In situ catalytic growth of large-area multilayered graphene/MoS$_2$ heterostructures

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Stacking various two-dimensional atomic crystals on top of each other is a feasible approach to create unique multilayered heterostructures with desired properties. Herein for the first time, we present a controlled preparation of large-area graphene/MoS$_2$ heterostructures via a simple heating procedure on Mo-oleate complex coated sodium sulfate under N$_2$ atmosphere. Through a direct in situ catalytic reaction, graphene layer has been uniformly grown on the MoS$_2$ film formed by the reaction of Mo species with S species, which is from the carbothermal reduction of sodium sulfate. Due to the excellent graphene “painting” on MoS$_2$ atomic layers, the significantly shortened lithium ion diffusion distance and the markedly enhanced electronic conductivity, these multilayered graphene/MoS$_2$ heterostructures exhibit high specific capacity, unprecedented rate performance and outstanding cycling stability, especially at a high current density, when used as an anode material for lithium batteries. This work provides a simple but efficient route for the controlled fabrication of large-area multilayered graphene/metal sulfide heterostructures with promising applications in battery manufacture, electronics or catalysis.

With superb electronic and mechanical properties, two dimensional (2D) atomic crystals have shown great promise in a plethora of applications$^{1-7}$. Efforts have been devoted to the development of atomic-scale heterostructures made from a combination of alternating layers of graphene, MoS$_2$, hexagonal boron-nitride and so on$^{8-12}$. Such heterostructures provide a higher electronic quality for lateral graphene devices$^{13-15}$ and also allow for a conceptually new degree of flexibility in designing films for applications in battery manufacture, electronics or catalysis$^{16-20}$. Accordingly, interest has been directed to the exploitation of reliable methods for the fabrication of large-area high-quality heterostructures$^{21,22}$. So far, the most popular strategy for the preparation of atomic-scale heterostructures is based on the poly-methylmethacrylate (PMMA) transfer of one atomic layer to the top of another$^{23}$. However, the atomic layers involved have to be prepared in advance by epitaxial growth, mechanical exfoliation$^{22}$, liquid-phase exfoliation$^{23,24}$ or chemical vapor deposition (CVD)$^{25-27}$, making this approach quite complicated. In addition, the achievement in rational stacking between atomic layers is still challenging for the atomic layer transfer strategy. Recently, a templating CVD method has been developed, realizing the epitaxial growth of graphene on h-BN, ZnO and ZnS$^{28-29}$. Although the quality of the atomic-scale heterostructures is guaranteed, the CVD reactions had to be stimulated through a plasma or arc-discharge treatment and expensive, complicated instruments had to be used. The growth of MoS$_2$ on graphene was also reported through a hydrothermal method$^{30}$, but it is not feasible to use such a method to generate high quality atomic layer heterostructures because the formation of nanoparticles is more favorable than atomic layers for MoS$_2$ under hydrothermal conditions. Thus, the development of a simple, controllable, and cost-effective method for the fabrication of large-area, high-quality multilayered heterostructures with superb properties is highly desirable.

Herein, we describe a transfer-free method for the preparation of large-area, high-quality multilayered graphene/MoS$_2$ heterostructured films in a controlled manner. The films have been fabricated through an in situ catalytic process by simply heating Mo-oleate complex coated on sodium sulfate particles under a N$_2$ atmosphere. Taking advantage of the greatly shortened lithium ion diffusion distance and the outstanding electronic conductivity, the graphene/MoS$_2$ heterostructured films exhibit high specific capacity, excellent rate performance and cycling stability, even at high current densities, when used as an anode material for lithium batteries.

The preparation procedure of graphene/MoS$_2$ heterostructured films is provided in Supplementary Fig. S1. First, Mo-oleate was obtained by aging the mixture of molybdenum pentachloride (MoCl$_5$), sodium oleate and a small amount of de-ionized water at 358 K for 3 h. The Mo-oleate formed was uniformly coated on the surface of
sodium sulfate particles and then transferred to a tube furnace and heated in a N₂ atmosphere. After the product was washed with de-ionized water and dried at 353 K, graphene/MoS₂ heterostructured films were obtained.

