In situ formation of carbon encapsulated nanosheet-assembled MoSe₂ hollow nanospheres with boosting lithium storage

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Abstract

Carbon encapsulated nanosheet-assembled MoSe₂ hollow nanospheres were in situ fabricated via a facile hydrothermal treatment and subsequent annealing treatment. When evaluated as anode material for lithium-ion batteries, the MoSe₂/C hybrid hollow spheres manifest prodigious cycling stability (a high reversible capacity of 795 mAh g⁻¹ after 250 cycles at 0.2 A g⁻¹ and 744 mAh g⁻¹ after 300 cycles at 1 A g⁻¹) and compelling rate capability (370 mAh g⁻¹ even at a high current density of 10 A g⁻¹) compared to the bare MoSe₂ hollow nanospheres. The impressive lithium storage properties of the as-prepared MoSe₂/C nanocomposites can be attributed to the introduction of glucose- derived conductive carbon and the design of hollow structure, which facilitates fast electron and ion transfer, relieves the stress caused by volume variation upon cycling and improves the electric conductivity. Such remarkable electrochemical performances together with universal approach endow this material with potential application for next generation lithium-ion batteries.

Key words: MoSe₂, nanocomposites, hollow spheres, anode, lithium-ion batteries

Introduction

Nowadays, with the fast development of multiple portable electronics and smart grids, exploiting advanced electrode materials for rechargeable lithium-ion batteries (LIBs) has become the booming tidal current on account of their high energy density

and environmental benignity.[1-6] The commercially used anode material, graphite, is confined to a relatively low specific capacity (372 mAh g^{-1}) and a poor rate capability, accordingly failing to satisfy the ever-increasing demands of green applications, such as electric vehicles (EVs) and hybrid electric vehicles (HEVs).[7, 8] Therefore, scrupulous design and fabrication of high-performance anode materials are exceedingly desirable and imperative.

Recently, two- dimensional layered transition metal dichalcogenides (TMDs) have been hailed as potential anode candidates due to their unique sandwiched structure and distinguished physical and chemical properties.[9-12] MoSe_2 , as a member of TMD family, has a layered Se-Mo-Se structure bound by strong covalent bonds, where the stacked atom layers bound through weak van der Waals interactions.[13, 14] Such layered structure is demonstrated beneficial for the insertion/extraction of Li ions once used in LIBs. Moreover, the high theoretical specific capacity (422 mAh g^{-1}) and the large interlayer spacing (0.65 nm) compared with graphite make MoSe_2 advantageous in the copious applications, particularly in LIBs.[15-18]

Albeit promising and intriguing for lithium storage, the electrochemical performances of MoSe_2 is suppressed by its severe mechanical stress, intrinsic pulverization and low electronic conductivity, which induces quick capacity deterioration, poor cycling stability and limited rate capability. To ameliorate these deficiencies, tremendous efforts have been devoted to improve the lithium-storage properties of MoSe_2 anodes. Alternatively, integrating MoSe_2 with carbonaceous material, like grapheme, carbon cloth and carbon nanotubes and so on, has been proposed as an effective strategy, which is generally anticipated to serve as buffer layer as well as elevate the electronic conductivity of anode materials.[19-21] For example, MoSe_2 nanosheets grown on carbon cloth prepared by Zhang and co-workers show superior electrochemical performance with a capacity of 452.6 mAh g^{-1} after 100 cycles at 0.2 A g^{-1} . [22] Numerous attempts have been implemented to realize the facile integration with conductive carbon. Nevertheless, the in-situ encapsulation of carbon for MoSe_2 has rarely been reported. Besides, the construction of hierarchical hollow structures can availably increase the electrolyte/electrode

contact area and cushion the volume variations.[23, 24] For instance, Yang et al synthesized porous carbon spheres decorated with MoSe₂ nanosheets as anodes, exhibiting enhanced electrochemical performance.[25]

Herein, with meticulous and rational manufacture, hollow spheres nanocomposites of MoSe₂/C were prepared by introducing a conductive carbon via a simple hydrothermal process employing SiO₂ nanospheres as templates. Glucose not only serves as carbon source, but also restricts the stacking of MoSe₂ nanosheets, thus leading to the ultrathin shells and few-layered nanosheets. When used in LIBs, the MoSe₂/C hybrid hollow spheres manifest prodigious cycling stability and compelling rate capability even at a current density as high as 10 A g⁻¹. It can be concluded that the high rate behavior, long cycle life and excellent capacity retention of as-prepared material are definitely related to the fascinating architecture, *i. e.* the design of hollow spheres, the participation of carbon.

