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Fabrication Of Titania Nanotubes By A Modified Hydrothermal Method

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Abstract

The main setback of the fabrication of titania nanotubes by the hydrothermal method is the long dissolution time and the usage of highly concentrated NaOH. Our group has managed to develop a modified hydrothermal process that is capable of fabricating titania nanotubes in a shorter timespan while using a more dilute NaOH solution. The study shows that the titania nanotubes starts to form from 7 hours of dissolution, and more nanotubes is produced as the dissolution duration is extended. Similarly, we are able to produce titania nanotubes from a more dilute NaOH solution than those reported earlier. By varying the parameters of the fabrication process, different nanostructures can be obtained such as single, branched nanowires and nanobelts.

Keywords: titania nanotube; hydrothermal; sodium titanate; nanowire; nanobelt

1 INTRODUCTION

The chemical structure for titania nanotubes (TNT) can either be titanium dioxide in the anatase or rutile crystal form, sodium titanate such as that of $Na_4Ti_1O_4$ and $Na_2Ti_6O_{13}$ or hydrogen titanate as in the $H_2Ti_3O_7$ structure (1). Nanotitania powder is an important photocatalyst material due to its strong oxidizing power, inertness and nontoxicity. Although it has great potential, one main obstacle for the widespread commercial application of this nanomaterial is its small surface area and its ability to reduce/halt electron transfer after a certain amount of time. Titania nanostructures in the form of tubes, wires, rods or belts were found to be more effective than that of the nanopowders. Adachi M. et al, 2003 (2) showed that TNT increased short circuit current density by 100% when compared to nanoparticles in thin film dye-sensitized solar cells. Similarly Srimala et al., 2009 (3) showed that TNT has better photocatalytic properties and is capable of degrading tobacco smoke 50% faster than titania nanopowder.

The three main methods of fabrication of TNT are the template-assisted method, the electrochemical anodic oxidation method and hydrothermal treatment. TNT was first reported by Hoyer, 1996 (4) via the template-assisted method and thereafter electrochemical anodic oxidation and hydrothermal treatment succeeded in fabricating TNTs. Each fabrication method has unique advantages and functional features. Ou H. H. et al, 2007 (1) reviewed these three different fabrication methods and the advantages and disadvantages of these methods. The template assisted method is capable of moderately controlling the scale of the nanotubes, and it produces TNT in powder form with ordered arrays. Its disadvantages include a fairly complicated fabrication process and the danger of the TNT being damaged during the fabrication process. The electrochemical anodic oxidation method is more desirable for practical applications, with ordered alignments along with high aspect ratios. The TNT produced is in thin film forms with oriented arrays. However, the potential for mass production using this method is fairly limited; and the formation of TNT depends largely on the utilization of HF (aq), contributing to the relatively high cost of the fabrication apparatus. Finally, the hydrothermal treatment is an easy route for obtaining TNTs, and the technique is easily modifiable, and it produces powder TNTs in random alignments. Concerns regarding this method include the long duration of its reactions, the requirement of highly concentrated NaOH, and the overall difficulty in achieving a uniform size in the TNTs.

There is a strong interest in using the hydrothermal method for this purpose mainly due to its relative simplicity for large scale synthesis of titanate nanowire in a single reaction process Hydrothermal fabrication method may also yield TNT of very low dimensional size, is well separated and in highly crystallized form. TNT produced from the hydrothermal method can also be modified into other nanostructures such as single nanowire, branched nanowire, nanorods and nanobelts. These nanostructures could further enhance the properties of the TNT.

In this study an alkaline fusion stage was included in the hydrothermal process to reduce the disadvantages of the fabrication method due to the long NaOH dissolution stage as well as highly concentrated NaOH of more than 10M that is required for the process.

2 EXPERIMENTAL

The starting material used for this study is synthetic rutile, produced by Tor Minerals in Lahat, Perak. The samples' morphology, crystal phase and chemical content were determined by the SEM, XRD and EDXRF techniques respectively. Following that a hydrothermal process was used to produce the titanate nanowire from this synthetic rutile. The synthetic rutile was first fused with NaOH at 550oC for 3 hours to form a sodium titanate compound. The next stage involves NaOH leaching where 30 to 50% of NaOH were used at 90 - 100oC for 7 hours. After cooling and solid-liquid filtration, the liquid portion of the sample was recovered and heated to induce recrystallization. The sample was then washed with 0.01M HCl to remove the unwanted sodium hydroxide that might still be present. The washed sample was then dried overnight at 70oC after which its crystalline phase was determined by using Panalytical X'pert XRD spectrometer. The morphology and size of the product was also tested by using the FEI Scanning Electron Microscope.

