



# Anchoring hollow MoO<sub>2</sub> spheres on graphene for superior lithium storage



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## ARTICLE INFO

### Keywords:

Molybdenum dioxide  
Graphene  
Hollow structure  
Lithium storage

## ABSTRACT

Hollow MoO<sub>2</sub> spheres anchored on nitrogen-doped graphene (H-MoO<sub>2</sub>@rGO) are synthesized with an *in situ* self-assembly approach. The hollow structure could provide sufficient space to accommodate the volume variation of MoO<sub>2</sub> during the discharge-charge process, thus improving the cycling stability. Nitrogen-doped graphene can accelerate the charge transfer. Moreover, the graphene and MoO<sub>2</sub> are proved to be strongly connected through C–O–Mo linkage, which provide good pathways for charge transfer and thus allowing an improved rate capability. Benefiting from the above features, H-MoO<sub>2</sub>@rGO delivers impressive cycling stability with a capacity of 414 mAh g<sup>-1</sup> after 1000 cycles at 2 C. Even at a high discharge/charge rate of 5 C, the composite still could deliver a capacity of 478 mAh g<sup>-1</sup>.

## 1. Introduction

Rechargeable Lithium-ion batteries (LIBs) have been widely used in portable electronic devices for their high energy density and long cycle life compared with other kinds of electrochemical power sources [1]. However, the common used graphite anode could not meet the increasing demand of electric vehicles and energy storage facilities due to its low theoretical specific capacity (372 mA h g<sup>-1</sup>) and poor rate capability. In order to develop candidate anode materials with superior performances, transition metal oxides (TMOs) have been investigated due to their high theoretical capacity, such as FeO<sub>x</sub>, [2–4] CoO<sub>x</sub>, [5,6] and MoO<sub>2</sub> [7,8] et al. Among them, MoO<sub>2</sub> is an attractive anode material due to its high theoretical specific capacity (838 mAh g<sup>-1</sup>) and affordable cost [9–13]. However, MoO<sub>2</sub> usually suffers from poor rate capability and cycle stability because of their low electron conductivity and severe volume variation during discharge/charge process.

In order to accommodate the volume variation of MoO<sub>2</sub> during cycling process, various nanostructures have been fabricated, such as heterostructure, [14] nanoparticles, [11] nanosheets [9] and spheres [12,15,16]. Recently, hollow structure has attracted great attention in lithium storage, supercapacitors and electrocatalyst for its high surface area and sufficient inner space [17–20]. These advantages enable the easy access of electrolyte to electrode interface, increase ion and electron transport capability and provide sufficient inner space for volume changes, thus improving the rate capability and cycling performance of LIBs.

Besides the serious volume variation, metal oxides usually suffer

from poor electronic conductivity. Binding active materials with other matrix is becoming a promising strategy to solve this problem [13,14,21–24]. As a fantastic two-dimension (2D) carbon material with excellent electrical conductivity and mechanical properties, graphene could improve the conductivity and serve as structural buffer to maintain the integrity of electrode. Therefore, MoO<sub>2</sub>/graphene composites have been reported and delivered enhanced electrochemical performance [7,15,25]. However, the details of the interfacial interaction between MoO<sub>2</sub> and graphene is not clear.

In this work, hollow MoO<sub>2</sub> spheres are anchored on graphene (H-MoO<sub>2</sub>@rGO) through a facile one-pot solvothermal method. The combination of hollow structure and graphene provide several advantages for improved MoO<sub>2</sub> Li-storage performance. First, the hollow structure and small nanoparticles provide plenty space to accommodate the volume variation of MoO<sub>2</sub> during cycling process, thereby improves the cycling stability [26,27]. Second, graphene could enhance the conductivity and structural stability of H-MoO<sub>2</sub>@rGO [15]. Moreover, MoO<sub>2</sub> and graphene are bound through C–O–Mo linkages and provide good pathways for charge transfer during cycle process, which could improve the conductivity and favorable for the rate capability. Benefiting from the advantages mentioned above, H-MoO<sub>2</sub>@rGO exhibited enhanced lithium storage performance. The composite can deliver a capacity of 414 mAh g<sup>-1</sup> after 1000 cycles at 2 C. Even under a high charge/recharge rate of 5 C, the composite still delivers a capacity of 478 mAh g<sup>-1</sup>.

