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Polypyrrole-assisted synthesis of roselike MoS$_2$/nitrogen-containing carbon/graphene hybrids and their robust lithium storage performances

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Introduction
Rechargeable lithium-ion batteries (LIBs) have been regarded as one of the most promising power technology in the applications of energy storage stations, electric vehicles and so on.$^{1,2}$ High energy and power density, excellent security, long cycling performance is a key technology for the development of LIBs.$^3$ Nowadays, commercially used carbon-based anode materials are limited by their intrinsically low theoretical capacity value of $372$ mAh g$^{-1}$$^4$ Molybdenum disulfide (MoS$_2$), a layered transition metal dichalcogenide, in which  $\sigma$–Mo–$\sigma$ layers are held together by weak interactions, has attracted tremendous interest owning to its novel geometrical structure and excellent electrical conductivity.$^5$ Meanwhile, it is an ideal substrate for growth and anchoring nanoparticles, such as metal, metal oxide, metal sulfide nanoparticles, functionally as catalysts for hydrogen evolution reaction.$^6$ Graphene, a single layer of $sp^2$ carbon atoms, has attracted tremendous interest owing to its novel inorganic nanomaterials, such as metal, metal oxide, metal sulfide nanoparticles, to which the abundant nitrogen-containing functional groups of NC. When used as an anode materials for lithium ion batteries, the MoS$_2$/NC/G hybrids exhibit enhanced electrochemical energy storage performances compared with the bare MoS$_2$ nanosheets, including high specific capacity (1570.6 mAh g$^{-1}$ at 0.1 A g$^{-1}$), excellent rate capability (704.8 mAh g$^{-1}$ at 5 A g$^{-1}$) and good cycling stability (96.4% capacity retention after 100 cycles at 0.2 A g$^{-1}$). The enhanced lithium storage properties of the MoS$_2$/NC/G hybrids can be ascribed to the boosted electronic conductivity arising from the novel hybrids nanostructures of MoS$_2$/NC/G.

Architectures constructed by single-layered MoS$_2$ via a mixed solution reaction, and exhibited greatly improved Li$^+$ storage properties. Lou et al.$^9$ have reported a simple glucose-assisted hydrothermal method to directly grow MoS$_2$ nanosheets on the CNT backbone, which shown greatly enhanced lithium storage properties compared with the pure MoS$_2$. Graphene, a single layer of $sp^2$ carbon atoms, has attracted tremendous interest owing to its novel geometrical structure and excellent electrical conductivity.$^5$ Mean while, it is an ideal substrate for growth and anchoring nanoparticles, such as metal, metal oxide, metal sulfide nanoparticles, functionally as catalysts for hydrogen evolution reaction.$^6$ Graphene, a single layer of $sp^2$ carbon atoms, has attracted tremendous interest owning to its novel geometrical structure and excellent electrical conductivity.$^5$ Nevertheless, owing to the general incompatibility between graphene and inorganic nanoparticles, the growth of inorganic nanoparticles with uniform morphology and controllable sizes on a graphene substrate is difficult technically.

Recently, nitrogen-containing carbon (NC) has received considerable interest because nitrogen-containing functional groups can not only provide more active sites for lithium storage, but also be used for the conjugation of metallic ions to help the growth of MoS$_2$ on the surface of graphene.$^{10-20}$ Polypyrrole (PPy) is one of the most promising conducting polymers, which facilitates the incorporation of nitrogen-containing functional groups into carbon matrix. In addition, the pyrrole monomers can be easily polymerized on both surfaces of graphene oxide (GO) due to the $\pi$-$\pi$ stacking between PPy and GO layers,$^{21,22}$ which inspires us to find a new route to fabricate hybrids nanostructure in which MoS$_2$ could grow uniformly on the surfaces of PPy/GO. Herein, we report an efficient strategy for the synthesis of MoS$_2$/NC/G hybrids by a facile PPy-assisted synthesis of roselike MoS$_2$/nitrogen-containing carbon/graphene hybrids and their robust lithium storage performances.

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assisted hydrothermal approach in combination with high-
temperature calcination, which exhibit excellent lithium storage 
performances including high specific capacity, excellent rate 
capability and good cycling stability.

