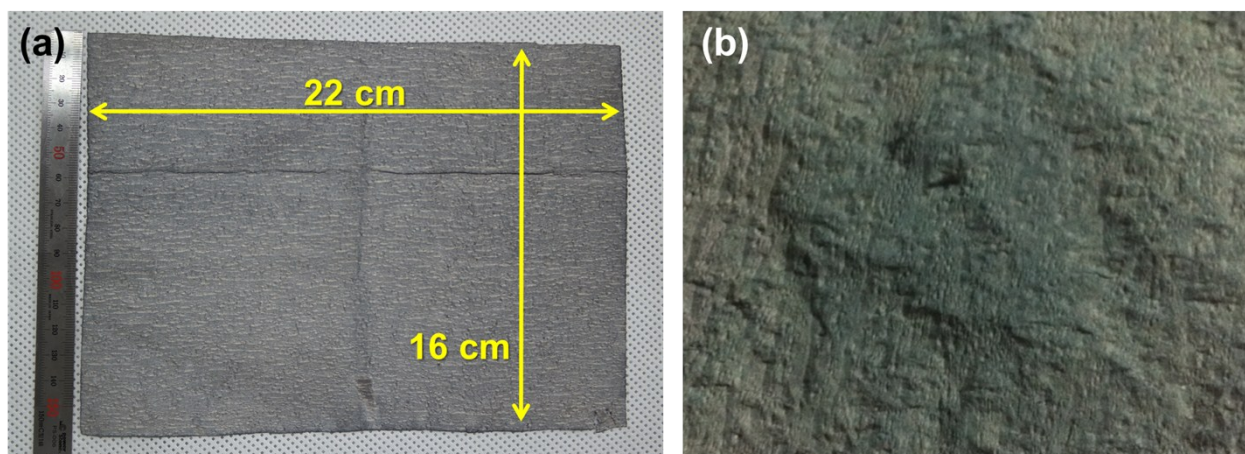


Fig. S5 Digital images of the Al-coated Kimwipes interlayer for (a) dimension and (b) surface state.

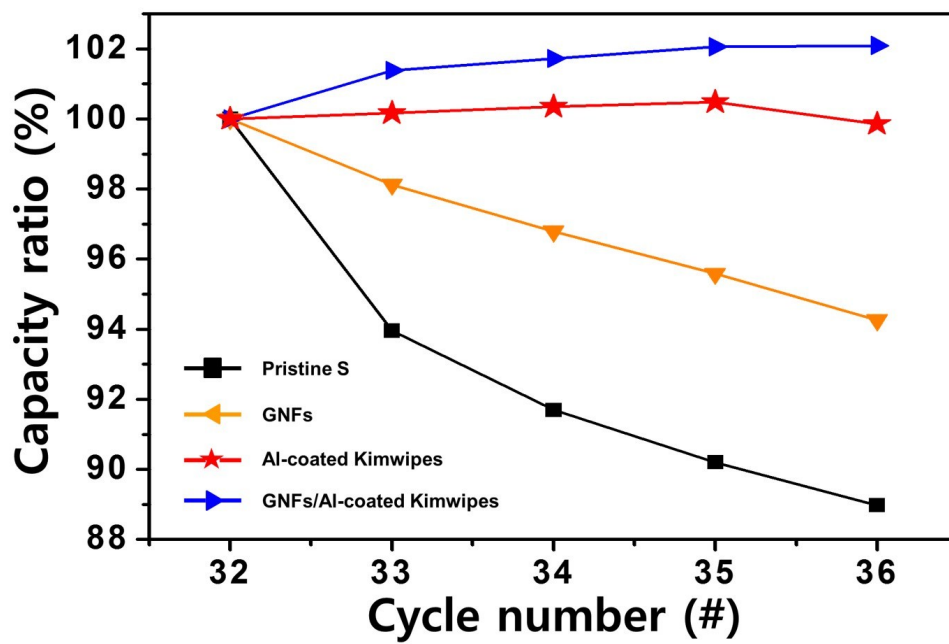


Fig. S6 Recovery capacities after the 2C rate cycling in Fig. 4b.

