A critical review on the recent progress of synthesizing techniques and fabrication of TiO$_2$-based nanotubes photocatalysts

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ABSTRACT

One-dimensional titanium dioxide (TiO$_2$)-based nanotubes have attracted great interest to be used as photocatalysts in the field of environmental applications. Three main approaches via template-assisted, electrochemical anodic oxidation and alkaline hydrothermal treatment used to prepare the nanostructured TiO$_2$-based nanotubes are reviewed. The parameters that affect the formation of TiO$_2$-based nanotubes via hydrothermal method such as phases and particle sizes of starting materials, types and concentrations of alkali solution, temperature and duration of hydrothermal treatment, ultrasonication and microwave-assisted hydrothermal synthesis, acid washing and calcination have been reviewed in details. This paper also discussed the possible crystal structure and formation mechanism of TiO$_2$-based nanotubes via alkaline hydrothermal treatment. In addition, the recent research progress on the structural modification of TiO$_2$-based nanotubes to be used as photocatalysts is summarized in this review. Modification strategies investigated include metal nanoparticles deposition, single- and co-doping of metal ions/non-metal ions, coupled with other semiconductors to form binary composites and hybrid with carbon nanomaterials.

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1. Introduction

Titanium dioxide (TiO₂) is a very well-known photocatalysis material due to its superior photo-reactivity, non-toxicity, long term stability, high corrosion resistance and available in low cost [1–3]. The key to photolysis of water (H₂O) molecule under illumination of light is the positions of the conduction and valence bands relative to the redox potential of water [4]. TiO₂ fulfills the particular requirement as compared to the other metal oxides, where the conduction band edge lay higher than that of the species to be reduced (hydrogen ion/hydrogen) and the valence band edge located lower than that of the species to be oxidized (H₂O/oxygen (O₂)).

The drawbacks of TiO₂ nanoparticles photocatalyst include the requirement of large amount of catalysts, difficulty in catalyst recycling and problematic agglomeration of TiO₂ nanocrystals into large particles [5]. Although immobilized TiO₂ is a feasible option, the overall photocatalytic activity has been compromised due to the reduction of surface area and limitation in mass transfer [6]. In order to enhance photocatalytic activity and facilitate catalyst separation after photocatalytic reaction, one-dimensional (1D) nanostructured materials such as nanotubes, nanowires and nanorods have been investigated. Besides, charge recombination probability within TiO₂ nanoparticles also increases due to the presence of defects, surface states and grain boundaries which act as electron trapping sites [7]. Meanwhile, 1D nanostructured materials are expected to have faster electron transport and lower charge recombination due to 1D channel for electron transportation and decrement of inter-crystalline contacts, respectively.

The present review focuses on TiO₂-based nanotubes rather than nanowires and nanorods due to the internal layer of the hollow nanotubes provide larger surface area and easily functionalized by filling the hollow nanotubes [8]. However, TiO₂ is a wide band gap semiconductor with 3.2 eV for anatase [1,9], 3.0 eV for rutile [1,9] and nanotubes material is reported to have a mobility band gap of about 3.1–3.87 eV [10,11]. The blue shift of the absorption edge wavelength is attributed to the quantum size effect of TiO₂ nanotubes, which is due to the thin nanotube wall thickness of around 1 nm [12]. This is the major drawback that limits the use of TiO₂ photocatalysts for large scale application. Therefore, intense effort focuses on the modification of TiO₂ nanotubes by various strategies such as metal nanoparticles deposition, single or co-doping metal ions/non-metal ions, coupling with other semiconductors and hybrid with carbon nanomaterials. These efforts alter the electronic properties of TiO₂ nanotubes by narrowing the band gap energy, resulting in higher reaction rates for the photocatalytic degradation of organic pollutants.

The review begins with a brief overview of the synthesis techniques including template-assisted, electrochemical anodization and hydrothermal treatment with their research progress, advantages and disadvantages. Extensive applications of template-assisted method often encounter difficulties like pore size limitation of the prepared template and post-removal template usually results in impurities [13]. The method of electrochemical anodization is based on the anodization of titanium foil to obtain nanoporous TiO₂ film [14] and can be considered as an expensive technique for large scale production of TiO₂ nanotubes [3]. Besides, this method may lead to un-separable tubes and uneven length distribution of tubes over a large surface area [9,10]. Thus, the recent research progress of the formation of TiO₂-based nanotubes photocatalysts through hydrothermal treatment has been emphasized in this review. The factors during the hydrothermal reaction which affect the formation of TiO₂-based nanotubes, possible mechanism, modification of TiO₂-based nanotubes and their effects on the photocatalytic reactions have been reviewed in details.

2. TiO₂ nanoparticles, randomized and oriented nanotubes for photocatalytic reactions

For better clarification, the mechanism of photocatalytic reaction is briefly summarized in Eqs. (1)–(6) [13,15]. Photocatalytic process occurs based on the sufficient energy obtained from absorption of light radiation which equals to or is greater than the semiconductor band gap energy. This will lead to the excitation and transfer of electrons from the valence band to the conduction band, leaving behind holes at the valence band. The electrons could react with electron acceptors such as O₂ adsorbed on the catalyst surface or dissolved in water and reduce to superoxide radical anion ("O₂⁻"). Meanwhile, holes tend to oxidize directly on the organic molecules or react with hydroxyl group and oxidize to hydroxyl radical ("OH"). The resulting radicals are capable of promoting oxidation reactions to mineralize organic pollutant.

\[
\text{TiO}_2 + \text{energy(heatlight)} \rightarrow h_{\text{vb}}^+ + e_{\text{cb}}^- \quad (1) \\
\text{O}_2(\text{ads}) + e_{\text{cb}}^- \rightarrow \text{O}_2^- \quad (2) \\
\text{H}_2\text{O} + h_{\text{vb}}^+ \rightarrow \text{OH} + \text{H}^+ \quad (3) \\
h_{\text{vb}}^+ + \text{pollutant} \rightarrow \text{pollutant}^+ \rightarrow \text{degradationproducts} \quad (4) \\
\text{O}_2^- + \text{pollutant} \rightarrow \text{degradationproducts} + \text{CO}_2 \quad (5) \\
\text{OH} + \text{pollutant} \rightarrow \text{degradationproducts} + \text{CO}_2 \quad (6)
\]

where h_{\text{vb}}^+ and e_{\text{cb}}^- are the positive hole in the valence band and the electron in the conduction band, respectively while subscripts ‘ads’ denote the adsorbed forms of the O₂ molecule.

In randomly packed TiO₂ nanoparticles, the transportation of photo-excited electron is limited due to low electron diffusion coefficient and scattering effect of free electrons [7]. The electron trapped sites could occur at defects, surface states and grain boundaries between nanoparticles [16]. Consequently, charge collection efficiency was diminished due to the increment of charge recombination at the trapping sites. Moreover, other drawbacks of TiO₂ nanoparticles are often related to the separation and recycling of the particulate catalysts from the reaction media [5]. Filtration of ultra-fine nanoparticles is a tedious and time consuming separation process.

In order to improve these behaviors, recent researches have moved toward the use of 1D nanostructures of TiO₂ such as nanotubes, nanorods and nanowires. The unique properties of high aspect ratio of TiO₂ nanotubes include large surface area, high cation exchangeability, high catalytic activity, easier separation and recyclability [8]. These advantages make nanotubes attractive for industrial scale applications. Ohsaki et al. [17] found that the use of TiO₂ nanotubes, even in a randomly disordered system, was able to suppress the possibility of charge recombination. At the same electron diffusion coefficient of TiO₂ nanoparticles and randomly packed TiO₂ nanotubes, TiO₂ nanotubes with longer diffusion length and longer electron lifetime would exhibit excellent electron transport. In addition, TiO₂ nanotubes can provide strong
light scattering effect and enhance light harvesting properties [16]. The special features of internal and external surface area are available for the adsorption and chemical reaction of organic pollutant molecules.

It should be highlighted that TiO2 nanotubes can be synthesized into randomized powdery or immobilized nanotubes arrays. The immobilized nanotubes are self-organized, vertically oriented and supported on a surface to form an integrated unit. Immobilization of nanocatalyst on a support can prevent catalyst agglomeration and facilitate catalyst recycling. The arrangement of highly ordered TiO2 nanotubes array is perpendicular to the titanium substrate, providing channels for efficient charge transfer from the solution to the collecting substrate [7]. This reduces the losses incurred by charge trapping across the nanoparticles grain boundaries [16].

Fig. 1 shows the electron transporting pathways in nanoparticles, randomized and oriented nanotubular structured TiO2. The ordered TiO2 nanotubes arrays are expected to improve the charge collection efficiency due to the fast electron transportation along 1D channel with minimum charge recombination site. Consequently, a lot of research works had been concentrating on the formation of ordered arrays of nanotubes especially in the application of photoelectrochemical water splitting and dye sensitized solar cells [7-9]. However, dispersed non-ordered nanotubes showed great potential as heterogeneous catalyst to accelerate photocatalytic degradation of organic pollutants in liquid medium [18]. Thus, the research progresses on the formation of nanotubes via different synthesizing techniques are discussed in details in subsequent section.

3. Synthesizing techniques of TiO2 nanotubes

Three popular synthesizing techniques of TiO2 nanotubes have been investigated in recent years including template-assisted, electrochemical anodization and hydrothermal treatment. A comparison between unique features of these three fabrication methods is summarized in Table 1.