**Experimental**

**Synthesis of GO**

Graphene oxide (GO) was synthesized from natural graphite 
flakes by a modified Hummer method.23

**Synthesis of PPy/GO composite**

Pyrrole (4 mL) and GO (200 mg) at the weight ratio of 10:1 were 
dispersed in 900 mL of 0.1 mol L\(^{-1}\) HCl aqueous solution by 
ultrasonication for 20 min. Then 100 mL of HCl (0.1 mol L\(^{-1}\) 
aqueous solution containing ammonium peroxydisulfate (13.6 g) 
was rapidly added to the above mixture suspension solution at 0– 
5°C. The polymerization reaction was carried out for 12 h without 
any disturbance. Then the black precipitate was filtered off, washed 
with ammonium hydroxide, deionized water, and ethanol several 
times, and then dried at 80 °C for 24 h.

**Synthesis of MoS\(_2\)/NC/G hybrids**

The obtained PPy/GO composite (ca. 120 mg) were redispersed 
into 60 mL H\(_2\)O with assistance of ultrasonication about 30 min. 
Then 0.8 g sodium molybdate (Na\(_2\)MoO\(_4\)\cdot 2H\(_2\)O) and 1.0 g thiourea 
were added to the PPy/GO suspension by ultrasonication for another 
30 min. The mixture was transferred a Teflon-lined autoclave and 
kept at 200 °C for 20 h. After cooling down to room temperature, the 
black precipitate was collected by centrifugation, washed with 
ethanol and water for several times, and dried at 80 °C for 24 h. 
Afterwards, the MoS\(_2\)/PPy/GO products were further annealed at 
800 °C for 2 h under the atmosphere of 5% H\(_2\) balanced by Ar for 2 
h with a heating rate of 3 °C min\(^{-1}\).The preparation of the bare MoS\(_2\) 
nanosheets is similar to the one for MoS\(_2\)/NC/G hybrids except the 
addition of PPy/GO.

**Characterization**

The crystalline structures of the samples were characterized by X-
ray powder diffraction (XRD Rigaku D-max-\(\gamma\)A XRD with Cu K\(_{\alpha}\) 
radiation, \(\lambda = 1.54178\) Å) from 5° to 90°. SEM images were 
measured by Field-emission scanning electron microscopy (FE-SEM, 
JSM-6700F from JEOL) and TEM images were measured by a 
transmission electron microscopy (TEM, FEI Tecnai G20).

**Results and discussion**

The synthetic procedure of the MoS\(_2\)/PPy/GO hybrids is illustrated in Fig. 1. To improve the compatibility between GO (Fig. 
S1 a) and MoS\(_2\), PPy was first coated uniformly on both surfaces of 
GO by in-situ polymerization of pyrrole. As shown in Fig. 1b, the 
thickness and lateral dimension of the PPy/GO composite 
nanosheets (Fig. S1 b) are 20–25 nm and 1–2 \(\mu\)m, respectively. After 
hydrothermal growth of MoS\(_2\), it is found that roselike MoS\(_2\) 
composed of nanosheets were coupled on the PPy/GO composite 
nanosheets due to the strong interaction between MoS\(_2\) and PPy (Fig. 
1c). The MoS\(_2\)/PPy/GO hybrids can be converted into MoS\(_2\)/NC/G 
hybrids by high temperature calcination.

Fig. 1 The overall synthetic procedure of MoS\(_2\)/PPy/GO hybrids. The 
corresponding SEM images of GO (a), PPy/GO (b), MoS\(_2\)/PPy/G (c).

Fig. 2 a and b show typical SEM images of the MoS\(_2\)/NC/G 
hybrids. Low-magnification SEM image (Fig. 2 a) reveals that the 
product has a two-dimensional structure and the surface is covered 
with roselike MoS\(_2\) subunits. As shown in high-magnification SEM 
image (Fig. 2b), it is clear that the PPy/GO composite nanosheets are 
converted into NC/G composite nanosheets as indicated by an arrow 
due to the carbonization and thermal reduction process. Moreover, 
the roselike MoS\(_2\) subunits comprising of thin nanosheets are
coupled strongly on the surfaces of NC/G composite nanosheets, which is similar to that of the MoS$_2$/PPy/GO hybrids, indicating that the MoS$_2$/NC/G hybrids possess high thermal stability. Compared with the MoS$_2$/NC/G hybrids, bare MoS$_2$ tends to form microphases composed of nanosheets (Fig. S2 a and b). The roselike MoS$_2$ subunits closely attached on the surfaces of the NC/G nanosheets can be further confirmed by TEM observation (Fig. 2 c). In addition, the NC/G nanosheets can be also found in the TEM image as described by an arrow. Typical HRTEM image of the MoS$_2$ nanosheets is represented in Fig. 2d. The observed fringes correspond to the interplanar distance of 0.66 nm, which are in good agreement with the lattice spacing of the (002) planes of the bare MoS$_2$ nanosheets (Fig. S2 c). Meanwhile, the fringes with interplanar spacing of 2.09 Å corresponding to (200) facet of the Mo$_2$N based on a face-centered cubic crystal structure be clearly observed in the HRTEM image (Fig. S2 d). Intriguing transition metal nitrides have superior properties in some respects such as high conductivity, which are desired for LIBs.

