Catalysis Communications 47 (2014) 32–35

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Hydrothermal synthesis of anatase and brookite nanotubes with superior photocatalytic and Li^{+} insertion/extraction performances

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ARTICLE INFO

Article history:
Received 22 October 2013
Received in revised form 9 December 2013
Accepted 17 December 2013
Available online 21 December 2013

Keywords:
Anatase
Brookite
Nanotube
Photocatalysis
Lithium battery

ABSTRACT

Anatase and brookite TiO_2 nanotubes were prepared separately with hydrothermal method in aqua media by simply adjusting the electrolyte in the system. Both kinds of nanotubes show superior photoactivity as well as excellent performance in lithium batteries, due to their larger surface areas and the unique structure. It is noted that for brookite, this is the first time that a high discharge capacity of 372 $mAh \cdot g^{-1}$ has ever been reported.

1. Introduction

Nowadays one-dimensional TiO_2 nanomaterials have attracted considerable attention because of their unique properties and potential applications in photocatalytic, photovoltaic, and electrochemical fields as well as lithium batteries [1–3]. Various titanate nanotubes can be prepared from P25 or commercial anatase when they were hydrothermally treated under certain temperature in high concentrated alkali solution followed by acid washing [4]. However, the poor photocatalytic property of titanate limits its application in photocatalysis. To achieve superior photocatalytic performances, literature works lately attempt to transform the as-prepared titanate nanotubes to TiO_2 phase through calcining them under high temperatures [5,6]. Nevertheless, subjecting to the Ostwald Step Rule and the significantly internal stress, some serious problems occur in obtaining perfect TiO_2 nanotube morphology as the fragile nanotubes are practically prone to break down into small particles during lattice transition at high temperatures. So far, the preparation of perfect anatase nanotubes is still a great challenge. Further, due to its low asymmetric and complex structure [7,8], brookite is much more difficult to be prepared in nanotubes. Although the synthesis of pure brookite nanotubes has been reported once before [9], the only instance requires accurate pH control, which involves complex manipulation and is practical low-probability to successfully duplicate. In our work, aqua ammonia was used as the reaction solvent, which provides an appropriate media for brookite formation under a quite wide range of NaCl concentration. As a result, the production of pure brookite is highly guaranteed and the experimental operation is greatly simplified. What's more, the potential application of the only brookite nanotube was not involved in the published work at all [9].

In our previous work [10,11], a facile method was developed to hydrothermally prepare either anatase or brookite TiO_2 from amorphous titanate precursor in aqua ammonia media. By tuning the concentration of the electrolyte, we can selectively get anatase, brookite or their mixtures in different morphologies. Inspired by the previous works, we speculate that if the phase transition from titanate into TiO_2 can be carried out as mild as possible in aqua ammonia media, it is likely to prepare perfect anatase and brookite nanotubes from the desired well-crystallized titanate nanotubes by maintaining its original nanotube morphology.

In this work, we firstly report a preparation method of anatase and brookite nanotubes in an aqua ammonia media by simply tuning the electrolytes under hydrothermal treatment. Interestingly, both anatase and brookite nanotubes show superior photocatalytic activity as well as good Li^{+} intercalation/deintercalation properties.

2. Experimental

2.1. Synthesis of titanate nanotube

The titanate nanotube was prepared with commercial P25 and NaOH (10 M, 75 ml). The mixture of P25 and NaOH was transferred into an autoclave (100 ml) and treated at 120 °C for 24 h. Then the obtained white powder was separated and washed with 0.1 M HCl and deionized water for several times till a pH of 7 was reached. The powder was then dried under infrared light overnight to obtain the

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http://dx.doi.org/10.1016/j.catcom.2013.12.017

final product, which was characterized as titanate nanotube and referred to as TNT.

