Study of synthesis parameters and photocatalytic activity of TiO₂ nanostructures

Mahdi Shahrezaei, Sajjad Habibzadeh, Ali Akbar Babaluo, Hossein Hosseinkhani, Mohammad Haghighi, Amin Hasanzadeh and Roghiyeh Tahmasebpour

Article History
Received 13 December 2015
Accepted 30 October 2016

ABSTRACT
In this present study, various types of TiO₂ nanostructures were synthesised via hydrothermal method from a commercial titanium dioxide. The effects of the initial concentration of titanium dioxide and the reaction time on the morphology of synthesised nanostructures were investigated. The TiO₂ nanostructures were calcined at 500°C and examined for the photocatalytic performance by decomposing formic acid as an organic pollutant. Scanning electron microscopy, transmission electron microscopy, Brunauer–Emmett–Teller and X-ray diffraction were employed to characterise the synthesised TiO₂ nanostructures. The outcomes showed more influence of reaction time rather than initial TiO₂ concentration on the properties of TiO₂ nanostructures. Various TiO₂ nanostructures such as, nanorods and nanotubes were fabricated at different initial TiO₂ concentrations and reaction times. In addition, the synthesised nanorod structures showed higher photocatalytic activity than the nanotubes. This is owing to the presence of rutile–anatase combined crystalline phases in the nanorod structures.

1. Introduction
Nanostructure materials have attracted enormous attention due to their interesting properties which differ from those of bulk materials [1–5]. Among various types of ceramics, titanium dioxide as a significant inorganic functional material has extensively been investigated because of its useful chemical, optical and electronical properties [6–10]. Photocatalytic property is observed when TiO₂ absorb light at a wavelength smaller than 384 nm. Consequently, valence band electrons are promoted through the band gap into the conduction band, generating an electron–hole (e⁻/h⁺) pair. These pairs are able to initiate oxidation and reduction reactions at TiO₂ surface [11,12]. Considering this property, TiO₂ nanostructure attracts wide scientific interest in view of their applications in
photocatalytic water splitting [13,14], environmental protection procedures such as, air and water purification [15,16], gas sensors [17–20], solar cell [13,21–24], cancer cell killing [25], hip and dental implant [26] and ion change [27]. It has been reported that photocatalytic activity of TiO₂ nanostructures is related to their size, specific surface area, morphology/structure (nanorods, nanowires and nanotubes) and the synthesis method of the nanomaterials [8,28]. TiO₂ nanotube is considered as one of the promising structures due to its large specific surface area and low density [2,28,29]. This thereby leads to an efficient use in catalysts, semiconductor devices and photovoltaic cell [2]. There are various methods of TiO₂ nanotubes synthesis such as, template method, electrochemical anodic oxidation and alkali hydrothermal method [30–37]. In this work, we considered the synthesis of TiO₂ nanostructures via hydrothermal treatment of TiO₂ nanoparticles. This synthesis process is an affordable one-step reaction, which requires neither expensive instruments nor especial chemicals [38,39]. Different types of TiO₂ nanostructures were synthesised from the commercial titanium dioxide (P25 Degussa Company) via hydrothermal method where over the past years several parameters have been considered, including reaction temperature [13,38,40], reaction time [40,41], initial amount of TiO₂ [2] and NaOH concentration [13,40].

To the best of our knowledge, both of the effects of reaction time and TiO₂ content have not simultaneously been so far studied. We focused on the impact of these parameters (reaction time and TiO₂ content) on the morphology of TiO₂ nanostructures. In addition, photocatalytic properties of the synthesised nanopowders have been investigated. It was found that not only the specific surface area is key parameter but also crystalline structures are more important than the first one. Morphology, specific surface area and crystalline structures of the synthesised nanostructures were determined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) and X-ray diffraction (XRD). The samples were calcined at 500 °C for 30 min. Formic acid was used as an organic pollutant for measuring the photocatalytic activity of the samples under the UV lamp exposure.

2. Materials and methods

2.1. Materials

Commercial titanium dioxide (P25) was purchased from Degussa Co., Germany, and formic acid, sodium hydroxide (NaOH, %96) and sulphuric acid (H₂SO₄, %98) were purchased from Merck Co., Germany. All the chemicals were used as received without further purification.

