Double-Shelled NiO-NiCo$_2$O$_4$ Heterostructure@Carbon Hollow Nanocages as an Efficient Sulfur Host for Advanced Lithium–Sulfur Batteries

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Double-shelled NiO-NiCo$_2$O$_4$ heterostructure@carbon hollow nanocages as efficient sulfur hosts are synthesized to overcome the barriers of lithium–sulfur (Li–S) batteries simultaneously. The double-shelled nanocages can prevent the diffusion of lithium polysulfides (LiPSs) effectively. NiO-NiCo$_2$O$_4$ heterostructure is able to promote polysulfide conversion reactions. Furthermore, the thin carbon layer outside can improve the electrical conductivity during cycling. Besides, such unique double-shelled hollow nanocage architecture can also accommodate the volumetric effect of sulfur upon cycling. As a result, the prepared S/NiO-NiCo$_2$O$_4$@carbon (C) electrode exhibits good rate capacities and stable cycling life up to 500 cycles at 0.5 C with a very low capacity decay rate of only ≈0.059% per cycle.

1. Introduction

Li-S batteries, as a promising candidate of next-generation energy storage devices for the ever-growing demand, have received wide attention in terms of their high theoretical energy density and low price and environment benignity of the sulfur cathode.[3] Nevertheless, the commercial application of Li-S batteries is impeded by several obstacles. Primarily, the intrinsic insulating properties of sulfur (5 × 10$^{-30}$ S cm$^{-1}$) and the discharged end products inevitably cause the poor utilization of sulfur.[2] Next, there is a significant volume expansion (~80%) occurring during the discharge process, leading to the instability of electrode structure.[3] Last but the foremost, the unavoidable dissolution of polysulfides in electrolyte as well as the depressed reaction kinetics of the transformation of polysulfides to Li$_2$S$_2$/Li$_2$S will result in the “shuttle effects.”[4]

To tackle aforementioned challenges, intensive efforts have been carried out to design optimized carbon/sulfur cathodes, such as compositing sulfur with mesoporous carbon,[5] carbon nanofibers,[6] carbon nanotubes,[7] carbon spheres,[8] and graphene.[9] Although these carbon-based materials greatly improve the electric conductivity of electrode thereby providing high capacities,[10] the weak interaction between nonpolar carbon and polar polysulfides is not sufficient to limit the dissolution of LiPSs. To further boost the polysulfides adsorption capability and promote the redox reaction kinetics, various polar sulfur host, including metal, metal oxides, metal sulfides, and perovskite[11–14] are engineered as ideal candidates to not only possess good bonds between polar material and LiPSs, but also accelerate the conversion of LiPSs to solid Li$_2$S$_2$/Li$_2$S, giving rise to a good cycling stability.

Heterostructures constructed from coupling nanocrystals with different bandgaps have attracted extensive attention and widely used in photocatalysis, sensor, and energy storage.[15] Benefiting from the internal electric field at heterointerfaces, heterostructures can facilitate charge transport and enhance the surface reaction kinetics.[16] Inspired by the unique advantages of heterostructures, we propose and construct a double-shelled NiO-NiCo$_2$O$_4$ heterostructure@C hollow nanocages as an efficient sulfur host for advanced Li-S batteries. NiO has much better electrical conductivity and higher redox activity into nickel oxides can promote electron transfer for LiPSs conversion reactions. Introducing NiCo$_2$O$_4$ that possesses much better electrical conductivity and higher redox activity into nickel oxides can promote electron transfer for LiPSs conversion reactions.[18]

The synthetic approach to the S/NiO-NiCo$_2$O$_4$@C composite is schematically shown in Figure 1a (for experimental details, see the Supporting Information). Uniform Ni-Co prussian blue analogue (PBA) nanocube precursor was first prepared by a facile coprecipitation strategy. Afterward, double-shelled NiO-NiCo$_2$O$_4$ heterostructure@C nanocages were obtained through a facile calcination treatment coupled with a simple hydrothermal carbon-coating process. After a melt-diffusion process,
sulfur was successfully introduced into the NiO-NiCo$_2$O$_4$ heterostructure@C hollow nanocages. This double-shelled NiO-NiCo$_2$O$_4$@C hollow nanocage as the sulfur host exhibits multifold features (Figure 1b): (i) The hollow structure not only can provide sufficient space for loading sulfur but also mitigate volumetric variation of sulfur during cycling; (ii) NiO-NiCo$_2$O$_4$ heterostructure nanocages effectively prevent polysulfide diffusion and accelerate electron transfer for polysulfide conversion reactions, thus remitting the shuttling effect of LiPSs; and (iii) the outside carbon layer improves the electrical conductivity for electron transport during cycling. With this desired design, the S/NiO-NiCo$_2$O$_4$@C composite manifests considerable specific capacity and remarkable cycle stability.

