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Synthesis of lithium titanate nanorods as anode materials for lithium and sodium ion batteries with superior electrochemical performance

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HIGHLIGHTS

- $Li_4Ti_5O_{12}$ nanorods were successfully synthesized using TiO_2–B as titanium source and template.
- The synthesis mechanism of $Li_4Ti_5O_{12}$ nanorods was proposed.
- $Li_4Ti_5O_{12}$ is one of promising anode materials for lithium ion batteries and sodium ion batteries.

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ABSTRACT

$Li_4Ti_5O_{12}$ nanorods have been successfully synthesized via hydrothermal method using TiO_2–B as titanium source and template. Such $Li_4Ti_5O_{12}$ nanorods with sizes of 100–200 nm in diameter and 1–2 μm in length can be observed. The $Li_4Ti_5O_{12}$ nanorods exhibit high discharge capacity of about 101.1 mAh g^{-1} after 1000 cycles at 20C for the lithium ion battery anode. The $Li_4Ti_5O_{12}$ nanorods also show excellent sodium storage performance, which have a reversible capacity of approximately 131.6 mAh g^{-1} after 100 cycles at 0.1C. Based on the electrochemical performance, it is suggested that $Li_4Ti_5O_{12}$ nanorods have a great potential for lithium and sodium ion battery that are available as large-scale storage devices for applications such as automotive and stationary energy storage.

1. Introduction

Currently, demands for rechargeable batteries are increasing for applications in mobile devices, electric-powered transportation, and stationary energy storage. For these applications, lithium ion batteries (LIBs) have been the most promising system due to their long cycle life, high energy density, safety, and so on [1]. However, its success is still limited due to their high cost on dollars per kilowatt hour basis [2]. In this background, room-temperature sodium ion batteries (NIBs), which were originally investigated in parallel with lithium-ion batteries, have again aroused interest recently because of their low cost and the infinite sodium resources [3–5]. It is well known that there are many restrictions for these battery technologies, such as separators, electrolytes and electrode materials. Among all of those restrictions, anode material is a crucial factor for both LIBs and NIBs in electrochemical property and safety [6–8]. The Na ion has a larger ionic radius than that of the Li ion, making it more difficult to identify suitable anode materials for NIBs. Recently, extensive researches have been centered on anode materials, mainly carbon-based composites [9,10]. The graphite, which is the most common anode for Li-ion batteries, is unavailable for a Na^+-insertion host [11]. It was found that hard carbon is a suitable anode material for Na-ion batteries because it has large interlayer distance and disordered structure [12]. However, as the sodium storage voltage in hard carbon is relatively low and near zero versus Na^+/Na, this would result in sodium metal deposition on its surface in an improper operation or during fast charging, giving rise to major safety concern [3]. Most notably, the operating voltage close to the electroplating potential of Li or Na that raises concern about a Li-metal or Na-metal dendrite formation, which triggers internal short, especially at high rates [13,3]. Therefore, it is desirable to develop other new anode materials with relatively high storage voltage. Spinel $Li_4Ti_5O_{12}$ has been considered as a promising anode material for LIBs application. Recently, this well-known 'zero-strain' anode material for Li-ion batteries has

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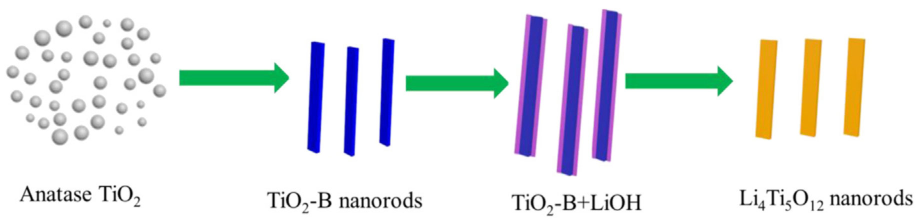

Fig. 1. Schematic illustration for the formation of $Li_4Ti_5O_{12}$ nanorods.

also been reported for Na-ion batteries. Liu et al. prepared tiny $Li_4Ti_5O_{12}$ nanoparticles embedded in carbon nanofibers using electrospinning method and exhibited a reversible capacity of approximately 162.5 mAh g^{-1} at 0.2C during the first 100 cycles for sodium ion battery anode [14]. $Li_4Ti_5O_{12}$ shows an average storage voltage of approximately 0.9 V (vs. Na/Na^+) and theoretical capacity of 175 mAh g^{-1}, according to the following three-phase separation mechanism [3,4].

$$2Li_4Ti_5O_{12} + 6Na^+ + 6e^{-1} \rightarrow Li_7Ti_5O_{12} + LiNa_6Ti_5O_{12}$$

Similar to the anode for Li-ion batteries, the relatively higher storage voltage versus Na metal makes spinel $Li_4Ti_5O_{12}$ anode for Na-ion batteries intrinsically much safer than hard carbon anode.

