Fast three-dimensional assembly of MoS₂ inspired by the gelation of graphene oxide

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Two-dimensional (2D) materials, such as graphene, transition metal dichalcogenides (TMDs) and MXene [1–5], have attracted great attention in various applications due to their unique electronic properties, large surface area and sheet-like structure. However, the severe aggregation of the nanosheets (NSs) leads to the loss of accessible surface area and high ion diffusion resistance in practical uses. According to the previous reports [6], the assembly of graphene into a three-dimensional (3D) structure can effectively prevent the aggregation of the graphene NSs and form 3D interconnected conductive networks. Graphene oxide (GO) with a large number of functional groups has excellent processability in solution [7,8] and is always used as the starting material for the assembly because the functionalized surface makes it possible to assemble through various approaches, such as decreasing the repulsion force between GO NSs by removing the functional groups by hydrothermal or chemical reduction [9]. Introducing linkers is another way to assemble the NSs together by their interaction with the functional groups [10].

However, other 2D materials cannot be decorated by a similar oxidation. As a result, the absent functional groups and insufficient bonding sites limit the above two approaches for the assembly of 2D materials such as TMDs [11–14]. Furthermore, their poor dispersibility in solution results in inferior processability. Although some reports show the assembly of GO with other 2D materials to form the 3D hybrid materials, the GO plays a dominating role in the formation of 3D structure. Thus, a simple method for the 3D assembly of 2D materials

besides graphene is desired [15,16].

Here, we report an ultra-fast assembly of GO by introducing a molecular linker (1,4-butanediol diglycidyl ether, BDGE) in an acidic solution. A hydrogel monolith was immediately formed when the GO solution, acid solution and the linker were mixed. The interaction between carboxyl groups and BDGE is the key factor in such a gelation process. Inspired by this, the surfactant sodium cholate (SC), which contains hydroxyl and carboxyl groups, was selected as the agent to disperse other 2D materials (e.g., MoS₂) and realize their fast assembly. The SC molecules were adsorbed onto the MoS₂ NS, which not only increased the dispersing ability but also realized surface functionalization to trigger the assembly. After drying and the following pyrolysis of BDGE, the obtained 3D structured MoS₂ showed an improved electrochemical performance for sodium ion storage compared with randomly aggregated MoS₂, demonstrating that the assembled 3D network has less aggregation of the NSs. Furthermore, this method is facile and promising to be a universal method for the assembly of different 2D materials.

Fig. 1a and Fig. S1 illustrate the assembly of GO with the assistance of BDGE. In a typical process, the BDGE was added to the GO dispersion and mixed by shaking. The mixture was added to HCl solution and a hydrogel formed immediately (see Supplementary movie 1). As shown in Fig. 1a, no gelation occurred solely with the BDGE (denoted GO-B) or HCl (denoted GO-H), and the hydrogel (denoted GO-BH) can only form with both of them, demonstrating the synergistic effect of BDGE

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Figure 1 Photos (a), XRD patterns (b) and SEM images (c–f) of GO, GO+BDGE, GO+HCl and GO+(BDGE/HCl mixture).

linkers and an acidic environment. The influence of the pH and the amount of BDGE on the assembly is investigated as shown in Fig. S2. The hydrogel forms till the pH less than 0.7, because the H^+ ions restrain the ionization of the $-COOH$ and promote the interaction between the GO NSs. In addition, 0.06 vol.% of BDGE in the dispersion is enough to trigger the hydrogel formation. The hydrogel can withstand the tube inversion test [17], and the samples obtained were usually dried for the following characterization.

The X-ray diffraction (XRD) patterns in Fig. 1b show that the typical (002) peak of GO-H is broader and slightly shifts to left compared with that of dried GO at 11.3° due to the aggregation of NSs, and the GO-B peak shifts more left and is much broader, demonstrating that BDGE as the spacer effectively prevents layer-by-layer stacking. While, the GO-BH shows no obvious peaks due to the formation of a random 3D structure that effectively prevents the restacking of GO NSs. These results are evidenced by the photos of the dried samples (Fig. S3). These samples were pyrolyzed at $800^\circ C$, and Fig. 1c–f show their scanning electron microscopy (SEM) images. An interlinked network of GO-BH-800 can be observed while the others show tightly or randomly aggregated structures. Fig. S4 shows the nitrogen adsorption and desorption isotherms of GO-800 and GO-BH-800, and the increased specific surface area (SSA) and adsorption volume at the mediate and high relative pressure range indicate the increased accessible surface area and the well-developed pore structure in the 3D assembly [18].