2.2. TiO₂ nanostructures synthesis

Different types of TiO₂ nanostructures were synthesised by a simple one-step hydrothermal reaction between NaOH and titanium dioxide (P25). In this experiment, 0.4 and 0.8 g of titanium dioxide (P25 Degussa – 70% anatase and 30% rutile) were added to a 25 ml solution of 10 M NaOH in a polytetrafluoroethylene (PTFE) pipe. The solution was placed in an autoclave with rotation speed of 20 rpm and heated for 12, 18 and 24 h at 150 °C. The filtered materials were thoroughly washed with deionised water until the solution...
reached the pH value of 7. Next, the samples (see Table 1) were washed with sulphuric acid and deionised water, respectively. Then, the samples were dried in vacuum oven at 80 °C. Furthermore, we used electric furnace (model: M2L-1200) to calcine all the synthesised nanostructures at 500 °C for 30 min with the heating rate of 5 °C/min.

### 2.3. Characterisation of samples

The BET specific surface area of the synthesised TiO₂ nanostructures was measured using a CHEMBET-3000 (Quantachrome) apparatus. Before N₂ adsorption measurement, samples were outgassed at 150 °C for 1 h. Morphological studies were conducted using a SEM (Viga II, 3 × 105, USA and Cam Scan MV-5300) and TEM (JEOL JSM-5300). XRD (Siemens D5000) was employed to analyse the crystalline structure of the synthesised TiO₂; the analyses were performed using a Cu-Kα as radiation (λ = 1.54 Å) in the range of 20° ≤ 2θ ≤ 70°.

### 2.4. Photocatalytic performance test

In order to measure the photocatalytic activity of synthesised titanium dioxide, 500 μl of formic acid (0.01 M) as an organic pollutant was added to 0.02 g of the TiO₂ nanostructures suspended in 100 ml of deionised water. Prior to the UV irradiation, the suspensions were stirred in dark for 30 min to reach the adsorption equilibrium. Then, the solution was subjected to a 125 W medium pressure mercury lamp irradiation (Philips-HPK). A magnetic stirrer was used to homogenously mix the TiO₂ nanostructures in the aqueous media. In addition, the decomposition of formic acid was tracked using a digital pH meter (see Figure 1).

### 3. Results and discussion

#### 3.1. Morphology of nanostructures TiO₂

TiO₂ nanostructures were synthesised by a hydrothermal method using Degussa P25 as precursor and 10 M NaOH aqueous solution. Figure 2 shows the SEM images of the products acquired at 150 °C for 12, 18 and 24 h with the lower TiO₂ content (0.4 g). Titanium dioxide nanotubes can be formed in the range of reaction temperature of 100–150 °C while commercial P25 was used as the raw materials [40]. SEM images of samples TiL12 and TiL18 synthesised at the lower concentration of the initial titanium dioxide nanoparticles (Figure 2(a,b)) indicate not quite conclusive structures. However, with increasing the reaction time up to 24 h, the TiO₂ Degussa shows a significant morphological
Figure 1. Experimental set-up of photocatalytic performance test.

Figure 2. SEM images of the synthesised TiO$_2$ nanostructures from 0.4 g TiO$_2$ at 150 °C with different reaction times: (a) 12, (b) 18 and (c) 24 h.
transition from nanoparticles to well-defined nanorods (sample TiL24, Figure 2(c)). It shows that the nanorod structures become longer and more protrusive in comparison with synthesised nanostructures with 12 and 18 h reaction time (samples TiL12 and TiL18).

In order to corroborate the TiO₂ nanostructures and to perform a detailed study, TEM images of the samples with high magnification were depicted in Figure 3. According to the literature [24,33,42], the most widely accepted formation mechanism of TiO₂ nanotubes during the hydrothermal process involves four stages: (1) dissolution of TiO₂ precursor and breaking of Ti–O–Ti bonds in the concentrated alkaline solution; (2) formation and growth of layered nanosheets; (3) exfoliation of nanosheets and finally (4) growing the nanosheets with the increasing tendency of curling which leads to the formation of nanotubes. Moreover, we can evidently see in Figure 3(a) (sample TiL12) the stages encompassing not only the nanosheets mostly as edge-shared octahedral layers (TiO₆) but the nanotubes as well [21,43]. Increasing the hydrothermal reaction time from 12 to 18 h (sample TiL18) causes the growth of the nanosheets where they have a tendency to wrap and form nanotubes. As shown, in Figure 3(b) a large amount of nanotubes with narrow size distribution were obtained. The diameter of nanotubes is around 10 nm and their lengths range from several tens to one hundred nanometres. TEM images of the TiL24 indicate (Figure 3(c,d)) that no more nanotubes and nanoparticles structures were observed when the reaction time increases up to 24 h where only nanorods structure can be found. From the TEM images, the diameter and the length of the nanorods were about 20–200 and 200 nm to several micrometres, respectively.

