

Efficient Immobilization and Bidirectional Catalysis of Polysulfide Conversion by FeCoP Quantum Dot for Lithium-sulfur Batteries

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Experimental

Visualized Adsorption of Polysulfides

Li₂S₆ solution was selected as a representative of polysulfides, which was prepared by mixing Li₂S and sulfur with a molar ratio of 1:5 in a solution containing 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v = 1/1) under vigorous stirring. Then, NCS, FeCo-NCS and FeCo-NCS samples were added separately into the as-prepared Li₂S₆ solution to evaluate their adsorption abilities.

Assembly and Measurements of Symmetric Cells

To prepare the sulfur-free electrodes for symmetric cells, the active materials (NCS, FeCo-NCS and FeCo-NCS) were ground with Super P and PVDF binder in a weight ratio of 8:1:1 in NMP solvent to form a slurry and coated onto Al foil. Then the electrodes were punched into disks with a diameter of 10 mm and the areal loading of electrodes disks were around 0.6 mg cm⁻². The Li₂S₆ electrolyte was prepared by dissolving Li₂S and sulfur with a molar ratio of 1:5 in a mixed solvent of DOL/DME (v/v = 1/1) with bis(trifluoromethanesulfonyl)imide lithium (LiTFSI, 1.0 M) and LiNO₃ (1.0 wt%) under vigorous stirring. The symmetric cells were assembled by sandwiching a Celgard 2400 polypropylene separator (diameter = 12 mm) between two identical sulfur-free electrodes (NCS, FeCo-NCS and FeCo-NCS) with 40 μL Li₂S₆ electrolyte in a CR2032 coin cell. Both CV and EIS were conducted on a CHI 760E workstation.

Measurements for the Li₂S Deposition

The Li₂S₈ electrolyte was prepared by dissolving the Li₂S and sulfur with a molar ratio of 1:7 in tetraglyme solvent with LiTFSI (1.0 M) under vigorous stirring. The cells were assembled by sandwiching a Celgard 2400 polypropylene separator between the sulfur-free electrodes (NCS, FeCo-NCS and FeCo-NCS) and Li foil in a CR2032 coin cell.

The Li_2S_8 electrolyte was dropped onto the sulfur-free electrodes, while the blank electrolyte without Li_2S_8 was added in the Li foil side. The assembled cells were galvanostatically discharged at 0.112 mA to 2.06 V, and subsequently kept potentiostatically discharged at 2.05 V.

Measurements for the Li_2S Dissolution

The cells identical to those in the above tests of Li_2S deposition were employed for the tests of Li_2S dissolution. The cells were firstly galvanostatically discharged at 0.10 mA to 1.80 V, and subsequently galvanostatically discharged at 0.01 mA to 1.80 V for full transformation of S species into solid Li_2S . Then the cells were potentiostatically charged at 2.40 V.

Assembly and Measurements of Li–S Cells

To prepare the cathode, S@NCS, Super P, and PVDF binder were mixed in a mass ratio of 70:20:10 to form a homogeneous slurry. Then, the slurry was coated on Al foil and dried at 60 °C for 12 h to obtain S@NCS cathode (diameter = 10 mm). The routine mass loading of sulfur in the electrode is about 1 mg cm^{-2} (4.5 mg cm^{-2} for high S loading test). CR2032 coin cells were assembled by employing the as-prepared sulfur cathodes, Celgard 2400 polypropylene separator (diameter = 12 mm), and Li foil as the anode. The electrolyte was LiTFSI (1.0 M) in a mixed solvent of DOL/DME (v/v=1/1) with LiNO_3 (1.0wt%). The electrolyte/sulfur (E/S) ratio is about 40 $\mu\text{L mg}^{-1}$ unless otherwise noted (4 $\mu\text{L mg}^{-1}$ for lean electrolyte test). The galvanostatic charge/discharge (GCD) tests were measured using a Neware battery system within a voltage window of 1.7–2.8 V. The current density is defined as 1 C = 1675 mA g^{-1} . CV tests were conducted between 1.7 and 2.8 V. EIS was performed in the frequency range of 0.01 Hz to 100 kHz.