The oxygen-containing groups on GO were selectively removed by different reducing agents to further investigate the different interactions of the functional groups on GO with BDGE [19]. According to the photos

Figure 2 (a) Photos of GO with different functional groups after assembly, (b) FT-IR profiles of GO reduced by different reducing agents and decorated with different functional groups. Graphene and MoS_2 gels (c) and aerogels (d) made by the same method as GO.

shown in Fig. 2a, reduced GO (rGO) by hydroiodic acid (HI) (denoted HI-rGO) also gels, which can sustain the tube inversion test. However, no hydrogel formed in $NaBH_4$ reduced GO (denoted $NaBH_4$ -rGO). Hydroxyl and carboxyl groups can be easily removed by HI and $NaBH_4$, respectively, which can be evidenced by Fourier-transform infrared (FT-IR) spectroscopy (Fig. 2b). This result suggests that carboxyl groups play a key role in the interaction between rGO and BDGE. At the same time, the HI provides excess H^+ ions, which restrains the ionization of the $-COOH$ groups and promotes interaction between them.

Based on the result of the above assembly process, we speculate that the assembly of other 2D materials should be achieved through surface functionalization by carboxyl

Figure 3 (a) XRD patterns of pristine MoS₂ and assembled MoS₂. TG-DSC profiles (b), and SEM images (c, d) of pristine MoS₂ and assembled MoS₂ after heat treatment to remove BDGE and the residual HCl.

groups and BDGE linkers. Graphene annealed at high temperature to remove the functional groups and MoS₂ prepared by a hydrothermal process were dispersed by SC in an aqueous solution. At the same time, the adsorption of SC molecules decorated the surfaces of these materials with hydroxyl and carboxyl groups, evidenced by the FTIR profiles in Fig. S5. As shown in Fig. 2c and d, both graphene and MoS₂ (see Supplementary movie 2) assembled, and after drying, 3D porous aerogels were obtained.

XRD patterns show the structural differences of the assembled MoS₂ (denoted MoS₂-BH) and pristine MoS₂. In Fig. 3a, the (002) peak which indicates the stacking of the MoS₂ NSs shifts to a much lower angle, suggesting that the BDGE acts as a spacer to prevent restacking. The MoS₂-BH was heated at 700°C for 2 h to pyrolyze the BDGE (denoted MoS₂-BH-700) for thermogravimetric-differential scanning calorimetry (TG-DSC). The TG-DSC profile measured in air (Fig. 3b) shows a higher weight-loss of the assembled MoS₂-BH-700 indicating increased chemical activity compared with MoS₂-700. The 3D structure improves the contact of the MoS₂ NSs with oxygen, indicating high surface utilization and fast mass transfer in such a 3D assembly. According to the TG curves in Fig. 3b, the calculated carbon contents in MoS₂-700 and MoS₂-BH-700 are only about 3.4 and 7.8 wt% based on the mass loss of the transformation of MoS₂ to MoO₃ and the burn of carbon in the air. The pristine MoS₂ NSs obtained by the hydrothermal process were the

small flakes with the size of 200 nm, which randomly aggregated together. The SSA of MoS₂-BH-700 and MoS₂-700 calculated by the nitrogen adsorption and desorption isotherms (Fig. S6) are about 48 and 3 m² g⁻¹, respectively, suggesting the 3D structure increases its surface accessibility. As shown in Fig. 3c, d and Figs S7 and S8, all the samples after drying and thermal treatment show flat surface in low magnification, but the magnified SEM images clearly show that the assembled MoS₂-BH-700 has a 3D interconnected network which is different from the restacked structure of MoS₂-700 and MoS₂-B-700 and the randomly aggregated structure of MoS₂-H-700. The TEM images (Fig. S9) also show the MoS₂ sheets are stacked to form the thick layers. However, the assembled MoS₂-BH-700 shows interconnected structure formed by the corrugated MoS₂ nanosheets with about 2–3 layers according to the TEM images in Fig. S9b and c, further demonstrating the improved surface utilization. Such a 3D structure prevents the aggregation of the MoS₂ NSs, which can greatly improve their performance for electrochemical energy storage. In contrast, the assembly process did not occur only with BDGE or HCl (Fig. S10), and the severe aggregations (Fig. S7 SEM) appeared after the drying of the dispersion. The XPS spectra in Fig. S11 show the existence of Mo⁶⁺ peaks suggesting a slight oxidation of MoS₂ after the thermal treatment, but for the MoS₂-BH-700, such oxidation is suppressed because its surface is coated by BDGE. Raman spectra in Fig. S12 show two peaks of E_{2g}¹ and A_{1g} of MoS₂ and the D band

Figure 4 CV curves (a), the rate performance (b), cycling stability (c) and (d) EIS of pristine and assembled MoS₂ samples.

and G band of carbon derived from the pyrolysis of the surfactant and BDGE. These carbons are beneficial to improving the conductivity to enhance the electrochemical performance [20].

