Electronic supplementary information (ESI)

A Phenyl Disulfide@CNT Composite Cathode for Rechargeable Lithium Batteries

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Experimental Section:

Materials: Diphenyl disulfide ($C_{12}H_{10}S_2$, 99%, Sigma Aldrich), carbon nanotubes (CNT, 95%, OD: 10-20 nm, L: 30-100 μm, Nanostructure and Amorphous Materials, Inc.), methanol (CH_3OH, low water, Fisher Chemical), poly(ethylene oxide) (PEO, Sigma Aldrich), Toray carbon paper (TGP-H-030, fuelcellstore.com), lithium bis(trifluoromethanesulfonimide) (LiTFSI, $LiN(CF_3SO_2)_2$, 99%, Acros Organics), lithium nitrate ($LiNO_3$, 99.999%, Acros Organics), 1,2-dimethoxyethane (DME, 99.5%, Sigma Aldrich), 1,3-dioxolane (DOL, 99.8%, Sigma Aldrich), and potassium bromide (KBr, FTIR Grade, Alfa Aesar) were purchased and used as received.

Phenyl disulfide@CNT cathode preparation: Phenyl disulfide (PDS) and CNT were taken 3:1 wt. ratio and vigorously stirred in with about 200 mL of methanol. After stirring for 15 minutes to dissolve the PDS, the mixture was ultrasonicated using a vibracell VC505 sonicator for 15 minutes causing the CNT to interweave. 150-200 mL of D.I. water was added dropwise under stirring into the PDS-CNT mixture to precipitate out the PDS and deposit it on the CNTs. The products were vacuum filtered on to a 7 cm filter paper and washed repeatedly with copious amount of D.I. water. The cathodes thus formed were free-standing, flexible films of approximately 300 micron thickness and 7 cm in diameter. The cathode was dried under vacuum at 50-60°C for 24 h to obtain the cathode sheet. They were cut into 7/16 inch cathode disks that were used for further testing.

Cathode composition determination: The PDS content in the composite was determined by thermogravimetric analysis (TGA) performed on a TA instruments SDT Q600 analyzer under air flow at 50 mL min^{-1} while heating from 25°C to 500°C at 10°C min^{-1}. Samples of CNT and pure PDS were run as a comparison.

Phenyl disulfide slurry cast cathode preparation: A slurry of PDS and CNT with PEO as the binder in 7:2:1 wt. ratio respectively was prepared using D.I. water as the solvent. The slurry was impregnated into Toray carbon paper using doctor blade casting technique. The carbon paper served as both the slurry confining substrate as well as the current collector. The cast cathode was dried under vacuum at 50-60°C for 24 h to obtain the cathode sheet. They were cut into 7/16 inch cathode disks that were used for further testing. Typical PDS loadings on these cathodes were about 4 mg cm^{-2}. The cast cathode is designated as PDS/CNT.

Cell fabrication and electrochemical evaluation: PDS@CNT cathode disks were ~0.97 cm^2 and typically weighed 6-8 mg for regular cells (areal PDS loading is between 4.6-6.2 mg cm^{-2}). Cathodes prepared with high, practical level loadings weighed about 23-25 mg (corresponding to an areal PDS loading of 17.8-19.3 mg cm^{-2}). CR2032 coin cells were made in an Ar-filled glove box with an ether electrolyte composed of 1.0 M LiTFSI and 0.2 M $LiNO_3$ in mixture solvent of DME and DOL (1:1 v/v). Typically, the PDS@CNT cathode was placed without any additional current collectors and 20 μL electrolyte was added into the cathode. Then, a Celgard 2400 separator was placed on the top of the electrode followed by adding 10 μL electrolyte on the separator. Finally, a piece of lithium foil and nickel foam as a spacer was placed on the separator.

The high loading cathode used 50 μL electrolyte on the cathode side and 25 μL on the anode side. The cells were crimped and taken out of the glove box for electrochemical evaluation.

Cyclic voltammetry (CV) was performed on a BioLogic VSP potentiostat. The potential was swept from open circuit voltage to 1.8 V and then cycled between 1.8 and 3 V at a scanning rate of 0.2 mV s^{-1}. Cells were galvanostatically cycled on an Arbin BT2000 battery cycler at different C rates (1C = 245 mA g^{-1} of PDS in the cathode) between 1.8 and 2.8 V.

