



Conductive polymer armor strategy enables metal sulfides with super long-life sodium storage

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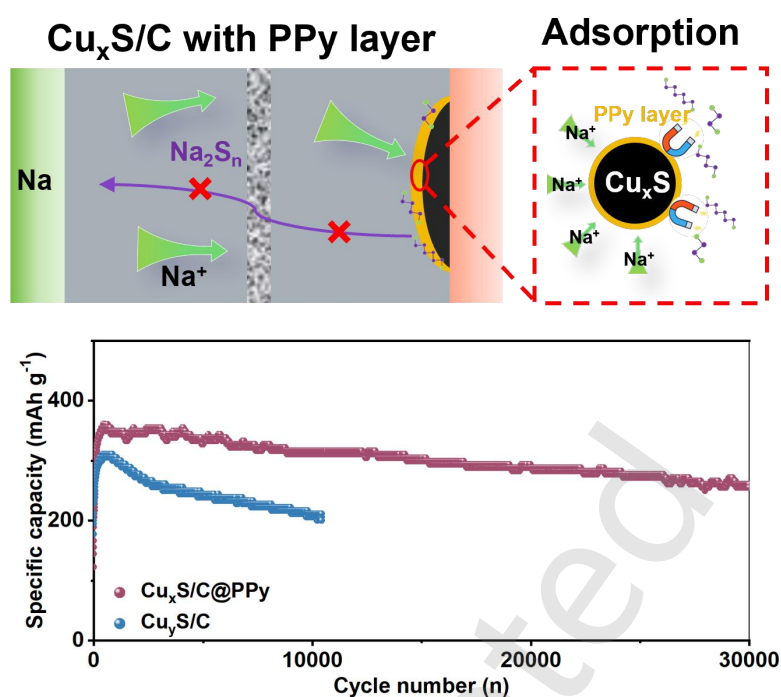
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An ultrathin polypyrrole (PPy) layer with a thickness of 4.0 nm is armored on the surface of Cu_xS/C microspheres through in-situ polymerization method and the Cu_xS/C@PPy composite anode is obtained. Owing to the strong polysulfide chemisorption capability and high sodiophilicity of PPy layer, the volume change and polysulfide shuttle behavior of Cu_xS/C@PPy anode are greatly restrained, endowing it long-term cyclic stability and outstanding rate performance.

Conductive polymer armor strategy enables metal sulfides with super long-life sodium storage

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Abstract

Metal sulfide anode for sodium-ion batteries (SIBs) have attracted widespread attention for the merits of abundant resources, low cost and high capacity. Unfortunately, its practical application still subjects to the low electron conductivity, severe micro-volume deformation, and grievous polysulfide shuttle during cycling process, leading to rapid capacity attenuation and poor cyclic behavior. To address these issues, the designed Cu₂S/C microsphere anode is armored with polypyrrole (PPy) layer, which intrinsically holds high sodiophilicity and strong chemisorption capability for polysulfides. As the protective shell layer of Cu₂S/C anode, both the volume change and polysulfide shuttle effect are greatly suppressed, achieving excellent sodium storage performance. Briefly, Cu₂S/C@PPy anode delivers high reversible capacity of 300 mAh g⁻¹ after 3000 cycles at 5 A g⁻¹, and 257 mAh g⁻¹ after 30000 cycles at 20 A g⁻¹. When matched with the commercial AC cathode, the optimized dual-ion battery also exhibits stable sodium storage capacity of 274 mAh g⁻¹ after 4000 cycles at 5 A g⁻¹. This work demonstrates the positive effect of conductive polymer armor strategy on the performance improvement of metal sulfide anode, and provides new strategy for the design of organic-inorganic hybrid electrodes.

Keywords: Metal sulfides; Conductive polymer armor; Organic-inorganic hybrid electrode; Polysulfide chemisorption; Sodium-ion batteries

1. Introduction

Global energy shortage is increasingly severe, and it is an urgent need to develop large-scale energy storage devices[1-3]. Among the current energy storage technologies, sodium-ion batteries (SIBs) are regarded as dazzling future star owing to the low cost, abundant resources and wide operating temperature range compared to lithium-ion batteries. Hard carbon, with a theoretical capacity of 372 mAh g⁻¹ was the primary anode for SIBs[4-6], but the extremely-low initial Coulombic efficiency, low voltage plateau, low compaction density and the high safety risks brought by the sodium dendrites seriously restricted the practical application of hard carbon[7, 8]. Thus, it is also necessary requirement to design new-type anode materials for SIBs with practical application potential[9-11].

Metal sulfides possessed high theoretical capacity and rapid phase transition reaction kinetics, and have been widely studied as anodes of SIBs[12-14]. However, in-situ real-time magnetic monitoring technology has found that due to the large Na ion radius and severe powdering of surface metal sulfides, the kinetics is sluggish, resulting in the existence of an “inactive core” inside the SIBs, which leads to its low capacity and poor cycling performance[15]. Therefore, the micro-nano structure design of metal sulfides with short ion transport paths is conducive to the insertion/extraction process of Na⁺. In addition, the crushing caused by volume expansion during the conversion reaction process usually requires the construction of hollow nanostructures and carbon-based composites[16-18]. Among the various metal sulfide-based anodes for SIBs, CuS had attracted widespread concern for the advantages of abundant resource and high capacity[19-21]. Unfortunately, CuS anode always suffered from low electron conductivity, severe volume deformation, and notorious polysulfide shuttle during the cycling process, leading to rapid capacity attenuation and inferior cyclic stability[22, 23]. Enlightened by the ideas in the field of metal-sulfur batteries, conductive polymers generally held strong polysulfide adsorption ability, which contributed to reduce the polysulfide shuttle effect[24-26]. Therefore, coating conductive polymer on the surface of CuS is considered

as an effective strategy to develop long-cycle-life metal sulfide anodes for SIBs.

Herein, an ultrathin polypyrrole (PPy) layer with a thickness of 4.0 nm is armored on the surface of $\text{Cu}_x\text{S}/\text{C}$ microspheres through in-situ polymerization method and the $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ composite anode is obtained. Owing to the strong polysulfide chemisorption capability and high sodiophilicity of PPy layer, the volume change and polysulfide shuttle behavior of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode are greatly restrained, endowing it long-term cyclic stability and outstanding rate performance. In details, $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode delivers stable sodium capacity of 300 mAh g^{-1} after 3000 cycles at 5 A g^{-1} , which is much higher than that of raw $\text{Cu}_x\text{S}/\text{C}$ anode. Even at high current density of 20 A g^{-1} , $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode still maintains high reversible capacity of 257 mAh g^{-1} after 30000 cycles, far higher than that of the previously reported CuS-based anodes.

2. Results and discussion

Notorious polysulfide shuttle during the cycling process is an important factor affecting the cycle life of sulfide-based sodium anode electrodes. As detailedly depicted in **Fig. 1a**, the nitrogen-containing ring has a high adsorption capacity for sodium polysulfides. As a modified coating layer, PPy conductive macromolecule is expected to reduce the shuttle problem of polysulfides in the negative electrode based on copper sulfide during the cycling process. Furthermore, **Figs. 1b, S1 and Tabs. S1, S2** presented the adsorption energies calculated by density functional theory (DFT). In brief, PPy molecule exhibited higher adsorption energy for Na_2S_2 (-1.85 eV) than that of carbon model (-0.22 eV). Meanwhile, PPy molecule also held stronger adsorption behavior for both Na_2S_4 (-1.77 eV) and Na_2S_6 (-1.56 eV), demonstrating the intrinsic chemisorption capability of PPy for polysulfides. Hence, in this work, a strategy for in-situ growth of conductive polymer coatings for modification was proposed. As shown in **Fig. 1c**, the $\text{Cu}_x\text{S}/\text{C}$ precursor was prepared through the initial hydrothermal reaction and the following calcination treatment under nitrogen atmosphere, while the targeted $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ composite was obtained via the in-situ polymerization coating process of pyrrole monomer. Scanning electron microscope (SEM) was carried out to observe the

morphology of these two samples. As compared in **Figs. 1d, S2a**, Cu_yS/C sample delivered microsphere morphology assembled by wire pellets. It is worth noting that a small fraction of distorted or agglomerated particles can be observed in the Cu_yS/C sample (**Fig. S2a**). This structural deformation is rationally ascribed to the necessary high-temperature calcination process (600 °C). During this stage, the intense carbonization of organic precursors and the concurrent release of pyrolytic gases induce uneven volume shrinkage, while partial sintering between adjacent spheres further causes morphological distortion. Nevertheless, the predominant morphology remains as microspheres, and this minor distortion does not compromise the overall structural integrity or phase purity. After in-situ polymerization process, the wire pellets on the surface of Cu_xS/C@PPy became coarse and smooth (**Figs. 1e, S2b**), which was ascribed to the successful coating of PPy. Additionally, as confirmed by the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images, an obvious PPy coating layer with amorphous structure and thin thickness of 4 nm was visually observed, demonstrating the right coverage of PPy on the surface of Cu_xS/C@PPy microspheres (**Figs. 1f, S3**). Energy-dispersive spectroscopy (EDS) mapping images further demonstrated the uniform distribution of Cu, S, C, N element on both Cu_yS/C and Cu_xS/C@PPy samples (**Figs. 1g, S4**).

X-ray diffraction (XRD) patterns revealed the mixed phase of Cu_{1.96}S and Cu_{1.8}S in Cu_yS/C and pure phase (Cu_{1.8}S) in Cu_xS/C@PPy sample phase proportion (**Fig. S5a**). Besides, The XRD refinement spectrum in **Fig. S6** show the mixed phase of Cu_yS/C sample and single crystal phase of Cu_xS/C@PPy. Based on the thermogravimetric analysis (TGA) curves, the mass residue of these two samples was higher than 93% after 900 °C, and the slightly higher mass loss of Cu_xS/C@PPy sample was attributed to the degradation of PPy component (**Fig. S5b**). The distinct *D*-band and *G*-band in Raman spectra confirmed the existence of amorphous carbon component in both Cu_yS/C and Cu_xS/C@PPy samples (**Fig. S5c**) [27, 28]. Meanwhile, Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) were adopted

to verify the attendance of PPy component in $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ sample. As detected in **Fig. S5d**, an obvious peak around 1631 cm^{-1} can be ascribed to the pyrrole rings[29], implying the presence of PPy layer. The high-resolution N 1s spectra of $\text{Cu}_y\text{S}/\text{C}$ sample was divided into graphitic N, pyrrolic N and pyridinic N (**Fig. S5e**)[30-32], which was attributed to the existence of nitrogen-doped carbon. In contrast, the high-resolution N 1s spectra of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ sample delivered typical conjugate nitrogen structure ($-\text{NH}^+/\text{=NH}^+/-\text{NH}$) derived from PPy polymer (**Fig. S5f**)[33-35]. In addition to the PPy component, the high-resolution XPS spectra of other elements (C 1s/Cu 2p) showed almost no difference within $\text{Cu}_y\text{S}/\text{C}$ and $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ samples (**Fig. S7**).

