Hierarchical 3D graphene nanoribbons/carbon nanotubes–molybdenum disulfide (GR/CNT-MoS2) nanocomposites have been facilely and controllably prepared. The GR/CNT matrix, which is prepared by partial unzipping of multiwalled CNTs, possesses good conductive networks by bridging graphene nanoribbons on different CNTs. MoS2 with monolithic morphologies is anchored on the GR/CNT conductive networks, achieving the formation of hierarchical GR/CNT-MoS2 nanocomposites. As a result of the good dispersion of MoS2, a large specific surface area (238 m² g⁻¹) of GR/CNT-MoS2 nanocomposite has been achieved. Excellent electrochemical performance including high specific capacity (1245 mA h g⁻¹) and good cycling stability (90.9% capacity retention after 200 cycles) of the GR/CNT-MoS2 nanocomposites is achieved due to the full exposure of the active sites of MoS2 nanoflakes, and high electron transport ability of the GR/CNT substrate. These novel GR/CNT-MoS2 nanocomposites show promising application in lithium ion batteries, and further provide a new way to design and develop new anode materials.

1. Introduction
Lithium ion batteries (LIBs) have been proven to be promising candidates for prospective high-power electronics due to their superior energy storage ability, especially their high energy density and long-cycle life. Nowadays, a critical challenge for further boosting their performance is to design and synthesize novel electrode materials with upgraded conductivity and electrochemical properties. 2D transition-metal dichalcogenides MX2 (M = Mo, Ta, Ti, Nb; X = S, Se, Te), acting as alternative anode materials for traditional graphite, have drawn considerable interests due to their high specific capacity and abundant active sites. The layered structures of MX2 are predominately connected with covalent bonds with regnant van der Waals forces between layers, and severe destruction upon repetitive lithium insertion during alloying and dealloying.

However, the practical application of MoS2 is still seriously restricted by its poor capacity retention over longterm charge/discharge cycling. This problem mainly originates from their intrinsically poor ionic/electrical conductivity between two adjacent S–Mo–S layers, and severe destruction upon repetitive lithium insertion during alloying and dealloying. Moreover, it is proved that the lithiation product Li2S will react with the electrolyte, which results in the formation of thick gel-like polymeric layers with irrecoverable capacity fading. In addition, the exfoliated MoS2 layers are prone to aggregate or restack during the drying process and repetitive cycling due to the existed van der Waals interactions.

Nanostructural engineering of MoS2 and hybridization bulk MoS2 with superior conductive matrices have been demonstrated as two effective approaches to improve the electrochemical performance of MoS2 material. First, it has been definitely demonstrated that the battery performance of MoS2 is highly
dependent on its particle size and morphology. Microscaled MoS\(_2\) exhibits initial specific capacitance over 600 mA h g\(^{-1}\), but suffers quick decline in the following cycles. Nanosized MoS\(_2\) (usually nanosheets resulting from its layered structure) is confirmed to be able to enhance the interfacial contact area between MoS\(_2\) and electrolyte, as well as to reduce the diffusing distance of lithium ions, thus improving the storage capacity. Second, constructing hierarchical 3D architectures with nanosized MoS\(_2\) on 2D conductive carbon networks can effectively improve the conductivity and long-term stability of the electrode materials by promoting the electron transport in the poorly conductive MoS\(_2\), and remarkably prevent the restacking and aggregation of MoS\(_2\), thus greatly enhancing their electrochemical performance. Moreover, integrating the aforementioned two design principles to prepare hierarchical MoS\(_2\) hybrid nanomaterials supported on conductive carbon networks may provide new advanced electrode materials for highly efficient lithium storage.

