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Robust binder-free anodes assembled with ultralong mischcrystal TiO_2 nanowires and reduced graphene oxide for high-rate and long cycle life lithium-ion storage

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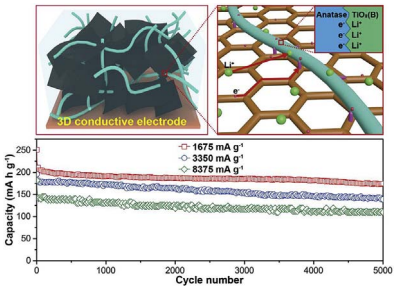
HIGHLIGHTS

- Ultralong nanowires are used to form a network avoiding auxiliary agents.
- A binder-free electrode is prepared by assembling ultralong TiO_2 nanowires with RGO.
- RGO enhances electronic conductivity and enlarges surface area of TiO_2/RGO anode.
- The robust network avoids agglomeration and provides fast Li^+/e^- transport paths.
- The binder-free electrode exhibits high reversible capacities and long lifespan.

GRAPHICAL ABSTRACT



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ABSTRACT

To satisfy increasing power demands of mobile devices and electric vehicles, rationally designed electrodes with short diffusion length are highly imperative to provide highly efficient ion and electron transport paths for high-rate and long-life lithium-ion batteries. Herein, binder-free electrodes with the robust three-dimensional conductive network are prepared by assembling ultralong TiO_2 nanowires with reduced graphene oxide (RGO) sheets for high-performance lithium-ion storage. Ultralong TiO_2 nanowires are synthesized and used to construct an interconnecting network that avoids the use of inert auxiliary additives of polymer binders and conductive agents. By thermal annealing, a small amount of anatase is generated in situ in the TiO_2(B) nanowires to form abundant TiO_2(B)/anatase interfaces for accommodating additional lithium ions. Simultaneously, RGO sheets efficiently enhance the electronic conductivity and enlarge the specific surface area of the TiO_2/RGO nanocomposite. The robust 3D network in the binder-free electrode not only effectively avoids the agglomeration of TiO_2/RGO components during the long-term charging/discharging process, but also provides direct and fast ion/electron transport paths. The binder-free electrode exhibits a high reversible capacity of 259.9 mA h g^{-1} at 0.1 C and an excellent cycling performance with a high reversible capacity of 111.9 mA h g^{-1} at 25 C after 5000 cycles.

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1. Introduction

High-performance lithium-ion batteries (LIBs) with ultrafast charging/discharging rate and long cycle life are regarded as promising energy sources for portable electronic devices and electric vehicles applications [1–3]. However, the commercial LIB anodes are easy to form lithium (Li) dendrite and solid-electrolyte interphase (SEI) film due to the low operating voltages (less than 1 V vs. Li/Li^+), leading to severe impacts on safety and rate performances [4,5]. Besides, most of the state-of-art anodes of LIBs, such as Si and Sn, suffer from short cycle life and low rate performances because of their structural instability [6,7]. It is hence highly desirable to develop robust anode materials with high rate and long cycle life performances for safe LIBs [3,8].

Titania (TiO_2) is considered as one of promising anode materials for high rate and long cycle life performances of LIBs [9,10]. Moreover, its high operating voltage (3-1 V vs. Li/Li^+) and small volume change (3–4%) make the batteries more secure by avoiding the formation of Li dendrite and SEI film [11,12]. Additionally, as an environmentally friendly and natural abundant material, TiO_2 is one of the key materials for large-scale manufacturing of batteries [13,14]. Therefore, various polymorphs of TiO_2, including anatase, rutile, and TiO_2(B), have been extensively studied as anode materials of LIBs [4,15,16]. However, it is noted that TiO_2 has not been widely used for high-rate and long cycle life anodes because of its long-range ion diffusion path, poor electronic conductivity, and limited ability of Li-ion storage [8,17].

The synthesis of TiO_2 nanowires [18], nanorods [19], nanotubes [20], nanosheets [21], and mesoporous microspheres [9] is an effective way to improve the Li-ion diffusion kinetics and electronic conductivity [3]. However, the TiO_2 nanomaterials are often at the risk of agglomeration after long-term cycles, consequently causing quick capacity decay [22]. Also, the long-range ion diffusion path is still an issue resulted from the use of inert auxiliary additives of polymer binders or conducting agents that usually do not contribute to any capacity [23,24]. It is therefore imperative to construct a 3D network as a robust binder-free electrode for direct ion/electron transports [25].

