



Article N–Doped Porous Carbon Microspheres Derived from Yeast as Lithium Sulfide Hosts for Advanced Lithium-Ion Batteries

Sheng Liang ^{1,*,†}, Jie Chen ^{1,†}, Xuehua He ², Lingli Liu ¹, Ningning Zhou ¹, Lei Hu ¹, Lili Wang ¹, Dewei Liang ¹, Tingting Yu ¹, Changan Tian ³ and Chu Liang ^{2,*}

- ¹ School of Energy, Materials and Chemical Engineering, Hefei University, Hefei 230601, China; ntrdchenjie@126.com (J.C.); liull@hfuu.edu.cn (L.L.); zhnn@hfuu.edu.cn (N.Z.); hulei@hfuu.edu.cn (L.H.); wangll@hfuu.edu.cn (L.W.); liangdw@hfuu.edu.cn (D.L.); yutt@hfuu.edu.cn (T.Y.)
- ² College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, China; hzhexh@zjut.edu.cn
- ³ School of Chemistry and Civil Engineering, Shaoguan University, Shaoguan 512005, China; tca2204@126.com
- * Correspondence: liangsheng8866@126.com (S.L.); cliang@zjut.edu.cn (C.L.)
- + These authors contributed equally to this work.

Abstract: Lithium sulfide (Li₂S) is considered to be the best potential substitution for sulfur-based cathodes due to its high theoretical specific capacity (1166 mAh g⁻¹) and good compatibility with lithium metal-free anodes. However, the electrical insulation nature of Li₂S and severe shuttling of lithium polysulfides lead to poor rate capability and cycling stability. Confining Li₂S into polar conductive porous carbon is regarded as a promising strategy to solve these problems. In this work, N-doped porous carbon microspheres (NPCMs) derived from yeasts are designed and synthesized as a host to confine Li₂S. Nano Li₂S is successfully entered into the NPCMs' pores to form N-doped porous carbon microspheres–Li₂S composite (NPCMs–Li₂S) by a typical liquid infiltration–evaporation method. NPCMs–Li₂S not only delivers a high initial discharge capacity of 1077 mAh g⁻¹ at 0.2 A g⁻¹, but also displays good rate capability of 198 mAh g⁻¹ at 5.0 A g⁻¹ and long-term lifespan over 500 cycles. The improved cycling and high-rate performance of NPCMs–Li₂S can be attributed to the NPCMs' host, realizing the strong fixation of LiPSs and enhancing the electron and charge conduction of Li₂S in NPCMs–Li₂S cathodes.

Keywords: lithium sulfide; porous carbon microsphere; nitrogen doping; lithium-ion battery

1. Introduction

With the ever-growing demand for lightweight electric vehicles with high mileages, there is an urgent need to develop new energy storage devices with higher energy density to replace the current intercalation-type lithium-ion batteries (LIBs) [1-7]. Lithium-sulfur (Li-S) batteries based on the multi-electron conversion reaction between S and Li₂S are regarded as one of the most promising energy storage devices due to their high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}) [8–14]. However, the actual electrochemical performance of Li-S batteries is limited by the low conductivity of S, the large volume expansion of S cathodes during the discharge process and the serious shuttle of intermediate products of lithium polysulfides (LiPSs) [15–18]. Moreover, we know that the S cathode is usually required in order to use lithium metal as the matching anode, which will greatly increase the safety hazards caused by lithium dendrite [19–21]. In this regard, replacing S with full lithiation-state Li₂S is considered to be the most effective way to avoid the formation of lithium dendrite since Li₂S has good compatibility with lithium metal-free anodes (e.g., carbonaceous material, siliceous material and metallic oxide) [22–25]. Li₂S not only has high theoretical specific capacity (1166 mAh g^{-1}), but also effectively avoids structural damage caused by volume expansion during discharge [26,27]. Nevertheless, Li₂S is also accompanied by low electron conductivity and severe LiPSs shuttling, similar to S [28–31].



Citation: Liang, S.; Chen, J.; He, X.; Liu, L.; Zhou, N.; Hu, L.; Wang, L.; Liang, D.; Yu, T.; Tian, C.; et al. N–Doped Porous Carbon Microspheres Derived from Yeast as Lithium Sulfide Hosts for Advanced Lithium-Ion Batteries. *Processes* **2021**, *9*, 1822. https://doi.org/10.3390/ pr9101822

Academic Editor: Mingxia Gao

Received: 24 September 2021 Accepted: 11 October 2021 Published: 14 October 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

To improve the electrochemical performance of Li₂S, various strategies are proposed, including adding conductive metals, combining sulfides or oxides and introducing carbon materials [32–35]. Among them, mixing Li₂S with carbon materials, especially porous carbon, to form Li₂S/C composites is considered to be the most effective approach because the abundant pore structure, high specific surface area and good conductivity of porous carbon are conducive to the improvement in the electrochemical performance of Li₂S [26,32,36]. However, most porous carbons exhibit non-polar characteristics, leading to weak immobilization between polar LiPSs and porous carbons [37]. Therefore, exploring porous carbon frameworks with a strong polar surface as a Li₂S host to improve the conductivity of Li₂S and achieve strong chemical fixation with LiPSs is an important step in the development of Li₂S cathodes. Nitrogen-doped (N-doped) carbon, as a common carbon material modification method, can improve the surface polarity and electronic conductivity of carbon material, and maintain the integrity of the microstructure [38,39]. The synthesis of N-doped porous carbon is mainly through high temperature pyrolysis of N-containing polymer materials (such as polyaniline, melamine, polypyrrole, and metal–organic framework) [37,40]. The high cost, severe toxicity and low reproducibility of N-containing polymers determine that such precursors are difficult to be scaled up to mass production. Consequently, it is urgent to develop a facile, green and low-cost way to prepare N-doped porous carbon for Li₂S cathodes.

