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A strongly coupled CoS₂/ reduced graphene oxide nanostructure as an anode material for efficient sodium-ion batteries



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Kongyan Xie^a, Li Li^{b, **}, Xiang Deng^a, Wei Zhou^a, Zongping Shao^{a, b, c, *}

^a Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), State Key Laboratory of Materials-Oriented Chemical Engineering, College

of Chemical Engineering, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009, China

^b School of Energy Science and Engineering, Nanjing Tech University, Nanjing 210009, China

^c Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia

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ABSTRACT

Sodium-ion batteries (SIBs) are highly attractive electrochemical devices for massive energy storage because of their low cost and abundance of sodium, but insufficient anode performance remains a key challenge for the commercialization of this attractive technology. In this study, a hierarchically porous CoS₂/graphene composite with an architecture of CoS₂ nanoparticles embedded in reduced graphene oxide (rGO) is synthesized through a one-step hydrothermal route allowing the growth of the CoS₂ phase and the reduction of the graphene oxide simultaneously. This composite is applied as an anode material for SIBs, delivering favorable performance. The CoS2 phase consists of nanoparticles of ~10 nm that are uniformly anchored on the rGO, forming a CoS₂/rGO hybrid with strong phase interaction. As a conversion-type anode for SIBs, the electrochemical testing results show significantly enhanced sodiumstorage properties for the CoS₂/rGO composite compared with that of bare CoS₂. Impressively, the CoS₂/ rGO nanostructure exhibits a high discharge capacity of approximately 400 mAh g^{-1} after 100 cycles at specific current of 100 mA g^{-1} , corresponding to approximately 80% of the discharge capacity in the second cycle. Such improvement may be due to the two-dimensional conductive network, homogeneous dispersion and immobilization of the CoS₂ nanoparticles, as well as the enhanced wettability of the active material in the electrolyte by introducing rGO. The results suggest that this well-designed conversion-type CoS₂ is a promising anode material for high-performance SIBs.

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1. Introduction

Currently, sodium-ion batteries (SIBs) are known as the most potential substitute for lithium-ion batteries (LIBs) because of their natural abundance, low cost, and similar operating principles [1–4]. Unfortunately, the actual applications of SIBs have been blocked, at least in part, by the lack of proper anode materials to host Na⁺, which has a larger radius than Li⁺. Therefore, the foremost issue that needs to be solved for SIBs is the development of suitable electrode materials with favorable high specific capacity and cycling performance. To date, various alternative materials, including metal chalcogenides, alloy-based materials, layered metal oxides and carbon, have been exploited as promising anodes for SIBs [1,5–8]. Although some dramatic progress has been made, further research on anode materials is still urgently needed to improve the capacity, cycling stability and rate capability of SIBs, thus making them practically applicable.

Recently, multifarious cobalt sulfides with a certain range of stoichiometry, such as $Co_{1-x}S$, Co_9S_8 , CoS, Co_3S_4 and CoS_2 , have drawn a lot of attention because of their remarkable physical, chemical, magnetic properties [9–12]. In particular, their potential application in electrochemical energy storage fields, e.g., as electrode materials for supercapacitors, LIBs and SIBs, has received tremendous attention in recent years [13–16]. As anodes for LIBs and SIBs, the energy storage in these materials involve a conversion-type reaction mechanism with high theoretical capacity. However, the practical application of bulk-phase CoS_2 electrodes suffers from a couple of problems. For example, the dissolution of the polysulfide intermediates in organic solvent will bring about quick capacity decaying during cycling and the pulverization issue coming from the volume expansion during the



^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: LILI6023@njtech.edu.cn (L. Li), shaozp@njtech.edu.cn (Z. Shao).

charge-discharge process [17,18]. The formation of a composite with an elastic material such as carbon may provide buffer space to adapt the volume change of such conversion-type electrode materials, thus improving the cycling stability and increasing the electrode capacity by suppressing the pulverization of the active materials. For example, superior Li-storage properties of Co_9S_8 have been realized through surface coating the active material with carbon [19]. To date, however, the application of metal sulfides in SIBs has been less reported, likely due to the lower sodium diffusivity in these materials, which required strict control over the electrode microstructure and morphology to achieve favorable electrode performance.

Graphene, as a popular star in materials science with its clearly two-dimensional honeycomb-like network of carbon atoms, has aroused wide attention in many fields, including electrochemical energy storage and conversion, because of its large theoretical specific surface area, outstanding thermal stability, superior electronic conductivity, and remarkable structural flexibility [20]. For example, graphene has been widely used to form composite electrodes for SIBs and LIBs, in which a synergistic effect between graphene and the main active material may occur, significantly improving the electrode performance. For example, a brief freezedrying and then hydrazine treatment process was used to get Co₃S₄ porous nanosheets embedded in graphene sheets, which delivered an attractive reversible capacity of 450 mAh g^{-1} at 500 mA g^{-1} as the anode for SIBs [13]. However, after 50 cycles, a charge capacity of only 329 mAh g⁻¹ was retained, suggesting the importance of further cycling stability improvement. The nanocomposite of Co₃S₄ nanosheets and graphene sheets as reported by Bao was formed through weak van der Waals interaction. An increase in the interaction between cobalt sulfide and graphene may further improve the electrode performance by increasing the charge transfer efficiency and reducing the isolation of cobalt sulfide. On the other hand, as the charge carrier could shorten the diffusion length, 2D nanostructures are very hopeful to supply more active sites for fast electrochemical reactions [21–23]. Through optimizing the nanostructure and the interaction between graphene and cobalt sulfide, a further improvement in the performance (capacity, cycling stability and rate capacity) of a CoS₂ nanoparticles and reduced graphene oxide composite as an anode for SIBs may be realized.

