



# Synthesis and Photocatalytic Performance of Titanium Dioxide Nanofibers and the Fabrication of Flexible Composite Films from Nanofibers

Ming-Chung Wu<sup>1,4</sup>, Geza Tóth<sup>1</sup>, András Sápi<sup>2</sup>, Anne-Riikka Leino<sup>1</sup>, Zoltán Kónya<sup>2</sup>,  
Ákos Kukovecz<sup>2</sup>, Wei-Fang Su<sup>3</sup>, and Krisztián Kordás<sup>1,5,\*</sup>

<sup>1</sup>Microelectronics and Materials Physics Laboratories, Department of Electrical and Information Engineering, University of Oulu, 90014 Oulu, Finland

<sup>2</sup>Department of Applied and Environmental Chemistry, University of Szeged, H-6720 Szeged, Hungary

<sup>3</sup>Department of Materials Science and Engineering, National Taiwan University, Taipei 106-17, Taiwan

<sup>4</sup>Department of Chemical and Materials Engineering, Chang Gung University, Tao-Yuan 333-02, Taiwan

<sup>5</sup>Technical Chemistry, Department of Chemistry, Chemical-Biological Center, Umeå University, SE-901 87 Umeå, Sweden

Mon, 16 Apr 2012 12:16:27

Titanium dioxide nanofibers were synthesized and applied in flexible composite films that are easy to handle and recycle after use. The nanofibers were obtained in a multi-step procedure. First, sodium titanate nanofibers were prepared from TiO<sub>2</sub> nanoparticles through the alkali hydrothermal method. In the next step, sodium hydrogen titanate nanofibers were made by washing the sodium titanate nanofibers in HCl solution. Finally, the sodium hydrogen titanate nanofibers were transformed to TiO<sub>2</sub> anatase nanofibers by calcination in air. The photocatalytic activity of TiO<sub>2</sub> anatase nanofibers were evaluated and compared to a TiO<sub>2</sub> nanoparticle catalyst by decomposing methyl orange dye in aqueous solutions. The achieved reaction rate constant of TiO<sub>2</sub> anatase nanofibers was comparable to that of Degussa P25. Paper-like flexible composite films were prepared by co-filtrating aqueous dispersions of TiO<sub>2</sub> catalyst materials and cellulose. The composite films made from the nanofibers exhibit better mechanical integrity than those of the nanoparticle-cellulose composites.

**Keywords:** TiO<sub>2</sub>, Nanofiber, Nanowire, Nanoparticle, Flexible Film, Photocatalyst.

## 1. INTRODUCTION

Production of renewable energy sources as well as degradation of organic contaminants using photochemical processes are of great economical and environmental interest.<sup>1–4</sup> Several studies have focused on indoor as well as outdoor air quality and waste water treatment due to the significantly increased emission of volatile organic compounds, coloring agents, and industrial dye wastes amongst others.<sup>5–7</sup>

In the recent years, for such applications, alkali titanates (A<sub>2</sub>Ti<sub>n</sub>O<sub>2n+1</sub>) have attracted considerable attention due to their good photocatalytic performance, ion-exchange/intercalation properties, and multiplex shapes.<sup>8,9</sup> Titanium dioxide (TiO<sub>2</sub>) is another reasonable choice for photocatalytic applications since it is an abundant material, affordable for a broad spectrum of various applications, shows advantageous photocatalytic properties

(good activity and photostability) and environmentally friendly.<sup>10,11</sup> TiO<sub>2</sub> is a wide-band-gap semiconducting material with three different natural crystalline phases.<sup>12</sup> According to several studies, the anatase based photocatalysts offer the most viable alternative for degradation of organic contaminants in both water and air.<sup>13–15</sup>

The alkaline hydrothermal synthesis<sup>16–18</sup> has opened new possibilities for large scale and simple production of various types of titanate nanostructures such as nanoparticles, nanofibers and nanotubes. These titanates can be then used as starting materials for the synthesis of nanostructured highly photoactive TiO<sub>2</sub>-based materials by a simple thermal annealing procedure.

In this work, high quality anatase nanofibers were synthesized, and used to prepare paper-type composite films by co-filtrating the nanofibers with cellulose. The photocatalytic activity of the anatase nanofibers are compared to commercial TiO<sub>2</sub> nanoparticles and the mechanical behavior of catalyst-cellulose composite films are also studied.

