A facile sol–gel route to prepare functional graphene nanosheets anchored with homogeneous cobalt sulfide nanoparticles as superb sodium-ion anodes†

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Hybrid metal sulfides with a graphene matrix is an efficient design to buffer the volume expansion and fragmentation of vulnerable metal sulfides. However, the preparation of graphene oxide is commonly the first step to obtain metal sulfide/graphene composites. In this work, we integrated the preparation of functional graphene nanosheets (FGNs) and the growth of electrochemically active cobalt sulfide (Co1–xS) nanoparticles into the same synthesis procedure by a facile sol–gel method to prepare Co1–xS/FGN nanocomposites. The FGNs not only function as a powerful support for the loading of electrochemically active Co1–xS nanoparticles, which can effectively prevent the re-stacking of the FGNs in turn, but also furnish additional electrochemically active sites for sodium ion storage. Consequently, the Co1–xS/FGN composites delivered a high reversible capacity of 466 mA h g−1 as sodium-ion battery (SIB) anodes, exhibiting a good rate capability with 211 mA h g−1 capacity retained at a large current density of 10 A g−1 and a noticeably improved cycle performance.

With the rapid development of electric vehicles, smart grids, and other large-scale energy storage devices,1–3 sodium-ion batteries (SIBs) gradually show more competitive advantages, such as low cost and abundance, for next-generation batteries compared to lithium-ion batteries (LIBs).4 However, finding a suitable anode material to promote and commercialize SIBs is still considered to be one of the major challenges because the large size of Na+ ions precludes their intercalation into graphite, which is generally utilized as the anode material for LIBs.4 Among various anode material candidates, transition metal sulfides, such as MoS2,5 SnS6 FeS2,7 and CoSx, are widely investigated because of their high theoretical capacities and abundant resources.8–10 In particular, cobalt sulfides (CoS, Co9S8, Co1–xS, etc.) shed light upon the highly promising applications.11,12 Nevertheless, the poor cycle performance and rate capability of cobalt sulfides, resulting from large volume change and electrode pulverization, have limited their practical application in SIBs.13 For example, the specific capacity of bare CoS nanoparticles is reported up to 601 mA h g−1 in the first cycle, which drops rapidly to 68 mA h g−1 after only 40 cycles when tested as the SIB anode.14 To circumvent these critical issues, nanostructured cobalt sulfides hybridized with carbon materials have been studied. For example, sandwich-like CoS/reduced graphene oxide (rGO) composites reported by Zhou et al. can maintain a discharge capacity of 230 mA h g−1 after 100 discharge/charge cycles.14 Undoubtedly, carbonaceous materials are proved to be efficient supports for the loading of metal sulfides because they can buffer the volume change and suppress interfacial reactions due to their good flexibility and chemical stability.15,16 However, the reported preparation procedures of cobalt sulfide/graphene (or reduced graphene oxide) composites are commonly tedious and cost-inefficient, involving the first preparation of graphene oxide. And, the separated syntheses of cobalt sulfide and graphene result in complicated procedures and high cost. Moreover, the composites usually deliver poor performances due to the deficient contact of heterogeneous interfaces and long transport distance of thick graphene sheets due to their restacking and agglomeration nature.

In this work, nanocomposites with high-capacity cobalt sulphide (Co1–xS) in situ grown in functional graphene nanosheets (Co1–xS/FGNs) were rationally synthesized by a newly developed sol–gel method. Different from previous studies, the growth of inorganic nanoparticles and formation of FGNs were integrated into the same synthesis procedure and thus these two components coupled with each other, significantly simplifying the synthesis of the graphene-involved composites. In the nanocomposites, the heteroatom-enhanced FGNs not only function as good buffer layers to protect Co1–xS from volume
expansion and electrode pulverization, but also contribute to large Na ion storage capability due to the enhanced electrochemically active sites originating from the heteroatoms.\textsuperscript{17} Consequently, the Co\textsubscript{1−x}S/FGN nanocomposites exhibited a large specific capacity, good cycle performance, and excellent rate capability, opening a new direction towards high-performance and low-cost anode materials for SIBs.