MoS₂ is a promising anode for sodium ion batteries (SIBs) [21]. Here the electrochemical performance of the above two MoS₂ samples was compared with the results reported for sodium ion storage. Fig. 4a shows the cyclic voltammetry (CV) curves of the assembled MoS₂-BH-700 and pristine MoS₂ with a scan rate of 0.2 mV s⁻¹ for the first two cycles (0.005–3 V). In the first cycle, the CV curve has two cathodic peaks at 0.68 and 0.83 V and a sharp peak at 0.1 V, indicating the intercalation of sodium ions into MoS₂ and the decomposition of the electrolyte into a solid electrolyte interface (SEI) layer. For the second cycle, these peaks become broad due to the formation of 2H-Na_xMoS₂ (1.6 V) and 1T-Na_xMoS₂ (0.7 V). The peak for the assembled MoS₂ shows a lower shift of around 0.7 V in the second cycle compared with the pristine MoS₂, indicating the lower polarization and a better reversible charge-discharge process [22,23]. Fig. S13 shows the first charge-discharge profiles of MoS₂ at a current density of 100 mA g⁻¹, which is in

accordance with the CV profiles.

The assembled MoS₂-BH-700 also shows superior rate performance as shown in Fig. 4b. A significant improvement of reversible capacity (546 mA h g⁻¹) at a current density of 0.1 A g⁻¹ was obtained compared with that of pristine MoS₂ (451 mA h g⁻¹). Even at high rates (1 A g⁻¹), the capacity of the assembled MoS₂ NSs remains high at 420 mA h g⁻¹, while it dropped to 334 mA h g⁻¹ for the original MoS₂, indicating that the assembled 3D structure significantly improves the intercalation of Na⁺ ions and the phase transformation. Its cycling stability at a high current rate of 500 mA g⁻¹ was evaluated (Fig. 4c). Due to its 3D interconnected structure, the assembled MoS₂ delivers a much better cycling stability after 50 cycles. In contrast, the pristine MoS₂ shows a dramatically decrease from 392 to 154 mA h g⁻¹. The electrochemical impedance spectroscopy (EIS) curves are shown in Fig. 4d. The similar semicircles at high frequencies for the assembled MoS₂ electrodes indicate that the connected 3D network has a stable structure during cycling. However, the larger semicircle for the pristine MoS₂ electrode after cycling demonstrates increasing reaction resistance due to its

unstable aggregated structures. The larger slope at low frequency also confirms faster ion diffusion for the 3D assembled MoS₂ electrodes.

The improved electrochemical performance of MoS₂-BH can be ascribed to the following reasons. First, the assembled 3D structure effectively prevents the aggregation of MoS₂ NSs and the individual sheets are fully utilized during the electrochemical process. Second, the assembled MoS₂ has more exposed reactive sites for sodium ions producing a lower polarization and higher reversible capacitance during the electrochemical process. Third, the 3D structure formed efficiently prevents volume expansion during sodium ion intercalation and ensures a stable cycling performance.

A fast and universal approach has been proposed for the assembly of 2D materials into 3D structures inspired by the assembly of GO. In the gelation process, the interaction of carboxyl groups with linkers and the acidic environment play a key role in achieving this assembly. As a typical example, the assembly of MoS₂ has been achieved and the sodium ion storage based on the resulting material shows improved performance because the 3D structure ensures high surface utilization and fast ion diffusion. Such a strategy indicates a simple way to prevent the aggregation of nanomaterials which is important for their practical applications.

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Supplementary information Experimental details and supporting data are available in the online version of the paper.

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二维材料的快速三维自组装: 从氧化石墨烯到二硫化钼

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摘要 本工作借助1,4-丁二醇二缩水甘油醚(BDGE)与氧化石墨烯上羧基的相互作用, 实现了氧化石墨烯的快速三维组装. 基于此方法, 我们通过表面活性剂分散其他二维材料并实现材料表面官能化, 借助于这些表面官能团与BDGE的相互作用, 发展出一种普适的二维材料快速三维自组装方法. 以二硫化钼为例, 组装形成的三维结构显著提高了表面利用率, 极大地改善了其作为钠离子电池负极材料的电化学性能.