Accepted Article

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To be cited as: ChemElectroChem 10.1002/celc.201600327

Link to VoR: http://dx.doi.org/10.1002/celc.201600327
Solvothermal synthesis of mesoporous MnS nanoparticle supported on nitrogen and sulfur co-doped graphene with superior lithium storage performance

Gangyong Li, Binhong He, Minjie Zhou, Guoxiang Wang, Ningbo Zhou, Wenyuan Xu, and Zhaohui Hou

Abstract: Aimed at enhanced cyclic stability and rate capability for lithium storage of MnS-based anode materials, a composite consists of mesoporous MnS nanoparticles and N, S co-doped graphene (NS-G/MnS) was synthesized via a facile one-pot solvothermal procedure employing thiourea as the single N and S precursor. The resultant composite was served as an anode active material for lithium-ion batteries (LIBs), which exhibited large specific capacity, good rate capability, and excellent cyclic stability. The superior lithium storage property can be ascribed to the synergistic effect between the NS-G nanosheets and the mesoporous MnS nanoparticles. The NS-G/MnS composite with superior lithium storage properties can be considered as a promising candidate for high performance LIBs anode.

Introduction

Electrochemical energy storage and conversion (EESC) materials, like fuel cells, solar

[a] G. Li, B. He, Dr. M. Zhou, Dr. G. Wang, Dr. N. Zhou, Dr. W. Xu, and Prof. Dr. Z. Hou

School of Chemistry and Chemical Engineering

Hunan Institute of Science and Technology

Qijialing Street, Yueyang, Hunan, 414006 (China)

Tel: +86 730 8648502; Fax: +86 730 8640122

E-mail: zhaohuihou@126.com
cells, LIBs and supercapacitors, are served as alternative energy sources owing to its high energy density and environment-friendly characteristic \cite{1-3}. Among EESC technologies, LIB is one of the most promising candidates. In recent years, the range of application of LIBs has expanded particularly to daily electronic products to achieve a sustainable world \cite{4}. At present, graphitized-carbon materials are the most extensively used anodes for traditional LIBs because of their benefits of many advantages \cite{5}. However, graphitized-carbon materials have two inherent defects as anodes for LIBs. These defects include a poor rate capability and a low theoretical capacity (372 mA h g\(^{-1}\)), which are the main obstacles impeding the further application of graphite-based anode \cite{6}.

Transition metal sulfides (TMSs), which are similar to oxides, possess high theoretical capacities between 500 and 1200 mA h g\(^{-1}\) via the chemical conversion reactions; TMSs attract increasing research interests as the promising alternatives to replace traditional graphite-based anode materials \cite{7-9}. Despite these promising characteristics, TMSs-based anodes often suffer from huge volume expansion and contraction during charge/discharge process, as well as from mechanical stress that induces material agglomeration and electrode pulverization. These deficiencies result in rapid capacity fade and poor cycling performance. Among the TMSs, MnS is a promising material with potential applications in photoluminescence \cite{10}, microwave absorption \cite{11}, supercapacitors \cite{12,13}, and LIBs \cite{14}. When used as an active material for LIBs anode, MnS crystal can react with lithium through the following electrochemical reaction: \(\text{MnS + 2Li}^+ + 2\text{e}^- \leftrightarrow \text{Mn + Li}_2\text{S}\). The resulting theoretical
capacity of MnS (616 mA h g\(^{-1}\)) \cite{15} is higher than the currently used graphite-based anode, which attracted the researcher’s tremendous attention. Zhang et al. prepared \(\alpha\)-MnS submicrocrystals through a hydrothermal route; they initially investigated the lithium storage performances of \(\alpha\)-MnS crystals as anodes for LIBs \cite{14}. Lou et al. reported that single-crystal MnS microboxes display enhanced electrochemical performance as anodes for LIBs \cite{15}. Nevertheless, all of the pristine MnS anode materials show poor anodic performances because of their inherent drawbacks. To enhance the anodic performance of these materials, carbonaceous materials [e.g. graphene or reduced graphene oxide (rGO), carbon nanotubes, carbon nanofiber, and pyrolysis carbon] were usually served as a matrix to prepare the nanocomposite with these TMSs; this approach has captured considerable attention in the past few years \cite{7-9,11}. Some examples of MnS-based nanocomposite anode material are hollow \(\alpha\)-MnS spheres/RGO hybrids \cite{11}, coral-like \(\alpha\)-MnS/N-doped carbon \cite{16}, 3D graphene cross-linked with mesoporous MnS clusters \cite{17}, mesoporous MnS sub-microspheres/graphene composite \cite{18}, \(\gamma\)-MnS/rGO nanocomposites \cite{19}, MnS hollow microspheres/RGO composite \cite{20}, and \(\gamma\)-MnS nanowires/carbon \cite{21}. Among these carbonaceous materials, graphene is a superior substrate for hosting active materials for LIBs application due to its superior mechanical, electrical, and chemical properties \cite{22,23}. Recently, researches have demonstrated that heteroatoms-doped graphene can tailor its electronic structure and significantly improve their electrochemical activity \cite{24-26}. However, despite these promising findings, most of the doping processes in previous studies required a thermal annealing process \cite{3,6b,25,26}. 

