Hierarchical Self-Supported TiO₂/NC-MoS₂ Composite as a Stable Anode for Enhanced Lithium-Ion Batteries

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Ultrafine MoS_2 nanosheets are embedded with nitrogen-doped carbon-coated TiO_2 nanofibers $(TiO_2/NC-MoS_2)$ via a facile hydrothermal reaction and annealing treatment. Applied in the anode of a lithium-ion battery, the as-prepared $TiO_2/NC-MoS_2$ hybrid delivers a good cycling performance of 629.9 mA h g⁻¹ at 0.1 A g⁻¹ after 200 cycles and a rate capability of 471.2 mA h g⁻¹ at 1 A g⁻¹ over 1000 cycles. The superior electrochemical performance results from both the unique hierarchical morphology and the synergic effects among various interfaces and components. Nitrogen doping in carbon materials can facilitate the transfer of Li ions and TiO_2 nanofibers to prevent the aggregation of MoS_2 nanosheets. The MoS_2 nanosheets provide more active sites for electrochemical reactions. This work demonstrates that the obtained composite holds great potential for high-performance energy storage applications.

Keywords: MoS₂, hydrothermal, electrochemical, anode

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been intensively studied and applied in electric products due to their low cost and lack of pollution. [1-3] Graphite is a typical anode material; however, its low capacity cannot meet the future demand for large-scale applications in batteries. To date, many studies have investigated developing substitutes with increased energy density and safety.[4-6] Transition-metal oxides and sulfides have attracted great interest in terms of achieving improved anodes.[7,8] As a typical 2D metal sulfide, molybdenum disulfide (MoS₂), which has a layered structure with layer spacings of 0.62 nm, is good for Li⁺ embedding; thus, it is a good anode material for LIBs.[9,10] One challenge is that the strength of MoS₂ nanosheets is too low to endure the great stress variation accompanying the

discharge and charge process, which results in severe restacking and structural pulverization, with fast capacity fading. [11, 12]

Interconversion-type TiO₂ has been proposed as an excellent material owing to its long cycle life, nontoxicity and low cost. Moreover, there is very little volume expansion (<4%) during the Li insertion/extraction process. However, the low lithium-ion diffusivity and electronic conductivity restrict the applications of such a material. [13,14] TiO_2 has been generally applied as a composite substrate, and the strength of MoS₂-based electrode materials may be improved by the integration of TiO₂. [15-17] Several MoS₂/TiO₂ composites have been reported very recently. One example involved filling ultrathin MoS₂ nanosheets into the nanoscale voids of TiO₂ microspheres, which were then encased with graphene.[18] TiO₂/MoS₂ nanofibers were synthesized through MoS₂ nanoparticles wrapped in a TiO₂ nanofibrous backbone via a facile method.[19] The preparation of core-shell TiO₂@MoS₂ was reported by using thin titania nanosheets coated with MoS₂ shells.[20] Fish-scale-like MoS₂ could be decorated in the interspace of flower-like TiO₂/C microspheres.[21] While the Li storage has been enhanced in these examples, these nanohybrid anodes are still subject to the inferior intrinsic conductivity of TiO₂ and MoS₂. Recently, some researchers have discovered the benefits of N-doping in carbon materials, specifically in electrode materials.[22-24] Doping with nitrogen can improve the electronic properties by providing more active sites and ion diffusion pathways. [25,26] Polydopamine (PDA) is a catecholamine polymer derived from the oxidation polymerization of dopamine.[27] Carbonized PDA with a high nitrogen content can release volumetric strains and display high electrical conductivity.[28-29] MoS₂@TiO₂ nanofiber hybrid nanostructures have been prepared with a template-assisted hydrothermal approach, and they present good electrochemical performance.[30] However, the complicated synthesis procedure requires removal of the template by methods such as calcination at high temperature or etching in harsh solutions, thus restricting the following applications.

Based on the above considerations, a rational structure of MoS_2/TiO_2 nanomaterials still needs to be designed, which would enable many advantages in one hybrid material. Herein, we report the preparation of a MoS_2 hybrid with N-doped carbon-coated TiO_2 ($TiO_2/NC-MoS_2$) via a simple and economical PDA-assisted carbonization and hydrothermal process. Benefiting from the merits of 1D TiO_2 nanofibers and 2D MoS_2 nanosheets, the hybrids can integrate the high capacity of MoS_2 and superior cycling stability of TiO_2 . In addition, PDA can provide carbon and nitrogen sources, and the introduction of PDA can improve the rate capacity by increasing the conductivity. Thus, the prepared $TiO_2/NC-MoS_2$ anodes exhibit excellent cycling performance and outstanding high-rate capability. The $TiO_2/NC-MoS_2$ composite delivers a high discharge capacity of 649.4 mA h g⁻¹ at 0.1 A g⁻¹ and exhibits outstanding cycling stability, with a capacity retention of 97% after 200 cycles.