2. Results and Discussion

The Ni-Co PBA nanocube precursors are highly uniform with a rather smooth surface and an average size of 400 nm, as confirmed by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) (see Figure S1a–c, Supporting Information). X-ray diffraction (XRD) pattern (see Figure S1d, Supporting Information) of the precursor indicates the typical diffraction peaks of Ni$_3$[Co(CN)$_6$]$_2$ (JCPDS Card No. 89-3738). After annealed in air at 450 °C, these Ni-Co PBA nanocubes can be converted into Ni-Co mixed oxide nanocubes with rough surface, which is composed of NiO (JPCDS Card No. 47-1049) and NiCo$_2$O$_4$ (JPCDS Card No. 20-0781) (see Figures S2 and S3, Supporting Information). The increase of heating treatment is able to obtain high-crystallinity hollow NiO-NiCo$_2$O$_4$ heterostructure nanocages (see Figure S4, Supporting Information). As depicted in Figure 2a,b, the heterostructure nanocages constructed from metal oxide building blocks possess rather rough surface. The size of nanocages is slightly reduced to ≈300 nm. Besides, the hollow structure of the NiO-NiCo$_2$O$_4$ nanocage is also observed (Figure 2c). Energy-dispersive spectroscopy (EDS) mapping (see Figure S5, Supporting Information) indicates the homogenous distribution of Ni, Co, and O in the NiO-NiCo$_2$O$_4$ heterostructure. From the high-magnification TEM image (Figure 2d,e), the NiO-NiCo$_2$O$_4$ nanocage with a wall thickness of 30 nm is assembled by nanoparticles with a particle size of 10–20 nm. The high-resolution TEM (HRTEM) image in Figure 2f shows the lattice fringes of the NiO-NiCo$_2$O$_4$ heterostructure with d-spacing of 0.47 and 0.20 nm, corresponding to the (111) and (200) crystal planes of NiCo$_2$O$_4$ and NiO, respectively. Moreover, the interface between NiCo$_2$O$_4$ and NiO can be observed clearly, which can act as the highly active sites in both adsorption and electron transfer. Figure S6 (Supporting Information) shows the fast Fourier transforms (FFT) of the NiO-NiCo$_2$O$_4$ heterostructure taken from different domains of HRTEM image, further confirming the evidence of the physical phases of the NiO (Figure S6b, Supporting Information), NiCo$_2$O$_4$ (Figure S6c, Supporting Information), and NiO+NiCo$_2$O$_4$ (Figure S6d, Supporting Information), respectively.

Subsequently, a uniform carbon layer derived from glucose is coated onto the surface of NiO-NiCo$_2$O$_4$ heterostructure nanocages (Figure 2g,h). Meanwhile, the hollow feature of the nanocages can still be well-maintained (Figure 2i–k). Thermogravimetric analysis (TGA) indicates the content of carbon in the NiO-NiCo$_2$O$_4$@C composite is ≈20 wt% (see Figure S8, Supporting Information). From the magnified TEM image (Figure 2l), it can be found that the thickness of the carbon shell is ≈10 nm, indicating the successful synthesis of double-shelled NiO-NiCo$_2$O$_4$@C hollow nanocages. There is no characteristic peak of carbon due to its much lower signal when compared to metal oxide. Raman spectra of the NiO-NiCo$_2$O$_4$@C show two broad peaks around 1369 and 1574 cm$^{-1}$ (Figure S10, Supporting Information) due to the vibration of carbon atoms with dangling bonds of disordered graphite and the vibration in all sp$^2$ bonded carbon atoms in a 2D hexagonal lattice, respectively.[19] Besides, the X-ray photoelectron spectroscopy (XPS)
The morphology of the materials is well maintained after loading sulfur. Moreover, there is no extra sulfur outside, demonstrating the successful diffusion of sulfur into the nanocages (Figure 3a,b). From the XRD pattern (Figure 3c), the peaks between 20° and 25° are due to the crystalline sulfur in the S/NiO-NiCo2O4@C composite. TEM observations (Figure 3d,e) clearly show that the contrast of inner void spaces of the S/NiO-NiCo2O4@C becomes much darker than that of the NiO-NiCo2O4 heterostructure@C host, which reveals the successful accommodation of sulfur into the hollow host. The mass proportion of sulfur in the S/NiO-NiCo2O4@C composite was determined by TGA as 73 wt% (see Figure 3f). EDS elemental mapping and linear scan of the S/NiO-NiCo2O4@C composite show the homogeneous encapsulation of sulfur within the host (Figure 3g,h), proving that sulfur has been infused into the inner part of the NiO-NiCo2O4 heterostructure@C host.