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that uses toxic and hazardous precursors (NH$_3$ or H$_2$S) \cite{27,33}. Despite their effectiveness, these methods require both special equipment and harsh conditions. Up to now, Bag et al. reported a one-step method for the synthesis of N and S co-doped graphene by refluxing graphene oxide and thiourea in ethylene glycol (EG) for 3 h at 180 °C \cite{31}.

Inspired by this synthesis method, herein, we demonstrate a facile one-pot procedure to synthesize mesoporous MnS nanoparticles supported on N and S co-doped graphene nanosheets through a facile one-pot solvothermal procedure using thiourea as the single N and S sources without surfactant. When employed as LIBs anode, the resulting NS-G/MnS composite exhibited excellent anodic performance. Such composite shows superior lithium storage performances when compared with the performance of the previously reported MnS-based anode material \cite{11,16-21}. These results can be explained as the following two reasons: on the one hand, N and S co-doping can introduce additional defects and disorders into the graphene framework, these defects are very favorable to Li$^+$ ion storage and thus improves the capacity of LIBs. It is worth noting that Li$^+$ ion storage is determined not only by the amount of heteroatoms or defects but also by the synergistic effect between the dopants \cite{24a}. It is known that the electronegativity of N is much stronger than that of C. Thus, the doping of N atoms into graphene framework can improve the adsorption energy and decrease the energy barrier for Li$^+$ ion intercalation \cite{26}. On the other hand, as the atomic radius of S is larger than C, S-doping causes more structural distortion \cite{24b}, which could result in more defects in graphene, so the Li$^+$ ion trapping could be
increased. Additionally, mesoporous MnS nanoparticles are beneficial to the permeation of electrolytes and can provide multi-dimensional channels for the transport of electrons and the diffusion of Li$^+$ ions during cycles, generating in a remarkable rate capability.

**Results and discussion**

**Structure and Morphology**

Scheme 1 shows the synthesis procedure of NS-G/MnS composite. Graphene oxide (GO) was synthesized by chemical exfoliation of natural graphite flakes using the Hummers’ method $^{[27]}$ with modification and then followed by ultrasonic treatment in EG. Thiourea decomposed into NH$_3$ and H$_2$S under the solvothermal reaction. Notably, the N and S co-doping process, the reduction of GO, and the formation of mesoporous MnS nanoparticles take place simultaneously during solvothermal reaction, resulting in the uniform dispersion of mesoporous MnS nanoparticles onto the NS-G nanosheets.

**Scheme 1.** Schematic diagram of the synthesis procedure of NS-G/MnS composite.
The phase constitution and crystal structure of the products were investigated through X-ray diffraction (XRD). As shown in Figure 1a, the diffraction peaks of the NS-G/MnS composite indicate that the MnS crystal synthesized by such a facile method in the EG-H\(_2\)O system was a coexisting polymorphs of \(\alpha\)-MnS (JCPDS No. 72-1534) and \(\gamma\)-MnS (JCPDS No. 65-3413). The diffraction intensity of pure MnS is stronger then the MnS in NS-G/MnS composite, suggesting that the degree of crystallinity of the pure MnS crystal is better then that of in NS-G/MnS composite. The diffraction peaks of the NS-G nanosheets were not obvious in the XRD patterns of NS-G/MnS composite sample, which may be attributed to the result of restacking-inhibited and well-uniform dispersion of the NS-G nanosheets in the as-prepared composite. The (002) facets of MnS in the NS-G/MnS composite were also in a dominant position similar to the position of the (100) facets. This result suggests that the (002) facet is one of the preferentially growing directions in the NS-G/MnS composite.

