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Porous TiO_2 urchins for high performance Li-ion battery electrode: facile synthesis, characterization and structural evolution

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ABSTRACT

Porous TiO_2 urchins have been synthesized by a hydrothermal route using TiO_2/oleylamine as precursors with subsequent ion-exchange and calcination. The resultant material consists of porous spherical cores and nanochains-constructed shells with straight channels. Electrochemical measurements indicate the TiO_2 urchins deliver superior lithium storage capability in terms of high capacity (206.2 mA h g^{-1} at 0.5 C), superior rate performance (94.4 mA h g^{-1} at 20 C) and stable cycling stability (94.3% capacity retention over 1000 cycles at 10 C versus the third cycle). Such performance enhancement is mainly due to the increased electrode/electrolyte contact interface, reduced Li^+ diffusion pathways and improved mass transfer of electrolyte in the unique 3D interconnected hierarchical network. In addition, ex-situ XRD, SEM and TEM analyses further reveal high structure integrity of the porous TiO_2 urchins during the electrochemical lithiation, leading to enhanced lithium storage stability. Moreover, we detected that some anatase nanocrystals evolved into electrochemically inactive Li_1TiO_2 dots (~10 nm in size) during long-term electrochemical cycling. Our findings provide more insights for better understanding of the structure evolution and capacity decay mechanism in porous TiO_2 nanostructures.

1. Introduction

Lithium ion batteries (LIBs) have played a crucial role in powering portable electronic devices in the past two decades [1]. They are now being further improved for emerging energy-storage applications in (hybrid, plug-in) electric vehicles, smart grids and intermittent renewable energies from solar and wind. Despite their commercial success, improvements in power, cost, durability and safety are still highly desired [2]. Among various electrode materials, TiO_2 has attracted considerable interest as alternative anode because of its high abundance, nontoxicity, high activity, small volume changes upon Li^+ uptake/removal, and absence of solid-electrolyte interphase layer for better operation safety [3–5].

The electrochemical performance of TiO_2 strongly relies on its polymorphs [6,7], crystallinity [8], grain size [9], morphology [10,11], porosity and composition [12,13], which can determine the Li^+ diffusion and electron transport. In particular, much work has been devoted to the controllable synthesis and electrochemical characterization of various TiO_2 nanostructures with tunable morphologies [14–16] and compositions [17,18], either in pure phases or mixed polymorphs [19–25], as well as nanocomposites hybridized with carbon nanotubes [26], and reduced graphene oxides [6,27–29]. Among these, urchin-like TiO_2 has gained much attention due to its unique structure and electrochemical performance [30–32]. For example, Park et al. synthesized urchin-like rutile TiO_2 submicron spheres composed of single-crystalline nanorods. After coating with amorphous carbon layer, it could deliver a reversible capacity of 165.7 mA h g^{-1} after 100 cycles at 0.2 C [33]. Meanwhile, porous or hollow TiO_2 nanostructures [34–43] can offer more active sites for Li^+ storage due to their high surface area, good accommodation of volume change during (de)lithiation and shortened pathways for fast Li^+ and

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electron transport, leading to enhanced electrochemical performance. Porous TiO_2 nanostructures with well-defined morphologies and pore structures can be prepared by template-directing approaches. For example, TiO_2 nanocages with uniform shells and tunable sizes have been fabricated by using Cu_2O polyhedra as sacrifice templates [44]; however, conventional template-based synthetic routes may require the removal of hard- or soft-templates in the following steps, leading to increased synthetic costs and environmental concerns.

In addition, recent study discloses mesoporous TiO_2 material can undergo evident structure degradation and capacity loss upon electrochemical cycling in opposition to what is expected for a long time [45]. The structure change has been primarily ascribed to irreversible lattice swelling/shrinkage caused by Li^+ concentration gradient in porous framework during initial (de)lithiation. Therefore, design of rational pore structure and deeper understanding of structure evolution of porous TiO_2 electrode during cycling are very important and highly desired.

In this work, we report the designed synthesis of porous TiO_2 urchins constructed from nanochains using TiO_2/oleylamine composite as precursor via an in-situ self-sacrificing template method. The resultant TiO_2 material exhibits superior electrochemical performance as anode for LIBs. Post-mortem characterizations validate high structure stability of the TiO_2 material during cycling. More importantly, we observe the evolution of trace 10-nm Li_1TiO_2 crystalline dots that are randomly distributed within the TiO_2 host after long-term cycling. Our findings can provide more insights into the deeper understanding of the high Li^+ storage capability of porous TiO_2 nanostructures as well as their capacity decay mechanism upon cycling.

