



# Enhanced electrochemical performances of anatase TiO<sub>2</sub> nanotubes by synergetic doping of Ni and N for sodium-ion batteries



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## ABSTRACT

The main challenge of using TiO<sub>2</sub> as anode for sodium-ion batteries (SIBs) is its inherent low electrical conductivity, which leads to its unsatisfied capacity, short cycle life and low initial Coulombic efficiency. Herein, we report that synergistically doped anatase TiO<sub>2</sub> nanotubes with Ni and N via a simple sol-gel process, subsequent alkali-thermal reaction, and final thermal treatment in NH<sub>3</sub> can optimize the relationship among the phase structure, electrical conductivity and sodium-ion diffusion kinetic performance of anatase TiO<sub>2</sub> to enhance its sodium-ion storage and transport performances. The resultant Ni and N co-doped anatase TiO<sub>2</sub> nanotubes (Ni-N/TNTs) exhibit a high charge capacity of 303 mA h g<sup>-1</sup> after 500 cycles at a current density of 50 mA g<sup>-1</sup> with an initial Coulombic efficiency of 65% and even at a high current density of 5 A g<sup>-1</sup>, a capacity of 143 mA h g<sup>-1</sup> is maintained after 8000 cycles with a capacity retention of ≥100%. The bandgap estimation, phase structure evolution, and electrochemical impedance spectroscopy analysis combined with the electrochemical test results indicate that the significantly improved sodium-ion storage and transport performances of Ni-N/TNTs should be mainly ascribed to the increased electrical conductivity, stable phase structure during the electrochemical processes, lower charge transfer resistance, and enhanced sodium-ion diffusion coefficient after Ni and N co-doping. The high capacity, improved Coulombic efficiency, excellent rate performance and long cycle life enable Ni-N/TNTs to be an applicable anode material for SIBs.

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## 1. Introduction

Nowadays, the expensive raw materials and limited lithium resources have severely hindered the development of lithium-ion batteries (LIBs) [1–3]. To meet the growing demands of energy, sodium-ion batteries (SIBs) have been regarded as the next generation rechargeable battery system instead of the LIBs especially in the large-scale energy storage field due to its low cost and abundant sodium resources [4–6]. However, compared with the mature LIBs techniques, the current performances of SIBs in such aspects as Coulombic efficiency, specific capacity, rate performance, and cycle life still need to be greatly enhanced to realize their wide applications [6–8]. Therefore, it is crucial to develop advanced electrode materials with applicable performances for SIBs [1–8].

One major factor limiting the sodium-ion storage and transport performances of SIBs is the larger radius of sodium ion (1.02 Å) than lithium ion (0.76 Å), which leads to one problem that some commercial electrode materials used in LIBs, especially graphite anode, cannot store sodium ions reversibly [9–17]. Thus, recently there have been many efforts put into developing suitable host materials capable of reversible, fast and substantial sodium-ion storage, of which several types of anode materials including carbonaceous materials, metal alloys, metal oxides, metal sulphides and their composites have been developed with improved electrochemical performances [9–17]. For carbon anodes, hard carbons and partially graphitic materials can afford a reversible capacity of 200–400 mA h g<sup>-1</sup> with a long cycle life [12,13], but their sodium-ion storage processes occurring mainly below 0.1 V (vs. Na/Na<sup>+</sup>) will cause the inevitable safety hazards owing to the plenty of sodium dendrites growth. Some metals (e.g. Sn, Sb, Co, Ni, Cu, Fe, Mo and Mn etc.) based compounds, and alloying P, Sn and Sb anodes with high theoretical specific capacities can store a great quantity of sodium ions via the conversion and/or alloying reactions [7,8,14–17]. Nevertheless, they possess the disadvantages