The weight percentage of NS-G nanosheets in NS-G/MnS composite is determined by termogravimetric analysis (TGA). Figure 2b shows that the weight increase between 400 and 550 °C was related to the formation of MnSO\(_4\) and Mn\(_3\)O\(_4\) \(^{[11]}\). The small weight loss observed with the temperature range of 550-600 °C indicate that the decomposition of NS-G nanosheets and the formation of MnSO\(_4\) and Mn\(_3\)O\(_4\) were occurred simultaneously. The main weight loss between 700 and 900 °C was associated with the transformation of MnSO\(_4\) into Mn\(_3\)O\(_4\). The XRD pattern of the NS-G/MnS composite after TGA measurement is shown in the inset of Figure 1b. All
the diffraction peaks consistent well with the pure phase of Mn$_3$O$_4$ (JCPDS No. 75-1560). This result is different from that in previous reports$^{[7,11,18]}$ because of the different final temperature in the TGA measurement (900 °C in their study and 1000 °C in our study). The weight loss of pure MnS is about 10%. Hence, the weight percentage of NS-G nanosheets in NS-G/MnS composite is evaluated at around 36%. Such a considerable amount of NS-G nanosheets ensures the NS-G/MnS composite a good electronic conductivity and effectively protects the MnS nanoparticles from aggregation during the charge/discharge process.

The as-prepared samples were characterized by Fourier transform infrared spectroscopy (FTIR) to demonstrate the oxygen-containing functional groups of GO, NS-G nanosheets, and NS-G/MnS composite. Figure 1c shows that the strong absorption peak of hydroxy at 3420 cm$^{-1}$, carbonyl at 1729 cm$^{-1}$, carbon-carbon double bond at 1630 cm$^{-1}$, and carbon-oxygen bond at 1400 cm$^{-1}$ were obviously detected in the GO sample$^{[28a]}$. As regards the NS-G nanosheets and NS-G/MnS composite, the absorption peak of hydroxy is weaker than that in GO, and the absorption peak of carbonyl has disappeared. These results indicate the effective reduction of GO into the NS-G nanosheets during the solvothermal reaction. The Raman spectroscopy measurements were employed to further characterize the structural changes of GO after the solvothermal process. Figure 1d depicts the identified peaks at ~1580 cm$^{-1}$ and ~1340 in the Raman spectra of GO and NS-G/MnS composite, which are assigned to the G band and D band, respectively. The value of $I_D/I_G$ (Raman intensity ratio of the D band and the G band) is extensively
used to assess the quality of carbon-based materials \[12\]. The Raman spectra outcomes exhibit a considerable increase of $I_D/I_G$ value from 1.09 for GO to 1.40 for NS-G/MnS composite. This result indicates that the solvothermal reduction has changed the structure of GO and introduced additional defects and disorders into the graphene framework because of the N and S dual-doping process. These defects are helpful to the lithium storage and improve the capacity of LIBs.

**Figure 1.** (a) the typical XRD patterns of pure MnS nanoparticles and NS-G/MnS composites; (b) TGA curves of MnS and NS-G/MnS composite, inset shows the XRD pattern of NS-G/MnS composite after TGA measurement; (c) FT-IR spectra of GO, NS-G nanosheets, and NS-G/MnS composite; (d) Raman spectra of GO and NS-G/MnS composite.

Specific surface area and pore structure of the NS-G/MnS composite were
estimated by \( \text{N}_2 \) isothermal adsorption-desorption experiment. In Figure 2a, the isotherm shows a type IV adsorption-desorption behavior, and a large hysteresis loop in the relative pressure range from 0.45 to 1.0 can be observed, suggesting the coexistence of mesopores and macropores \[^{[28b]}\]. The specific surface area of NS-G/MnS composite calculated by Brunauer-Emmett-Teller (BET) method is 79.7 \( \text{m}^2 \text{ g}^{-1} \), and the pore volume of the composite is 0.37 \( \text{cm}^3 \text{ g}^{-1} \). These results show that the as-prepared NS-G/MnS composite possesses acceptable value of surface area and pore volume, which can augment the number of accessible sites for the adsorption of \( \text{Li}^+ \) ions when it was used in LIBs. Figure 2b shows the Barrett-Joyner-Halenda (BJH) pore size distribution curve calculated from the adsorption branch, which further demonstrates the mesoporous feature of the NS-G/MnS composite.

