

## 1. Materials

1,4-dicyanobenzene (DCB) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Sigma Aldrich and TCI. The air-laid paper (AP, 45% polyester and 55% cellulose) was purchased from VWR. All the reagents and materials used directly without any further purification or modification.

## 2. Experimental procedures

CTF-LiF (65 mg, yield 50%) was synthesized by mixing DCB (100 mg, 1 equiv) and LiTFSI (336 mg, 1.5 equiv) in an ampoule (10 mL) inside the glove-box. For the LiF (15 mg, 49.6%), the same ampoule reaction was performed using only LiTFSI (336 mg). All the ampoules were evacuated and sealed at room temperature and transferred into a box furnace and kept at 300 °C for 48 h (1 °C min<sup>-1</sup> ramping). After cooling to room temperature, the samples were taken out and washed with acetone, CH<sub>2</sub>Cl<sub>2</sub> and deionized water.

For the AP-CTF-LiF and AP-LiF, CTF-LiF or LiF were grounded in a mortar to form a fine powder, added in acetone (40 mL, 2 mg mL<sup>-1</sup>) and sonicated for 1 h using a probe sonicator. Afterwards, AP was immersed into the solution for 30 seconds and dried at 80 °C in the oven, and this immersion process was repeated 5-6 times to achieve the loading of 0.2 mg cm<sup>-2</sup>. Lastly, AP-CTF-LiF and AP-LiF were punched to discs with the diameter of 14 mm for electrochemical analysis.

## 3. Material characterizations

Powder X-ray diffraction (PXRD) analysis was performed for CTF-LiF and LiF using Rigaku Ultima IV at 1° min<sup>-1</sup> from 5–50°. Fourier transform infrared (FT-IR) was conducted by using Bruker TENSOR II to reveal the bonding structure over the wavelength range of 3500-600 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was conducted to detect elemental state and composition by using PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany) with a monochromatic Al K $\alpha$  X-ray source. The morphology and energy-dispersive spectroscopy (EDS) were characterized by field emission scanning electron microscopy (FE-SEM, Tescan Mira3 LM FE). Elemental analysis (EA) was done by using FLASH 2000 Organic Elemental Analyzer (C, H, N). Thermogravimetric analysis (TGA) was conducted by TGA 3+ (METTLER TOLEDO) with ramping rate of 5 °C min<sup>-1</sup> under air atmosphere. <sup>13</sup>C

magic angle spinning (MAS) solid-state nuclear magnetic resonance (ssNMR) was conducted by Bruker AV NEO 400 MHz NMR spectrometer with spinning frequency of 5 kHz. N<sub>2</sub> isotherms were measured using a 3Flex physisorption analyzer (Micromeritics, USA) at 77 K.

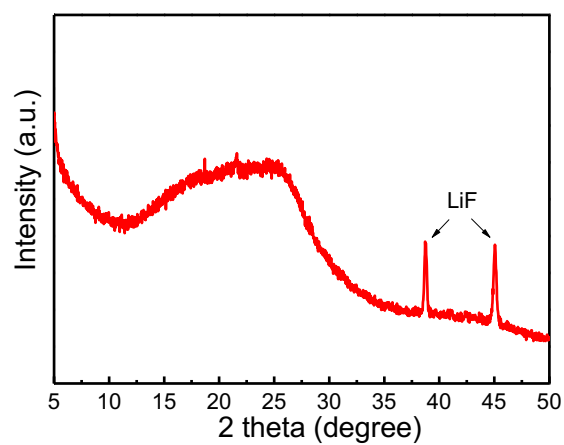
#### **4. Electrochemical characterizations**

All of battery cells were assembled in a glove-box in the form of CR2032-type coin cells taking Celgard 2400 as separator. The electrolyte was 1 M LiTFSI in the mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume) with 2 wt% LiNO<sub>3</sub>. The electrolyte amount of 60  $\mu$ L was injected for each coin cell, and all battery tests were done using a Land 2001A battery system.

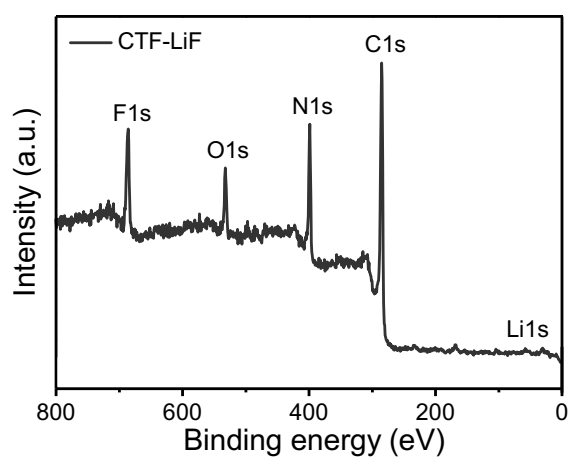
For Li metal anode characterization, all batteries were first cycled at 50  $\mu$ A in the potential range of 0–1.5 V (versus Li<sup>+</sup>/Li) for 10 cycles to stabilize the interface. In order to measure Coulombic efficiency (CE), the cells were assembled in a way that Cu foil ( $\varnothing$  14 mm) on which AP, AP-CTF-LiF or AP-LiF disc ( $\varnothing$  14 mm) was placed was used as the working electrode, and Li foil ( $\varnothing$  16 mm) was used as the counter/reference electrode. In each cycle of this CE test, Li of a constant capacity was plated on the Cu side and then stripped at a constant current density until the potential reached the top cut-off of 1 V. All the CEs are averaged values in the given cycling range. Electrochemical impedance spectra (EIS) analysis was conducted by a Solartron impedance analyzer with an amplitude of 5 mV in the frequency range of 1 MHz to 50 mHz for the cells operated at 3 mA cm<sup>-2</sup> with 1 mAh cm<sup>-2</sup>. For the overpotential test with the symmetric cells, 1.5 mAh cm<sup>-2</sup> of Li was first pre-deposited at 0.5 mA cm<sup>-2</sup> to the working electrode, and the cells were then cycled at 5 mA cm<sup>-2</sup> for 0.2 h (1 mAh cm<sup>-2</sup>) for each charge and discharge.

