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## Three-dimensional graphene-supported nickel disulfide nanoparticles promise stable and fast potassium storage†

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Nickel sulfide ( $\text{NiS}_2$ ) is generally regarded as an appropriate anode for manufacturing new-type potassium-ion batteries (PIBs), while the development and application of  $\text{NiS}_2$  are hampered by poor intrinsic electrical conductivity and huge volumetric change during potassiation/de-potassiation. Herein, we construct self-adaptive  $\text{NiS}_2$  nanoparticles confined to a three-dimensional graphene oxide ( $\text{NiS}_2/3\text{DGO}$ ) electrode *via* *in situ* sulfurization and self-assembly processes. The as-obtained  $\text{NiS}_2/3\text{DGO}$  exhibits high reversible capacity ( $391 \text{ mA h g}^{-1}$ ) and outstanding rate behavior (stable cycling at  $1000 \text{ mA g}^{-1}$ ) for PIBs. Furthermore, *in situ* X-ray diffractometry and *ex situ* Raman test results elucidate partially reversible transformation from the cubic  $\text{NiS}_2$  phase to the  $\text{K}_x\text{NiS}_2$  intermediate, followed by generating a  $\text{Ni}^0$  and  $\text{K}_2\text{S}_4$  product. This phenomenon is caused by the conversion reaction mechanism of  $\text{NiS}_2$  nanocrystals along with an amorphous phase transition during the initial cycle. Such understandings may shed new light on the application of metal sulfides and give directions to design novel electrodes with desirable structural stability and lifespan.

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## Introduction

With the popularization of 5th generation (5G) wireless systems and the Internet of Things (IoT) technologies, the era in which everything is interconnected has set in motion a new wave in energy revolution.<sup>1</sup> Nowadays, lithium-ion batteries (LIBs) have been widely used in all aspects of our life and almost entirely equipped with mobile terminal equipment.<sup>1–3</sup> Nevertheless, considering the uneven distribution of lithium resources (0.0017 wt%) and high prices,<sup>4</sup> the economic benefits of LIBs for grid-scale energy storage are less attractive. Researchers have gradually turned their attention to potassium-ion batteries (PIBs) owing to their sustainable competitive advantages of abundant potassium reserves (1.5 wt%), high operating voltage, and fast ion conductivity in electrolytes.<sup>4</sup> Compared with that of sodium, the standard reduction potential of potassium is more near to lithium,<sup>4,5</sup> which brings

about a relatively high energy density of the PIBs. Besides, aluminium foil can be substituted in place of copper foil as a current collector at the anode side. This improvement not only significantly lowers the cost of the PIB but also effectively lessens the overall weight of the battery pack.<sup>6</sup> However, although some significant research work has been carried out,<sup>4,7–12</sup> the development and application of PIBs are still in the toddler stage. At present, considerable research work has been devoted to carbon materials because of their excellent electrical conductivity and high cost-benefit effectiveness.<sup>13–20</sup> However, the inherent defects of low theoretical specific capacity limit its further development.<sup>21–23</sup> Therefore, the development of ideal PIB anode materials with high specific energy and long-life is a pressing issue that needs to be overcome.

Transition metal sulfides have long been regarded as promising anode materials for secondary ion batteries owing to productive two-dimensional interlayer channels and numerous active sulfur sites;<sup>8,24–28</sup> however, only a few typical metal sulfides ( $\text{CoS}$ ,<sup>10</sup>  $\text{SnS}_2$ ,<sup>11</sup>  $\text{MoS}_2$ ,<sup>12,29</sup>  $\text{VS}_2$ ,<sup>30</sup>  $\text{SnS}$ ,<sup>31</sup> *etc.*) have received researcher's attention and been investigated in PIBs. Among such transition metal sulfides, nickel disulfide ( $\text{NiS}_2$ ) has rarely been empirically studied for its potassium-ion storage behaviour. Different from the intercalation reaction behaviour exhibited by graphite,  $\text{NiS}_2$  is a typical pyrite-type structure compound,<sup>32</sup> which exhibits a conversion reaction mechanism during the potassiation/de-potassiation process, thereby

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showing three times high theoretical capacity (*ca.* 870 mA h g<sup>-1</sup>) compared to graphite. Nevertheless, the unstable sulfur electrochemistry during cycling and the inherently slow kinetic properties of metal sulfide result in fast capacity decay and inferior rate performance.<sup>32–35</sup> One useful way to promote the improvement of electrochemical performance is to rationally design nanostructures with large surface areas and short ion diffusion pathways.<sup>36–40</sup> Another effective solution against these drawbacks is to combine the nanostructured NiS<sub>2</sub> with a conductive carbon matrix.<sup>8,10–12,26</sup> Recently, Ji and co-workers reported hierarchical flowerlike NiS<sub>2</sub> decorated with a multi-functional carbon anode material with enhanced cycling stability and rate performance,<sup>41</sup> further demonstrating the effectiveness of this strategy. However, due to the inherent complexity of the multi-electron transfer reaction process, the author's research on the structure and phase evolution of electrode materials still encounters some difficulties and lacks authentic evidence.

