

Porous nitrogen-doped carbon/MnO coaxial nanotubes as an efficient sulfur host for lithium sulfur batteries

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© Tsinghua University Press and Springer-Verlag GmbH Germany, part of Springer Nature 2018 Received: 11 March 2018 / Revised: 14 August 2018 / Accepted: 13 September 2018

ABSTRACT

As a promising candidate for next generation energy storage devices, lithium sulfur (Li-S) batteries still confront rapid capacity degradation and low rate capability. Herein, we report a well-architected porous nitrogen-doped carbon/MnO coaxial nanotubes (MnO@PNC) as an efficient sulfur host material. The host shows excellent electron conductivity, sufficient ion transport channels and strong adsorption capability for the polysulfides, resulting from the abundant nitrogen-doped sites and pores as well as MnO in the carbon shell of MnO@PNC. The MnO@PNC-S composite electrode with a sulfur content of 75 wt.% deliveries a specific capacity of 802 mAh·g⁻¹ at a high rate of 5.0 C and outstanding cycling stability with a capacity retention of 82% after 520 cycles at 1.0 C.

KEYWORDS

nitrogen doping, porous, MnO, carbon nanotubes, sulfur batteries

1 Introduction

The increasing demand for electric vehicles and large-scale smart grid is hardly satisfied by the current energy storage systems [1, 2]. Lithium sulfur (Li-S) batteries, due to the high theoretical capacity (ca. 1,675 mAh·g⁻¹) and extremely low cost [2, 3], have garnered enormous attention in recent years. However, several obstacles, including the insulating nature of both sulfur and its ultimate discharged products (Li₂S/Li₂S₂), as well as the "shuttle effect" of the soluble intermediate polysulfides during the cycling process, need to be circumvented before the practical applications [3–7].

To tackle the above issues, one-dimensional (1D) carbon materials have been widely employed as the hosts for sulfur loading due to the high electron conductivity and large surface area [2]. When assembled into an interconnected conductive network, 1D carbon material with high aspect ratio shows sufficient surface to facilitate the electrochemical reaction and the effective utilization of sulfur [3, 8, 9]. And the design of porous structure in the carbon material is also commonly employed to shorten the ion diffusion distance and improve the electrochemical reaction kinetics, which are supposed to result in a desirable rate performance at a high sulfur content [2, 10-12]. However, the non-polar nature of carbon material manifests weak interaction with polysulfides. This property is disadvantageous for carbon material to efficiently anchor the polysulfide for a long term when the carbon sulfur composite has a high sulfur content (>70 wt.%) [13, 14].

Recently, significant progress has been made by modifying the carbon materials with heteroatom, which can mitigate the "shuttle effect" through creating strong chemical bonds with polysulfide ions [15–18]. Among the heteroatoms, nitrogen atoms have been demonstrated to strengthen the chemical bonding and improve the conductivity of carbon effectively [17–20]. Alternatively, polar

oxide materials, such as MnO₂, TiO₂, MnO, have been verified to be advantageous for chemically binding the polysulfides [21–24]. Based on the aforementioned consideration, it is rational and significant to enhance the overall electrochemical performance of Li-S batteries through the integration of heteroatoms and polar materials into the porous 1D carbon materials.

In this work, we report porous N-doped carbon nanotubes composited with MnO (MnO@PNC) as the sulfur host for Li-S batteries. This MnO@PNC composite has large hollow space and numerous hierarchical pores, which is beneficial for the high sulfur loading and fast ion transport. Furthermore, the embedded MnO and abundant N-doped sites on the carbon shell can efficiently keep the polysulfides inside the hollow carbon nanotubes through chemical bonding. With the synergistic combination of multiple components, the as-prepared MnO@PNC-S composite exhibits an enhanced electrochemical performance when served as the cathode material for Li-S batteries.

2 Experiment

All the chemicals were of analytical grade and were used as received without any purification.

Synthesis of the MnO_2 nanowires: In a typical synthesis procedure, 4.0 mmol of $MnSO_4$ ·H₂O, 7.0 mmol of KClO₃, and 7.0 mmol of CH₃COOK were dissolved in 70 mL of deionized water. Subsequently, 3.2 mL of CH₃COOH was added to the above solution under vigorous stirring. Then, the obtained homogeneous solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 200 °C for 5.0 h. After naturally cooling down to room temperature, the precipitates were collected by vacuum filtration with common filter paper, and washed with deionized water for several times, and finally dried at 70 °C in air.

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Synthesis of the hierarchical polypyrrole coated MnO₂ (MnO₂@PPy): Typically, 200 mg of the as-prepared MnO₂ nanowires were dispersed in 200 mL of 0.1 M HCl solution under vigorous stirring for 1.0 h. Then, 150 μ L of pyrrole monomers were added dropwise into the above suspension. After 6.0 h stirring, the color of the suspension was totally evolved from brown to black, suggesting that the *in-situ* interfacial polymerization was completed. The black product was collected and washed using deionized water by vacuum filtration, and finally dried in an oven at 70 °C overnight.

