Influence of Thermal Treatment and Fe-Loading on Morphology, Crystal Structure, and Photocatalytic Activity of Sodium Titanate Nanotubes

INDERPREET SINGH GROVER, SATNAM SINGH, and BONAMALI PAL

School of Chemistry and Biochemistry, Thapar University, Patiala, Punjab, India

An understanding of collective influence of Fe-loading and calcination on changes in the crystal structure, morphology, phase composition, and photocatalytic activity of titanate-nanostructures is investigated here. Bare sodium-titanate nanotubes (TNT) having a BET-surface-area ($S_{\text{BET}}$) of 176 m$^2$ g$^{-1}$ were transformed to sodium-titanate nanorods (TNT(S)) of $S_{\text{BET}} = 21$ m$^2$ g$^{-1}$ when calcined at 800°C. Whereas, calcination of Fe-loaded-TNT at 800°C led to a variety of fragmented particles having different crystal structures, $S_{\text{BET}}$ (21–39 m$^2$ g$^{-1}$), shape, and sizes (50–70 nm) attributed to the strain induced thermal-decomposition of TNT after Fe-loading. The comparative photocatalytic activity of as-prepared catalysts under UV-light irradiation was evaluated by photooxidation of naphthalene to CO$_2$, with the identification of its photoproduced intermediates by GC-MS analysis. These results are well explained in correlation with the surface area, size, and shape of as-prepared catalysts.

Keywords: Crystal phases of Na-titanate, effect of calcination on titanates, Na-titanate nanostructures, photoactivity of Fe-titanate

1. Introduction

Nanotubes are ubiquitous to the scientific world due to their spectacular properties such as high surface-to-volume ratio, hollow interior, high pore volume, and surface area (Morgado et al. 2006; Qamar et al. 2006; Yu et al. 2006; Lee et al. 2007; Qamar et al. 2008). Recently, a number of nanotubes made of inorganic materials showed intriguing properties that are quite different from those of carbon nanotubes and possess a wide range of potential applications (Bavykin et al. 2006). Among such materials, sodium titanate nanotubes have received great attention as piezoelectric and/or magnetic materials (Pookmanee and Phanichphant 2005; Nath et al. 2008) in a wide range of applications such as photocatalysis (Morgado et al. 2006; Qamar et al. 2006; Yu et al. 2006; Lee et al. 2007) and sensing (Chen and Mao 2007). It is well documented that TNT possesses crystalline and scroll structures (Yu et al. 2006, Qamar et al. 2008) that could be easily prepared by hydrothermal treatment of crystalline TiO$_2$ with concentrated aqueous solution of NaOH. A number of different crystal structures and compositions for TNT are reported (Morgado et al. 2006) and have been confirmed by the products formed after its calcination. Calcination of TNT at elevated temperatures causes changes in its crystal structure and morphology. For instance, Qamar et al. (2008) claimed that TNT after calcination at 700–800°C transformed into crystalline sodium titanate nanorods having a monoclinic Na$_2$Ti$_6$O$_{13}$ crystal structure that confirms the presence of an orthorhombic Na$_2$Ti$_3$O$_7$ crystal structure in TNT.

It is known that TNT having a layered structure can also be used as an ion exchanger (Chen and Mao 2007; Nath et al. 2008) resulting in the formation of better metal dispersed photocatalysts. Nonetheless, there are very few reports on exploration of the ion exchange ability of TNT, e.g., Tsai et al. (2009) and Si et al. (2011) exchanged Na$^+$ ions in TNT with Fe$^{3+}$ and Au$^{3+}$ ions and studied the photooxidation of CO and H$_2$ production, respectively. However, the effect of these exchanged metal ions on the crystal structure and morphology of TNT has not been well considered, as the exchange of these ions may induce a strain in the crystal structure (Garcia et al. 2004; Adan et al. 2007) that may cause changes in its properties. Moreover, the effect of calcination temperatures on such strained TNT toward changes in its crystal structure, composition, and morphology is not documented. Thus, the present work demonstrates the effect of postthermal treatment (800°C) on the crystal structure, phase composition, morphology of bare, and Fe$^{3+}$ ion exchanged (0.2 and 0.5 wt%) TNT. The comparative photocatalytic activity of as-prepared catalysts has been assessed by photooxidation of naphthalene (C$_{10}$H$_8$), a probable human carcinogen.
2. Experimental Section

2.1 Materials

Sodium hydroxide (AR), methanol (AR), ferric chloride (AR), naphthalene (AR), and nitric acid (AR) were purchased from Loba Chemie, India. Commercially available P25-TiO2 was obtained from Evionik (formerly Degussa Corporation, Frankfurt, Germany). All the chemicals were used without further purification.