Herein, we designed a self-adaptive strain-relaxed PIB anode, which was constructed by three-dimensional graphene-supported nickel disulfide nanoparticles (NiS<sub>2</sub>/3DGO). Such a hierarchical structure of NiS<sub>2</sub>/3DGO greatly enhances ionic and electronic conductivity and makes full use of the transport capacity of an individual nanoparticle. Besides, the presence of 3DGO provides a highly elastic protective layer for the volume expansion of NiS<sub>2</sub> and effectively increases the electrostatic attraction to S<sub>2</sub><sup>2-</sup>. When it is applied in PIBs, the as-obtained NiS<sub>2</sub>/3DGO electrode exhibits an enhanced reversible capacity of 391 mA h g<sup>-1</sup> and remarkable rate behavior (260 mA h g<sup>-1</sup> at 1000 mA g<sup>-1</sup>). Furthermore, with advanced *in situ* X-ray diffractometer and *ex situ* Raman technology, the structure evolution and phase transition mechanism of the nickel disulfide anode during potassiation/de-potassiation were systematically investigated. We believe that such understandings are indispensable for exploring the transition metal sulfide materials and give directions to design novel electrode materials for large-scale energy storage.

## Experimental

### The synthesis of a Ni(OH)<sub>2</sub> precursor

First, 3 mmol of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was first dissolved in 80 mL deionized water. Then, 2 mmol NH<sub>4</sub>F and 5 mmol urea were added to obtain a transparent green solution after stirring for 10 min. Then, the obtained solution was transferred into a Teflon-lined (100 mL) stainless-steel autoclave. The autoclave was heated at 120 °C and kept for 6 hours, and then naturally cooled. The obtained green precipitate was washed several times and then put into a 60 °C vacuum oven and dried for later use.

### The synthesis of NiS<sub>2</sub>/3DGO

A self-adaptive strain-relaxed NiS<sub>2</sub>/3DGO hybrid material was synthesized *via* facile *in situ* sulfurization and self-assembly processes. The prepared nickel-based precursor (80 mg) was

redistributed in deionized water (30 mL). Subsequently, graphene oxide (GO) dispersion (5 mL, 2 mg mL<sup>-1</sup>) was dissolved in it. Finally, an appropriate amount of thioacetamide (TAA) was added. Then, the as-obtained solution was transferred into Teflon-lined (50 mL) and kept for 8 hours at 180 °C. The black solid was repeatedly washed several times before vacuum drying at 80 °C overnight.

### The synthesis of NiS<sub>2</sub> microflowers

The method for synthesizing NiS<sub>2</sub> microflowers is the same as that for preparing NiS<sub>2</sub>/3DGO. The difference is that the GO solution component is not introduced into the NiS<sub>2</sub> microflower synthesis process.

### Materials characterization

The microscopic characteristics of samples were investigated using a Japanese JEOL7100FA scanning electron microscope (SEM, 15–20 kV) and transmission electron microscopy with a scanning voltage of 200 kV (TEM, JEM-2100F). This equipment is also equipped with an X-ray energy spectrum analysis system, which can assist in the qualitative analysis of the chemical composition and distribution of materials. The D8 Advance powder X-ray diffractometer detected the structures of the as-prepared materials with Cu K $\alpha$ . The corresponding voltage and current parameters are 20 kV and 10 A, respectively, and the test angle is 10–80°. Thermogravimetric analysis measurement (Netzsch STA 449C) was performed from 30 °C to 800 °C at a heating rate of 10 °C min<sup>-1</sup> to detect the content of NiS<sub>2</sub>. Raman spectra were recorded using a Horiba Jobin Yvon Lab RAM HR800 Raman spectrometer with He-Ne laser excitation at 633 nm. X-ray photoelectron spectroscopy (XPS) was investigated using a VG Multilab 2000 system.

*In situ* X-ray diffractometer (XRD) was employed to analyze the crystal structure evolution and phase transition mechanism during the charging/discharging process. The XRD signals were acquired every 120 s using a Bruker D8 Discover X-ray diffractometer with a planar detector in still mode.

