General approach for preparing sandwich-structured metal sulfide@reduced graphene oxide as highly reversible Li-ion battery anode

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ABSTRACT
A general method for preparing sandwiched nanostructures consisting of reduced graphene oxide (rGO) and metal sulfides is presented. As a demonstrating example, the sandwiched MoS$_2$@rGO nanocomposites show a good electrochemical performance including a high reversible capability of 1345 mAh g$^{-1}$ at 0.5 A g$^{-1}$ over 400 cycles, and a superior rate performance. Moreover, this method has been verified to fabricate a large set of transition metal sulfides- and double metal sulfides-based rGO composites such as CoS@rGO, NiS@rGO, NiCo$_2$S$_4$@rGO, and CuCo$_2$S$_4$@rGO, enabling the preparing approach presented here applicable for many possible anode and cathode chemistries.

IMPACT STATEMENT
A general strategy for the fabrication of sandwiched nanostructures consisting of reduced graphene oxide (rGO) and metal sulfides for highly reversible Li-ion battery anode has been developed.

1. Introduction
To achieve a higher performance than currently commercial graphite anodes, many materials have been investigated as potential anode candidates for rechargeable lithium-ion batteries (LIBs). Among them, metal sulfides such as MS$_x$ (M = Mo, Co, Ni, Sn, Fe, Mn, etc.) have attracted increasing attention due to their high theoretical capacity [1,2]. However, metal sulfides commonly suffer from cracking and crumbling due to their large volume expansion/shrinkage upon repeated lithiation/delithiation, which leads to a severe capacity decay [3,4]. Nanostructured materials have been confirmed offering significant merits including a short pathway for Li$^+$ ion diffusion, large electrode/electrolyte contact area, and strain accommodation, which are benefit for a high rate capacity and a long cycling life [5,6]. Since that, there have been great efforts for preparing nanostructured metal sulfides and their composite anodes for LIBs [7,8].

Recently, there have been enormous investigations about the fabrication of metal sulfides-based composites with amorphous carbon, carbon nanotube, carbon nanofiber, graphene, etc., to achieve high conductivity and cycling stability [9–12]. Among them, graphene is considered ideal for the composite preparation due to its large surface area, high electrical conductivity, and mechanical flexibility [13–15]. Three-dimensional (3D) porous graphene has been demonstrated being able to enhance the rate performances and cycling stabilities, since 3D graphene provides not only channels for fast ion transport, but also improve the electric conductivity...
through interconnected graphene network [12,16–18]. However, it remains a great challenge to establish a generally applicable approach for making broad composites consisting of various MS\textsubscript{x} and graphene.

Herein, we present a general method for the preparation of sandwich-structured MS\textsubscript{x}@rGO nanocomposites which consist of MS\textsubscript{x} confining on both sides of rGO scaffold. The method involves immersing 3D rGO in a solution containing MS\textsubscript{x} precursors followed by solvothermal synthesis. The sandwiched MS\textsubscript{x}@rGO anodes exhibit high stable capacity and rate performance. Using MoS\textsubscript{2}@rGO as a demonstrating example, the MoS\textsubscript{2}@rGO nanocomposite anodes in both MoS\textsubscript{2}@rGO//Li half-cells and MoS\textsubscript{2}@rGO//LiCoO\textsubscript{2} full-cells show good electrochemical performance, with the expectation that the rGO matrix provides a flexible conductive scaffold, promotes the electronic and ionic transportation, and accommodates the volume change of the MoS\textsubscript{2} during lithiation/delithiation.

