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Rational Design of Three-layered TiO₂@Carbon@MoS₂ Hierarchical Nanotubes for Enhanced Lithium Storage

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Abstract

Here we demonstrate the rational design and synthesis of three-layered TiO₂@carbon@MoS₂ hierarchical nanotubes for anode applications in lithium-ion batteries (LIBs). Through an efficient step-by-step strategy, ultrathin MoS₂ nanosheets are grown on nitrogen-doped carbon (NC) coated TiO₂ nanotubes to achieve the TiO₂@NC@MoS₂ tubular nanostructures. This smart design can effectively shorten the diffusion length of Li⁺ ions, increase electric conductivity of the electrode, relax volume variation of electrode materials upon cycling, and provide more active sites for electrochemical reactions. Owing to these structural and compositional features, the hierarchical TiO₂@NC@MoS₂ nanotubes manifest remarkable lithium storage performance with good rate capability and long cycle life.

Key words: MoS₂, TiO₂, hollow, nanotubes, lithium-ion batteries.

Rechargeable lithium-ion batteries (LIBs) have attracted considerable attention in view of their great opportunities as the power source for portable electronic devices/vehicles.^[1-3] Although graphite is widely used as the anode material in commercial LIBs, its low theoretical capacity (372 mAh g⁻¹) cannot meet the rapidly rising demand of large-scale high energy/power density.^[4-6] Recently, transition metal oxides and sulfides have emerged as promising electrode materials for LIBs because of their high specific capacity, low cost, design flexibility and other appealing properties.^[7-10] Particularly, molybdenum sulfide (MoS₂), a representative two-dimensional (2D) material with graphene-like crystalline structure, has been actively investigated owing to its high specific capacity (669 mAh g⁻¹) from the four-electron transfer reaction.^[11-14] However, MoS₂ electrodes still face great challenges in the practical application such as fast capacity fading caused by the drastic volume change upon cycling and inferior rate performance due to the poor conductivity.^[14-16]

To overcome the intrinsic drawbacks of MoS₂ electrodes, various strategies have been proposed to boost their lithium storage properties.^[8,11,13-15,17-20] One effective way is to integrate MoS₂ and other active materials into smart hybrid nanostructures.^[16,21-23] The hybrid configuration can not only preserve all the advantages from each component, but also bring some unique synergetic effects to enhance their electrochemical properties such as electrical/ionic conductivity, electrochemical reactivity and mechanical stability. As an important insertion-type electrode material, titanium oxide (TiO₂) with minor volume variation during the cycling process is usually considered as a suitable backbone or protective layer for other metal oxides/sulfides through smart hybridization.^[16,21,24-28] Recently, several MoS₂ and TiO₂ hybrid materials have thus been reported for enhanced lithium storage, such as TiO₂ nanowire@MoS₂ nanosheet composites,^[24] TiO₂@MoS₂ microspheres,^[28] and TiO₂@MoS₂ nano-onion heterostructures.^[26] Despite these advances, the lithium storage performance of these composite anodes still suffers from poor intrinsic electronic conductivity, sluggish Li⁺ ions transport kinetics and inevitable volume changes during the lithium

insertion/deinsertion process.^[16,23,25,27,29-31]

Due to the good electric conductivity, carbonaceous materials are always chosen as functional additives to ameliorate electric conductivity of electrode materials with inspiring results.^[15,18,32-34] In addition, it is believed that nitrogen-doping can further increase the electronic conductivity of carbon-based materials and thus enhance the electrochemical performances.^[11,35-36] On the other hand, many studies demonstrate that the employment of hierarchical hollow nanostructures is an attractive way to accommodate the large volume changes associated with electrochemical reactions.^[37-38] Moreover, the permeable nanoshells can greatly reduce the diffusion length for both Li^+ ions and electrons. Besides, some internal voids within hollow nanostructures guarantee the sufficient electrode-electrolyte contact area and plenty of electrochemical active sites.