<table>
<thead>
<tr>
<th>Fabrication method</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Template-assisted method</td>
<td>• Ordered arrays&lt;br&gt;• Advantages: The dimension of nanotubes can be controlled by the size and type of applied templates&lt;br&gt;Uniform size of nanotubes can be formed&lt;br&gt;• Disadvantages: Nanotubes morphology may be destroyed during post-removal of the templates&lt;br&gt;Disolution of template may result in contamination of nanotubes</td>
</tr>
<tr>
<td>Electrochemical anodization method</td>
<td>• Oriented arrays&lt;br&gt;• Advantages: The dimension of nanotubes can be controlled by varying the voltage, electrolyte, pH and anodizing time&lt;br&gt;Ordered alignment of nanotubes with high aspect ratio can be formed&lt;br&gt;• Disadvantages: The requirement of fabrication apparatus&lt;br&gt;Length distribution and separation of nanotubes over a large surface area is not well-developed</td>
</tr>
<tr>
<td>Hydrothermal treatment</td>
<td>• Random alignment or can be aligned&lt;br&gt;• Advantages: Easy route to obtain nanotubes in relatively large amount&lt;br&gt;• Disadvantages: Difficult in achieving uniform size of nanotubes</td>
</tr>
</tbody>
</table>

3.1. Template-assisted method

The dimensions (diameter and length) of TiO2 nanotubes formed through hard template approach membranes can be controlled easily by the dimension of templates [20]. Generally, TiO2 nanotubes derived from the templates are obtained after removal of templates by selective chemical etching [21] or thermal decomposition [22]. Template can be divided into two types: positive and negative templates as shown in Fig. 2 [20]. Positive template synthesis
Table 2
Template-assisted method for preparation of TiO2 nanotubes.

<table>
<thead>
<tr>
<th>Template categories</th>
<th>Types of precursors</th>
<th>Preparation methods of TiO2 nanotubes</th>
<th>Dimensions of nanotubes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive template</td>
<td>(i) Amorphous TiO2 (ii) Anodized aluminum oxide (AAO) (&gt;3 h)</td>
<td>(i) Two-step anodization (ii) Template-based electrochemical deposition process (iii) Low-temperature aqueous solution method (iv) Template-based liquid phase deposition</td>
<td>Internal diameter (D) = 70–100 nm Outer diameter (Dx) = 140–180 nm Average length (L) = 8 μm Wall thickness = 50–120 nm for deposition times of 3–10 h</td>
<td>Hoyer [24]</td>
</tr>
<tr>
<td></td>
<td>(i) TiO2 (ii) Zinc oxide (ZnO) nanorod template (5 h)</td>
<td>(i) Sol–gel followed by hydrothermal method (ii) Layer-by-layer absorption and reaction technique (iii) Template-assisted method</td>
<td>Average diameter (D) = 400–600 nm L = 30 μm Shell thickness = 150 nm Ds and L of TiO2 branches were 60 nm and 1 μm, respectively</td>
<td>Qiu et al. [21]</td>
</tr>
<tr>
<td></td>
<td>(i) TiO2 sol (ii) ZnO nanorod template (no fabrication time is reported)</td>
<td>(i) Rapid thermal chemical vapor deposition (ii) Sol–gel method</td>
<td>Ds = 60 nm Wall thickness = 15 nm</td>
<td>Kim et al. [22]</td>
</tr>
<tr>
<td>Negative template</td>
<td>(i) Titanium (IV) iso-propoxide (ii) AAO</td>
<td>(i) Commercially available (ii) Template-based gas phase atomic layer deposition</td>
<td>Ds = 80–100 nm L = 30 μm Wall thickness = 2.5 nm Wall thickness = 7 nm Specific surface area = 400 m²/g</td>
<td>Bae et al. [26]</td>
</tr>
<tr>
<td></td>
<td>(i) Titanium (IV) t-butoxide (ii) AAO</td>
<td>(i) Commercially available (ii) Template-based alcoholate hydrolysis</td>
<td>Ds = 200 nm L = 60 μm Wall thickness = 10–45 nm at precursors concentration of 0.1–2.0 M</td>
<td>Yuan et al. [27]</td>
</tr>
</tbody>
</table>

is employed when oxide materials are coated on the outer surface of the template [21]. Meanwhile, negative template synthesis involved oxide materials which are deposited inside the template channel space [23]. Table 2 shows several selected research works on the production of TiO2 nanotubes through positive and negative templates.

In 1996, Hoyer [24] was the first researcher reported the preparation of TiO2 nanotubes via template-assisted method. TiO2 nanotubes were formed by electrochemical deposition method into polymethyl methacrylate (PMMA) mold. Anodically grown of porous anodized aluminum oxide (AAO) membrane consists of an array of parallel straight nanopores with uniform diameter and length. It served as negative template to produce a positive type polymer mold. TiO2 nanotubes were obtained after dissolution of the polymer mold using acetone. Recently, Karanman et al. [28] demonstrated that TiO2 nanotubes thin films could be deposited over electrospray PMMA fibers by hot filament chemical vapor deposition method. Post-heat treatment of the deposited materials leads to the decomposition of polymeric inner layer and formation of randomly distributed anatase TiO2 nanotubes. Several types of soft template had been reported in the literature such as core–shell–corona cylindrical polymer brushes, self-assembled block copolymers and biological superstructures [29], Ku et al. [30] introduced silicon moiety into a block copolymer, polystyrene-block-poly(4-tert-butylmethysilylethyl)oxyxystrene) to enhance template properties such as thermal stability, dielectricity and mechanical strength. They found that the wall thickness of the TiO2 nanotubes can be easily tuned by adjusting the number of atomic layer.

On the other hand, zinc oxide (ZnO) nanostructure was employed as a template due to the low material cost and ease of fabrication [31]. It has characteristic of amphoteric in nature, which can be easily dissolved in mild acids or bases [31]. Lee et al. [25] demonstrated that TiO2 nanotubes could be produced without using chemical medium to dissolve ZnO nanorod template. The removal of ZnO could be achieved by the reaction with hydrogen ions during liquid phase deposition process. However, the sample could be contaminated easily by precipitation resulting from the liquid phase deposition process of TiO2. Qiu et al. [21] formed three-dimensional (3D) branched TiO2 nanotube arrays on transparent conducting oxide substrates using ZnO nanorods and ZnO spacers as template. The ZnO nanorods template and sacrificial spacers can be removed by selective chemical etching in dilute aqueous solution of titanium tetrachloride, which might lead to the collapse of TiO2 tubes.

Recently, carbon nanotubes have been considered to be an ideal template to synthesis TiO2 nanotubes due to the template easily being removed, small diameter of carbon nanotubes and can support tubular morphology [22]. A sintering process at an appropriate temperature is performed after coating TiO2 on carbon nanotubes to burnout the carbon nanotubes template and high crystallinity of TiO2 nanotubes could be obtained [22]. Meng et al. [32] reported crystalline anatase TiO2 nanotubes were prepared using atomic layer deposition on carbon nanotubes and calcination at 250°C. Meanwhile, Kim et al. [22] successfully synthesized anatase TiO2 nanotubes by performing a simply calcination process above 500°C on TiO2 coated multi-walled carbon nanotubes composite materials via sol–gel method.

The advantages of positive template are inner diameters and length of the resulting nanotubes could be determined by the outer diameters and length of the original template, whereas outer diameters are determined by the thickness of deposited wall layers [20]. Meanwhile, the disadvantage of this type of template is high difficulty in fabrication of uniform length and open ended nanotubes. Thereby, the use of negative template has attracted attention.

Nanoporous AAO, which prepared by electrochemical oxidation of aluminum in acidic solution has been extensively used as a negative template. The attractive advantages of anodic AAO membranes are large specific surface area, ordered pore geometry, adjustable structured properties such as pore diameter and length and the ease of dissolution with chemical solvents [23]. Assisted by AAO templates, various methods have been developed to prepare TiO2 nanotubes such as electrochemical technique, sol–gel and atomic layer deposition [27]. By controlling the conditions of anodization process, 10–400 nm of pore diameter, 50–600 nm of inter-pore distance, pore aspect ratio of 10 to 5000 and 10 nm to 150 μm of thickness of porous aluminum oxide layer can be prepared [23].
This makes the anodic AAO membrane as an excellent template material for 1D of ordered arrays nanostructures. Bae et al. [26] successfully fabricated multi-walled anatase TiO2 nanotubes using AAO as a negative template. Multi-walled nanotubes were produced by alternating TiO2 and aluminum oxide nanolaminates structures onto porous aluminum oxide templates with atomic layer deposition method, followed by wet etching of the sacrificial aluminum oxide. The structural parameters including diameter, length, wall thickness, inter-wall spacing and number of wall layers of the multi-walled TiO2 nanotubes can be adjusted. In addition, Yuan et al. [27] synthesized TiO2 nanotubes through an AAO template-based titanium (IV) t-butoxide (Ti[OC4H9]4) hydrolysis process. In their experiment, the wall thickness of the TiO2 nanotubes can be controlled by adjusting the concentration of Ti[OC4H9]4 solutions.

In short, both types of template show the disadvantage of obtaining smaller nanotubes due to the restriction of pore sizes of the prepared template. Besides, it requires multi-step of prefabrication template and post-removal of template which are time-consuming for the practical applications. In the case of the post-removal for hard template, array of nanotubes may be collapsed, contaminated or become bundles onto the substrate during the wet-chemical etching in acidic or alkaline solution [30].

