Unique Cobalt Sulfide/Reduced Graphene Oxide Composite as an Anode for Sodium-Ion Batteries with Superior Rate Capability and Long Cycling Stability

Shengjie Peng, * Xiaopeng Han, Linlin Li, Zhiqiang Zhu, Fangyi Cheng, Madhavi Srinivansan, Stefan Adams, and Seeram Ramakrishna *

**Exploitation of high-performance anode materials is essential but challenging to the development of sodium-ion batteries (SIBs). Among all proposed anode materials for SIBs, sulfides have been proved promising candidates due to their unique chemical and physical properties. In this work, a facile solvothermal method to in situ decorate cobalt sulfide (CoS) nanoplates on reduced graphene oxide (rGO) to build CoS@rGO composite is described. When evaluated as anode for SIBs, an impressive high specific capacity (540 mAh g\(^{-1}\) at 1 A g\(^{-1}\)), excellent rate capability (636 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) and 306 mAh g\(^{-1}\) at 10 A g\(^{-1}\)), and extraordinarily cycle stability (420 mAh g\(^{-1}\) at 1 A g\(^{-1}\) after 1000 cycles) have been demonstrated by CoS@rGO composite for sodium storage. The synergetic effect between the CoS nanoplates and rGO matrix contributes to the enhanced electrochemical performance of the hybrid composite. The results provide a facile approach to fabricate promising anode materials for high-performance SIBs.**

1. Introduction

As an alternative energy storage technology to the predominantly employed lithium-ion batteries (LIBs), sodium-ion batteries (SIBs) have revitalized increasing scientific attention for large-scale applications, mainly because of the low cost, large resource availability, and similar chemistry of sodium with lithium.\(^\text{[1–3]}\) However, the main bottleneck to the commercialization of SIBs is the limited choice of anode materials. It is well known that Na ions are about 55% larger in radius compared with Li ions, which significantly hinders the utilization...
of well-developed electrode materials in LIBs owing to the insufficient interlayer spacing. Therefore, it is difficult to find suitable materials that can accommodate Na ions and allow reversible ion insertion/deinsertion. Up to now, various alternative materials, including carbon, layered metal oxides, alloy-based materials and metal chalcogenides, have been explored as potential anodes for SIBs. Although some encouraging progress have been made, developing appropriate electrode materials with high capacity and good reversibility is less successful and still requires further research.

Recently, metal chalcogenides have been intensively studied as anode materials for SIBs due to their high capacities. In particular, it was found that layered sulfides (MoS₂ and SnS₂) and their composites with reduced graphene oxide (rGO) could exhibit high electrochemical properties, because of the unique layered structures in favor of the initial ion intercalation/de-intercalation, and the followed conversion or intercalation chemistry enables high theoretical capacity. More recently, FeS₂ and FeSe₂ have also been synthesized and demonstrated superior electrochemical performance in SIBs. However, as the same first-row transition metal dichalcogenides, cobalt sulfides have been rarely investigated in SIBs, while intense work only has been focused on catalysis, supercapacitors, lithium-ion batteries, etc. owing to their unique physical, chemical, and electronic properties. Nevertheless, it is known that cobalt sulfides possess similar electronic conductivity and thermal stability compared to iron sulfides. As continuation and broadness of our work in anode materials, cobalt sulfides are expected to be promising materials in SIBs. Additionally, with the purpose of expanding and enriching the family of materials suitable as advanced anode for SIBs, numerous efforts should be paid to explore the sodium-storage properties of cobalt sulfides.

Apart from the intrinsic properties, the optimization and design of electrode composition and configuration also plays a crucial role in determining their electrochemical performance. It has been demonstrated that combinations with graphene materials cannot only provide conducting networks but also buffer the large volume changes during charge/discharge processes. Besides, 2D nanostructures with secondly building blocks are highly desirable to provide more active sites for fast electrochemical reactions, as well as shorten the diffusion length of the charge carriers. Also, it is well known that the unique 2D architecture is structurally compatible with graphene. Thus, by integrating the aforementioned design rationales, it is believed that CoS@rGO composite is anticipated to be high-performance anode for SIBs.