2. EXPERIMENTAL

2.1 Synthesis of TiO₂/NC-MoS₂, TiO₂/NC and MoS₂

 TiO_2 nanofibers were prepared as previously described.[31] TiO_2 (130 mg) was added to Tris-HCl (200 mL), and then, dopamine (30 mg) was added to the solution. The mixture was stirred for 3 h. Afterwards, the product was rinsed with ethanol and deionized water and then dried at 60°C for 12 h. TiO₂/PDA was carbonized at 300°C for 3 h under an Ar atmosphere at a heating rate of 3°C min⁻¹. The product TiO₂/NC was obtained.

TiO₂/NC-MoS₂ was obtained by a hydrothermal method. TiO₂/NC was added to a glucose solution (0.1 M, 40 mL). Then, NaMoO₄•2H₂O (80 mg) and thiourea (160 mg) were added and stirred for 0.5 h. Next, the hydrothermal reaction was performed at 180°C for 12 h. The sample was rinsed with a large amount of deionized water and dried. The product was heated at 700°C at 5°C min⁻¹ in a N₂ atmosphere for 1 h. Black powder was obtained. Pristine MoS₂ and TiO₂/NC were synthesized using a similar procedure.

2.2 Characterization

The products were characterized by X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., Cu K α radiation, λ =1.5418 Å), transmission electron microscopy (TEM, JEM-2010F, JEOL, Japan), Raman spectroscopy (Jobin Yvon LabRam HR800, excitation wavelength 532 nm), X-ray photoelectron spectroscopy (XPS, Newcastle, U.K.), scanning electron microscopy (SEM, Carl Zeiss AG, Germany), and nitrogen adsorption-desorption isotherms (Quantachrome, USA).

2.3 Electrochemical performance

The electrochemical performance was assessed with a 2032-type half coin cell. The products were mixed with carbon black and polyvinylidene fluoride (PVDF) (mass ratio= 80:10:10) in N-methyl-pyrrolidone and then cured on copper foil. The electrolyte was mixed ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1 M LiPF₆. Cyclic voltammetry (CV) was performed from 0.01–3.0 V on a Vertex.C. DC electrochemical workstation (Metrohm, Netherlands). Electrochemical impedance spectroscopy (EIS) was also performed (100 kHz~0.01 Hz). The galvanostatic charge-discharge test was conducted under the following conditions: scan rate of 0.2 mv s⁻¹ and voltage range of 0.01–3.0 V at 25°C (LAND-CT2001A battery-testing instrument).

3. RESULTS AND DISCUSSION

The synthetic route of the $TiO_2/NC-MoS_2$ nanocomposite is shown in Fig. 1. First, TiO_2/NC was synthesized by PDA coating, followed by calcination in an Ar atmosphere. Then, the MoS_2 nanosheets grew on the surface of TiO_2/NC nanowires with the assistance of glucose through the hydrothermal reaction. The hydrothermal sample was treated at 700°C under a N₂ atmosphere to obtain the annealed $TiO_2/NC-MoS_2$ hybrid.

The crystallographic properties of $TiO_2/NC-MoS_2$ and TiO_2/NC were analyzed based on the XRD patterns (Fig. 2a). The diffraction pattern revealed that anatase TiO_2 (JPCDS: No. 21-1272), TiO_2 -B (JPCDS: No. 46-1238), and hexagonal MoS₂ phase (JCPDS: No. 37-1492) were obtained. [32,33] The (002), (100), and (110) peaks of hexagonal MoS₂ appeared after the hydrothermal and carbonization

processes, indicating the successful coexistence of MoS₂ and TiO₂.[34] Notably, the (002) diffraction peak at 14° corresponding to the c plane of MoS₂ was absent. This result indicated that the MoS₂ nanosheets along the TiO₂ nanofibers were not in a stacked arrangement, and they contained few-layered MoS₂ nanosheets.[35] The obvious peaks at 2 θ values of 25.3, 37.8 and 53.9° were assigned to the (101), (004) and (105) planes of the anatase TiO₂ phase, respectively, becoming sharper and more intense than those for TiO₂/NC, which indicated that the crystallinity of the sample was slightly improved after annealing.