### Electrochemical measurements

Electrochemical characterization was performed using 2016 coin cells. The working electrode was prepared by applying a slurry containing NiS<sub>2</sub>/3DGO or NiS<sub>2</sub> microflowers (70 wt%), acetylene black (20 wt%), and a sodium carboxymethyl cellulose (10 wt%) binder on an aluminium foil, respectively. Then, the coated aluminium foil was put in a vacuum oven and dried at 80 °C for 24 hours. The dried aluminium foil was further cut into small square slices with a diameter of 10 mm and a thickness of 100  $\mu$ m, in which the average loading mass of NiS<sub>2</sub>/3DGO or NiS<sub>2</sub> microflowers is about 1.0 mg cm<sup>-2</sup>. The electrolyte used in the experiment was 1 M bis(fluorosulfonyl) imide potassium salt in ethylene carbonate/diethyl carbonate (EC : DEC = 1 : 1 Vol.%). The galvanostatic discharge/charge data measurement is performed using a LAND system. A Biologic VMP-3 electrochemical workstation was used to complete cyclic voltammetry and impedance testing.

## Results and discussion

The overall fabrication process of  $\text{NiS}_2$  microflowers ( $\text{NiS}_2$  MF) and  $\text{NiS}_2$ /3DGO is briefly illustrated in Fig. 1, including (i) the formation of 2D nickel hydroxide ( $\text{Ni(OH)}_2$ ) microflower precursor (Fig. S1†) and (ii) the *in situ* sulfurization and self-assembly processes. During the sulfurization step, thioacetamide is uniformly dispersed in the solvent and reacts quickly with water to form  $\text{H}_2\text{S}$  at high temperatures. The produced  $\text{H}_2\text{S}$  reacts with the 2D nickel hydroxide nanosheets, resulting in the transformation from a 2D  $\text{Ni(OH)}_2$  nanosheet template

to  $\text{NiS}_2$  nanoparticles (Fig. S2a†). Due to the lack of necessary bonding force between particles, the structure of  $\text{NiS}_2$  MF is unstable and easy to collapse (Fig. S2b†). Interestingly, with the introduction of GO into the system,  $\text{NiS}_2$  nanoparticles are preferentially nucleated and grown on the surface of GO<sup>42</sup> (Fig. S2c†). Meanwhile, the shrinking force generated by multi-layer self-assembly of GO firmly anchors nano-sized  $\text{NiS}_2$  particles between GO layers<sup>43</sup> (Fig. S2d†). This unique structure not only provides a highly elastic protective layer to alleviate the massive volume expansion but also stabilizes the dissolution of sulfides in the electrolyte.<sup>31</sup>

XRD patterns were investigated to detect the phase and crystal structure information of the finally obtained samples (Fig. 2a). All characteristic diffraction peaks of both  $\text{NiS}_2$  MF and  $\text{NiS}_2$ /3DGO can be well indexed with cubic pyrite  $\text{NiS}_2$  (JCPDS No. 89-3058), manifesting the as-prepared  $\text{Ni(OH)}_2$  precursor does successfully convert into  $\text{NiS}_2$  after long-time sulfurization. No distinct diffraction peak located at  $22.5^\circ$  resulting from the (002) plane of the graphene nanosheets was detected in  $\text{NiS}_2$ /3DGO. This phenomenon was caused by the growth of nanocrystalline  $\text{NiS}_2$  on the GO sheet surface, thus preventing the re-stacking of the GO sheet and covering the weak GO signal.<sup>44</sup> Meanwhile, based on Scherer's formula, the size of the  $\text{NiS}_2$  nanoparticles can be further reckoned to be in the range of 100–120 nm, which in accordance with the particle size statistics shown in Fig. S3.† For  $\text{NiS}_2$ /3DGO, two weak

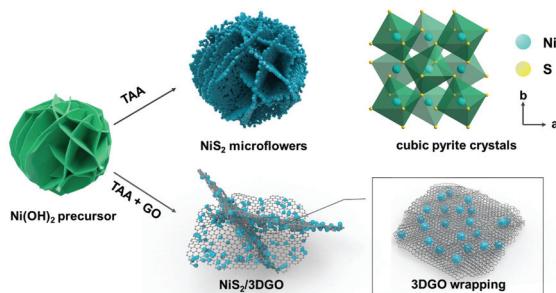


Fig. 1 Schematic illustration of the synthesis process for  $\text{NiS}_2$ /3DGO and  $\text{NiS}_2$  MF and the proposed stabilizing effects of 3DGO on the  $\text{NiS}_2$  electrode.