Preparation of N-doped porous carbon from biomass has become a recent research hotspot due to its abundant resources, low price, diverse structures and nontoxic characteristics. Yeast, as a microorganism, has a uniform submicron size structure (1–4 μ m) and a rich nitrogen content (7.5–10 wt%) [41]. Herein, we used yeast as a precursor to synthesize N-doped porous carbon microspheres (NPCMs) through carbonization and etching. NPCMs exhibit abundant micropores and mesopores, ultra-high specific surface area (2005.6 m² g⁻¹) and strong chemical polarity. When using NPCMs to confine Li₂S, the obtained NPCMs–Li₂S composites exhibit high discharge capacity, excellent rate capability and cycling stability.

2. Materials and Methods

Materials Synthesis: The yeast powder (Yichang Angel Yeast Co., Ltd., China), Li₂S (99.9%, Alfa Aesar), CuCl₂·2H₂O (99%, Macklin), formaldehyde solution (37%, Macklin), anhydrous ethanol (EtOH) (99.5%, <0.005% water, Sigma Aldrich), H₂SO₄ (50%, Alfa Aesar) and H_2O_2 (35%, Alfa Aesar) were used as raw materials. A total amount of 15 g yeast powder was immersed in 100 mL deionized water for 1 h to wake up the yeast cells. The woken yeast cells were mixed with 10% formaldehyde solution and stirred for 1 h to achieve cell morphology fixation. Subsequently, the above solution was transferred to Teflon lined autoclave for 10 h at 180 °C. After heat treatment, the dark brown product was filtered, washed and dried at 80 °C for 10 h. The obtained dark brown powder was mixed with $CuCl_2 \cdot 2H_2O$ in a weight ratio of 3:50, and then calcined the mixture at 900 °C under argon for 2 h. The calcined product was immersed in a mixed solution of $0.5 \text{ M H}_2\text{SO}_4$ - $1.2 \text{ M H}_2\text{O}_2$ to remove Cu-based impurities. Finally, NPCMs were obtained by filtering, washing and drying the black powder from above solution. The synthesis of N-doped carbon microspheres (NCMs) is similar to that of NPCMs, except that the CuCl₂·2H₂O pore former is not added. NPCMs-Li₂S and NCMs-Li₂S were prepared via a typical liquid infiltration-evaporation method. Firstly, 0.24 g Li₂S was added in 10 mL EtOH and stirred 6 h to synthesize Li₂S solution. Secondly, the EtOH–Li₂S solution was slowly and periodically dropped on 0.16 g NPCMs (or NCMs) to ensure that the Li₂S can effectively enter into the pore channels. Finally, the above powder was dried at 360 °C for 1.5 h under vacuum to remove EtOH and obtain NPCMs-Li2S (or NCMs-Li2S) composite.

Characterizations: The X-ray diffraction (XRD) patterns were employed to study the crystal structural of samples. The morphologies of samples were observed by using scanning electron microscope (SEM, Hitachi SU8010). The microstructure and element composition of samples were investigated by transmission electron microscopy (TEM, JEM2100) attached with an energy dispersion X-ray spectroscopy (EDS) detector. The nitrogen adsorption analyzer (Micromeritics ASAP 2020 plus) was used to measure the surface area and porous characteristic. The pore size distribution was calculated by the density functional theory (DFT) method. The X-ray photoelectron spectroscopy (XPS) spectra analysis was conducted on ESCALAB 250XI spectrometer by using an Al-Ka radiation source. The ultraviolet-visible (UV-VIS) absorption spectra test was performed on a spectrophotometer (Agilent Technologies Cary 60).

Electrochemical Measurements: The electrochemical performances of NPCMs-Li₂S and NCMs-Li₂S were evaluated in the 2025 coin-type cell by using lithium foil as the reference electrode and Celgard 2400 membrane as the separator. For the working electrode, 80 wt% active material (NPCMs-Li₂S or NCMs-Li₂S), 10 wt% polyvinylidene fluoride (PVDF) binder and 10 wt% acetylene black (Super-p) were added to the Nmethyl-2-pyrrolidinone (NMP) and stirred to from a uniform slurry. Then, the above slurry was coated on aluminum foil and dried at 120 °C for 6 h under argon protection. The average mass loading is ~ 1.2 mg cm⁻² and 4.1 mg cm⁻² for the thin and thick electrodes, respectively. The used electrolyte is composed of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt, 1 wt% LiNO₃, 50 vol% DOL and 50 vol% DME. Cyclic Voltammetry (CV) curves were measured on a CHI760E electrochemistry workstation (Shanghai Chenhua, China) with a scan rate of 0.1 mv s⁻¹. The scan voltage range is set at from open circuit voltage to 3.8 V and 1.5 V to 3.0 V for the first and subsequent scans, respectively. Galvanostatic charge-discharge tests were performed on the battery test system (Wuhan LAND, China). The first charge activation of electrode was realized by using high charging cut-off voltage (3.8 V) and low current density (0.05 A g^{-1}). The subsequent charge–discharge test voltage range is adjusted to 1.8–2.8 V. Electrochemical impedance spectroscopy (EIS) measurements were tested by a CHI760E electrochemistry workstation with a frequency range of 10^{-2} – 10^{5} Hz.

3. Results

Figure 1 shows the main synthesis process of the NPCMs–Li₂S composite. In a typical process, the EtOH–Li₂S solution was slowly and periodically dropped on the NPCMs to ensure that the Li₂S can effectively infiltrate into the pore channels of NPCMs. As depicted in Figure 2a, several characteristic XRD peaks at 27.0, 31.2, 44.8, 53.1, 55.6, 65.2, 71.9 and 74.1° were observed in both the NPCMs–Li₂S and NCMs–Li₂S composites, which correspond to the standard peaks of Li₂S (PDF#26–1188). Compared with NCMs–Li₂S, the NPCMs–Li₂S displayed a weaker diffraction peak, signifying that most of the Li₂S enters into the pore channels of NPCMs. It is worth noting that the characteristic peaks belonging to NPCMs and NCMs did not appear in the above two composites due to the weak XRD peaks of both NPCMs and NCMs (Figure S1).