Synthesis of the nitrogen-doped carbon coated MnO (MnO@NC): The as-prepared MnO₂@PPy were heated to 800 °C at a ramping rate of 3 °C·min⁻¹ under the nitrogen atmosphere, and then maintained at this temperature for 3.0 h. During the period, the polypyrrole (PPy) was carbonized to nitrogen-doped carbon and the MnO₂ was reduced to MnO, resulting a composite of MnO@NC.

Synthesis of MnO@PNC and PNC: The obtained MnO@NC were heated to 800 °C at a heating rate of 5 °C·min⁻¹ and kept at this temperature for 3.0 h in a flowing mixture gas of H_2O/N_2 . After naturally cooling down, MnO@PNC was obtained. To get the PNC, a certain amount of MnO@PNC was immersed into sufficient 1.0 M HCl solution overnight under stirring and then washed with deionized water and finally dried at 70 °C for 12 h.

Preparation of MnO@NC-S, PNC-S and MnO@PNC-S: The appropriate amounts of MnO@PNC were mixed with sulfur at a mass ratio of 1:4 in 10 mL carbon disulfide (CS₂) and stirred until the solution was evaporated. Then, the obtained MnO@PNC/S mixture was dried at 70 °C for 10 h. Subsequently, the mixture was transferred into a sealed bottle and heated at 155 °C for 12 h in an oven. Finally, the product was heated at 200 °C for 0.5 h under argon flow in a tube furnace to remove the redundant sulfur. The MnO@NC-S and PNC-S composite were fabricated following the same route.

Materials characterization: The crystallographic characterization of the as-synthesized samples was performed with a Bruker D8 Advance X-ray diffractometer with a non-monochromatic Cu Ka X-ray source. Field emission scanning electron microscopic (FESEM) images and energy dispersive X-ray spectrum (EDS) were obtained with a JEOL-7100F microscope. Transmission electron microscopic (TEM) images and corresponding elemental mappings were collected with a JEM-2100F STEM/EDS microscope. The thermogravimetric analysis (TGA) data were collected with a Pyris1 Thermogravimetric Analyzer at a heating rate of 10 °C·min⁻¹. The Brunauer-Emmett-Teller (BET) surface area was measured using a Tristar II 3,020 instrument at 77 K. Raman spectra were achieved using a Renishaw RM-1000 laser Raman microscopy system. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Multi Lab 2,000 instrument. Utralviolet-visble (UV-Vis) absorption spectra were obtained with a V-670 (Jasco).

Electrochemical testing: The MnO@NC-S, PCN-S or MnO@PCN-S cathode was prepared by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) binder in a mass ratio of 8:1:1 in N-methylpyrrolidinone (NMP) to form a homogeneous slurry. The slurry was spread onto aluminum foils with a 300 mm doctor blade and dried at 50 °C in a vacuum oven for 24 h. The dried foil sheets were pressed and cut into a circular disk with a diameter of 10 mm served as a cathode. The areal mass loading of sulfur was $\sim 3 \text{ mg} \cdot \text{cm}^{-2}$. The electrochemical performance was evaluated by using coin cells with lithium metal as the counter and reference electrode and Celgard 2400 membrane as the separator. The electrolyte solution was 1.0 M bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) in a solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 in volume) with 0.1 M LiNO3 additive. Galvanostatic measurements were conducted using a LAND CT2001A battery test system between 1.8 and 2.8 V (vs. Li⁺/Li). The specific capacity was calculated based on the mass of sulfur. The tested cells were disassembled in the glove box and the cathode in the cell was washed with a solvent of DOL:DME before the morphology characterization of the cycled electrode. Cyclic voltammograms (CV) experiments and electrochemical impedance spectroscopy (EIS) measurements were conducted using a CHI 760E electrochemical workstation. The CV was recorded at a scan rate of 0.1 mV·s⁻¹ within a cutoff window of 1.8–2.8 V. The EIS was measured by applying a disturbance amplitude of 5 mV in a frequency range of 10^{-2} – 10^{5} Hz.

Polysulfide adsorption study: A Li₂S₆ solution with concentration of 0.2 mol·L⁻¹ (calculated based on sulfur content) was prepared by dissolving stoichiometric ratio of Li₂S and elemental S into DME:DOL (1:1 in volume) at 60 °C overnight. 10 mg of PNC and MnO@PNC powder was separately added to 4.0 mL of Li₂S₆ solution and the mixtures were stirred to obtain thorough adsorption. A blank glass vial was also filled with the same Li₂S₆ solution as a comparison.

