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Effect of alkalinity on the hydrothermal synthesis of Li_2ZrO_3 nanotube arrays

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Abstract High aspect-ratio Li_2ZrO_3 nanotube (NT) layers were obtained by hydrothermal synthesis in LiOH solution using anodic ZrO_2 NT arrays as templates. Characterizations of SEM, XRD, and TEM were performed. The results showed that tetragonal Li_2ZrO_3 NTs arrays containing a little monoclinic ZrO_2 can be obtained using this simple method. The mean diameter of the NTs is approximately 150 nm. The alkalinity of hydrothermal solution was proved to have significant effect on the formation of the Li_2ZrO_3 NT arrays. Under different alkalinity, different growth mechanisms dominated the formation of the nanotubular layers.

Introduction

In recent years, Li_2ZrO_3 ceramics have been extensively studied for their applications as electronic devices in batteries and breeder materials for nuclear fusion reactors [1, 2]. Moreover, Li_2ZrO_3 is a promising candidate for CO_2 sorption at high temperature [3, 4]. Separation of CO_2 is a significant industrial technology in a lot of fields such as enhancing oil recovery, preparing hydrogen from methanol or methane, etc. [5, 6]. The main challenge is to find a Li_2ZrO_3 acceptor with fast kinetics, excellent capture capacity and structure stability under the high working temperature. As we know, the microstructure can influence the performance of some materials. Therefore, synthesis of Li_2ZrO_3 ceramic with nano-scaled size has become a promising research field [7–9]. Comparing to the nanoparticle-shape Li_2ZrO_3, the nanotubular arrays would be more proper for CO_2 absorbent due to their large surface area, improved kinetic property and high regeneration ratio. In addition, the agglomeration and losing of porosity could be prevented during the regeneration process for the Li_2ZrO_3 nanotubes (NTs) acceptor. As we know, a higher temperature (above 700 °C) is generally requested for the regeneration of Li_2ZrO_3 from Li_2CO_3. And the agglomeration of particles is inevitable during the sorption–desorption cycles [10]. The Li_2ZrO_3 layers with a NT array configuration would be more stable in this process.

As reported, solid-state reaction is the most common synthesis route for the Li_2ZrO_3 ceramic. However, a high temperature (850–1000 °C) and long reaction time is usually required [11]. And it is difficult to control the particles size. Therefore, preparation of nano-scaled Li_2ZrO_3, especially those with nanotubular structure remains a challenge in the materials science. The hydrothermal method is known for the controllable synthesis route of high-purity materials at low temperatures [12, 13]. Up to now, the formation of barium titanate [14] and barium strontium titanate [15] NTs by hydrothermal reaction have been well studied. But little reports focus on the in situ synthesis of Li_2ZrO_3 NTs. In this article, we employed anodized ZrO_2 NTs as templates to prepare the Li_2ZrO_3 NT arrays on Zr substrates by hydrothermal route. In order to thoroughly understand the growth mechanism, different hydrothermal conditions were used. This work is helpful for preparation of other zirconate NTs in the future.

Experiments

Zirconium foils (10 × 7 × 0.5 mm) with a purity of 99.7% were used for anodization to obtained ZrO_2 NT

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arrays. Electrolytes in the anodizing process were formamide and glycerol (GE) (volume ratio 1:1) containing 0.5 wt% NH_4F. The anodization details could be found in our early study [16]. The as-synthesis ZrO_2 NT layers were annealed at 400 °C for 3 h to obtain a crystalline structure [16]. Then the samples were held in the center of Teflon reaction vessels. The LiOH solutions prepared by CO_2-free deionized water filled to 70% of the vessels. Then, the hydrothermal vessels were placed into an oven heated to 200 °C, and holding this temperature for 4 h. Finally, the samples were removed out, rinsed in CO_2-free deionized water and dried. For comparison, LiOH solution with concentrations of 0.01, 0.05, 0.1, and 0.5 M were used under the same hydrothermal conditions mentioned above.