2.2 Synthesis, Characterization, and Photoactivity of Bare and Fe\textsuperscript{3+} Exchanged Samples

TNT was prepared through a hydrothermal route by autoclaving P25-TiO2 with NaOH as recently reported by our group (Grover et al. 2013). Thus, the obtained TNT (0.3 g) was stirred for 3 h with an appropriate amount of aqueous solution of FeCl\textsubscript{3} (equivalent to 0.2 and 0.5 wt% of Fe\textsuperscript{3+} ions), dried at 60°C with stirring to obtain Fe\textsuperscript{3+}-loaded TNT and denoted as 0.2- and 0.5-Fe-TNT. Afterwards, bare and Fe\textsuperscript{3+}-loaded TNT samples were calcined at 800°C in an alumina crucible (heating rate 5°C/min, for 2 h) using the muffle furnace (Jupiter Scientific) and abbreviated as TNT(S) (for bare) and 0.2- and 0.5-Fe-TNT(S) (for Fe-loaded).

The samples were characterized by XRD (Panalytical X’pert using Cu Kα, λ = 1.54178 Å). Phase composition (%) and d\textsubscript{spacing} were determined using the X’Pert High Score Plus software. The strain in the as-prepared samples was determined (Singla et al. 2012) from the slope of the line obtained by plotting a graph between βcosθ vs 4sinθ, where β = full width at half-maxima, θ (in radians), i.e., half of the 2θ (from XRD) diffraction line. Transmission electron microscopic (TEM) images were recorded on a Hitachi 7500 electron microscope, using 120 kV accelerating voltage. The BET surface area was measured with Smart Sorb 93 using 150 mg of the sample preheated at 150°C for 1 h. The photocatalytic activity (PCA) was analyzed in a rubber capped test tube containing 5 ml aqueous solution of naphthalene (10 ppm) with 5 mg of as-prepared sodium titanate nanoparticles under UV-light (Phillips 125 W) irradiation for 60 min. The reaction solution was analyzed using a UV-Visible spectrophotometer (Champion). Quantitative estimation of the formation of CO\textsubscript{2} during photoreaction was monitored using a gas chromatograph (GC, Nucon 5676) equipped with a thermal conductivity detector. Analysis was performed by taking gas samples in a gas-tight syringe (Hamilton, capacity 2.5 ml) and by injecting 1 ml of gas into a Porapak-Q column having flow of N\textsubscript{2} gas as a carrier @ 30 ml/min. The oven was isothermally maintained at 50 ± 3°C, while the injector and the detector were kept at 70 and 100°C, respectively. Identification of intermediates formed during photosynthesis of naphthalene was carried at through a GC (45X-GC)-mass spectrometer (MS-Scion-4SP), by injecting 1 μl of the extracted sample (Electronic Supplementary Information (ESI)-figure S1) in the HP-5MS column (15 m × 0.25 mm × 0.25 μm) having a flow (1 ml/min) of helium as a carrier gas. The oven was programmed from 60°C (5 min hold) to 240°C@6°C, while the transfer line and the injector were kept isothermally at 250°C and 275°C, respectively.