For the lithium-sulfur (Li-S) batteries, elemental sulfur was first melted into graphene (sulfur@graphene) at 155 °C for 12 h by weight ratio of 85:15. The cathode was then prepared by mixing sulfur@graphene, super-P and polyvinylidene difluoride (PVDF) in *N*-methyl-2-pyrrolidone (NMP) in weight ratio of 60:30:10. The areal loading of sulfur was about 0.8 mg cm<sup>-2</sup>. For the Li electrode, 3 mAh cm<sup>-2</sup> of Li was plated on the bare Cu foil or the bare Cu foil with AP or AP-CTF-LiF.

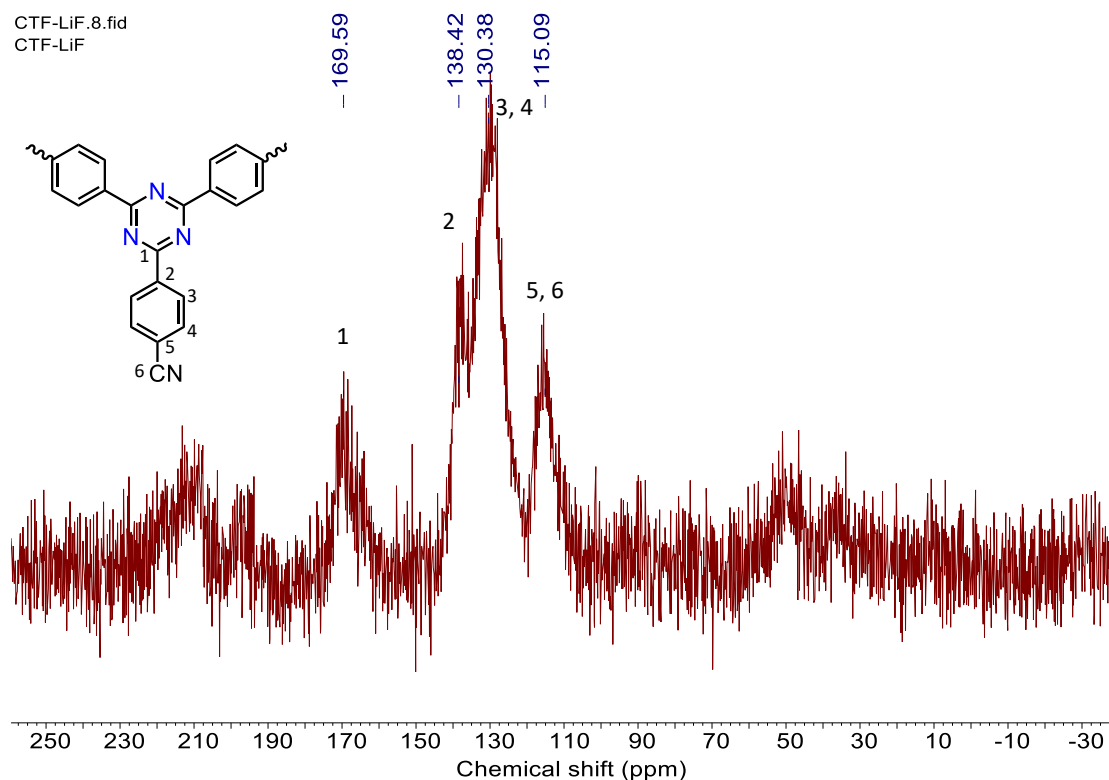
## 5. Supporting figures and tables



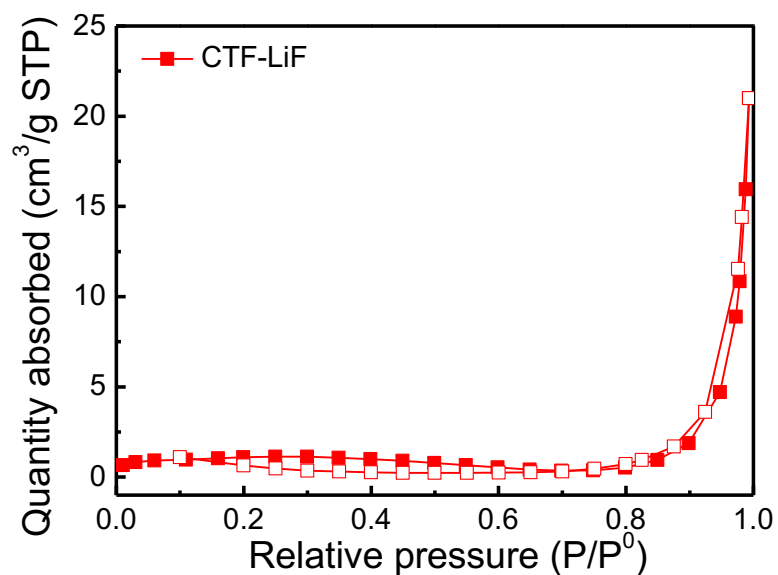
