



Enhanced lithium-storage performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated with boron-doped carbon layer for rechargeable Li-ion batteries

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ABSTRACT

In this study, the B-doped carbon coating has been applied to enhance the lithium-storage performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material for Li-ion batteries. The designed B-doped carbon improved $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite (abbreviated as $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{@C-B}$) is successfully synthesized using a sol-gel approach followed by a microwave heating route. The XRD and HRTEM results demonstrate that the well-crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles are uniformly coated with the B-doped carbon layer with a thickness of about several nanometers. The existence of boron doping in the carbon layer is also confirmed by XPS and EDX mapping. Compared with the undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{@C}$, the $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{@C-B}$ anode shows superior electrochemical performances such as higher reversible capacity and better cycling stability. The enhanced lithium-storage property can be attributed to the doped boron element which could bring many amazing improvements on the carbon coating. Therefore, this novel strategy of B-doped carbon coating can be widely used to improve the electronic conductivity of other electrode materials for electrochemical energy storage.

1. Introduction

Nowadays, rechargeable Li-ion batteries with high-energy density and long cycle-life are extending to automotive and stationary energy storage applications such as hybrid electric vehicles (HEVs), electric vehicles (EVs), portable electronic devices and renewable energy integration [1, 2]. As one of the promising candidates, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode is regarded as the most attractive candidate for substitution of the commercial graphite in energy storage due to its good safety, low cost and excellent cycling stability [3, 4]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material can accommodate up to 3 Li^+ per formula unit, resulting in an end-phase $\text{Li}_7\text{Ti}_5\text{O}_{12}$ with a theoretical capacity of 175 mAh g^{-1} [5]. Furthermore, it shows a flat discharge profile at about 1.55 V (vs. Li^+/Li), which makes it safe by avoiding the formation of solid electrolyte interphase film [6, 7]. Unfortunately, the commercialization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode is restricted by two problems, including the bad electronic conductivity (ca. $10^{-13} \text{ S cm}^{-1}$) and sluggish Li^+ -ion diffusion (ca. $10^{-13}\text{--}10^{-9} \text{ cm}^2 \text{ s}^{-1}$) [8].

In this context, various approaches have been devoted in the past decades to solve these challenges. One general method is to prepare the nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles to reduce the Li^+ -ion diffusion pathway [9, 10]. Additionally, heteroatom doping such as Co^{2+} [11], V^{5+} [12] and Mg^{2+} [13], has an enhancing effect on the intrinsic

electronic conductivity for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material. The most effective approach is to construct the conductive networks by carbon materials [4, 7, 8, 14–16] amount the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. Especially, the carbon coating can greatly inhibit the growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles during the annealing process, prevent the direct contact of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with the electrolyte solution and improve the apparent electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Recently, it is reported that doping boron into the carbon layer can further enhance the electronic conductivity of the bulk [17]. However, to the best of our knowledge, there are rare reports to explain in-depth how B-doping can further enhance the electrochemical property of carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite so far.

Herein, the B-doped carbon is adopted to improve the lithium-storage performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for rechargeable Li-ion batteries. The designed $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{@C-B}$ composite has been synthesized through a sol-gel method followed by a microwave heating route. Compared with the undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{@C}$ electrode, the $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{@C-B}$ shows superior electrochemical performances such as higher reversible capacity and better cycling stability. This can be attributed to the doped boron element which could bring many amazing improvements on the carbon coating. As a result, the B-doped carbon coating is an effective approach to improve the apparent electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for electrochemical energy storage.