The electrochemical properties of the S/NiO-NiCo2O4@C composite are evaluated as the cathode for Li-S batteries. Figure 4a shows the cyclic voltammetric (CV) curves of the S/NiO-NiCo2O4@C electrode for the first three cycles. During
the cathodic scanning, two stabilized reduction peaks located at 2.27 and 2.04 V correspond to the transformation of sulfur (S₈) to long-chain lithium polysulfides and the conversion of long-chain lithium polysulfides to short-chain lithium polysulfides (Li₂Sₓ/Li₂S). Figure 4b shows the galvanostatic charge–discharge voltage profiles at various current densities from 0.2 to 2 C. Two typical discharge plateaus and one charge plateau are obvious even at 2 C, indicating a low polarization. Rate capability of the S/NiO-NiCo₂O₄@C cathode is shown in Figure 4c. The cathode delivers discharge capacities of 1063.2, 920, 821.7, and 697.9 mAh g⁻¹ at the current densities of 0.2, 0.5, 1, and 2 C, respectively. When the current density recovered to 0.2 C, the capacity can be almost maintained, indicating the excellent stability of the S/NiO-NiCo₂O₄@C composite. It is worth mentioning that the NiO-NiCo₂O₄@C nanocages cannot contribute to the capacity under the same conditions, as displayed in Figure S12 (Supporting Information).

The long-term cycling performance (Figure 4d) was evaluated at 0.5 C to confirm the stability of the S/NiO-NiCo₂O₄@C cathode. After 500 cycles, a high capacity of 716.9 mAh g⁻¹ with high coulombic efficiency of over 98% can still be maintained. Meanwhile, a low capacity fading of 0.059% per cycle was obtained. This performance is superior to that of many other metal oxides electrodes (Figure S22, Supporting Information). As a contrast, the S/carbon black (S/CB) cathode displays a comparatively low initial capacity of 690 mAh g⁻¹ and suffers from rapid capacity decay in the following cycles.

Electrochemical impedance spectra (EIS) analysis of the S/NiO-NiCo₂O₄@C electrode in Figure S13 (Supporting Information) shows that the charge-transfer resistance decreases clearly after cycling, which can be attributed to the activation process. Besides, the low charge-transfer resistances indicate that the irreversible deposition of insoluble reduction products on the surface of the S/NiO-NiCo₂O₄@C electrode is very limited. The electric conductivity of NiO-NiCo₂O₄@C is about 0.1 S cm⁻¹ using four-point probe operation.

In order to further show the superiority of the heterostructure, we also prepared the NiO@C and NiCo₂O₄@C nanocage...
hosts and studied their electrochemical performance. As shown in Figures S14 and S15 (Supporting Information), both the NiO@C and NiCo2O4@C nanocages show an average size of 300 nm, which are similar to that of the NiO-NiCo2O4@C nanocages. XRD patterns of the samples show the characteristic diffraction peaks of NiO and NiCo2O4. The contents of sulfur in the S/NiO@C and S/NiCo2O4@C composites are ≈ 72 and 73 wt%, respectively. Both the S/NiO@C and S/NiCo2O4@C composites deliver lower capacities at 0.2, 0.5, 1, and 2 C when compared to the S/NiO-NiCo2O4@C composite (Figure S16, Supporting Information). Moreover, they also suffer from faster capacity decay. These results indicate the unique advantages of heterostructure we prepared. In addition, the carbonization process for the prepared samples is able to improve the electrochemical performance of the electrodes. However, high heating treatment can reduce the samples to from some Ni particles and destroy the morphology of hollow structure, which will greatly decrease the electrochemical performance of the electrodes (Figures S17–S19, Supporting Information). To further verify the NiO-NiCo2O4 heterostructure can effectively restrict the diffusion of LiPSs from the electrode, lithium metal foils disassembled from different coin cells were compared by FESEM and EDS analysis, as displayed in Figure 4e and Figure S20 (Supporting Information). The lithium foil from the S/NiO-NiCo2O4@C cell almost maintains its original morphology, and low-intensity signals of sulfur can be observed from elemental mapping and EDS spectrum, suggesting the excellent absorption ability of the NiO-NiCo2O4 for LiPSs. For the S/CB cell, lithium metal foil shows a looser and rougher surface, indicating a serious shuttle of LiPSs in the cell. In addition, the shape and structure of the S/NiO-NiCo2O4@C can be well retained after 500 cycles (Figure 4f,g). Meanwhile, the separator from the S/NiO-NiCo2O4@C cell shows less color than that from the S/CB cell, further confirming that the NiO-NiCo2O4 heterostructure effectively restricts LiPSs dissolution upon cycling (Figure 4h).

