1 **Preparation of Ultrathin 2D MoS₂/Graphene Heterostructure Assembled**
2 **Foam-like Structure with Enhanced Electrochemical Performance for**
3 **Lithium-ion Batteries**

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7 **Abstract:** A simple one-step surfactant-free hydrothermal approach is presented for the facile synthesis
8 of ultrathin 2D MoS₂/graphene heterostructure (rGO@MoS₂) assembled foam-like structure. The
9 morphology and structure of the rGO@MoS₂ nanocomposite are characterized by scanning electron
10 microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectra,
11 X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). It is
12 found that numerous of ultrathin MoS₂ nanosheets are homogeneously self-assembled on the surface of
13 the foam-like reduced graphene oxide which acts as the skeleton of the nanocomposite. The
14 electrochemical performance of the composite electrode is investigated. Due to countless exposed
15 active sites of the ultrathin 2D MoS₂ nanosheets and rapid ion diffusion and electron transport of the
16 foam-like reduced graphene oxide with high strength and large specific surface area, the rGO@MoS₂
17 composite shows superior electrochemical performance based on the cycling stability (retaining 657
18 mAh g⁻¹ after 150 cycles while retaining 110 mAh g⁻¹ after only 60 cycles of MoS₂), and specific
19 capacity (achieving more than 786 mAh g⁻¹ at 100 mA g⁻¹) compared with the pure MoS₂ when used as
20 electrode materials in LIBs.

21 **Keywords:** MoS₂ nanosheet; Graphene; Foam-like structure; Self-assembled; Lithium-ion batteries

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22 **1. Introduction**

23 Transition metal sulfides (TMS), since first used in lithium batteries in the 1970s, were found to be
24 able to act as host lattice when reacting with a range of guest atoms or forming intercalation
25 compounds, showing the great potential of being used as electrode materials for lithium ion batteries
26 (LIBs). In recent years, TMS have attracted widely attention as electrode materials based on the lithium
27 ion storing mechanism of conversion or alloying reaction [1].

28 Among them, MoS₂, as a two dimensional and layered compound, has particularly gained much
29 interest in that it could accommodate lithium ions at a lower potential and exhibit high lithium ion
30 capacity through conversion reaction [2]. It has been considered as promising alternative to
31 carbonaceous anode materials due to its high specific capacity about 670 mAh g⁻¹ [3]. Layered MoS₂
32 nanosheets have structures analogous to that of graphene, the layered structures are composed of
33 covalently bonded two dimensional sandwiched S-M-S layers stacked together through weak Van der
34 Waals interactions [4]. MoS₂ nanosheets have been reported exhibiting more outstanding
35 electrochemical properties than other traditional anode materials, which could be attributed to their
36 facile lithium ion intercalation properties through the interval between the layers and the reversible
37 conversion reaction to form Mo metal and Li₂S phase [5]. What's more, nano-sized layered MoS₂ could
38 offer remarkable advantages in favor of high-performance LIBs, including shortened diffusion path for
39 Li⁺, large electrode/electrolyte contact area and strain accommodation [1]. However, the cyclic stability
40 and rate capability of the MoS₂ electrodes are still unsatisfactory due to the intrinsically poor electrical
41 conductivity and the structural instability of MoS₂ [6, 7]. In order to combat these drawbacks, extensive
42 research has been done to improve the performance of MoS₂ electrodes. It has been reported that
43 constructing stable hybrid structure of MoS₂ with conductive and high-strength materials was an

44 effective way to improve the stability and conductivity of the MoS₂ electrode materials [8].

45 Since first reported in 2004 [9], graphene has attracted enormous attention owing to its
46 exceptional physicochemical properties: a high specific surface area ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$), extraordinary
47 electronic transport properties ($20,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and good material flexibility [10-13]. In recent years,
48 there were a variety of strategies to fabricate MoS₂-based hybrids aimed at developing excellent
49 electrodes, amongst which integration of MoS₂ nanosheets with graphene has been confirmed to be
50 effective. Because the above mentioned problems of 2D MoS₂ can be satisfactorily solved by
51 introducing graphene due to graphene's high electrical conductivity and good structure stability. The
52 few-layer MoS₂/graphene composite delivers a reversible specific capacity as high as 900-1200 mAh
53 g^{-1} , and a 3D MoS₂/graphene architecture prepared by hydrothermal process exhibits a high specific
54 capacity about 1200 mAh g^{-1} [14, 15]. When combined MoS₂ nanosheets with graphene, graphene
55 could act as both a conducting medium to promote electron transport and electrical contact with active
56 materials, and a "buffer zone" to buffer the internal stress caused by the volume swing of these
57 electrochemically active phases during Li⁺ intercalation and deintercalation process [16]. Moreover, the
58 better structure stability of the hybrid could be also ascribed to the interactions between graphene and
59 MoS₂ and the so-called synergistic effect [17]. To this end, it is highly desirable to develop hybrid
60 nanosheets by integrating high capacity layered MoS₂ with conductive and flexible graphene.

