



A review on TiO₂ nanotubes: synthesis strategies, modifications, and applications

O. Zakir^{1,2} · A. Ait-Karra¹ · R. Idouhli¹ · M. Khadiri¹ · B. Dikici³ · A. Aityoub¹ · A. Abouelfida¹ · A. Outzourhit²

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Abstract

In the field of nanotechnology, titanium dioxide nanotubes (TiO₂ NTs) are one of the most valued inventions. They were discovered in 1996, and have since been used in several fields including photocatalytic degradation of pollutants, hydrogen production, and dye-sensitized solar cells. This review provides a comprehensive overview of TiO₂ NTs and their synthesis methods, highlighting recent progress and modifications that improve their properties. The influence of anodization parameters, the effect of annealing temperature, and modified TiO₂ NT arrays, including doping and heterostructure were discussed also in detail. In addition, this article summarizes some of the recent advances in the applications of TiO₂ nanotubes in photocatalysis, hydrogen production, dye-sensitized solar cells (DSSC), and the detection of heavy metal ions. Finally, the existing problems and further prospects of this renaissance and rapidly developing field are also briefly addressed.

Keywords Electrochemical anodization · Doped nanotubes · Modified TiO₂ · Nanostructures · TiO₂ Nanotubes

Introduction

Nanotechnology has opened up new opportunities to design and develop materials with unique properties and applications. Recently, those materials have played an important role in new technologies to attain high-performance devices for various applications. The geometry, shape, and morphology of the used nanomaterials significantly determine the performance of these devices. Transition metal oxide nanomaterials such as titanium dioxide (TiO₂) [1–3] zinc oxide (ZnO) [4, 5], tungsten trioxide (WO₃) [6, 7], ferric oxide (Fe₂O₃) [8, 9], and copper/cuprous oxides (CuO/Cu₂O) [10] have extensively been investigated for various applications.

Among all transition metal oxides, TiO₂ is the most studied material because it has a wide range of functional properties. Various nanostructures of TiO₂ have been successfully synthesized including; nanowires [11], nanoparticles [12], nanorods [13], nanosheets [14], nanotubes [15], and microspheres [16] (Fig. 1). Nanotube structures have attracted significant research interest due to their high specific surface area, enhanced charge transfer, stability, and remarkable photo-catalytic and photo-electrocatalytic properties. These unique characteristics make them promising candidates for various applications, including but not limited to photo-catalytic [17–20], photo-electrochemical [21–23], water splitting [24–27], solar cells [28, 29], biomedicine [30], etc. The TiO₂-based nanotubes were first reported in 1996 by Hoyer using the template-assisted method [31].

To achieve the desired properties and characteristics of TiO₂ nanotubes, the synthesis method plays a critical role. Thus, several techniques have attracted considerable attention to synthesize the TiO₂ nanotubes and ameliorate their properties. The most used techniques to elaborate TiO₂ nanotubes are the template-assisted method [32, 33], sol-gel process [34, 35], electrochemical anodization of titanium (Ti) [36–46], and the hydrothermal method [47]. Each technique has its own advantages and limitations. Therefore, it is essential to have a good understanding of the different methods and their influencing factors to obtain the desired nanotube structure.

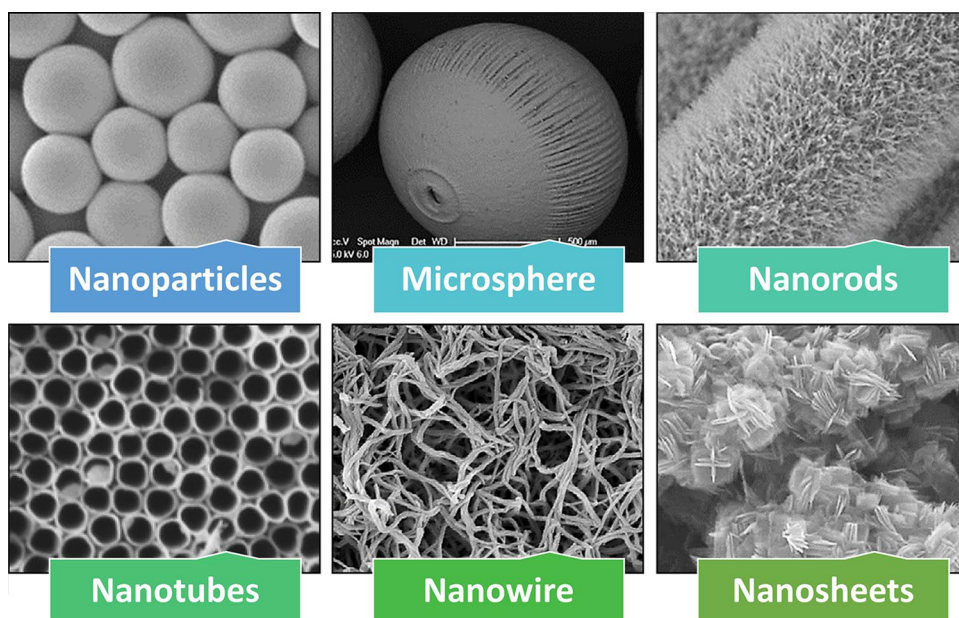
✉ O. Zakir
othmane.zakir@gmail.com

¹ Laboratory of Applied Chemistry and Biomass, Department of Chemistry, Faculty of Science Semlalia, University Cadi Ayyad, BP 2390 Marrakech, Morocco

² Laboratory of Nanomaterials for Energy and Environment, Department of Physics, Faculty of Science Semlalia, University Cadi Ayyad, BP 2390 Marrakech, Morocco

³ Department of Metallurgical and Materials Engineering, Faculty of Engineering, Ataturk University, 25240 Erzurum, Turkey

Fig. 1 Different nanostructures of TiO₂ (Derivated from refs. [11–16])



The fundamental principles of anodized TiO₂ nanotubes were proposed in 1999 and 2001 by Zwilling et al. [48, 49] and Gong et al. [50], respectively. Since then, several studies focused on the determination of the optimal experimental conditions have been performed to efficiently obtain high-quality TiO₂, such as smooth and high-aspect-ratio nanotubes [51], highly ordered nanotubes by multistep anodization [52], tapered and conical-shaped nanotubes [53], free-standing and open-ended nanotubes [54, 55], and transparent nanotubes [56]. Despite these efforts, the wide band gap (> 3 eV) and the recombination of photo-generated charges are major disadvantages of TiO₂. Several attempts to activate TiO₂ under visible light have been investigated. Many studies have reported that the absorption capacity of TiO₂ can be increased from UV to visible range by doping or coupling the TiO₂ with other semiconductors [57–60].

This review provides an analysis of the recent developments in TiO₂ NTs synthesis methods and modifications that enhance their performance. Besides, the review aims to provide an overall understanding of the current state of the art, the novelty, and the future perspectives of TiO₂ NTs, which can inspire further research and development of these materials for various practical applications.

Synthesis of TiO₂ nanotubes

The synthesis of TiO₂ nanotubes has been the subject of extensive research over the past few decades. Several methods have been developed to fabricate these nanotubes up to now, as shown in Fig. 2. The first method developed was the template-assisted method in 1996, followed by the sol-gel method in 1998, the hydrothermal method in 1999, and the currently used electrochemical anodization method performed in 2001 [61, 62].