Electrochemical impedance spectroscopy (EIS) data was collected using a Bio-Logic VSP impedance analyzer in the frequency range of 200 kHz – 200 mHz with Li metal foil as both counter and reference electrodes.

Material Characterizations:

Cells for characterization were cycled appropriately at C/10 and opened inside the glovebox to recover the cathodes. They were mildly washed with pure DME to remove traces of the Li salts. They were then dried for an hour inside the glovebox prior to characterization.

The X-ray diffraction (XRD) data were collected on a Bruker D8 Discover XRD Instrument equipped with Cu Kα radiation. The scan rate was 2° min^{-1}, and 2θ was set between 20° and 60°. All electrodes were protected by a Kapton tape and its background was removed using Bruker's DIFFRAC.EVA software.

The morphological characterization of the electrodes was performed using a JEOL JSM-7800F field emission scanning electron microscopy (SEM). The elemental mapping was performed with energy-dispersive X-ray spectroscopy (EDS) attached to the SEM with 10 kV to confirm the presence of sulfur in particles of PDS. The air-sensitive samples were transferred in an argon filled, air-tight container to prevent its decomposition.

Fourier Transform Infrared (FTIR) absorption spectra were recorded on a Thermo Scientific-Nicolet iS10 FTIR spectrometer. 32 scans between 400 cm^{-1} to 4000 cm^{-1} were recorded per sample. Samples were prepared by grinding the cathodes with KBr within the glovebox and pelletizing it using an FTIR die set. The pellet contained within the die was transferred in an argon filled, air-tight container to the spectrometer.

Additional Data:

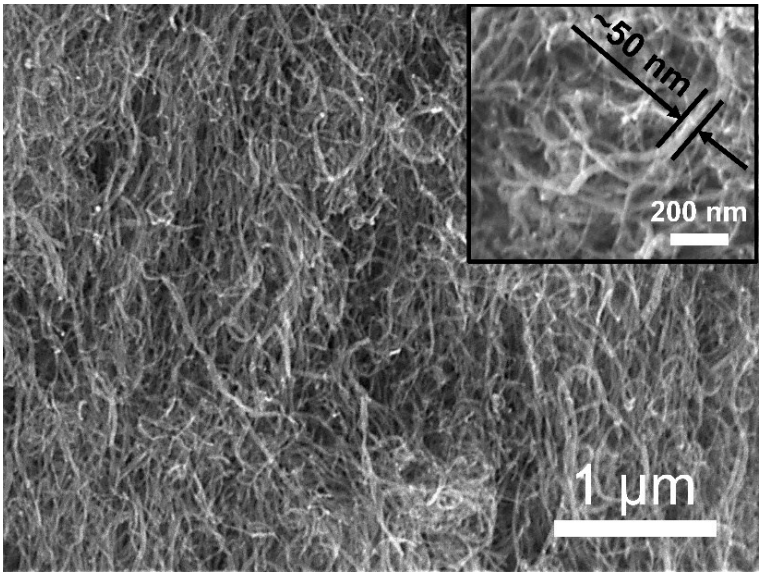

Figure S1. SEM micrograph of CNT paper showing the diameter of CNT fibril to be ~50 nm.

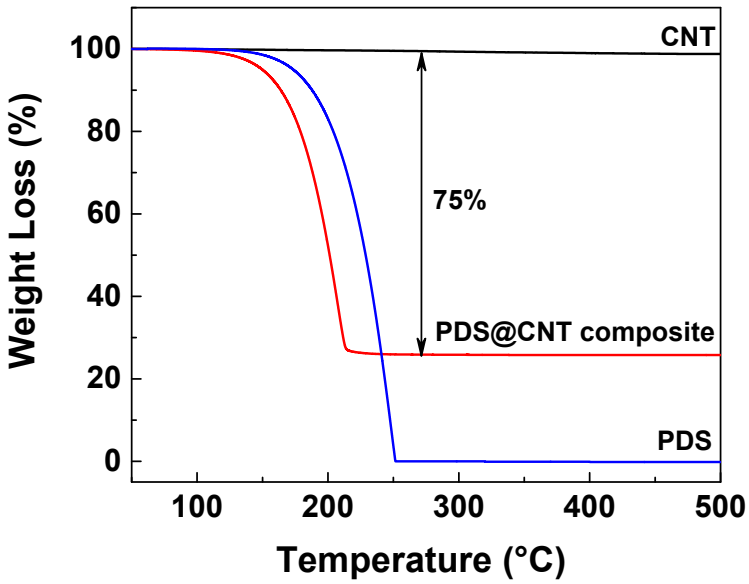

Figure S2. TGA analysis of CNT, PDS@CNT composite cathode, and pure commercial PDS.

