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Short communication

Synthesis and Li electroactivity of dandelion-like nanorutile

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Abstract

We report the synthesis of dandelion-like rutile TiO_2 (D-TiO_2) nanostructures composed of numerous single-crystalline nanorods using a facile wet-chemical route without any templates or surfactants. The effects of the addition of an inorganic salt, i.e., LiCl, during the synthesis on the morphology of the D-TiO_2 nanorutile powders are investigated. When applied as an anode for Li-ion batteries, the resultant D-TiO_2 nano-structured powders with 1.0 M LiCl exhibited good electrochemical properties that are attributed to the combined effects of the decreased powder aggregation and the enhanced one-dimensional character of each nanorod.

Keywords: Rutile TiO_2; Dandelion-like; LiCl; Li-ion batteries

1. Introduction

Titanium dioxide (TiO_2) polymorphs, which include rutile, anatase, and brookite, are among the most widely used inorganic materials and are applied in diverse fields such as dye-sensitized solar cells, photocatalysts, gas sensors, and energy-storage devices due to their low cost, abundance, and safety [1–5]. In particular, nanorutile TiO_2, which electrochemically reacts with more Li ions than bulk rutile, is commonly used as an anode for Li-ion batteries [6]. Therefore, many researchers have attempted to synthesize morphology-controlled rutile nanostructures in the form of nanoparticles, nanorods, nanowires, nanotubes, and hierarchical structures [1,4,7]. One-dimensional rutile nanostructures have received the most attention as anodes for Li-ion batteries because these nanostructures act as channels, thereby enabling facile electron transport to the current collector. Accordingly, dandelion-like rutile TiO_2 (D-TiO_2) comprising numerous nanorods should be a good candidate as an anode material for Li-ion batteries.

Herein, we report the low-temperature (100 °C) formation of D-TiO_2 nanorutile powders via a facile wet-chemical route without any templates or surfactants. In addition, the morphological changes of the D-TiO_2 nanostructures with varying concentrations of LiCl were investigated and their electrochemical activities were evaluated.

2. Experimental procedure

Titanium chloride (0.16 M, $TiCl_3$, Kanto, aqueous solution of ~20%) and anhydrous lithium chloride (0–1.0 M, LiCl, Sigma–Aldrich, >99.0%) were dissolved in deionized water (200 mL) in a 250 mL glass bottle with magnetic stirring. The pH values of the solutions were ~1.0 regardless of the concentration of LiCl. The glass bottles were sealed and maintained at 100 °C for 12 h. The resultant suspensions were centrifuged, washed repeatedly with deionized water, and then washed once with anhydrous ethanol. Subsequently, the precipitates were dried at 60 °C for 4 h in a vacuum oven. The obtained rutile TiO_2 samples were named TR-L0, TR-L1, TR-L3, TR-L5, and TR-L10 according to their LiCl concentrations of 0, 0.1, 0.3, 0.5, and 1.0 M, respectively.

The prepared powders were characterized via X-ray diffraction (XRD, Miniflex II, Rigaku, Tokyo, Japan), field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Tokyo, Japan), and high-resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL, Tokyo, Japan). The specific surface areas were

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examined using Brunauer–Emmett–Teller (BET, Belsorp-mini II, BEL Japan Inc., Osaka, Japan) analysis.

For the electrochemical evaluation of the prepared powders, positive electrodes were fabricated by mixing the powders with Super *P* carbon black (MMM Carbon, Brussels, Belgium) and Kynar 2801 binder (PVdF-HFP) at a mass ratio of 70:15:15 and pasting the mixture on a Cu foil. Swagelok-type cells with a Li metal foil as the anode and a separator Celgard 2400 film were assembled and saturated with a liquid electrolyte comprising 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1 v/v, Techno Semichem Co., Ltd., Korea). The assembled cells were cycled galvanostatically between 1.0 and 2.5 V using an automatic battery cycler (WBCS 3000, WonaTech, Korea).

3. Results and discussion

Fig. 1a shows the XRD patterns of the TiO_2 powders synthesized with various amounts of LiCl. The XRD pattern of TR-L0 primarily corresponds to a tetragonal TiO_2 rutile phase (JCPDS No. 21-1276) with additional peaks, marked by asterisks in Fig. 1a that correspond to a small amount of orthorhombic TiO_2 brookite phase (JCPDS No. 29-1360). As the amount of LiCl increased from 0 to 1.0 M, the intensities of the peaks corresponding to the brookite phase gradually decreased and eventually disappeared. Accordingly, high-purity rutile TiO_2 powders were prepared from a $TiCl_3$ aqueous solution containing 1.0 M LiCl (i.e., sample TR-L10). The phase formation of TiO_2 depends upon several factors including reactant concentration, pH, and type of inorganic salt used.