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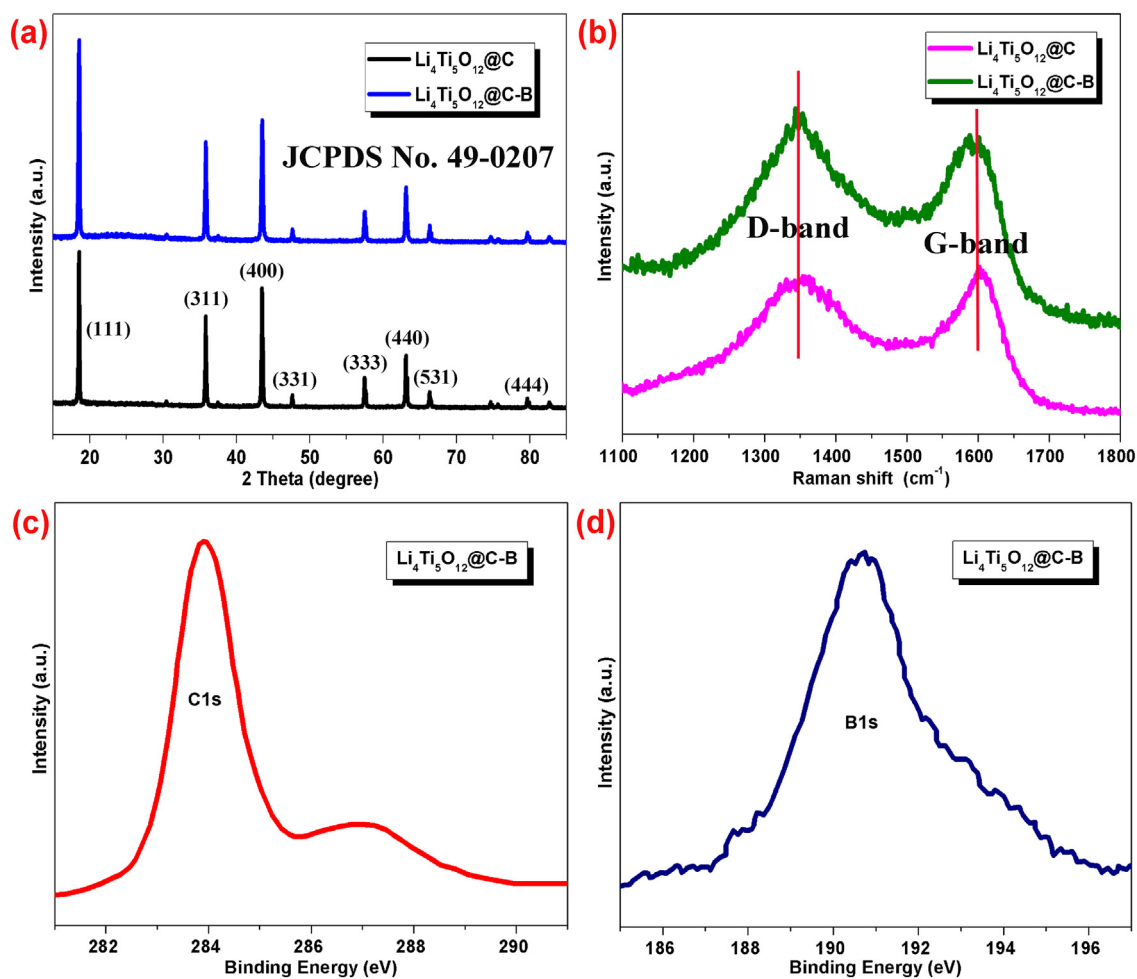


Fig. 1. (a) XRD patterns and (b) Raman spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{C}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{C-B}$; XPS spectra core level of (c) $\text{C}1\text{s}$ and (d) $\text{B}1\text{s}$ for the $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{C-B}$ composite.

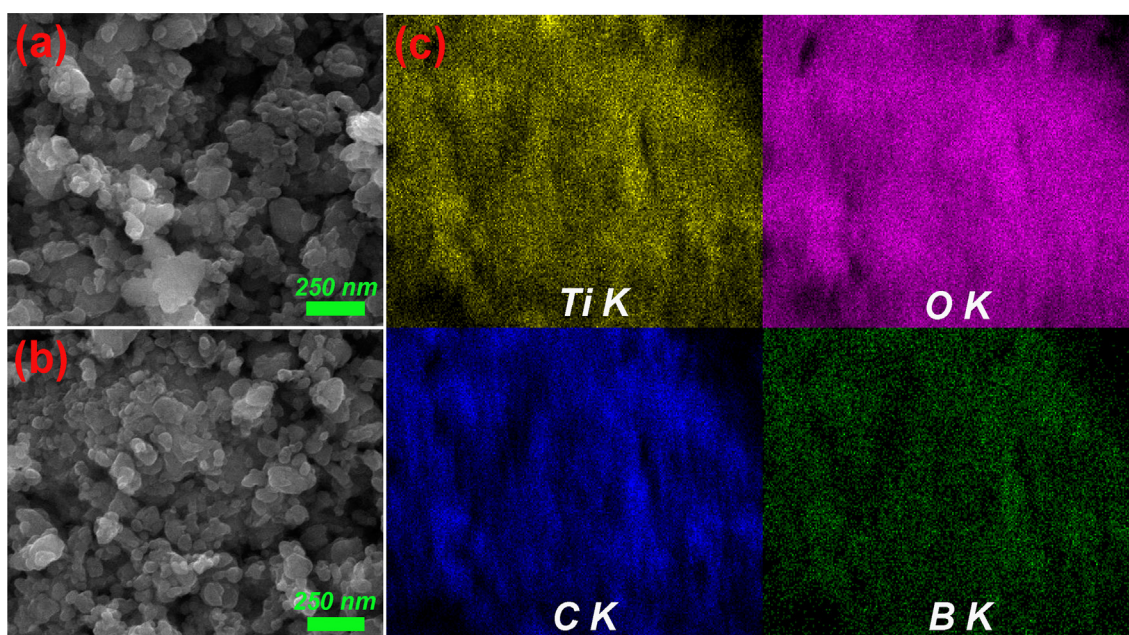


Fig. 2. SEM images of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{C}$ and (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{C-B}$; (c) The EDX elemental mapping images of $\text{Li}_4\text{Ti}_5\text{O}_{12}@\text{C-B}$ sample.

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