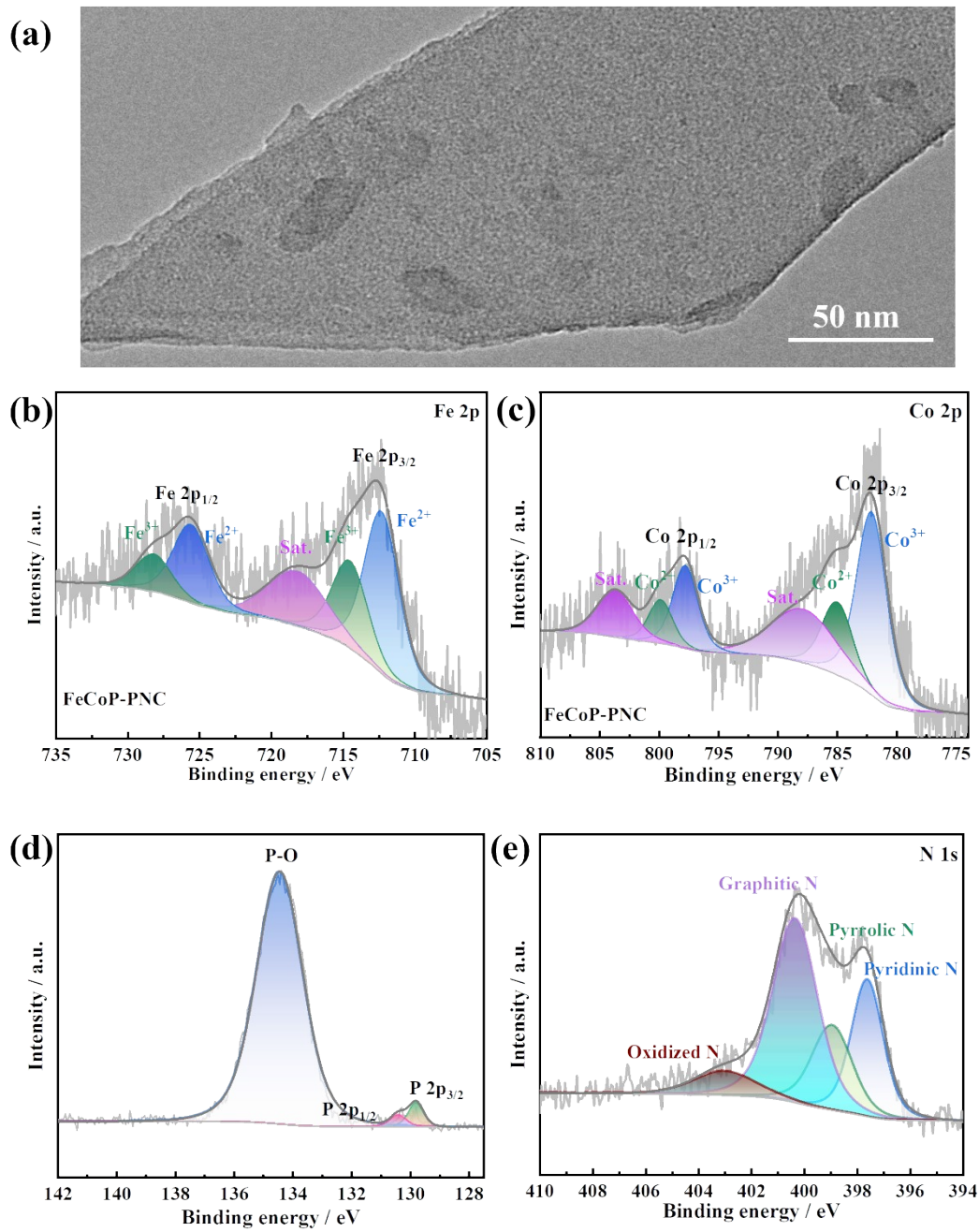


Fig. S1. (a) TEM image of NCS; High-resolution XPS spectra of (b) Fe 2p, (c) Co 2p and (d) P 2p and (e) N1s.