The crystallographic structure and phase purity of annealed MoS$_2$/NC/G hybrids are measured by XRD analysis (Fig. S3). The XRD pattern of the products in the first step can be well indexed to hexagonal MoS$_2$, in good agreement with the standard data (JCPDS card no.37-1492; space group P63/mmc; a = 3.161 Å, c = 12.299 Å). Besides the XRD peaks of hexagonal MoS$_2$, the XRD patterns of the products in the second step show another peak, which can be well matched with a strong peak (111) and (200) of cubic Mo$_2$N (JCPDS card no.25-1366), which may be caused by slow nitridation under the circumstance of PPy pyrolysis.

![Fig. 3 Typical high-resolution XPS spectra of N 1s and Mo 2p (a), Mo 3d and S 2s (b) for the MoS$_2$/NC/G hybrids.](image)

![Fig. 4 N$_2$ adsorption-desorption isotherms (a) and pore size distribution (b) of the MoS$_2$/NC/G hybrids and the bare MoS$_2$ nanosheets.](image)

XPS measurement was applied to analyze the chemical states of the elements in MoS$_2$/NC/G hybrids and the bare MoS$_2$ nanosheets. It can be clearly seen that a peak corresponding to N 1s appears at around 399 eV, suggesting the presence of N in the hybrids (Fig. S4). There is no peak related to N and C species detected from the bare MoS$_2$ nanosheets. The surface elemental compositions from XPS analysis shows that 3.7 at.% N are contained in MoS$_2$/NC/G hybrids. XPS N1s spectrum of the MoS$_2$/NC/G hybrids is displayed in Fig. 3 a, and fitted by three components of binding energies of about 401.0, 398.3, and 397.7 eV. The peaks at 398.3 and 401.0 eV are assigned to pyridinic N and quaternary N, respectively. The peak at around 397.7 eV can be assigned to N 1s which is characteristic for a metal nitride material, which is in agreement with XRD and HRTEM results. The presence of nitrogen at the carbon surface enhance the reactivity and electric conductivity according to previous reports.

![Fig. 5 CV curves of the MoS$_2$/NC/G hybrids (a), and the bare MoS$_2$ nanosheets (b) measured in the voltage range of 0.01–3.0 V with a scan rate of 0.1 mV s$^{-1}$.](image)

CV measurements were performed to investigate the phase transformation and ionic diffusion process of the MoS$_2$/NC/G hybrids and the bare MoS$_2$ nanosheets during the electrode reaction process. In the first cathodic scan (Fig. 5a), the 0.96 V peak is assigned to the Li$^+$ intercalation into MoS$_2$ layers for forming Li$_x$MoS$_2$. 0.36 V peak is attributed to the complete reduction of MoS$_2$ to Mo and Li$_2$S. These peaks disappears completely in the subsequent processes. Instead, new peaks at 1.90, 1.06, and 0.25 V emerge, which perhaps are attributed to combustion of NC and graphene, and oxidation of MoS$_2$ to MoO$_x$. We confirmed that the remaining product after the TG measurement is MoO$_3$ (XRD pattern in Fig. S6), which has a weight fraction of about 79%, estimate that the MoS$_2$ content in the MoS$_2$/NC/G hybrids is approximately 87%.
nanosheets, the CV profile (Fig. 5b) in the first cycle is similar with that of the MoS$_2$/NC/G hybrids. However, higher potentials of oxidation peaks and lower potentials of corresponding reduced peaks compared to MoS$_2$/NC/G hybrids are observed, indicating the large polarization of the bare MoS$_2$ nanosheets during the charge and discharge process. The polarization is associated with the transfer delay of the electrons on the active material/electrolyte interface.$^{32,33}$ In contrast, the MoS$_2$/NC/G hybrids electrode facilitates electron and ion transfer during the electrochemical reaction process.

