Influence of Na⁺ content on the structure and morphology of TiO₂ nanoparticles prepared by hydrothermal transformation of alkaline titanate nanotubes

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Abstract

The objective of this study is to investigate the role of Na⁺ content in the morphology evolution of TiO₂ nanoparticles prepared by hydrothermal approach. Various TiO₂ morphology from 0-dimensional (0D) nanoparticles to 1-dimensional (1D) nanorods were synthesised by hydrothermally treating the alkali titanate nanotubes with different Na⁺ content. The XRD patterns show the phase transformation and crystallographic nature of alkali titanate nanotubes are strongly dependent on the Na⁺ content, the cation exchange of Na⁺ by H⁺ ion exchange affects the crystallinity of the tubes and causes disorder of the interlayers of nanotubes. The SEM and TEM images confirm that Na⁺ rich titanate nanotubes were thermally stable. Moreover, BET measurements revealed that the Na⁺ content plays an important role on the specific surface area of formed TiO₂ nanoparticles. The photocatalytic activity of the TiO₂ nanoparticles was characterised via the decomposition rate of an aqueous solution of methyl orange (MO) under UV light irradiation. The TiO₂ nanoparticles prepared by hydrothermally treating the alkali titanate nanotubes with no Na⁺ content has a surface area of 55.1 m²/g with nearly 100% photodecomposition of MO in 20 min.

1. Introduction

Synthesising TiO₂ nanomaterials with controlled structures has attracted considerable interests due to the beneficial properties of the architectures [1,2]. In particular, one dimensional (1D) TiO₂ with high aspect ratio are used in a range of applications such as photocatalysis, sensing, H₂ storage and biology [3–5]. Methods for preparing TiO₂ nanostructures include electro-chemical synthesis, chemical synthesis and alkaline hydrothermal method. Among them, the hydrothermal approach is quite simple and enables the production of various TiO₂ nanostructures, especially for TiO₂ 1D structures [6,7].

In 1998, Kasuga et al. [8] first reported the synthesis of titanate nanotubes by reacting TiO₂ nanoparticles and concentrated NaOH solution followed by acid washing. The titanate nanotubes have been found to possess different crystal structures and components,
including H$_2$Ti$_2$O$_4$(OH)$_2$/Na$_2$Ti$_2$O$_4$-(OH)$_2$/Na$_2$H$_2$-xTiO$_5$(H$_2$O), H$_2$Ti$_3$O$_7$/Na$_2$Ti$_3$O$_7$/Na$_x$H$_{2-x}$Ti$_3$O$_7$, and H$_x$Ti$_{2-x}$/4Ax/4O$_4$ (x ≈ 0.7, A stands for vacancy). More importantly, the later research in this field found that the synthesis conditions (the temperature, the sodium concentration, and post-synthesis treatments, etc.) could be adjusted to produce other structures, such as nanorods, nanowires, nanoribbons and nanobelts [9]. According to the previous reports [10], the phase and morphology transformation of formed titanate nanotubes to TiO$_2$ after post-synthesis process are strongly dependent on the Na$^+$ content. For instance, for protonated titanate nanotubes, pure anatase phase is formed, whereas for Na$^+$ rich nanotubes, post-annealing leads to a mixture phases. The presence of protons facilitates acid catalysed condensation of OH groups during annealing treatments [11]. However, the mechanism of phase transformation, crystallographic nature and the role of Na$^+$ content during the post-synthesis treatments in the hydrothermal process still need to be studied.

In this work, the neutralisation process was evaluated in order to clarify the role of cation exchange reaction in the formation of TiO$_2$ nanostructures by hydrothermal synthesis from commercial P25 powder. The morphology and structural modification of TiO$_2$ products which were obtained by the second hydrothermal treatment after washing and acid treatments were followed by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET analysis.

2. Experimental

2.1. Synthesis of TiO$_2$ nanoparticles

The TiO$_2$ nanomaterials were synthesised by hydrothermal method. First, 1.5 g of commercially available P25 (Nippon Aerosil) was added into a Teflon-lined stainless-steel autoclave (100 mL) that had been filled with 60 mL of 10 M NaOH aqueous solution. Then the autoclave was maintained at hydrothermal temperature of 150°C for 24 h. After the first hydrothermal process, the product were filtrated and washed with deionised water until pH ≈ 7 was reached, and then dried at 70°C to obtain the alkali titanate nanotubes. Subsequently, 0.75 g of the alkali titanate sample was immerged into different amounts of 0.1 M HNO$_3$ solution (0, 5, 10, 15, 20, 100 mL) for 6 h in order to make the precursors with different Na$^+$ content (7.37%, 4.03%, 2.72%, 1.70%, 0%), respectively. After filtrated, washed with deionised water and dried at 70°C. Finally, the precursors with different Na$^+$ content were added into autoclave (50 mL) filled with 30 mL deionised water and subjected to the second hydrothermal treatment at 180°C for 24 h. All the products were filtered, washed with deionised water and dried at 70°C to obtain the TiO$_2$ samples.