As illustrated in Scheme 1, a green and facile sol−gel method with two steps of thermal treatments was introduced. Different from the traditional methods for preparing metal sulfide/graphene hybrid materials, in this work, a sol−gel procedure was adopted with urea as the soft template and N source, and citric acid as the carbon source. It is well known that urea can decompose and transform into two-dimensional (2D) layered graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) during heat treatment, which could act as a self-sacrificing template for the growth of 2D graphene frameworks.\textsuperscript{18} In the meantime, Co\textsuperscript{2+} ions are homogenously dispersed in the organic precursor during the premier sol−gel stage, and turn into Co nanoparticles during the first step of heat treatment, accompanied by the formation of nitrogen-doped graphene. After the second step of heat treatment with sulfur powder, the Co nanoparticles in situ transform into Co\textsubscript{1−x}S nanoparticles on the 2D FGNs doped with abundant heteroatoms (N, O, and S), and the final Co\textsubscript{1−x}S/FGN composites can be obtained. This synthesis procedure is also applicable for preparing other transition metal sulfide (oxide)−FGN composites, and can be easily amplified for large-scale production.

X-ray diffraction (XRD) patterns of the intermediate Co/FGNs and final product Co\textsubscript{1−x}S/FGN composites are displayed in Fig. 1a. For both samples, a small hump at about 26° can be observed, which can be attributed to the (002) reflection of graphitic carbon. The weak (002) peak suggests that the hetero-interface of Co\textsubscript{1−x}S and graphene is effective in suppressing graphene restacking. Consequently, a few layers of graphene can be obtained for the final composites. Except for the graphene diffraction peak, all other diffraction peaks of the intermediate product can be assigned to metallic Co (JCPDS card no. 15-0806) while all other diffraction peaks of the final product can be ascribed to Co\textsubscript{1−x}S (JCPDS card no. 42-0826), implying the successful conversion from Co to Co\textsubscript{1−x}S. Co\textsubscript{1−x}S shares the same structure with stoichiometric CoS crystallites (Fig. S1†), which is a space group of P\textsubscript{6}3/mmc of a hexagonal phase with a NiAs-type structure.

The field emission scanning electron microscopy (FESEM) image in Fig. 1b shows that the in situ grown Co nanoparticles are homogeneously distributed and embedded in the FGNs, and thus the further Co\textsubscript{1−x}S/FGN composites exhibit a similar morphology and texture (Fig. 1c and d). The ultrathin and transparent morphology of the FGNs indicates that few-layer graphene was obtained. Pristine FGNs were prepared under the same conditions without the addition of a metal source. The pronounced (002) XRD peak of the FGNs in Fig. S2† indicates severe restacking of graphene nanosheets. Also, the FESEM images in Fig. S3† display the poor transparency of the crumpling nanosheets. Pure Co\textsubscript{1−x}S was obtained by a hydrothermal method and the particle size is about 500 nm. The agglomerating substance (Fig. S4†) is assigned to the same Co\textsubscript{1−x}S phase (Fig. S5†). Obviously, the ultrathin Co\textsubscript{1−x}S/FGN morphology is partially attributed to the hetero-interface that can effectively suppress the agglomeration for both the Co\textsubscript{1−x}S nanoparticles and graphene nanosheets. The Raman spectrum of the Co\textsubscript{1−x}S/FGNs in Fig. S6† shows the characteristic D, G, and 2D bands, agreeing with the literature on graphene nanosheets.\textsuperscript{19} The broadened 2D-peak relates to a large number of edge defects in the FGNs.\textsuperscript{20}

The chemical states and electronic structures of different elements were investigated by X-ray photoelectron spectroscopy (XPS). Co, S, C, O, and N elements were identified from the full-survey-scan XPS spectrum (Fig. S7†). Discarding the involved Co\textsubscript{1−x}S component, the content of N and S in the surface of the FGN support is about 16 at% and 3 at%, respectively. As shown in Fig. 1e, the C 1s core-level spectrum can be fitted with three components. The main component at 284.6 eV is attributed to sp\textsuperscript{2}-hybridized carbon,\textsuperscript{21} and two minor components centered at 285.6 and 287.2 eV are ascribed to C−N/C−S and C≡O, respectively,\textsuperscript{21,22} indicating the successful doping of heteroatoms in the graphene framework. The N 1s core-level spectrum shown in Fig. 1f demonstrates peaks with binding energies located at 398.5, 399.5 and 400.8 eV, which can be assigned to the pyridine N, pyrrole N and graphitized N, respectively. Another small peak at about 403.0 eV is ascribed to the oxidized N.\textsuperscript{21,24} The electron rich characteristic of nitrogen alters the electronic properties of the adjacent carbon network, thus inducing an electron donor effect.\textsuperscript{23} Therefore, metal ions like Co\textsuperscript{2+} could pre-occupy the N-doped sites and further in situ grow into nanocrystals.

