Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

In-situ decorated cathode by LiF and F@C for performance enhanced Li-S battery

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Experimental section

Materials:

CF_x was purchased from YuanchengChem. Sulfur was brought from Adamas. Li foils, and Al foils were purchased from Ke Jing Materials Technology CO., Ltd., Super P and polyvinylidene fluoride (PVDF) were obtained from DoDoChem. The electrolyte of Li–S battery and Polypropylene-based separator with commercial name Celgard 2500 were obtained from ZhongyanChem. N-methyl pyrrolidone (NMP) was purchased from Sinopharm Chemical Reagent Co., Ltd. LiF was from Shanghai Macklin Biochemical Co., Ltd. Li_2S and 1, 2-dimethoxyethane (DME) were from Sigma-Aldrich.

Preparation of S, and S/CF_x cathodes:

The S/CF_x composite was obtained by grinding S and CF_x with a ratio of 5:2 in the agate mortar. For the fabrication of a homogeneous S and S/CF_x cathodes, the 70 wt% composite material, 20 wt% Super P and 10 wt% the binder PVDF were mixed together by grinding for 30 min. The mixture was transferred to a weighing bottle and NMP was used as solvent to prepare a slurry. Then, the slurry was coated onto an Al foil with blade and dried in a 60 ºC vacuum oven for overnight. The S loading is around 1 mg cm^{-2}.

Adsorption tests:

Li_2S_6 solution was prepared by the reaction of sulfur and Li_2S powder (n:n = 1:5) in 15 mL DME. The solution was stirred at 80 ºC overnight[1-5]. An appropriate amount of Super P, LiF and the discharge products of CF_x (LiF&F@C) were added to 2.5 mL Li_2S_6 solution (2 mM). All processes were carried out in an argon-filled glove box. The adsorption ability of Super P, LiF and LiF&F@C on Li_2S_6 was investigated by UV-vis spectroscopy using SHIMADZU UV-175 spectrometer.

Material Characterization:

Field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F) was used to characterize the morphologies of the samples. Energy dispersive spectrometry (EDS, OXFORD) was performed to analyze element ratio. The structures of the CF$_x$ and the discharge products of CF$_x$ were characterized by a SmartLab3Kw X-ray diffractometer (XRD) using Cu Kα (λ = 1.5418 Å) radiation at a scanning speed of 20° per minute. X-ray photoelectron spectroscopy (XPS, thermo scientific escalate 250XI) was used to characterize the discharge products of CF$_x$.

Electrochemical measurements:

Before using as cathode, various electrodes were cut into a disc-shaped electrode and kept in a 60 ºC vacuum oven for 24 h. Coin cells (2025 type configurations) were assembled in a glove box with argon using Li foil as anode and PP membrane as the separator. The electrolyte usually consisted of 1 mol L^{-1} lithium bis-trifluoromethanesulphonylimide (LiTFSI) and 0.2 mol L^{-1} LiNO$_3$ additive in a mixed solution of DME and 1,3-dioxolane (DOL) (V_{DME}:V_{DOL} = 1:1). The cyclic voltammetry (CV) tests were operated on a BioLogic Science Instruments (VMP-300) between 1.8 and 3.0 V. The electrochemical impedance spectroscopy (EIS) was tested on the BioLogic Science Instruments (VMP-300) with the frequency range from 100 kHz to 0.01 Hz. The charge–discharge cycles were carried out in a potential range from 1.8 to 3.0 V using LAND battery testers. The specific capacity was calculated based on the weight of S.