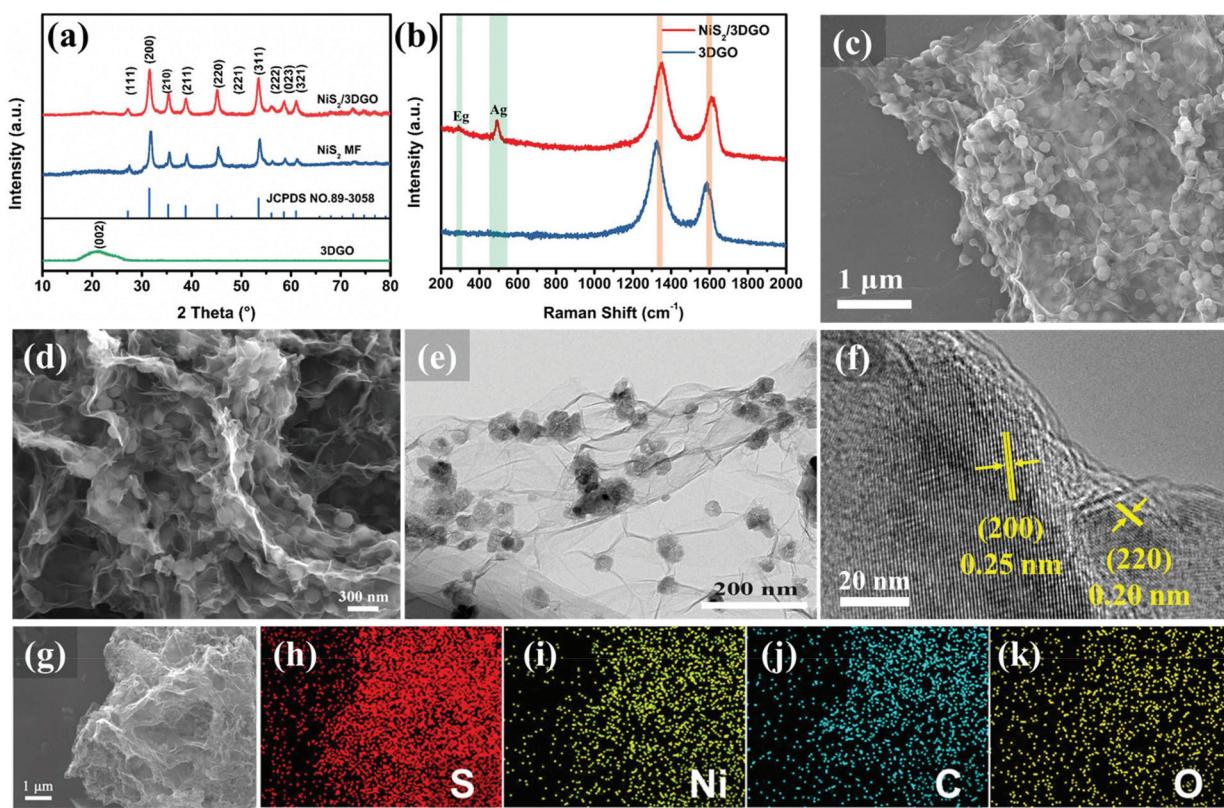


Fig. 2 (a) XRD comparison of  $\text{NiS}_2$ /3DGO,  $\text{NiS}_2$  MF and 3DGO; (b) Raman spectrum of  $\text{NiS}_2$ /3DGO and 3DGO; (c and d) Representative SEM images of  $\text{NiS}_2$ /3DGO; (e and f) TEM and HRTEM images of  $\text{NiS}_2$ /3DGO; (g–k) SEM images and corresponding elemental mapping analysis of  $\text{NiS}_2$ /3DGO.

Raman peaks are detected at 289 and 490  $\text{cm}^{-1}$ , which is attributed to  $E_g$  and  $A_g$  modes of  $\text{NiS}_2$ , respectively.<sup>45,46</sup> Besides, the Raman peaks at 1353 and 1608  $\text{cm}^{-1}$  are assigned to the D-band and G-band in GO.<sup>47</sup> The intensity ratio ( $I_D/I_G$ ) of these two adjacent peaks is about 1.24 and lower than that of the 3DGO (1.44), confirming that more defects and disorder exists in the  $\text{NiS}_2$ /3DGO structure.<sup>31</sup> Meanwhile, the D and G peaks of 3DGO samples are shifted toward lower wavenumbers compared to those of  $\text{NiS}_2$ /3DGO samples, manifesting that the number of GO layers in 3DGO has increased significantly (Fig. 1b). This phenomenon further illustrates the fact that the presence of  $\text{NiS}_2$  nanoparticles can effectively suppress the shrinkage of the GO layer.

The microscopic morphology of the  $\text{NiS}_2$ /3DGO is shown in Fig. 2c–f. Repprehensive SEM and TEM images show that  $\text{NiS}_2$ /3DGO composite exhibits a 3D interconnected structure and  $\text{NiS}_2$  nanoparticles *in situ* nucleated and grown on the layers of the 3DGO substrate during the self-assembly process (Fig. 2c–e). Moreover, high-resolution TEM shows that the lattice fringes of  $\text{NiS}_2$ /3DGO exhibit interplanar spacings of 0.25 nm and 0.20 nm, which corresponds to the (200) and (220) planes of  $\text{NiS}_2$ , respectively (Fig. 2f). The corresponding elemental mapping of  $\text{NiS}_2$ /3DGO verifies that the Ni, S, C, and O elements were uniformly distributed in the hierarchical 3D interconnected structure (Fig. 2g–k and Fig. S4†).