Herein, we report the synthesis and investigation of a composite being composed of strongly coupled CoS_2 nanoparticles and reduced graphene oxide (CoS_2/rGO) as a potential anode material for SIBs. The CoS_2/rGO nanostructure was synthesized directly from graphene oxide(GO) and cobalt nitride through hydrothermal treatment with L-cysteine as the sulfur source. As an anode for SIBs, good cycling stability (approximately 400 mAh g⁻¹ at 100 mA g⁻¹ after 100 cycles) was achieved. In addition, an outstanding rate capability with capacity of 247 mAh g⁻¹ at 5000 mA g⁻¹ was demonstrated. Besides, the electrolyte is critical to the electrochemical properties of the SIBs, and different electrolyte will bring back different electrochemical performance [24–26]. Explanations of this outstanding performance are discussed.

2. Experimental section

2.1. Materials synthesis

The hydrothermal synthesis of the CoS_2/rGO nanostructure was conducted as follows. First, graphene oxide (GO) powders were prepared by an improved version of the graphene preparation method [27]. To synthesis GO, we employed graphite flakes (sigma-Aldrich, cat # 33246, ~150 µm falkes), H₃PO₄ (Sinopharm chemical reagent co., Ltd), H₂SO₄ (Shanghai Lingfeng chemical reagent co., Ltd), KMnO₄ (Shanghai Lingfeng chemical reagent co., Ltd), H₂O₂ (Shanghai Lingfeng chemical reagent co., Ltd). H₂SO₄: H₃PO₄ (180: 20 ml) solution were added to a mixture of graphite flakes (1.5 g) and KMnO₄ (9.0 g) slowly. The reaction was then heated to 50 °C and stirred for 12 h. The mixture was cooled to room temperature and poured onto ice with 30% H₂O₂ and centrifuged several times. Then, 50 mg of GO powders was diffused in a 53.3 ml of a mixed solution of ethylene glycol and DI water (1:3 by volume) by ultrasonication for 1 h, followed by the addition of 120 mg of L-cysteine and 0.4 mmol of Co(NO₃)₂·6H₂O. The mixture solution was stirred for 1 h and shifted to a 100 ml of Teflon-lined autoclave, tighten and heated in an oven at 160 °C for 8 h. The final product was treated separately with ethanol and DI water several times, and then dried in a freeze dryer. Finally, the as-obtained precipitate was treated at 400 °C for 4 h in argon atmosphere to result in the CoS₂/rGO nanostructure. As a control, pristine CoS₂ nanoparticles were also prepared via the similar experimental process but without the presence of GO in the mixture solution. Pristine graphene sheets were also prepared by adding GO into the mixture solution, but without cobalt nitride and the sulfur source.

2.2. Material characterization

The crystallographic information of the samples were evaluated through RT powder X-ray diffraction (XRD) measurement on a Bruker D8 Advance diffractometer with Cu K α source over a 2θ range from 10° to 80°. The microstructure images were observed with field-emission scanning electron microscope (FE-SEM, Hitachi, Japan). Transmission electron microscope (TEM) was obtained using a field emission TEM equipped at 300 kV (Tecnai G2 F30 S-TWIN, USA). X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI550 system and the as-obtained spectra were fitted through XPSPEAK41 software. Raman spectra were collect by an HR800 UV micro-Raman spectrometer. Thermogravimetric (TG) analysis was performed employing a WCT-1 TG Analyzer under air flow to determine the carbon content of the product. AutoSorb-iQ3 was employed to character BET made by Quantachrome. The pore size distribution and specific surface area of the samples were calculated using the Brunauer-Emmett-Teller (BET) equation. Besides, we also use DHG-9070A type oven made by Shanghai Yiheng Science Instrument Co., Ltd., autoclave made by Zhenghong, SCIENTZ-10Z type freeze dryer was made by Ningbo Scientz Biotechnology Co., Ltd. DZF-6050 type vacuum oven was made by Shanghai Boxun Industry Co., Ltd., TG1650-WS type centrifuge was made by Shanghai Lu Xiangyi Centrifuge Instrument Co., Ltd.

2.3. Electrochemical measurements

To prepare the working electrode, the active material, conductive Super P (Shanghai Hersbit chemical) and sodium carboxymethyl cellulose (Na-CMC, Chemical reagents of national medicine) were mixed in proper weight ratios (80:10:10) by planet pulp mixer (ARM-30), which were pasted onto copper foil (Hefei Ke Jing material technology Co., Ltd) current collectors by doctor blade, and dried at 100 °C for 12 h in vacuum. Each electrode plate contained 1-1.2 mg of active material. The CR2025 coin-type cells were assembled in a pure-argon filled glove box with 1.0 M NaClO₄ in PC: FEC (98:2 in volume, Cathay Huarong chemical new materials Co. Ltd) as the electrolyte, metallic sodium (Aladdin chemical reagent) as the reference and counter electrode and microporous polyethylene film (Celgard 2400) as the separator. RT-galvanostatically discharge/charge cycling performance was conducted over the potential range of 3.00–0.01 V on the NEWARE BTS multichannel battery testing system (5 V, 10 mA). Cyclic voltammetry profiles were acquired from a PARSTAT 273A electrochemical workstation and the scanning rate was set as 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was tested using a Princeton 2273 electrochemical system at a frequency range of 100 kHz to 100 mHz at open circuit voltage (OCV) over the single cell. The voltage amplitude is 10 mV, and the applied voltage is 3 V.