Herein, we demonstrate a simple solvothermal method to in situ decorate 2D CoS nanoparticles on rGO nanosheets. The resulting CoS@rGO hybrid architecture offers unique characteristics, which is needed for advanced anode. Benefiting from the novel structure and improved electric conductivity, CoS@rGO hybrid composite exhibits high capacity (540 mAh g⁻¹ at 1 A g⁻¹), superior rate capability (636 mAh g⁻¹ at 0.1 A g⁻¹ and 306 mAh g⁻¹ at 10 A g⁻¹), and ultralong cycle life (420 mAh g⁻¹ at 1 A g⁻¹ after 1000 cycles) as anode for SIBs. These results endow CoS@rGO composite as advanced anode for SIBs. Remarkably, a full cell, which is based on CoS@rGO hybrid anode and electrospun Na₃V₂PO₄carbon (NVP@C) cathode, has been assembled and manifests high capacity and outstanding cycle stability, indicating its huge potential as promising anode for SIBs industry.

2. Results and Discussion

CoS@rGO hybrid composite has been prepared by a one-pot solvothermal strategy using Co(CH₃COO)₂ (Co(Ac)₂), thiourea (Tu), and GO as precursors in ethanol medium at 200 °C for 10 h. As shown in the schematic illustration in Figure 1a, in situ directly growth of CoS@rGO composites is induced by the heterogeneous nucleation of CoS on graphene. During the reaction process, GO provides large amounts of defects/functional groups as nucleation sites for in situ growth of CoS on nanosheets. The presence of carboxyl and hydroxyl groups on the GO sheets can make the thiourea grafted on the GO through surface functional groups, as the amino groups in thiourea are activated by the C=S bonds. Moreover, Co²⁺ could incorporate on the GO sheet by electrostatic force. As a consequence, the absorbed Co²⁺ reacts with the gradual release of S²⁻ ions deriving from the decomposition of Tu to form CoS nuclei that are tightly anchored onto graphene sheet with well dispersion. Meanwhile, GO sheets are reduced to rGO sheets with ethanol medium as a mild reductant. Thus, the continuous solvothermal reaction resulted in oriented alignment of CoS nanoparticles grown on rGO sheets. This unique structure is expected to provide high accessibility to the electrolyte and fast sodium-ion transport pathways.

The phase purity and composition of the CoS@rGO composite were analyzed by X-ray diffraction (XRD), Raman spectra, X-ray photoelectron spectroscopy (XPS), and thermogravimetric (TGA). The XRD pattern of the CoS@rGO composite (Figure 2a) is the same as that of bare CoS, indicating that all of the diffraction peaks can be assigned to the

![Figure 1. Schematic illustration for the synthesis of CoS@rGO.](image-url)
hexagonal CoS (JCPDS card no. 75-605) (Figure S1, Supporting Information). In addition, no characteristic diffraction peak of graphene ($2\theta = 24.5^\circ$) was detected due to the low amount and relatively low diffraction intensity of graphene. Raman spectroscopy is used to confirm the existence of rGO in the as-prepared composite. The Raman spectra of GO, bare CoS, and CoS@rGO are presented in Figure 2b. It can be observed that both of CoS and CoS@rGO exhibit Raman peaks at 473, 517, and 683 cm$^{-1}$, which are assigned to $E_g$, $F_{2g}$, and $A_{1g}$ modes of CoS materials, respectively.$^{[38]}$ In contrast to CoS, CoS@rGO composite presents two characteristic peaks at 1353 and 1584 cm$^{-1}$, corresponding to the D band and the G band, respectively. The high D/G intensity ratio in the CoS@rGO composite indicates the existence of rGO compared to that of GO. XPS analysis in Figure 2c,d was further used to examine chemical states of cobalt and sulfur in the composite. As shown in Figure 2c, the Co 2p signal was quite complex owing to the presence of various species at surface level. After fitting, the Co 2p2/3 spectrum has peaks at 778.3 and 781.6 eV that can be attributed to sulfided Co-S, whereas the peak at 786.5 eV could be assigned to the surface-adsorbed hydroxide species because cobalt ions have a very strong affinity for atmospheric oxygen and rGO.$^{[39-41]}$ The peaks between 791.0 and 810.0 eV are the corresponding Co 2p1/2 signals of their Co 2p3/2 counterparts and the satellite signal.$^{[42]}$ The S 2p peak centered at 1621.5 eV is ascribed to the binding energies of Co–S.$^{[43]}$ Therefore, the Co 2p and S 2p peaks in the XPS spectra are characteristic of cobalt sulfide. The weight loss from 400 $^\circ$C to 600 $^\circ$C in the TGA curves determined that the weight composition of the CoS@rGO nanocomposite was about 19 wt% graphene and 81 wt% CoS (Figure S2, Supporting Information).

