Rational design of three-dimensional graphene encapsulated core–shell FeS@carbon nanocomposite as a flexible high-performance anode for sodium-ion batteries†

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The development of high-performance electrochemical energy storage systems is highly dependent on the synergistical structural design of electrode materials and whole electrodes with appropriate compositions. Here we create a novel flexible three-dimensional graphene (3DG) hybrid electrode with a core–shell FeS@carbon (FeS@C) nanocomposite encapsulated within 3DG by one-step thermal transformation of the deliberately designed 3DG wrapped metal–organic framework (3DG/MOF) composite based on the newly disclosed spatially confined phase separation of the metal and organic moieties of MOFs and the following in situ composition transformation mechanism. Benefitting from effective ion/charge transport in the whole electrode and the robust structural stability of FeS during electrochemical processes guaranteed by the highly interpenetrated porous conductive network of 3DG and the carbon protective layer with N- and S-codoping, the free-standing 3DG/FeS@C electrode delivers an ultrahigh specific capacity of 652 mA h g⁻¹ after 80 cycles at 100 mA g⁻¹ and excellent rate capacities of 363.3 and 152.5 mA h g⁻¹ at 1 and 6 A g⁻¹ with unprecedented cycling stability with a capacity retention of 97.9% after 300 cycles at 1 A g⁻¹, which is the best ever reported result for FeS-based anode materials for sodium ion batteries. This study opens up a new MOF-based phase separation avenue to construct sophisticated 3DG wrapped core@shell nanocomposites and represents an important step to the structural design of high-performance electrodes for electrochemical energy storage.

1. Introduction

The ever-growing demand for further portable electronics, electric vehicles and grid applications is urgently calling for new alternative high-performance electrochemical energy storage systems with unique advantages over current commercial lithium-ion batteries (LIBs), such as lithium–sulfur batteries (LSBs), lithium–oxygen batteries (LOBs) and sodium-ion batteries (SIBs). Extensive research studies have demonstrated that the deliberate structural design of electrode materials and whole electrodes with appropriate compositions is a prerequisite to obtain desirable electrochemical properties. For example, anode materials (such as silicon for LIBs) and cathode materials (such as sulfur for LSBs) with high theoretical capacity have attracted tremendous attention in recent years. However, the poor structural stability of these electrode materials (such as huge volume changes for silicon) or intermediate products (such as the shuttle of polysulfides for LSBs) during ion insertion/de-insertion severely encumbers their practical applications. Thus, they have to be tailored to sophisticated nano-architectures such as porous structures and/or core@shell composite structures to mitigate these issues. In addition, these electrode materials usually show poor electronic conductivity and exist in the form of powder. In this case, extra inactive conductive agents and binders have to be pre-mixed with them and then the mixtures have to be coated on the surfaces of heavy metal current collectors to form available electrodes, which not only largely decreases the energy density of full cells, but also hinders their potential applications in the next generation of functional devices, such as flexible and/or stretchable electronics. In this regard, integrating electrode materials into free-standing and light-weight carbon-based porous materials with an interpenetrated porous structure and conductive network such as three-dimensional graphene (3DG) aerogels is indispensable. Therefore, it is of great importance to construct a series of new electrodes...
which meet all the above merits and make an in-depth investigation into the structure–property relationship.

Recently, great concerns have been raised for lithium-based batteries in light of increasing costs as well as safety problems caused by limited lithium resources and lithium dendrites, which might be bound to impede the large scale use of lithium-based batteries in future. Therefore, tremendous attention has been paid to SIBs owing to the similar electrochemical properties of sodium to lithium and the natural abundance of sodium.⁵–⁷ Recently, the exploitation of suitable anode materials with low cost and high capacity for SIBs is an urgent task and extensive research studies have been conducted to evaluate the electrochemical properties of carbon-based materials, metal oxides (MOs),⁵–⁷ and metal sulfides (MSs)⁵–⁷ for SIBs. Due to the larger ion diameter (1.02 Å for Na⁺ vs. 0.76 Å for Li⁺) as well as the higher redox potential (E⁰Na⁺/Na = −2.71 V, E⁰Li⁺/Li = −3.04 V versus the standard hydrogen electrode) of sodium ions than those of lithium ions, these anode materials show different electrochemical responses to sodium ion insertion/de-insertion. For example, graphite and many metal oxides offer very low capacity.⁶ In this respect, MSs have attracted considerable attention because of their higher theoretical specific capacity than carbon-based materials and superior electrochemical kinetics and smaller volumetric variation during the electrochemical process than MOs.⁶,²⁶ Nevertheless, as a kind of conversion reaction-based anode material for SIBs, MSs face the aforementioned issues including poor intrinsic electron/ion conductivity, a huge volume change during sodium ion insertion/de-insertion processes and being in powder form. Considering the capability of carbon shell based core@shell structures in enhancing the electronic conductivity and alleviating the volume change of electrode materials,²⁶,²⁷ it is highly desirable to combine nanostructured core–shell MS@carbon composites with 3DG aerogels to build high-performance anodes for SIBs.