Microstructure of the NTs was observed by a field emission scanning electron microscope (FESEM, LEO-1530, LEO, Oberkochen, Germany). The cross-section images and selected area electron diffraction (SAED) patterns were obtained by a high resolution transmission electron microscope (HRTEM, JEOL-2010, Japan). Crystal structures of the specimens were determined by X-ray diffraction (XRD 2500, Rigaku, Tokyo, Japan).

Results and discussion

Figure 1a shows the FESEM image of the as-prepared ZrO_2 templates anodic grown on Zr substrates. The layers consist of highly ordered NT arrays with an open porous structure at the top end. The diameters of the NTs range from 150 to 200 nm with smooth and straight walls (inset of Fig. 1a). Figure 1b, c, d show the FESEM images of the NT arrays obtained after hydrothermal treatment of ZrO_2 templates in solutions with different LiOH concentration. At a lower LiOH concentration (0.01 M), no distinct changes can be found on the samples. Morphology of the layers is nearly the same to the as-prepared ZrO_2 NTs arrays (SEM images are omitted). Minor differences are revealed for the samples obtained in 0.05 M LiOH solutions (Fig. 1b). The tubal wall becomes a little thicker and a quantity of particles is attached on the outer side of the walls. After hydrothermal treatment of the templates in 0.1 M LiOH solutions, an ordered porous structure still existed in the layer. But evident distinctions are displayed. The wall of the NTs becomes thicker and the spacing between NTs is not apparent (Fig. 1c). It could be explained by the crystal cell expansion during the in situ

