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Titanium dioxide@titanium nitride nanowires on carbon cloth with remarkable rate capability for flexible lithium-ion batteries

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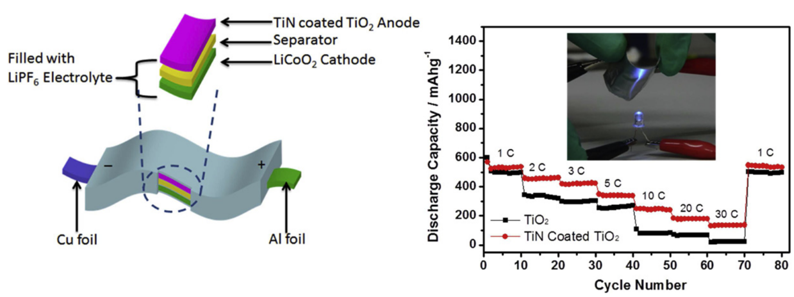
HIGHLIGHTS

- TiO_2@TiN core–shell nanowires was synthesized via hydrothermal and annealing.
- Improved rate capability was achieved by the TiO_2@TiN core–shell electrode.
- The TiO_2@TiN core–shell electrode exhibited good cyclic stability.
- Flexible lithium ion battery device was fabricated.
- Attractive electrochemical performance was delivered by the flexible device.

GRAPHICAL ABSTRACT



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ABSTRACT

Flexible lithium-ion batteries have attracted tremendous attention as a promising power source in the growing field of flexible electronic devices. In this article, we report a simple and binder free for the synthesis of TiO_2@TiN nanowires on carbon cloth by hydrothermal method and annealing. This method is highly effective in improving the rate capability of TiO_2 with discharge capacity of 136 mAh g^{-1} at high current rate to 30C. The TiO_2@TiN nanowires on carbon cloth also show remarkable cyclic performance retaining 84% of the initial capacity (240 mAh g^{-1}) after 650 cycles at 10C. High performance full flexible battery device based on TiO_2@TiN nanowires/carbon cloth composite anode and $LiCoO_2$ cathode exhibiting superior capacity retention with high discharge capacities of 227 mAh g^{-1} and 222 mAh g^{-1} at the flat and 90° bending position respectively during 30 cycles at 1C.

1. Introduction

Due to the fact that the properties of electrode materials are the most important in the performance of the lithium-ion batteries, development of energy storage materials that will account for high capacity, high stability, low volume expansion and high rate capability are highly desirable for lithium ion batteries electrode [1,2]. Titanium dioxide (TiO_2) has received numerous interests as anode material for lithium-ion batteries in terms of its chemical stability, low cost and environmental friendliness [3,4]. However, the major disadvantage of TiO_2 in their application as electrode material in lithium ion batteries is its poor lithium intercalation/deintercalation capability and electronic conductivity [5,6]. Recent

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efforts dedicated to address these limitations include nanostructuring [7] such as nanotubes [8], nanowires [9], hollow nanostructures [10]. These nanostructures have been extensively studied as anode material for lithium ion batteries with enhanced lithium electroactivity but still suffer from poor conductivity. Another approach to improve the conductivity of TiO_2 is nanocomposites. For TiO_2, they combines with metal oxides such as SnO_2 [11], Fe_2O_3 [12], metal sulphides like MoS_2 [13], coupled with other active/conductive materials [14], such as carbonaceous materials [15] and interesting improvement have been reported. Despite these achievements, there is still need for further improvement of the electronic conductivity and lithium electroactive behaviour of TiO_2 anode.

Compared to oxides, transition metal nitrides such as Mo_2N [16], VN [17], TiN [18], have superior properties in some respects such as high conductivity [19], high chemical resistance and hardness [20], mechanical stability and high melting points [21]. Liu et al. reported improvement in the electrochemical properties of MoO_2 anodes by firstly applying a direct coating of Mo_2N nanolayers [22]. They pointed out that Mo_2N nanolayer coated MoO_2 hollow nanostructures exhibits excellent electrochemical performance due to the relatively high specific surface area, porous shell and interconnected wall. Inspired by Liu's work, we extended such approach to TiO_2 by coating a shell of TiN (well known for its superior electrical conductivity around 4000–55500 S cm^{-1}) [18] on the surface of TiO_2 and expect that the nanocomposites might enhance the electrochemical performance of TiO_2. Paik et al. demonstrated nitrided TiO_2 hollow nanofibers [10]. However, the synthesis employed in the preparation method is quite tedious and the nitridated TiO_2 hollow nanofibers could only delivered about 25 mAh g^{-1} at a current rate of 10C. Such rate capability still demands further improvement. Moreover, carbon cloth as a conductive flexible substrate holds great promise as an electrode material for electrochemical storage devices due to some advantages such as highly conductive textile, excellent mechanical flexibility and also commercially available [23,24]. Recently, some works has been reported based on carbon cloth and improved electrochemical properties have been achieved [25]. They disclosed that carbon cloth can serve as a binder free and flexible substrate [26]. Thus, utilization of carbon cloth as binder free and flexible substrate requires further development. We proposed that TiO_2 nanowires coated with a thin TiN shell grown on a carbon cloth could also enrich the rate capability of TiO_2.

