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Phosphorus-doped TiO₂-B nanowire arrays boosting robust pseudocapacitive properties for lithium storage

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HIGHLIGHTS

- Phosphorus-doped TiO₂-B nanowire arrays are successfully synthesized.
- P doping promotes electronic conductivity of the TiO₂-B nanowire arrays.
- P doping endows the TiO₂-B nanowire arrays with high surface reactivity.
- The P-TNAs exhibit robust pseudocapacitive properties for lithium storage.

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ABSTRACT

TiO₂-B has received increasing interest as a possible anode for lithium-ion batteries, but its properties are restricted by the intrinsically low electronic conductivity. Herein, we first demonstrate that phosphorus doping can be an efficient approach to boost the pseudocapacitive properties of TiO₂-B nanowire arrays. The phosphorus doping not only promotes electronic conductivity of TiO₂-B nanowire arrays by modifying their electronic structure, but also significantly enhances the electrochemical surface reactivity. Density functional theory calculations further reveal that the phosphorus doping could improve the surface lithium affinity of TiO₂-B nanowire arrays. Consequently the phosphorus-doped TiO₂-B nanowire arrays simultaneously exhibit high reversible capacity (350.9 mAh g⁻¹), remarkable rate capability (142.6 mAh g⁻¹ at 30 C), and impressive cyclability (approximately 80% capacity retention efficiency over 3000 continuous cycles at 10 C), holding promise in high-energy and high-power lithium-ion batteries application.

1. Introduction

Advanced electrochemical energy storage techniques such as lithium-ion batteries (LIBs) have been playing a critical role in portable electronic devices owing to their high energy density, long cycle life and environmental friendliness [1,2]. Nowadays, in order to meet the increasing energy and power demands of electric vehicles and hybrid electric vehicles, development of advanced electrode materials simultaneously with relatively large capacity, long-term cyclability and high rate capability has become significantly important to the LIBs [3,4]. In this regards, the pseudocapacitive electrode materials have attracted numerous attention because of they can store considerable amounts of Li⁺ in a reversible and rapid manner [5,6]. Unlike the diffusion-controlled intercalation reaction mechanism, the

pseudocapacitive charge storage occurs at or in the vicinity of electrode surface through Faradaic charge transfer [5]. As one of the most studied anode materials for LIBs, the TiO₂-B is well-known for its natural pseudocapacitance, intrinsic safety and low cost [7–9]. The pseudocapacitive properties of TiO₂-B are closely associated with its favorable open framework structure that provides both active sites and diffusion channels for Li⁺ [9]. Besides, the theoretical capacity of TiO₂-B is 335 mAh g⁻¹ (corresponding 1.01 Li⁺ per Ti), which is much higher than those of the other TiO₂ polymorphs (anatase and rutile, ~170 mAh g⁻¹) and the spinel Li₄Ti₅O₁₂ (175 mAh g⁻¹). Despite of these merits, the poor electronic conductivity (10⁻¹³ to 10⁻⁷ S cm⁻¹) has seriously restricted the pseudocapacitive properties of TiO₂-B [10,11].

Different strategies have been proposed to address this problem. The

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most common one is to hybridize TiO₂-B with carbonaceous materials (e.g., amorphous carbon, carbon nanotubes, and graphene) [12–14], thus effectively improving the pseudocapacitive properties. Nevertheless, it is difficult to distinguish the contribution of TiO₂-B from that of carbonaceous materials. As a promising new approach, doping of TiO₂-B with aliovalent ions has received increasing attention. By now, several dopant ions such as Fe³⁺, Cu²⁺, and N³⁻ have shown the ability of improving pseudocapacitive properties of TiO₂-B [15–17]. The structural modulation of TiO₂-B by an atomic level doping process shows great importance for considerably increasing electronic conductivity and Li⁺ diffusion within the materials. However, as far as we know, no research has been devoted to investigate the surface reactivity of TiO₂-B materials by doping with aliovalent ions, although the electrochemical surface reactivity has been proved to play a key role in pseudocapacitive properties [18–20].

In this work, we present a phosphorus doping strategy to enhance pseudocapacitive properties of TiO₂-B nanowire arrays (TNAs). In order to synthesize the phosphorus-doped TiO₂-B nanowire arrays (P-TNAs), a heat treatment process under phosphorous atmosphere is conducted to transform the hydrogen titanates (H₂Ti₂O₅·H₂O) nanowire arrays into TNAs, in which the phosphorus is simultaneously introduced into the product. The phosphorus doping is verified to modify the electronic structure of TiO₂-B, thereby realizing the improvement of electronic conductivity. Density functional theory (DFT) calculations reveal that the phosphorus doping could boost surface lithium affinity of TNAs. Consequently, the pseudocapacitive properties of TNAs are effectively improved, owing to the electronic structure modulation and the enhanced surface reactivity. When working as additives-free anodes for LIBs, the P-TNAs can afford a high reversible capacity of up to 350.9 mAh g⁻¹ at 1 C and retain a capacity of 152.6 mAh g⁻¹ over 3000 continuous cycles at 10 C, which outperform most other TiO₂-B based nanostructured materials reported to date.