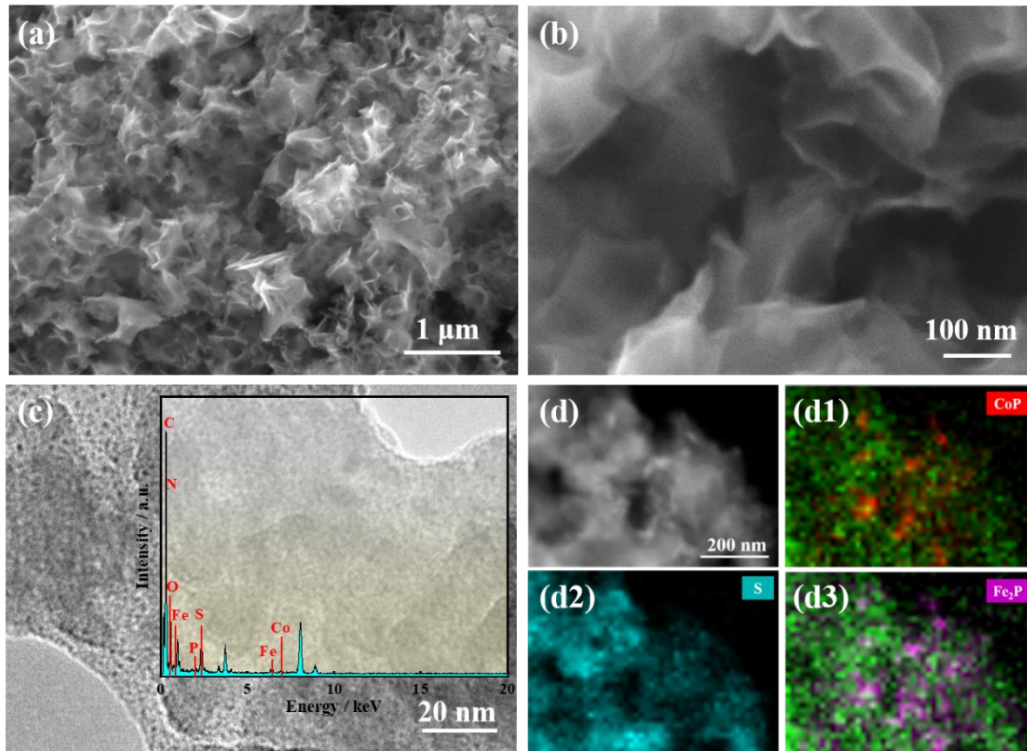


Fig. S2. (a, b) SEM and (c) TEM images on different scales (Insert: EDX spectrum); (d) STEM image and the high magnification elemental mapping images of S@FeCoP-NCS sample.

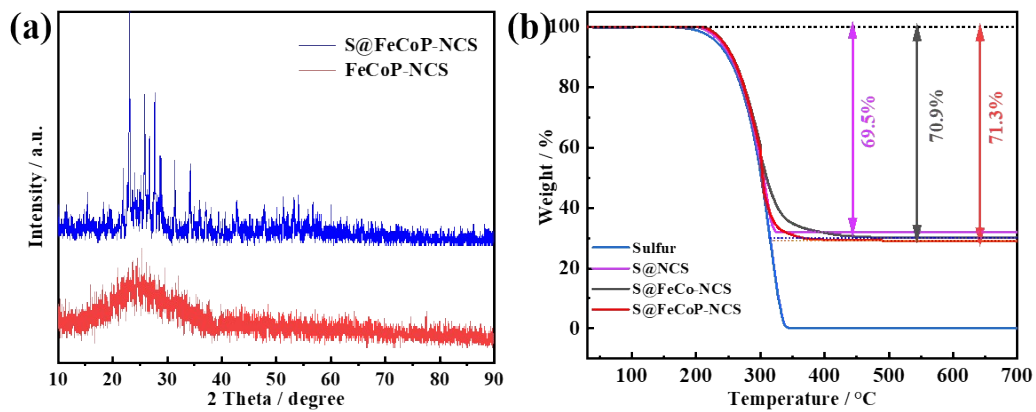


Fig. S3. (a) XRD patterns of S@FeCoP-NCS sample; (b) TGA curve of S@NCS, S@FeCo-NCS and S@FeCoP-NCS samples with 70% S-loading under a nitrogen atmosphere from 25 °C to 600 °C.

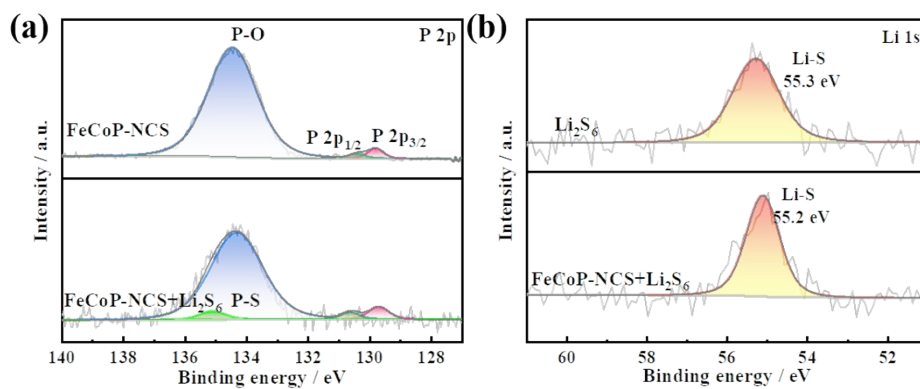


Fig. S4. (a) XPS spectra of P 2p before and after adsorbing Li₂S₆; (b) Li 1s of pristine Li₂S₆ and Li₂S₆@FeCoP-NCS composite before and after absorption.

