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Synthesis and characterisation of TiO₂-derived nanotubes

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TiO₂-based nanotubes were synthesised via hydrothermal and reflux methods in a 10 N NaOH solution at 403 K under stirring for 20–72 h from nano TiO₂ and industrial TiO₂ powders. The results show that the yield of nanotube formed through the hydrothermal method is higher than that of the reflux method. The samples were characterised by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images and X-ray diffractometer (XRD) patterns to investigate the phase of the nanotubes. The results from XRD patterns show that nanotubes consist of a titanate structure with general formula Na_xH_{2-x}Ti₃O₇, where 0 ≤ x ≤ 2, depending on degree of proton exchanged after acid washing. TEM images show the inner and outer diameters to be about 3 and 9 nm, respectively, for nanotubes. Also the SEM images show that the lengths of nanotubes are about several 10 μm.

Keywords: nanotube; TiO₂; titanate; hydrothermal; reflux

1. Introduction

The synthesis of nanoscale materials of various elements has become one of the most important areas of research in nanotechnology. Among them, fine TiO₂ semiconductor materials have attracted considerable attention because of their photocatalyst application in elimination of pollutants [1]. The surface area of the materials, depending on the morphology, plays a significant role in governing the photocatalyst reaction. A large surface area of photocatalyst corresponds to more effective photocatalysis. The surface area became larger as the particle became smaller or more tubular [2]. Various nanotubular materials have been produced during the last decades and the synthesis of them has become one of the most important research subjects in nanotechnology [3]. TiO₂-based nanotubes with high specific surface area and ion-exchangeable ability have been considered for extensive applications such as catalyst support [4–7], photocatalysts [8–13], sensors [14], hydrogen generation [15] and storage [16], water splitting [17], solar cells [18] and medicine [19].

TiO₂-based nanotubes with specific surface area of 400 m² g⁻¹ and 8 nm in diameter, via hydrothermal treatment followed by HCl washing, were first reported by Kasuga et al. [20]. These authors claimed that the tubular products obtained were of the anatase form of TiO₂ formed during the washing process.

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After this, a number of papers were published on the structure and formation mechanisms of nanotubes. However, the conclusions of these reports are quite controversial. Du *et al.* [21] obtained $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes by a hydrothermal process at 130°C similar to that reported by Kasuga but without washing.

However the present debate over the crystal structure of TiO_2 -based nanotubes is as follows: anatase TiO_2 [20], lepidocrocite $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ ($x \sim 0.7$, \square : vacancy [22], $\text{H}_2\text{Ti}_3\text{O}_7$ [21] $\text{Na}_2\text{Ti}_3\text{O}_7/\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ [23], $\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2/\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2/\text{Na}_x\text{H}_{2-x}\text{Ti}_2\text{O}_5(\text{H}_2\text{O})$ [24] and $\text{H}_2\text{Ti}_4\text{O}_9$ (H_2O) [25]. Three main methods have been reported for the preparation of TiO_2 -based nanotubes: template method [26], anodisation [27] and NaOH treatment [20]. Each of them has unique advantages and affects selection of applications. For example, nanotubes that are used in sensors [14] usually are produced via anodisation and nanotubes that are used in catalyst support are produced via NaOH treatment [3]. In template method, the template material is sacrificial and needs to be destroyed after synthesis, leading to an increase in cost of materials [28]. Also this method is not appropriate for smaller nanotubes, because of its high dependence on the template mold [28]. In anodisation, the average internal diameter of the nanotubes exceeded 50 nm. One end of nanotubes was always open while the other end, which was in contact with the electrode, was always closed [28]. On the other hand, hydrothermal method is a simple and cost effective method for large-scale production of TiO_2 -derived nanotubes with small diameters that can be used in catalyst and photocatalyst aims [28]. NaOH treatment can be done either chemically or hydrothermally. Herein, we used both procedures to prepare nanotubes and compared the obtained results from them to elucidate which method is the best. Also, several factors that affect the nanotube formation yield, such as type of TiO_2 precursor, time treatment and washing procedure, were investigated. For large-scale nanotube production in industrial applications, the yield of the product is very important. Also, we examined a cheap industrial TiO_2 powder beside nanoparticle in synthesis of nanotubes to reduce cost of products and, to the best of our knowledge, this is the first report of the preparation of nanotubes using industrial TiO_2 powder as precursor.