\* Author to whom correspondence should be addressed.

## 2. EXPERIMENTAL DETAILS

Sodium titanate nanofibers were prepared by suspending 30.0 g TiO<sub>2</sub> anatase powder in 15.0 M NaOH aqueous solution of 1 L volume, followed by a treatment in a teflon-lined autoclave at 155 °C for 24 hours, applying 28 rpm revolving around its short axis. The product was washed with deionized water and finally filtered and dried in air at 70 °C.

For the preparation of sodium hydrogen titanate nanofibers, we use a similar process as described above but the TiO<sub>2</sub> powder was dispersed in aqueous 10.0 M NaOH solution at 175 °C for 24 hours and the applied revolution rate of the autoclave was 120 rpm. The product, i.e., sodium titanate nanofibers was then washed in 0.10 M HCl to exchange Na<sup>+</sup>-ions to protons. The product was washed with deionized water and finally filtered and dried in air at 70 °C.

In order to prepare highly crystalline anatase TiO<sub>2</sub> from sodium titanate and sodium hydrogen titanate nanofibers, a quick screening for finding the optimum calcination temperature was carried out (calcination in air at 300, 400, 500, 600 and 700 °C for 6 hours).

The heat-treated nanofibers were tested by UV light-induced photodegradation of methyl orange in aqueous solutions (widely accepted and used model reaction in photocatalysis). The 10 different samples were suspended in the dye solutions and after 20 min UV irradiation (mercury vapor lamp, 125 W) the decoloration of the dye in the dispersion was evaluated by visual observation. Since the sample of sodium hydrogen titanate calcined at 600 °C performed the best amongst all catalyst, in the subsequent experiments we have selected this material and temperature of calcination for the more detailed studies.

The sodium hydrogen titanate nanofibers were calcined at 600 °C with a heating rate of 1 °C/min for 12 hours to obtain the anatase form. The comparison between photocatalytic activity of TiO<sub>2</sub> anatase nanofibers and commercial TiO<sub>2</sub>-based photocatalyst (Degussa P25) was performed by monitoring the decoloration of methyl orange. In a typical experiment, 10.0 mg of catalyst was sonicated for 2 min in 10 mL methyl orange (Reanal) aqueous solution (10 mg/L). (Note: Degussa P25 is a common standard to compare TiO<sub>2</sub>-based photocatalyst materials. It contains anatase and rutile nanoparticles in a ratio of about 3:1 having size of 85 and 25 nm, respectively<sup>19</sup>).

The suspension was irradiated with UV light (Mercury-vapor lamp, 80 W) under vigorous stirring at ambient conditions. After a centrifuging process (for 15 min at 3200 rpm), the UV-Vis spectrum of remained methyl orange and its derivatives in the supernatant was recorded in the spectral range from 200 nm to 700 nm (Hitachi U-2001, UV-Vis spectrophotometer). The methyl orange concentration was calculated from the absorbance at  $\lambda = 464$  nm extrapolated to a previously plotted calibration curve.

Two types of freestanding flexible catalyst films were made by dispersing 70.0 mg cellulose fibers (Sigma-Aldrich, C6288) and 60.0 mg of TiO<sub>2</sub> anatase nanofibers or Degussa P25 in 20 mL deionized water with ultrasonic agitation for 30 min followed by subsequent stirring for 30 min. The dispersion was then filtered through membranes of 0.2  $\mu$ m pore size then dried at room temperature for 12 hours, and finally detached from the membrane. These freestanding flexible catalyst films were cut to  $\sim 5$  mm  $\times$   $\sim 30$  mm for tensile test measurements. The thickness of the films was about 200  $\mu$ m.

The microstructure of composite films and the morphology of individual nanofibers were studied by field-emission scanning electron microscopy (FESEM, Zeiss Ultra plus) equipped with an EDX-analyzer, transmission electron microscopy (EFTEM, LEO 912 OMEGA, 120 kV) and by X-ray diffraction (XRD, Siemens D5000 and Philips PW 1380, Cu K $\alpha$  radiation).

## 3. RESULTS AND DISCUSSION

The microstructure of the sodium titanate nanofibers synthesized by the alkaline hydrothermal method is shown in Figure 1(a). The nanofibers are having length of up to a few micrometers and diameter of 80–150 nm. Elemental analysis by EDX showed that the sodium content of the acid washed fibers is considerably lower ( $\sim 1.3$  wt%) than that of the non-treated material ( $\sim 6.1$  wt%). The washing procedure causes no visible change in the microstructure of the samples (Fig. 1(b)).

