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CONTROLLABLE SYNTHESIS AND PROPERTIES OF $MoSe_2$ NANOSTRUCTURES

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Three kinds of $MoSe_2$ nanostructures, 3D nanoflowers, hollow nanospheres and monodisperse solid nanospheres have been fabricated by a simple hydrothermal approach. The structure and morphology of these samples were characterized by X-ray powder diffraction (XRD), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). The electrochemical hydrogen storage behaviors of the as prepared $MoSe_2$ nanostructure were also investigated. It is found that the morphology plays a key role in the hydrogen storage capacity of $MoSe_2$ nanostructures. The as-derived $MoSe_2$ hollow nanospheres exhibit excellent hydrogen storage capacity (118.2 mA h g^{-1}) after 40 cycles than that of $MoSe_2$ nanoflowers (94.3 mA h g^{-1}), and monodisperse nanospheres (45.1 mA h g^{-1}). The enhanced electrochemical performance of the 3D $MoSe_2$ hollow nanospheres could be attributed to their hollow spherical structure, and their unique layered structure.

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Keywords: Electrochemical; $MoSe_2$; Hollow nanospheres; Hydrogen storage; Layered structure

1. Introduction

Recently, hollow nano spherical inorganic functional materials are one of the most charming materials structural forms [1-2], and they have potential applications in catalysis [3-4], nanoreactors [5], lithium-ion batteries anodes [5-6],drug-delivery carriers [7], supercapacitors and photovoltaics [8],water treatment [9], photothermal therapy [10], gas sensing [11] and so on. To date, diverse approaches such as template method [11-12], electrospinning method [3,13], hydrothermal or solvothermal method [14-15], gas/liquid interfacial microwave-assisted process [16] and the layer-by-layer assembly mechanism [17] have been employed to synthesize hollow nanospheres with controllable structure and composition. Among these, hydrothermal or solvothermal is most popular, which can be easily control the phase and morphology of the resultant products through adjusting the synthesis conditions such as composition of the solution, pH, temperature, duration, etc.

Molybdenum selenide ($MoSe_2$) is a typical layered transition metal chalcogenides, which has been of particular interest to researchers due to its application in photoluminescence devices [18-19], lubricants [20], solar cells [21-22], field-effect transistors [23-24], etc. Because of the above advantages, various procedures including mechanical exfoliation [18, 23] thermal decomposition approach [25] solid-state reactions [26] liquid exfoliation [27], and solution process [28] have been adopted to synthesize $MoSe_2$ nanomaterials. However, $MoSe_2$ hollow nanospheres have rarely been reported, therefore, it is still a great challenge to develop a facile and effective process to fabricate $MoSe_2$ hollow nanospheres. In addition, it was found that transition metal chalcogenides has an excellent electrochemical property [29-32]. However, to the best of our knowledge, limited work has been carried out on the electrochemical hydrogen storage properties of $MoSe_2$.

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Herein, we successfully fabricated $MoSe_2$ nanoflowers, hollow nanospheres and solid nanosphere by utilizing a facile hydrothermal method. This synthetic approach is simple, effective, low cost and environmentally friendly. The electrochemical hydrogen storage ability with different morphologies was measured. The $MoSe_2$ hollow nanospheres presented higher electrochemical hydrogen storage ability than those of $MoSe_2$ nanoflowers and solid nanosphere.

2. Experimental

Synthesis of $MoSe_2$ nanostructures

All chemical reagents (analytical purity) were purchased from Sinopharm (Shanghai) Chemical Reagent Co., Ltd. and used directly without further purication. The experiment was designed by three different preparation nanostructures of $MoSe_2$ as the following; Sample 1 (nanoflowers): 0.483 g $Na_2MoO_4 \cdot 2H_2O$, 0.316 g Se powder and 10 mL hydrazine hydrate($N_2H_4 \cdot H_2O$), Sample 2 (hollow nanospheres): 0.507 g $(NH_4)_2MoO_4 \cdot 2H_2O$, 0.316 g Se powder and 10 mL hydrazine hydrate($N_2H_4 \cdot H_2O$) , Sample 3 (solid nanospheres): 0.507 g $(NH_4)_2MoO_4 \cdot 2H_2O$ and 0.79g $Na_2SeO_3 \cdot 5H_2O$. In the typical procedure, 0.483 g $Na_2MoO_4 \cdot 2H_2O$, 0.316 g Se powder were dissolved in mixture of 10 mL hydrazine hydrate($N_2H_4 \cdot H_2O$) and 60 mL distilled water under magnetic stirring and stirred into a red solution, and then the pH value was adjusted to about 12 with the addition of NaOH solution. After violent stirring, the resulted solution was transferred into a 100 mL Teflon-lined stainless autoclave and sealed tightly, which was held in an oven at 200 ^oC for 48 h. Subsequently, the autoclave was taken out and cooled down to room temperature naturally. The resulting black precipitates were collected and washed with ethanol and distilled water for several times. Finally, it was dried in vacuum at 70 ^oC for 12 h, and black $MoSe_2$ was obtained. The product was directly characterized without further processing by various analytic techniques.

