Growth Mechanism of Hollow TiO₂(B) Nanocrystals as Powerful Application in lithium-Ion Batteries

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Abstract: This article deduces the formation mechanism of hollow TiO₂(B) nanocrystals by Oriented Attachment and Kirkendall effect. Charge density distribution and total energy can be calculated using SCC-DV-X α -ECM. The diameter of the hollow nanocrystals is about 10 to 18 nm and the wall thickness of hollow nanocrystals is about 3 to 5 nm. The dimensions are smaller than other previous reports. In addition, their best discharge specific capacity has already reached nearly 360 mAhg⁻¹ at 0.2 C. Comparing with other structures of TiO₂(B), the hollow nanocrystals have a high rate capability and stable cycling.

Keywords: TiO₂(B); Hollow nanostructures; Li-ion batteries

1. Introduction

Nanostructures of titanium dioxide attracted more and more attentions recently due to their powerful characters. The sizes of tiny particles below 100 nm could have significant changes in the physical and chemistry properties. The size reduction into

the nano-scale (<100 nm) leads to increased electrode/electrolyte contact areas and shortened Li^+ transport distance, permitting batteries to operate at higher power [1]. Titanium dioxide has the advantages of non-toxicity, high efficiency, good stability, solar cells/ batteries, field emission and so on. Crystal structures of titanium dioxide have anatase, rutile, brookite, monoclinic crystal and so on. Researchers are interested in the anatase, rutile. On the contrary, they made few investigations on brookite and monoclinic crystal. The monoclinic crystal titanium dioxide belongs to the metastable fabrications. The lattice structure of $\text{TiO}_2(\text{B})$ is shown in Figure S1. Marchand et al. reported the synthesis of them named $\text{TiO}_2(\text{B})$ via one way based on high temperature solid phase to synthesize them in 1980 [2]. Zhu et al. put forward that composites of nano-fiber materials and anatase nanocrystals have higher activity than the P25 by the photocatalytic degradation of Rhodamine B in 2009 [3]. Zhao et al pointed out that Monoclinic $\text{TiO}_2(\text{B})$ was prepared by hydrothermal treating the peroxotitanium complex precursor produced from titanium sulfate and sodium peroxide [4].

Until recently, there was some lack of knowledge about $\text{TiO}_2(\text{B})$ nano hollow spheres whose average size was less than 18 nm. On the contrary, their structures in this dimension exhibit more powerful performance in lithium-ion batteries and photocatalysis. On the one hand, few researchers concerned about the lattice parameters of $\text{TiO}_2(\text{B})$, charge density distribution and total energy. On the other hand, predecessors have little work to expound formation mechanism of hollow $\text{TiO}_2(\text{B})$ nanocrystals using the nanoscale Kirkendall effect and Oriented Attachment as previously described. Obviously, the revolution of sizes and theoretical innovation

have great significance to the performance of the materials.

Our group has already synthesized hollow TiO_2 nanocrystals using the nanoscale Kirkendall effect and explained formation mechanism of hollow TiO_2 nanocrystals in 2015 [5]. Accordingly we continue to explore that the structure of hollow $\text{TiO}_2(\text{B})$ nanocrystals is synthesized from series titanium sulphate and sodium hydroxide by calcination and hydrothermal procedures. The nanoparticles and unique structure of $\text{TiO}_2(\text{B})$ hollow nanocrystals have largely improved material properties about lithium-ion batteries and photocatalysis. In this article, a new approach developed to describe the formation mechanism of $\text{TiO}_2(\text{B})$ and the formation mechanism of $\text{TiO}_2(\text{B})$ hollow nanocrystals will be more efficiently.

2. Experimental

2.1 Materials synthesis

In a typical synthesis, $\text{TiO}_2(\text{B})$ hollow nanocrystals were synthesized via a simple hydrothermal process. An aqueous solution of $\text{Ti}(\text{SO}_4)_2$ was added in a vessel. NaOH solution was then added drop wise to the vessel under stirring at room temperature. A gelatinous white precipitate was formed instantly. The resulting precipitate was separated from the mother liquor by centrifugation and washed with distilled water until the absence of residual SO_4^{2-} (tested by reaction with a BaCl_2 solution). Subsequently, further treatment with 6.5 g of $\text{LiOH}\cdot\text{H}_2\text{O}$ and 30 ml of deionized water aqueous solution in a Teflon vessel at $180\text{ }^\circ\text{C}$ was carried out for 48 h. After the hydrothermal treatment, the precipitates were separated by filtration and washed with

diluted HCl solution and deionized water. At last, the samples were calcined at 400 °C for 4 h.