Benefitting from the inorganic–organic hybrid compositions with high tunability, metal–organic frameworks (MOFs) have been widely explored as appropriate precursors for porous metal oxides, porous carbon and carbon shell-based core@shell composites.⁹,¹⁹,²¹,²⁷–²⁹ Thus, the combination of MOFs with 3DG might provide unlimited opportunities for the construction of new functional materials that meet the aforementioned merits. For example, a series of 3DG/MOF composites with MOFs simply deposited on the surface of 3DG and well encapsulated within 3DG have been successfully fabricated by us and other groups,²⁰–²³ and then transformed into 3DG/porous MOs with highly enhanced electrochemical properties for use as anodes for LIBs.²¹,²² However, fundamental scientific problems, such as concrete thermal transformation mechanisms for MOFs with different organic ligands and the influence of 3DG supports on the electrochemical properties of carbon-based materials, and extensive research studies have been conducted to evaluate the electrochemical properties of carbon-based materials, metal oxides (MOs), and metal sulfides (MSs) for SIBs. Due to the larger ion diameter (1.02 Å for Na⁺ vs. 0.76 Å for Li⁺) as well as the higher redox potential (E⁰Na⁺/Na = −2.71 V, E⁰Li⁺/Li = −3.04 V versus the standard hydrogen electrode) of sodium ions than those of lithium ions, these anode materials show different electrochemical responses to sodium ion insertion/de-insertion. For example, graphite and many metal oxides offer very low capacity. In this respect, MSs have attracted considerable attention because of their higher theoretical specific capacity than carbon-based materials and superior electrochemical kinetics and smaller volumetric variation during the electrochemical process than MOs. Nevertheless, as a kind of conversion reaction-based anode material for SIBs, MSs face the aforementioned issues including poor intrinsic electron/ion conductivity, a huge volume change during sodium ion insertion/de-insertion processes and being in powder form. Considering the capability of carbon shell based core@shell structures in enhancing the electronic conductivity and alleviating the volume change of electrode materials, it is highly desirable to combine nanostructured core–shell MS@carbon composites with 3DG aerogels to build high-performance anodes for SIBs.

Benefitting from the inorganic–organic hybrid compositions with high tunability, metal–organic frameworks (MOFs) have been widely explored as appropriate precursors for porous metal oxides, porous carbon and carbon shell-based core@shell composites. Thus, the combination of MOFs with 3DG might provide unlimited opportunities for the construction of new functional materials that meet the aforementioned merits. For example, a series of 3DG/MOF composites with MOFs simply deposited on the surface of 3DG and well encapsulated within 3DG have been successfully fabricated by us and other groups, and then transformed into 3DG/porous MOs with highly enhanced electrochemical properties for use as anodes for LIBs. However, fundamental scientific problems, such as concrete thermal transformation mechanisms for MOFs with different organic ligands and the influence of 3DG supports on the architecture of MOF derived functional materials, have not been comprehensively understood, which plays a key role in the construction of new 3DG-based composites with a sophisticated structure.