Figure 1. The synthetic route of TiO₂/NC-MoS₂



Figure 2. (a) XRD patterns, (b) Raman spectra, (c) N₂ adsorption/desorption isotherms, and (d) pore size distributions of the TiO₂@NC-MoS₂ hybrids, TiO₂@NC and MoS₂.

The Raman spectrum is depicted in Fig. 2b. Four peaks at 151, 198, 254 and 643 cm⁻¹ are assigned to the Eg, B_{2g} , B_{3g} and Eg bands of TiO₂, respectively.[31,36] In addition, the peak at 420 cm⁻¹ was due to the A_{1g} mode of MoS₂, suggesting that MoS₂ was successfully embedded in the TiO₂/NC nanofiber. Moreover, a blueshift of the E_{2g} mode of MoS₂ was observed for the composite, which was probably owing to the surface strain induced by the MoS₂ decorated on the surface of the TiO₂/NC nanofiber. [37,38] Two peaks at 1358 cm⁻¹ and 1593 cm⁻¹, which were attributed to the D band and G band, respectively, demonstrated the existence of carbon.^[38] The intensity ratio I_D/I_G was calculated to be 1.27, indicating a low graphitic degree. [40]

The N₂ adsorption-desorption results showed the BET-based surface area (Fig 2. 3c), which was $21.6 \text{ m}^2 \cdot \text{g}^{-1}$ and $14.1 \text{ m}^2 \cdot \text{g}^{-1}$ for TiO₂/NC and MoS₂, respectively, and $41.7 \text{m}^2 \cdot \text{g}^{-1}$ for the TiO₂/NC-MoS₂ hybrid. The TiO₂ nanofibers suppressed the stacking of MoS₂, and the surface area of the hybrid was further enlarged by the regular growth of MoS₂ nanosheets. The BJH plots showed that the TiO₂/NC-MoS₂ MoS₂ hybrid is in the mesoporous range, with a sharp peak at 3.5 nm.



Figure 3. SEM images of (a) TiO₂ nanofibers, (b) TiO₂/NC-MoS₂ hybrids, (c) high-magnification TEM images, (d) HRTEM images, and (e) TEM-EDS mapping of the as-synthesized TiO₂/NC-MoS₂ hybrids.

The morphology of the prepared samples is presented in Fig. 3a. The diameter of the TiO_2 nanotubes was approximately 200 nm, presenting a smooth surface. As shown in Fig. 3b, a layer of MoS_2 nanosheets is uniformly coated on the TiO_2 nanotubes after the solvothermal and carbonization processes. Fig. 2c clearly shows the hierarchical structure of the $TiO_2/NC-MoS_2$ composite surface. From the HRTEM image in Fig. 3d, the (002) planes of MoS_2 and (101) planes of anatase TiO_2 can be observed, indicating a well-defined structure and heterojunction. Molybdenum, titanium, oxygen and

sulfur can be found in the elemental mappings, proving that TiO₂/NC-MoS₂ composites were obtained (Fig. 3e). [41]



Figure 4. XPS spectra of TiO₂/NC-MoS₂: (a) survey scan, (b) Mo 3d, (c) C 1s, (d) Ti 2p, (e) S 2p and (f) N 1s



Figure 5. Electrochemical tests: a) CV curves at 0.01-3 mVs⁻¹ with a scan rate of 0.2 mV s⁻¹. b) Galvanostatic charge-discharge profiles from the 1st to 3rd cycle at current densities of 0.1 A g⁻¹. c) Cycling performance. d) Rate capability. e) Long cycling performance (1 A g⁻¹) of the TiO₂/NC-MoS₂ composite electrode. f) Nyquist plots of the TiO₂/NC-MoS₂ hybrids, TiO₂/NC and MoS₂.

