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## REVIEW

# Recent advances in the use of TiO<sub>2</sub> nanotubes powder in biological, environmental, and energy applications

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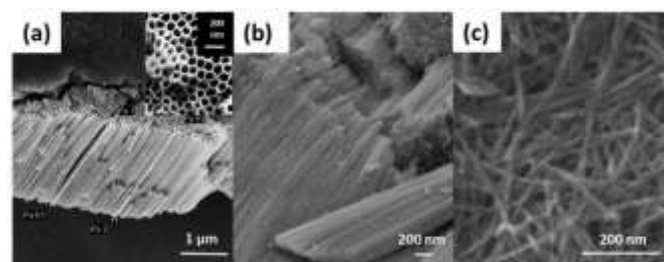
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The use of titanium dioxide nanotubes in the powder form (TNTP) has been a hot topic for the past decades in many applications. The high quality of the fabricated TNTP by various synthetic routes may meet the required threshold of performance in a plethora of fields such as drug delivery, sensors, supercapacitors, and photocatalytic applications. This review briefly discusses the synthesis techniques of TNTP, their use in various applications, and future perspectives to expand their use in more applications.

## Introduction

Nanomaterials with tubular morphology enjoy unique properties over other morphologies, making them the target for many applications. Therefore, a plethora of fabrication techniques have been demonstrated in the literature to synthesize such nanotubes from different materials. Specifically, a huge interest has been shown in the synthesis of titania nanotubes and their applications due to their biocompatibility,<sup>1–3</sup> antimicrobial properties,<sup>4,5</sup> high chemical stability, specific surface area, and catalytic activity.<sup>6–8</sup> In addition, the high UV absorption and the possibility to modify the band gap promote titania as a good candidate for photocatalysis, making it useful for sunscreen protection materials<sup>9</sup> and water treatment.<sup>10–13</sup> Of special interest, titania nanotubes in the powder form (TNTP) have recently gained a great interest within the scientific community. To this end, many synthesis methods have been established to fabricate TNTP as shown in **Figure 1**, including ultra-sonication after anodization, rapid break down anodization, and hydrothermal techniques. In this mini-review, the properties of TNTP will be highlighted by giving insights on their different synthesis techniques and use in a plethora of applications.

subdivided into two techniques. While the first approach includes the anodization of Ti foil followed by controlled ultrasonication<sup>14</sup>, the second technique is a one-step process known as rapid breakdown anodization.<sup>15,16</sup> The second approach is the hydrothermal synthesis of TNTP.<sup>17,18</sup> Although there are other methods for producing tubular titania such as sol-gel

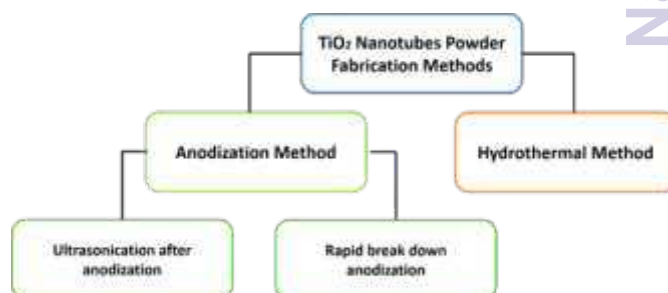


**Figure 1.** FESEM images of TNTP prepared by the authors via (a) ultrasonication, (b) rapid break down anodization, and (c) hydrothermal techniques.

and template-based synthesis methods<sup>19–21</sup>, they are not commonly used.

## Fabrication methods of TNTP

There are two main approaches to fabricate TiO<sub>2</sub> nanotubes in the powder form as presented in **Scheme 1**. The first approach, is the anodization of Ti foil, which can be



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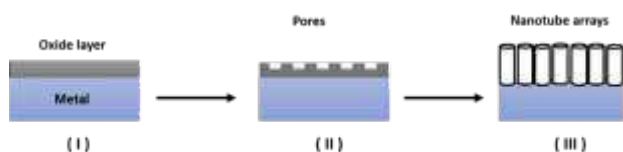
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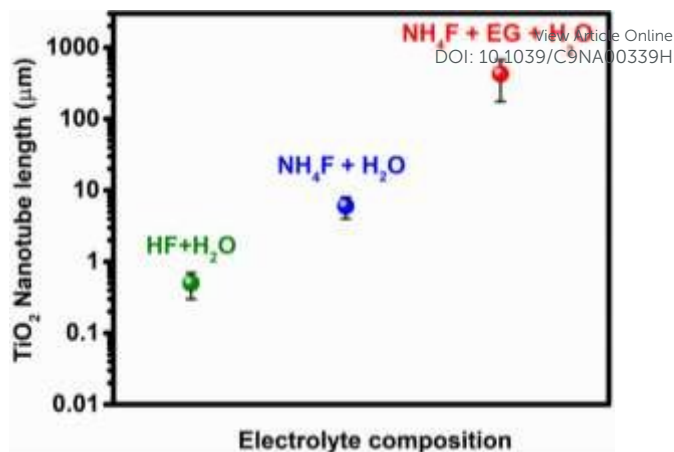
**Scheme 1.** Fabrication methods of titania nanotubes in the powder form.

## Anodization Technique

Anodization process, a top-down fabrication technique, is an electrochemical method that develop an oxide layer on the surface of the metals.<sup>22</sup> In order to achieve the tubular arrays formation, there are three main processes: the first process is the field assisted oxidation of Titanium metal to produce an oxide layer on its surface and to form ( $\text{TiO}_2$ ). The second is the field assisted dissolution of Titanium metal ions in the electrolyte. The final one is the surface etching resulting from the chemical dissolution of Titanium and  $\text{TiO}_2$  as shown in **Figure 2**.<sup>3,19,23,24</sup> Extensive research studies have been investigated the factors that govern the nanotubes formation with tuned tube diameter and length.<sup>25–29</sup> The formed oxide layer structure on the metal surface mainly depends on the concentration and composition of the electrolyte solution and the applied voltage.<sup>5,8</sup> The effect of the electrolyte composition on the length of titania nanotubes is summarized in **Figure 3**.