3. Results and discussion

Fig. 1a shows the XRD patterns of the as-prepared CoS_2/rGO composite, bare CoS_2 , and rGO. Diffraction reflections at 2θ of approximately 32.4, 36.1, 39.5, 47.2 and 55.2° were observed from the XRD patterns of the as-synthesized CoS_2/rGO , which can be indexed based on the cattierite CoS_2 phase (JCPDS card 41–1471) at the (200), (210), (211), (220) and (311) diffraction planes, confirming the formation of the CoS_2 crystalline phase. Besides, diffraction reflections at 2θ of approximately 26, 43° were observed from the XRD patterns of the as-synthesized CoS_2/rGO , which can be due to the presence of rGO phase at the (002) and (100). The broadened diffraction reflections of both the bare CoS_2 and the CoS_2/rGO composite reveal the nanocrystallinity of the CoS_2 phase.

Fig. 1b shows the Raman spectra of GO, rGO and CoS_2/rGO . All samples display two bands at approximately 1355 and 1604 cm⁻¹, corresponding to the disordered/defected (D) and graphitic (G) bands of the graphene sheet [17]. The intensity ratios of the D band to the G band (I_D/I_G) are 1.004, 0.89, and 1.28 for GO, rGO, and CoS_2/rGO , respectively, indicating a further decreased sp² carbon domain [28] when CoS_2 nanoparticles formed the composite with rGO, in good agreement with the disappearance of the characteristic XRD peaks of graphitized graphene in the CoS_2/rGO composite. The CoS_2/rGO composite, as determined by TGA (Fig. S1), was found to be composed of approximately 50 wt% rGO and 50 wt% CoS_2 .

In addition, elements in the CoS₂/rGO composite are detected by the XPS survey spectrum from 0 to 1100 eV (Fig. 2a). Specifically, the C 1s XPS spectra of CoS₂/rGO (Fig. 2b) can be fitted into four peaks which located at 284.7, 286.3, 286.8 and 288.9 eV, corresponding to the carbon atoms in C–C, C–O, C=O, O–C=O groups, respectively [13,29]. Two peaks related to the Co 2p_{3/2} and Co 2p_{1/2} orbitals in the Co 2p XPS spectrum can be deconvolved into six peaks located at 779.2, 782.9, 786.6 eV, 798.1, 799.7 and 803.7 eV, respectively (Fig. 2c). The first three peaks can be assigned to the Co $2p_{3/2}$ spin-orbit peaks. The peak at 779.2 eV can be ascribed to the Co²⁺ ion of CoS₂ [30,31], the peak located at 782.9 eV can be attributed to the Co–NH coordination bond in the L-cysteine-Co [32], and the peak at 786.6 eV can be ascribed to the Co²⁺ ion of Co–O bond [33]. The last three peaks corresponded to the Co $2p_{1/2}$ orbital. In addition, the peak located at 799.7 eV can be due to the Co–O bond [13]. Meanwhile, the existence of CoS₂/rGO can be further verified by the S 2p peak at 162.6 (S $2p_{3/2}$) and 164.1 eV (S $2p_{1/2}$) [34] (Fig. 2d). The presence of oxygen-containing groups suggests the GO was not fully reduced, which is, however, helpful to fix CoS₂ on the rGO surface.

Fig. 3 presents the N₂ adsorption-desorption isotherm and the pore size distribution diagram of the as-prepared CoS_2/rGO composite. The specific surface area of the CoS_2/rGO composite was calculated to be 83.7 m² g⁻¹, and the main pores were in the range of 1–10 nm, as shown from the inset of Fig. 3. In comparison, the specific surface areas of the bare CoS_2 and the pristine rGO were calculated to be 24.5 and 490.7 m² g⁻¹, and the main pores of the bare CoS_2 and the pristine rGO, respectively, were approximately 3.83 and 3.42 nm, as marked in the inset of Fig. S2. This results indicated that the surface area of the CoS_2/rGO nanocomposite was relatively enhanced with the addition of GO compared to the bare CoS_2 , which would benefit for the diffusion of electrolyte to active sites and improve the electrochemical performance of CoS_2/rGO as anode in SIBs.

The morphology and microstructure of the CoS₂/rGO composite and the bare CoS₂ were examined by SEM and TEM. For the bare CoS₂, as shown in Fig. 4a, they gave rise to large aggregates with size ranging from 500 nm to 2 µm after calcination. Such large particle size may inhibit the penetration of the electrolyte, increasing the diffusion distance for Na⁺ due to smaller surface area $(24.5 \text{ m}^2 \text{ g}^{-1})$ and pore size (~3.83 nm) compared to that of CoS₂/ rGO (83.7 m² g⁻¹, ~4.3 nm) as indicated by BET results in Fig. S2a and Fig. 3. In contrast, as shown in Fig. 4b, the size of CoS₂ dramatically decreased to approximately 10 nm when it formed the composite with rGO, and these CoS₂ nanoparticles were homogeneously distributed on both sides of the rGO. The intimate interaction between the negatively charged graphene oxide and the positively charged cobalt ions during the early hydrothermal reaction stage likely played an important part both in inhibiting the growth of the CoS₂ nanoparticles and limiting the aggregation of the crystalline CoS₂ particles to some extent [35], and in allowing the uniform distribution over the reduced graphite surface. All of the CoS₂ nanoparticles still adhered to the reduced graphene oxide firmly even after vigorous ultrasonic treatment, further confirming



Fig. 1. (a) XRD patterns of the CoS₂/rGO nanocomposite, rGO and bare CoS₂, (b) Raman spectra of CoS₂/rGO, rGO and GO from 300 to 1800 cm⁻¹.



Fig. 2. (a) XPS survey spectrum of CoS₂/rGO; (b) XPS spectra of C 1s; (c) Co 2p and (d) S 2p.



Fig. 3. N₂ adsorption-desorption isotherms of the CoS₂/rGO nanocomposite.

the presence of strong interactions between the CoS_2 nanoparticles and the rGO in the composite. The natural curvature of the reduced graphene and the separation of the sheets with the presence of CoS_2 nanoparticle could enrich mesopores inside the CoS_2/rGO composite, which is also consistent with the results in Fig. 3 that the pore size of the composite is the largest than that of bare CoS_2 and rGO in Fig. S2, and these rich pores in the sample may provide more effective ionic and electron transport during sodiation/desodiation and buffer space for mediating the volume change during the electrochemical conversion reaction. An improved capacity and cycling stability are then expected.