2.2 Materials characterization

X-Ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray Diffractometer. Transmission electron microscope (TEM) images were taken on a Tecnai G2 S-Twin F20 microscope.

High resolution TEM (HRTEM) analyses were performed on a Tecnai G2 S-Twin F20 microscope.

2.3 Electrochemical measurements

The working electrode consisted of the active material (i.e, hollow $\text{TiO}_2(\text{B})$ nanocrystals), carbon black, and a polymer binder polyvinylidene fluoride, PVDF) in a weight ratio of 8:1:1. The lithium foil was used as both the counter electrode and the reference electrode. 1 M LiPF_6 in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. The cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. Cyclic voltammetry measurements were performed on a CHI660C electrochemical workstation. The galvanostatic charge–discharge tests were performed on a LAND(CT2001A) battery test system.

3. Results and discussion

Based on above information, the total energy of $\text{TiO}_2(\text{B})$ is calculated via Hartree-Fock-Slater and Ho-henberg-Kohn-Sham, and equations are established based on Schrödinger equation (Figure S2) [6]. We use SCC-DV- $X\alpha$ -ECM theory, which can

improve the computational efficiency and can be used in the program. In our application, the α is adjustable, the total energy can be obtained by solving the Schrödinger equation (Figure S3) [7].

The wave function Φ_i and the energy eigenvalue E_i are obtained from the equation. However, the results of $\sum E_i$ are not equal to the total energy of the system, because, the Coulomb energy and the exchange energy could be calculated once again, the total energy of the system should be E_{tot} (Figure S4).

In order to calculate conveniently, the article uses the method of freezing internal electron. In this way, charge density distribution is calculated using Matlab 7.0 based on Monte Carlo model. Figure 1 shows the charge density distribution of the five atoms (one oxygen atom and four titanium atoms). Substituting charge density into total energy equation, the system total energy E_{tot} can always be obtained by integral. $E_{tot} = -3979.7 \text{ eV}$.

In order to clarify the basic theories of formation mechanism for nano powder material, there are some aspects of this problem can be addressed. (The 3rd theory and 4th theory can turn to Supporting Information).

The first theory relates to Kirkendall effect. In 1947, Smigelskas and Kirkendall reported the Kirkendall effect, which was the first experimental proof that atomic diffusion occurs through vacancy exchange and not by the direct interchange of atoms [8]. In 2004, Yin et al. reported the synthesis of hollow nanocrystals using the nanoscale Kirkendall effect for the first time [9]. In 2015, Liang et al. reported the synthesis of titanium dioxide hollow nanocrystals using the nanoscale Kirkendall

effect. As a result, Kirkendall effect can effectively explain the formation of hollow nanostructures or the formation of nanostructures.

The second theory relates to Oriented Attachment, Oriented Attachment recently attracted people's attention in 2010,[10] scientists noted in many other synthesis conditions, the crystal growth of titanium dioxide nano materials also follow Oriented Attachment. For example, using nano grain oriented attachment growth could gain a one-dimensional titanium dioxide nanowire structure.

In scientific research work, the research on the crystal structure of nanomaterial with anisotropic structure, scientific research workers could have already turned attentions to Oriented Attachmen in this field. The mechanism is first presented in the research work of Penn and Banfield on TiO_2 and FeOOH [9]. The Oriented Attachment mechanism [10] has some characteristics. The primary single crystal units are rotated and the lattice is changed via the orientation of the crystal surface, and then the primary single crystal units are aggregated and the crystal surface is completely coincident with crystal surface of their same direction. In one direction they gradually form a larger, two-stage single crystal.