**Figure S1.** XRD spectrum of CTF-LiF. The two sharp diffraction peaks at  $38.7^\circ$  and  $45.0^\circ$  are (111) and (200) crystal facets well-matched with LiF JCPDS 72-1538 diffraction card.



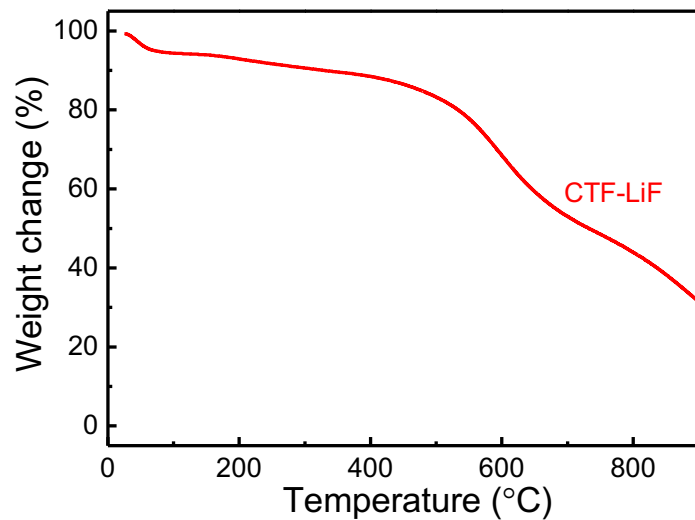
**Figure S2.** XPS survey spectrum of CTF-LiF



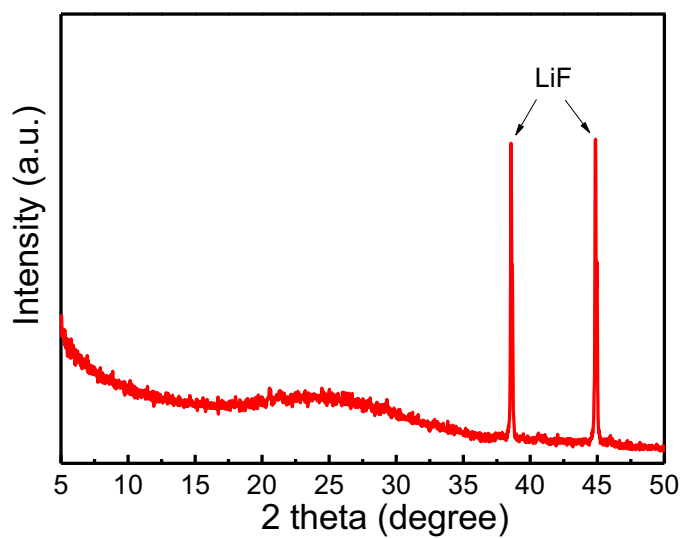
**Figure S3.**  $^{13}\text{C}$  CP MAS solid-state NMR spectra of CTF-LiF. The signal at 170 ppm is assigned to the carbon atoms of triazine ring, while the other strong signals at 138 and 130 ppm correspond to the phenyl ring. The signal at 115 ppm is attributed to nitrile group as well as the carbon atom of the phenyl ring attached to it.



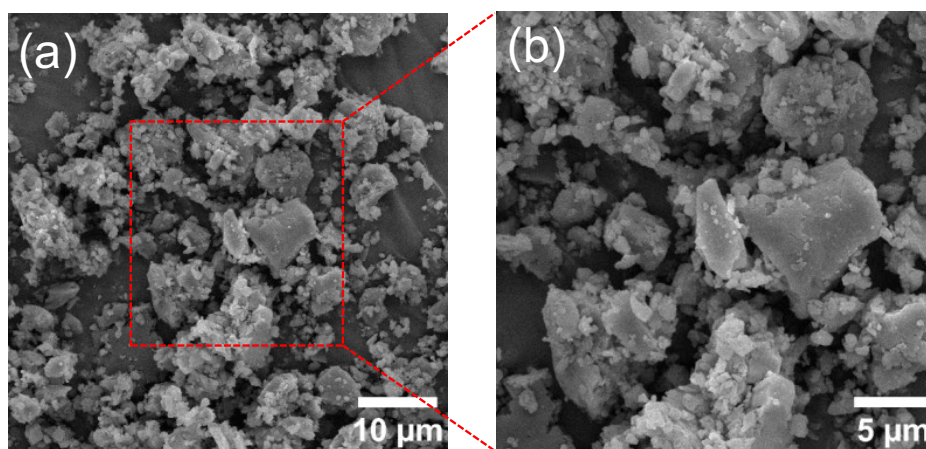
**Figure S4.** Nitrogen adsorption–desorption isotherms at 77 K of CTF-LiF.