Each of these methods has its advantages and disadvantages, and the choice of method depends on the specific application and desired properties of the nanotubes. In the following sections, details of the methods used to synthesize TiO₂ nanotubes and the parameters that influence their growth and properties were discussed.

Template-assisted method

Template-assisted synthesis is an easy, cost-effective approach to fabricating TiO₂ nanotubes. Porous materials, usually anodic aluminum oxide, were used as a template,

Fig. 2 The chronology of fabrication methods for TiO₂ nanotubes



and TiO₂ layers were deposited on their bottom. Firstly, the template surface is covered with a thin layer of gold, then the pores of the treated aluminum oxide are entirely filled with a poly(methyl) methacrylate polymer. Finally, the polymeric block is separated from the Al₂O₃ mold and used as the secondary template for the growth of the TiO₂ nanotube arrays. After the deposition of TiO₂, the second template is removed to obtain the TiO₂ nanotubes. A template-assisted method is a mainly used technic to synthesize the TiO₂ nanotube arrays. Michailowski et al. [33] synthesized a TiO₂ nanotube material via an impregnation-decomposition of titanium (IV) isopropoxide to TiO₂ at 500 °C using anodic Al₂O₃ as a template. Additionally, Yuan et al. [63] revealed the synthesis of TiO₂ nanotubes by template-based Ti(OC₄H₉)₄ hydrolysis process using an anodic Al₂O₃ membrane as a template between H₂O and the Ti(OC₄H₉)₄ solution. Similar results are reported by immersing anodic Al₂O₃ in an aqueous (NH₄)₂TiF₆ solution [64]. Liang et al. showed the synthesis of TiO₂ nanotubes by depositing the TiCl₄ on anodic Al₂O₃ using atomic layer deposition [65]. Liu et al. [66, 67] have produced a very innovative class of TiO₂ photonic crystals functionalized nanoporous anodic alumina broadband-distributed Bragg reflectors for visible-light-driven photocatalysis.

Sol-gel method

The sol-gel method has been widely used to produce TiO₂ materials of high purity and homogeneity. In this method, a titanium precursor undergoes hydrolysis/condensation to form a sol, which then transforms into a gel. The solvent is then evaporated, and a xerogel is obtained. The xerogel is further processed through milling and heat treatment to produce highly crystalline TiO₂.

To produce highly ordered TiO₂ nanotubes, the sol-gel method is usually combined with another process, such as the hydrothermal or the template-assisted method. For instance, Pang et al. [68] have successfully obtained TiO₂ nanotubes via the sol-gel process in conjunction with the hydrothermal method to degrade Rhodamine B in an aqueous solution. Similarly, Liu et al. [69] used the nanorods of ZnO as a template to elaborate TiO₂ nanotube arrays by the sol-gel process. The combination of the sol-gel method with other techniques has provided an effective means of producing highly ordered and functional TiO₂ nanotubes for various applications.

Hydrothermal method

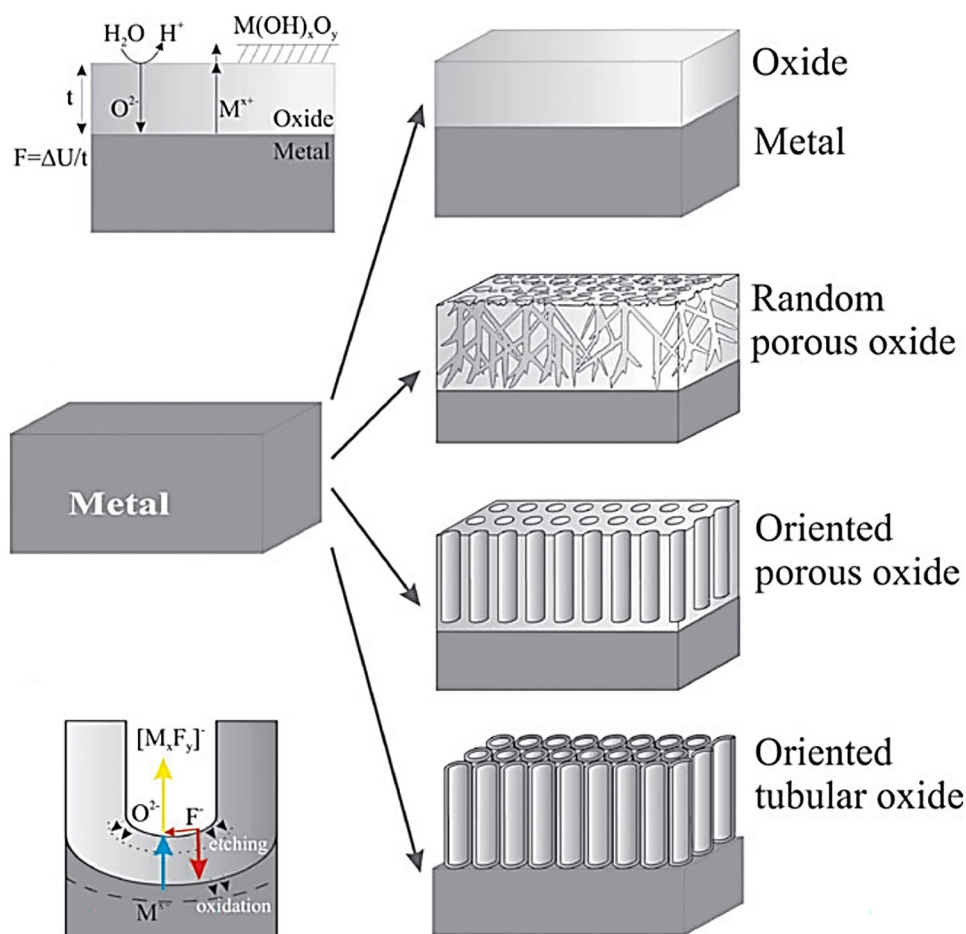
Hydrothermal treatment has received wider attention because it gave pure TiO₂ nanotubes with a high crystallinity [70]. It consisted of mixing titanium dioxide powder and highly

concentrated sodium hydroxide solution at a temperature below 150 °C and under high pressure using a Teflon-sealed autoclave [71, 72]. Using this method, the properties of the formed TiO₂ nanotubes depend on many parameters, such as the starting materials [73], hydrothermal temperature [74], and post-treatment [75]. Xu et al. [76] obtained TiO₂ nanotubes with a diameter of about 10 nm using the hydrothermal process at 110 °C after approximately 20 h. In another study, Dong et al. [77] successfully produced TiO₂ nanotubes with multilayered sheets and an outer diameter varying from 10 to 15 nm. Tsai and Teng [78] investigated the role of post-treatment acidity on the properties of TiO₂ nanotubes. It is found that with the increase in acidity, the TiO₂ layer transformed into nanotubes and eventually into the anatase phase during the post-treatment acid wash. In addition, it was reported that the main factor in the formation of the nanotubes is the acid-washing process [35, 79, 80]. Nevertheless, other researchers concluded that acid washing does not affect the properties of TiO₂ nanotubes [81]. Tsai and Teng postulated that the contradiction observed between these studies is due to the synthesis conditions such as the time and temperature of NaOH treatment [78].