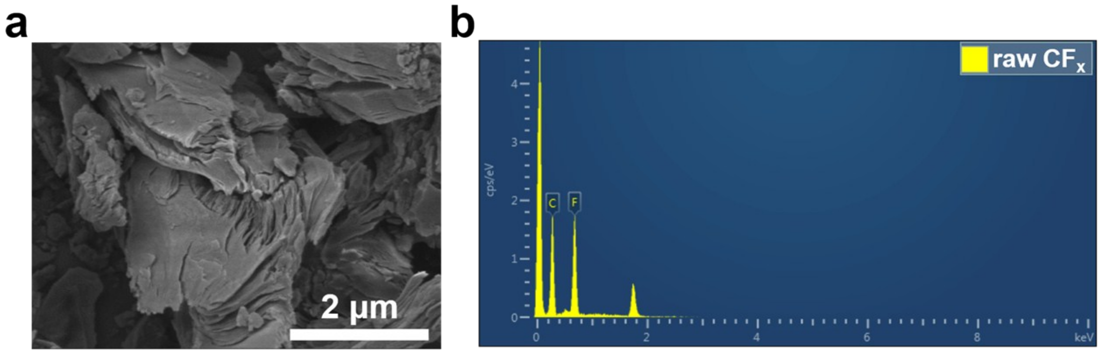

Fig. S1 (a) SEM image of CF$_x$. (b) EDS spectra of CF$_x$.

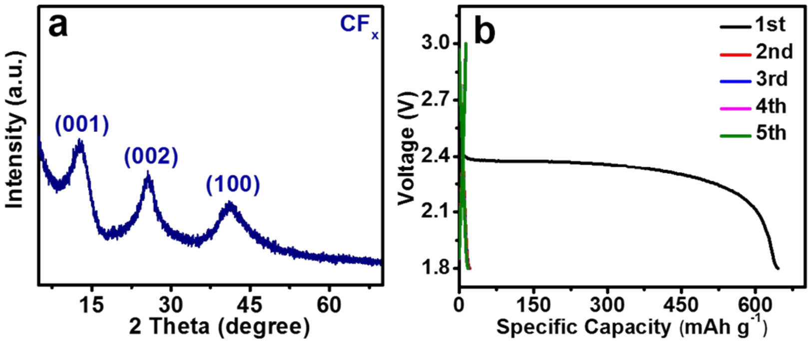

Fig. S2 (a) XRD pattern of CF_x. (b) Charge and discharge curves of Li-CF_x battery at 0.1 C.

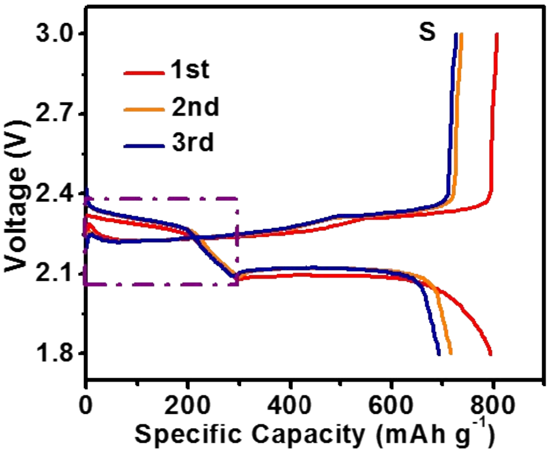

Fig. S3 Voltage profiles of S electrode at 0.1 C for the first three cycles.

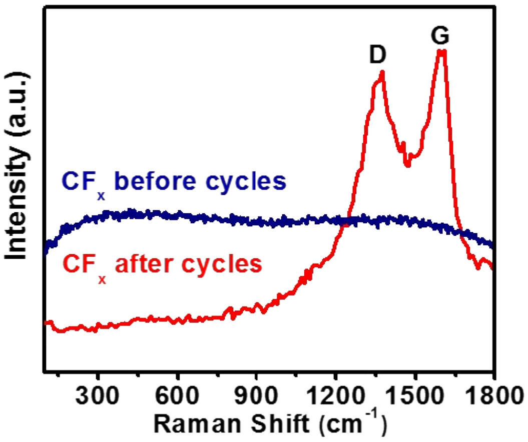

Fig. S4 Raman spectrum of CF_x before and after discharge.