**Figure S5.** TGA plot of CTF-LiF with ramping rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  under air atmosphere.



**Figure S6.** XRD spectrum of LiF synthesized by pure LiTFSI at  $300\text{ }^{\circ}\text{C}$  for 48 h.



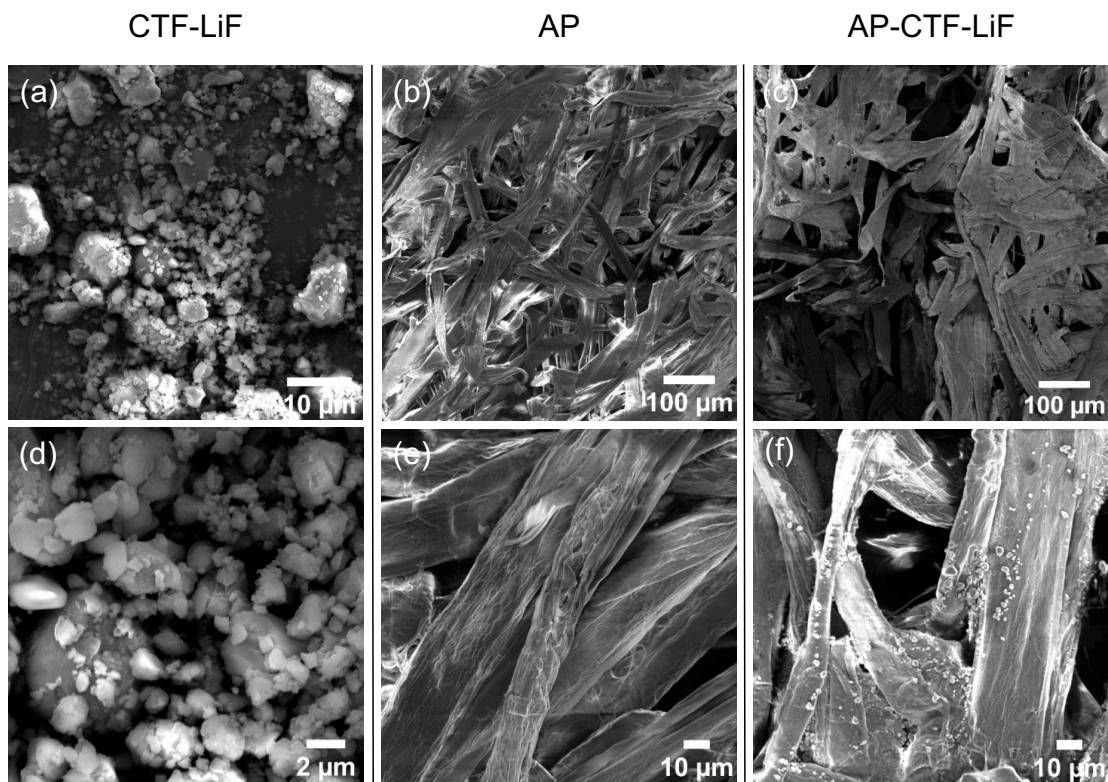
**Figure S7.** SEM images of LiF synthesized from LiTFSI at  $300\text{ }^{\circ}\text{C}$  for 48 h.

**Table S1.** EA and XPS analysis results of CTF-LiF. The theoretical elemental composition of CTF-LiF was calculated based on the initial ratio between DCB and LiTFSI (1:1.5)

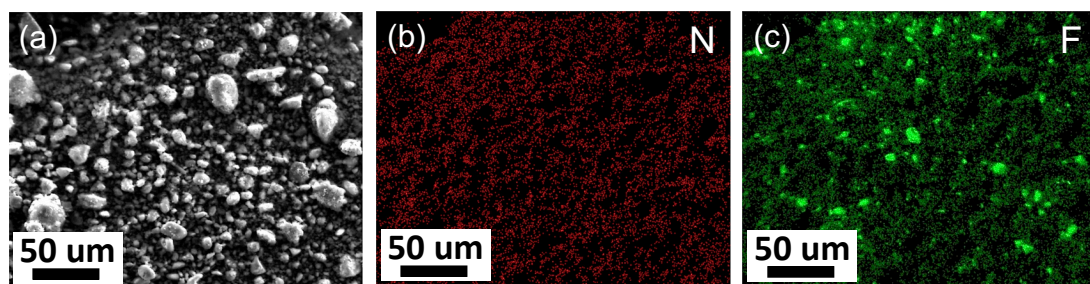
Technique	C	H	N	F	Li	Total
Theoretical (wt%)	57.52	2.41	16.77	17.06	6.23	100
EA (wt%)	54.57	2.09	19.72	-	-	76.38
XPS (at%)	62.52	-	16.70	8.64	5.37	93.23