3 Results and discussions

The synthesis process of MnO@PNC-S composite is schematically illustrated in Fig. 1. First, MnO₂ nanowires were used as the template and oxidation initiator. The MnO₂@PPy nanotubes were converted from these MnO₂ nanowires through the pyrrole-induced reductive transformation reaction [25]. Via the carbonization of MnO₂@PPy nanotubes in N₂ atmosphere at 800 °C for 3.0 h, the MnO@NC nanotubes were obtained. MnO@NC nanotubes were then treated with a mixture gas flow of H₂O/N₂ at 800 °C for 3.0 h to create pores on the surface to obtain the MnO@PNC. Finally, sulfur was incorporated into the MnO@PNC nanotubes through the melt-diffusion method [3].

Ultralong MnO₂ nanowires were prepared through a hydrothermal method. The length of hundreds of micrometers and an average diameter of approximately 110 nm (Figs. S1(a) and S1(b) in the Electronic Supplementary Material (ESM)), suggests a high aspect ratio over 1,000 of MnO₂ nanowires. The X-ray diffraction (XRD) pattern of as-prepared MnO₂ nanowires was indexed to tetragonal α -MnO₂ (Reference pattern: 01-072-1982, Fig. S2(a) in the ESM). After *in situ* interfacial polymerization of pyrrole, PPy was uniformly coated on the MnO₂ nanowires and the average diameter of the nanowires increased to about 180 nm (Figs. S1(c) and S1(d) in the ESM). The subsequent annealing process of MnO₂@PPy transformed PPy into N-doped carbon and reduced MnO₂ to MnO (Reference pattern: 01-075-1090, Fig. S2(b) in the ESM). The transformation gave rise to a relatively rough surface, but the ultralong nanostructure was well maintained (Figs. S1(e) and S1(f) in the ESM). After



Figure 1 Illustration of the synthesis process for MnO@PNC-S composite. The left and the right flow charts are the longitudinal section view and the cross section view, respectively.

treatment of MnO@NC with steam at an elevated temperature, mesopores and micropores (Fig. 2(a), and Figs. S3(a), S3(b) and S4(b) in the ESM) were generated in the carbon sheath, leading to the formation of product MnO@PNC nanotubes, while the MnO phase and the nanotube morphology maintained (Fig. 2(b) and Fig. S4 in the ESM). The average diameter of the inner MnO@PNC nanotubes is about 80 nm. Benefiting from the unique structural features, element sulfur was successfully incorporated into the MnO@PNC nanotubes, and no bare sulfur particle was observed on the outer surface of the MnO@PNC nanotubes (Fig. 2(c) and Fig. S5(a) in the ESM). The XRD pattern of MnO@PNC-S composite shows that sulfur exists as orthorhombic S₈ in the composite (Fig. 2(d)). An EDS line scan (Fig. 2(e)) and elemental mappings (Figs. S5(b)-S5(e) in the ESM) confirmed that the sulfur, carbon, nitrogen and manganese elements were uniformly distributed in the MnO@PNC-S composite. And sulfur was proved to be encapsulated in the hollow carbon nanotubes and in the pores of PNC (Fig. 2(f) and Fig. S6 in the ESM).

The porous structures of MnO@PNC, PNC and MnO@NC were investigated by the N2 adsorption-desorption measurements. MnO@PNC and MnO@NC manifest a typical I and IV isotherms [9, 26] (Fig. 3(a)), revealing a hierarchical microporous and mesoporous structure. MnO@PNC possesses a surface area of 691 m²·g⁻¹ and a pore volume of 0.595 cm³·g⁻¹ as calculated through the BET method. After the etching of MnO, the inner MnOblocked pores of MnO@PNC were exposed, resulting in a higher surface area of 743 $m^2 \cdot g^{-1}$ and a larger pore volume of 0.639 $cm^3 \cdot g^{-1}$ for PNC. However, for the MnO@NC sample, the surface area is merely 60 m²·g⁻¹ and the total pore volume is only 0.124 cm³·g⁻¹. The increase in the surface area and the pore volume for MnO@PNC and PNC samples suggest the effective carbon etching and pore generation through the activated process. To further confirm the carbon state, Raman spectra were recorded (Fig. 3(b)). The Raman spectra of both MnO@PNC and MnO@NC exhibit two distinct peaks at 1,582 (G band) and 1,355 (D band) cm⁻¹, which represent sp²-type graphitic carbon and sp³-type disordered carbon, respectively [17, 27]. The relative intensity of I_D/I_G of MnO₂@NC is 0.90, suggesting that the carbon component in MnO₂@NC is semi-crystalline. Moreover, the following pore-generating process has little influence on the degree of graphitization in carbon shell as the ratio of I_D/I_G is 0.89 for MnO@PNC sample.