2. Experimental

We used different types of TiO_2 powders as precursors for nanotube synthesis: a home prepared nano-powder anatase TiO_2 (indicated as A), industrial anatase TiO_2 (COSMO) (indicated as I) and amorphous TiO_2 (Degussa P25) (indicated as P). The treatment in NaOH 10 N was conducted both hydrothermally and chemically. In the hydrothermal method 1.6 g of TiO_2 precursors were treated with 50 mL 10 N NaOH in a Teflon autoclave at 130°C in an oil bath for 20 h and in another experiment for 72 h with stirring. In the chemical method 0.5 g of precursors were treated with 50 mL 10 N NaOH and refluxed in a 130°C oil bath for 20 and 72 h with stirring. After treatment and cooling, the products were washed with ethanol, deionised water, 0.1 and 1 N HCl and then deionised water, respectively.

The phase identification of nanotube samples was conducted with powder X-ray diffractometer (XRD, Philips BW 3710) equipped with Cu-K α radiation. The microstructure and morphology of nanotubes were explored with transmission electron microscopy (TEM, Philips CM 200 FEG) and scanning electron microscopy (SEM, LEO 1455VP and Philips XL30).

3. Results and discussion

Figure 1 shows the SEM images of nanotubes, which were prepared by reflux and hydrothermal methods from the industrial anatase (I) and washed with deionised water. As is obvious from the SEM images, nanotubes were formed in both hydrothermal and reflux methods. When preparing the nanotubes with the reflux method, after treatment and cooling a white suspension similar to the initial one is obtained. While using the hydrothermal method, a white-layered paste, which was several orders in volume with respect to the initial suspension, formed. In the SEM images (Figure 1(c)), the layered product is seen truly; also it seems that in this case the long nanotubes formed are open-ended. The products obtained using reflux method are spongy and seems that the short nanotubes formed are closed-ended. When using the reflux method, some of precursor was left unreacted (Figure 1(a) and (b)). It seems that influence of pressure in autoclave using hydrothermal method must be the key point to produce the nanotubes with higher yield with respect to the reflux method.

To investigate the influence of the type of the precursor on yield of nanotube formation using hydrothermal method, three types of TiO_2 powders including home-prepared nano powder anatase TiO_2 (A), industrial anatase TiO_2 (COSMO) (I) and amorphous TiO_2 (Degussa P25) (P) were used. Precursors A and I consist of anatase phase of TiO_2 species with particle sizes of 10 nm and 0.25–0.35 μm , respectively. Precursor P is amorphous. Figure 2 shows the SEM images of specimens prepared from A (Figure 2(a)) and P (Figure 2(b)) after 20 h treatment and washing with deionised water using the hydrothermal method.