The TEM images give further evidence that the CoS_2 nanoparticles were distributed on the surface of the rGO in the form of single particles or small particle clusters, and the nature of CoS_2 nanoparticles was confirmed by their selected area electron diffraction (SAED) pattern (inset of Fig. 4c) since the respective diffraction rings can be well indexed to the (200), (210), (220) and (311) diffraction planes of CoS_2 . The HR-TEM image in Fig. 4d shows crystal lattice fringes with a d-spacing of 0.31 nm of the nanoparticles, matching well with the (210) plane of CoS_2 , which further confirms the CoS_2 nature of the nanoparticles. The reduced graphene layer in the CoS_2/rGO is rather thin, possibly consisting of single or few-layer sheets, which can be observed from the wrinkles and its transparent nature.

As we known, the electrochemical performance of a SIB is strongly affected by its electrolyte. Four types of electrolyte, i.e., (1) 1.0 M NaClO₄ in propylene carbonate and fluoroethylene carbonate (PC:FEC, 98:2 v/v), (2) 1.0 M NaClO₄ in ethylene carbonate and diethylcarbonate (EC:DEC, 1:1 v/v), (3) 1.0 M NaClO₄ in ethylene carbonate and propylene carbonate (EC:PC, 1:1 v/v), and (4) 1.0 M NaCF₃SO₃ in diethyleneglycol dimethylether (DEGDME), were tested in sodium half cells. The four different organic solvents was



Fig. 4. (a) A low-magnification SEM image of bare CoS₂; (b) an SEM image of the CoS₂/rGO composite; (c) a TEM image of the CoS₂/rGO composite. The inset shows the SAED pattern with indexed diffraction rings, and (d) shows an HR-TEM image of CoS₂ nanoparticles in the CoS₂/rGO composite.

used to detect the charge-discharge reaction of the CoS2/rGO composite at an specific current of 100 mA g^{-1} in the potential window of 0.01–3.0 V vs Na⁺/Na. As shown in Fig. S3, the CoS₂/rGO electrode in 1.0 M NaClO₄ in PC: FEC exhibited the best property with the discharge capacity kept at 400 mAh g^{-1} after 100 cycles. In contrast, although the electrode in 1.0 M NaClO₄ in EC:PC demonstrated a high initial discharge capacity of 419 mAh g^{-1} , the discharge capacity decayed quickly to only approximately 230 mAh g^{-1} after 20 cycles and less than 100 mAh g^{-1} after 100 cycles. The CoS₂/rGO electrode in 1.0 M NaClO₄ in EC: DEC and 1.0 M NaCF₃SO₃ in DEGDME also presented low capacities and a quick capacity decay with cycling. In both of electrolytes, a capacity of approximately 100 mAh g^{-1} was maintained after 100 cycles. With such clear differences, the electrolyte clearly has an outstanding effect on the electrochemical property of the as-prepared CoS₂/rGO electrode. The excellent cycling stability of the CoS₂/rGO electrode in the electrolyte of 1.0 M NaClO₄ in PC: FEC suggests that a propylene carbonate-based electrolyte could likely restrain the reaction between the electrolyte and active material, and this reaction may cause the fast loss of active materials [36–40].

The electrochemical properties of the CoS₂/rGO electrode were first studied by galvanostatic charge-discharge tests. Fig. 5a show the 1st, 2nd, 50th and 99th charge-discharge curves of the CoS₂/rGO electrode between 0.01 and 3.0 V at a specific current of 100 mA g⁻¹. Here, the specific capacities of the CoS₂/rGO electrode are calculated based on the whole mass of CoS₂ and graphene. As the capacity of CoS₂/rGO electrode, 483 and 744 mAh g⁻¹ was reached in the first charge and discharge, respectively, corresponding to a coulombic efficiency of 67%. However, the discharge capacity decreased to 464 mAh g⁻¹ in the second cycle. Fortunately, capacities of 376 mAh g⁻¹ can be maintained in the 99th cycle. Cyclic voltammetry (CV) of the CoS₂/rGO electrode at a scan rate of 0.1 mV s⁻¹ in the potential range from 0.01 to 3 V was further measured in Fig. 5b. For the bare CoS₂ electrode, there were two reduction peaks at 0.9 and 0.7 V in the first cycle. According to the literature, the first reduction peak is associated with the electrochemical reactions of $CoS_2 + xNa^+ + xe^- \rightarrow Na_xCoS_2$ and $Na_xCoS_2 + (4-x)Na^+ + (4-x)e^- \rightarrow Co + 2Na_2S$, and we supposed that the reduction peak at 0.9 V involved with the formation of a solid-electrolyte interphase (SEI) film on the surface of the electrode materials [41]. Accordingly, there was only one oxidation peak at 1.4 V, which can be associated with the reactions of Co + $2Na_2S \rightarrow CoS_2 + 4Na^+ + 4e^-$. In the second cycle, only one peak at approximately 0.7 V was observed. This result suggests the reduction peak at 0.9 V was shifted to 0.7 V, while the initial 0.7 V reduction peak disappeared because SEI is usually formed during the first cycle. Such a shift may result from the improved kinetics of the electrode [42].