Figure 1. Illustration of synthesis process of NPCMs-Li₂S composite.



Figure 2. (a) XRD patterns of NCMs–Li₂S and NPCMs–Li₂S composites; (b) N₂ adsorption–desorption isotherms and (c) corresponding pore size distributions of NCMs, NPCMs NCMs–Li₂S and NPCMs–Li₂S; XPS spectra of NPCMs (d) N 1s spectrum and (e) C 1s spectrum; (f) UV-VIS absorption spectra of NCMs and NPCMs in Li₂S₆ solution.

To further characterize the porosity and surface area of NCMs, NPCMs, NCMs–Li₂S and NPCMs–Li₂S, N₂ adsorption–desorption isothermal measurement was carried out. A typical mixed type I and IV adsorption–desorption curve can be seen in the NPCMs, suggesting hierarchical porosity consisting of micropores and mesopores (Figure 2b). The micropores and mesopores displayed a continuous pore diameter distribution in the ranges of 0.8–1.9 nm and 2.1–2.8 nm, respectively (Figure 2c). However, NCMs showed typical non-porous characteristics (Figure 2b,c). The specific surface area of NPCMs is as high as 2005.6 m² g⁻¹, which is ~32 times higher than that of NCMs (63.1 m² g⁻¹). After impregnating Li₂S into the NPCMs host, the NPCMs–Li₂S exhibited a typical type I adsorption–desorption curve, indicating the micropores feature of NPCMs–Li₂S (Figure 2b). The disappeared mesopores in the NPCMs–Li₂S composite can be attributed to the fill-

ing of Li₂S (Figure 2c). In addition, the specific surface area and total pore volume of NPCMs dramatically decreased from 2005.6 m² g⁻¹ to 590.2 m² g⁻¹ and 0.97 cm³ g⁻¹ to 0.44 cm³ g⁻¹, respectively, for NPCMs–Li₂S (Figure 2b). In contrast, NCMs–Li₂S also shows typical non-porous characteristics (Figure 2b,c). Based on the above results, we can infer that most of Li₂S may enter into the mesopore channels of NPCMs.

The XPS was used to confirm the elemental composition and chemical state of NPCMs. Three peaks at 531.3, 401.3 and 285.3 eV can be clearly observed in the NPCMs surface, assigning to the O 1s, N 1s and C 1s, respectively (Figure S2) [42,43]. For the N 1s spectrum, three different peaks located at 404.9, 400.9 and 398.4 eV can be fitted and divided, corresponding to the N–O, pyrrolic N and pyridinic N, respectively (Figure 2d) [44–46]. Meanwhile, the peaks related to the C–N (287.5 eV) and C=C (284.8 eV) bonds can be fitted and observed in the C 1s spectrum (Figure 2e) [44,47]. This high nitrogen content (7.2 wt%) endows NPCMs with a strong chemical polarity, resulting in powerful capture ability for LiPSs.

The ability of NPCMs to capture LiPSs is confirmed by the adsorption experiment combined with the UV-VIS absorption spectra test. In this case, the same amounts of NPCMs and NCMs were employed and added to 0.005 M Li₂S₆ in DOL/DME (1:1, v/v) solution to measure the capture effect on LiPSs. Two obvious peaks centered at 265 and 280 nm are appeared in the original Li₂S₆ solution, which can be ascribed to the S₆²⁻ species (Figure 2f) [48]. After NPCMs adding, the NPCMs containing Li₂S₆ solution is gradually changed from brown to transparent and the peak intensity of S₆²⁻ is sharply decreased (Figures 2f and S3), suggesting the strong LiPSs capture ability. However, both S₆²⁻ peak intensity and color of NCMs contained Li₂S₆ solution are no obvious change (Figures 2f and S3). This phenomenon can be attributed to the low specific surface area and absent pore structure of NCMs, which caused a significant reduction in nitrogen adsorption sites toward LiPSs, resulting in weak LiPSs capture ability.

The morphologies and microstructures of as-synthesized samples were investigated by using SEM and TEM. As shown in Figure 3a,c, the NPCMs display a typical microsphere structure with an average size of 2 µm and hierarchical porous structure. The low graphitization degree of NPCMs is further confirmed in HRTEM, in good agreement with the XRD result (Figures S1 and S4). After Li₂S was loaded into NPCMs host, NPCMs-Li₂S still maintains a microsphere structure as NPCMs do, signifying that most of the Li₂S enters into the mesopores of NPCMs (Figure 3b). Meanwhile, the disappearing porous structure of NPCMs–Li₂S further proves that most of the pores in NPCMs are loaded with Li₂S (Figure 3c,d). For comparison, NCMs–Li₂S shows irregular morphology accompanied by serious particle agglomeration (Figure S5). This phenomenon can be attributed to the fact that NCMs lack the pores and space to confine Li₂S, resulting most of Li₂S direct depositing and covering on the surface of NCMs (Figures 2c and S5). The particle size and state of Li₂S in the NPCMs host are displayed in Figure 3e. The Li₂S nanoparticles in the diameter range of 6–8 nm are coated with amorphous carbon, demonstrating that the Li₂S is confined in the pores of NPCMs (Figure 3e). Moreover, the uniformly distribution signals of C, N and S in elemental mapping signify that the Li₂S is homogeneous distributed in the NPCMs host (Figure 3f-i). Therefore, it can be believed that the NPCMs host improves the electrochemical performance of Li₂S due to its abundant porous structure, ultra-high specific surface area and strong polar surface.