The morphology and the phase purity of the CoS@rGO hybrid were further characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-magnified transmission electron microscopy (HRTEM), as shown in Figure 3. Figure 3a,b demonstrate fairly well distribution of CoS nanoplates on both sides of graphene sheets. The thickness and average length in lateral direction of CoS nanoplates are around 10 and 100 nm, respectively (Figure 3b,d). Significantly, it should be noted that only 2D nanostructures can be identified in this hybrid composites, suggesting a nearly complete CoS nanoplates yield. In addition, the lattice spacing in the HRTEM was calculated to be 0.25 nm, matching well with the (101) lattice plane of hexagonal CoS. In contrast, the same synthesis procedure in the absence of GO nanosheets produced bare CoS nanospheres, which are constructed by interconnected nanoplates (Figure S1, Supporting Information). The drastic morphological differences highlight the dispersion function of GO sheets, which favors the growth of plate-like structures and restrains the stacking of CoS nanoplates. The energy-dispersive X-ray spectroscopy (EDS) mapping of the CoS@rGO hybrid reveals that Co, S, C elements were homogeneously distributed over the hybrid nanocomposites. All the results confirm that CoS@rGO hybrid composites with the unique structure can be easily fabricated through the facile in situ solvothermal method.
To evaluate the electrochemical performance of the as-prepared samples, CR2032-type coin cells were fabricated. It is known that electrolyte have important influence to determine the sodium storage performance. The effect of various electrolytes, such as 1.0 m NaCF$_3$SO$_3$ in diethyleneglycol dimethylether (DEGDME), ethylene carbonate and diethyl carbonate (EC/DEC), and propylene carbonate (PC), was firstly investigated in Na half cells. The charge–discharge behavior of CoS@rGO hybrid composites using various electrolytes was measured at a current density of 0.1 A g$^{-1}$ in the voltage range of 0.01–2.9 V versus Na$^+/Na$. As shown in Figure S3 (Supporting Information), it can be clearly seen that a smaller voltage polarization and larger capacity retention can be identified for the CoS@rGO electrode with ether-based electrolyte (DEGDME). Moreover, the cycling performance in Figure S3d also confirms the merits of ether-based electrolyte in our present studies. Specifically, the specific capacity of CoS@rGO using the carbonate-based electrolytes decays rapidly, while CoS@rGO using the ether-based electrolyte presents no obvious capacity fading from the second cycle onwards. These results demonstrate that the selection of electrolyte has prominent effect on the electrochemical properties of CoS@rGO electrode and suitable electrolyte would be beneficial for the enhancement of battery performance. The superior cycling stability of CoS@rGO electrode in ether-based electrolyte suggests that ether-based electrolyte would possibly suppress the reaction between electrolyte and polysulphides, leading to the fast loss of active materials, which was observed before.$^{[24,25,30,44,45]}$ Although the reaction mechanism requires further identification, we propose that the combination of ether-based (DEGDME) electrolyte and CoS@rGO electrode contributes to the enhanced electrochemical properties in the measured system.

