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# 3D MoS<sub>2</sub>/graphene nanoflowers as anode for advanced lithium-ion batteries

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Abstract: Vertical  $MoS_2$  nanosheets were controllably patterned onto graphene as nanoflowers through a two-step hydrothermal method. The interconnected network and intimate contact between  $MoS_2$  nanosheets and graphene by vertical channels enabled a high mechanical integrity of electrode and cycling stability. In particular,  $MoS_2$ /graphene nanoflowers anode delivered an ultrahigh specific capacity of 901.8 mA·h/g after 700 stable cycles at 1000 mA/g and a corresponding capacity retention as 98.9% from the second cycle onwards.

Key words: MoS<sub>2</sub>; graphene; 3D nanoflowers; nanosheets; lithium-ion batteries

### **1** Introduction

There is an urgent requirement for sustainable development of new energy accompanying the global warming and energy crisis [1]. The demand for high-power vehicles and smart grid arises the rapid evolution of lithium-ion batteries. With the appearance of monolayer graphene, a variety of two-dimensional (2D) materials, such as transition metal dichalcogenides (TMDs) [2,3], transition metal oxides (TMOs) [4,5] and transition metal carbide and nitrides (MXenes) [6,7] nanosheets, are once again on the horizon as its structure analogues.

Molybdenum disulfide (MoS<sub>2</sub>), one of the most important members of TMDs, has attracted much attention because of its graphene-like lamellar structure [8]. Recently, layered MoS<sub>2</sub> has become the potential candidate for anode material of lithium-ion batteries due to the higher theoretical specific capacity (670 mA·h/g) compared with the conventional graphite anode (372 mA·h/g), and the

large theoretical interspacing (0.615 nm), which creates favorable conditions for Li<sup>+</sup> insertion and desertion [9]. However, the poor electronic/ionic conductivity and rapid capacity fading limit its practical applications. At the same time, the intermediate product Li<sub>2</sub>S of the transformation reaction is easy to react with the electrolyte to form a thick gel-like polymer layer, which will inhibit the reaction and damage the cyclic stability and rate performance of the active material [10].

Reducing the number of  $MoS_2$  layers or increasing their lamellar spacing is often used to overcome these issues. Designing novel hybrid nanostructures has been an alternative way by integrating diverse functionalities into a single system [11,12]. Extensive research has proven that the combination of graphene and its derivatives can improve the conductivity and stability of the entire hybrid, due to the high electrical conductivity and excellent structure stability of graphene [9,13,14]. For example, WANG et al [15] reported that vertically aligned  $MoS_2$  nanosheets patterned on

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electrochemically exfoliated graphene (EG) and the prepared anode delivered an ultrahigh-specific capacity of 1250 mA·h/g after 150 cycles at 1 A/g. Although a large number of hybrids (MoS<sub>2</sub>/ graphene nanosheets [16], MoS<sub>2</sub>/N-doped grapheme [17], 3D MoS<sub>2</sub>/grapheme [18]) have been developed recently, these hybrids were not well controlled in structure, hindering further development of MoS<sub>2</sub>-based composites for highperformance energy storage. This would result from the fact that the anticipated advantages of graphene in grapheme/MoS<sub>2</sub> composite were not fully exerted and can be solved by developing new grapheme/ MoS<sub>2</sub> hybrid nanostructures.

In this work, flower-like  $MoS_2$  with nanosheets on the surface of graphene was designed as 3D  $MoS_2$ /graphene nanoflowers via solvothermal and hydrothermal methods. The flower-like  $MoS_2$ vertical nanosheets is conducive to the penetration of electrolyte and can shorten the diffusion distance of Li<sup>+</sup>, and 3D conducting graphene networks also enhance the electrical conductivity of the whole electrode.

### 2 Experimental

### 2.1 Preparation of MoO<sub>2</sub>/graphene composite

MoO<sub>2</sub>/graphene composite was prepared according to our previous literature [19]. In detail, 0.3 g commercial MoO<sub>3</sub> was added into the mixture of 10 mL ethylene glycol, 3 mL grapheme oxide (GO) suspension (10 mg/mL) and 30 mL distilled water under continuous stirring. Then, the mixture was transferred into a 50 mL Teflon-lined stainlesssteel autoclave and kept at 180 °C for 12 h. The sample was collected after washing by deionized water and ethanol, as well as drying in vacuum overnight. Finally, the dark MoO<sub>2</sub>/graphene composites were obtained through heat treatment at 500 °C for 2 h in 5%H<sub>2</sub>/Ar atmosphere.