The lithium storage performances of the MoS$_2$/NC/G hybrids and the bare MoS$_2$ nanosheets were further evaluated by galvanostatic charge-discharge cycling. As shown in Fig. 6a, the plateaus on the charge/discharge curves of MoS$_2$/NC/G hybrids and the bare MoS$_2$ nanosheets are in consistent with the conversion peaks on its CV curves (Fig. 5a and b). The initial discharge and charge capacities of the MoS$_2$/NC/G hybrids were found to be 1570.6 and 1143.7 mAhg$^{-1}$, respectively. Such a high initial lithium storage capacity might be associated with the hybrids nanostructure of MoS$_2$/NC/G. The irreversible capacity loss of approximately 27.2% can be mainly attributed to the formation of the solid-electrolyte interface (SEI). Rate performances of the MoS$_2$/NC/G hybrids and the bare MoS$_2$ nanosheets were examined at various current densities in the range of 0.1–5 A g$^{-1}$ (Fig. 6c). Reversible capacities of around 1570.6, 1182.9, 1153.7, 1056.4, 947.0, and 704.8 mA h g$^{-1}$ are achieved for the MoS$_2$/NC/G hybrids at 0.1, 0.2, 0.5, 1, 2, and 5 A g$^{-1}$, while the bare MoS$_2$ nanosheets deliver inferior capacities of 1226.5, 721.3, 548.3, 443.9, 375.5, and 248.6 mA h g$^{-1}$ at 0.1, 0.5, 1, 2, and 5 A g$^{-1}$, respectively. When the current rate reverses back to 0.1 A g$^{-1}$, the discharge capacities can recover to the original value immediately, indicating that the MoS$_2$/NC/G hybrids possess good cycling stability due to the high structure stability.

Kinetic differences of the MoS$_2$/NC/G hybrids and MoS$_2$ electrodes were investigated by EIS after CV test. As shown in Fig. 6d, the high-frequency semicircle corresponds to the solid SEI film resistance ($R_s$) and the constant phase element (CPE1), the semicircle in the medium-frequency region is assigned to the charge-transfer impedance ($R_{ct}$) and the constant phase element of the electrode-electrolyte interface (CPE2), and W is associated with the Warburg impedance. Obviously, the SEI film resistance ($R_f$) and charge-transfer resistance ($R_{ct}$) of the MoS$_2$/NC/G hybrids based on the modified equivalent circuit (the inset in Fig. 6d) are fitted to be 52.3 and 56.8 $\Omega$, respectively, which are significantly lower than those of the bare MoS$_2$ nanosheets (119 and 614 $\Omega$). The results confirm that the NC/G nanosheets have distinctly boosted the electronic conductivity of the MoS$_2$/NC/G hybrids and facilitate the efficient and fast transfer of electrons and Li$^+$ ions, leading to the high rate capability of the MoS$_2$/NC/G hybrids.

Fig. 6 Galvanostatic discharge-charge profiles of the bare MoS$_2$ nanosheets electrode (a) and the MoS$_2$/NC/G hybrids electrode (b) at various rates. Comparison of the rate performance of the MoS$_2$/NC/G hybrids electrode and the bare MoS$_2$ nanosheets electrode (c). EIS spectra of the of the MoS$_2$/NC/G hybrids and the bare MoS$_2$ nanosheets cells after CV test (d). Equivalent circuits for the MoS$_2$/NC/G hybrids electrode (The inset in d).

Fig. 7 gives the long-term cycling performance of the MoS$_2$/NC/G hybrids and the bare MoS$_2$ electrodes at a current rate of 0.2 A g$^{-1}$. During the first 40 cycles, the discharge capacity stabilizes around 1021 mAh g$^{-1}$, and then gradually increases to 1093 mAh g$^{-1}$ at the 100 th cycle (96.4% of the second cycle capacity). The increasing specific capacity with cycling is common for various nanostructured metal oxide/sulfide electrodes and could be attributed to the growth of the gel-like polymeric layer and possibly electrochemical activation of hybrids composites.$^{34,35}$ In contrast, the bare MoS$_2$ nanosheets delivers fast capacity fading, and a capacity of only around 285 mAhg$^{-1}$ was retains after 100 cycles (42.3% of the second cycle capacity). These results reveal the excellent electrochemical stability and cycling performance of the MoS$_2$/NC/G hybrids.

Conclusions

In conclusion, we have developed a facile PPy-assisted approach to successfully synthesize the MoS$_2$/NC/G hybrids in which roselike MoS$_2$ subunits composed of nanosheets are closely attached on the surfaces of the NC/G nanosheets. The presence of PPy can not only couple the MoS$_2$ with graphene oxide, but also be converted into NC to increase electronic conductivity of the hybrids. As a result, the MoS$_2$/NC/G hybrids exhibit improved lithium ion storage performances including higher specific capacity, superior rate performance, and good cycling stability in comparison with the bare MoS$_2$ nanosheets. This facile strategy can be extended to fabricate other hybrid electrode materials to couple two incompatible components which may serve as ideal candidates in catalyst, sensors, supercapacitors, as well as LIBs.
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Notes and references

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