After the exchange of sodium titanate nanowires (Figure 2a) using dilute hydrochloric acid, the nanowires are fragmented into a bulk state (Figure 2b) of the primary single crystal cell. The integration of the primary single crystal interface will result in the reduction of the total surface energy, which drives the growth of oriented attachment. Using rotation of units and aggregation of the primary crystal units (Figure 2c), small intergranular cracks could be eliminated, and the boundary gap is

gradually widening, thus forming a hollow cavity and special appearance (Figure 2d). Finally, the hollow cavity and special appearance could form hollow nanocrystals (Figure 2e) because of the decrease of total surface energy.

According to the above information, hollow $\text{TiO}_2(\text{B})$ nanocrystals were obtained using Titanium sulphate as titanium source and Sodium hydroxide as the matrix material. This chemical change could be expressed by some equations (Figure S5) based on Ostwald's rule [11].

In the preparation stage, titanium hydroxide was generated by titanium sulfate and sodium hydroxide. In the drying stage, titanium hydroxide could decompose into metatitanic acid and water, and then metatitanic acid could continue to decompose into water and Titanium dioxide whose structure is irregular short-range order.

In hydrothermal stage, after the amorphous TiO_2 was added to solutions of lithium hydroxide, the hydroxide and water moleculars could diffuse into the amorphous $\text{TiO}_2(\text{B})$ particles, and they reacted with the titanium atoms or oxygen atoms in the lattice to produce Titanium hydroxyl, titanium hydroxyl is likely to be HTiO_3^- . And then Li_2TiO_3 was generated by HTiO_3^- and Li^+ . Figure S6 shows the process changes. According to the Kirkendall effect, in the process, the formation of the HTiO_3^- will be out of the original position to the external diffusion. According to the characteristics of ion crystal defect, in the ionic crystals, the system must maintain the neutral, a negative ion produces a vacancy, and there is a positive ion vacancy near it. They form the positive and negative ion vacancies called Schottky defect. Therefore, a large number of vacancy flow will be formed via lots of OH^- and TiO_2 . The chemical

equations indicate that production of Li_2TiO_3 cause the reaction to move forward. Finally, a large number of amorphous titanium dioxide could be consumed by production of Li_2TiO_3 . In the end, the difference between the migration rate of the vacancy and HTiO_3^- leads to the formation of hollow nanocrystals in the reaction of the system.

However, the synthesis of hollow spheres is so difficult that we racked our brains until we came up with an extremely important formation mechanism of $\text{TiO}_2(\text{B})$ hollow nanocrystals. About Stability of hollow spheres, the nucleation of the solid transformation is almost uniform. There are many defects in the solid phase. Such as vacancy, grain boundary, location inclusion, free surface, these defects can be used as a form of nuclear. At this time, crystal defect caused by the increase of energy, they have the formation of the crystal nucleus reduced, because heterogeneous nucleation is much easier than the homogeneous nucleation. The total variation of the free energy of the system is described in the form of a heterogeneous nucleation. In order to express formulas, they can be written as follows Figure S7.

In the formula of the heterogeneous nucleation, V , ε , ΔG_V , σ are supposedly fixed, ΔG is determined by ΔG_d and S . ΔG_d is caused by the disappearance or decrease of crystal defects. The formula of ΔG can be rewritten into another form. $\Delta G = K + S\sigma - \Delta G_d$ [12].

In the formula of the heterogeneous nucleation, K , σ is supposedly fixed, ΔG is determined by ΔG_d and S , In order to reduce ΔG , S must be reduced and ΔG must be increased. Because of the large surface area of the hollow spheres, the

nucleation is not easy. This is the reason why the formation of the hollow spheres is difficult and unstable.