**Table S2.** Summary of reaction temperature vs nitrogen content in CTFs.

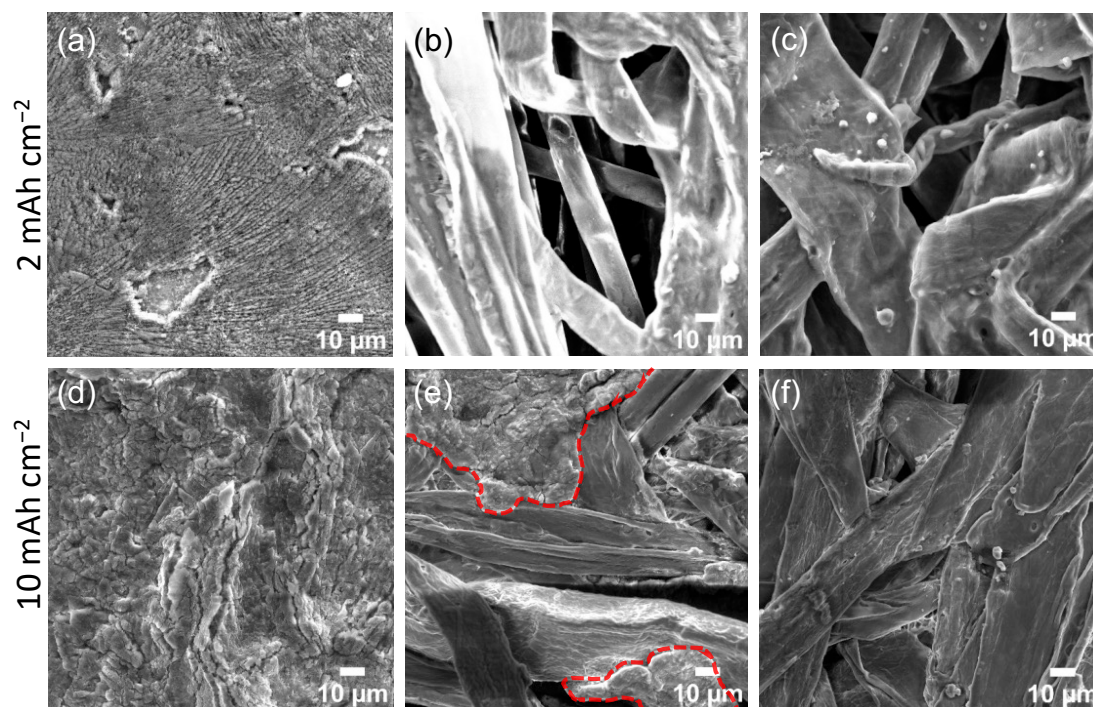
Catalyst	Reaction Temperature	Theoretical content (Nitrogen)	Experimental content (Nitrogen)	Reference
LiTFSI	300 °C	16.77 %	19.72 %	This work
ZnCl <sub>2</sub>	400 °C	21.86 %	17.45 %	Angew. Chem. Int. Ed. 2008, 47, 3450–3453
P <sub>2</sub> O <sub>5</sub>	400 °C	19.65 %	14.38 %	Angew. Chem. Int. Ed. 2018, 57, 8438–8442
ZnCl <sub>2</sub>	400 °C	13.0 %	8.6 %	ACS Appl. Mater. Interfaces 2017, 9, 8, 7209-7216
ZnCl <sub>2</sub>	450 °C	13.0 %	7.9 %	ACS Appl. Mater. Interfaces 2017, 9, 8, 7209-7216
ZnCl <sub>2</sub>	500 °C	13.0 %	6.6 %	ACS Appl. Mater. Interfaces 2017, 9, 8, 7209-7216
ZnCl <sub>2</sub>	550 °C	27.44 %	17.67 %	J. Am. Chem. Soc. 2015, 137, 219–225
ZnCl <sub>2</sub>	600 °C	27.44 %	15.29 %	J. Am. Chem. Soc. 2015, 137, 219–225
ZnCl <sub>2</sub>	650 °C	27.44 %	11.54 %	J. Am. Chem. Soc. 2015, 137, 219–225
ZnCl <sub>2</sub>	700 °C	27.44 %	7.67 %	J. Am. Chem. Soc. 2015, 137, 219–225



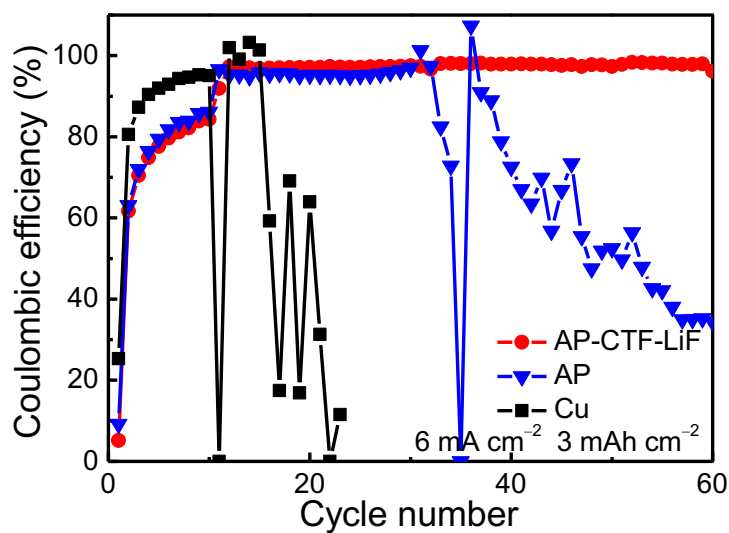
**Figure S8.** SEM images of CTF-LiF at magnification of (a)  $\times 10$  k and (d)  $\times 30$  k, AP at magnification of (b)  $\times 800$  and (e)  $\times 4$  k, AP-CTF-LiF at magnification of (c)  $\times 800$  and (f)  $\times 4$  k.