X-ray diffraction patterns of the thermally treated sodium titanate and sodium hydrogen titanate nanofibers (Fig. 2) show a phase-transformation occurred. The sodium titanate changes to a mixture of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>, Na<sub>2</sub>O and TiO<sub>2</sub> phases.<sup>17,20</sup> However, sodium hydrogen titanate nanofibers underwent a different phase-transformation.<sup>9</sup> The results show that the SHT600 nanofibers calcined at 600 °C for 6 hours present optimal TiO<sub>2</sub> anatase phase [PDF no. 89-4921]. At 700 °C the formation of the catalytically less active rutile-phase starts as

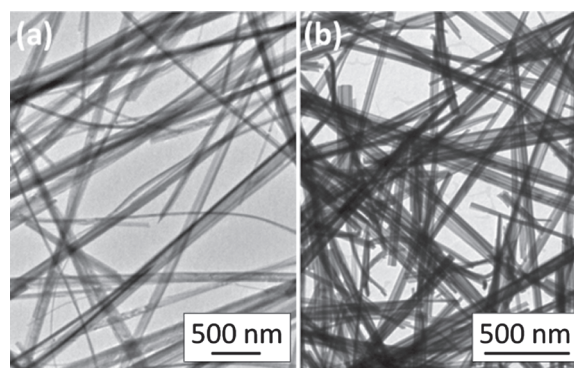
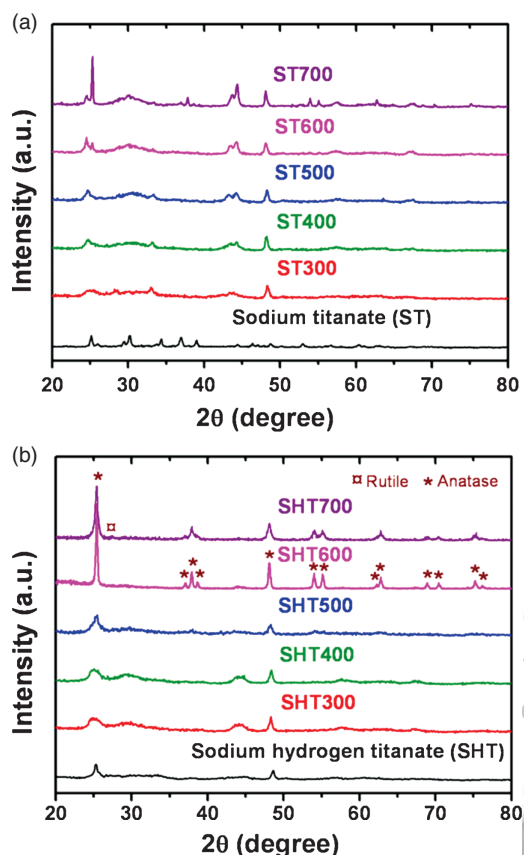


Fig. 1. TEM images of (a) sodium titanate nanofibers and (b) sodium hydrogen titanate nanofibers.



**Fig. 2.** XRD patterns of (a) sodium titanate nanofibers and (b) sodium hydrogen titanate nanofibers calcined in air at 300, 400, 500, 600 and 700 °C for 6 hours, respectively.

shown by the appearance of (110) reflection at  $\sim 27.2^\circ$  [PDF no. 77-0445].

