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Synthesis of Highly Uniform Mo-glycerate Spheres and Their Conversion to Hierarchical MoS₂ Hollow Nanospheres for Lithium-Ion Batteries

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Abstract

Highly uniform Mo-glycerate solid spheres are synthesized for the first time through a novel solvothermal process. The size of these Mo-glycerate spheres can be easily controlled in the range of 400 - 1000 nm by varying the water content in the mixed solvent. As a precursor, these Mo-glycerate solid spheres can be converted to hierarchical MoS₂ hollow nanospheres through a subsequent sulfidation reaction. Owing to the unique ultrathin subunits and hollow interior, the as-prepared MoS₂ hollow nanospheres exhibit appealing performance as the anode materials for lithium-ion batteries. Impressively, these hierarchical structures deliver a high capacity of ~ 1100 mAh g⁻¹ at 0.5 A g⁻¹ with good rate retention and long cycle life.

Keywords: MoS₂; hollow spheres; nanosheets; lithium-ion batteries.

Molybdenum disulfide (MoS_2) is a well-known two-dimensional (2D) material with graphene-like crystalline structure.^[1-3] Recently, it has been recognized as a promising electrode material in the energy conversion and storage areas owing to its rich intercalation chemistry.^[4-9] In particular, significant attention has been drawn on its potential use as the anode material in lithium-ion batteries (LIBs) because MoS_2 leads to a 4-electron transfer reaction during the charge/discharge process with a high theoretical capacity of 669 mAh g^{-1} .^[10-14] Nonetheless, it still faces some challenges in the practical applications such as the substantial volume change during cycling and poor rate performance. To solve these problems, various strategies have been reported to optimize the electrochemical performance of MoS_2 by rationally designing its geometric shapes and morphologies at nanoscale.^[15-26]

Amongst the various approaches, the employment of hollow nanostructures has been considered as an attractive avenue to mitigate the above-mentioned obstacles and improve the lithium storage performance.^[27, 28] To be specific, the nanosized building blocks could effectively shorten the diffusion distance of the Li^+ ions, relax the strain and lower the barrier for lithium intercalation during the charge/discharge processes.^[6, 12, 29] Meanwhile, the cavities in hollow structures ensure their high surface-to-volume ratio, which offers larger specific surface area for plenty of electrochemical active sites. Of note, the interior voids of the material could help preserve the integrity of the electrodes by accommodating the large volume variation associated with various electrochemical reactions.^[30-33]

The templating method is the most common strategy to generate diverse hollow materials.^[34-36] Usually, template-based synthesis involves the coating of the shell material on either hard or soft templates and the subsequent removal of the inner templates. For instance, we have recently prepared hollow MoS_2 supported on carbon box using cubical Fe_2O_3 particles as a hard sacrificial template.^[37] Despite its versatility, the templating method would face the potential incompatibility issue between the core and shell materials. A self-templating method, on the other hand, directly transforms a precursor template into the final product. Since it does not require the heterogeneous process, better control over

the size uniformity can be easily achieved.^[27, 38] Self-templating approaches have been widely applied to generate a great variety of metal sulfides with distinct morphologies and compositions.^[39-43] Recently, Zhang and co-workers developed an anion-exchange reaction of MoO₃-amine hybrid nanowires to produce hierarchical MoS₂ nanotubes.^[5] However, such modified templating strategies have not been widely practiced yet due to the paucity of applicable Mo-based templates with high size uniformity.

Herein we report the first synthesis of highly uniform Mo-glycerate (MoG) solid spheres by a facile solvothermal process. Afterwards, these MoG spheres are successfully sulfurized by thiourea in a mixed solvent to obtain the MoS₂ hollow nanospheres (HNS) constructed by nanosheets. By tuning the composition of the reaction system and preparation temperature in the sulfidation treatment, the size and internal architectures of the MoS₂ HNS can be adjusted to generate a series of complex derivatives with the yolk-shell or double-shell structural features. The MoS₂ HNS are further annealed and applied as the anode materials for LIBs showing enhanced electrochemical performance.