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of poor cycling stability, short cycle life, and unsatisfactory rate performance due to their drastic volume variation during the sodium-ion storage processes, which limit their further practical applications. Among the reported advanced anode materials,  $\text{TiO}_2$  with low cost, high safety, satisfied theoretical capacity ( $335 \text{ mAh g}^{-1}$ ), superior structural stability during electrochemical processes (less than 4% volume variation), appropriate (de-)insertion voltage potential ( $>0.3 \text{ V}$ ) and suitable sized tunnels for sodium-ion diffusion, is regarded as one of the most promising anode materials for SIBs [18–51]. In the past five years, various advanced  $\text{TiO}_2$  anode materials have been developed [18–51]. Xiong et al. firstly reported  $\text{TiO}_2$  as anodes in SIBs, and amorphous  $\text{TiO}_2$  nanotubes (TNTs) were prepared through an electrochemical anodization process, which showed a capacity of  $150 \text{ mAh g}^{-1}$  after 15 cycles at a current density of  $50 \text{ mA g}^{-1}$  [29]. Wang's group synthesized bicrystalline (anatase@ $\text{TiO}_2(\text{B})$ )  $\text{TiO}_2$  spheres via a solvothermal method, and found that they delivered a stable capacity of  $131 \text{ mAh g}^{-1}$  after 50 cycles at a current density of  $170 \text{ mA g}^{-1}$  [30]. Ji's group developed novel  $\text{TiO}_2$  nanocubes through a simple hydrothermal reaction, and discovered that they exhibited a capacity of  $176 \text{ mAh g}^{-1}$  after 40 cycles at a current density of  $84 \text{ mA g}^{-1}$  with an excellent rate performance, and a good capacity retention of 94.6% after 1000 cycles at a current density of  $1.68 \text{ A g}^{-1}$  [31]. Despite the above encouraging studies to date,  $\text{TiO}_2$  as one semiconducting material shows a large band gap (around 3.1 eV) with poor electrical conductivity and low sodium-ion diffusion coefficient, leading to its poor reversible capacity, unsatisfied cycle life and low initial Coulombic efficiency, and thus influencing its further applications in SIBs [32–51].

In order to further improve the sodium-ion storage and transport performances of  $\text{TiO}_2$ , plenty of effective methods have been dedicated to overcome these inherent drawbacks. One popular strategy is incorporating highly conductive carbons with unique structured  $\text{TiO}_2$ , such as carbon tuning yolk-like  $\text{TiO}_2$  (a capacity of  $242 \text{ mAh g}^{-1}$  after 200 cycles at  $167.5 \text{ mA g}^{-1}$ ) [32], carbon coated  $\text{TiO}_2$  hollow spheres (a capacity of  $185 \text{ mAh g}^{-1}$  after 500 cycles at  $167.5 \text{ mA g}^{-1}$ ) [33],  $\text{TiO}_2$ /carbon nanodots composites (a capacity of  $245.3 \text{ mAh g}^{-1}$  after 300 cycles at  $83.75 \text{ mA g}^{-1}$ ) [34], carbon wrapped olive-like  $\text{TiO}_2$  (a capacity of  $243 \text{ mAh g}^{-1}$  after 300 cycles at  $84 \text{ mA g}^{-1}$ ) [35],  $\text{TiO}_2$ -carbon nanofibers (a capacity of  $310 \text{ mAh g}^{-1}$  after 90 cycles at  $67 \text{ mA g}^{-1}$ ) [36], carbon coated  $\text{TiO}_2$  nanorods (a capacity of  $168 \text{ mAh g}^{-1}$  after 100 cycles at  $165 \text{ mA g}^{-1}$ ) [37], graphene coupled  $\text{TiO}_2$  (a capacity of  $263 \text{ mAh g}^{-1}$  after 200 cycles at  $50 \text{ mA g}^{-1}$ ) [38], carbon coated TNTs (a capacity of  $170 \text{ mAh g}^{-1}$  after 500 cycles at  $168 \text{ mA g}^{-1}$ ) [39],  $\text{TiO}_2$  embedded on carbon nanotubes (a capacity of  $210 \text{ mAh g}^{-1}$  after 100 cycles at  $100 \text{ mA g}^{-1}$ ) [40], and carbon coated  $\text{TiO}_2$  nanoparticles (a capacity of  $196 \text{ mAh g}^{-1}$  after 300 cycles at  $335 \text{ mA g}^{-1}$ ) [41]. These studies achieved the remarkable progresses for the application of  $\text{TiO}_2$  as anodes in SIBs, and proved that carbon additives can significantly enhance the electrochemical performances of  $\text{TiO}_2$ . However, the introduction of abundant carbons in  $\text{TiO}_2$  may lead to the mass growth of sodium dendrites or low active materials loading in the electrodes, and thus causes safety hazards or low energy densities, which can influence their further applications.

