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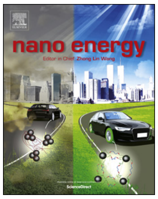

Full paper

N-doped C-encapsulated scale-like yolk-shell frame assembled by expanded planes few-layer $MoSe_2$ for enhanced performance in sodium-ion batteries

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ABSTRACT

To meet the pressing needs of fast development of energy and environmental science, sodium ion batteries (SIBs) are considered as the promising novel generation of power storage system, due to abundant reserves and low price of sodium sources. In this work, N-doped C-encapsulated scale-like yolk-shell structured $MoSe_2$-C materials assembled by expanded (002) planes few-layer $MoSe_2$ nanosheets are successfully synthesized by a facile general strategy. The few-layer crystal fringes are no more than 4 layers. Notably, the interlayer spacing of (002) planes is expanded to 1.15 nm, which is larger than its intrinsic value of pristine $MoSe_2$ (0.64 nm). Particularly, the few-layer nanosheets with expanded (002) planes are spaced-restricted growing in the inner wall and the surface of hollow carbon frame and form scale-like yolk-shell hybrid $MoSe_2$-C structure. When evaluated as anode for SIBs, the $MoSe_2$-C materials show ultra-long cycling life, maintaining 378 $mA\,h\,g^{-1}$ over 1000 cycles at 3 $A\,g^{-1}$. It also exhibits outstanding rate capability and the Coulombic efficiencies for all the rate performance reaching more than 98.3% except the first one. The expanded (002) planes, 2D fewer-layer nanosheets and unique N-doped C-encapsulated scale-like yolk-shell frame are responsible for the enhanced electrochemical performance.

1. Introduction

Sodium-ion batteries have attracted great attention recently as the attractive alternative to Li-ion batteries due to abundant reserves and low price of sodium sources [1–3]. However, the large radius of Na ions (1.02 Å) compared with that of Li ions (0.76 Å) leads to many impacts. For example, graphite and silicon are electrochemical inactive for Na-ion batteries [4–6]. Meanwhile the anode materials for the SIBs still face severe challenges, such as low conductivity, large volume expansions, foot-dragging reaction dynamics, unsatisfied cycling time and inferior capacity and difficulty in seeking proper host materials for Na-ion storage [7–9]. Up to now, designing novel anodes with enhanced electrochemical performance including high reversible capacity, good rate capability, stable and long cycling life remains a major challenge unresolved, even though reports on cathodes of Na-ion battery have shown capability comparable to their Li-ion battery counterparts recently.

Two-dimension layered transition metal dichalcogenides (TMDs) have received considerable attention in the energy and environmental application field [10–13]. Particularly, MoS_2 has been extensively investigated as promising materials for LIBs and SIBs [9,14–17]. Chen et al fabricated hybrid MoS_2@C nanosheets, showing enhanced reversible capacity about 993 $mA\,h\,g^{-1}$ at 1 $A\,g^{-1}$ [18]. Nonetheless, it exhibits inferior cycling stability and low reversible capacities for SIBs. The short distance between neighboring layers of MoS_2 materials should be responsible for their poor electrochemical performance in SIBs. Furthermore, the MoS_2 nanosheets are easily to agglomerate together because of their high surface energy. Therefore, their practical application in SIBs is severely limited. It is noticed that $MoSe_2$ exhibits improved electrochemical performance for SIBs compared with MoS_2 due to its large pristine interlayer spacing (0.64 nm) and higher electrical conductivity due to little band gap, which is benefit to fast charge transfer and electrochemical cycling process [19–22].

To further increase the achieving performance $MoSe_2$ anodes, allowing the electrochemical reaction to proceed in a hybrid matrix of distinct material systems, such as coupling with electrically conductive carbon is a popular technology. Kang and coworkers prepared $MoSe_2$-rGO-CNT microsphere by a spray pyrolysis process, which exhibit final discharge capacities of 411 $mA\,h\,g^{-1}$ at 0.2 $A\,g^{-1}$ [23]. Unfortunately, the simple composite application of $MoSe_2$-C only improves their electrical conductivity, whereas the large volume change (ca. 300%) during charge/discharge process is difficult to buffer. Therefore, they

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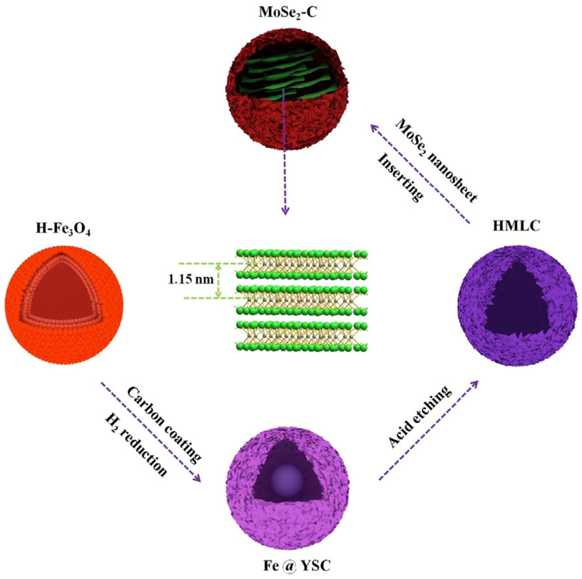
normally deliver low rate capability.