2.2. Characterisation of the catalysts

X-ray diffraction (XRD) patterns of the samples were obtained on an X-ray diffractometer (D/max-3A, Japan) equipped with Cu K$_\alpha$ radiation ($\lambda$ = 0.15 405 nm). The data was recorded for scattering angles (2θ) ranging from 5° to 60° with a step size of 0.1°, operated at 40 kV and 30 mA. The morphology and microstructure of the samples were characterised by scanning electron microscope (SEM) (Nova Nano 430, Holland). Transmission
electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images of the samples were obtained using a transmission electron microscope (JEM-2010F, JEOL, Japan) operated at an accelerating voltage of 200 kV. For TEM sample preparation, the powders were suspended in ethanol, and then a drop of this suspension was deposited onto a holey carbon film supported by copper grid. The TEM specimen was dried in air prior to the TEM examination. The specific surface area, pore size and pore volume were measured by the Brunauer–Emmett–Teller (BET) method (Micromeritics ASAP 2010 system). The samples were degassed in vacuum at 473 K until the pressure was lower than $10^{-6}$ Torr before each measurement.

### 2.3. Photocatalytic reaction

The photocatalytic activity was measured in a XPA-II photochemical reactor (Nanjing Xujiang Machine-electronic Plant), equipped with a magnetic stirrer, a quartz cool trap and a condensation tube and a 300 W UVA lamp (centred at 365 nm). 0.014 g of catalysts was added into a 280 mL of 20 mg/L methyl orange (MO) solution in a 500 mL cylindrical glass vessel. Before irradiation, the suspension was sonicated in the dark for 15 min to ensure the powder disperse well in the solution, and then bubbled with 150 mL/min air and stirred magnetically for 1 h in the dark to achieve absorption equilibrium. After that, turn on the lamp and conduct the photocatalytic experiment. About 6 mL of the suspension was sampled at intervals of 5 min and separated by centrifugation at 11,000 rpm for 15 min. The remaining solution concentrations were measured by the U3010 spectrophotometer ((U3010, Hitachi, Japan). The whole photocatalytic process was carried out under sparing air of 150 mL/min and magnetic stirring. The degradation ration of MO can be calculated by $(A_0 - A)/A_0 \times 100\%$, and $A_0$ is the absorbance of the 20 mg/L MO at 465 nm, $A$ is the absorbance of the samples at different sampling time.

### 3. Results and discussion

#### 3.1. Effect of Na$^+$ content on the crystalline phase and morphology of products

Alkali titanate nanotubes prepared by the first hydrothermal treatment of TiO$_2$ nanoparticles in a concentrated NaOH aqueous solution were immersed into different amounts of 0.1 M HNO$_3$ solution (0, 5, 10, 15, 20, 100 mL) for 6 h in order to make the precursors with different Na$^+$ content (7.37, 4.03, 2.72, 1.70, 0%), respectively. It has been reported that treating TiO$_2$ nanoparticles in NaOH resulted in formation of lamellar sheets because of the break of Ti-O-Ti bonds [12]. Washing the treated sample with water acid to partially remove the electrostatic charge leading to formation of nanotubular structure. The phase composition of the alkali titanate nanotubes were examined by XRD carefully. Figure 1 shows the XRD patterns of the precursors obtained from hydrothermal treatment of TiO$_2$ nanoparticles in a concentrated NaOH aqueous solution, followed by immersing with different amounts of 0.1 M HNO$_3$ solution. We observed that the pattern of the precursors consisted of five primary characteristic peaks at $2\theta$ values of 10.5°, 24.3°, 28.5°, 31.6°, 48.6°, respectively. It was reported that these peaks corresponded to the layered structure of nanotube titanium oxide [12]. The structure has been assigned to $A_2$Ti$_3$O$_7$, lepidocrocite-type species, or $A_2$Ti$_2$O$_5$$\cdot$H$_2$O, where $A$ represents Na and/or H. A
comparison of the samples and \( \text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O} \) from the Joint Committee on Powder Diffraction (JCPD) Standards (bottom of Figure 1), indicated that the pre-synthesised titanate nanotubes should be layered \( \text{A}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O} \) titanate with an orthorhombic unit cell (JCPD-47–0124) [10,13]. After ion exchange the intensity ratio of diffraction peak at 24.3° and 28.5° changed. The ratio of H/Na in the titanate nanotubes raised due to Na⁺ was displaced by H⁺ in \( \text{Na}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O} \) when the added HNO₃ solution increased from 0 to 20 mL. However, the replacement was not thoroughly, hence, the \( \text{A}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O} \) contained different Na⁺ content. Finally, \( \text{Na}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O} \) transformed into \( \text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O} \) completely when the added HNO₃ solution increased to 100 mL, thereby indicating the tube chemical composition strongly dependents on the ion exchange process.