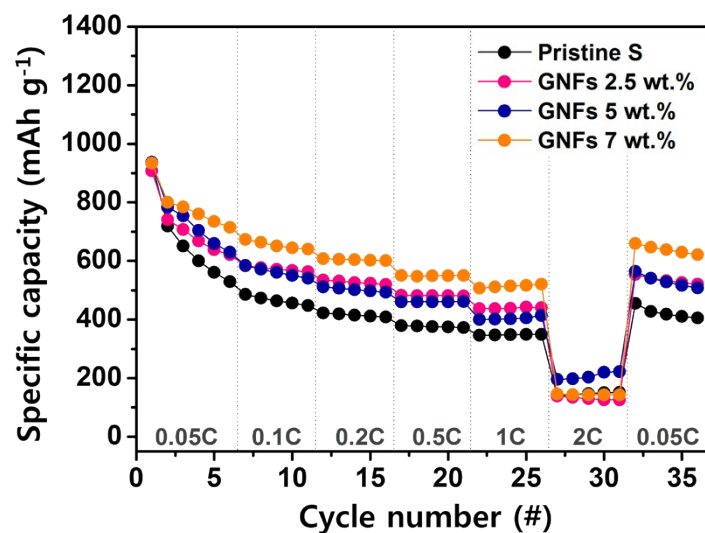


Fig. S7 Rate capabilities of the GNF electrode with different mass loading of the GNFs.

Discussion of Fig. S7:

To find optimal interlayers, the controlled rate capability evaluations were performed in terms of loading amount of the GNFs. When the amount of the GNFs increases up to 7 wt%, the better cycle performance with various current rates was observed compared to the lower amount (0, 2.5 and 5 wt%) of the GNFs. The results are in good agreement with the morphological feature (Fig. 2) of the GNFs layers, demonstrating that the intimate contact between the carbon interlayer and sulfur would improve the cell efficiency in terms of a conductivity and the dissolved polysulfides utilization. All of the cathodes including only the GNFs interlayer have poor electrochemical stability at a high C rate (at 2C), meaning that the sole GNFs interlayer cannot serve as effective screen for the polysulfides anymore at high C rate.

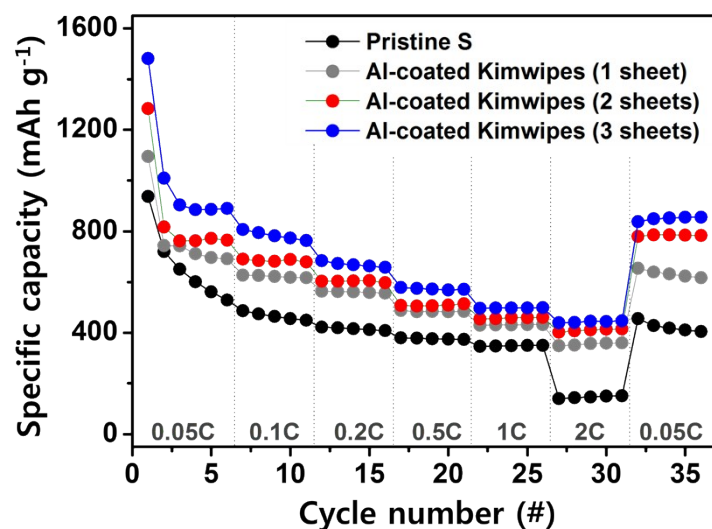


Fig. S8 Rate capabilities of the Al-coated Kimwipes interlayer electrodes with the different number of the Al-coated Kimwipes sheets.