Herein, we synthesized TiO_2@TiN nanowires on carbon cloth composited electrode (denoted as TiO_2@TiN/CC) and study their electrochemical performance in a half-cell. Electrochemical measurements show that the TiO_2@TiN/CC electrode exhibited high rate capability. It delivers a discharge capacity of 203 mAh g^{-1} when cycled at a high current rate of 10C, which is substantially higher than the TiO_2/CC (116 mAh g^{-1}) electrode. The TiO_2@TiN/CC composite electrode also has a remarkable cycling stability. It retains a capacity of 84% of the initial capacity after 650 cycles at 10C and a capacity of 76% of the initial capacity after 200 cycles at 1C. A full flexible lithium ion battery device was fabricated employing the TiO_2@TiN/CC as anode. The developments of the flexible and wearable electronic devices have stimulated great interest to explore the flexible and lightweight energy storage devices with high energy and power densities [27]. Lithium-ion batteries have attracted great attention as a favourable power source due to their high energy density, low self-discharge, high operating voltage and low maintenance cost [28]. In this context, flexible lithium-ion batteries holds great promise as a new class of energy storage devices in the field of flexible and portable electronics since they have high energy density and good flexibility [29]. In recent years, a lot of efforts have been devoted to the fabrication and application of flexile lithium-ion batteries, and remarkable advances have been made [30]. For example, Li et al. have reported hierarchical binary metal oxides nanowire arrays/carbon textile Anodes [25], microfibrillated cellulose–graphite nanocomposites for highly flexible paper-like Li-ion battery electrodes was reported by Jabbour et al. [31], vanadium oxide nanowire–graphene flexible electrodes were also demonstrated by Lee and his co-workers [32]. However, reports based on flexible TiO_2 anode in full flexible lithium ion batteries are limited. Recently, flexible free-standing graphene–TiO_2 hybrid paper and Flexible TiO_2–B were reported by Lian et al. [33] and Lou et al. [34,35] respectively but were not demonstrated as anode material in full flexible lithium ion batteries. Huang's group demonstrates full lithium ion batteries based on TiO_2 nanorod anode and $LiFePO_4$ but in a coin cell [36]. Thus, it is still a vital challenge to develop flexible lithium ion batteries with good flexibility and electrochemical performance based on TiO_2 anode. Our fabricated TiO_2@TiN/CC//$LiCoO_2$ flexible lithium-ion battery device displays outstanding flexibility and excellent electrochemical performance. It delivers a discharge capacity of 227 mAh g^{-1} after 30 cycles at a current rate of 1C and 2% loss when cycled at 90° bending angle. This is the first time that flexible TiO_2 nanostructure will be reported as anode material in full flexible lithium ion battery.

2. Experimental

2.1. Preparation of TiO_2 nanowires on the carbon cloth

TiO_2 nanowires were grown on a carbon cloth by hydrothermal method according to our previous report with slight modification [37]. In a typical synthesis, 3 cm × 5 cm carbon cloth was cleaned with deionized water and ethanol ultrasonically and then allowed to dry at room temperature. The carbon cloth was then immersed in 0.2 M aqueous titanium (IV) chloride solution for 2 min and then allowed to be dried by blowing in the compressed air. The blow dried carbon cloth was then heated on a hotplate at about 320 °C for few minutes which generates a nanoparticle on the surface of the carbon cloth. This process was repeated about four times to ensure uniformity. 40 mL of concentrated hydrogen chloride acid was diluted in 40 mL deionized water and then mixed with 1.2 mL of tetrabutyl titanate and then stirred on a magnetic stirrer until a clear solution was obtained. The carbon cloth was then immersed in the clear solution and transferred to a 50 mL Teflon-lined stainless steel autoclave. The sealed autoclave was heated in an electric oven at 160 °C for 5.5 h. The autoclave was then allowed to cool down at room temperature and a white TiO_2 nanowires coated uniformly was obtained on the carbon cloth surface. The sample was then washed thoroughly with deionized water and allows to air dry.

2.2. Preparation of the TiO_2@TiN composite

The TiO_2@TiN core–shell nanowires on carbon cloth were obtained by calcined TiO_2 nanowires in NH_3 atmosphere at 800 °C with different annealing time. The detailed process was described as follow: The synthesized TiO_2 on carbon cloth was annealed in N_2 at 800 °C at a ramping rate of 5 °C min^{-1} and then changed to the flow of pure NH_3 gas for 5 min to obtain the TiO_2@TiN nanowires (denoted as TiO_2@TiN/CC). The NH_3 gas was introduced into the furnace while the temperature was maintained at 800 °C. After annealing, the furnace was allowed to cool to room temperature before the samples were collected. Pristine TiO_2 nanowires were directly obtained by annealing as-prepared TiO_2 nanowires at 800 °C in air (denoted as TiO_2/CC).