2. Experimental

2.1. Materials synthesis

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

Amorphous TiO_2/oleylamine spheres were synthesized referring to literature work [46] with little modification (oleylamine was used as surfactant) and served as precursor for following experiments.

Titanate urchins were prepared by hydrothermal reaction of TiO_2/oleylamine precursor in an alkaline solution. In a typical procedure, 0.2 g of precursor was dispersed in 40 mL of H_2O and 20 mL of ethanol containing 12 g of NaOH. Then, the suspension was transferred into an autoclave (with a PTFE liner, 100 mL capacity) and heated at 160 °C for 12 h. The resultant white precipitates were rinsed with ethanol and distilled water, and dried at 80 °C in air for 12 h. Protonated titanate (H-titanate) sample was obtained by soaking the titanate sample in 0.12 M of HCl solution for 2 h to exchange the interlayer Na^+ with H^+ and then thoroughly rinsed with deionized water and dried at 80 °C for 12 h in air.

Porous TiO_2 urchins were obtained after thermal treatment of the H-titanate sample at 450 °C for 2 h in air with a heating rate of 2 °C min^{-1}.

2.2. Material characterizations

Crystal structures of the samples were analyzed by powder X-ray diffraction (XRD) patterns recorded on a Bruker Diffractometer operated at 40 kV and 40 mA with Cu Kα radiation. Rietveld

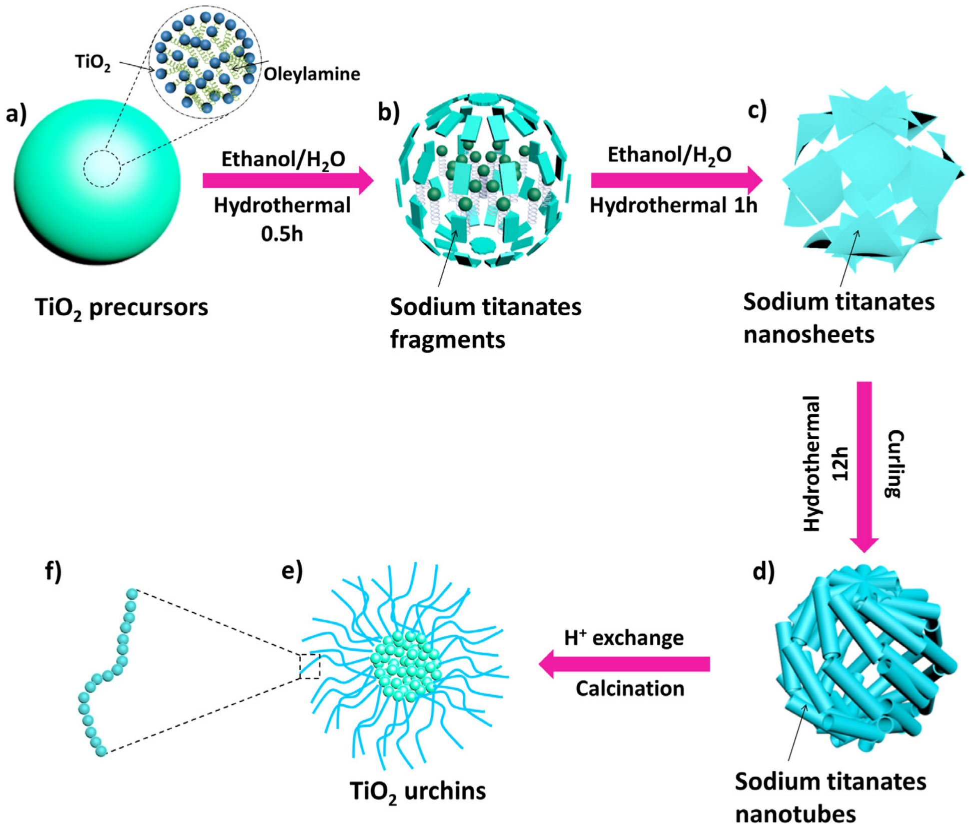

Fig. 1. Schematic illustration of the fabrication process of the porous TiO_2 urchins. (a) TiO_2/oleylamine composites, (b) out-diffusion of oleylamine from precursor and partial conversion of TiO_2 nuclei into titanate fragments during hydrothermal process, (c) titanate nanosheets-assembled flowers, (d) titanate nanotubes-constructed urchins, (e) porous TiO_2 urchins, (f) magnified portion of a TiO_2 nanochain constructed from connected nanocrystals.