The content of 3DGO in the as-prepared  $\text{NiS}_2$ /3DGO electrode was investigated by thermogravimetric analysis (TGA, Fig. S5†). The weight loss (2.92 wt%) occurring below 150 °C results in the vaporization of adsorbed water.<sup>48</sup> This part should be deducted during the calculation to reflect the authenticity of the result accurately. In the following stage, the weight loss and weight gain can be ascribed to the decomposition of 3DGO and the oxidation of  $\text{NiS}_2$ , respectively. Accordingly, the mass ratio of 3DGO in the  $\text{NiS}_2$ /3DGO composite is calculated to be 9.86%.

The surface chemical bonding states of Ni, S, C, and O in  $\text{NiS}_2$ /3DGO were further examined by XPS (Fig. 3a). Four peaks recorded at 284.6, 285.5, 286.7, and 288.6 eV can be separated from the C 1s spectrum (Fig. 3b), which corresponds to C=C, C-C, C-O, and O-C=O groups, respectively.<sup>49,50</sup> This further proved the existence of GO in  $\text{NiS}_2$ /3DGO. In Fig. 3c, two pairs of peaks can be detected at 856 and 874 eV, which is in agreement with 2p<sub>3/2</sub> and 2p<sub>1/2</sub> of Ni in cubic pyrite  $\text{NiS}_2$ .<sup>41</sup> Moreover, the S 2p spectra could be fitted to two adjacent peaks at 162.5 and 163.7 eV that is ascribed to 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks for  $\text{S}_2^{2-}$ , respectively (Fig. 3d).

The electrochemical tests of the  $\text{NiS}_2$  MF and  $\text{NiS}_2$ /3DGO hybrid electrode for potassium ion storage were evaluated ranging from 0.01 to 2.0 V (vs.  $\text{K}^+/\text{K}$ ). A noticeable reduction peak appeared at ~1.0 V and disappeared in the subsequent cycles during the initial negative scan process (Fig. 4a). This process was ascribed to an amorphous intermediate phase  $\text{K}_x\text{NiS}_2$  formed due to the original cubic  $\text{NiS}_2$  lattice break and reconstructed during  $\text{K}^+$  intercalation.<sup>51</sup> The following two reduction peaks at 0.68 V and 0.55 V are ascribed to the irreversible solid-electrolyte interface film (SEI) and the further

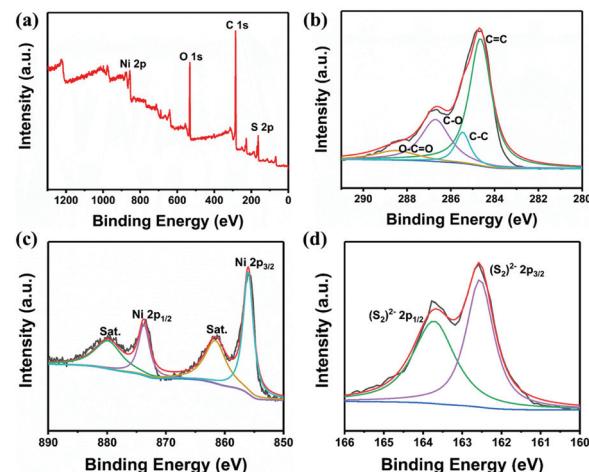


Fig. 3 (a) The XPS survey spectra of  $\text{NiS}_2$ /3DGO; (b) C 1s; (c) Ni 2p; (d) S 2p.