**Figure 2.** A schematic diagram of nanotubes formation by anodization.



**Figure 3.** Effect of the electrolyte Composition on the length of titania nanotubes formed during anodization.

It has been reported that the formation of highly oriented  $\text{TiO}_2$  nanotubes with lengths approximately ( $\approx 500$  nm) achieved by the use of the HF acidic aqueous electrolyte in the anodization of the titanium metal.<sup>30</sup> Many researchers have been paid attention to further synthesis approaches to enhance the titanium tube length and reduce the dissolution of the oxide layer on the surface of the Ti Metal in the robust acidic medium. Therefore, several studies have been conducted to replace acidic HF electrolyte with fluoride salts such as  $\text{NH}_4\text{F}$ , NaF, and KF at adjusted pH in order to increase the titanium nanotube length up to  $6 \mu\text{m}$ .<sup>31–35</sup> A novel approach was conducted to fabricate the highly oriented titania nanotubes with highly tube length that reached up to  $720 \mu\text{m}$  using the combination of non-aqueous organic electrolytes such as ethylene glycol (EG) or formamide (FA) with HF, KF, NaF,  $\text{NH}_4\text{F}$ .<sup>19,30,32–34</sup>

## Anodization and ultrasonication

Following the anodization of Ti foil, the TNTP can be formed via ultra-sonication of the pre-grown titania nanotubes followed by repetitive anodization and ultra-sonication processes until all the Ti foil has been fully converted into aligned nanotubes powder. This process is also known as two-step anodization because the metal foil is used, recycled until it is fully consumed and converted into fine tubular powders.<sup>14</sup>

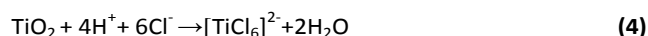
Although this method produces high surface area and well-defined structures of  $\text{TiO}_2$  tubular array, it has several drawbacks. In fact, it is considered time-consuming to extract the tubes and recycle the metal foil with extremely small yield of the powder via ultra-sonication. In other words, the electrochemical reaction takes 2 hours per one  $\text{cm}^2$  of foil to produce only 0.01 g after annealing at  $450^\circ\text{C}$ . In addition, due to the increasing temperature during ultra-sonication, the titania tubular architecture might be collapsed. Furthermore,



the tubes are usually contaminated by the electrolyte impurities, which could negatively affect their properties.<sup>14</sup>

### Rapid breakdown anodization

Using rapid breakdown anodization technique to produce TNTP is considered the simplest and most cost-effective approach because it provides high yield and can be achieved through single electrochemical anodization step. The produced TNTP can be easily used in different applications due to their high surface area and aspect ratio. As discussed before, the formation mechanism of TNTP is mainly attributed to the chemical oxidation and dissolution of the metal substrate. In the rapid breakdown anodization, chloride ions are mainly used instead of the fluoride ions in the electrolyte (e.g. perchloric acid).<sup>14</sup> During the initial phase, the oxide layer is formed through the hydrolysis of titanium metal surface. Once the electric field is applied, migration and transport of ions occurs: through the dissolution process where  $\text{Ti}^{4+}$  cations migrate toward the electrolyte solution and via the oxidation process, where oxygen anions diffuse towards the metal/oxide interface forming thick oxide layer. After that, the electrolyte resistance is increased causing anodic oxidation to be stopped. Then, the chloride anions start to dissolve the metal oxide layer forming pores that resulted from the localized breakdown of the oxide interface. The titanium dioxide white layer leaving the substrate and breakdown gradually in one dimension developing vertically oriented nanotubes in the electrolyte in the powder form as indicated by Eq. 1-4.<sup>15,16,38</sup>



The chemical interactions explained above are due to the mechanical stress established at the Ti/TiO<sub>2</sub> interface. Moreover, the strong chemical reactions between the Ti substrate and chloride ions causes hydrogen evolution at the Pt electrode.<sup>15,16</sup> A comparison between ultra-sonication, rapid break down anodization, and hydrothermal techniques is summarized in Table 1.<sup>15,16</sup> Figure 4 summarizes the factors controlling the formation of TNTP such as the applied voltage, type and concentration of the electrolyte, temperature, pH, and fabrication processing period that definitely affects the tube diameter, tube length, etching rate, homogeneity, and roughness.<sup>29</sup>

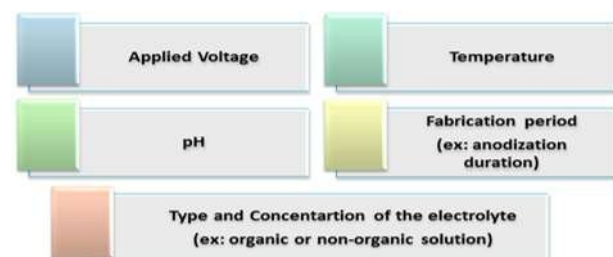


Figure 4. Factors affecting TNTP formation.

### Hydrothermal processing

The hydrothermal process is used for crystal formation and growth.<sup>39</sup> It is considered the most commonly used technique for the synthesis of TNTP due to its simplicity and high yield. Typically, amorphous TNTs are treated at high temperature in a concentrated sodium hydroxide solution.<sup>40,41</sup> According to Moazeni et al<sup>42</sup>, the formation of TNTP via hydrothermal processing involves six main steps. Initially, TiO<sub>2</sub> and NaOH are mixed and stirred for 1h then moved for ultra-sonication for another hour. The obtained suspension is then moved to a Teflon-lined autoclave to be heated for 2 days. The resulting powder is washed then aged in HCl to reach pH 2. The powder is then washed several times by