Figure 4(a) shows the SEM image of the sample TiH12 treated with the higher TiO₂ content (0.8 g) alkali solution for 12 h. The different morphology of TiO₂ nanostructures can be clearly seen in Figure 4(a) compared to that in Figure 2(a). It can be concluded that an increase in the molar ratio of the TiO₂ to NaOH decreases the probability of the
synthesis of nanotubes structure. In addition, at the lowest reaction time (e.g. 12 h, as shown in Figure 4(a)) some aggregated nanoparticles were observed in the products. In addition, TEM image of TiH12 (Figure 5(a)) indicates the nano-sized dispersion of synthesised TiO$_2$ particles. However, upon further prolonging the reaction time up to 18 h (sample TiH18), no specific pattern can be observed in this SEM image (see Figure 4(b)).

According to the TEM observation in Figure 5(b), TiH18 nanoparticles mostly are nanotubes in which they are by about 10–50 nm long with the diameters of less than 10 nm. Further observation indicated that the nanosheets and little TiO$_2$ nanorods were produced as well. Increasing the hydrothermal reaction time to 24 h causes the formation of numerous nanorods. According to the SEM observation in Figure 4(c) (sample TiH24), nanorods show a desirable and narrow diameter distribution (<100 nm). High aspect ratio of these nanorods might lead to employing this type of nanostructure materials in the polymeric application in order to produce nanocomposites with improved mechanical properties [44].

Figure 4. SEM images of the synthesised TiO$_2$ nanostructures from 0.8 g TiO$_2$ at 150 °C with different reaction times: (a) 12, (b) 18 and (c) 24 h.
Figure 5(c,d) show TEM images of the synthesised TiH24 sample, indicating the nano-rods structure. As observed, a large amount of nanorods with diameter less than 100 nm to several hundred nanometres while having the length of several microns are found. As discussed above, for both TiL24 and TiH24, quite some nanorods are produced, meanwhile morphological features of TiH24 seem to be similar to TiL24. Nevertheless, for TiH24, the nanorods structure shows a higher aspect ratio than TiL24 with longer nanorods. On the other hand, for sample synthesised with high content of TiO2 nanoparticles, nanorods were produced at shorter times (18 h). These trends might be attributed to more reacting nanoparticles at higher concentrations.

3.2. Specific surface area (S\textsubscript{BET})

The specific surface area of initial TiO\textsubscript{2} powder (P25 Degussa) was measured about 50 m\textsuperscript{2}/g. The BET specific surface area (S\textsubscript{BET}) of initial powder P25 and all of the synthesised nanostructures are presented in Figure 6. It is evident that the synthesis conditions of the hydrothermal method have significant effect on the specific surface area since the chemical structure and morphology of the synthesised nanostructures changed in different conditions. From Figure 6, when P25 transformed into the nanotubes structure for both TiL12 and TiL18 samples, there was a noticeable increase in the specific surface area from 50 up to 250 and 320 m\textsuperscript{2}/g, respectively. Besides, owing to the larger surface area of TiL18 than TiL12, one can conclude that more nanotubes are formed in the former sample, which is in agreement with the TEM images (see Figure 3). However, nanorods are formed as a result of decreasing the interlayer spacing of TiO\textsubscript{2} nanotubes by raising the reaction time (up to 24 h). This, in turn, decreases the respective S\textsubscript{BET}, which dramatically drops to 35 m\textsuperscript{2}/g in the case of TiL24 sample with the nanorod structures. This trend confirms the synthesis of titanium dioxide by the structures of nanotubes and nanorods.
A typical isotherm for the nitrogen adsorption–desorption of TiL18 and TiL24 with nanotube and nanorod structures, respectively, together with their corresponding pore volume and pore size distribution were implemented (see Figure 7 and Table 2). The representative results of the synthesised TiO2 nanostructures (TiL18 and TiL24) are shown in Figure 7(a) in which the larger pore volume of TiL18 than TiL24 is observed. Moreover, the corresponding pore size distribution calculated by Barrett–Joyner–Halenda (BJH) algorithm is also displayed in Figure 7(b). It can be found that TiL18 and TiL24 are composed of mesopore and macropore structures, accordingly. This justifies the much higher specific surface area of TiL18, i.e. 320 m²/g, compared to that of TiL24 (ca. 35 m²/g). In addition, with an increase in the reaction time, the hysteresis loops shift to the region of higher relative pressure and the areas of the hysteresis loops gradually become smaller. Considering the morphology of the TiL18 observed in Figure 3, the smaller pores (<10 nm) might correspond to the pores inside the nanotubes and the diameters of these pores are in the range of the inner diameter of the nanotubes, while the larger pores can be attributed to the voids in the aggregation of the nanotubes. This observation can be found in the other studies as well [45,46].

