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# Hierarchical self-supported C@$TiO_2$-$MoS_2$ core-shell nanofiber mats as flexible anode for advanced lithium ion batteries

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ABSTRACT

The requirements of high power density, excellent cycling ability, flexibility and low cost, are of paramount importance and critical to develop flexible lithium ion batteries (LIBs) for wearable instruments. Here we reported the rational design and fabrication of a flexible self-supported lithium ion anode material, which consists of thin $MoS_2$ nanosheets grown on the surfaces of carbon@$TiO_2$ core-shell nanofibers. The resulting hierarchical ternary nanocomposites exhibited high reversible specific capacity (~1460 mA h $g^{-1}$ at 100 mA $g^{-1}$), excellent cyclability (little capacity loss even after 1000 cycles) and rate performance (928 mA h $g^{-1}$ at 2 A $g^{-1}$) as anode in LIB. Furthermore, the binder-free anode material demonstrated new opportunities for flexible lithium ion batteries. The superior lithium storage performance is derived from the present well-designed hierarchical nanofiber structure and the synergic effect of different components and numerous interfaces.

## 1. Introduction

Numerous applications such as portable electronic devices and electric vehicles have posed great demands for advanced lithium ion batteries (LIBs), the key of which is to develop efficient electrode materials [1,2]. Up to now, various efforts have been devoted on exploration of novel electrode materials [3,4]. Graphite is one of the most often used anode materials. Unfortunately, low theoretical capacity restricts its further application [5]. In recent years, transition metal oxides and dichalcogenides have been extensively studied for LIBs electrodes because of high energy density, cycling stability, design flexibility and environmental benign [6,7]. Especially, transition metal dichalcogenides (TMD), such as molybdenum disulfide ($MoS_2$), possess a sandwich-like layered structure of one Mo atoms layer and two S atoms layers. The Mo–S interactions represent the strong covalent bonding, while the interactions between individual layers are behaved with van der Waals forces [8]. As a result, $Li^+$ can be easily intercalated and de-intercalated, endowing $MoS_2$ a promising application in LIBs. Although various $MoS_2$ nanostructures have been used as active electrodes, the inferior cycling stability impedes their practical goal. Anatase $TiO_2$ exhibits favorable cycling life and high rate capability because of low volume change in discharge/charge processes. The poor electrolyte ions diffusivity and electronic conductivity lead to a low theoretical capacity [9].

To overcome the inherent drawbacks of the $MoS_2$ and $TiO_2$ electrode materials, an optimal strategy is to design hybrid structures made of both components. By coupling the individual constituent, enhanced properties difficult to realize in a single component can be expected, such as the ability to tolerate the volume changes and to react with massive lithium reversibly [10–12]. Therefore, various hybridized nanostructures including $TiO_2$ nanobelt@few-layered $MoS_2$ structure [13], $MoS_2$ nanosheet@$TiO_2$ nanotube [14] and mesoporous $MoS_2$-$TiO_2$ nanofibers [15], have been applied to enhance the performance of LIBs.

Despite the great synergy advances of hybridized materials, the inherent low electronic/ionic conductivity of metal oxides/sulfides is still barrier for their further application in electrochemical performance. Additionally, due to the drastic volume changes in a process of Li insertion/extraction, mechanical strain often cause the electrode pulverization and delamination from current collectors, leading to a fast fade of the capacity [16]. Thus, an essential strategy to acquire self-supported flexible integrating electrodes, in which all the materials can exert their roles for lithium storage is highly desired [17–19]. However, the design of a robust, flexible, and high-performance electrode for LIBs still remains a great challenge [20,21]. Electrospinning is a promising and straightforward

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technique to produce self-supported nanofiber membranes with high flexibility, which avoids the conventional tedious preparation process of electrodes. In particular, electrospun carbon nanofibers (CNFs) network can not only provides a facile pathway for the access of electrolytes but also alleviates the mechanical stress as a flexible matrix, simplifying the practical mass production of binder-free anodes for mobile electronic devices [22–24].