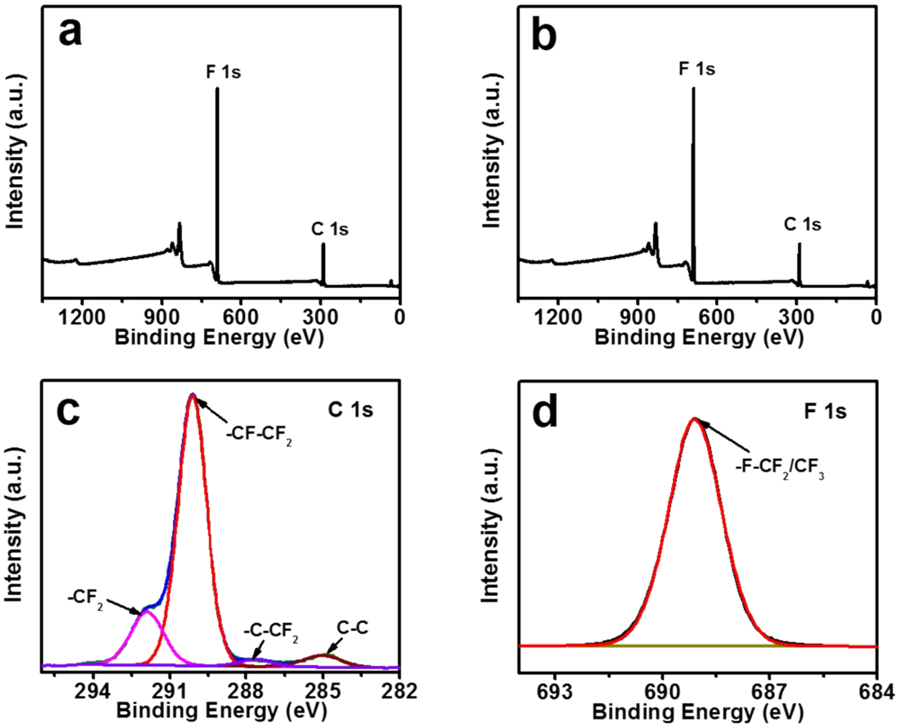

Fig. S5 (a) XPS survey spectrum of the CF_x discharge products, (b) XPS survey spectrum, (c) high-resolution spectra of C 1s and (d) F 1s of CF_x.

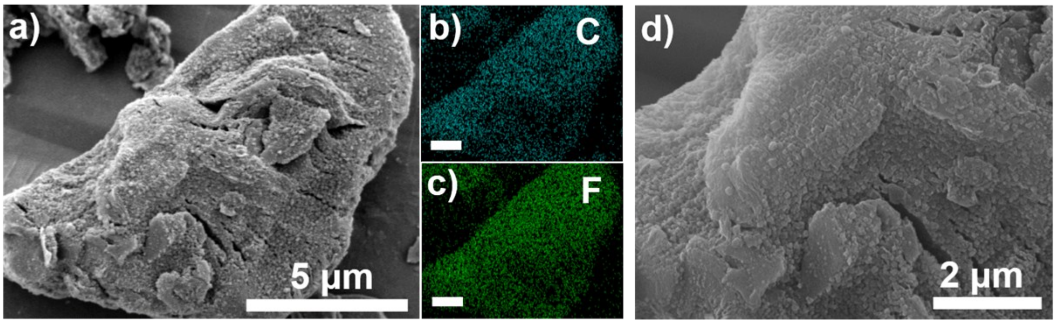

Fig. S6 (a, d) SEM images of CF_x after discharge. (b, c) Elemental EDS mapping images of CF_x after discharge (the scale bar in b, c represents 2 μ m).

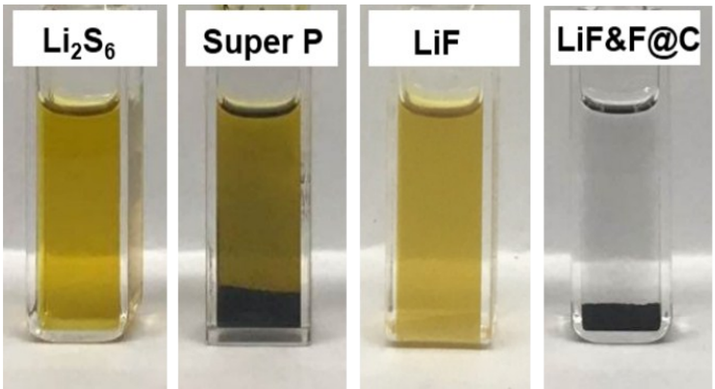

Fig. S7 Optical photos of original Li_2S_6 solution, Super P, LiF and LiF&F@C powders soaked in Li_2S_6 solution.