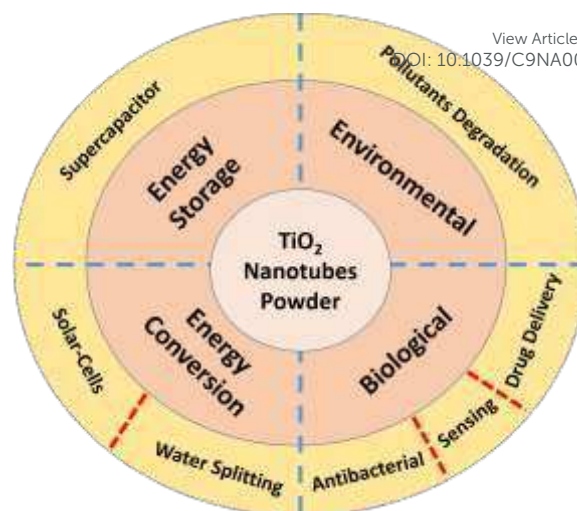
deionized water and ethanol and dried at 40 °C for one whole day. It was noted that the alkaline solution caused some of the Ti and O bonds to be broken to form lamellar fragments as the growth mechanism was attributed to slow dissolution of TiO<sub>2</sub> in a highly concentrated alkali solution. As titanate ions react with sodium from the alkali solution, they merge to form layered nanosheets. The induced mechanical stress caused by titanate ions at the borders of the sheets makes them scroll and wrap in the form of tubes.<sup>42</sup> Zeng et al<sup>43</sup> used a similar technique to produce powder nanotubes. However, instead of treating TiO<sub>2</sub> with NaOH at room temperature and stirring, they used NaOH solution inside a Teflon-lined autoclave at elevated temperature for 24h. Upon subsequent cooling of the solution, it was titrated to reach the desired pH and dried. The obtained nanotubes have outer diameter less than 10 nm and length that is less than 1 μm.<sup>43</sup> Zavala et al<sup>39</sup> investigated the effect of hydrothermal treatment, annealing temperature, and acid washing on the morphology of TiO<sub>2</sub> nanotubes. They realized that the hydrothermal treatment alters the TiO<sub>2</sub> from anatase to monoclinic phase. In addition, a temperature ranges between 400 °C and 600 °C maintained highly stable tubular structure. Increasing the temperature above 600 °C resulted in the formation of irregular nanoparticles that are larger than the precursor TiO<sub>2</sub> particles size. Moreover, the crystalline phase was changed from anatase to rutile. Finally, they proved the importance of the acid washing as the exchange of Na<sup>+</sup> ions promoted the formation of highly pure nanotubes.<sup>18,39</sup> The hydrothermal processing is considered a relatively cost-effective method that produces highly pure TiO<sub>2</sub> nanotubes. However, some drawbacks of the method should be taken into consideration, including non-uniformity, short length, and long synthesis time. However, it was shown that sonication pre-treatment would aid to increase the length of the resulting nanotubes.<sup>44</sup> Also, the stirring revolving speed



was manipulated as a mechanical force to enhance the diffusion and the reaction rate of  $\text{TiO}_2$  nanocrystals to produce longer TNTP.<sup>45,46</sup>

## Applications of TNTP

Although  $\text{TiO}_2$  nanotubes in the powder form have been used in many applications, this review is focused on the specific applications shown in **Figure 5**.



**Figure 5.** Selected TNTP Applications

**Table 1.** Comparison between the three main techniques for producing  $\text{TiO}_2$  Nanotube Powders (TNTP).

	Ultra-Sonation Technique	Rapid Breakdown Anodization	Hydrothermal Technique
<b>Advantages</b>	<ul style="list-style-type: none"> <li>- Produce aligned nanotube arrays</li> <li>- High surface area</li> <li>- Cost-effective</li> </ul>	<ul style="list-style-type: none"> <li>- Produce dispersed crystalline <math>\text{TiO}_2</math> NTs</li> <li>- High surface area</li> <li>- Cost-effective</li> <li>- High yield in few minutes.</li> </ul>	<ul style="list-style-type: none"> <li>- Produce highly pure randomly aligned <math>\text{TiO}_2</math> NTs.</li> <li>- High surface area</li> <li>- Cost-effective</li> <li>- High yield.</li> <li>- Applicable for large scale</li> </ul>
<b>Drawbacks</b>	<ul style="list-style-type: none"> <li>- Under any circumstances, the tubular structure may collapse leading to reduced surface area.</li> <li>- Very low yield (0.01 g for 1 <math>\text{cm}^2</math> of foil).</li> <li>- Time-consuming.</li> <li>- Repetitive and risky process, due to its two steps.</li> <li>- Electrolyte may contain impurities that adversely influence the biological applications.</li> </ul>	<ul style="list-style-type: none"> <li>- Need to rinse by DI water to ensure that <math>\text{TiO}_2</math> nanotubes are free of electrolyte impurities.</li> </ul>	<ul style="list-style-type: none"> <li>- Time-consuming (long processing time).</li> <li>- Chemicals-consuming.</li> <li>- Produce non-uniform TNTs.</li> <li>- Short length by default.</li> </ul>

## Biological Applications

### Drug delivery applications

$\text{TiO}_2$  nanotubes has been recently utilized to address the shortcomings of the conventional drug therapeutic solutions, particularly with the excellent physicochemical properties and