The synthesis process is schematically illustrated in **Figure 1**. The whole synthesis process generally involves two stages. First, a solvothermal method is developed to synthesize highly uniform MoG solid spheres using MoO₂(acac)₂ as the molybdenum source, and glycerol, isopropanol (IPA) together with a certain amount of water as the mixed solvent.^[44] In the following sulfidation step, sulfide (S²⁻) ions released from thiourea at high temperature react with metal ions from the surface of the MoG spheres. Further anion exchange reaction between the inward diffused S²⁻ ions and faster outward diffused metal ion species can create a void space between the newly formed MoS₂ layer and the inner MoG core.^[31, 40, 44] Eventually after reaction for 6 h, the original MoG spheres are chemically transformed into MoS₂ HNS composed of nanosheets.

Figure 2 shows the morphologies of the MoG precursor spheres and the as-formed MoS₂ HNS. Field-emission scanning electron microscope (FESEM) and transmission electron microscopy (TEM)

images (Figure 2a-c) show that the highly uniform MoG spheres are solid in nature with an average diameter of 580 nm. Besides, the well-separated spheres possess a rather smooth surface over the whole particle without any crystalline facets. Energy-dispersive X-ray (EDX) spectroscopy data confirms the existence of elements of Mo, C and O in the spheres (Figure S1, Supporting Information). The weak peaks of the X-ray diffraction (XRD) pattern imply the amorphous nature of the MoG spheres and the existence of possible MoO₂ phase (Figure S2, Supporting Information). Only a small loss in weight can be observed from the thermogravimetric analysis (TGA; Figure S3, Supporting Information), suggesting the small amount of organic components. The size and uniformity of the MoG spheres can be adjusted by tuning the volume fraction of water in the mixed solvent. Generally speaking, the spheres will grow bigger with compromised uniformity when the water content is reduced. While a slight increase of the water content to 37.5 vol% would still give uniform MoG spheres with a reduced average size of ~ 400 nm (Figure S4a, Supporting Information). As the water content is reduced to 12.5 vol%, the obtained MoG spheres possess an increased average size of ~ 1 μm (Figure S4b, Supporting Information). In the absence of water, some irregular spheres with larger size could be obtained (Figure S4c, Supporting Information). When the IPA/H₂O volume ratio is increased to 1, the MoG spheres experience a rapid reduction in size with much higher surface roughness (Figure S4d, Supporting Information). Other Mo sources, such as (NH₄)₆Mo₇O₂₄·4H₂O and H₂MoO₄, could also be employed to generate MoG spheres. Nonetheless, the size distribution of corresponding products is quite difficult to control (Figure S5, Supporting Information).

After sulfidation under solvothermal conditions, the MoG spheres are converted into MoS₂ HNS. The panoramic FESEM image (Figure 2d) indicates the overall spherical morphology of the as-prepared MoS₂ structures is well preserved with a uniform diameter of ~ 580 nm, almost same as the solid MoG spheres. The magnified observations (Figure 2e,f) further reveal the surface of these hierarchical structures are constructed by nanosheet subunits. As depicted by TEM studies in Figure

2g-h, the hollow structures and well-defined inner cavities of MoS₂ HNS are clearly elucidated by the sharp contrast between the centre and the edge. From a closer examination of an individual sphere (Figure 2i), it can be observed that the hierarchical shell has a thickness of about 140 nm. Moreover, the dark strips demonstrate the ultrathin feature of the exposed 2D nanosheets. XRD study of the hollow product (Figure S6, Supporting Information) can be assigned to the hexagonal phase of MoS₂, consistent with the previous reports.^[5, 45] In addition, the visible (002) diffraction peak further confirms the formation of a well-stacked layered structure of MoS₂. As determined by N₂ sorption measurement (Figure S7, Supporting Information), these MoS₂ HNS possess a Brunauer-Emmett-Teller specific surface area of 31.48 m² g⁻¹ with the pore sizes mostly below 10 nm.

