Design of coherent anode materials with 0D Ni$_3$S$_2$ nanoparticles self-assembled on 3D interconnected carbon networks for fast and reversible sodium storage†

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There has been tremendous progress in development of nanomaterials for energy conversion and storage, with sodium-ion batteries (SIBs) attracting attention because of the high abundance of raw materials and low cost. However, inferior cycling stability, sluggish reaction kinetics, and poor reversibility hinder their practical applications. In the present study, Ni$_3$S$_2$/carbon nanocomposites with coherent nanostructures were successfully used as anodes in half- and full-cells. Outstanding cycling and rate performances are attributed to a synergistic effect between the Ni$_3$S$_2$ nanoparticles and interconnected carbon networks. The coherent porous framework effectively alleviated volume changes of Ni$_3$S$_2$, shortened the Na$^+$ diffusion path, and accelerated electron transport and ionic diffusion during the electrochemical reaction. Moreover, conversion reaction products can be confined by the entangled carbon networks, leading to reversible redox reactions as demonstrated in ex situ XRD studies. The coherent Ni$_3$S$_2$/C nanocomposites demonstrated a highly reversible charge capacity of 453 and 430 mA h g$^{-1}$ at a current density of 0.1 and 0.4 A g$^{-1}$ over 100 cycles, respectively. At a current density of 2.0 A g$^{-1}$, high rate capacities of 408 mA h g$^{-1}$ can be attained over 200 cycles. The high performance of Na$_3$V$_2$(PO$_4$)$_3$/Ni$_3$S$_2$ full-cells enrich prospects for future practical applications.

1. Introduction

The ever-increasing global consumption of fossil fuels and their consequent environmental pollution have become a pressing challenge in modern society.$^{1,2}$ A variety of clean renewable energy conversion and storage technologies have been investigated and some have been successfully commercialized, such as solar cells, supercapacitors, lithium ion batteries, and thermoelectric devices.$^{3-5}$ Intensive research and industrial development of lithium ion batteries (LIBs) over the past 30 years$^6$ have made them an indispensable portable power source, pervasive in our electronic device-dependent modern life, because of their high-energy density, high power density, and environmental friendliness as well as their long cycle life. Despite the great success and steady advancement of LIB technology, there remain some challenges.$^{2,3}$ The relatively low abundance of Li has forced researchers to pursue alternative technologies with materials in higher abundance with broader distribution.$^{7-9}$ Sodium ion batteries (SIBs) are one of the most promising alternatives studied in recent years, as sodium is one of the most abundant elements on the Earth.$^{2,9-12}$ In addition, sodium shares similar structure and energy storage mechanism with its lithium counterpart. Hence, there is strong interest in developing high-performance anodes$^{13,14}$ and cathodes$^{15,16}$ for SIBs. As the sodium ion possesses a larger ionic radius than the lithium ion ($1.02$ Å vs. $0.76$ Å),$^4$ electrodes commonly suffer from slow sodium ion diffusion and large pulverization during discharge/charge processes. Various nanostructured materials have been studied to circumvent the slow kinetics in development of new electrodes for SIBs. In addition to metal oxides, transition metal sulfides (MS$_x$) have been explored as alternative anodes in LIBs and SIBs because of their good mechanical stability and enhanced reversibility.$^{17-20}$ The weaker chemical bonding of M–S than that of M–O could also be favorable for the electrochemical processes.$^{18}$

Nickel sulfides (Ni$_x$S) including NiS, NiS$_2$, Ni$_3$S$_4$, and Ni$_9$S$_8$ are widely known as promising anode materials.$^{21-24}$ Among them, Ni$_3$S$_2$ exhibits some unique properties in various clean
energy technologies, including photocatalytic and electrocatalytic production of H₂ and supercapacitors.²⁵–²⁷ Ni₃S₂ has attracted attention as a promising anode in SIBs because of its stable forms and smaller volume change than other nickel sulfides.²⁸ Commonly known as a “Heazlewoodite”-type mineral,²⁹ it is naturally abundant, cheap, and stable. The overall reaction of Ni₃S₂ in SIBs is given in eqn (1):

\[ \text{Ni}_3\text{S}_2 + 4\text{Na}^+ + 4\text{e}^- \rightarrow 3\text{Ni} + 2\text{Na}_2\text{S} \]  