In addition to the influence of electrolyte, the potential window also plays a significantly role to achieve excellent cycling stability. Noted that the capacity of CoS@rGO electrode rapidly faded to 148.3 mAh g$^{-1}$ after 500 cycles at 1 A g$^{-1}$ in the voltage range of 0.1–2.9 V (Figure S4, Supporting Information), which might be due to the huge volume change caused by the deep discharge. Besides, considering that the initial irreversible capacity loss mainly derives from the discharge capacity in the voltage range of 0.5–0 V. Hence, it is anticipated that highly reversible electrochemical reaction could be realized by simply restricting the potential window to 0.6 V.$^{[24,25,46,47]}$ To understand the main difference between CoS and CoS@rGO electrodes, the galvanostatic charge–discharge performance for both electrodes was evaluated with the optimized test parameters (at a current density of 1 A g$^{-1}$ within a voltage range of 0.6–2.9 V), as shown in Figure 4a,b. The reaction mechanism of CoS@Na proposed here is consistent with previous report$^{[30]}$ and the CoS crystal recovers after the initial CV cycle (Figure S5, Supporting Information).
It is evident that the discharge/charge voltage profiles of CoS@rGO are almost identical with those of bare CoS electrode, implying that similar working mechanism exists in both cases. Specifically, from the second cycle onwards, both cases possess similar discharge/charge curves with two discharge plateaus in the potential ranges of 1.5–1.1 V and 1.1–0.8 V and two charge plateaus at about 1.6–1.8 and 1.8–2.1 V, demonstrating that introducing of rGO cannot change the electrochemical mechanism of CoS electrode. More significantly, CoS@rGO delivers a high initial discharge/charge capacity of 581/540 mAh g\(^{-1}\) with a coulombic efficiency of 93%, while the value for bare CoS is only 550/492 mAh g\(^{-1}\) with a relatively low coulombic efficiency of 89%. Besides, the overlapping voltage profiles of CoS@rGO electrode demonstrate the good cycle stability during cycling sustaining. Even after 50th cycles, the discharge capacity is still as large as around 447 mAh g\(^{-1}\). However, for the bare CoS electrode, not only is its first discharge capacity lower than the CoS@rGO electrode, there is also rapid capacity fading leading to a discharge capacity of only 310 mAh g\(^{-1}\) after 50th cycles, further confirming the excellent electrochemical reversibility of CoS@rGO electrode. Then, to deep insight into the charge/discharge behavior of the CoS@rGO composite, cyclic voltammetry (CV) analysis was performed at a scan rate of 0.1 mV s\(^{-1}\) from 0.6 to 2.9 V versus Na\(^+\)/Na. As shown in Figure 4c, the first sweeping cycle is different from the others, in accordance with the previously reported results.\[48\] Two main reduction peaks are centered at 0.92 and 0.75 V and two oxidation peaks are located at 1.70 and 1.95 V in the first cycle. Considering the similar working mechanism with LIBs,\[48,49\] they might originate from the initial insertion of sodium and the following displacement reaction to the formation of Na\(_2\)S and Co, respectively. Whereas, in the subsequent cycles, the main cathodic peaks shift toward to the higher potential of 1.3 and 0.93 V, respectively, also in good agreement with the voltage profiles in Figure 4a,b. Additionally,
electrochemical impedance spectra (EIS) was also used to compare the electrochemical properties of CoS@rGO composite and bare CoS electrode. Figure 4d shows the typical Nyquist plots, which consist of a compressed semicircle in the medium frequency region and an inclined line in the low frequency range. As seen, the semicircle is related to the charge-transfer resistance ($R_{ct}$) at the interface of electrode, while the inclined line is associated with Warburg impedance, reflecting the diffusion of Na$^+$ into the bulk of the active materials. Apparently, CoS@rGO possesses a much lower $R_{ct}$ value compared with that of bare CoS electrode, which can be attributed to the conducting effect of rGO.\[50–52\] Moreover, the relatively steeper low-frequency tail of CoS@rGO suggests higher sodium-ion diffusivity, ensuring much easier Na-intercalation kinetics. Therefore, all of these are beneficial for electrode materials, and consequently, enhance the sodium storage properties of CoS@rGO electrode.