For the preparation of large-area uniform graphene/MoS₂ heterostructures, sodium sulfate single crystals were used as a substrate and a source of sulfur, while Mo-oleate complex as the sources of Mo and carbon. 2D atomic crystals usually grow on flat substrates and the nature of substrates gives an important impact on the quality of the 2D atomic crystals generated. The substrates with inactive surfaces such as SiO₂ film function only as flat supports for the growth of atomic layers31, while the metal-based substrates, such as Cu32, Ni33 or Ru34, not only work as supports but also prompt the formation of atomic layers. However, the removal of the metal substrates usually caused contamination of the formed layers by metal impurities. For the preparation of graphene/MoS₂ heterostructures, we chose sodium sulfate crystals as a substrate. In addition to the smooth crystal facets which provide an ideal support for the growth of the heterostructures, sodium sulfate solid functions as a sulfur source for the generation of MoS₂ through a local CVD reaction. More importantly, the sodium sulfate substrate can be easily removed to generate free-standing atomic layers by washing with de-ionized water after the reactions.

A proposed formation mechanism for the graphene/MoS₂ heterostructured films is illustrated in Fig. 1 and the possible chemical reactions are listed in Supplementary Equations. Upon stirring sodium sulfate crystals with pre-prepared Mo-oleate gently, a uniform Mo-oleate ultrathin layer was coated on the surface of sodium sulfate particles (Fig. 1a). After heated at high temperature in a N₂ atmosphere, amorphous carbon thin films are formed through carbonization of the coating molybdenum oleate complex on the surface of sodium sulfate particles. The amorphous carbon thin films would reduce sulfate on the surface of the sulfate particles to form Na₂S₃ and the hydroslysis of Na₂S₃ leads to the formation of hydrogen sulfur. A local CVD reaction was expected to take place to generate uniform MoS₂ atomic layer through the reaction of hydrogen sulfur with Mo species, resulting in an amorphous carbon/MoS₂ film supported on the surface of the remaining sodium sulfate crystals was obtained (Fig. 1b). Transmission electron microscopy (TEM) and the selected area electron diffraction (SAED) of the amorphous carbon/MoS₂ film supported on the surface of the remaining sodium sulfate crystals was obtained (Fig. 1b). Transmission electron microscopy (TEM) and the selected area electron diffraction (SAED) of the amorphous carbon/MoS₂ films prepared by heating at 873 K for 0.5 h are shown in Fig. S2. From the TEM image, it is seen that the amorphous carbon/MoS₂ films are rather uniform. The SAED pattern of the films shows one set of six-fold symmetry diffraction spots and diffraction rings, ascribed to MoS₂ crystal and the amorphous carbon, respectively. The SAED pattern demonstrates the existence of crystalline MoS₂ and amorphous carbon species in the films generated. Compared with traditional CVD methods using external H₂S or S as a source of sulfur31,35, this local CVD process is simple in producing uniform MoS₂ atomic layer.

Further heating the reactant for 3 h in a N₂ atmosphere leads to growth of graphene on MoS₂ through the conversion of the amorphous carbon, generating graphene/MoS₂ heterostructures on the surface of sodium sulfate (Fig. 1c). The scanning electron microscopy (SEM) image shows that the coated film has a lateral size of >140 μm (Fig. S3). After removal of Na₂SO₄ substrate by simply washing with de-ionized water, an ultrathin graphene/MoS₂ heterestructured film was obtained (Fig. 1d–e). The uniformity and high quality of the heterostructured film are well demonstrated by the TEM observation (Fig. 2a). The SAED pattern of the film shows one set of strong single crystal diffraction spots (labeled in white color) and another set of weak single crystal spots (labeled in yellow color), attributing to the crystalline MoS₂ and few-layered graphene, respectively (Fig. 2b). The X-ray photoelectron spectra (XPS) technique has been used to further identify the nature of carbon in the heterostructured films (Fig. S4). The C 1 s XPS spectra show a main peak near 284.5 eV, ascribed to the sp²-hybridized carbon36. The presence of the sp²-hybridized carbon indicates the catalytic growth of graphene on MoS₂ layer from the amorphous carbon. The high-resolution TEM observation at the edge of the film obviously shows the stacking of MoS₂ layer on the top of graphene atomic layer (Fig. 2c). From the analyses of the AFM and the corresponding height profiles (Fig. 2d–g), the thicknesses of individual graphene and MoS₂ layers are measured to be approximately 1.6 and 1.2 nm, respectively. This result might suggest that the heterostructured film consists of a carbon layer composed of four single graphene sheets and one single MoS₂ sheet. To further prove the existence of both graphene and MoS₂, we performed the large area spatially Raman mapping (532 nm), collecting spectra on a 15 × 30 μm grid with 6 × 6 spots. The Raman spectra are shown in Figure S5 a–d and the E₁₂g, A₁g, D and G peaks intensities of the spectra are plotted as maps, respectively. From the Raman mapping images of E₁₂g, A₁g, D and G intensities (Figure S5 e–h), the characteristic peaks of E₂g and A₁g for MoS₂, and those of D and G for graphene are detected in each spot of the selected large-area region of our material, revealing the growth of large area graphene/MoS₂ heterostructure in our material. Moreover, the scanning transmission electron microscopy (STEM) technique was also used to identify the elemental distribution of carbon, sulfur and Mo in a film. The STEM image of GM1 is shown in Figure S6. It exhibits uniform distribution of carbon, sulfur and