### 3.2. Electrochemical anodization method

TiO2 nanotubes with ordered arrangement and high aspect ratio can be produced by using electrochemical anodization method. Basically, TiO2 nanotubes grow on the surface of the anode of titanium foils or thin sheets. The dimensions of nanotubes formed in various electrolytes can be controlled by applying different electrolyte composition, applied voltage, pH and anodizing time [33,34]. The development of electrochemical anodization method can be divided into three generations based on the length of TiO2 nanotubes or type of electrolyte as shown in Table 3.

In 1999, Zwilling et al. [40] had reported that the titanium metal surface became porous when using anodization in chromic acid electrolytes containing hydrofluoric acid. They recognized that small addition of fluoride ions (F−) to electrolyte was a crucial ingredient in the formation of self-organized porous structures. The latter work done by Gong et al. [33] demonstrated clearly self-organized and highly uniform nanotubes on titanium substrate using an aqueous dilute hydrofluoric solution as electrolyte. The high chemical dissolution rate of titanium and TiO2 in hydrofluoric acid containing electrolytes and high H2O content of the electrolytes could result in limitation of length to few hundred nanometers and non-ideal tubular shape of nanotubes [33,35]. Hence, the first generation of nanotubes length with approximately 500 nm or less could not meet the requirement of practical applications.

Subsequently, the use of buffered neutral electrolytes containing various fluoride salts such as sodium fluoride [36] and ammonia fluoride [34] had been proposed to slow down the TiO2 dissolution rate. For this second generation of nanotubes, longer nanotubes with lengths up to several micrometers can be produced as the ultimate concentration of F− and hydrofluoric acid are determined by the solution pH. Taking into account the importance of the pH during anodization, Sreekantan et al. [34] reported that the reduction of acidity could decrease the chemical dissolution of titanium. This allowed the formation of nanotube arrays up to 2.5 μm long.

On the other hand, electrochemical anodization in non-aqueous organic solvent electrolyte containing F− can be considered as third generation of nanotubes [37]. This method appeared as a promising approach to form smooth and long nanotube arrays. Various types of organic solvents such as glycerol [37,38], ethylene glycol [37,38], formamide [41], N-methylformamide [41] and dimethyl...
sulfoxide [41] had been successfully employed for the formation of TiO₂ nanotube arrays. Paulose et al. [41] found that the key to obtaining very long nanotube arrays was to minimize the amount of water to be less than 5 wt% during anodization process. Addition of small amount of water allowed sufficient titanium oxidation rate since the oxidation process was difficult in pure organic electrolyte [38,41].

According to the literature, the most widely accepted formation mechanism of TiO₂ nanotubes during electrochemical anodization involves several stages [35,38,42]. At the initial stage of anodization, a dense TiO₂ layer was formed on the titanium surface by field-assisted oxidation via reaction (7). Ion migration occurred within metal/metal oxide interface under the applied electric field. Titanium ions could dissolve and react with oxygen ion (O₂⁻) or hydroxyl ion (OH⁻) provided by water to form TiO₂ or titanium hydroxide, respectively. In the next stage, the titanium metal and oxide layer, which were in contact with the electrolyte, would etch by F⁻ ions through chemical dissolution to form soluble hexafluorotitania complex (Eq. (8)). The localized dissolution of oxide resulted in the formation of tiny pits on the oxide layer and gradually grew into bigger pores with increasing anodization time.

\[
\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (7)
\]

\[
\text{TiO}_2 + 4\text{H}^+ + 6\text{F}^- \rightarrow \text{[TiF}_6\text{]}^{2-} + 2\text{H}_2\text{O} \quad (8)
\]

It is believed that the competition between rate of oxide growth at the metal/metal oxide interface (Eq. (7)) and the rate of oxide dissolution at the metal oxide/electrolyte interface (Eq. (8)) is the key factor in determining nanotube formation [35]. When the rate of electrochemical etching equals to the rate of chemical dissolution of the nanotubes, the tube length remains the same. Thus, the final stage determines the length of the nanotubes during the reaction.

The crucial key factors to achieve high degree arrangement of hexagonal close-packed nanotubes structured are anodic voltages for a given electrolyte before dielectric breakdown [43], purity of the material [43] and multi-step anodization [42]. By altering the electric field during the growth of nanotubes, several types of tube geometry can be achieved such as bamboo- [44], nanolace- [45] and branched-type nanotubes [45]. For example, bamboo-type nanotubes were obtained by alternating voltage and holding time on the microstructure [44], nanolace-type nanotubes were obtained when extending the etching process of bamboo-type nanotubes [45], while tube branching morphology could be obtained when altering a higher to a lower anodization voltage [45]. Meanwhile, Ji et al. [46] found that double-walled nanotubes with bamboo-like morphologies could be formed if the anodization process was carried out under alternating voltage conditions. The double-walled structure could be further tuned by heat treatment.

In addition to the dilute fluoride electrolyte approach, alternative approach using electrolyte containing perchlorate [14], chloride [39,47], bromide [47] or nitrate [36] ion is possible to form bundles of TiO₂ nanotubes on titanium substrate under very rapid growth conditions. This method is known as rapid breakdown anodization and micrometers long nanotubes can be obtained in a few min [39]. Hence, it is not easy to tune the morphology of tube bundles into highly ordered self-organized TiO₂ nanotubes through this ultra-fast anodization technique.

Production of TiO₂ nanotubes via electrochemical anodization method requires two/three electrode configurations with anodization voltage and the help of a power supply. Besides, the disadvantages of this method include the length distribution of tubes is not well-defined [9], nanotubes are not separated from each other in an organized manner and do not have well-developed gaps between the tubes over a large surface area [10]. Hydrogen gas is evolved at the cathode in the form of gas bubble nucleates, which will accumulate at the electrode surfaces and increase the electrical resistance of the cell [48]. As a result, more electric energy must be used and consequently increases the cost of operating electrochemical anodization.

3.3. Hydrothermal method

Among these preparation methods, hydrothermal method has attracted more attention from the scientific community due to the simple, cost-effective and environmental friendly method for large scale production of nanotubes. This synthesis conditions could be adjusted to fabricate alternative low dimensional of TiO₂ nanostructures [10]. These nanostructures included TiO₂ nanotubes, nanofibers, nanowires, nanoribbons and nanorods by controlling various parameters during hydrothermal synthetic conditions. The term nanotube was used for high aspect ratio materials with a hollow inner channel and nanowire for high aspect ratio materials without an inner void. Meanwhile, nanofibers are similar to nanowires but with significantly larger diameter [49]. Nanorods usually featured shorter aspect ratio as compared to nanowires. Fig. 3 shows the HRTEM images for the morphology of nanotubes, nanowires, nanofibers and nanorods, adapted from Yuan and Su [50].

In year 1998, Kasuga et al. [51] first reported the synthesis of TiO₂ nanotubes by employing an alkaline hydrothermal treatment of TiO₂ nanoparticles. With respect to the described methods, the alkaline hydrothermal route could produce nanotubes with tunable diameters (~8–200 nm) [52]. After further investigation, majority of the researchers found that the so-called “TiO₂ nanotubes” obtained via hydrothermal method were actually titana nanotubes [53,54]. Thus, the term of titanate nanotubes was used for the subsequent review instead of TiO₂ nanotubes.

Although this synthesis method had been carried out extensively over the past decade, the crystalline structure, composition, thermal stability and formation mechanism are still in controversy. Several factors can influence the formation of titana nanotubes such as phases and particle sizes of the starting materials [55], types and concentrations of the alkaline solution [56], hydrothermal temperature and duration [57] and post-treatment processes (acid washing and calcination) [58]. Table 4 shows several selected works on the conventional- [59], ultrasonication- [57,60] and microwave-hydrothermal [11,61] methods for synthesizing titana nanotubes. The details of these combination techniques will be further discussed in Section 4.4.

The main disadvantage of this nanotube fabrication method is the requirement of long reaction time in concentrated sodium hydroxide (NaOH) medium, which lead to the excessive intercalation of sodium ions in the produced nanotubes. Hence, more efforts have to be made in order to shorten the synthesis time and produce ordered alignment of TiO₂ nanotubes apart from the random alignment powder form [62].

4. Factors influencing the formation of titana nanotubes via hydrothermal treatment

The microstructure of titana nanotubes is easily affected by the starting materials, concentrations and types of the alkaline solution, synthesize conditions (reaction time and synthesis temperature) and post-hydrothermal treatments (acid washing and calcination temperature).

4.1. Starting materials: phases and particle sizes

The effects of different phases and particle sizes of the starting materials for titana nanotubes are still debatable. Table 5 summarizes several selected results on the formation morphology
of titanate nanotubes using different types of starting materials, alkaline solution and hydrothermal treatment. Morgan et al. [55] observed that the dissolution process of anatase precursor corresponded to zero-order kinetic, where the dissolution was independent of precursor concentrations. Meanwhile, the dissolution kinetic for the rutile phase was second-order, indicated TiO₂ rutile was affected by the diffusion of products and replenishment of reactants to the surface. Anatase has often been observed to react rapidly to produce nanotubes, whereas rutile has been observed to react incompletely with remaining unreacted rutile in the product or nanorods shaped after similar hydrothermal conditions. They also observed that anatase with small crystalline and rutile phase with big crystalline size could produce nanotubes with lengths up to several hundred nanometers, but the former starting material could produce nanotubes with smaller average external diameter.