### 2.2 Preparation of MoS<sub>2</sub>/graphene nanoflowers

1 mmol MoO<sub>2</sub>/graphene composite, 2 mmol Na<sub>2</sub>S·9H<sub>2</sub>O and 15 mL distilled water were mixed and stirred for 30 min. And then 10 mL HCl solution was added into the mixture. The mixture was stirred for another 10 min and transferred into a 50 mL Teflon-lined stainless-steel autoclave and kept at 230 °C for 6 h. The MoS<sub>2</sub>/graphene nanoflowers were collected after washing by distilled water and ethanol and drying at 60 °C. The schematic diagram of the synthesis process for MoS<sub>2</sub>/graphene nanoflowers is shown in Fig. 1.

### 2.3 Materials characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2500 using Cu Ka radiation ( $\lambda$ =0.15405 nm) scanning in a range of 10°-80° at a sweep speed of 8 (°)/min. Raman spectroscopy was detected using a LabRAM HR 800 Raman spectrometer (HORIBA Jobin Yvon, France) in a scanning range of 100–500 cm<sup>-1</sup>. The surface and cross-section morphologies were determined using a scanning electron microscope (SEM, Nano SEM 230, FEI, America). Thermal gravimetric analysis (TGA, STA449F3, NETZSCH, Germany) was used to detect the content of every component with a heating rate of 10 (°)/min in air. And the crystal structures of micro-sized composite were collected using a transmission electron microscope (TEM, Tecnai G2 F20, FEI, America).

### 2.4 Electrochemical tests

CR2016 coin cells were assembled and used for the electrochemical experiment. The  $MoS_2/$ graphene nanoflowers, acetylene black, and polyvinylidene fluoride (PVDF) were used as active material, conductive agent, and binder at a mass ratio of 7:2:1. Then, the slurry was pasted on a copper foil and dried in a vacuum oven at 110 °C for 12 h. The electrolyte consists of ethylene



Fig. 1 Schematic illustration of formation process for MoS<sub>2</sub>/graphene nanoflowers

carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (volume ratio 1:1:1) with 1 mol/L LiPF<sub>6</sub>. The electrode performance was characterized by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD). These tests were performed on an electrochemical workstation (CHI604E and IM6ex, China) and a Land automatic battery tester (Wuhan, China). The test parameters were as follows, in regard of galvanostatic charge–discharge,  $\varphi_{initial}$ =3.0 V,  $\varphi_{end}$ =0.01 V (vs Li/Li<sup>+</sup>), with respect to CV, voltage=0.01–3.0 V (vs Li/Li<sup>+</sup>), scan rate=0.1 mV/s.

### **3** Results and discussion

## 3.1 Phase structure and chemical component analysis

The crystal structure of as-obtained MoO<sub>2</sub>/ graphene composites and MoS<sub>2</sub>/graphene nanoflowers are shown in Fig. 2(a). In the XRD pattern of MoO<sub>2</sub>/graphene composites, the characteristic peaks located at  $2\theta=26^{\circ}$ ,  $37^{\circ}$  and  $53.5^{\circ}$  are well indexed to the (001),  $(\overline{2}11)$  and  $(\overline{3}11)$  planes of MoO<sub>2</sub> (monoclinic, JCPDS: 65-5787), respectively. As for MoS<sub>2</sub>/graphene nanoflowers, the dominant characteristic peaks located at  $2\theta = 13.8^{\circ}$ ,  $33.2^{\circ}$ ,  $39.5^{\circ}$  and  $58.9^{\circ}$  are well indexed to the (002), (110), (103) and (110) planes of  $2H-MoS_2$  (hexagonal, JCPDS: 37-1492). No redundant peaks of other phases are detected, indicating that the purity of sample is very high. The widths of those peaks are narrow, suggesting that both composites are finegrained. Besides, the theoretical  $2\theta$  corresponding to (002) plane in the standard PDF card of  $MoS_2$  is  $14.4^{\circ}$ , with an interplanar spacing as 0.63 nm [20]. However, the experiment value of  $2\theta$  is  $13.8^{\circ}$ , meaning a higher interplanar spacing as 0.65 nm, which is benefit for the insertion and extraction of Li<sup>+</sup>. Furthermore, Raman tests were carried out to confirm the existence of carbon, as shown in Fig. 2(b). The broad peaks at 1350 and 1580  $\text{cm}^{-1}$ are characteristic features of carbon. The intensity ratio of D-band to G-band  $(I_D/I_G)$  is large than 1, showing the partially graphitizing of the carbon which could improve the matrix, electron transportation of both composites. The carbon content in the MoS<sub>2</sub>/graphene nanoflowers was determined by TGA as shown in Fig. 2(c), which was calculated to be about 19.5 wt.%.