The crystal structure of the samples was characterized by using X-ray diffraction. Figure S8 shows the representative powder XRD patterns of the samples recorded at various hydrothermal times. The diffraction peaks can be indexed to the monoclinic metastable polymorph of $\text{TiO}_2(\text{B})$ (space group C2/m , JCPD No. 35-0088) [13]. The framework of the $\text{TiO}_2(\text{B})$ structure is constructed from corrugated sheets of edge and corner-sharing TiO_6 octahedra that are linked by bridging oxygen atoms to form a three-dimensional network. This structure is more open than those of rutile and anatase, consequently making the material an effective host for lithium ion storage. $\text{TiO}_2(\text{B})$ hollow nanocrystals show a relatively high Brunauer–Emmett–Teller (BET) specific surface area of $139\text{m}^2/\text{g}$ [14]. The plots of pore size distribution are calculated from the desorption isotherm using the Saito–Foley (SF statistical micropore $<2\text{nm}$) and Barrett–Joyner–Halenda (BJH statistical mesoporous) models. Figure S8 shows that hollow TiO_2 -48h nanocrystals possess the microporous and mesoporous structures. From Figure S8, the characteristic peak of 2θ in 14.186° , 15.207° , 24.979° , 28.596° , 29.798° , 48.634° respectively corresponding to crystal planes which are (0 0 1), (2 0 0), (1 1 0), (0 0 2), (-4 0 1), (0 2 0) in $\text{TiO}_2(\text{B})$. This results are in good agreement with the reported Arm-strong et al [15] characteristics of the $\text{TiO}_2(\text{B})$, but the diffraction peak of the sample is wide, which shows that the degree of crystallinity in $\text{TiO}_2(\text{B})$ prepared by sodium hydroxide and titanium sulfate is appropriate, and they could have higher specific surface areas.

The morphological characterization of $\text{TiO}_2(\text{B})$ hollow nanocrystals is shown in Figure 3a, the sample shown in Figure 3a has not agglomeration but good dispersion and crystallization. The sample shown in Figure 3b has obviously exhibited that the diameter of hollow $\text{TiO}_2(\text{B})$ nanocrystals is about 10 to 18 nm, this size is smaller than that of other materials, and the wall thickness of hollow nanocrystals is about 3 to 5 nm, this thickness is moderate in comparison with other material hollow spheres, as shown in Figure 3a, hollow $\text{TiO}_2(\text{B})$ nanocrystals have a certain reunion phenomenon. There are some lamellae in addition to a certain number of hollow nanocrystals. This phenomenon is due to presence of a large S in these areas, the increase of S makes ΔG come larger, the unsteady structure with the large ΔG makes TiO_2 hollow nanocrystals collapse. It was some lamellae that they finally made. Figure 3c show the inter-planar distance between the lattice fringes is measured to be 0.31nm, 0.37nm and 0.63 nm, which can be indexed to and (0 0 2), (2 0 1) and (0 0 1) crystal planes of and $\text{TiO}_2(\text{B})$ respectively in the scale of 5 nm, this conclusion is consistent with XRD. Figure 3d shows the SAED patterns of the samples. The samples reveal the diffraction ring radii $R_1=1.59$, $R_2=2.81$, $R_3=3.21$ can be indexed the monoclinic $C2/m$ crystal structure of $\text{TiO}_2(\text{B})$. According to Figure 3d, the diffraction ring radii can not only be matched the $\text{TiO}_2(\text{B})$ lattice planes of (0 0 1), (2 0 0), (0 0 2) but also correspond to the XRD results. The TiO_2 hollow nanocrystals indicate the polycrystalline nature of the samples and each of the diffraction rings can be indexed readily to $\text{TiO}_2(\text{B})$, which are consistent with the XRD results.

Li-reaction with the titanium dioxide polymorphs is conveniently expressed as:

The electrochemical properties of $\text{TiO}_2(\text{B})$ were analyzed by charge-discharge test and cyclic voltammetry. Figure 4a shows the cycling curve of discharge current density at 0.2 C of $\text{TiO}_2(\text{B})$ calcined at 400 °C for 4 hours. It can be seen from the figure that the first discharge capacity was 358.3 mAhg^{-1} . After 100 cycles, the discharge capacity is attenuated to 212.8 mAhg^{-1} . Charge-discharge efficiency of $\text{TiO}_2(\text{B})$ is relatively stable. Because of more pores, the structure of $\text{TiO}_2(\text{B})$ nano hollow spheres has larger specific surface area and increase of the vacancies is conducive to more of the lithium ion insertion and extraction, so the structure has been higher initial specific capacity.

