A single-source molten salt synthesis of uniform octahedral Na$_2$Ti$_3$O$_7$
particels composed of nanorods

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Abstract

Na$_2$Ti$_3$O$_7$, as one of the most potential anode electrode materials, is expected to play an important role in various fields. In this work, we synthesized uniform hollow octahedral Na$_2$Ti$_3$O$_7$ particles through directly sintering a kind of precursors obtained by (NH$_4$)$_2$TiF$_6$ and NH$_4$OH in the presence of sodium-containing cationic polyacrylamide. XRD, SEM, TEM were used to characterize precursors and Na$_2$Ti$_3$O$_7$ particles. In addition, the synthesis conditions and the formation mechanism were discussed in detail. This single-source molten salt method is flexible, efficient and controllable. Moreover, the strategy of this method makes it possible for us to synthesize other sodium titanate materials.

Key words:

Inorganic chemistry; Single-source molten salt method; Sodium titanates
1. Introduction

In recent years, sodium-ion batteries have attracted extraordinary attention owing to their low cost and raw materials in abundance. They offer a promising scalable energy storage alternative to current lithium-ion batteries (LIBs) [1-3]. As a kind of anode electrode materials, sodium titanates, having the general formula of Na$_2$Ti$_n$O$_{2n+1}$ (2 ≤ n ≤ 9), exhibit high ionic exchange ability and high Na$^+$ ion conductivity [4,5]. Na$_2$Ti$_3$O$_7$ (sodium trititanate), a kind of Na$_2$Ti$_n$O$_{2n+1}$ (n=3), has been proved to be a very potential anode material with low voltage plateau (around 0.3 V) [6,7], high charge capacity [8,9] and stable storage capacity [3,10]. It has received considerable attention in various fields such as sodium-ion batteries [4,11,12], ion exchangers [10,13], photocatalysts [14], bioactive ceramics [15] and sensors [16]. Up to now, some methods have been reported for synthesis of Na$_2$Ti$_3$O$_7$ crystals, such as solid-state molten salt reaction [1,6,7,13,14], sol-gel reaction [3,17], hydrothermal reaction [9,12,18]. However, there are some shortages in these methods, such as the long sintering time for solid-state molten salt reaction (10 h ~20 h), the long sol drying time for sol-gel reaction, the high temperature (and a Teflon-lined autoclave is essential) for hydrothermal reaction. These shortages limit the massive production of Na$_2$Ti$_3$O$_7$. In order to synthesize Na$_2$Ti$_3$O$_7$ with high crystallinity more efficiently, an efficient and flexible method is demanded.

In our previous work, we synthesized rod-like Na$_2$Ti$_6$O$_{13}$ particles through a single-source molten method [19]. This method is flexible and efficient, which just needs to directly sinter a kind of precursors obtained by (NH$_4$)$_2$TiF$_6$ and H$_3$BO$_3$ in the presence of sodium salts. Due to the similarities of crystal structure between Na$_2$Ti$_6$O$_{13}$ and Na$_2$Ti$_3$O$_7$ [20], this single-source molten salt approach may be applied to synthesize Na$_2$Ti$_3$O$_7$ particles, only if we can successfully prepare suitable precursors.

In this study, we synthesized uniform hollow octahedral Na$_2$Ti$_3$O$_7$ particles through directly sintering a kind of precursors obtained by (NH$_4$)$_2$TiF$_6$ and NH$_4$OH in the presence of sodium-containing cationic polyacrylamide. The hollow octahedral Na$_2$Ti$_3$O$_7$ particles are composed of nanorods with high crystallinity. In addition, the
formation process and the reaction conditions of this single-source molten salt method were discussed. In comparison with the conventional methods, this method is more flexible, efficient and controllable. Moreover, the strategy of this method also makes it possible for us to synthesize other sodium titanate materials.