61 It has been reported that researchers have synthesized layered MoS₂/graphene composites by an
62 L-cysteine-assisted or CTAB-assisted solution-phase method and demonstrated that the obtained
63 MoS₂/graphene composites show excellent electrochemical performances as electrode materials for
64 Li-ion batteries due to their robust composite structure and the synergistic effects between layered
65 MoS₂ and graphene [14, 18]. Gong's group and Zhang's group also fabricate MoS₂/graphene

66 nanosheets hybrids by hydrothermal treatment. The resulting MoS₂-graphene architectures exhibit high
67 reversible capacity, with very good cycling performance [19, 20]. Although the MoS₂/grapheme
68 composites were proved to be promising anode materials for LIBs, however, during most of the
69 reported synthesis procedures of MoS₂/graphene composites, different surfactants were used and the
70 electrode reaction may be influenced by the surfactants, the interaction strength between MoS₂ and
71 graphene is also depended on the surfactants [14, 18-20]. Thus, it is of great value to preparing
72 MoS₂/graphene heterostructure with high strength and good stability by surfactant-free approaches.

73 In this work, we present a strategy to fabricate ultrathin 2D MoS₂/graphene heterostructure
74 (rGO@MoS₂) assembled foam-like structure by a simple one-step surfactant-free hydrothermal
75 approach, in which sodium molybdate and as-prepared graphene oxide (GO) are used as starting
76 materials, as shown in **Scheme 1**. The obtained products were evaluated as the anode materials of LIBs.
77 Numerous of ultrathin 2D MoS₂ nanosheets intimately integrate with the high-strength and conductive
78 reduced graphene oxide substrate, which not only provide countless exposed active sites for lithium-ion
79 storage, but also improve the conductivity and stability of the hybrid structure, thus enhancing rapid
80 and reversible Li⁺ diffusion and electron transport during Li⁺ insertion/extraction. Therefore, the
81 rGO@MoS₂ composite shows superior electrochemical performance based on the specific capacity,
82 cycling performance, and rate capability compared with the pure MoS₂ when used as electrode
83 materials in LIBs.

84 **2. Experimental Section**

85 **2.1 Materials and Reagents**

86 Sodium molybdate (Na₂MoO₄·2H₂O), graphite powers, thiourea (NH₂CSNH₂), sulphuric acid
87 (H₂SO₄, 98wt%), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂) and polyvinylidene

88 difluoride (PVDF) were purchased from Sigma Chemical Reagent Co., Ltd. All reagents were
89 analytical grade, and used without further purification. Deionized water was supplied with a Millipore
90 Water System (18.2 MΩ cm).

91 **2.2 Synthesis of rGO@MoS₂ composite**

92 Graphene oxide (GO) was prepared by a modified Hummers methods using natural graphite
93 powders as the starting materials [21, 22]. rGO@MoS₂ composite was synthesized by using a simple
94 one-step hydrothermal method. In a typical procedure, 1 mmol of Na₂MoO₄ • 2H₂O and 5 mmol of
95 NH₂CSNH₂, respectively, were dissolved in 100 mL of GO (0.25mg mL⁻¹) suspension, which
96 containing 40ml of distilled water and 60ml of ethanol, under the continuously stirring for 30min. Next,
97 the homogeneous solution was transferred into a 60mL Teflon-lined autoclave and held at 180°C for 24
98 h. After that, the black precipitate was collected by centrifugation, washed three times with distilled
99 water and ethanol, and then dried in an oven at 60°C for 12 h. In order to investigate the effects of GO
100 on crystal structures and morphologies of the samples, the pristine MoS₂ was prepared by the similar
101 procedure without the addition of GO, in which 1 mmol of Na₂MoO₄•2H₂O and 5 mmol of NH₂CSNH₂,
102 respectively, were dissolved in 100 mL deionized water and then maintained at 180°C for 24h. Pure
103 MoS₂ was collected by centrifugation, washed several times with distilled water and ethanol.