Anodization: an electrochemical synthesis strategy

Recently, the electrochemical technique has been the commonly used method to elaborate TiO₂ nanotube layers. This method has many advantages, such as good mechanical adhesion strength and high electronic conductivity since the layer grows directly on the titanium metal substrate [82]. This method offers easy control of the thickness and morphology of the TiO₂ by adjusting the anodization parameters such as applied voltage, anodization time, electrolyte composition, and the temperature of the solution. The anodization method can obtain a layer of TiO₂ nanotubular with a controlled and uniform diameter. It has been demonstrated that different morphologies of TiO₂ can be obtained depending on the anodization parameters (Fig. 3). Compact TiO₂ films are generally obtained in fluoride-free electrolytes, whereas nanoporous/nanotubular films can be prepared in electrolytes containing fluoride ions [83, 84]. Using the anodization method, Kulkarni et al. successfully obtained thick and adherent TiO₂ nanotubes on the titanium surface. They showed that the thickness and diameter of the nanotubes depend on the anodization time and applied voltage [85]. However, Jankulovska et al. [86] successfully fabricated TiO₂ nanotubes with an internal diameter of 90 nm, an external diameter of 120 nm, and a length of approximately 4 μm. In another study, Ghicov et al. [87] fabricated TiO₂ nanotubes in a fluoride-ion-containing phosphate electrolyte with diameters varied between 40 and 100 nm and lengths between 100 nm and 4 μm.

Fig. 3 The schematic illustration of anodization setup (Reprinted with permission from ref. [88], Copyright 1996, Royal Society Of Chemistry)



Among all these methods, electrochemical anodization is the most effective way to produce highly ordered nanotubular TiO_2 films.

Influence of anodization parameters

The anodization method has focused on the formation of TiO_2 nanotubes. All these showed that the synthesis of TiO_2 nanotubes is strongly influenced by anodization parameters, which have a significant impact on their morphology, composition, and structure. The ability to control these parameters has been a major focus of research to achieve desirable properties and performance of TiO_2 nanotubes for various applications. In this section, the influence of these parameters on the formation of TiO_2 nanotubes and their properties were reported with recent literature.

Effect of electrolyte composition

The composition and concentration of electrolytes significantly affect the formation of nanotube arrays. Based on the electrolyte we use, the nanotubes are essentially

classified into four generations: 1st generation of nanotubes prepared in hydrofluoric acid, which were only 0.5 μm long and characterized as poorly self-organized [50, 89–91]. Second generation of nanotubes up to 5 μm long grown in an aqueous solution containing fluoride ions. 3rd generation of smooth and longer nanotubes, up to 100–1000 μm grown in organic solvents such as ethylene glycol [40, 92–94], glycerol [36, 51, 95–97], dimethyl sulfoxide [98], formamide or diethylene glycol [99], containing fluoride species (NH_4F , NaF , and KF) and small amounts of water. The 4th generation nanotubes and nanopores have been developed in the last few years. A highly ordered hexagonal structure characterizes this generation. Yeonmi and Seonghoon [100] have improved the regular nanopores structure using two-step anodization. Macak et al. [101] developed highly hexagonal TiO_2 nanotubes using a multi-step approach in other studies. Similar results have also been achieved by Albu et al. [102]. They produced the hexagonal self-ordered TiO_2 nanotube of about 250 μm by operating within optimal anodization parameters (F^- concentration, anodizing voltage, and time). Table 1 summarizes the anodization conditions and the characteristics diameter (D), and length (L) of the

Table 1 Evolution of TiO₂ nanotubes from the 1st to 4th generation

	Electrolyte	Anodization conditions	Characteristics of NTs	Ref
1st Generation	- Aqueous solution + 0.5 wt% HF	20 V 20 mins	D = 60 nm L = 250 nm	[50]
2nd Generation	- Aqueous solutions of fluoride salts; (0.5 wt% NaF + 0.5 M H ₃ PO ₄ + 0.5 M Na ₂ SO ₄ + 0.2 M sodium citrate)	20 V 18 h	Organized nanotube D = 110 nm L = 2.6 μm	[103]
3rd Generation	- Glycerol + 1.48 wt% NH ₄ F	60 V 1 h	Organized nanotube D = 128 nm L = 1.5 μm	[36]
	- Ethylene glycol + 0.3 wt % NH ₄ F + 2 vol.% H ₂ O	60 V 18 h	Organized nanotube D = 100 nm L = 45 μm	[104]
	- Glycerol + 0.3 wt% NH ₄ HF ₂	30 V 2 h Annealing (500 °C)	D = 100 nm	[105]
4th Generation	Ethylene glycol + 0.3 wt% NH ₄ F + 2 vol% H ₂ O	Pure Ti Two-step anodization 50 V 1st step; • Freshly electrolyte • 1 h 2nd step; • Freshly electrolyte • 30 minutes	Hexagonal shape D = 75 nm L = 6 μm	[24]

resulting TiO₂ nanotubes in different generations. Figure 4 shows the morphology of TiO₂ nanotubes depending on the generation.

Effect of applied voltage

The anodic charge is the critical factor controlling film thickness and pore diameter. Several studies showed that the diameter and length of the nanotube vary linearly with the electric charge applied during the anodization process [106–108]. For this reason, the morphology of the nanotube arrays can be predicted by applying the suitable voltage (Fig. 5) [36, 109–111]. The applied voltage usually ranges from 10 to 60 V and 5 to 30 V in organic and aqueous solutions, respectively [112, 113]. At low applied voltage, tubes of a few nanometers in diameter and a few hundred nanometers in length were obtained. At intermediary voltage, the ordered nanotubes are formed. If a higher voltage is applied, the dissolution rate is too high, resulting in high dissolution of the oxide layer and no tube formation could be observed [114]. Zakir et al. [36] reported that the highly ordered nanotubes are formed at 60 V, and the mean inner diameter of TiO₂ nanotubes increased from 59 to 128 nm when the applied voltage was increased from 30 to 60 V. Other studies suggested that the linear relation between the inter-tube distance and anodization voltage is limited to low voltages [115], whereas at higher voltages, the dependence is not linear [116, 117].

On the other hand, the anodization voltage affects the photo-electrochemical and photo-catalytic activity of the TiO₂ nanotubes. Sun et al. [44] investigated the effect of anodization voltage on photo-electrochemical properties and hydrogen production. The hydrogen production rate increased by increasing anodization voltage, and a maximum rate was denoted at 93.6 μmol/h.cm² with photo-conversion efficiency of 3.51% for TiO₂ formed at 50 V. Atyaoui et al. [118]. studied the photocatalytic activity of TiO₂ nanotubes arrays on the degradation of Black Amido and shown that the photo-decolorization efficiency of about 100% is achieved after 30 min of irradiation using a nanotube formed at the optimal voltage of about 60 V.