To verify our hypothesis on the formation mechanism of the unique MoS₂ HNS, time series analysis is carried out to monitor the morphological evolution during the sulfidation reaction. The morphology of the MoG solid spheres appears unchanged and their surfaces remain smooth after heating treatment at 200 °C for 1 h (Figure S8a, Supporting Information). When the solvothermal process prolongs to 1.5 h, a thin hierarchical shell made of MoS₂ nanosheets can be identified around the outermost layer of the spheres (Figure S8b, Supporting Information). Over an extended period of 2 to 6 h, the continuous anion exchange reaction further supports the growth of the sulfurized shell accompanied by the formation of an obvious hollow interior within the spheres (Figure S8c, Supporting Information). After the complete sulfidation process, the morphology of the hierarchical architectures will not change any more, even when the reaction is extended to 12 h (Figure S8d, Supporting Information).

Figure 3 shows the FESEM and TEM images of the MoS₂ HNS after the thermal treatment at 700 °C in Ar/H₂ for 2h. Despite the ultrathin feature, the FESEM images (Figure 3a,b) indicate that the hierarchical MoS₂ shell exhibits good structural stability to endure the harsh calcination conditions without apparent deformation in appearance. As elucidated by TEM observations in Figure 3c,d, the average size of the annealed HNS shrinks to about 450 nm with a reduced shell thickness about 100 nm.

From the XRD pattern (Figure S9, Supporting Information), the crystallinity of the HNS increases significantly after calcination. All Bragg peaks can be indexed to the MoS₂ phase (JCPDS card no. 37-1492).^[37] No residues or impurity phases are detected, further demonstrating complete transformation of the MoG spheres after sulfidation. In agreement with the XRD analysis, the inter-layer spacing of 0.66 nm and a distinct set of visible lattice fringes with an inter-planar distance of 0.27 nm can be clearly observed in the high resolution TEM (HRTEM) images, which are consistent with the expanded *d* spacing of the (002) planes and (100) facet of hexagonal MoS₂ (Figure 3e,f).

Next, the hollow MoS₂ HNS are evaluated as the anode materials for LIBs to demonstrate their promising application. **Figure 4a** shows the representative galvanostatic charge/discharge voltage profiles of the hollow nanospheres in the voltage range of 0.1-3.0 V vs. Li/Li⁺ at a current density of 0.5 A g⁻¹. Two voltage plateaus located at 1.1 and 0.6 V can be observed in the first discharge, corresponding respectively to the formation of Li_xMoS₂ by the insertion of Li⁺ ions into the interlayer MoS₂ lattice and the generation of Li₂S and Mo through the further reaction between Li_xMoS₂ and Li⁺.^[15, 46, 47] In the first charge process, a pronounced peak at around 2.3 V can be assigned to the delithiation of Li₂S to sulfur. In the following discharge process, the discharge plot with two voltage plateaus located at 2.0 and 1.3 V is observed, indicating a multi-step lithium insertion mechanism.^[16, 48, 49] To further study the mechanism of lithium storage, the cyclic voltammograms (CV) curves of the hollow nanospheres (Figure S10, Supporting Information) obtained at various cycles are investigated. In the CV plots, the representative cathodic/anodic peaks can be clearly identified, which is consistent with the above charge-discharge voltage profiles. In addition, the CV profiles are approximately overlapping except for the initial cycle, suggesting the excellent stability of these hollow structures for reversible lithium storage. Galvanostatic charging-discharging measurements confirm that these unique MoS₂ HNS can be reversibly cycled at various current densities. As shown in Figure 4b, the average specific capacities of the hollow nanospheres are ~ 944, 895, 831, 762, 711 and 576 mAh g⁻¹ at the