3. Results and Discussion

The XRD pattern of bare and Fe\textsuperscript{3+} (0.2 and 0.5 wt%) ion exchanged TNT at 800°C before and after heat treatment is shown in Figure 1(a) and 1(b), respectively. Before calcination, bare and Fe-TNT samples were composed of orthorhombic Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} crystal structures as evidenced by their characteristic peak at 2θ = 24.0519° for the (1 1 0) plane, which is in accordance with the reported work (Morgado et al. 2006; Qamar et al. 2006; Yu et al. 2006; Lee et al. 2007; Qamar et al. 2008). There was no peak corresponding to any crystalline phase related to \( x \)-Fe\textsubscript{2}O\textsubscript{3} or any other iron oxide due to a very low amount of Fe\textsuperscript{3+} ions (0.2 and 0.5 wt%), suggesting the amorphous phase of iron oxide and/or its fine dispersion on/ between layers of TNT. After calcination at 800°C, bare TNT consisting of orthorhombic (Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}) crystal structures transforms into a crystalline monoclinic (Na\textsubscript{2}Ti\textsubscript{9}O\textsubscript{19}) unit cell, as confirmed by its characteristic peak at 2θ = 24.49° (ICDD data card: 01-073-1398).

---

**Fig. 1.** XRD pattern of (a) bare and Fe\textsuperscript{3+}-ion exchanged TNT and (b) corresponding patterns after calcination: Na\textsubscript{2}Ti\textsubscript{6}O\textsubscript{13}(●), Na\textsubscript{2}Ti\textsubscript{9}O\textsubscript{19} (◆), and NaTiO\textsubscript{2} (□).
This structural transformation has been explained (Jin et al. 2003; Morgado et al. 2006; Qamar et al. 2006; Yu et al. 2006; Lee et al. 2007; Qamar et al. 2008) by condensation of corrugated layers of trittanate having three edge-sharing TiO$_6$ octahedral units into the Na$_2$Ti$_6$O$_{13}$ structure by connecting the corners of opposite octahedra for linking the layers together. This change in the crystal phase as a function of temperature is observed in typical piezolectric materials, which largely affects the magnetic and electronic properties (Pookmanee and Phanichphant 2005; Nath et al. 2008).

Calcination of 0.2-Fe-TNT at 800°C resulted in a mixture of crystalline monoclinic Na$_2$Ti$_9$O$_{19}$ (95%) and rhombohedral NaTiO$_2$ (5%) crystal structures, as confirmed by their characteristic peaks corresponding to 20 = 24.715° (ICDD data card: 01-073-2256) and 40.712° (ICDD data card: 01-089-0803), respectively.

In order to explain the formation of NaTiO$_2$, it is proposed that Fe$^{3+}$ ions got exchanged with Na$^+$ ions in Na$_2$Ti$_6$O$_{13}$, and during calcination, the exchanged Na$^+$ ions are transformed into Na$_2$O$_6$ octahedra. During the formation of NaTiO$_2$ crystals by heating anatase TiO$_2$ with Na, Clarke et al. 1998 suggested alternating layers of edge-sharing NaO$_6$ and TiO$_6$ octahedra with elongation and compression along their the C$_3$-axis, respectively. Our proposal has been further confirmed by the fact that addition of a higher amount of Fe$^{3+}$ ions (0.5 wt%) to TNT replaces a more number of Na$^+$ ions resulting in the formation of a more number of Na$_2$O$_6$ octahedra and hence a higher amount of expected NaTiO$_2$ crystals (95%).

In order to investigate the exchange of Fe$^{3+}$ ions by interlayered Na$^+$ ions, the change in lattice parameters and $d_{\text{spacing}}$ corresponding to the (1 1 0) peak of Na$_2$Ti$_3$O$_7$ was determined. It has been found that there is no significant change in $d_{\text{spacing}}$ due to the presence of Fe$^{3+}$ ions (0.2 and 0.5 wt%) in TNT (Table 1), indicating the absence of Fe$^{3+}$ ions in the lattice of Na$_2$Ti$_3$O$_7$. However, a small decrease in lattice parameters (Table 1, along the a-axis) with the corresponding shift in the peak (Figure 1a) suggested that distortion has been created due to the exchange of larger size Na$^+$ (0.99 Å) with Fe$^{3+}$ ions (0.69 Å). It must be emphasized that such a type of lattice distortion might result from exchange of one Fe$^{3+}$ ion with three Na$^+$ ions to maintain charge balance.

