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Novel porous anatase TiO₂ nanorods and their high lithium electroactivity

Shu-Juan Bao^a, Qiao-Liang Bao^{a,b}, Chang-Ming Li^{a,}, Zhi-Li Dong^c*

^a *School of Chemical and Biomedical Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*

^b *Department of Physics, Wuhan University, Wuhan 430072, PR China*

^c *School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*

Abstract

We demonstrated a simple approach for the synthesis of a kind of novel porous anatase TiO₂ nanorods. The method is based on a reaction in composite-hydroxide eutectic system and normal atmosphere without using an organic dispersant or capping agent. The synthesis technique is cost effective, easy to control and is adaptable to mass production. This is the first time TiO₂ nanorods with a porous structure are fabricated by using this method. The as-prepared material was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), nitrogen adsorption and desorption experiments and electrochemical measurements. The results showed that the anatase TiO₂ nanorods obtained in our experiment have a large specific surface area with a porous structure which makes it have a potential application in catalysts and battery materials, especially in lithium ion batteries. In this study, we mainly tested their electrochemical performance as negative materials for lithium ion batteries. Further research to optimize synthesis conditions, particularly to develop their application in the field of catalysis is currently in progress.

1. Introduction

TiO₂ (anatase) has been extensively studied during the past decade [1]. This interest arises from its potential application in photovoltaic cells [1–3], catalysts [4–6], gas sensing [7], electrochromic devices [8], and rechargeable lithium ion batteries [1,9–12]. Especially, in recent years, one-dimensional nanostructured TiO₂ such as nanotubes and nanowires have attracted considerable academic and industrial interest due to their superior properties and unique features arising from their nanoscale structures [13,14]. To realize these promising high-performance applications, the

control of the physicochemical properties through tailoring their nanostructures is a great challenge.

Because the synthesis of one-dimensional nanostructured TiO_2 is very important for understanding its fundamental properties, considerable effort has recently been concentrated on exploring the various synthetic methods ranging from vapor-phase techniques to solution-growth processes [13,15–17]. At present, the main approach to fabricate TiO_2 nanotubes and nanowires is the hydrothermal method which provides access to uniform and distinct morphologies with excellent reliability, selectivity and efficiency [18–20]. However, the method is complicated and restricted by a high reaction pressure and its completion in an autoclave. Although the sample obtained using the hydrothermal method has a good performance, the complicated equipment is considered to be a big obstacle for commercialization. Therefore, it is of significance to explore an alternative method to synthesize nanostructured TiO_2 with homogeneous particle morphology in which the process is simple and controllable.

Here we report a novel nanostructure TiO_2 synthesis method. The method involves the synthesis of the sample in a solution of molten mixed potassium hydroxide and sodium hydroxide eutectic at 200 °C and normal atmosphere without using an organic dispersant or a capping agent. This provides a convenient, low-cost and mass-production route for the fabrication of nanostructures of functional oxide materials with various structure types [21]. Although the method has been widely applied in preparing of complex oxide nanostructures of scientific and technological importance, it has never been used to synthesize nanostructured TiO_2 .

The results of nitrogen adsorption and desorption experiments and HRTEM analysis indicated that the TiO_2 nanorods prepared in binary eutectic mixture system has a large specific surface area and a porous structure. Recently, nano-sized materials with porous structure have attracted great research interest in the field of catalysts, molecular sieves, host materials and battery materials, especially in electrochemistry-related applications [22–24], essentially because of their substantial advantages in terms of mass transport. Transport in porous nanostructured system typically encompasses shorter lengths for electrons and Li^+ transport, higher electrode–electrolyte contact area, and a better accommodation of the strain of Li^+ insertion/extraction.

Furthermore, nanosized TiO_2 has been widely investigated as a key material for lithium ion batteries, because it is not only a low-voltage insertion host for Li, but also a fast Li insertion/extraction host [25]. Hence, in this work, we mainly report a novel porous TiO_2 nanorods synthesized from a binary eutectic mixture system; at the same time we test their electrochemical performance as a negative electrode material of the Lithium ion battery.