Based on the above considerations, it is highly desirable to combine these strategies into a one-electrode design to fully exploit their respective advantages. Herein, we demonstrate the design and synthesis of hierarchical tubular structures by sequential coating nitrogen-doped carbon (NC) layer and ultrathin MoS_2 nanosheets on TiO_2 nanotubes (designated as $\text{TiO}_2@\text{NC}@\text{MoS}_2$). The design of this unique sandwich-like three-layered $\text{TiO}_2@\text{NC}@\text{MoS}_2$ hollow nanostructure has multiple apparent advantages for LIBs. Specifically, the overall one-dimensional (1D) coaxial nanostructures with a middle layer of NC can provide an electron/ion pathway for charge storage and delivery. Besides, the hierarchical tubular structures constructed of nanosized subunits will effectively address the volume stress related with the electrochemical reactions. Therefore, the synergistic effects between MoS_2 and TiO_2 can be ideally utilized to achieve high capacity and long cycle life for LIBs application. Impressively, the optimized hierarchical $\text{TiO}_2@\text{NC}@\text{MoS}_2$ nanotubes exhibit high specific capacity of around 900 mAh g^{-1} at 0.1 A g^{-1} , excellent cycling stability up to 200 cycles, and superior rate performance.

The multi-step synthesis process for the $\text{TiO}_2@\text{NC}@\text{MoS}_2$ tubular nanostructures is depicted in **Figure 1**. High-aspect ratio MnO_2 nanowires are selected as the starting template. In step I, a TiO_2

layer is coated on the surface of MnO₂ to produce the core-shell MnO₂@TiO₂ nanowires. Then, the MnO₂@TiO₂ nanowires are deposited with a layer of polydopamine (PDA) to yield coaxial MnO₂@TiO₂@PDA nanowires (step II). Afterwards, the resultant composite nanowires are carbonized in a N₂ atmosphere and treated in acid to remove the MnO₂ templates (step III). Meanwhile, the outer PDA layer is converted into the NC shell for the core-shell TiO₂@NC nanotubes. In the last step, a layer of ultrathin MoS₂ nanosheets is grown on the surface of TiO₂@NC nanotubes through a hydrothermal reaction and a subsequent annealing process to produce the three-layered hierarchical TiO₂@NC@MoS₂ tubular nanostructures (step IV).

MnO₂ nanowires with an average diameter of *ca.* 40 nm are first synthesized by a hydrothermal method as the starting template (Figure S1 and Figure S2, Supporting Information).^[39] Then, a TiO₂ layer is deposited on the MnO₂ nanowires through a modified cooperative assembly-directed strategy.^[40] Field-emission scanning electron microscope (FESEM) images show that the core-shell MnO₂@TiO₂ nanowires are quite uniform with a smooth surface (**Figure 2a** and Figure S3a, Supporting Information). Transmission electron microscope (TEM) image and energy-dispersive X-ray spectroscopy (EDX) result indicate the successful coating of TiO₂ shell on the surface of MnO₂ (Figure 2b and Figure S3b, Supporting Information). As a result, the diameter of nanowire increases to *ca.* 120 nm for the MnO₂@TiO₂ sample. X-ray diffraction (XRD) pattern confirms the TiO₂ coating layer is anatase phase after annealing treatment in air at 450 °C for 2 h (Figure S4, Supporting Information). The core-shell hybrid nanowires are then coated with a PDA layer to obtain the coaxial MnO₂@TiO₂@PDA nanowires. FESEM images reveal that the MnO₂@TiO₂@PDA product well preserves the 1D wire-like structure with slightly rougher surface (Figure 2c and Figure S5a, Supporting Information). In addition, TEM image reveals the thickness of the PDA layer is about 10 nm (Figure 2d). EDX spectrum also suggests the existence of PDA layer (Figure S5b, Supporting Information). After a carbonization treatment under N₂ atmosphere at 500 °C for 3 h and a follow-up acid etching process, the MnO₂ core is eliminated completely

