Supporting Information (SI)

Critical thickness of surface functionalization for enhanced lithium storage: a case of nanoscale polypyrrole-coating on FeS₂ for Li-ion battery

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Section 1

1.1. Material Characterization

The crystallographic phases of the samples were performed by Powder X-ray diffraction (DX-2700 diffractometer with a Cu-K α radiation source (λ =1.54056Å)) and FT-IR spectrometer (Nicolet 6700). Thermogravimetric (TG) analysis was performed with NETZSCH STA 449C instrument. The morphologies, sizes and EDX spectrum were characterized by scanning electron microscopy (SEM, Nova NanoSEM230). Transmission electron microscope (TEM) images, and selected area electron diffraction (SAED), High-resolution transmission electron microscope (HRTEM) image were recorded by using FEI Tecnai G2 f20 s-twin 200kV transmission electron microscope.

1.2. Electrode Fabrication

The FeS₂ or FeS₂@PPY (-1, -3, -5, -10 and -18, respectively) core-shell (80wt%), Super P (10 wt%) and polyvinylidene fluoride (PVDF) binder (10 wt%) were mixed in N-methyl-2-pyrrolidinone to form a uniform slurry, which was then coated on copper foil and dried in a vacuum oven at 50 °C for 12 h. The mass loading of the active material was around 1.0 mg cm⁻² (based on the weight of FeS₂ or FeS₂@PPY). The electrodes were assembled into CR2025-type coin cells in a glovebox (Mbraun, Germany) filled with ultra-high-purity argon. Lithium chips was used as the counter and reference electrodes, whereas 1 M LITFSI, 0.1 M lithium nitrate (LiNO₃) in 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) (volume ratio 1:1) was used as electrolyte.

1.3. Electrochemical Measurement

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were measured by a Gamry Interface 1000T electrochemical work station. CV curves were detected in the voltage range 1.0-3.0 V (vs. Li⁺/Li). The electrochemical impedance was tested in the frequency range of 100 kHz to 0.01 Hz. The galvanostatic charge–discharge measurements were conducted on a Neware BTS4000 battery tester (Shenzhen, China) between 1.0 and 3.0 V.

Section 2



Fig. S1. (a) XRD pattern; (b) EDAX pattern; (c) SAED pattern; (d) HRTEM image of FeS₂.

The FeS₂ particles with a size of around 2.5 μ m were prepared according to our previous work.^{S1} The XRD, EDAX, SAED and HRTEM characterization were used to determine the successful synthesis of a pure cubic phase of FeS₂, as exhibited in Fig. S1. The XRD pattern of FeS₂ (Fig. S1a) confirmed the formation of a pure cubic phase of FeS₂ (JCPDS card No. 42-1340). The EDAX pattern (Fig. S1b), SAED pattern (Fig. S1c) and HRTEM image (Fig. S1d) further confirmed the synthesis of FeS₂. In the SAED pattern (Fig. S1c), the selected area electron diffraction of FeS₂ showed a series of discontinuous concentric rings, indicating the polycrystalline characteristic. From inside to outside, the diffraction rings could be indexed to the (200), (311), (222) and (331) diffractions of FeS₂. In the HRTEM image (Fig. S1d), the clear space of the lattice fringes of 0.271 nm could be assigned to the (200) plane of FeS₂.



Fig. S2. (a) XRD patterns of F, FP-1, FP-3, FP-5, FP-10 and FP-18; (b) FTIR curves of F, FP-1, FP-3, FP-5, FP-10 and FP-18 powders.

The FeS₂@PPY core-shell composites were prepared by vapor-phase polymerization method (VPM) reported by Yu's group with minor modifications.^{S2} The XRD patterns and FTIR curves of F, FP-1, FP-3, FP-5, FP-10 and FP-18 are provided in Fig. S2. The XRD diffraction peaks intensity gradually decreased and no obvious peak shifts following the increasing PPY content in the FeS₂@PPY system, indicating the increase of PPY content did not significantly change the lattice structure of FeS₂, in addition to reducing the degree of crystallization (Fig. S2a). These characteristic chemical bonds (C=C, C-H, C-N, =C-H) of PPY appeared in FP-1, FP-3, FP-5, FP-10 and FP-18 but not in F, indicating that PPY existed in the FeS₂@PPY system.^{S2, S3}



Fig. S3. SEM images: (a) F; (b) FP-1; (c) FP-3; (d) FP-5; (e) FP-10; (f) FP-18 powders.