As seen in Figure 6, the results of the nitrogen adsorption test show that the $S_{BET}$ of the samples synthesised with higher initial concentration of titanium dioxide are lower than those of lower initial TiO2 concentration [38]. The $S_{BET}$ of the formed TiO2 nanostructures (TiH12 and TiH18) increased after treatment at 150 °C, which are 181 and 290 m²/g, respectively. Furthermore, the $S_{BET}$ of the TiO2 nanorods (TiH24) is even smaller than that of synthesised using the precursor P25 Degussa (20 m²/g), indicating the long structure with high aspect ratio for the obtained nanorods. As a result, one can find that an increase in the molar ratio of TiO2 to NaOH results in a decrease in the specific surface area.

### 3.3. Crystallographic characterisation

XRD were used to demonstrate phase structure of the synthesised TiO2 nanotubes and nanorods before and after calcination at 500 °C. Figures 8 and 9 show the XRD patterns
of the synthesised nanostructures by reaction times of 18 and 24 h, and the as-received TiO₂ powder, while treated at 150 °C. As shown in Figure 8(e), the as-received powder consists of mixture of rutile and anatase crystalline structures, whereas the crystalline structure of the P25 powder was changed in the course of hydrothermal process.

Figure 7. (a) Nitrogen adsorption–desorption isotherms and (b) the corresponding pore size distributions of TiL18 (BJH desorption pore volume of 0.92 cm³/g) and TiL24 (BJH desorption pore volume of 0.29 cm³/g).

| Sample | Pore size (nm) | Pore volume (cm³/g) | Nanostructures                      |
|--------|---------------|---------------------|------------------------------------|
| TiL18  | 18.1          | 0.92                | Nanotubes                          |
| TiH18  | 22.4          | 0.68                | Nanosheets, nanotubes and nanorods |
| TiL24a | 30.2          | 0.29                | Nanorods                           |
| TiH24a | 29.3          | 0.32                | Nanorods                           |
| P25    | 8.3           | 0.09                | Nanoparticles                      |

*Pores of these samples are resulted from the voids among formed nanorods.
Figure 8. XRD patterns of samples: (a) TiL18 and (b) TiH18 before and (c) TiL18 and (d) TiH18 after calcination at 500 °C and (e) as-received TiO$_2$ powder.

Figure 9. XRD patterns of samples: (a) TiL24 and (b) TiH24 before and (c) TiL24 and (d) TiH24 after calcination at 500 °C and (e) as-received TiO$_2$ powder.
According to the XRD patterns of the TiO₂ nanotubes and nanorods, the amorphous features of the synthesised TiO₂ nanorods and nanotubes are formed before the calcination step (see Figures 8 and 9(a,b)). It is worth to mention that a number of experiments show that at temperatures higher than ca. 280 °C, TiO₂ with the nanotubes structure can be transformed to anatase phase or a mixture of anatase and rutile is formed at temperatures higher than about 450 °C [1]. It has been notified that the temperature range of phase transformation mostly depends on the particle size, morphologies of crystals, addition of additives and synthesis temperature [47,48]. Namely, Zhang et al. [49] found that TiO₂ nanotube was turned into anatase–rutile form at 500 °C. Thus, the synthesised nanostructures (nanotubes and nanorods) were calcined at 500 °C for a short period of time (30 min) in air. XRD patterns of calcined TiL18 and TiH18 samples (nanotubes structures) indicate anatase phase (see Figure 8(c,d)). The presence of two diffraction peaks assigned at 25.3° and 48.0° (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 21–1272) indicates the anatase phase. The XRD pattern of calcined TiL18 and TiH18 samples indicate that the product only contains the anatase phase, confirming the formation of the single phase. Furthermore, the results show that there is no difference between the diffractograms of the TiL24 and TiH24 samples (synthesised nanorods – see Figure 9(c,d)). In addition, the XRD patterns of TiL24 and TiH24 nanostructures reveal a few peaks after calcination corresponding to the anatase and rutile phases (anatase as a dominant phase) of the commercial TiO₂.