without apparent damage to the integral 1D structure (Figure 2e and Figure S6, Supporting Information). Meanwhile, TEM image confirms the formation of the well-defined double-shelled $\text{TiO}_2@\text{NC}$ nanotubes with an ultrathin NC shell (~ 8 nm) derived from PDA layer (Figure 2f). XRD pattern indicates that the interior TiO_2 layer still maintains the anatase phase after carbonization procedure, which agrees with the lattice fringes in high-resolution TEM (HRTEM) image and the diffraction fringes in selected area electron diffraction (SAED) result (Figure S7 and Figure S8, Supporting Information). Of note, after these multi-step processes, the resultant $\text{TiO}_2@\text{NC}$ nanohybrids maintain the relatively smooth surface, which favours the following growth of highly dispersive MoS_2 nanosheets.

Finally, a layer of ultrathin MoS_2 nanosheets is grown on the surface of $\text{TiO}_2@\text{NC}$ nanotubes by a facile hydrothermal method. After this process, few-layered MoS_2 nanosheets are uniformly covered on the surface of $\text{TiO}_2@\text{NC}$ nanotubes (**Figure 3a,b**). FESEM image at high magnification clearly shows that the hierarchical MoS_2 shell is composed of randomly assembled ultrathin nanosheets (Figure 3c). XRD pattern of the as-prepared $\text{TiO}_2@\text{NC}@\text{MoS}_2$ product reveals the nearly amorphous feature of the deposited MoS_2 nanosheets (Figure S9, Supporting Information). After an annealing treatment in a H_2/Ar atmosphere at 700°C for 2 h, the crystallinity of MoS_2 is significantly increased in the final $\text{TiO}_2@\text{NC}@\text{MoS}_2$ hybrid sample. All the diffraction peaks in the XRD pattern of annealed $\text{TiO}_2@\text{NC}@\text{MoS}_2$ can be readily identified as anatase TiO_2 and hexagonal MoS_2 (Figure S10, Supporting Information) without any residuals or impurity phases. The contents of TiO_2 , NC and MoS_2 in the three-layered $\text{TiO}_2@\text{NC}@\text{MoS}_2$ material are determined by EDX measurement to be about 17.0, 23.4 and 59.6 wt.%, respectively (Figure S11, Supporting Information). It should be noted that the as-prepared MoS_2 sample does not exhibit a (002) deflection peak, indicating that the MoS_2 nanosheets contain five or less number of graphene-like MoS_2 layers.^[22,24,32] Moreover, the overall 1D hierarchical structure is well retained with a minor shrinkage of the MoS_2 nanosheets, and the average diameter of the annealed $\text{TiO}_2@\text{NC}@\text{MoS}_2$

nanotubes is about 250 nm (Figure 3d-f). TEM images clearly reveal the hollow structure of the $\text{TiO}_2@\text{NC}@\text{MoS}_2$ hybrid materials (Figure 3g,h). However, the internal layers of NC and TiO_2 cannot be identified clearly from the TEM observations due to the lower contrast compared with the thick MoS_2 layer. HRTEM image shows the edge view of some interconnected MoS_2 nanosheets with visible lattice fringes (Figure 3i). The interplanar distance is measured to be about 0.62 nm, which corresponds to the (002) plane of hexagonal MoS_2 . Elemental mappings are conducted to confirm the inhomogeneous distribution of TiO_2 , NC and MoS_2 in the $\text{TiO}_2@\text{NC}@\text{MoS}_2$ tubular nanostructures. The results show that the intensity of Ti, O, and N is slightly enhanced within the inner part of the hierarchical nanohybrid, which is different from that of Mo and S (Figure S12, Supporting Information).

