



Morphology-controlled synthesis of MoS₂ nanostructures with different lithium storage properties



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ABSTRACT

A one-step hydrothermal process was employed to prepare a series of MoS₂ nanostructures via simply altering the surfactant as soft template and hydrothermal reaction temperature. Three kinds of MoS₂ nanostructures (three-dimensional (3D) hierarchical nanospheres, one-dimensional (1D) nanoribbons, and large aggregated nanoparticles) were successfully achieved and investigated well by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), and Brunauer–Emmett–Teller analysis (BET). Electrochemical tests reveal that these MoS₂ samples could deliver high initial discharge capacities (higher than 1050.0 mA h g^{−1}), but various cycling performances. The hierarchical MoS₂ nanospheres assembled by sheet-like subunits show the highest specific capacity of 1355.1 mA h g^{−1}, and 66.8% of which can be retained after 50 cycles. The good lithium storage property of hierarchical MoS₂ nanospheres can be attributed to the higher electrolyte/MoS₂ contact area and stable 3D layered structure.

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1. Introduction

Li-ion batteries (LIBs) are the main power sources for portable electronic devices and hybrid electric vehicles [1–3]. Graphite has been commonly used as anode materials in commercial LIBs. However, the limited theoretical capacity of graphite (372 mA h g^{−1}) could not meet the requirement of future energy storage system [4]. As one type of two-dimensional (2D) layered materials, transition metal disulfides (TMDs) MS₂ such as MoS₂ [5], SnS₂ [6], WS₂ [7] and ZrS₂ [8] have been exploited as the novel anode materials of LIBs owing to their graphene-like structure, in which atoms are covalently bonded within the individual layers that are bound by weak van der Waals force. This graphene-like structure enables the convenient insertion and extraction of Li⁺ ions.

Among the graphene analogous TMDs, MoS₂ is found to be one of the most promising anode material for LIBs because there is a 4-electron transfer reaction occurring at lower potential during the charge/discharge process achieving high capacities up to 1000 mA h g^{−1}. However, the rapid capacity fading and poor rate performance result in its limited practical application due to the gel-like polymeric layer formed by the reaction between the lithiation product Li₂S and electrolyte, which will prevent the successive lithiation/delithiation reaction [9–12]. An extensive used

strategy to address this issue is to design different nanostructure. Du et al. reported the synthesis of restacked MoS₂ nanostructures that gave a high specific capacity of 750 mA h g^{−1} after 50 cycles, while the raw MoS₂ faded to 226 mA h g^{−1} [13]. MoS₂ nanorods prepared by a sulfidation method demonstrated an excellent cycling stability with a high capacity of 621 mA h g^{−1} after 80 cycles [14]. Other MoS₂ nanostructures including nanosheets [15], nanoflowers [16], nanoplates [17], nanowalls [18] and hollow nanoparticles [19] have also been reported as LIBs anode materials. Although there are many reports about MoS₂ nanostructures with improved lithium storage properties, most of them only focused on one type of MoS₂ nanostructures. The morphology could have an important impact on the surface area, active site and ion kinetics of materials, which could effectively influence its electrochemical performance [20,21]. Therefore, it is necessary to investigate the morphology-depending electrochemical performance of various MoS₂ nanostructures.

Meanwhile, even though various synthetic methods have been developed, it is still a challenge to achieve the shape-controlled MoS₂ nanostructure through a facile and environmentally friendly method. Among all synthesis strategies, the surfactant-assisted hydrothermal method is considered to be a direct reaction route to control both the morphology and phase of inorganic materials. MnWO₄ [22], Mn₂O₃ [23] and NiS_x [24] nanostructures have been prepared by a hydrothermal process in presence of different surfactant.