2. Experimental

2.1. Preparation of materials

All the chemicals were of analytical grade and used without further purification. The preparation process is described as follows: (1) an amount of mixed hydroxides ($\text{NaOH/KOH} = 1:1$) was placed in a 50 mL Teflon vessel with a cover for preventing dust, and then, added 1 g TiO_2 (commercial TiO_2 nanopowder, Aldrich) was added on the top of the hydroxide in the vessel; (2) the vessel was put into a furnace at 200 °C for 3 h, the covered vessel was shaken to ensure that the samples were mixed completely and (3) the vessel was kept in the furnace at 200 °C for another 36 h, then washed with 0.1 M HCl solution and distilled water several times till the pH reached 7.0. The final step was to calcine the obtained sample at different temperatures. In addition, the sample was also prepared following the same procedure but just using water washing for comparison.

2.2. Structure and morphology characterization

The crystal structure of the product was characterized by X-ray diffraction (XRD, D/max-2400 Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) operating at 50.0 kV and 200.0 mA. Morphology and microstructure of the synthesized materials were investigated by field emission scanning electron microscopy (FESEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, Hitachi 600 Japan). The structure and composition of nanostructures were measured by a high-resolution transmission electron microscope (HRTEM, JEM-2010F, Japan). Nitrogen adsorption and desorption experiments were carried out at 77.3 K by means of an Autosorb-1 (Quantachrome Instruments) analyzer. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Pore-size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch of the isotherm.

2.3. Electrochemical measurements

To prepare the tested negative electrode material in a lithium battery, the produced TiO_2 powder was mixed with 15 wt% acetylene black. Polyvinylidene fluoride (5 wt%, PVDF as binder, dissolved in N-methyl pyrrolidone) was added until a slurry solution was obtained. The slurry was pasted on an aluminum foil, as depicted in Refs. [13,18], followed by vacuum drying at 100 °C for 24 h. The cell consisted of the TiO_2 electrode, Li metal and an electrolyte of 1 M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). A Celgard 2400 membrane was used as the cell separator. The assembly of the cell was conducted in

an Ar-filled glove box. The cell was charged and discharged from 1.0 to 3.0 V at different current rates (Land CT2001A). Cyclic voltammetry was performed over a potential range of 1.0–3.0 V with a scan rate of 0.1 mV/s using a CHI 760 Electrochemical Workstation (CH Instruments, Austin, TX).

3. Results and discussion

A possible reaction mechanism as follows could happen in this experiment. Although the melting points of both sodium hydroxide and potassium hydroxide are over 300 °C ($T_m = 323$ °C for NaOH and $T_m = 360$ °C for KOH), the eutectic point at NaOH/KOH = 51.5:48.5 is only about 165 °C [21]. This is likely to be the key for synthesizing the sample at ~200 °C or lower. During the reaction process, hydroxides played a role not only as the solvent but also as the reactant for decreasing the reaction temperature. In the molten hydroxide, Ti–O–Ti building units in TiO₂ particles were broken and formed Ti–O–Na (Ti–O–K) and Ti–OH bonds. During the process of acid washing, sodium ions, potassium ions and hydroxyl groups in the Ti–O–Na (Ti–O–K) and Ti–OH ion exchange with H⁺ and convert the sodium (potassium) titanate into hydrogen titanate [26–28]. The formed hydrogen titanate is further converted into TiO₂ after high temperature sintering.

Fig. 1 (left) displays the XRD patterns of the powders obtained by acid washing and different heat-treatment processes. It can be clearly seen that all of the diffraction peaks correspond to the pure phase TiO₂ without any other impurity peaks, which is in good agreement with the standard spectrum (JCPDS, card no: 21-1272). It is notable that the crystallinity of TiO₂ drastically increases by sintering at 500 °C for 2 h (the relative intensity of the main XRD peak (101) of the two samples is above 2:1).