When used in SIB anodes, Ni₃S₂ suffers from poor electrical conductivity, large pulverization, and insufficient surface area for electrolyte contact.³⁰,³¹ Several strategies have been reported to improve the electrochemical properties through hybridizing Ni₃S₂ with conductive polymer,³² carbon nanotube,³³ graphene,³³ and nickel foam.³³ However, despite some success, the SIB performances are still unsatisfactory because of the irreversible conversion reaction. This drawback is usually a result of multiple electron transfers occurring per metal centre during the conversion reactions,³³ making conversion of the Ni₃S₂ to metal Ni and Na₂S in the initial sodiation process irreversible. As a result, most of the Na₂S generated in situ cannot effectively react with the Ni to recover the Ni₃S₂ phase in the recharge process. The unreacted Na₂S can be oxidized to poly-sulfides during the desodiation process, which experience a dissolving/shuttle effect leading to severe capacity losses, as known in Li-S batteries.³⁴–³⁶ Xie et al. introduced a protected carbon layer on the surface of MoSe₂ and CVD-graphene nano-composites to suppress the “shuttle effect” resulting in a high performance SIB anode.³⁷ George et al. used “double wall carbon nanotubes (DWCNTs)” in the MoS₂ electrode to form an entangled network to migrate the shuttle effects, achieving promoted LIBs performance.³⁷ However, the high cost of preparation procedures and high-rate performances are still not ideal. Therefore, development of a Ni₃S₂ electrode with fast kinetics for high storage capacity at a high rate remains challenging.

From this perspective, this study demonstrates fast and reversible sodium ion storage in coherent Ni₃S₂/carbon nano-composites (referred as Ni₃S₂/C). First, coherent carbon networks derived from NaCl as template and citric acid as carbon precursor, not only provide sufficient contacts between Ni₃S₂ and electrodes, but also shorten sodium-ion diffusion pathways and enhance electrical conductivities.³⁸–³⁹ Moreover, the entangled confinement, coherent structure effectively promoted the reversible reaction by confining discharge products. The resulting unique interconnected structures demonstrated excellent cyclic and rate properties (retention 85% and 87% at 0.1 and 0.4 A g⁻¹ for 100 cycles, respectively. 408 mA h g⁻¹ at 2.0 A g⁻¹ over 200 cycles). A Na₃V₃(PO₄)₉/rGO ∥ Ni₃S₂/C full cell with excessive cathode materials was assembled and found to deliver a storage capacity of 101 mA h g⁻¹ over 30 cycles at 0.5 A g⁻¹. Enhanced sodium ion diffusion and high reversibility lead to high-rate capacity and cyclic performance. The purposely designed coherent Ni₃S₂/C nanostructure exhibits higher reversible capacity and rate capability when used as an SIB anode compared with reported Ni₃S₂-based electrodes.

2. Experimental sections

2.1 Chemicals and materials

All chemicals were used without further purification. Nickel(II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O, 98%], sodium carbonate (Na₂CO₃, 98%), and sodium chloride (NaCl, 99.0%) were bought from Alfa Aesar, USA. Thiourea (CH₄N₂S, 99.0%), citric acid (C₆H₈O₇·3H₂O, 99%), ammonium dihydrogen phosphate (NH₄H₂PO₄, 99.999%), and vanadyl acetylacetonate (V(acac)₃, 98%) were purchased from Sigma-Aldrich, USA. Ultrapure deionized water was used for preparation of all aqueous solutions.

2.2 Synthesis of coherent Ni₃S₂/C nanocomposites

In a typical synthesis process, 0.29 g of Ni(NO₃)₂·6H₂O and 0.38 g of thiourea were dissolved in 20 mL deionized (DI) water with stirring at room temperature. Then 0.18 g of citric acid and 4 g NaCl were added, and stirred for 30 min. Then the mixture was frozen in a refrigerator at −20 °C overnight, followed by freeze-drying under vacuum for 48 h. The obtained gel was ground and further annealed under high-purity nitrogen (N₂) for 2 h at 800 °C with a ramping rate of 5 °C min⁻¹, then cooled to room temperature naturally under the protection of N₂. The obtained black powders were washed five times using DI water to completely remove the NaCl template. After drying in air at 45 °C for 12 h, the final products were obtained.