biocompatibility they possess.<sup>3</sup> As current drug therapies may suffer from short circulating time, tedious pharmacodynamics, low resistance to the gastrointestinal system, and limited drug solubility, TNTP can help providing an innovative delivery route for drugs to reach their target sites.<sup>47</sup> It is worthwhile noting that diffusion process of TNTP when implanted in the body is governed by Fick's first law. This indicates that the drug release process will be dependent on several elements such as the nanotubes charge, dimensions, surface chemistry, the drug loaded charge, molecular size, and diffusion coefficient, as well as the type of interaction between the drug molecules and TiO<sub>2</sub> inner surface, see **Figure 6**.<sup>48,49</sup> Accordingly, controlling the drug release profile is expected to depend on the fabrication and implementation conditions of TNTP. It is also of importance to mention that the most commonly drug release strategy is of the zero-order type, in which the release rate is constant regardless of the duration.<sup>48</sup> In this regard, several studies tried to modify the nanotubular structure to suite the desired therapeutic strategy. These modifications include the adjustment of their length, thickness, pore opening, or stimulating their releasing process by polymeric coatings or other external sources.<sup>50,51</sup> For instance, Aw et al found that extending the tubular length from 25-100  $\mu\text{m}$  resulted in an increase the release duration for TiO<sub>2</sub> nanotubes drug delivery implants.<sup>52</sup> Other types of drug release strategies consider varying dynamic change of the release kinetics, improving the drug loading and release patterns, multi-drug release, etc. which all were pursued in numerous studies through functionalization of the nanotubular surface.<sup>53,54</sup> For example, TiO<sub>2</sub> nanotubes functionalized by 2-carboxyethyl-phosphonic acid and organic silanes such as penta-fluorophenyl dimethyl chlorosilan and 3-aminopropyl triethoxysilane have been utilized to modify the kinetics of both drug loading and release. This was obtained by changing the hydrophilic and hydrophobic properties of the nanotubular surface, which altered the interaction mechanism between the loaded drug and its carrier, the functionalized TiO<sub>2</sub> nanotubes.<sup>55</sup> For better controlled and sustained release profiles, several studies have reported exposing TiO<sub>2</sub> nanotubes to external triggers such as ultrasound waves, radiofrequency, magnetic fields, and electric fields.<sup>56</sup> As an example, the concept of ultrasonic-sensitive systems of drug delivery has been proved by Aw et al using TiO<sub>2</sub> nanotubes. The drug-micelles release profile has shown a promising chance to be enhanced in accordance to the power intensity, pulse amplitude, length, and duration. This may be attributed to the combination of both cavitation and thermal processes triggered by the ultrasonic waves. Accordingly, better interaction between the drug loaded and TiO<sub>2</sub> nanotubes is expected.<sup>57</sup> This sort of modification would be of a significant importance in local and complex delivery systems such as in brain and stents applications. Regarding the cytotoxicity effect of anodized TiO<sub>2</sub> nanotubes on different types of cells, Li et al<sup>58</sup> have argued that the cytotoxicity of different nanostructures relies on their physiochemical factors

such as size, shape, dose, surface charge, and chemical composition. In fact, the three main factors that manage the use of metal oxides in biomedical applications are size, shape, and dose.<sup>58</sup> Chassot et al<sup>59</sup> performed a study to test the cytotoxicity of TiO<sub>2</sub> nanotubes fabricated via anodization method using Protozoan *T. pyriformis* cells for in vitro studies. The research did not observe any cytotoxicity and confirmed that TiO<sub>2</sub> nanotubes are not toxic.<sup>59</sup> However, with all these possibilities and remarkable potential for TiO<sub>2</sub> nanotube powders to be used for drug delivery systems, further ex vivo and vivo animal studies are needed to examine the long-term tolerability and cytotoxicity of the material.



**Figure 6.** Governing strategies for drug release profile using TNTP.

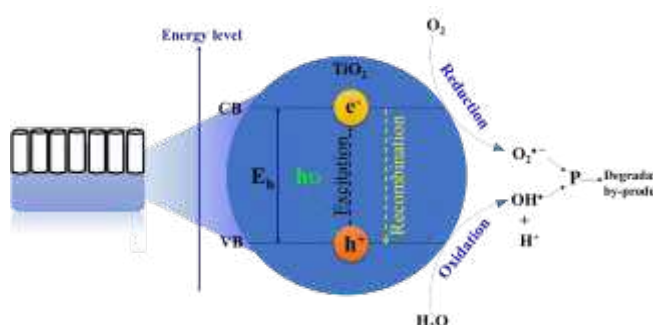
#### Antibacterial applications

A remarkable attention has been devoted to the use of TiO<sub>2</sub> nanomaterials in the field of photocatalytic bacterial disinfection.<sup>60,61</sup> TNTP, as nanostructured semiconductor materials, are potent photoactive catalysts. They were utilized for eradicating the harmful microorganisms and bacteria from water using solar irradiation.<sup>62</sup> Using its different morphologies in the nano-scale, TiO<sub>2</sub> have proven several advantages such as superior antimicrobial activity, high photo-stability (high corrosion resistance), biocompatibility, and strong photochemical oxidative activity. All



these properties have qualified  $\text{TiO}_2$  to be an excellent material for water microbial purification.<sup>63</sup> Basically, the mechanism of using TNTP for water disinfection relies on the hydroxylation reactions that start by the formation of hydroxyl radicals ( $\text{OH}^\bullet$ ). Upon light absorption by TNTP, the created electron-hole pairs trigger electrochemical redox reactions that produce free radicals such as hydroxyl radicals ( $\text{OH}^\bullet$ ).<sup>64</sup> In the aqueous medium, these active radicals are strong enough to destroy the bacterial cell wall along with different other cellular components with extremely low survival levels as shown in **Figure 7**.<sup>65</sup> Typically, these ( $\text{OH}^\bullet$ ) radicals are produced by the reactions of holes with either  $\text{H}_2\text{O}$  molecules, their hydrolysed  $\text{OH}^-$  ions, or even bacterial membrane lipids.<sup>66</sup> The radicals cause some deleterious effects on the extracellular medium of the bacteria, leading to serious chemical/biomolecular transformations. On the other hand, the electron counterparts are combined with the proton ions ( $\text{H}^+$ ) in the same physiological environment to complete the other half of the electrochemical reaction.<sup>67,68</sup>

The effect of the concentration of titania in the Lysogeny Broth (LB) nutrient medium was tested against bacterial growth of drain water. The study by Carroll et al.<sup>69</sup> has concluded that titania powder holds the ability to diminish the growth of bacterial colonies even in the dark conditions, with a reverse proportionality between the bacterial growth rate and the titania powder concentration.<sup>69</sup> Interestingly, Abbas et al.<sup>70</sup> have studied how different types of the TNTP can deactivate the growth of *Escherichia coli* (*E. coli*) in contaminated water. The TNTP studied were prepared by both hydrothermal and rapid breakdown anodization techniques, along with other titania structures. The study has revealed that the hydrothermally synthesized TNTP was the best among other titania nanostructures, resulting in the highest inactivation rate of the *E. coli* bacteria under both dark and light conditions for 120 min.<sup>70</sup> It was suggested that the hydrothermally-prepared TNTP hold a high abundance of -OH functional groups on their surfaces, mixed rutile and anatase phases, and remarkably high surface area. All these factors offered this particular structure the highest potential to result in the highest efficacy against bacterial growth in waste water.<sup>70</sup>