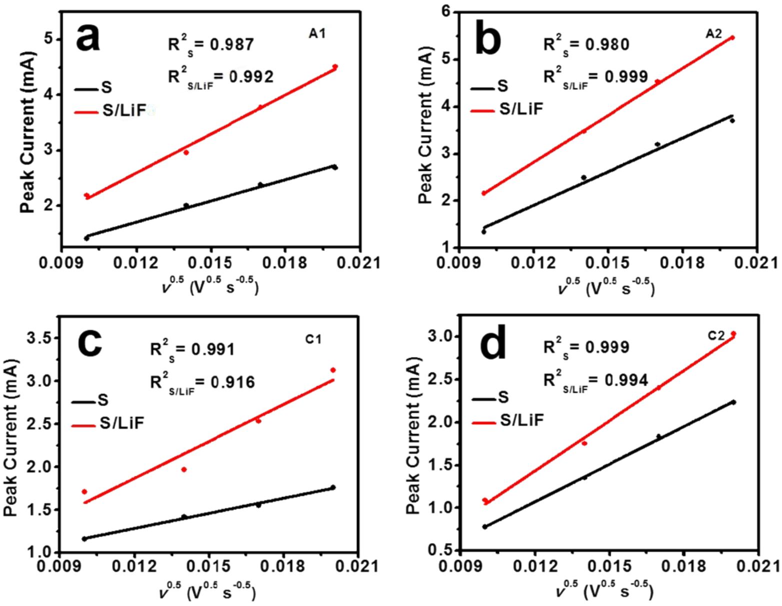

Fig. S8 Plots of CV peak current for (a-b) the anodic oxidation processes (A1 and A2) and (c-d) cathodic reduction processes (C1 and C2) versus the square root of the sweep rates.

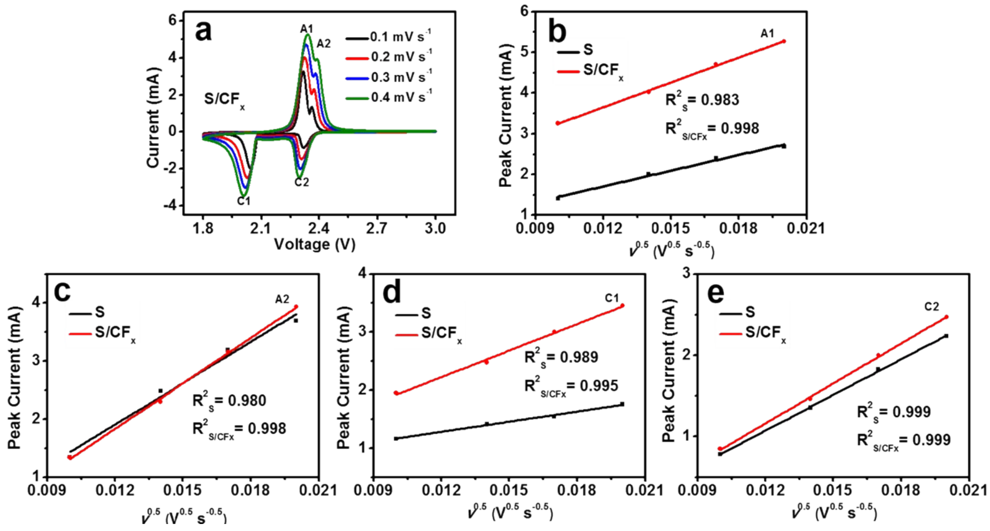

Fig. S9 CV curves of (a) S/CF$_x$ electrodes at various voltage sweep rates.[6] Plots of CV peak current for (b-c) the anodic oxidation processes (A1 and A2) and (d-e) cathodic reduction processes (C1 and C2) versus the square root of the sweep rates.