Herein, a novel exquisite 3DG hybrid structure with a core–shell FeS@C nanocomposite encapsulated in 3DG is successfully designed and fabricated by one-step thermal transformation of the 3DG/MOF composite for the first time. Prussian blue (PB, Fe₆[Fe(CN)₆]₉)⁸,¹⁹ a typical low-cost, resource abundant and environmentally benign MOF, is chosen as the precursor of the core–shell FeS@C nanocomposite. In this case, unusual 3DG confined phase separation of the metal and organic moieties of PB is revealed to lead to the formation of a well-dispersed core–shell FeS@C nanocomposite, which is then in situ transformed into a core–shell FeS@C nanocomposite with a small gap between FeS and C at higher temperature due to the smaller molar volume of FeS than FeS₂. Meanwhile, N derived from the cyanide ligand of PB and sulfur are simultaneously doped in the carbon shell and 3DG framework. Different from previous reports where homogeneous phase particles are simply deposited on the surface of 3DG, the monolithic 3DG/FeS@C aerogel for the first time integrates the core@shell structure, robust 3D porous conductive network of graphene and sandwich-like graphene/core@shell composite/graphene structure together, thus holding great potential for electrochemical applications. When directly used as a flexible anode for SIBs upon mechanical pressing, the 3DG/FeS@C delivers an ultrahigh specific capacity of 632 mA h g⁻¹ after 80 cycles at 100 mA g⁻¹, and excellent rate capacities of 363.3 and 152.5 mA h g⁻¹ at 1 and 6 A g⁻¹, and shows unprecedented cycling stability with a capacity retention of 97.9% after 300 cycles at 1 A g⁻¹, which is the best result ever reported for FeS-based anode materials.

2. Experimental section
2.1 Synthesis
2.1.1 Synthesis of graphene oxide (GO). GO was prepared by oxidation of natural graphite powder according to a modified Hummers’ method. Briefly, graphite (3.0 g) was added to concentrated sulfuric acid (70 mL) under stirring at room temperature, then sodium nitrate (1.5 g) was added, and the mixture was cooled to 0 °C. Under vigorous agitation, potassium permanganate (9.0 g) was added slowly to keep the temperature of the suspension lower than 20 °C. Successively, the reaction system was transferred to a 35–40 °C water bath and allowed to remain for about 0.5 h, forming a thick paste. Then, 140 mL of water was added, and the solution was stirred for another 15 min. An additional 500 mL of water was added followed by a slow addition of 20 mL of H₂O₂ (30%), turning the color of the solution from brown to yellow. The mixture was filtered and washed with 1 : 10 HCl aqueous solution (250 mL) to remove metal ions followed by repeated washing with water and centrifugation to remove the acid. The resulting solid was dispersed in water by ultrasonication for 1 h to make a GO aqueous dispersion (0.5 wt%). The obtained brown dispersion was then subjected to 30 min of centrifugation at 4000 rpm to remove any aggregates. Finally, it was purified by dialysis for 1 week to remove the remaining salt impurities for the following experiments.

2.1.2 Preparation of the 3DG/PB composite and PB. Typically, 0.02 mL sodium ferrocyanide (Na₄[Fe(CN)₆]·10H₂O, 0.5 M) was dissolved in 2 mL GO solution (2 mg mL⁻¹) under stirring. Then 0.2 mL ferrous sulfate (FeSO₄, 0.5 M) was slowly added

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into the above solution under strong stirring to obtain the GO/PB solution. After aging for 0.5 h, the solution was centrifuged at 4000 rpm for 10 min three times to remove the excess FeS$^\text{2-}$. 3 mL deionized water was added after centrifugation. To obtain a 3DG/PB hydrogel, the GO/PB solution was heated at 95 °C for 2 h after the addition of 0.2 mL sodium ascorbate (0.5 M). The obtained 3DG/PB hydrogel was washed three times, and then freeze-dried overnight to get the 3DG/PB aerogel. 3DG/PB-H and 3DG/PB-L were obtained in the same way with different concentrations of Na$_2$Fe(CN)$_6$·10H$_2$O and FeSO$_4$ (0.8 and 0.3 M for Na$_2$Fe(CN)$_6$·10H$_2$O and FeSO$_4$, respectively). Pure PB was fabricated in the same way without addition of GO.