Effect of anodization time

The duration of anodization affects the nanotubes principally in two aspects. Firstly, the formation or not of the nanotube structure, and secondly, the length of the nanotubes [119]. At the beginning of the anodization, a thin and compact TiO₂ film is formed. In this case, if the duration is too short, a disordered porous layer is formed at the substrate surface. In addition, with an increase in the anodization time, porous structures progressively become thicker, converting into the TiO₂ nanotube array [112, 120]. If the duration is sufficient, highly nanotube arrays can be formed [109]. If the other anodization parameters are kept constant, the length of the nanotubes increases over time

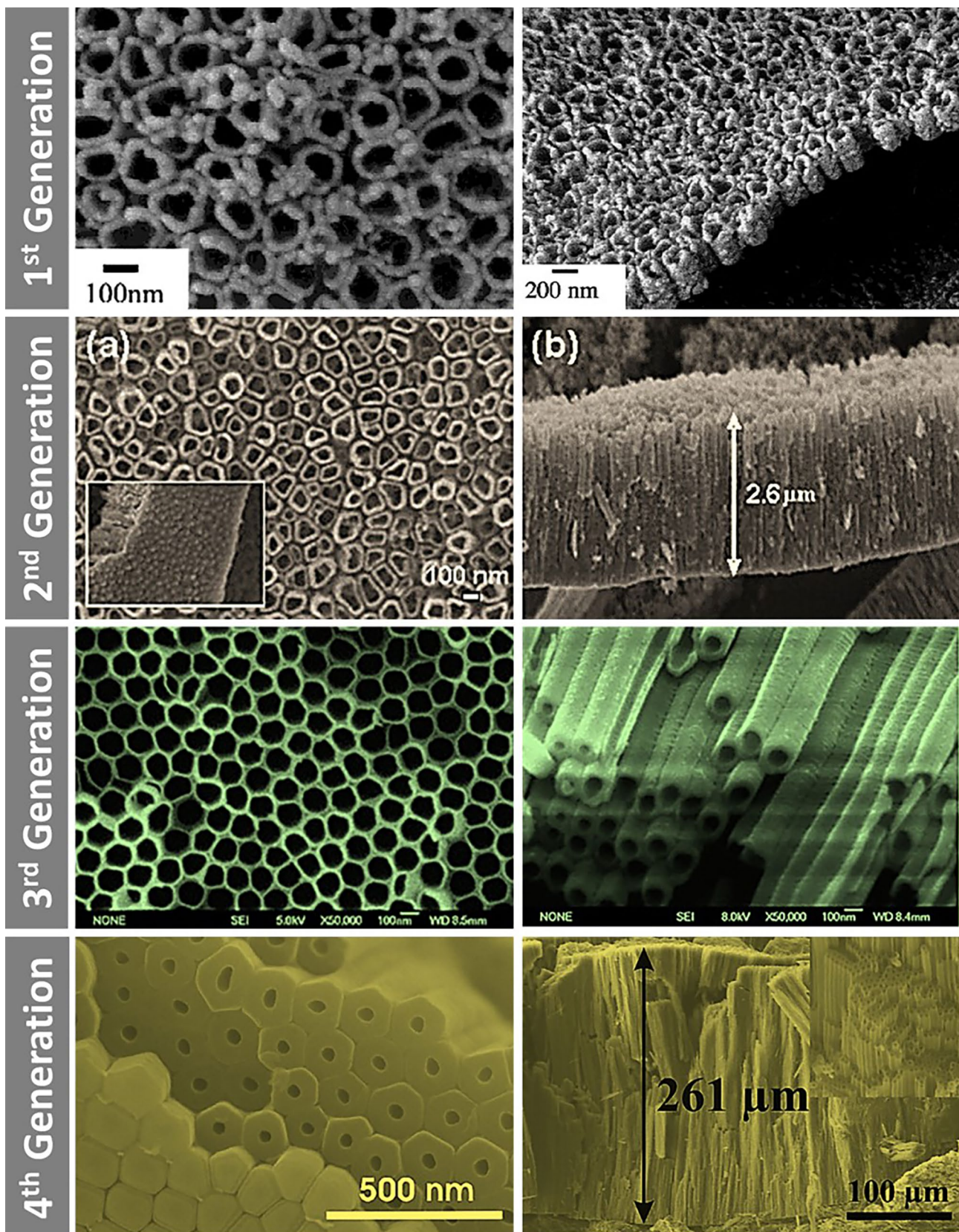


Fig. 4 Evolution of the anodized TiO₂ nanotube from 1st to 4th generation (Derived from refs. [50, 102–104] with permission from their publishers)

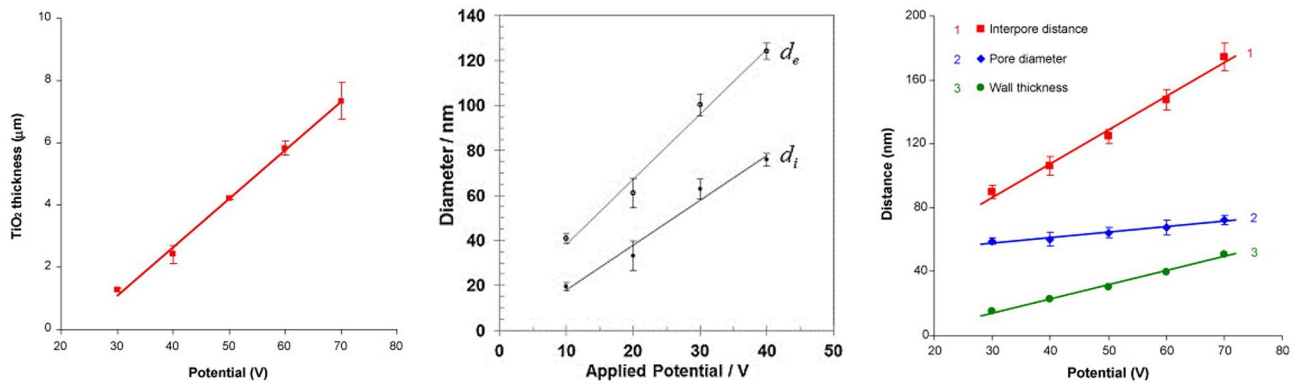


Fig. 5 Linear relationship between the applied voltage and nanotube parameters (Reprinted with permission from refs. [95, 111], Copyright 2010 and 2012, Elsevier)

[88, 109, 121]. However, the growth rate of nanotubes is reduced with anodization time because of the decreasing diffusion rate of $[\text{TiF}_6]^{2-}$ within the nanotube [112]. Ghicov et al. [87] also suggested that after reaching a stable condition between nanotube growth at the metal/TiO₂ interface and electrochemical/chemical dissolution at the top of the tube, we will no longer find an increase in nanotube length (Fig. 6a). Macak et al. [101] showed that the wall thickness and inner tube diameter is not a constant along the TiO₂ nanotube and that the inner tube diameter increases from 50 nm at the bottom to 110 nm at the tube top, while the wall thickness decreased from 65 to 12 nm. Bervian et al. [122] have suggested that the anodization duration is less than 30 min, a compact TiO₂ structure will occur and the nanotube structure is not yet formed until reaching 60 min of anodization time, using a mixture of fluorinated glycerol and ethylene glycol electrolyte. The average length of the nanotubes was varied between 650 nm to 6 μm by changing

the anodization time from 1 to 3 h. This study also shows that the length of the nanotubes plays a crucial role in the photo-electrochemical water splitting properties of TiO₂ and that the best performance is obtained using nanotubes formed at 120 min. Figure 6b show that the photo-current response increases with anodization duration to reach a maximum for TiO₂ nanotubes formed at 60 min, while the photocurrent response decreased when the anodization duration reached to 120 min. This result was explained by a simple transfer of photo-generated electrons from TiO₂ to the counter electrode in the TiO₂ NTs formed at 60 min.