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## 2. Experimental section

### Preparation of H-MoO<sub>2</sub>@rGO and H-MoO<sub>2</sub>

Graphene oxide (GO) was firstly prepared through a modified Hummers method. H-MoO<sub>2</sub>@rGO were synthesized through a one-pot solvothermal method. In a typical synthesis process, 80 mg GO was dispersed in 50 mL deionized water by ultrasonication for 1 h. Then 0.27 g ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O) and 10 mL concentrated hydrochloric acid were added in the mixture. After that, 50 mg polyvinylpyrrolidone (PVP) and 50 mg ascorbic acid were dissolved in the mixture and ultrasonication for 30 min. Subsequently, the mixture was sealed in a 100 mL Teflon-lined stainless steel autoclave and heated under 180 °C for 48 h. After natural cooling to room temperature, the aerogel was washed with deionized water and alcohol several times and freeze dried. Finally, H-MoO<sub>2</sub>@rGO were obtained after annealing in Ar at 600 °C for 4 h. Hollow MoO<sub>2</sub> spheres and reduced graphene oxide (rGO) were prepared with a similar solvothermal method separately and mixed together with a mass ratio of 72:28 (noted as H-MoO<sub>2</sub>/rGO).

### Electrochemical measurements

Electrochemical performance were tested using CR2025 type coin cells. The active materials (H-MoO<sub>2</sub>@rGO or H-MoO<sub>2</sub>/rGO) were grinded and mixed with poly (vinylidene fluoride) (PVDF) binder with a ratio of 8:2 in N-methylpyrrolidone (NMP). The slurry was spread onto copper foil with a mass density around 1 mg cm<sup>-2</sup> and dried at 100 °C for 12 h. The coin cells were assembled in a glove box filled with argon. 1 mol L<sup>-1</sup> LiPF<sub>6</sub> dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a 1:1 vol ratio was used as the electrolyte and lithium foil were used as the counter and reference electrodes.

## 3. Results and discussion

The fabrication process of H-MoO<sub>2</sub>@rGO is illustrated in Fig. 1. When the concentration of PVP was beyond its critical micelle concentration, PVP molecules were spontaneously self-assembled into spherical micelles and acted as micro reactors, in which the hydrophilic groups pointed outwards while the hydrophobic groups were oriented inwards. During the following hydrothermal process, ammonium molybdate was reduced to MoO<sub>2</sub>. Mo<sup>2+</sup> ions chemisorbed on MoO<sub>2</sub> nanoparticles may react with GO to form C–O–Mo linkage and some Mo<sup>2+</sup> ions bonded with GO also form C–Mo bonding and then combine with MoO<sub>2</sub> nanoparticles [28]. MoO<sub>2</sub> nanoparticles were restricted in

the inner of the PVP micelles. These MoO<sub>2</sub> nanoparticles tend to precipitate together to decrease the high surface energy, but restricted in the inner space of PVP micelles, thereby assembled to hollow spheres through Ostwald ripening process (Fig. 1b). At the same time, GO was reduced, meanwhile hollow spheres were bound in graphene sheets (Fig. 1a). The hollow MoO<sub>2</sub> nanospheres and rGO were also separately prepared and mixed together (H-MoO<sub>2</sub>/rGO).

As shown in SEM images (Fig. 2), MoO<sub>2</sub> demonstrates a sphere morphology with diameter around 300 nm. All the nanospheres are anchored on graphene sheets. The roughness of MoO<sub>2</sub> nanospheres surface implies that these nanospheres are consisted with small nanoparticles, which will be further confirmed by TEM characterization. The SEM images of hollow MoO<sub>2</sub> spheres and H-MoO<sub>2</sub>/rGO are also provided in Fig. S1. It is obvious that the distribution of H-MoO<sub>2</sub> on rGO is not uniform and detached.