Fig. S4. TEM images: (a) F; (b) FP-1; (c) FP-3; (d) FP-5; (e) FP-10; (f) FP-18 powders.



Fig. S5. TG curves of F, FP-1, FP-3, FP-5, FP-10 and FP-18 powders.

Thermogravimetric analysis (TGA) (shown in Fig. S5) in air was carried out to determine the FeS_2 content of these $FeS_2@PPY$ composites. The initial weight loss between 300 and 450 °C can be attributed to not only the combustion of PPY in air, but also the combustion of residual carbon in asprepared FeS_2 , and the oxidation of FeS_2 in air. The chemical equation were provide as follows:

$$PPY + O_2 \rightarrow CO_2 + H_2O \quad (S1)$$

$$C + O_2 \rightarrow CO_2 \quad (S2)$$

$$2FeS_2 + 7O_2 \rightarrow Fe_2(SO_4)_3 + SO_2 \quad (S3)$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \quad (S4)$$

The second weight loss between 500 and 700 °C can be ascribed to the following chemical reaction: ^{S4, S15}

$$2Fe_2(SO_4)_3 \rightarrow 2Fe_2O_3 + 6SO_2 + 3O_2$$
 (S5)

Assuming the final products was Fe_2O_3 , the calculated FeS_2 contents in F (FeS_2), FP-1 (FeS_2@PPY-1), FP-3 (FeS_2@PPY-3), FP-5 (FeS_2@PPY-5), FP-10 (FeS_2@PPY-10) and FP-18 (FeS_2@PPY-18) were estimated to be 99.3%, 97.3%, 94.1%, 90.7%, 86.6%, and 80.7%, respectively. The corresponding PPY contents in FeS_2@PPY composites were calculated to be 0%, 2%, 5.2%, 8.6%, 12.7% and 18.6% with the increase of PPY thickness from 0 nm to 18 nm.



Fig. S6. CV curves of (a) F, (b) FP-1, (c) FP-3, (d) FP-5, (e) FP-10, (f) FP-18 cathode.

The CV curves at a scan rate of 0.1 mV s⁻¹ of F, FP-1, FP-3, FP-5, FP-10 and FP-18 cathodes were investigated in the voltage region of 1.0-3.0V, exhibited in Fig. S5. On the CV curve, all samples showed a similar shape, indicating that the coating layer did not have a remarkable influence on the electrochemical reaction. The charge-discharge mechanism was analyzed by taking the relatively stable 2nd cycle as an example, all the samples exhibited two cathodic peaks and three anodic peaks. According to the previous literature, ^{S4, S5} the two cathodic peaks, theoretically, corresponded to lithiation (Equation S6) and conversion (Equation S7) reactions, respectively.

Peak 1:

$$FeS_2 + 2Li^+ + 2e^- \rightarrow Li_2FeS_2 \quad (S6)$$

Peak 2:

$$Li_2FeS_2 + 2Li^+ + 2e^- \rightarrow Fe + 2Li_2S \quad (S7)$$

On the other hand, the three anodes peaks respectively corresponded to the following three reactions (Equation S8, 9 and 10):

Peak 3:

 $Fe + 2Li_2S \rightarrow Li_2FeS_2 + 2Li^+ + 2e^-$ (S8)

Peak 4:

 $Li_2FeS_2 \rightarrow Li_{2-x}FeS_2 + xLi^+ + xe^- (0.5 < x < 0.8)$ (S9)

Peak 5:

$$Li_{2-x}FeS_2 \rightarrow 0.8 ortho - FeS_2 + 0.2FeS_8 + 0.175S + (2-x)Li^+ + (2-x)e^- (S10)$$



Fig. S7. (a) 1st; (b) 50th voltage–capacity curves at 0.1 A g⁻¹ of F, FP-1, FP-3, FP-5, FP-10 and FP-18 in the voltage region of 1.0-3.0 V; (c) Voltage–capacity curves at 0.1 A g⁻¹ of FP-5 cathode at different cycles; (d) Voltage–capacity curves of FP-5 cathode at different rates (from 0.1 to 10 A g⁻¹).