2.3 Synthesis of Na₃V₃(PO₄)₉ cathode material

Na₃V₃(PO₄)₉/graphene composites (named NVP/rGO) were synthesized as reported in the literature.⁴⁰ 0.75 mmol Na₂CO₃, 1 mmol V(acac)₃, and 1.5 mmol NH₄H₂PO₄ were dissolved in 30 mL DI water and stirred for 12 h at room temperature. NVP gel was obtained via a hydrothermal reaction at 180 °C for 6 h. Then 4.5 mL graphene oxide solution (prepared by modified Hummers’ method, 2 mg mL⁻¹) was added with strong stirring. After freeze-drying, NVP/rGO precursors were obtained through heat treatment with the condition of Ar/H₂, 95 : 5 in vol% and 750 °C for 8 h.

2.4 Structural characterizations

Crystal structures of the samples were identified using X-ray diffraction (PANalytical XPert Pro with Cu-Kα radiation). The Raman spectrum was obtained using a Renishaw inVia system (Renishaw inVia Raman Microscope, the USA) with a laser wavelength of 514 nm. Thermogravimetric analysis (TGA) was performed on a TG instrument (NETZSCH STA 409 C) from room temperature to 700 °C in air with heating rate of 10 °C min⁻¹. Morphologies were characterized using a field emission scanning electron microscope (SEM, FEI Sirion XL30). Microstructures were investigated using a transmission electron microscope (TEM, FEI Tecnai G2 F20). XPS measurements were performed using an X-ray microprobe (Thermo Fisher Scientific ESCALAB 250Xi) with Al Kz radiation. Nitrogen adsorption-desorption isotherms were measured using a Quanta-chrome NOVA 4200e system. Specific surface areas were determined using a multi point-Brunauer–Emmett–Teller (BET) method.
2.5 Electrochemical measurements

Half cells were performed using coin-type 2016 cells at room temperature. The working electrode was prepared by mixing the active materials, carbon black (Super-P), and poly(vinylidene fluoride) (PVDF) at a weight ratio of 8 : 1 : 1, and then pasting on pure Cu foil, followed by drying at 80 °C under vacuum overnight. For the SIB half cell, sodium pieces were used as both the counter electrode and reference electrode, vacuum overnight. For the SIB half cell, sodium pieces were used as both the counter electrode and reference electrode, glass fiber (Whatman GF/A) as the separator, and 1 M NaClO4 in ethylene carbonate/diethyl carbonate/fluoroethylene carbonate (EC/DEC/ FEC, 1 : 1 : 0.05 in volume%) as electrolyte. Cyclic voltammetry (CV) curves were recorded on a CHI 605C electrochemical workstation (the scan rate was 0.2 mV s⁻¹). The coherent Ni₃S₂/C composites before and after removal of NaCl as templates for pores. In addition to strong peaks of NaCl (JCPDS no. 44-1418), other peaks are in good accordance with Ni₃S₂ of Heazlewoodite phase. The influence of annealing temperature on phase purity is shown in Fig. S3.† At low annealing temperature (600 °C), a mixture of several nickel sulfides containing Ni₀.₉₆S, Ni₉S₈, and Ni₃S₂ can be detected, which may be ascribed to insufficient reactions of the precursors. Increasing the temperature to 700 °C, the Ni₀.₉₆S disappeared and the main phases were indexed to Ni₃S₂ and Ni₉S₈. On increasing the temperature further to 800 °C, the as-obtained products were all pure Ni₃S₂ without other nickel sulfides. Results indicate that Ni₃S₂ is more stable than other nickel sulfides, which is helpful for practical applications. Thermogravimetric analyses (TGA) of “Ni(NO₃)₂ + thiourea + citric acid + NaCl” composites were conducted under N₂ from room temperature to 800 °C (Fig. S4a†), with a ramping rate of 5 °C min⁻¹. The initial weight losses (<300 °C) could be assigned to evaporation of crystal water and decomposition of Ni-salt. From 300 °C to 800 °C, together with results shown in Fig. S3,† continuous sulfurization processes occurred.

Fig. 2a presents the X-ray diffraction (XRD) pattern of coherent Ni₃S₂/C nanocomposites. All the diffraction peaks match well with crystalline Ni₃S₂ (JCPDS no. 44-1418) with peaks at 2θ of 21.7°, 31.1°, 37.8°, 44.3°, 49.7° and 55.1° readily assigned to respective (101), (110), (003), (202), (113), and (122) facets of Ni₃S₂.