MnO content in the MnO@PNC was determined to be about 14 wt.% (Fig. S7(a) in the ESM) by TGA. MnO has been shown to be an excellent polysulfides mediator, which possesses strong adsorption capability for polysulfides and facilitates the uniform deposition of solid state Li₂S and Li₂S [22, 28, 29]. After the filtration of sulfur, the sulfur loading into the MnO@PNC is determined to be approximately 75 wt.% (Fig. 3(c)). To confirm the chemical composition and chemical bonds in the MnO@PNC-S composite, XPS was conducted. The full XPS spectrum of MnO@PNC-S mainly contains peaks related to C, S, N, O and Mn elements that are marked in Fig. S7(b) in the ESM. Specifically, the N 1s spectrum of MnO@PNC-S is resolved into two peaks (Fig. 3(d)). The peaks at 397.08 and 399.58 eV are attributed to pyridinic-type and pyrrolictype of N atoms, respectively, which create numerous extrinsic defects and active sites and thus improve the electronic conductivity [16, 17, 30]. The atomic percentage of N was calculated to be 2.7 at.%. Through the theoretical calculation of the N atoms at different positions of carbon, pyridinic and pyrrolic N are demonstrated to have strong coordination interaction with lithium polysulfides for enhancing the electrochemical performances of sulfur cathodes [16, 17, 21].

To further explore the adsorption ability of the as-prepared MnO@PNC on lithium polysulfides, ex-situ adsorption measurement was utilized. After adding 10 mg of PNC and MnO@PNC powder to Li₂S₆ solution respectively for 2 h, the MnO@PNC decolored the polysulfide solution completely, whereas the color of the solution containing PNC powder only faded slightly (inset of Fig. S8 in the ESM). The UV-Vis spectra were also collected to investigate the concentration changes of Li2S6 solution after adding PNC or MnO@PNC. The blank Li₂S₆ solution exhibited strong absorbance in the 400-500 cm⁻¹ region [17, 31], which agreed well with the previous report. The absorption peak for Li₂S₆ solution exposed to MnO@PNC almost disappeared while Li₂S₆ solution exposed to MnO@PNC still showed absorbance (Fig. S8 in the ESM). These differences strongly revealed that the MnO can remarkably strengthen the adsorption of lithium polysulfides [22]. As a result, MnO@PNC is supposed to effectively trap the soluble polysulfides during cycling, alleviating the loss of active materials.

To evaluate the electrochemical performance of MnO@PNC-S as a cathode material for Li-S batteries, CR2025 coin cells were assembled. MnO@NC-S and PNC-S cathodes were also prepared for demonstrating the structural advantages of MnO@PNC-S. The CV curves (Fig. 4(a)) and the galvanostatic charge–discharge profiles (Fig. 4(b)) show the typical electrochemical behaviors of the sulfur cathodes. In details, the cathodic scans of the MnO@PNC-S cathode show two peaks corresponding to the formation of long-chain polysulfides (Li₂S_x, 4 < X < 8) at around 2.3 V and short-chain polysulfides (Li₂S₂ and Li₂S) near 2.1 V [10, 21]. The anodic peak between 2.3 and 2.4 V is associated with the oxidation of Li₂S₂/Li₂S



Figure 2 (a) and (b) FESEM images (a) and XRD pattern (b) of MnO@PNC, the inset image of (a) shows cross-section for MnO@PNC; (c) FESEM image of MnO@PNC-S; (d) XRD pattern of MnO@PNC-S; (e) linear EDS element distributions of carbon, sulfur, nitrogen and manganese; (f) TEM image of MnO@PNC-S.



Figure 3 (a) Nitrogen adsorption–desorption isotherms of MnO@PNC, MnO@NC and PNC; (b) Raman spectra of MnO@NC and MnO@PNC; (c) TG curve of MnO@PNC-S; (d) high-resolution N 1s XPS spectrum of MnO@PNC-S.

to Li₂S₈ and eventually sulfur [3, 32]. These reversible redox peaks are consistent with the typical voltage plateaus of Li-S batteries (Fig. 4(b)), agreeing well with the previous reports [21, 31, 33]. The plateaus of the three cathodes are similar at low current densities of 0.2 and 0.5 C. In contrast, the plateaus of PNC-S and MnO@PNC-S cathodes are longer and flatter with lower polarization at high current density (over 1.0 C) and are well retained even at 5.0 C when compared with those of MnO@NC-S (Fig. 4(b) and Figs. S9(a)-S9(c) in the ESM), suggesting that better redox reaction kinetics is associated with the pores in the carbon shell. Notably, the shapes of CV curves for PNC-S (Fig. S10(a) in the ESM), MnO@PNC-S (Fig. 4(a)), and MnO@NC-S (Fig. S10(b) in the ESM) electrodes are similar, suggesting MnO in the composites has little influence on the redox reaction mechanism of the sulfur cathode [3]. Besides, the initial five cycles of the CV profiles for MnO@PNC-S electrode (Fig. 4(a)) overlap better than that of PNC-S, indicating a relatively stable cyclic performance. And this phenomenon mainly arises from the polysulfide adsorption capability of MnO.