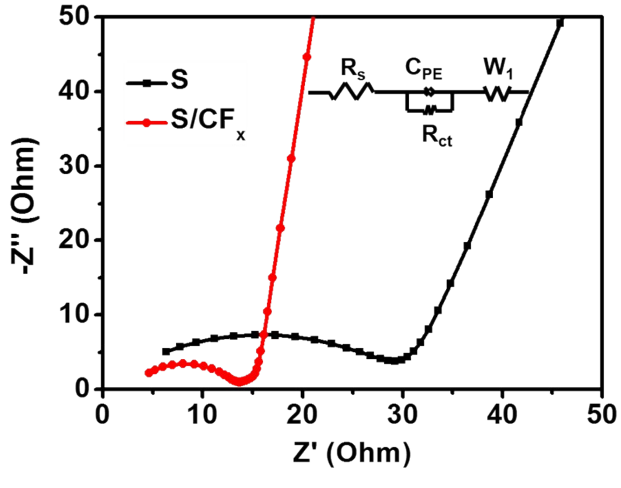

Fig. S10 EIS spectra of the S and S/CF$_x$ electrodes after CV test, the inset is the simulation equivalent for fitting the experimental spectra.

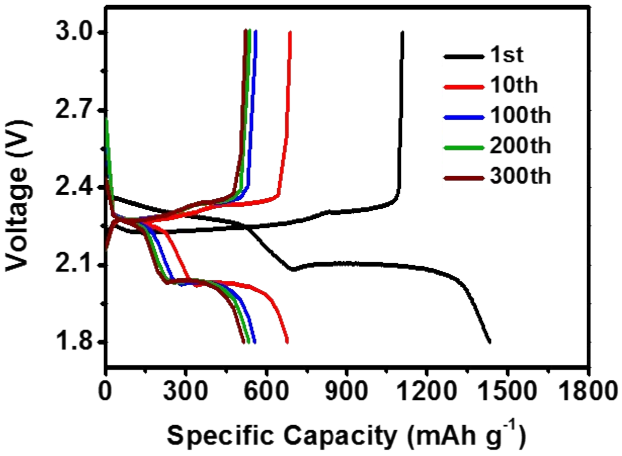

Fig. S11 Charge-discharge curves of S/CF$_x$ cathode for 1st, 10th, 100th, 200th and 300th cycles.

Table S1. The specific lithiun ion diffusion coefficient of Li–S batteries with S and S/CF$_x$ cathodes.

Parameters	**S**	**S/CF$_x$**
D_{Li+} at peak A1 [cm^2 s^{-1}]	**1.19×10^{-8}**	**3.07×10^{-8}**
D_{Li+} at peak A2 [cm^2 s^{-1}]	**4.20×10^{-8}**	**5.07×10^{-8}**
D_{Li+} at peak C1 [cm^2 s^{-1}]	**2.59×10^{-9}**	**1.71×10^{-8}**
D_{Li+} at peak C2 [cm^2 s^{-1}]	**1.58×10^{-8}**	**2.0×10^{-8}**

Table S2. The specific data resulting from simulation equivalent circuits of the Li–S batteries with S and S/CF$_x$ electrodes.

Cathode	**R_s (Ω)**	**R_{ct} (Ω)**
S	**2.64×10^{-6}**	**31.18**
S/CF$_x$	**2.86**	**10.37**

References

1. L. Zhang, M. Ling, J. Feng, G. Liu and J. Guo. *Nano Energy*, 2017, **40**, 559-565.
2. W. Wu, J. Pu, J. Wang, Z. Shen, H. Tang, Z. Deng, X. Tao, F. Pan and H. Zhang. *Adv. Energy Mater.*, 2018, **8**, 1702373.
3. C. Dai, J.-M. Lim, M. Wang, L. Hu, Y. Chen, Z. Chen, H. Chen, S.-J. Bao, B. Shen, Y. Li, G. Henkelman and M. Xu. *Adv. Funct. Mater.*, 2018, **28**, 1704443.
4. Z. Yuan, H.-J. Peng, T.-Z. Hou, J.-Q. Huang, C.-M. Chen, D.-W. Wang, X.-B. Cheng, F. Wei and Q. Zhang. *Nano Lett.*, 2016, **16**, 519-527.
5. X. Wang, T. Gao, F. Han, Z. Ma, Z. Zhang, J. Li and C. Wang. *Nano Energy*, 2016, **30**, 700-708.
6. S. Bai, X. Liu, K. Zhu, S. Wu and H. Zhou. *Nat. Energy*, 2016, **1**, 16094-16103.