Figure 3. SEM images of (**a**) NPCMs and (**b**) NPCMs–Li₂S; TEM images of (**c**) NPCMs and (**d**) NPCMs–Li₂S; (**e**) HRTEM image of NPCMs–Li₂S; (**f**) STEM image of NPCMs–Li₂S and corresponding elemental distributions of (**g**) C, (**h**) N and (**i**) S.

The electrochemical performance of NPCMs-Li₂S and NCMs-Li₂S composites were evaluated by 2025 coin-type cell and tested at room temperature. For Li₂S-based cathodes, a high cutoff voltage should be adopted to overcome the kinetic barrier of phase nucleation from Li₂S to LiPSs in the first charge, which is referred to the initial activation process of Li₂S cathodes [25,43]. According to our previous study [25,43], 3.8 V was employed to activate Li₂S in the initial charge. Three anodic peaks located at 2.39, 3.36 and 3.76 V can be observed in the first anodic scanning of NCMs-Li₂S cathode, corresponding to the transition from Li_2S to S and the initial charge kinetic barrier (Figure S6) [25,43]. For NPCMs-Li₂S cathode, three slightly lower anodic peaks at 2.38, 3.19 and 3.68 V are appeared in the first anodic scanning, signifying the slightly increased activation barrier (Figure 4a). After the initial charge activation, both NPCMs-Li₂S and NCMs-Li₂S are displayed in the typical CV curves of S cathodes. EIS was used to further study the electrochemical reaction kinetics of NPCMs-Li₂S and NCMs-Li₂S. As shown in Figure 4b, the EIS curves of both NPCMs-Li₂S and NCMs-Li₂S consist of a line in the low frequency region and a semicircle in high frequency range, which correspond to the Warburg diffusion process and the charge transfer resistance (R_{ct}), respectively [49,50]. The R_{ct} of NPCMs Li_2S (49.8 Ω) is smaller than that of NCMs– Li_2S (122.2 Ω), representing faster electron and charge transfer rate of NPCMs– Li_2S , which could be attributed to the abundant porous structure providing fast channesl for electron and charge transport.



Figure 4. (a) CV curves of NPCMs–Li₂S cathode; (b) EIS spectra of NPCMs–Li₂S and NCMs–Li₂S electrodes in the fresh state; (c) charge–discharge profiles of the NPCMs–Li₂S cathode in the first three cycles; (d) cycling performance of NPCMs–Li₂S and NCMs–Li₂S electrodes at 0.2 A g^{-1} .

Figure 4c depicts the first three charge–discharge profiles of the NPCMs–Li₂S cathode. Similar to CV test, a high cutoff voltage (3.8 V) was employed for the initial activation of Li₂S. The voltage plateaus of the NPCMs–Li₂S cathode are consistent with the CV result. The NPCMs–Li₂S exhibits higher first discharge capacity of 1077 mAh g⁻¹ at 0.2 A g⁻¹, which is greater than that of 639 mAh g⁻¹ for NCMs–Li₂S, indicating the high Li₂S utilization rate in NPCMs–Li₂S (Figures 4c and S7). In subsequent cycles, NPCMs–Li₂S composite displays high discharge capacities of 872 and 762 mAh g⁻¹ at the 2nd cycle and 60th cycle with a high average coulomb efficiency of ~98%. By contrast, both discharge capacity and coulomb efficiency of NCMs–Li₂S are lower than those of NPCMs–Li₂S (Figure 4d).

The rate capability of NPCMs–Li₂S and NCMs–Li₂S at current densities from 0.2 A g^{-1} to 5.0 A g^{-1} are shown in Figure 5a. The discharge capacities of NPCMs–Li₂S at 0.2, 0.5, 1.0, 2.0 and 5.0 A g^{-1} are around 869, 663, 519, 362 and 198 mAh g^{-1} , respectively. After various rate cycles, the discharge capacity of NPCMs–Li₂S recovers to 805 mAh g^{-1} when the current density is returned to 0.2 A g^{-1} . It should be noted that the rate capability of NPCMs–Li₂S is higher than that of NCMs–Li₂S and other reported Li₂S cathodes (Figures 5a and S8). The excellent rate and cycle performance of NPCMs–Li₂S composites can be attributed to the host of NPCMs, which can not only improve the electron and charge transfer rate of Li₂S, but also realize the strong fixation of LiPSs.



Figure 5. (a) Rate performance of NPCMs–Li₂S and NCMs–Li₂S electrodes; (b) cycling performance of the NPCMs–Li₂S cathode at 0.5 A g^{-1} with a mass loading of 4.1 mg cm⁻²; (c) long-term cycle life of NPCMs–Li₂S and NCMs–Li₂S electrodes at 1.0 A g^{-1} .

Long-term cycling and high-rate performance are considered important factors for Li_2S cathodes. As depicted in Figure 5c, NPCMs–Li₂S delivers a high initial discharge capacity of 704 mAh g⁻¹ at 1.0 A g⁻¹, and retains 465 and 354 mAh g⁻¹ after 100 and 500 cycles, respectively. However, NCMs–Li₂S only displays the discharge capacities of 396, 288 and 205 mAh g⁻¹ for the 1st, 100th and 500th, respectively, which are much lower than that of NPCMs–Li₂S. The capacity decay of NPCMs–Li₂S and NCMs–Li₂S cathodes during the long cycling can be attributed to the slow shuttle of lithium polysulfides and cumulative deposition of insulating Li_2S_2/Li_2S on electrode surface [51,52]. The high mass loading properties are also as a crucial factor for the commercialization of Li-ion batteries. For the NPCMs–Li₂S, the thick electrode with 4.1 mg cm⁻² was employed to investigate the high mass loading performance. As shown in Figure 5b, the NPCMs–Li₂S exhibits a discharge capacity of 670 mAh g⁻¹ at 0.5 A g⁻¹, and still maintains a considerable discharge capacity of 421 mAh g⁻¹ after 50 cycles. It is noted that this electrochemical performance of NPCMs–Li₂S is superior to other Li₂S-based electrodes (Table S1).

