Formation of TiO$_2$ based nanoribbons and the effect of post-annealing on its photocatalytic activity

D Ariyanti$^{1,2}$, S Mo'ungatonga$^1$, Y Li$^3$, and W Gao$^4$

1Department of Chemical & Materials Engineering, the University of Auckland, Auckland 1142, New Zealand
2Department of Chemical Engineering, Universitas Diponegoro Semarang 50275, Indonesia
3School of Mechanical & Electrical Engineering, Henan Institute of Science and Technology, Xinxiang 453003, China
E-mail: dari293@aucklanduni.ac.nz

Abstract. The formation of TiO$_2$ based nanoribbons via alkaline hydrothermal methods and the post-annealing effect on its photocatalytic activity were investigated. The structure features and physical properties were characterized using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier-transform infrared (FTIR). The result shows that the morphology evolution of starting material (TiO$_2$ nanopowder) into TiO$_2$ based nanoribbons is initiated at low temperature (100°C), while the structure transformation occurred at higher temperatures (150-180°C). The process includes formation of layered titanate and dissolution-crystallisation with the ion exchange. The post-annealing process applied to the TiO$_2$ based nanoribbons improves its photocatalytic activity as it provides more active sites. The nanoribbon annealed at 500°C possesses high photocatalytic activity with kinetics constant of 0.082/min.

1. Introduction
Titanium oxide can be made to have many 0-2D layered titanates and 3D crystalline polymorphs, which possess special physical properties and wide range of commercial applications in pigment, photocatalysis, electronics, electrochemical and ceramic industries [1]. Different morphologies such as nanorods, nanotubes, nanosheets, nanoribbons and nanowires can be produced with different methods. Alkaline hydrothermal technique was first introduced by Kasuga et al in 1998 to produce TiO$_2$ nanotubes [2], which converts amorphous TiO$_2$ into nanotubes with almost 100% efficiency [2,3]. TiO$_2$ based nanostructures produced via alkaline hydrothermal methods possess unique physicochemical properties and can be used as catalysis, gas adsorption [4], in lithium battery [5,6] and solar cells [7]. This method can also produce TiO$_2$ nanoribbons, which have the specific surface area and pore volume of 20–25 m$^2$/g and ~0.1, cm$^3$/g respectively [3,4]. In this study, TiO$_2$ based nanoribbons were synthesised via alkaline hydrothermal methods. The effect of post-annealing on its photocatalytic activity was explored. By applying different process parameters, the evolution of morphology and transformation of crystal structure were studied. Its application on photodegradation of organic pollutants was also investigated.

2. Experimental procedures

2.1. Synthesis
Pristine TiO$_2$ powder (anatase, Sigma Aldrich Co. particle size < 25nm) was used as a starting material. TiO$_2$ based nanostructure was prepared by using an alkaline hydrothermal method. 0.2 g anatase powder was dispersed in 30 mL 10 M NaOH solution in a beaker, then immediately transferred to a Teflon-lined autoclave, which was sealed and placed in an oven at 180°C for 20 h. The products then washed first with 0.1 M HCl, followed by deionized water, and then dried at 120°C for 4 h. For the investigation of post-annealing process, TiO$_2$ based nanostructure were annealed at different temperature (400, 500 and 700°C) for 4 h.

2.2. Characterization
Samples was characterized by X-ray diffraction (XRD), Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM-EDS, Philips XL30S FEG), and FTIR (Perkin Elmer FT-IR Spectroscopy ATR). TriStar 3000 surface area analyser was used to evaluate the Brunauer–Emmett–Teller (BET) total surface area, along with the cumulative pore volume and average pore diameter using Barrett–Joyner–Halenda (BJH) method.

2.3. Photocatalytic degradation
Photocatalytic activity was evaluated by monitoring the decomposition of Rhodamine B (RhB) in an aqueous solution under simulated solar and visible light irradiation. TiO$_2$ based nanoribbons (50 mg) was mixed with RhB solution (50mL, 5ppm). After stirring for 60 min in the dark to reach the adsorption equilibrium, the solution was illuminated with simulated sunlight (ULTRA VITALUX, 300W 230V E27). A sample (2 mL) was taken every particular time and filtered by 0.2 µm PVDF syringe filter prior analysis. The concentration of aqueous RhB was determined with a UV-Vis spectrophotometer (Perkin Elmer Instrument) by measuring the peak intensity at 553 nm.

