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# Carbon-bonded, oxygen-deficient $TiO_2$ nanotubes with hybridized phases for superior Na-ion storage

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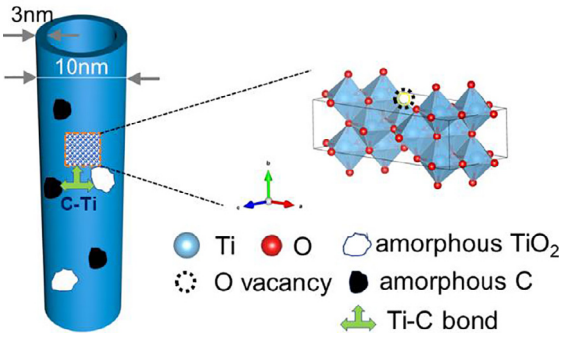
## HIGHLIGHTS

- Ultrathin $TiO_2$ nanotubes were synthesized by a hydrothermal and annealing process.
- Oxygen vacancies and Ti—C bonding in the $TiO_2$ boosted electrical conduction.
- Coherent amorphous/$TiO_2$(B) junctions enabled rapid electron/Na-ion transport.
- The material exhibited a fast, pseudocapacitance-dominant Na-ion storage.

## GRAPHICAL ABSTRACT

Ultrathin carbon-bonded, oxygen-deficient $TiO_2$(B) with hybridized phases were controlled synthesized by a facile hydrothermal process following heat-treatment, which displays fast pseudocapacitance-dominant Na-ion storage capability.

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## ABSTRACT

$TiO_2$ shows great potential as anode materials for sodium-ion batteries (SIBs). However, its practical application has been deferred by the sluggish electronic/ionic transport. In this work, we report the controlled synthesis of ultrathin, carbon-bonded $TiO_2$ nanotubes with oxygen vacancies ($V_o$) and hybridized amorphous/$TiO_2$(B) phases via a hydrothermal reaction and heat-treatment. The introduction of $V_o$ and carbon in $TiO_2$ by C-Ti bonding effectively boosts its electron transport. Meantime, the ultrathin $TiO_2$ nanotubes (with diameter of ~10 nm and tube thickness of ~3 nm) enable a large electrode/electrolyte contact interface with shortened $Na^+$ diffusion distance. In addition, the formed coherent amorphous/$TiO_2$(B) junctions further promote the charge transport and transfer at heterointerface. These synergic effects endow the resultant $TiO_2$ material with superior $Na^+$ storage capability in terms of high capacity (191 mA h/g at 0.2 C) and rate property (141 mA h/g at 10 C). Kinetics analysis further discloses a pseudocapacitive $Na^+$ storage exerts a significant contribution to the total

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capacity. The proposed strategy based on synergic engineering of vacancy defects, chemical bonding and phase composition can pave the way for exploration of novel electrode materials for beyond lithium-ion batteries.

## 1. Introduction

Lithium-ion batteries (LIBs) have successfully powered a wide array of portable electronic devices since their commercialization [1]. Currently, various novel electrode materials with high (rate) capacity, long-term cyclability, and good safety are being intensively studied for next-generation LIBs with emerging applications in electric vehicles, smart grid, and storage of renewable energies [2–6]. However, a major concern about LIBs stems from the growing cost and limited resources of lithium. As an alternative technology, sodium-ion batteries (SIBs) are very promising for large-scale energy storage applications because of low-cost and resource abundance of sodium (Na). Recently, several cathode materials have been proposed for SIBs, including $Na_3V_2(PO_4)_3$ [7], P2-$Na_xVO_2$ [8], and Prussian blue [9] etc. In contrast, commercial graphite, despite widely used in LIBs with a high capacity of 372 mA h/g for more than two decades, cannot host an acceptable capacity for $Na^+$-storage (< 35 mA h/g) [10]. Some hard carbon materials can offer a high capacity of ~300 mA h/g at low potentials (< 0.1 V vs. $Na^+$/Na), but raise safety concerns due to the possible growth of Na-dendrites [11]. Other candidates based on alloy- and conversion-reactions exhibited high initial capacity but suffered from poor cyclability due to the large volume change and sluggish kinetics [12]. These issues can be partially mitigated by rationally blending them into flexible, conductive carbon matrix [13,14], morphology control [15] and optimizing electrolyte composition [16]. Recently, Lu et al. delicately designed and synthesized a class of organic anodes for SIBs with high capacity and cyclability by stabilizing intermediate radicals via steric effects [17]. Besides, some transition metal oxides, especially titanium oxides were also proposed as promising anode materials for SIBs due to their relatively high theoretical capacity (340 mA h/g), good safety and low cost [18]. $TiO_2$ with various polymorphs, such as anatase [19], rutile [20–23], and amorphous structure [24–28] has been studied as anode materials in SIBs. Recently, $TiO_2$(B), a superior anode for LIBs [29,30], receives increasing attention for $Na^+$ storage. Compared to rutile, anatase or brookite, $TiO_2$(B) has a more open 3D network structure which is formed by oxygen atoms linking to corrugated sheets with edge- and corner-sharing $TiO_2$ octahedra. Therefore, the opened channel structure and low mass density render $TiO_2$(B) fast $Na^+$ transport and good strain/stress relief during sodiation/desodiation [10,31,32].