Indeed, such a trend is expected to produce strain in the crystal structure and correlates with the observation on titania doped with transition metals (Mallick et al. (2009)). It has been found that the strain in the crystal structure of TNT increases with an increase in the amount (0.2–0.5 wt%) of Fe$^{3+}$ ions (Table 1), ascribed to exchange of interlayer Na$^+$ ions with Fe$^{3+}$ ions in TNT. In contrast to negligible strain in the crystal structure of Na$_2$Ti$_9$O$_{13}$ (for TNT(S)), the crystal structures (Na$_2$Ti$_9$O$_{19}$ and NaTiO$_2$) of 0.2-Fe-TNT(S) are found to be highly strained, becoming ~2 times for 0.5-Fe-TNT(S) (Table 1), suggesting more replacement of interlayered Na$^+$ ions by Fe$^{3+}$ ions.

TEM analysis of TNT (Figure 2a) shows its open ended cylindrical morphology with diameter (D) 9–12, length (L) 82–113 nm, and small wall thickness 0.8–1.1 nm. Whereas, fine deposits of iron (3–6 nm) could be seen at the surface of TNT for the 0.5-Fe-TNT sample (Figure 2b). The sample TNT upon heating at 800°C transformed into well crystalline, stick like cylindrical titanate nanorods of dimensions $D = 25–30$ nm, and $L = 250–500$ nm (Figure 2c), indicating complete disappearance of TNT and its thermal instability at this temperature. In contrast, calcination of 0.2-Fe-TNT at 800°C resulted in the formation (Figure 3a and 3b) of titania nanopolgons (TNP) having particles in the size range of 60–70 nm (Figure 4a). Such a drastic change in morphology of TNT(S) could be ascribed to the presence of Fe$^{3+}$ ions in TNT. These findings are in conformity with the report of Bryan et al. 2005, suggesting hampering of kinetics for potassium TiO$_2$ particle growth with Co$^{2+}$, Ni$^{2+}$, and Mn$^{2+}$ during temperature treatment, as growth of such materials is likely to be dominated by the surface processes rather than the bulk transport of ions. In the presence of Fe$^{3+}$ ions (exchanged by Na$^+$), the surface free energy (SFE) of TNT decreases and thereby reduces the thermodynamic driving force for the particle growth. This fact in turn was further confirmed by increasing the amount of Fe$^{3+}$ ions (0.5 wt%), where a more decrease in SFE is expected, resulting in the formation of smaller TNP (size ranging from 50 to 60 nm for most of the particles (Figure 4b) than 0.2-Fe-TNT

| S. No | Catalyst | Chemical composition (crystal structure) | Lattice parameters (Å) | Strain |
|-------|----------|----------------------------------------|------------------------|--------|
|       |          |                                        | Calculated              | Reported | $d_{\text{spacing}}$ (Å) |      |
|       |          |                                        | $a$ | $b$ | $c$ | $a$ | $b$ | $c$ | $d_{\text{spacing}}$ (Å) |      |
| 1     | TNT      | Na$_2$Ti$_3$O$_7$ (orthorhombic)       | 20.1 | 3.7 | 3.0 | 19.3 | 3.7 | 3.0 | 3.59 | 7.4 $\times$ 10$^{-4}$ |
| 2     | TNT(S)   | Na$_2$Ti$_6$O$_{13}$ (monoclinic)      | 15.2 | 3.7 | 9.1 | 15.1 | 3.7 | 9.1 | – | 1.5 $\times$ 10$^{-4}$ |
| 3     | 0.2-Fe-TNT | Na$_2$Ti$_3$O$_7$ (orthorhombic)       | 19.2 | 3.7 | 3.0 | 19.3 | 3.7 | 3.0 | 3.64 | 6.9 $\times$ 10$^{-3}$ |
| 4     | 0.2-Fe-TNT(S) | Na$_2$Ti$_9$O$_{19}$ (95%) (monoclinic) | 12.2 | 3.7 | 15.7 | 12.2 | 3.7 | 15.6 | – | 1.5 $\times$ 10$^{-2}$ |
| 5     | 0.5-Fe-TNT | Na$_2$Ti$_3$O$_7$ (orthorhombic)       | 19.1 | 3.6 | 3.0 | 19.3 | 3.7 | 3.0 | 3.69 | 9.1 $\times$ 10$^{-3}$ |
| 6     | 0.5-Fe-TNT(S) | Na$_2$Ti$_9$O$_{19}$ (95%) (monoclinic) | 12.0 | 3.7 | 15.6 | 12.2 | 3.7 | 15.6 | – | 2.4 $\times$ 10$^{-2}$ |

$\frac{1}{2}$, not determined.
**Fig. 2.** TEM images of sodium titanate nanotubes (a) bare, (b) after 0.5 wt% Fe$^{3+}$ loading, and (c) after calcination of bare at 800°C.