To directly illustrate the superiority of CoS@rGO nanostructures, the cycling performance, as a critical indicator for the real use, was investigated. Figure 4e compares the long-term cycling stability of pure CoS and CoS@rGO at a current density of 1 A g$^{-1}$. Impressively, the CoS@rGO nanostructure exhibits an ultrahigh discharge capacity of around 420 mAh g$^{-1}$ even after 1000 cycles corresponding to around 88% of the value in the second cycle. The high coulombic efficiency and energy efficiency further demonstrate the good cyclability of CoS@rGO anode (Figure S6, Supporting Information). However the capacity of the bare CoS drops rapidly to 263 mAh g$^{-1}$ only after 100 cycles, which further proves the remarkable long-term electrochemical stability of CoS@rGO nanostructures. More importantly, it should be noted that the unique structure of CoS@rGO promote the integrity of the electrode. Even after 50 cycles, the unique structure of CoS@rGO composite still can be maintained after 50 cycles (Figure S7, Supporting Information), thereby resulting in improved cycling stability.

As good rate capability of electrode materials could efficiently reduce the charge/discharge time in practical applications, we studied the rate performance of CoS@rGO at various current densities and depicted in Figure 5a,b. According to the detailed discharge/charge profiles, only small increase in the charge plateau can be observed from 0.1 to 5 A g$^{-1}$, illustrating rapid reaction kinetics and low polarization of CoS@rGO. Moreover, the CoS@rGO electrodes are able to deliver stable discharge capacity of 636, 549, 455, 420, and 359 mAh g$^{-1}$ at current densities of 0.1, 0.5, 1, 2, and 5 A g$^{-1}$ (Figure 5b). Even a 100-fold increase in current density is implemented, a discharge capacity of around 306 mAh g$^{-1}$ still can be retained at 10 A g$^{-1}$, confirming the superior rate capability for CoS@rGO electrode. When the current density is reduced back to 0.1 A g$^{-1}$ after 60 cycles, CoS@rGO can still regain a reversible capacity of about 630 mAh g$^{-1}$. This means that CoS@rGO electrode could tolerate high-rate cycling without damaging its structural integrity. More significantly, when comprehensively considering the capacity, cycling stability, and applied current density, the obtained CoS@rGO composite shows comparable or even higher electrochemical performance than many other metal sulfide anode materials, which renders CoS@rGO as one of the best anode candidates for SIBs (Figure 5c) (Table S1, Supporting Information).

In order to clarify the reversible sodiation/desodiation process of CoS@rGO electrode, ex situ XRD, Raman spectra, and HRTEM analysis were conducted after ten cycles. Figure 6a gives the XRD patterns of the CoS@rGO electrode
at different charge/discharge states. Parafilm is used to protect the electrode from air, and its characteristic peaks located at 21.5° and 23.9°. Also some peaks belonged to conductive carbon (KS6) and current collector (Cu) can be observed in each pattern of the samples. At discharged state of 1.0 V, the peak of Co can be found at 44.3°, while a very weak signal of CoS still can be observed at about 36°. When fully discharged to 0.6 V, the Co signal significantly increases, and meanwhile a new peak, which is the characteristic peak of Na₂S, appears at 45.8°. Although, no obvious characteristic signal of CoS in the XRD pattern can be identified at fully charged state of 2.9 V, the Raman spectra confirms the existence of CoS (Figure S8, Supporting Information), indicating the excellent reversibility of electrochemical reactions. Besides, these also imply that the final electrochemical reaction products are in low crystallinity or amorphous, and uniformly dispersed in the whole electrode, thereby resulting in the invisible of X-ray signals. When discharged to 1.0 V and charged to 1.8 V, the intermediate Na₂CoS phase could not be detected, implying that the Na₂CoS might have low crystallinity. Moreover, the HRTEM images of the fully discharged and charged CoS@rGO electrodes are shown in Figure 6d,e. As discharged to 0.6 V, the lattice fringe with interplanar spacing of 0.20 nm is in good agreement with the (111) plane of Co, and the d-space distance of 0.23 nm is indexed to the (220) planes of Na₂S. When fully charged, the (101) plane of CoS appears, suggesting that the Na⁺ insertion and extraction reaction is completely reversible. Furthermore, the SAED patterns also prove the reaction processes. When discharged to 0.6 V, the rings in the SAED pattern are indexed to metallic Co and Na₂S (Figure 6b). At fully charged state of 2.9 V, the rings of CoS are observed (Figure 6c). Combining the above analysis, the reaction mechanism of CoS can be proposed as following