Next, we evaluate the electrochemical properties of the sandwich-like hierarchical $\text{TiO}_2@\text{NC}@\text{MoS}_2$ tubular nanostructures as an anode material for LIBs. **Figure 4a** displays the representative galvanostatic charge/discharge voltage profiles of the $\text{TiO}_2@\text{NC}@\text{MoS}_2$ nanotubes in a cut-off voltage range of 0.01-3.0 V versus Li/Li^+ at a current density of 0.2 A g^{-1} . The $\text{TiO}_2@\text{NC}@\text{MoS}_2$ electrode delivers high initial discharge and charge capacities of 1410 and 838 mAh g^{-1} , respectively, corresponding to a Coulombic efficiency (CE) of 59.4%. The relatively low initial CE is mainly caused by the decomposition of electrolyte or some irreversible processes such as the formation of the solid-electrolyte interface (SEI) film during the first cycle.^[11,17,19] This intrinsic drawback can be efficiently minimized through a room temperature pre-lithiation treatment of the as-prepared $\text{TiO}_2@\text{NC}@\text{MoS}_2$ electrode, which could bring the initial CE of nearly 100 % (Figure S13, Supporting Information). It should be mentioned that the first discharge curve is usually different from the discharge curves in the subsequent cycles.^[20,32,41] The difference might imply that the material undergoes substantial structural and compositional variation during the initial cycle and remains stable afterwards.^[41] In the following discharge processes, two pronounced voltage plateaus located around 2.0 and 1.5 V can be observed, which might be ascribed to multi-

step lithium insertion mechanisms for MoS₂ and TiO₂ to form Li_xMoS₂ and Li_xTiO₂.^[22,28,40] Meanwhile, the small voltage plateau located around 0.7 V indicates the further decomposition of Li_xMoS₂ into Mo nanoparticles embedded into a Li₂S matrix.^[17,19,27] In the charge processes, the apparent voltage plateaus around 2.0 V are corresponding to the delithiation of Li₂S and Li_xTiO₂.^[20,40] These results suggest both MoS₂ and TiO₂ are contributing to the total specific capacity of the hierarchical hollow nanostructures. After the first cycle, the capacity quickly stabilizes and the discharge-charge curves almost coincide with each other, suggesting the electrochemical reactions are highly stable and reversible in the electrode. The rate capability of the TiO₂@NC@MoS₂ electrode is investigated through galvanostatic measurements at various current densities. As shown in Figure 4b, the average specific discharge capacities are approximately 925, 855, 756, 670 and 612 mAh g⁻¹ at the current densities of 0.1, 0.2, 0.5, 1.0 and 2.0 A g⁻¹, respectively. When the current density is reduced back to 0.1 A g⁻¹, the capacity of TiO₂@NC@MoS₂ electrode quickly resumes to 955 mAh g⁻¹, revealing the good reversibility of the electrode materials. The cycling performance of the TiO₂@NC@MoS₂ electrode at a high current density of 1.0 A g⁻¹ is presented in Figure 4c. From the second cycle onwards, the discharge capacity quickly stabilizes at around 680 mAh g⁻¹. After a relatively slow fading, a high reversible capacity of 590 mAh g⁻¹ can still be retained after 200 cycles. Importantly, the CE is nearly 100% except the first few cycles. Besides, the TiO₂@NC@MoS₂ electrode can be cycled over 100 cycles with a high reversible capacity of 770 mAh g⁻¹ at a small current density of 0.2 A g⁻¹, which further reveals its high stability (Figure S14, Supporting Information). As also shown in Figure 4c, the electrochemical properties of TiO₂@NC nanotubes, NC@MoS₂ nanotubes (Figure S15-S17, Supporting Information) and bulk MoS₂ (Figure S18 and Figure S19, Supporting Information) are rather inferior compared with the TiO₂@NC@MoS₂ composite nanotubes. Although the cycling of this two-layered TiO₂@NC electrode is quite good, it can only deliver a low specific capacity of 205 mAh g⁻¹. Whereas, the NC@MoS₂ electrode and bulk MoS₂ electrode with relatively high