**Fig. 3.** TEM images after calcination at 800°C of (a and b) 0.2 wt% Fe-loaded sodium titanate nanotubes and (c and d) 0.5 wt% Fe-loaded sodium titanate nanotubes.
Moreover, a variety of particles of different shapes viz., hexagons, pentagons, heptagons (highlighted by lines in Figure 3d), are formed, which could have a more number of surface exposed atoms and more surface area necessary for better photocatalytic activity.

The calcination of bare TNT resulted in a decrease of $S_{\text{BET}}$ from 176 to 21 m$^2$g$^{-1}$, due to collapse of its hollow interior. The exchange of Na$^+$ ions by 0.2 wt% Fe$^{3+}$ ions in TNT decreases its $S_{\text{BET}}$ (168 m$^2$g$^{-1}$) and this decrease in $S_{\text{BET}}$ becomes more significant (159 m$^2$g$^{-1}$) with an increase in the amount of Fe$^{3+}$ ions (0.5 wt%). However, the small particle size of 0.2-Fe-TNT(S) and 0.5-Fe-TNT(S) resulted in an increase (1.8 times) in $S_{\text{BET}}$ of 28 and 39 m$^2$g$^{-1}$, respectively, than TNT(S).

The PCA of various TNP was assessed by photooxidation of 10 ppm aqueous naphthalene solution under exposure of UV-light for different time intervals (Figure 5). It has been observed that the amount of naphthalene photooxidized by TNT (5.1 ± 0.8 ppm) increases with an increase in the amount of iron (0.2-Fe-TNT = 7.6 ± 0.2; 0.5-Fe-TNT = 9 ± 0.2 ppm) and is found to be ~2 times higher than TNT. However, after calcination of bare and Fe-loaded TNT catalysts, PCA decreases in comparison to their precursors and is least for TNT(S). The photodegradation of naphthalene was found to follow pseudo-first order kinetics (Figure 6). The value of apparent rate constant ($k$) was found to increase from TNT ($1.4 \times 10^{-2}$ min$^{-1}$) to 0.2-Fe-TNT ($2.7 \times 10^{-2}$ min$^{-1}$) and turns into the highest for the 0.5-Fe-TNT catalyst ($5.1 \times 10^{-2}$ min$^{-1}$), while after calcination of these catalysts, $k$ was reduced and became least for TNT(S) ($3.7 \times 10^{-3}$ min$^{-1}$).

Although almost complete oxidation of naphthalene was found using 0.5-Fe-TNT, yet its complete mineralization is not certain, as aerobic oxidation of organic compounds (Grover et al. 2013) often forms other oxidized products instead of complete mineralization. Hence, in order to identify intermediate compounds of naphthalene during photooxidation, GC-MS (Figure 7) analysis was carried out confirming the formation of 1-napthol ($m/z$ = 145) and 1,4-naphthalenedione ($m/z$ = 158) as intermediate compounds, indicating the requirement of more UV-light irradiation for further degradation of intermediate compounds.
compounds and ultimately for their complete mineralization to CO₂ and H₂O.