2.1.3 Preparation of 3DG/FeS@C and FeS/NC composites. The 3DG/FeS@C nanocomposite was obtained by one-step calcination of the 3DG/PB aerogel. Typically, 3DG/PB and sulfur powder with a mass ratio of 1 : 3 were put into a ceramic crucible, and the heating temperature was increased to 800 °C at a rate of 10 °C min$^{-1}$, and maintained for 2 h under an argon atmosphere. The FeS/NC composite was fabricated in the same way by replacing 3DG/PB with PB.

2.2 Material characterization

The morphological characterization was conducted on a Zeiss Ultra-55 field emission scanning electron microscope (FESEM) and FEI Tecnai G2 20 TWIN transmission electron microscope (TEM, 200 kV). X-ray diffraction (XRD) analysis from 10° to 80° was carried out on a PANalytical X’pert PRO X-ray diffraction system (Cu Kz). Raman spectra were recorded on an Xplora Laser Raman spectrometer. A Pyris1 thermogravimetric analyzer (TGA) was used to perform the TGA test at a heating rate of 10 °C min$^{-1}$ under air conditions from 100–700 °C. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000C ESCA system.

2.3 Electrochemical characterization

The free-standing 3DG/FeS@C aerogel in a quantity of about 1 mg and with a diameter of about 0.8 cm (2.0 mg cm$^{-2}$) was pressed and cut into circular shapes to serve as the anodes directly for SIBs. FeS anodes were prepared by mixing the FeS nanocomposites, Super P and polyvinylidene fluoride (PVDF) binder in a mass ratio of 7 : 2 : 1 to form a homogeneous slurry. The slurry was spread onto copper foils and vacuum dried at 110 °C for 12 h. The dried foil sheet was directly cut into circular disks to serve as the anodes. The galvanostatic experiments were carried out on a battery testing system (LAND, Wuhan China) in the voltage window from 0.01 V to 3 V at different current densities. Electrochemical impedance spectroscopy (EIS) was conducted on a CHI 760D electrochemical workstation in the frequency range of 100 kHz to 0.01 Hz. The CHI 760D electrochemical workstation was also used to record cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s$^{-1}$ in the potential range of 0.01–3 V.

3. Results and discussion

The representative synthetic procedure of 3DG/FeS@C is schematically shown in Fig. 1. The 3DG/PB aerogel is first prepared by the excessive metal ion induced combination and the following spatially confined Ostwald ripening strategy that was developed by us recently with some modifications.36,37 After heat treatment with sulfur, phase separation of metal and organic moieties in PB occurs, and iron reacts with sulfur to form FeS$_2$ nanoparticle aggregates while cyanide ligands decompose to N-containing gas and then carbonize on the surface of FeS$_2$, resulting in the formation of a core–shell FeS$_2@C$ nanocomposite (Fig. 1a). Along with the increase of temperature, the FeS$_2$ nanoparticle aggregates fuse into FeS$_2$ particles by Ostwald ripening (Fig. 1b). At higher temperature, FeS$_2$ decomposed to FeS and core@shell FeS@C nanocomposites with a small gap between FeS and C are successfully obtained due to the smaller molar volume of FeS than FeS$_2$ (Fig. 1c). At the same time, N derived from the cyanide ligand of PB and sulfur are simultaneously doped in the carbon shell and 3DG framework. As a result, yolk–shell FeS@C nanocomposites encapsulated in 3DG with nitrogen and sulfur co-doping are obtained.