The rate capabilities of the composites were compared at various current densities from 0.2 to 5.0 C (Fig. 4(c)). As the current density increased, the MnO@PNC-S electrode delivered specific capacities of 1,138, 1,056, 1,011, 948, 906 and 802 mAh·g^-1 at 0.2, 0.5, 1.0, 2.0, 3.0 and 5.0 C, respectively, indicating a high discharge and charge capability and excellent reaction kinetics [3, 33]. In contrast, the MnO@NC electrode exhibited a much lower capacity of 245 mAh·g⁻¹ at 5.0 C. When the current density returned to 0.2 C, the discharge capacity was recovered to 982 mAh·g⁻¹ for MnO@PNC-S electrode, suggesting that the material structure remained stable after the impact of high current densities. Specifically, although the MnO@PNC-S delivered a lower specific capacity (1,138 mAh \cdot g⁻¹) at the current density of 0.2 C than PNC-S (1,260 mAh·g⁻¹), it exhibited slightly higher specific capacity in the following 0.5, 1.0, 2.0, 3.0 and 5.0 C rates. This is mainly because that the strong polysulfides adsorption ability of MnO keeps the capacity retention of MnO@PNC-S is higher than that of PNC-S at each current density, resulting in the better rate performance. Furthermore, the reversible capacities of MnO@PNC-S and PNC-S electrodes are much higher than that of MnO@NC-S, revealing that the pores in the nanotubes are beneficial for the promotion of rate capability [9].

The cycling performance of the MnO@PNC-S was investigated to clarify the effects of the MnO@PNC on retarding the polysufide dissolution. For comparison, the MnO@NC-S and the PNC-S cathode were also tested. As shown in Fig. 4(d), the initial discharge capacity of 862 mAh g^{-1} for MnO@PNC-S electrode at 4.0 C was relatively



Figure 4 (a) CV curves of MnO@PNC-S for five cycles; (b) voltage profiles of MnO@PNC-S cathode cycled between 1.8–2.8 V under increasing C-rates; (c) discharge capacites of MnO@NC-S, MnO@PNC-S and PNC-S; (d) cycling stability of MnO@PNC-S in comparison with MnO@NC-S and PNC-S at a high current density of 4.0 C rate; (e) prolonged cycling performance of MnO@PNC-S and the corresponding Coulombic efficiency.

close to the initial discharge capacity of 928 mAh·g⁻¹ achieved by the PNC-S electrode, whereas the MnO@NC-S electrode delivered a much lower discharge capacity of 562 mAh·g⁻¹. After 200 cycles, the MnO@PNC-S and MnO@NC-S electrodes exhibited the capacity retentions of 89% and 67%, respectively, which are superior to that of PNC-S electrode (28%). The capacity decay rates of the MnO@PNC-S is only 0.055% per cycle. Notably, the introduction of MnO does not significantly increase the impedance while the introduction of pores accelerates the ions diffusion process (Fig. S11 in the ESM). Based on the above analyses, the enhancement of rate capability is attributed to the introduction of pores whereas the improvement of cycling performance is ascribed to the existence of MnO. The MnO@PNC-S cathode was also examined at 1.0 C for long-term cycle test (Fig. 4(e)). The electrode delivered an initial discharge capacity of 1,015 mAh·g⁻¹ and maintained 832 mAh·g⁻¹ after 520 cycles with a capacity retention of 82% (a decay of 0.034% per cycle). Even after the prolonged cycling test, the 1D structure exhibited little change (Fig. S12 in the ESM), revealing superior robustness. Besides, the Coulombic efficiency of MnO@PNC-S showed an obvious enhancement compared to that of PNC-S. (Fig. S13 in the ESM), demonstrating that MnO is beneficial for the restriction of polysulfides. Considering the relatively high sulfur content of 75% and an areal sulfur mass loading of 3.0 mg·cm⁻², the cyclability and the rate capability is competitive to many other sulfur-based cathodes in the literature (Table S1 and Fig. S14 in the ESM) [3, 4, 8, 10, 16, 27, 33-39].

The above excellent electrochemical performance of MnO@PNC-S is ascribed to the multiple advantages of our cathode structure design. First, the 1D nitrogen doping carbon nanotube favorably interconnected as a superior electron conductive network. Second, the robust hollow structure provides sufficient void space for loading a large number of sulfur and alleviates the volume variation during its discharge and charge process. Third, the adsorption ability of polysulfide of MnO can efficiently suppress the shuttle effect of polysulfides and thus keep good cycling stability. Fourth, the pores

on the nanotube supply effective lithium ions diffusion pathway, which is critical to the promotion of rate performance.