**Figure 7.** The principal mechanism for using TNTP in the process of water microbial disinfection

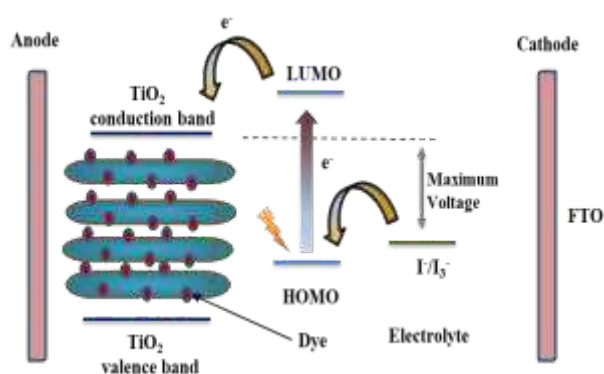
## Energy Conversion Applications

### Solar cells applications

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Vast majority of the commercially available solar cells are made from silicon with different solid state junctions. The overall conversion efficiency is varied according to whether silicon is mono- or multi-crystalline. Several approaches now are being explored attempting to achieve higher efficiencies with cost-effective materials. A promising photoelectrochemical concept is utilizing dye-sensitized  $\text{TiO}_2$  solar cells. In 1985, a Ru-based dye was adsorbed on  $\text{TiO}_2$  nanoparticles, which allowed the conversion of solar energy to electricity with 80% quantum efficiency.<sup>71</sup> Later on, Grätzel implemented the concept to fabricate a full dye-sensitized solar cell (DSSC).<sup>72</sup> The classic DSSC is mainly made of  $\text{TiO}_2$  crystalline nanoparticles attached to conductive substrate, Ru-based dye as a sensitizer, electrolyte, and platinum as a counter electrode.<sup>73</sup> A fundamental aspect of the dye selection is that the LUMO of the dye has to be energetically higher than the  $\text{TiO}_2$  conduction band. Upon exposure to sunlight, the excited electrons of the dye are injected from the LUMO into the semiconductor's conduction band (see **Figure 8**). The dye gets reduced through the redox reaction catalyzed by the electrolyte. The electrolyte is either an ionic liquid or an organic solvent. In addition to the crucial thermodynamic considerations, reaction kinetics have to be fulfilled, the electron injection from the semiconductor conduction band has to be faster than dye de-excitation, also the dye regeneration time constant has to be fast enough to minimize any depletion effects.<sup>74,75</sup> The struggle between effective electron transport within  $\text{TiO}_2$  and electron recombination possibilities is a limiting factor. Generally,  $\text{TiO}_2$  nanoparticles suffer from slow transport time constants owing to trapping/de-trapping effects. The hindered diffusion coefficient of the  $\text{TiO}_2$  nanoparticles is due to grain boundaries, defects, surface states, etc., which drastically contribute to diminished electron flow as they act as trapping sites.<sup>76,77</sup> In this regard, one-dimensional nanostructures such as TNTP can significantly improve the overall electron transport mechanism owing to limited inter-crystalline traps that lower the possibilities of recombination. However, although many types of solar cells have been produced using 1D  $\text{TiO}_2$  morphologies, the multidirectional orientations of the misaligned 1D nanostructures don't guarantee the best unidirectional flow of the electrons along the longitudinal length. The perfect 1D nanostructures provide rapid, conductive electron transport and the orientation becomes of less importance. This may apply for the single crystalline nanostructures free from defects. Current approaches tend to grow polycrystalline  $\text{TiO}_2$  nanotubes, where vertical alignment can compromise between electron transport and the charge efficiency. Anodic oxidation approaches for synthesis of self-assembled titania nanotubes is becoming of great interests.<sup>78,79</sup>





**Figure 8.** Schematic diagram for DSSC using TNTP as an anode

The sole role of  $\text{TiO}_2$  in DSSCs is to harvest the injected electrons from the dye. Although other oxides could be considered as an alternative, till now  $\text{TiO}_2$  is the best choice. TNTs synthesized via rapid breakdown anodization (RBA) lead to the formation of flower-like bundles with very high aspect ratios using perchlorate or chloride electrolytes. These TNTP show excellent performance in DSSC.<sup>80</sup> The  $\text{TiO}_2$  DSSC performance is mainly dictated by the degree of crystallinity. Upon elevating the temperature, the rutile phase dominates with possibility of collapse. Thus, anatase is phase of choice for efficient titanium-based solar cells as it is the most photoactive phase. Different groups have already reported several results but it is hard to compare these results because the overall produced efficiency is not only dictated by the intrinsic properties of the  $\text{TiO}_2$  NT but to the entire solar cell structure i.e. the actually investigated active area within the solar cell, the distance between the nanotubes, and the counter electrode.<sup>81</sup>