To mitigate the sluggish $Na^+$ diffusion in $TiO_2$, various nanostructures, such as nanoparticles [33–35], nanowires [36], nanosheets (NSs) [37], have been synthesized to provide a large electrode/electrolyte interface and shorten $Na^+$ diffusion paths [38]. Particularly, porous nanostructures comprised of nanosized building blocks are very appealing because they can avoid the undesired particle aggregation while maintain a high electrode/electrode interface for facile electrochemical reactions [39]. In addition, heteroatom-doping or self-doping via $V_o$ [31,40–42] as well as compositing with conductive nano-carbon [43–46] has been successfully used to boost the electron transport in $TiO_2$ [47]. Especially, it is assumed that dual-functionalization of $TiO_2$ via synergetic doping and carbon decoration can better enhance electronic conductivity and rate property of $TiO_2$ electrode.

Recently, heterostructured electrodes with rationally designed phase hybridization and morphologies have also attracted increasing attention. Such electrode usually exhibits superior rate capability due to the rapid electron/ion transport and separation at the heterointerfaces driven by a self-building electric field [3,4,6]. Additionally, increased capacity storage can be achieved at such nanosized phase interfaces following a “job-sharing mechanism” [48].

In this paper, we report the rational design and synthesis of $TiO_2$ nanotubes-constructed porous spheres with hierarchical structure by a hydrothermal process following annealing. The $TiO_2$ nanotubes are characterized by ultrathin diameters of ~10 nm with hybridized amorphous/$TiO_2$(B) phases. Moreover, $V_o$ and amorphous carbon have also been introduced into the $TiO_2$ nanotubes possibly during the carbonization of residual organic species upon heat-treatment. The synergy of $V_o$, carbon doping in form of C—Ti bonding, and coherent amorphous/$TiO_2$(B) phases integrated in the ultrathin $TiO_2$ nanotubes enables the material superior pseudocapacitive $Na^+$ storage capability. The current methodology may cast new insights on the development of novel electrode materials for post lithium-ion batteries.

## 2. Material and methods

### 2.1. Materials synthesis

All chemicals used were analytically pure grade and used as received without further purification.

The schematic fabrication procedure of the $TiO_2$ nanotubes is shown in Fig. 1. Herein, amorphous $TiO_2$/oleylamine hybrid spherical particles were first synthesized by a facile sol–gel process and used as precursor (Fig. 1a). In subsequent hydrothermal reaction, some oleylamine molecules were dissolved out from the precursor and the inner $TiO_2$ colloids could react with NaOH to form lamellar titanates nanosheets (Fig. 1b), which then curved into nanotubes (Fig. 1c) to reduce the system’s total surface energy. After cation-exchange and thermal treatment, $TiO_2$ nanotubes could be obtained (Fig. 1d).

#### 2.1.1. Synthesis of $TiO_2$/oleylamine hybrids

The synthesis of $TiO_2$ nanotubes referred to our previous work [29] with little modifications. In a typical procedure, tetrabutyl titanate (4.5 mL) was poured in 200 mL ethanol containing oleylamine (1.8 mL) and trace water ($H_2O$, 0.8 mL) under vigorous stirring at room temperature. The resulting precipitates were kept static at room temperature overnight, then collected by centrifugation and washed with ethanol three times and finally dried at 80 °C for 12 h in air.

#### 2.1.2. Synthesis of titanates intermediate

The titanate spheres were prepared by hydrothermal treatment of

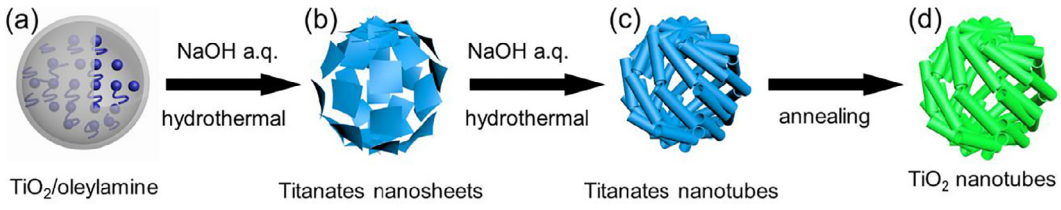


**Fig. 1.** Schematic synthesis procedure of $TiO_2$ nanotubes.