In this work, 3D hybrid materials of graphene nanoribbons/carbon nanotubes (GRs/CNTs) and MoS\(_2\) (GR/CNT-MoS\(_2\)) were facilely and controllably prepared with monolithic MoS\(_2\) nanoflakes anchored on 3D conductive carbon networks of GR/CNT. The GR/CNT materials were prepared by partial unzipping of multiwalled CNTs, resulting in the internally bridged 3D conductive carboonic networks with excellent codispersion stability. The structural design of MoS\(_2\) nanoflakes anchored on carboonic networks ensures the transport of electrons/lithium ions to be greatly improved for better electrochemical performance. In addition, the porous nanostructure of the GR/CNT-MoS\(_2\) hybrid can promote their adequate contact with the electrolyte, so as to fully utilize the active sites on MoS\(_2\). With these GR/CNT-MoS\(_2\) hybrids as active anode materials for LIB, a high capacity of 1245 mA h g\(^{-1}\) (at 0.1 A g\(^{-1}\)) with good cycling ability up to 200 times (90.9% retention) was achieved.

2. Results and Discussion

The GR/CNT conductive matrix used here was prepared via a longitudinal partial unzipping treatment of pristine CNTs, as illustrated in our previous report. The unzipped GR nanosheets were nearby bridged on the residual CNTs, which form a 3D conductive network with internally cross-linked nanostructure. During the unzipping process, oxygen-containing groups are introduced onto the surface of GRs and residual CNTs, which endows carbon atoms with defects and lone pair electrons, and can act as active sites for the deposition of MoS\(_2\) nanoflakes. Finally, monolithic MoS\(_2\) nanoflakes rather than aggregated flower-like MoS\(_2\) were grown onto GR/CNT substrate, resulting in the formation of 3D GR/CNT-MoS\(_2\) hybrids with hierarchical structures.

Scanning electron microscopy (SEM) images of GR/CNT matrix, GR/CNT-MoS\(_2\) hybrids, as well as pure MoS\(_2\) materials are presented in Figure 2. The obtained GR/CNT composites show apparent existence of GR nanosheets with larger size in width (Figure 2a) compared with the pristine CNTs (Figure S1, Supporting Information). Figure 2b–e shows the GR/CNT-MoS\(_2\) hybrids with different GR/CNT and MoS\(_2\) mass ratios of 1:1, 1:2, 1:3, and 1:4, which were, respectively, named as GR/CNT-MoS\(_2\)(1), GR/CNT-MoS\(_2\)(2), GR/CNT-MoS\(_2\)(3), and GR/CNT-MoS\(_2\)(4) in the following discussion. Thermogravimetric analysis (TGA) of these four samples is carried out in order to measure the accurate content of MoS\(_2\) in the GR/CNT-MoS\(_2\) hybrids, as seen in Figure S2 (Supporting Information). Four steps of weight loss can be observed in the TGA curves. Taking TGA curve of GR/CNT-MoS\(_2\)(3) as a sample (Figure S2b, Supporting Information), the weight loss of first stage is 3.5% before 200 °C belongs to the water evaporation. Oxidization of MoS\(_2\) to MoO\(_3\) occurs at 310–405 °C (stage I). The slopping part between 405 and 600 °C (stage II) can be assigned to the combustion of carbon matrix. Also, the weight loss at the temperature higher than 675 °C (stage III) is due to the evaporation of MoO\(_3\). According to these results, the weight percent of GR/CNT in GR/CNT-MoS\(_2\)(1), GR/CNT-MoS\(_2\)(2), GR/CNT-MoS\(_2\)(3), and GR/CNT-MoS\(_2\)(4) hybrids is 48%, 33%, 22%, and 18%, respectively. Clearly, monolithic MoS\(_2\) nanoflakes were homogeneously anchored on the surface of GR/CNT matrix. As a comparison, the pure MoS\(_2\) nanomaterial prepared with the same method exhibits flower-like structures with heavy aggregation. Compared with the aggregated MoS\(_2\) structure, the homogeneous GR/CNT-MoS\(_2\) hybrids with hierarchical structures provide much larger surface area for lithium ion accommodation. However, when the molar ratio of MoS\(_2\) and GR/CNT was increased to 4:1, partial aggregation of MoS\(_2\) appeared (Figure 2e), which may decrease the performance of GR/CNT-MoS\(_2\) hybrids. The unique structure of GR/CNT-MoS\(_2\) hybrids can effectively combine the merits of excellent electrical conductivity of GR/CNT matrix and superior electrochemical performance of MoS\(_2\) nanoflakes, realizing the synergistic effect of MoS\(_2\) and GR/CNT. Meanwhile, the GR/CNT matrix used here also exhibits good porous structures that could buffer and absorb the mechanical stress from the volume change of active materials during the insertion and extraction of lithium ions. According to the energy dispersive spectroscopy (EDS) results (Figure S3, Supporting Information), both S and Mo elements...
are uniformly distributed in the GR/CNT-MoS2 hybrids, confirming the homogeneous deposition of MoS2 nanoflakes onto the surface of GR/CNT composites. The detailed hierarchical structure of the prepared samples can be further observed from the transmission electron microscopy (TEM) images (Figure 3). Compared with pristine CNTs (Figure 3a), GR/CNT composites exhibit desired conductive networks with residual CNTs bonded on the obtained GNR sheets (Figure 3b). Moreover, MoS2 nanoflakes were totally connected with GR/CNT matrix, which further confirms the homogeneous composition of the GR/CNT-MoS2 hybrids (Figure 3c,d). The discontinuous crystal fringes of MoS2 indicate the existence of abundant defects along the curled edge of MoS2 (Figure 3f). TEM image of pure MoS2 (Figure 3e) further confirms their flower-like morphology as detected by the SEM image. In addition, the defect-rich structures in MoS2 flakes can provide additional active sites that notably facilitate the rapid insertion/extraction process for lithium ions, contributing to the remarkable improvement in lithium storage ability.\[14\]