2. Experimental section

2.1. Synthesis of H₂Ti₂O₅·H₂O nanowire arrays (HTNAs) on Ti foil

The synthesis method of HTNAs on Ti foil refers to the previous reports [10,21]. The other reaction conditions are the same except that the reaction time of hydrothermal process was decreased to 12 h.

2.2. Synthesis of TiO₂-B nanowire arrays (TNAs) and phosphorus-doped TiO₂-B nanowire arrays (P-TNAs)

P-TNAs were prepared by heating treatment of the HTNAs under phosphorous atmosphere at 400 °C for 3 h. In detail, 1.0 g NaH₂PO₂ was placed on the upstream side of a tube furnace at carefully adjusted locations to set the temperature, and Ar gas was used as the precursor carrier. For comparison, the samples were prepared following the same procedures but using 0, 0.5, and 2.0 g NaH₂PO₂ were marked TNAs, P-TNAs-S1, and P-TNAs-S2, respectively. The mass loading of the grown nanowire arrays on Ti foil is about 1.0 ± 0.05 mg cm⁻² determined by peeling off the film from Ti foil and measuring the weight difference by a Sartorius analytical balance (CPA225D, with a resolution of 10 μg).

2.3. Materials characterization

The morphology, crystalline structure and elemental distribution of the materials were investigated by using Field emission scanning electron microscopy (FSEM, Nova NanoSEM 450) and high-resolution transmission electron microscopy (HR-TEM, Tecnai G2 F30) equipped with energy dispersive spectroscope (EDS). An X'Pert PRO X-ray diffractometer with Cu Kα radiation was used for recording the X-ray diffraction (XRD) patterns of the products in the 2θ range of 10°–60°. Raman spectra were obtained with a Thermo scientific FT-Raman spectrometer using an Nd-line laser source with an excitation

wavelength of 532 nm. The chemical state and composition of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600 W). The UV–vis absorption spectrum was obtained with a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan) at room temperature.

2.4. Electrochemical measurements

The electrochemical measurements were carried out with 2032-type coin cells, which were assembled in an Ar-filled dry glove box. The Ti foils supported TNAs or P-TNAs with cutting size of 1 × 1 cm² were directly used as the working electrodes and metallic lithium foils were the counter electrodes. The electrolyte is 1.0 M LiPF₆ dissolved in a mixture of EC (ethylene carbonate) and DEC (diethyl carbonate) with a volume ratio of 1:1 and the cell separators are Celgard 2400 membranes. Galvanostatic charge-discharge tests at different current densities were performed using a LAND CT-2001A battery tester between the potential region of 0.01 and 3.0 V. Cyclic voltammetry (CV) tests were performed on a CHI660D electrochemical workstation between 0.01 and 3.0 V (vs. Li⁺/Li) at different scan rates. Electrochemical impedance spectroscopy (EIS) measurements were measured on an AC voltage of 5 mV amplitude in the frequency range from 100 kHz to 10 mHz using the CHI660D electrochemical workstation.

2.5. DFT calculations

The first-principles calculations were carried out employing the CASTEP package, using a plane-wave pseudopotential formalism which was aided by the Accelrys Materials Studio (Accelrys Inc.) graphical front-end interface [22]. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional was used for describing the exchange correlation energy [23]. For the optimized geometries of all the systems, a conjugated gradient technique was used in a direct minimization of the Kohn–Sham energy functional and the core electrons were described by pseudopotentials. A plane-wave basis set with an energy cutoff of 500 eV was used for ensuring good convergence and the k-points were sampled on Monkhorst–Pack grid of 8 × 8 × 4 for the unit cell. The atomic forces, maximum displacement, and total energy variation were less than 3.0 × 10⁻² eV Å⁻¹, 1.0 × 10⁻³ Å, and 1.0 × 10⁻⁵ eV atom⁻¹, respectively.

3. Results and discussion

As schematically presented in Scheme 1, the P-TNAs were synthesized via a facile hydrothermal method and subsequent heating treatment under phosphorous atmosphere. The obtained HTNAs sample is composed of well-ordered vertical nanowires and its XRD pattern is well-indexed to H₂Ti₂O₅·H₂O (Fig. S1) [24,25]. During the heating treatment process, the H₂Ti₂O₅·H₂O is converted into TiO₂-B by a topotactic phase transition, and the phosphorus is simultaneously introduced into the product. If the phosphorous atmosphere is absent, the product is TNAs. Compared to HTNAs, the P-TNAs (Fig. 1a and b) and TNAs (Fig. S2) samples maintain the similar nanowire morphology and well-ordered vertical arrays structure, with a length of about 10 μm and diameter in the range of 40–100 nm. The well-ordered vertical nanowire arrays with large aspect ratio (~140) of length to diameter ensure their full contact with electrolytes during cycling process, possessing high Li⁺ accessibility. Moreover, the phosphorus doping could not only enhance the lithium reaction kinetics of the nanowire arrays by improving their electronic conductivity, but also more importantly increase the surface lithium affinity due to the high surface reactivity, thus significantly boosting the pseudocapacitive properties.

The morphology and microstructure of the materials were confirmed with TEM analysis. As displayed in Fig. 1c, the P-TNAs consist of the nanowires with a diameter of 40–80 nm, being consistent well with the SEM investigation. Fig. 1d presents the HR-TEM images of P-TNAs, in

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