Experimental section

Synthesis

Hollow spheres nanocomposites of MoSe₂/C were synthesized by employing SiO₂ nanospheres as templates and glucose as the carbon source. Firstly, SiO₂ spheres were produced by the well-known Stöber method.[26] Then, MoSe₂/C nanosheets could be assembled onto the SiO₂ nanospheres according to the following process. Typically, 1 mmol Se powder was dissolved into 10 mL N₂H₄·H₂O solution under constant stirring to obtain a red-brown solution. Simultaneously, 100 mg as-prepared SiO₂, 200 mg glucose and a stoichiometric of (NH₄)₆Mo₇O₂₄ was dispersed in 30 mL deionized water and stirred for 1 h. Then, the hydrazine hydrate-Se solution was added to the above mixture slowly and transferred into a Teflon-lined autoclave, then heated in an oven at 200 °C for 10 h. After cooling to room temperature naturally, the black precipitates were collected by vacuum filtration before annealed in a conventional tube furnace at 600 °C for 2 h under highly-pure Ar flow. The silica cores were then removed by immersed in 2 M NaOH at 80 °C for 6 h. For comparison purposes, the bare MoSe₂ hollow spheres were prepared adopting a similar process without the addition of glucose.

Characterization

The x-ray diffraction (XRD) patterns were obtained on the X-ray diffraction instrument (D/Max 2550, Rigaku Corporation, Cu-K α radiation $\lambda=0.15406$ nm). Morphology and structure analyses were conducted by a field emission scanning electron microscope (FESEM, Nova Nano SEM 230 FEI) and a field emission transmission electron microscope (FTEM, JEM-2100F, JEOL). X-ray photoelectron spectroscopy (XPS) was acquired on a Thermo ESCALAB 250G XPS spectrometer. Thermogravimetric analysis (TGA) was conducted with a TGA instrument (SDT Q600) in air heating to 600 °C at rate of 10 °C min⁻¹.

Electrochemical measurements

The electrochemical properties of as-synthesized samples were tested in CR2016 coin cells assembled in an argon-filled glove box. Lithium metal was served as the reference electrodes and a Celgard 2500 microporous polypropylene was used as the separator. The electrolyte was 1 M LiPF₆ in a mixture of EC/DMC/DEC (1: 1: 1 in volumn). For preparing the working electrode, a slurry, composed of active materials, carbon black and carboxyl methyl cellulose (CMC) (8:1:1 in mass) dispersed in a mixture of distilled water/alcohol, was pasted onto a copper foil, followed by drying in vacuum oven at 70 °C overnight. Then, it was punched into round pieces with a diameter of 12 mm. The discharge-charge cycling characteristics were conducted using a battery tester (LAND CT2001A) at different current rate with the potential ranging of 0.01 to 3 V. Cyclic voltammetry (CV) was performed using an electrochemical workstation (PARSTAT 4000, A metek) at a scanning rate of 0.2 mV s⁻¹ from 0.01 to 3 V. Electrochemical impedance spectrometry (EIS) was measured on a PARSTAT 4000 potentiostat with a 5 mV AC amplitude over the frequency range of 100 kHz to 0.1 Hz.