Characterization

The X-ray diffraction (XRD) patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu Ka radiation (λ=0.1546 nm). The 2θ range used in the measurement was from 10 to 80^O with a velocity of 5^O min^{-1}, data analysis with Jade software. The composition was characterised by energy-dispersive spectroscopy (EDS).The morphologies and structures of the samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2100) equipped with LaB_6 cathode using an accelerating voltage of 200 kV. The samples for the EDS studies were prepared by placing the $MoSe_2$ powders on to a copper disk with conducting resin followed by metal spraying. The samples for the TEM studies were prepared by dispersing the powders in ethanol through ultra-sonication and drop casting the dispersion onto a carbon coated copper grid.

Electrochemical measurements

The electrochemical hydrogen storages were performed using three electrode cell in 6 M KOH under normal atmosphere following the reported method.[33-34]. The $MoSe_2$ powders with different morphologies were used as the working electrode, $Ni(OH)_2$/ NiOOH as the counter electrode, and Hg/HgO as a reference electrode. The working electrode was fabricated by directly pressing the as synthesized samples into a sheet of nickel foam under 20 MPa pressure. All electrochemical hydrogen storage experiments carried out on a Land battery system (CT2001A) with charged for 4 h at a current density of 50 mA g^{-1}.

3. Results and Discussion

Structure and morphology characterization of $MoSe_2$

The crystallographic structure and phase purity of the three $MoSe_2$ products obtained at 200 ^oC were determined by XRD and EDS. As shown in Fig. 1a, all the diffraction peaks can be assigned to those of the hexagonal ($P6_3/mmc$ space group) $MoSe_2$ phase, with lattice constants

a=3.288Å, c=12.930Å, which are in good agreement with the reported values (JCPDS card no.87-2419), and no other noticeable peaks from impurities can be detected, indicating that the sample was of high purity.

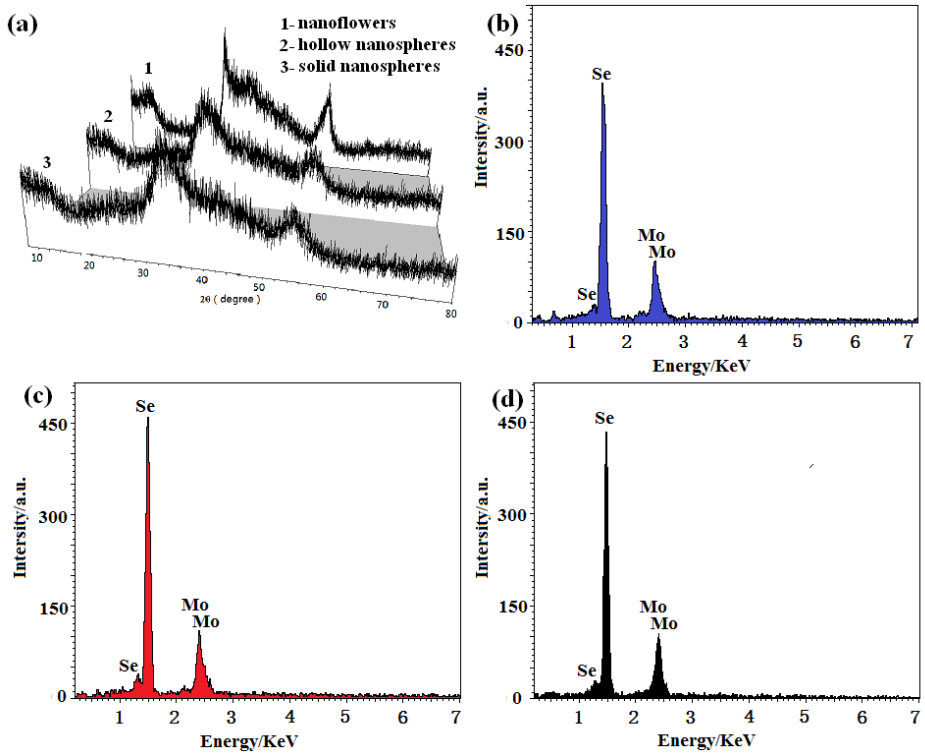

Fig. 1: (a) XRD pattern and (b-d) EDS of the prepared $MoSe_2$ nanoflowers (Sample 1), hollow nanospheres (Sample 2) and solid nanospheres (Sample 3)

Moreover, the XRD patterns reveal wide and weak diffraction peaks, which is evidence of the formation of nanoparticles. Energy-dispersive X-ray Spectrometer (EDS) results were shown in Fig. 1b-d, which reveals that the samples consist of element Mo and Se, no other element was observed.

