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A hierarchical carbon@TiO_2@MoS_2 nanofibrous composite derived from cellulose substance as an anodic material for lithium-ion batteries

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ABSTRACT

A filter paper derived hierarchical carbon@TiO_2@MoS_2 nanofibrous composite was fabricated by employing natural cellulose substance (*e.g.*, commercial filter paper) as both scaffold and carbon source. The nanofibers of the filter paper pre-coated with an ultrathin titania-gel film were further modified with polydiallyldimethylammonium chloride (PDDA) and polysodium-p-styrenesulfonate (PSS) polyelectrolytes based on the layer-by-layer self-assemble method. Afterwards, the composite sheet was served as a host to grow MoS_2 nanosheets by a hydrothermal process. Finally, the as-prepared composite sheet was carbonized in Ar atmosphere at 800 °C for 3 h to yield the carbon@TiO_2@MoS_2 composite. The resultant composite consists of titania thin layer coated carbon nanofibers with wrinkled MoS_2 nanosheets (with a thickness of *ca.* 6 nm) anchored as an external coating layer on the surfaces. When evaluated as an anodic material for lithium-ion batteries, the carbon@TiO_2@MoS_2 composite delivered an initial discharge capacity of 1314.4 mAhh g^{-1} and a stable reversible capacity of 597.2 mAhh g^{-1} after 100 discharge/charge cycles at the current rate of 100 mA g^{-1}, which is higher than the theoretical capacity of the as-prepared composite electrode. The enhanced electrochemical performances of this composite were benefited from its unique three-dimensional network structures, as well as the buffering effect arising from the titania-coated carbon nanofibers, which effectively alleviates the serious volume change of MoS_2 and maintains the structural integrity of the electrode during the repeated lithiation/delithiation processes.

1. Introduction

As one of the most promising power sources, rechargeable lithium-ion batteries (LIBs) have been extensively applied in portable electronic devices and electric vehicles, due to the high energy density, long cycle life and environmental friendliness [1,2]. The battery performance largely depends on the electrochemical properties of electrode materials adopted [3]. Currently, graphite-based materials are utilized as the anodic materials in commercial LIBs. However, the low theoretical capacity (*ca.* 372 mAhh g^{-1}) and working energy density, as well as the poor rate performance of the anodes limit the widely applications; therefore, enormous efforts have been devoted to explore next-generation high-performance anodic materials.

Transition metal sulfides have drawn considerable attention as the potential anodic materials for lithium storage, due to the unique physicochemical properties and high theoretical capacities [4]. Molybdenum disulfide (MoS_2), as the most studied one among the various transition metal sulfides, has unique two-dimensional layered structure, in which the hexagonal molybdenum atom layer is sandwiched between two layers of sulfide atoms, and the Mo—S interconnected through strong covalent bonding, while S—S combined *via* weak van der Waals forces [4]. Due to the particular layered structures, MoS_2-based matters possess large specific area and two-dimensional permeable channels, which facilitate electrode/electrolyte contact [5]. In addition, a number of MoS_2 nanostructures such as nanospheres [6], nanotubes [7], nanocages [8], nanofilms [9] and hollow nanoparticles [10] have been synthesized and utilized as anodic materials for LIBs, which displayed improved electrochemical performances as compared with the macro-sized and bulk analogues. Unfortunately, most of the MoS_2-based electrodes still suffer from inferior cycling stability and poor rate

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capability caused by the low electrical/ionic conductivity and the structure deterioration upon repeated cycling [11].

To address these problems, one feasible strategy is to fabricate the composite materials composed of MoS_2 and specific metal oxides. Among the different metal oxides, titanium dioxide (TiO_2) has been regarded as a favorable hybridization candidate, owing to the good security and low volume change during the discharge/charge cyclings, which endows the TiO_2-based composite anodes with superior structural integrity and remarkable cycling stability. Therefore, some MoS_2—TiO_2 composites have been synthesized as low-cost anodic materials for LIBs [12,13]. However, the electrochemical behaviors of the MoS_2—TiO_2 hybrid anodes are still undesirable, due to the weak interaction between the MoS_2 and TiO_2 components [14].

Another available approach is to assemble MoS_2 nanosheets onto various conductive carbon supports, such as graphene [15,16], carbon nanotubes [17], carbon nanofibers [18] and carbon sheath [19], which improve the conductivity and stability of the electrode materials, leading to the enhanced lithium-storage capabilities. To date, various approaches have been proposed to construct MoS_2/carbon composites, such as magnetic field-induced method [20], chemical vapour deposition [21], electrospinning [22], solid/gas phase reaction [23], and hydro/solvo-thermal process. Among which, the hydrothermal method is the most popular one due to the low cost, simple operation and eco-benignity [15,24]. For example, layered MoS_2/graphene composites were synthesized by series of hydrothermal routes assisted by *L*-cysteine [25], cationic surfactant [15] as well as supramolecule [11], and their electrochemical performances were greatly improved when employed as anodic materials for LIBs. Furthermore, MoS_2/carbon composites with MoS_2 nanoflakes encapsulated into amorphous, hollow and porous carbon nanofibers were fabricated hydrothermally with excellent electrochemical performance for LIBs, benefited from the good electro-conductivity and enlarged interlayer spacing to relax the large volume change of MoS_2 upon cyclings [22]. Although the synergistic reactions of MoS_2 and carbon matters in the above-mentioned composites contribute to the improved lithium storage performances, the growth orientation of MoS_2 onto these carbon substrates is usually random in most cases. Thus, the development of a more versatile and reliable approach to control the growth of MoS_2 onto the carbon substrates is still a great challenge.