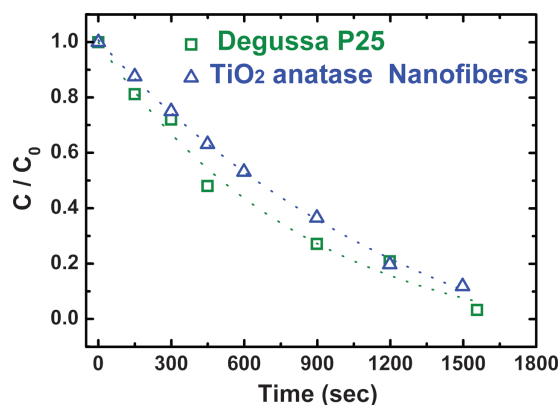
In the photocatalytic screening experiments (visual observation of methyl orange decoloration after 20 min UV irradiation) the thermally treated sodium titanate nanofibers (all) and the low temperature annealed (300 °C and 400 °C) hydrogen titanate fibers showed poor activity. The sodium hydrogen titanate nanofibers calcined at 500 °C, 600 °C and 700 °C however performed well. The overall order of photocatalytic activity results are SHT600 > SHT700 > SHT500 > SHT400~SHT300 indicating that the nanofibers treated at 600 °C consisting of only the anatase crystalline phase are the most promising ones for photocatalytic applications. In a subsequent experiment, we have also checked whether longer calcination at 600 °C may help improving the activity. The results showed samples calcined for 12 h perform better than those annealed only for 6 h. The crystal structure remained the same anatase phase however with a better crystallinity. Therefore, we decided to use 12 h calcination time for preparing anatase nanofibers for an in-depth kinetic study of methyl orange photodegradation model reaction.

The TiO<sub>2</sub> catalyzed photodegradation of organic dyes obeys well the Langmuir–Hinshelwood mechanism. For low dye concentrations, the kinetics is of first-order

and can be described as  $\ln(c_0/c) = kt$ , where  $c$  is the concentration of the dye at time  $t$ ,  $c_0$  denotes the initial concentration and  $k$  is the apparent reaction rate constant.<sup>21</sup> The methyl orange decoloration over both the TiO<sub>2</sub> anatase nanofibers and the commercial Degussa P25 (Fig. 3) show very similar rates with calculated rate constants of  $\sim 0.078 \text{ min}^{-1}$  and  $\sim 0.082 \text{ min}^{-1}$ , respectively.<sup>22</sup> Consequently, we may assume that the obtained TiO<sub>2</sub> anatase nanofibers might be reasonable alternatives of the traditional Degussa P25 for photocatalytic applications.

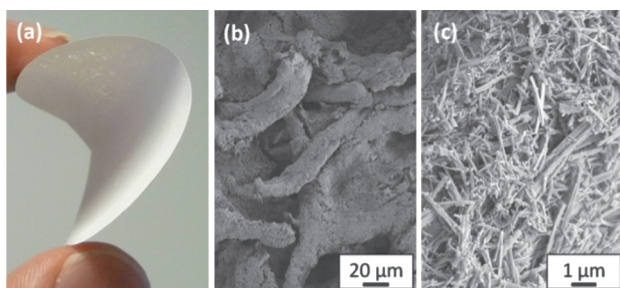
In the recent years, photocatalytic degradation of organic contaminants is intensively researched; however recycling the photocatalyst is problematic because of the separation of catalyst from the reactants. Here, we propose the use of composite membranes made of cellulose and TiO<sub>2</sub> anatase nanofibers (Fig. 4(a)) to overcome difficulties normally associated with powder type catalyst materials. Even without serious optimization of the co-filtration process, the cellulose composite membranes have reasonable mechanical integrity, and are easy to handle and reuse. The cellulose microfibrils are uniformly coated with the catalyst materials as show in Figures 4(b and c). The as-prepared membranes are flexible and can be folded until a curvature radius of  $\sim 5 \text{ mm}$  (when the membrane buckles and then breaks). The different shapes of TiO<sub>2</sub> catalyst coating the cellulose fibers in the composite films seems to influence the mechanical friction and stick behavior of the adjacent microscopic cellulose fibers. The membranes based on the commercial TiO<sub>2</sub> nanoparticles are significantly softer than those made of the nanofibers. The Young's moduli of two types of freestanding flexible catalyst/cellulose films were  $\sim 7 \text{ MPa}$  (cellulose/nanoparticle) and  $\sim 54 \text{ MPa}$  (cellulose/nanofiber) with corresponding tensile strength values of  $\sim 15 \text{ kPa}$  and  $\sim 90 \text{ kPa}$ , respectively.

In conclusion, sodium hydrogen titanate nanofibers calcined at 600 °C for 12 hours led to the formation of TiO<sub>2</sub> anatase nanofibers showing almost the same photocatalytic activity as Degussa P25. The potential advantage of using nanofibers instead of nanoparticles becomes conspicuous in film-type photocatalyst applications. Since composites



**Fig. 3.** Photocatalytic activities of Degussa P25 and TiO<sub>2</sub> anatase nanofibers over the photodegradation of methyl orange.