Effect of electrolyte temperature

The electrolyte temperature affects the growth and quality of TiO₂ nanotube arrays by affecting the oxide growth rate and, consequently, the wall thickness and the length of the nanotubes [28, 45, 123]. Wang and Lin published the first

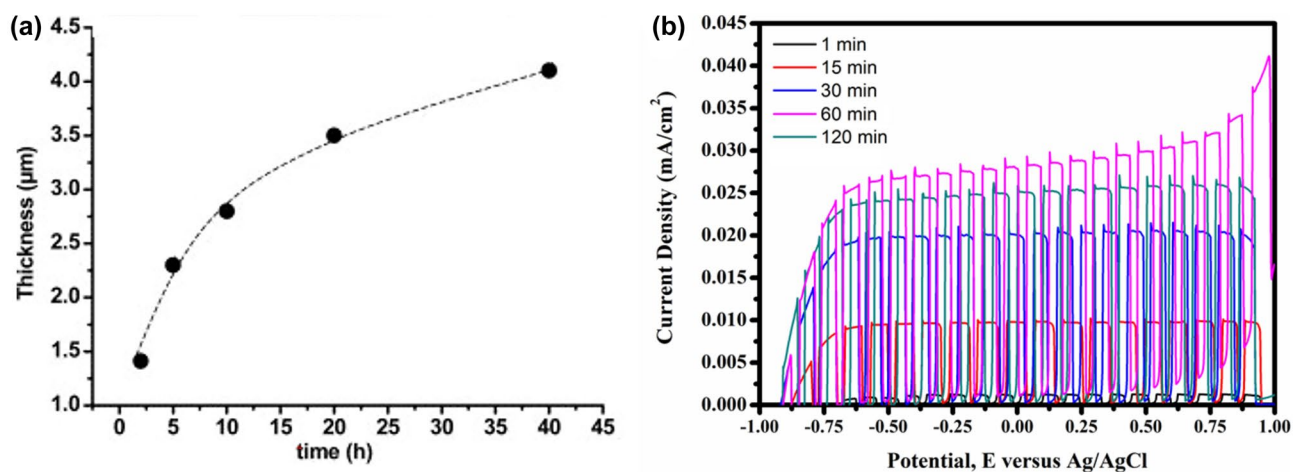


Fig. 6 Evolution of length (a) and photo-current responses (b) of TiO₂ nanotubes prepared at different anodization duration (Reprinted with permission from ref. [21, 87])

work demonstrating the effect of electrolyte temperature in an aqueous and non-aqueous electrolyte on the anodic TiO₂ properties [91]. In an aqueous electrolyte, a slight decrease in internal diameter was observed with increasing temperature while the external diameters remained unchanged [124]. This can be due to the fact that the etching of TiO₂ induced by the electric field and fluoride ions is similar, while the rate of oxide formation is higher than at low temperatures [91]. Prida et al. suggest that in aqueous solutions, low temperatures inhibit the growth of TiO₂ nanotubes [45]. In organic electrolytes containing fluoride ions, the temperature between 0 and 40 °C is the most range of temperature suitable for the growth of highly ordered TiO₂ nanotubes [125]. In addition, the outer diameter of the nanotubes fabricated in glycerol/NH₄F (0.14 M) electrolyte was significantly increased by increasing the temperature of the electrolyte from 0 °C to 40 °C [126]. These suggestions can be explained by the fact that at low temperatures, the ionic mobility of fluorine in some organic electrolytes is reduced, resulting in a slower dissolution of the formed TiO₂ and, consequently, a smaller nanotube diameter [91].

Effect of fluoride ion (F⁻) concentration

The presence of fluorides in the electrolyte affects strongly the anodization process. On one hand, complexation occurs with Ti⁴⁺ ions that are ejected at the TiO₂/electrolyte interface to form a water-soluble complex [TiF₆]²⁻ and on the other hand by chemical attack of the formed TiO₂ [127–129]. Various studies showed that three different electrochemical characteristics can be obtained depending on the fluoride concentration [88, 95, 130–132]. At low fluoride concentrations, a stable compact oxide layer is formed after anodization [133]. At higher fluoride concentrations, the Ti⁴⁺ formed immediately reacts with the abundant fluoride to form soluble [TiF₆]²⁻ and no oxide formation can be observed [134]. For the intermediate fluoride concentrations, the growth of the NTs layers is controlled by a competition between the formation of a compact oxide layer and the chemical dissolution of the oxide by F⁻ ions [135–137].

Effect of water content

In addition to the applied voltage and the anodization time, the water content is another crucial factor in the electrochemical anodization process of titanium because the growth of one-dimensional nanotubes can be accelerated by enhancing the corrosive effect [138]. Water is the source of oxygen to form efficiently TiO₂ during the anodization process, but it is also an essential factor for the formation of tubes rather than pores [139]. The effect of water on oxide formation has

been studied by many researchers. Wei et al. [140] suggested that the transition from nanopores to nanotubes is favored by increasing the water content from 0 to 0.7% in NH₄F (0.05 M) -containing ethylene glycol electrolyte at an anodization voltage of 20 V. Yin et al. [141] showed that when the water content is in the range of 4–12%, the TiO₂ NTs are growth with a reasonable rate and that the barrier layer thickness increases while the growth rate decreases with increasing water content in NH₄F (0.25 wt.%) -containing ethylene glycol electrolyte. When the water content is beyond 12%, compact titania is formed.

Effect of annealing temperature

The morphology and crystallinity of the TiO₂ nanotube arrays, as well as their optical and electrical properties, depend on the annealing temperature [142–146]. Varghese et al. [147] published the first comprehensive study demonstrating the effect of annealing temperature on anodized TiO₂ nanotubes, demonstrating that the NTs were stable up to 580 °C when annealed in an oxygen atmosphere. Other previous studies showed that the as-prepared TiO₂ is amorphous and could be transformed to anatase or rutile phase, or mixtures of the phases relying when be annealed on specific temperature [120, 148, 149]. The amorphous character of mesoporous TiO₂ results in low thermal stability and limits their applications. In contrast, the crystallized structures offer enhanced thermal properties and improved electrical, optical, and catalytic properties [150]. Sun et al. [151] showed that at a temperature less than 450 °C, the TiO₂ nanotubes consist of a pure anatase phase, while the rutile phase starts to appear at 550 °C so that a mixture of anatase and rutile phases are detected between 550 °C and 750 °C (Fig. 7a). Recently, Gavrilin et al. [152] studied the influence of thermal treatment in vacuum and air on the structural properties of multi-walled anodic TiO₂ NTs. It was found that the composition of samples annealed in the air was different from those annealed in a vacuum. Talla et al. [153] synthesized TiO₂ NTs and annealed them in different atmospheres, such as air, nitrogen, oxygen, and vacuum at 450 °C. They reported that the atmosphere affected the phase composition of TiO₂ and that the transformation from the anatase into rutile is retarded in a vacuum and the anatase phase remained the dominant phase even at 800 °C.