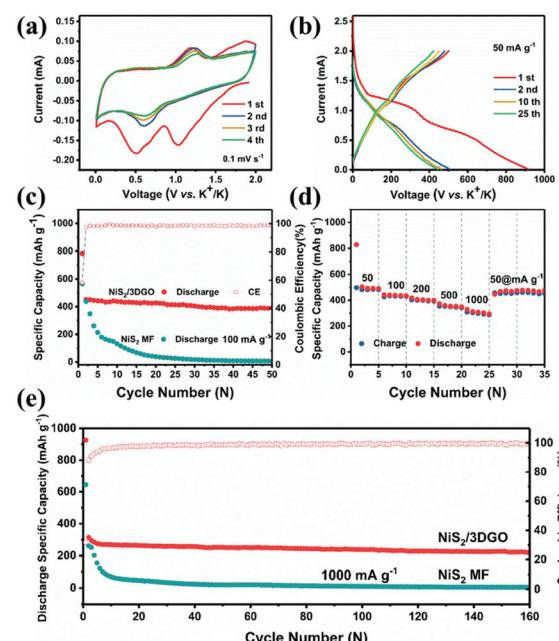


Fig. 4 (a) CV test result for the initial four cycles of  $\text{NiS}_2$ /3DGO at 0.1  $\text{mV s}^{-1}$ . (b) Representative galvanostatic discharge/charge curves of  $\text{NiS}_2$ /3DGO at 50  $\text{mA g}^{-1}$ . (c) Cycling performance of  $\text{NiS}_2$ /3DGO and  $\text{NiS}_2$  MF at 100  $\text{mA g}^{-1}$ . (d) Rate performance of  $\text{NiS}_2$ /3DGO at a different density. (e) Long-term cycling stability of  $\text{NiS}_2$ /3DGO at 1000  $\text{mA g}^{-1}$ .

conversion process of  $\text{K}^+$  with  $\text{K}_x\text{NiS}_2$ , respectively. For the reversed positive scan, two distinct peaks are detected at 1.18 V and 1.87 V, which are attributed to the conversion reaction of  $\text{Ni}^0 + \text{K}_2\text{S}_4$  to form  $\text{K}_x\text{NiS}_2$  and the further extraction of  $\text{K}^+$  to form amorphous  $\text{NiS}_2$ , respectively. Both the oxidation peak and the reduction peak shifted slightly in the subsequent cycles, which indicates that an activation process may occur in

the initial cycle,<sup>52</sup> thereby achieving better  $K^+$  transport kinetics.

Fig. 4b and Fig. S6<sup>†</sup> show the comparison of galvanostatic discharge/charge (GDC) curves of the  $\text{NiS}_2$ /3DGO composite and  $\text{NiS}_2$  MF anode at  $50 \text{ mA g}^{-1}$ , respectively. The  $\text{NiS}_2$ /3DGO sample showed a distinct higher discharge platform (1.0 V) and a highly consistent GDC curve compared to  $\text{NiS}_2$  MF (0.8 V) during the charging/discharging process, manifesting that  $\text{NiS}_2$ /3DGO has much less polarization and better capacity retention compared to  $\text{NiS}_2$  MF. According to the cycling performance of  $\text{NiS}_2$ /3DGO and  $\text{NiS}_2$  MF at  $100 \text{ mA g}^{-1}$  (Fig. 4c). The  $\text{NiS}_2$ /3DGO electrode showed a high initial discharge capacity with a reasonable initial coulombic efficiency (ICE) of 59%. The slightly low ICE is relative to the irreversible SEI and the reconstruction of original cubic  $\text{NiS}_2$  lattice during  $K^+$  intercalation.<sup>41</sup> The  $\text{NiS}_2$ /3DGO electrode exhibits a high capacity retention of 88% after 50 cycles (compared with the second cycle). However, the cycling curve of  $\text{NiS}_2$  MF without 3DGO supported shows an inferior cycling performance. Accurately, the  $\text{NiS}_2$  MF only delivered a specific capacity of  $793.5 \text{ mA h g}^{-1}$  with poor cycling performance. This result further demonstrates that the presence of the elastic GO protective layer dramatically enhances the structural stability of  $\text{NiS}_2$ /3DGO and makes full use of the transport capacity of individual  $\text{NiS}_2$  nanoparticle.

When gradually increasing the current density at rate stages of  $50, 100, 200, 500$ , and  $1000 \text{ mA g}^{-1}$ , the GDC curves remain stable and keep reversible capacities of  $494, 398, 339, 283$ , and  $235 \text{ mA h g}^{-1}$ , respectively. When returning to  $50 \text{ mA g}^{-1}$ , the  $\text{NiS}_2$ /3DGO quickly recovers to a high specific capacity of  $477 \text{ mA h g}^{-1}$  (about 97% capacity recovery rate). Moreover,  $\text{NiS}_2$ /3DGO still showed an excellent capacity retention of  $260 \text{ mA h g}^{-1}$  after 160 cycles and high CE of approximately 100% at each cycle (Fig. 4e), far beyond the reversibility of  $\text{NiS}_2$  MF ( $<20 \text{ mA h g}^{-1}$  after 50 cycles). Meanwhile, pioneering studies of typical transition metal sulphides were compared with our work. As shown in Table S1<sup>†</sup> and Fig. S7,<sup>†</sup> the obtained  $\text{NiS}_2$ /3DGO electrode had a competitive electrochemical performance in KIBs. Especially in the term of capacity, which is much better than those previously reported metal sulphide anodes. The EIS results verify that after the first discharge/charge, the impedance decreases significantly (Fig. S8<sup>†</sup>). After short activation, the impedance remained stable after 10, 30, and 50 cycles, which further proves that the  $\text{NiS}_2$ /3DGO electrode has a stable interface structure.