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CoS + 2Na^+ + 2e^- \rightarrow Co + Na_2S
\]  

With the aim to realize industry application of the unique CoS@rGO as electrode for SIBs, a full battery was assembled by coupling CoS@rGO and Na₃VPO₄@C nanowires (NVP@C) as anode and cathode, respectively. The structure of the fabricated full battery was demonstrated in Figure 7a. The electrospun NVP@C nanowires, which is prepared using electrospinning technique, showed a superior specific capacity of 105.5 mAh g⁻¹ at 0.5 C and could still retain 97% of its specific capacity after 100 cycles (Figures S9 and S10, Supporting Information). As the NVP possesses a theoretical capacity of 118 mAh g⁻¹, the
active materials of the anode and cathode were balanced with the mass ratio of ≈1:6.0 to optimize the electrochemical performance of the as-prepared full battery. Figure 7b presents the discharge/charge curves of as-prepared full battery for the 1st, 5th, 50th, and 100th cycles at a current density of 0.5 A g⁻¹ over the potential range of 0.5–3.5 V. c) Long-term cycling performance of the sodium-ion full cell at a current density of 0.5 A g⁻¹. The inset is a digital picture for the as-assembled sodium-ion full cell to light a red LED.

Figure 7. Electrochemical test of CoS@rGO//NVP@C sodium-ion full cell. a) Schematic structure of the sodium-ion full cell. b) Galvanostatic charge/discharge curves for the 1st, 5th, 50th, and 100th cycles at a current density of 0.5 A g⁻¹ over the potential range of 0.5–3.5 V. c) Long-term cycling performance of the sodium-ion full cell at a current density of 0.5 A g⁻¹. The inset is a digital picture for the as-assembled sodium-ion full cell to light a red LED.

3. Conclusions

In summary, the novel CoS@rGO hybrid composites with precisely controlled unique configurations have been successfully developed by an efficient in situ solvothermal technique. The well-defined CoS nanoplates with a thickness of around 10 nm are uniformly grown on rGO frames with strong adhesion, which provides structurally stable host for Na-ion intercalation and deintercalation. Surprisingly, as anode for SIBs, an impressive high specific capacity (540 mAh g⁻¹ at 1 A g⁻¹), excellent rate capability (636 mAh g⁻¹ at 0.1 A g⁻¹ and 306 mAh g⁻¹ at 10 A g⁻¹), and extraordinarily cycle stability (420 mAh g⁻¹ at 1 A g⁻¹ after 1000 cycles) have been demonstrated by CoS@rGO for sodium storage. The 2D conductive framework of rGO, ultrathin feature and small lateral size of CoS plate-like structure are favorable for the fast electron/ion transport. Third, the unique structure possesses many free spaces, which could efficiently absorb the stress that is created by the large volume variations during repetitive cycling, and meanwhile, easily get access to the electrolyte, thus benefiting the rapid diffusion of Na⁺ across the interface between electrode and electrolyte. Last but not least, the optimization of electrolyte (ether-based electrolyte) and rationally controlling the terminal voltage guarantee the exceptional electrochemical reversibility and structure integrity of the whole electrode. Compared to previous reports on the similar materials, the combination of graphene sheets supported uniform distribution small lateral size of CoS plate-like structure and the stable ether-based electrolyte toward sulfide anionic group contributes to the superior electrochemical properties for Na⁺ storage.
4. Experimental Section