**Figure S9.** SEM image of (a) CTF-LiF and its EDS elemental mappings with respect to (b) nitrogen and (c) fluorine atoms.



**Figure S10.** SEM images of (a) Cu, (b) AP and (c) AP-CTF-LiF after Li plating of 2 mAh cm<sup>-2</sup>, (d) Cu, (e) AP and (f) AP-CTF-LiF after Li plating of 10 mAh cm<sup>-2</sup> at a higher magnification ( $\times 4$  k).

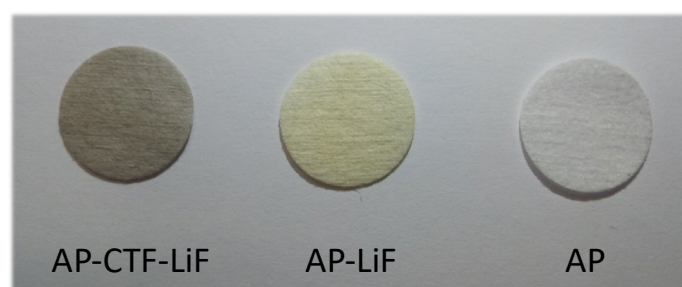


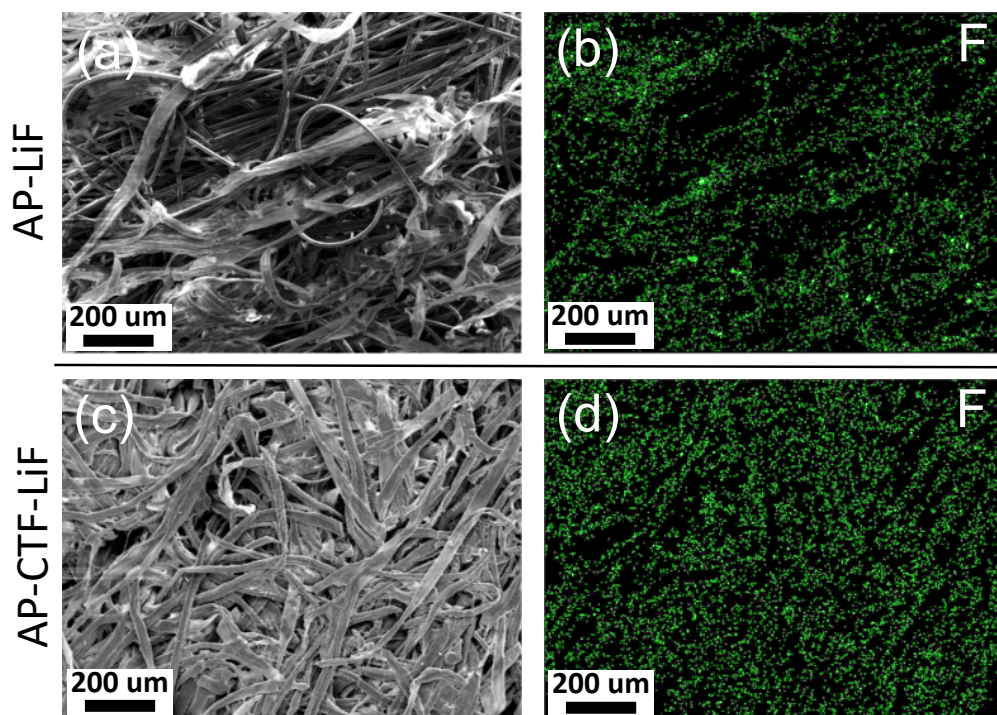
**Figure S11.** Comparison of Li plating/stripping CE for bare Cu, AP and AP-CTF-LiF electrodes when measured at 6 mA cm<sup>-2</sup> with areal capacity of 3 mAh cm<sup>-2</sup>.



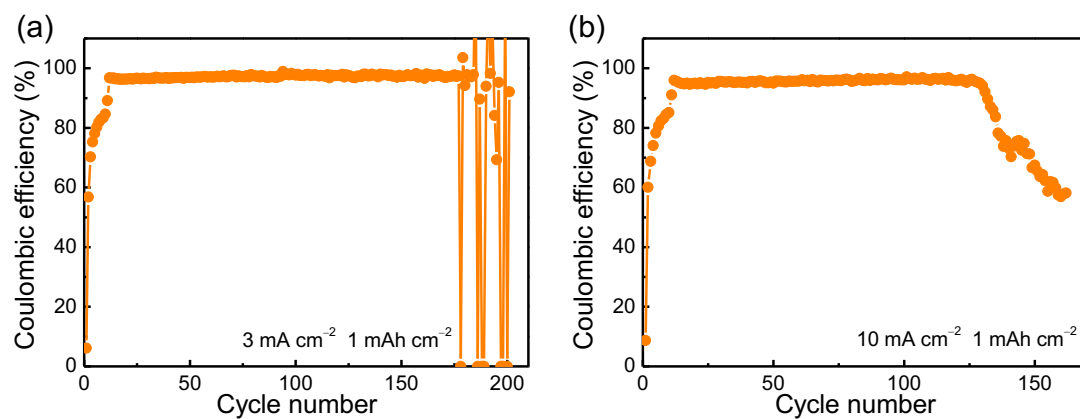
**Table S3.** Summary of electrochemical performance comparison.