Figure 2. SEM images of a) GR/CNT hybrid, b–e) GR/CNT-MoS2 nanocomposites with different GR/CNT and MoS2 mass ratios of 1:1 (b), 1:2 (c), 1:3 (d), and 1:4 (e). f) Pure MoS2 with flower-like morphology.

The crystallographic structure and crystallinity of the as-prepared samples were examined by X-ray diffraction (XRD) (Figure 4a). GR/CNT-MoS2 hybrids exhibit typical hexagonal phase with sharp diffraction peaks just like pure MoS2, which can be readily indexed from a JCPDS card (37-1492).\[15\] The primary diffraction peak at 2θ = 14.2° with a d-spacing of 0.62 nm can be ascribed to the (002) crystal plane of MoS2, indicating that the layered MoS2 with flower-like morphology grows well along the c-axis during the annealing process.\[44\] Diffraction peak at 2θ = 26.1° of GR/CNT can be also clearly observed in GR/CNT-MoS2(1) and GR/CNT-MoS2(2) hybrids, but becomes ambiguous in GR/CNT-MoS2(3) and GR/CNT-MoS2(4) hybrids, which can be ascribed to the increased content of MoS2. GR/CNT-MoS2 hybrids exhibit similar diffraction peaks as pure MoS2 sample, which confirms the successful deposition of MoS2 nanoflakes on GR/CNT composites and further illustrates the incorporation of GR/CNT guests does not affect the crystallization of MoS2. Lattice fringes with interlayer distance of 0.62 and 0.26 nm in the high-resolution TEM image of GR/CNT-MoS2(3) (Figure 4b) are in good agreement with the d-spacing of (002) and (100) crystal planes of MoS2. Furthermore, the GR/CNT-MoS2(3) hybrid achieved a high specific surface area up to 238 m² g⁻¹ compared with that of 87 m² g⁻¹ for pure MoS2 flowers according to the results of Brunauer–Emmett–Teller (BET) analysis (Figure 4c), which indicates much more active sites of MoS2 can be exposed for lithium ion accommodation in GR/CNT-MoS2(3) hybrid. In addition, the surface electronic state and chemical composition of GR/CNT-MoS2(3) hybrid were further investigated by X-ray photoelectron spectroscopy (XPS) analysis (Figure 4d). Two peaks at 229.3 and 232.5 eV can be observed in the high-resolution Mo 3d spectrum (Figure 4e), corresponding to the doublet Mo 3d5/2 and Mo 3d3/2 binding energies, respectively, which are characteristics of Mo⁴⁺ in MoS2. A small peak located at 226.6 eV with slightly lower binding energy than the Mo 3d5/2 peak can be ascribed to the existence of S 2s peak.\[14a\] Figure 4f shows the binding energies of S 2p peaks, corresponding to the S 2p1/2 (163.3 eV) and S 2p3/2 (162.1 eV) orbitals of divalent sulfide ions (S²⁻), respectively.\[16\] Most of the oxygen-containing functional groups introduced during the unzipping process have been effectively removed after the solvent thermal and thermal reduction process (Figure S4, Supporting Information), resulting in excellent conductive properties of the GR/CNT networks.