Herein, to integrate the merits of 1D CNFs and $TiO_2$ nanotube, and 2D $MoS_2$ nanosheets, we have presented the preparation of self-supported C@$TiO_2$-$MoS_2$ nanofiber mat through a combination of electrospinning, carbonization and hydrothermal process [25]. In the as-prepared fibrous mat, 1D core-shell nanostructures composed of thin $TiO_2$ nanoshells on the surface of the CNFs increase the elctroactive interfaces for the transfer of $Li^+$, providing a good electronic conduction path along each nanofiber and a high interfacial contact area with electrolytes. Meanwhile, few-layered $MoS_2$ nanosheets standing out the surfaces of $TiO_2$ shell further form quantities of channels, which are beneficial for the fast charge transfer and rapid lithiation/delithiation. Especially, self-supported nanofiber mat endows the electrode excellent mechanical flexibility and high capacity. The synergistically enhancement of electrochemical performance over the as-made mat is achieved with a specific capacity as high as 1500 mA h $g^{-1}$ at 100 mA $g^{-1}$ after 50 cycles and outstanding rate capacity (~900 mA h $g^{-1}$ at 2 A $g^{-1}$). Moreover, the hybridized mats also exhibit good cycling performance at high current densities (i.e., 1072 mA h $g^{-1}$ at 1 A $g^{-1}$, 898 mA h $g^{-1}$ at 2 A $g^{-1}$, 455 mA h $g^{-1}$ at 10 A $g^{-1}$, and 150 mA h $g^{-1}$ at 20 A $g^{-1}$ after 1000 cycles, respectively). The excellent performance makes the C@$TiO_2$-$MoS_2$ nanofiber mat a promising self-supported electrode for flexible high-energy LIBs.

## 2. Experimental section

### 2.1. Chemicals

Polyacrylonitrile (PAN, Mw = 150,000) were purchased from Aldrich Reagent Co. N, N-dimethyl formamide ( > 95%), tetrabutyl titanate ($Ti(OBu)_4$, TBOT), sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and ethanol were purchased as analytical reagents from Sinopharm Chemical Reagent Co., Ltd (China). N-butyl alcohol was purchased from Beijing Chemical Company (China). Thioacetamide ($C_2H_5NS$) was purchased from Aladdin Industrial Corporation (China). All chemicals were used without any purification.

### 2.2. Preparation of C@$TiO_2$ core-shell nanofibers

PAN nanofibers were electrospun from 7% PAN solutions at 12 kV with a power supply (gamma high-voltage supply, ES30-0.1P) and collected on a ground aluminum foil target 15 cm away from the orifice. 1.5 g of TBOT was dissolved in 15 mL mixed solvent of *n*-butyl alcohol and ethanol (2:1 in v/v). Amorphous $TiO_2$/PAN core-shell nanofibers were prepared by dripping diluted TBOT in *n*-butanol/alcohol mixture onto the PAN nanofiber mat. It was completely infiltrated before hydrolysing under moisture atmosphere. The obtained amorphous $TiO_2$/PAN core-shell nanofibers were treated via pre-oxidation and carbonization at 600 °C in argon finally. CNFs were prepared by the same thermal treatment of PAN nanofibers. The preparation of pristine $TiO_2$ nanotubes is similar to that used for $TiO_2$@CNFs core-shell nanofibers except the thermal treatment in air.

### 2.3. Preparation of C@$TiO_2$-$MoS_2$ nanofiber mat

Typically, 30 mg of sodium molybdate and 60 mg of $C_2H_5NS$ were dissolved in 20 mL deionized water. 20 mg flexible C@$TiO_2$ core-shell nanofibers mat was added into the mixed solution and transferred to a Teflon-lined stainless steel autoclave. It was sealed and kept at 200 °C for 24 h. A black self-supported mat, C@$TiO_2$-$MoS_2$ nanofiber, was harvested after being washed and dried at 50 °C overnight. For comparison, $MoS_2$ nanosheets coated CNFs (first treated in a bath of 98% $H_2SO_4$ for 30 min and thoroughly washed to neutral) and $TiO_2$ nanotubes heterostructures were also prepared through a similar process.