The development of accurate designing molecular architecture of TMDs with functional nanostructures is another effective way to improve their electrochemical properties. Particularly, assembling 3D spatial structures with few layers 2D nanosheets has several advantages to overcome the shortcomings of bulk materials, because the single 2D nanosheets are easy to aggregate into large blocks during synthesis and electrochemical cycling process. Among them, yolk-shell structures attract great interest due to their unique structural features, fascinating physicochemical properties and widespread applications [24–28]. The core in the yolk-shell structures increase the energy density of SIBs through enhancing the weight ratio of the active contents. Meanwhile, the void part between the core and shell can effectively accommodate the severe volume variation of electrode materials upon cycling and prevent self-aggregation of the nanoscale subunits, which could alleviate the pulverization of active materials and significantly improve the cycling performance. The void structures can also facilitate electrolyte penetration and provide large contact area between the electrode and the electrolyte. Furthermore, it can short transport length for sodium ions and electrons, and thus improve the rate capability. Yu and coworkers prepared yolk-shell MoS_2 nanospheres used as anodes materials for lithium-ion battery, exhibiting long cycle life (94% of capacity retained after 200 cycles) and high rate behaviour ($830\,mA\,h\,g^{-1}$ at $5\,A\,g^{-1}$) [29]. Whereas, the synthesis of yolk-shell structure is typically related to the template fabrication and multistep/high-cost procedures, which is easily to result the collapse of hollow structures. Thus, a novel controllable synthesis design for yolk-shell TMDs with high reversible capacity and long cycling life for SIBs is highly expected.

In most recently, it is interesting to notice that expanding the (002) planes of $MoSe_2$ can significantly improve the dynamics for sodium ion intercalating and deintercalating, and thus enhance sodium storage performance. Xu and coworkers prepared interlayer-expanded $MoSe_2$ nanosheets used as a highly durable electrode for sodium storage, exhibiting a reversible discharge capacity of $228\,mA\,h\,g^{-1}$ after 1500 cycles at a high current density of $1000\,mA\,g^{-1}$ [30]. However, most reports show unsatisfied capacities, particularly when the current density is higher than $2\,A\,g^{-1}$. Additionally, the nitrogen introducing defects within the carbon material can increase the electronic conductivity and create abundant active sites [31]. As compared to pure carbon, it is well documented that N-doping not only can tailor electronic structure and increase the chemical activity, but also benefit the contact between carbon and active materials [32].

Though these procedures are effective, each design strategy alone always leads to limited improvement on the electrochemical properties of TMDs for SIBs. Therefore, the development of a facile, scalable and controllable fabrication of durable hybrid yolk-shell structured TMDs materials with satisfactory cycling ability and high capacity is still highly desirable for SIBs. Herein, we design N-doped C-encapsulated scale-like yolk-shell frame $MoSe_2$-C assembled by few-layer $MoSe_2$ with expanded (002) planes to demonstrate our concept and propose a facile general strategy as illustrated in Scheme 1. The unique N-doped scale-like yolk-shell structures are benefit to the enhanced rate capability and long cycling life, The hollow multi-layer mesporous carbon sphere (HMLC) with ultrathin thickness acts as nanoreactors and can prohibit the restacking of $MoSe_2$, which is good to control the confined formation of few-layer $MoSe_2$ nanosheets with expanded interlayer spacing structure. Meanwhile the $MoSe_2$ nanosheets with expanded (002) planes are inclined to insert in HMLC matrix uniformly. As a result, the N-doped $MoSe_2$-C anode is rendered a higher reversible capacity, and the kinetics for sodium ion intercalating and deintercalating during electrochemical cycling are also improved as well.



Scheme 1. Representative illustration of the assembly process of N-doped C-encapsulated scale-like yolk-shell structured $MoSe_2$-C.

2. Experimental section

2.1. Materials

$FeCl_3{\cdot}6H_2O$, sodium citrate, urea, polyacrylamide, tris, dopamine (PDA), hydrochloric acid solution (36–38%), Na_2MoO_4, ethylenediamine, selenium and hydrazine hydrate ($N_2H_4H_2O$, 80%) solution were all analytical grade and were used without further purification. Water used was purified using an Ulu-pure system (Shanghai China).

2.2. Synthesis of hollow Fe_3O_4 (H-Fe_3O_4) precursor

Typically, $FeCl_3{\cdot}6H_2O$ (1.08 g), sodium citrate (2.35 g), urea (0.72 g) were dissolved in 80 ml deionized water and stirred for 30 min to form a homogeneous solution. Then 0.8 g PAM (polyacrylamide) was added to the above solution with a continual stirring for 1.5 h. Subsequently, the above solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and held at 200 °C for 12 h. Finally, the products were harvested through several rinse-centrifugation cycles with deionized water and absolute ethanol, then dried at 70 °C under vacuum condition overnight.

2.3. Synthesis of yolk-shell Fe@carbon (Fe@YSC)

The as-prepared H-Fe_3O_4 80 mg was dissolved in 100 ml 10 mM tris solution. Subsequently, 40 mg dopamine was added with magnetic stirring for 5 h to form the Fe_3O_4@PDA. Then, the Fe_3O_4@PDA was washed with ethanol and distilled water three times, and dried under vacuum at 60 °C overnight. Finally, the above product was sintered and reduced at 600 °C for 2 h under 20% H_2, 80% Ar atmosphere to turn into york-shell Fe@carbon (Fe@YSC).

2.4. Synthesis of hollow multi-layer mesporous carbon sphere (HMLC)

The Fe cores of Fe@YSC were removed by 4 M hydrochloric acid solution after 3 h of etching to prepare hollow multi-layer mesporous carbon sphere (HMLC).

2.5. Synthesis of $MoSe_2$-C

15.79 mg selenium was dissolved in 10 ml hydrazine hydrate