### 3.4. Photocatalytic activity

Figure 10(a,b) shows the photocatalytic activity of the synthesised TiO₂ nanostructures before and after calcination at 500 °C, respectively. The experiment was conducted by the photodecomposition of formic acid as an organic pollutant. The schematic of pollutant degradation is presented in Figure 11. According to the literature [50,51] and our experiment results, we propose a mechanism for the degradation of acid formic as pollutant as follows:

\[
\begin{align*}
\text{HCOOH} & \rightarrow \text{COOH}^- + \text{H}^+ \\
\text{TiO}_2 & \rightarrow \text{TiO}_2(e^- + h^+) \\
\text{O}_2 + e^- & \rightarrow \text{O}_2^- \\
\text{O}_2 + 2e^- + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{O}_2^- & \rightarrow \text{OH}^* + \text{OH}^- + \text{O}_2 \\
\text{COOH}^- + \text{OH}^* & \rightarrow \text{COOH}^* + \text{OH}^- \\
\text{COOH}^* + \text{HO}^* & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

The organic pollutant \((C/C_0)\) residue percentage was calculated and plotted versus time as shown in Figure 10.

Here, \(C_0\) is the initial organic concentration and \(C\) is the organic concentration at time \(t\). Before subjecting UV lamp to the suspension, the samples were first assessed for the formic acid adsorption in the dark condition, indicating less than 5.8% adsorption of
formic acid onto TiO₂ nanostructures (see Table 3). In addition, the adsorption capacity decreases in the following order: TiL18 > TiH18 > P25 > TiL24 > TiH24. This is in accordance with the order of the specific surface areas of the synthesised nanostructures.

It should be mentioned that the synthesised TiO₂ nanostructures prior to the calcination at 500 °C did not reveal a satisfactory photocatalytic performance in terms of formic acid degradation (Figure 10(a)). This was confirmed as the formic acid concentration remained nearly unchanged during photocatalytic experiment [46,47], this might be attributed to the absence of crystalline structures in the synthesised materials. However, the photocatalytic outcomes showed better photodecomposition performance of the calcined nanostructure powders than that of uncalcined ones under 125 W medium pressure.
mercury lamp, which is in line with the other studies [51]. In addition, the synthesised nanotubes (samples TiL18 and TiH18) showed almost the similar photocatalytic activity, photodecomposing the organic pollutant with a close trend (see Figure 10(b)). However, there exists a difference between the photocatalytic activities of the nanotube materials, i.e. the photodecomposition process for the TiL18 sample reaches nearly 95% after about 95 min, while TiH18 takes this time ca. 95 min to complete 85% of decomposition process. This can be ascribed to their different specific surface areas. Furthermore, it has been reported that the mixture of anatase and rutile crystal phases (anatase as a dominant crystalline structure) has been indicated better photocatalytic activity than pure anatase or pure rutile crystal phase [50,52]. Therefore, the enhanced photocatalytic activity of P25 compared to TiL18–TiH18 (with nanotube structures) after 60% decomposition of formic acid is owing to the mixture of anatase and rutile crystal phases present in its structure. There are two theories which can address this phenomenon. First, rutile acts as a sink for the electrons generated in anatase, leading to physically separate the electron-hole and thereby depress rates of recombination (Figure 12(a)). This model is consistent with the fact that the band edges of rutile lie within those of anatase, i.e. the potential of the conduction band edge of anatase is more negative than that of rutile. However, the second scenario has been recently shown that the opposite occurs: rutile undergoes band gap activation, and electrons are shuttled from rutile to anatase sites, which must be of lower energy (Figure 12(b)). This implies that one or more trap sites exist on anatase at potentials more positive than the conduction band edge of either anatase or rutile. This was

Table 3. The amount of adsorption of formic acid (%) in dark for the synthesised TiO2 nanostructures.

| Photocatalyst | Formic acid adsorption % |
|---------------|--------------------------|
| TiL18         | 5.7                      |
| TiL24         | 2.4                      |
| TiH18         | 4.9                      |
| TiH24         | 1.7                      |
| P25           | 3                        |