2. Experimental

2.1. Preparation of materials

2.1.1. Preparation of 3D rGO

Graphene oxide (GO) was prepared from graphite powders on the basis of a modified Hummers’ method as follows [19]: 5 g of graphite powders (Nanjing Geruifa Carbon Material Co., Ltd.) was mixed with 3.75 g of NaNO\textsubscript{3} (Sinopharm Chemical Reagent Co., Ltd) in a beaker. Subsequently, 150 mL of concentrated H\textsubscript{2}SO\textsubscript{4} (Sinopharm Chemical Reagent Co., Ltd) was added slowly under mechanical stirring. Then, 20 g of KMnO\textsubscript{4} (Sinopharm Chemical Reagent Co., Ltd) was added within 0.5 h. After continuous stirring for 20 h, the mixture was placed for 5 days. Afterwards, 500 mL of de-ionized water was added to the mixture; whereas 30 mL of H\textsubscript{2}O\textsubscript{2} was added after that. At last, the mixture turned into brilliant yellow. After the mixture was centrifuged, it was dialyzed over 7 days with deionized water to remove metal ions and acid thoroughly.

A certain amount of the GO was dispersed in 10 mL of ultra-pure water. Then, the solution was ultrasonicated for approximately 5 h to form a 0.9 mg mL\textsuperscript{-1} GO suspension. Two milliliters of concentrated H\textsubscript{2}SO\textsubscript{4} (98 wt\%) was slowly added under mechanical stirring until the solution was totally mixed. Finally, the mixture was transferred into a Teflon-lined stainless steel autoclave, and heated at 200°C for 20 h. After the mixture cooled down to room temperature naturally, a columnar 3D rGO was obtained.

The digital photograph of the 3D rGO was shown in Figure S1. The products were washed for several times with deionized water until the pH was \(\sim 7\).

2.1.2. Synthesis of MoS\textsubscript{2}@rGO

In a typical procedure, 0.6 g of thioacetamide (CH\textsubscript{3}CSNH\textsubscript{2}, Sinopharm Chemical Reagent Co., Ltd) and 0.4 g of urea (Sinopharm Chemical Reagent Co., Ltd) were dissolved in 14 mL of N,N-dimethylformamide (DMF)/water mixture solvent (1:1 v/v) containing 0.24 g of Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O (Sinopharm Chemical Reagent Co., Ltd). The solution was stirred to form a transparent solution at room temperature using a magnetic stirrer. Then, a columnar rGO was soaked in the solution for 2 days. After that, the system was transferred into a Teflon-lined stainless steel autoclave and maintained at 200°C for 24 h. When it cooled down to room temperature, the product was taken out and rinsed for several times with deionized water and ethanol, respectively. At last, the product was vacuum-dried at 60°C for 10 h. To improve its crystallinity, the product was calcined in H\textsubscript{2}/Ar (H\textsubscript{2}:5 vol.\%) at 700°C for 2 h. For control experiments, MoS\textsubscript{2}/rGO mixtures were prepared by the similar process, in which the columnar rGO was replaced by GO solution.

2.2. Electrochemical measurements

The electrochemical performance of the prepared samples was evaluated using a coin cell systems including half-cells and full-cells. The electrodes were fabricated by using active MoS\textsubscript{2}@rGO (85 wt\%), carbon black (5 wt\%) and sodium carboxymethyl cellulose binder (CMC, 10 wt\%) with styrene-butadiene rubber (SBR), while for NiCo\textsubscript{2}S\textsubscript{4}@rGO electrode, the using active material percentage was 80%. The mixture was mixed into a homogeneous slurry and coated onto a copper foil, and dried in vacuum at 80°C for 12 h. The cells were assembled in an argon-filled glovebox (H\textsubscript{2}O < 0.1 ppm and O\textsubscript{2} < 0.1 ppm, Mikrouna, Super 1220/750/900), with MoS\textsubscript{2}@rGO and NiCo\textsubscript{2}S\textsubscript{4}@rGO as the working electrode, lithium foil as the counter/reference electrode and 1.0 M LiPF\textsubscript{6} in a mixture of EC/DMC/DEC (1:1:1 by volume) as the electrolyte. To assemble a full-cell, the as-prepared MoS\textsubscript{2}@rGO anode was coupled with a commercial LiCoO\textsubscript{2} cathode. The electrochemical performance was tested using a galvanostatic discharge/charge method on a Neware battery tester (Shenzhen Neware Technology Co., Ltd). The voltage cut-off windows were 0.01–3.0 V for half-cells and 1.5–4.1 V for full-cells, respectively. Cyclic voltammetry (CV, 0.01–3.0 V, 0.1 mV s\textsuperscript{-1}) and electrochemical impedance spectrum (EIS) measurements (from 100 MHz to 100 kHz) were
performed on an electrochemical work station (CHI-660E, Shanghai Chenhua Instruments Co., Ltd).