2. Experiment

2.1 Materials and methods

Synthesis of precursors: Sodium-containing cationic polyacrylamide (labeled as Na-CPAM) (Tianjin Zhiyuan Chemical Reagent) and \((\text{NH}_4)_2\text{TiF}_6\) (Sigma-Aldrich) were dissolved in 50 ml distilled water, then \(\text{NH}_4\text{OH}\) solution (25 wt%) was added drop by drop with stirring. The final concentrations of \((\text{NH}_4)_2\text{TiF}_6\), \(\text{NH}_4\text{OH}\), Na-CPAM were 0.5 M, 1.0 M and 4 wt%, respectively. After the addition of \(\text{NH}_4\text{OH}\) solution, the mixture solution became turbid and was treated at 25 °C for 30 min. The precipitates were collected and separated by centrifugation, washed \((\times 3)\) with distilled water and dried at 35 °C for 12 h.

Synthesis of \(\text{Na}_2\text{Ti}_3\text{O}_7\): The furnace was preheated to 800 °C. Then the precursor powders were directly put into the furnace and sintered at 800 °C for 2 h.

2.2. Characterization

Scanning electron micrographs (SEM) and EDX spectrum were obtained using a FEI Nova Nano SEM 450. Powder X-ray diffraction (XRD) studies were performed using a PANalytical X’Pert PRO diffractometer. Transmission electron micrographs (TEM) were obtained using a FEI Tecnai G2 F30.

3. Results and discussion

A kind of stable precursors with octahedral morphology was synthesized in the hydrolysis system of \((\text{NH}_4)_2\text{TiF}_6\) and \(\text{NH}_4\text{OH}\) with adding sodium-containing cationic polyacrylamide (labeled as Na-CPAM). SEM images and XRD patterns of the samples prepared by adding different concentrations of Na-CPAM are shown in Figure 1 and Figure 2, respectively. When the Na-CPAM was not added in the hydrolysis system (0 wt% Na-CPAM), the products are rod-like particles (Figure 1a), and the XRD result (Figure 2a) confirms the particles are pure \((\text{NH}_4)_2\text{TiOF}_4\). With adding Na-CPAM, a kind of octahedral particles was synthesized. Under low
Na-CPAM concentration (< 4 wt%), the octahedral particles coexist with rod-like \((\text{NH}_{4})_2\text{TiOF}_4\) particles (Figure 1b and 1c). With increasing the Na-CPAM concentration, the number of octahedral particles increases, together with the decreasing of rod-like \((\text{NH}_{4})_2\text{TiOF}_4\) particles. Especially, when the Na-CPAM concentration is higher than 4 wt%, the products are almost octahedral particles (Figure 1d and 1e), and the peaks of \((\text{NH}_{4})_2\text{TiOF}_4\) (JCPDS-49-0161) phase are almost wiped out (Figure 2d and 2e). These SEM and XRD results demonstrate that a kind of octahedral precursors was synthesized.

To identify the component of octahedral precursors, EDX spectrum was carried out. As shown in Figure 1f, the octahedral precursor particle contains N, F, Na, Ti, O elements. According to our previous work, \(\text{Na}^+\) can partly substitute the position of \(\text{NH}_4^+\) in \(\text{NH}_4\text{TiOF}_3\) [19]. Similarly, in this system, \(\text{Na}^+\) coming from Na-CPAM could partly substitute the position of \(\text{NH}_4^+\) in \((\text{NH}_4)_2\text{TiOF}_4\) and form the precursors. In addition, Na-CPAM, as a cationic surfactant, is crucial to stabilize the structure of precursor particles, which can bond with the inorganic species and control the growth rate of various faces [21]. Since, it seems very probable that the chemical formula of precursor is \((\text{NH}_4)_x\text{Na}_y\text{Ti}_z\text{O}_{\beta}F_{x+y+4z-2\beta}\).