Sample	Performance	Reference
AP-CTF-LiF	10 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup> 220 cycles CE: 96.2%	This work
fCNT-PRPAA	4.5 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup> 140 cycles CE: 97.6%	Adv. Mater. 2019, 31, 1901645
RPC-stabilized Li anode	2 mA cm <sup>-2</sup> 4 mAh cm <sup>-2</sup> 300 cycles CE: 99.1%	Nat. Mater. 2019, 18, 384–389
g-C <sub>3</sub> N <sub>4</sub> @Ni foam	1 mA cm <sup>-2</sup> 2 mAh cm <sup>-2</sup> 140 cycles CE: 97%	Adv. Energy Mater. 2019, 9, 1803186
3D Cu@Al	0.5 mA cm <sup>-2</sup> 2 mAh cm <sup>-2</sup> 85 cycles CE: 98.6%	Angew. Chem. Int. Ed. 2019, 58, 1094–1099
TiC/C	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup> 100 cycles CE: 98.5%	Adv. Energy Mater. 2018, 8, 1702322
Zircone Coatings	1 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup> 80 cycles CE: 97.7 %	DOI:10.1002/anie.20190775 9

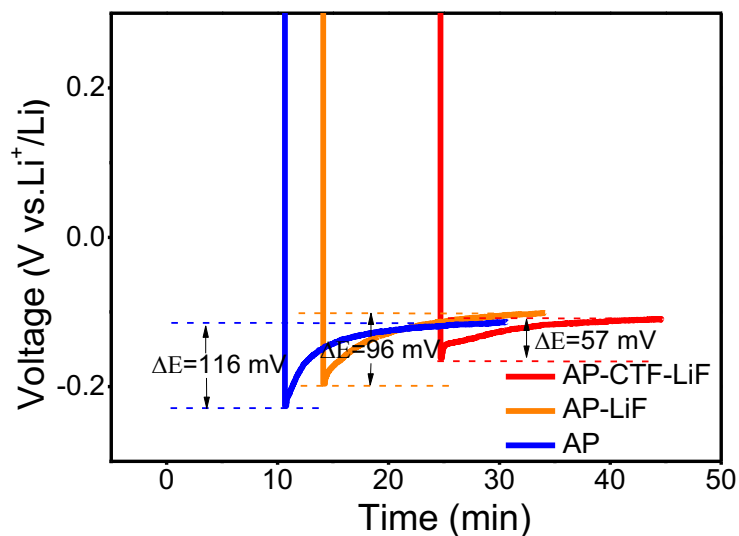
**Figure S12.** Digital photographs of AP-CTF-LiF, AP-LiF and AP.



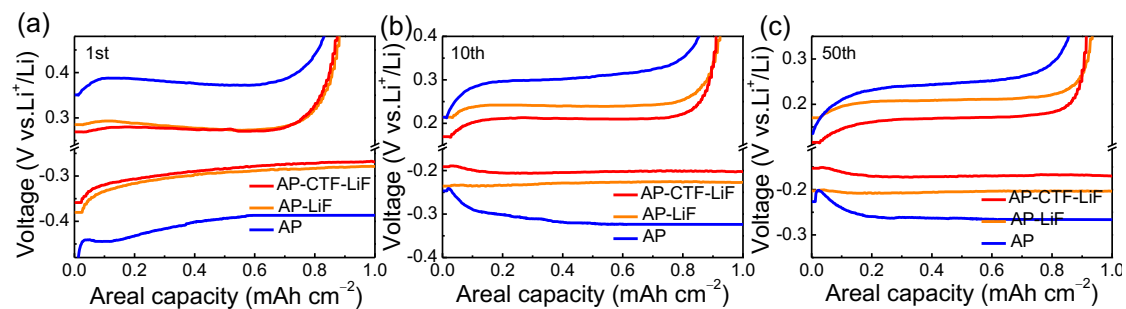
**Figure S13.** SEM images and EDS elemental mappings with respect to fluorine atom of (a, b) AP- LiF and (c, d) AP-CTF-LiF.