3. Results and discussion

3.1. Physicochemical characterization

As illustrated in Figure 1, firstly, a 3D rGO scaffold was prepared using GO sheets via a solvothermal route. Subsequently, the 3D rGO was impregnated into a solution containing MS\textsubscript{x} precursors. Within this process, metal ions diffuse into the cavity of 3D rGO and were captured by the functional groups (e.g. –COOH, –OH) on the surface of the rGO confirmed by FTIR (Figure S2), which is crucial for the homogeneous nucleation and secondary growth of MS\textsubscript{x} nanostructures. At last, the sandwich-structured MS\textsubscript{x}@rGO architectures were obtained through a secondary solvothermal synthesis.

Figure 2 shows the morphology of the MoS\textsubscript{2}@rGO nanocomposites. Dense nanosheets are uniformly anchored on the surface of rGO, as shown in Figure 2(a,b). In Figure 2(b), the nanosheets are \sim 150 nm in length and 8–12 nm in thickness, as confirmed in Figure 2(c,d). The high-resolution TEM (HRTEM, Figure 2(e)) shows a single nanosheet with a clear lattice fringe. The inter-planar distance is \sim 0.62 nm, corresponding to the plane (002) of hexagonal MoS\textsubscript{2}. The ring-like profile in the selected area electron diffraction (SAED) pattern (Figure 2(f)) indicates that the nanosheets are polycrystalline.

The energy dispersive spectroscopy (EDS) mappings of the MoS\textsubscript{2}@rGO (Figure S3) show the homogeneous distribution of the molybdenum, sulfur, and carbon, in which the atomic ratio of Mo/S is \sim 1:2. Thermogravimetric analysis was employed to determine the amount of graphene within the MoS\textsubscript{2}@rGO nanocomposite (Figure S4), which showed that the weight content of the rGO is around 10.4 wt%.

X-ray diffraction (XRD) peaks (Figure S5a) are assigned to the hexagonal MoS\textsubscript{2} (JCPDS card no. 37-1492) [20]. In Raman spectra (Figure S5b), the peaks at 1346 and 1599 cm\textsuperscript{-1} are indexed to the D and G bands of graphene, respectively; whereas the peaks at 377.1 and 404.3 cm\textsuperscript{-1} are assigned to the E\textsubscript{2g} and A\textsubscript{1g} modes of the MoS\textsubscript{2} crystal, respectively [21]. In addition, Figure S6a shows the survey XPS spectrum of the MoS\textsubscript{2}@rGO, in which the signals of Mo (Mo 3d\textsubscript{5/2}, 3d\textsubscript{3/2}) and S (S 2p) are detected [20,22]. From the N\textsubscript{2} adsorption–desorption isotherm (Figure S7), a distinct hysteresis loop can be identified, indicating a mesoporous structure. The Brunauer–Emmett–Teller (BET) surface area of
the MoS$_2$@rGO nanocomposite is 46.9 m$^2$ g$^{-1}$; while the dominate pore-size is $\sim$ 17.2 nm.

The preparing method for constructing the sulfides/rGO was generalized to many other composites further. Figure 3 shows the SEM and TEM images of the CoS@rGO and NiS@rGO composites. As seen, similar sandwich-structured composites were generally synthesized in a large yield with sulfides densely anchored on the rGO. Each XRD pattern (Figure S8) can be well indexed to the corresponding phases without impurity. In addition, the synthesis strategy can be extended to prepare a broad set of rGO-based structures including NiCo$_2$S$_4$@rGO and CuCo$_2$S$_4$@rGO, as shown in Figures S9 and S10, indicating a good general applicability.