Fig. 5c compares the cycling stability of the CoS₂/rGO nanostructure, the bare CoS₂ and the pristine rGO at a specific current of 100 mA g^{-1} . The CoS₂/rGO electrode exhibited improved cycling stability compared with the bare CoS₂. After 40 cycles, a capacity of over 400 mAh g^{-1} was retained for the CoS₂/rGO electrode. In comparison, the capacity of the bare CoS₂ electrode decayed promptly to below 20 mAh g^{-1} after 40 cycles. Impressively, the CoS₂/rGO nanostructure exhibited a high discharge capacity of approximately 400 mAh g⁻¹ after 100 cycles, suggesting a capacity retention of approximately 80% with respect to the discharge capacity in the second cycle. The excellent cycling ability of the CoS₂/ rGO nanostructures was demonstrated by the average 97.3% coulombic efficiency as an anode for SIBs. To illustrate the superiority of the as-fabricated CoS2/rGO nanostructures for sodium storage, the rate performance was further investigated to determine their practical use in SIBs. Fig. 5d show that the CoS₂/rGO electrode delivered stable discharge capacities of 408, 352, 325, 297, and 275 mAh g^{-1} at specific current of 100, 200, 500, 1000, and 2000 mA g⁻¹. In addition, even though a 50-fold increase in specific current was tested, a discharge capacity of approximately 247 mAh



Fig. 5. (a) Charge-discharge curves of CoS_2/rGO composite in the voltage range of 0.01–3.0 V at a specific current of 100 mA g^{-1} , (b) CV plots of CoS_2/rGO scanned at 0.1 mV s^{-1} in a potential window of 0.01–3.0 V. (c) rate performance of the CoS_2/rGO electrode at current densities of 100, 200, 500, 1000, 2000, and 5000 mA g^{-1} in a potential window of 0.01–3.0 V. (d) Cycling performance (left y-axis) and coulombic efficiency (right y-axis) of the bare CoS_2 , rGO and CoS_2/rGO composite at a current density of 100 mA g^{-1} .

 g^{-1} was still maintained at 5000 mA g^{-1} , suggesting the outstanding rate capability of the CoS₂/rGO electrode. According to the detailed discharge/charge profiles depicted in Fig. 6a, only a

slight increase in the charge plateau appeared when the specific current was increased from 100 to 5000 mA g^{-1} , illustrating the low polarization and rapid reaction kinetics of the CoS₂/rGO electrode.



Fig. 6. (a) Charge-discharge curves of the CoS_2/rGO electrode at various current densities of 0.1 A g^{-1} , 0.2 A g^{-1} , 0.5 A g^{-1} , 1 A g^{-1} , 2 A g^{-1} , 5 A g^{-1} in a potential window of 0.01–3.0 V. (b) The cycling stability of the CoS_2/rGO electrode at three different current densities of 0.1 A g^{-1} , 0.2 A g^{-1} , 0.5 A g^{-1} in a potential window of 0.01–3.0 V.

This means that the CoS₂/rGO electrode could conquer high-rate cycling without damage the integrity of its structural. Such outstanding rate performance may be explained by the following three factors: (i) the highly conductive rGO supplies efficient conducting channels for the CoS₂ nanoparticles; (ii) nanoscaled and well-distributed CoS₂ nanoparticles on the surface of graphene are favorable for rapid Na-ion diffusion: and (iii) the loosely stacked CoS₂/rGO flakes are conductive for better infiltration of the electrolyte and quick Na-ion transport across the electrode/electrolyte interface. Furthermore, the CoS2/rGO could still achieve a high specific capacity of 206 mA g^{-1} even when the specific current increased to 500 mA g^{-1} (Fig. 6b). As a comparison, the capacity of the bare CoS₂ electrode dropped quickly to approximately 20 mAh g⁻¹ after 100 cycles. Similar poor cycling stability for a bare CoS₂ electrode has also been reported by other groups [43–48]. Such enhanced cycling stability can be due to the incorporation of reduced graphene oxide in the composite, which not only restrained the aggregation of the CoS₂ nanoparticles but also buffered the large volume changes during the conversion reactions by immobilizing them on the rGO. In addition, the highly conductive rGO would enhance the electrical conductivity of the whole electrode, and the loosely stacked CoS₂/rGO nanocomposite is conductive for better infiltration of the electrolyte and quick Na-ion transport across the electrode/electrolyte interface.

Fig. 7a shows the typical EIS in a Nyquist plot, the two partly semicircles in the high-to-medium frequency zone and a linear tail in the low frequency zone. Apparently, owing to the highly conductive rGO, R_{ct} of the CoS₂/rGO electrode show a lower value contrasted with the bare CoS₂ electrode [49–51]. Moreover, the relatively sharper low-frequency region of the CoS₂/rGO electrode suggests the higher sodium-ion diffusivity inside the CoS₂/rGO electrode, ensuring rapid Na-intercalation kinetics [14]. To calculate the diffusion coefficient of Na-ion through the electrode materials, we employed the following formula:

 $D=R^2T^2/2n^4F^4A^2C^2\sigma^2$

In which R is the gas constant, n is the number of electrons involved in the oxidation/reduction reaction per molecule, T is the temperature, F is the Faraday constant, C is the concentration of sodium ions, A is the surface area of the electrode, and σ is the Warburg factor [52]. Fig. 7b show the Z' versus $\omega^{-1/2}$ curves in the

low frequency region of the pristine CoS₂ and CoS₂/rGO composite. The D_{Na+} values of the pristine CoS_2 and CoS_2/rGO composite are calculated to be 4.10×10^{-23} and 2.65×10^{-21} cm² s⁻¹, respectively. Every character of the electrode materials are conductive, and furthermore improve the sodium storage properties of the $CoS_2/$ rGO electrode. According to the fitting results, the R_{ct} of the bare CoS_2 electrode is 298.2 Ω , while it is only 109.8 Ω for the CoS_2/rGO electrode. We listed the results in Table S1, in which the R_s, R_f and R_{ct} represented for the ohmic resistance of the electrolyte, the resistance of Na ion transport through the SEI on the electrode surface and the resistance of charge transfer reactions inside or on the surface of active materials, respectively. Meanwhile, the constant phase elements (CPEs) represented the interfacial capacitance between electrolyte/SEI film/electrode materials and some surface confined faradic capacitance as well. W is referred to the Warburg impedance. The restricted particle aggregation is responsible for the low R_{ct} value for the CoS₂/rGO electrode. A lower R_{ct} of the CoS₂/ rGO electrode can also explain its better rate capacity compared with the bare CoS₂ electrode. Clearly, the introduction of reduced graphite sheets to form the composite electrode played a decisive role in improving the overall capacity and cycling stability of CoS₂ even at high specific current.