3 RESULTS AND DISCUSSION

In the fabrication of TNT by the hydrothermal process, locally produced pigment grade synthetic rutile was used as the starting material. Characterization using XRD, SEM and XRF were performed on these samples and the results are as that shown in Figs. 1 – 2 below.

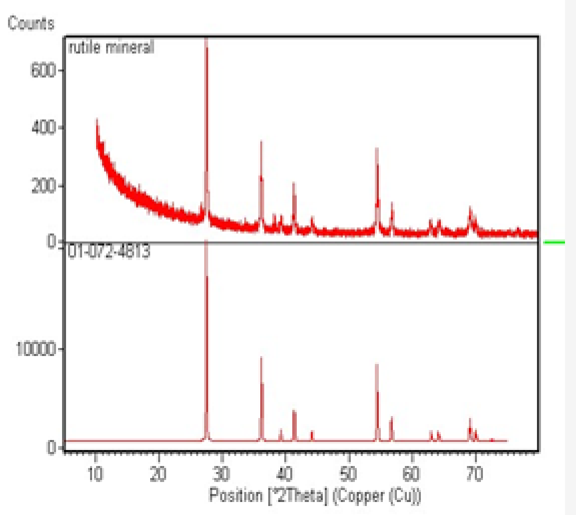

Figure 1 : XRD diffractogram of synthetic rutile

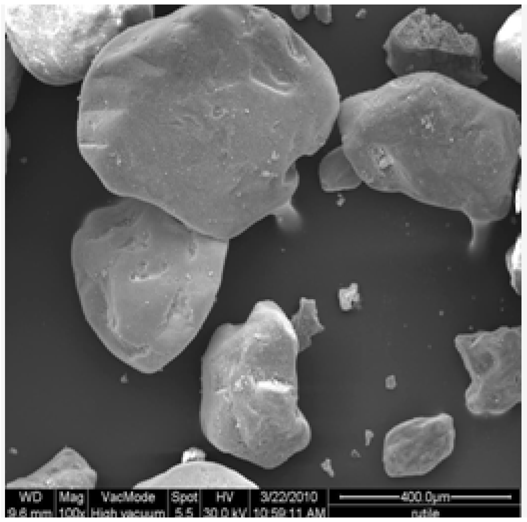

Figure 2 : SEM micrograph of synthetic rutile

An XRD pattern was obtained for the synthetic rutile (Fig. 1) and using the ICDD reference pattern 01-072-4813, it was seen that the diffractogram obtained matches that of rutile. The SEM micrograph (Fig. 2) also shows a different morphology from the previous sample where single large rounded crystals can be seen. TiO_2 content analyzed by the XRF technique shows a 92% drop compared to the previous sample. The main feature of the modified hydrothermal process is the fusion of the starting material with NaOH to produce sodium titanate fused complex. The rationale for the inclusion of this stage is that the sodium titanate complex is more readily dissolved compared to the titanium starting materials. Previous researchers had used extended durations of 28 - 60 hours in autoclave machines to dissolve these materials (1). Figs. 3 – 6 below show the effect of dissolution time on the fabrication of TNT.