3. Results and discussions

3.1 Growth strategy and structure characterization of coherent Ni₃S₂/C

The coherent Ni₃S₂/C nanocomposite was synthesized via template-directed sol-gel processing and post-annealing, as illustrated in Fig. 1. First, precursor was prepared by dissolving Ni(NO₃)₂, thiourea, citric acid, and NaCl in DI water at room temperature to form a homogenous solution. The solution was then frozen in a freezer for 24 hours at −20 °C. During this step, NaCl crystallizes to form small crystallites that serve as hard templates. Afterwards, water was removed via a freeze-drying process (−20 °C for 2 days). As shown in Fig. S1a,† NaCl cubic crystals with an average diameter of 10 microns were formed. Subsequent annealing treatment at 800 °C in high purity N₂ for 2 h resulted in black mixtures containing Ni₃S₂/C adsorbed on the surface of cubic NaCl (Fig. S1b†). Finally, coherent Ni₃S₂/C was obtained by dissolving NaCl in water (Fig. S1c†).

Fig. 2b shows scanning electron microscopy (SEM) images of the product before washing NaCl templates. Micro-sized cubic NaCl crystals are encapsulated uniformly in a thin film-like Ni₃S₂/C nanocomposite. As-mentioned self-assembly strategies
provide a surface for directing synthesis of the Ni$_3$S$_2$/carbon networks. From the SEM image of Fig. 2c, the laminar Ni$_3$S$_2$/carbon foam-like structure with a 3D interconnected macro-porous network was retained. The product has unique interconnected sub-micrometer sized macro-porous networks, and the walls of the interconnected 3D porous networks demonstrate a clear curved profile and a very low contrast, which arise from the ultrathin thickness and high mechanical flexibility (Fig. 2d). If the sulfur precursor was replaced by L-cysteine (free of nitrogen functional group), some aggregated sub-micron particles with a diameter of about 200 nm on carbon sheets were clearly distinguished (Fig. S4b†). The morphology shown in Fig. 2d is significantly different through use of L-cysteine, perhaps because of a linking role of nitrogen. SEM images and XRD results of “bare Ni$_3$S$_2$” (prepared by adding NaCl but without citric acid) and “bulk Ni$_3$S$_2$/C” (obtained by adding citric acid as carbon precursors but without NaCl template) are also shown for comparison in Fig. S5.† Only large particles were obtained in bare Ni$_3$S$_2$, confirming that carbon can provide abundant surfaces and prevent Ni$_3$S$_2$ nanoparticles from agglomeration during the annealing process (Fig. S5a†). In Fig. S5b† only Ni$_3$S$_2$ embedded in carbon layers could be attained. It should be emphasized that no coherent nanostucture was formed in bulk Ni$_3$S$_2$ + C products, demonstrating the key guiding role of the NaCl template. Results strongly indicate that the NaCl templates and carbon precursors play indispensable roles in formation of homogeneous coherent nanostructures. XRDS results of coherent Ni$_3$S$_2$/C, bare Ni$_3$S$_2$, and bulk Ni$_3$S$_2$ + C (Fig. S2a†) show a pure phase of crystalline Ni$_3$S$_2$. The microstructures of the coherent Ni$_3$S$_2$/C were further studied by TEM, revealing a continuous ultrathin carbon layer anchored with uniform Ni$_3$S$_2$ nanoparticles (5–10 nm) (Fig. 2e). The carbon layers are about 5 nm in thickness, which facilitates rapid transport of electrons and sodium ions to Ni$_3$S$_2$ nanoparticles. Close examination under high-resolution TEM (Fig. 2f) reveals individual Ni$_3$S$_2$ nanocrystals with clear lattice fringes attached to carbon substrates.