Fig. 2 XRD patterns (a) and Raman spectra (b) of  $MoO_2/$ graphene composites and  $MoS_2/$ graphene nanoflowers, and TGA curve of  $MoS_2/$ graphene nanoflowers heated at 10 °C/min in air atmosphere (c)

### 3.2 Morphology and microstructure

SEM and TEM images are characterized to obtain the morphology and structure of the  $MoO_2$ /graphene composites and  $MoS_2$ /graphene nanoflowers in Fig. 3. The particles of  $MoO_2$  are very fine (5–10 nm) and evenly dispersed in  $MoO_2$ /graphene composites (Fig. 3(a)). The ultrafine  $MoO_2$  nanoparticles grow on the surface



Fig. 3 SEM images of  $MoO_2/graphene$  (a) and  $MoS_2/graphene$  nanocomposite (b), and TEM (c) and HRTEM (d) images of  $MoS_2/graphene$  nanoflowers

of the graphene, in return the graphene tightly covers the surface of the active material. After sulfidation, MoO<sub>2</sub>/graphene composites change into 3D MoS<sub>2</sub>/graphene nanoflowers as shown in Fig. 3(b). Plenty of MoS<sub>2</sub> nanoflowers with an average size of 150-250 nm pattern closely and uniformly on the graphene substrate, forming a whole piece of huge nanoflowers. The vertical MoS<sub>2</sub> nanosheets, which connected with each other through local cross contact instead of overlapping, are controllably patterned onto graphene as nanoflowers. MoS2 nanoflowers were packed tightly onto the graphene sheets, which is benefit for the diffusion of Li<sup>+</sup>, and also improving the contact area of active materials and electrolyte. As shown in Fig. 3(c), the transparent and curly  $MoS_2$ nanosheet with thickness of 3-6 nm is growing on the graphene substrate, which is consistent with Fig. 3(b). Figure 3(d) shows the HRTEM of  $MoS_2/$  graphene nanoflowers, which further clarifies that the  $MoS_2$  nanoflowers are lamellar structure consisting of several layers stacked on top of each other. In addition, the interlayer space is 0.65 nm, which corresponds to the specific (002) surface of the orthorhombic  $MoS_2$ .

TEM image and corresponding EDS patterns (Fig. 4) illustrate that Mo, S and C elements are homogeneously distributed in MoS<sub>2</sub>/graphene nanoflowers, which proves the presence of graphene. Graphene enhances the electrical conductivity of the material and makes the structure more stable.

### 3.3 Electrochemical performance

To further explore the structural advantages of the  $MoS_2$ /graphene nanoflowers as an alternative electrode material of lithium-ion batteries, electrochemical tests were conducted. Figure 5(a) displays