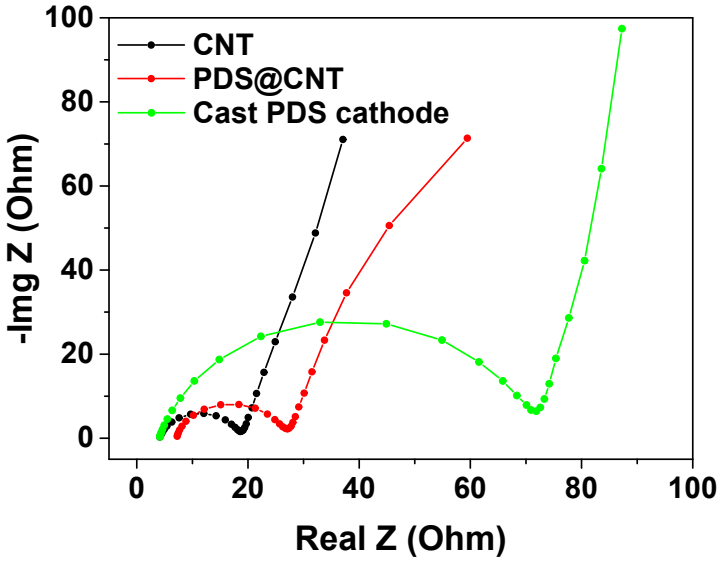

Figure S3. Electrochemical impedance spectroscopy (EIS) analysis of CNT, PDS@CNT composite cathode, and slurry cast PDS cathode.

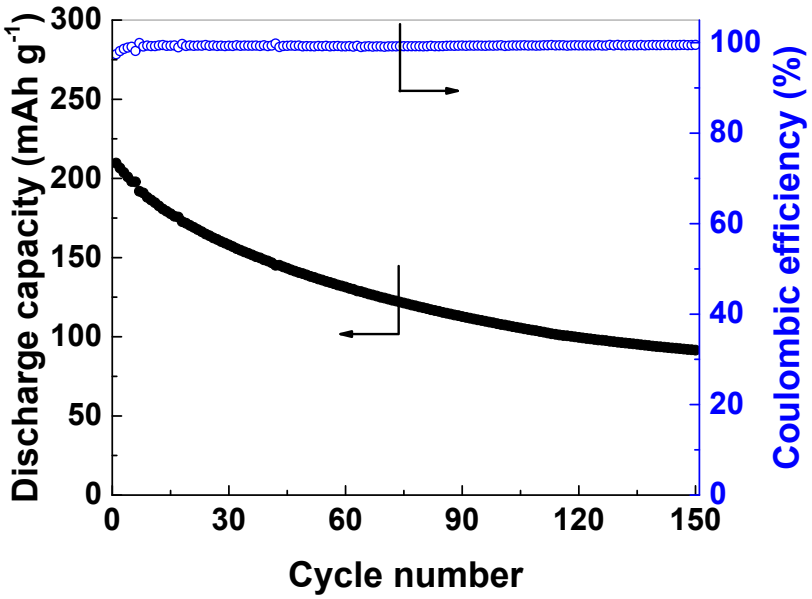

Figure S4. Cycle life of PDS/CNT cast cathode cycled at C/5.