3. Results and discussion
3.1. TiO$_2$ based nanoribbons formation via alkaline hydrothermal method
Figure 1 shows the SEM images of raw pristine TiO$_2$ to TiO$_2$ based nanoribbons via alkaline hydrothermal method. This is a simple process conducted by mixing pristine TiO$_2$ with 10 M NaOH solution, followed by hydrothermal process at certain temperature for 20 hours. In the relatively low temperature (100°C), the hydrothermal method abruptly changed the nanoparticle into a torn sheet-like shape (Figure 1B).

![Figure 1](image_url)

Figure 1 SEM images of TiO$_2$ based nanoribbons formation: (A) Pristine TiO$_2$, (B) by hydrothermal process at 100°C, (C) at 150°C, and (D) at 180°C.
The sheets were decorated with irregular needle-like whiskers. It was suggested that during hydrothermal process with concentrated NaOH, some Ti-O bonds from TiO$_2$ would be broken under high pressure inside the autoclave, resulting in the recrystallization of nanoparticles into lamellar sheet [6]. By increasing the temperature to 150°C, the whisker-like morphology evolves to nanorods of 200 nm long and 10-20 nm in diameter (Figure 1C). By setting up hydrothermal process at 180°C, regular thin nanoribbons were produced (Figure 1D), with width between 200-300 nm and length up to several microns.

![Figure 2](image)

**Figure 2** (A) XRD patterns and (B) FT-IR analysis of TiO$_2$ based nanostructures prepared at different temperatures.

XRD analysis in Figure 2A shows the crystal structure of hydrothermally treated TiO$_2$. Sheet-like structure formed at 100°C is confirmed to be crystalline TiO$_2$ anatase (JCPDS 78-2486), similar to the started material, evidence that only morphology change occurred at 100°C. The nanorods and nanoribbons formed at 150 and 180°C respectively are confirmed to be layered monoclinic structure hydrogen tititanate (H$_2$Ti$_3$O$_7$) with the peaks at 11, 24.5, 33, and 48.4° (JCPDS 47-0561). During hydrothermal process, there are several possibilities of layered protonated titanates may be produced, such as H$_2$Ti$_3$O$_7$, H$_2$Ti$_3$O$_4$,(OH)$_2$, H$_2$Ti$_3$O$_7$·H$_2$O, TiO$_2$·B and H$_2$Ti$_3$O$_7$·H$_2$O, depending on the parameters used during alkaline hydrothermal treatment and acid washing [3,8].

In general, there are two reaction steps during the hydrothermal process at higher temperatures, (1) formation of layered titanate, and (2) dissolution-crystallisation along with ion exchange. The chemical reactions are suggested below [8,12]:

- TiO$_2$ dissolved in 10 M NaOH solution for 15-20 h:
  $3\text{TiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 + \text{H}_2\text{O}$

- Washing with HCl for 24 h:
  $\text{Na}_2\text{Ti}_3\text{O}_7 \rightarrow 2\text{Na}^+ + \text{Ti}_3\text{O}_7^{2-}$
  $2\text{Na}^+ + \text{Ti}_3\text{O}_7^{2-} + \text{H}^+ + \text{Cl}^- \rightarrow \text{H}^+ + \text{Ti}_3\text{O}_7^{2-} + 2\text{Na}^+ + \text{Cl}^-$
  $2\text{H}^+ + \text{Ti}_3\text{O}_7^{2-} \rightarrow \text{H}_2\text{Ti}_3\text{O}_7$

Figure 2B shows the FT-IR result of TiO$_2$ based nanostructures prepared at different temperatures. The absorption peaks located at 443 cm$^{-1}$ correspond to the vibrational frequency of Ti–O–Ti. Vibration mode at 908 cm$^{-1}$ is associated with the stretching vibrations of Ti-O hydrogen titanates [3]. In addition, broad spectrum was observed at 3210 cm$^{-1}$ and strong absorption at 1633 cm$^{-1}$ for
hydrothermally treated sample. While the former attributes to the presence of –OH groups on the surface, the latter indicates the deformation vibration of H-O-H bonds in the physically absorbed water. IR absorption in the range of 1600-3600 cm\(^{-1}\) indicates the presence of –OH groups and H-O-H molecules that are weakly bound in different active sites of TiO\(_2\) [9,10,11].