TGA of coherent Ni$_3$S$_2$/C composites in air were recorded from room temperature to 700 °C. As shown in Fig. 3a, slight weight loss in the initial stage results from removal of water and residual organics. Approximately 73% of the original sample weight remained after TGA in air. The resultant solid combustion product is NiO (Fig. S6†, JCPDS: 47-1049). The overall reaction is given in eqn (2).

$$2\text{Ni}_3\text{S}_2 + 7\text{O}_2 \rightarrow 6\text{NiO} + 4\text{SO}_2$$  (2)

The Ni$_3$S$_2$ content in the sample was estimated to be ~78.2%. The Raman spectrum (Fig. 3b) of the coherent Ni$_3$S$_2$/C composites presents two distinguishable peaks at 1351.7 cm$^{-1}$ and 1591.7 cm$^{-1}$, which belong to the D-band and G-band of carbon, respectively. The D-band is related to the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite. The G-band is the result of a C–C stretching mode of sp$^2$-bonded carbon. In general, the intensity ratio between the D-band and G-band ($I_D/I_G$) provides a key parameter for the graphitized degree of carbon materials. The $I_D/I_G$ ratio of coherent Ni$_3$S$_2$/C is 0.98, which is beneficial for achieving high electrical conductivity. Well-graphitized carbon with high electrical conductivity may be very beneficial for fast electron transport. Fig. 3c shows the nitrogen isotherms of coherent Ni$_3$S$_2$/C composites. The hysteresis loops shown in isotherms of samples (type III) suggest the presence of macro-pores in the samples, consistent with the SEM results. The unique interconnected nanostructure shows a BET specific surface area of 275 m$^2$ g$^{-1}$, which is much higher than that of bulk Ni$_3$S$_2$ + C and bare Ni$_3$S$_2$ (as shown in Fig. S7a†). It also indicates that a broad pore size distribution of meso-pores (2–50 nm) with a pore volume of 0.334 cm$^3$ g$^{-1}$ can be attained (Fig. 3d), which is superior to those of bulk Ni$_3$S$_2$ + C and bare Ni$_3$S$_2$ (Fig. S7b and c†).

XPS analysis was conducted to study the elemental composition and chemical states of the coherent Ni$_3$S$_2$/C nanocomposite. As shown in Fig. 4a, the scanned C 1s spectrum can be deconvoluted into four peaks of C–C (284.4 eV, sp$^2$-hydridized carbon), C–N (285.3 eV), C–O (286.5 eV), and O–C=O (288.8 eV). The oxygen can be derived from decomposition of oxygen-containing groups in citric acid during the pyrolysis process. In Fig. 4b, three forms of nitrogen, namely, graphitic N (400.5 eV), pyrrolic N (399.6 eV), and pyridinic N (398.2 eV) can be visualized. The presence of nitrogen is derived from decomposition of thiourea. As observed, pyridinic N may be the dominant nitrogen species in Ni$_3$S$_2$/C nanocomposite. The presence of pyridinic nitrogen can increase electron conduction of the composite material by donation of the lone electron pair from N species to the graphitic carbon matrix, leading to improved rate property of the electrode. In addition, the presence of N heteroatoms helps to enhance the whole architecture stability via the strong affinity of nanoparticles to the
carbon surface and the formation of defects for extra sodium storage.22-24 In the Ni 2p XPS spectrum (Fig. 4c), the main peak at 854.5 eV can be assigned to Ni 2p3/2. The peak located at about 862 eV corresponds to the accompanied satellite peaks.25-29,31-33 In the S 2p region (Fig. 4d), the peaks at 161.8 eV and 160.7 eV originate from S 2p1/2 and S 2p3/2 of S2. In general, the peaks in Ni 2p and S 2p spectra show obvious characteristics of Ni3S2, which consistent with the XRD and high resolution TEM results.33