Another widely used approach to improve the conductivity of electrodes is to introduce reduced graphene oxide (RGO) as conductive agents [26]. As a typical precursor of RGO, graphene oxide (GO) can be completely dispersed in water or some organic solvents and quickly reduced to conducting RGO sheets by chemical reduction or thermal annealing [5]. Furthermore, GO can be well attached to the current collector to prepare binder-free electrodes because of its large specific surface area and high van der Waals adsorption [27,28]. Thus, binder-free electrodes with a 3D conductive architecture may obtain high rate performance by facilitating electrode-electrolyte contact and ion/electron transports. In the present work, we demonstrate an efficient and facile methodology to fabricate 3D conductive TiO_2(B)/anatase/RGO nanocomposites as a binder-free anode for high-rate and long cycle life LIBs. By hydrothermal synthesis [25], ultralong TiO_2 nanowires (longer than 100 μm) are interwoven into a robust interpenetrating network, thus avoiding the issue of agglomeration of the nanocomposites during long-term charging/discharging processes and providing direct ion/electron transport pathways. Furthermore, a small amount of anatase (3.7 wt%) is formed in situ in the TiO_2(B) nanowires by thermal treatment at 400 °C to generate abundant grain boundaries, promoting additional Li-ion accommodation. What's more, the thermally reduced RGO sheets are introduced to construct the 3D conductive networks with TiO_2 nanowires and thus enhance the electrical conductivity of TiO_2(B)/anatase/RGO nanocomposite. The resultant binder-free electrode with robust 3D conducting network exhibits a high reversible capacity of 259.9 mA h g^{-1} at 0.1 C (33.5 mA g^{-1}) in the sixth cycle and excellent cycling performance with a high reversible capacity of 111.9 mA h g^{-1} even at a high current density of 25 C (8375 mA g^{-1}) after 5000 cycles. The mechanism of the electron/ion transports in the 3D conductive network is also investigated.

2. Experimental section

2.1. Materials

Hydrogen peroxide (30%) and anatase TiO_2 were purchased from Aladdin (Shanghai, China). Graphite flakes (300 mesh), sodium nitrate, ethanol, sulfuric acid, potassium permanganate, nitric acid, hydrochloric acid, and sodium hydroxide were obtained from Beijing Chemical Works (China).

2.2. Syntheses of hydrogen titanate nanowires and their nanocomposites with interpenetrating networks

GO was prepared with a modified Hummers' method [29]. The as-prepared GO was exfoliated and dispersed in ethanol by ultrasonication, and the supernatant was collected by centrifuging at 10000 rpm for 30 min and concentrated to a concentration of 10 mg mL^{-1} for further use. Ultralong nanowires of sodium titanate were synthesized using a hydrothermal approach [25]. In a typical process, 6 g of NaOH and 0.1 g of anatase TiO_2 powder were dispersed in 15 mL of deionized water. After the mixture was stirred for 10 min and ultrasonically treated for 15 min, the resulting homogeneous suspension was transferred into a Teflon-lined stainless-steel autoclave (25 mL) and kept at 180 °C for 24 h with a stirring speed of 550 rpm. The sodium titanate product was concentrated and washed with deionized water for 6 times to neutral pH value, followed by an ion-exchange process for 6 h, in which the initial sodium ions were replaced with hydrogen ions by immersing the sodium titanate product into a 0.1 M nitric acid to obtain hydrogen titanate (HTO). After centrifuging and washing with deionized water for 8 times to neutral pH value, the precipitate was dispersed in ethanol at a concentration of 10 mg mL^{-1}. By mixing 2.0 mL of the HTO dispersion, 0.2 mL of GO dispersion, and 2.6 mL of ethanol and stirring for 6 h at 550 rpm, the HTO/GO nanocomposite with an interpenetrating network was fabricated.

2.3. Characterization

Malvern Instruments particle size analyzer MS2000 (UK) was used to analyze the Zeta potentials of HTO, GO, and HTO/GO nanocomposite in ethanol solution. Crystal structures of the nanocomposites were analyzed with a Rigaku D/Max 2500 X-ray diffractometer (Japan). The microstructure and morphology of nanocomposites were investigated by a Hitachi S4700 field-emission scanning electron microscope (SEM), a JEOL JEM-3010 transmission electron microscope (TEM), and a JEOL scanning TEM (STEM). Energy dispersive spectroscopy (EDS) attached to the SEM was used to analyze the component elements. Composition and chemical states of the nanocomposites were measured on a Thermo VG RSCAKAB 250X high-resolution X-ray photoelectron spectroscopy (XPS). Raman spectra were obtained using a Renishaw inVia at the laser wavelength of 514 nm (Britain).

2.4. Preparation of electrodes and measurements of electrochemical performances

Coin-type half-cells (CR 2032) using Li metal as the reference electrode were assembled to measure the electrochemical performances of the TiO_2(B)/anatase and TiO_2(B)/anatase/RGO electrodes. First, both the TiO_2(B)/anatase and TiO_2(B)/anatase/GO nanocomposite slurries were prepared by dispersing the as-prepared nanocomposites in ethanol with vigorous stirring for 6 h. 5 mL of the slurry with a concentration of 4–6 mg mL^{-1} was spread over the 4 × 4 cm^2 copper foil, dried in air at 50 °C for 6 h, and then thermally annealed with a heating rate of 5 °C min^{-1} under vacuum at different temperatures (300, 400, and 500 °C) for 3 h to obtain TiO_2 electrodes with anatase/TiO_2(B) mischcrystal boundaries in the TiO_2 nanowires, which were denoted as AB300, AB400, and AB500, respectively. The TiO_2/RGO

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