3 Conclusion

In summary, 1D N-doped porous carbon nanotubes with MnO embedded in have been designed and synthesized as a sulfur host material for Li-S batteries. The MnO@PNC-S composite delivers a specific capacity of 802 mAh·g⁻¹ at a high rate of 5.0 C and outstanding cycling stability with a capacity retention of 82% after 520 cycles at 1.0 C at a high sulfur content (75%) and an areal sulfur loading of 3 mg·cm⁻². The concept of integrating multiple features into carbon nanotubes will provide a new strategy for future development of high performance Li-S batteries.

Acknowledgements

This work was supported by the National Natural Science Fund for Distinguished Young Scholars (No. 51425204), the National Natural Science Foundation of China (Nos. 51521001 and 51702247), the National Key Research and Development Program of China (No. 2016YFA0202603), the Programme of Introducing Talents of Discipline to Universities (No. B17034), and the Fundamental Research Funds for the Central Universities (WUT: 2016III001, 2017III009, 2017III005, 2017III030).

Electronic Supplementary Material: Supplementary material (FESEM images and XRD patterns of MnO₂ nanowires and MnO@NC; FESEM images of MnO₂@PPy and MnO@PNC; FESEM, TEM images and elemental mapping of MnO@PNC-S; TGA curve and XPS spectrum of MnO@PNC; polysulfides adsorption study; voltage profiles and CV curves of PNC-S and MnO@NC-S; comparison of the potential difference and EIS profiles of MnO@NC-S, MnO@PNC-S and PNC-S; SEM images of MnO@PNC-S electrode before and after cycling; the Coulombic efficiency of PNC-S; comparison of electrochemical performance with literature) is available in the online version of this article at https://doi.org/10.1007/s12274-018-2203-9.

References

- Ji, X. L.; Lee, K. T.; Nazar, L. F. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat. Mater.* 2009, *8*, 500–506.
- [2] Li, Z.; Wu, H. B.; Lou, X. W. Rational designs and engineering of hollow micro-/nanostructures as sulfur hosts for advanced lithium-sulfur batteries. *Energy Environ. Sci.* 2016, 9, 3061–3070.
- [3] Li, Z.; Zhang, J. T.; Lou, X. W. Hollow carbon nanofibers filled with MnO₂ nanosheets as efficient sulfur hosts for lithium-sulfur batteries. *Angew. Chem., Int. Ed.* 2015, 54, 12886–12890.
- [4] Zhang, J. T.; Hu, H.; Li, Z.; Lou, X. W. Double-shelled nanocages with cobalt hydroxide inner shell and layered double hydroxides outer shell as high-efficiency polysulfide mediator for lithium-sulfur batteries. *Angew. Chem., Int. Ed.* 2016, 55, 3982–3986.
- [5] Pang, Q.; Liang, X.; Kwok, C. Y.; Nazar, L. F. Advances in lithium–sulfur batteries based on multifunctional cathodes and electrolytes. *Nat. Energy* 2016, *1*, 16132.
- [6] Chen, J. Z.; Han, K. S.; Henderson, W. A.; Lau, K. C.; Vijayakumar, M.; Dzwiniel, T.; Pan, H. L.; Curtiss, L. A.; Xiao, J.; Mueller, K. T. et al. Restricting the solubility of polysulfides in Li-S batteries via electrolyte salt selection. *Adv. Energy Mater.* **2016**, *6*, 1600160.
- [7] Xu, N.; Qian, T.; Liu, X. J.; Liu, J.; Chen, Y.; Yan, C. L. Greatly suppressed shuttle effect for improved lithium sulfur battery performance through short chain intermediates. *Nano Lett.* **2017**, *17*, 538–543.
- [8] Mi, K.; Jiang, Y.; Feng, J. K.; Qian, Y. T.; Xiong, S. L. Hierarchical carbon nanotubes with a thick microporous wall and inner channel as efficient scaffolds for lithium-sulfur batteries. *Adv. Funct. Mater.* 2016, *26*, 1571–1579.
- [9] Lee, J. S.; Kim, W.; Jang, J.; Manthiram, A. Sulfur-embedded activated

multichannel carbon nanofiber composites for long-life, high-rate lithium-sulfur batteries. *Adv. Energy Mater.* **2017**, *7*, 1601943.