To obtain pure \(\text{Na}_2\text{Ti}_3\text{O}_7\), the furnace was preheated to 800 °C before sintering. Then the precursor powders were directly put into furnace for sintering at 800 °C for 2 h. After sintered, the white powders were characterized by XRD and SEM. The XRD pattern (Figure 3a) indicates that the products are pure \(\text{Na}_2\text{Ti}_3\text{O}_7\). SEM and HRSEM image of a \(\text{Na}_2\text{Ti}_3\text{O}_7\) particle are displayed in Figure 3b and 3c. After the sintering process, the previous overall octahedral shape remains, although the surface is rougher (Figure 3b). HRSEM image of a \(\text{Na}_2\text{Ti}_3\text{O}_7\) particle confirms that the hollow octahedral particle is constructed by large nanorods (Figure 3c) with a length of 3~5 \(\mu\text{m}\) and a diameter of ~300 nm. The details of the \(\text{Na}_2\text{Ti}_3\text{O}_7\) nanorods were further investigated using TEM and SAED. The results are given in Figure 3d. It confirms the \(\text{Na}_2\text{Ti}_3\text{O}_7\) nanorods are highly crystalline, which are consistent with conventional molten salt methods [1,6,7,13,14]. These results indicate that the single-source molten salt method is a highly efficient strategy to synthesize hollow octahedral \(\text{Na}_2\text{Ti}_3\text{O}_7\).
particles composed of nanorods. Furthermore, the hollow octahedral structure may enhance the contact area between the electrode and electrolyte and can improve the efficiency of electrolyte penetration [2,13]. Therefore, the hollow octahedral Na$_2$Ti$_3$O$_7$ particles obtained in this method may have a potential application in battery field.

For the single-source molten salt method, sintering time is very important. In order to investigate the effect of sintering time, the as-prepared precursor powders were sintered at 800 °C for different times, and corresponding XRD patterns are displayed in Figure 4. At the early stage of sintering (1 h), peaks of TiO$_2$ (rutile phase and anatase phase) appear. This evidence suggests that the Ti$^{4+}$ from precursor particles convert to TiO$_2$ and the Na$^+$ form precursor particles may convert to some amorphous sodium salts, which is consistent with our previous work [19]. With the sintering process proceeding, TiO$_2$ and amorphous sodium salts convert to Na$_2$Ti$_3$O$_7$. The Na$_2$Ti$_3$O$_7$ particles obtained in this method are thermodynamic stable without any generation of impurity for longer sintering time (> 3 h). In this process, it is worth noting that the amorphous sodium salts formed at the early stage are essential for the subsequent molten salt reaction. To prove it, the powders prepared by sintering precursor at 800 °C for 1 h were washed with deionized water for three times (amorphous sodium salts were almost eliminated), and later sintered at 800 °C for 2 h. The XRD pattern shows that the products are rutile phase (Figure 4e) without any evidence of Na$_2$Ti$_3$O$_7$. SEM images of samples during the sintering process are shown in Figure 5. At the beginning of the sintering process, the previous smooth surface of octahedral shape becomes rough due to the formation of TiO$_2$ particles and amorphous sodium salts (Figure 5a). When the precursors were sintered at 800 °C for 2 h, the stable hollow octahedral shape Na$_2$Ti$_3$O$_7$ particles composed of nanorods were formed (Figure 5b). However, long sintering time (over 2 h) would lead to the collapse of octahedral shape (Figure 5c and 5d), which could be caused by excessive crystal growth of nanorods. This result suggests that the sintering time is crucial for final component and particle morphology of products.

Moreover, the sintering temperature, as the driving force for phase transformation and crystal growth, is another vital factor for the single-source molten salt reaction. In
order to further investigate the effect of sintering temperature, the as-prepared precursor powders were sintered at different temperatures (400 °C ~700 °C) for 2 h. The corresponding XRD patterns and SEM images are displayed in Figure 6 and Figure 7, respectively. In comparison with 800 °C samples (Figure 3), it is obvious that lower temperature cannot drive the formation of Na$_2$Ti$_3$O$_7$. For the XRD patterns of samples obtained at 400 °C ~600 °C, only peaks of anatase phase particles appear (Figure 6a, 6b and 6c). Even at 700 °C, the XRD pattern shows mixed peaks of anatase and rutile (Figure 6d). SEM images show that the octahedral precursor particles just become rougher (Figure 7a) or collapse into some nanoparticles (Figure 7b-7d) at low sintering temperatures (< 800 °C) condition. These results indicate that 800 °C is essential for molten salt reaction between TiO$_2$ and amorphous sodium salts.