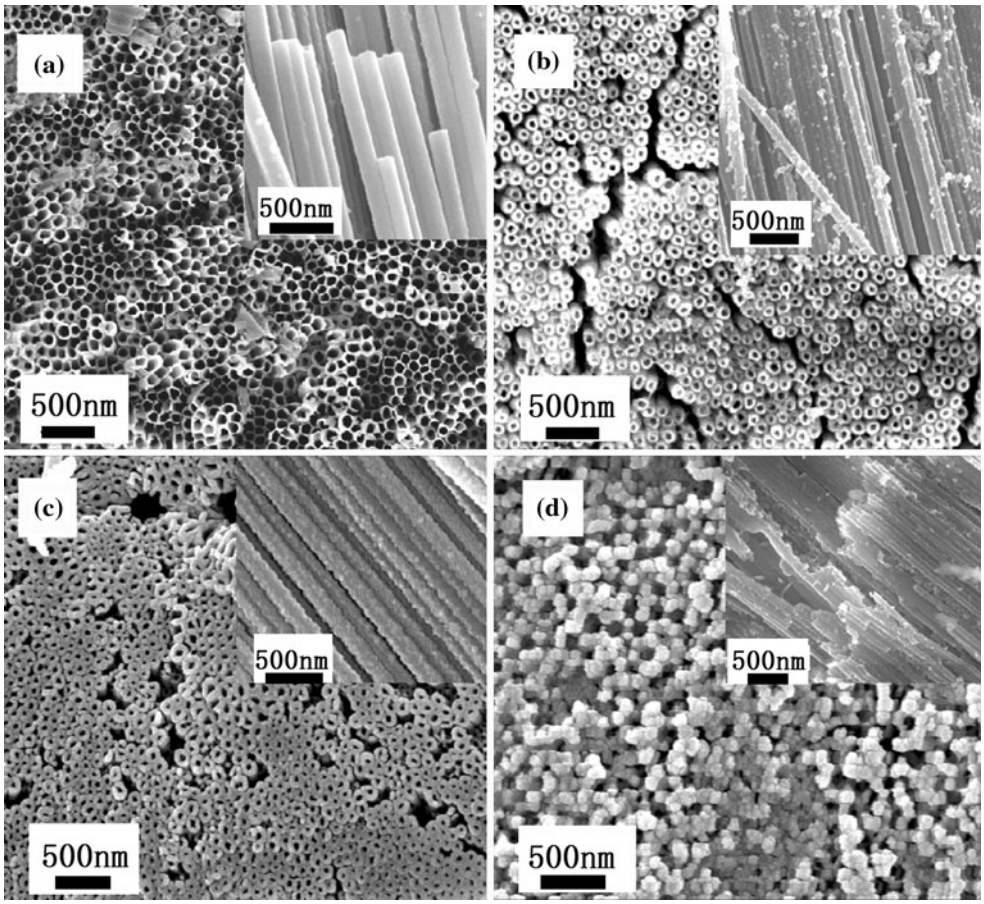

Fig. 1 SEM images of anodized ZrO_2 NTs (**a**), and ZrO_2 templates after hydrothermal reaction in 0.05 M (**b**), 0.1 M (**c**), and 0.5 M (**d**) LiOH solution at 200 °C for 4 h

formation of Li_2ZrO_3 NTs [14, 15]. Li^+ are transmitted into zirconia lattice and react with the templates by the assisting of high temperature and pressure in hydrothermal vessel. The reaction formulation is as follow:

$$2LiOH + ZrO_2 \rightarrow Li_2ZrO_3 + H_2O \quad (1)$$

With addition of 0.5 M LiOH in hydrothermal vessels, the obtained NT arrays collapse severely on the walls and the surface of the layer is overlaid by nano-scaled particles. Only a few pores can be found under the grainy layer (Fig. 1d). This is not favorable on their application for the un-stability and low porosity.

X-ray diffraction patterns of the as-synthesized materials under different alkalinity are shown in Fig. 2. Diffraction peaks marked with triangles in the patterns can be assigned to the tetragonal Li_2ZrO_3 with some indication of other crystalline by-products such as lithium carbonate (marked with tetragons) or monoclinic ZrO_2 remain (marked with rotundities). Evidently, the intensity of the peaks for crystalline Li_2ZrO_3 increases along with the enhancing of hydrothermal alkalinity (Fig. 2a: 0.01 M, b: 0.05 M, c: 0.1 M, and d: 0.5 M). A fairly pure Li_2ZrO_3 NTs layer can be obtained in the solutions with LiOH concentrations above 0.1 M. However, the higher alkalinity (0.1 and 0.5 M) gives rise to the formation of Li_2CO_3 impurity in the layers. Weak peaks for monoclinic ZrO_2 indicate a little partial ZrO_2 remain in the templates.

The results presented above suggest that Li_2ZrO_3 NT arrays can be achieved by hydrothermal reaction of ZrO_2 NTs and LiOH solutions. The content of Li_2ZrO_3 in the layers increases with the hydrothermal alkalinity (0.01–0.5 M LiOH). But the ordered porous structure would be damaged under the LiOH concentration higher than 0.1 M. Considering both the purity and morphology of the obtained layer, 0.1 M LiOH solution is preferable to the synthesis of the Li_2ZrO_3 NT arrays. TEM observation is also performed on the specimens obtained in 0.1 M LiOH solution. In contrast to the as-prepared ZrO_2 NT (inset of Fig. 3a), the Li_2ZrO_3 NT gets thicker and rougher after hydrothermal reactions (Fig. 3a). This agrees well with the SEM images. Fig. 3b shows the HRTEM image and SAED patterns of an isolated Li_2ZrO_3 NT. The diffraction spots (inset of Fig. 3b) provide evidence that the isolated Li_2ZrO_3 NT has a single crystal structure. The *d* spacing estimated from the lattice fringes of the HRTEM pattern is about 0.33 nm (Fig. 3b),

