



# Compositional dependence of the alignment of three-dimensionally macroporous architectures assembled by two-dimensional hybrid nanosheets



Xu Yu <sup>a,1</sup>, Qasim Mahmood <sup>b,1</sup>, Ying Bo Kang <sup>a</sup>, Woo Sik Kim <sup>b,\*\*</sup>, Ho Seok Park <sup>a,\*</sup>

<sup>a</sup> School of Chemical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 440-746, Republic of Korea

<sup>b</sup> Department of Chemical Engineering, Kyung Hee University, Suwon, 440-746, Republic of Korea

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## ABSTRACT

The composition and pore alignment of three-dimensional (3D) internetworked materials may be a critical parameter for determining the electrochemical properties, but it has yet to be explored. Herein, hierarchically structured reduced graphene oxide (rGO)/MoS<sub>2</sub> frameworks (GMfs), as lithium ion batteries (LIB) electrode, are assembled via an ice-templating process on a basis of the interaction between 2D MoS<sub>2</sub> and 2D rGO. The morphology and chemical structure of GMfs are investigated by various microscopic and spectroscopic methods and their alignment is dependent on the compositional variations. The as-obtained GMfs exhibit randomly networked and crumpled morphology, achieving the enhanced electrochemical performances for LIB anodes due to the redox-active MoS<sub>2</sub> deposited on the 3D macroporous internetworks. The GMfs with 16% MoS<sub>2</sub> (GMfs-16) shows high discharge capacity of 1362 mAh g<sup>-1</sup> at the specific current of 100 mA g<sup>-1</sup> along with a reasonable rate capability of 53.4% from 50 to 1000 mA g<sup>-1</sup> and good cycle capability of 86.4% after 100 charge/discharge cycles. It is concluded that for the case of the randomly networked GMfs-16 composites, MoS<sub>2</sub> is the key active component to lithium ions storage, while rGO is the skeleton to improve conductivity and maintain the structural stability for MoS<sub>2</sub> nanosheets.

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## 1. Introduction

Lithium ion batteries (LIBs) are promising candidate of the main power sources for a variety of powerful electronic devices and electrical vehicles due to its high capacity, high rate capability and long cycle life [1–3]. In commercial LIBs, the graphitic material have been employed as the anode material by their structural stability during cyclic performance. However, the graphite anodes are bottlenecked by the limited theoretical capacity of 372 mAh g<sup>-1</sup> [4]. In order to improve the specific capacity of LIB anodes, the graphite has been replaced by various nanocarbon-based materials such as CNT [5,6], graphene [7,8] and graphene aerogel [9]. Despite the excellent electronic conductivity and high surface area, the specific capacity of nanocarbons is still limited.

Molybdenum disulfide (MoS<sub>2</sub>), as a typical transition-metal chalcogenide with layered structure, is constructed by S–Mo–S atomic layer through the weak van der Waals interaction. When lithium (Li) ions are intercalated into the MoS<sub>2</sub> layers, the formation of Li–S bond results in the volume expansion, in a similar manner to TiS<sub>2</sub> with 10% expansion of the lattice parameter *c* during the intercalation process [10]. For MoS<sub>2</sub>, Santa-Ana et al. reported an increment of the *c*-axis of 0.25 Å for 1 mol of lithium intercalation, which is considered as a negligible change in the electrode geometry [11]. So, the electrochemical stress must be properly accommodated or relieved during the lithiation/delithiation cycling process. Increase of lattice parameter *c*, constant MoS<sub>2</sub> can provide large space for Li ion to diffuse without a significant increase in volume expansion [12]. The theoretical Li storage capacity of MoS<sub>2</sub> accounts for 670 mAh g<sup>-1</sup>, which is two-fold greater than that of graphite. On a basis of these superior capacity, MoS<sub>2</sub> has been regarded as an important candidate for LIBs anode material [13–16]. Various reports have demonstrated the combination of graphene with exfoliated layer-structural MoS<sub>2</sub>, which exhibit a significant increase in reversible capacity and rate capacity,

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [wskim@khu.ac.kr](mailto:wskim@khu.ac.kr) (W.S. Kim), [phs0727@skku.edu](mailto:phs0727@skku.edu) (H.S. Park).