3.2. TiO\(_2\) based nanoribbons formation via alkaline hydrothermal method
The photocatalytic activity of TiO\(_2\) based nanoribbons were evaluated by the degradation of RhB under solar light simulation. Figures 3A and 3B show RhB degradation curve and kinetics constant respectively of the as produced and TiO\(_2\) based nanoribbons annealed at different temperatures. Direct light degradation of RhB solution in the absence of photocatalyst was not detected.

![Figure 3](image)

**Figure 3** (A) Rhodamine B degradation profile and (B) the kinetics constant of photocatalysis using TiO\(_2\) based nanoribbons at different annealing temperatures.

| Samples                | \(S_{\text{BET}}\) (m\(^2\)/g) | Pore volume (cm\(^3\)/g) | Pore size (nm) |
|------------------------|-------------------------------|--------------------------|----------------|
| As produced nanoribbon | 89.805                        | 0.384                    | 15.896         |
| Annealed at 500°C      | 37.8735                       | 0.340                    | 36.480         |
| Annealed at 700°C      | 12.1093                       | 0.056                    | 23.352         |

After the adsorption equilibrium reached at 60 min, the as produced nanoribbon shows higher adsorption capacity than TiO\(_2\) based nanoribbons annealed at different temperatures. The former adsorb almost 50% of RhB while the latter adsorb less than 30%. The adsorption capacities of TiO\(_2\) based nanoribbons follow the order of annealed at 500°C > 400 and 700°C. At first, it was expected that the high adsorption capacity will result in high photocatalytic activity, as the absorbed RhB could have higher chance to be degraded in the surface of catalyst. However, the experimental result shows that the kinetics constants of TiO\(_2\) based nanoribbons follow the order of annealed at 500°C > 400 > 700°C > as produced nanoribbons (Figure 3B). The degradation rate follows the pseudo first-order reaction kinetics; and kinetics constant is calculated by using equation \(\ln(C_0/C) = kt\).
Adsorption capacity is largely influenced by pore size and pore volume of adsorbent [13,14]. Based on the surface area and pore size distribution analysis (Table 1), the as produced nanoribbons contain higher mesopores and pore volume compared to the annealed samples, which favour the adsorption of RhB molecules to the inner and narrow micropores.

![Figure 4](image-url) (A) XRD patterns and (B) FT-IR analysis of TiO$_2$ based nanoribbons annealed at different temperatures.

On the other hand, photocatalytic activity is mainly governed by TiO$_2$ crystallinity, defect structure, active site and specific surface area. Even the as produced nanoribbons possess high specific surface area; it has low number of active sites compared to TiO$_2$ based nanoribbons annealed at different temperatures. Figures 4A and AB shows XRD patterns and FT-IR analysis of TiO$_2$ based nanoribbons after annealing at different temperatures. During the annealing, the as produced nanoribbons (H$_2$Ti$_3$O$_7$) undergo rearrangement as a consequence of heating and continuous water loss [15], yielding anatase TiO$_2$ (JCPDS 78-2486) and small percentage of rutile TiO$_2$ JCPDS 78-1508 (annealed at 700°C) with the degree of crystallinity determined by the annealing temperature. Anatase structure is desirable for the photocatalytic reaction [16] due to the highly active sites. The nanoribbon annealed at 500°C demonstrates high photocatalytic activity over nanoribbon annealed at 700°C. The former has a higher specific surface area, ~3 times compared to the latter. High specific surface area provides larger contact area for RhB molecules to the catalyst. It also associated with the surface area which provides additional active sites for absorbing light to generate charge for photocatalytic reaction. Thus the combination of TiO$_2$ crystallinity, number of active site and specific surface area improves photocatalytic degradation of RhB.

4. Conclusions

TiO$_2$ based nanoribbons produced via alkaline hydrothermal methods and post-annealing effect on its photocatalytic activity has been investigated. Two reaction steps that determine its structure during the hydrothermal process at 150-180°C include formation of layered titanate and dissolution-crystallisation along with the ion exchange. The morphology evolution is initiated at 100°C and mostly driven by the high pressure in the autoclave. The post-annealing improves the photocatalytic activity
of TiO$_2$ based nanoribbons at a certain extent (500°C) as it can maintain the surface area and pore volume while providing higher active sites for photocatalytic reaction.

5. References
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Acknowledgments
The authors would like to thank the group of Advanced Materials and Department of Chemical and Materials Engineering, the University of Auckland for their assistances. Dessy Ariyanti also thank the Directorate General of Resources for Research, Technology and Higher Education, Ministry of Research, Technology, and Higher Education of Indonesia for the scholarship support.