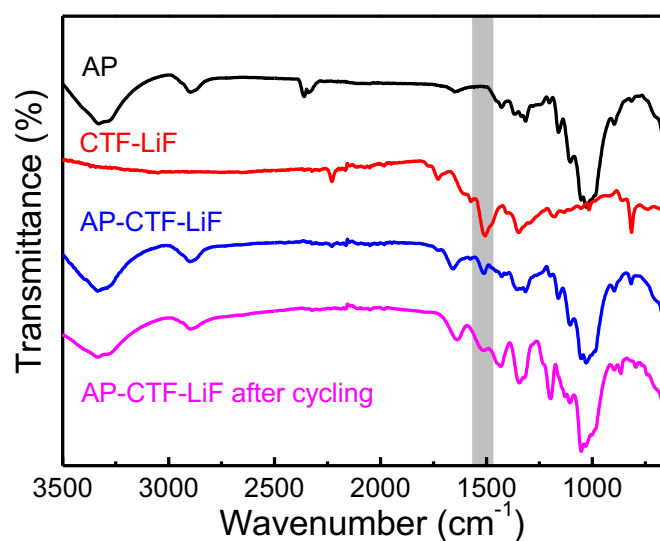
**Figure S14.** CE of Li plating/stripping for AP-LiF electrode when measured at (a) 3 mA cm<sup>-2</sup> with 1 mAh cm<sup>-2</sup> and (b) 10 mA cm<sup>-2</sup> with 1 mAh cm<sup>-2</sup>.



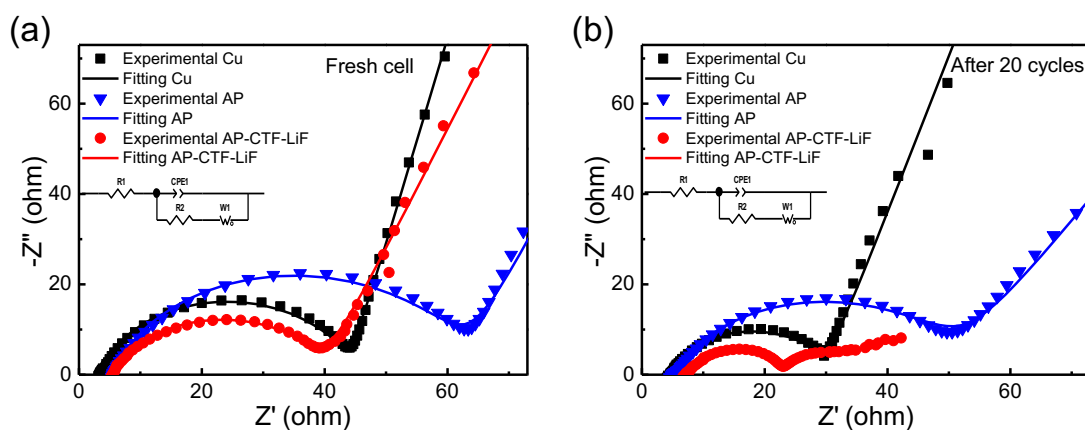
**Figure S15.** Nucleation overpotentials of the cells with AP-CTF-LiF, AP-LiF and AP.



**Figure S16.** Charge-discharge profiles of the cells at  $10 \text{ mA cm}^{-2}$  with  $1 \text{ mAh cm}^{-2}$  Li at (a) 1st cycle, (b) 10th cycle and (c) 50th cycle.



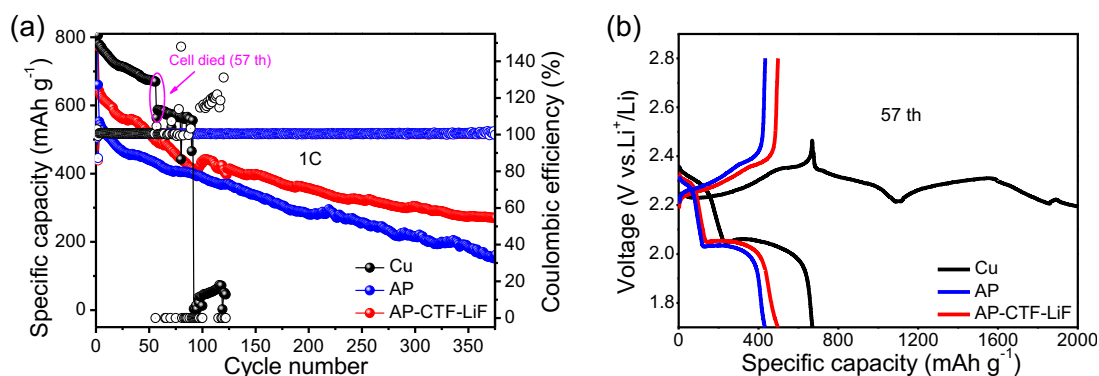
**Figure S17.** FT-IR spectra of AP, CTF-LiF, AP-CTF-LiF and AP-CTF-LiF after cycling.



**Figure S18.** EIS curves of (a) fresh cells with bare Cu, AP and AP-CTF-LiF and (b) the same cells after 20 cycles at  $3 \text{ mA cm}^{-2}$  with  $1 \text{ mAh cm}^{-2}$ .

**Table S4.** Fitting results to the equivalent circuit displayed in Figure S11.

	Fresh cell			After 20 cycles		
	Cu	AP	AP-CTF-LiF	Cu	AP	AP-CTF-LiF
$R_0$ (ohm)	3.48	5.50	5.37	4.59	5.25	7.15
$R_{ct}$ (ohm)	40.96	58.11	35.33	25.49	46.32	12.82



**Figure S19.** (a) Cycling performance and CEs of Li-S cells with bare Cu, AP and AP-CTF-LiF. (b) Galvanostatic discharge-charge profiles at 57<sup>th</sup> cycle for the three Li-S cells.