- [10] Yang, X. F.; Yan, N.; Zhou, W.; Zhang, H. Z.; Li, X. F.; Zhang, H. M. Sulfur embedded in one-dimensional French fries-like hierarchical porous carbon derived from a metal–organic framework for high performance lithium–sulfur batteries. J. Mater. Chem. A 2015, 3, 15314–15323.
- [11] Papandrea, B.; Xu, X.; Xu, Y. X.; Chen, C.-Y.; Lin, Z. Y.; Wang, G. M.; Luo, Y. Z.; Liu, M.; Huang, Y.; Mai, L. Q. et al. Three-dimensional graphene framework with ultra-high sulfur content for a robust lithium–sulfur battery. *Nano Res.* 2016, *9*, 240–248.
- [12] Liu, X.; Huang, J.-Q.; Zhang, Q.; Mai, L. Q. Nanostructured metal oxides and sulfides for lithium–sulfur batteries. *Adv. Mater.* 2017, 29, 1601759.
- [13] Li, Z.; Zhang, J. T.; Chen, Y. M.; Li, J.; Lou, X. W. Pie-like electrode design for high-energy density lithium-sulfur batteries. *Nat. Commun.* 2015, 6, 8850.
- [14] Zhang, J.; Yang, C. P.; Yin, Y. X.; Wan, L. J.; Guo, Y. G. Sulfur encapsulated in graphitic carbon nanocages for high-rate and long-cycle lithium-sulfur batteries. *Adv. Mater.* 2016, 28, 9539–9544.
- [15] Zhou, W. D.; Wang, C. M.; Zhang, Q. L.; Abruña, H. D.; He, Y.; Wang, J. W.; Mao, S. X.; Xiao, X. C. Tailoring pore size of nitrogen-doped hollow carbon nanospheres for confining sulfur in lithium-sulfur batteries. *Adv. Energy Mater.* **2015**, *5*, 1401752.
- [16] Pang, Q.; Tang, J. T.; Huang, H.; Liang, X.; Hart, C.; Tam, K. C.; Nazar, L. F. A nitrogen and sulfur dual-doped carbon derived from polyrhodanine@ cellulose for advanced lithium-sulfur batteries. *Adv. Mater.* 2015, *27*, 6021–6028.
- [17] Guo, J. L.; Du, X. Y.; Zhang, X. L.; Zhang, F. X.; Liu, J. P. Facile formation of a solid electrolyte interface as a smart blocking layer for high-stability sulfur cathode. *Adv. Mater.* 2017, 29, 1700273.
- [18] Song, J. X.; Yu, Z. X.; Gordin, M. L.; Wang, D. H. Advanced sulfur cathode enabled by highly crumpled nitrogen-doped graphene sheets for high-energy-density lithium-sulfur batteries. *Nano Lett.* **2016**, *16*, 864–870.
- [19] Cao, J.; Chen, C.; Zhao, Q.; Zhang, N.; Lu, Q. Q.; Wang, X. Y.; Niu, Z. Q.; Chen, J. A flexible nanostructured paper of a reduced graphene oxide-sulfur composite for high-performance lithium-sulfur batteries with unconventional configurations. *Adv. Mater.* **2016**, *28*, 9629–9636.
- [20] Lin, C.; Niu, C. J.; Xu, X.; Li, K.; Cai, Z. Y.; Zhang, Y. L.; Wang, X. P.; Qu, L. B.; Xu, Y. X.; Mai, L. Q. A facile synthesis of three dimensional graphene sponge composited with sulfur nanoparticles for flexible Li-S cathodes. *Phys. Chem. Chem. Phys.* **2016**, *18*, 22146–22153.
- [21] Liang, X.; Hart, C.; Pang, Q.; Garsuch, A.; Weiss, T.; Nazar, L. F. A highly efficient polysulfide mediator for lithium-sulfur batteries. *Nat. Commun.* 2015, 6, 5682.
- [22] Yu, M. P.; Ma, J. S.; Song, H. Q.; Wang, A. J.; Tian, F. Y.; Wang, Y. S.; Qiu, H.; Wang, R. M. Atomic layer deposited TiO₂ on a nitrogen-doped graphene/sulfur electrode for high performance lithium-sulfur batteries. *Energy Environ. Sci.* 2016, 9, 1495–1503.
- [23] An, T. H.; Deng, D. R.; Lei, M.; Wu, Q.-H.; Tian, Z. W.; Zheng, M. S.; Dong, Q. F. MnO modified carbon nanotubes as a sulfur host with enhanced performance in Li/S batteries. *J. Mater. Chem. A* 2016, *4*, 12858–12864.
- [24] Lei, T. Y.; Xie, Y. M.; Wang, X. F.; Miao, S. Y.; Xiong, J.; Yan, C. L. TiO₂ feather duster as effective polysulfides restrictor for enhanced electrochemical kinetics in lithium-sulfur batteries. *Small* **2017**, *13*, 1701013.
- [25] Zhang, J.; Shi, Y.; Ding, Y.; Zhang, W. K.; Yu, G. H. *In situ* reactive synthesis of polypyrrole-MnO₂ coaxial nanotubes as sulfur hosts for high-performance lithium-sulfur battery. *Nano Lett.* 2016, *16*, 7276–7281.
- [26] Guo, D. Y.; Chen, X. A.; Wei, H. F.; Liu, M. L.; Ding, F.; Yang, Z.; Yang, K. Q.; Wang, S.; Xu, X. J.; Huang, S. M. Controllable synthesis of highly uniform flower-like hierarchical carbon nanospheres and their application in high performance lithium–sulfur batteries. *J. Mater. Chem. A* 2017, *5*, 6245–6256.
- [27] Jeong, Y. C.; Lee, K.; Kim, T.; Kim, J. H.; Park, J.; Cho, Y. S.; Yang, S. J.; Park, C. R. Partially unzipped carbon nanotubes for high-rate and stable lithium-sulfur batteries. *J. Mater. Chem. A* 2016, *4*, 819–826.
- [28] Qian, X. Y.; Jin, L. N.; Zhao, D.; Yang, X. L.; Wang, S. W.; Shen, X. Q.; Rao, D. W.; Yao, S. S.; Zhou, Y. Y.; Xi, X. M. Ketjen black-MnO composite coated separator for high performance rechargeable lithium-sulfur battery. *Electrochim. Acta* 2016, 192, 346–356.
- [29] Guo, J. L.; Zhang, X. L.; Du, X. Y.; Zhang, F. X. A Mn₃O₄ nano-wall array based binder-free cathode for high performance lithium–sulfur batteries. *J. Mater. Chem. A* 2017, *5*, 6447–6454.