Besides the sintering process used above, we also tried another sintering process. Contrary to preheat the furnace to 800 °C before sintering, the precursor was put into furnace first. Then the precursor powders were heated from room temperature to the required 800 °C and sintering at 800 °C for 2 h. The XRD pattern (see Figure 8a) indicates that the products obtained by this sintering process are composites of Na$_2$Ti$_3$O$_7$ and Na$_2$Ti$_6$O$_{13}$. SEM (Figure 8b) and HRSEM (Figure 8c) image show that the previous overall octahedral shape of precursor particles cannot maintain and collapse into some random rods. The result indicates that the first sintering process is better to prepare pure octahedral Na$_2$Ti$_3$O$_7$ particles composed of nanorods.

With all results and discussions described above, the process of single-source molten salt reaction can be summarized in Figure 9. At the early sintering stage, the octahedral shape precursor particles, as the single reactant, would convert to TiO$_2$ and amorphous sodium salts. With the sintering process proceeding, a molten salt reaction occurs between TiO$_2$ and amorphous sodium salts to form Na$_2$Ti$_3$O$_7$. During the whole process, the previous octahedral shape maintains and the final Na$_2$Ti$_3$O$_7$ particles are composed of nanorods.

**4. Conclusions**

In this work, we synthesized a kind of stable octahedral precursors in the hydrolysis system of (NH$_4$)$_2$TiF$_6$ and NH$_4$OH with adding Na-CPAM. After a
sintering process, the octahedral precursor particles convert to hollow octahedral Na$_2$Ti$_3$O$_7$ composed of nanorods through a single-source molten salt reaction. The sintering condition and the formation mechanism of Na$_2$Ti$_3$O$_7$ were discussed. In comparison with conventional approaches, this approach is more flexible, efficient and controllable. Moreover, the Na$_2$Ti$_3$O$_7$ particles obtained in this method may have a potential application in battery field due to the hollow octahedral overall structure, and the strategy of this method makes it possible for us to synthesize other sodium titanate materials.

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6. References

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Figure 1 SEM images of samples obtained by adding different concentrations of Na-CPAM. (a) 0 wt%; (b) 1 wt%; (c) 2 wt%; (d) 4 wt%; (e) 8 wt%. (f) EDX result and HRSEM image of samples obtained by adding 4 wt% Na-CPAM.
Figure 2 XRD patterns of samples obtained by adding different concentrations of Na-CPAM. (a) 0 wt%; (b) 1 wt%; (c) 2 wt%; (d) 4 wt%; (e) 8 wt%. 
Figure 3 XRD pattern (a), SEM image (b), HRSEM image (c) and TEM image (d) of samples obtained by sintering precursor powders at 800 °C for 2 h. The inset is the SEAD pattern.
Figure 4 XRD patterns of samples obtained by sintering precursor powders at 800 °C for different times. (a) 1 h; (b) 2 h; (c) 3 h; (d) 4 h; (e) After sintering precursor powders at 800 °C for 1 h, the powders were washed by deionized water (3 times), and later sintered at 800 °C for 2 h.
Figure 5 SEM images of samples obtained by sintering precursor powders at 800 °C for different times. (a) 1 h; (b) 2 h; (c) 3 h; (d) 4 h.
Figure 6 XRD patterns of samples obtained by sintering precursor powders at different temperatures for 2 h, (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C.
Figure 7 SEM images of samples obtained by sintering precursor powders at different temperatures for 2 h, (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C.
Figure 8 XRD pattern (a), SEM image (b) and HRSEM image (c) of samples obtained by slowly sintering precursor powders at 800 °C for 2 h.
Figure 9 The formation mechanism of the Na$_2$Ti$_3$O$_7$ synthesized through the single-source molten salt method.