Results and discussion

The phase composition and crystalline structure of the bare MoSe₂ and MoSe₂/C hollow nanospheres were detected by XRD. As delineated in **Figure 1**, all the diffraction peaks of these two samples can be indexed to the 2H-MoSe₂ phase (JCPDS 29-0914). Compared to the bare MoSe₂, the (002) peak of MoSe₂/C hollow

spheres located at $2\theta = 13.7^\circ$ became weaker, which demonstrates the presence of graphene-like MoSe₂ layers in the nanocomposites. This interesting phenomenon could be ascribed to the fact that the introduction of carbon formed by the carbonization of glucose decrease the stacking of the MoSe₂ layers, which will tremendously elevate the diffusion efficiency of Li⁺ because of the shorted diffusion length .[27, 28]

The MoSe₂/C hollow spheres were synthesized by a facial hydrothermal-calcination-etching route, as illustrated in **Figure S1**. SiO₂ nanospheres with uniform diameter of ~300 are obtained and chosen as the templates. The morphology of SiO₂ and SiO₂@MoSe₂/C are presented in **Figure S2**. The intact and monodispersed spheres are apparent. **Figure 2a** shows a scanning electron microscope (SEM) image of as-prepared MoSe₂/C hybrid hollow spheres, illustrating well-defined and uniform spheres with a diameter of 300~400 nm as well as the hollow structure inferred from some broken ones. Transmission electron microscopy (TEM) image, as depicted in **Figure 2b**, demonstrates that the spherical morphology is well inherited after etching, which is well unanimous with SEM images. A high-resolution TEM (HRTEM) analyses are fulfilled, seeing **Figure 2c** and **Figure 2d**. It can be distinctly observed that each intertwined MoSe₂ nanosheet is comprised of 2~5 layers and the interlayer spacing is measured to be 0.67 nm, which is larger than the d-spacing of (002) planes of hexagonal phase MoSe₂ thus anticipated to accommodate more Li⁺. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping images in **Figure 3** testify a homogenous distribution of Mo, Se and C almost overlaps each other. For comparison, **Figure 4a** and **Figure 4b** presents the SEM images and TEM images of the bare MoSe₂, which is similar with the MoSe₂/C nanocomposites but more little particle aggregation. The HRTEM image (**Figure 4c**) displays the view of the stacking structure of the bare MoSe₂ with an interplanar distance of ~0.65 nm.

Thermogravimetric analysis (TGA) was employed under air atmosphere to examine the loading of MoSe₂ in MoSe₂/C hybrid hollow spheres, as shown in **Figure 5**. The weight increase around 300-400°C appeared in two samples is derived from the formation of SeO₂. For pure MoSe₂, the weight loss of 41.71 % at approximately

450 °C can be attributed to the oxidation of MoSe₂ into MoO₃. While in the case of MoSe₂/C hybrid hollow spheres, a larger weight loss of 45.73 % is relevant to the oxidation reaction of MoSe₂ combined with carbon. Therefore, the MoSe₂ ratio in composite is calculated to be about 93.10 %. Such high content of active materials in nanocomposites is significant for actual application in LIBs.

To investigate the surface element composition and the valence states of the as-prepared MoSe₂/C hybrid hollow spheres, X-ray photoelectron spectroscopy (XPS) was carried out (**Figure 6**). The XPS survey spectrum is shown in **Figure 6a**, clearly indicating the presence of Mo, Se and C these three elements.[17] The C 1s spectrum in **Figure 6b** could be deconvoluted into five peaks, the carbon in C=C at 284.5 eV, the carbon in C-C at 285.2 eV, the carbon in C-O at 286.21 eV, the carbon in C=O at 287.1 eV and the carbon in O-C=O at 288.5 eV.[29, 30] The high resolution Mo 3d in **Figure 6c** displays two peaks centered at 228.94 eV and 232 eV, which can be ascribed to the Mo 3d_{5/2} and the Mo 3d_{3/2}. [16, 31] In **Figure 6d**, the binding energy of Se 3d_{5/2} at 54.4 eV and 3d_{3/2} at 55.3 eV confirms the existence of the Se II state. [16]