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In this work, we report a facile approach to prepare MoS₂ nanostructures with different morphologies and sizes via a hydrothermal method by controlling the added surfactant and hydrothermal reaction temperature. MoS₂ nanostructures with nanospheres, nanoribbons and nanoparticles morphologies have been successfully synthesized. The electrochemical properties of three kinds of as-prepared MoS₂ samples were investigated as anode materials for LIBs. Among these samples, the MoS₂ hierarchical nanospheres with high specific surface area and stable structure show the best cycling stability and rate performance.

2. Experiment

2.1. Preparation of MoS₂ nanostructures

MoS₂ nanoribbons (NSs) were fabricated as the following procedures: 0.5 g sodium molybdate (Na₂MoO₄·2H₂O) and 0.6 g thioacetamide (TAA) were dissolved in 40 mL de-ionized water under vigorous stirring. After stirring for 15 min, 0.14 g polyvinyl pyrrolidone (PVP) was added to the above solution. Then, the transparent solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated to 200 °C with a heating rate of 5 °C min⁻¹ and held for 24 h. After that, the autoclave was cooled to room temperature. The black products deposited at the bottom were washed by centrifugation for three times using de-ionized water and dried in oven at 60 °C for 12 h.

The MoS₂ nanoribbons (NRs) were synthesized by the similar procedures above except that 0.4 g poly(ethylene glycol octylphenol ether) (Triton X-100) was used to substitute PVP in reaction solution.

For the synthesis of MoS₂ nanoparticles (NPs), both the surfactant and hydrothermal reaction temperature were changed. 0.54 g cetyltrimethyl ammonium bromide (CTAB) was added into a mixed solution of Na₂MoO₄ and TAA. The mixture was hydrothermally treated at 160 °C for 24 h.

2.2. Materials characterization

The crystal structure of samples was measured by X-ray diffractometer (XRD, Rigaku D/max 2550VB*) from 10° to 80° with Cu K α radiation (λ = 1.54056 Å). The product morphology was characterized by scanning electron microscope (SEM, Nova NanoSEM 230), transmission electron microscope (TEM, Tecnai G2 20ST). Nitrogen adsorption/desorption measurements were performed by using Quantachrome instrument (Quabrasorb SI-3MP) at 77 K.

2.3. Electrochemical measurements

The electrochemical characterization was carried out using a CR-2025 type coin cell with a lithium metal sheet as the counter and reference electrode and a Celgard 2400 film as separator. The working electrode was prepared by casting a slurry consisted of 80 wt% active materials, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) on a copper foil. Then, the slurry was dried at 100 °C under vacuum overnight. The test cells were assembled in an argon-filled glove box (Universal 2440/750). The electrolyte was 1.0 M LiPF₆ solution in a 1:1:1 v/v mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diethyl carbonate (DMC).

The charge/discharge tests were carried out in potential window of 0.01–3.0 V with a LAND CT2001A battery-testing system. The EIS were measured in the frequency range of 100 k–0.1 Hz with AC voltage amplitude of 5 mV at open-circuit voltage on PARSTAT 2273 electrochemical measurement system.

3. Results and discussion

3.1. Structure and morphology characterizations

Fig. 1 shows the XRD patterns of as-prepared MoS₂ nanostructures. All diffraction lines of three samples can be indexed to hexagonal 2H-MoS₂ (JCPDS No. 37-1492), which belongs to the space group *P6₃/mmc* (No. 194). Intensive diffraction peaks at 2θ = 34.5°, 42.0° and 59.2° which correspond to (100), (103) and (110) planes of MoS₂, could be observed in XRD patterns of three samples. The intense peaks of MoS₂ NPs at 14.0°, corresponding to the (002) reflection, indicates a well-stacked layered structure with a much larger *d*-spacing (0.62 nm) than natural graphite (0.34 nm). The MoS₂ NRs exhibit a broadened and shortened (002) peaks (2θ = 12.5°) than MoS₂ NPs, suggesting a smaller crystallite size and a less number of layers in direction of the *z*-axis per-