Figure 1 | Schematic representation of the preparation procedure and formation mechanism of multilayered graphene/MoS₂ heterostructure.
Mo in the film, revealing the existence of 2D heterostructure of graphene and MoS$_2$.

To reveal the nature of graphene layers catalytically grown on MoS$_2$ more clearly, we removed the MoS$_2$ layer from the heterostructured film using strong acids. The TEM image shows that the remaining ultrathin film is quite large and uniform (Fig. 3a). The related EDX analysis shows that only carbon element is present in the film, indicating that the MoS$_2$ layer has been removed completely (Fig. S7). The SAED pattern (Inset of Fig. 3a) of the carbon film presents a hexagonal symmetry of graphene. The AFM image (Fig. 3b) and the corresponding height profile (Inset of Fig. 3b) shows that the thickness of the graphene film is approximately 1.66 nm, in good agreement with that of the graphene/MoS$_2$ heterostructured films.

It is believed that the MoS$_2$ atomic layers function as both a template and a catalyst during the formation of the graphene. The growth of large-area graphene is catalyzed by the in situ formed MoS$_2$ hexagonal atomic crystals. Under intense conditions graphene has also been prepared on hexagonal atomic layers previously$^{37,38,29}$. Employed graphite flake as carbon source and ZnO or ZnS as catalysts, Liu et al$^{37}$ obtained graphene sheets by using an arc-discharge method. Yang et al$^{37}$ reported the epitaxial growth of graphene on h-BN by breaking down the methane with a remote plasma source. A catalyst-free transformation of amorphous carbon into graphene via current-induced annealing was reported by Barreiro et al$^{38}$. It is worth noting that for the growth of large-area graphene on the MoS$_2$ layer, no external forces are involved, making our in situ catalytic process simple and environmentally friendly.

The number of MoS$_2$ sheets in the graphene/MoS$_2$ heterostructured films can be controlled by varying the molar ratio of MoCl$_5$ to sodium oleate. When the molar ratio is 1:5, the heterostructured film, denoted as GM1 is mainly composed of one MoS$_2$ sheet and one graphene layer (Fig. 2). Increasing the molar ratio to 2:5, the heterostructured film, denoted as GM2, mainly contains three MoS$_2$ sheets (Fig. S8 a,b). Further increasing the molar ratio to 4:5, the number of MoS$_2$ sheets in the heterostructured film, denoted as GM3, is mainly six (Fig. S8 c,d). In the AFM images, the thickness of a heterostructured film measured is approximately 2.7 and 5.6 nm for the samples GM2 and GM3, respectively, consistent with the results of the high-resolution TEM observation. Interestingly, in GM2 and GM3, the interlayer distance between adjacent single-layer MoS$_2$ is approximately 1.0 nm, equal to the sum of $d(002)$ spacing of MoS$_2$ (0.62 nm) and the thickness of single-carbon layer (0.34 nm). Furthermore, the Raman spectrum was used to identify the nature of single-carbon layer. It shows two sharp G and 2D bands at around 1576 and 2686 cm$^{-1}$ respectively, revealing that the interlayer carbon might...
be graphene (Fig. S9). The possible synthesis mechanism for heterostructures with different number of MoS$_2$ sheets (as illustrated in Fig. S10) is that the increase in sheet number of MoS$_2$ with molar ratio of MoCl$_5$ might be due to increased number of MoO$_x$ sheets derived from the hydrolysis of MoCl$_5$. The subsequent local CVD reaction of these MoO$_x$ sheets with hydrogen sulfur generates the corresponding MoS$_2$ sheets.