In order to understand the adsorption capacity of the PPy coating for sodium polysulfides, the polysulfide adsorption experiment was carried out to intuitively observe the chemisorption effect of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$. In details, 10 mg PPy, $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ and $\text{Cu}_y\text{S}/\text{C}$ powder were respectively added into glass bottles with 2 mL Na_2S_2 -containing DME solution. After standing for 12 h, the solution containing PPy and $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ powder gradually turned colorless (**Fig. 2a**). Moreover, the corresponding UV-vis spectra demonstrated the strong chemisorption ability of PPy component for polysulfides (**Fig. 2b**), which can be regarded as the primary reason for the superior sodium storage performance of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode. Meanwhile, the obtained $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ and $\text{Cu}_y\text{S}/\text{C}$ anodes at fully discharge state after 100 and 500 cycles were soaked into 5 mL dimethoxyethane (DME) solution for 2 h hours. As detected by the Ultraviolet-visible (UV-vis) spectra, $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode presented weaker absorption peaks of polysulfides[36, 37], which can be ascribed to the strong chemisorption capability of PPy for polysulfides. As a comparison, $\text{Cu}_y\text{S}/\text{C}$ anode delivered much stronger absorption peaks, indicating its more residual polysulfides (**Figs. 2c, d**). Additionally, when the discharge cut-off voltage was set as 0.2 V, the corresponding absorption peaks were also weaker, manifesting the discharge voltage had great influence on the metal sulfide anodes of SIBs. The above UV-vis spectroscopy tests were all based on steady-state

observations. However, the changes of the electrode during the cycling process are dynamic. Therefore, in this work, in-situ UV-vis technology was employed to observe the electrolyte during the cycling process, in order to understand the polysulfide shuttle situation of the electrode material during the cycling process. As shown in **Fig. S8**, in-situ observation battery was assembled with the work electrode ($\text{Cu}_x\text{S/C@PPy}$ and $\text{Cu}_y\text{S/C}$), counter electrode (Na metal), electrolyte and UV-vis cell. Obviously, electrolyte in the UV-vis cell with $\text{Cu}_y\text{S/C}$ electrode shown much stronger absorption peak around 200-350 nm than that of $\text{Cu}_x\text{S/C@PPy}$ electrode (**Figs. 2e, f**), which indicates that the less shuttle of polysulfides in UV-vis cell based on $\text{Cu}_x\text{S/C@PPy}$ electrode during cycle process. To further understand the function of PPy layer for the interface of anode materials, the electrochemical impedance spectroscopy (EIS) plots after different cycles were conducted. Briefly, the semicircle at high frequency represented the charge transfer resistance (R_{ct}), and $\text{Cu}_x\text{S/C@PPy}$ anode invariably delivered smaller R_{ct} values than $\text{Cu}_y\text{S/C}$ anode after different cycles (**Fig. S9**), suggesting fewer side effect. Based on the above analysis, due to its strong adsorption of polysulfides, the PPy coating layer will contribute to the development of high-performance copper sulfide negative electrodes.

The positive effect of PPy layer on the sodium storage performances of $\text{Cu}_x\text{S/C@PPy}$ anode was comprehensively investigated through electrochemical tests[38-40]. As compared in **Fig. 3a**, $\text{Cu}_x\text{S/C@PPy}$ and $\text{Cu}_y\text{S/C}$ anodes delivered similar cyclic voltammetry (CV) curves, *i.e.*, similar redox reaction mechanism, which can be attributed to their similar crystal phase composition. Based on the galvanostatic charge/discharge curves, the $\text{Cu}_x\text{S/C@PPy}$ anode exhibited an initial discharge capacity of 423 mAh g^{-1} (**Fig. 3c**), higher than that of $\text{Cu}_y\text{S/C}$ (380 mAh g^{-1} , **Fig. 3b**). The charge-discharge voltage platforms were well corresponding with the redox peaks in CV curves. The high sodiophilicity of the PPy layer, as evidenced by the DFT calculations (**Fig. S10**), plays a crucial role in regulating the interfacial Na^+ transfer kinetics. Specifically, the strongly electronegative nitrogen atoms in the PPy chains provide abundant active sites that

effectively lower the desolvation energy barrier of Na^+ ions at the solid-liquid interface. This strong surface affinity accelerates the uniform accumulation and subsequent transport of Na^+ ions, thereby markedly reducing the interfacial charge transfer resistance (R_{ct}), which aligns perfectly with the EIS results showing a lower R_{ct} for the $\text{Cu}_x\text{S}/\text{C}@PPy$ electrode (**Fig. S9**). Consequently, at high current densities (e.g., up to 20 A g^{-1}), the highly sodiophilic armor effectively mitigates concentration polarization and reduces the nucleation overpotential, ensuring rapid charge transfer and explaining the superior rate capability of $\text{Cu}_x\text{S}/\text{C}@PPy$ shown in **Figs. 3d-f**. In order to test the intrinsic electronic conductivity of the material, Herein, I-V test through the linear volt-ampere test was carried out. Interestingly, the I-V test (**Fig. S11**) reveals that the electronic conductivity of the pristine $\text{Cu}_y\text{S}/\text{C}$ sample is 7.5 times higher than that of the modified $\text{Cu}_x\text{S}/\text{C}@PPy$ sample. Unlike most metal oxides, copper sulfides inherently exhibit near-metallic conduction behavior with exceptionally high absolute conductivity. While PPy is a conductive polymer, its conductivity is moderately lower than that of metallic copper sulfides. Furthermore, the 4 nm PPy coating acts as a physical barrier between the highly conductive $\text{Cu}_y\text{S}/\text{C}$ particles, inevitably increasing the interparticle contact resistance in the bulk powder. Nevertheless, although the PPy armor slightly sacrifices the bulk electron conductivity, it still provides sufficient electrical pathways. More importantly, it endows the electrode with robust structural confinement and high sodiophilicity (accelerating ion diffusion), which collectively result in the comparable and even superior high-rate capability of the $\text{Cu}_x\text{S}/\text{C}@PPy$ electrode.

In addition to the promoted rate capability, $\text{Cu}_x\text{S}/\text{C}@PPy$ anode also held an excellent cyclic stability of 300 mAh g^{-1} after 3000 cycles at 5 A g^{-1} (**Figs. 3g, S12**), which is much higher than that of $\text{Cu}_y\text{S}/\text{C}$ anode ($\sim 100 \text{ mAh g}^{-1}$). when at a high current density of 20 A g^{-1} , $\text{Cu}_x\text{S}/\text{C}@PPy$ anode can deliver an impressive reversible capacity of 257 mAh g^{-1} after 30000 cycles (**Fig. 3h**), far better than the previously reported CuS-based anodes (**Figs. 3i, Tab. S3**). When adjusting the discharge cut-off voltage to 0.2 V, long-term cycling stability of 40000 cycles can be achieved for $\text{Cu}_x\text{S}/\text{C}@PPy$ anode (**Fig. S13**). It is worth noting that

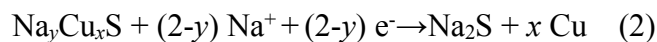
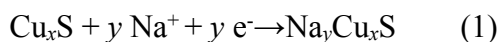
an initial capacity increase (capacity climbing) is observed at the early stage of cycling when the cut-off voltage is 0.2 V. This phenomenon originates from a milder and progressive electrochemical activation process. Due to the restricted deep discharge at 0.2 V, the electrolyte infiltration and the in-situ nanocrystallization of Cu_xS proceed more gradually, leading to a continuous and slow awakening of internal active sites over more cycles. Importantly, this gentle activation process averts abrupt volume expansion and structural pulverization, which, in synergy with the restricted polysulfide dissolution at 0.2 V, fundamentally contributes to the ultra-long lifespan of 40,000 cycles. Generally, metal sulfides as anode for SIBs suffered from inferior cycling stability, which was induced by the poor electroconductibility, distinct volume change, and polysulfide shuttle effect. Herein, the superior cyclic behavior of $\text{Cu}_x\text{S}/\text{C}@PPy$ anode can be attributed to the introduction of PPy coating layer, effectively contributing to the inhibited volume change and polysulfide shuttle during the cycling process.

The differences in sodium storage mechanism and reaction kinetics of $\text{Cu}_x\text{S}/\text{C}@PPy$ and $\text{Cu}_y\text{S}/\text{C}$ anodes were further investigated by CV curves at different scan rates (**Figs. 4a, b**). Generally speaking, the peak current (i_p) is composed of Faraday intercalation (ion diffusion) and surface-controlled adsorption (pseudo-capacitance behavior)[41, 42]. Based on the **Eqs. S1, S2** and **Figs. 4c, d**, the corresponding b values of $\text{Cu}_x\text{S}/\text{C}@PPy$ and $\text{Cu}_y\text{S}/\text{C}$ anodes were calculated as 0.64 and 0.78, respectively, indicating their combination reaction mechanism of ion diffusion and pseudocapacitive effect. By analyzing the CV results under different sweeping speeds, the proportion of pseudocapacitance can also be obtained. As detected in **Figs. 4e-h**, both types of electrodes have a high proportion of pseudocapacitance, especially at high sweep rates, which matches well up with great rate performance in **Fig. 3d**. Meanwhile, the corresponding ion diffusion kinetics can be further evaluated by the galvanostatic intermittent titration technique (GITT)[43, 44]. According to the **Eqs. S3, Figs. 4i, S14**, the diffusion coefficients of Na^+ ions in $\text{Cu}_x\text{S}/\text{C}@PPy$ and $\text{Cu}_y\text{S}/\text{C}$ anodes were calculated, revealing a little higher ion transport kinetics of $\text{Cu}_x\text{S}/\text{C}@PPy$ electrode

during cycling process (**Fig. 4j**), it is demonstrated that conductive polymers layer can facilitate the transmission of Na ions. In summary, the introduction of the PPy coating creates an additional physical interface, requiring sodium ions to travel through this polymer layer during transport. This inevitably increases the proportion of the ion diffusion-controlled mechanism, thereby leading to a decrease in the b value. Although the PPy layer slightly reduces the relative contribution of pseudocapacitance, it significantly enhances the structural stability of the material. By effectively mitigating volume expansion and the polysulfide shuttle effect, the PPy layer prevents the structural degradation that typically hinders ion transport. Consequently, as demonstrated by the GITT and cycling results, both the sodium-ion diffusion kinetics and the overall rate performance of the $\text{Cu}_x\text{S/C@PPy}$ electrode are significantly improved. Furthermore, semi-in-situ EIS test was also conducted to assess the charge transfer kinetics during cycling process. As displayed in **Figs. 4k, S15** $\text{Cu}_x\text{S/C@PPy}$ electrode delivered the R_{ct} value that first rises and then falls, indicating the formation of SEI (solid electrolyte interphase) film and the alloying reaction process. It is worth noting that during the subsequent charging and discharging process, the R_{ct} value change regularly, indicating that the electrode is operating stably with fewer side reactions[45, 46].