The effect of combining TNTP and  $\text{TiO}_2$  nanoparticles prepared via sol-gel and hydrothermal methods, respectively have been studied through measuring the performance of the solar cell. Various weight ratios of the TNTP and  $\text{TiO}_2$  nanoparticles were mixed together. The open TNTP structure facilitated better penetration of the electrolyte and enhanced the contact between the dye, tubes, and the electrolyte. The high surface area of the nanotubes and the nanoparticles enhanced the amount of adsorbed dye. The crystal property of the anatase phase was found to be the best at a hydrothermal temperature of  $150^\circ\text{C}$  for 12 h. The overall conversion efficiency of the DSSC reached 4.56 % under AM 1.5 illumination. It is worth mentioning that the photovoltaic performance of the hybrid titania nanoparticles and nanotubes showed enhanced performance than the DSSC made purely of  $\text{TiO}_2$  nanoparticles.<sup>82</sup> Also, the hybrid nanotubes and nanoparticles were tested in perovskite solar cells (PSCs). A  $(\text{CH}_3\text{NH}_3)\text{PbI}_3$  PSC based on  $\text{TiO}_2$  nanotubes and nanoparticles hybrid photo-anode was successfully constructed without affecting the nanotubular structure. The charge efficiency was maximized and the recombination rates were suppressed. In this assembled device, the nanotubes boosted the light scattering and hence absorption by the

sensitizer. The nanoparticles enhanced the adhesion of the cell components. Using carbon as a counter electrode, the conversion efficiency of the PSC reached 9.16 % under 1.5 AM illumination.<sup>83</sup> Hydrothermal annealed TNTP were sensitized with poly [2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene] (MEHPPV) as a conducting polymer used to improve the donor- acceptor mechanism for the hybrid solar cell. The different thermal treatments of the  $\text{TiO}_2$  nanotubes revealed drastic morphological, structural, electrical and optical alterations for the nanotubes, in addition to the remarkable induction of crystallinity and hence charge transfer enhancement. Here, the nanotubes act as an acceptor material and MEHPPV polymer acts as a donor material, which improved the energy conversion of the organic solar cell.<sup>84</sup> In an attempt to study the effect of different sensitizers on the efficiency of the TNTP, Zinc porphyrin-imide dye was adsorbed on the  $\text{TiO}_2$  nanotubes by immersion for 24 h. The absorption spectra of the used Zinc porphyrin-imide dye are usually seen at 439 nm and 620 nm. Upon adsorption on the  $\text{TiO}_2$  nanotubes, the peaks were shifted to 421 nm and 640 nm. The assembled DSSC showed a conversion efficiency of 1.914 % from the front side and 1.147 % from the backside.<sup>85</sup>

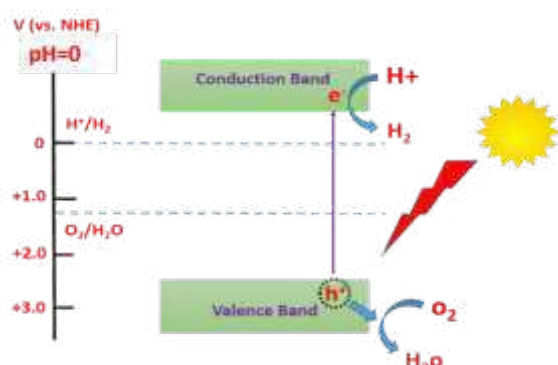
### Photocatalytic water splitting

Environmental pollution and depletion of fossil fuels have become serious issues. In this regard, enormous studies have been done to utilize a renewable energy source that should be efficient as fossil fuels but pollutant free. Harvesting solar energy has been utilized in photocatalytic hydrogen production via water splitting.<sup>86</sup> Photocatalytic processes are reactions that can be accelerated or activated by means of the absorption of photons.<sup>87</sup> Absorbed photons yield photogenerated electron/hole pairs that can derive certain redox reactions such as degradation of organic pollutants and water splitting. Among the photocatalytic materials, semiconductors are of a great interest due to their potential applications in solar energy harvesting. However, for a semiconductor to allow a certain photocatalytic reaction, it must satisfy some criteria including a relatively small band gap to harvest as much energy as possible from the solar spectrum and convert these photons to well-separated charge carriers ( $e^-/h^+$  pairs).<sup>88,89</sup> It also needs to exhibit high chemical stability in aqueous electrolytes as well as being earth abundant to be cost-effective. **Figure 9** illustrates the conditions that should be satisfied by a semiconducting material for use in solar water splitting.<sup>88</sup>

In this regard,  $\text{TiO}_2$  has been considered as an outstanding photocatalyst owing to its high chemical stability, availability, low-cost, and environmentally friendly nature. Despite all these advantages,  $\text{TiO}_2$  suffers from its restricted absorbance to the UV region of the solar spectrum as well as the fast recombination rate of the photogenerated charge carriers.<sup>90,91</sup> In order to overcome these drawbacks, the morphology of  $\text{TiO}_2$  was modified to obtain one dimensional  $\text{TiO}_2$  nanotubes that can offer an enhanced photocatalytic performance due to the enhanced separation of



photogenerated charge carriers by decoupling the direction of light absorption and charge carrier collection.<sup>92</sup> Moreover, band gap engineering via doping, decoration and/or alloying with different elements (metals or non-metals) were reported to extend its light harvesting into the visible region of the solar spectrum.<sup>93,94</sup>