Heteroatom doping is another effective approach to improve the electron and phase structure of  $\text{TiO}_2$ , and thereby enhance its sodium-ion storage and transport performances [42–51]. Encouragingly, our preliminary work reported that Ni doped TNTs (Ni/TNTs) with an optimized doping concentration could effectively enhance the electrical conductivity and phase structure reversibility of  $\text{TiO}_2$  during the electrochemical processes, and thus achieved an obviously increased reversible specific capacity (a capacity of  $286 \text{ mAh g}^{-1}$  after 100 cycles at  $50 \text{ mA g}^{-1}$ ) [42]. Nevertheless, the obtained low initial Coulombic efficiency (57%) and unsatisfied cycle life still need to be further improved. Recently, it has been

established that N doping can substitute O in the  $\text{TiO}_2$  lattices, and thus facilitates the formation of oxygen vacancies, which can improve the electrical conductivity, sodium-ion storage and transport performances of  $\text{TiO}_2$  [36,49]. Therefore, a synergetic doping of Ni and N into  $\text{TiO}_2$  can take advantage of improved electrical conductivity and stable phase structure as well as enhanced sodium-ion diffusion kinetic performance, which would endow the  $\text{TiO}_2$  anodes with excellent sodium-ion storage and transport performances.

Inspired by above previous studies, we herein fabricated Ni and N co-doped TNTs (Ni-N/TNTs) via a simple sol-gel process with a subsequent alkali-thermal reaction, and final sintering in  $\text{NH}_3$  atmosphere. The as-prepared Ni-N/TNTs were used as an anode in SIBs for the first time, and showed a much improved initial Coulombic efficiency (65%), a high reversible specific capacity ( $303 \text{ mAh g}^{-1}$  at  $50 \text{ mA g}^{-1}$  with a capacity retention of 96% after 500 cycles), and a remarkable superior long cycle life at a high current density (8000 cycles at  $5 \text{ A g}^{-1}$ ). More significantly, the improvement mechanism for enhanced electrochemical performances was also discussed and revealed. Consequently, this work offers insights into fully understanding the importance of the optimizing relationship among the electronic structure, phase structure, sodium-ion diffusion kinetic performance, and the electrochemical performances of  $\text{TiO}_2$ .

## 2. Experimental

### 2.1. Sample synthesis

All chemicals including tetrabutyl titanate,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , ethanol, acetylacetone, NaOH and  $\text{HNO}_3$  were obtained from Sinopharm Chemical Reagent Co., Ltd. with AR grade, and used without additional treatments. The processes to synthesize Ni-N/TNTs were proceeded as follows. A mixed solution of  $0.46 \text{ g NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $20 \text{ mL}$  ethanol and  $2 \text{ mL}$  acetylacetone solution was stirred in a beaker for 1 h. Afterward,  $10 \text{ mL}$  tetrabutyl titanate and  $50 \text{ mL}$  ethanol were mixed, and then slowly dropped into the above obtained solution under the vigorous magnetic stirring. Subsequently, the formed mixture solution was aged for 48 h at the room temperature to obtain the gel, and then dried at  $70^\circ\text{C}$  under vacuum. Next, the prepared powders were transferred into a Teflon-lined stainless steel autoclave with a  $70 \text{ mL}$   $10 \text{ mol L}^{-1}$  NaOH aqueous solution. The powders in the autoclave was then placed in a sealed oven at  $120^\circ\text{C}$  for 24 h to form a nanotube structure, where the nanoparticles were etched into nanosheets by NaOH at first, and then self-coiled to nanotubes. The precipitates were obtained by the centrifugation, washed by  $\text{HNO}_3$ , deionized water and ethanol several times with an ion exchange process, and then dried at  $70^\circ\text{C}$  under vacuum overnight. Ni-N/TNTs were finally obtained by the thermal treatment at  $400^\circ\text{C}$  for 12 h in a flowing  $\text{NH}_3$  atmosphere. In addition, TNTs were prepared according to the above similar processes without the addition of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and the final atmosphere of thermal treatment is  $\text{N}_2$ . Ni/TNTs were also synthesized using the same procedures as applied in the synthesis of Ni-N/TNTs except that the atmosphere of thermal treatment is  $\text{N}_2$ .

### 2.2. Material characterizations

X-ray photoelectron spectroscopy (XPS) data were collected by the Thermo ESCALAB 250XI. Raman spectra were measured on the Renishaw inVia. X-ray diffraction (XRD) measurements were carried out on the Bruker D8 Advance. The field emission scanning electron microscopy (FESEM), transmittance electron microscopy (TEM), high resolution transmittance electron microscopy (HRTEM), and energy dispersive X-ray spectroscopy (EDS)

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