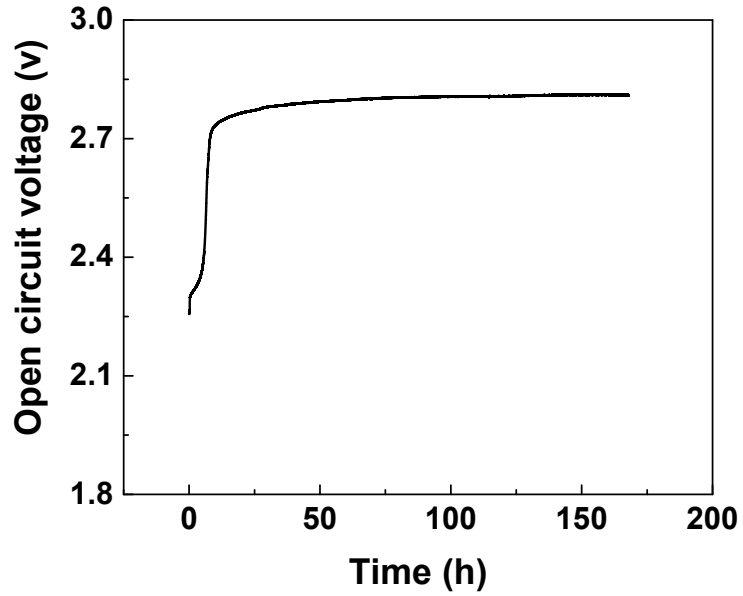

Figure S5. Open circuit voltage (OCV) of a cell with PDS@CNT cathode monitored over one week.

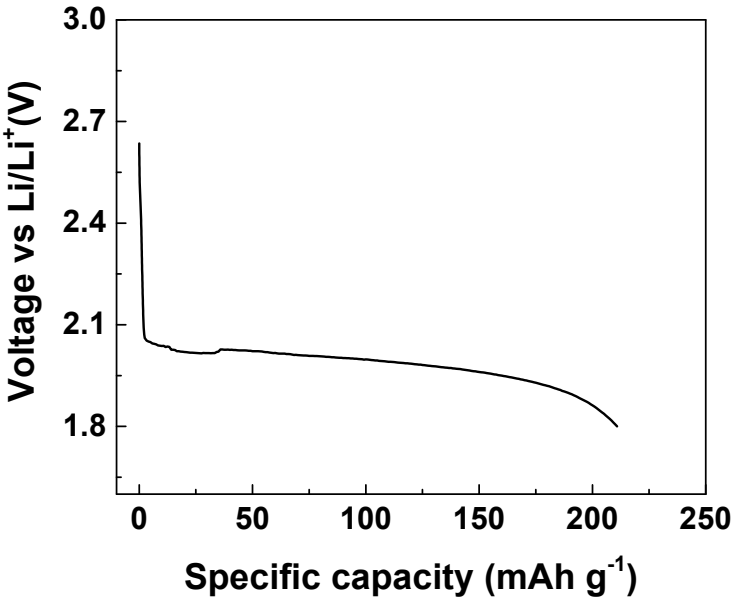

Figure S6. First discharge of the cell held at OCV for one week at C/10. This capacity shows the low self-discharge rate and active material retention capability of the cathode.

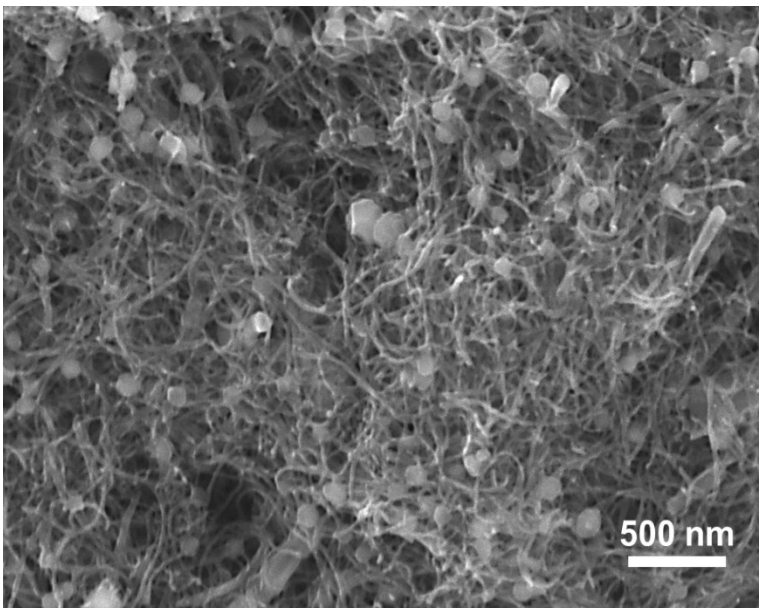

Figure S7. SEM micrograph of cycled PDS@CNT cathode at the end of 150th cycle (charged state). The cell was cycled at 1C. The cell was partially rinsed with DME to reveal the underlying CNT.