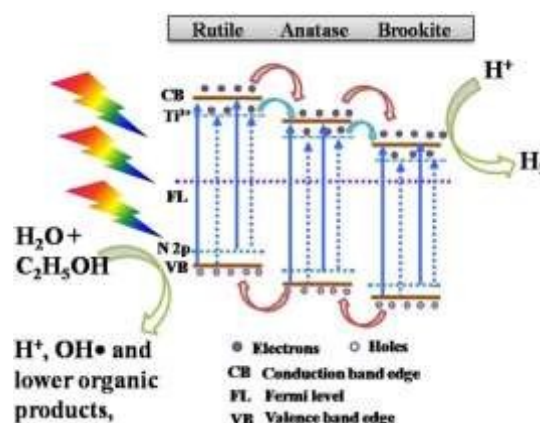


**Figure 9.** Semiconductor requirements for solar water splitting.

David et al.<sup>95</sup> reported the impact of loading TNTs, fabricated via rapid breakdown anodization, with Pt, Pd and Ni nanoparticles on the efficiency of hydrogen generation via solar water splitting. The as-prepared TNTs were annealed at 450 °C for 3h then sensitized with the metal nanoparticles through the chemical reduction approach using  $\text{NaBH}_4$ . The XRD patterns showed that all the samples exhibited pure anatase phase without any induced crystal structure modification. The metal nanoparticles were loaded on TNTs with two different concentrations, 5 wt% (noted as PtA, PdA and NiA) and 10 wt% (noted as PtB, PdB and NiB). The samples loaded with Pt and Pd nanoparticles exhibited enhanced hydrogen generation due to the created Fermi level of the metal just beneath the conduction band of the TNTs, resulting in increased life time for the photogenerated charge carriers to drive the corresponding water splitting process. At high concentration of metal NPs loading, the samples showed a decreased photocatalytic performance due to the agglomeration of the metal NPs at the active sites of the TNTs, thus preventing the penetration of light to these sites. On the other hand, sensitizing the TNTs resulted in deterioration in the hydrogen generation rate of the Ni sensitized TNTs compared to the pristine one. This behaviour was attributed to the created impurity level, which was far below the CB of the TNTs, making it difficult for the photogenerated electrons in the CB to be transferred to the Fermi level of the Ni NPs.<sup>95</sup>

For non-metal doping, Preethi et. al. showed that N-doped triphase (anatase-rutile-brookite) TNTP exhibited a superior photocatalytic activity for solar water splitting compared to the pristine triphase TNTs. This enhancement was ascribed to engineering the band gap by N-doping from 3.06 eV down to 2.87 eV, which resulted in extending the photocatalytic activity into the visible region of the solar spectrum as illustrated by the charge transfer mechanism in **Figure 10**. The pristine triphase TNTP was prepared via the rapid breakdown anodization method. While the N-doped sample was prepared by adding different concentrations

of hydrazine hydrate to the electrolyte solution, rather than annealing the pristine  $\text{TiO}_2$  in  $\text{NH}_3$  atmosphere since annealing in  $\text{NH}_3$  atmosphere resulted in the formation of N-doped biphasic TNTs. The XRD patterns confirmed that both pristine and N-doped TNTP exhibited diffraction peaks that are indexed to the three phases (anatase- rutile-brookite). Also, it was illustrated that increasing the concentration of N dopant induced phase transformation from brookite to anatase. The photocatalytic measurements revealed that doping  $\text{TiO}_2$  with nitrogen concentration of 0.29 atomic percentage exhibited the best photocatalytic performance in hydrogen production (30.2 mmol/g) via solar water splitting.<sup>94</sup>



**Figure 10.** Schematic diagram for the charge transfer mechanism in 0.29 atomic % N-doped triphase TNTPs. Reproduced from Ref. 94 with permission from Nature Publishing group under Creative Commons Attribution 4.0 International License.

## Energy Storage Applications

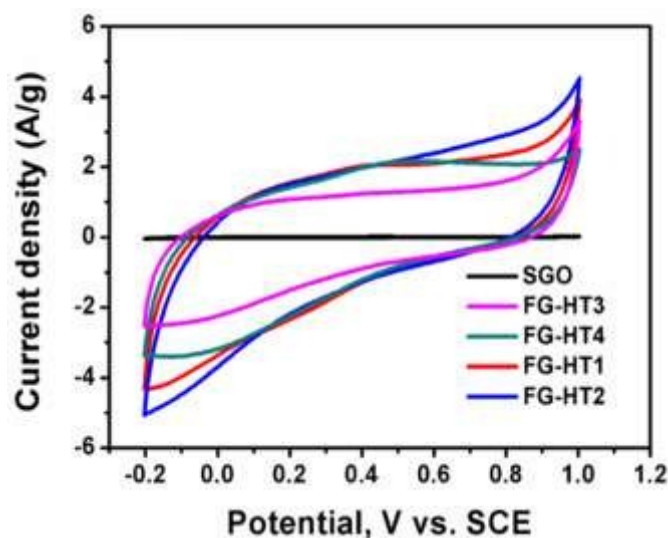
Due to the increased need for energy in our daily life, it is mandatory to fabricate long-lasting energy storage devices. In this regard, supercapacitors are considered the energy storage devices of the future. Electrochemical capacitors (EC) can store energy in the form of electrical charges.<sup>96</sup> The materials used for supercapacitors can be divided into three main categories.<sup>97–99</sup> Firstly, materials that store energy in the form of electric double layers (EDLs), which are mainly carbon allotropes such as graphite, graphene, and carbon nanotubes. Secondly, materials that store energy through a fast-redox reaction from different chemical groups such as oxides, sulfides, nitrides, or conducting polymers.<sup>100,101</sup> Thirdly, composite materials of both active and double layer materials.<sup>96,99</sup> In battery-like materials, the capacitance is subject to change over the potential window.<sup>102</sup> The process of storing energy through a redox reaction is usually referred to as “faradaic process”. In the faradaic process, a fast reversible redox reaction occurs at the surface of the electrode material resulting in adsorption of the electrolyte ions and exchange of electron charges between the electrolyte and the electrode material.<sup>96,103</sup> The surface of the material is the main factor that controls the adsorption of the ions and the charge exchange. Thus, the



morphology of the material is a good subject to be studied as it affects the mechanism and the quality of the pseudocapacitor material.<sup>103</sup>