Fig. S8. The initial Coulombic efficiency versus thickness of F, FP-1, FP-3, FP-5, FP-10 and FP-18 cathodes.



Fig. S9. SEM images after cycling at 0.1 A g^{-1} for 50 cycles: (a) F; (b) FP-1; (c) FP-3; (d) FP-5; (e) FP-10; (f) FP-18 powders.



Fig. S10. Kinetic analysis of the electrode of FP-5: (a) CV curves with scan rates from 0.1 to 0.9 mV s⁻¹; (b) CV peak current (Ip) logarithmically potted as a function of the sweep rates (v) to give the slops (b); (c) Separation of the capacitive and diffusion currents at a scan rate of 0.9 mV s⁻¹; (d) Contribution ratio of the capacitive and diffusion-controlled charge versus scan rate.

The kinetics of the FP-5 electrode was analyzed with CV measurement at different sweep rates from 0.1 to 0.9 mV s⁻¹ to further investigate the excellent high-rate capacitive behavior of the FP-5 electrode (Fig. S10). As exhibited in Fig. S10a, the CV profiles at different sweep rates increasing from 0.1 to 0.9 mV s⁻¹ displayed a similar shape with two cathodic peaks (Peak 1, Peak 2) and three anodic peaks (Peak 3, Peak 4 and Peak 5). According to the Dunn's work,^{S4, S6, S7} the contributions of diffusion-pseudocapacitance behavior could be analyzed by referring to the following equations:

$$i(V) = av^{b}$$
 (S11)
 $i(V) = k_{1}v^{1/2} + k_{2}v$ (S12)
 $i(V)/v^{1/2} = k_{1}v^{1/2} + k_{2}$ (S13)

where v is the sweep rate (mV s⁻¹) of a cyclic voltammogram and i(V) is the current (mA) at the corresponding v, and a, b stand for empirical parameters in Equation S11. Here, the b-value of 0.5 represents a diffusion controlled behavior, whereas the value of 1 indicates an ideal capacitive one. In this work, the b-values of FP-5 can be determined to be 0.805 (Peak 1), 0.938 (Peak 2), 0.921 (Peak

4) and 0.945 (Peak 5), as shown in Fig. S10b, indicating surface capacitive-controlled process kinetically favored the FP-5 electrode. Furthermore, the total capacitive contribution at a given scan rate could be distinguished into two parts (the diffusion-controlled fraction $k_1 v^{1/2}$ and capacitorlike one k_2v at a fixed potential (V), as depicted in Equation S12, k_1 and k_2 can be facilely achieved by plotting $i(V)/v^{1/2}$ vs $v^{1/2}$ (Equation S13), and thus the capacitive current $i_c(V) = k_2 v$ could be extracted from the total one with the value of k₂. For instance, the CV profile for the capacitive current (marked as the red shadow) compared with that of the diffusive current (marked as the cyan shadow) of FP-5 was 88.6%, at a scan rate of 0.9 mV s⁻¹ (Fig. S10c). Based on the same method, the total contributions of the pseudocapacitive behaviors (FP-5) were 77.1%, 81.8%, 84.3%, 86.8% and 88.6% at scan rates of 0.1, 0.3, 0.5, 0.7 and 0.9 mV s⁻¹, summed up in Fig. S10d. The FP-5 electrode exhibited the trend that the capacitive contribution increased as expected with the scan rate increase. Comparison of such results clearly revealed that the pseudocapacitive charge-storage amount of FP-5 did occupy a high portion of the whole capacity. The nanoscale PPY-coating-layer effectively improved the surface conductivity of the FeS₂ micro-particles, thus changed the path of some lithium ions from volume diffusion to surface diffusion, thereby achieved the fast lithium-ion storage performance of the FP-5 electrode.