In-situ XRD test was carried out to explore the sodium storage mechanism of $\text{Cu}_x\text{S/C@PPy}$ anode during the cycling process. As shown in **Figs. 5a, S16**, in-situ XRD test was applied by self-designed coin cell with Be windows and was placed into snap-type fixture on XRD sample stage. **Fig. 5b** represented the corresponding contour results of XRD patterns in the initial two cycles. Notably, the variation of diffraction peaks in the first cycle was completely different from the results in the second cycle, indicating the irreversible reaction of initial sodiation process. During the initial discharge process, $\text{Cu}_{1.82}\text{S}$ undergoes the transformation from $\text{Na}_y\text{Cu}_x\text{S}$ to Cu[47, 48]. In the the following charge and discharge cycles, Cu undergoes the transformation of $\text{Cu}_{1.75}\text{S}$ in the charge peocess, and the transformation of Cu_2S to Cu[49, 50]. Besides, ex-situ HR-TEM images of $\text{Cu}_x\text{S/C@PPy}$ electrodes under different voltage was shown in **Figs. 5c-f, S17**,

which matches well up with in-situ XRD results. Hence, as detected in **Fig. 5g**, the corresponding reaction equations of $\text{Cu}_x\text{S}/\text{C}@PPy$ during the initial sodiation process were listed as follows:



In the desodiation process, there is no characteristic peak of $\text{Na}_y\text{Cu}_x\text{S}$, while the characteristic peaks of Cu gradually disappeared. In addition, the characteristic peaks of copper sulphide were also not detected at fully charged state, which can be attributed to the trace product and low signal to noise ratio. In the charge process, the characteristic peaks of Cu reversibly appeared, confirming the phase transformation within Cu and $\text{Cu}_{1.75}\text{S}$. During the second cycle, a complex phase transition of $\text{Cu}_{1.75}\text{S}$ occurs during the discharge process, including Cu_2S , $\text{Na}_y\text{Cu}_x\text{S}$ and Cu. Then the charging and discharging processes that follow are the same as those mentioned earlier. Therefore, the sodium storage mechanism of $\text{Cu}_x\text{S}/\text{C}@PPy$ anode can be reasonably summarized as the conversion reactions in **Figs. 5g, h**.

To further investigate the practicability of $\text{Cu}_x\text{S}/\text{C}@PPy$ anode, the full cells were assembled with $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (NVP) and $\text{Cu}_x\text{S}/\text{C}@PPy$ as cathode and anode materials, respectively (**Figs. 6a, S18**). According to the results in **Figs. 6b, c**, the $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode delivered reversible capacity of 107.5 mAh g^{-1} at 0.2 C (1 C=118 mAh g^{-1}), and the voltage range of NVP// $\text{Cu}_x\text{S}/\text{C}@PPy$ full cells was determined as 0.1-3 V. As expected, the optimized full cells achieved high capacity of 105 mAh g^{-1} at 0.2 C on basis of the mass loading of NVP cathode (**Fig. 6d**). Meanwhile, the NVP// $\text{Cu}_x\text{S}/\text{C}@PPy$ full cells displayed remarkable rate performance, and the specific capacity decreased from 106 to 55 mAh g^{-1} when the current density increased from 0.2 C to 10 C (**Fig. 6e**). Moreover, stable cycling performance was also realized in the optimized full cells, corresponding to a reversible capacity of 74 mAh g^{-1} at 1.0 C after 300 cycles (**Fig. 6f**). Based on the extremely high-rate performance of $\text{Cu}_x\text{S}/\text{C}@PPy$ anode, the dual-ion capacitor was assembled with AC (active carbon) and $\text{Cu}_x\text{S}/\text{C}@PPy$ as cathode and anode materials ((**Fig. 6g**). The

optimized dual-ion battery (0-3.8V) can deliver a stable sodium storage capacity of 274 mAh g⁻¹ after 4000 cycles at 5 A g⁻¹ and a cycle time of 3.36 min.

3. Conclusion

In summary, conductive polymer (PPy) armor strategy is proposed to intrinsically holds high sodiophilicity and strong chemisorption capability for polysulfides of Cu_yS/C microsphere anode for SIBs. Owing to the strong adsorption behavior of PPy layer for polysulfides, the shuttle effect of the optimized Cu_xS/C@PPy anode during cycling process is greatly reduced, effectively facilitating the structural stability and cyclic stability. As expected, Cu_xS/C@PPy anode displays high specific capacity of 300 mAh g⁻¹ after 3000 cycles at 5 A g⁻¹, and high cycling durability of 257 mAh g⁻¹ for 30000 cycles at 20 A g⁻¹. In addition, the home-made sodium-ion full cells with Na₃V₂(PO₄)₃/C and Cu_xS/C@PPy as cathode and anode also present stable cycling performance for 300 cycles. When matched with the commercial AC cathode, the optimized dual-ion battery also exhibits stable sodium storage capacity of 274 mAh g⁻¹ after 4000 cycles at 5 A g⁻¹, manifesting the practical application possibility of Cu_xS/C@PPy anode. These satisfying results indicate the necessity and significance of developing organic-inorganic hybrid electrodes for secondary batteries.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

Electronic Supplementary Material: Supplementary material (please send us a short summary regarding the Supporting info, thanks) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120281>.

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Figures and captions

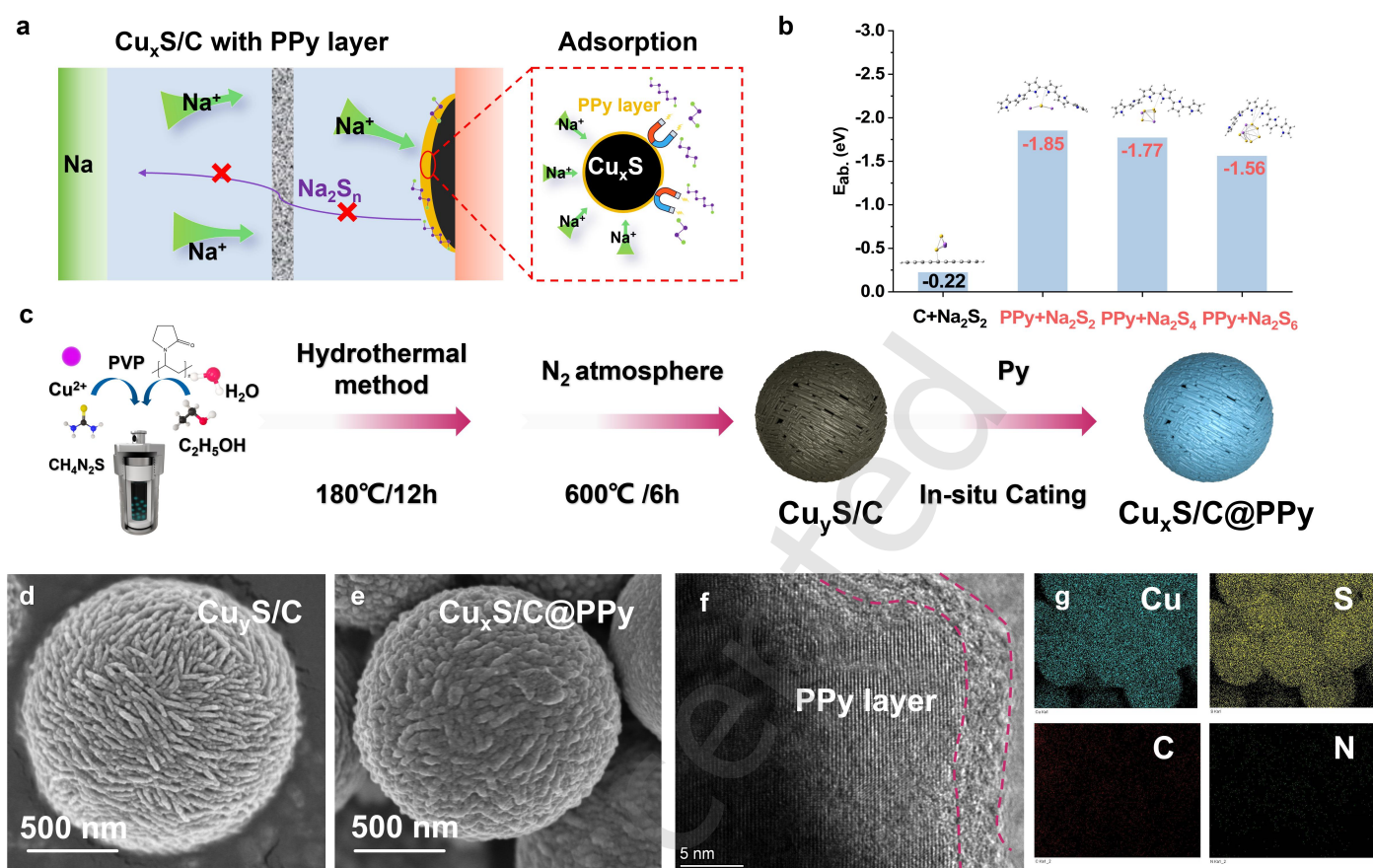


Figure 1 (a) Schematic illustration of the function of PPy coating; (b) Calculation of the adsorption energy of carbon and PPy for sodium polysulfides; (c) Schematic diagram of sample synthesis; (d-e) FE-SEM images of $\text{Cu}_y\text{S}/\text{C}$ and $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ sample; (f) High-resolution TEM image and (g) EDS mapping of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ sample.

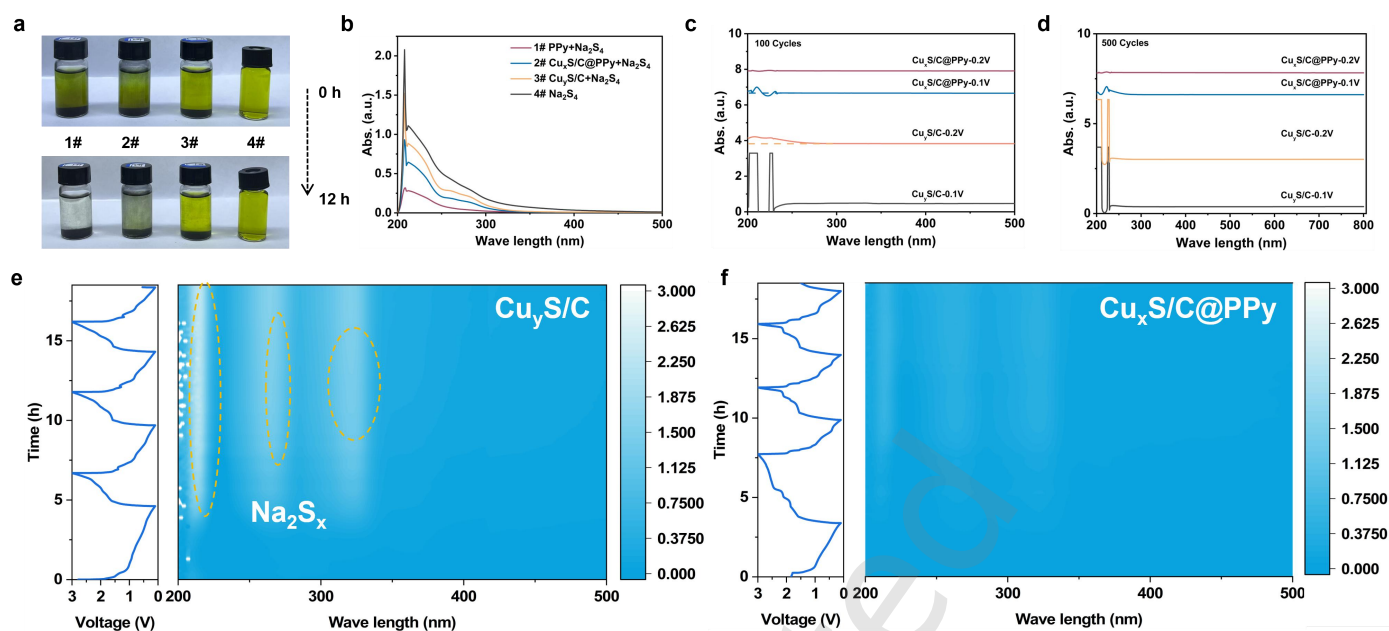


Figure 2 (a) Polysulfide adsorption experiment of PPy, Cu_xS/C@PPy and Cu_yS/C samples, and (b) the UV-vis spectra of their corresponding mixed solution; (c-d) UV absorption spectroscopy tests of Cu_xS/C@PPy and Cu_yS/C anodes after different cycles; (e-f) Electrochemical in-situ ultraviolet tests of Cu_xS/C@PPy and Cu_yS/C electrodes during the cycling process.