As shown in Fig. 1g, multiple peaks can be observed in the Co 2p core-level spectrum owing to the various species at the surface. After fitting, the two peaks at around 782.2 eV and 798.2 eV are ascribed to Co 2p\textsubscript{1/2} and Co 2p\textsubscript{3/2}, respectively.\textsuperscript{25} The energy separation between the Co 2p\textsubscript{1/2} and Co 2p\textsubscript{3/2} peaks is 16 eV, which is smaller than that of metallic Co, agreeing well with the literature on cobalt sulfide.\textsuperscript{26} Another two components located at 778.8 and 794.8 eV can be attributed to surface

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**Scheme 1** Schematic diagram of the synthetic procedure of Co\textsubscript{1−x}S/FGN nanocomposites.
absorbed hydroxide species as the cobalt ions have a very strong affinity to oxygen in air.28,29 The O 1s core-level spectrum (Fig. S8†) can be deconvolved into three components with peaks at around 531.3, 532.7 and 534.2 eV, corresponding to the C\(\text{O} / \text{Co}\)–\(\text{O}\), S–O and N–O, respectively.30–32 The S 2p core-level spectrum shown in Fig. 1h reveals three types of S species at the surface. The first two peaks at 162.9 and 161.7 eV can be attributed to S 2p\(\text{1/2}\) and S 2p\(\text{3/2}\) of S\(_2\)/Co\(_2\) in Co\(_1\)/Co\(_x\)S. Another two peaks at 163.8 and 165.0 eV correspond to the S 2p\(\text{1/2}\) and S 2p\(\text{3/2}\) of thiophenic S atoms incorporated into carbon frameworks.21 The last high energy doublet at 169.0 and 170.2 eV can be assigned to the oxidized S, perhaps resulting from the oxidation in air.32,33

A transmission electron microscopy (TEM) image of the Co\(_1\)/Co\(_x\)S/FGN composites is shown in Fig. 2a. The particle size distribution analysis in the insets shows that the Co\(_1\)/Co\(_x\)S nanoparticles are about 25–45 nm in size. Note that these small Co\(_1\)/Co\(_x\)S nanoparticles are well confined in the FGNs. The selected-area electron diffraction (SAED) pattern (inset in Fig. 2a) shows multiple diffraction rings, which are well attributed to the crystal planes of Co\(_1\)/Co\(_x\)S. The high-resolution TEM (HRTEM) images shown in Fig. 2b and c reveal clear lattice fringes with an interplanar spacing of 0.255 nm, which can be indexed to the (101) planes of Co\(_1\)/Co\(_x\)S. A scanning transmission electron microscopy (STEM) image and the corresponding elemental mapping images of C, N, Co, and S are shown in Fig. 2d. It demonstrates the homogeneous distribution of C and N elements. The overlapped distributions of Co and S reveal the fruitful anchoring of Co\(_1\)/Co\(_x\)S nanoparticles on the FGNs. Fig. 2e shows the atomic force microscopy (AFM) image of a single nanosheet, and the corresponding height profiles of the line scan are shown in Fig. 2f. The left average height difference of \(~48.1\) nm is attributed to the anchored Co\(_1\)/Co\(_x\)S nanoparticles, and the right average height difference of \(~3.5\) nm is assigned to the thickness of the FGNs.

Thermogravimetric analysis (TGA) was performed to estimate the Co\(_1\)/Co\(_x\)S content in the composites (Fig. S9†). FGNs lose their total weight by the evaporation of adsorbed water, oxidation of functional groups and burning of carbon backbones. Based on the TGA curve of the Co\(_1\)/Co\(_x\)S/FGN and Co/FGN composites and weight loss, the content of Co\(_1\)/Co\(_x\)S in the Co\(_1\)/Co\(_x\)S/FGN composites is estimated to be about 43 and 46 wt%, respectively.