2.2. Synthesis of anatase and brookite nanotubes

0.5 g as-synthesized TNT was put into 75 ml aqua ammonia, then a certain amount of NaCl (0–0.5 M) was added into the mixture under stirring. The mixture was then transferred into an autoclave and treated at 220 °C for 72 h. The obtained white powder was washed with 0.1 M HCl and deionized water for several times till a pH of 7 was reached, then the powder was dried under infrared light overnight. The final product can be anatase nanotube (ANT) or brookite nanotube (BNT), according to the amount of NaCl used.

3. Results and discussion

The crystalline phases of titanate nanotube and its hydrothermally treated products in aqua ammonia with various concentrations of NaCl were detected by XRD technique (Fig. 1). The titanate nanotube precursor shows a typical structure of layered titanate ($Na_2Ti_2O_5 \cdot H_2O$, PDF# 47-0124), which possesses typical layered structure formed by edge-sharing, with cations like Na^+ embedding in the interspaces of host layers [12,13]. While washing with HCl, $H_{2-x}Na_xTi_2O_5 \cdot H_2O$ would be formed through the exchange of Na^+ by H^+. After $H_{2-x}Na_xTi_2O_5 \cdot H_2O$ was hydrothermally treated, the typical peak at 9.8° disappeared completely; meanwhile, the peaks which belong to anatase (PDF# 21-1272) at 25.3, 36.9, 37.8, 38.6 and 48.0° appear, which suggests the phase transition from titanate to anatase. While adding NaCl electrolyte (0.05 M) into the hydrothermal system, a new peak at 30.8° appeared. This peak does not overlap with any peaks of anatase or other TiO_2 polymorphs, so the appearance of this peak demonstrates the production of brookite phase TiO_2 (PDF# 29-1360). The sample obtained here is the mixture of brookite and anatase TiO_2. When increasing the concentration of NaCl from 0.05 M to 0.25 M, the typical brookite peak at 30.8° intensifies accordingly, i.e., the content of brookite in the mixture increases gradually. Generally, the ratio of XRD peaks of brookite at 30.8° and 25.3° is ca. 9:10, while the presence of anatase would increase the relative intensity of the XRD peak at 25.3° and cause the ratio of these two peaks less than 9:10. The computed result shows that the ratio of XRD peak at 30.8 and 25.3° is almost 9:10 for the TiO_2 product obtained from the 0.10 M NaCl aqua ammonia, which is consistent with the ratio presented in the standard PDF of brookite (PDF# 29-1360). Thus, pure brookite TiO_2 was produced with a NaCl concentration of 0.10 M. Continue increasing the concentration of NaCl to 0.25 M lead to the production of mixed brookite and titanate [14]. Academically, by prolonging the hydrothermal time, the phase transition from titanate into TiO_2 can go on completely [10].

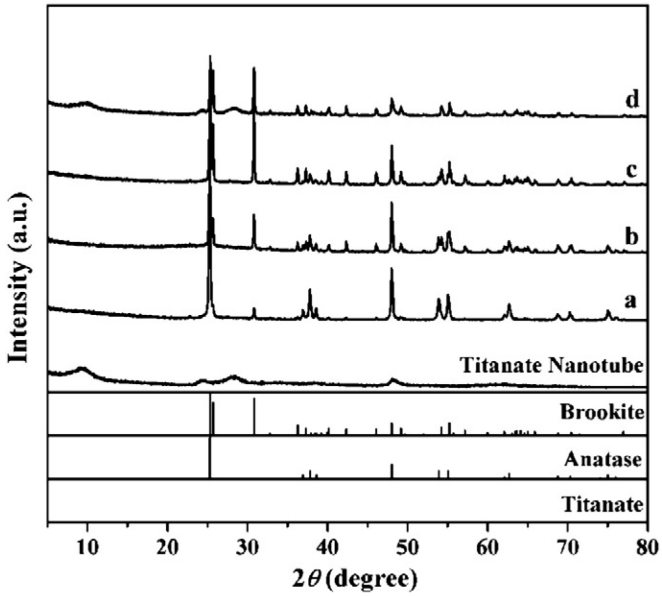

Fig. 1. XRD patterns of as-prepared titanate nanotube and samples prepared in aqua ammonia with various NaCl concentrations, (a) 0 M, (b) 0.05 M, (c) 0.10 M and (d) 0.25 M. The bar charts show the standard PDF patterns of titanate, anatase and brookite.