To further demonstrate the stability of the NPCMs host, SEM and XPS were adopted to measure the NPCMs–Li₂S electrode after 500 cycles at 1.0 A g⁻¹ (Figures 6 and S9). The NPCMs–Li₂S electrode displays a relatively smooth surface, which can be attributed to the chemical interaction between electrolyte and electrode material during the long-term repeated de/intercalation of lithium ion (Figure 6a) [25,43]. After detached from the current collector, NPCMs–Li₂S composite still retains a typical microsphere structure, suggesting the excellent electrochemical structural stability (Figure 6b). Three peaks at 168.9, 164.3 and 161.7 eV can be fitted and divided from the S 2p spectrum of NPCMs–Li₂S, which are assigned to the S-O, S-C and Li-S bonds, respectively (Figure 6c) [53–55]. Meanwhile, two peaks related to Li-N (55.9 eV) and Li-S (55.3 eV) bonds can be fitted and divided into the Li 1s spectrum of NPCMs–Li₂S (Figure 6d) [56]. According to the XPS results, we can further confirm that the NPCMs host has a strong capture ability for LiPSs. Based on the above analysis and results, the good electrochemical performance of NPCMs–Li₂S is



mainly attributed to the NPCMs host, which can not only improve the electronic charge conductivity and structural stability, but also achieve strong capture and fixation for LiPSs.

Figure 6. SEM images of NPCMs–Li₂S electrode after 500 cycles at 1.0 A g^{-1} (**a**) attached on current collector and (**b**) detached from current collector. XPS spectra of NPCMs–Li₂S electrode after 500 cycles at 1.0 A g^{-1} ; (**c**) S 2p spectrum and (**d**) Li 1s spectrum.

4. Conclusions

In summary, submicron NPCMs with an abundant pore structure, ultra-high specific surface area and strong chemical polarity were successfully synthesized for Li₂S cathodes. The abundant pore structure of NPCMs can not only offer sufficient space for Li₂S storage, but also provides a high-speed channel for electron and charge conduction. The ultra-high specific surface area and strong chemical polarity of NPCMs can achieve strong chemical adsorption and immobilization of LiPSs, thereby inhibiting the shuttle of LiPSs. Moreover, the unique submicron microsphere structure of NPCMs host can effectively improve the electrochemical structural stability. Benefiting from the above advantages of the NPCMs host, NPCMs–Li₂S displays a high discharge capacity and long-term lifespan. This research will provide a valuable reference for the application of biological carbon host in the alkaline metal–sulfur battery.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/pr9101822/s1, Figure S1: XRD patterns of NPCMs and NCMs. Figure S2: XPS spectra of NPCMs. Figure S3: Digital images of Li₂S₆ adsorption at different time. Figure S4: HRTEM image of NPCMs. Figure S5: SEM images of (a) NCMs and (b) NCMs–Li₂S. Figure S6: CV curves of NCMs–Li₂S cathode. Figure S7: Charge–discharge curves of NCMs–Li₂S cathode in the first three cycles. Figure S8: Comparison of the rate capabilities of NPCMs–Li₂S and various Li₂S cathodes. Figure S9: XPS survey spectra of NPCMs– Li_2S after 500 cycles at 1.0 A g⁻¹. Table S1: Electrochemical performance of various lithium sulfide–based cathodes.