Lithium storage properties of MoSe₂/C hybrid hollow spheres and bare MoSe₂ hollow spheres probed by cyclic voltammetry (CV) and galvanostatic tests are described in **Figure 7** and **Figure S3**. **Figure 7a** shows the CV curves of MoSe₂/C composites for the initial four cycles. Conspicuously, a sharp peak at 0.89 V and a broaden one at 0.35 V in the first cathodic step are easy to be noticed, which can be attributed to the insertion of Li⁺ into the interlayer of MoSe₂ forming Li_xMoSe₂ and the conversion reaction of Li_xMoSe₂ into Mo and Li₂Se accompanied by the formation of solid electrolyte interface (SEI) film.[32] The overall reaction during this process is based on the equation: MoSe₂ + 4Li⁺ + 4e⁻ → Mo + 2Li₂Se. In the first anodic step, two peaks located at about 1.68 V and 2.2 V are related to the partial oxidation of Mo to MoSe₂ and the oxidation of Li₂Se to Se, respectively. Therefore, the electrode consists of Mo and Se rather than the initial MoSe₂ in the subsequent cycles.[19, 20, 33, 34] From the second cathodic step onwards, the peaks shifted to 1.82 V and 1.21 V, 0.37 V, corresponding to the conversion of Se to Li₂Se and the association of Li with Mo.[35-37] The CV curves keep consistent in terms of the

shape and the peaks from the first cycle onward, manifesting a prominent stability and reversibility of MoSe₂/C electrode material. For bare MoSe₂ electrode in **Figure S3a**, it shows no great difference but smaller integrated area of CV curves, indicating a higher specific capacity for MoSe₂/C hybrid hollow spheres.

The discharge-charge voltage profiles of MoSe₂/C electrode at current densities of 0.2, 0.5, 1, 2, 5, 10 A g⁻¹ are shown in **Figure 7b**. An exceptionally high discharge capacity of 789 mAh g⁻¹ at 0.2 A g⁻¹ are released by MoSe₂/C nanocomposites with a coulombic efficiency of 77.4 %. In addition, the material delivers still relatively high capacities of 516, 460, 426, 395, 370 mAh g⁻¹ at high densities of 0.5, 1, 2, 5, 10 A g⁻¹, respectively, together with coulombic efficiency of nearly 100 %. The considerable high specific capacity of 370 mAh g⁻¹ at 10 A g⁻¹ is very impressive. Besides, it is noteworthy that two potential plateau around 0.9 V and 0.4 V in the first discharge curve can be viewed followed by a higher discharge plateau at about 2.2 V after subsequent discharge cycles, which is in accordance with the CV curves. By contrast, the bare MoSe₂ electrode only possesses a discharge capacity of 403 mAh g⁻¹ with coulombic efficiency of 68.7 % at 0.2 A g⁻¹ and a low high-rate capacity of 194 mAh g⁻¹ at 10 A g⁻¹, which is far less than the that of MoSe₂/C composites.

The rate capabilities of MoSe₂/C hybrid hollow spheres and bare MoSe₂ are evaluated at various current densities of 0.2, 0.5, 1, 2, 5, 10 A g⁻¹ (**Figure 7c**). Comparatively, with the increase of current density, the MoSe₂/C hybrid hollow spheres exhibits a higher specific discharge capacity and a more obvious high-rate performance than the bare MoSe₂. Notably, MoSe₂/C hybrid hollow spheres gained a capacity as high as 370 mAh g⁻¹, greater than the bare MoSe₂ (194 mAh g⁻¹). Remarkably, when the current density returned to 0.2 A g⁻¹, the capacity of MoSe₂/C composites is retained and even increased without decay, which is common in TMDs.[31, 38, 39] More impressively, a high capacity of 795 mAh g⁻¹ is achieved and remains stable after 250 cycles at 0.2 A g⁻¹. While a severe degeneration of capacity after long-term cycle appeared in the case of bare MoSe₂. The results corroborate that the introduction of C can effectively buffer volume variation and improve the capacity and cycling stability.