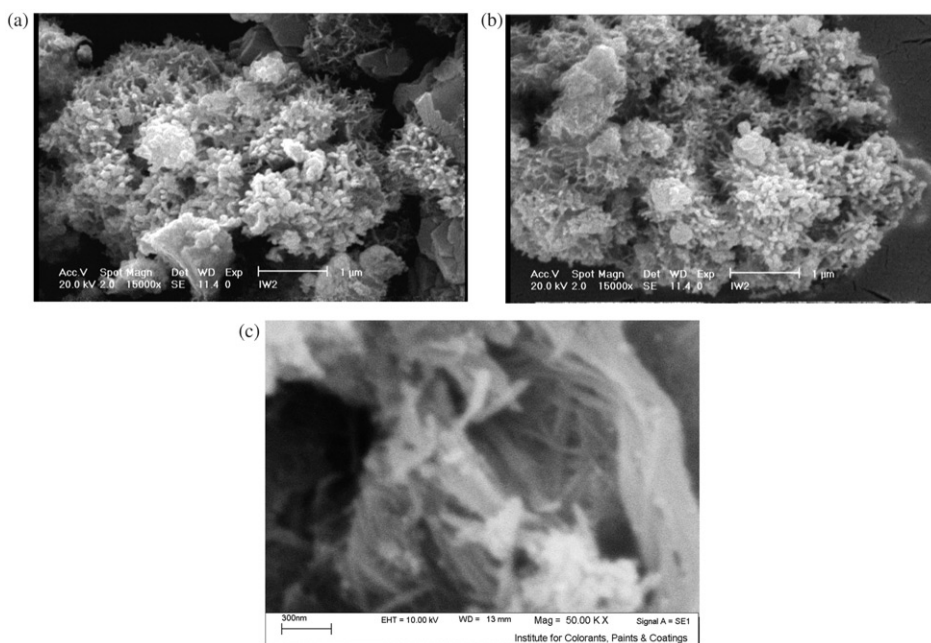


Figure 1. SEM images of nanotubes prepared using reflux (a) and (b) and hydrothermal (c) methods from industrial anatase (I) after 20 h treatment and washed with deionised water.

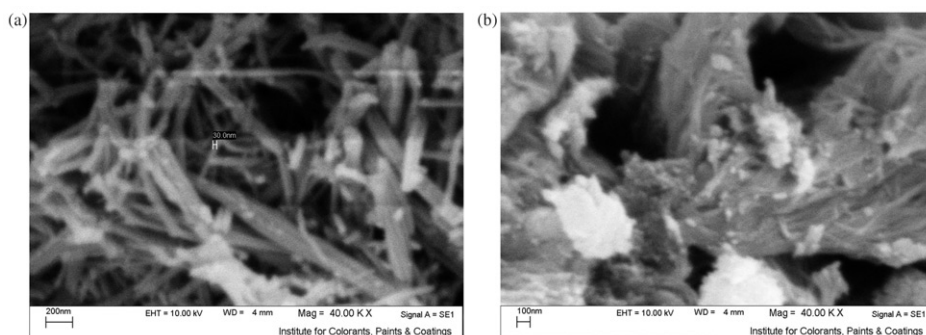


Figure 2. SEM images of nanotubes prepared using hydrothermal method after 20 h treatment and washing with deionised water from A (a) and P (b).

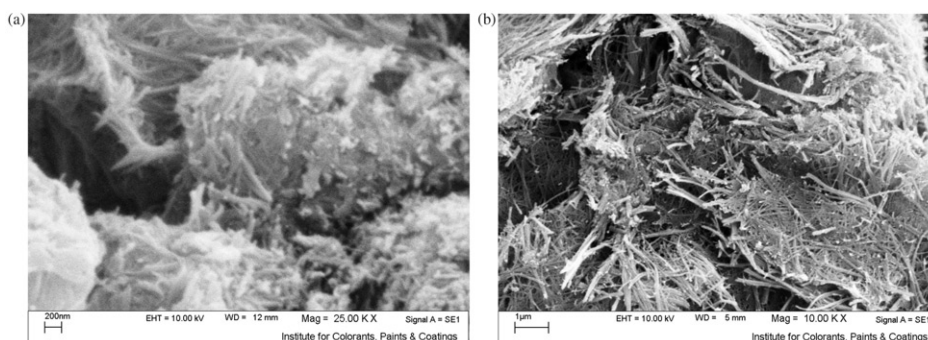


Figure 3. SEM images of nanotubes prepared using hydrothermal method after 20 h treatment and washed with HCl 0.1 N until pH = 7, from I (a) and A (b) as precursor.

According to SEM images, higher yields obtained for nanotubes were prepared from A (Figure 2(a)) and I (Figure 1(c)) with respect to the P (Figure 2(b)) as precursor. It seems that the crystalline phase of the precursor is probably an effective factor to increase the yield of nanotube formation. Also, it should be noted that the specimen prepared from A shows to have higher yield than those prepared from I. It seems that the crystalline size of the particles could be another effective factor for preparing the nanotubes. Thus, by applying a crystalline precursor with small size, the yield of the nanotubes is increased.

In order to investigate the effect of washing on the yield of the nanotubes, a part of the product was washed with 0.1 N HCl. Figure 3 shows the SEM images of nanotubes which were obtained using hydrothermal method and washed with 0.1 N HCl from I (Figure 3(a)) and A (Figure 3(b)). It seems that much clearer nanotubes were formed with respect to the specimens that were washed with deionised water (Figures 1(c) and 2(a)).