discharge capacities at initial cycles experience rapid capacity fading after about 100 cycles. Moreover, the 1D morphology of the $\text{TiO}_2@\text{NC}@\text{MoS}_2$ electrode can be maintained after charging/discharging for 200 cycles (Figure S20, Supporting Information). Nonetheless, the outermost MoS_2 nanosheets become less discernable due to the formation of solid-electrolyte interfaces during the electrochemical reactions. Compared with the control samples, the $\text{TiO}_2@\text{NC}@\text{MoS}_2$ nanotubes own the highest electric conductivity and the smallest charge-transfer resistance (R_{ct}) of 184 Ω according to the equivalent circuit in the electrochemical impedance spectroscopy tests (Figure S21, Supporting Information). Whereas, the R_{ct} values of $\text{NC}@\text{MoS}_2$, bulk MoS_2 and $\text{TiO}_2@\text{NC}$ electrodes are calculated to be about 225, 263 and 310 Ω , respectively. These improvements might be ascribed to the synergetic effect of the three functional layers in the sandwich-like $\text{TiO}_2@\text{NC}@\text{MoS}_2$ nanotubes. Specifically, the inner layer of TiO_2 nanotubes, serving as a skeleton of the hybrids, can not only buffer the large volume variation of electrode materials for stable cycling performance, but also shorten the diffusion distance of Li^+ ions for high rate capacities. The middle NC layer is more conductive to facilitate electron transfer within the hybrid, protect the overall 1D hollow structure, and prevent the MoS_2 nanosheets from restacking. The outer layer of ultrathin MoS_2 nanosheets with high surface area can provide sufficient electrode/electrolyte contact area and reduced diffusion length for electrons and Li^+ ions transfer to realize the high specific capacity.

In summary, hierarchical three-layered $\text{TiO}_2@\text{NC}@\text{MoS}_2$ tubular nanostructures are rationally synthesized by a step-by-step method. The hollow nanohybrid possesses remarkable structural features with increased electric conductivity, shortened diffusion length for Li^+ ions, reduced volume variation, and more active sites for electrochemical reactions. As a result, the hybrid $\text{TiO}_2@\text{NC}@\text{MoS}_2$ material exhibits enhanced lithium storage properties in terms of high capacity, long cycle life and good rate performance. All these results demonstrate that the rational selection and design of hierarchical hollow nanostructures can be an effective strategy to obtain advanced

electrode materials for lithium-ion batteries.

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Figures and Captions

Figure 1. Schematic illustration of the synthesis process of $\text{TiO}_2@\text{NC}@\text{MoS}_2$ tubular nanostructures. (I) TiO_2 coating, (II) PDA coating, (III) annealing in N_2 and acid etching, (IV) growth of MoS_2 nanosheets.

Figure 2. (a,c,e) FESEM and (b,d,f) TEM images of (a,b) $\text{MnO}_2@\text{TiO}_2$ nanowires, (c,d) $\text{MnO}_2@\text{TiO}_2@\text{PDA}$ nanowires and (e,f) $\text{TiO}_2@\text{NC}$ nanotubes.

Figure 3. (a-c) FESEM images of as-prepared hierarchical nanotubes after the growth of MoS₂ layer. (d-f) FESEM and (g,h) TEM images of annealed TiO₂@NC@MoS₂ nanotubes. (i) HRTEM image of the MoS₂ nanosheets.

Figure 4. Electrochemical performance of annealed $\text{TiO}_2@\text{NC}@\text{MoS}_2$ tubular structures for lithium storage. (a) Discharge/charge voltage profiles for the first five cycles at a current density of 0.2 A g^{-1} . (b) Rate performance at various current densities. (c) Cycling performance of $\text{TiO}_2@\text{NC}@\text{MoS}_2$, $\text{NC}@\text{MoS}_2$, MoS_2 and $\text{TiO}_2@\text{NC}$ at a current density of 1.0 A g^{-1} and the corresponding Coulombic efficiency of $\text{TiO}_2@\text{NC}@\text{MoS}_2$.

Table of Content Entry

Hierarchical TiO₂@carbon@MoS₂ tubular-like nanostructures have been rationally synthesized via an efficient multi-step route. The unique architecture and composition of this nanohybrid can effectively improve electric conductivity, promote transport kinetics of Li⁺ ions and buffer volume variation upon cycling. With these benefits, the nanohybrid electrode manifests enhanced electrochemical properties as an anode material for lithium-ion batteries.