Except the outstanding rate capability, the MoSe₂/C hybrid hollow spheres also exhibit brilliant cycling behavior (**Figure 7d**). In the case of MoSe₂/C composites, the first discharge specific capacity of 723 mAh g⁻¹ with a coulombic efficiency of 74.8 % is acquired. Then it undergoes an increasing trend followed by a tiny decline and ultimately tends to be steady. For MoSe₂ electrode, a sharp fall of capacity emerges after 140 cycles in spite of the early rise. The calculation of the specific capacity for MoSe₂/C nanocomposites was based on the total mass of composite material. Obviously, the value is much higher than the theoretical specific capacity of MoSe₂ (422 mAh g⁻¹), which confirms that MoSe₂ in composite has been sufficiently activated and utilized on account of the vast contact area between the electrode and electrolyte, the quick charge transfer and the promoted structure stability. The observed excess over the theoretical capacity of MoSe₂ could be derived from the additional lithium storage sites, as reported previously.[40, 41]

In order to gain further insight into the cause of better electrochemical performance for MoSe₂/C hybrid hollow spheres, electrochemical impedance spectra (EIS) after 50 cycles were carried out. **Figure 8** displays the Nyquist plots of MoSe₂/C nanocomposite and bare MoSe₂ after 50 cycles and after 100 cycles. Clearly, both plots are composed of a semicircle in the medium-high frequency region and a sloping line in the low frequency region, corresponding to a charge transfer process and a Warburg diffusion process. Apparently, the MoSe₂/C nanocomposites obtain a smaller diameter of semicircle than that of bare MoSe₂, demonstrating a vastly decreased charge-transfer resistance. Furthermore, only a slight increase was found in semicircle diameters for the MoSe₂/C electrode after 50 cycles and after 100 cycles. It can be concluded that the introduction of amorphous carbon effectively improve the electric conductivity.

It is noteworthy that the as-prepared MoSe₂/C hybrid hollow spheres present much better electrochemical properties than those of previously reported MoSe₂-based anode materials, as displayed in Table S1. The enticing performance of MoSe₂/C hybrid hollow spheres can be interpreted as the following reasons: (1) The large interface contact between MoSe₂ nanosheets and carbon facilitate the high-efficiency

diffusion of electrons and Li^+ . (2) Enlarged interlayer distance of 0.67 allows for more Li^+ and lowers the activation energy for intercalation. (3) Hollow structure relieves the stress caused by volume variation in constant discharge/charge process. (4) The carbon in composite acts as conductive matrix to elevate the electric conductivity and maintains the structural integrity (Figure S4 (a) and (b)). Motivated by the above consideration, MoSe_2/C hybrid hollow spheres can be deemed to be promising anode material for LIBs.

Conclusions

In summary, MoSe_2/C hybrid hollow spheres were in situ fabricated with meticulous and rational manufacture. The as-prepared hybrid material presents a well-defined and intact hollow spherical morphology, which provides effective protection against the structure collapse. The MoSe_2/C hybrid hollow spheres electrode manifests distinguished cycling stability and rate capability. It can be accounted as the synergistic effect between conductive carbon and ultrathin MoSe_2 nanosheets as well as the design of hollow structure, which exert collectively considerable influence on the prominently improved lithium storage properties. The remarkable lithium-storage performance together with the universal approach endows the MoSe_2/C composite with potential application for next generation lithium-ion batteries.

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Figure captions

Figure 1 XRD patterns of bare MoSe₂ and MoSe₂/C hybrid hollow spheres

Figure 2 (a) SEM, (b) TEM and (c, d) HRTEM images of MoSe₂/C hybrid hollow spheres

Figure 3 Elemental mapping images of MoSe₂/C hybrid hollow spheres

Figure 4 (a) SEM, (b) TEM and (c, d) HRTEM images of bare MoSe₂

Figure 5 TG curves of bare MoSe₂ and MoSe₂/C hybrid hollow spheres

Figure 6 XPS spectra of MoSe₂/C hybrid hollow spheres: (a) Survey spectrum and high resolution spectrum of (b) C 1s, (c) Mo 3d and (d) Se 3d

Figure 7 (a) CV curves and (b) discharge/charge voltage profiles of MoSe₂/C hybrid hollow spheres, (c) Rate and (d) cycling performance of bare MoSe₂ and MoSe₂/C hybrid hollow spheres

Figure 8 Nyquist plots of bare MoSe₂ and MoSe₂/C hybrid hollow spheres: (a) after 50 cycles and (b) after 100 cycles