current densities of 0.1, 0.2, 0.5, 1, 2 and 5 A g⁻¹, respectively. When the current density is reduced back to 0.1 A g⁻¹, the high capacity of 1000 mAh g⁻¹ is immediately resumed, suggesting the good reversibility of the electrode materials. The cycling performance of the MoS₂ HNS electrodes is presented in Figure 4c. The reversible capacity of the MoS₂ hollow nanospheres in the first cycle is 1270 mAh g⁻¹, which is much higher than that of solid MoS₂ spheres (640 mAh g⁻¹). The irreversible capacity of 238 mAh g⁻¹ in the first cycle corresponding to a Coulombic efficiency (CE) of 83 % could be attributed to irreversible processes such as the formation of the solid-electrolyte interface (SEI) film and decomposition of electrolyte.^[14, 20] The MoS₂ HNS deliver a reversible specific capacity of 1100 mAh g⁻¹ at 0.5 A g⁻¹ without obvious capacity decay after 100 cycles, while the reversible specific capacity of solid MoS₂ sample is only 500 mAh g⁻¹. The Coulombic efficiencies are nearly 100 % after the first few cycles. The superior electrochemical performance of the hollow spheres might be related to the increment of electrochemical active sites compared with the solid sample. Clearly, the hierarchical MoS₂ HNS exhibit interesting properties as potential anode materials for LIBs benefitting from their unique structural features such as the ultrathin subunits and well-defined hollow interior to withstand the structural strain.

In summary, we have developed a facile solvothermal method to synthesize highly uniform Mo-glycerate spheres with size in the range of 400 - 1000 nm. These Mo-glycerate spheres can be used as precursor to synthesize MoS₂ hollow nanospheres constructed of nanosheets. The process allows good quality control on the uniformity and structure of the obtained MoS₂ materials. By slightly altering the reaction conditions, we demonstrate that the size and shell thickness of the products can be readily tuned. After thermal treatment in inert environment, hollow MoS₂ nanospheres show excellent electrochemical performance as the anode of lithium-ion batteries with high specific capacities and excellent cycling stability. It is worth mentioning that the ease of the structural tailoring provides the possibilities to further optimize the properties of the MoS₂-based functional materials.

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Figures and Captions

Figure 1. Schematic illustration of the formation process of the MoS₂ hollow sphere. Mo-glycerate (MoG) solid sphere were firstly formed by a modified solvothermal process, and then sulfurized by thiourea at 200 °C to obtain the MoS₂ hollow nanospheres (HNS).

Figure 2. FESEM and TEM images of the (a-c) MoG solid spheres and (d-i) the corresponding hierarchical MoS₂ HNS after sulfidation process.

Figure 3. (a,b) FESEM and (c,d) TEM images of the MoS₂ HNS after annealing in Ar/H₂ at 700 °C for 2 h. (e,f) HRTEM images of the MoS₂ sheets.

Figure 4. (a) Charge-discharge voltage profiles at 0.5 A g⁻¹, (b) rate capability test and (c) cycling performance at 0.5 A g⁻¹ of the MoS₂ HNS.

for Table of Content Entry

Hierarchical MoS₂ hollow nanospheres are synthesized with a novel self-templating method from highly uniform Mo-glycerate solid spheres. By altering the solvent composition, the size of Mo-glycerate solid spheres can be readily tuned. After a sulfidation reaction and a subsequent annealing treatment, these Mo-glycerate solid spheres can be converted to hierarchical MoS₂ hollow nanospheres. Owing to their unique structures, the hierarchical nanospheres show enhanced electrochemical properties as the anode materials for lithium ion batteries.

Supporting Information

Experimental Section

Synthesis of Mo-glycerate (MoG) solid spheres. All chemicals were purchased and used without further purification. MoG spheres were synthesized with a modified solvothermal process. 120 mg of molybdbl acetoacetate ($\text{MoO}_2(\text{acac})_2$) and 8 mL of glycerol were dispersed in 40 mL of isopropanol (IPA)/ H_2O ($\text{V/V} = 3:1$). The mixture was sonicated for 15 min to obtain a uniform dispersion, and then transferred to a Teflon-lined stainless steel autoclave with a capacity of 100 mL and kept at 190 °C for 3 h. After cooling down, the dark brownish product was centrifuged, washed with ethanol and redispersed in 5 mL of ethanol.