Finally, in Table S2 [13,53–59], we compare the electrochemical performance of the CoS₂/rGO nanostructure as an anode for SIBs with other recently reported cobalt sulfide-based electrodes. As can be seen, electrochemical properties of our CoS₂/rGO electrode outperformed the most of previous reports on cobalt sulfur-based electrodes in terms of reversible capacity, cycling performance and initial coulombic efficiency.

4. Conclusions

In summary, a CoS_2/rGO hybrid was successfully prepared by using a hydrothermal method. The CoS_2 nanoparticles, with sizes of 1–10 nm, were uniformly embedded on both sides of the rGO, which provided a structurally stable host for sodium storage through the conversion reaction. The rGO played an important part in the formation of the CoS_2 nanoparticles. As an anode for SIBs, good cycle stability (approximately 400 mAh g⁻¹ at 100 mA g⁻¹ after 100 cycles) have been proved by the CoS_2/rGO composite. The improved cycling stability of CoS_2/rGO compared to bare CoS_2 can be due to the introduction of the versatile rGO that not only



Fig. 7. (a) Electrochemical impedance spectra of the bare CoS_2 and CoS_2/rGO composite electrodes. (b) Z' versus $\omega^{-1/2}$ curves in the low frequency region of the pristine CoS_2 and CoS_2/rGO composite.

buffered the volume changes but also prevented the CoS_2 nanoparticles from aggregating. The rGO also offered efficient conductive networks to enhance the charge transfer rate. As a result, an enhanced rate capacity was also realized. Such intriguing electrochemical properties of the CoS_2/rGO composite make it a potential anode material for advanced SIBs.

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Appendix A. Supplementary data

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References

- Y. Kim, K.H. Ha, S.M. Oh, K.T. Lee, High-capacity anode materials for sodiumion batteries, Chem.-Eur. J. 20 (2014) 11980–11992.
- [2] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, Chem. Rev. 114 (2014) 11636–11682.
- [3] S.W. Kim, D.H. Seo, X. Ma, G. Ceder, K. Kang, Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithiumion batteries, Adv. Energy Mater. 2 (2012) 710–721.
- [4] H. Pan, Y.S. Hu, L. Chen, Room-temperature stationary sodium-ion batteries for large-scale electric energy storage, Energy Environ. Sci. 6 (2013) 2338–2360.
- [5] S.H. Choi, Y.N. Ko, J.K. Lee, Y.C. Kang, 3D MoS₂-graphene microspheres consisting of multiple nanospheres with superior sodium ion storage properties, Adv. Funct. Mater. 25 (2015) 1780–1788.
- [6] S. Hariharan, K. Saravanan, P. Balaya, α-MoO₃: a high performance anode material for sodium-ion batteries, Electrochem. Commun. 31 (2013) 5–9.
- [7] N. Zhang, X. Han, Y. Liu, X. Hu, Q. Zhao, J. Chen, 3D porous γ-Fe₂O₃@C nanocomposite as high-performance anode material of Na-ion batteries, Adv. Energy Mater. 5 (2015) 1401123.
- [8] S. Yuan, X. Huang, D. Ma, H. Wang, F. Meng, X. Zhang, Engraving copper foil to give large-scale binder-free porous CuO arrays for a high-performance sodium-ion battery anode, Adv. Mater. 26 (2014) 2273–2279.
- [9] R. Wu, D.P. Wang, X. Rui, B. Liu, K. Zhou, A.W. Law, Q. Yan, J. Wei, Z. Chen, In-Situ formation of hollow hybrids composed of cobalt sulfides embedded within porous carbon polyhedra/carbon nanotubes for high-performance lithium-ion batteries, Adv. Mater. 27 (2015) 3038–3044.
- [10] Y. Wang, J. Wu, Y. Tang, X. Lü, C. Yang, M. Qin, F. Huang, X. Li, X. Zhang, Phasecontrolled synthesis of cobalt sulfides for lithium ion batteries, ACS Appl. Mater. Interfaces 4 (2012) 4246–4250.
- [11] S.J. Bao, Y. Li, C.M. Li, Q. Bao, Q. Lu, J. Guo, Shape evolution and magnetic properties of cobalt sulfide, Cryst. Growth Des. 8 (2008) 3745–3749.
- [12] V.R. Shinde, S.B. Mahadik, T.P. Gujar, C.D. Lokhande, Supercapacitive cobalt oxide (Co₃O₄) thin films by spray pyrolysis, Appl. Surf. Sci. 252 (2006) 7487–7492.
- [13] Y. Du, X. Zhu, X. Zhou, L. Hu, Z. Dai, J. Bao, Co₃S₄ porous nanosheets embedded in graphene sheets as high-performance anode materials for lithium and sodium storage, J. Mater. Chem. A 3 (2015) 6787–6791.
- [14] S. Peng, X. Han, L. Li, Z. Zhu, F. Cheng, M. Srinivansan, S. Adams, S. Ramakrishna, Unique cobalt sulfide/reduced graphene oxide composite as an anode for sodium-ion batteries with superior rate capability and long cycling stability, Small 12 (2016) 1359–1368.
- [15] B. Wang, J. Park, D. Su, C. Wang, H. Ahn, G. Wang, Solvothermal synthesis of CoS₂-graphene nanocomposite material for high-performance supercapacitors, J. Mater. Chem. 22 (2012) 15750–15756.
- [16] J. He, Y. Chen, P. Li, F. Fu, Z. Wang, W. Zhang, Self-assembled CoS₂ nanoparticles wrapped by CoS₂-quantum-dots-anchored graphene nanosheets as superior-capability anode for lithium-ion batteries, Electrochim. Acta 182 (2015) 424–429.
- [17] B. Qiu, X. Zhao, D. Xia, In situ synthesis of CoS₂/RGO nanocomposites with enhanced electrode performance for lithium-ion batteries, J. Alloys Compd. 579 (2013) 372–376.
- [18] Q. Wang, R. Zou, W. Xia, J. Ma, B. Qiu, A. Mahmood, R. Zhao, Y. Yang, D. Xia,