- [30] Wang, C.; Su, K.; Wan, W.; Guo, H.; Zhou, H. H.; Chen, J. T.; Zhang, X. X.; Huang, Y. H. High sulfur loading composite wrapped by 3D nitrogen-doped graphene as a cathode material for lithium–sulfur batteries. *J. Mater. Chem. A* 2014, 2, 5018–5023.
- [31] Sun, Z. H.; Zhang, J. Q.; Yin, L. C.; Hu, G. J.; Fang, R. P.; Cheng, H.-M.; Li, F. Conductive porous vanadium nitride/graphene composite as chemical anchor of polysulfides for lithium-sulfur batteries. *Nat. Commun.* 2017, *8*, 14627.
- [32] Strubel, P.; Thieme, S.; Biemelt, T.; Helmer, A.; Oschatz, M.; Brückner, J.; Althues, H.; Kaskel, S. ZnO hard templating for synthesis of hierarchical porous carbons with tailored porosity and high performance in lithiumsulfur battery. *Adv. Funct. Mater.* **2015**, *25*, 287–297.
- [33] Zhou, G. M.; Paek, E.; Hwang, G. S.; Manthiram, A. Long-life Li/polysulphide batteries with high sulphur loading enabled by lightweight three-dimensional nitrogen/sulphur-codoped graphene sponge. *Nat. Commun.* 2015, *6*, 7760.
- [34] Ma, Z. L.; Tao, L.; Liu, D. D.; Li, Z.; Zhang, Y. Q.; Liu, Z. J.; Liu, H. W.; Chen, R.; Huo, J.; Wang, S. Y. Ultrafine nano-sulfur particles anchored on *in situ* exfoliated graphene for lithium–sulfur batteries. *J. Mater. Chem. A* 2017, *5*, 9412–9417.

- [35] Tan, Y. B.; Zheng, Z. H.; Huang, S. T.; Wang, Y. Z.; Cui, Z. H.; Liu, J. J.; Guo, X. X. Immobilization of sulfur by constructing three-dimensional nitrogen rich carbons for long life lithium–sulfur batteries. *J. Mater. Chem. A* 2017, *5*, 8360–8366.
- [36] Yang, X.; Zhang, L.; Zhang, F.; Huang, Y.; Chen, Y. S. Sulfur-infiltrated graphene-based layered porous carbon cathodes for high-performance lithium-sulfur batteries. ACS Nano 2014, 8, 5208–5215.
- [37] Zhao, M. Q.; Liu, X. F.; Zhang, Q.; Tian, G. L.; Huang, J. Q.; Zhu, W. C.; Wei, F. Graphene/single-walled carbon nanotube hybrids: One-step catalytic growth and applications for high-rate Li-S batteries. ACS Nano 2012, 6, 10759–10769.
- [38] Zheng, Z. M.; Guo, H. C.; Pei, F.; Zhang, X.; Chen, X. Y.; Fang, X. L.; Wang, T. H.; Zheng, N. F. High sulfur loading in hierarchical porous carbon rods constructed by vertically oriented porous graphene-like nanosheets for Li-S batteries. *Adv. Funct. Mater.* **2016**, *26*, 8952–8959.
- [39] Wang, Q.; Wang, Z. B.; Li, C.; Gu, D. M. High sulfur content microporous carbon coated sulfur composites synthesized via *in situ* oxidation of metal sulfide for high-performance Li/S batteries. *J. Mater. Chem. A* 2017, *5*, 6052–6059.