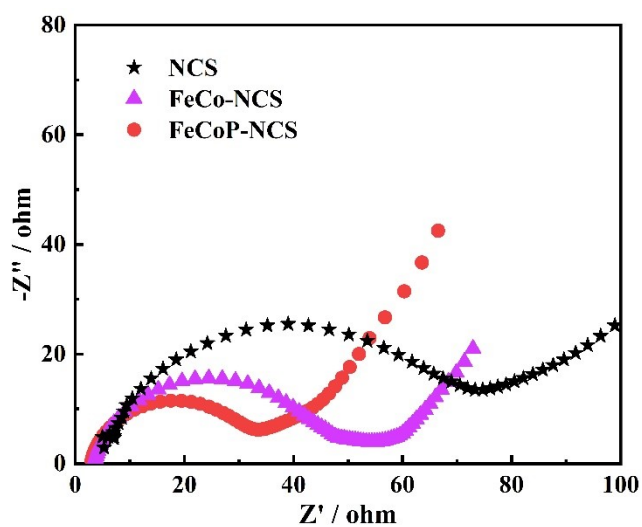


Fig. S5. EIS spectra of Li-S cells with S@NCS, S@FeCo-NCS and S@FeCoP-NCS electrodes.

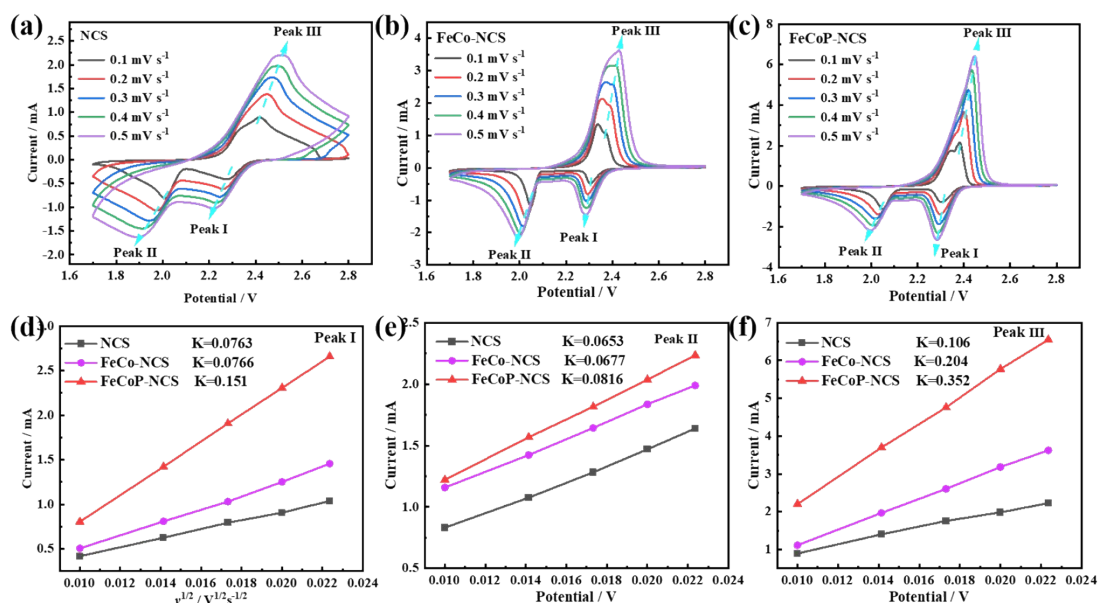


Fig. S6. Lithium-ion diffusion characteristics of the fabricated electrodes at different voltage scan rates. (a-c) CV curves of the S@NCS, S@FeCo-NCS and S@FeCoP-NCS electrodes; (d-f) cathodic reduction process and anodic oxidation process against the square root of the scan rates.