Fig. S11. (a) Impedance parameters versus thicknesses of F, FP-1, FP-3, FP-5, FP-10 and FP-18 at 1st, 10th and 30th cycles and inset of the equivalent circuit model; (b) Relationship plot of Z' versus $\omega^{-1/2}$ at low-frequency region.

The equivalent circuit model (Inset of Fig. S11a) was used to better understand the impedance spectrum, which is composed of Rs (the sum of electrolyte resistance and ohmic resistances), Rf (the SEI resistance), Rct (the interfacial charge-transfer resistance), CPE1 (the constant phase element of the SEI), CPE2 (the double-layer capacitance), and W (the Warburg impedance).^{S8, S9, S10} The impedance parameters (Rs, Rf, Rct, R(Rs+Rf+Rct)) values versus thickness of 1st, 10th, 30th cycles gotten from fitting calculation to impedance spectrums are provided in Fig. S11a. Relationship plot of Z' versus $\omega^{-1/2}$ at low-frequency region of F, FP-1, FP-3, FP-5, FP-10 and FP-18 at 1st, 10th and 30th cycles were provided in Fig. S11b.

The calculation formula is shown as follows:

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \qquad \qquad Equation \,S14$$

Where R represents the gas constant, T is the test temperature, A is the surface area of electrode, F is the Farady constant, n represents the number of electrons per molecule attending the chargedischarge reaction, C is the concentration of lithium ion in our composite electrode, and σ is the slope of the line Z'- ω -^{1/2} (shown in Fig. S11b).^{S6, S9}

| Materials This work | Cycle stability (mAh g ⁻¹) | | Rate performance (mAh g ⁻¹) | | |
|---|---|---|--|---------------------------|----------------------------|
| | 0.1A g ⁻¹ 739(50 th) | 1A g ⁻¹ 504(500 th) | 0.1A g ⁻¹ 808 | 2A g ⁻¹ 543 | 10A g ⁻¹ 489 |
| Pitaya-structured | 0.3A g ⁻¹ | 1.5A g ⁻¹ | 0.2A g ⁻¹ | 2A g ⁻¹ | 10A g ⁻¹ |
| $FeS_2(a)C^{[S4]}$ | 614(100 th) | 455(100 th) | 660 | 499 | 400 |
| Carbon-Encapsulated | 0.5C | | 0.5C | 1C | 5C |
| $\operatorname{FeS}_{2}^{[S5]}$ | 500(50 th) | | 571 | 439 | 256 |
| $FeS_2/C^{[S11]}$ | 0.1A g ⁻¹ | 0.3A g ⁻¹ | 0.2A g ⁻¹ | 0.5Ag-1 | 1A g ⁻¹ |
| 2 | 682(100 th) | 446(100 th) | 820 | 615 | 440 |
| FeS_2/C nanotubes | 0.25C | 1C | 0.25C | 1C | 1.5C |
| arrays ^[S12] | 689(100 th) | 390(100 th) | 735 | 581 | 482 |
| FeS_2/C shells on cobalt | 0.25C | | 0.25C | 1C | 1.5C |
| nanowires ^[S13] | 536(70 th) | | 703 | 568 | 478 |
| FeS ₂ /CNT micro- | 0.1C | 1C | | | |
| spherical ^[S14] | 491(50 th) | 370(50 th) | | | |
| Nano-FeS2@N-doped | | 0.5A g ⁻¹ | 0.05A g ⁻¹ | 1A g ⁻¹ | 5A g ⁻¹ |
| graphene ^[S15] | | 402(400 th) | 768 | 445 | 285 |
| Porous FeS ₂ @rGO ^[S16] | 1A g-1 | 10A g ⁻¹ | 0.1A g ⁻¹ | 2A g-1 | 10A g ⁻¹ |
| | 435(200 th) | 170(2000 th) | 531 | 371 | 193 |
| FeS ₂ hollow | 0.2C | 1C | 0.1C | 0.5C | 1C |
| microspheres ^[S17] | 537(30 th) | 393(30 th) | 800 | 480 | 370 |
| FeS_2 nanocrystals ^[S18] | 0.2A g ⁻¹ 630(100 th) | 1A g ⁻¹ 600(50 th) | | | |
| FeS ₂ nanocubes ^[S19] | 1A g ⁻¹ | | 0.1A g ⁻¹ | 1A g ⁻¹ | 5A g ⁻¹ |
| | 540(150 th) | | 890 | 530 | 220 |
| FeS ₂ microsphere ^[S20] | 0.1C | | 0.1C | 0.5C | 2C |
| | 372(50 th) | | 372 | 295 | 162 |
| FeS ₂ via an upper cut- | 0.2C | 0.5C | 0.1C | 1C | 5C |
| off ^[S21] | 533(50 th) | 398(50 th) | 800 | 437 | 268 |
| FeS ₂ with ether-based | 1A g ⁻¹ | 2A g ⁻¹ | 0.5A g ⁻¹ | 3A g-1 | 8A g ⁻¹ |
| electrolyte ^[S22] | 540(100 th) | 495(100 th) | 615 | 496 | 318 |