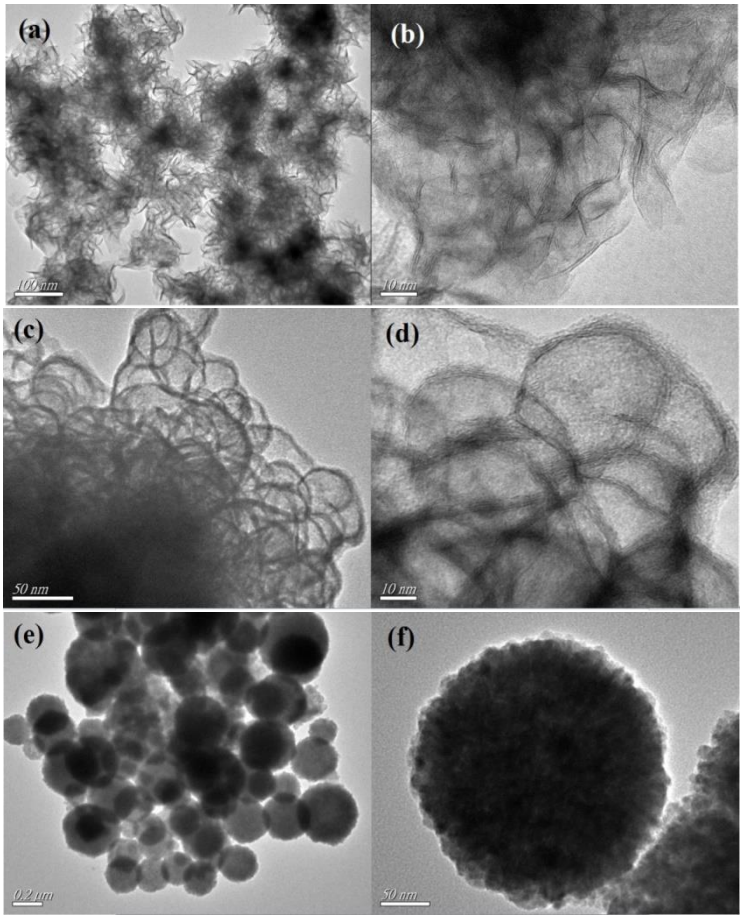

Fig. 2: TEM and HRTEM images of the prepared $MoSe_2$ (a and b) nanoflowers (Sample 1), (c and d) hollow nanospheres (Sample 2) and (e and f) solid nanospheres(Sample 3)

The size and morphologies of all $MoSe_2$ nanostructures were primarily investigated by TEM measurement. Fig. 2a shows that the $MoSe_2$ sample fabricated by the hydrothermal reaction $Na_2MoO_4 \cdot 2H_2O$ and Se powder in mixture of hydrazine hydrate and distilled water at 200 ^oC for 48 h are nanoflowers assembled of many irregular nanosheets. The high- magnification TEM image, as shown in Fig. 2b, typical layered $MoSe_2$ with a few layers (~4 layers) bond together tightly by van der Waals force to form thin sheets which then curl up to form the $MoSe_2$ nanoflowers, and further indicated that the as-prepared $MoSe_2$ nanoflowers might be built up with a sheetlike structure [20]. Fig. 2c indicates that the $MoSe_2$ sample fabricated by the reaction $(NH_4)_2MoO_4 \cdot 2H_2O$ and Se powder are composed of hollow nanospheres, and shows that the diameter of the nanospheres is about 30-50 nm and shell thickness is 3-5 nm. More details for $MoSe_2$ structure are illustrated by HRTEM images in Fig. 2d, which indicates that the hollow nanospheres consist of 3~ layers structures, the interlayer separation between the $MoSe_2$ layers is about 0.67 nm. Fig. 2e clearly shows that the $MoSe_2$ spheres obtained by the reaction $(NH_4)_2MoO_4 \cdot 2H_2O$ and $Na_2SeO_3 \cdot 5H_2O$ are in diameters of 200-400 nm. The corresponding HRTEM image in Fig.2f indicates that the obtained products are solid nanospheres, and the nanospheres were formed without any sheetlike structures