![Figure 2](image)

**Figure 2.** (a) \( \text{N}_2 \) adsorption-desorption isotherms and (b) BJH pore size distribution curve of NS-G/MnS composite.

The microstructure of the products were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 3a and b present that NS-G nanosheets were restacked owing to the recovery of the \( \pi \)-conjugated system from the GO sheets upon solvothermal reduction \[^{[29]}\]. Figure 3c
and d show that the pure MnS nanoparticles were agglomerated severely, and some large bulk solids can be observed, which may be attributed to their nanosized dimensions and high surface energies. Additionally, the structural stability of pure MnS nanoparticles could be destroyed by the aggregation and/or pulverization. By contrast, MnS nanoparticles were uniformly distributed and inserted into the NS-G nanosheets in NS-G/MnS composite as shown in Figure 3e and f. The MnS nanoparticles can serve as spacers that inhibit the restacking of NS-G nanosheets, and the NS-G nanosheets can also work as cushions to restrain the aggregation of the MnS nanoparticles. The synergistic effects between the two components make the composite a stable structure upon cycling.
Figure 3. Different magnification SEM images of NS-G nanosheets (a, b), pure MnS nanoparticles (c, d), and NS-G/MnS composite (e, f).

The detailed micromorphology information of the NS-G/MnS composite was further characterized by TEM and is shown in Figure 4. Figure 4a and b show the
micromorphologies of NS-G nanosheets at different magnifications. These images present that the NS-G nanosheets with a wrinkled and scrolled architecture, this result may be ascribed to the microexplosion reaction under ultrasonic-assisted \(^{[30]}\). The high-resolution TEM images of the pure MnS nanoparticles (Figure. 4c and d) show clear lattice spacing of 0.235 nm and 0.345 nm, corresponding to the (102) and (100) facet of \(\gamma\)-MnS, respectively. Figure 4e depicts that the MnS nanoparticles with a particle size range of 100–200 nm are dispersed uniformly into the NS-G nanosheets. The high-resolution TEM images of NS-G/MnS composite (Figure. 4f) exhibit clear porous morphology with a diameter of approximately 4 nm in MnS. This outcome is consistent with of the BJH pore size analysis (Figure 2b). Such a mesoporous structure provides multi-dimensional channels for electron transport and Li\(^+\) ion diffusion during charge/discharge process and will be beneficial to facilitate the permeation of electrolyte, thereby, giving rise to a high cycling performance and rate capability.
Figure 4. (a, b) TEM images of NS-G nanosheets and (e) NS-G/MnS composite, HRTEM images of pure MnS nanoparticles (c, d) and NS-G/MnS composite (f).
XPS measurements were performed to characterize further the chemical composition and bonding configurations in the NS-G nanosheets and NS-G/MnS composite. Figure 5a shows that five elements (C, N, O, S, Mn) can be identified through the characteristic peaks of C1s (284.9 eV), N1s (400.0 eV), O1s (531.9 eV), S2p (163.9 eV), and Mn2p (642.9 eV) in NS-G/MnS composite. Four elements (C, N, O, S) can also be detected in NS-G nanosheets. These findings suggest that graphene framework is successfully co-doped with N and S atoms. There are four peaks locating at 289.2, 286.2, 285.7, and 284.6 eV can be fitted for the high-resolution spectrum of C1s (Figure 5b), corresponding to the carbonyl (C=O), carbon-nitrogen bond (C–N), carbon-oxygen bond (C–O) or carbon-sulfur bond (C–S), and carbon-carbon double bond (C=C, sp2 C) groups, respectively. Figure 5c shows the high-resolution spectrum of N1s, which presents that there are exist three types of N atoms in the graphene framework. The fitted three peaks locating at 401.2, 400.1, and 398.9 eV, corresponding to the graphitic-N, pyridinic-N, and pyrrolic-N, respectively. Notably, 83.1% of the total N in NS-G/MnS composite have a pyridinic-N and pyrrolic-N atomic structure. This type of atomic structure can cause considerable defects and vacancies and is considered to be the most active site for the Li+ ion adsorption, thereby improving the capacity of the LIBs. Figure 5d depicts the high-resolution spectrum of S2p, which is fitted by three peaks locating at 162.5, 164.9, and 169.1 eV; these peaks associated with the thiophene-S of carbon-sulfur-carbon bond, carbon-sulfur double bond and some oxidized S (C-SOx, x = 2, 3, etc.), respectively.
Figure 5. (a) XPS surface survey scan spectra of NS-G nanosheets and NS-G/MnS composite and high-resolution spectra of C1s (b), N1s (c) and S2p (d).