To analyze the chemical components of the TiO₂/NC-MoS₂ hybrid, XPS was performed (Fig. 4). There were characteristic peaks of Mo, Ti, C, S, O and N. In the high-resolution Mo 3d spectra, the peaks at 232.1 and 228.7 eV corresponded to Mo $3d_{3/2}$ and Mo $3d_{5/2}$, respectively. The peak at 235.2 eV resulted from the oxidation of molybdenum.[42] In the high-resolution C 1s spectrum (Fig. 4c), there was an obvious peak of graphitic C at 284.1 eV. The peaks at 285.5 and 288.1 eV corresponded to C–N and C=O bonds, respectively. The peaks of the Ti 2p spectrum included Ti $2p_{1/2}$ at 458.3 eV and Ti $2p_{3/2}$ at 463.8 eV (Fig. 4d), which correspond to the classic values for TiO₂. [43] For S 2p, the S²⁻ $2p_{3/2}$ and S²⁻ $2p_{1/2}$ of the TiO₂/NC/MoS₂ composites were at 161.5 and 162.8 eV, respectively, which is consistent with a previous report.[44] For the N 1s spectrum, there were two nitrogen species: pyridinic-N at 397.9 eV and graphitic-N at 400.1 eV (Fig. 4f), and the introduction of nitrogen-doped carbon was good for ion and electron transport.[45]

The CV behavior of the TiO₂/NC-MoS₂ composite is in good agreement with the behavior of other previously reported TiO₂/MoS₂ materials.[46] In the primary discharge process of the TiO₂/NC-MoS₂-based electrode material, the reduction peaks at 0.71 V indicate that Li⁺ was inserted into the MoS₂ layers to form LixMoS₂ based on the following process:[47] MoS₂+xLi⁺+x e⁻→LixMoS₂. The peak at 0.48 V corresponds to further conversion of LixMoS₂ into Mo and Li₂S:[48] LixMoS₂+(4-x)Li⁺+(4-x)e⁻→Mo+2Li₂S. In addition, in the CV curves, the two reduction peaks disappeared after the first discharge, indicating that the conversion of MoS₂ to Li₂S and Mo was irreversible. The peak at 1.12 V is attributed to Li⁺ embedded in TiO₂, which causes TiO₂ to convert to LixTiO₂ via the following reaction:[49,50] TiO₂+xLi⁺+x e⁻→Li_xTiO₂. At the same time, a new discharge peak of 1.86 V appeared in the next cycle, which was due to the lithiation process of S to Li₂S:^[51] S+2Li⁺+2e⁻ →Li₂S. Then, during charging, the two anode peaks observed near 1.63 V and 2.32 V indicated the release of Li⁺ from LixTiO₂ and the oxidation of Li₂S, respectively. The CV curves remained stable after the primary charge and discharge process, indicating the excellent stability of the TiO₂/NC-MoS₂ electrode.

The galvanostatic charge-discharge profiles of TiO₂/NC-MoS₂ for the first three cycles are shown in Fig. 5b. During the first discharge process, the plateaus appear at 0.75 V and 0.5 V, owing to the formation of LixMoS₂ and the transformation of LixMoS₂ into Mo and Li₂S, respectively.[52] The peak forming at 1.86 V in the subsequent discharge cycles suggests the formation of Li₂S.[53] These results are also in agreement with the CV results. The CE for the electrode was calculated as 66%, with a discharge capacity of 981.2 mA h g⁻¹ and a charge capacity of 650.9 mA h g⁻¹. The side reaction and solid electrolyte interface layer led to the loss of capacity. [54] In the 2nd cycle, the CE was 95% (668.5 vs 633.6 mA h g⁻¹). Moreover, the overlapping charge–discharge curves indicated the superior cycling stability of the TiO₂/NC-MoS₂ anode.

The cycling performance of the TiO₂/NC-MoS₂ hybrid was tested at 0.1 A g⁻¹ (Fig. 5c). The specific capacity of the TiO₂/NC-MoS₂ hybrid can be retained at 629.9 mA h g⁻¹ after 200 cycles, corresponding to 97% retention of the reversible capacity (649.4 mA h g⁻¹). However, the TiO₂/NC hybrid and MoS₂ exhibited relatively low discharge capacities down to 79 and 247.8 mA h g⁻¹, respectively. Moreover, the CE of the hybrid was increased from 66% to more than 98% in the subsequent cycles. These results suggest a good cycling stability of the TiO₂/NC-MoS₂ electrodes. TiO₂/NC-MoS₂ could deliver values of 603.9, 566, 515.6, 465.6, 376.8 and 190.5 mA h g⁻¹ at 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 A g⁻¹, respectively, compared to those of TiO₂/NC at 70.5, 48.3, 27.2, 10.9, 2.7 and