When increasing the heat treatment temperature of 3DG/PB with sulfur to 400 °C, the PB nanoparticles are transformed into carbon coated FeS$_2$ aggregates (Fig. S1a–c†). It can be clearly observed that a thin layer of carbon is uniformly deposited on the external surface of FeS$_2$ aggregates (Fig. S1c†), which is quite different from previous reports where MS nanoparticles dispersed within the carbon matrixes (MSCMs) are often fabricated by thermal decomposition of MOFs in the presence of sulfur.34,35 In those cases, the organic moieties of MOFs usually decomposed to solid phase organic residues and some gases and thus MSCMs could be formed. However, the formation of core–shell FeS$_2@C$ nanocomposites cannot be explained clearly by the above mechanisms. This transformation process should originate from the unique chemical nature of the cyanide ligands of PB,34,35 which might all decompose into N-containing gases without solid organic residues in the presence of sulfur. That is to say, phase separation of metal and organic moieties in PB occurs in this work, and iron reacts with sulfur to form FeS$_2$ nanoparticle aggregates while cyanide ligands decompose to N-containing gas and then carbonize on the surface of FeS$_2$. This is very similar to the chemical vapor deposition process,36,37 except that the gas is not provided by an external gas source, but originates from the decomposition of the organic ligand of the MOF. Along with the increase of temperature, the FeS$_2$...
nanoparticle aggregates fuse into core–shell FeS₂ particles by Ostwald ripening at 600 °C (Fig. 2c and d). Interestingly, the carbon shell adapts its shape to the morphological change of FeS₂, which might be caused by further carbonization. It should be noted that the encapsulation of the MOF by graphene is very important in the whole process. Otherwise, micro-sized FeS other than core–shell FeS@C would be obtained when heating pure PB rather than 3DG/PB with sulfur (Fig. S2 and S3†). This means that the 3DG framework not only confines the cyanide derived gas around FeS₂ and promotes the formation of the carbon shell, but also prevents the aggregation and fusion of FeS₂ during the high-temperature reaction and guarantees the formation of a well-dispersed FeS₄@C nanocomposite. At higher temperature (800 °C), FeS₂ decomposes to FeS and core@shell FeS@C nanocomposites wrapped within 3DG are also successfully obtained. As shown in Fig. 2d and e, the 3DG/FeS@C inherits the 3D interconnected porous structure of 3DG/PB and FeS@C nanocomposites are well-dispersed on the 3DG framework. TEM pictures in Fig. 2f and S4a–c demonstrate that the obtained FeS@C nanocomposites possess a well-defined core–shell structure. Moreover, a small gap between the FeS core and the carbon shell is observed, which is further confirmed by dark-field TEM (Fig. 2g). The gap might be caused by the smaller molar volume of FeS (18.16 cm³ mol⁻¹) than FeS₂ (23.99 cm³ mol⁻¹) as well as further carbonization. Elemental mapping analyses were also carried out on the 3DG/FeS@C hybrid materials. The concentrated distribution of Fe and S signals in the core section (Fig. 2h and i) and the uniform distribution of C and N on the whole composite (Fig. S4d–i†) verify that the core is FeS and N and S have been co-doped in the 3DG/FeS@C.

Composition analysis was carried out to demonstrate the transformation process. As shown in Fig. 3a, four dominant peaks are located at 17.4, 24.7, 35.1 and 39.5° that correspond to the (100), (110), (200), and (210) planes of PB (JPCDS # 01-0239) in the XRD pattern of 3DG/PB. After calcinating 3DG/PB with sulfur, the obtained products transformed into FeS₂ (JPCDS # 42-1340) at 400 °C and then FeS (JPCDS # 37-0477) at 800 °C (Fig. S5†). At last, these XRD peaks are replaced by four new peaks located at 30.1, 34.1, 43.9 and 53.2° that are ascribed to the (110), (112), (114), and (300) planes of FeS (JPCDS # 37-0477), indicating the successful fabrication of FeS.³⁸ In addition, the appearance of a broad peak at ~26° with gradually increased intensity demonstrates the effective reduction and more dense stacking of graphene during high temperature transformation. This transformation process could be further confirmed by Raman spectra and X-ray photoelectron spectroscopy (XPS) analysis. As shown in Fig. 3b, there are two bands located at 2120 and 2160 cm⁻¹ in 3DG/PB, which can be assigned to the Fe–CN–Fe linkage of PB.²⁶,³¹ They disappear in 3DG/FeS@C and three bands are located at 238, 312, and 377 cm⁻¹ (inset image of Fig. 3b) that are ascribed to FeS appearance.²⁹ In the XPS spectra, two peaks at 711.1 and 724.1 eV (Fig. 3c) and other two

