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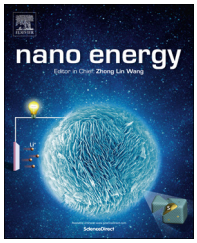


FULL PAPER

# Hierarchical nanotubes assembled from $MoS_2$-carbon monolayer sandwiched superstructure nanosheets for high-performance sodium ion batteries

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**Abstract**

Interface engineering on 2D layered nanomaterials plays pivotal roles in achieving novel properties and superior device performance. In this work, hierarchical nanotubes consisting of 2D monolayer $MoS_2$ and carbon ($MoS_2$:C) interoverlapped superstructure nanosheets have been synthesized, in which the $MoS_2$ and carbon layers are alternately sandwiched. The hierarchical architectures assembled from the $MoS_2$:C superstructures are beneficial for: (i) providing substantially expanded (002) interlayer spacing (0.98 nm) of 2H-$MoS_2$ which facilitates fast $Na^+$ insertion/extraction reaction kinetics, (ii) improving electrical conductivity of $MoS_2$ by carbon monolayer insertion with ideal heterointerface contact, (iii) preventing aggregation of $MoS_2$ nanosheets, and (iv) accommodating volume change upon sodiation/desodiation. The superstructure nanotubes are demonstrated as a robust anode material for sodium storage with

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superior electrochemical performance. They deliver a high rate-capability and maintain discharge capacities of 295 and 187 mAh $g^{-1}$ at high current densities of 10.0 and 20.0 A $g^{-1}$, respectively. Furthermore, they show durable cycling life (capacity retention of 101.3%, 108.2% and 107.8% after 200 cycles at current densities of 0.2, 0.5 and 1.0 A $g^{-1}$, respectively, in comparison to those of the 2nd cycles), and an initial Coulombic efficiency as high as 84%. The $MoS_2$:C superstructure nanotubes perform among the best of current $MoS_2$-based electrode materials.


## Introduction

Sodium-ion batteries (SIBs) is attracting increasing attention as a promising alternative to the widely used lithium-ion batteries (LIBs) owning to the earth-abundant and cheap sodium resource [1-5]. However, as $Na^+$ has larger ionic radius (ca. 1.02 Å) than $Li^+$ (ca. 0.76 Å), SIBs are typically encountering slower reaction kinetics, poor cycling stability and low rate capability [1-5]. Therefore, it is necessary to explore suitable host materials to satisfy fast sodiation/desodiation kinetics and high charge/discharge capacities. $MoS_2$ with a 2D layered structure and a high theoretic capacity of 670 mAh $g^{-1}$ is of particular interest as a promising sodium storage material [6-10]. $MoS_2$ is covalently bonded (S-Mo-S) to form 2D monolayers, which are stacked together through weak Van der Waals interactions. Owing to the anisotropic structure, the 2D layered structures can offer large surface area and 2D permeable channels to facilitate $Na^+$ insertion/extraction and promote fast electron transport within individual monolayer [11-13]. Nevertheless, bare $MoS_2$ nanosheets usually show unsatisfactory electrochemical performance for SIBs due to poor conductivity, limited interlayer distance between adjacent $MoS_2$ monolayers, and serious aggregation during charge/discharge cycles [8,9,14,15]. Therefore, atomic interface engineering of layered $MoS_2$ nanosheets to improve the intrinsic conductivity and expand adjacent layers is a promising approach to improve sodium storage application. Recent advances are mainly focusing on decorating $MoS_2$ nanosheets with low-cost conductive carbon materials (carbon fibers, graphene, carbon nanotubes) [7,10,16-21], which can facilitate fast electron/ion transport and improve electrochemical performance of SIBs. However, these composites usually have very limited interface contact between $MoS_2$ and carbon. Therefore, maximizing the hetero-interface between $MoS_2$ and carbon by rationally constructing $MoS_2$-carbon hybrid architectures becomes very significant for optimizing performance of $MoS_2$-based SIBs to gain high rate capability and long cycle life.

On the other hand, past studies on LIBs have revealed that porous, hollow or hierarchical architectures can allow efficient electrolyte penetration and support rapid $Li^+$ diffusion as well as provide buffer for accommodating volume changes during cycling, resulting in much enhanced structural stability and cycling performance [22-31]. Also, formation of 3D hierarchical architectures is beneficial to rechargeable battery applications, as 3D hierarchical organization can effectively prevent aggregation and maintain the superior intrinsic properties of the building units (such as large surface area, ultrathin thickness, structural stability, and novel physical properties for layer $MoS_2$) [22-31]. Therefore, reasonable design as well as smart organization of 2D $MoS_2$ nanosheets into 3D hierarchical hollow architectures is a promising route for preparing robust sodium host materials with outstanding structural stability, cycling stability and high-rate performance of SIBs.

Herein, to address the key challenges on $MoS_2$-based SIBs, we report a smart design on the synthesis of novel hierarchical nanotubes assembled from 2D superstructure nanosheets consisting of alternative monolayers of $MoS_2$ and carbon. Unlike previously reported $MoS_2$ hollow structures [17,25,29-31], the present $MoS_2$ hollow architecture shows a significantly expanded (002) interlayer spacing as large as 0.98 nm. Comparing to commonly reported $MoS_2$ and carbon composites, the 2D superstructure possesses an ideal interface contact between $MoS_2$ and carbon coupled with a substantially enlarged interlayer distance, allowing faster sodiation/desodiation kinetics. Formation mechanisms of the $MoS_2$:C 2D superstructures and their organization into hierarchical nanotubes featuring with one closed-tip are investigated. The $MoS_2$:C superstructure architectures are further employed as a robust anode material for SIBs and show excellent rate and cycling performance.

## Experimental section

### Synthesis

In a typical synthesis, S powder (1.2 mmol) was dissolved in octylamine (12 mL) in a Teflon-lined autoclave (50 mL) and followed with addition of $MoO_3$ powder (0.5 mmol) and finally absolute ethanol (15 mL). The mixture was magnetically stirred for 5 min and turned to a light yellow suspension. The autoclave was then sealed and kept in an oven at 190 °C for 3-8 h, and finally cooled down naturally to room temperature. A black product was collected by centrifugation and washed with absolute ethanol and distilled water several times, and then dried in vacuum at 60 °C for 12 h. The as-prepared $MoS_2$:C sample was finally annealed at 700 °C for 1 h in mixed Ar-$H_2$ (5% $H_2$) atmosphere to remove possible organic contaminations.

### Characterization

Structures, morphologies and compositions of the samples were characterized with X-ray diffraction (XRD) with a Rigaku D/MAX2500V diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) was carried out with a Philips XL30 FEG SEM. Transmission electron microscopy (TEM) was carried out with a Philips CM 20 FEG TEM or a JEOL JEM-2100 TEM



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