104 **2.3 Structural characterizations**

105 The morphology and microstructure of the as-prepared products were performed by FE-SEM
106 (Hitachi S-4800) and TEM (JEM-3010). The products were analyzed by X-ray diffraction (XRD,
107 D/max-2200) using Cu K_α radiation (λ=0.154 nm). Raman spectra of GO and rGO@MoS₂ composite
108 samples were obtained at room temperature with Nicolet Almega XR Dispersive Raman Spectrometer
109 with the laser excitation of 532 nm. Fourier transform infrared spectroscopy (FT-IR) spectra were

110 obtained on a Bruker TENSOR27 instrument. X-ray photoelectron spectroscopy (XPS) measurements
111 were performed by using an ultrahigh vacuum VG Scientific Corp MK-II electron spectrometer
112 equipped with a multichannel detector.

113 **2.4 Electrochemical measurements**

114 The electrochemical performance of rGO@MoS₂ composite electrode was measured with a
115 half-cell lithium ion battery (LIBs) configuration. The working electrode material slurry was prepared
116 by mixing rGO@MoS₂ composite, carbon black and polyvinylidene difluoride at a weight ratio of
117 80:10:10, several drops of 1-methyl-2-pyrrolidinone solvent were added into the mixture to prepare the
118 active materials slurry. The slurry was coated onto a copper foil current collector and dried at 110°C for
119 12 h. Lithium wafer was used as the counter electrode and reference electrode, and 1.0 M LiPF₆
120 solution in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 in volume) as
121 electrolyte. The coin cells (CR2016) with Li foil as cathode and rGO@MoS₂ as anode were assembled
122 in an Ar-filled glove-box to test the electrochemical performance of the as-prepared electrodes.
123 Galvanostatic charge/discharge cycles were carried out on a LAND CT2001A (Land, China) battery
124 tester between 0.01 and 3.00 V vs. Li⁺/Li at various current densities at room temperature.
125 Electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical
126 workstation (CHI660D) in the frequency range between 100kHz and 10mHz, and the applied initial
127 voltage and ac amplitude were set at 0.5 V and 5 mV, respectively. The discharge state were chosen for
128 EIS measurements. All electrochemical measurements were performed at room temperature. The EIS
129 data were fitted by Zsimpwin software and the equivalent circuit model can be acquired.

130 **3. Results and discussion**

131 **3.1 Characterization of the rGO@MoS₂ composite**

132 The morphology of the as-prepared MoS₂ and rGO@MoS₂ composite was characterized by SEM
133 (Fig 1). From Fig 1 (a), it is obvious that the pure MoS₂ microspheres show relatively uniform
134 morphology with the radius of about 600 nm, and the MoS₂ microspheres possess flower-like structure
135 self-assembled by scale-like nanosheets. Fig 1 (b-d) presents the rGO@MoS₂ assembled foam-like
136 structure with different magnifications. The foam-like reduced graphene oxide matrix provides a
137 skeleton structure for MoS₂ growth, as shown in Fig 1 (b), the foam-like structure consists of plenty of
138 porous channels which could not only provide a large number of channels for electrolyte access, but
139 also buffer the strain from volume change during charge-discharge process. From the high resolution
140 SEM images (c) and (d), it can be clearly seen that ultrathin 2D scale-like MoS₂ nanosheets grow
141 intensively along the foam-like reduced graphene oxide surfaces being connected by
142 van der Waals force. Numerous of ultrathin 2D scale-like MoS₂ nanosheets provide quite a lot of
143 exposed edges for Li-ion intercalation. Also, the ultrathin 2D MoS₂ nanosheets promote the kinetics of
144 Li⁺ storage due to their more and shortened pathways for Li⁺ fast diffusion. From the Fig 1(d), it could
145 be seen that the ultrathin 2D MoS₂ nanosheets are anchored on the foam-like reduced graphene oxide.
146 In such structure, reduced graphene oxide could effectively improve the stability of the hybrid structure,
147 as well as enhance the electron transfer for the electrode reaction.