![Fig. 2 SEM (a and b) and TEM (c) images of 3DG/PB; SEM (d and e), TEM (f) and dark-field TEM (g) images of core–shell 3DG/FeS@C; elemental mapping pictures of Fe (h) and S (i) of 3DG/FeS@C. Specifically, excess ferrous sulfate (FeSO₄) is directly added into the graphene oxide (GO)/sodium ferrocyanide (Na₄Fe(CN)₆) solution to form a PB/GO suspension, which is then thermally treated with sodium ascorbate to self-assemble into the 3DG/PB hydrogel. Compared with our method reported before,³²,³³ this process reduces one centrifugation step and simplifies the synthetic process of the 3DG/PB aerogel. Similar to our previous report, excess iron ions adsorbed on the surface of PB could interact with GO through coordination and electrostatic interactions, ensuring the effective combination of PB and GO. Then, the 3DG/PB hydrogel with PB particles encapsulated by graphene layers could also be obtained by heating the GO/PB suspension in the presence of sodium ascorbate, which results in the dissolution of PB particles anchored on the surface of graphene while other particles wrapped within graphene grow into larger particles because of the unstability of PB in sodium ascorbate solution. As shown in (a–c), the obtained 3DG/PB aerogel possesses an interconnected 3D porous network and PB nanoparticles with sizes of 50–80 nm wrapped in the interior of the graphene framework with good dispersion.

![Fig. 3 XRD patterns (a) and Raman spectra (b) of 3DG/PB and 3DG/FeS@C. Raman spectra of 3DG/FeS@C from 200–400 cm⁻¹; XPS spectra of 3DG/FeS@C, (c) Fe 2p, (d) S 2p and (e) N 1s.]

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peaks at 160 and 161.5 eV (Fig. 3d) could be assigned to the characteristic peaks of Fe$^{2+}$ and S$^{2-}$ in FeS, respectively.\textsuperscript{39,40} Notably, N signals (397.1, 399.3, and 401.3 eV) and S signals (163.1 and 164.4 eV) that are chemically bonded to carbon (Fig. 3d and e) are also observed for 3DG/FeS@C.\textsuperscript{41,42} The above analysis indicates that N and S are simultaneously doped into carbon during the formation process of 3DG/FeS@C, which is consistent with the above elemental mapping results. In addition, the content of FeS in 3DG/FeS@C is determined to be about 60.5% by thermogravimetric analysis (TGA) in Fig. S6.\textsuperscript{†} This value could be facilely adjusted by changing the concentration of Fe$^{2+}$ and [Fe(CN)$_6$]$^{4-}$, and 3DG/FeS@C-H and 3DG/FeS@C-L containing 70.8 and 51.2% of FeS, respectively, have also been fabricated (Fig. S7†). In a word, core–shell FeS@C nanocomposites encapsulated in an interpenetrated 3DG network with N and S co-doping have been successfully fabricated via simple calcination of 3DG/PB and sulfur. This result not only opens up a new route to construct MOF derived core–shell nanocomposites by spatially confined phase separation, but also reveals a new thermal transformation mechanism of MOFs and enriches the fundamental knowledge in this field. The monolithic 3DG/FeS@C aerogel for the first time integrates the core@shell structure, robust 3D porous conductive network of graphene and sandwich-like graphene/core@shell composite/graphene structure as well as heteroatom doping together, thus holding great potential for electrochemical applications.

To test the possibility of 3DG/FeS@C as a flexible and free-standing anode for SIBs, mechanical property and electronic conductivity tests were carried out. As shown in Fig. 4a, the typical 3DG/FeS@C aerogel could be compressed into a robust film with a thickness of about 18 μm and a density of 1.1 g cm$^{-3}$. SEM measurements on the cross section of the film show that the interpenetrated porous 3DG graphene network remains intact after being pressed and FeS@C nanoparticles are still tightly encapsulated between graphene layers (Fig. 4b and c). Moreover, this pressed film possesses an electrical conductivity of 5.9 S cm$^{-1}$, and could be folded 50 times at a folding angle of 180° without any structural or electrical degradation. Thus, the 3DG/FeS@C films can be directly used as light-weight anodes without binders, conductive agents and metal collectors. However, all these materials are necessary for pure FeS to prepare a common electrode, which unavoidably decreases the energy density of electrochemical storage systems as well as increases the operation cost.