Fig. 4 TEM image (a) and corresponding EDS mappings (b, c, d) of MoS<sub>2</sub>/graphene nanoflowers

the CV spectra of the first three cycles of the MoS<sub>2</sub>/graphene nanoflowers at a scan rate of 0.1 mV/s in a range of 0-3 V (vs Li/Li<sup>+</sup>), respectively. The two reduction peaks at 0.4 and 1.4 V in the first cathodic scan can be detected. The former is attributed to the reaction of Li<sub>x</sub>MoS<sub>2</sub>+  $(4-x)Li^++(4-x)e \rightarrow Mo+2Li_2S$  and the forming of SEI film, resulting in the capacity loss. The latter is owing to the reaction of Li<sup>+</sup> embedding MoS<sub>2</sub> to form Li<sub>x</sub>MoS<sub>2</sub> and the transformation of MoS<sub>2</sub> from 2H (tri-prism) to 1T (octahedron). The first anode scan only has two obvious oxidation peaks located at 1.7 and 2.3 V, respectively, which are related to the partial oxidation of Mo to form MoS<sub>2</sub>, the desulfurization process of Li<sub>2</sub>S and the formation of S. In the subsequent discharge, the peak at 0.4 V disappears and that at 1.4 V is reinforced as well as the peak at 1.9 V appears. The first two is caused by the combination of Mo and Li, the 3rd one shows the formation of Li<sub>2</sub>S. The overlapping of next two cycles indicates the remarkable reversibility of MoS<sub>2</sub>/graphene anode.

In order to study the cyclic properties of

MoS<sub>2</sub>/graphene anode, the galvanostatic chargedischarge curves are tested from the 1st to 100th cycles at the current density of 100 mA/g as shown in Fig. 5(b). The initial discharge capacity of the MoS<sub>2</sub>/graphene anode is 1460 mA·h/g and corresponding coulombic efficiency is 57.9%, which is related to the formation of SEI film and decomposition of electrolyte. From the 5th cycle onwards, the coulombic efficiencies stay above 98% and from the 2nd cycle onwards, the capacity retention is 91.1% after 100 cycles. For comparison, the galvanostatic charge-discharge curves of pure MoS<sub>2</sub> anode are also presented in Fig. 5(c). The initial discharge capacity of the pure MoS<sub>2</sub> anode is 338.1 mA·h/g and corresponding coulombic efficiency is 69.6%. With the increase of cycle number, the specific capacity of pure MoS<sub>2</sub> anode first increases over 800 mA·h/g and then quickly fades to 256 mA·h/g after 75 cycles. Meanwhile, charge-discharge profiles of MoS<sub>2</sub>/graphene anode in the first three cycles are also illustrated under the same conditions as shown in Fig. 5(d). The voltage platform at about 0.5 and 1.0 V of the first



**Fig. 5** Electrochemical properties: CV curves of MoS<sub>2</sub>/graphene electrode at 0.1 mV/s (a), cycling performance of MoS<sub>2</sub>/graphene electrode (b) and pure MoS<sub>2</sub> electrode (c) at 100 mA/g, galvanostatic charge/discharge voltage profiles at 100 mA/g (d), cycling performance at 1000 mA/g (e), and rate performance ranging from 100 to 2000 mA/g (f) of MoS<sub>2</sub>/graphene electrode

discharge curve is consistent with the results of CV curve, corresponding to the irreversible transformation reaction of  $\text{Li}_x\text{MoS}_2$  and the embedding reaction of  $\text{Li}^+$ , respectively. Meanwhile, the charge capacities of the first three cycles are 845.4, 863.9 and 861.4 mA·h/g, respectively. The well-overlapped curves in the subsequent cycles imply that MoS<sub>2</sub>/graphene anode has excellent reversibility. In addition, the MoS<sub>2</sub>/graphene anode composite also demonstrates excellent durability under high current density in the long-term cycling

tests. Figure 5(e) displays that the cycling stability of  $MoS_2$ /graphene nanoflowers anode is 901.8 mA·h/g under a current density of 1000 mA/g over 700 cycles, and the corresponding capacity retention is 98.9% from the 2nd cycle onwards. Except the excellent durability, the  $MoS_2$ /graphene anode also demonstrates stable bate performance. As illustrated in Fig. 5(f), the anode also renders high reversible specific capacities of 992, 1067, 1037, 1000, 930, and 788 mA·h/g under the current densities of 100, 200, 300, 500, 1000, and 2000 mA/g, respectively. When the rate comes back to 100 mA/g, a stable specific capacity of 1077 mA·h/g can be recovered. With the increase of current density in the first 20 cycles, the reversible capacity exhibits an upward tendency, attributing to the slow activation of MoS<sub>2</sub>. The superior cycling ability is obtained owing to the unique huge nanoflowers structure of MoS<sub>2</sub>/graphene composite, which effectively alleviates the pulverizing of nanoparticles for the volume expansion of MoS<sub>2</sub> in the process of charge–discharge.