The kinetic research based on CV analysis at scan rates of  $0.1$  to  $1.0 \text{ mV s}^{-1}$  is employed to acquire a deeper understanding of the outstanding rate performance of  $\text{NiS}_2$ /3DGO. Fig. 5a shows that the CV curve at each scanning speed shows similar peak positions and gradually broadened as the scan rate increases. These observations indicate that the  $\text{NiS}_2$ /3DGO electrode has typical pseudocapacitive potassium storage and excellent surface-dominated characteristics, allowing for ultra-fast potassium ion insertion and extraction. A general method to measure the degree of pseudocapacitive effect is to make a

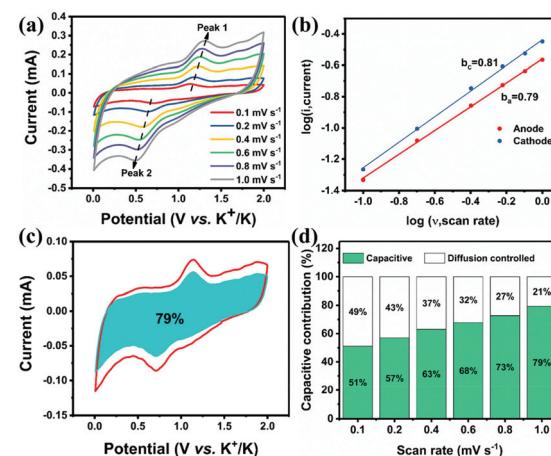
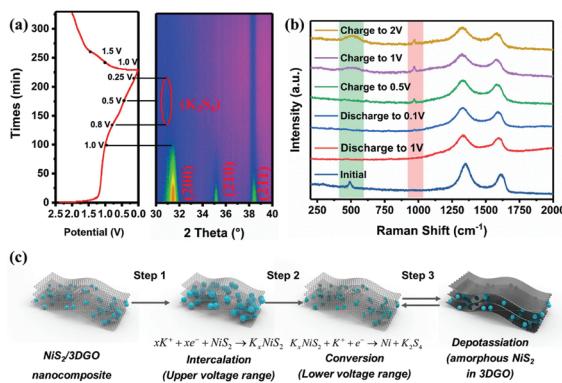


Fig. 5 (a) CV curves of  $\text{NiS}_2$ /3DGO at scan rates range from  $0.1$  to  $1.0 \text{ mV s}^{-1}$ . (b) Linear relationship of  $\log(i)$  vs.  $\log(v)$ . The contribution ratio of the capacitive capacities and diffusion-limited capacities at  $1 \text{ mV s}^{-1}$  (c) and at different scan rates (d).

qualitative analysis based on the following equation:  $i = av^b$ , where  $a$  and  $b$  are constants.<sup>53</sup> Generally, for the ideal Faraday intercalation process controlled by the diffusion effect, the  $b$  value is  $0.5$ ; for a surface-dominated process without diffusion control, the  $b$  value is  $1.0$ .<sup>15</sup> Hence, the higher  $b$ -value of  $\text{NiS}_2$ /3DGO ( $0.81/0.76$ ) was determined by the cathodic/anodic peaks, suggesting a more favoured surface capacitance-dominated process of  $\text{NiS}_2$ /3DGO (Fig. 5b). Moreover, by further dividing the response current at the same potential into a surface-dominated process ( $k_1v$ ) and a diffusion-dependent process ( $k_2v^{1/2}$ ) as the following equation:  $i = k_1v + k_2v^{1/2}$ , the percentage of capacitive contribution can be quantified. In consequence, 79% of the total capacity can be considered to be the capacitance contribution of the  $\text{NiS}_2$ /3DGO electrode at a scan rate of  $1.0 \text{ mV s}^{-1}$ , explaining the fundamental reason for the excellent rate performance of  $\text{NiS}_2$ /3DGO (Fig. 5c). Fig. 5d shows the investigation of the contribution of capacitance at all scan rates. As expected, the capacitance contribution is gradually increasing along with the scan rate. Such excellent pseudo-capacitive storage behaviour is primarily related to the abundant topological defects and excellent conductivity on the GO surface. It can maximize the surface charge storage and effectively improve the rapid pseudocapacitive processes at the interface between  $\text{NiS}_2$  and the electrolyte.<sup>54</sup>

In order to further reveal the phase transition process, *in situ* XRD analysis was performed. Fig. 6a shows that the as-fabricated  $\text{NiS}_2$ /3DGO electrode exhibits the characteristic peaks of (200), (210) and (211) at  $31.5^\circ, 35.3^\circ$ , and  $38.8^\circ$ , respectively. When the cell discharged to  $1.0 \text{ V}$ , the intensity of each diffraction peak decreased clearly, suggesting that  $K^+$  is gradually inserted into the  $\text{NiS}_2$  host material along with an intermediate phase  $\text{K}_x\text{NiS}_2$  formation (Fig. 6a and Fig. S9<sup>†</sup>). The standard peak of  $\text{NiS}_2$  disappears when discharged to  $0.8 \text{ V}$ . Simultaneously, an obvious peak well consistent with  $\text{K}_2\text{S}_4$