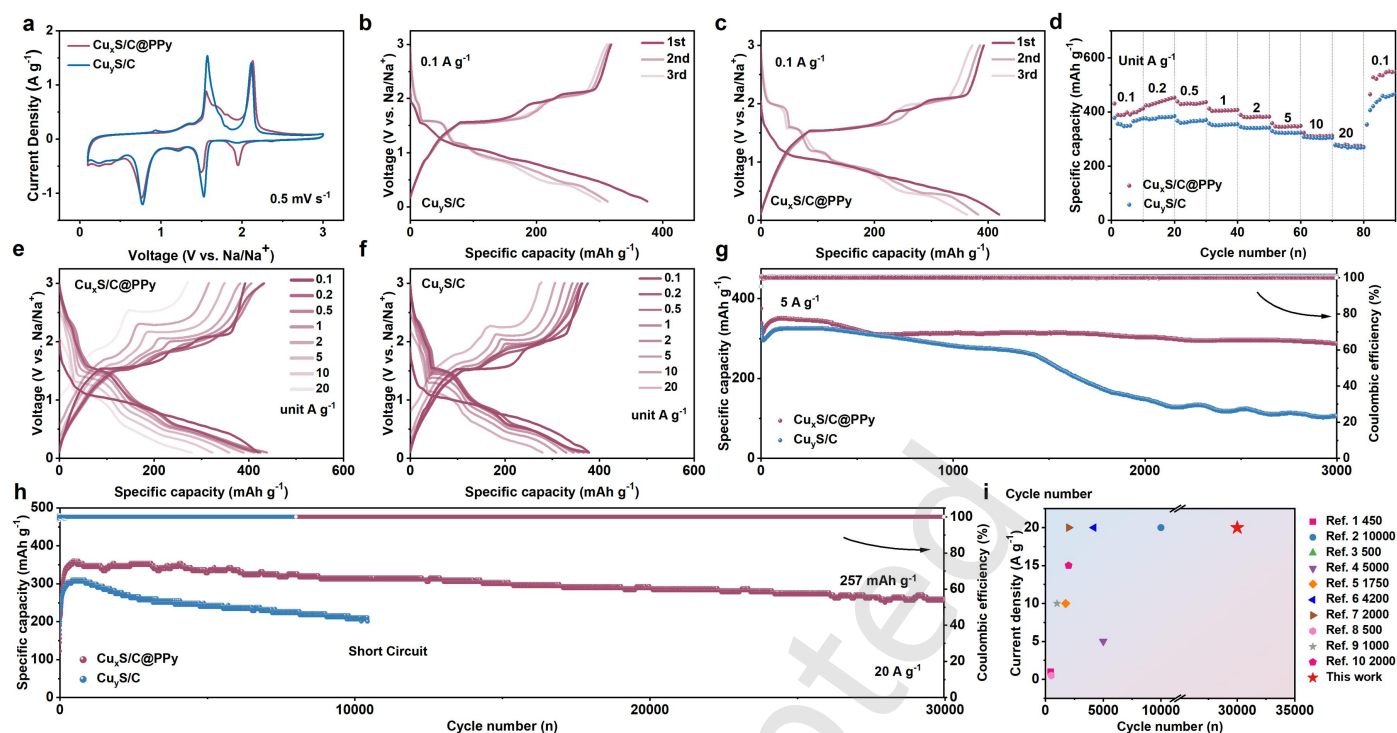


Figure 3 (a) CV curves of $\text{Cu}_x\text{S/C@PPy}$ and $\text{Cu}_y\text{S/C}$ anodes at 0.5 mV s^{-1} ; Galvanostatic charge/discharge curves of (b) $\text{Cu}_y\text{S/C}$ and (c) $\text{Cu}_x\text{S/C@PPy}$ anodes at 0.1 A g^{-1} ; (d) Rate performances and the corresponding charge/discharge curves of (e) $\text{Cu}_x\text{S/C@PPy}$ and (f) $\text{Cu}_y\text{S/C}$ anodes at different current densities; Long-term cycle performances of $\text{Cu}_x\text{S/C@PPy}$ and $\text{Cu}_y\text{S/C}$ anodes at (g) 5 A g^{-1} and (h) 20 A g^{-1} ; (i) Comparison of the achieved sodium storage performances with the reported literatures.

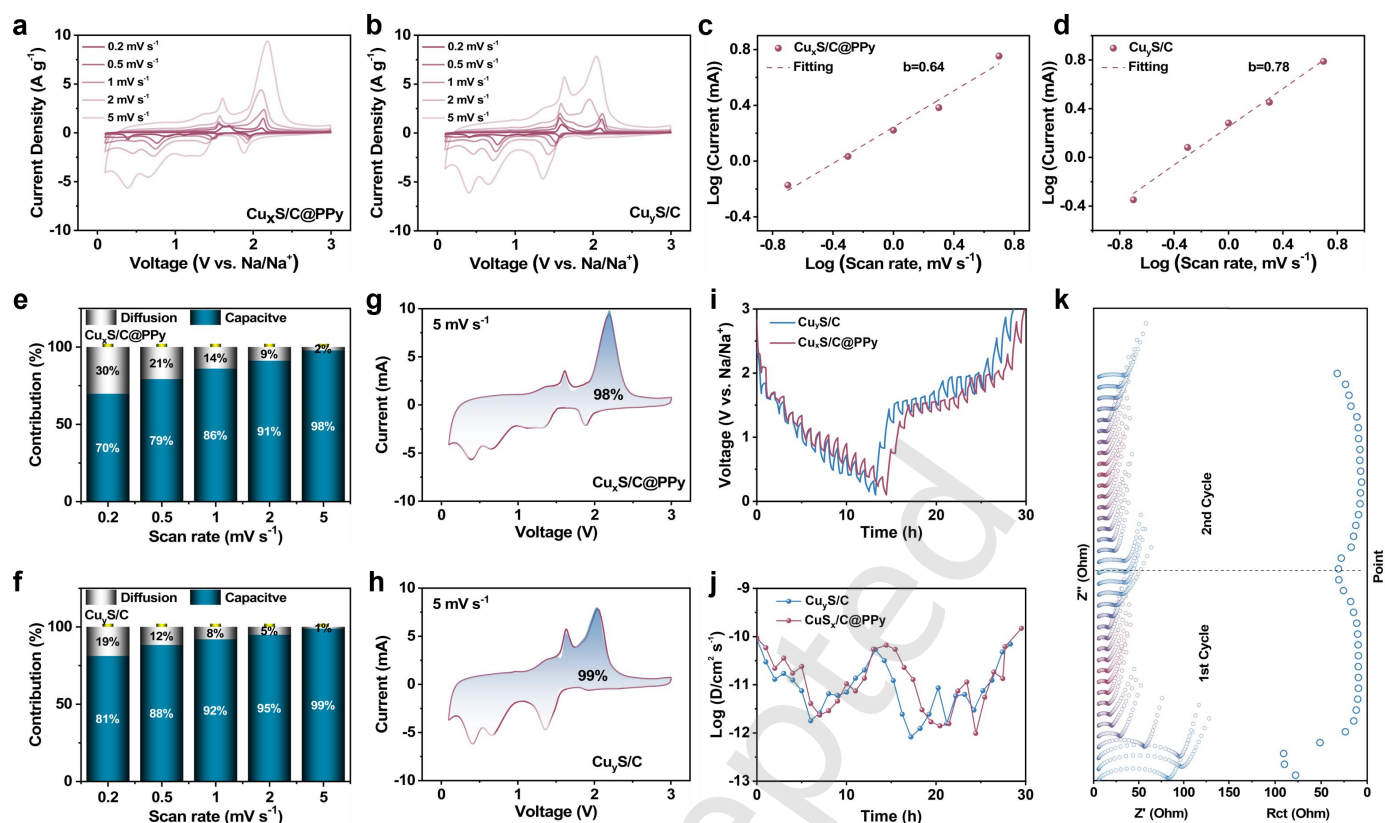


Figure 4 CV curves of (a) $\text{Cu}_x\text{S/C@PPy}$ and (b) $\text{Cu}_y\text{S/C}$ anodes tested at different scan rates; The calculated b values of (c) $\text{Cu}_x\text{S/C@PPy}$ and (d) $\text{Cu}_y\text{S/C}$ anodes; (e-h) Pseudocapacitance calculation of $\text{Cu}_x\text{S/C@PPy}$ and $\text{Cu}_y\text{S/C}$ anodes; (i) Test results by GITT method and (j) The calculated diffusion coefficient of $\text{Cu}_x\text{S/C@PPy}$ and $\text{Cu}_y\text{S/C}$ anodes; (k) In-situ EIS test during the cycling process of $\text{Cu}_x\text{S/C@PPy}$ anode.

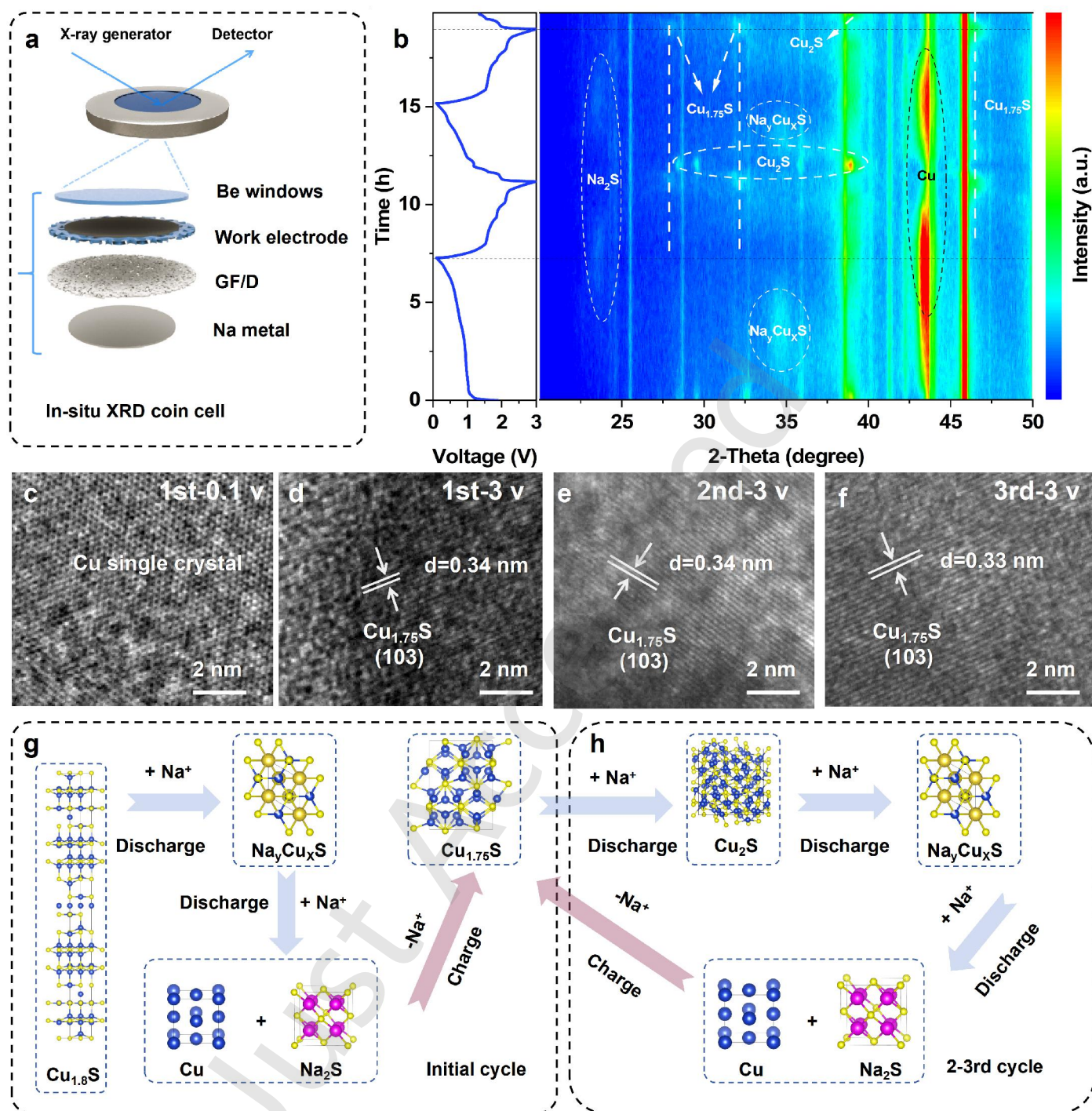


Figure 5 (a) Self-designed in-situ XRD coin cell model; (b) In-situ XRD patterns of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode in the initial two cycles; (c-f) Ex-situ HR-TEM images of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ electrode at different voltage states; (g-h) The inferred sodium storage mechanism of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode.