### 3.2. Electrochemical properties

The electrochemical properties of the sandwich-structured MoS$_2$@rGO composites are shown in Figure 4. Figure 4(a) displays the charge/discharge curves of the MoS$_2$@rGO at a current density of 0.5 A g$^{-1}$ over the potential range of 0.01–3.0 V. Two voltage-plateaus located at $\sim$ 1.4 and 0.7 V in the first discharge cycle indicate the formation of Li$_x$MoS$_2$ by the insertion of Li$^+$ [23,24]. In contrast, the plateau at 2.2 V is assigned to the delithiation of Li$_2$S to sulfur, which can be identified by the CV curves (Figures S11 and S12). In Figure 4(b), the MoS$_2$@rGO shows higher specific capacities than the MoS$_2$/rGO which were prepared by mechanically mixing of MoS$_2$ and rGO (Figures S13–S15). The capacities of the MoS$_2$@rGO are 1475, 1401, 1336, 1271, 1191, and 935 mAh g$^{-1}$ at current densities of 0.1, 0.2, 0.5, 1, 2, and 5 A g$^{-1}$, respectively. When the current density was back to 0.1 A g$^{-1}$, the capacity was 1273 mAh g$^{-1}$, exhibiting a good capacity retention.

Figure 4(c) shows the charge/discharge stability and Columbic efficiency of the MoS$_2$@rGO composite and MoS$_2$/rGO mixtures at a current density of 0.5 A g$^{-1}$ over 400 cycles. The sandwich-structured MoS$_2$@rGO composite exhibits a high performance compared to the mixtures, delivering a reversible capacity of 1345 mAh g$^{-1}$ after cycling for 400 times. It should be indicated that the reversible capacity is higher than the theoretical capacity of MoS$_2$ (670 mAh g$^{-1}$), which is attributed to that the porous structure would provide numerous physical adsorption sites for Li$^+$ insertion/extraction [3,24,25]. In contrast, the MoS$_2$/rGO mixtures exhibit a capacity decrease from 951 to 127 mAh g$^{-1}$ after 400 cycles. The capacity of the MoS$_2$@rGO increases during the initial 40 cycles, which is ascribed to the improved access of Li$^+$ into the inner part of the porous nanostructure, and the possible electrochemical activation of the nanomaterials [26,27]. The Coulombic efficiency of the MoS$_2$@rGO rapidly increases since the 2nd cycle and remains $\sim$ 95.0% during subsequent cycles. The irreversible capacity loss in the first cycle is attributed to the formation of the solid electrolyte interface film [28]. The electrochemical performance of MoS$_2$@rGO nanocomposite is attributed to the following aspects. First, the rGO scaffold in the MoS$_2$@rGO nanocomposite improves the electric conductivity of the electrode; second, the agglomeration of MoS$_2$ nanosheets is minimized by rGO scaffold, which enhances the contact between the electrode and electrolyte. Additionally, the rGO buffers the structural change upon lithiation/delithiation.

The corresponding rate capability and cycling performance of NiCo$_2$S$_4$@rGO nanocomposite are shown in Figure S16. The NiCo$_2$S$_4$@rGO nanocomposite delivers capacities of 646.4, 575.7, 485.5, 385.6, 263.6 mAh g$^{-1}$ at current densities of 0.1, 0.2, 0.5, 1, and 2 A g$^{-1}$, respectively. When the current density was back to 0.1 A g$^{-1}$, the capacity was 689 mAh g$^{-1}$, exhibiting a good capacity retention. While the NiCo$_2$S$_4$@rGO nanocomposite electrode was cycled at 0.1 A g$^{-1}$ for 140 times, the capacity retained 708.3 mAh g$^{-1}$ as shown in Figure S16b, which also illustrated its preferable electrochemical property.