3.2 Sodium ion storage performance

Fig. 5 illustrates the electrochemical properties of the resultant samples in Na-half cells. Fig. 5a displays the CV curves for the first three cycles of coherent Ni3S2/C nanocomposites at a scan rate of 0.2 mV s-1 in the voltage window of 0.01–3 V (vs. Na+/Na). In the initial scan, a broad peak at about 0.43 V may be attributed to the conversion reaction and formation of the solid-electrolyte interphase (SEI) layer.30-32 In the following cycles, this peak disappears and a couple of redox peaks can be observed at about 0.88/1.66 V, indicating the sodiation/desodiation of the electrode. Overlapping of CV curves in the second and third cycles indicates good electrode reversibility with reduced polarization after initial activation. The potential differences (ΔV) increase slightly (from 84 mV to 88 mV), indicating that reactions are highly reversible.34 Fig. 5b shows the typical discharge/charge curves for coherent Ni3S2/C hybrids at a current density of 0.1 A g-1 between 0.01 and 3.0 V. Specifically, the initial discharge and charge capacities were 1012 and 598 mA h g-1, respectively, with a coulombic efficiency (CE) of 59%. To examine whether the potential at which the SEI layer is formed correlates with that in similar lithium electrolytes, the LIBs were assembled using similar solvent composition (home-made 1 M LiPF6 in EC/DEC/FEC, 1 : 1 : 0.05 in volume%). The corresponding CV curve is shown and discussed in Fig. S8.† The irreversible capacities of most transition metal sulfides (TMS) in Li or Na ion batteries are possibly caused by formation of the SEI layer and decomposition of electrolyte in the first cycle, which is common in many TMS-based anodes.35,36,44 Also, the capacity loss of bare carbon was only 34% (Fig. S9†), which might cause the low CE in coherent Ni3S2/C electrode. The voltage platform hysteresis (about 0.3 V) in the first cycle may be caused by polarization of the anodes, possibly caused by a typical conversion reaction.10,45-46 From the second cycle, the observed voltage plateaus are in accordance with the above CV results. In addition, the discharge and charge capacities in the second cycle were 656 and 590 mA h g-1, respectively, corresponding to a higher CE of 90%. The CE was further increased to over 97% in the third cycle, suggesting good electrode reaction kinetics with high reversibility upon cycling. Fig. 5c shows the rate performance of the two samples as prepared, evaluated at various current densities from 0.1 to 2.0 A g-1. Coherent Ni3S2/C composites showed a better rate performance overall than those of bulk Ni3S2 + C composites and bare Ni3S2. In the initial current density, the specific capacities showed a downwards trend mainly resulting from activation of anode materials. As the current densities increased from 0.1 to 0.2, 0.4, 0.8, 1.6, 2.0 A g-1, the discharge capacities slightly decreased from 583 to 529, 491, 459, 421, 408 mA h g-1, respectively, indicating superior rate capability of coherent Ni3S2/C composites. The specific capacity recovers 538 mA h g-1 after the current density is lowered to 0.1 A g-1, with a retention rate of about 92%. The CE can be observed at over 99% after activating in the initial few cycles. Volumetric capacity was also roughly determined using whole anode volume (Fig. S10†). Low volumetric capacity might be caused by the loose packing of nanostructured materials. The bare carbon matrix was prepared by a similar route, with rate performance displayed in Fig. S11†. The low capacities of the single Ni3S2 and poor rate performance of the carbon matrix electrode indicate that the Ni3S2 and porous carbon networks could have a favorable synergistic effect that contributes to stabilizing reversible capacities and improving rate performances. In Fig. 5d, coherent Ni3S2/C nanocomposites deliver high and stable specific capacity of 453 and 431 mA h g-1 over 100 cycles with retention rates of 83% and 87% at 0.1 and 0.4 A g-1, respectively. As seen from Fig. 5e, coherent Ni3S2/C nanocomposites possessed a reversible capacity of 427 mA h g-1 after three cycles of activation and only 4.4% capacity loss after 200 cycles, with the CE approaching 100%

The preliminary results of the full-cell (Na2V3PO4)1/rGO cathode || Ni3S2/C anode) demonstrate great potential for the as-prepared coherent Ni3S2/C to be used as an anode material in future SIBs. The choice of Na2V3PO4 (named as NVP) cathode is mainly because of its high theoretical capacity and stable sodium super-ion conductor (NASICON) structure.15-16 NVP/rGO was prepared via a sol-gel route (Fig. S12a†). Fig. S12b† shows the lamellar nanostructure with multi-stacked layers. Fig. S7c† shows a stable cyclic curve at 2C (1C ≈ 110 mA g-1) for 100 cycles between 1.5 V and 4.0 V of NVP/rGO. The inset shows the NVP/rGO coupled flat charge and discharge plateaus at around 3.3 and 3.5 V, corresponding to the redox pair of V5+/V4+. Fig. S13† highlights the composition and cycling performance of the full cell at a current density of 0.5 A g-1. The full cell with
NVP (mass ratio between cathode and anode materials was 6 : 1) delivers an initial discharge capacity of 167 mA h g$^{-1}$ at 0.5 A g$^{-1}$ based on the mass of anode with an average discharge voltage platform of 1.7 V. The capacity was retained at 101 mA h g$^{-1}$ after 30 cycles. In comparison with many similar anodes based on Ni$_3$S$_2$ (Table S1 in ESI†), the coherent Ni$_3$S$_2$/C electrode in this study exhibits much enhanced capacities and very attractive cycling stability at high rates.