Although it is known that strongly acidic conditions and inorganic salts such as NaCl and NH_4Cl are favorable for rutile formation [8,9], brookite is often obtained as a byproduct when using the hydrothermal method [10]. In this work, the solution pH was ~ 1; this is not sufficiently acidic to form phase-pure rutile induced by the slow rate of hydrolysis of the Ti source, and hence, leads to the formation of small amounts of brookite phase. However, Cl^- ions provided by the hydrolysis of LiCl can accelerate the formation of the rutile phase. Therefore, the TR-L10 sample, which was synthesized in solution with a higher concentration of LiCl, comprised a high-purity rutile phase.

Fig. 1b–f shows the morphologies of the rutile TiO_2 samples obtained with different LiCl concentrations. All the powders had dandelion-like shapes composed of numerous nanorods. The lengths of the nanorods and the sizes of the D-TiO_2 nanostructures increased with increasing LiCl concentration, as shown in Fig. 1b–f and

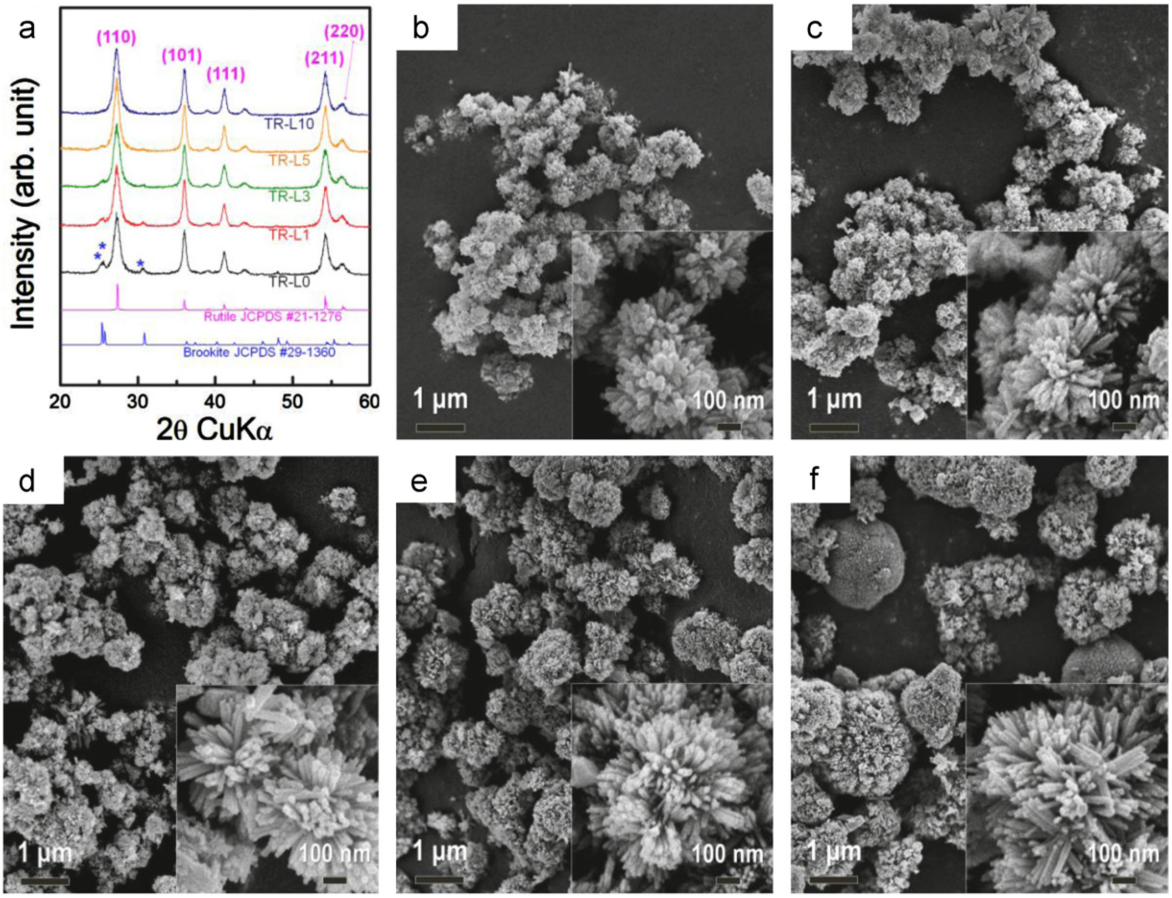

Fig. 1. (a) X-ray diffraction patterns of dandelion-like TiO_2 with various amounts of LiCl and (b–f) their corresponding typical FE-SEM images (TR-L0, TR-L1, TR-L3, TR-L5, and TR-L10, respectively). The insets in (b–f) show magnified FE-SEM images.

their insets; the inserts display a magnified view of each sample. It is well known that Cl^- ions play an important role in the one-dimensional growth of rutile TiO_2 [4]. Generally, Cl^- ions preferentially adsorb to and delay the growth of the (1 0 0) planes of rutile TiO_2, leading to enhanced growth along the [0 0 1] direction and resulting in the formation of TiO_2 nanorod arrays. In this work, D-TiO_2 nanostructures were formed by the commonly known "nucleation-growth-assembly" mechanism. For TR-L0, self-assembly occurred after the growth of short nanorods, whereas TR-L10 was obtained by the growth of long nanorods followed by self-assembly; this is the cause for the differences in the sizes of the two D-TiO_2 nanostructures. This also affects their specific surface areas, which gradually decreased with increasing D-TiO_2 nanostructure and LiCl concentration and reached a minimum of $\sim 55\ m^2\ g^{-1}$ at LiCl concentrations above 0.5 M (Fig. S1).