To investigate the electrochemical performance, galvanostatic discharge/charge measurements were carried out. Fig. 3a shows the charge/discharge curves of the Co\(_1\)/Co\(_x\)S/FGN electrode.
in the 1st, 2nd, and 5th cycles between 0.01 and 3 V (vs. Na+/Na) at a current density of 100 mA g⁻¹. It delivered an initial discharge/charge capacity of 609/499 mA h g⁻¹ with an excellent initial coulombic efficiency (ICE) of 82%, and the reversible capacity is 466 mA h g⁻¹. The high ICE could be ascribed to the rational hybrid design and utilization of polyacrylic acid (PAA) as the binder. A distinct plateau arose at around 0.75 V for the initial discharge process and disappeared in the 2nd cycle, which was probably caused by the electrolyte decomposition and inevitable formation of a solid electrolyte interface (SEI) film. For comparison, the discharge/charge profiles of the 1st cycle, rate and cycle performance are presented. The bare FGN electrode only delivered a low reversible charge capacity of 310 mA h g⁻¹. Therefore, the capacitive contribution of the Co₁₋ₓS (≈45 wt%) in the hybrid composites is estimated to be around 295 mA h g⁻¹, with an assumed equivalent capacity of 656 mA h g⁻¹ for 100% Co₁₋ₓS, which is very close to the theoretical specific capacity of the Co₁₋ₓS component (≈701 mA h g⁻¹). The bare Co₁₋ₓS electrode exhibited a rather large capacity of 566 mA h g⁻¹ (Fig. 3b), while its reversible capacity dropped quickly during increasing the current density from 0.1 to 10 A g⁻¹ and could not maintain the stability when returns back to 0.1 A g⁻¹ (Fig. 3c). After 130 cycles at a current density of 1 A g⁻¹, its capacity remains at only ≈50 mA h g⁻¹ (Fig. 3d). Conversely, the reversible capacity of Co₁₋ₓS/FGNs is still retained at over 210 mA h g⁻¹ at a large rate of 10 A g⁻¹ (466 mA h g⁻¹ at 0.1 A g⁻¹). When returns back to 0.1 A g⁻¹, the large reversible capacity can be fully recovered, indicating the excellent reversibility of the electrode. The superb rate capability can be attributed to the short diffusion paths for both Na⁺ ions and electrons, owing to the small particle size of electrochemically active Co₁₋ₓS and the highly conductive graphene matrix. After 200 discharge/charge cycles at 1 A g⁻¹, the Co₁₋ₓS/FGN electrode can still maintain a large capacity of 251 mA h g⁻¹, which is distinctly superior to that of bare Co₁₋ₓS. The electrochemical performances of the reported metal sulfide/carbon composites are summarized in Table S1.† Obviously, the present Co₁₋ₓS/FGN electrode exhibits a superior cycle performance as well as an improved rate capability.

Fig. 3  (a) The discharge and charge profiles of Co₁₋ₓS/FGNs in the 1st, 2nd and 5th cycles at a current density of 100 mA g⁻¹. (b) The discharge and charge profiles in the 1st cycle at a current density of 100 mA g⁻¹. (c) rate performance at varied current densities, and (d) cycling performance at a current density of 1 A g⁻¹ of Co₁₋ₓS/FGNs, FGNs and Co₁₋ₓS.
The cyclic voltammograms (CVs) demonstrated in Fig. 4a show the initial three cycles of the Co$_{1-x}$S/FGN electrode at a scan rate of 0.1 mV s$^{-1}$ in the voltage range between 0.01 and 3 V (vs. Na$^+$/Na). In the first cathodic scan, the broad peak located at 0.77 V is attributed to the SEI layer formation, agreeing well with the discharge/charge curves. In the second cathodic scan, the first two reduction peaks at 1.28 and 0.95 V are ascribed to the insertion of Na$^+$ into Co$_1$S as shown in eqn (1). The peak at 0.58 V is assigned to the conversion reaction with further Na$^+$ insertion as shown in eqn (2).

$$\text{Co}_1\text{S} + y\text{Na}^+ + ye^- \rightarrow \text{Na}_x\text{Co}_{1-x}\text{S}. \quad (1)$$

$$\text{Na}_x\text{Co}_{1-x}\text{S} + (2 - y)\text{Na}^+ + (2 - y)e^- \rightarrow (1 - x)\text{Co} + \text{Na}_2\text{S}. \quad (2)$$

Accordingly, the three oxidation peaks at 1.56, 1.73, and 1.96 V correspond to the extraction of Na$^+$ from the electrode. A pair of sharp peaks near 0 V are observed, which can be ascribed to the Na$^+$ insertion/extraction into/from the graphene nanosheets. In the following cycles, the reduction peaks and the oxidation peak are still visible, which indicates the reversible reaction of Co$_1$S to Co and Na$_2$S as shown in eqn (3).

$$\text{Co}_1\text{S} + 2\text{Na}^+ + 2e^- \leftrightarrow (1 - x)\text{Co} + \text{Na}_2\text{S}. \quad (3)$$