3.3 Kinetics analyses

To further investigate the capacity–rate relationship in the coherent Ni$_3$S$_2$/C nanocomposites, the charge and discharge voltage profiles at various current densities are given in Fig. 6. Well defined, flat, and symmetric charge–discharge plateaus are clearly observed in Fig. 6a. When current densities increased, the charge and discharge plateaus were still clearly distinguishable. In contrast, bulk Ni$_3$S$_2$ + C and bare Ni$_3$S$_2$ show a rapid capacity drop when the current density is increased (Fig. 6b and c). The overpotential between charge and discharge voltage plateaus at various current densities further confirmed that the Ni$_3$S$_2$/C electrode possesses much less polarization and better reaction kinetics than of the bulk Ni$_3$S$_2$ + C and bare Ni$_3$S$_2$ electrodes (Fig. 6d), which can be attributed to the unique coherent structure inducing excellent electronic and ionic conductivity.47

Fig. 7a exhibits CV curves of coherent Ni$_3$S$_2$/C nanocomposite between 0.01 and 3.0 V at different scan rates. Two peaks are distinct in each curve at all scan rates. In cathodic scan, the peak shifts to a low potential area, while the peak shifts to a high potential area in anodic scan with increasing scan rate.48 This is because redox reactions can occur over the
entire active surface area while the scan rate is low; however, diffusion of sodium ions will be limited and the electrodes polarized at high scan rates. Therefore, only the outer active surface is effective for redox reactions, which results in position shift of both reduction and oxidation peaks.\(^{14}\) Comparing Fig. 7 and S14,\(^{†}\) there are clear redox peaks in the coherent Ni\(_3\)S\(_2\)/C nanocomposite with increasing scan rate to 1 mV s\(^{-1}\), whereas the peaks become inconspicuous in the bulk Ni\(_3\)S\(_2\) + C and bare Ni\(_3\)S\(_2\) electrodes. Results demonstrate excellent reversibility and good electronic conductivity of the coherent Ni\(_3\)S\(_2\)/C electrodes. Based on the Randles–Sevchik equation for semi-infinite diffusion of sodium ions into electrodes, the apparent diffusion coefficients \(D, \text{ cm}^2 \text{ g}^{-1}\) were calculated according to eqn (3).\(^{49}\)

\[
D = \frac{F^2 RT}{0.446vN_A} \text{ cm}^2 \text{ g}^{-1}
\]

where \(I\) (A) is peak current, \(R\) \([8.314 \text{ J mol}^{-1} \text{ K}^{-1}]\) is gas constant, \(T\) (K) is the absolute temperature, \(F\) \([96,485 \text{ C mol}^{-1}]\) is the Faraday constant, \(N\) is the number of electrons transferred per molecule, \(A\) (cm\(^2\)) is the active surface area of the electrode, \(C\) (mol cm\(^{-3}\)) is the concentration of sodium ions in the electrolyte, and \(v\) (V s\(^{-1}\)) is the scanning rate. From the slope of the fitting line collected from oxidation and reduction peak current \(I\) (Fig. 7b), the diffusion coefficients \(D\) of the coherent Ni\(_3\)S\(_2\)/C electrode are \(1.3 \times 10^{-12} \text{ cm}^2 \text{ g}^{-1}\) and \(0.9 \times 10^{-12} \text{ cm}^2 \text{ g}^{-1}\) for the cathodic peak and anodic peak, respectively.