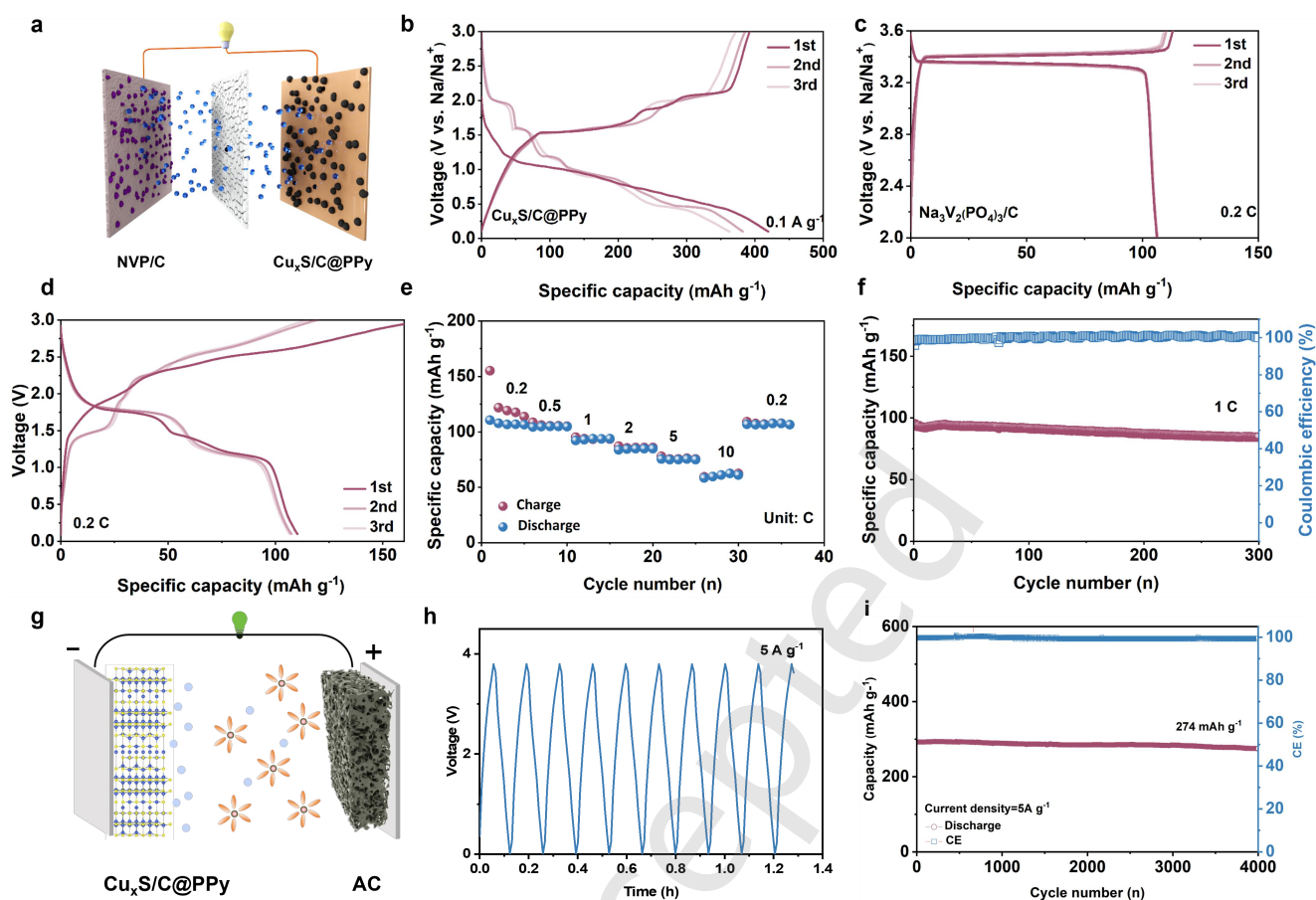


Figure 6 (a) Schematic diagram of the NVP//Cu_xS/C@PPy full cells; (b) Galvanostatic charge/discharge curves of Cu_xS/C@PPy anode at 0.1 A g⁻¹, (c) Na₃V₂(PO₄)₃/C cathode at 0.2 C (1C=118 mAh g⁻¹), and (d) NVP//Cu_xS/C@PPy full cells at 0.2 C; (e) Rate capability and (f) Cycling performance of NVP//Cu_xS/C@PPy full cells; (g) Dual-ion battery model of the AC//Cu_xS/C@PPy full cells; (h) Galvanostatic charge/discharge curves and (i) cycling performance of Cu_xS/C@PPy anode at 5 A g⁻¹.

Author Profile



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Electronic Supplementary Materials

Conductive polymer armor strategy enables metal sulfides with super long-life sodium storage

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1. Experimental section

1.1 Chemical reagents

Cupric nitrate ($\text{Cu}(\text{NO}_3)_2$), Thiourea, ethanol, polyvinyl pyrrolidone (PVP), pyrrole, hydrochloric acid, Ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and N-Methylpyrrolidone (NMP) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ketjen Black (KB), Polytetrafluoroethylene (PTFE), Poly

(1,1-difluoroethylene) (PVDF) and electrolyte 1M sodium hexafluorophosphate (NaPF_6) in dimethoxyethane (DME) were provided by Nanjing Mojiesi Chemical Technology Co. Ltd.

1.2 Synthesis of $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ and $\text{Cu}_y\text{S}/\text{C}$ samples

In a typical synthesis process, 7.0 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 14.0 mmol thiocarbamide, 0.778 g polyvinylpyrrolidone and 1.0 g glucose were added into a mixed solution of 40 ml deionized water and 30 ml alcohol. After magnetic stirring for 1 hour, the mixture was poured into teflon-line stainless steel autoclave, and then placed into an oven and maintained at 180 °C for 12 hours. After the reaction, precipitate was collected and washed with deionized water and alcohol for several times, and dried in a vacuum oven overnight to obtain CuS/CRP (carbon-rich polysaccharide) precursor. After treatment at 600 °C under a N_2 atmosphere for 6 hours, the $\text{Cu}_y\text{S}/\text{C}$ was obtained. To obtain the PPy coating Cu_xS composite, a multistep strategy was carried out. First, 0.3 g of copper sulfide powder was dispersed in a mixture containing 160 μl of pyrrole and hydrochloric acid, after stirring for half an hour, 10 ml of aqueous solution containing 100 mg ammonium persulfate is added in three drops. The whole process is an ice bath reaction for 8h, and the as-prepared PPy cating Cu_xS composite was obtained via filtration and drying treatment.

1.3 Preparation of polysulfide solution

Sodium polysulfide adsorption experiment, preparation of 0.1M Na_2S_4 : In a glove box, Na_2S and S powder were dissolved in 20mL of DME solution in a molar ratio of 1:3, and stirred at 60 °C for 2 hours to dissolve, obtaining a dark green solution.

1.4 Material characterizations

The sample crystal structure was analyzed via X-ray diffraction (XRD) with a copper (Cu) $\text{K}\alpha$ source (Bruker D2 Phaser). X-ray photoelectron spectroscopy (XPS, Thermo Fisher 250Xi, USA) was performed to analyze the chemical states of the samples. To observe the chemical functional group composition. Fourier transform infrared (FTIR, Perkin-ElmerFrontier, USA) spectra were recorded in attenuated total reflectance

mode in the range of 4000-400 cm^{-1} . Scanning electron microscopy (SEM, Phenom ProX, Netherlands) and transmission electron microscopy (TEM, TecnaiF 20, USA) were applied to investigate the morphological characteristics and crystallinity of the samples. To reveal the thermodynamic properties of the as-prepared samples, thermogravimetric analysis (TGA) was performed under a N_2 atmosphere with a thermogravimetric analyzer (TA Instruments, USA) using a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Ultraviolet-visible (UV-vis) spectroscopy was performed (UV-3600 plus, Shimadzu) to evaluate the solubility of the electrodes.

1.5 Computational methods and details

All calculations were carried out with the Gaussian 16 software. The B3LYP functional was adopted for all calculations in combination with the Grimme's DFT-D3(BJ) empirical dispersion correction. The geometry optimization, frequency and singlet point energy calculations were performed with basis set of the 6-311G(d, p). Furthermore, the frequencies had been calculated at the same level to verify that all optimized structures did not have imaginary frequency, which corresponded to the local minima on the potential energy surfaces. In this article, the calculation of adsorption energy was obtained via a intermolecular force between PPy (C) model and Na_2S_n . Moreover, table S2-S3 show the details of the calculation value.

1.6 Electrochemical characterization of as-prepared samples

To prepare the working electrode for battery testing, the active material, Ketjen black, and the polyvinylidene fluoride (PVDF) binder were adequately mixed in a specific weight ratio of 70:20:10 with a paste mixer. A slurry with suitable viscosity was obtained by adding an appropriate amount of NMP. This slurry was coated onto a copper current collector with a blade coating machine, then vacuum-dried at $110\text{ }^\circ\text{C}$ overnight. The working electrodes were cut into wafers with 10 mm diameters by using a slicer. The active material mass loading of each electrode wafer was about 1.2 mg/cm^2 . SIBs 2032 button half-cells were assembled in an argon-filled glove box. Each cell contained a Na metal lamina, separator (GF/D, Whatman), working electrode, and electrolyte (1 M NaPF_6 in DME). The batteries were subjected to the

constant-current charge and discharge cycling tests on an automatic battery test system (Neware Shenzhen). Electrochemical impedance spectroscopy (EIS) was performed with a Bio-logic VSP-300 electrochemical workstation in the frequency range of 0.01 Hz to 100 kHz. Cyclic voltammetry (CV) was performed with the same electrochemical workstation at room temperature. For the construction of full cells, the cathode was composed of commercial $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (NVP/C), acetylene black, and PVDF at a weight ratio of 80:10:10, which were coated on an aluminum foil. The cathode loading mass was about 5 mg cm^{-2} . The $\text{Cu}_x\text{S}/\text{C}@PPy$ anode was pre-cycled five times in a half-cell before being assembled into a full cell. The mass ratio of cathode to anode was approximately 4:1, and the corresponding capacity ratio of cathode to anode was about 1:1.13. The battery separator and electrolyte in the $\text{NVP}/\text{C}||\text{Cu}_x\text{S}/\text{C}@PPy$ full cells were the same as those used in the half-cells. The cycling tests were carried out within a voltage range from 0.1 V to 3 V. The current density and specific capacity of the full cells were calculated based on the mass of NVP/C cathode. The dual-ion capacitor were assembled with AC (active carbon) and $\text{Cu}_x\text{S}/\text{C}@PPy$ as cathode and anode materials. It is worth noting that the electrolyte chosen here is a lipid-based one (1 M NaPF_6 in EC/DMC).