As can be seen from the schematic illustration of anatase TiO₂ (Fig. 1 (right)), anatase TiO₂ has a tetragonal space group $I4_1/amd$ with Ti⁴⁺ ions (octahedral sites) at positions 4a sites and O²⁻ ions at positions 8e. The octahedral sites at the 4b positions are vacant positions. When electrons are inserted in Ti⁴⁺ ions (d⁰) at positions 4a, Ti³⁺ ions (d¹) are formed at the same positions [10]. Electrons on Ti³⁺ ions may travel along 4a sites with the aid of thermal energy (hopping mechanism) and an external electric field. Excess charges may be compensated by the accommodation of foreign ions (Li⁺ ion in this case) at 4b sites in the anatase TiO₂ matrix. Thus, Li⁺ ions are mobile along 4b sites (three-dimensional channel) during the electrochemical reaction.

The morphology evolution of samples after different washes and heat-treatment processes is displayed in Fig. 2. Only the nano-particle aggregation was observed for the as-prepared sample after using DI water washing adequately and sintering at 300

°C for 2 h (Fig. 2a). After the same washing process and sintering at 500 °C for 2 h, the sample consisted of some irregular shaped nanorods, which was aggregated by nanoparticles (Fig. 2b). Fig. 2c and d exhibited the SEM images of the as-prepared sample after washing with a 0.1 M HCl solution followed by washing with DI water adequately, and heating at different temperatures. After acid washing and sintering at 300 °C for 2 h, a kind of rod-shaped sample was formed. After acid washing and sintering at 500 °C for 2 h, the rod-shaped structure becomes more uniform and regular (Fig. 2d).

From the above results of XRD and SEM analyses, it is clearly indicated that the conditions of the post-treatment and washing significantly affected the formation, crystalline structure and chemical composition of the final products; further high temperature treatment could accelerate the formation of rod-shaped TiO₂ and increase the crystalline growth.

Fig. 3a shows the TEM images of TiO₂ obtained by using acid washing and sintering at 500 °C for 2 h. It is seen from Fig. 3a, the TiO₂ nanorods are composed of many very small interconnected nanoparticles, which indicated that the material might have a predominately porous structure. The inset of Fig. 3a shows the selected area of electron diffraction (SAED) patterns of the TiO₂ sample, where polycrystalline diffraction rings (101), (004) and (200) of anatase TiO₂ are clearly observed. The HRTEM image recorded on the nanorods provided a further insight into the microstructures of this material as shown in Fig. 3b. The nanorods were composed of many randomly oriented 10 nm nanocrystallites with sets of clearly resolved lattice fringes, giving evidence that the TiO₂ material was highly crystallized. The anatase (101) lattice plane was observed in this HRTEM image. The fine crystallinity of the nano-rods was identified by this image. The results of XRD and HRTEM strongly support our proposed approach as a desirable process for the fabrication of a large quantity of high quality TiO₂ nanorods.

In order to further analyze the structure of the novel TiO₂ material, the nitrogen adsorption–desorption isotherms were measured. The results are shown in Fig. 4. The hysteresis loop appears in the relative pressure (P/P_0) range of 0.45–0.80 in the isotherm of the sample and the adsorption curve exhibited an abrupt increase in the high-pressure region ($>0.8P/P_0$), which indicates the presence of a porous structure in the TiO₂ sample. This result is consistent with that of the TEM analysis. The Brunauer–Emmett–Teller (BET) surface area of the sample is 99.3 m²/g, and BJH analysis shows further that the TiO₂ exhibits porous distributions, of which the most probable pore sizes are ca. 5 nm.

This kind of porous structure would be much more attractive than 2D hexagonal

phase for applications in photocatalysis and electrochemistry requiring diffusion of species in and out of the pore structure material.