As a typical 2D chalcogenide, atomic layered MoS$_2$ is promising for use as an electrode material in rechargeable lithium ion batteries due to the large specific capacity and high rate performance$^{6,39–41}$. However, the poor electronic/ionic conductivity between two adjacent S-Mo-S layers still limits their further applications$^{42}$. Furthermore, the lithiation product Li$_2$S is prone to reacting with the electrolyte to produce a thick gel-like polymeric layer, which leads to the capacity fading and inferior rate capability$^{43,44}$. It is expected that these issues can be resolved by switching to the multilayered graphene/MoS$_2$ heterostructures, in which atomic layers of MoS$_2$ are coated with graphene to enhance the electronic/ionic conductivity and to reduce the reactions at the interface between MoS$_2$ atomic layer and electrolyte$^{45,46}$.

In this work, the electrochemical performance of the graphene/MoS$_2$ heterostructured films has been evaluated as an electrode material for lithium-ion batteries. The initial three consecutive cyclic voltammograms (CVs) of the three MoS$_2$-layered films are shown in Fig. 4a. There are two cathodic peaks located at 0.87 and 0.22 V in the first cycle. The peak at 0.87 V corresponds to the intercalation of Li$^+$ into the MoS$_2$ lattice to form Li$_x$MoS$_2$. The other peak at 0.22 V is attributed to the decomposition of MoS$_2$ into Mo nanoparticles following the reaction, MoS$_2$ + 4Li$^+$ + 4e$^-$ → Mo + 2Li$_2$S. The Mo nanoparticles generated are embedded in a Li$_2$S matrix. In the reverse anodic curve, a very small oxidation peak at 1.77 V is detected, attributed to the partial oxidation of Mo into MoS$_2$. The distinct peak located at 2.43 V is ascribed to the conversion of Li$_2$S into S. After the first cycle, the electrode is mainly composed of Mo and S instead of the initial MoS$_2$. In the following cycles, the cathodic peaks at around 1.83, 1.0 and 0.2 V are ascribed to the formation of Li$_2$S, LixMoS$_2$, and Mo, respectively, as illustrated in equations (1–3). The CV curves with distinct redox peaks are consistent with those reported in the literature for MoS$_2$ materials$^{47–49}$. Stable redox peaks for the conversion between Li$_2$S and S are clearly observed upon cycling, indicating that the stability of the heterostructured films upon lithiation and delithiation. The graphene sheets in the heterostructured films not only improve the electronic conductivity, but also prevent the dissolution of intermediate lithium polysulfide products, ensuring the cycling stability.

$$2\text{Li}^+ + \text{S} + 2\text{e}^- \rightarrow \text{Li}_2\text{S}$$  \hspace{1cm} (1)

$$\text{MoS}_2 + x\text{Li}^+ \rightarrow \text{Li}_x\text{MoS}_2$$  \hspace{1cm} (2)

$$\text{Li}_x\text{MoS}_2 + (4-x)\text{Li}^+ + (4-x)\text{e}^- \rightarrow \text{Mo} + 2\text{Li}_2\text{S}$$ \hspace{1cm} (3)
MoS₂ heterostructured films are cycled stepwise. (b) The diffusion of Li ions into the heterostructured film from the front and side surfaces of MoS₂ layers. (c) The electron conduction in the graphene layer. These graphene/MoS₂ heterostructured films enhance the high contact area, shorten the Li ion diffusion length and promote the faster transfer of electrons in the material.

Figure 5 | Schematic representation of diffusions of Li⁺ and electron in GM2 during charge and discharge processes. (a) The multilayered graphene/MoS₂ heterostructures. (b) The diffusion of Li ions into the heterostructured film from the front and side surfaces of MoS₂ layers. (c) The electron conduction in the graphene layer. These graphene/MoS₂ heterostructured films enhance the high contact area, shorten the Li ion diffusion length and promote the faster transfer of electrons in the material.

observed, corresponding to the formation of Li₂S and Li₄MoS₂, respectively, upon lithium ion insertion. The distinct plateau at approximately 2.3 V in the charge profiles is ascribed to the generation of S upon the Li⁺ extraction. The negligible variation of this plateau upon cycling indicates that insertion and extraction of lithium ion in and from S is highly reversible. The initial discharge and charge capacities of the MoS₂-layered films are 936 and 820 mAh g⁻¹, respectively, giving a coulombic efficiency of 88%. The irreversibility of approximately 116 mAh g⁻¹ is due to the formation of solid electrolyte interface (SEI) film, decomposition of electrolyte, and reduction of oxygen-containing groups⁴⁹. The coulombic efficiency increases to over 99% in the subsequent cycles. Compared with the MoS₂-based electrode materials reported in the literature⁴⁵–⁵⁰, the heterostructured films show distinctly high coulombic efficiency and large capacities at high current densities, attributing to the unique heterostructure of these graphene/MoS₂ thin films.