Electrochemical Performances

NS-G/MnS composite was served as a LIBs anode to evaluate its anodic performances by assembling the material into 2025 coin-type cells. Figure 6a depicts the initial three CV curves of the NS-G/MnS composite. In the first cycle, one broad cathodic peak in the range of 1.1–1.6 V can be attributed to the insertion of Li$^+$ ions into the MnS crystal lattice to form the Li$_x$MnS phase. A cathodic peak below 0.5 V is ascribed to the formation of solid electrolyte interface (SEI) layer. Three anodic peaks are detected in the range of 1.0–1.7 V, 1.8–2.1 V, and 2.3–2.6 V, suggesting three steps of electrochemical oxidation reaction proceeds, the reversible formation of Li$_x$MnS and MnS phases, and the extraction of Li$^+$ ions from the defects in the composite. The
The electrochemical reaction mechanism between the NS-G/MnS composite and lithium can be described as follows:\[^{16,20}\):

\[
\text{MnS} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Mn} + \text{Li}_2\text{S} \quad (1)
\]

\[
\text{NS-G} + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{NS-G} \quad (2)
\]

Figure 6b depicts the 1\(^{st}\), 20\(^{th}\), 50\(^{th}\) and 100\(^{th}\) charging and discharging curves of the NS-G/MnS anode at 200 mA g\(^{-1}\). A first-cycle discharge capacity of 1662.6 mA h g\(^{-1}\) was obtained, and a reversible capacity as high as 1004.9 mA h g\(^{-1}\) at the first-cycle was also achieved. The irreversible capacity loss could be ascribed to the inevitable formation of the SEI layer, phenomena that are similar for most anode materials\[^{18,36-38}\]. The reversible capacity reached 989.2 mA h g\(^{-1}\) after 100 cycles. This result shows that the obtained reversible capacity of the composite is higher than the theoretical capacity of MnS, which could be assigned to the additional capacity of the NS-G nanosheets because N and S dual-doping induces abundant active sites into graphene layer and further enhances extra interfacial lithium storage\[^{6,25,26}\]. Figure 7b shows a comparison cycling performance of pure MnS nanoparticles, NS-G nanosheets, and NS-G/MnS composite electrode. The reversible capacity of the NS-G/MnS composite electrode decreased during the first 20 cycles and gradually increased in the following cycles (capacity retention of 98.4\% after 100 cycles in comparison to the first cycle). The phenomenon of increasing capacity over cycling may be ascribed to the porous structure activating process, as well as N and S co-doping active sites of the NS-G/MnS composite electrode. This result could also be assigned to the partial reversible reaction of the SEI layer, and it is a common
phenomenon for numerous electrode materials \[^{[3,26,38]}\]. As regards the NS-G and MnS electrode, both of them are exhibited low charge-discharge capacity and poor cyclic performance. This outcome could be ascribed to the restacking of NS-G nanosheets and the agglomeration of MnS during the charge/discharge process.

The rate performance of the NS-G/MnS composite electrode was also tested at various charge rates range from 0.1 to 2.0 A g\(^{-1}\). The result is shown in Figure 6d. First, the discharge/charge process was conducted at each charge rate for 5 cycles and at 2.0 A g\(^{-1}\) for 10 cycles. Second, the charge rate was gradually returned from 2.0 to 0.1 A g\(^{-1}\) at the same gradient, and retested for 10 cycles at each charge rate of 0.5, 1.0, and 2.0 A g\(^{-1}\), respectively. Finally, the charge rate was reset to 0.5 A g\(^{-1}\). At the rate of 0.1 A g\(^{-1}\), the NS-G/MnS composite electrode given a high average reversible capacity of \(~ 873.5\) mA h g\(^{-1}\). Specific capacity decreased regularly with the increasing rate from 0.1 to 2.0 A g\(^{-1}\). At the high rate of 2.0 A g\(^{-1}\), a charge capacity of \(~ 635.5\) mA h g\(^{-1}\) can still be obtained. The average charge capacity about \(~ 884.4\) mA h g\(^{-1}\) was regained when recycling at 0.1 A g\(^{-1}\). After cycled at 1.0 and 2.0 A g\(^{-1}\), an average charge capacity of \(~ 852.3\) mA h g\(^{-1}\) was recovered when recycling again at 0.5 A g\(^{-1}\). The specific capacity decreases is only \(~ 13.3\) mA h g\(^{-1}\) as the charge rate increased from 0.1 to 0.5 A g\(^{-1}\). These outcomes demonstrate the superior rate capability and electrochemical reversibility of the composite electrode.