148 The microstructure of the rGO@MoS₂ hybrid is further investigated by TEM and HRTEM. As
149 shown in Fig 2(a) and (b), the rGO@MoS₂ hybrid displays highly wrinkled surfaces which cater for
150 lithium ion storage. It is confirmed that graphene is acted as the skeleton for ultrathin 2D MoS₂
151 nanosheets growth (Fig 2a), consistent with the SEM observation. From Fig 2b, it could be found that
152 the basic unit of the MoS₂ layers is ultrathin 2D nanosheets and they are uniformly distributed on the
153 surface of the foam-like reduced graphene oxide matrix. Graphene provides an intimate face-to-face

154 contact with MoS₂ nanosheets to form the hybrid system due to their structural and morphological
155 similarity. From Fig 2a and b, it's easily to find that the composites show large electrolyte-electrode
156 contact areas in favor of faster reaction. From Fig 2c, it could be clearly seen that the MoS₂ nanosheets
157 are assembled on the graphene surface and the layer number of MoS₂ nanosheets is approximately ~3
158 layers. The interface between them is distinct and the characteristic lattice fringes related to 0.63nm and
159 0.26nm are corresponding to the (002) and (100) lattice of MoS₂, as shown in the enlarged image (the
160 yellow rectangle) of yellow circles. The characteristic lattice fringe shown in Fig 2d related to 0.63nm
161 should be also attributed to the (002) lattice of MoS₂, from the yellow circles, the few-layered structural
162 MoS₂ is found and the foam-like reduced graphene oxide is acted as the substrate for MoS₂ growth,
163 which is consistent with the XRD measurement and SEM photos. To further manifest the evenly
164 distribution of MoS₂ on graphene surfaces, the element distribution is studied by EDS, element
165 mapping studies of the rGO@MoS₂ hybrid show a uniform distribution of the C, Mo and S elements,
166 indicating the rGO@MoS₂ nanocomposite have been successfully synthesized (Fig 2h). Fig 2 (e-g)
167 shows the crystal structures of MoS₂ and graphene. The thicknesses of them are 0.62nm and 0.34nm,
168 respectively (Fig 2e). The schematic diagrams of the rGO@MoS₂ hybrid show that the smaller layered
169 MoS₂ nanosheets are assembled on the larger layered graphene. Benefiting from this unique 2D
170 layer-structure assembled foam-like structure, the rGO@MoS₂ hybrid exhibits superior electrochemical
171 performance compared with the bare MoS₂ when used as electrode materials.

172 The crystal structures of the samples are measured by X-ray diffraction. Fig 3a presents XRD
173 patterns of MoS₂ (red) and rGO@MoS₂ (black), respectively. All the diffraction peaks of the two curves
174 are good agreement with that of the hexagonal-phase MoS₂ (JCPDS 37-1492). However, the (002) peak
175 of the rGO@MoS₂ hybrid is left-shifted compared with the pure MoS₂, indicating that the MoS₂ grow

176 into ultrathin nanosheets along with the foam-like reduced graphene oxide surface and the layer
177 became thinner and thinner. Moreover, the sharp and strong (002) peak found in pure MoS₂ suggests
178 that there are lots of layers arranged along the (002) direction. However, the (002) peak in the
179 composite is much weaker, further to indicate the fewer layers of MoS₂ nanosheets [23]. The (103)
180 peak is disappear in the rGO@MoS₂ hybrid, this change can be ascribed to the influence of the layered
181 and highly wrinkled graphene, what's more, it also indicates that the MoS₂ nanosheets are too thin to
182 investigate by XRD measurement. In Fig 3a, all the diffraction peaks of the rGO@MoS₂ hybrid are
183 much broader and lower than that of MoS₂; this phenomenon is suggesting that continuously crystal
184 growth of MoS₂ has been effectively suppressed by the combination with graphene.