Author Contributions: The experimental work, original draft preparation, and modification, S.L. and J.C.; methodology for experiments, manuscript review and editing, X.H. and L.L.; conceptualization and data analysis, resources, project administration, funding acquisition, S.L., N.Z., T.Y., C.T. and C.L.; data analysis, L.H.; formal analysis, L.W. and D.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work is supported by the National Natural Science Foundation of China (51902079, 52072342), Anhui Provincial Natural Science Foundation (2008085QE271, 2008085QE277), Talent Scientific Research Foundation of Hefei University (18–19RC21, 18–19RC22), Research Development Foundation of Hefei University (19ZR12ZDA), Guangdong Basic and Applied Basic Research Foundation (No.2021A1515010671,2020A1515011221).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Yang, W.; Liu, H.; Ren, Z.; Jian, N.; Gao, M.; Wu, Y.; Liu, Y.; Pan, H. A novel multielement, multiphase, and B–containing SiO_x composite as a stable anode material for Li–ion batteries. *Adv. Mater. Interfaces* **2019**, *6*, 1801631. [CrossRef]
- Wang, D.; Gao, M.; Pan, H.; Wang, J.; Liu, Y. High performance amorphous–Si@SiO_x/C composite anode materials for Li–ion batteries derived from ball–milling and in situ carbonization. *J. Power Sources* 2014, 256, 190–199. [CrossRef]
- Yang, Y.; Liu, Y.; Pu, K.; Chen, X.; Tian, H.; Gao, M.; Zhu, M.; Pan, H. Highly stable cycling of amorphous Li₂CO₃–Coated α–Fe₂O₃ nanocrystallines prepared via a new mechanochemical strategy for Li–ion batteries. *Adv. Funct. Mater.* 2017, 27, 1605011. [CrossRef]
- Yang, Y.; Qu, X.; Zhang, X.; Liu, Y.; Hu, J.; Chen, J.; Gao, M.; Pan, H. Higher than 90% initial coulombic efficiency with staghorn–coral–like 3D porous LiFeO_{2-x} as anode materials for Li–ion batteries. *Adv. Mater.* 2020, *32*, 1908285. [CrossRef] [PubMed]
- 5. Wang, P.; Gao, M.; Pan, H.; Zhang, J.; Liang, C.; Wang, J.; Zhou, P.; Liu, Y. A facile synthesis of Fe₃O₄/C composite with high cycle stability as anode material for lithium–ion batteries. *J. Power Sources* **2013**, *239*, 466–474. [CrossRef]
- 6. Huang, J.; Wang, S.; Xu, W.; Shi, W.; Fernandez, C. A novel autoregressive rainflow–integrated moving average modeling method for the accurate state of health prediction of lithium–ion batteries. *Processes* **2021**, *9*, 795. [CrossRef]
- 7. Wang, L.; Wu, H.; Hu, Y.; Yu, Y.; Huang, K. Environmental sustainability assessment of typical cathode materials of lithium–ion battery based on three LCA approaches. *Processes* **2019**, *7*, 83. [CrossRef]
- Wang, Y.; Deng, Z.; Huang, J.; Li, H.; Li, Z.; Peng, X.; Tian, Y.; Lu, J.; Tang, H.; Chen, L.; et al. 2D Zr–Fc metal–organic frameworks with highly efficient anchoring and catalytic conversion ability towards polysulfides for advanced Li–S battery. *Energy Storage Mater.* 2021, 36, 466–477. [CrossRef]
- 9. Wu, Y.; Gao, M.; Li, X.; Liu, Y.; Pan, H. Preparation of mesohollow and microporous carbon nanofiber and its application in cathode material for lithium–sulfur batteries. *J. Alloy. Compd.* **2014**, *608*, 220–228. [CrossRef]
- 10. Zhao, M.; Chen, X.; Li, X.Y.; Li, B.Q.; Huang, J.Q. An organodiselenide comediator to facilitate sulfur redox kinetics in lithium–sulfur batteries. *Adv. Mater.* 2021, 33, 2007298. [CrossRef]
- Zhang, H.; Zhou, W.; Huang, D.; Ou, L.; Lan, Z.; Liang, X.; Huang, H.; Huang, D.; Guo, J. Functionalized hierarchical porous carbon with sulfur/nitrogen/oxygen tri–doped as high quality sulfur hosts for lithium–sulfur batteries. *J. Alloy. Compd.* 2021, 858, 157647. [CrossRef]
- 12. Li, M.; Feng, W.; Wang, X. The dual–play of carbon nanotube embedded with CoNi N codoped porous polyhedra toward superior lithium–sulfur batteries. *J. Alloy. Compd.* **2021**, *853*, 157194. [CrossRef]
- 13. Shao, Q.; Guo, D.; Wang, C.; Chen, J. Yolk–shell structure MnO₂@Hollow carbon nanospheres as sulfur host with synergistic encapsulation of polysulfides for improved Li–S batteries. *J. Alloy. Compd.* **2020**, *842*, 155790. [CrossRef]
- Shi, Z.; Feng, W.; Wang, X.; Li, M.; Song, C.; Chen, L. Catalytic cobalt phosphide Co₂P/carbon nanotube nanocomposite as host material for high performance lithium–sulfur battery cathode. *J. Alloy. Compd.* 2021, 851, 156289. [CrossRef]
- Wang, W.P.; Zhang, J.; Chou, J.; Yin, Y.X.; You, Y.; Xin, S.; Guo, Y.G. Solidifying cathode–electrolyte interface for lithium–sulfur batteries. *Adv. Energy Mater.* 2021, *11*, 2000791. [CrossRef]
- 16. Zhao, Z.; Yi, Z.; Li, H.; Pathak, R.; Yang, Z.; Wang, X.; Qiao, Q. Synergetic effect of spatially separated dual co–catalyst for accelerating multiple conversion reaction in advanced lithium sulfur batteries. *Nano Energy* **2021**, *81*, 105621. [CrossRef]