Biomimetic nanomaterials syntheses based on the facile and versatile self-assembly technique could give a solution for this purpose [26–33]. It is considered that the duplication of the sophisticated biological structures by the self-assembly approach brings the unique structural features of the bio-matters into synthetic materials. In addition, the biological templates are abundant, low-cost and environmental friendliness. As demonstrated by our previous works [34–38] and the colleagues' studies [39–42], the natural cellulose substance (*i.e.*, commercial filter paper) can be utilized as an ideal template or scaffold for the fabrication of functional materials with unique hierarchical structures from macro-to nanosizes. And a variety of filter paper derived metal-oxides [34,35,37,38–41] and silicon-based nanomaterials [36] showed the desirable electrochemical behaviours as employed as anodic materials for LIBs, due to the unique three-dimensional porous structures that originated from the initial filter paper. Here in the present work, a new hierarchically nanofibrous carbon@TiO_2@MoS_2 composite was fabricated by employing natural cellulose substance (filter paper) as both scaffold and carbon sources. The typical procedure involves modification of the cellulose nanofiber surfaces with ployelectrolyte multilayers, which can effectively control the uniform growth of MoS_2 nanosheets and their distribution on the titania-precoated cellulose nanofiber surfaces. The as-prepared composite contains titania thin layer coated carbon nanofibers with wrinkled MoS_2 nanosheets anchored as an external coating layer on the surfaces. When this composite was utilized as an anodic material for LIBs, it showed improved cycling stability and capacity retention as compared with the pristine MoS_2 microspheres. This is attributed to the synergetic interaction of the MoS_2, titania and carbon components, as well as the unique hierarchical nanostructural features of the carbon@-TiO_2@MoS_2 composite.

2. Experimental section

2.1. Chemicals

PDDA (average $M_W < 100{,}000$, 35 wt% aqueous solution) and PSS (average M_W 70,000) were bought from sigma-Aldrich. Titanium *n*-butoxide [$Ti(O^nBu)_4$, TBT], anhydrous sodium molybdate (Na_2MoO_4) and thioacetamide (TAA) were purchased from J&K Chemical Ltd. The commercial filter paper (quantitative #202, ashless, made from cotton) was bought from Hangzhou Xinhua Paper Industry Co. Ltd. (China). All the other chemicals were guaranteed reagents and were utilized without further purification. Milli-Q water with resistivity higher than 18.2 MΩ cm was used in all relevant cases.

2.2. Fabrication of the nanofibrous carbon@TiO_2@MoS_2 composite

As presented in Scheme 1, one piece of filter paper ($d = 3.0$ cm) was placed in a suction filter funnel, and washed by suction filtration of ethanol, followed by drying with air flow for 15 min prior to use. Then, an ultrathin titania-gel film (thickness of *ca.* 2.5 nm) was deposited onto the surface of the cellulose nanofibers of the filter paper (Scheme 1b), according to our previous report [43]. Afterwards, 20.0 mL of polycation PDDA aqueous solution (1.0 mg mL^{-1} in 0.5 M sodium chloride) was added to the filter funnel, and the initial 10.0 mL of which was slowly suction filtered through the filter paper. The remaining solution was kept for 15 min to allow PDDA adsorption on the titania-gel layer surface. Then the rest 10.0 mL solution was suction-filtered, and after that, 60.0 mL of sodium chloride aqueous solution and 60.0 mL of water were filtered successively to remove the un-assembled reagents, yielding the cellulose/titania-gel/PDDA composite fibres (Scheme 1c). After that, polyanion PSS aqueous solution (1.0 mg mL^{-1} in 0.5 M sodium chloride) was deposited onto the cellulose/titania-gel/PDDA composite nanofiber surface with the same procedure (Scheme 1d), followed by the deposition of an additional PDDA layer to generate the cellulose/titania-gel/PDDA/PSS/PDDA composite nanofibers with positively charged surfaces (Scheme 1e).

The growth of MoS_2 nanosheets on the composite nanofiber surfaces was achieved by a facile hydrothermal process. Briefly, the composite sheet (20.0 mg, which was cut into small pieces to increase the solid/liquid contact areas) was added into 40.0 mL of aqueous Na_2MoO_4 solution (0.1 mM), and the mixture was stirred for 12 h to allow adsorption of MoO_4^{2-} anions on the positively charged surfaces of the composite nanofibers driven by the electrostatic interaction. Next, thioacetamide (0.0163 g, 0.22 mM) was dissolved into the mixture under stirring for 1 h. Then, the resulting mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed tightly and heated at 200 °C for 16 h. The surface adsorbed MoO_4^{2-} anions thus reacted with H_2S that formed by the decomposion of thioacetamide to yield MoS_2. After cooling to room temperature, the black cellulose/titania/PDDA/PSS/PDDA/MoS_2 composite sheets formed (Scheme 1f) were collected by centrifugation, and washed several times with water and ethanol, followed by dried in a vacuum oven at 80 °C overnight. The as-prepared