185 Fig 3b presents Raman spectra of GO (black curve) and rGO@MoS₂ hybrid (red curve). GO
186 shows the Raman shift at 1355 and 1598 cm⁻¹ corresponding to the D- and G-bands of graphene (Fig
187 3b black curve). There are the same peaks in the hybrid confirming the existence of rGO in the
188 rGO@MoS₂ hybrid. However, it could be found that the D/G intensity ratio increased from 0.95 (GO)
189 to 1.04 (rGO@MoS₂ or rGO) after the hydrothermal treatment, which can be attributed to the increase
190 in the number of smaller sp² domains and a re-establishment of conjugated graphene networks
191 (rearomatization) [24], suggesting a successful transformation of GO to rGO [25, 26]. Meanwhile, the
192 Raman spectra of MoS₂ shows the four characteristic peaks at 273.4, 327.4, 377.5 and 400.6 cm⁻¹
193 corresponding to the E_{1g}¹, LA, E_{2g}¹ and A_{1g} mode of the hexagonal MoS₂ crystal, respectively [27, 28].
194 The E_{2g}¹ mode arises from opposite vibration of two S atoms with respect to the Mo atom, while the
195 A_{1g} mode is related to the out-of-plane vibration of only S atoms in opposite direction [29]. The E_{1g}¹
196 and LA mode peaks are less distinguishable, this phenomenon may be ascribed to the few-layered
197 structure of MoS₂ and being anchored on the foam-like reduced graphene oxide surface [30, 31]. All

198 the Raman bands for MoS₂ and rGO can be found in the rGO@MoS₂ composite, which confirms the
199 co-existence of MoS₂ and rGO in the nanocomposite.

200 XPS measurements are then carried out to characterize the elemental compositions and chemical
201 states of the rGO@MoS₂ hybrid. The XPS spectrum indicates the co-existence of C, O, Mo, and S
202 elements in the hybrid, as shown in Fig 4a, the existence of Mo 3p peaks could be ascribed to the
203 partial oxidation of MoS₂ and the O1s may be attributed to the oxygen-containing functional groups of
204 rGO and the oxygen in the testing environment. The high-resolution Mo 3d and S 2p spectra show that
205 the peaks were located at 232.3, 229.2, 163.1, 161.9eV, corresponding to the Mo 3d_{3/2}, Mo 3d_{5/2}, S 2p_{1/2}
206 and S 2p_{3/2} components of MoS₂, respectively(Fig 4b and 4c) [32]. Additionally, the high-resolution O
207 1s and C 1s spectra show that the peaks at 532.5, 284.4eV are related to the C-O and C=C of graphene
208 oxide, respectively [33]. While the C1s spectrum shows other two peaks at 288.6 and 285.9ev, these
209 two peaks may be attributed to the C-S and C-O bonds. When investigating the O1s and C1s spectra,
210 no O1s and C1s electrons of C=O bond are found, indicating that the C=O bonds are replaced by C-O
211 bonds and forming C-S bonds (Fig 4d and 4e). The existence of C-S bond may cause the S vacancy
212 defects in the MoS₂ nanosheets, thus, by the sides of Mo3d and S2p peaks, there are two peaks existed,
213 which are ascribed to Mo loss and S loss [34].

214 To further prove the existence of the C-S bond in the rGO@ MoS₂ hybrid, the FT-IR spectra of
215 MoS₂, GO and rGO@ MoS₂ hybrid material are presented in Fig 4f. The peak at 1623 cm⁻¹ could be
216 attributed to the aromatic C=C stretch. And at 1390 cm⁻¹, there is a peak that corresponds to O-H
217 deformation [35], 1156 cm⁻¹ could be ascribed to the stretching modes of C-O [36]. It is worth noting
218 that the peak located at 1725 cm⁻¹ which is ascribed to the C=O bond in the graphene oxide cannot be
219 found in the rGO@MoS₂ hybrid, and the intensity of the C-O peak in rGO@MoS₂ is much stronger

than that of GO, indicating the reduction of GO to rGO and the C=O bond transforms into C-O bond. Moreover, the much weaker O-H peak in rGO@MoS₂ is also suggesting the reduction of GO to rGO. However, in the rGO@MoS₂ hybrid, there is a peak at 950 cm⁻¹ corresponding to the C-S bond that could not be found in both GO and MoS₂, indicating that the formation of C-S bond in the rGO@MoS₂ composite, consistent with the XPS results.