1.7 Pseudocapacitance calculations

It is known that the contribution of capacitance can be determined by calculating the relationship between the peak current (i) and the scan rate (v), as shown in the following equations:

$$i = av^b \quad (1)$$

$$\log(i) = b \log(v) + \log(a) \quad (2)$$

1.8 GITT Measurement details

To estimate the kinetics of electrochemical reactions of as-prepared electrodes, GITT measurements were carried out. Typically, the cell was subjected to a current pulse discharge/charge at a current density of 50 mA g^{-1} for a duration t of 1800 seconds, followed by an open circuit rest period of 1800 seconds.

According to the following equation, the Li^+ diffusion coefficients (D_{GITT}) in PI electrodes can be calculated via GITT data:

$$D_{\text{GITT}} = \frac{4}{\pi\tau} \left(\frac{mV_m}{MA} \right)^2 \left(\frac{\Delta E_s}{\Delta E\tau} \right)^2 \quad \left(\tau \ll \frac{L^2}{D_{\text{GITT}}} \right) \quad (3)$$

In **Equation S3**, M and m correspond to the molecular weight and active material mass (the value of $\text{Cu}_x\text{S/C@PPy}$ electrode is 0.88 mg), respectively. Additionally, the molar volume is denoted as V_m , while the electrode area (0.79 cm^2) is represented by the symbol A . The electrode thickness (L) was measured to be $150 \text{ }\mu\text{m}$, while ΔE_s refers to the change in steady-state potential after a discharge (charge) pulse and open circuit standing, and ΔE_t represents the voltage discharge (charge) during a discharge (charge) pulse. Herein, the value of V_m/M can be estimated by the inverse of the mass density ρ .

2. Figures and captions

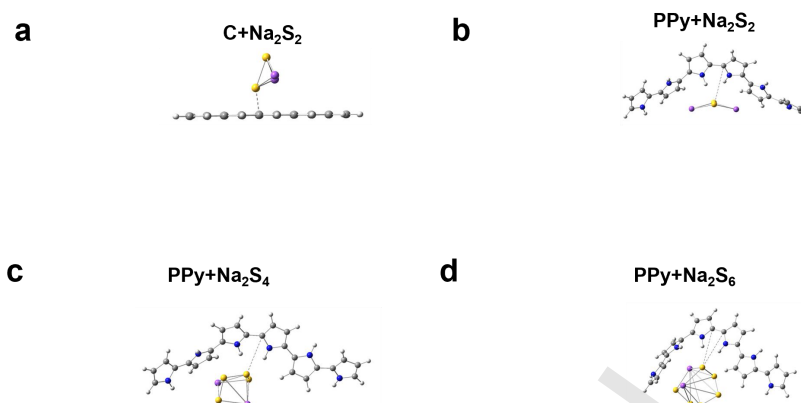


Figure S1 The adsorption energies calculated by density functional theory (DFT).

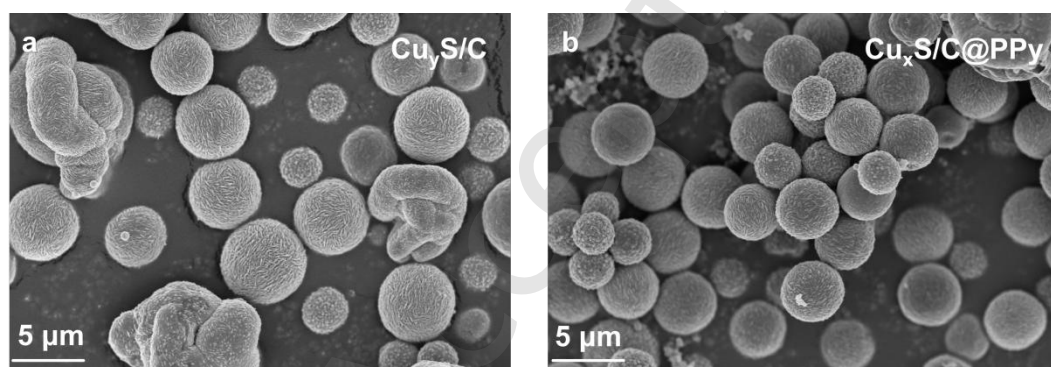


Figure S2 FE-SEM images of Cu_yS/C and $Cu_xS/C@PPy$ samples.

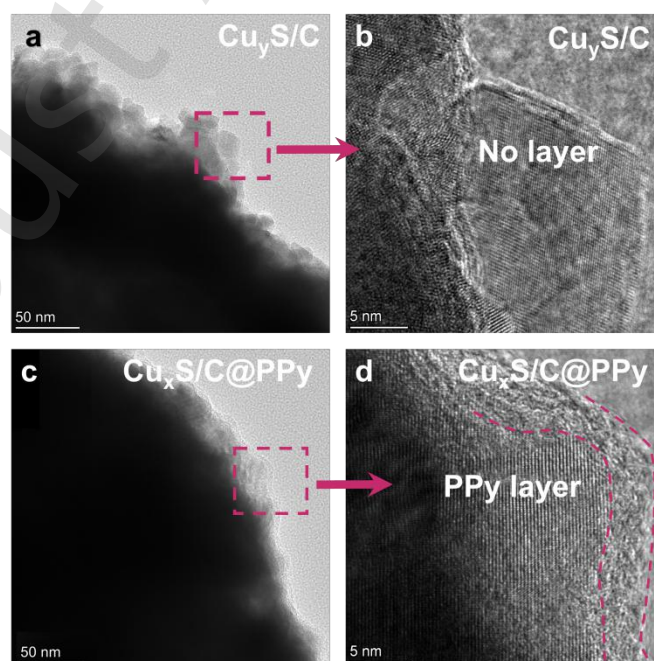


Figure S3 HR-SEM images of Cu_yS/C and $Cu_xS/C@PPy$ samples.

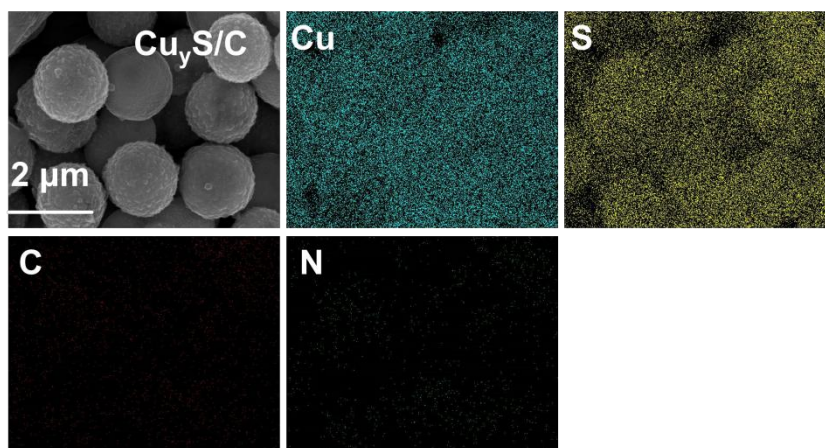


Figure S4 EDS mapping images of Cu_yS/C sample.

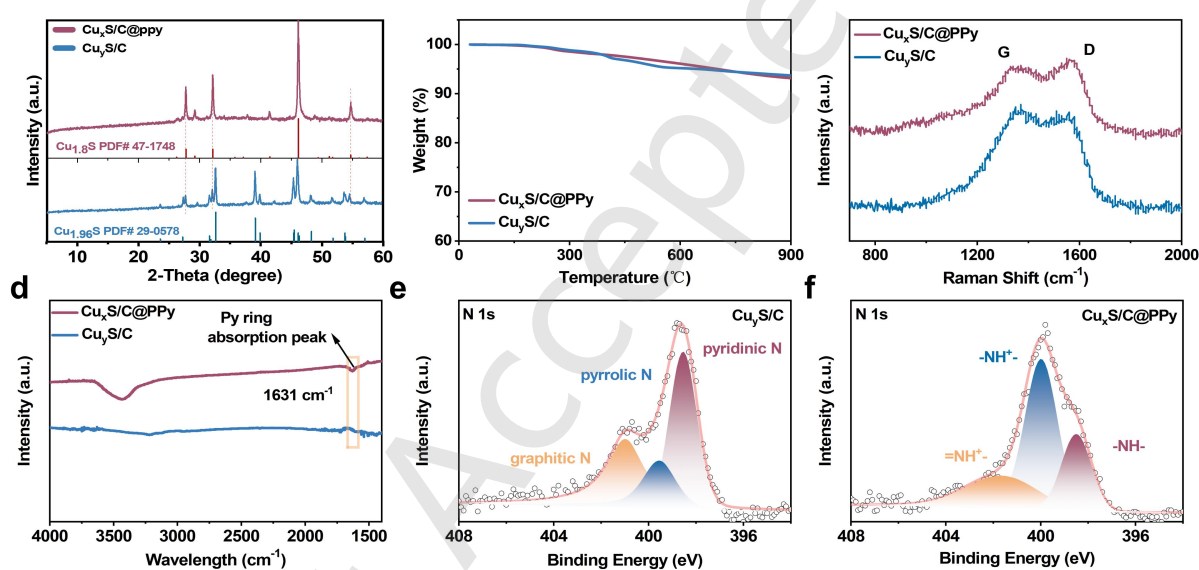


Figure S5 (a) XRD patterns, (b) TGA curves, (c) Raman spectra, (d) FT-IR spectra, and high-resolution N 1s spectra of the as-prepared Cu_yS/C and Cu_xS/C@PPy samples.

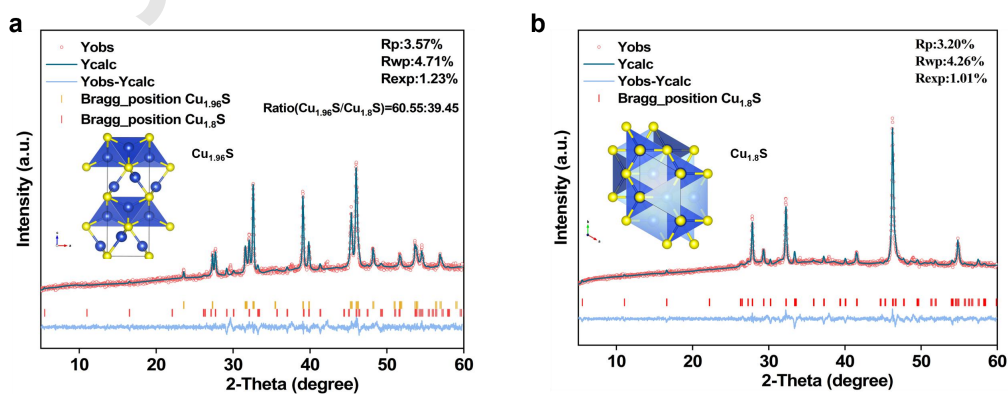


Figure S6 The XRD refinement spectrum of Cu_yS/C and Cu_xS/C@PPy samples.