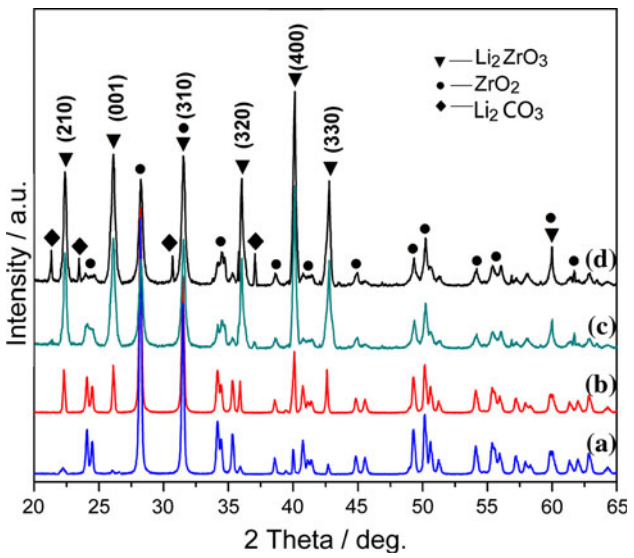

Fig. 2 XRD patterns of the as-prepared NTs arrays obtained in 0.01 M (*a*), 0.05 (*b*), 0.1 M (*c*), and 0.5 M (*d*) LiOH solution at 200 °C for 4 h

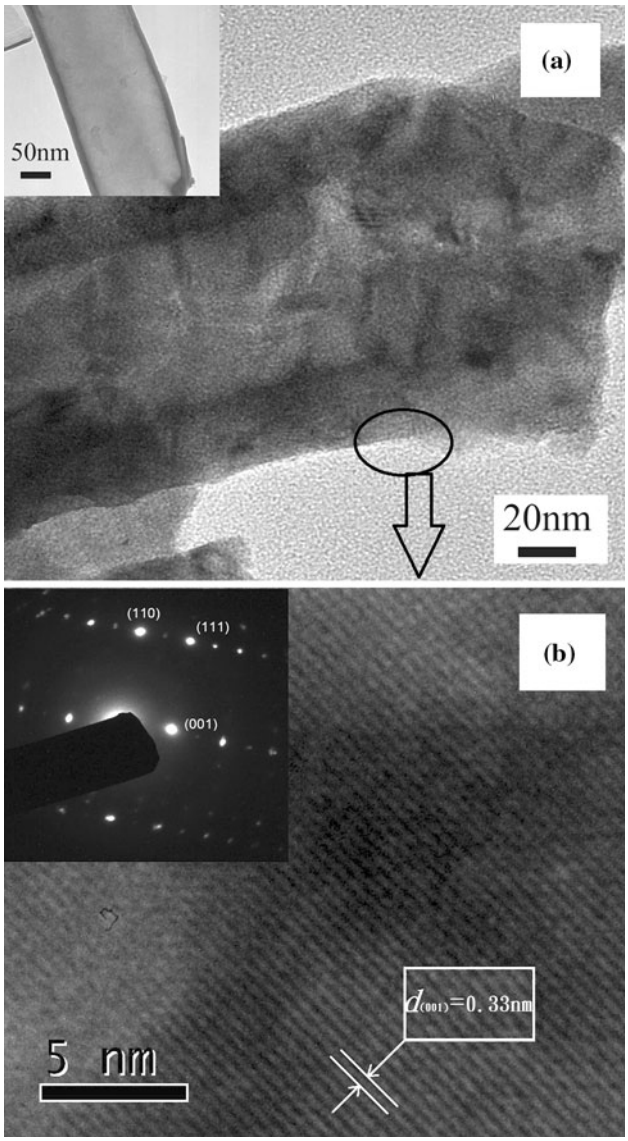

Fig. 3 **a** TEM images of Li_2ZrO_3 NT obtained in 0.1 M LiOH solution (with anodized ZrO_2 NT in the *inset*), and HRTEM images of (**a**), *inset* corresponding SAED pattern

which is close to the {001} inter-planar spacing of tetragonal Li_2ZrO_3 crystal, 0.34 nm (PDF Card No. 20-647).