Figure S9 is the charge-discharge curve of $\text{TiO}_2(\text{B})$ at 0.2 C and voltage range of 2.5~1 V. The charging platform is 2.0 V, and the discharge platform is 1.7 V. First discharge specific capacity and charge specific capacity are respectively 358.3 mAhg^{-1} and 261.3 mAhg^{-1} . The discharge capacity is stable in the vicinity of about 275 mAhg^{-1} , which could show good stability. Irreversible capacity loss is 25 %, which is due to the formation of irreversible Li_xTiO_2 after lithium ion is embedded into titanium dioxide crystal into titanium dioxide crystals, the results reflect the irreversible capacity is restricted to the surface structure of titanium dioxide. Because of the reduction of the vacancy of surface, the case enables the reduction of the lithium ion embedded into titanium dioxide, reducing the specific capacity.

Figure S10 shows the cycling curve of discharge current density at 10C of $\text{TiO}_2(\text{B})$. It can be seen from the first discharge capacity in the Figure S10 was 186.6 mAhg^{-1} .

After 1000 cycles, the discharge capacity is attenuated to 105 mAhg⁻¹. It is worth noting that from 200 circles to 600 circles, discharge specific capacity is gradually building up. We conclude that Li⁺ which could slip in and out of the structure may cause the structure to collapse, this situation has led to the decrease of volumetric strain energy, in the end discharge specific capacity is gradually gradually increase. Charge-discharge efficiency of TiO₂(B) not only owns relatively stable but shows powerful vitality as well.

In order to test the electrical properties of this structure, Figure 4b shows cyclic performance of various discharge rate at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10 C. The first discharge capacity reached 258.7 mAhg⁻¹ and the second discharge capacity decreased to 224.9 mAhg⁻¹. It is due to the formation of the volume strain after lithium ions enter monoclinic crystal structure, which has resulted in a loss of approximately 13 % of the irreversible capacity.

In order to obtain electrochemical property of hollow TiO₂(B) nanocrystals, Figure S11 has not only shown the potential range of 1-2.5 V and the scanning rate of 0.1 mVs⁻¹ via TiO₂(B) cyclic voltammetry(CV) curve but also shown a pair of oxidation/reduction peaks at 1.72V and 2.01 V on the CV curves. The average specific capacity of the battery is calculated using formula (Figure S12), $C_m=240.28$ mAhg⁻¹.

4. Conclusions

In conclusion, the charge density distribution can be shown and the system total energy E_{tot} can be calculated $E_{tot}=-3979.7\text{eV}$. We indicate the formation mechanism

of $\text{TiO}_2(\text{B})$ hollow nanocrystals by Oriented Attachment within the lattice structure. We illustrate the formation mechanism of hollow $\text{TiO}_2(\text{B})$ nanocrystals using the nanoscale Kirkendall effect in the range of morphologies, and this chemical change based on Ostwald's rule can be expressed by chemical reaction equation conjectured by us. Hollow $\text{TiO}_2(\text{B})$ nanocrystals have been synthesized by hydrothermal and calcination procedures. The diameter of the hollow nanocrystals is about 10 to 18 nm and the wall thickness of hollow nanocrystals is about 3 to 5 nm. The dimensions are smaller than previous reports. The test results show that hollow $\text{TiO}_2(\text{B})$ nanocrystals have powerful electrical performance. Moreover, the low manufacturing cost could make the nanocrystals come future candidates for lithium ion batteries.

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Figure 1. The charge density distribution of the five atoms based on Monte Carlo model.

Figure 2. The formation mechanism of $\text{TiO}_2(\text{B})$ by Oriented Attachment.

Figure 3. (a) and (b) TEM images of $\text{TiO}_2(\text{B})$ nano hollow spheres. (c) HRTEM image indicating the presence of crystalline nanograin and (d) SEAD image showing lattice planes corresponding to the $\text{TiO}_2(\text{B})$.

Figure 4. Electrochemical performance of Nano structure of $\text{TiO}_2(\text{B})$ hollow spheres as an anode material in LIBs: (a) cycling performance of the electrode at a constant ratio of 0.2C; (d) rate capability at various current rates from 0.1C to 10C.