The present of Na⁺ in prepared alkali titanate nanotubes should be associated with two mechanisms: (i) Na⁺ only adsorbed on the tube surface and/or (ii) structural Na⁺ (which means the cations belong to the tube). As shown in Figure 1, with an increase in the amount of HNO₃ solution, there appears to be a corresponding decrease in the intensity of 10.5° peak, which is anticipated that the Na⁺/H⁺ ion exchange affects the crystallinity of the tubes. Besides, the 10.5° peak is shifted toward higher angle values while more HNO₃ solution were introduced indicating a decrease in the interlayer distance for this plane, this has been ascribed to the decrease in the Na⁺/H⁺ ratio of alkali titanate nanotubes caused by the replacement of Na⁺ with H⁺ during the acid treatment with HNO₃ solution. Therefore, we proposed that Na⁺ belongs to the nanotube structure, the Na⁺/H⁺ ratio decreases due to the cation exchange of Na⁺ by H⁺ and the nanotube composition is appropriately described by a \( \text{Na}_{2-x}\text{H}_x\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O} \) chemical formula. The x value changes from zero to two depending on the amounts of HNO₃ solution is used. The ion exchange of Na⁺ by H⁺ in bulk titanates is a well-known mechanism reported in the literature and it should be somewhat similar in alkali titanate nanotubes [14].

Then, the prepared titanate nanotubes with different Na⁺ content transformed into diverse TiO₂ nanomaterials by another hydrothermal reaction at 180 °C for 24 h. The
XRD patterns of the samples obtained from the second hydrothermal treatment (180 °C for 24 h) are displayed in Figure 2. As shown in Figure 2, with an decrease in the Na+/H+ ratio, the profile of 25° peak belongs to anatase phase become broader and more asymmetric and suggests that the chemical environment between the layers is disordered. More sharpening of the intensity and lower of the full width at half maximum (FWHM) of diffraction peaks reflect the grain size of the samples were getting bigger with the increase of Na+ content of the precursors. The average grain sizes of the anatase nanoparticles prepared from 0%, 2.72%, 7.37% Na+ content of precursors were 17 nm (Figure 2(e)), 21 nm (Figure 2(c)) and 50 nm (Figure 2(a)) respectively, which were determined from the broadening of corresponding X-ray diffraction peaks by Scherer’s formula. Such variations should be associated with different lattice distortions affected by the ion exchange, thus indicating the exchanged H+ ions were incorporated into the lattice rather than only absorbed in outside surface.

3.2. SEM and TEM analysis of the TiO2 nanomaterials synthesised from hydrothermal transformation under different Na+ content of precursors

Figure 3 displays the SEM images of P25 powder and TiO2 products synthesised from the hydrothermal transformation (at 180 °C for 24 h) of precursors with different Na+ content, respectively. We can see that the particle size and shape had been altered with the increasing Na+ content of precursors. As shown in Figure 3(a), the commercially available P25 powder contained many orbicular particles with an average diameter size of ca. 100 nm. However, the TiO2 products obtained from the precursors with different Na+ content presented novel morphology evolution. Figure 3(b) shows that the sample obtained from the precursor without Na+ contained many globular nanoparticles with very small size compared with P25 particles. With an increase in the Na+ content from 1.7% to 7.37%, the morphology of the TiO2 products showed a clear tendency from round shape to rod.
shape (as shown in Figure 3(c–f)), and the particle size became larger and larger. The result has reflected the enlargement of the nanoparticles to be anisotropic [15].