The unique structure and exceptional electronic properties of GR/CNT-MoS2 hybrid enable it to be a promising material for electrochemical application. Herein, cyclic voltammetry (CV), galvanostatic charge/discharge measurements,
and electrochemical impedance spectroscopy (EIS) analysis were conducted to evaluate their electrochemical properties as anode materials in LIBs. Figure 5 shows the first three cycles of CV curves (at 0.1 mV s\(^{-1}\)) and charge/discharge curves (at 0.1 A g\(^{-1}\)) of GR/CNT, GR/CNT-MoS\(_2\) (3) hybrid, and pure MoS\(_2\) in the voltage range of 0.01–3.0 V. Compared to CV curves of GR/CNT (Figure 5a), the obtained CV curves of GR/CNT-MoS\(_2\) (3) (Figure 5b) exhibit apparent anodic/cathodic peaks with increased current intensity. In its first cathodic sweep, an ambiguous peak at 1.10 V emerged as a result of intercalating lithium ions into defect sites of MoS\(_2\), resulting in the formation of Li\(_x\)MoS\(_2\) according to Equation (1), which may be due to the phase transition from trigonal prismatic to octahedral coordination driven by a lowering of the electronic energy for the octahedral structure when electrons are donated from the lithium ions to MoS\(_2\).[6] A strong reduction peak located at 0.38 V was also observed in the first cathodic curve of GR/CNT-MoS\(_2\) (3) (Figure 5b) exhibit apparent anodic/cathodic peaks with increased current intensity. In its first cathodic sweep, an ambiguous peak at 1.10 V emerged as a result of intercalating lithium ions into defect sites of MoS\(_2\), resulting in the formation of Li\(_x\)MoS\(_2\) according to Equation (1), which may be due to the phase transition from trigonal prismatic to octahedral coordination driven by a lowering of the electronic energy for the octahedral structure when electrons are donated from the lithium ions to MoS\(_2\).[6] A strong reduction peak located at 0.38 V was also observed in the first cathodic curve of GR/CNT-MoS\(_2\) (3), which is related to the in situ decomposition of MoS\(_2\) into Mo nanoparticles embedded into Li\(_2\)S matrices (Equation (2)) and the subsequent formation of an solid electrolyte interface (SEI) film as a result of electrolyte decomposition.[17] In the following anodic scan, a newly emerged small peak located at 1.70 V can be ascribed to the partial oxidation of Mo, and a pronounced peak at 2.30 V is attributed to the delithiation of Li\(_2\)S to S monomer according to Equation (3).[9b] In the subsequent cycles, the reduction peaks at 0.38 V and 0.90/1.10 V are replaced by two new cathodic peaks at 1.10 and 1.90 V resulted from the multistep conversion from S with lithium ions to the finally formed Li\(_2\)S, indicating that active MoS\(_2\) nanomaterials experience an irreversible phase transition in the initial discharge process.[18] CV curves of other GR/CNT-MoS\(_2\) samples (Figure S5, Supporting Information) exhibit the similar cathodic/anodic peaks as those of pure MoS\(_2\) (Figure 5c) with lower current intensities, indicating that the same lithiation/delithiation process was occurred on the active sites of MoS\(_2\), but achieving lower capacities for lithium ion storage.