Another factor, which is probably important to produce high-yield nanotubes, could be the time of treatment with NaOH. So, reaction time was increased from 20 to 72 h. Figures 4 and 5 show the SEM images of nanotubes, which were prepared from I and A, respectively, as precursor, using hydrothermal method for 72 h, and washed with deionised water (Figures 4(a) and 5(a)) or 0.1 N HCl to reach to pH = 7 (Figures 4(b) and 5(b)).

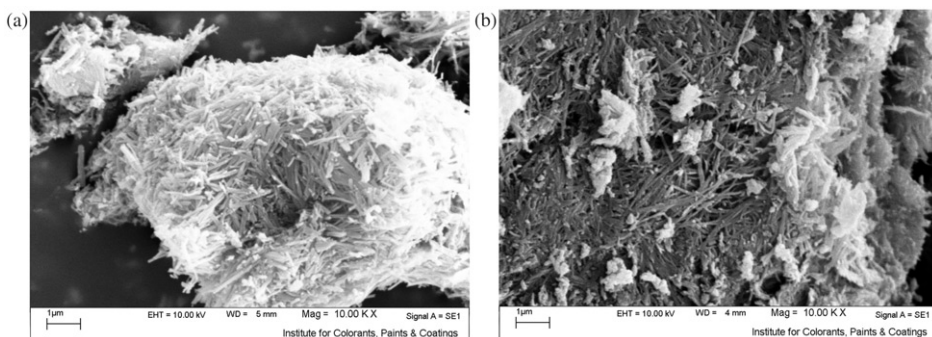


Figure 4. SEM images of nanotubes prepared using hydrothermal method after 72 h treatment from I, washed with deionised water (a) or 0.1 N HCl to reach pH = 7 (b).

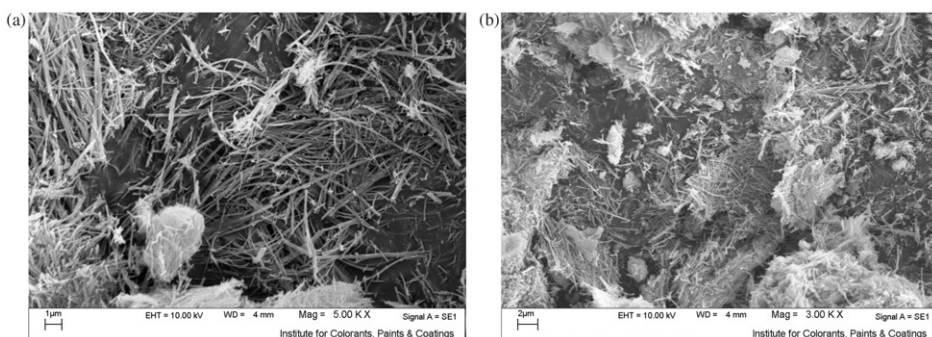


Figure 5. SEM images of nanotubes prepared using hydrothermal method after 72 h treatment from A, washed with deionised water (a) or HCl 0.1 N to reach pH = 7 (b).

When comparing Figure 1(c) with Figure 4(a) and (b) it is clear that the time of NaOH treatment and washing treatment both have distinct effects on the yield increases of the nanotube formation. Also, comparison of Figure 5(a) and (b) with Figure 2(a) confirms this consideration. The scale bar in Figure 5(b) is 2 μm and, with precise investigation, it can be seen that nanotubes are the only specimens occurring in this image having length of about several tens of micrometre. Therefore, it can be said that by increasing the time of the reaction, use of a suitable precursor and good washing programme, the yield of nanotube formation can reach close to 100%.

It has been pointed out by Kasuga et al. [20] that washing is critical in the formation of nanotubes. To investigate the effect of washing on nanotube formation we attempt to produce the nanotubes from I as precursor, using ethanol for washing treatment instead of water or acid solution. Figure 6 shows the SEM images of product prepared from I and washed with ethanol. In this case, only a few nanotubes were seen and most of the product was still in the form of particles, which is in agreement with the data of Kasuga et al. [20]. Unlike water and acid solution, ethanol is not able to remove Na⁺ attached to the surface of the layer structures formed during NaOH treatment.