Electrochemical hydrogen storage properties of three $MoSe_2$ nanostructures

The potential applications of the $MoSe_2$ nanostructure in electrochemical hydrogen storage were examined. Fig. 8(a) presents the cycle performances of the $MoSe_2$ nanoflowers, hollow nanospheres and solid nanosphere respectively. After 40 cycles at the charge-discharge current density of 50 mA g^{-1}, the capacity of the $MoSe_2$ hollow nanospheres decreases from 193.1 mA h g^{-1} to 118.2 mA h g^{-1}, higher than that of $MoSe_2$ nanoflowers (94.3 mA h g^{-1}) and solid nanosphere

(45.1 mA h g^{-1}). It is evident that the hierarchical structure of hollow nanospheres possesses have a higher capacity and stability. However, the capacity fading is still obvious, which can be attributed to the large volume variation during charge/discharge process [33]. The large volume variation will lead to the polarization of the electrodes, resulting in the structure collapse of the sample.

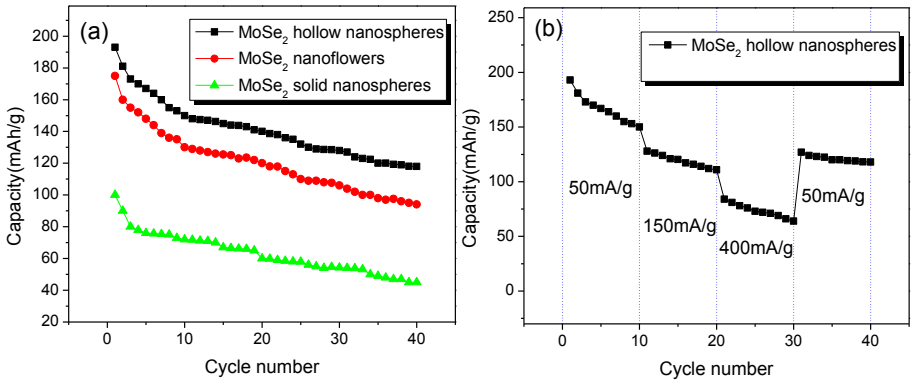

Fig. 3: (a) Cycle performances of the synthesized different $MoSe_2$ nanostructure at a constant current density of 50 mA g^{-1}, (b) cycle performance of the $MoSe_2$ hollow nanospheres at different current density.

The cycle performance of the $MoSe_2$ hollow nanospheres was also investigated at different current density, as shown in Fig. 3(b). After 10 cycles at a charge–discharge current density of 50 mA g^{-1}, the discharging capacities of the electrode still remain above 150.1 mA h g^{-1}.When the current density is increased to 150 mA g^{-1}, the discharging capacity is decreased to 110.8 mA h g^{-1} after the 10th cycle, and the current density is increased to 400 mA g^{-1}, the discharging capacity is decreased to 64 mA h g^{-1}. Due to the larger potential polarization of the electrodes, the hydrogen storage properties quickly decreased at high current density [34]. However, when the current density returns to 50 mA g^{-1}, the composite electrode can recover its original capacity, which shows the electrode has good reversibility. The excellent hydrogen storage capacities suggesting that the $MoSe_2$ hollow nanospheres could be used as a material for electrochemical hydrogen storage.

As a consequence, the excellent electrochemical performance of hierarchical structure of $MoSe_2$ hollow nanospheres with ultrathin layers might be attributed to the following reasons. Firstly, the distinct layered structure of $MoSe_2$ could provide more reaction surface area of electro-catalytic reaction and reactivity of the electrodes, which are helpful for the spread of hydrogen to increase hydrogen storage capacity of the electrode. In addition, hierarchical structure of hollow nanospheres own lots of open spaces and larger specific surface area, which can effectively buffer volume variation and store large quantity hydrogen during the charge and discharge process, so endow the electrode with cycling stability.

4. Conclusion

In summary, a simple solvothermal method has been developed to synthesize hierarchical $MoSe_2$ nanoflowers, hollow nanospheres and solid nanosphere. The electrochemical measurement shows that the $MoSe_2$ hollow nanospheres present the higher electrochemical hydrogen storage than that of nanoflowers and solid nanosphere. The excellent electrochemical performance is related with their unique hierarchical structure with ultrathin nano layers subunits and hollow interior, which implies their application in hydrogen storage, high-energy battery and catalytic fields.

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