### 2.4. Characterization

The samples were characterized on a field emission scanning electron microscope (FESEM, Hitachi S-480 equipped with energy dispersive X-ray spectroscopy) and a high resolution transmission electron microscope (HRTEM, JEOL JEM-2100UHR), respectively. An X-ray powder diffractometer (XRD, Siemens D5005) with Cu K radiation was used to characterize the structures of hybrid materials. Brunauer-Emmett-Teller (BET) surface area was measured with a Micromeritics ASAP 2020 nitrogen adsorption apparatus by $N_2$ physisorption at 77 K. X-ray photoelectron spectroscopy (XPS) analyses were measured on an ESCALAB 250Xi system (Thermo Scientific) with Al K radiation.

### 2.5. Electrochemical measurements

The self-supported CNFs, C@$TiO_2$, CNFs-$MoS_2$ and C@$TiO_2$-$MoS_2$ nanofiber mat (0.2 mg in weight with 12 mm in diameter and 20 μ m in thickness) were used as anode directly. 2032 coin-type half-battery cells assembled in an argon-filled glovebox (Lab 2000) were used to test electrochemical performance. $LiPF_6$ (1 M) in EC and EMC (1/1 in v/v) was used as the electrolyte and a Celgard-2400 membrane as the separator. Galvanostatic charge-discharge and rate-performance measurements at different current densities were performed in a LAND CT2001A (Wuhan Rambo Testing Equipment Co. Ltd, China) in a voltage ranging from 0.05 to 3.0 V. The other electrochemical tests including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were studied on an electrochemical workstation (CHI 660E). For comparison, $TiO_2$-$MoS_2$ hierarchical nanotubes, carbon black and PVDF (8:1:1 in mass) were dispersed in N-methyl-2-pyrrolidinone uniformly before being cast onto a copper foil as the electrode. Finally, a flexible battery was assembled using a self-supported C@$TiO_2$-$MoS_2$ nanofiber mat as anode, lithium metal film as counter electrode, and steel foil as current collectors.

## 3. Results and discussion

The preparation of self-supported C@$TiO_2$-$MoS_2$ nanofiber mat electrode involves the bottom-up synthesis of C@$TiO_2$ core-shell nanofibers and the following attachment of $MoS_2$ nanosheets. SEM image (Fig. 1a) shows the as-spun PAN precursor nanofibers have smooth surface with a diameter of 200 nm. An in-situ treatment of PAN nanofibers with TBOT results in the formation of PAN@$TiO_2$ coaxial nanocables (Fig. 1b). The beaded rough surface of the nanocables is caused by the hydrophilic layer with cyano groups inducing a favorable adsorption of TBOT. Carbonizing the PAN@$TiO_2$ core-shell nanofibers in argon easily make the PAN templates totally convert to CNFs, and C@$TiO_2$ core-shell nanofibers was resulted (Fig. 1c). A zoom-in observation of C@$TiO_2$ core-shell nanofibers shows the $TiO_2$ layer is 8 nm in thickness (Fig. 1d). If calcined in air, the PAN templates can also be removed, and concurrently $TiO_2$ nanotubes would be resulted (Fig. S1a). Corresponding TEM image (Fig. S1b) clearly demonstrates that the shell of the nanotubes has a porous structure.

Fig. 2a shows the hierarchical structure of C@$TiO_2$-$MoS_2$ nanofiber mat, revealing that $MoS_2$ nanosheets are uniformly grown on C@$TiO_2$ core-shell nanofibers. Magnified observation