Tighineanu et al. [154] have investigated the effect of annealing treatment on the conductivity of anodic TiO₂ nanotube arrays. This study demonstrates that the resistance of the TiO₂ layer decreases when the amorphous nanotube arrays are converted into the anatase phase at about 350–450 °C. Similar results are found by Bakri et al. [155], who show that the resistivity decreases from 1.40×10^5 to 7.19×10^2 Ω·cm by varying the annealing

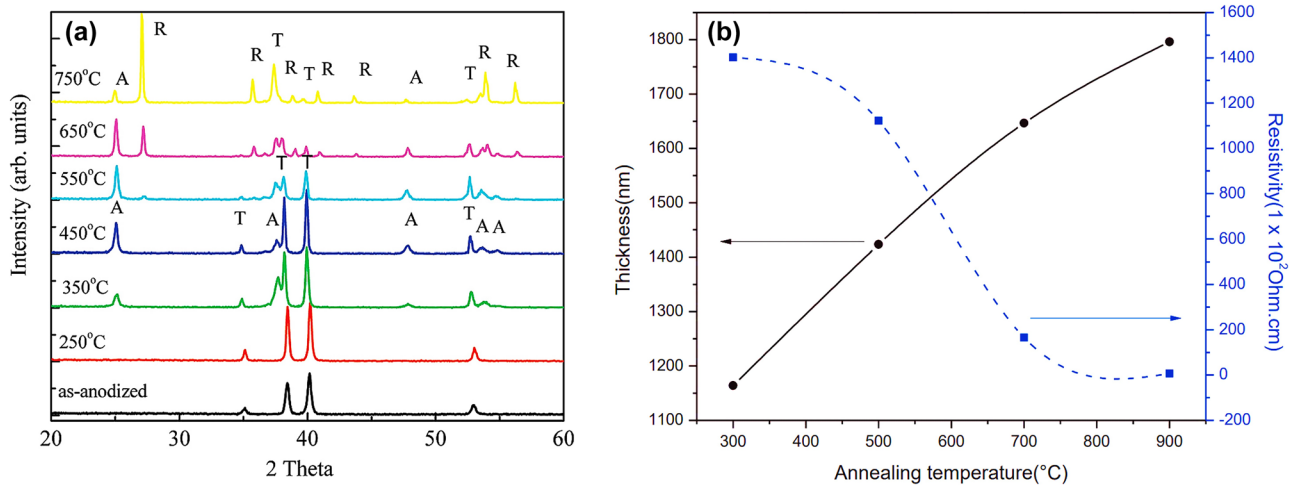


Fig. 7 Evolution of phase composition, thickness, and resistivity of TiO_2 after annealing at indicated temperatures (Reprinted with permission from refs. [151, 155], Copyright 2011 and 2017, American Chemical Society and AIP Publishing)

temperature between 300 and 900 °C (Fig. 7b). Zhao et al. [156] show that the extinction coefficient and the refractive index increase with the increase in the annealing temperature. This study also shows that the anatase is the dominant phase until the temperature lower than 900 °C above the rutile phase becomes the dominant crystal phase.

Modified TiO_2 nanotube arrays

Despite its excellent physical and chemical properties, the higher band gap of TiO_2 makes this material almost inactive under visible light (Fig. 8a). In this regard, several studies have been made to: firstly broaden the absorption of TiO_2

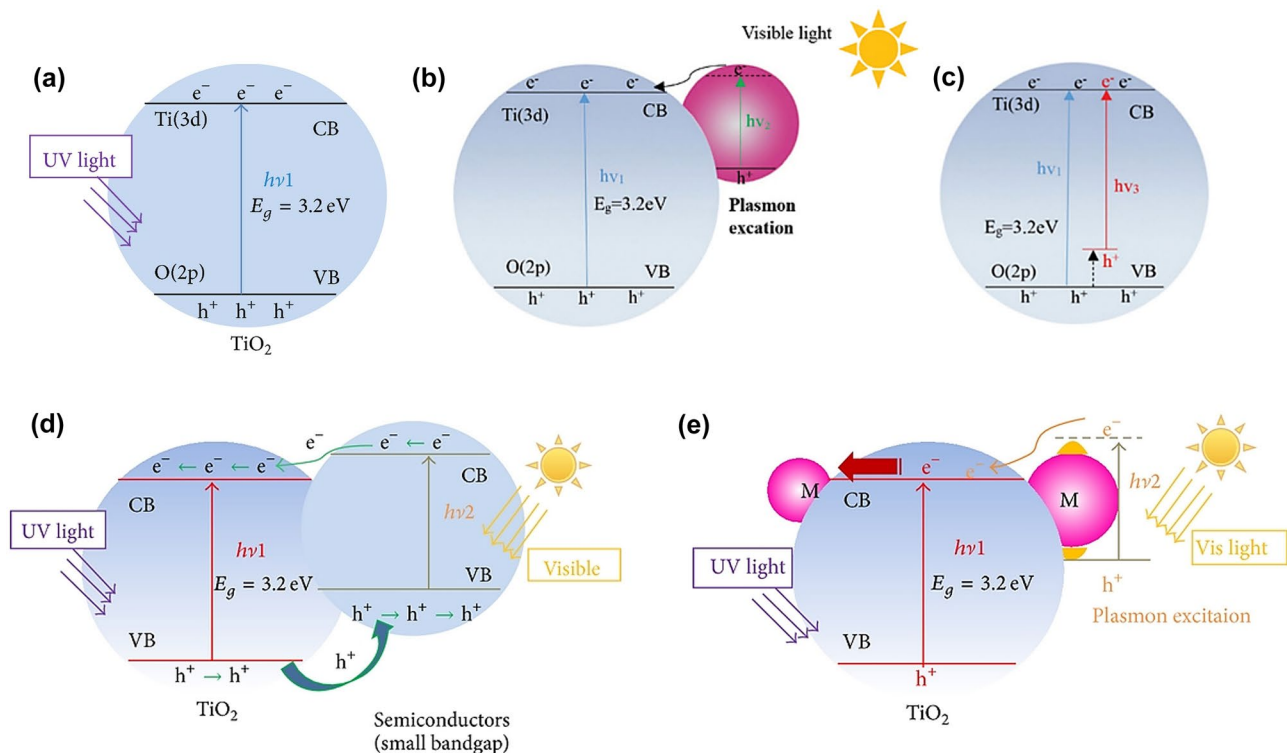


Fig. 8 Schematic of energy level and electron/hole separation of pure TiO_2 (a), doping with metal (b), non-metal (c), coupling with semiconductors (d), and noble metals (e) (Reprinted with permission from refs. [157, 158], Copyright 2013 and 2012, Hindawi and De Gruyter)

in the visible wavelength range and more efficient charge transfer by modifying its optical and electronic properties, and secondly to promote the separation between the electrons and holes photo-generated and inhibit their recombination. To achieve these objectives, different approaches are proposed such as; firstly, doping of TiO₂ with metal ions (Co²⁺, Fe²⁺, Ni²⁺, Cu²⁺, Zn²⁺, etc.) or non-metallic (C, S, N, P, etc.) is one of the typical approaches that have been widely applied (Fig. 8b, c). Or coupling the TiO₂ with a semiconductor material with a narrow band gap (Fig. 8d). The decoration of TiO₂ with different noble metals (Ag, Pt, Au, Pd, etc.) represents another approach (Fig. 8e). In the below subsections, some of the modifications were made to TiO₂ nanotube arrays, including doping and heterostructure formation. These modifications have shown promising results in improving the properties and expanding the applications of TiO₂ nanotubes.