Even though several authors reported that amorphous TiO₂ could only produce nanofibers not nanotubes [50], Ylhäinen et al. [68] claimed to have obtained nanotube products from amorphous precursors. Hence, it seems that there were other parameters playing a role apart from crystallite form of TiO₂. Yuan and Su [50] reported that the effect of particle size of the starting material toward the yield of the produced nanotubes was quite small in comparison to the hydrothermal temperature and concentration of alkaline solution. On the other hand, Dawson et al. [69] concluded that the length of titanate nanotubes was influenced by both phase and particle size of the starting material. Pure anatase phase with a particle size of 300 nm could produce nanotubes with 1 μm in length, micrometer sized of TiO₂ with mixed phases produced tubes with lengths between 200 and 500 nm, while P25 mixed phases with particle size of 30 nm produced lengths less than 100 nm. Viriya-empikul et al. [57] reported that interlayer spacing of nanotubes was not significantly affected by the size of the starting material. They verified that smaller crystal size of starting material could lead to titanate nanotubes with a higher surface area.

In addition, Morgado et al. [63] reported that TiO₂ anatase raw materials with smaller crystal size usually led to faster rate of thermal transformations of TiO₂ nanotubes. Anatase with smaller crystalline size could produce larger external diameter as compared to those produced from anatase phase with bigger crystalline size. However, Papa et al. [70] found that anatase particles with a grain size of less than 17 nm could not form nanotubes at hydrothermal temperature of 150 °C even with prolong treatment duration from 36 h to 72 h. They concluded that too many small primary germs involved in the dissolution/recrystallization reactions and it was hard to obtain super-saturation condition for the growth of the nanotubes. Meanwhile, Miao et al. [71] used 14 nm diameter anatase aerogel powders as the starting material and produced nanotubes after treatment duration of 40 h at 150 °C. These conflicted results reported by both of the studies might probably due...
Table 4: Hydrothermal method for preparation of titania nanotubes.

<table>
<thead>
<tr>
<th>Auxiliary methods</th>
<th>Conditions hydrothermal reaction</th>
<th>Dimensions of nanotubes</th>
<th>References</th>
</tr>
</thead>
</table>
| Conventional hydrothermal          | • 5 g TiO2 powder in 10 M sodium hydroxide (NaOH)  
  • 150 °C for 20 h  
  • Acid washing with 0.1 M nitric acid (HNO3)  
  | Average $D_a = 9$ nm  
  Average $D_i = 6$ nm  
  Interlayer spacing = 0.7 nm (2–4 walls)  
  $L = 0.3–3.0$ μm  
  Specific surface area = 423 m2/g  | Kitano et al. [59]                                    |
| Ultrasonication-assisted hydrothermal | • 150 mg TiO2 powder in 30 ml of 10 M NaOH  
  • Mixture was sonicated at 280 W for 60 min  
  • 110 °C for 4 h  
  • Acid washing with 0.1 M HNO3  
  • 0.5 g TiO2 powder in 50 ml 10 M NaOH  
  • Mixture was sonicated at 7.6, 38.1 W for 8 min  
  • 150 °C for 3 days  
  • Acid washing with 0.1 M hydrochloric acid (HCl)  
  | Average $D_a = 5$ nm  
  Wall thickness = 1.3 nm  
  $L = 200–300$ nm  
  $D_i = 4–6$ nm  
  Interlayer spacing = 0.8 nm (2–6 walls)  
  | Zhu et al. [60]                                    |
| Microwave-assisted hydrothermal    | • 0.5 g TiO2 rutile in 25 ml of 10 M NaOH  
  • Microwave power for 45 min at 200 °C  
  • Acid washing with 0.1 M HNO3  
  | $D_a = 3–5$ nm  
  $D_i = 8–10$ nm  
  $L = 100–500$ nm  
  Interlayer spacing = 1 nm (3–4 walls)  
  Specific surface area = 214 m2/g  | Huang and Chien [11]                                  |
|                                   | • 0.6 g P25 TiO2 in 70 ml 10 M NaOH  
  • Microwave power of 70, 400, and 700 W at 130 °C for 3 h  
  • Acid washing with 0.5 M HCl  
  | Average $D_a = 9.9$ nm  
  Average $D_i = 5.1$ nm  
  Interlayer spacing = 0.82, 0.86, and 0.90 nm at microwave power of 70, 400, and 700 W (4–5 walls)  
  Specific surface area = 323, 367, and 320 m2/g at microwave power of 70, 400, and 700 W  | Ou et al. [61]                                    |


to the different conditions used such as fabrication vessels, amount of starting materials and concentrated alkaline solution.

4.2. Alkaline solution: types and concentrations

The alkaline type and their concentrations play important role in hydrothermal process. The most favorable titane nanotubes were prepared via hydrothermal treatment of TiO2 powders in a 10 M NaOH solution [63,70]. There was only small proportion of nanotubes formed when NaOH concentration was lower than 5 M or higher than 18 M [56]. The concentration of dissolved Ti4+ in solution can determine the rate of crystallization of titane nanosheets, which in turn control the morphology of the final nanostructures [10].

Bavkyin et al. [72] found that an increment in the molar ratio of TiO2 to NaOH generally resulted in higher average pore diameter and a reduction in the specific surface area. Meanwhile, the pore volume of nanotubes was independent of the molar ratio of TiO2 to NaOH. Furthermore, Huang et al. [64] demonstrated that nanosheets, nanotubes and nanowires were three kinetic products from the reaction of TiO2 with NaOH when increasing alkaline condition from 5 to 12 M. They observed that the nanowires had wider diameter and longer length as compared to nanotubes morphology. However, Sikhivivhilu et al. [56] reported that a small portion of shorter nanotubes was produced when concentration of NaOH solution increased to 18 M. Thus, the concentration of NaOH could influence in the yield of tubular morphology.

Furthermore, Bavkyin et al. [73] discovered that titane nanotubes could be prepared using 10 M potassium hydroxide (KOH) and low temperature of 56 °C after 12 days. Thus, titane nanotubes could also be produced using a NaOH/KOH binary aqueous mixture at 100 °C [74]. Recently, Sikhivivhilu et al. [56] found that potassium titane nanotubes could also be produced by hydrothermal treatment in 10 M KOH at 120 and 150 °C for 24 h. They reported that KOH was more reactive with TiO2 to yield different shapes of nanostructured materials compared to NaOH. Ammonium hydroxide solution showed no influence on the microstructure of TiO2. Meanwhile, similar spherical morphology was observed in 10 M lithium hydroxide (LiOH) at the temperatures of 120 and 150 °C [56], whereas flower-like structure on the TiO2 surface could be obtained when treated in 10 M LiOH solution at temperature of 80 °C [75].

4.3. Hydrothermal treatment: temperature and duration

In general, the amount, length and crystallinity of titane nanotubes increase with the hydrothermal temperature [76]. However, there exists an optimal temperature, which usually reported in the range of 130–150 °C to obtain high purity of nanotubes with high surface area [49,57]. During higher reaction temperatures (>180 °C), the main products were nanoribbons or nanowires like morphologies [19]. Yuan and Su [50] reported that TiO2 nanotubes could be formed in the reaction temperature ranged from 100 to 180 °C when either crystalline anatase or rutile or commercial P25 were used as the raw materials. Nanoribbons were produced when increasing reaction temperature from 180 to 250 °C, while nanowires were obtained when reaction temperature ranged from 130 to 240 °C if KOH were used as the alkaline solution.

Bavkyin et al. [72] found that increasing temperature from 120 to 150 °C for 22 h resulted in larger average diameter of titane nanotubes. Subsequent increment of temperature resulted in a sharp reduction in pore volume of produced samples and wider size distribution in the diameter of fibers morphology. However, Sreekantan and Wei [76] observed that the average outer diameters of the nanotubes produced at 110, 130 and 150 °C for 24 h were similar, at about 10 nm. Seo et al. [66] observed that increasing the synthesis temperature up to 150 °C would improve crystallinity of the tube and increased tube lengths from few hundred nanometers to few micrometers, but with the same diameters. Meanwhile, Lan et al. [67] found that the outer diameter of the nanotubes increased slightly when increasing hydrothermal temperature above 150 °C. This indicates that reaction temperature is a key factor in determining the overall morphology of the product. Hence, the effect of hydrothermal temperature on the formation of the nanotubes products is similar to that of the alkaline concentration.
Table 5  
Effects of starting materials, alkaline solution and hydrothermal treatment on the morphology of titanate nanotubes.