Table S1. A comparison of cycle stability and rate performance between the FP-5 cathode and the other recently reported FeS₂ cathodes for lithium storage.

References

- [S1] Y.Y. Li, Q. Xiao, S.P. Huang, Highly active nickel-doped FeS₂ nanoparticles trigger non-enzymatic glucose detection. Mater. Chem. Phys. 193 (2017) 311-315.
- [S2] X.R. Sun, H.W. Zhang, L. Zhou, X.D. Huang, C.Z. Yu, Polypyrrole-Coated Zinc Ferrite Hollow Spheres with Improved Cycling Stability for Lithium-Ion Batteries. Small 27 (2016) 3732–3737.
- [S3] H.C. Liang, J.F. Ni, L. Li, Bio-inspired engineering of Bi₂S₃-PPY yolk-shell composite for highly durable lithium and sodium storage. Nano Energy 33 (2017) 213–220.
- [S4] X.J. Xu, J. Liu, Z.B. Liu, J.D. Shen, R.Z. Hu, J.W. Liu, L.Z. Ouyang, L. Zhang, M. Zhu, Robust Pitaya-Structured Pyrite as High Energy Density Cathode for High-Rate Lithium Batteries. ACS Nano 11 (2017) 9033-9040.
- [S5] J. Liu, Y.R. Wen, Y. Wang, P.A. van Aken, J. Maier, Y. Yu, Carbon-Encapsulated Pyrite as Stable and Earth-Abundant High Energy Cathode Material for Rechargeable Lithium Batteries. Adv. Mater. 26 (2014) 6025–6030.
- [S6] P. Ge, S.J. Li, H.L. Shuai, W. Xu, Y. Tian, L. Yang, G.Q. Zou, H.S. Hou, X.B. Ji, Engineering 1D chain-like architecture with conducting polymer towards ultra-fast and high-capacity energy storage by reinforced pseudocapacitance. Nano Energy 54 (2018) 26–38.
- [S7] J. Wang, J. Polleux, J. Lim, B. Dunn, Pseudocapacitive Contributions to Electrochemical Energy Storage in TiO₂ (Anatase) Nanoparticles. J. Phys. Chem. C 111 (2007) 14925-14931.
- [S8] Y. Wu, Q. Xiao, S.P. Huang, K. Wang, Facile synthesis of hierarchically γ-Al₂O₃@C yolk-shell microspheres for lithium-sulfur batteries, Mater. Chem. Phys. 221 (2019) 258–262.
- [S9] B. Yin, X.X. Cao, A.Q. Pan, Z.G. Luo, S. Dinesh, J.D. Lin, Y. Tang, S.Q. Liang, G.Z. Cao, Encapsulation of CoS_x Nanocrystals into N/S Co-Doped Honeycomb-Like 3D Porous Carbon for High-Performance Lithium Storage. Adv. Sci. 5 (2018) 1800829.
- [S10] Y.X. Wang, L. Huang, L.C. Sun, S.Y. Xie, G.L. Xu, S.R. Chen, Y.F. Xu, J.T. Li, S.L. Chou, S.X. Dou, S.G. Sun, Facile synthesis of a interleaved expanded graphite-embedded sulphur nanocomposite as cathode of Li-S batteries with excellent lithium storage performance, J. Mater. Chem. 22 (2012) 4744-4750.