6.7 mA h g⁻¹. When the current density was 5 A g⁻¹, TiO₂/NC-MoS₂ still presented a charge specific capacity of 190.5 mA h g⁻¹, whereas MoS₂ and TiO₂/NC only possessed capacities of 52.1 and 6.7 mA h g⁻¹ at the same current density, respectively. The TiO₂/NC-MoS₂ mixture maintained 471.2 mA h g⁻¹ over 1000 cycles at 1 A g⁻¹. Compared to previous MoS₂-based anode materials (Table 1), our TiO₂/NC-MoS₂ mixture showed the best cycle stability and rate capacity. Both the activity and stability of the electrode could be improved with TiO₂ nanofibers, N-coated carbon, and MoS₂ nanosheets.[57]

	Cycling stability after		Reference
Electrode materials	100 cycles at current	Rate performance	
	density		
TiO ₂ /NC-MoS ₂ nanofibers	603.9 mA h g ⁻¹ at 0.1 A	603.9, 465.6, 649.4 mA h g ⁻¹	This work
	g^{-1}	at 0.1, 1.0, 0.1 A g ⁻¹	
TiO ₂ /MoS ₂ nanobelts	479.7 mA h g ⁻¹ at 0.1 A	495.1, 303,474 mA h g ⁻¹ at	20
	g ⁻¹	0.1, 1, 0.1 A g ⁻¹	
$TiO_2@MoS_2$	519 mA h g^{-1} at 0.1 A g^{-1}	550, 400,598 mA h g ⁻¹ at	21
nano-onions		0.1, 1, 0.1 A g ⁻¹	
TiO ₂ /C/MoS ₂ microspheres	$621 \text{ mA h g}^{-1} \text{ at } 0.1 \text{ A g}^{-1}$	663, 270,664 mA h g ⁻¹ at	22
		0.1, 1, 0.1 A g ⁻¹	
core-shell TiO ₂ @MoS ₂	$467 \text{ mA h g}^{-1} \text{ at } 0.1 \text{ A g}^{-1}$	722, 464,720 mA h g ⁻¹ at	30
		0.1, 1, 0.1 A g ⁻¹	
MoS ₂ /TiO ₂ nanowire array	350 mA h g ⁻¹ at 0.03 A	437, 287, 399 mA h g ⁻¹ at	54
	g ⁻¹	0.03, 0.34,0.03 A g ⁻¹	
MoS ₂ /C/TiO ₂	$472 \text{ mA h g}^{-1} \text{ at } 0.1 \text{ A g}^{-1}$	713, 461, 611 mA h g ⁻¹ at	55
nanotube		0.1, 1, 0.1 A g ⁻¹	
MoS ₂ /C/TiO ₂	$544 \text{ mA h g}^{-1} \text{ at } 0.1 \text{ A g}^{-1}$	724, 414, 563 mA h g ⁻¹ at	56
nanowire		0.1, 1, 0.1 A g ⁻¹	
TiO ₂ nanowire@MoS ₂	501mA h g^{-1} at 0.1 A g $^{-1}$	581, 555, 470 mA h g ⁻¹ at	57
nanosheet		0.1, 0.5, 0.1 A g ⁻¹	

Table 1. A comparison of the electrochemical performance of TiO2 and MoS2 composites as anode materials for LIBs

The EIS test for $TiO_2/NC-MoS_2$ and TiO_2/NC is shown in Fig. 5f. The semicircle of the EIS curves consisted of the high-frequency region representing the charge transfer resistance and the straight sloping line at the low-frequency region showing the diffusion resistance. Compared with that of TiO_2/NC and MoS_2 , the semicircle of $TiO_2/NC-MoS_2$ was smaller, demonstrating lower interfacial and charge transfer resistance. [53] These results are attributed to the synergistic effects of the TiO_2 nanowires, the superior conductivity of C, and the MoS_2 nanosheets. First, the MoS_2 sheets might be convenient for lowering the activation energy for Li^+ diffusion and shortening the diffusion pathway. Second, N-coated carbon was beneficial to the conductivity. [58,59] Third, the TiO_2 nanofibers acting as a framework provided large channels for Li^+ insertion/extraction.

4. CONCLUSION

In conclusion, MoS_2 nanoflakes with nitrogen-doped carbon-coated TiO_2 nanofibers were successfully prepared through a facile process. The $TiO_2/NC-MoS_2$ nanocomposites were proved to be outstanding anode materials for LIBs due to their good cycle stability and rate capability. This favorable performance may result from the strength of TiO_2 and the activity of MoS_2 for Li^+ storage. The $TiO_2/NC-MoS_2$ nanocomposites show promising applications in LIBs.

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