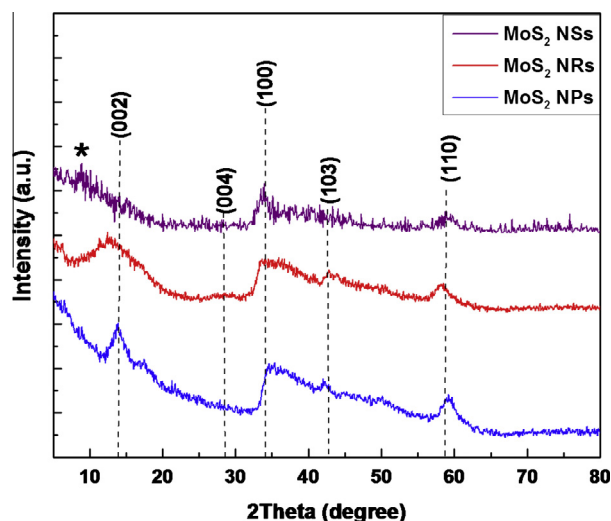


Fig. 1. XRD patterns of MoS₂ nanospheres, nanoribbons and nanoparticles.

pendicular to the atomic layers [11]. The (002) reflection even could not be observed in the XRD pattern of MoS₂ NSs, implying that this material may consist of five or less graphene-like MoS₂ layers [17]. A weak peak at 8.5° can be attributed to the diffraction of adjacent few-layered MoS₂ sheets. By using the Bragg equation, the interlayer distance of MoS₂ NRs and NSs are calculated to 0.69 and 0.98 nm respectively, providing a larger space for Li ions intercalation [25].

Morphologies of all MoS₂ nanostructures were examined with FESEM. Fig. 2a and b shows that the 3D MoS₂ NSs are in diameters of 600–900 nm and composed of the sheet-like subunits. The MoS₂ nanosheets could form MoS₂ nanoflakes and then MoS₂ nanoflakes aggregate to form the loose cauliflower-like architectures, which are similar to other reported 3D MoS₂ microspheres [18,26,27]. As shown in Fig. 2c and d, the MoS₂ NRs demonstrate a one-dimensional rod or ribbon shape with a width of 200–300 nm and a length up to several micrometers. It is noteworthy that the MoS₂ NRs exhibit a relatively smooth surface. To our best knowledge, the one-pot hydrothermal synthesis of 1D MoS₂ nanostructures has not been reported yet. Fig. 2e illustrates that the spherical MoS₂ NPs do not exhibit a good dispersions. The higher magnification FESEM (Fig. 2f) shows these particles are with a relatively uniform size of 600 nm and possess quite rough surfaces.

In order to further investigate structural information of three MoS₂ samples, HRTEM and selected area electron diffraction (SAED) are presented in Fig. 3. It can be obviously seen from Fig. 3a and b that the MoS₂ NSs and NRs consist of few-layered MoS₂ sheets in random orientation. For MoS₂ NSs and NRs, the interlayer distance of (002) plane measured from HRTEM images are 0.69 and 0.98 nm respectively, which coincide with the results from XRD analysis. MoS₂ (002) planes do not stack together in the MoS₂ NSs, confirming the absence of the (002) reflection in XRD pattern. For the MoS₂ NPs in Fig. 3c, a well-layered structure with *d*₍₀₀₂₎ spacing of 0.62 nm is observed, in good agreement with previous XRD results. More than 5 layers bond together tightly by van der Waals force to form thin sheets which then curl up to sphere-like particles. The SAED in inset of Fig. 3 reveal that the all three MoS₂ nanostructures are weakly crystalline.

To characterize the specific surface area of three MoS₂ nanostructures, N₂ adsorption-desorption analysis were performed using Brunauer-Emmett-Teller (BET) method. Fig. 4 shows the N₂ adsorption-desorption isotherms of these samples, and the insets exhibit the corresponding pore size distribution by Barrett-Joyner-Halenda (BJH) method. The isotherm curves of three

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