<table>
<thead>
<tr>
<th>Starting materials (phase, composition, particle size)</th>
<th>Alkaline solution (types, concentration)</th>
<th>Hydrothermal treatment (temperature, duration)</th>
<th>Dimensions of nanotubes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Anatase, &gt;95%, 112 ± 1 nm</td>
<td>9 M NaOH</td>
<td>(i) 160 °C, 2–8 h</td>
<td>(i) L = several hundred nanometers, average D = 3.7 ± 0.7 nm, interlayer spacing = 0.74–0.75 nm (3–5 walls)</td>
<td>Morgan et al. [55]</td>
</tr>
<tr>
<td>(ii) Rutile, &gt;93%, 320 ± 10 nm</td>
<td>(ii) 160 °C, 4 h</td>
<td></td>
<td>(ii) L = several hundred nanometers, average D = 3.6 ± 0.7 nm, interlayer spacing = n.d. (6–7 walls)</td>
<td></td>
</tr>
<tr>
<td>(i) Anatase, 220 nm</td>
<td>10 M NaOH</td>
<td>(i) 120 °C, 30 h</td>
<td>(i) L = several hundred nanometers, average D = 3–5 nm, average D = 6–10 nm, interlayer spacing = n.d. (4–5 walls), pore size distribution = 2–5 nm; 5–60 nm</td>
<td>Morgado et al. [63]</td>
</tr>
<tr>
<td>(ii) Anatase, 8 nm</td>
<td>(ii) 120 °C, 15 h</td>
<td></td>
<td>(ii) L = several hundred nanometers, average D = 4–10 nm, average D = 10–30 nm, interlayer spacing = 0.74–0.75 nm (&gt;5 walls), pore size distribution = 2–10 nm</td>
<td></td>
</tr>
<tr>
<td>Anatase</td>
<td>(i) 3 M NaOH</td>
<td>180 °C, 24 h</td>
<td>(i) Nanosheets</td>
<td>Huang et al. [64]</td>
</tr>
<tr>
<td></td>
<td>(ii) 5 M NaOH</td>
<td></td>
<td>(ii) Nanotubes, L = several hundred nanometers, average D = 2–4 nm, average D = 7–10 nm, interlayer spacing = n.d. (3–5 walls)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iii) 10 M NaOH</td>
<td></td>
<td>(iii) Mixture of nanotubes and nanowires, L = several tens of micrometers, average D = 40–250 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iv) 12 M NaOH</td>
<td></td>
<td>(iv) Mixture of nanowires and amorphous particles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(v) 15 M NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P25 Degussa</td>
<td>(i) 5 M NaOH</td>
<td>140 °C, 24 h</td>
<td>(i) Fibrous structures, L = 100–200 nm, average D = 25–140 nm</td>
<td>Camposeco et al. [65]</td>
</tr>
<tr>
<td></td>
<td>(ii) 7 M NaOH</td>
<td></td>
<td>(ii) Nanotubes structures, average D = 3–4 nm, average D = 8–10 nm, wall thickness = 2.5 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iii) 10 M NaOH</td>
<td></td>
<td>(iii) Nanotubes structures, average D = 4 nm, average D = 8 nm, wall thickness = 3.5 nm, interlayer spacing = 0.7 nm (2–4 walls)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iv) 12 M NaOH</td>
<td></td>
<td>(iv) Nanowires structures, L = 300–500 nm, average D = 15–20 nm</td>
<td></td>
</tr>
<tr>
<td>P25 Degussa, 25 nm</td>
<td>10 M NaOH</td>
<td>(i) 70 °C, 48 h</td>
<td>(i) 2D nanosheets</td>
<td>Seo et al. [66]</td>
</tr>
<tr>
<td></td>
<td>(ii) 90 °C, 48 h</td>
<td>(ii) Nanosheet and fiber-like mixed phase</td>
<td>(ii) 1D fiber/tube-like, L = few hundred nanometers, average D = 10–20 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iii) 110 °C, 48 h</td>
<td>(iii) 1D separated fibers/tube, L = few micrometers, average D = 10–20 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iv) 150 °C, 48 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rutile powder, 120–280 nm</td>
<td>10 M NaOH</td>
<td>(i) 100 °C, 48 h</td>
<td>(i) Nanotubes, average D = 7–11 nm</td>
<td>Lan et al. [67]</td>
</tr>
<tr>
<td></td>
<td>(ii) 125 °C, 48 h</td>
<td>(ii) Nanotubes, average D = 8–12 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iii) 150 °C, 48 h</td>
<td>(iii) Nanotubes, L = 50–200 nm, average D = 2–3 nm, average D = 8–15 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iv) 180 °C, 48 h</td>
<td>(iv) Nanorods, L = several micrometers, average D = 40–120 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: n.d. is defined as no data provided.

At relatively low reaction temperature around 90 °C, nanosheets [76], nanofibers [68] or nanotubes [57] could be formed after 24 h, 48 h, 72 h, respectively. This proved that the yield of nanotubes could increase with duration treatment. However, prolonged reaction duration (72 h to 1 week) might lead to the transformation of nanotubes to nanofibers or nanowires [77]. The width of the obtained nanofibers or nanowires was about 100–300 nm, which was significantly larger than the diameter of nanotubes. Thus, an increment in the average nanotubes diameter can be observed at longer synthesis time. Hence, the treatment duration could be reduced if higher reaction temperature was performed in order to obtain nanotubular structures.

4.4. Assisted hydrothermal synthesis

The purposes of the application of sonication- or microwave-assisted hydrothermal treatment are due to the advantages such as shorter synthesis duration [11,60] and enhance the yield and length of titanate nanotubes [57]. The power of sonication and irradiation duration played an important role in fabricating titanate nanostructured materials. Sonication showed a strong influence on the morphology and properties of titanate nanotubes [57], apart from dispersing TiO2 uniformly in alkaline solution. Meanwhile, microwave irradiation is able to deliver energy to the reactants through molecular interactions and heat treatment using microwave is an economic, rapid and homogeneous heating method [11].

Zhu et al. [60] found that titane whiskers and nanotubes were obtained when sonication powers used were 580 W and 280 W, respectively and the synthesis duration was shortened from 20 to 4 h. Meanwhile, nanosheet-, nanofiber- and nanotube-like morphologies were observed under sonication of 100, 280 and 380 W, respectively [78]. Appropriate sonication power and duration may help the reaction of sodium and hydroxyl species on the de-agglomerated TiO2 particles and the dissolution/breaking of Ti–O–Ti bonding. This resulted in smooth unhindered peeling of large nanosheets and consequently rolled into longer titanate nanotubes [57,78]. Ou et al. [61] reported that higher microwave irradiation power was beneficial to the intercalation of Na atoms into titanate nanotubes in order to enlarge the spacing between interlayers. Titane nanotubes could be obtained after 45 min under microwave irradiation [11].
In addition, organic solvent–controlled hydrothermal synthesis had been investigated to achieve different 1D nanostructures morphology of TiO\textsubscript{2}. Solvents with different physical and chemical properties have a strong effect on the solubility, reactivity and diffusion behavior of the reactants, which are able to influence the structure and morphological features [79]. It had been reported that the samples prepared using ethanol [80], methanol [80], methyl ethyl ketone [80] and ethylene glycol [81] exhibited nanotube structures. However, Das et al. [81] found that nanosheets were transformed to nanorods and nanowires in water–ethanol and water–ethylene glycol mixed solvents, respectively. Meanwhile, Santara and Giri [82] obtained nanoporous nanoribbons products in water–ethylene glycol mixed solvents. On the other hand, titanate nanotubes with ultrahigh crystallization can be obtained after hydrogen peroxide treatment under reflux at 40 °C for 4 h [83]. This proves that titanate microstructures are more easily affected by the preparation conditions, rather than the types of organic solvent.

### 4.5. Post-hydrothermal treatments

In order to achieve high catalytic activity of titanate nanotubes and control the tubular structure of nanotubes, the investigation of post-hydrothermal treatment has received more attention compared to hydrothermal synthetic conditions. Post-hydrothermal treatments include acid washing and calcination steps. Acid washing might affect the nanotubes formation [84], crystalline structure or even chemical composition of the final nanotubes product [53]. Meanwhile, it is believed that calcination process can induce the transformation of titanate to anatase phase, modify microstructure based on the amount of sodium present in nanotubes, improve crystallinity and reduce surface defects of the material [79]. From the point of view of practical usage, it is an important issue to study the structural stability of the titanate nanotubes and their corresponding microstructure changes at various calcination temperatures.

#### 4.5.1. Acid washing

Kasuga et al. [84] considered that the acid washing process was a crucial step for the formation of titanate nanotubes. They proposed that the purpose of acid washing was to remove electrostatic repulsion of residual charge, in which Ti–O–Na converted to Ti–OH. Then, the dehydration of Ti–OH bonds could result in the formation of nanotubes from nanosheets.

Meanwhile, several researchers suggested that acid washing was only applied for the ion-exchange process as they found that titanate nanotubes were formed during hydrothermal reaction [53,55,66]. When proton replaces sodium ion in the structure, acid washed titanate nanotubes possess stronger hydroxyl bonds, results in decrement of interlayer spacing and increment in specific surface area [53]. Papa et al. [70] found that acid washing turned out to be necessary when nanoribbons structure was obtained after hydrothermal treatment. Researchers often reported an optimum concentration of hydrochloric acid (HCl) during acid washing in order to prepare sodium-free nanotubular structure effectively. Further increment of the concentration of HCl would destroy nanotubular structures [58].

The quantity of sodium ions plays a crucial role in the morphological, structural stability and phase transformation of the nanotubes [53]. The detailed discussions on the role of sodium in stabilizing the nanotubular structure of titanate nanotubes had been reported by Zhang et al. [85]. They demonstrated that heat-treatment of sodium titanate nanotubes may induce the dehydration of interlayered OH groups, whereas hydrogen titanate nanotubes experienced dehydration of intralayered and interlayered OH groups. These types of dehydrations did not only reduce the interlayer distance and nanotube length, but also destroyed the nanotube morphology.

#### 4.5.2. Calcination

The level of sodium ions in titanate nanotubes had been identified as an important factor that can influence thermal stability and phase transformation of the materials [53]. Hence, the thermal behavior of titanate nanotubes could be categorized into three groups: high, medium and low or non-sodium titanate nanotubes. The structural changes in high, medium and low sodium titanate nanotubes generally follow the sequence as shown in Fig. 4 [53].