Synthesis of MoS_2 hollow nanospheres (HNS). MoG spheres were further sulfidated to obtain the hollow MoS_2 nanospheres. Typically, 1 mL of MoG solution (~ 10 mg) was added into 20 mL of ethanol (EtOH)/ H_2O ($\text{V/V} = 3:1$) solution containing 50 mg of thiourea. The mixture was then transferred to a Teflon-lined stainless steel autoclave with a capacity of 50 mL and kept at 200 °C for 6 h. The black precipitates were centrifuged, washed three times with ethanol and dried at 80 °C. The as-prepared MoS_2 HNS were annealed under Ar/H_2 atmosphere for 2 h with a temperature ramp of 2 °C min^{-1} .

Materials characterization. The crystal phase was examined by X-ray powder diffraction (XRD; Bruker, D8-Aavance X-ray Diffractometer, $\text{Cu K}\alpha$ radiation, $\lambda = 1.5406$ Å). The microstructures of products were characterized with a field-emission scanning electron microscope (FESEM; JEOL-6700) and transmission electron microscopy (TEM; JEOL, JEM-2010; JEOL, JEM-1400). Elemental mapping was recorded using energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM. Thermogravimetric analysis (TGA, Pvriss Diamond) was carried out in a flow of air with a heating rate of 10 °C min^{-1} . The nitrogen sorption measurement was conducted by Autosorb 6B at 77 K.

Electrochemical measurements. To make the anode electrode, MoS₂ hollow spheres, Super P and PVDF binder were mixed in N-Methyl-2-pyrrolidone (NMP) with a weight ratio of 70:20:10. Afterwards, the slurry was spread onto copper foil with the areal mass loading of about 1mg cm⁻². The electrode film was dried in a vacuum oven at 80 °C overnight. The 2032-type coin cells were assembled using Celgard 2300 membrane as separator. The electrolyte was a 1 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. The cell was assembled in an argon-filled glovebox with concentration of moisture and oxygen below 5 ppm. Galvanostatic discharge-charge tests were performed on a Neware Battery Measurement System (Neware, China) in the voltage range of 0.01-3.0 V. Cyclic voltammetry (CV) tests were conducted on a CHI 660D electrochemical workstation.

Figure S1. EDX spectrum of the MoG solid spheres.

Figure S2. XRD pattern of the MoG spheres.

Figure S3. TGA curve of the MoG spheres in air with a heating rate of 10 °C min⁻¹.

Figure S4. MoG products formed in different reaction systems. (a) The IPA/H₂O volume ratio is 5:3, (b) the IPA/H₂O volume ratio is 7:1, (c) pure ethanol and (d) the IPA/H₂O volume ratio is 1:1.

Figure S5. MoG products formed with (a) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 25 vol% water, (b) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 50 vol% water and (c) H_2MoO_4 and 50 vol% water.

Figure S6. XRD pattern of the as-synthesized MoS_2 hollow nanospheres by sulfidation of the MoG intermediates formed at 25 vol% water content.

Figure S7. (a) N₂ adsorption/desorption isotherms and (b) the pore-size distribution curve of the MoS₂ HNS.

Figure S8. TEM images of the products formed by reacting the MoG solid spheres with thiourea at 200 °C for (a) 1 h, (b) 1.5 h, (c) 2 h and (d) 12 h.

Figure S9. XRD pattern of the MoS₂ hollow nanospheres after annealing at 700 °C in Ar/H₂ for 2 h.

Figure S10. CV plots of the MoS₂ electrodes in the voltage range of 0-3.0 V at a scan rate of 0.2 mV s⁻¹.