The electrochemical performance of the 3DG/FeS@C anode is first demonstrated by its cycling stability at 0.1 A g$^{-1}$. As shown in Fig. 5a, the initial discharge and charge specific capacities are 844.4 and 507.7 mA h g$^{-1}$, respectively. The low coulombic efficiency (60.1%) should be mainly caused by the degradation of the electrolyte and the formation of a solid–electrolyte interface (SEI) in the first discharge cycle. However, the coulombic efficiency increases to about 97% at the second cycle and stays constant for the following cycles. It can be observed that the discharge capacity of 3DG/FeS@C undergoes a slight decrease during the initial cycles and then gradually increases to as high as 639 mA h g$^{-1}$ after 80 cycles. In contrast, the initial discharge capacity of pure FeS as the anode is only 487.8 mA h g$^{-1}$, and then decreases to 27.6 mA h g$^{-1}$ rapidly after 60 cycles. These results fully prove that this unique hybrid structure of core–shell FeS@C encapsulated in interconnected porous 3DG can largely improve the electrochemical performance of FeS. It should be noted that the capacity value of 3DG/FeS@C is higher than the theoretical capacity of FeS (about 609.5 mA h g$^{-1}$) based on the conversion mechanism, and also that of 3DG/HC obtained by chemical etching of 3DG/FeS@C and 3DG (Fig. S8†). Thus it is highly desirable to reveal the sodium ion storage mechanism of 3DG/FeS@C. Firstly, the morphologies and compositions of 3DG/FeS@C after different cycles were examined by TEM and XRD analysis. As shown in Fig. S9, the morphology of 3DG/FeS@C during the whole cycling process has no obvious changes due to its double layered carbon protection. In addition, these products at different discharge/charge cycles exhibit similar XRD results as shown in Fig. S10 and S11† Unfortunately, the weak peaks in these products could not be well-assigned to any of the possible

![Fig. 4](image-url) (a) Digital pictures of 3DG/FeS@C prepared as a flexible and free-standing anode. (b and c) SEM images of pressed 3DG/FeS@C at different scale bars.

![Fig. 5](image-url) (a) Cycling performance and (b) discharge–charge curves of 3DG/FeS@C at a current of 0.1 A g$^{-1}$. (c) Rate performance of 3DG/FeS@C and pure FeS. (d) Cycling performance of 3DG/FeS@C at 1 A g$^{-1}$.
compositions that might be created by discharge and charge, such as Na2S, Fe and Na2CO3.46,47 Thus the discharge/charge curves and cyclic voltammetry (CV) results were analyzed in detail. As revealed in Fig. S12† the 3DG/FeS@C exhibits similar CV curves to previous reports during the initial several cycles,48,49 and thus a similar sodium ion storage mechanism should be employed by 3DG/FeS@C. For example, at the first cathodic scan, the peak at 0.68 V might be related to the formation of a solid-electrolyte interface (SEI) on the surface of the materials and the conversion from FeS to Fe and Na2S according to eqn (1).

\[
\text{FeS} + 2\text{Na}^+ + 2e^- \rightarrow \text{Na}_2\text{S} + \text{Fe}
\]

At the same time, the sharp peak at ~1.44 V and the broad peak at ~1.85 V in the first anodic scan should correspond to the desodiation reaction, where Na2FeS2 and NaFeS2 species are probably formed based on eqn (2) and (3).

\[
2\text{Na}_2\text{S} + \text{Fe} \rightarrow \text{Na}_2\text{FeS}_2 + 2\text{Na}^+ + 2e^-
\]

\[
\text{Na}_2\text{FeS}_2 \rightarrow \text{NaFeS}_2 + (2 - x)\text{Na}^+ + (2 - x)e^-
\]

From the second cathodic scan, two pairs of cathodic peaks at 1.67 and 0.87 V, and anodic peaks at 1.46 V and 1.97 V that are attributed to the reversible reaction (2) and (3) appeared and almost remained stable,48,49 indicating the good reversibility and cycling stability of 3DG/FeS@C during the initial cycles. This is in good agreement with the discharge/charge curves in Fig. 5b. However, along with the increase of the cycle number, a new discharge plateau that resides above 2.0 V and the corresponding charge plateau that lies above 2.4 V (as indicated by red arrows) appeared and the length of them increased gradually. This indicates an alternative sodium ion storage mechanism that is different from the common conversion mechanism based on eqn (1)–(3), which is the origin of the extraordinary capacity of 3DG/FeS@C. Nevertheless, the accurate reasons that cause the above extra sodium ion storage could not be disclosed by our present TEM and XRD analysis, and more advanced characterizations should be carried out.