High sodium titanate nanotubes without acid washing showed the best thermal stability and it could remain its nanotubular structure when increasing temperature from 300 to 500 °C [85]. The coexistence of sodium hexatitanate (Ti\textsubscript{6}O\textsubscript{13}) and rutile appeared after calcined at 600–800 °C. A few studies found that the tubular structures of medium sodium titanate nanotubes can be maintained up to 300–400 °C [53]. Conversion of titanate nanotubes into anatase occurred at about 500 °C. Meanwhile, low or
non-sodium titanate nanotubes could only retained the tubular shape at 250–350 °C. Further increment of temperature, they transformed into the intermediate phases of hydrogen Ti₅O₁₃, followed by monoclinic and metastable TiO₂[58]. Anatase usually appeared during calcination temperature above 450 °C. This phase transformation temperature might be different at varying synthetic conditions.

In addition, annealing as-prepared titanate nanotubes at elevated temperature in an oxygen-poor environment such as a pure helium, nitrogen, argon gas atmosphere or vacuum condition would create oxygen vacancies [86]. Zhang et al. [85] reported that single electron trapped oxygen vacancy and hydrogen vacancy were produced during intralayered dehydration of titanate nanotubes. However, these as-formed oxygen vacancies on titanate nanotubes will slowly disappeared while the material was exposed to air, even at room temperature [86]. Hence, modification of titanate nanotubes can be considered to stabilize the oxygen vacancies.

5. Crystal structure, formation mechanism and structural-activity of titanate nanotubes

A number of crystalline structures for as-synthesized titanate nanotube materials including anatase TiO₂ [84], lepidocrocite-type titanate (HₓTi₂₋₄xV₄/₃O₄, where x ~ 0.7, V represents vacancy) [87], dititanate acid (NaₓH₂₋ₓTiO₂·H₂O, where 0<x<2) [54,88], trititanate acid (NaₓH₂₋ₓTi₂O₄) [53] and tetratitanate acid (HₓTi₄O₈·H₂O) [89] had been proposed. Fig. 5 shows the structure models of anatase TiO₂ [88], H₂TiO₂ [87], H₂Ti₂O₄·H₂O [88] and lepidocrocite-type titanate (HₓTi₂₋₄xV₄/₃O₄, where x ~ 0.7, V represents vacancy) [87]. The crystal system of anatase is tetragonal, lepidocrocite-type titanate and H₂TiO₂·OH are orthorhombic, while H₂Ti₃O₇ and H₂Ti₅O₈·H₂O are monoclinic structures. Similar to anatase TiO₂, all titanate acids consist of edge-shared TiO₆ octahedra and zigzag ribbons configurations [90]. The arrangement of layers of TiO₆ octahedrons is diverse in different crystal structures. Three edge-sharing octahedral is in the unit cell of trititanate acid while four edge-sharing octahedra is in tetratitanate acid. Particularly, titanate acid TiₓO₂ₓ₋₁ (where n = 3–5) consists of parallel corrugated layers of edge-sharing TiO₆ octahedra, where octahedra joins at the corners and stepped by every n-th octahedral [77]. Lepidocrocite-type titanate lattice is composed of two-dimensional (2D) lepidocrocite-type or flat host layers sheets in which TiO₆ octahedra are connected to each other via edge-sharing [91]. This depicts that the preparation conditions play an important role in determining morphologies and microstructures of titanate nanostructures.

The mechanism of formation of the various types of nanotubes has been the subject of intense research. According to the literature, acid washing after hydrothermal was essential for sodium exchange purpose as well as formation of nanotubes [51,84]. Meanwhile, strong evidences state that the key step for the formation of nanotubes is during hydrothermal reaction [53]. However, it is widely accepted that the formation mechanism of nanotubes follows the 3D → 2D → 1D model [92]. Chemical bonds in the starting 3D TiO₂ will break under hydrothermal reaction, in which 2D layered entities will be formed and then convert into 1D nanotubes through sheet folding mechanism. Bavykin’s group [72] had proposed three possible mechanisms for the formation of multilayered titanate nanotubes. These included (a) the helical scrolling of a single-layer nanosheet, (b) the curving of several conjoined nanosheets and (c) direct production of a multi-layered nanotube, as shown in Fig. 6.

Among these mechanisms of formation, the wrapping of a single nanosheet has been favored by a number of research groups [53,93]. This would result in the inequality number of wall layers on two sides of nanotubes and interlayer spacing of approximately 0.78 nm. Zhang et al. [93] indicated that the imbalance charge of hydrogen or sodium ion concentration at two different sides of nanosheets may introduce excess surface energy to strain driving the peeling process and resulting in wrapping of nanotubes. This kind of hydrogen deficiency driving force in surface layers is unable to bend multiple layers of nanosheets although it can be done through mechanical stress. On the other hand, Kukovecz et al. [94] argued that particle surfaces were cut up into small terraces before curving up of the nanoloop resulted from nanosheets.

Meanwhile, Bavykin et al. [72] demonstrated the imbalance width of different layers during crystallization and rapid growth of layers which might lead to nanosheet with a single curved layer
and then several conjoined curved layer in order to decrease the excess energy. They suggested that formation of nanotubes underwent several steps: (i) dissolution of TiO$_2$ accompanied by epoxidal growth of layered nanosheets; (ii) dissolution–recrystallization of nanosheets; (iii) curving of nanosheets and (iv) exchange of sodium ions to proton during washing of nanotubes.

Morgado et al. [95] found that small crystal TiO$_2$ possessed fast dissolution rate which accelerated recrystallization of nanosheets. When the rate of nanosheet crystallization was higher than the rate of their curvature into nanotubes, the formation of thicker planar entities with multiple layers would be favored before they could be easily rolled up. Thus, small crystal TiO$_2$ led to low yields of nanotubes and non-hollowed layered particles with thicker walls and larger external diameter. They also suggested that this was the reason for those researchers who were not able to obtain nanotubular materials from freshly precipitated amorphous TiO$_2$ due to the fast dissolution rate under alkali solution.

Both titanate and anatase structures contain zigzag ribbons of TiO$_6$ octahedra that share four edges with each other [96], while rutile structure is composed of TiO$_6$ octahedrons that share two edges with each other [97]. This can be surmised that anatase easily converted into titanate nanotubes, while rutile requires a higher temperature in order to convert into titanate nanotubes due to the structural dissimilarity. Dawson et al. [69] reported that pure anatase phase with large particle size able to allow the dissolution–recrystallization processes and no other phase impurity to impede greater growth for the nanotubes. The mixture of phases in the starting material would inhibit the reaction of anatase and thus produced shorter tubes than the pure phase. The rutile structure cannot simply undergo the dissolution and exfoliation processes, thereby, total structural destruction and recrystallization become necessary [97].

Zhu et al. [96] revealed that the phase transition from titanate to anatase was a topochemical reaction process, rather than dissolution of titanate and recrystallization of anatase. They found that the anatase retained the morphology of the reactant titanate because the large structural units remained relatively unchanged during dehydration process. It is noted that more investigations, evidences and discussions need to be done in order to support the formation mechanism of titanate nanotubes.

In general, photocatalytic activity of titanate nanotubes was determined by three structural factors which were specific surface area, pore volume and amount of anatase phase in titanate nanotubes [98]. It was often reported that larger specific surface area would allow more reactants to adsorb to the surface of the catalyst, which was beneficial for the subsequent oxidation reaction. Higher pore volume would result in more rapid diffusion of various compounds during the photocatalytic reaction. Moreover, it is well known that more anatase phase can induce faster photocatalytic reaction. Turki et al. [58] demonstrated that large surface area was not the only crucial factor to achieve the highest photocatalytic activity. A good crystalline quality of anatase phase and coherent crystallographic domains of TiO$_2$ must be fulfilled in order to achieve high photo-degradation activity.

A straightforward comparison of the photocatalytic activity results obtained in different studies is difficult because final products with different specific structural and optical properties can be obtained. For example, in the literature, the amount of sodium content present in the titane nanotubes might lead to different photocatalytic activities. According to Qamar et al. [99], titane nanotubes with high, medium or free sodium content without calcination showed no photocatalytic activity for the degradation of the amaranth dye. The photocatalytic activities of free sodium titanate nanotubes calcined at 400 °C and medium sodium titanate nanotubes calcined at 500 °C were less active than P25 though they reached their maximum activity with increasing calcination temperature. In contrast, Turki et al. [58] observed that photocatalytic activity of free sodium titanate nanotubes calcined at 400 °C showed 4 times more active than P25 for the degradation of formic acid. Meanwhile, Lee et al. [98] found that medium content of sodium titanate nanotubes possessed higher photocatalytic activity as compared to low and high medium content of titanate nanotubes. However, its activity was still lower than P25 in the photocatalytic oxidation of a basic dye. All these results indicated that the role of sodium was not precisely evaluated while the relationship between photocatalytic activity and morphology of titane nanotubes was not clearly defined.

6. Modification of titanate nanotubes as photocatalysts

It should be noted that the photocatalytic activity of TiO$_2$ is limited by the light absorption properties, electron–hole recombination rate, reduction and oxidation reaction rates on the surface by the electrons and holes [1,79]. Many efforts on the modification of titane nanotubes have been made to modify the electronic band structure in order to promote the separation of electron–hole pair and improve catalytic activity. Titane nanotubes can be modified by various strategies such as deposition of metal nanoparticles, single- and co-doping with two or more foreign ions, coupling with other semiconductors and hybrid with carbon nanomaterials. Several recent research works on the modification of titane nanotubes classified according to different methods have been summarized in Table 6.