Figure 7(a), (b) and (c), (d) show the SEM images of specimens prepared from I and A, respectively, and washed with 1 N HCl until pH < 0.5. In Figure 7(a) and (b) beside some

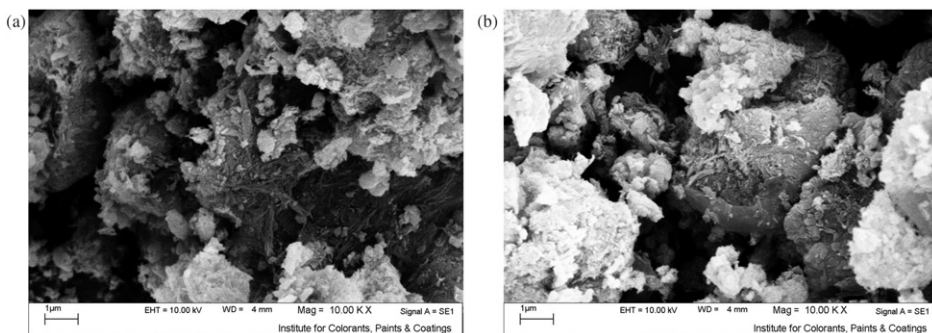


Figure 6. SEM image of specimen prepared from I and washed with ethanol.

particles many nanotubes are also seen. In Figure 7(c) and (d) most of the product is nanotubes and only a very small amount of particles that are put in square are seen. From these images it can be suggested that in very low pH still some of the nanotubes exist and the product was not destroyed completely. Although it has been reported that in very low pH (0.38) nanotubes are destroyed and samples are mainly composed of anatase particles [29].

Figure 8 shows the TEM images of nanotubes prepared from I (Figure 8(a) and (b)), washed with deionised water and A (Figure 8(c) and (d)) washed with HCl treated by hydrothermal method for 20 h.

As can be seen from Figure 8, all nanotubes are open-ended. The specimen prepared from I (Figure 8(a) and (b)) shows nanotubes with different sizes. Figure 8(b) demonstrates a nanotube with inner and outer diameter about 2.87 and 6.89 nm, respectively. The specimen prepared from A shows nanotubes with narrow size distribution (Figure 8(c)) and Figure 8(d) shows a nanotube with inner and outer diameter of 3.2 and 8.9 nm, respectively, similar to the results supported by Kasuga et al. [20]. The number of layers in the wall of the nanotubes is different. A nanotube in Figure 8(d) has three layers in one side and four layers in another side of the nanotube's wall.

In Figure 8(a), we can see a sheet (shown in square) and a nanotube that is wrapping. It was inferred from this image that nanotubes were formed by rolling up the single-layer sheets. This explains why the walls viewed on the two sides of a nanotube are generally unequal.

The phases of nanotubes were investigated by XRD pattern. Figure 9 shows the XRD pattern of the nanotubes obtained by hydrothermal method, washed with deionised water (IW) and HCl until pH = 7 (IA) and calcined in 623 K.

Characteristic peaks at $2\theta = 10^\circ$ have been assigned to $\text{Na}_2\text{Ti}_3\text{O}_7$ [23]. The peaks at 11° and 24° are assigned to $\text{H}_2\text{Ti}_3\text{O}_7$ and indicate that some of Na^+ are replaced with H^+ ions. In the specimen prepared from I and washed with deionised water and acid, all the peaks belonging to $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{H}_2\text{Ti}_3\text{O}_7$ are seen. These data suggest a chemical formula of the nanotube: $\text{Na}_{2-x}\text{H}_x\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$, where $0 \leq x \leq 2$ for nanotubes. The x -value depends on the washing conditions.

Figure 10 indicates the XRD pattern of nanotubes prepared from A and washed with deionised water (AW) or 0.1 HCl (AA) to reach pH = 7 and calcined at 623 K.

In the specimen washed with deionised water, there is a peak at $2\theta = 10^\circ$ that can be assigned to $\text{Na}_2\text{Ti}_3\text{O}_7$. Also, the peaks at 11° and 24° are related to $\text{H}_2\text{Ti}_3\text{O}_7$ phase.