- Yan, W.; Wei, J.; Chen, T.; Duan, L.; Wang, L.; Xue, X.; Chen, R.; Kong, W.; Lin, H.; Li, C.; et al. Superstretchable, thermostable and ultrahigh–loading lithium–sulfur batteries based on nanostructural gel cathodes and gel electrolytes. *Nano Energy* 2021, *80*, 105510. [CrossRef]
- Li, Z.; Zhang, Q.; Hencz, L.; Liu, J.; Kaghazchi, P.; Han, J.; Wang, L.; Zhang, S. Multifunctional cation–vacancy–rich ZnCo₂O₄ polysulfide–blocking layer for ultrahigh–loading Li–S battery. *Nano Energy* 2021, *89*, 106331. [CrossRef]
- 19. He, Y.; Chang, Z.; Wu, S.; Qiao, Y.; Bai, S.; Jiang, K.; He, P.; Zhou, H. Simultaneously inhibiting lithium dendrites growth and polysulfides shuttle by a flexible MOF–based membrane in Li–S batteries. *Adv. Energy Mater.* **2018**, *8*, 1802130. [CrossRef]
- 20. Li, L.; Basu, S.; Wang, Y.; Chen, Z.; Hundekar, P.; Wang, B.; Shi, J.; Shi, Y.; Narayanan, S.; Koratkar, N. Self–heating–induced healing of lithium dendrites. *Science* 2018, 359, 1513–1516. [CrossRef]
- Pang, Q.; Shyamsunder, A.; Narayanan, B.; Kwok, C.Y.; Curtiss, L.A.; Nazar, L.F. Tuning the electrolyte network structure to invoke quasi-solid state sulfur conversion and suppress lithium dendrite formation in Li–S batteries. *Nat. Energy* 2018, *3*, 783–791. [CrossRef]
- Chen, Y.; Lu, S.; Li, Y.; Qin, W.; Wu, X. A high-performance Li₂S/MnO₂ rechargeable battery. *Mater. Lett.* 2019, 248, 157–160. [CrossRef]
- Hao, Z.; Chen, J.; Yuan, L.; Bing, Q.; Liu, J.; Chen, W.; Li, Z.; Wang, F.R.; Huang, Y. Advanced Li₂S/Si full battery enabled by TiN polysulfide immobilizer. *Small* 2019, 15, 1902377. [CrossRef] [PubMed]
- 24. Seita, T.; Matsumae, Y.; Liu, J.; Tatara, R.; Ueno, K.; Dokko, K.; Watanabe, M. Graphite–lithium sulfide battery with a single–phase sparingly solvating electrolyte. *ACS Energy Lett.* **2020**, *5*, 1–7. [CrossRef]
- Liang, S.; Xia, Y.; Liang, C.; Gan, Y.; Huang, H.; Zhang, J.; Tao, X.; Sun, W.; Han, W.; Zhang, W. A green and facile strategy for the low-temperature and rapid synthesis of Li₂S@PC-CNT cathodes with high Li₂S content for advanced Li–S batteries. *J. Mater. Chem. A* 2018, *6*, 9906–9914. [CrossRef]
- Li, X.; Gao, M.; Du, W.; Ni, B.; Wu, Y.; Liu, Y.; Shang, C.; Guo, Z.; Pan, H. A mechanochemical synthesis of submicron–sized Li₂S and a mesoporous Li₂S/C hybrid for high performance lithium/sulfur battery cathodes. *J. Mater. Chem. A* 2017, *5*, 6471–6482. [CrossRef]
- 27. Chen, Y.; Lu, S.; Zhou, J.; Wu, X.; Qin, W.; Ogoke, O.; Wu, G. 3D graphene framework supported Li₂S coated with ultra–thin Al₂O₃ films: Binder–free cathodes for high–performance lithium sulfur batteries. *J. Mater. Chem. A* **2017**, *5*, 102–112. [CrossRef]
- Zhang, X.; Li, J.; Gao, C.; Shi, C.; He, L.; Xiang, Q.; Hong, B.; Lai, Y.; Zhang, Z.; Zhang, K. Promoting the conversion of Li₂S by functional additives phenyl diselenide in Lithium–Sulfur batteries. *J. Power Sources* 2021, 482, 228967. [CrossRef]
- 29. Chen, X.; Peng, L.; Yuan, L.; Zeng, R.; Xiang, J.; Chen, W.; Yuan, K.; Chen, J.; Huang, Y.; Xie, J. Facile synthesis of Li₂S@C composites as cathode for Li–S batteries. *J. Energy Chem.* **2019**, *37*, 111–116. [CrossRef]
- He, J.; Chen, Y.; Lv, W.; Wen, K.; Li, P.; Qi, F.; Wang, Z.; Zhang, W.; Li, Y.; Qin, W.; et al. Highly–flexible 3D Li₂S/graphene cathode for high–performance lithium sulfur batteries. *J. Power Sources* 2016, 327, 474–480. [CrossRef]
- 31. Wang, D.; Wu, Y.; Zheng, X.; Tang, S.; Gong, Z.; Yang, Y. Li₂S@NC composite enable high active material loading and high Li₂S utilization for all–solid–state lithium sulfur batteries. *J. Power Sources* **2020**, 479, 228792. [CrossRef]
- Chen, Y.; Lu, S.; Zhou, J.; Qin, W.; Wu, X. Synergistically assembled Li₂S/FWNTs@reduced graphene oxide nanobundle forest for free-standing high-performance Li₂S cathodes. *Adv. Funct. Mater.* 2017, 27, 1700987. [CrossRef]
- Hayashi, A.; Ohtsubo, R.; Ohtomo, T.; Mizuno, F.; Tatsumisago, M. All–solid–state rechargeable lithium batteries with Li₂S as a positive electrode material. J. Power Sources 2008, 183, 422–426. [CrossRef]
- 34. He, J.; Chen, Y.; Manthiram, A. Metal sulfide–decorated carbon sponge as a highly efficient electrocatalyst and absorbant for polysulfide in high–loading Li₂S batteries. *Adv. Energy Mater.* **2019**, *9*, 1900584. [CrossRef]
- 35. Wang, X.; Bi, X.; Wang, S.; Zhang, Y.; Du, H.; Lu, J. High–rate and long–term cycle stability of Li–S batteries enabled by Li₂S/TiO₂–impregnated hollow carbon nanofiber cathodes. *ACS Appl. Mater. Interfaces* **2018**, *10*, 16552–16560. [CrossRef]
- Cai, K.; Song, M.K.; Cairns, E.J.; Zhang, Y. Nanostructured Li₂S–C composites as cathode material for high–energy lithium/sulfur batteries. *Nano Lett.* 2012, 12, 6474–6479. [CrossRef]
- Xia, Y.; Fang, R.; Xiao, Z.; Huang, H.; Gan, Y.; Yan, R.; Lu, X.; Liang, C.; Zhang, J.; Tao, X.; et al. Confining sulfur in N-doped porous carbon microspheres derived from microalgaes for advanced lithium-sulfur batteries. ACS Appl. Mater. Interfaces 2017, 9, 23782–23791. [CrossRef]
- Qie, L.; Manthiram, A. Uniform Li₂S precipitation on N, O-codoped porous hollow carbon fibers for high-energy-density lithium-sulfur batteries with superior stability. *Chem. Commun.* 2016, 52, 10964–10967. [CrossRef] [PubMed]
- 39. Zhang, J.; Shi, Y.; Ding, Y.; Peng, L.; Zhang, W.; Yu, G. A conductive molecular framework derived Li₂S/N, P–codoped carbon cathode for advanced lithium–sulfur batteries. *Adv. Energy Mater.* **2017**, *7*, 1602876. [CrossRef]
- 40. He, J.; Chen, Y.; Lv, W.; Wen, K.; Xu, C.; Zhang, W.; Li, Y.; Qin, W.; He, W. From metal–organic framework to Li₂S@C–Co–N nanoporous architecture: A high–capacity cathode for lithium–sulfur batteries. *ACS Nano* **2016**, *10*, 10981–10987. [CrossRef]
- 41. Li, Y.; Cai, Y.; Cai, Z.; Xu, J.; Sonamuthu, J.; Zhu, G.; Militky, J.; Jin, W.; Yao, J. Sulfur–infiltrated yeast–derived nitrogen–rich porous carbon microspheres@reduced graphene cathode for high–performance lithium–sulfur batteries. *Electrochim. Acta* 2018, 285, 317–325. [CrossRef]
- Li, W.K.; Feng, J.T.; Ma, Z.Q. Nitrogen, sulfur, boron and flavonoid moiety co-incorporated carbon dots for sensitive fluorescence detection of pesticides. *Carbon* 2020, 161, 685–693. [CrossRef]