Doping

Asahi et al. [159] reported for the first time the doping of TiO₂ with nitrogen by sputtering in a nitrogen-containing gas mixture and showed that N-doped TiO₂ exhibits photo-electrochemical activity under visible light irradiation. Recently, other doping species, such as several non-metals such as fluorine [160–162], carbon [163, 164], phosphor [165, 166], sulfur [167–169], and boron [170, 171] have been inserted into TiO₂ using different methods. These studies show that the visible-light activities of doped TiO₂ were not only influenced by the value of the energy gap, the distribution of impurity level, and the property of impurity levels but were also affected by the location of Fermi level and the energy in the edges of the band gap [172, 173]. It was found that doping TiO₂ nanotubes with nitrogen received significant attention because of their improved charge transfer properties. Different approaches have been published concerning the doping of TiO₂, including the annealing of TiO₂ in gaseous atmospheres [174], sputtering [175], sol-gel [176], and anodization of titanium alloys [177]. Among these methods, heat treatment of TiO₂ in gaseous atmospheres of the dopant species is considered an easy one-step doping technique [174, 178]. Moreover, the surface of doped nanotubes exhibits significant photo-response in the visible range compared to undoped nanotubes. On the other hand, TiO₂ doped with transition metal ions (Cu [179–181], Cr [182], Ni [183, 184], Zn [185, 186], Ag [181], Co [187], Zr [188], and Fe [22, 187]) has also been reported to broaden the visible light absorption range, and improve the conversion efficiency by extending the lifetime of photo-generated electrons and holes. Choi et al. [189] studied the photo-reactivity of quantum-sized TiO₂ doped with metal ions. Doping with Fe, Mo, Ru, Os, Re, V, and Rh significantly

increased the photo-reactivity efficiency of TiO₂ nanotubes, while doping with Co and Al ions decreased the photo-reactivity. In other studies, Momeni and Ghayeb [190] obtained Fe-TiO₂ nanotube composites using iron (potassium ferricyanide) to decorate anodic TiO₂ nanotubes. They indicated that Fe doping accelerates the photocatalytic performance of TiO₂ nanotubes for water splitting.

Heterostructure

In recent years, many attempts have been made to extend the light absorption range of TiO₂ nanotubes and reduce the charge carrier recombination, such as the formation of hetero-junctions between TiO₂ nanotubes and narrow band gap semiconductors [191]. In 1986, Gerischer and Lübke fabricated the TiO₂ photo-electrodes sensitized by thin deposit CdS semiconductor [192]. Recently, this approach is improved, and other semiconductors are used CdSe [193, 194], Cu₂O [195, 196], ZnO [197], WO₃ [198], and BiOI [199]. Indeed, all these semiconductors can absorb part of the visible light. One of the following schemes to elaborate the p-n heterojunction for highly efficient photo-electrocatalytic devices is the direct deposition of p-type semiconductors on TiO₂ nanotubes [196, 199]. Wang et al. [200] deposited p-type Cu₂O on n-type TiO₂ nanotube arrays to fabricate Cu₂O/TiO₂ p-n heterojunction photo-electrodes using ultrasonic-assisted sequential chemical bath deposition. This study shows that the Cu₂O/TiO₂ p-n photo-electrodes exhibited higher photo-conversion capacity and higher photo-electrocatalytic activity in the degradation of rhodamine B compared to single TiO₂ nanotubes. This result was explained by the efficient separation of photo-generated electrons and holes. Similar results have also been achieved by Davaslıoğlu et al. [198] using WO₃/TiO₂ p-n heterojunction photo-electrodes prepared by electrochemical deposition of WO₃ on the TiO₂ nanotubes array by subsequent cycling the potential between -0.6 –1.0 V vs Ag/AgCl. However, the major disadvantage of this approach is that many narrow bandgap semiconductors are not stable, not only due to corrosion or photo-corrosion but also due to the instability of some of the materials under applied voltage.

Applications of TiO₂ nanotubes

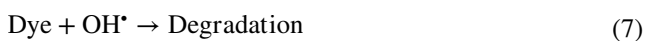
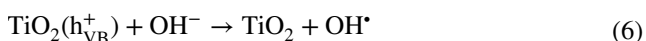
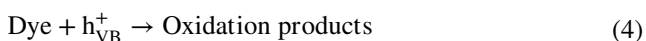
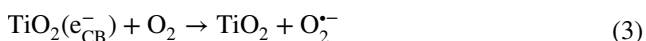
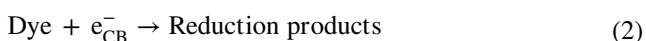
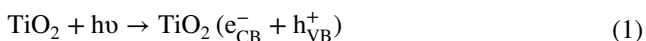
TiO₂ nanotubes have attracted considerable attention due to their applications in photo-catalysis, water splitting, photo-voltaic cells (solar cells), and other aspects.

This TiO₂ nanotube is a promising material for these applications due to its multifunctional semiconductor properties which are based on its excellent physical and chemical behavior, high specific surface area, and fast charge transfer [201].

Photocatalysis

Today, one of the most useful applications of TiO₂ is the photocatalytic degradation of toxic pollutants water contains [83, 202, 203]. It has been shown that TiO₂ nanotube layers can be more efficient photo-catalysts than comparable nanoparticle layers. After Fujishima and Honda demonstrated, for the first time, the photo-electrochemical decomposition of water on TiO₂ surfaces [204, 205]. TiO₂ has been investigated for applications in heterogeneous catalysis [206, 207]. On the other hand, TiO₂ has been used to convert carbon dioxide (CO₂) into energy-intensive hydrocarbon compounds [208, 209]. Savchuk et al. [210] are studied the efficient conversion of CO₂ in the gas phase to methane and methanol on the surface of TiO₂-Cu_xO NTs. In another study, Park et al. [211] successfully reduced the CO₂ to methane by photocatalysis using Cu_xO-TiO₂ hybrid heterostructures under solar irradiation. The basic mechanisms of the photo-catalytic process can be explained as follows:

When the TiO₂ is excited by UV light, the electrons of the valence band (VB) will move to the conduction band (CB). Then the holes and electrons photo-generated (Eq. 1) will be transported to the TiO₂/solution interface and react with the adsorbed molecules. The photo-generated e⁻_{CB} could reduce the dye (Eq. 2) or react with electron acceptors such as adsorbed O₂ on the TiO₂ surface or dissolved in water, reducing it to the superoxide radical anion O₂^{•-} (Eq. 3). On the other hand, the photo-generated h⁺_{VB} can oxidize the organic dye (Eq. 4), or react with H₂O (Eq. 5) or OH⁻ (Eq. 6) to form OH[•] radicals. The resulting OH[•] radical, being a very strong oxidizing agent, can oxidize most of the molecule dyes to the mineral end-products (Eq. 7) [14, 212–217].