Discussion of Fig. S8:

With the results in Fig. S7, we also elaborately controlled the number of Al-coated Kimwipes interlayers and examined their cycle performance with different current rates as well. When the Al-coated Kimwipes was inserted between the separator and sulfur cathode, the higher capacity values were achieved as the number of the Al-coated Kimwipes sheets increased. The electrode with three sheets of the Al-coated Kimwipes showed higher capacities at most of rates than the electrodes with one or two sheets of the Al-coated Kimwipes. This difference would be mainly caused by the blocking ability and electrolyte uptake ability, which are important factors as a container for capturing the active polysulfides. However, it is noticeable that the electrode with three sheets of the Al-coated Kimwipes interlayers has better rate capabilities compared to the electrode with two sheets of the Al-coated Kimwipes interlayers, but their capacities at high C-rate (1 and 2C) are almost the same. From the insight gained by these performances, we conclude that three sheets are a saturation point for the number of the Al-coated interlayer sheets to maximize the cell stability.

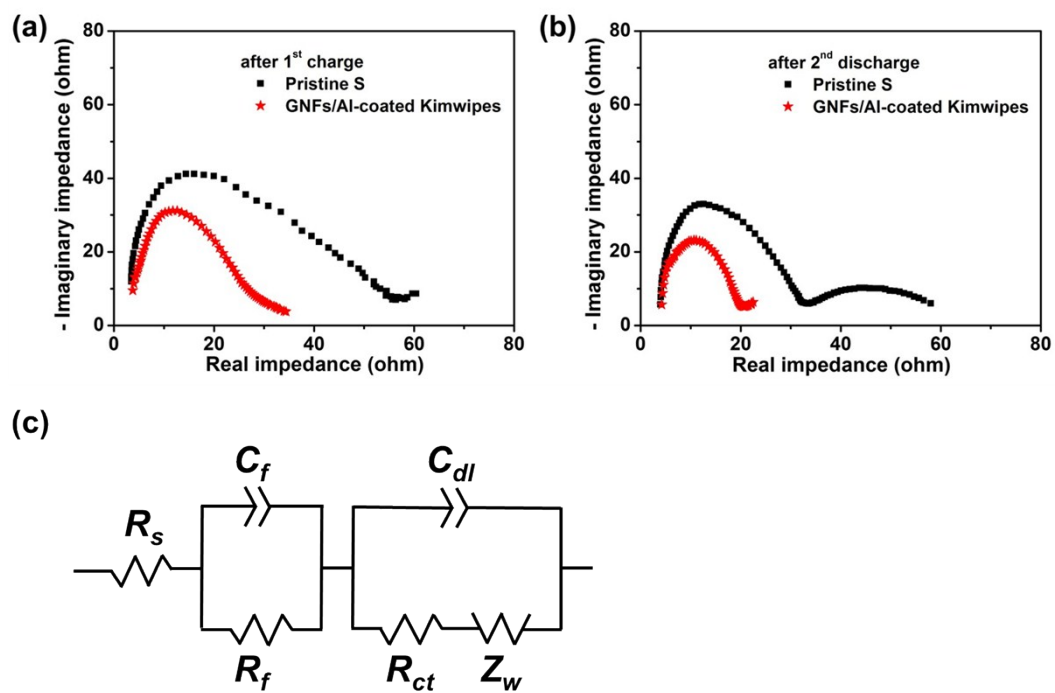


Fig. S9 Impedance data of the pristine sulfur and the GNFs/Al-coated Kimwipes interlayer electrodes (a) after 1st charge and (b) after 2nd discharge. (c) equivalent circuit of both of (a) and (b).