Previously, a great many interesting nanostructures of $Li_4Ti_5O_{12}$ have been prepared, including nanorods [15], nanowires [16] and nanotubes [17]. Typically, $Li_4Ti_5O_{12}$ nanorods have been demonstrated to be capable of providing more channels for efficient electron transportation than particle-based electrodes [15]. It is well known that nanostructured TiO_2 can serve as a structure framework for fabricating the titanate-based compounds with desirable morphologies, which is hardly generated from the conventional synthesis methods using the bulk materials [18,19]. Specifically, $Li_4Ti_5O_{12}$ nanowires and nanotubes have been fabricated using TiO_2 nanowires and nanotubes as a precursor [15,16], suggesting that different shapes of $Li_4Ti_5O_{12}$ rely on the precursor structure. Among various polymorphs of TiO_2, TiO_2–B with a relatively open tunnel structure and large interlayer spacing can provide a better electrochemical activity, which is also considered as a suitable active material for lithium storage and sodium ion intercalation [20,21]. Considering that the synthesized $Li_4Ti_5O_{12}$ using TiO_2–B as titanium source and template might have excellent electrochemical activity. So, it would be of great interest to fabricate $Li_4Ti_5O_{12}$ using TiO_2–B as titanium source and template with excellent electrochemical performance in LIBs and NIBs.

Here, we report a hydrothermal synthesis process for the fabrication of $Li_4Ti_5O_{12}$ nanorods using TiO_2–B nanorods as titanium source and template, which has not been reported in previous paper. Benefiting from the one-dimensional (1D) nanostructure with large contact surface areas with the electrolyte and significantly shortened transport lengths of lithium ions, the as-prepared $Li_4Ti_5O_{12}$ nanorods show superior electrochemical performance in terms of specific capacity, cycling performance, and rate performance, when used as anode materials for lithium and sodium ion batteries.

2. Experimental

2.1. Synthesis of TiO_2–B nanorods

The TiO_2–B nanorods were prepared via hydrothermal process. In a typical procedure, 1 g of TiO_2-anatase and 0.1 g cetyltrimethyl

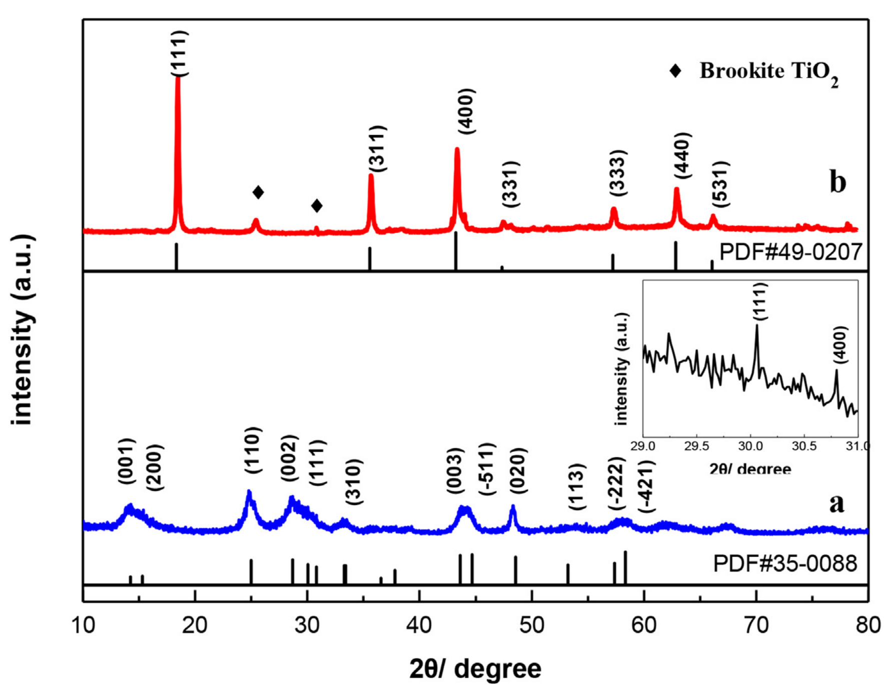

Fig. 2. XRD patterns of TiO_2–B nanorods (a) and $Li_4Ti_5O_{12}$ nanorods (b).