The typical morphology and crystallinity of the TR-L0 and TR-L10 samples were further investigated using TEM and HR-TEM (Fig. 2a and b, respectively). Both samples clearly show dandelion-like morphologies that are composed of a large number of nanorods, although they were of different sizes. On the basis of the HR-TEM analysis of each sample (insets of Fig. 2), individual rutile TiO_2 nanorods from TR-L0 and TR-L10 each feature a highly ordered single-crystalline nature, (1 1 0) surface planes with a d-spacing value of 0.324 nm, and a [1 1 1] growth direction; this indicates that the prepared nanorods have very similar fundamental properties regardless of the LiCl concentration. Unfortunately, we were unable to isolate the brookite phases in the TR-L0 sample through TEM analysis because there were not enough of them.

Fig. 3 shows voltage-specific capacity curves at a rate of C/5 ($33.6\ mA\ g^{-1}$) based on the theoretical capacity ($168\ mA\ h\ g^{-1}$) of the TR-L0 and TR-L10 samples. The variation of the discharge–charge capacity versus the cycle number at a rate of C/5 for all D-TiO_2 samples (i.e., TR-L0, TR-L1, TR-L3, TR-L5, and TR-L10) is also shown in Fig. S2. The high specific capacities of all electrodes during the first discharge reaction originated from an undesirable side reaction with the electrolyte or irreversible changes in the structure of the rutile TiO_2 [11]. The reversible capacities of the TR-L0 electrodes faded rapidly even during the initial cycles, resulting in a poor reversible capacity of $\sim 90\ mA\ h\ g^{-1}$ after 30 cycles. Of the fabricated D-TiO_2 nanostructure electrodes, the TR-L10 electrodes exhibited the best electrochemical performance ($128\ mA\ h\ g^{-1}$ after 50 cycles) (Fig. S2).

Generally, a large specific surface area results in high reversible capacity due to increased contact area with the electrolyte. However, it should be noted that the TR-L10 electrode delivered higher capacities than the TR-L0 electrode despite its smaller specific surface area. This