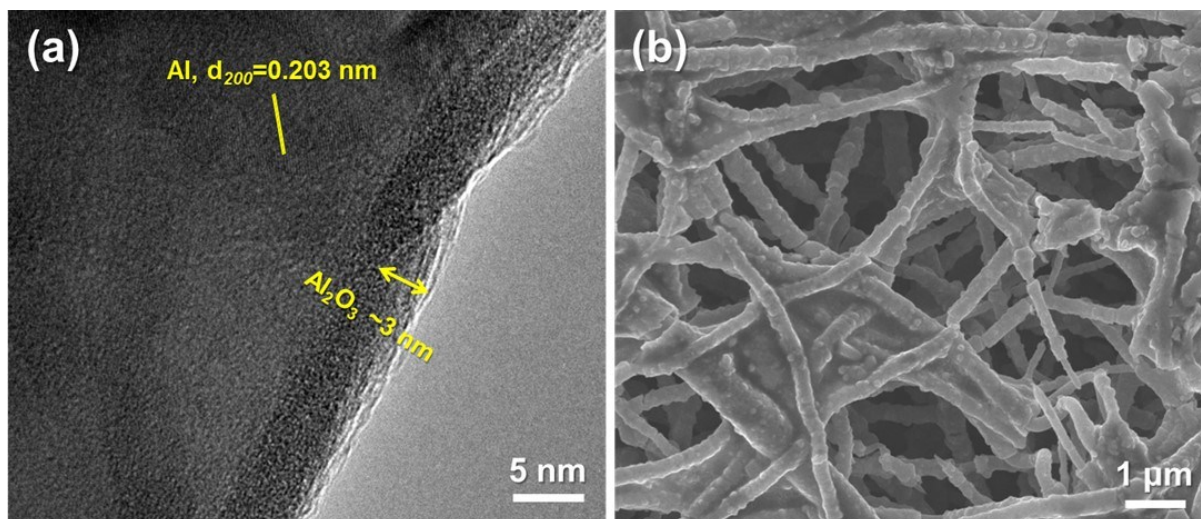


Fig. S10 (a) HRTEM and (b) SEM images of the Al-coated polyimide nanofibers. The thickness of the native Al_2O_3 was analyzed from the Al-coated polyimide nanofibers instead of the Al-coated Kimwipes because TEM analysis of the Al-coated Kimwipes was very difficult. The Al-coated polyimide nanofibers were synthesized by our chemical-solution coating method, exhibiting nanofibrous structure with high weave density.

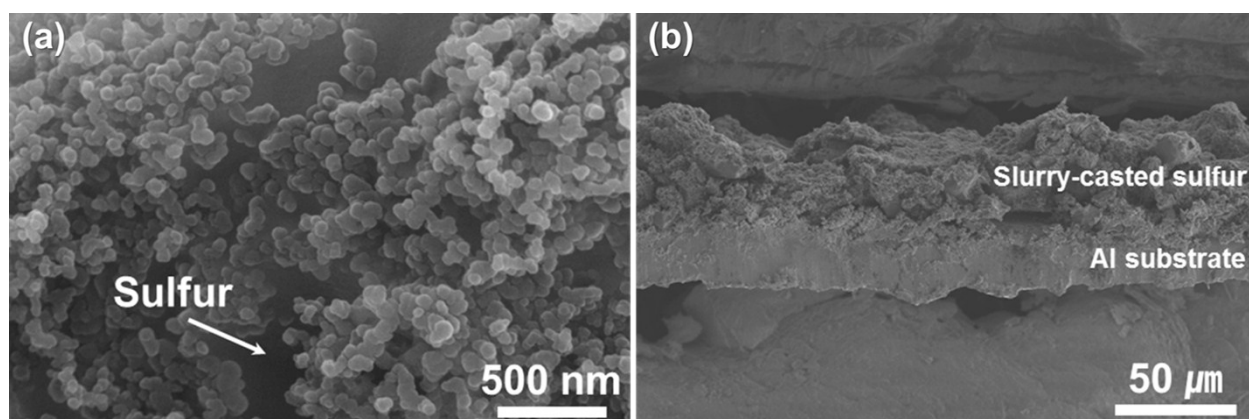


Fig. S11 SEM images of pristine sulfur electrode which was prepared by mixing with bulk sulfur, Super P, and PVDF binder. (a) Surface morphology and (b) cross-section image of the pristine sulfur electrode.