Charge/discharge curves of GR/CNT-MoS\(_2\) hybrids (Figure 5e and Figure S6 (Supporting Information)) exhibit apparent potential plateaus compared with the results of GR/CNT (Figure 5d), due to the incorporation of active MoS\(_2\) into GR/CNT matrix. Here, taking GR/CNT-MoS\(_2\) (3) hybrid (Figure 5e) as an example, two potential plateaus approximately at 1.2 and 0.9 V in the first cycle were observed, which can be ascribed to the intercalation of lithium ions to form Li\(_x\)MoS\(_2\), indicating that the conversion reaction occurs via a two-step process. In the discharge curves at the second and third cycles, new potential plateaus at 2.0, 1.2, and 0.5 V emerged in the region of the pre-existing plateaus in the first discharge, which mirrors the corresponding changes in the CV curves after the first scan, as indicated in Figure 5b. For the charge process, a conspicuous potential plateau at 2.3 V can be clearly observed, corresponding to the reversible extraction of lithium ions.[19] The initial discharge capacities of GR/CNT-MoS\(_2\) hybrids (Figure 5e) and pure MoS\(_2\) (Figure 5f) are found to be 1522 and 825 mA h g\(^{-1}\) while the charge capacities are 1250 and 619 mA h g\(^{-1}\), respectively. The Coulombic efficiency of GR/CNT-MoS\(_2\) hybrids and pure MoS\(_2\) is 82.1% and 75.0% as a result of serious decay in the first cycle, which is in agreement with the obvious decrease of the intensity of cathodic peak in their first CV curves.

\[
\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2
\]  
\[
\text{Li}_x\text{MoS}_2 \rightarrow x\text{Li}_2\text{S} + \text{Mo}
\]  
\[
\text{Li}_2\text{S} - 2e^- \rightarrow 2\text{Li}^+ + \text{S}
\]

Figure 6a shows the CV curves of GR/CNT, pure MoS\(_2\), and GR/CNT-MoS\(_2\) hybrids at the tenth cycle in the voltage range of 0.01–3.0 V at a scan rate of 0.1 mV s\(^{-1}\). As we can see, the peak current density increases with the introduction of MoS\(_2\) into GR/CNT and reaches the largest value at GR/CNT-MoS\(_2\).
ratio of 1:3, then drops with further increasing the MoS$_2$ content in the hybrid. The charge/discharge performance of GR/CNT, pure MoS$_2$, and GR/CNT-MoS$_2$ hybrids at the tenth cycle can be seen in Figure 6b. The specific storage capacity increases with increasing the MoS$_2$ content in the GR/CNT-MoS$_2$ hybrids and reaches the peak value at a GR/CNT:MoS$_2$ ratio of 1:3 and decreases with further increasing the content of MoS$_2$ (Figure 6c), which shows quite similar trend as the CV measurement. The specific capacitance of all samples calculated based on the active materials including GR/CNT and active MoS$_2$ nanoflakes is about 400, 870, 1056, 1245, 1112, and 550 mA h g$^{-1}$ for GR/CNT matrix, GR/CNT-MoS$_2$(1), GR/CNT-MoS$_2$(2), GR/CNT-MoS$_2$(3), and GR/CNT-MoS$_2$(4), respectively. GR/CNT-MoS$_2$(3) hybrid shows a topmost lithium ions storage capacity of 1245 mA h g$^{-1}$, which is much higher than GR/CNT (401 mA h g$^{-1}$) and pure MoS$_2$ (565 mA h g$^{-1}$). Therefore, it can be sure that GR/CNT-MoS$_2$ hybrid with GR/CNT-MoS$_2$ ratio of 1:3 exhibits the best electrochemical performance due to the synergistic effect of hierarchical GR/CNT matrix and MoS$_2$. Here, a lower specific capacitance (1112 mA h g$^{-1}$) exhibited by GR/CNT-MoS$_2$(4) hybrid compared to 1245 mA h g$^{-1}$ of GR/CNT-MoS$_2$(3) can be ascribed to the aggregation of MoS$_2$ nanoflakes, as indicated by Figure 2e. The closely aggregated nanoflakes may decrease the utilization efficiency of the active sites of MoS$_2$, which will further damage the electrochemical performance of sample GR/CNT-MoS$_2$(4).