The variation of the specific charge capacities of the graphene/MoS₂ heterostructured films is plotted as a function of cycling number (Fig. 4c). The cycling performance of the heterostructured films GM1, GM2, and GM3 is tested at a current density of 1.0 A g⁻¹. A slight increase in the charge capacity with charge/discharge cycles is observed for both GM1 and GM2, attributed to the gradual activation of the electrode upon lithiation and delithiation. Large discharge capacities of approximately 1100, 800, and 730 mAh g⁻¹ are retained for the GM2, GM3, and GM1, respectively after 50 cycles, distinctly higher than those presented in the literature (580 mAh g⁻¹)⁴⁹,⁵¹. Compared with GM1 and GM3, GM2 exhibits the highest charge capacity and the best cycling stability. In addition to the remarkable cycleability, the heterostructures also exhibit excellent rate performance. Figure 4d shows the variations of the reversible capacities with current densities and charge-discharge cycles. The cells were first cycled at 0.1 A g⁻¹ for 5 cycles, followed by cycling at current densities increasing stepwise to as high as 10 A g⁻¹. Compared with GM1 and GM3, GM2 exhibits superior rate performance. For GM2, a reversible capacity of approximately 990 mA h g⁻¹ is achieved at a current density of 0.1 A g⁻¹, 970 mAh g⁻¹ at 0.5 A g⁻¹, 930 mAh g⁻¹ at 2.0 A g⁻¹, and 820 mAh g⁻¹ at 10.0 A g⁻¹. Cycled at 10.0 A g⁻¹, reversible capacities of 269 and 606 mAh g⁻¹ are obtained for GM1 and GM3, respectively, much lower than that of GM2. Decreasing the current density back to 0.1 A g⁻¹ after cycling at 10.0 A g⁻¹, reversible capacities of 920, 1360, and 1202 mAh g⁻¹ are restored for GM1, GM2, and GM3, respectively, indicating the good reversibility and structural stability of these heterostructured films. To the best of our knowledge, such a remarkably high electrochemical performance has never been reported so far for MoS₂ materials in the literature.

The electrochemical performance of MoS₂-based heterostructured films depends on the film thickness and the weight of MoS₂ content in a hybrid active material. GM1 has the highest content of graphene in the composite, while GM3 shows the highest content of MoS₂ in the composite (Table S1). However, as shown in Fig. 4, GM2 exhibits the highest charge capacity and the best cycling stability. The superb electrochemical performance of GM2 is ascribed to its appropriate mass ratio of graphene/MoS₂ in the composite. The appropriate MoS₂ content in GM2 ensures the high specific capacity of the electrode, while the thin graphene layers improve the electronic conductivity of the electrode and ensure the cycling stability of S generated electrochemically.

It is believed that the high capacity and excellent rate performance is associated with the unique multilayered graphene/MoS₂ heterostructures. As demonstrated by the schematic illustration in Fig. 5, the graphene/MoS₂ heterostructure is composed of appropriate number of graphene and MoS₂ atomic layers, ensuring the structure stability and facilitating the transport of electrons and the diffusion of lithium ions (Fig. 5a). Due to the small thickness of the films, the Li⁺ ions may get sufficient contact with the atomic layers of MoS₂ (Fig. 5b). The interlayered graphene not only improves the electronic conductivity of the electrode, but also helps with the reversible insertion and extraction of lithium ions in the material.
We have synthesized large-area multilayered graphene/MoS2 heterostructures with a tunable sheet number through in situ catalytic growth of graphene on MoS2 atomic crystal. The uniform heterostructured films exhibit excellent electrochemical performance when used as an electrode material for LIBs. For the heterostructure with mainly three MoS2 sheets, large discharge capacities of approximately 1100 mA g$^{-1}$ are delivered at a current density of 1.0 A g$^{-1}$ for 50 cycles. Taking advantage of uniformity, large area, and high electronic quality, these heterostructured films may find use in more traditional fields such as electronics or catalysis. This simple, controllable, and inexpensive synthetic strategy is also applicable for the preparation of other multilayered graphene/metal sulfide heterostructures with attractive properties.

Methods

Materials. All the reagents for synthesis and preparation were of analytic grade and used as received without further purification. Molybdenum pentachloride were purchased from Acros. Sodium oleate and sodium sulfate were purchased from TCI and Aldrich, respectively.