Polysulfide adsorption measurement, UV–vis absorption test, and XPS measurement were performed to further verify the absorption ability of NiO-NiCo2O4. As elucidated in Figure 5a, the color of the LiPSs solution is basically unchanged after the addition of CB. In contrast, the LiPSs solution changes from brown to colorless after adding NiO-NiCo2O4. Figure 5b shows the concentration change of Li2S4 after the addition of CB and NiO-NiCo2O4, the peak at 420 nm is linked to S42− species.21 The absorbance intensity of Li2S4 solution with NiO-NiCo2O4 is much weaker than that of Li2S4 solution with CB. These findings indicate the strong interaction between LiPSs and NiO-NiCo2O4. Figure 5c displays the Ni 2p3/2 XPS spectra comparison of the initial and cycled NiO-NiCo2O4. The Ni 2p3/2 XPS spectrum of the initial NiO-NiCo2O4 exhibits a spin–orbit doublet at 855.6 and 853.7 eV, corresponding to Ni3+ and Ni2+ ions, respectively. After cycling, the peaks of Ni3+ and Ni2+ shift to
856.2 and 854.3 eV, respectively. Figure 5d shows the Co 2p 3/2 spectrum in comparison of the initial and cycled NiO-NiCo 2O 4. Before cycling, the peaks of Co 2p 3/2 spectrum locate at 781 and 779 eV.[22] After cycling, the peaks of Co 2p 3/2 spectrum shift to 781.4 and 779.5 eV, respectively. The results are in good agreement with the others.[23] The peak position variation of Ni 2p 3/2 and Co 2p 3/2 spectrums can be attributed to the electron transfer between Li2Sx and Ni/Co atoms,[13c,24] manifesting the strong chemical interaction between the NiO-NiCo 2O 4 and LiPSs.

A combination of CV and galvanostatic discharge–charge tests was carried out to investigate the catalytic effect of the NiO-NiCo 2O 4 heterostructure on LiPSs redox reactions. As shown in Figure 5e and Figure S21a (Supporting Information), two deformed and widened cathodic peaks of pure S electrode locate at 2.18 and 1.91 V and the anodic peak at 2.56 V. For the NiO-NiCo 2O 4+S electrode, two sharp cathodic peaks at 2.29 and 2.0 V and the anodic peak at 2.39 V can be observed, indicating that NiO-NiCo 2O 4 can significantly suppress the electrochemical polarization. The analysis of the onset potentials provides further evidence that the NiO-NiCo 2O 4 heterostructure accelerates the redox processes (Figure S21b, Supporting Information). Compared with pure S electrode, the NiO-NiCo 2O 4+S electrode shows higher onset potentials of cathodic peaks (2.4 and 2.1 V) and a lower anodic peak (2.2 V). Figure 5f shows discharge/charge voltage profiles of pure S and the NiO-NiCo 2O 4+S electrode at 0.1 C. The NiO-NiCo 2O 4+S electrode shows a discharge capacity of 950.4 mAh g−1, which is much larger than that of the pure S electrode. Furthermore, when compared to pure S electrode the NiO-NiCo 2O 4+S electrode possesses a relatively lower polarization value of 179 mV. Both the improved discharge capacity and reductive polarization show that the
NiO-NiCo_{2}O_{4} heterostructure is able to boost the electrochemical reaction kinetics during cycling.

3. Conclusion

In summary, we propose and design an efficient double-shelled sulfur host in which hollow NiO-NiCo_{2}O_{4} heterostructure nanocages are coated by a thin carbon layer. The NiO-NiCo_{2}O_{4} heterostructure can efficiently confine LiPSs due to the polar chemisorptive capability, and promote electron transfer for polysulfide transform into Li_{2}S_{2}/Li_{2}S. This unique structure can maximize the sulfur loading and provide enough space for accommodating the volumetric effect of sulfur upon cycling. Benefiting from the structural and compositional superiorities, the S/NiO-NiCo_{2}O_{4}@C composite cathode delivers a high specific capacity and a low capacity fading of 0.059% per cycle over 500 cycles. We believe that our present work would offer effective ideas in fabricating various electrode materials with excellent electrochemical properties for Li-S batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

double-shelled hollow nanocages, heterostructures, lithium–sulfur batteries, NiO-NiCo_{2}O_{4}, reaction kinetics

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