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Cationic surfactant-assisted hydrothermal synthesis of few-layer molybdenum disulfide/graphene composites: Microstructure and electrochemical lithium storage

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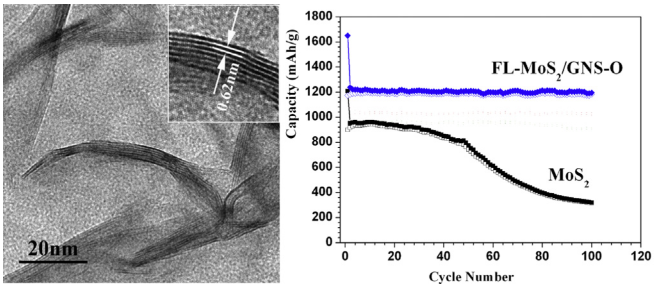
HIGHLIGHTS

- FL-MoS_2/GNS composites are prepared by a facile cationic surfactant–hydrothermal route.
- Cationic surfactants show some ability to control layer number of FL-MoS_2 in the composites.
- FL-MoS_2/GNS exhibits outstanding electrochemical properties as a reversible lithium storage host.

GRAPHICAL ABSTRACT



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ABSTRACT

Few-layer molybdenum disulfide/graphene (FL-MoS_2/GNS) composites are fabricated by a facile hydrothermal route and a post-annealing with the assistance of various cationic surfactants (dodecyltrimethylammonium bromide, DTAB; octyltrimethylammonium bromide, OTAB; and tetrabutylammonium bromide, TBAB), which have different alkyl-chain lengths and stereo configurations. The effects of these cationic surfactants on the microstructures and electrochemical performances of the FL-MoS_2/GNS for lithium storage are investigated. It is demonstrated the cationic surfactants show some ability to control the microstructure (layer number) of FL-MoS_2 in composites. The electrochemical performances of FL-MoS_2/GNS composites for lithium storage are greatly improved compared to the bare MoS_2. Especially, FL-MoS_2/GNS with ~6 MoS_2 layers prepared with the assistance of OTAB exhibits very high reversible capacity of ~1200 mAh g^{-1} with excellent cycle stability and enhanced rate capability. Electrochemical impedance spectrum also confirms that the FL-MoS_2/GNS composite electrodes exhibit much lower electron-transfer resistance than the MoS_2. The remarkable electrochemical performances of FL-MoS_2/GNS composites can be attributed to the synergistic interaction between FL-MoS_2 and graphene and their quasi-3D architectures, which promote lithium diffusion, electron transfer and electrolyte access.

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1. Introduction

With the advent of plug-in hybrid electric vehicles and a new greater political awareness toward the importance of energy storage, the advanced energy storage and conversion technology have become an increasingly pivotal part of the modern era [1]. As the most advanced rechargeable batteries, lithium-ion batteries (LIBs) have attracted the great attention due to their high energy/power densities, long life and environment-friendly characteristics [2,3]. The capability of LIBs largely depends on the electrode materials, especially anodes. Graphite anodes have been ubiquitous in current designs but are limited by its low theoretical capacity of 372 mAh g^{-1}. Thus, it is of great significance to design and create the novel electrode materials with higher capacity, excellent cycle and rate capability for next-generation high-performance LIBs [4].

Two-dimensional (2D) nanomaterials have long been regarded as attractive materials owing to their unique properties and promising applications in energy storage and conversion, particularly for LIBs due to their shortened paths and more channels for lithium ion fast-diffusion and insertion [5,6]. Among these 2D crystals, graphene nanosheet (GNS) is an unequivocal champion and exhibits superior conductivity, high charge mobility, crystal and electronic quality [7,8]. GNS have been used as an appealing platform for preparing a variety of composites and hybrids with exceptional properties and mass potential applications [9,10]. Apart from graphene, other 2D crystal nanosheets, especially 2D transition metal dichalcogenide (TMD, such as MoS_2 and WS_2) sheets with single-layer (SL) or few-layer (FL), have recently attracted considerable attention for their unexpectedly exotic behaviors compared with the bulk counterparts [6,11]. As a typical TMD, MoS_2 crystals have a sandwich interlayer structure formed by stacking of the (S—Mo—S) layers in *c*-direction, which are loosely bound to each other by van der Waals [12]. This layered structure is favorable to exfoliation of layers into SL- or FL-MoS_2 nanosheets. Currently, the exfoliation of the bulk MoS_2 into SL- or FL-nanosheets can be achieved by mechanical cleavage [13–15] and liquid exfoliation based on N-butyllithium [16]. However, the efficiency of the former is very low and the latter consumes a large amount of organic solvent and is sensitive to environmental conditions [16,17]. A few new approaches toward the SL- or FL-MoS_2 nanosheets can be now available, such as the modified liquid exfoliation under sonication [18–20], electrochemical lithiation-assisted exfoliation [21,22], laser/plasma thinning [23] and other solution-phase approaches (e.g. hydrothermal or solvothermal synthesis [24,25], oleylamine-assisted wet-chemical approach [26]).