Preparation of graphene/MoS2 heterostructures. In a typical procedure, a certain amount of molybdenum pentachloride (MoCl5, Acros) was dissolved in 2.0 ml of de-ionized water and then mixed with 1.22 g sodium oleate (TCL 95%). The mixture was aged at 358 K for 3 h, leading to the formation of molybdenum oleate. 10.0 g of sodium sulfate (Aldrich, 98%) was mixed well with the above molybdenum oleate by grounding. During this process, molybdenum oleate was uniformly coated on the surface of sodium sulfate particles. The ground mixture was heated at 873 K with a ramping rate of 10 K min$^{-1}$ under a N2 atmosphere for 3 h. After cooled down naturally, the product was washed with de-ionized water to remove unreacted sodium sulfate and then dried at 353 K for 12 h. In order to control the number of MoS2 layers, the molar ratios of MoCl5 to sodium oleate were chosen to be 1 : 5, 2 : 5 and 4 : 5, and the corresponding products are denoted GM1, GM2 and GM 3, respectively.

General characterization. The transmission electron microscopy (TEM) images were taken with a JEM-2100F microscope operated at an acceleration voltage of 200 kV. The scanning electron microscopic (SEM) images were obtained with a FEI Topcon microscope (Brucker AG). XPS measurements were conducted on a Kratos Axis Ultra DLD spectrometer using a monochromated Al Kα radiation. The atomic force microscope (AFM) images were taken on a Multimode-NanoscopeIII microscope (Digital Instrument).

The battery performance. The working electrode was fabricated as follows. First, the MoS2 (70 wt%), Super-P carbon black (15 wt%, Timcal), and sodium carboxymethyl cellulose (15 wt%) were mixed in an ethanol/water solution to form a slurry. The mixture was aged at 358 K for 3 h, leading to the formation of molybdenum oleate (TCL 95%). The mixture was aged at 358 K for 3 h, leading to the formation of molybdenum oleate (TCL 95%). The mixture was aged at 358 K for 3 h, leading to the formation of molybdenum oleate (TCL 95%). The mixture was aged at 358 K for 3 h, leading to the formation of molybdenum oleate (TCL 95%). The mixture was aged at 358 K for 3 h, leading to the formation of molybdenum oleate (TCL 95%). The mixture was aged at 358 K for 3 h, leading to the formation of molybdenum oleate (TCL 95%).
43. Zheng, G. et al. Amphiphilic surface modification of hollow carbon nanofibers for improved cycle life of lithium sulfur batteries. *Nano Lett.* 13, 1265–1270 (2013).
44. Yang, Y. et al. High-capacity micrometer-sized Li$_2$S particles as cathode materials for advanced rechargeable lithium-ion batteries. *J. Am. Chem. Soc.* 134, 15387–15394 (2012).
45. Hassoun, J. & Scrosati, B. A high-performance polymer tin sulfur lithium ion battery. *Angew. Chem. Int. Ed.* 49, 2371–2374 (2010).
46. Armand, M. & Tarascon, J. M. Building better batteries. *Nature* 451, 652–657 (2008).
47. Yu, H. et al. Three-dimensional hierarchical architectures constructed by graphene/MoS$_2$ nanoflake arrays and their rapid charging/discharging properties as lithium-ion battery anodes. *Chem. – Eur. J.* 19, 5818–5823 (2013).
48. Gong, Y. et al. A bottom-up approach to build 3D architectures from nanosheets for superior lithium storage. *Adv. Funct. Mater.* 24, 125–130 (2014).
49. Yang, L. et al. Hierarchical MoS$_2$/polyaniline nanowires with excellent electrochemical performance for lithium-ion batteries. *Adv. Mater.* 25, 1180–1184 (2012).
50. Rout, C. S. et al. Synthesis and characterization of patronite form of vanadium sulfide on graphitic layer. *J. Am. Chem. Soc.* 135, 8720–8725 (2013).
51. Wang, Z. et al. CTAB-assisted synthesis of single-layer MoS$_2$-graphene composites as anode materials of Li-ion batteries. *J. Mater. Chem. A* 1, 2202–2210 (2013).

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Author contributions

W.F. and K.X.W. developed the idea and designed the experiments. W.F. performed the sample fabrication, measurements and data analysis. F.H.D. performed the electrochemical experiments. W.F., K.X.W., F.H.D., X.H.L., X.W., T.N.Y., J.S. and J.S.C. analyzed the data, and discussed the results. W.F., K.X.W. and J.S.C. co-wrote the paper. J.S.C. planned and supervised the project.

Additional information

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