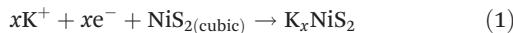


**Fig. 6** (a) *In situ* XRD results of NiS<sub>2</sub>/3DGO during the first cycle at the cut-off voltage of 0.01–2.0 V. (b) *Ex situ* Raman spectrum of NiS<sub>2</sub>/3DGO at different discharged/charged states. (c) Schematic illustration of the potassium storage mechanism.

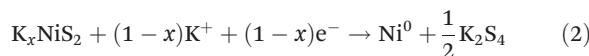
(JCPDS No. 43-0795) appeared at about 30.9°. The final product is K<sub>2</sub>S<sub>4</sub> instead of K<sub>2</sub>S, while Li<sub>2</sub>S/Na<sub>2</sub>S (analog of K<sub>2</sub>S) is usually formed in LIBs/NIBs,<sup>51,55</sup> manifesting that the conversion reaction occurs and a new phase K<sub>2</sub>S<sub>4</sub> and Ni<sup>0</sup> formation. No obvious metallic Ni characteristic diffraction peaks were observed in XRD. The reasonable interpretation is that the *in situ* formed Ni nanoparticles that are presumably smaller than the X-ray coherence length.<sup>56</sup> Moreover, no significant peak was observed during the subsequent charging process, suggesting an irreversible amorphous phase transition accompanied by the destruction of the original cubic NiS<sub>2</sub> lattice during K<sup>+</sup> intercalation. To confirm this point, *ex situ* Raman analysis was performed at different stages. As shown in Fig. 6b, with the progress of discharge, the intensity of NiS<sub>2</sub> characteristic peak reflection at 490 cm<sup>-1</sup> disappeared. Then, a broadening peak is observed when charged to 1 V, demonstrating that the original ordered cubic phase NiS<sub>2</sub> (denoted as NiS<sub>2</sub>(cubic)) transformed into a disordered amorphous phase NiS<sub>2</sub> (denoted as NiS<sub>2</sub>(amorphous)), which is consistent with the test results of *in situ* XRD. The Raman peak at around 245 cm<sup>-1</sup> was not detected, which may be ascribed to the addition of acetylene black and the binder reduced the Raman intensity of the original material. Interestingly, an additional Raman peak at 969.1 cm<sup>-1</sup> was detected when discharged to 0.1 V and kept persisting in the subsequent charging process, which may correspond to the SEI film formed during the initial cycle.<sup>57</sup> Therefore, the overall reaction process in the initial cycle was proposed as the following equation (Fig. 6c):

During the discharging process:

From OCV to 1.0 V:

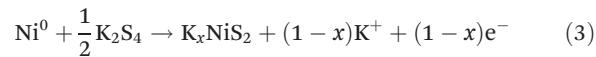


From 1.0 V to 0.2 V:

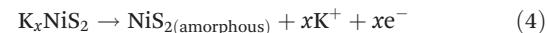


During the charging process:

From 0.2 V to 1.2 V:



From 1.2 V to 2.0 V:



## Conclusions

In summary, a self-adaptive strain-relaxed NiS<sub>2</sub>/3DGO hybrid electrode was fabricated through *in situ* sulfurization and self-assembly processes. NiS<sub>2</sub>/3DGO presents a well-defined 3D conductive network in which 3DGO provides rich electronic conductive channels and effectively improves the rapid pseudocapacitive processes at the interface between NiS<sub>2</sub> nanoparticles and the electrolyte. Besides, the high flexibility and elasticity GO layer can be self-adaptive to the volumetric change of NiS<sub>2</sub>. When applied in PIBs, NiS<sub>2</sub>/3DGO exhibits high specific reversible capacity (451 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>), good cycling stability (260 mA h g<sup>-1</sup> at 1000 mA g<sup>-1</sup> after 160 cycles), and excellent rate performance (97% recovery ratio). Furthermore, the combination of *in situ* XRD and *ex situ* Raman observations confirmed that NiS<sub>2</sub> undergoes a deep conversion reaction of K<sub>x</sub>NiS<sub>2</sub> to form K<sub>2</sub>S<sub>4</sub> and Ni<sup>0</sup> during the initial cycle. This study describes the great potential of the NiS<sub>2</sub>/3DGO electrode applied in PIBs and gives directions to design novel high-performance electrode materials.

## Conflicts of interest

There are no conflicts to declare.

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