In order to investigate the electrochemical properties of the novel nanostructure TiO_2 as a negative electrode material for lithium ion batteries, a typical cyclic voltammogram at a scan rate of 0.1 mV/s and initial two-cycle charge–discharge curve for TiO_2 obtained via acid washing followed by sintering at 500 °C for 2 h were conducted (Figs. 5 and 6)

In Fig. 5, a pair of well-defined anodic and cathodic peaks was observed. Apparently, the peaks at 1.59 and 1.99 V were associated with lithium insertion/extraction in the anatase lattice, which was consistent with those reported previously [29]. The measured value of the ratio for peak currents i_{pa}/i_{pc} is nearly 1, demonstrating that the reaction of Li ion-extraction/insertion relatively is reversible in this compound.

Fig. 6 shows the charge–discharge curves of the TiO_2 nanorods for different cycles. It shows a distinct charge and discharge voltage plateau related to the redox peaks in the CV, indicating the typical electrochemical characteristics of anatase TiO_2 .

Fig. 7 presents the cycling performance of the porous structure TiO_2 nanorods as the negative electrode in a lithium ion battery at different current densities (60 mA/g and 120 mA/g). The TiO_2 nanorod electrode exhibited a remarkably high initial discharge capacity at a current density of 60 mA/g, up to 266.4 mAh/g, which was near the stoichiometry $\text{Li/Ti} = 0.8$. After a relatively large capacity drop in the first cycle, the capacity in the second cycle was still great (212.4 mAh/g) and presented a favorable cycling capability during the subsequent charge/discharge. When a higher current density was employed (120 mA/g), the material still had an excellent capacity retention. It is very interesting that TiO_2 nanopowder has a lower capacity (150 mAh/g) [30] although it could have a higher specific surface area than the nanorods developed in this work. This may be caused by the poor pore structure of the nanopowder based electrode, such as pores with dead ends formed from the aggregation of the small nanoparticles (10–20 nm) during preparation. The TiO_2 nanorods in our work are composed of many small interconnected nanoparticles (10 nm) to form a network pore structure, which was kept during the electrode preparation. This was confirmed by HRTEM observation and nitrogen adsorption and desorption experiments. Thus, TiO_2 nanorodes obtained by the binary eutectic mixture method provide not only a high specific surface area, but also a superior nanopore structure for a high utilization efficiency to result in a high capacity. The irreversible capacity loss might originate from irreversibly inserted lithium, which was in agreement with the irreversible structure formation at a deeper Li insertion [13]. However, after the

first cycle, the retention of capacity and rate capability of this material were still excellent in comparison to others such as TiO₂ nanowires and nanopowders [13,30]. In addition, the preparation method of the nanorods in this work is convenient, low-cost and easily adaptable to mass production. Hence, it is a promising negative electrode material for lithium ion batteries in terms of its high performance and low manufacturing cost.

4. Conclusions

Novel TiO₂ nanorods with a porous structure have been synthesized by using a binary eutectic mixture system. The novel materials exhibited a high-specific surface area with a ca. 5 nm pore-size distribution, uniform and regular rod-shaped structures. The good cycleability and a high rate capability coupled with the low cost and environmentally benign nature of the preparation method may make this material attractive for large applications. Further research to optimize synthesis conditions, particularly its application in the field of catalysis, is currently in progress.