Figure 11. The proposed mechanism for the degradation formic acid by TiO₂.
recently confirmed by a photoacoustic spectroscopy study of anatase, which found trap sites on anatase at an average energy of 0.8 eV below the conduction band edge [50]. Moreover, it is shown (see Figure 10(b)) that the synthesised nanorods demonstrate better photocatalytic activity than the nanotubes for the samples of TiL24 and TiH24. This can be related to the amount of rutile–anatase combined crystalline structures in the synthesised nanorods (see the XRD patterns). It is clear that no significant difference has been observed between the TiL24 and TiH24. However, TiH24 sample shows lower photocatalytic activity than TiL24. This can be also due to the lower specific surface area of sample TiH24. In addition, the enhanced photocatalytic activity of TiL24 versus P25 (even with relatively close specific surface areas) can be ascribed to its higher pore volume (see Table 2). In particular, higher pore volume results in the faster diffusion of the products from formic acid decomposition during the photocatalytic reaction [47,53]. As for TiH24 and P25 samples, the trend of both photocatalysts for the decomposition of formic acid is similar until which \( C/C_0 = 75\% \), however, the larger specific area of P25 improves the respective photocatalytic activity.

### 4. Conclusion

Titanium dioxide nanotubes and nanorods were successfully synthesised via hydrothermal method employing P25 Degussa in 10 M NaOH solution at 150 °C. The synthesised nanotubes found to have high specific surface area with the nanometric diameter of less than 100 nm. However, nanorods were synthesised with low specific surface area but we fabricated nanometric diameter and micron-size length. Our results clearly demonstrated that the reaction time shows more significant effect than TiO₂ initial concentration on the final properties, i.e. surface morphology, crystallinity and photocatalytic performances. In addition, lower initial concentration of titanium dioxide leads to shortening the reaction time of the nanotubes synthesis while increasing the corresponding specific surface area of the final products. In addition, after calcination of the TiO₂ nanorods where there was a mixture of anatase–rutile phases, a higher photocatalytic activity was achieved comparing to that of TiO₂ nanotubes. It was found that the photocatalytic efficiency of our

![Figure 12. Models of mixed-phase TiO₂: (a) rutile islands surround anatase particles, and rutile is an electron sink; (b) a small rutile core surrounded by anatase crystallites, where electrons are shuttled from rutile to anatase.](image-url)
products highly depends on the crystalline structures. Therefore, we think that titanium dioxide nanorods are one of the ideal and novel photocatalysts.

**Acknowledgments**

The Authors wish to acknowledge Sahand University of Technology (SUT) for this work supporting. We acknowledge co-workers and technical staff in the Department of Chemical Engineering and Nanostructure Materials Research Center (NMRC) of SUT and National Science Council (NSC) of Taiwan for their help during various stages of this work.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**References**

[1] Neupane MP, Park IS, Lee MH, et al. Influence of heat treatment on morphological changes of nano-structured titanium oxide formed by anodic oxidation of titanium in acidic fluoride solution. Bio-Med Mater Eng. 2009;19:77–83.

[2] Wei M, Konishi Y, Zhou H, et al. Formation of nanotubes TiO₂ from layered titanate particles by a soft chemical process. Solid State Commun. 2005;133:493–497.

[3] Wen B, Liu C, Liu Y, et al. Synthesis of titane nanofibers and nanotubes. J Nanosci Nanotechnol. 2004;4:1062–1066.

[4] Angeles-Chavez C, Toledo-Antonio JA, Cortes-Jacome MA, et al. Structural characterization of Pt–Ir bimetallic clusters on TiO₂ nanotubes prepared by simultaneous reduction. Powder Technol. 2014;258:78–84.

[5] Usha K, Kumbhakar P, Mondal B. Effect of Ag-doped TiO₂ thin film passive layers on the performance of photo-anodes for dye-sensitized solar cells. Mater Sci Semicond Process. 2016;43:17–24.

[6] Djenadic RR, Nikolic LM, Giannakopoulos KP, et al. One-dimensional titanate nanostructures: synthesis and characterization. J Eur Ceram Soc. 2007;27:4339–4343.

[7] Wang B, Sun Q, Liu S, et al. Synergetic catalysis of CuO and graphene additives on TiO₂ for photocatalytic water splitting. Int J Hydrogen Energy. 2013;38:7232–7240.

[8] Pelaez M, Nolan NT, Pillai SC, et al. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl Catal B. 2012;125:331–349.

[9] Chen X, Mao SS. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. Chem Rev. 2007;107:2891–2959.

[10] Takahashi J, Itoh H, Motai S, et al. Dye adsorption behavior of anatase- and rutile-type TiO₂ nanoparticles modified by various heat-treatments. J Mater Sci. 2003;38:1695–1702.