To further testify the superior cycling performance of NS-G/MnS composite, a new cell was measured at 1 A g\(^{-1}\) with prolonged 500 cycles. Figure 6e shows that the NS-G/MnS composite electrode exhibited the perfect cyclic performance, wherein a
reversible capacity as high as 882.9 mAh g\(^{-1}\) was obtained after 500 cycles. The capacity retention is about \(\sim 118.7\%\); this result demonstrates an extraordinary extended cyclic performance. The average coulombic efficiency is close to 99\% after the 5\(^{th}\) cycle, which indicates excellent electrochemical reversibility. Table 1 displays a comparison of the electrochemical performance of various MnS-based composite anodes. The result shows that our NS-G/MnS composite exhibits superior anodic performance in comparison with the results of recent reports related to MnS-based composite anodes.

**Table 1** Comparison of the electrochemical performance of various MnS-based composite anodes.

<table>
<thead>
<tr>
<th>MnS-based composite anodes</th>
<th>Voltage window (V vs. Li/Li(^+))</th>
<th>Current density (mA g(^{-1}))</th>
<th>Reversible capacity (mA h g(^{-1}))</th>
<th>Initial coulombic efficiency (%)</th>
<th>Cycle number</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow α-MnS spheres/RGO</td>
<td>0.005–3.0</td>
<td>50</td>
<td>500</td>
<td>68.8%</td>
<td>50</td>
<td>[11]</td>
</tr>
<tr>
<td>Coral-like α-MnS/N-doped carbon</td>
<td>0.01–3.0</td>
<td>500</td>
<td>699</td>
<td>—</td>
<td>400</td>
<td>[16]</td>
</tr>
<tr>
<td>Mesoporous MnS clusters/graphene MnS</td>
<td>0.005–3.0</td>
<td>50</td>
<td>980</td>
<td>66.3%</td>
<td>30</td>
<td>[17]</td>
</tr>
<tr>
<td>MnS sub-microspheres/graphene</td>
<td>0.005–3.0</td>
<td>200</td>
<td>735</td>
<td>71.3%</td>
<td>300</td>
<td>[18]</td>
</tr>
<tr>
<td>γ-MnS/rGO</td>
<td>0.005–3.0</td>
<td>200</td>
<td>600</td>
<td>69%</td>
<td>100</td>
<td>[19]</td>
</tr>
<tr>
<td>MnS hollow microspheres/RGO</td>
<td>0.01–2.6</td>
<td>1000</td>
<td>640</td>
<td>—</td>
<td>400</td>
<td>[20]</td>
</tr>
<tr>
<td>Mesoporous MnS/NS-G</td>
<td>0.005–3.0</td>
<td>1000</td>
<td>882.9</td>
<td>62.9%</td>
<td>500</td>
<td>This work</td>
</tr>
</tbody>
</table>

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Figure 6. (a) CV curves of NS-G/MnS composite electrode at a scanning rate of 0.5 mV s\(^{-1}\); (b) galvanostatic charge-discharge curves of NS-G/MnS composite electrode at 0.2 A g\(^{-1}\) in different cycles; (c) a comparison cycling performance of pure MnS, NS-G nanosheets, and NS-G/MnS composite electrode at 0.2 A g\(^{-1}\); (d) rate capability of NS-G/MnS composite electrode; (e) long-term cyclic performance of NS-G/MnS composite electrode.