<sup>1</sup> These authors equally contributed to this work.

prepared by chemical vapor decomposition (CVD) [17], solvent thermal process [18] and liquid phase exfoliation [19,20]. Chang et al. [16] demonstrated the synthesis of MoS<sub>2</sub>/graphene composites by an *L*-cysteine assisted solution method, which exhibited the specific capacity of ~1100 mAh g<sup>-1</sup> at a current of 100 mA g<sup>-1</sup>. Cao et al. [17] reported the specific capacity of 1029 mAh g<sup>-1</sup> at a current of 100 mA g<sup>-1</sup> of the three-dimensional (3D) graphene/MoS<sub>2</sub> composites prepared by CVD method. However, the ice-templating, co-assembly of 2D hybrid nanosheets into a hierarchical structure has yet to be explored.

Here, we report hierarchically structured graphene/MoS<sub>2</sub> frameworks (GMfs) that are co-assembled by interacting single or few-layered MoS<sub>2</sub> with graphene *via* an ice-templating method for the application into LIB anodes. The ice-templating method, which consists of unidirectional freezing of hydrogel and pore-preserving drying method, is more versatile and simpler compared to the afore-mentioned synthetic methods for the construction of the 3D networking structure as exemplified by the graphene sponge [21]. The unidirectional freezing could be achieved by immersion freezing or contact freezing. During the freezing process, the solidification and sublimation of water as the solvent crystal following the phase transition diagram form the macro- or microporous texture. Fully taking advantages of ice-templating method, the 3D internetworked structure was constructed by assembling 2D hybrid nanosheets as building blocks and its alignment was controlled with compositional variations. The compositional effect of hierarchically structured GMfs on the battery performance was investigated to optimize hybrid composition.

## 2. Experimental

### 2.1. Synthesis of 2D MoS<sub>2</sub> nanosheets

The mono or few layer MoS<sub>2</sub> nanosheets were synthesized by a lithium exfoliated method. Firstly, 300 mg of bulk MoS<sub>2</sub> was taken in a 250 mL round flask and 150 mL of *n*-hexane was added as the solvent. The flask was placed in the oil-bath and then, the temperature was increased up to 90 °C step by step under N<sub>2</sub> atmosphere. After steadily raising the temperature of the mixture up to 90 °C, 8 mL of *n*-butyl lithium was added and the solution was refluxed at 90 °C for 3 days. The intercalated MoS<sub>2</sub> solution was retrieved by vacuum filtration and repeatedly washed by *n*-hexane to remove the organic residues and *n*-butyl lithium. The exfoliated MoS<sub>2</sub> powder was diluted by deionized (DI) water and ultrasonicated for 6 h in a closed container for the exfoliation of 2D MoS<sub>2</sub> nanosheets. The dispersion was centrifuged 3 times at 4500 rpm to remove excess lithium in the LiOH and unexfoliated MoS<sub>2</sub>. The as-prepared homogenous solution maintains a concentration of 0.17–0.2 mg mL<sup>-1</sup> for the 2D MoS<sub>2</sub> precursor.

### 2.2. Synthesis of hierarchical structured GMfs

1 mL of aqueous graphene oxides (GO) dispersion [22] (20 wt%) was diluted in 3 mL of DI water and ultrasonicated for 3 h to get the homogeneous dispersion. 16 mL of the as-prepared 2D MoS<sub>2</sub> dispersion was taken in a test tube at pH = 7.0. Then, the two dispersions were mixed together for 30 min. The well-mixed dispersion was immersed in liquid N<sub>2</sub>, which solidifies the water, and then, freeze-dried for 3 days. During the freeze drying process, the GMfs with compositional variations were obtained by completely removing the water molecules and then, annealed at 300 °C for 4 h in N<sub>2</sub> atmosphere. The 3D GMfs were notated as Gfs, GMfs-4, GMfs-8, GMfs-16 and GMfs-20 with respect to the concentrations of MoS<sub>2</sub> (0%, 4%, 8%, 16% and 20%). In comparison of the electrochemical performance, the graphene oxide powder and 2D