[11] Carrier M, Perol N, Herrmann J-M, et al. Kinetics and reactional pathway of Imazapyr photocatalytic degradation Influence of pH and metallic ions. Appl Catal B. 2006;65:11–20.

[12] Tan Z, Sato K, Ohara S. Synthesis of layered nanostructured TiO₂ by hydrothermal method. Adv Powder Technol. 2014;26:296–302.

[13] Wong CL, Tan YN, Mohamed AR. A review on the formation of titania nanotube photocatalysts by hydrothermal treatment. J Environ Manage. 2011;92:1669–1680.

[14] Su Y-f, Lee M-c, Wang G-b, et al. An innovative method to quickly and simply prepare TiO₂ nanorod arrays and improve their performance in photo water splitting. Chem Eng J. 2014;253:274–280.

[15] Lee C-K, Wang C-C, Lyu M-D, et al. Effects of sodium content and calcination temperature on the morphology, structure and photocatalytic activity of nanotubular titanates. J Colloid Interface Sci. 2007;316:562–569.
[16] Usman M, Rasool K, Batool SS, et al. Humidity effect on transport properties of titanium dioxide nanoparticles. J Mater Sci Technol. 2014;30:748–752.
[17] Li G, Liu Z, Zhang Z, et al. Preparation of titania nanotube arrays by the hydrothermal method. Chin J Catal. 2009;30:37–42.
[18] Ryu WH, Park CJ, Kwon HS. Effects of highly ordered TiO2 nanotube substrates on the nucleation of Cu electrodeposits. J Nanosci Nanotechnol. 2010;10:3671–3675.
[19] Zhong X, Yu D, Song Y, et al. Fabrication of large diameter TiO2 nanotubes for improved photoelectrochemical performance. Mater Res Bull. 2014;60:348–352.
[20] Zhang X, Li D, Wan J, et al. Hydrothermal synthesis of TiO2 nanosheets photocatalyst on Ti mesh for degradation of norfloxacin: influence of pickling agents. Mater Sci Semicond Process. 2016;43:47–54.
[21] Wu X, Jiang Q-Z, Ma Z-F, et al. Synthesis of titania nanotubes by microwave irradiation. Solid State Commun. 2005;136:513–517.
[22] Farsinezhad S, Mohammadpour A, Dalrymple AN, et al. Transparent anodic TiO2 nanotube arrays on plastic substrates for disposable biosensors and flexible electronics. J Nanosci Nanotechnol. 2013;13:2885–2891.
[23] Liu R, Qiang L-S, Yang W-D, et al. The effect of calcination conditions on the morphology, the architecture and the photo-electrical properties of TiO2 nanotube arrays. Mater Res Bull. 2013;48:1458–1467.
[24] Chao C, Ren Z, Yin S, et al. Dissolution/recrystallization growth of titanian nanostructures by amorphous precursor. Adv Powder Technol. 2014;25:745–751.
[25] Kalbacova M, Macak JM, Schmidt-Stein F, et al. TiO2 nanotubes: photocatalyst for cancer cell killing. Phys Status Solidi. 2008;2:194–196.
[26] Peng L, Eltgroth ML, LaTempa TJ, et al. The effect of TiO2 nanotubes on endothelial function and smooth muscle proliferation. Biomaterials. 2009;30:1268–1272.
[27] Sun X, Li Y. Synthesis and characterization of ion-exchangeable titanian nanotubes. Chem Eur J. 2003;9:2229–2238.
[28] Tang G, Liu S, Tang H, et al. Template-assisted hydrothermal synthesis and photocatalytic activity of novel TiO2 hollow nanostructures. Ceram Int. 2013;39:4969–4974.
[29] Uchida S, Chiba R, Tomiha M, et al. Hydrothermal synthesis of titania nanotube and its application for dye- sensitized solar cell. In: Sang-Eon Park RRW-SACWL, Jong-San C, editors. Studies in surface science and catalysis. Vol. 146. Netherlands: Elsevier; 2003. p. 791–794.
[30] Huang K-C, Chien S-H. Improved visible-light-driven photocatalytic activity of rutile/titania-nanotube composites prepared by microwave-assisted hydrothermal process. Appl Catal B 2013;140:140–141:283–288.
[31] Jiang F, Zheng S, An L, et al. Effect of calcination temperature on the adsorption and photocatalytic activity of hydrothermally synthesized TiO2 nanotubes. Appl Surf Sci. 2012;258:7188–7194.
[32] Wang X, Li H, Liu Y, et al. Hydrothermal synthesis of well-aligned hierarchical TiO2 tubular macrochannel arrays with large surface area for high performance dye-sensitized solar cells. Appl Energy. 2012;99:198–205.
[33] Weng LQ, Song SH, Hodgson S, et al. Synthesis and characterisation of nanotubular titanates and titania. J Eur Ceram Soc. 2006;26:1405–1409.
[34] Gao M, Li Y, Guo M, et al. Effect of substrate pretreatment on controllable growth of TiO2 nanorod arrays. J Mater Sci Technol. 2012;28:577–586.
[35] Hou Q, Tao X, Yang Y-J, et al. Optimal synthesis of mesostructured hollow titania nanotubes templated on CaCO3 nanoparticles. Powder Technol. 2010;198:429–434.
[36] Chen J, Wang H, Wei X, et al. Characterization, properties and catalytic application of TiO2 nanotubes prepared by ultrasonic-assisted sol-hydrothermal method. Mater Res Bull. 2012;47:3747–3752.
[37] Lei B-X, Luo Q-P, Sun Z-F, et al. Fabrication of partially crystalline TiO2 nanotube arrays using 1, 2-propanediol electrolytes and application in dye-sensitized solar cells. Adv Powder Technol. 2013;24:175–182.
Bavykin DV, Parmon VN, Lapkin AA, et al. The effect of hydrothermal conditions on the mesoporous structure of TiO$_2$ nanotubes. J Mater Chem. 2004;14:3370–3377.