Deduced from the experimental results, two mechanisms can be used to explain the synthesis of the Li_2ZrO_3 NTs: in situ mechanism and dissolution-precipitation process as seen in Fig. 4. In the initial stage of the hydrothermal treatment, the dispersed Li^+ ions concentrate around the ZrO_2 NTs arrays (Fig. 4a). Partial supersaturated Li^+ ions enter the crystal lattice of ZrO_2 under high pressure and form a tetragonal Li_2ZrO_3 NTs (Fig. 4b). During this in situ growth process, the NTs walls become thicker and rougher due to the crystal cell expansion. However, for the blocking of the outer tubal walls, especially on the compact position (root of the NT or bottom barrier layer) of the layer, Li^+ ions are deficient and segmental ZrO_2 template remains (Fig. 4b, c). Accompanying with the formation of Li_2ZrO_3 NTs, little portion of ZrO_2 is dissolved in the alkaline solution assisted by the high temperature and pressure. When ZrO^{2+} and Zr^{4+} are introduced into the solution, Li^+ are combined with the ZrO^{2+} or Zr^{4+} and agglomerate on the heterogeneous-nucleation sites provided by the NT arrays. Herein, the grainy Li_2ZrO_3 is formed on or in the already-formed Li_2ZrO_3 NTs (Fig. 4c). This dissolution–precipitation process is mainly involved with the alkalinity of the hydrothermal solution [17]. With addition of LiOH concentration (0.5 M), the dissolution rate of ZrO_2 is elevated. The NT layers collapse severely under the same hydrothermal time and temperature (Fig. 1d). This destructive process is unfavorable for the formation and application of the Li_2ZrO_3 NT layers. Consequently, in order to in situ growth Li_2ZrO_3 NTs arrays under a certainly reaction time and temperature, avoid the deposition of Li_2ZrO_3 particles on the surface of the already-formed layers, suitable hydrothermal alkalinity should be applied.

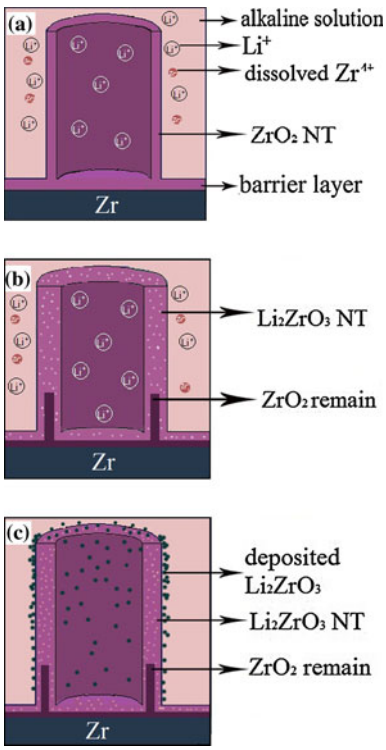

Fig. 4 Growth mechanism of Li_2ZrO_3 NT by hydrothermal method in LiOH solution. **a**, **b** The supersaturated Li^+ ions enter the crystal lattice of ZrO_2 and form a tetragonal Li_2ZrO_3 structure. **c** Partially dissolved Zr^{4+} ions react with the superfluous Li^+ ions and form tiny Li_2ZrO_3 particles on the top and wall of the already-formed NT

Conclusions

Using anodic ZrO_2 NTs arrays as templates, Li_2ZrO_3 NTs arrays have been obtained by hydrothermal synthesis in alkaline solutions (LiOH). The alkalinity of the hydrothermal solution has significant effect on the growth mechanism of Li_2ZrO_3. At a lower alkalinity, the in situ formation is dominant in the reactions. The addition of LiOH concentration results in the dissolution of ZrO_2 and formation of Li_2ZrO_3 particles on the surface of the Li_2ZrO_3 NTs. For synthesis of Li_2ZrO_3 layers with NTs structure, proper alkalinity should be adopted in the hydrothermal reactions.

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