Briefly, layered titanate has typical capability of exchanging its cations in the interlayers with surrounding counterparts [15], of which H^+ is a good candidate with priority to exchange. When washing with HCl, the Na^+ in the interlayers of $Na_2Ti_2O_5 \cdot H_2O$ was exchanged with H^+, which leads to the crimping of titanate layers and the formation of $H_{2-x}Na_xTi_2O_5 \cdot H_2O$ nanotube. Subsequently, hydrothermal treatment in the aqua ammonia leads to a Na^+ deintercalation process and a dehydration process. Generally, the dehydration process between the layers that induces the closure of layered structure leads to the formation of anatase. Nevertheless, the adjacent Na^+ ions interfere with the closure process, which delays some of the structural transformation locally. Consequently, the asynchronous closure of titanate layers leads to the distortion of lattice structure, which results in the formation of brookite. Therefore, brookite TiO_2 was obtained as the predominant phase or even the only phase at moderate concentration of Na^+ (~0.1 M). Further increasing the concentration of Na^+ causes more Na^+ residual in the interlayer of titanate, which is adverse to the hydroxyl condensation (i.e., the dehydration process). Hence, the layered structure of titanate was maintained at high concentration of NaCl even after a long time hydrothermal treatment.

Fig. 2 shows the TEM images of TNT, ANT and BNT nanotubes. TNT exhibits uniform hollow tube-like morphology, with length of about tens of micrometers (Fig. 2A). As labeled in Fig. 2B, the outer diameter of a typical nanotube is ca. 10.2 nm, and corresponding inner diameter is ca. 6.2 nm. ANT presents a clearly tube-like morphology (Fig. 2C&D). However, the length of ANT (ca. 200–300 nm) is much less than that of TNT, indicating that some breakage still happened during the hydrothermal treatment. Nevertheless, the nanotube profile is perfectly remained. Similar results can be reached in the case of BNT. Nanotubes with length of 200–300 nm interweave together to form mesh-like plate (Fig. 2E). A closer observation shows that the nanotube of BNT has a clearly hollow structure (Fig. 2F). The selected area electron diffraction (SAED) patterns of ANT (Fig. 2G) and BNT (Fig. 2H) show a series of rings, which correspond with the nanocrystalline anatase and brookite, respectively. These results confirm the formation of crystal nanotubes of anatase and brookite again.

According to BET analysis, the S_{BET} of TNT, ANT and BNT nanotubes is 109.9, 103.4 and 95.1 $m^2 \cdot g^{-1}$, respectively, much larger than the anatase nanoparticle and brookite nanoflower synthesized with a just similar process before [10]. The minor change of S_{BET} between TNT and ANT&BNT also demonstrated the structural stability of nanotubes.

A frequently used target organic, acid orange 7 (AO7, 10 mg/l), was used to estimate the photoactivity of the ANT and BNT nanotubes under UV light (300 W high-pressure Hg lamp, the strongest emission at 365 nm). Degradation of AO7 with a commercial anatase TiO_2 ($S_{BET} = 73.2\ m^2 \cdot g^{-1}$) was also checked for reference. Fig. 3 shows the degradation of AO7. ANT shows the highest photocatalytic activity. The AO7 was degraded by 88.7% in first 30 min and became totally colorless in 60 min with ANT. BNT shows a comparable photocatalytic activity, which degraded 84.1% AO7 in 30 min, and completely in 90 min. Meanwhile, the degradation of AO7 with referential commercial anatase was only 65.7% in 30 min, which is much lower than those with ANT and BNT. TNT, as a titanate precursor, shows the lowest activity. Only 86.8% AO7 was degraded even after 120 min UV irradiation. One-dimensional structures like nanobars and nanotubes have been reported to show much better performances than those of bulked