As a control group, the CVs of the FGNs at a scan rate of 0.1 mV s$^{-1}$ are also plotted (Fig. S10†). During the cathodic scan, the peaks near 0 V are ascribed to the insertion of Na$^+$ into the carbonaceous material, which is the same with Co$_{1-x}$S/FGNs. Besides, the two weak peaks at 1.96 V and 2.44 V in the anodic scan could be attributed to the electrochemical reactions of C–S bonds. Besides, the CV curves at different scan rates depicted in Fig. 4b further confirm the good rate capability of the hybrid composites. Besides, the morphological images after discharging/charging cycles verify the good combination of the hybrid integrity (Fig. S11†).

The depressed semicircles in the electrochemical impedance spectra (EIS, Fig. 4c) relate to the charge transfer resistance ($R_{ct}$) and the inclined lines signify the diffusion of Na$^+$ into the solid phase.$^{41-43}$ The hybrid Co$_{1-x}$S/FGNs possess the lowest electronic resistance and $R_{ct}$, indicating the potential synergistic effect of Co$_{1-x}$S nanoparticles and ultrathin FGNs. Further, the EIS of the Co$_{1-x}$S/FGNs are fitted with the equivalent circuit model (Fig. S12†). The corresponding internal resistance ($R_i$), resistance of the SEI layer ($R_l$) and $R_{ct}$ values are listed in Table S2.† $R_i$ increased slightly. $R_{ct}$ increased from 66.3 Ω to 105.8 Ω after the initial 3 cycles due to the formation of the SEI film, and decreased to 6.8 Ω after 15 cycles because of the enhanced reaction kinetics of Co$_{1-x}$S/FGNs upon cycling and the reduced diffusion distance caused by grain fragmentation, reinforcing inter-particle contact between the carbon matrix and particles.$^{45}$

As illustrated in Fig. 4d, the electron-rich nitrogen doped into the graphene matrix improves the electronic conductivity and meanwhile is conducive to enhancing the contact between the electrolyte and active nanoparticles. The rational design of Co$_{1-x}$S nanoparticles incorporated into ultrathin FGNs could withstand larger current densities and exhibit a longer cycle.
stability by reducing the diffusion path of Na+ ions. Moreover, the doping of heteroatoms of N and S could provide additional electrochemically active sites to accommodate Na+ ions, further boosting the reversible capacity.

Conclusions

By integrating the preparation of functional graphene nanosheets (FGNs) and the growth of cobalt sulfide (Co1−xS) nanoparticles into the same synthesis procedure, Co1−xS/FGN nanocomposites were prepared by a newly developed sol−gel method. Benefiting from the ultrathin texture and enriched heteroatoms, the FGNs not only function as a powerful support for the loading of electrochemically active cobalt sulfide, which can effectively prevent the agglomerating of the FGNs in turn, but also furnish additional electrochemically active sites for sodium ion storage. The ultrathin FGNs and the small size of Co1−xS particles capably shorten the transmission path, facilitating the transferring of both electrons and ions. When investigated as a SIB anode, the Co1−xS/FGN electrode delivers a large and reversible capacity of 466 mA h g−1 with a high initial coulombic efficiency of 82%. Particularly, it possesses an excellent cycle stability with a capacity of 251 mA h g−1 at a large rate of 1 A g−1 after 200 cycles, along with an outstanding rate capability (211 mA h g−1 at 10 A g−1). The presented sol−gel method offers a new, facile, green, and large-scale route for the production of homogeneous metal sulfide hybrids with functional graphene, and also provides a novel insight into general materials design towards high-performance electrodes for energy storage systems.

Experimental

All the reagents were of analytical grade and directly used without further purification. Co/FGN nanocomposites were first prepared via a sol−gel method, followed by heat treatment. The final product of Co1−xS/FGNs was obtained by sintering the Co/FGN materials with sulfur powder. In a typical synthesis process, 0.8 g cobalt sulfate (CoSO4·7H2O), 10.0 g urea (CO(NH2)2) and 1.0 g citric acid (C6H8O7) were dissolved in a mixed solution composed of 150 mL ethanol and 50 mL distilled water and then stirred in a water bath at 75 °C for 10 h. The presented sol−gel method offers a new, facile, green, and large-scale route for the production of homogeneous metal sulfide hybrids with functional graphene, and also provides a novel insight into general materials design towards high-performance electrodes for energy storage systems.

Notes and references