To further understand the reason why the composite electrode exhibits such good electrochemical performances, the NS-G/MnS composite electrode was chosen for EIS tests in the full-charged state by comparing with pure MnS nanoparticles and
NS-G nanosheets electrode obtained after five cycles. Figure 7a shows that the shapes of the Nyquist plots are similar. These plots are made up of one circular arc followed with a sloped line. The circular arc represents the resistance of the cell and the sloped line relates with the Li$^+$ ion diffusion inside the electrode \[^{39,40}\]. Figure 7b depicts the relationships between $Z'$ (real part of impedance) and $\omega^{-1/2}$ (angular frequency in the low-frequency region); this relationship indicates that a low slope of $Z'$ versus $\omega^{-1/2}$ results in a high Li$^+$ ion diffusion rate \[^{41-43}\]. The NS-G nanosheets and NS-G/MnS composite electrode have similar slopes, and both exhibit slopes lower than those of MnS electrode. These results indicate that the Li$^+$ ion diffusion rate of the NS-G and NS-G/MnS composite are higher than that of the pure MnS. This finding is attributed to the introduction of NS-G nanosheets into the NS-G/MnS composite. Such introduction significantly enhances the conductivity of the NS-G/MnS composite when compared with pure MnS, which can be attributed to the high electrical conductivity of graphene materials. Figure 7c presents the equivalent circuit model for pure MnS, NS-G nanosheets and NS-G/MnS composite electrode. In this model, constant phase element (CPE) was used to replace the pure capacitance because the electrode is non-ideal. $R_s$, $R_p$, and $R_{ct}$ represent the resistance of electrolyte, the resistance of the SEI layer, and the charge-transfer resistance, respectively. According to the fitting results, the $R_{ct}$ value of the NS-G/MnS composite electrode (84.7 $\Omega$) is lower than those of in NS-G nanosheet (88.0 $\Omega$) and pure MnS electrode (118.3 $\Omega$). This result suggests that the good conduction structure that formed in the composite electrode is due to the synergistic effect between the NS-G nanosheets and the MnS.
nanoparticles.

**Figure 7.** (a) Nyquist impedance plots of pure MnS, NS-G nanosheets and NS-G/MnS composite electrode; (b) the relationships between $Z'$ and $\omega^{-1/2}$; (c) equivalent circuit model for pure MnS, NS-G nanosheets and NS-G/MnS composite electrode.

**Conclusions**

A composite fabricated by mesoporous MnS nanoparticles supported on NS-G nanosheets was successfully synthesized via a facile one-pot solvothermal treatment without surfactant. The as-prepared NS-G/MnS composite was endowed with the merits of mesoporous MnS architectures and defects-riched and high electric conductivity NS-G nanosheets. Given these advantages, the NS-G/MnS composite exhibits superior anodic performance when employed as anode active material for LIBs. Such composite shows a big potential application as next-generation anode active material for LIBs. This kind of synthetic strategy can be employed as a
platform for the synthesis of multi-heteroatoms doped with graphene-based material composite formation with transition metal sulfides.

**Experimental section**

**Preparation of GO hydrogel**

GO hydrogel was prepared via a chemical oxidation of graphite flakes (325 mesh, 99.8%, Alfa Aesar) using a modified Hummers’ method[27]. Typically, 1 g of graphite flakes was mixed with 25 ml of concentrated H$_2$SO$_4$ in a 250 ml of round-bottom flask with ice-water bath. Next, 3 g of KMnO$_4$ (97%, Sinopharm Chemical Reagent) was then gradually added into the mixture with stirring. The mixture was kept stirring at 35 °C for 30 min. Afterward, 100 ml of deionized water (DW) was poured into the mixture with vigorous stirring at a temperature below 100 °C. The mixture was continuous stirring for 30 min. Another 100 ml of DW was then poured into the mixture to dilute the mixture. 5 ml of H$_2$O$_2$ (30%) was then dropwise added into the mixture. After that, a yellow-colored colloid solution was obtained. The colloid solution was centrifuged and washed with 1 mol L$^{-1}$ HCl and DW to remove the SO$_4^{2-}$ ions (detected by BaCl$_2$ aqueous solution) and the metal ions. After the washing process, the resulting GO hydrogel was formed.