More clear information of the TiO₂ products morphology evolution can be found in Figure 4, which are the TEM and HRTEM images of TiO₂ products synthesised from the hydrothermal transformation (at 180 °C for 24 h) of precursors with different Na⁺ content respectively. As shown in Figure 4(a1), the formed nanoparticles without Na⁺ has a relative regular spherical shape, the HRTEM (Figure 4(a2)) of the nanoparticles indicated the average particle size is around 20–30 nm. The sample obtained from the precursor with 1.7% Na⁺ consisted of rhombic nanoparticles in the majority and spherical nanoparticles in the minority. The HRTEM (Figure 4(b2)) of the nanoparticles indicated the rhombic particles size are around 30–40 nm. We observed from the Figure 4(c1) and Figure 4(c2) that the shape of nanoparticles has a significant change from rhombic to rod structure. The average length of the nanorods is ca. 100 nm. With an increase in the Na⁺ content from 4.03% to 7.37% (Figure 4(d,e)), the length of the nanorods became longer than the sample with less Na⁺ content, and the average length of the sample obtained from the precursor with 7.37% Na⁺ (Figure 4(e1,e2)) is ca. 500 nm. These results reveal that the Na⁺ content in the precursor has a significant influence on the morphology of TiO₂ products synthesised from the hydrothermal transformation. When the Na⁺ content in the precursor higher than 1.7%, the alkali titanate nanotubes are predominately transformed into nanorod particles. To our knowledge, this is the first time to report the effect of Na⁺ content on the hydrothermal transformation process from alkali titanate nanotubes to nanorods. The SEM and HRTEM images indicate that the layered structure of titanate nanotubes with higher Na⁺ content is better defined than the protonated one. According to previous report [16], Na⁺ ions play very important role on the thermal
Figure 4. TEM and HRTEM images of TiO$_2$ products synthesised from hydrothermal transformation (at 180 °C for 24 h) of precursors with (a1, a2) 0%, (b1, b2) 1.70%, (c1, c2) 2.72%, (d1, d2) 4.03%, (e1, e2) 7.37% Na$^+$ content, respectively.
behaviour and Na⁺ rich nanotubes are thermally stable due to the position of Na⁺ ions in the interlayer space.

The BET measurement was showed in Table 1, we can find that the surface area of formed TiO₂ products consisted with the results presented in the SEM and TEM images, the samples with smaller size has the largest surface area of ca.55.1 cm²/g, while the rod shape sample obtained from the precursor with 7.37% Na⁺ has the smallest value in surface area, only ca. 29.1 cm²/g.

### 3.3. Photocatalytic activity

The photocatalytic activity measurements of the obtained TiO₂ products synthesised from hydrothermal transformation at 180 °C for 24 h of precursors with different Na⁺ content are showed in Figure 5. We can observe that the photocatalytic activity of TiO₂ samples increased significantly when the precursor has a complete H⁺ ion exchange and no Na⁺ at all, compared with other samples which were synthesised from the precursors with different Na⁺ content. This can be ascribed to the relative larger surface area and pure anatase phase which both played a positive role in promoting the photocatalytic activity. However, one can notice that the samples prepared from the precursors with 1.7% and (7.37%) have very similar photocatalytic behavior, even the sample (1.7%) has smaller particle size and larger surface area. This is possible due to the sample (7.37%) with mixed crystal phase of

| Samples (Na⁺ content) | S_{BET} (cm²/g) |
|-----------------------|----------------|
| Sample A (0)          | 55.1           |
| Sample B (1.7%)       | 50.5           |
| Sample C (2.72%)      | 49.7           |
| Sample D (4.03%)      | 37.4           |
| Sample E (7.37%)      | 29.1           |

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**Figure 5.** The photocatalytic activity measurements of the obtained TiO₂ products synthesised from hydrothermal transformation at 180 °C for 24 h of precursors with different Na⁺ content, respectively.
large fraction of anatase and small fraction of rutile and 1 dimensional nanorod structure which facilitated the photocatalytic process make up the smaller surface area [17].

4. Conclusions
This study utilised Na⁺ content in the alkali titanate nanotubes to tailor the morphology of TiO₂ nanoparticles by hydrothermal method. Various parameters, such as hydrothermal reaction temperature and time were investigated. 0D nanoparticles and 1D nanorods of TiO₂ can be obtained by hydrothermally treating the alkali titanate nanotubes with different Na⁺ content. The XRD patterns show the crystal phase transformation and chemical environment of alkali titanate nanotubes are strongly dependent on the Na⁺ content, the cation exchange of Na⁺ by H⁺ ion exchange affects the crystallinity of the tubes and causes disorder of the interlayers of nanotubes. The SEM and TEM images confirm that Na⁺ rich titanate nanotubes were thermally stable and Na⁺ ions play very important role on the thermal behaviour due to the position of Na⁺ ions in the interlayer space. Moreover, BET measurements revealed that the Na⁺ content plays an important role on the specific surface area of formed TiO₂ nanoparticles. The existence of Na⁺ has a tendency to reduce the TiO₂ surface area. The Photocatalytic activity of the TiO₂ nanoparticles was characterised via the decomposition rate of MO under UV light irradiation. The TiO₂ nanoparticles prepared by hydrothermally treating the alkali titanate nanotubes with no Na⁺ content with nearly 100% photodecomposition of MO in 20 min, and only 50% MO was degraded when P25 was applied.

Disclosure statement
No potential conflict of interest was reported by the authors.

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