The electrochemical impedance spectra (EIS) of the MoS$_2$@rGO before and after cycling are shown in Figure S17. The fitting results show that the charge transfer resistance ($R_{ct}$) of MoS$_2$@rGO composite and the MoS$_2$/rGO mixtures are 66.7 and 175.6 $\Omega$ before cycling, and increase to 115.9 and 230.2 $\Omega$ after cycling for 200 times, respectively. The $R_{ct}$ of the MoS$_2$@rGO composite is much less than that of the MoS$_2$/rGO mixtures, indicating a significant enhancement of conductivity by the rGO.
Figure 4. (a) Charge/discharge profiles at 0.5 A g\(^{-1}\), (b) rate performance test, and (c) cycling capacity and Coulombic efficiency of the MoS\(_2@rGO\) composites and MoS\(_2/rGO\) mixtures at 0.5 A g\(^{-1}\) over 400 cycles.

Figure 5. (a) Charge/discharge curves of the MoS\(_2@rGO//LiCoO\(_2\) full-cells at 100 mA g\(^{-1}\) between 1.5 and 3.8 V, and (b) cycling performance at 500 mA g\(^{-1}\).

The structure and composition of the MoS\(_2@rGO\) after cycling were investigated using TEM, XRD, and EDS, respectively, as shown in Figure S18. Figure S18(a–d) shows the TEM images of the MoS\(_2@rGO\) before and after cycling. The sandwich-structured MoS\(_2@rGO\) composite keeps well; whereas the nanosheets anchored on the rGO transform to particles after 15 cycles. The size of the particles anchored on the rGO decreases depending on the increase of the cycling times. However, the particles transform to needle-like nanostructures after 400 cycles. The XRD pattern of the MoS\(_2@rGO\) after cycling (Figure S18e) confirms the
existence of MoS$_2$ within the electrode. The presences of Mo, S, C, and O are verified by EDS analysis (Figure S18(f)), which is consistent with the XRD results.

In addition, MoS$_2$@rGO/LiCoO$_2$ full-cells consisting of the commercial LiCoO$_2$ cathode and the presented MoS$_2$@rGO composite anode were investigated. The charge/discharge curves at a current density of 0.1 A g$^{-1}$ over the voltage range of 1.5–3.8 V are shown in Figure 5(a). The full-cell shows an initial charge capacity of 2393 mAh g$^{-1}$ (on the anode basis), accompanying with a Coulombic efficiency of 49.1% which increases to $\sim 83.0\%$ at the 2nd cycle. After cycling for 150 times at 0.5 A g$^{-1}$, the full-cell retains a capacity of 1004 mAh g$^{-1}$, accompanying with a Coulombic efficiency of $\sim 99.3\%$ (Figure 5(b)), indicating a good potential for practical applications.

4. Conclusions

In summary, we present a general strategy for the synthesis of MS$_x$@rGO nanocomposites. The chemical synthesis was confined within a cavity of the 3D rGO scaffold. A large variety of sandwich-structured MS$_x$@rGO including MoS$_2$@rGO, CoS@rGO, NiS@rGO, NiCo$_2$S$_4$@rGO, and CuCo$_2$S$_4$@rGO have been successfully prepared. As a demonstrating example, the MoS$_2$@rGO composite delivers a reversible capacity of 1345 mAh g$^{-1}$ over 400 cycles at a current density of 0.5 A g$^{-1}$, exhibiting a better performance compared to the mechanical mixtures of MoS$_2$ and rGO. In addition, the MoS$_2$@rGO/LiCoO$_2$ full-cell retains a capacity of 1004 mAh g$^{-1}$, accompanying with a Coulombic efficiency of $\sim 99.3\%$ after cycling 150 times. The high performances are ascribed to the reduced strain upon insertion/extraction, shortened Li$^+$ ion transfer pathway, improved conductivity, and electrode/electrolyte contact. It is believed that the general strategy presented here could be extended to synthesize a large variety of sandwich-like inorganic@graphene nanocomposites.

Disclosure statement

No potential conflict of interest was reported by the authors.

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