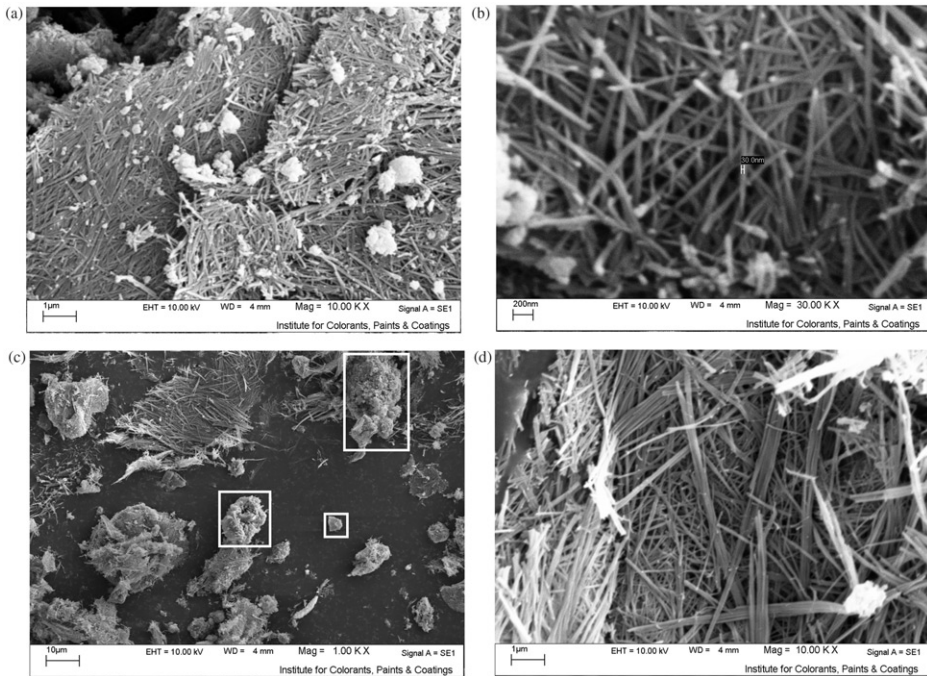


Figure 7. SEM image of nanotube prepared by hydrothermal method for 72 h, washed with HCl 1 N until pH < 0.5 from I (a) and (b) and from A (c) and (d).

Thus, the chemical formula for this specimen can also be $\text{Na}_{2-x}\text{H}_x\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$, where $0 \leq x \leq 2$. In the specimen washed with acid, peaks related to the $\text{H}_2\text{Ti}_3\text{O}_7$ are predominant and indicate that more replacement of Na^+ by H^+ ions has happened during acid washing treatment. In this case, the intensity of the characteristic peak at $2\theta = 10^\circ$ has decreased and the intensity of $\text{H}_2\text{Ti}_3\text{O}_7$ peaks has increased. Since the intensity of the peak at 25° (which is related to anatase and titanate phase) is higher in the case of acid washing than water washing, it can be suggested that this peak could be due to anatase phase, which has been formed by dehydration during calcination.



4. Conclusion

TiO_2 -based nanotubes were prepared through hydrothermal and reflux treatments and compared. The SEM images show that the yield of products in hydrothermal treatment because of pressure is higher than the reflux treatment. Several factors such as phase and particle size of precursor and time of reaction that affect the yield of nanotube formation were investigated. The results show that, by applying suitable phase, increasing of time reaction and decrease in precursor size, the yield of nanotube formation can increase.