- 43. Liang, S.; Chen, J.; Zhou, N.; Hu, L.; Liu, L.; Wang, L.; Liang, D.; Yu, T.; Tian, C.; Liang, C. CNT threaded porous carbon nitride nanoflakes as bifunctional hosts for lithium sulfide cathode. *J. Alloy. Compd.* **2021**, *887*, 161356. [CrossRef]
- 44. Wang, J.; Meng, Z.; Yang, W.; Yan, X.; Guo, R.; Han, W.Q. Facile synthesis of rGO/g–C₃N₄/CNT microspheres via an ethanol–assisted spray–drying method for high–performance lithium–sulfur batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 819–827. [CrossRef]
- Yuan, H.; Zhang, W.; Wang, J.G.; Zhou, G.; Zhuang, Z.; Luo, J.; Huang, H.; Gan, Y.; Liang, C.; Xia, Y.; et al. Facilitation of sulfur evolution reaction by pyridinic nitrogen doped carbon nanoflakes for highly–stable lithium–sulfur batteries. *Energy Storage Mater.* 2018, *10*, 1–9. [CrossRef]
- 46. Yang, J.; Wang, S.; Ma, Z.; Du, Z.; Li, C.; Song, J.; Wang, G.; Shao, G. Novel nitrogen–doped hierarchically porous coralloid carbon materials as host matrixes for lithium–sulfur batteries. *Electrochim. Acta* 2015, *159*, 8–15. [CrossRef]
- Zeng, X.; Ding, Z.; Ma, C.; Wu, L.; Liu, J.; Chen, L.; Ivey, D.G.; Wei, W. Hierarchical nanocomposite of hollow N–doped carbon spheres decorated with ultrathin WS₂ nanosheets for high–performance lithium–ion battery anode. ACS Appl. Mater. Interfaces 2016, 8, 18841–18848. [CrossRef]
- Xia, Y.; Zhong, H.; Fang, R.; Liang, C.; Xiao, Z.; Huang, H.; Gan, Y.; Zhang, J.; Tao, X.; Zhang, W. Biomass derived Ni(OH)₂@porous carbon/sulfur composites synthesized by a novel sulfur impregnation strategy based on supercritical CO₂ technology for advanced Li–S batteries. *J. Power Sources* 2018, *378*, 73–80. [CrossRef]
- 49. He, J.; Chen, Y.; Lv, W.; Wen, K.; Xu, C.; Zhang, W.; Qin, W.; He, W. Three–dimensional CNT/graphene–Li₂S aerogel as freestanding cathode for high–performance Li–S batteries. *ACS Energy Lett.* **2016**, *1*, 820–826. [CrossRef]
- Tao, X.; Wang, J.; Ying, Z.; Cai, Q.; Zheng, G.; Gan, Y.; Huang, H.; Xia, Y.; Liang, C.; Zhang, W.; et al. Strong sulfur binding with conducting magnéli–phase Ti_nO_{2n-1} nanomaterials for improving lithium–sulfur batteries. *Nano Lett.* 2014, 14, 5288–5294. [CrossRef] [PubMed]
- 51. Liu, J.; Nara, H.; Yokoshima, T.; Momma, T.; Osaka, T. Micro–scale Li₂S–C composite preparation from Li₂SO₄ for cathode of lithium ion battery. *Electrochim. Acta* 2015, *183*, 70–77. [CrossRef]
- 52. Zhang, B.; Qin, X.; Li, G.R.; Gao, X.P. Enhancement of long stability of sulfur cathode by encapsulating sulfur into micropores of carbon spheres. *Energy Environ. Sci.* 2010, *3*, 1531–1537. [CrossRef]
- 53. Chu, H.; Noh, H.; Kim, Y.J.; Yuk, S.; Lee, J.H.; Lee, J.; Kwack, H.; Kim, Y.; Yang, D.K.; Kim, H.T. Achieving three–dimensional lithium sulfide growth in lithium–sulfur batteries using high–donor–number anions. *Nat. Commun.* 2019, 10, 188. [CrossRef] [PubMed]
- 54. Wang, D.; Xia, X.; Xie, D.; Niu, X.; Ge, X.; Gu, C.; Wang, X.; Tu, J. Rational in–situ construction of three–dimensional reduced graphene oxide supported Li₂S/C composite as enhanced cathode for rechargeable lithium–sulfur batteries. *J. Power Sources* **2015**, 299, 293–300. [CrossRef]
- 55. Wang, D.H.; Xie, D.; Xia, X.H.; Zhang, X.Q.; Tang, W.J.; Zhong, Y.; Wu, J.B.; Wang, X.L.; Tu, J.P. A 3D conductive network with high loading Li₂S@C for high performance lithium–sulfur batteries. *J. Mater. Chem. A* **2017**, *5*, 19358–19363. [CrossRef]
- 56. Peng, Y.; Zhang, Y.; Wen, Z.; Wang, Y.; Chen, Z.; Hwang, B.J.; Zhao, J. Constructing fast electron and ion conductive framework for Li₂S as advanced lithium sulfur battery. *Chem. Eng. J.* **2018**, *346*, 57–64. [CrossRef]