3.2 Electrochemical performance of the rGO@MoS₂ composite

To clarify the electrochemical process, the electrochemical properties of the rGO@MoS₂ hybrid for the reversible lithium storage are investigated by discharge/charge test on a LAND CT2001A (Land, China) battery tester. Fig 5a shows the charge/discharge curves of the pure MoS₂ and the rGO@MoS₂ hybrid electrode for the first three cycles, measured at a current density of 100mA g⁻¹ between 0.01 and 3V. There are two potential plateaus at ~1.5 and ~0.6 V during the first discharge (lithiation process) for the rGO@MoS₂ hybrid electrode. The former corresponds to the insertion of Li⁺ into MoS₂ to form Li_xMoS₂, which resulted in the phase transformation from trigonal prismatic to octahedral, and the potential variation during the lithium intercalation could be attributed to the low crystalline nature and the insertion of extra Li⁺ in the different defect sites of the obtained MoS₂. The later could be attributed to the conversion reaction process related to the reduction of MoS₂ to Mo metal accompanied by the formation of Li₂S [37, 38]. The conversion reaction process: MoS₂ + 4Li → Mo + 2Li₂S [39]. The initial discharge and charge capacities are found to be 1297 and 868 mAh g⁻¹, respectively. The irreversible capacity loss of ca. 33% in the 1st cycle could be mainly caused by the irreversible processes including the electrolyte decomposition and inevitable formation of the solid-electrolyte interface (SEI) film, which are common for the nanostructured anode material. During the 2nd cycle, the discharge capacity decreases to 947 mAh g⁻¹ with a corresponding charge capacity of 813 mAh g⁻¹,

242 leading to a much higher Coulombic efficiency of 85.9%. This value further increased to 90.2% in the
243 3rd cycle. Such a high initial lithium storage capacity might be attributed to the numerous of ultrathin
244 2D MoS₂ nanosheets intensively grown on the foam-like reduced graphene oxide substrate, both the
245 MoS₂ nanosheets and graphene could provide large area for lithium storage. While from the dash line
246 shown in Fig. 5a, the pure MoS₂ shows much lower specific capacity in the initial discharge and charge
247 capacities of 451 and 400 mAh g⁻¹. Therefore, the rGO@MoS₂ hybrid electrode shows enhanced
248 specific capacity compared with pure MoS₂ electrode.

249 The cycling performance of pure MoS₂ and rGO@MoS₂ hybrid electrode at a current density of
250 100mA g⁻¹ is shown in Fig. 5b. It is worth noting that the capacity of MoS₂ sharply drops to 110 mAh
251 g⁻¹ after only 60 cycles, but the charge capacities of rGO@MoS₂ are retained 656 mAh g⁻¹ after 50
252 cycles, 654 mAh g⁻¹ after 100 cycles, 657 mAh g⁻¹ after 150 cycles, showing better cycling
253 performance than that of pure MoS₂. Such a high reversible capacity and excellent cycling behavior of
254 the rGO@MoS₂ is also exhibited in the rate performance, shown in Fig. 5c. It can be seen that
255 rGO@MoS₂ shows the average discharge capacities of 786, 458, 322 and 158 mAh g⁻¹ at current
256 densities of 100, 300, 500 and 1000 mA g⁻¹, respectively. More importantly, when the rate returns from
257 1000 mA g⁻¹ to the initial 100 mA g⁻¹, the specific capacity can return to 684mAh g⁻¹ at once and does
258 not ultimately change in following cycles, indicating the excellent rate performance. The high capacity,
259 cycling stability and rate capacity of rGO@MoS₂ hybrid materials are attributed to intimate
260 face-to-face contact between MoS₂ nanosheets and graphene matrix, which is facilitated to charge
261 carriers effectively and rapidly conducted back and forth from MoS₂ to graphene, and furthermore, the
262 foam-like reduced graphene oxide could also cushion the structural stress caused by the volume
263 expansion/shrinkage during Li⁺ insertion/extraction process.