### 3.4 Electrochemical reaction mechanism

Ex situ XRD analyses of coherent Ni\(_3\)S\(_2\)/C anodes were performed at different stages in the first cycle, as shown in Fig. 8. The fresh anode shows a clear pattern of crystallized Ni\(_3\)S\(_2\) (stage a). On discharge to 0.7 V (stage b), the Ni\(_3\)S\(_2\) peaks disappear; a new peak located at about 37° emerges and can be assigned to Na\(_2\)S.\(^{50}\) The main phase was Na\(_2\)S and no Ni\(_3\)S\(_2\) phase can be observed, implying that the Ni\(_3\)S\(_2\) lattice experienced a conversion reaction to Ni and Na\(_2\)S in the sodiation process. Although completing the discharge, the Na\(_2\)S peak was weak and no other obvious peaks were attained, suggesting that the discharge products were in amorphous states (stage c).\(^{51}\) On desodiation to 1.7 V, a broad peak appeared belonging to Ni\(_2\)S\(_2\) and the Na\(_2\)S was in an intensity reduction process, demonstrating the reversible reaction of the electrode. After charging to 3.0 V, the Ni\(_3\)S\(_2\) re-appeared but the peak intensity decreased, and Na\(_2\)S diminished (stage e). The broader peak and weaker peak intensity compared with the initial state indicate that the lattice expanded during the insert/extract of large sodium ions. Results reveal that sodium storage in our products is reversible. XRD patterns of bulk Ni\(_3\)S\(_2\) + C and bare Ni\(_3\)S\(_2\) in charge state (3.0 V) are shown in Fig. S9.\(^{†}\) During the first cycle, both bulk Ni\(_3\)S\(_2\) + C and bare Ni\(_3\)S\(_2\) cannot return to their initial Ni\(_3\)S\(_2\) phase. As certified in the literature,\(^{10,14,17,19}\) most metal sulfides or selenides experience an insertion–conversion reaction during the first discharge process and can hardly return to their initial state when the charge process is completed. The by-products, known as poly-sulfides or poly-selenides, can experience shuttle and dissolving effects as in Li–S or Li–Se batteries, causing severe capacity loss. As shown in Fig. 8 and S16,\(^{†}\) reactions in coherent Ni\(_3\)S\(_2\)/C are superiorly reversible to those of bulk Ni\(_3\)S\(_2\) + C and bare Ni\(_3\)S\(_2\). The coherent structures form an entangled network to confine the conversion reaction products in electrochemically active states, one possible explanation for the reversible reactions.

To evidence the effect of coherent networks on restrictions of poly-sulfides, cells were disassembled in a glove box after...

![Fig. 8](image-url) Ex situ XRD patterns of the electrode collected at various points carried out under 100 mA g\(^{-1}\), as indicated in the corresponding discharge/charge profiles: (a) pristine electrode, (b) after first discharge to 0.7 V, (c) after first discharge to 0.01 V, (d) after first charge to 1.7 V, and (e) after first charge to 3.0 V.
observed on the separator and Na anode for the disassembly, the Na pieces were covered with para and bare Ni3S2; (d) and (e) ex situ XRD patterns of the Na counter electrode after cycling collected from cells using coherent Ni3S2/C nanocomposites, bulk Ni3S2 + C composites, and bare Ni3S2 electrodes.

Fig. 9  Digital photos of separators from dissembled cells in glovebox: (a) coherent Ni3S2/C nanocomposites, (b) bulk Ni3S2 + C composites and (c) bare Ni3S2; (d) and (e) ex situ XRD patterns of the Na counter electrode after cycling collected from cells using coherent Ni3S2/C nanocomposites, bulk Ni3S2 + C composites, and bare Ni3S2 electrodes.

4. Conclusions
Phase-purity coherent Ni3S2/C nanocomposites were successfully prepared via template-directed sol-gel processing and post-annealing. Nano-structural composites delivered superior sodium storage properties, exhibiting 453 and 430 mAh g⁻¹ at a current density of 0.1 and 0.4 A g⁻¹ over 100 cycles, respectively. Even at a high current density of 2.0 A g⁻¹, only 4.4% capacity loss was observed after 200 cycles. The reaction mechanism of the as-prepared electrodes was investigated, demonstrating reversible conversion processes in the sodiation/desodiation reactions. The outstanding cyclic and rate behaviors and enhanced Na⁺ diffusion abilities, as well as superior reversibility, can be attributed to the unique structure. The novel coherent architectures afford an efficient electrode/electrolyte contact interface and enough active sites for sodium ion insertion/extraction, resulting in fast reaction kinetics. More importantly, the entangled networks in coherent Ni3S2/C nanocomposites can confine the discharge products, providing long-term cycling stability. Na3V2(PO4)3/Ni3S2 full cells with high performances are promising in development of commercial SIBs using Earth-abundant transition metal sulfide anodes.

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References