Long-term cyclic stability is another key parameter of ideal anode materials for LIBs. Figure 6d shows the cycling performance of GR/CNT, GR/CNT-MoS$_2$ hybrids, and pure MoS$_2$ tested at a current density of 0.1 A g$^{-1}$ up to 200 cycles. GR/CNT shows a low initial specific capacity of 378 mA h g$^{-1}$, while pure MoS$_2$ possesses a relative high specific capacity of 602 mA h g$^{-1}$ and suffers a continuous and drastic decay in the initial 50 cycles, and only retains 185 mA h g$^{-1}$ with retention of 30.7% after 200 cycles. In contrast, GR/CNT-MoS$_2$(3) hybrid exhibits an exceptional high initial specific of 1245 mA h g$^{-1}$ and can remain about 1142 mA h g$^{-1}$ with retention of 90.9% after 200 cycles. Furthermore, the Coulombic efficiency of GR/CNT-MoS$_2$(3) hybrid increases rapidly from 81% in the first cycle to 96% in the second cycle and remains ~99% in the following cycles up to 200 cycles, confirming stable lithium ions insertion/extraction throughout GR/CNT-MoS$_2$(3) hybrid during the long-term cycling process. Moreover, the charge/discharge curves at the 2nd, 5th, and 200th cycles of GR/CNT-MoS$_2$(3) hybrid are presented in Figure S7 (Supporting Information). It can be seen that the potential plateaus during the anodic and cathodic process were also distinct even after 200 cycles, indicating that the active GR/CNT-MoS$_2$(3) hybrid possesses high reversibility and excellent stability for the insertion/extraction of lithium ions. These results can be further confirmed by the stable CV profiles up to 20 cycles, which are stable without changes after the first cycle as seen in Figure S8 (Supporting Information).

Rate capabilities of GR/CNT, pure MoS$_2$, and GR/CNT-MoS$_2$ hybrids are also measured with sequential current density of 0.1, 0.2, 0.5, 1.0, and 2.0 A g$^{-1}$ as shown in Figure 6e. For pure MoS$_2$,
the reversible capacity fades to 243 mA h g\(^{-1}\) with 39.2% capacity retention when the current density increases from 0.1 to 1.0 A g\(^{-1}\). Moreover, serious capacity decay happens once charge/discharge current density shifts back from 1 to 0.2 A g\(^{-1}\).

However, all the GR/CNT-MoS\(_2\) hybrids show high retentions from 58.5% to 72.3% with the current density increased from 0.1 to 1.0 A g\(^{-1}\). The specific capacity can rebound to nearly the same initial values when charge/discharge current density shifts back to 0.2 A g\(^{-1}\), which confirms the excellent rate performance of the obtained GR/CNT-MoS\(_2\) hybrids. The excellent rate performance of GR/CNT-MoS\(_2\) hybrids can be ascribed to their unique 3D structures with nanostructured MoS\(_2\) flakes homogeneously anchored on hierarchical GR/CNT conductive networks, which not only effectively hinders the aggregation of MoS\(_2\) nanoflakes, but also buffers the volumetric expansion during the lithiation/delithiation process.