The crystal phase of bulk MoO<sub>2</sub> and H-MoO<sub>2</sub>@rGO were both confirmed by X-ray diffraction (XRD, Fig. 3a). All the peaks can be well indexed to monoclinic MoO<sub>2</sub> phase (Joint Committee on Powder Diffraction Standards 76-1807) and no other peaks were observed, confirming the high purity of products. No characteristic diffraction peaks of graphene are observed in H-MoO<sub>2</sub>@rGO because of its low content in the composite. This result confirms that MoO<sub>2</sub> with high purity and crystallization was successfully prepared. In order to measure the carbon content in H-MoO<sub>2</sub>@rGO, Thermal Gravity Analysis (TGA) was conducted from room temperature to 700 °C in air. According to the TGA result, the carbon content in H-MoO<sub>2</sub>@rGO is about 28% (Fig. S2).

In order to further confirm the hollow structure and structural details of H-MoO<sub>2</sub>@rGO, the TEM and HRTEM characterizations were carried out. As shown in Fig. 3b and c, the hollow structure is easily observed, and the shell layer is composed of small nanoparticles. The small nanoparticles could not only shorten the Li<sup>+</sup>/electron diffusion paths, but accommodate the volume change during the cycling process. At the same time, the hollow spheres are wrapped in graphene, which is beneficial for the fast transfer of electron and the stability of hollow structure. The HRTEM image (Fig. 4d) reveals that H-MoO<sub>2</sub>@rGO are well crystallized. The distance between two adjacent lattice fringes are 0.34 nm, corresponding to the interplanar spacing of (0 1 1) plane of MoO<sub>2</sub>.

X-ray photoelectron spectroscopy (XPS) was employed to study the chemical composite of H-MoO<sub>2</sub>@rGO. As shown in Fig. 4a, the survey spectrum involves four distinct peaks assigned to Mo 3d, C 1s, N 1s and O 1s, respectively, indicating the presence of Mo, C, O and N elements in H-MoO<sub>2</sub>@rGO composite. The Mo 3d peak can be deconvoluted into four peaks (Fig. 4b). The peaks at 229.4 and 232.7 eV are assigned to Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> of Mo<sup>4+</sup> [10,29]. The peaks at 232.1 and

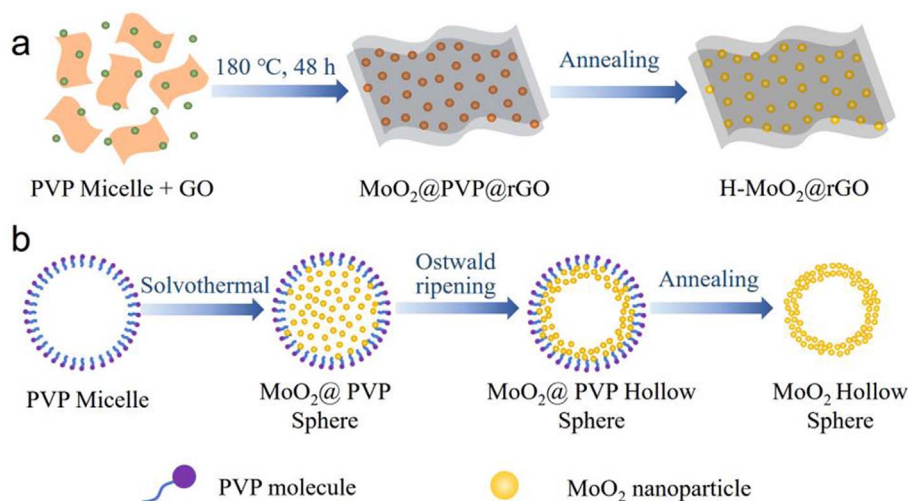


Fig. 1. Illustration of the formation mechanism of H-MoO<sub>2</sub>@rGO composite (a) and hollow MoO<sub>2</sub> spheres (b).

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