- [S11] L. Fei, Y.F. Jiang, Y. Xu, G. Chen, Y.L. Li, X. Xu, S.G. Deng, H.M. Luo, A novel solvent-free thermal reaction of ferrocene and sulfur for one-step synthesis of iron sulfide and carbon nanocomposites and their electrochemical performance, J. Power Sources 265 (2014) 1-5.
- [S12] G.X. Pan, F. Cao, X.H. Xia, Y.J. Zhang, Exploring hierarchical FeS₂/C composite nanotubes arrays as advanced cathode for lithium ion batteries, J. Power Sources 332 (2016) 383-388.
- [S13] F. Cao, G.X. Pan, J. Chen, Y.J. Zhang, X.H. Xia, Synthesis of pyrite/carbon shells on cobalt nanowires forming core/branch arrays as high-performance cathode for lithium ion batteries, J. Power Sources 303 (2016) 35-40.
- [S14] L. Liu, Z.Z. Yuan, C.X. Qiu, J.C. Liu, A novel FeS₂/CNT micro-spherical cathode material with enhanced electrochemical characteristics for lithium-ion batteries, Solid State Ionics 241 (2013) 25–29.
- [S15] R. Tan, J.L. Yang, J.T. Hu, K. Wang, Y. Zhao, F. Pan, Core-shell nano-FeS₂@N-doped graphene as an advanced cathode material for rechargeable Li-ion batteries. Chem. Commun. 52 (2015) 986-989.
- [S16] P.Q. Zhao, H.H. Cui, J. Luan, Z.F. Guo, Y.X. Zhou, H.T. Xue, Porous FeS₂ nanoparticles wrapped by reduced graphene oxide as high-performance Lithium-ion battery cathodes. Mater. Lett. 186 (2017) 62–65.
- [S17] Y.R. Wang, X.F. Qian, W. Zhou, H.T. Liao, S.Q. Cheng, Hierarchical nanostructured FeS₂ hollow microspheres for lithium-ion batteries. RSC Adv. 4 (2014) 36597–36602.
- [S18] M. Walter, T. Zünd, M.V. Kovalenko, Pyrite (FeS₂) nanocrystals as inexpensive high performance lithium-ion cathode and sodium-ion anode materials. Nanoscale 7 (2015) 9158-9163.
- [S19] W.L. Liu, X.H. Rui, H.T. Tan, C. Xu, Q.Y. Yan, H.H. Hng, Solvothermal synthesis of pyrite FeS₂ nanocubes and

their superior high rate lithium storage properties. RSC Adv. 4 (2014) 48770-48776.

- [S20] Y.M. Tao, K. Rui, Z.Y. Wen, Q.S. Wang, J. Jin, T. Zhang, T. Wu, FeS₂ microsphere as cathode material for rechargeable lithium batteries, Solid State Ionics 290 (2016) 47–52.
- [S21] S. Cheng, J. Wang, H.Z. Lin, W.F. Li, Y.C. Qiu, Z.Z. Zheng, X.L. Zhao, Y.G. Zhang, Improved cycling stability of the capping agent-free nanocrystalline FeS₂ cathode via an upper cut-off voltage control, J. Mater. Sci. 52 (2017) 2442–2451.
- [S22] Z. Hu, K. Zhang, Z.Q. Zhu, Z.L. Tao, J. Chen, FeS₂ microspheres with an ether-based electrolyte for highperformance rechargeable lithium batteries, J. Mater. Chem. A 3 (2015) 12898–12904.