In order to thoroughly understand the reason for higher electrochemical performance of GR/CNT-MoS\(_2\) hybrids compared with pure MoS\(_2\) for lithium ions storage, EIS was performed after the first cycle. Figure 6f shows the EIS curves of GR/CNT, pure MoS\(_2\), and GR/CNT-MoS\(_2\) hybrids and their corresponding equivalent circuit (inset in Figure 6f). GR/CNT, pure MoS\(_2\), and GR/CNT-MoS\(_2\) hybrids exhibit distinct EIS curves due to the difference in their unique microstructures. The fitted impedance parameters obtained by modeling Nyquist plots based on the equivalent circuit are listed in Table S1 (Supporting Information). Obviously, the SEI film resistance \((R_{SEI})\) and charge-transfer resistance \((R_{ct})\) (10.88 and 54.21 \(\Omega\)) of GR/CNT-MoS\(_2\) hybrids are much lower than those (14.31 and 98.71, respectively) of pure MoS\(_2\). Here, incorporation of GR/CNT networks can greatly enhance the internal conductivity of GR/CNT-MoS\(_2\) hybrids by providing more shortened channels for the access of electrolyte and rapid electron transport during the lithium ion insertion/extraction process, which results in a significant improvement of their electrochemical performances. Furthermore, the \(R_{SEI}\) and \(R_{ct}\) of GR/CNT-MoS\(_2\) hybrids almost remain the same after 200 charge/discharge cycles (Figure S9 and Table S2, Supporting Information), which further confirm their structural and performance stability. Figure 6g exhibits the photograph that a green light emitting diode (LED) can be easily lit up by the battery with GR/CNT-MoS\(_2\) hybrid as cathode electrode material, illustrating the practical application of these GR/CNT-MoS\(_2\) hybrids. Furthermore, the battery based on GR/CNT-MoS\(_2\) hybrid was long-term cycled up to 600 times even at high current density of 1 A g\(^{-1}\) (Figure 6h), and good capacity retention of 87% was achieved with Coulombic efficiencies of \(\approx\)99%. Moreover, the morphology of GR/CNT-MoS\(_2\) hybrid after 600 cycles has been investigated, as seen in Figure S10 (Supporting Information). Monolithic MoS\(_2\) nanoflakes that closely anchored on GR/CNT matrix can be clearly observed, which confirms the good cycling stability of GR/CNT-MoS\(_2\) hybrid.

In general, the high specific capacity, long-term cycling stability, and excellent rate performance of GR/CNT-MoS\(_2\) hybrid are associated with their unique 3D hierarchical structures with monolithic MoS\(_2\) nanoflakes tightly anchored on conductive GR/CNT networks. As demonstrated by the schematic illustration in Figure S11 (Supporting Information), the active sites of MoS\(_2\) can be completely exposed due to their structures of single nanoflake, resulting in sufficient interfacial contact between lithium ions and the atomic layers of MoS\(_2\). These features provide full utilization of active MoS\(_2\) nanomaterials and ensure adequate insertion and extraction of lithium ions into GR/CNT-MoS\(_2\) hybrids.\(^{[20]}\) Meanwhile, GR/CNT networks with porous structures not only
endow efficient diffusion of electrolyte but also accelerate the transfer of electrons inside the GR/CNT-MoS$_2$ hybrids. Incorporation of GR/CNT into the process for synthesizing active MoS$_2$ nanomaterials can effectively hinder their aggregation and achieve tight contact between MoS$_2$ and GR/CNT matrix, which can provide shortened channels for access of lithium ions, fast diffusion of electrolyte, and effective accommodation of volume change of MoS$_2$ during the cycling, resulting in the superior electrochemical performance of GR/CNT-MoS$_2$(3) hybrid compared with pure MoS$_2$ and the GR/CNT matrix.

3. Conclusion

In summary, hierarchical 3D GR/CNT-MoS$_2$ hybrids with unique structures have been designed by tightly anchoring monolithic MoS$_2$ nanoflakes on the surface of conductive GR/CNT network. This 3D structure provides a highly conductive network for lithium ion and electron transport, as well as a better contact between active material and electrolyte. After optimization, the GR/CNT-MoS$_2$(3) hybrid achieves a high capacity of 1245 mA h g$^{-1}$ at a current density of 0.1 A g$^{-1}$, coupled with good rate performance, as well as...
as excellent long-term cycling performance up to 200 cycles (retention of 90.9%). This novel GR/CNT-MoS₂ hybrid material not only shows promising application in LIBs, but also provides a new way to design and develop new anode materials for other electrodes.