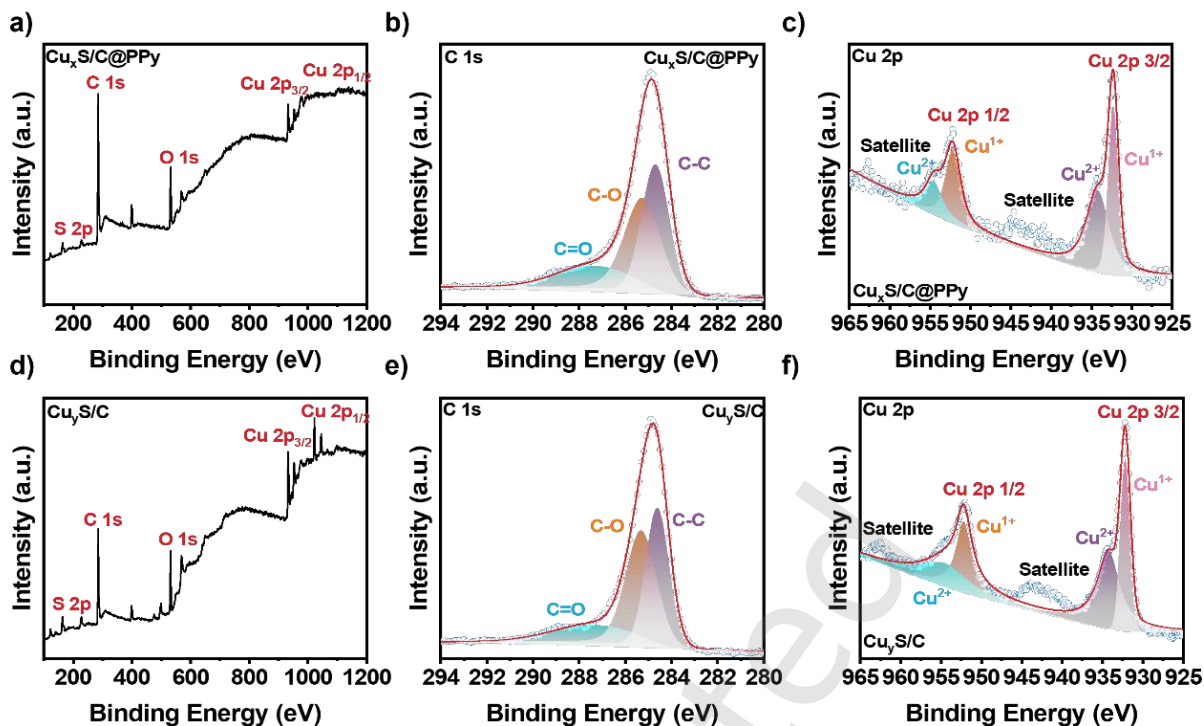


Figure S7 (a) Survey XPS spectra, (b) high-resolution C 1s spectra and (c) high-resolution Cu 2p spectra of $\text{Cu}_x\text{S/C@PPy}$ sample; (d) Survey XPS spectra, (e) high-resolution C 1s spectra and (f) high-resolution Cu 2p spectra of $\text{Cu}_y\text{S/C}$ sample.

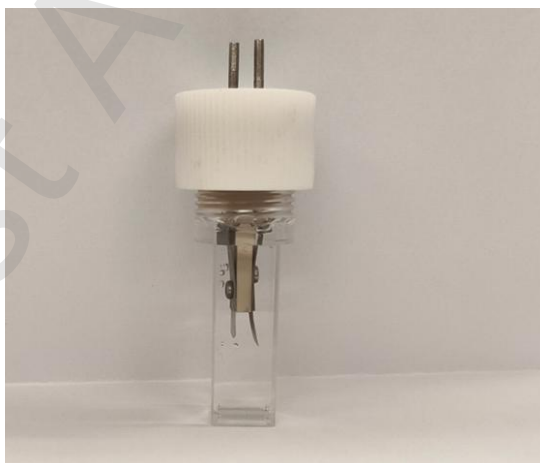


Figure S8 Image of In-situ ultraviolet cell.

In this work, the in-situ ultraviolet test was assembled with an in-situ cell, electrode plates, sodium sheets and electrolyte. The in-situ cell was purchased from Yuan Wei Gao Ke, and the electrode plates and sodium sheets were both made into rectangles. After the in-situ battery assembly is completed, it is placed in the ultraviolet spectrophotometer equipment for in-situ spectroscopy testing, and the Neware

charge-discharge instrument is used for constant current charge-discharge testing.

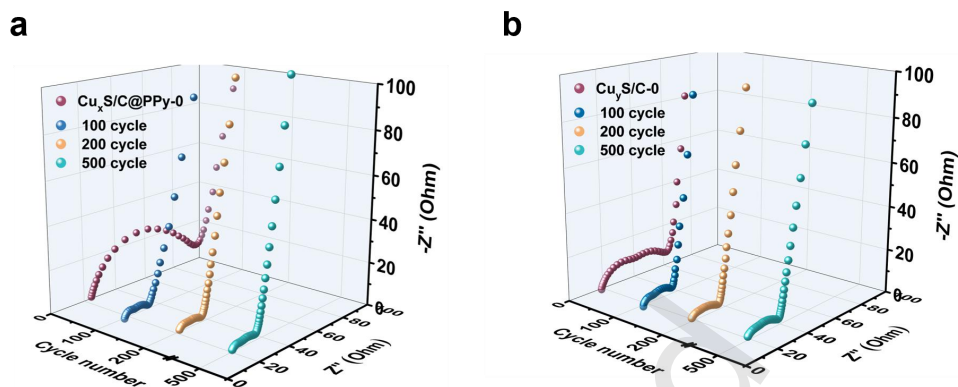


Figure S9 Electrochemical impedance spectroscopy (EIS) plots after different cycles.

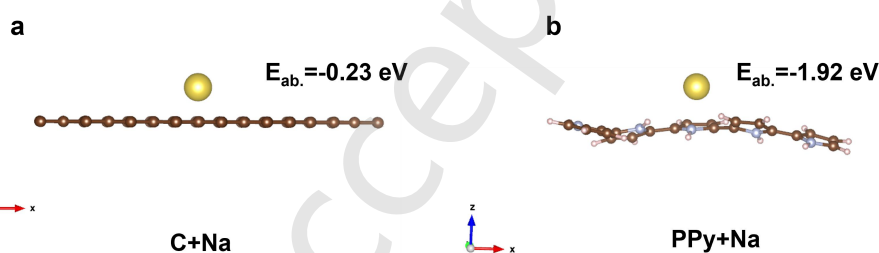


Figure S10 The adsorption energies calculated by density functional theory (DFT).

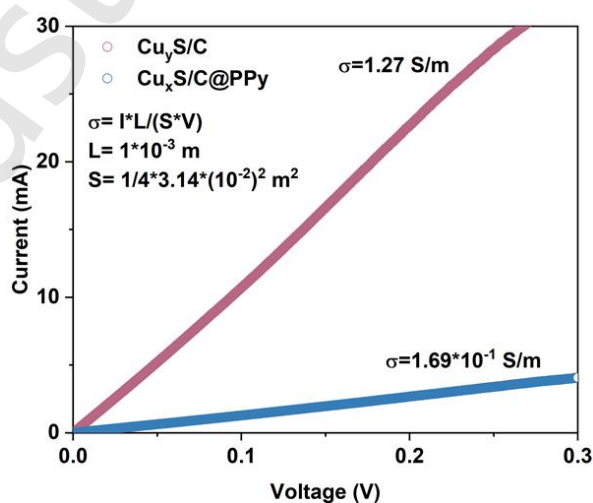


Figure S11 I-V test through the Linear volt-ampere test.

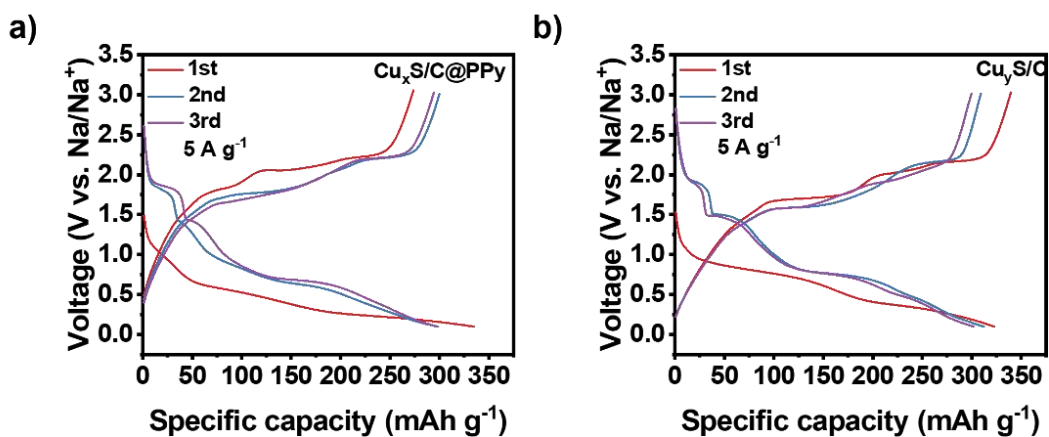


Figure S12 Galvanostatic charge/discharge curves of (a) $\text{Cu}_x\text{S/C@PPy}$ and (b) $\text{Cu}_y\text{S/C}$ anodes at 5 A/g.

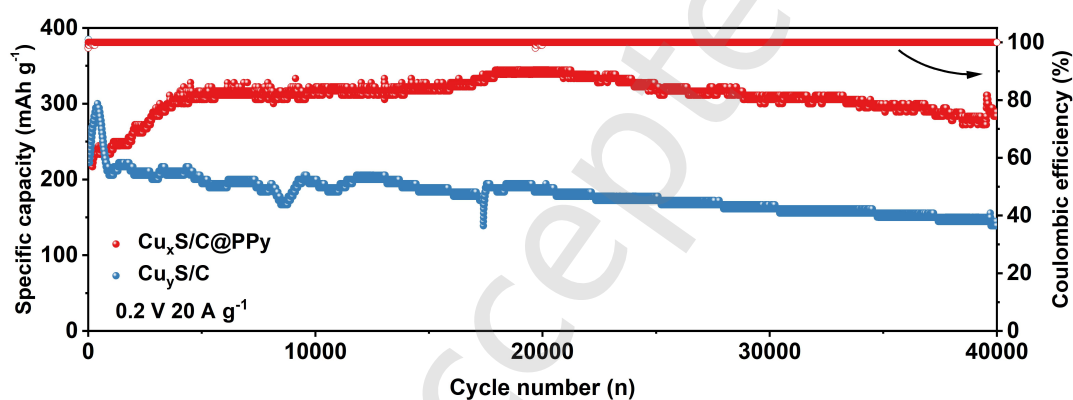


Figure S13 Durable cycle performances of $\text{Cu}_y\text{S/C}$ and $\text{Cu}_x\text{S/C@PPy}$ anodes at 20 A/g with a cut-off voltage of 0.2 V.