**Fig. 4.** (a) Photograph taken from a bent catalyst membrane, (b) SEM image of cellulose/TiO<sub>2</sub> anatase nanofiber composite, and (c) SEM image of TiO<sub>2</sub> anatase nanofibers on a cellulose fiber surfaces.

of nanofibers with cellulose (and probably with many other fibrous materials) enable mechanically strong structures, after some optimization, such catalyst films/membranes might be good candidates in large-area “intelligent” coatings and freestanding films produced in large volumes e.g., by paper and printing industries.

**Acknowledgment:** The authors are grateful for financial support received from TEKES (projects: 52423 and 52433) and Academy of Finland (projects: 120853, 124357, 128626 and 128908), the Hungarian Scientific Research Fund (projects: NNF-78920 and 73676) and National Science Council of Taiwan (projects: 98-3114-E-002-001 and 99-2120-M-002-011).

## References and Notes

1. A. Fujishima and K. Honda, *Nature* 238, 37 (1972).
2. U. I. Gaya and A. H. Abdullah, *J. Photochem. Photobiol. C* 9, 1 (2008).
3. F. E. Osterloh, *Chem. Mater.* 20, 35 (2008).
4. K. S. Deffeyes, *Beyond Oil: The View from Hubbert's Peak*, Hill and Wang, New York (2005).
5. C. Kim, J. T. Kim, K. S. Kim, S. Jeong, H. Y. Kim, and Y. S. Han, *Electrochim. Acta* 54, 5715 (2009).
6. Y. Wu, J. Zhang, L. Xiao, and F. Chen, *Appl. Catal. B* 88, 525 (2009).
7. H. H. Tseng, M. C. Wei, S. F. Hsiung, and C. W. Chiou, *Chem. Eng. J.* 150, 160 (2009).
8. Y. C. Pu, Y. C. Chen, and Y. J. Hsu, *Appl. Catal. B* 97, 389 (2010).
9. C.-H. Lin, J.-H. Chao, C.-H. Liu, J.-C. Chang, and F.-C. Wang, *Langmuir* 24, 9907 (2008).
10. M. Kitano, M. Matsuoka, M. Ueshima, and M. Anpo, *Appl. Catal. A* 325, 1 (2007).
11. J. Virkutyte, B. Baruwati, and R. S. Varma, *Nanoscale* 2, 1109 (2010).
12. K. Tanaka, M. F. V. Capule, and T. Hisanaga, *Chem. Phys. Lett.* 187, 73 (1991).
13. N. Negishi, S. Matsuzawa, K. Takeuchi, and P. Pichat, *Chem. Mater.* 19, 3808 (2007).
14. I. C. Kang, Q. Zhang, S. Yin, T. Sato, and F. Saito, *Appl. Catal. B* 80, 81 (2007).
15. M. Zlamal, J. Krysa, and J. Jirkovsky, *Catal. Lett.* 133, 160 (2009).
16. F. C. Wang, C. H. Liu, C. W. Liu, J. H. Chao, and C. H. Lin, *J. Phys. Chem. C* 113, 13832 (2009).
17. M. Qamar, C. R. Yoon, H. J. Oh, N. H. Lee, K. Park, D. H. Kim, K. S. Lee, W. J. Lee, and S. J. Kim, *Catal. Today* 131, 3 (2008).
18. E. Horvath, A. Kukovec, Z. Konya, and I. Kiricsi, *Chem. Mater.* 19, 927 (2007).
19. T. Ohno, K. Sarukawa, K. Tokieda, and M. Matsumura, *J. Catal.* 203, 82 (2001).
20. H. Liu, D. Yang, Z. Zheng, X. Ke, E. Waclawik, H. Zhu, and R. L. Frost, *J. Raman Spectrosc.* 41, 1331 (2010).
21. A. Katti, S. R. Venna, and M. A. Carreon, *Catal. Comm.* 10, 2036 (2009).
22. M.-C. Wu, A. Sapi, A. Avila, M. Szabó, J. Hiltunen, M. Huuhtanen, G. Tóth, Á. Kukovec, Z. Kónya, R. Keiski, W.-F. Su, H. Jantunen, and K. Kordás, *Nano Res.* 4, 360 (2011).

Received: 18 August 2010. Accepted: 3 November 2010.