6.1. Metal-loaded

Metal loading on titanate nanotubes surface is one of the methods used to improve the catalytic activity. Various metal nanoparticles such as Pt [100], Au [100] and Ag [1] have been employed in titanate nanotubes through photo-deposition, deposition–precipitation or ion-exchange. It is well known that Schottky junction formed by the interface of metal–semiconductor [100]. The noble-metal particles have the property of collective free electron charge at the interface when particles excited by light, known as the process of surface plasmon resonance [1]. When these noble-metal particles load on to titanate nanotubes surface, the plasmon-induced electrons are transported from the photo-excited noble-metal particles to the conduction band of the titanate nanotubes [100]. This facilitates electron–hole separation, promotes the interfacial electron transfer process and enhances photocatalytic performance of this hybrid catalyst [1,2]. Besides, metal ions with a standard redox potential is more positive than the conduction band of TiO$_2$ can be photo-reduced to the low-valent states and then be deposited on the surface of TiO$_2$ nanomaterials [15].

6.2. Doping

According to previous research, metal or non-metal ion doping tends to narrow the band gap energy, increases separation of electron–hole pairs and inhibits recombination photo-generated electron–hole pair [79,112]. Thereby, the overall catalytic activity of the catalyst can be enhanced. Various methods have been introduced to prepare doped titanate nanotubes through chemical (sol–gel, co-hydrothermal) or physical method (physical mixing).

It had been reported that the dopant cation with almost similar ionic radius was easier to substitute Ti$^{4+}$ cation and more difficult to replace an oxygen ion with other anion due to the difference in charge states and ionic radius [79]. In principle, the formation of oxygen vacancies on titanate nanotubes during doping process leads to the creation of unpaired electrons or Ti$^{3+}$ centers in order to keep the charge balance [86]. The excess electrons located on the
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<th>(i) Application</th>
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<td>Metal deposition</td>
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<td>Copper (Cu)</td>
<td>Hydrothermal, photodeposition&lt;br&gt;Source: 0.5–2.0 wt.% copper (II) nitrate pentahydrate</td>
<td>Cu served as the electron mediator to prolong the retention time of photo-generated radicals</td>
<td>(i) Photocatalytic degradation of bisphenol A (BPA)</td>
<td>(ii) The pseudo first-order rate constants for BPA photo-degradation by 1 wt.% Cu-deposited TiO₂/TNTs were 1.8–5.2 and 4.3–12.7 times higher than those of pure Degussa P25 and anatase TiO₂</td>
<td>Doong et al. [15]</td>
</tr>
<tr>
<td>Gold (Au) and platinum (Pt)</td>
<td>Hydrothermal, photodeposition&lt;br&gt;Source: 1 wt.% chloro-platinic acid (H₂PtCl₆·6H₂O) and auric chloride acid</td>
<td>Au or Pt formed a higher potential gradient of Schottky junction than at the TiO₂/electrolyte interface, which facilitated charge separation</td>
<td>(i) Photocatalytic degradation of methyl orange</td>
<td>(ii) The degradation rates of methyl orange solution were 96.1%, 95.1%, 88.9% and 82.6% in the presence of Au-TNTs, Pt–TNTs, TNTs and P25 catalysts, respectively after 40 min</td>
<td>Zhao et al. [100]</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>Hydrothermal, deposition–precipitation&lt;br&gt;Source: 1 at.% silver nitrate (AgNO₃)</td>
<td>Ag nanoparticles acted as additional separator of the electron and hole pair</td>
<td>(i) Photocatalytic degradation of caffeine</td>
<td>(ii) The hydrogenated TNTs@Ag sample showed two times photocatalytic activity higher than the hydrogenated TNTs</td>
<td>Ploidinec et al. [1]</td>
</tr>
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<td>Ag, AgX</td>
<td>Hydrothermal, deposition–precipitation and photo-deposition&lt;br&gt;Source: Ag₂O₃, hydrogen halide</td>
<td>Ag–AgCl–TNTs hybridized enhanced visible light absorption which induced by the surface plasmonic effect</td>
<td>(i) Photocatalytic degradation of methylene blue</td>
<td>(ii) Ag–AgCl–TNTs was found to possess the highest methylene blue removal rate as compared to Ag–AgCl and Ag–AgBr</td>
<td>Tang et al. [2]</td>
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<td>Single- and co-doping</td>
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<td>Carbon (C) and C-tungsten (W)</td>
<td>Sol–gel, hydrothermal&lt;br&gt;Source: 1 at.% melamine borate (as C dopant) and tungstic acid (C and W dopants)</td>
<td>W acted as an electron and hole recombination center. C-doped material exhibited high surface area, enhanced optical properties and charge separation</td>
<td>(i) Photocatalytic degradation of 4-chlorophenol</td>
<td>(ii) The degradation rates of 4-chlorophenol were 36.1%, 31.4%, 24.3% and 10% in the presence of C–TNTs, C–W–TNTs, TNTs and P25, respectively after 1 h</td>
<td>Neville et al. [18]</td>
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<tr>
<td>Silver ion (Ag⁺⁺)</td>
<td>Hydrothermal, photo-reduction&lt;br&gt;Source: 2.5 wt.% AgNO₃</td>
<td>Ag nanoparticles acted as electron acceptor and transferred to the adsorbed O₂ effectively</td>
<td>(i) Photocatalytic degradation of cefitoir sodium (CFS)</td>
<td>(ii) Photocatalytic degradation of CFS was about 6 times higher than bare TNTs</td>
<td>Pugazhenthiran et al. [3]</td>
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<td>Aluminum ion (Al³⁺)–iron ion (Fe²⁺)</td>
<td>Co–hydrothermal&lt;br&gt;Source: 0.1–5.0 at.% aluminum chloride and iron(III) nitrate</td>
<td>Fe³⁺ acted as shallow trapping sites. Al–Fe co-doping narrowed band gap energy and promoted the generation of OH radicals</td>
<td>(i) Photocatalytic degradation of humic acids</td>
<td>(ii) Al–Fe co-doping at 0.25: 0.75 at.% showed the highest degradation efficiency 79.4% as compared to 1 at.% Fe-doped (77.4%) and 1 at.% Al-doped (60.4%)</td>
<td>Yuan et al. [101]</td>
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<td>Pt–nitrogen (N)</td>
<td>Hydrothermal, photo-deposition&lt;br&gt;Source: 0.6 wt.% H₂PtCl₆ and 0.5 wt.% ammonium hydroxide</td>
<td>Pt doping used as electron trap to prevent charge recombination and increased stability of N in catalyst</td>
<td>(i) Photocatalytic production of hydrogen from glycerol–water mixture</td>
<td>(ii) Pt–N–TNTs produce H₂ amounts approximately 13 times, 6 times, and 20% higher as compared to P25, TNTs, and Pt–TNTs, respectively</td>
<td>Slamat et al. [102]</td>
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<td>N</td>
<td>Co–hydrothermal&lt;br&gt;Source: Weight ratio of TiO₂–urea was 1:1–1:10</td>
<td>N doping narrowed the band gap of TiO₂ and served as electron trap to inhibit the charge recombination</td>
<td>(i) Photocatalytic degradation of rhodamine B</td>
<td>(ii) N-doped TNTs at weight ratio of 1:2 exhibited the highest photocatalytic activity than the undoped TNTs and P25</td>
<td>Hu et al. [103]</td>
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<td>Gadolinium ion (Gd³⁺)–N</td>
<td>Hydrothermal, ion-exchange&lt;br&gt;Source: Molar ratio of gadolinium (III) nitrate:ammonium chloride were 1:1, 1:2 and 2:1</td>
<td>Gd³⁺ acted as electron-trapped agent to inhibit the charge recombination. Co-doping inhibited the particle growth and resulted in higher crystallinity</td>
<td>(i) Photocatalytic degradation of rhodamine B</td>
<td>(ii) The degradation rates were 81.4%, 61.5% and 37.1% in the presence of 1:1 Gd–N–TNTs, Gd–TNTs and N–TNTs, respectively after 2 h</td>
<td>Liu et al. [104]</td>
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<td>C–N–sulfur (S)</td>
<td>Hydrothermal, physical mixing, calcination&lt;br&gt;Source: Molar ratio of Ti:thiourea were 1:1, 1:2 and 1:3</td>
<td>C acted as a photo-sensitizer to inject electron to TNTs. N–S co-doping modified the electronic band structure and narrowed the band gap energy of TNTs</td>
<td>(i) Photocatalytic degradation of thiolene</td>
<td>(ii) The molar ratio of Ti:thiourea of 1:1 and 1:2 showed the highest pseudo first-order reaction rate constants under UV–vis light and visible light, respectively</td>
<td>Dong et al. [105]</td>
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<tr>
<td>Coupled semiconductors/binary composites</td>
<td>Hydrothermal, wet-impregnation&lt;br&gt;Source: 10–30 wt.% zinc acetate</td>
<td>ZnO–TNTs facilitated charge separation, increased the lifetime of the charge carriers and interfacial charge transferred to adsorbed substrates</td>
<td>(i) Photocatalytic degradation of rhodamine B</td>
<td>(ii) 20 wt.% of ZnO–TNTs nanocomposites exhibited the highest photocatalytic activity than pure TNTs, P25 and ZnO</td>
<td>Wang et al. [106]</td>
</tr>
</tbody>
</table>
Preparation and Important WO₃–TNTs Hydrothermal, wet-impregnation increased of visible light absorption. Grandcolas et al. [107], Liet al. [108].