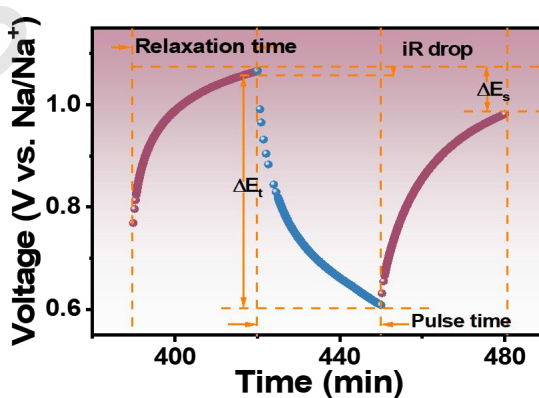


Figure S14 The pulse and relaxation threshold conditions of GITT test.

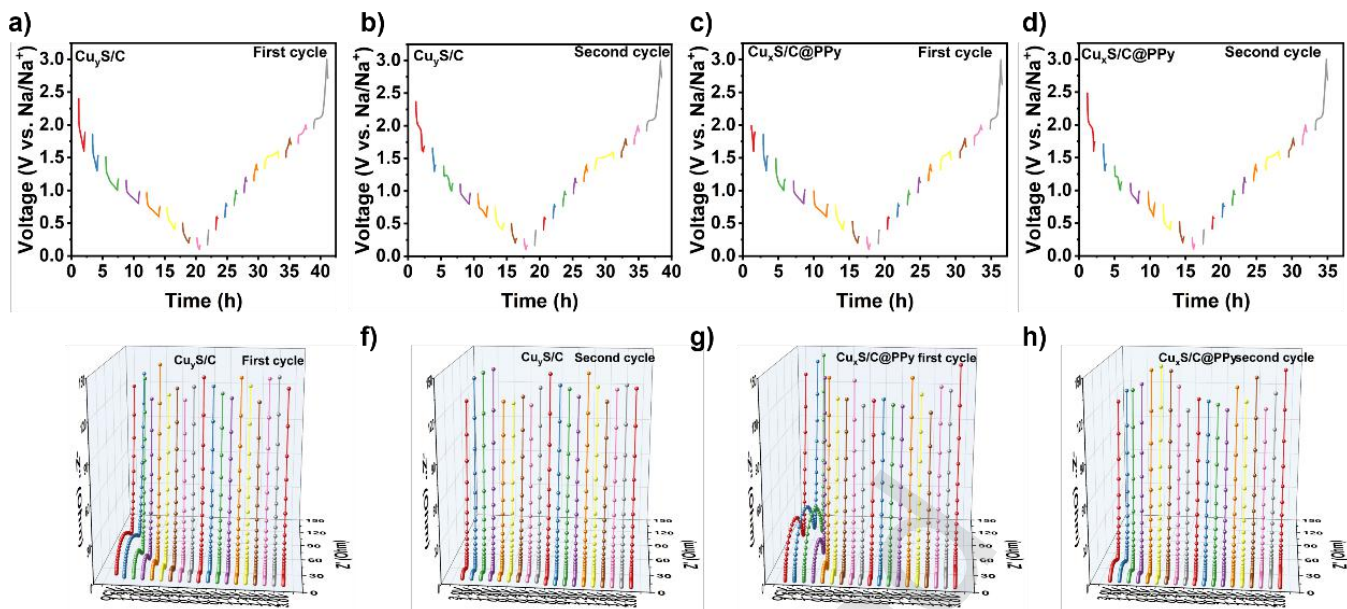


Figure S15 . Semi-in-situ EIS test of $\text{Cu}_y\text{S}/\text{C}$ and $\text{Cu}_x\text{S}/\text{C}@\text{PPy}$ anode.

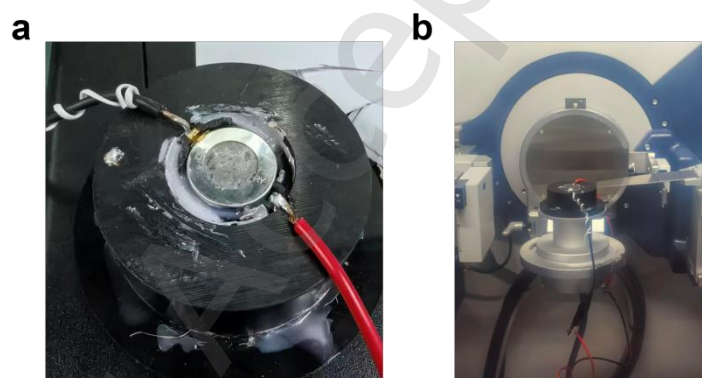


Figure S16 Image of in-situ XRD test device.

During the entire in-situ XRD testing process, the fabrication of the in-situ XRD battery positive electrode housing and the preparation of the mesh electrodes are the two core technological processes. The preparation of the positive electrode shell is achieved by bonding the perforated battery shell and the beryllium sheet with hot melt adhesive tape. The network electrode is completed through the process of applying the slurry and drying. Then, in the order of positive shell, wire electrode, separator, sodium sheet, foam nickel, electrolyte and negative shell, the button cell battery is encapsulated using a press machine. Place the self-made in-situ battery fixture on the surface of the XRD sample stage, and then insert the button-type battery to conduct the in-situ XRD test.

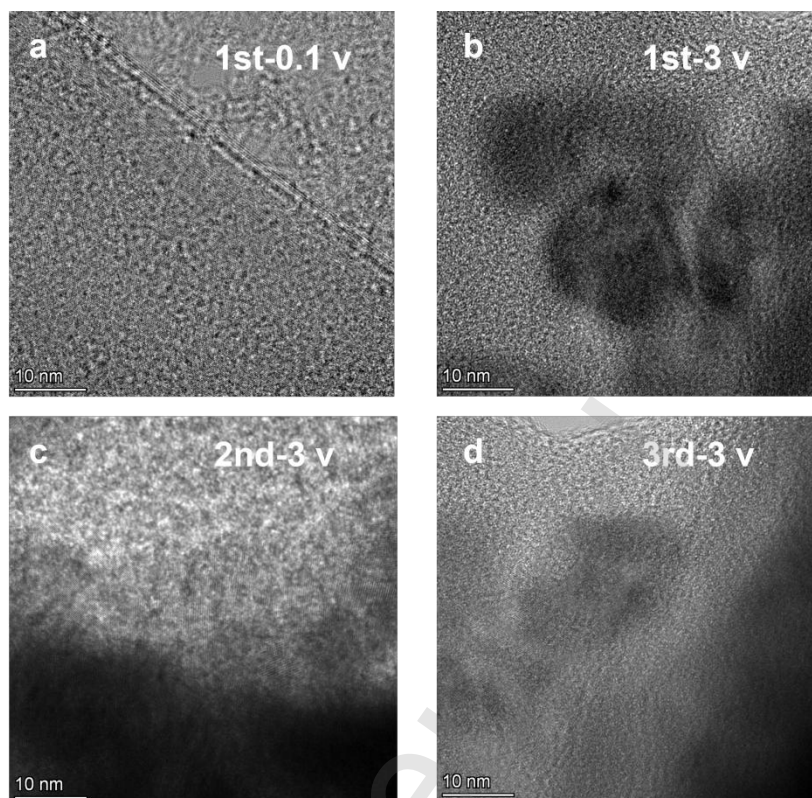


Figure S17 HR-TEM images of $\text{Cu}_x\text{S/C@PPy}$ electrodes under different voltage.

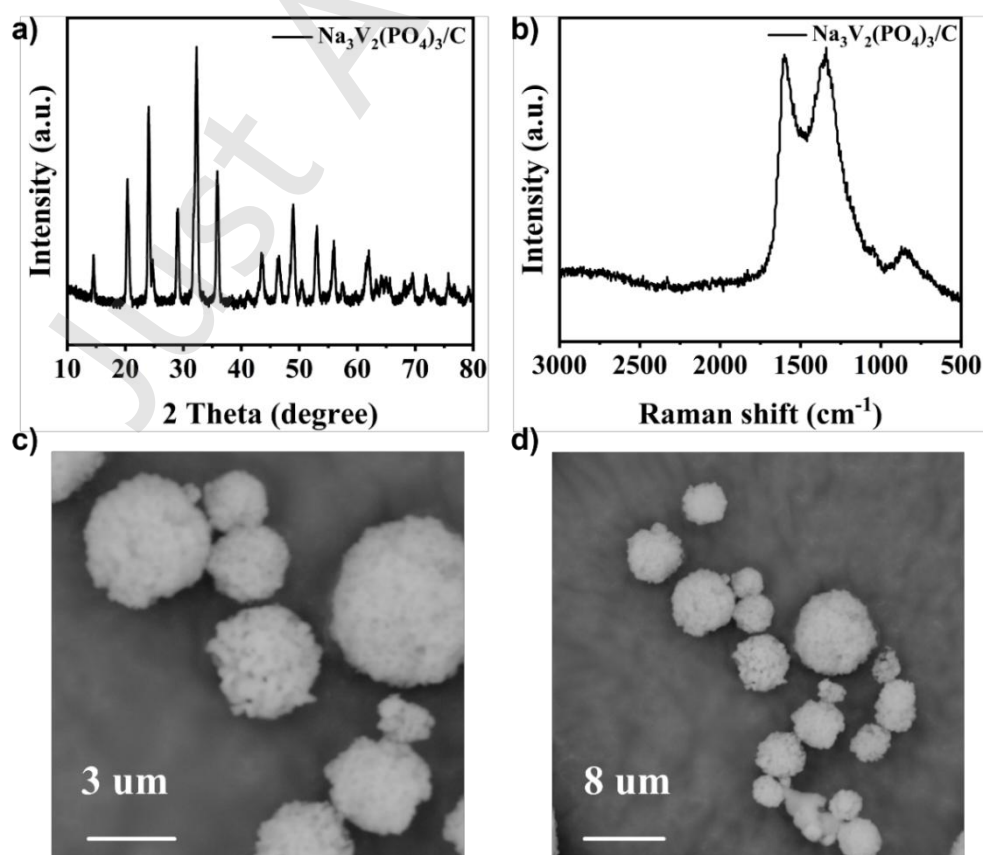


Figure S18 (a) XRD pattern, (b) Raman spectra and (c-d) SEM images of commercial NVP cathode.

Table S1 The intrinsic energy value of different material itself.

	Energy (Ha)	Energy (eV)
PPy	-1255.5274	-34164.1558
Na₂S₂	-1121.1436	-30507.4388
Na₂S₄	-1917.6261	-52180.5250
Na₂S₆	-2714.1106	-73853.6633
C	-1840.7050	-50087.4238

Table S2 Calculation of adsorption energies between PPy/C component and different polysulfides.

	Energy (Ha)	Energy (Ha)	E_{ab.} (eV)
PPy+Na₂S₂	-2376.7389	-0.0679	-1.85
PPy+Na₂S₄	-3173.2184	-0.0649	-1.77
PPy+Na₂S₆	-3969.6955	-0.0575	-1.56
C+Na₂S₂	-2961.8565	-0.0079	-0.22

Table S3 Comparison of sodium storage performances of different CuS-based anodes.

	Current (A g⁻¹)	Cycle number	capacity (mAh g⁻¹)	Ref s
Hydrangea-like CuS	1	450	336	[1]
CuS NWs@NC	20	10000	294.4	[2]
Platelet-like CuS	2	500	316	[3]
Micro-flower CuS	5	5000	132.6	[4]
ZnS/CuS@C	10	1750	282.7	[5]
Yolk-shell NiS₂/CuS	20	4200	283.4	[6]
CuS HNs	20	2000	250.1	[7]
CuS@CoS₂ DSNBs	0.5	500	483	[8]
CuS-CTAB	10	1000	312.5	[9]
CuS nanocables	15	2000	213	[10]

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