Li H, Zhu B, Feng Y, et al. Synthesis, characterization of TiO$_2$ nanotubes-supported MS (TiO$_2$NTs@MS, M=Cd, Zn) and their photocatalytic activity. J Solid State Chem. 2007;180:2136–2142.

Yuan Z-Y, Su B-L. Titanium oxide nanotubes, nanofibers and nanowires. Colloids Surf A. 2004;241:173–183.

Liu N, Chen X, Zhang J, et al. A review on TiO$_2$-based nanotubes synthesized via hydrothermal method: formation mechanism, structure modification, and photocatalytic applications. Catal Today. 2014;225:34–51.

Cui L, Hui KN, Hui KS, et al. Facile microwave-assisted hydrothermal synthesis of TiO$_2$ nanotubes. Mater Lett. 2012;75:175–178.

Wang W, Varghese OK, Paulose M, et al. A study on the growth and structure of titania nanotubes. J Mater Res. 2004;19:417–422.

Sokhandani P, Babaluo AA, Rezaei M, et al. Nanocomposites of PVC/TiO$_2$ nanorods: surface tension and mechanical properties before and after UV exposure. J Appl Polym Sci. 2013;129:3265–3272.

Lee C-K, Lin K-S, Wu C-F, et al. Effects of synthesis temperature on the microstructures and basic dyes adsorption of titanate nanotubes. J Hazard Mater. 2008;150:494–503.

Yu H, Yu J, Cheng B, et al. Synthesis, characterization and photocatalytic activity of mesoporous titania nanorod/titanate nanotube composites. J Hazard Mater. 2007;147:581–587.

Yu J, Yu H, Cheng B, et al. Effects of calcination temperature on the microstructures and photocatalytic activity of titane nanotubes. J Mol Catal A: Chem. 2006;249:135–142.

Ou H-H, Lo S-L. Review of titania nanotubes synthesized via the hydrothermal treatment: fabrication, modification, and application. Sep Purif Technol. 2007;58:179–191.

Zhang S, Zhou J, Zhang Z, et al. Morphological structure and physicochemical properties of nanotube TiO$_2$. Chin Sci Bull. 2000;45:1533–1536.

Khataee AR, Aleboyeh H, Aleboyeh A. Crystallite phase-controlled preparation, characterisation and photocatalytic properties of titanium dioxide nanoparticles. J Exp Nanosci. 2009;4:121–137.

Pipelzadeh E, Babaluo AA, Haghighi M, et al. Silver doping on TiO$_2$ nanoparticles using a sacrificial acid and its photocatalytic performance under medium pressure mercury UV lamp. Chem Eng J. 2009;155:660–665.

Bai X, Xie B, Pan N, et al. Novel three-dimensional dandelion-like TiO$_2$ structure with high photocatalytic activity. J Solid State Chem. 2008;181:450–456.

Lee C-K, Lyu M-D, Liu S-S, et al. The synthetic parameters for the preparation of nanotubular titanate with highly photocatalytic activity. J Taiwan Inst Chem E. 2009;40:463–70.