MoS<sub>2</sub> are mixed with the same weight ratio of GMfs-16, and heated at the same condition. The as-obtained graphene oxide/MoS<sub>2</sub> composite is noted as GM-16.

### 2.3. Characterization

All samples were analyzed by field emission scanning electron microscopy (Philips SEM 535M), equipped with a Schottky-based field emission gun. Transmission electron microscopy (TEM) images were collected on a JEM-3010 HR TEM (300 kV). X-ray diffraction (XRD) patterns were collected using a General Area Detector Diffraction System (GADDS) ( $\lambda = 1.5406 \text{ \AA}$ ) at  $2\theta$  between 10° and 70°. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo MultiLab 2000 system with an Al–Mg  $\alpha$  X-ray source to determine the chemical composition of GMfs-16. To compensate for charging effect, binding energies was corrected for covalent C1s at 284.6 eV after curve fitting. After background correction, curve fitting was carried out using a mixed Gaussian-Lorentzian function. Raman scattering was performed on a Jasco-Raman spectrometer with excitation by 520 nm laser light.

### 2.4. Application into LIB anode

The Li ion battery performance was analyzed by coin cell, which was fabricated in glove box with Ar atmosphere. The anode electrodes were fabricated by preparing a slurry consist of 90 wt% active material, and 10 wt% polyvinylidene fluoride as a binder. The two components were mixed and grinded in an agate mortar with few drops of *N*-methyl-2-pyrrolidone as solvent. The homogeneous slurry was pasted on the Cu foil, and dried overnight in vacuum oven at 80 °C. The specific capacity was measured based on the mass of active material. The coin cells were assembled by employing a composite electrode with metallic lithium foil and 1M LiPF<sub>6</sub> (Aldrich 99.99%) dissolved in a solution of ethylene carbonate (EC)/diethyl carbonate (DEC) at the same composition (1:1) as an electrolyte in a glove box filled with argon. The cell was galvanostatically cycled between 0.01 and 3.0 V vs. Li/Li<sup>+</sup> at various specific currents.

## 3. Results and discussion

As illustrated by Scheme 1, 2D hybrid colloids need to offer a high quality of aqueous dispersion arising from a complete exfoliation into single or few layers. A good dispersion of hybrid colloids resulting from the electrostatic repulsion of negatively charged GO and MoS<sub>2</sub> surfaces was achieved by solution chemistry as previously reported [23], and the layer number of 2D MoS<sub>2</sub> is single or few layers, as shown in AFM (Fig. S1) and TEM (Fig. S2). Ice crystals used as pore forming templates are created by freezing water molecules in a colloid dispersion. Hybrid particles are rejected from ice crystals *via* a phase separation and thus, entrapped and organized to construct 3D continuous networks above the percolation threshold. After defrosting or sublimating ice crystals, the reciprocal 3D macroporous architectures framed by 2D hybrid nanosheets are generated. Since the structure formation is controlled by coupled liquid-particle and particle-particle interactions, the surface charges of GO and MoS<sub>2</sub> (for a stable dispersion) and both  $\pi$ – $\pi$  stacking and van der Waals interactions are very critical for inducing 3D macroporous frameworks during a reorganization of structure. As shown in the optical image of final product (Fig. S3), the resulting hybrid solids were formed as monolithic frameworks with a density of 2.3 mg cm<sup>-3</sup>, which are suitable for energy storage devices because they can be free from binder and current collector.

The morphology of GMfs-16 was investigated by XRD spectra, SEM, TEM, and STEM images as shown in Fig. 1. The monolithic

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