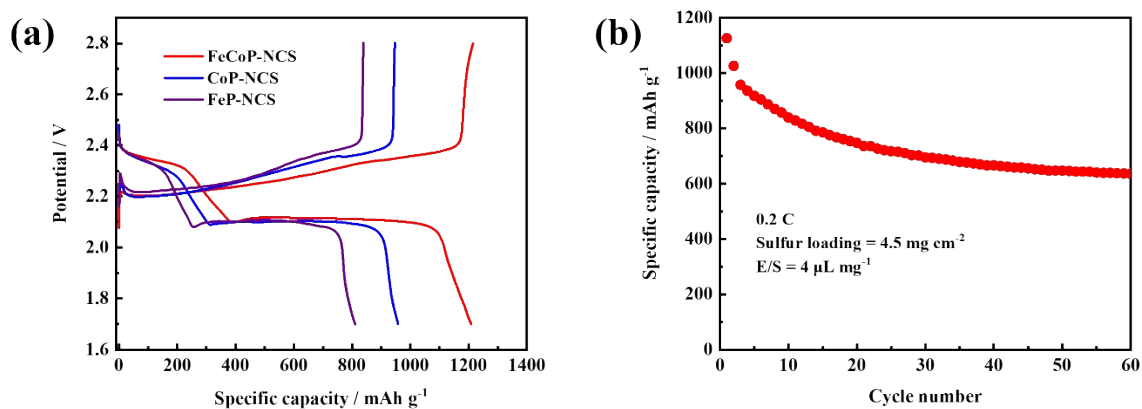


Fig. S7. (a) the first charge and discharge profiles of S@FeCoP-NCS, S@CoP-NCS and S@FeP-NCS cathodes; (b) cycling performance of S@FeCoP-NCS cathode with high sulfur loadings and lean electrolyte at 0.2 C.

Table S1. Diffusion coefficient of Li⁺ on S@NCS, S@FeCo-NCS and S@FeCoP-NCS electrodes.

	Peak I	Peak II	Peak III
S@NCS	1.97*10 ⁻⁷	1.44*10 ⁻⁷	3.81*10 ⁻⁷
S@FeCo-NCS	1.99*10 ⁻⁷	1.55*10 ⁻⁷	1.41*10 ⁻⁶
S@FeCoP-NCS	7.73*10 ⁻⁷	2.26*10 ⁻⁷	4.20*10 ⁻⁶

Table S2. Comparison of S@FeCoP-NCS assembled LSB performance with other electrodes reported in literature.

Sulfur cathodes	Current density	Cycle number	Remaining capacity	Capacity retention	Ref.
C/S/InOOH	2 C	500	558 mAh g ⁻¹	69.5%	1
S/PPy-MnO ₂	1 C	500	550 mAh g ⁻¹	64.7%	2
FMCTF-S	1 C	400	426 mAh g ⁻¹	62.6%	3
NPC/MoO ₂ @S	1 C	500	503 mAh g ⁻¹	63.3%	4
S-AQ-G	0.5 C	500	550 mAh g ⁻¹	65.0%	5
S/SnP _{0.94} @PHCA	0.5 C	300	442 mAh g ⁻¹	62.2%	6
S@FeCoP-NCS	1 C	500	605 mAh g ⁻¹	72.6%	This work

References

1. T. Zhao, J. Chen, K. Dai, M. Yuan, J. Zhang, S. Li, Z. Liu, H. He, C. Yang and G. Zhang, *J. Colloid Interface Sci.*, 2022, **610**, 418-426.
2. J. Zhang, Y. Shi, Y. Ding, W. K. Zhang and G. H. Yu, *Nano Lett.*, 2016, **16**, 7276-7281.
3. D.-G. Wang, L. Tan, H. Wang, M. Song, J. Wang and G.-C. Kuang, *ChemElectroChem*, 2019, **6**, 2777-2781.
4. H.-Y. Zhou, Z.-Y. Sui, F.-L. Zhao, Y.-N. Sun, H.-Y. Wang and B.-H. Han, *Nanotechnol.*, 2020, **31**, 315601.
5. G. Li, X. Wang, M. H. Seo, M. Li, L. Ma, Y. Yuan, T. Wu, A. Yu, S. Wang, J. Lu and Z. Chen, *Nat. Commun.*, 2018, **9**, 705.
6. X. Gao, Y. Huang, X. Li, H. Gao and T. Li, *Chem. Eng. J.*, 2021, **420**, 129724.