Therefore, time course quantitative estimation of CO₂ was carried out (Figure 8) to determine the extent of mineralization of naphthalene during its photooxidation. It has been observed that the trends for CO₂ formation by the aforementioned catalysts are similar to photodegradation of naphthalene. The highest amount (22.3 ± 1.3 ppm ~2.6 μmol) of CO₂ formed corresponded to only 65.0% of the actual photomineralization of naphthalene by the 0.5-Fe-TNT catalyst followed by 0.2-Fe-TNT (19.7 ± 0.9 ppm ~2.2 μmol ~55.0%), where 4 μmol (10 times the initial concentration (inset, Figure 8, ESI-table SI) of CO₂ was expected from complete mineralization of 0.4 μmol naphthalene. In contrast to observed complete degradation of naphthalene after 60 min of UV-light exposure, a steady increase in CO₂ formation was observed even after 120 min of its photooxidation corresponding to 65.0% (highest percentage) of the actual mineralization. This can be rationalized by the degradation of photoproduced intermediates into smaller molecules that eventually mineralize to CO₂.

The highest photoactivity of TNT could be ascribed to the collective effect of (i) hollow interior and high specific surface area favoring better adsorption of the substrate, (ii) the better delocalization of charge carriers along its length suppressing their recombination, and (iii) the presence of hydrated water in its crystal structure, which enhances the formation of more hydroxyl radicals, thus increasing the photocatalytic activity (Bavykin et al. 2006; Morgado et al. 2006; Qamar et al. 2006; Lee et al. 2007; Qamar et al. 2008; Grover et al. 2013, 2014). In Fe³⁺ ion exchanged nanoparticles, iron has the tendency to capture the photogenerated electrons from titania nanoparticles because of their suitable Fermi level position, thus favoring the charge separation, hence increasing the PCA. Since, more number of Na⁺ ions could be exchanged in the case of 0.5-Fe-TNT than in the case of 0.2-Fe-TNT, consequently, more number of electrons are expected to be captured by the former than the latter resulting in its higher PCA. However, after calcination of bare and Fe⁺⁺ ion exchanged TNT, the decrease in PCA could be attributed to the dehydroxylated surface, suppressing the formation of necessary hydroxyl radicals. Among these calcined catalysts, the order (0.5-Fe-TNT(S) > 0.2-Fe-TNT(S) > TNT(S)) of PCA is ascribed to the combined...
effect of (i) a higher amount of Fe in 0.5-Fe-TNT(S) and (ii) the presence of \( \text{Ti}^{3+} \) in NaTiO\(_2\) that captures the photoproduced electrons and thereby increases the life time of holes, thus facilitating the photooxidation of naphthalene. Moreover, formation of nanoparticles corresponding to smaller size, i.e., more number of surface exposed atoms (Chen and Mao 2007) and more surface area, which are known to facilitate the adsorption of reacting molecules may also contribute to the higher activity of 0.5-Fe-TNT(S) among these calcined catalysts.

4. Conclusions

In summary, the present work signified that Fe-loading produces strain in the crystal structure of sodium titanate nanotubes, thereby distorting its geometry and interfering with its crystal growth during calcination at 800°C. It has been found that the extent of strain induced in the crystal structure of TNT by the presence of Fe\(^{3+}\) ions influences the crystal phase, morphology, surface area, and particle size during its thermal treatment that in turn affects the photocatalytic activity. Among a variety of as-prepared crystal structures, high surface area with the aid of Fe\(^{3+}\) ions in 0.5-Fe-TNT causes superior photocatalytic activity for the mineralization of naphthalene to CO\(_2\).

Funding

The authors acknowledge the University Grants Commission and Department of Science and Technology, New Delhi, Government of India, for providing financial support.

Supplementary Material

Supplemental data for this article can be accessed on the publisher’s website.

References

Adan, C., A. Bahamonde, G. M. Fernandez, and A. A. Martinez. 2007. Structure and activity of nanosized iron-doped anatase TiO\(_2\) catalysts for phenol photocatalytic degradation. Applied Catalysis B: Environmental 72(1/2):11–17.

Bavykin, D. V., J. M. Friedrich, and F. C. Walsh. 2006. Protonated titanates and TiO\(_2\) nanostructured materials: synthesis, properties, and applications. Advanced Materials 18(21):2807–2824.

Bryan, J. D., and D. R. Gamelin. 2005. Doped semiconductor nanocrystals: synthesis, characterization, physical properties, and applications. Progress in Inorganic Chemistry 54:47–126.

Chen, X., and S. S. Mao. 2007. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. Chemical Reviews 107(7):2891–2959.