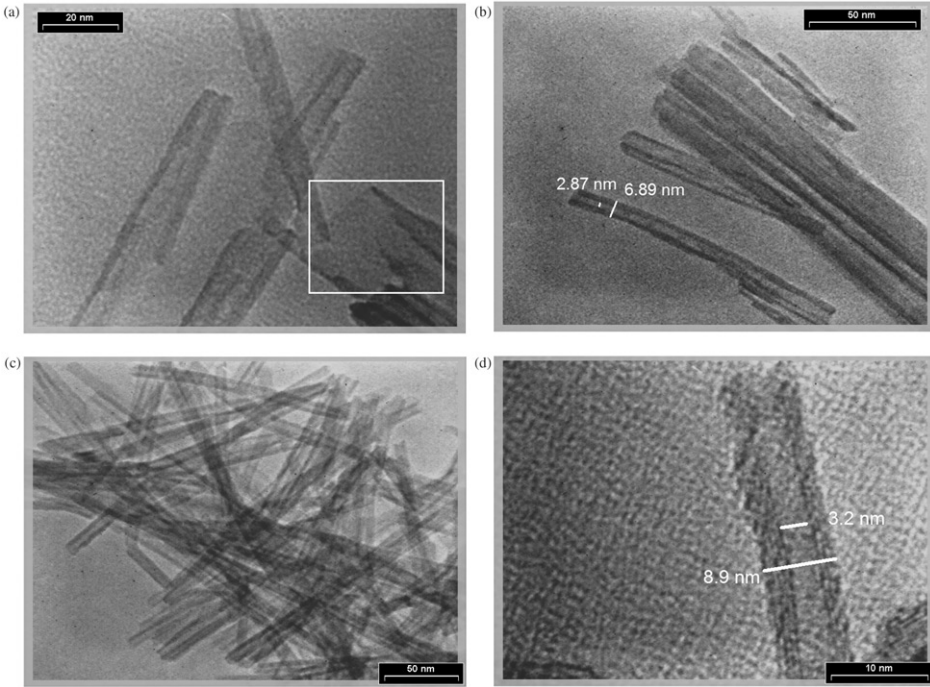


Figure 8. TEM images of nanotube prepared by hydrothermal method for 20 h, washed with deionised water from I (a) and (b) and washed with 0.1 N HCl until pH = 7 from A (c) and (d).

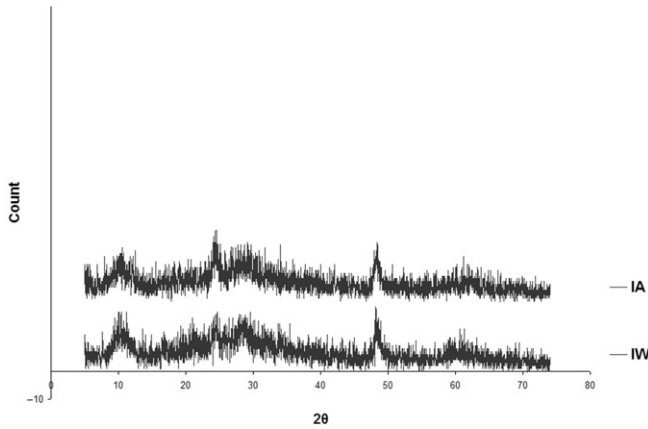


Figure 9. The XRD pattern of the nanotubes obtained with hydrothermal method, washed with deionised water (IW) and HCl until pH = 7 (IA) and calcinated in 623 K.

Also, the factors that affect the phase of nanotubes were explored. The results show that by increasing washing time, more Na^+ ions can be exchanged with H^+ ions and the composition of nanotubes can change from sodium titanate to hydrogen titanate. Also post-heat treatment at 623 K can change the phase of nanotubes from hydrogen titanate to

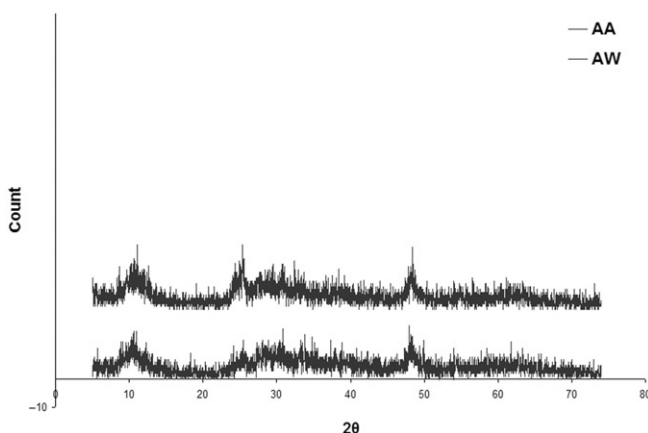


Figure 10. XRD pattern of nanotubes prepared from A and washed with deionised water (AW) or 0.1 HCl (AA) to reach pH = 7 and calcinated at 623 K.

titanium dioxide. TEM images show nanotubes prepared from nano and industrial TiO₂ powder have inner and outer diameter about 3 and 9 nm, respectively. Also SEM images show that the length of nanotubes can reach several 10 μm.

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