Q. Xu, Facile synthesis of ultrasmall CoS₂ nanoparticles within thin N-doped porous carbon shell for high performance lithium-ion batteries, Small 11 (2015) 2511–2517.

- [19] W. Shi, J. Zhu, X. Rui, X. Cao, C. Chen, H. Zhang, H. Hng, Q. Yan, Controlled synthesis of carbon-coated cobalt sulfide nanostructures in oil phase with enhanced Li storage performances, ACS Appl. Mater. Inter. 4 (2012) 2999–3006.
- [20] L. Li, Z. Guo, A. Du, H. Liu, Rapid microwave-assisted synthesis of Mn₃O₄graphene nanocomposite and its lithium storage properties, J. Mater. Chem. 22 (2012) 3600–3605.
- [21] T.J. Kim, C. Kim, D. Son, M. Choi, B. Park, Novel SnS₂-nanosheet anodes for lithium-ion batteries, J. Power Sources 167 (2007) 529–535.
- [22] Y. Sun, S. Gao, Y. Xie, Atomically-thick two-dimensional crystals: electronic structure regulation and energy device construction, Chem. Soc. Rev. 43 (2014) 530–546.
- [23] D. Su, S. Dou, G. Wang, Ultrathin MoS₂ nanosheets as anode materials for sodium-ion batteries with superior performance, Adv. Energy Mater. 5 (2015) 1401205.
- [24] F. Colò, F. Bella, J.R. Nair, M. Destro, C. Gerbaldi, Cellulose-based novel hybrid polymer electrolytes for green and efficient Na-ion batteries, Electrochim. Acta 174 (2015) 185–190.
- [25] J. Mindemark, R. Mogensen, M.J. Smith, M.M. Silva, D. Brandell, Polycarbonates as alternative electrolyte host materials for solid-state sodium batteries, Electrochem. Commun. 77 (2017) 58–61.
- [26] F. Bella, F. Colò, J.R. Nair, C. Gerbaldi, Photopolymer electrolytes for sustainable, upscalable, safe, and ambient-temperature sodium-ion secondary batteries, ChemSusChem 8 (2015) 3668–3676.
- [27] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. Alemany, W. Lu, J.M. Tour, Improved synthesis of graphene oxide, ACS Nano 4 (2010) 4806–4814.
- [28] J. Xie, S. Liu, G. Cao, T. Zhu, X. Zhao, Self-assembly of CoS₂/graphene nanoarchitecture by a facile one-pot route and its improved electrochemical Listorage properties, Nano Energy 2 (2013) 49–56.
- [29] Y. Zhu, X. Xu, G. Chen, Y. Zhong, R. Cai, L. Li, Z. Shao, Surfactant-free selfassembly of reduced graphite oxide-MoO₂ nanobelt composites used as electrode for lithium-ion batteries, Electrochim. Acta 211 (2016) 972–981.
- [30] L. Zhu, D. Susac, M. Teo, K.C. Wong, P.C. Wong, R.R. Parsons, D. Bizzotto, K.A.R. Mitchell, S.A. Campbell, Investigation of CoS₂-based thin films as model catalysts for the oxygen reduction reaction, J. Catal. 258 (2008) 235–242.
- [31] D.C. Higgins, F.M. Hassan, M.H. Seo, J.Y. Choi, M.A. Hoque, D.U. Lee, Z. Chen, Shape-controlled octahedral cobalt disulfide nanoparticles supported on nitrogen and sulfur-doped graphene/carbon nanotube composites for oxygen reduction in acidic electrolyte, J. Mater. Chem. A 3 (2015) 6340–6350.
- [32] S. Bao, Y. Li, C. Li, Q. Bao, Q. Lu, J. Guo, Shape evolution and magnetic properties of cobalt sulfide, Cryst. Growth Des. 8 (2008) 3745–3749.
- [33] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, Appl. Surf. Sci. 257 (2011) 2717–2730.
- [34] J. Xie, S. Liu, G. Cao, T. Zhu, X. Zhao, Self-assembly of CoS₂/graphene nanoarchitecture by a facile one-pot route and its improved electrochemical Listorage properties, Nano Energy 2 (2013) 49–56.
- [35] D. Li, M.B. Mueller, S. Gilje, R.B. Kaner, G.G. Wallace, Processable aqueous dispersions of graphene nanosheets, Nat. Nanotechnol. 3 (2008) 101–105.
- [36] A. Ponrouch, R. Dedryvère, D. Monti, A.E. Demet, J.M.A. Mba, L. Croguennec, C. Masquelier, P. Johansson, M.R. Palacín, Towards high energy density sodium ion batteries through electrolyte optimization, Energy Environ. Sci. 6 (2013) 2361–2369.
- [37] J. Gao, M.A. Lowe, Y. Kiya, H.D. Abruna, Effects of liquid electrolytes on the charge-discharge performance of rechargeable lithium/sulfur batteries: electrochemical and in-situ X-ray absorption spectroscopic studies, J. Phys. Chem. C 115 (2011) 25132–25137.
- [38] Z. Shadike, M.H. Cao, F. Ding, L. Sang, Z.W. Fu, Improved electrochemical performance of CoS₂-MWCNT nanocomposites for sodium-ion batteries, Chem. Commun. 51 (2015) 10486–10489.
- [39] Z. Hu, Z. Zhu, F. Cheng, K. Zhang, J. Wang, C. Chen, J. Chen, Pyrite FeS₂ for highrate and long-life rechargeable sodium batteries, Energy Environ. Sci. 8 (2015) 1309–1316.
- [40] K. Zhang, Z. Hu, X. Liu, Z. Tao, J. Chen, FeSe₂ microspheres as a highperformance anode material for Na-ion batteries, Adv. Mater. 27 (2015) 3305–3309.
- [41] Z. Li, W. Feng, Y. Lin, X. Liu, H. Fei, Flaky CoS₂ and graphene nanocomposite anode materials for sodium-ion batteries with improved performance, RSC Adv. 6 (2016) 70632–70637.
- [42] J.H. Kim, J.H. Lee, Y.C. Kang, Electrochemical properties of cobalt sulfidecarbon composite powders prepared by simple sulfidation process of spraydried precursor powders, Electrochim. Acta 137 (2014) 336–343.
- [43] J. Wang, S.H. Ng, G.X. Wang, J. Chen, L. Zhao, Y. Chen, H.K. Liu, Synthesis and characterization of nanosize cobalt sulfide for rechargeable lithium batteries, J. Power Sources 159 (2006) 287–290.
- [44] A. Débart, L. Dupont, R. Patrice, J.M. Tarascon, Reactivity of transition metal (Co, Ni, Cu) sulphides versus lithium: the intriguing case of the copper sulphide, Solid State Sci. 8 (2006) 640–651.
- [45] W. Luo, Y. Xie, C. Wu, F. Zheng, Spherical CoS₂@carbon core-shell nanoparticles: one-pot synthesis and Li storage property, Nanotechnol 19 (2008)