Lead(II) nitrate and PANi and exposed to high temperature and pressure. Kim et al. [109].

Grabenstein et al. [110].

Kim et al. [109].

Ghassemi et al. [111].

Table 6 (Continued)

Preparation methods, modifier Source

Modification effect

Modifier

Preparation methods, modifier source

Tungsten trioxide (WO₃)

Lead(II) nitrate (PANi) and GDS

Carbon nanotubes (CNTs)

Carbon nanotube (CNTs)

Graphene

Notes:

CNTs are defined as nitrogen-doped TiO₂ nanomaterials produced through hydrothermal treatment.

Oxygen vacancy states could serve as the centers to capture electrons [86]. This facilitates the efficient adsorption of oxygen and water on titannate surface and reaction with electrons and holes, leading to the formation of O₂⁻ and OH⁻, respectively. However, these oxygen vacancies can also act as recombination sites in the presence of high amount of dopants [112]. Hence, an optimum doping amount (with an acceptable amount of oxygen vacancies) could exhibit better visible light absorption and higher photocatalytic activity.

Titannate nanotubes doped with metal ions such as transition metals (Al [101] and Fe [101]), rare earth metals (Gd [104]) and noble metals (Ag [3]) have been widely investigated to enhance the photocatalytic activity of the titannate nanotubes. Among these elements, Fe³⁺ has been found to be the most used dopant due to its low band gap energy of 2.6 eV and the radius of Fe³⁺ (0.64 Å) is quite similar to that of Ti⁴⁺ (0.68 Å) [113]. A new energy level within the band gap of TiO₂ would be introduced when Fe³⁺ ions substituted Ti⁴⁺ sites, which enabled visible light absorption. This attributed to the charge transfer transition between the d-state electron of the dopant and the conduction band of TiO₂ or from valence band to the new energy level [114].

Moreover, Fe³⁺ dopants could act as hole and electron trapped sites and change the oxidation states to Fe⁴⁺ and Fe²⁺, respectively [113,114]. According to crystal field theory, the electronic configurations of Fe⁴⁺ and Fe²⁺ ions are relatively unstable as compared to Fe³⁺ ions (half-filled high spin d5) [114]. The electrons and holes are easily de-trapped to the adsorbed oxygen and surface hydroxyl groups, respectively and restores to its half-filled electronic configuration. Therefore, the recombination rate of electron and hole pairs can be retarded with the introduction of Fe³⁺. Besides, the effect of Fe doping is highly dependable on the dopant amount as the doping sites could also serve as charge recombination centers when present in high concentration [113]. The additional benefit of Fe doping is that the trace amount of Fe that might be leaching out from the photocatalyst could undergo fenton-like reactions [115].

Cationic doping materials suffer from thermal instability and cationic doping could be localized in the d-state deep of titannate band gap, which usually act as recombination center for electron–hole pairs [103]. Hence, non-metal ion doping appears as a promising way to avoid the disadvantages experienced by the cationic doping materials. Titannate nanotubes doped with non-metal elements show positive effect in catalytic performance.

Doping titannate nanotubes with non-metal ions including N [103], S [105] and C [18] have attracted considerable attentions due to the increasing photocatalytic activity performed under visible light irradiation. In 2001, Asahi et al. [116] found that nitrogen-doped TiO₂ nanomaterials exhibited superior photocatalytic activity among other non-metals (i.e. C, N, P, F and S) doped TiO₂ materials in various reactions. N element is the most investigated dopant for narrowing the band gap energy of titannate nanotubes as photocatalysts. N-doped TiO₂ could be obtained by adding different nitrogen sources such as ammonia, ammonium salts or urea [103,116]. The reason for the improvement of catalytic activity has been often related to the decrease of the band gap energy of TiO₂, which is due to either N 2p states mixed with O 2p states or the creation of an isolated impurity level above valence band [79,116]. In general, substitutional type of N-doping accompanied by oxygen vacancy is favored when the doping is carried out under highly reducing condition; whereas interstitial type N-doping takes place under oxygen-rich condition [102]. Substitutional (N–Ti–O and Ti–O–N) and interstitial (characteristic NO) states created localized states above the valence band, resulting in visible light response and faster photocatalytic degradation.

It should be bear in mind that the content of non-metal could decrease during annealing process, thereby, reducing its catalytic activity. Hence, co-doping materials have been investigated to
compensate the drawbacks of each single doped titanate nanotubes. For example, co-doping titanate nanotubes such as Gd$^{3+}$-N [104], Pt–N [102], and B–N [117] are proposed to be more advantageous over single nitrogen doping. Pt is used as electron trigger [102], Gd$^{3+}$ acted as a sensitizer to increase light absorption [104], while B could minimize the oxygen vacancies produced by N doping [117]. Consequently, photo-charge separation, electron transfer ability and photocatalytic activity can be enhanced as well as maintaining non-metal doping stability in the surface of photocatalysts.

6.3. Coupled semiconductors/binary composites

It has been reported that good matching of the conduction and valence bands of two semiconductors could enable efficient charge carrier transfer from one to another [106]. Wide band gap energy of titanate nanotubes coupling with small band gap semiconductor could result in the formation of heterojunctions [107]. This allows electron to be injected from small band gap of the semiconductor (sensitizer) to its neighbor counterpart (titanate nanotubes) and improve separation of electron–hole pairs.

The modification of titanate nanotubes with quantum dots of narrow band gap semiconducting materials such as CdS [108] and PbS [108] is more promising as couple nanomaterials since it can improve the photocatalytic activity effectively. CdS with a narrow band gap of 2.4 eV allows CdS to act as photo-sensitizer to absorb visible light irradiation [118]. The higher conduction band of CdS of about 0.5 eV with respect to that of TiO$_2$ could also enhance charge separation [118]. Owing to the photo-generated electron transfer from CdS to TiO$_2$, this charge separation restrains charge recombination. Thus, the coupling of CdS/titanate nanotubes has been applied to enhance the photocatalytic degradation organic pollutants [108]. In addition, the incorporation of WO$_3$ into titanate nanotubes has also gained much attention due to smaller band gap energy of WO$_3$ (2.8 eV) and higher corrosion stability in aqueous solution [107]. Both the valence band and conduction band of WO$_3$ are lower than those of titanate nanotubes. Photo-generated electrons would transfer from titanate nanotubes to that of WO$_3$ and the holes transferred from WO$_3$ to that of titanate nanotubes. Besides, titanate nanotubes composited with wide band gap energy of semiconductor such as ZnO (3.2 eV) [106] could suppress the charge recombination for higher photocatalytic activity.

6.4. Hybrid with carbon nanomaterials

Recently, titanate nanotubes composites with carbon nanotubes, graphene and fullerene have attracted increasing attention. Carbon nanotubes show excellent mechanical strength, thermal conductivity, unique electronic properties and thermal stability [110]. Meanwhile, graphene with zero band gap possesses excellent electrical and optical properties, large specific surface area and outstanding mechanical properties [111]. In addition, graphene can act as photo-sensitizer to transfer electron to the titanate nanotubes surface due to the more positive Fermi level of graphene [119]. Solid fullerenes in the form of C$_60$ with band gap energy of 1.6–1.9 eV and a unique structure of delocalized $\pi$ electrons may act as a sensitizer when attached to the surface of titanate nanotubes [120]. These outstanding structural characters enable them to be used as promising materials for environmental catalysts. In short, these hybrid materials showed large surface area with high quality of active sites and able to inhibit the recombination electron–hole pairs.

7. Conclusions

A series of comprehensive review on TiO$_2$-based nanotubes are discussed, which include three main routes used to synthesize TiO$_2$ nanotubes, factors affecting the formation of titanate nanotubes by hydrothermal treatment, crystal structure, mechanism, structural-activity correlation and modification of TiO$_2$-based nanotubes. Template-assisted method allows the fabrication of materials with regular and controlled morphology by adjusting the morphology of the applied template. However, it encounters difficulties such as time consuming due to pre-fabrication and post-removal template and contamination may occur during post-removal template. Electrochemical anodization method can build highly ordered self-organized TiO$_2$ nanotubes immobilized on a titanium foil surface with controllable pore size. However, this preparation method can be considered as an expensive technique for large scale production of TiO$_2$ nanotubes and length distribution of tubes is not well-defined over a large surface area. Meanwhile, TiO$_2$-based nanotube prepared by alkaline hydrothermal method is a simple and environmental friendly synthesis technique as compared to template-assisted and electrochemical anodization. Additional advantages are more cost-effectiveness and larger amount of TiO$_2$-based nanotubes can be produced in one-pot hydrothermal process.

TiO$_2$-based catalyst has become popular to be used as photocatalyst in the water treatment industry owing to its low cost, high safety and high photocatalytic activity. However, the lack of visible light activity limits its practical applications. Hence, the improvement in the photocatalytic activity of TiO$_2$-based nanotubes has been achieved via deposition with metal nanoparticles, single- or co-doping with metal ions/non-metal ions, coupled with other semiconductors and hybridized with carbon nanomaterials. The modification on TiO$_2$-based nanotubes exerts a substantial influence in modifying the optical interface and bulk properties of the pure TiO$_2$ nanotubes, which then reflects to the charge carrier separation and transfer behavior. In short, modified TiO$_2$-based nanotubes have higher potential to be utilized as photocatalyst in large scale applications.

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References