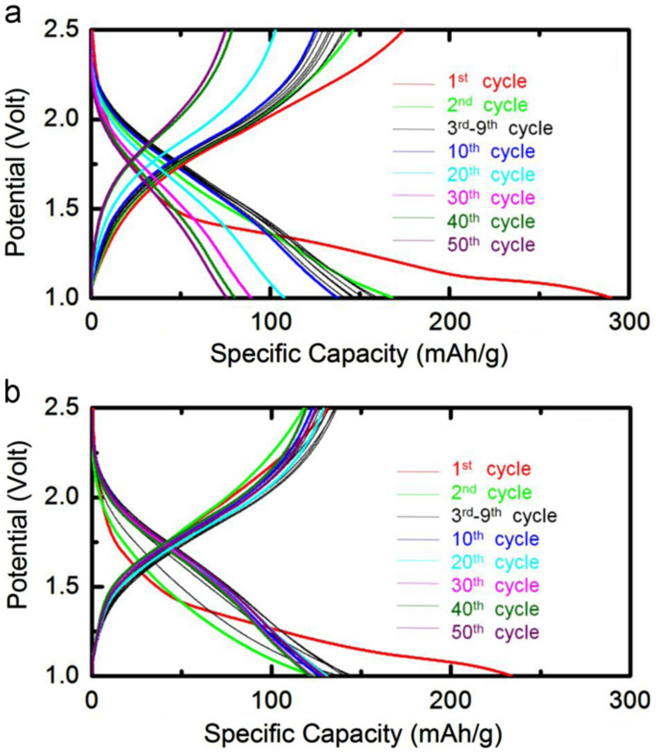

Fig. 3. Galvanostatic discharge–charge voltage profiles of (a) TR-L0 and (b) TR-L10 powders.

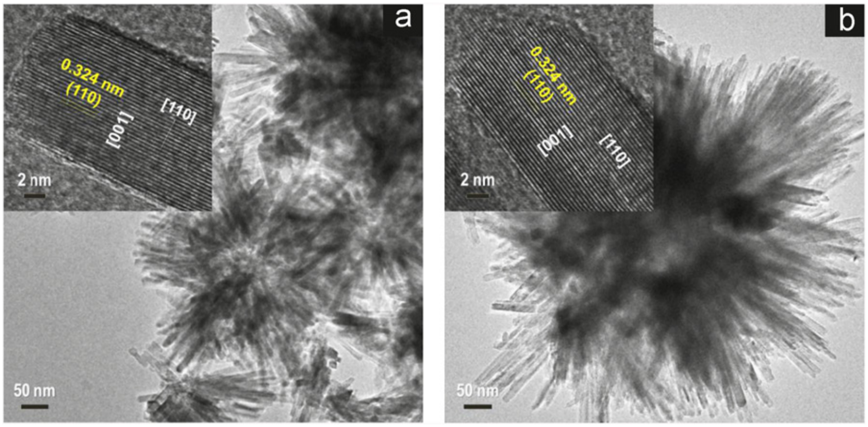

Fig. 2. Typical TEM images of (a) TR-L0 and (b) TR-L10 powders. The insets show HR-TEM images of each sample.

result can be explained through the differences in morphology. Although both D-TiO_2 samples comprise one-dimensional nanorods, the TR-L10 nanorods are longer than those in TR-L0, which leads to a much smaller number of nanorods per gram. As a result, the interparticle contact resistance that restricts the electronic conduction to the current collector is decreased. In other words, the longer nanorods in the TR-L10 electrode enable easy and efficient transport of electrons from the active materials to a current collector, thereby improving the reversible capacity and enhancing cyclability. Furthermore, the TR-L0 samples are more significantly agglomerated than the TR-L10 samples, as shown in Fig. 1b and f; this limits homogeneous mixing with conducting additives such as carbon black, which results in poor electrochemical properties. In general, the D-TiO_2 nanostructures and carbon black did not mix efficiently; therefore, in order to improve the electrochemical performance of the D-TiO_2 nanostructure-based anode, alternatives such as a carbon or conducting-polymer coating must be investigated.

4. Conclusions

In summary, we successfully synthesized D-TiO_2 nanostructures through a facile wet-chemical method. Although samples synthesized with lower LiCl concentrations (i.e., TR-L0, TR-L1, TR-L3, and TR-L5) have a second brookite phase in addition to the main rutile phase, the D-TiO_2 nanostructure synthesized with 1.0 M LiCl (i.e., TR-L10) has a high-purity rutile phase. In addition, the nanorods of the TR-L10 were longer than those of the other samples. These results originated from the effect of the Cl^- ions that were provided by the hydrolysis of LiCl. As anodes for Li-ion batteries, the TR-L10 electrode exhibited superior electrochemical performance than the TR-L0 electrode due to more efficient transport of electrons from the active materials to the current collector as a result of the elongation of the nanorods and the decrease in interparticle contact resistance caused by the decreased agglomeration of the samples.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2012.10.010.

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