Hydrogen production

Today, hydrogen energy is expected as a new clean energy source. In this regard, various technologies are proposed

to produce hydrogen, but only some of them can be considered environmentally friendly. Recently, solar hydrogen produced by photo-catalytic water splitting has attracted considerable attention and has been widely studied due to its great potential for low-cost clean hydrogen production [218]. For this purpose, low-dimensional semiconductor nanostructures are recently developed and applied to solar energy conversion fields [219–221]. The photocatalytic hydrogen production from water, alcohols, or organic pollutants with wide-gap semiconductors has been intensely studied [222]. TiO₂ nanotubes have been intensively studied as photoanodes in photo-electrochemical cells for hydrogen production due to their semiconductor properties, physical and chemical stability, abundance, and low cost [223, 224]. Theoretically, for efficient hydrogen production from water by photo-catalysis, the CB level should be negative than the hydrogen production level (E(H₂O/H₂)) while the VB should be positive than the water oxidation level (E(O₂/H₂O)) [225]. Recent studies show that the hydrogen production rate is highly dependent on the electrolyte, light intensity, external polarization, and the morphology and structure of TiO₂ [158]. Therefore, optimizing these parameters and fundamentally understanding their possible correlations is important to clarify approaches to constructing a highly efficient cell for hydrogen production. Hattori et al. [226] have successfully produced hydrogen from the photo-decomposition of ethanol using TiO₂ nanotubes. Moreover, they found that the length of the nanotubes is the most important factor in this process. They showed that the amount of hydrogen produced increases with the increase in the length of the nanotube. Mor et al. [227] found a hydrogen generation rate of 960 μmolcm⁻² h⁻¹ by using highly ordered TiO₂ nanotubes arrays of about 224 nm in length and 22 nm in diameter for water splitting under a constant voltage of -0.4 V. Recently, Li et al. [228] reported an enhanced hydrogen generation rate of 3.507 mmol h⁻¹ g⁻¹ under simulated solar light by a mesoporous-structured anatase TiO₂.

Solar cells applications

The TiO₂ nanotubes are one of the most promising materials for dye-sensitized solar cells (DSSCs) due to their improved charge-collection efficiency and enhanced separation of photo-generated electrons/holes [229–232]. For this reason, the ordered TiO₂ nanotubes significantly increase solar energy's conversion efficiency [233]. The DSSC consists of a layer of TiO₂ nanotubes deposited on a conductive substrate, a counter electrode (Pt), an adsorbed dye as a sensitizer, and an electrolyte. On the TiO₂ surface, adsorbed is a dye that serves as a light absorber and is attached to the TiO₂ surface by specific functional groups. For the choice of the dye molecule, the LUMO of the dye must be energetically placed slightly higher than the CB of TiO₂. Under solar irradiation,

HOMO–LUMO transitions occur in the dye. Excited electrons can then be injected from the LUMO (of the Dye) into the CB of the TiO₂ electrode [158]. However, the overall power conversion efficiency of the dye-sensitized TiO₂ nanotubes solar cells remained relatively low. Paulose et al. [234] found a conversion efficiency of about 4.24% using highly-ordered TiO₂ nanotube films sensitized by a monolayer of N719 under AM 1.5 sunlight source. These results can be explained by the incomplete coverage of the dye molecules on the TiO₂ nanotubes and insufficient electrolyte infiltration into the nanotubes [235, 236]. In another study, Mor et al. [56] compared the photo-conversion of anodic TiO₂ nanotubes formed on titanium substrate and nanotubes formed on FTO glass. They found that solar cells fabricated with nanotubes formed on the titanium surface have higher charge transfer efficiency and dye absorption than solar cells fabricated with nanotubes formed on FTO glass. Tsvetkov et al. [34] compared the photoconversion of the pure and Nb-doped TiO₂ nanotubes and nanoparticles. They found that the doping of TiO₂ nanostructures leads to an additional about 14% in CPE and that DSSCs based on Nb-doped TiO₂ NTs have an efficiency of 8.1%, which is 35% higher than that of a cell using TiO₂ nanoparticles. An open-ended TiO₂ NT ordering by anodization of titanium for the application of PE of DSSCs was prepared by Zhu et al. [237] The device obtained by using this material showed a PCE of 7.7%. In another study, Peighambardoust et al. [238] examined the effect of some parameters such as; annealing temperature and dopant on the efficiency of TiO₂ NTs electrodes for DSSCs, they found that the increasing of annealing temperature from 480 to 520 °C and doping of NTs improve the cell efficiency up to 70% and 40%, respectively.

Detection of heavy metal ions and organic pollutants

Toxic heavy metal ions such as Pb²⁺ and As³⁺, as well as organic pollutants present in water and soil, are a source of danger for the environment and human beings. Many methods have been developed to assess the environmental impact and control the amount of pollutants in water and soil, such as flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry, atomic fluorescence spectrometry, and inductively coupled plasma atomic emission spectrometry, etc. Recently, the sensors offered a new technique for monitoring heavy metals and organic pollutants. A modified TiO₂ nanotube array has been reported as a sensor for detecting heavy metals and organic pollutants in water. Liu et al. [239] have developed a DNA-modified TiO₂ nanotube array sensor to determine Pb²⁺ in water. The results showed that the concentrations detected by DNA-modified TiO₂ nanotubes were similar to those obtained by the atomic absorption spectrometry method. They also found that the modified TiO₂ nanotube sensor possesses a wide

linear calibration between 0.01 nM and 160 nM with detection limits of about 3.3 pM. Yang et al. [240] fabricated Au shrub-modified TiO₂ nanotube arrays as a novel and useful sensor to determine the arsenic concentration in water. The results showed a high sensitivity between the current changes and the arsenic concentration with a value of 25.7 μA/cm² corresponding to 5 μg/L of As³⁺. Cai et al. [241] reported molecularly imprinted polymer-modified TiO₂ nanotube arrays as a sensor to detect perfluorooctane sulfonate in water. The results showed that this sensor has good selectivity. Moreover, the direct detection of perfluorooctane sulfonate by electrocatalytic reduction reaction was achieved with a detection limit of 86 ng/mL.

Conclusion and future perspectives

The developments of the last decades have highlighted the importance of TiO₂-based materials. The different types of TiO₂ nanostructures, the synthesis strategies of TiO₂ nanotubes, and their applications in energy and environment fields have been discussed in this review. Ordered nanotubes have been synthesized by anodization and by regulating the operating conditions. These structures have considerably improved their performances and have found many applications in various fields. TiO₂-based materials have been widely used in photocatalytic applications, and solar-cell and continue to be active in other applications such as sensing, hydrogen production, etc.

As TiO₂ is a wide band gap (> 3 eV), the optimal use of solar energy is one of these materials' main challenges, reducing its photocatalytic performance. Therefore, doping with appropriate materials, development of composites, and new structural morphologies are expected to be developed in the coming days and will hopefully solve the problems mentioned above. Many innovative and cost-effective synthesis strategies are expected to emerge in the future. Preparing low-cost materials with high stability and environmentally friendly and with improved light adsorbed properties needs to be discovered to fulfill future needs. The development and commercialization of such light-harvesting materials will help to solve, to some extent, our ever-increasing energy needs and the environmental problems facing the world today.

In conclusion, TiO₂ nanotubes have demonstrated significant advantage in various technological fields, such as medicine, energy, and the environment. The review has discussed different synthesis methods and techniques for preparing highly ordered TiO₂ nanotubes with improved performance. However, there are still challenges to overcome, including reducing the band gap of TiO₂ for optimal use of solar energy and developing low-cost, stable, and environmentally friendly materials. The future of TiO₂ nanotubes looks promising, and further research and innovation are

expected to improve their performance and commercialization, contributing to a more sustainable future for our energy needs and the environment.

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