4. Experimental Section

Materials: Carbon nanotubes (diameter of 30–50 nm, 10 µm in length) were purchased from Aladdin Industrial Inc. Concentrated sulfuric acid (H₂SO₄, 98 wt%), potassium permanganate (KMnO₄), hydrochloric acid (HCl, 36.5 wt%), N,N-dimethylformamide (DMF), and ammonium tetrathiomolybdate ((NH₄)₂MoS₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout the experiments.

Synthesis of GR/CNT Matrix and GR/CNT-MoS₂ Hybrids: The GR/CNT matrix used in this work was facilely prepared by longitudinal unzipping of pristine CNTs as described in our previous reports.[13] The obtained GR/CNT oxide was washed several times and then dissolved into DMF to form a uniformly dispersed solution of 2 mg mL⁻¹. A certain amount of (NH₄)₂MoS₄ was dissolved into the solution following by strong stirring and sonication for 30 min. The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed tightly, and heated at 200 °C for 24 h. After cooling naturally, black precipitates were obtained by centrifugation and washed by ethanol and water (1:1) for five times before being dried at 60 °C for 12 h. The resulted composites were further annealed in a conventional tube furnace at 800 °C for 2 h in argon with a slow temperature increasing and decreasing speed of 1 °C min⁻¹, resulting in the formation of GR/CNT-MoS₂ hybrids with mass ratio of GR/CNT and MoS₂ of about 1:1 (denoted as GR/CNT-MoS₂(1)). GR/CNT-MoS₂ hybrids with other mass ratios can be easily obtained by increasing the amount of MoS₂ by two, three, and four times, which are denoted as GR/CNT-MoS₂(2), GR/CNT-MoS₂(3), and GR/CNT-MoS₂(4), respectively. Pure MoS₂ was prepared with the same procedure without the GR/CNT matrix.

Characterizations: SEM images were obtained on a field emission scanning electron microscope (Ultra 55, Zeiss) at an acceleration voltage of 5 kV, and corresponding EDS mappings were observed by an Oxford instrument (X-Max 50). TEM and HRTEM observations were performed on a JEOL JEM 2100 TEM with an acceleration voltage of 200 kV. X-ray analysis of samples was conducted on an X Pert Pro X-ray diffractometer with CuKα radiation under a voltage of 40 kV with current of 40 mA. XPS experiments were carried out using an RB upgraded PHI-5000C ESCA system (Perkin Elmer). BET analysis was performed by a Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) by N₂ physisorption at 77 K.

Electrochemical Measurements: The electrochemical measurements were carried out using a two-electrode testing system. Working electrode was fabricated by casting a slurry of 80 wt% active materials, 10 wt% conductive agent (ultraconductive carbon black), and 10 wt% binder (polyvinylidene fluoride) in N-methyl-2-pyrrolidinone on a copper foil. The coated electrodes were dried in vacuum oven at 80 °C for 12 h, followed by treatment of roll pressing. The mass loading of working electrode was controlled at about 3 mg cm⁻², according to the active materials. Lithium sheet was used as counter and reference electrode, and the test cells were assembled in an argon-filled glove box with an electrolyte of 1.0 v LiPF₆ in a mixture of ethylene carbonate and dimethyl carbonate (1:1 in v/v), and a polypropylene film (Celgard-2300) was used as a separator. CV curves were obtained in an electrochemical workstation of ARBIN (MSTAT-10 V/10 mA/48 Ch) in the potential range of 0.01–3.0 V versus Li/Li⁺ at a sweep rate of 0.1 mV s⁻¹. Galvanostatic discharging and charging measurements and rate performance tests were carried out on a LAND 2001A battery system between 0.01 and 3.0 V. EIS was performed on a Solartron electrochemical interface analysis system (SI 1260, SI 1287) with an amplitude of 10 mV in the frequency range from 100 kHz to 0.01 Hz.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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