SIBs with fast charge–discharge capability and long lifetime are necessary for large-scale energy storage applications such as electric grids,44–46 and thus the high rate performance and long-term cycling stability of 3DG/FeS@C are further evaluated. As shown in Fig. 5c, the 3DG/FeS@C anode delivers reversible capacities of 498.7, 426.7, 363.3, 294.6, 195.3 and 152.5 mA h g⁻¹ at 0.1, 0.4, 1, 2, 4 and 6 A g⁻¹, and recovers to 496 mA h g⁻¹ when the current density returns to 0.1 A g⁻¹. These are much better than those of the pure FeS anode under the same conditions, demonstrating that the hybrid structure endows FeS with excellent structural stability and superior rate performance. Furthermore, 3DG/FeS@C shows a pronounced cycling stability at high rates. It still offers a high capacity of 358 mA h g⁻¹ after 300 cycles at 1 A g⁻¹ with a capacity retention of 97.9%, highly superior to that of pure FeS. It should be noted that increasing or decreasing the content of FeS in 3DG does not improve the electrochemical properties of 3DG/FeS (Fig. S13†). This might be due to the insufficient electrochemical reaction of large-sized FeS as well as the poor 3DG wrapped structure in 3DG/FeS@C-H and decreased available active material in 3DG/FeS@C-L. Overall, the remarkable electrochemical performance of 3DG/FeS@C is the best ever-reported result among all FeS-based anodes, and superior to those of most MS anodes for SIBs (Table S1†).

To further clarify the underlying reasons of the excellent electrochemical performance of this 3DG hybrid electrode, electrochemical impedance spectroscopy (EIS) experiments were conducted before and after 80 cycles at 0.1 A g⁻¹. As illustrated in Fig. S14† the Nyquist plots of all the tested electrodes exhibit a depressed semicircle in the high-frequency region and a sloping line in the low frequency region, corresponding to the charge transfer process and the semi-infinite Warburg diffusion process, respectively.30,31 The 3DG/FeS@C exhibits smaller charge transfer resistance than pure FeS whether before or after cycling, indicating the superior electrochemical kinetics of 3DG/FeS@C. According to the results discussed above, the unique hybrid architecture of 3DG/FeS@C offers the following advantages. Firstly, the nanosize of the well-dispersed FeS particles, combined with the highly conductive N, S co-doped carbon shell and the tight graphene coating layer, shortens ion/electron transport pathways, ensuring fast ion/electron transport on FeS. Secondly, the interpenetrated porous 3D graphene network offers sufficient pathways for ion/electron transport, largely improving the electrochemical kinetics of the whole electrode. Thirdly, the robust protective carbon shell and graphene layers can alleviate volume expansion/shrinkage during the sodiation/desodiation process, preventing the pulverization and agglomeration of FeS particles (Fig. S9†). In addition, the free-standing flexible nature of the 3DG/FeS@C aerogel avoids the use of current collectors, conductive carbon and binders, making it a promising anode for flexible and lightweight electronics.

4. Conclusion

In conclusion, a novel hybrid electrode with core@shell FeS@C nanocomposites encapsulated within 3DG has been successfully prepared by one-step thermal transformation of 3DG wrapped metal–organic framework (3DG/MOF) composites. The core–shell FeS@C is revealed to be created by a new spatially confined phase separation of the MOF and the in situ composition transformation route. The monolithic 3DG/FeS@C aerogel for the first time integrates the core@shell structure, robust 3D porous conductive network of graphene, and sandwich-like graphene/core@shell composite/graphene structure as well as N and S co-doping together and could be directly used as a free-standing flexible anode for SIBs. This novel anode delivers an ultrahigh capacity and excellent rate performance as well as unprecedented cycle life. We believe that this study not only discloses a new thermal decomposition mechanism of MOFs, but also opens up a new avenue to construct sophisticated 3DG wrapped core@shell nanocomposites and provides a new 3DG-based hybrid electrode configuration that could
push the development of high-performance electrochemical energy storage systems.

Conflicts of interest
There are no conflicts to declare.

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