When the vertical  $MoS_2$  nanosheets are patterned onto graphene as nanoflowers, both cycle life and capacity retention are significantly enhanced, indicating that the nanoflower structures not only improve the electrochemical performance, but also maintain the structural integrity of the electrode, which can be proved by the SEM images before (Fig. 6(a)) and after (Fig. 6(b)) cycling. The images show that most  $MoS_2$ /graphene nanocomposites retain their original flower-like shape after 700 cycles under a current density of 1000 mA/g.

Overall. electrochemical the superior performance of the MoS<sub>2</sub>/graphene nanoflowers anode is attributed to the few-layered structure of MoS<sub>2</sub> and high conductive graphene. Such unique structures can effectively shorten the solid-state diffusion length for Li<sup>+</sup> owing to the flower-like and nanoscale MoS<sub>2</sub>, enhance the electrical conductivity of the whole electrode due to the three-dimensional conducting graphene network, and provide plenty of transmission routes for electrolyte-facilitating diffusion channels of Li<sup>+</sup> within the electrode Consequently, MoS<sub>2</sub>/graphene material. the nanoflowers exhibit outstanding reversible capacity, ultrahigh charge-discharge rate properties, and superior cycling performance compared to other nano-sized MoS<sub>2</sub>/carbon materials with different structures (Table 1).



Fig. 6 SEM images of MoS<sub>2</sub>/graphene nanocomposite before (a) and after (b) 700 cycles under current density of 1000 mA/g

Table 1 Performance comparison for MoS <sub>2</sub> /carbonaceous material with different	rent structures
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Material	Structure	Current density/(mA $\cdot$ g <sup>-1</sup> )	Capacity/(mA $\cdot$ h $\cdot$ g <sup>-1</sup> )	Cycle number
MoS <sub>2</sub> /graphene (this work)	Nanoflower	100 1000	961 901.8	100 700
MoS <sub>2</sub> /C [21]	Microfiber	100	335	100
MoS <sub>2</sub> /carbon [22]	Nanourchin	50	721	100
MoS <sub>2</sub> /C [23]	2D nanowall	200	880	50
MoS <sub>2</sub> /C [24]	2D mesoporous	100	1140	300
MoS <sub>2</sub> /RGO [13]	Nanoflower	100	1052	80 250
		300	800	230
MoS <sub>2</sub> /graphene [10]	Nanoflower	100	1100	00 50
		1000	090	50

### 4 Conclusions

(1) The vertically aligned  $MoS_2$  nanosheets were successfully patterned onto graphene substrate to produce 3D  $MoS_2$ /graphene nanoflowers through a two-step hydrothermal method.

(2) The unique vertical channels of  $MoS_2$  nanosheets and high conductivity of graphene endow 3D  $MoS_2$ /graphene nanoflowers anode with good mechanical and cycling stability.

(3) 3D MoS<sub>2</sub>/graphene nanoflowers anode delivered ultrahigh-specific capacities of 961 and 901.8 mA $\cdot$ h/g at and 1000 mA/g, respectively.

(4) Such a 3D hybrid structure design holds great promise for widespread applications such as catalyst and capacitors, and is ready to extend to other 3D sulfides, oxides and nitrides materials.

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### 先进锂离子电池用三维纳米花状 MoS<sub>2</sub>/石墨阳极

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摘 要:采用两步水热合成法将垂直的二硫化钼(MoS2)纳米片可控地负载于石墨烯表面形成纳米花。二硫化钼纳 米片和石墨烯形成紧密结合的垂直交互网络结构,使电极具有高的机械完整性和循环稳定性。所得 MoS2/石墨烯 纳米花阳极在 1000 mA/g 电流密度下稳定循环 700 次后,仍具有 901.8 mA·h/g 的超高比容量,且从第二次循环开 始,相应的容量保持率为 98.9%。

关键词: 二硫化钼; 石墨烯; 三维纳米花; 纳米片; 锂离子电池

(Edited by Xiang-qun LI)