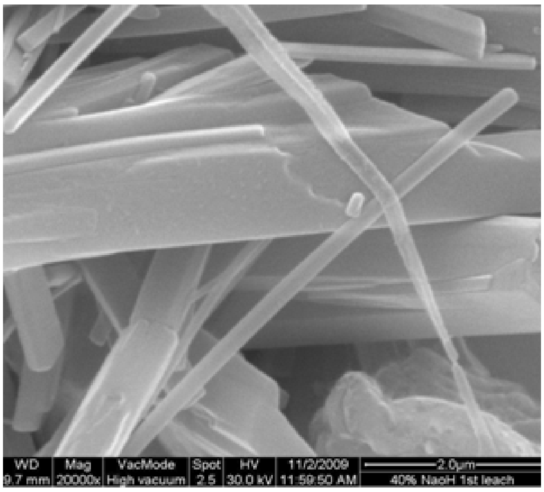

Figure 3 : SEM micrograph of TNT fabricated after 7 hours

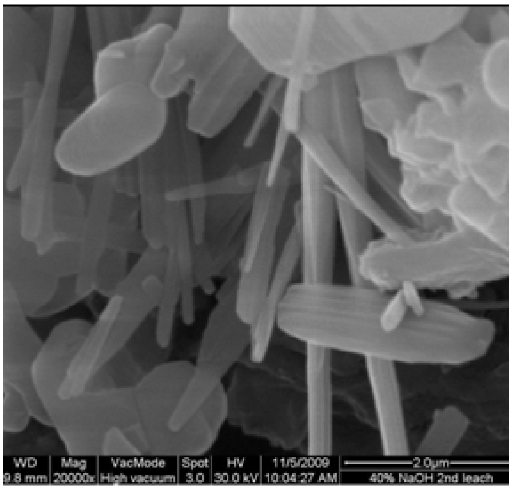

Figure 4 : SEM micrograph of TNT fabricated after 14 hours

After undergoing NaOH dissolution for 7 hours, the TNT begins to form (Fig. 3). When the dissolution time was further increased to 14 hours (Fig. 4), more of such nanowires are formed in the sample. Fig. 5 shows the morphology of TNT obtained is of the nanowire structure similar to those produce previously after 21 hours of dissolution. But in contrast to the Fig. 3 and 4, Fig. 5 shows that most of the formation is in tubular form of varying sizes. Finally after undergoing 28 hours of dissolution (Fig. 6) we obtained nanowires of different morphology as that fabricated earlier. The smooth surface formed earlier had turned into a rough surface. Also the yield of the TNT is better at longer process duration.

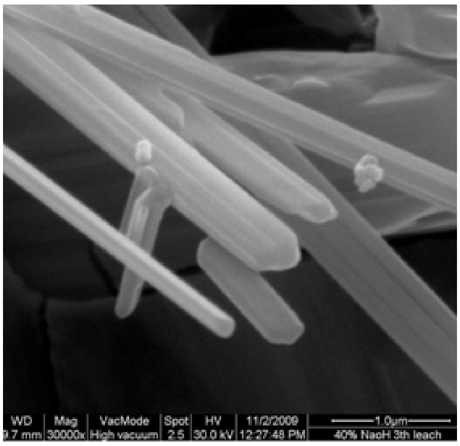

Figure 5 : SEM micrograph of TNT fabricated after 21 hours

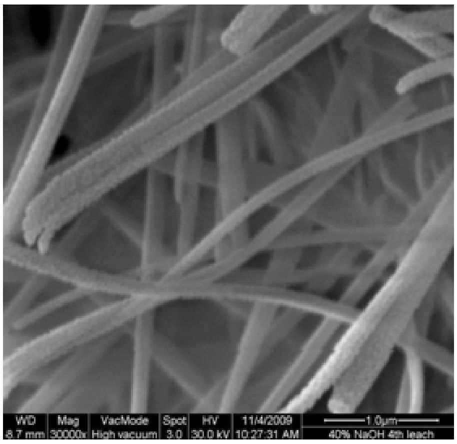

Figure 6 : SEM micrograph of TNT fabricated after 28 hours

The second parameter studied in our modified hydrothermal process is the effect on the nanostructure morphology when different concentrations of NaOH were used for the dissolution stage. For this purpose NaOH of concentrations from 30 – 60% were tested and the morphology of TNT is as that shown in Figs. 7 (a) – (d) below.

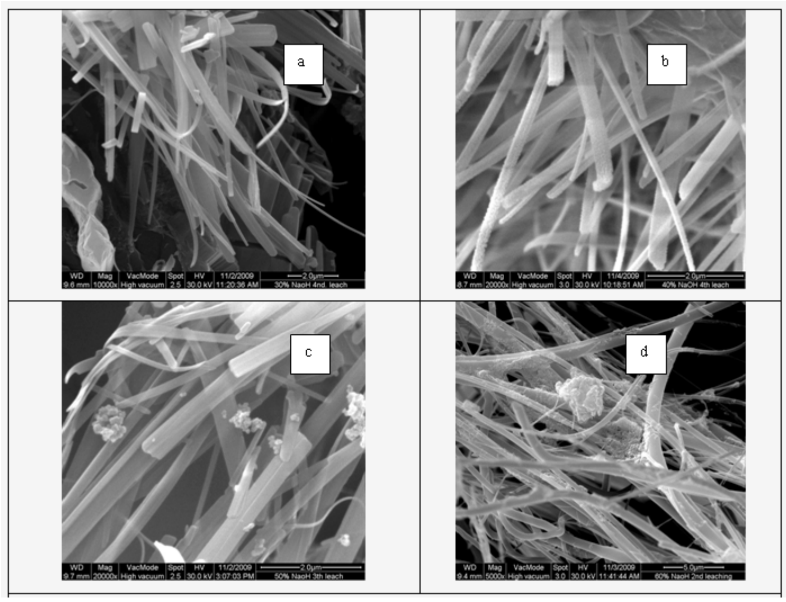

Figure 7 : SEM micrographs of titanate nanowire obtained by using different NaOH concentrations a) 30% NaOH b) 40% NaOH c) 50% NaOH d) 60% NaOH

The morphology of the titanate nanowire produced at different NaOH concentrations shows that by using 30 and 50% NaOH, flat surface nanostructure or nanobelts are formed. While by using 40% and 60% NaOH produces rough surface tubular nanowire. The result also shows that at higher concentration there is present of sodium hydroxide residue amongst the TNT.