Electrochemical impedance spectroscopy (EIS) is measured to reveal why the rGO@MoS₂ hybrid electrode shows much better electrochemical performance than the pure MoS₂. Fig 5d shows the Nyquist plots of MoS₂ and rGO@MoS₂ hybrid electrode. Inset of Fig 5d show enlarged Nyquist plots corresponding to the area marked by arrow. The Nyquist plots are composed of two semicircles at high and medium frequency regions following with a slope line at the low frequency region. The high frequency semicircle could be owing to the resistance of the SEI, and medium frequency semicircle to the charge transfer resistance of the electrode/electrolyte interface and the electrode reaction, and the slope line in the low frequency region to Li⁺ diffusion processes impedance (Warburg impedance) [18, 40]. The data were fitted by Zsimpwin software and the equivalent circuit model can be acquired (Inset of Fig 5d is the corresponding equivalent circuit mode). It can be seen that the rGO@MoS₂ system consists of R_e (represents the internal resistance of the test battery), R_f and CPE₁ (assigned to the resistance and constant phase element of SEI film), R_{ct} and CPE₂ (associate with the charge-transfer resistance and constant phase element of the electrode/electrolyte interface), and Z_W (ascribe to Warburg impedance corresponding to the lithium diffusion process). The kinetic parameters (R_f and R_{ct}) can be obtained by data fitting according to the equivalent circuit model. The values of R_f and R_{ct} of the rGO@MoS₂ anode are 11.97 Ω and 47.50 Ω respectively, which are obviously much lower than those of the pristine MoS₂ anode (793.6 Ω and 80.49 Ω). This confirms that the combination of MoS₂ with highly conductive graphene can improve the overall electrochemical conductivity of electrodes. From Fig 5d, it could be intuitively seen that the diameters of the semicircles in the plot of rGO@MoS₂ hybrid (Inset of Fig 5d) reduced dramatically, this indicate that the rGO@MoS₂ hybrid has much lower charge transfer resistance than that of pristine MoS₂ electrode, and because of this, the rGO@MoS₂ hybrid electrode showed superior electrochemical performance.

286 **4. Conclusions**

287 In summary, the ultrathin 2D MoS₂/graphene heterostructure (rGO@MoS₂) assembled foam-like
288 structure has been successfully synthesized by a simple one-step surfactant-free hydrothermal approach.
289 The rGO@MoS₂ can be used as anode materials for lithium-ion batteries, the results show that
290 rGO@MoS₂ hybrid electrodes possess better cycling performance (maintaining 657mAh g⁻¹ after 150
291 cycles), larger capacity (786 mAh g⁻¹ at 100 mA g⁻¹) and higher rate performance than the pure MoS₂
292 (retaining 110 mAh g⁻¹ after only 60 cycles), indicating that the integration of conductive and flexible
293 graphene with MoS₂ is an effective way to improve the electrochemical performance of MoS₂ electrode.
294 This work suggests that this ultrathin 2D rGO@MoS₂ assembled foam-like structure could be a
295 promising anode material for LIBs.

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406

407 **Figure captions**

408 **Scheme 1.** Schematic illustration of the prepared rGO@MoS₂ hybrid material.

409 **Fig 1.** SEM images of (a) pure MoS₂ and (b-d) rGO@MoS₂ hybrid material in different magnifications.

410 **Fig 2.** (a-d) TEM images of the prepared rGO@MoS₂ samples with different magnifications, (e-g)
411 crystal structures and schematic diagrams of MoS₂ anchored on the graphene, (h) its elemental
412 mapping images of C, Mo and S.

413 **Fig 3.** (a) XRD patterns of MoS₂ and rGO@MoS₂ samples, (b) Raman spectra of GO and rGO@MoS₂
414 samples, (i) and (ii) were the enlarged images of (I) and (II), respectively.

415 **Fig 4.** (a) XPS survey spectrum of rGO@MoS₂ material and high resolution scans of (b) Mo3d, (c) S2p,
416 (d) O1s, (e) C1s and (f) FT-IR spectra of MoS₂, GO and rGO@ MoS₂ hybrid.

417 **Fig 5.** (a) First three charge and discharge curves of rGO@MoS₂ hybrid and pure MoS₂ electrode at a
418 current density of 100mA g⁻¹, (b) Cycling stability for rGO@MoS₂ hybrid and pure MoS₂
419 electrodes charged-discharged at 100mA g⁻¹, (c) Rate capability of rGO@MoS₂ hybrid and pure
420 MoS₂ electrodes at various current densities, (d) Nyquist plots comparing rGO@MoS₂ hybrid
421 and pure MoS₂ electrodes in the frequency range between 100 kHz and 10 mHz. Inset: enlarged
422 Nyquist plots corresponding to the area marked by arrow, and the equivalent circuit model.

Scheme 1. Liu Hui et al

Figure 1. Liu Hui et al

Figure 2. Liu Hui et al

Figure 3. Liu Hui et al

Figure 4. Liu Hui et al

Figure 5. Liu Hui et al