**Preparation of NS-G/MnS composite**

NS-G/MnS composite was synthesized via a facile one-pot solvothermal procedure. In a typical synthesis process, 4 ml of GO hydrogel (11 mg ml$^{-1}$) was ultrasonically...
dispersed in 50 ml of EG for 60 min to obtain a brown colloidal solution, and then 2.54 g of manganese acetate tetrahydrate (99%, Tianjin Kermel Chemical Reagent) and 1.52 g of thiourea (99%, Aladdin) were dissolved in 50 ml of DW. The salt solution was then poured into the GO colloidal solution with vigorous stirring. After stirring for 60 min, the mixture was poured into a total capacity of 150 ml Teflon-lined autoclave. After sealed, the Teflon-lined autoclave was put in oven and kept at 180 °C for 15 h. The NS-G/MnS composite was obtained via centrifugation and washed thoroughly with DW and anhydrous alcohol. The collected samples were then dried in an oven at 60 °C overnight. MnS was synthesized in the same condition as the NS-G/MnS composite in the absence of GO solution. After etched the NS-G/MnS composite by 1 mol L⁻¹ HCl aqueous under ultrasonic-assisted, and washed thoroughly with DW and anhydrous alcohol, the NS-G nanosheet was obtained.

**Material characterization**

The phase constitution of the samples was characterized by XRD (Rigaku, Ultima IV) using copper (Cu) Kα radiation. The microstructures of the products were observed by TEM (JEOL, JEM-2100), and SEM (FEI, Nova NanoSEM 450). The molecular structure of the obtained samples was investigated by FTIR (Thermo Nicolet, AVATAR 370), and by Raman spectroscopy (Jobin Yvon, Labram-010) using 632 nm laser excitation. XPS (Axis Ultra DLD, Shimadza-Kratos) experiments were conducted using an aluminum Kα X-ray source (1486.6 eV). TGA (PerkinElmer, Diamond TG/DTA) test was conducted from ambient temperature to 1000 °C at a
heating rate of 10 °C min⁻¹ under air atmosphere. The N₂ adsorption-desorption isotherms and pore size distribution curves of the products were acquired at 77 K on the analyzer (ASAP 2020 HP, Micromeritics). BJH model and BET method were adopted to calculate the pore size distribution and specific surface area of the samples, respectively.

**Electrochemical measurements**

A conventional slurry-coating process was adopted to prepare the working electrode, which was contained active material (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (10 wt%). The mixture was then dispersed in 1-methyl-2-pyrrolidinone. After stirring for 6 h, the uniform slurry was then coated on pure Cu foil, and dried in a vacuum oven at 110 °C overnight to evaporate the solvent. Each electrode contains ~ 1.2 mg of active material.

The electrochemical performances of the active materials were examined by the use of coin-type cells (CR 2025). These cells were assembled in a glove box that was filled with argon and the water and oxygen contents are less than 1 ppm. The pure Li foil was served as the reference/counter electrode and microporous polypropylene film as the separator. 1 mol L⁻¹ LiPF₆ in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) with a volume ratio of 1:1:1 as the electrolyte. Cycling and rate performance of the as-assembled cells were tested on a battery test system (Land CT2001A, Wu Han JinNu electronics Corporation) at various charge rates of 0.1–2.0 A g⁻¹ within the voltage range of 0.005–3V (vs Li/Li⁺). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV)
measurements were curried out on an electrochemical workstation (CHI660B, Shanghai Chenhua Instrument Factory). EIS measurements were operated on open circuit potential in the frequency range from 0.01 Hz to 100 kHz. CV tests were measured at the scan rate of 0.5 mV s\(^{-1}\) within a voltage range of 0.005–3 V.

**Acknowledgements**

This work was supported by National Natural Science Foundation of China (No. 51272075, No. 51238002 and No. 51372080), and Hunan Provincial Innovation Foundation For Postgraduate (No. CX2016B668). We gratefully acknowledge Professor Xu-Biao Luo (Nanchang Hangkong University) and Dr. Fan-Yan Zeng (Jiangxi Normal University) for their help in XPS, SEM, and TEM tests.

**Keywords:** anode material • manganese sulfide • co-doped graphene • lithium-ion batteries


20957–20964.


NS-G/MnS composite was synthesized via a facile one-pot solvothermal procedure. The resultant composite was served as an anode active material for lithium-ion batteries and exhibited large specific capacity, good rate capability, and excellent cyclic stability.

G. Li, B. He, M. Zhou, G. Wang, N. Zhou, W. Xu, Z. Hou*

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Solvothermal synthesis of mesoporous MnS nanoparticle supported on nitrogen and sulfur co-doped graphene with superior lithium storage performance
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