On another hand, nanostructured MoS_2, especially the SL- or FL-MoS_2 nanosheets, have gradually emerged as a promising electrode material for LIBs owing to their more channels and shortened paths for the fast diffusion and insertion of lithium storage [11,27,28]. Even if the SL- or FL-MoS_2 nanosheets exhibit much higher specific capacity than graphite anodes, they suffer a lot from the poor cycling stability caused by particle pulverization and restacking of nanosheets during repeated lithiation/delithiation process, and a low rate-capability originating from the intrinsic low electronic conductivity of MoS_2 [29,30]. To circumvent the above drawbacks, a feasible strategy is to combine MoS_2 nanosheets with highly conductive and flexible matrix such as carbon nanotube and graphene as a buffer layer and a current micro-collector [31–36]. GNS appears particularly promising to improve the rate capability and cycle performance of MoS_2 nanosheets owing to their superior electrical conductivity, high charge mobility, large surface area and inherent flexibility [7,34]. More importantly, due to their structural and morphological similarity, GNS can provide a more intimate surface to surface contact with FL-MoS_2 nanosheets to form heterolayered composite compared to other 0D nanoparticles or 1D nanorods [9,10]. Indeed, the novel heterostructures made by the stacking of GNS and other 2D layered materials together have been paid more and more attention due to their unusual properties and more possibility of application including electronic/photoelectronic devices, clean energy storage and conversion [37]. To date, despite the fact that a few strategies have been developed to prepare SL or FL-MoS_2/graphene composites and great improvement has been achieved on their electrochemical performances, it is still imperative to hunt for a facile and scalable fabricating approach to FL-MoS_2/GNS heterostructural composites.

Recently, we have developed a facile and effective route to prepare SL- or FL-MoS_2/GNS composites by using cationic surfactants [38–40]. Cationic surfactants can be easily adsorbed on the negatively charged GOS surface through electrostatic interaction, and mediate the charge incompatibility between GOS and MoS_4^{2-} (or MoO^{4-}). It is also found that the cationic surfactants showed some ability to control the microstructure (layer number) of MoS_2 in the composites. In our previous works [38,39], the SL- or FL-MoS_2/GNS composites were prepared based on the simultaneous reduction of $(NH_4)_2MoS_4$ and GOS by hydrazine under refluxing with assistance of different cationic surfactants (CTAB, DTAB, OTAB and TBAB). Hydrothermal route is a facile and effective route for preparing various nanomaterials and nanocomposites, and has shown some advantages in homogeneous nucleation and grain growth of MoS_2 nanosheets compared with the liquid reduction under refluxing. In addition, $(NH_4)_2MoS_4$ is a special chemical, the price of which is much high than that of the general molybdate (Na_2MoO_4). Thus, FL-MoS_2/GNS composites were also prepared based on hydrothermal reduction of Na_2MoO_4 and L-cysteine in the presence of GOS with assistance of CTAB [40]. It was found that the microstructures and electrochemical performances of the MoS_2/GNS composites prepared by the above two strategies were different; and the FL-MoS_2/GNS composites prepared by hydrothermal method with assistant of 0.01–0.02 M CTAB exhibited better electrochemical lithium storage performance than other samples [39,40]. In order to further study the influence of different cationic surfactants on hydrothermal-synthesized MoS_2/GNS composites and continuously improve their electrochemical performances for LIB application, in this extended work, we demonstrate a facile approach to fabricating FL-MoS_2/GNS composites by a hydrothermal method and post-annealing with the assistance of other three cationic surfactants (DTAB, OTAB and TBAB), which possess different chain lengths and stereo configurations compared to CTAB. The FL-MoS_2/GNS composites were characterized by XRD, SEM, TEM, HRTEM, EDX and Raman spectra. The effects of the different cationic surfactants on the microstructures of the FL-MoS_2/GNS composites and their electrochemical performances of reversible lithium storage were investigated. Electrochemical measurements confirmed that the electrochemical performance of FL-MoS_2/GNS composites for lithium storage was greatly improved compared to the MoS_2. Especially, FL-MoS_2/GNS with ~6 MoS_2 layers prepared with the assistance of 0.02 M OTAB exhibits very high reversible capacity of ~1200 mAh g^{-1} with excellent cycle stability and enhanced rate capability, which is better than other samples both in this work and in our previous works [38–40].

2. Experimental section

2.1. Synthesis of FL-MoS_2/GNS composites

Graphene oxide was prepared by the oxidization of natural graphite powder using a modified Hummers method [41]. The graphene oxide prepared as such was re-dispersed in deionized water and then exfoliated to graphene oxide sheets (GOS) by