Synthesis of CoS@rGO Composite: Graphene oxide (GO) was prepared from natural graphite by a modified Hummers method. In a typical synthesis of cobalt sulfide/reduced graphite oxide (CoS@rGO), 30 mg of GO was put into 40 mL of H$_2$O and ultrasonicated at room temperature for 2 h to form a stable GO dispersion. Then, 2 mmol of Co(CH$_3$COO)$_2$·4H$_2$O and 2 mmol of thiourea (Tu) were sequentially added into the above GO dispersion under ultrasonication for another 30 min. The solution was transferred to a 50 mL Teflon-lined autoclave and heated at 200 °C for 10 h. After being cooled to room temperature, the precipitate was collected by centrifugation, then, washed with deionized water and ethanol several times, and finally dried at 60 °C. When keeping other experimental conditions unchanged, bare CoS spheres can be obtained in the absence of rGO.

Materials Characterization: The phase purity and the structure information of the as-prepared products were identified by X-ray diffraction (XRD) with Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) at a scan rate of 0.5° min$^{-1}$. The morphologies of the products were characterized by field-emission scanning electron microscopy (FESEM, JEOL, JSM-7600F) at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) were performed on a JEOL 2100F microscope with an accelerating voltage of 200 kV. Raman spectra were obtained by a WITec CRM200 confocal Raman microscopy system at a laser wavelength of 488 nm and a spot size of 0.5 mm. X-ray photoelectron spectroscopy (XPS) was conducted by KratosAxis Ultra DLD electron spectrometer at an accelerating voltage of 13 kV and a pass energy of 35.75 eV (PHI, PHI5300 system). Thermogravimetric analysis (TGA) was recorded on a TA Instruments SDT Q500 at a ramping rate of 10 °C min$^{-1}$.

Electrochemical Measurements: The electrodes were prepared by mixing the active material, conductive carbon (K56), and sodium carboxymethylcellulose (Na-CMC) binder with a weight ratio of 8:1:1. The viscous slurry was coated on copper foil with an active material loading of 1.0 mg cm$^{-2}$ and dried at 80 °C for 12 h in vacuum. Metallic sodium was used as the anode and reference electrode, glass fiber was used as the separator, and 1 M Na$_2$SO$_4$ in diethylene glycol dimethylether (DEGDME) was used as the electrolyte. As comparison, 1 M Na$_2$SO$_4$ in ethylene carbonate and diethyl carbonate (EC/DEC) and 1 M Na$_2$CO$_3$ in propylene carbonate (PC) electrolytes were used to evaluate the merits of ether-based electrolyte. The CR2032 coin-type cells were assembled in an Ar-filled glove box (Mikrouna Universal 2440/750, USA). The Galvanostatic discharge/charge cycling was evaluated on Neware multichannel battery tester at different current density. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on Solartron 1470E electrochemical workstation. For the sodium-ion full cell, CoS@rGO and electrospun N$_2$.V$_2$O$_5$@carbon (NVP@C) were used as anode and cathode, respectively. In a typical synthesis of NVP@C, 1 g of polyvinylpyrrolidone (PVP) was dissolved in 7 mL ethanol and 3 mL distilled water with stirring to obtain a homogeneous solution followed by addition of 3 mmol of Na$_2$HPO$_4$·2H$_2$O, 2 mmol of NH$_4$VO$_3$, and 5 mmol citric acid. After stirring at room temperature for 12 h, the precursor solution was then electrospun under an applied voltage of 20 kV with a flow rate of 0.5 mL h$^{-1}$. Finally, the obtained as-spun fibers were calcinated at 800 °C for 5 h under Ar atmosphere. The mass ratio of cathode and anode was controlled to be about ~6.0:1 in the full cell (mass loading of anode was about 1.0 mg cm$^{-2}$).

Supporting Information

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

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