075602.

- [46] Y. Yan, Y. Yin, Y. Guo, L. Wan, A Sandwich-like hierarchically porous carbon/ graphene composite as a high-performance anode material for sodium-ion batteries, Adv. Energy Mater. 4 (2014) 1301584.
- [47] X. Luo, C. Yang, Y. Peng, N. Pu, M.D. Ger, C.T. Hsieh, J. Chang, Graphene nanosheets, carbon nanotubes, graphite, and activated carbon as anode materials for sodium-ion batteries, J. Mater. Chem. A 3 (2015) 10320–10326.
- [48] J. Xu, M. Wang, N.P. Wickramaratne, M. Jaroniec, S. Dou, L. Dai, High-performance sodium ion batteries based on a 3D anode from nitrogen-doped graphene foams, Adv. Mater. 27 (2015) 2042–2048.
- [49] Q. Wang, L. Jiao, Y. Han, H. Du, W. Peng, Q. Huan, D. Song, Y. Si, Y. Wang, H. Yuan, CoS₂ hollow spheres: fabrication and their application in lithium-ion batteries, J. Phys. Chem. C 115 (2011) 8300–8304.
 [50] Q. Wang, L. Jiao, H. Du, W. Peng, Y. Han, D. Song, Y. Si, Y. Wang, H. Yuan, Novel
- [50] Q. Wang, L. Jiao, H. Du, W. Peng, Y. Han, D. Song, Y. Si, Y. Wang, H. Yuan, Novel flower-like CoS hierarchitectures: one-pot synthesis and electrochemical properties, J. Mater. Chem. 21 (2011) 327–329.
- [51] J.L. Gómez-Cámer, F. Martin, J. Morales, L. Sanchez, Precipitation of CoS vs ceramic synthesis for improved performance in lithium cells, J. Electrochem. Soc. 155 (2008) A189–A195.
- [52] A. Bhaskar, M. Deepa, T.N. Rao, MoO₂/Multiwalled carbon nanotubes (MWCNT) hybrid for use as a Li-ion battery anode, ACS Appl. Mater. Interfaces

5 (2013) 2555.

- [53] J.S. Cho, J.M. Won, J.K. Lee, Y.C. Kang, Design and synthesis of multiroomstructured metal compounds-carbon hybrid microspheres as anode materials for rechargeable batteries, Nano Energy 26 (2016) 466–478.
- [54] Q. Zhou, L. Liu, Z. Huang, L. Yi, X. Wang, G. Cao, Co₃S₄@ polyaniline nanotubes as high-performance anode materials for sodium ion batteries, J. Mater. Chem. A 4 (2016) 5505–5516.
- [55] L. David, R. Bhandavat, G. Singh, MoS₂/graphene composite paper for sodiumion battery electrodes, ACS Nano 8 (2014) 1759–1770.
- [56] D. Su, S. Dou, G. Wang, WS₂@ graphene nanocomposites as anode materials for Na-ion batteries with enhanced electrochemical performances, Chem. Commun. 50 (2014) 4192–4195.
- [57] J. Li, X. Shi, J. Fang, J. Li, Z. Zhang, Facile synthesis of WS₂ nanosheets-carbon composites anodes for sodium and lithium ion batteries, ChemNanoMat 2 (2016) 997–1002.
- [58] Y. Wang, C. Wang, Y. Wang, H. Liu, Z. Huang, Superior sodium-ion storage performance of Co₃O₄@ nitrogen-doped carbon: derived from a metal-organic framework, J. Mater. Chem. A 4 (2016) 5428–5435.
- [59] Z. Jian, P. Liu, F. Li, M. Chen, H. Zhou, Monodispersed hierarchical Co_3O_4 spheres intertwined with carbon nanotubes for use as anode materials in sodium-ion batteries, J. Mater. Chem. A 2 (2014) 13805–13809.