The chemical structure of the TNT was then determined and initially it was found that it comprises of both the sodium titanate and NaOH residue from the dissolution stage. Dilute HCl was introduced as a washing agent to remove the NaOH residue. Different molarities of HCl were used and the result of the XRD diffractograms for different acid molarities is shown in Fig. 8. Results from the XRD analysis shows the presence of both sodium titanate and NaOH phases when washed by 0.01 and 0.05M HCl. By using 0.1M HCl, all the NaOH are washed out and only the sodium titanate phase remains in the TNT sample.

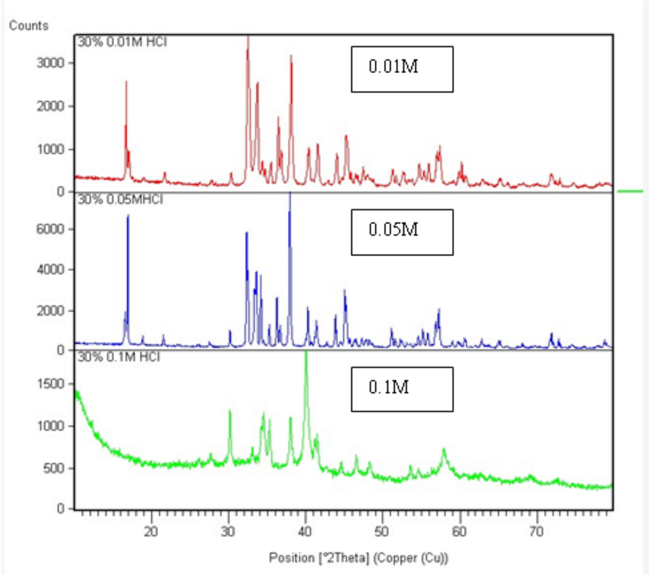

Figure 8 : XRD diffractograms of TNT washed by using different HCl molarities

Fig. 9 shows the SEM micrograph of our TNT product taken at low magnification after fabricating it under optimized conditions while Fig. 10 shows the same nanowire at high magnification. At low magnification, the TNT product obtained shows that it is in a random alignment form similar to that obtained by previous researchers (5, 6, 7, 8). The SEM morphology of Fig. 9 also shows that almost all of the structure is of similar forms. At higher magnification (Fig.10), the morphology of the nanowire shows that it has a smooth wall structure with a diameter of less than 100nm and a length of more than 4µm. These structures can be categorized as nanowire due to small dimension of its diameter. The formation of these nanowires is achieved by the swelling and peeling off the nanowire structure as proposed by Yang et al (4). This can be clearly seen from Fig. 10 where the nanowire seems to be peeling off from the bulk strip.

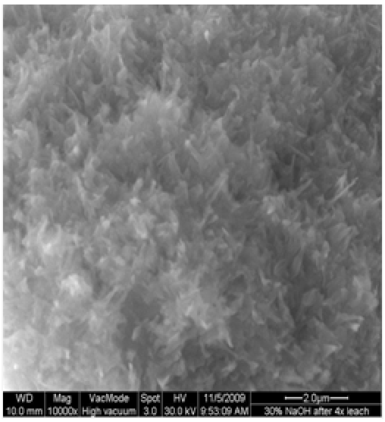

Figure 9 : SEM micrograph of TNT at low magnification (10,000x)

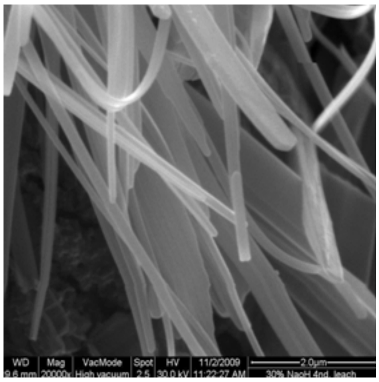

Figure 10 : SEM micrograph of TNT at high magnification (20,000x)

4 CONCLUSIONS

The study shows that TNT can be produced by the modified hydrothermal process within a shorter dissolution time and relatively low NaOH concentration. The morphology of the nanostructure changes with the usage of different concentrations of NaOH and the modified nanostructures are single and branched nanowires, nanobelts as well as porous nanowires. By utilizing the optimium process conditions, the sodium titanate had been converted into TNT and the mechanism of formation may be due to swelling and peeling from the bulk of the TNT.

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