Clarke, J. S., J. A. Fowkes, A. Harrison, M. R. Ibberson, and J. M. Rosseinsky. 1998. Synthesis, structure and magnetic properties of NaTiO\(_2\). Chemistry Materials 10:372–384.

Garcia, M. F., A. M. Arias, J. C. Hanson, and J. A. Rodriguez. 2004. Nanostructured oxides in chemistry: characterization and properties. Chemical Reviews 104(9):4063–4104.

Grover, I. S., S. Singh, and B. Pal. 2013. The preparation, surface structure, zeta potential, surface charge density and photocatalytic activity of TiO\(_2\) nanostructures of different shapes. Applied Surface Sciences 280:366–372.

Grover, I. S., S. Singh, and B. Pal. 2014. Enhanced photocatalytic activity of as-prepared sodium titanates for m-dinitrobenzene reduction and sulfosulfuron oxidation. Journal of Nanoscience and Nanotechnology doi:10.1166/jnn.2014.9072.

Jin, J. Z., X. Wang, W. Li, J. Zhang, S. Zhang, X. Guo, and Z. Zhang. 2003. Study on composition, structure and formation process of nanotube Na\(_2\)Ti\(_3\)O\(_4\)(OH)$_2$. Dalton Transactions 20:3898–3901.

Lee, C. K., C. C. Wang, M. D. Lyu, L. C. Juang, S. S. Liu, and S. H. Hung. 2007. Effects of sodium content and calcination temperature on the morphology, structure and photocatalytic activity of nanotubular titanates. Journal of Colloid and Interface Science 316(2):562–569.

Mallick, P., C. Rath, R. Biswal, and N. C. Mishra. 2009. Structural and magnetic properties of Fe doped NiO. Indian Journal of Physics 83(4):517–523.

Morgado, E., M. A. S. De-Abreu, O. R. C. Pravia, B. A. Marinkovic, P. M. Jardim, F. C. Rizzo, and A. S. Araujo. 2006. A study on the structure and thermal stability of titanate, nanotubes as a function of sodium content. Solid State Sciences 8(8):888–900.

Nath, R., S. Zhong, S. P. Alpay, B. D. Huey, and M. W. Cole. 2008. Enhanced piezoelectric response from barium strontium titanate multilayer films. Applied Physics Letters 92(1):012916-012918.

Pookmanee, P., and S. Phanichphant. 2005. Low temperature hydrothermal synthesis of bismuth sodium titanate nanopowder. International Journal of Nanoscience 4(4):637–641.

Qamar, M., C. R. Yoon, H. J. Oh, N. H. Lee, K. Park, D. H. Kim, K. S. Lee, W. J. Lee, and S. J. Kim. 2008. Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide. Catalysis Today 131(1–4):3–14.

Qamar, M., C. R. Yoon, J. H. Oh, D. H. Kim, J. H. Jho, K. S. Lee, W. J. Lee, H. G. Lee, and S. J. Kim. 2006. Effect of post treatments on the structure and thermal stability of titanate nanotubes. Nanotechnology 17(24):5922–5929.

Singla, G., K. Singh, and O. P. Pandey. 2013. Williamson–Hall study on synthesized nanocrystalline tungsten carbide (WC). Applied Physic A Material Science and Processing 113:237–242.

Si, X., F. Li, L. Sun, F. Xu, S. Liu, J. Zhang, M. Zhu, L. Z. Ouyang, D. Sun, and L. Y. Liu. 2011. Metals (Ni, Fe)-incorporated titanate nanotubes induced destabilization of LiBH\(_4\). Journal of Physical Chemistry C 115(19):9780–9786.

Tsai, J. Y., J. H. Chao, and C. H. Lin. 2009. Low temperature carbon monoxide oxidation over gold nanoparticles supported on sodium titanate nanotubes. Journal of Molecular Catalysis A: Chemical 298(1–2):115–124.

Yu, J., H. Yu, B. Chenga, and C. Trapani. 2006. Effects of calcination temperature on the microstructures and photocatalytic activity of titanate nanotubes. Journal of Molecular Catalysis A: Chemical 249(1–2):135–142.