References

- [1] W. Marnix, K. Roel Van de, P.M.K. Arno, A.A. van Well, M.M. Fokko, *J. Am. Chem. Soc.* 123 (2001) 1454.
- [2] F. Cao, G. Oskam, P.C. Searson, J.M. Stipkala, T.A. Heimer, F. Farzad, G.J. Meyer, *J. Phys. Chem.* 99 (1995) 11974.
- [3] A. Hagfeldt, M. Gratzel, *Chem. Rev.* 95 (1995) 49.
- [4] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [5] M. Anpo, M. Takeuchi, *J. Catal.* 216 (2003) 505.
- [6] D. Li, H. Haneda, S. Hishita, N. Ohashi, *Chem. Mater.* 17 (2005) 2596.
- [7] Y. Lei, L.D. Zhang, J.C. Fan, *Chem. Phys. Lett.* 338 (2001) 231.
- [8] A. Hagfeldt, N. Vlachopoulos, M. Gratzel, *J. Electrochem. Soc.* 141 (1994) L82.
- [9] S.Y. Huang, L. Kavan, M. Gratzel, I. Exnar, *J. Electrochem. Soc.* 142 (1995) 142.
- [10] T. Ohzuku, T. Kodama, T. Hirai, *J. Power Sources* 14 (1985) 153.
- [11] A.R. Armstrong, G. Armstrong, J. Canales, P.G. Bruce, *Angew. Chem., Int. Ed.* 43 (2004) 2286.
- [12] A. Kuhn, R. Amandi, F. Garcia-Alvarado, *J. Power Sources* 92 (2001) 221.
- [13] Q. Wang, Z.H. Wen, J.H. Li, *Inorg. Chem.* 45 (2006) 6944.
- [14] B. Zhang, W. Dai, X.C. Ye, W.Y. Hou, Y. Xie, *J. Phys. Chem. B* 109 (2005) 22830.
- [15] J.J. Wu, C.C. Yu, *J. Phys. Chem. B* 108 (2004) 3377.
- [16] P.D. Cozzoli, A. Kornowski, H. Weller, *J. Am. Chem. Soc.* 125 (2003) 14539.
- [17] S.M. Liu, L.M. Gan, L.H. Liu, W.D. Zhang, H.C. Zeng, *Chem. Mater.* 14 (2002) 2427.
- [18] Y.K. Zhou, L. Cao, F.B. Zhang, B.L. He, H.L. Li, *J. Electrochem. Soc.* 159 (2003) A1246.
- [19] D. Wu, J. Liu, X.N. Zhao, A.D. Li, Y.F. Chen, N.B. Ming, *Chem. Mater.* 18 (2006) 547.
- [20] G.R. Patzke, F. Krumeich, R. Nesper, *Angew. Chem., Int. Ed.* 41 (2002) 2446.
- [21] H. Liu, C.G. Hu, Z.L. Wang, *Nano. Lett.* 6 (2006) 1535.
- [22] Y.S. Tao, H. Kanoh, L. Abrams, K. Kaneko, *Chem. Rev.* 106 (2006) 896.
- [23] Y.Q. Wang, L.X. Yin, O. Palchik, Y.R. Hacohen, Y. Koitypin, A. Gedanken, *Langmuir* 17 (2001) 4131.
- [24] B. Lee, D. Lu, J.N. Kondo, K. Domen, *JACS* 124 (2002) 11256.
- [25] Y.S. Hu, L. Kienle, Y.G. Guo, J. Maier, *Adv. Mater.* 18 (2006) 1421.
- [26] Y. Lan, X. Gao, H. Zhu, Z. Zheng, T. Yan, F. Wu, S.P. Ringer, D. Song, *Adv.*

Funct. Mater. 15 (2005) 1310.

[27] C. Tsai, H. Teng, Chem. Mater. 18 (2006) 367.

[28] M.A. Khan, H. Jung, O. Yang, J. Phys. Chem. B 110 (2006) 6626.

[29] B. Zachau-Christiansen, K. West, T. Jacobsen, S. Atlung, Solid State Ionics 28–30 (1998) 1176.

[30] C. Natarajan, K. Setoguchi, G. Nogami, Electrochim. Acta 43 (1998) 3371.

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- Fig. 1. (left) XRD patterns of the sample obtained in different conditions: (a) the sample prepared by acid washing and sintering at 300 °C for 2 h and (b) the sample prepared by acid washing and sintering at 500 °C for 2 h). **Fig. 1(right)** is the schematic illustration of anatase TiO₂.
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