Although  $\text{TiO}_2$  is a cheap and stable material that can undergo redox reactions, it has a relatively low conductivity, making it a poor target for supercapacitor applications. To this end several modifications have been adopted to benefit from the unique properties of  $\text{TiO}_2$ <sup>103</sup> such as its large surface area.<sup>83–87</sup> Moreover, composites of  $\text{TiO}_2$  nanotube arrays with carbon materials are getting a great attention.<sup>108,109</sup>  $\text{TiO}_2$  nanotube arrays usually have a typical rectangular cyclic voltammogram (CV), indicating pseudocapacitive behaviour.<sup>104,110</sup> In addition, it also exhibits a minor EDL behaviour that is very beneficial in charge storage.<sup>111</sup> Some studies suggest that intercalation of the  $\text{TiO}_2$  with ions in the electrolyte might lead to a battery-like behaviour.<sup>112</sup> Meanwhile,  $\text{TiO}_2$  nanotube arrays have low capacitance due to their low conductivity, which motivates researchers to induce modifications to increase its capacitance.<sup>105,110,112–114</sup> Among those modifications, is to use alternative methods to produce titania nanotubes in the powder form.<sup>115</sup> To this end, Wu et. al<sup>116</sup> used hydrogen plasma treatment for the  $\text{TiO}_2$  nanotubes in order to enhance their capacitive properties. The prepared nanotubes were removed from the surface of the Ti foil using an adhesive tape then annealed in air at 450 °C. Sequentially, the obtained nanotubes were exposed to plasma enhanced chemical vapour deposition chamber at 320 °C under vacuum. The hydrogen plasma was then introduced along with hydrogen gas flow. The resulted hydrogenated  $\text{TiO}_2$  showed a darker colour indicating more defects and it was suggested that the hydrogen atoms were used to passivate the dangling bonds in the shell layer. The phase of the resulted  $\text{TiO}_2$  was mostly anatase, which has more electrical conductivity. The electrochemical properties of the hydrogenated titania were studied in a three-electrode system in a 2M  $\text{Li}_2\text{SO}_4$  as the electrolyte, Pt. foil as the counter electrode, and Ag/AgCl as the reference electrode. The resulted CV showed a quasi-rectangular shape with a potential window of -0.3 to 0.6 V, which indicates high EDL character. The CV curve of the plasma-treated titania was 7.2 times larger than that of the titania powder without treatment. The charge/discharge specific capacitance showed that plasma treatment greatly increased the capacitance of titania nanotubes. The increase in the capacitance was ascribed to the improvement of the conductivity of titania as a result of increasing the number of charge carriers due to the increasing  $\text{Ti}^{3+}$  sites. On the other hand, Dalia El-Gendy et. al<sup>117</sup> have used a  $\text{TiO}_2$ /spongy graphene composite for supercapacitor applications. The added graphene enhanced the capacitance of the hydrogenated  $\text{TiO}_2$  powder that reached 400 F/g at 1 mV/s scan rate and increased the potential window in the positive potential region. The study showed that the  $\text{TiO}_2$  powder affected the behaviour of the cyclic voltammetry that deviated from the ideal rectangular shape of the ideal EDL electrodes. On the other hand, the study showed that the more functionalized graphene oxide added to the powdered  $\text{TiO}_2$ , the higher the specific capacitance. **Figure 11** shows the enhancement of the spongy graphene capacitance with addition of  $\text{TiO}_2$  and the enhancement of the  $\text{TiO}_2$

powder capacitance with increasing the ration of the functionalized graphene.<sup>117</sup>  $\text{TiO}_2$  powders also showed high performance upon their use in Li-ion batteries. It was shown that allowing the  $\text{TiO}_2$  to self-crystallize and relax in its best structure gives the highest diffusion possibility of Li ions into the  $\text{TiO}_2$  crystals. The amorphous cubic structure of  $\text{TiO}_2$  showed a specific energy of 200 Wh/kg at a specific power of 30 W/Kg with high stability over 600 cycles.<sup>118</sup>



**Figure 11.** Cyclic voltammograms of spongy graphene oxide and hydrogenated  $\text{TiO}_2$  with different ratios of functionalized graphene oxide. Reproduced from Ref. 117 with permission from Royal Society of Chemistry.

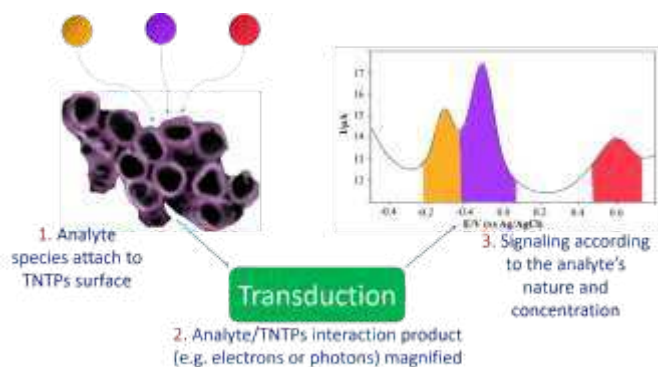
## Environmental Applications

### Sensing applications

Due to its chemical stability, biocompatibility, and remarkable catalytic properties,<sup>119</sup>  $\text{TiO}_2$  nanotubes have been utilized in different applications, particularly in the powder form.<sup>120</sup> one important example of these applications is sensing platforms, where  $\text{TiO}_2$  nanotubes can be used as a catalyst to bring the target molecules of the analyte all together on its surface to speed up the detection reaction, according to the sensing mechanism, see **Figure12**.<sup>121</sup> In brief, the nanotubular structure of titania, acting as a supporting platform, helping to increase the specific surface area of the sensor and leading to a higher probability of interaction between the target molecules and the TNTP, especially if they are functionalized with another sensitive material.<sup>122</sup> In this case, TNTP will also act as a scaffold to reduce the chances of agglomeration and increase the dispersity of the modifier, as it is usually added in minor amounts. It is worth mentioning that the thin wall thickness of TNTP plays an important role in the sensing mechanism by facilitating the pathways for charge collection after accumulation of the analyte species on the surface.<sup>122</sup> Typically, some ions may attach to the nanotubular nozzles,



while some others can be embedded onto the tubular surface. Some ions may even infiltrate inside the tubes to be adsorbed on the inner tubular walls.<sup>122</sup> This all increases the possibilities for the ionic species to be adsorbed and for their charges to be collected on the one-dimensional structure of TNTP. Accordingly, TNTP-based sensing platform can exhibit high specificity and selectivity toward the species of interest, especially with the enhanced charge collection that the tubular geometry can induce.<sup>29</sup> The sensing strategy itself can be utilized for different purposes. For instance, Abdullah et al have used TiO<sub>2</sub> nanotubes powder in a composite with reduced graphene oxide (RGO) for an environmental approach. The sensing platform was designed against Hg(II), Cu(II), and Mn(II) ions as toxic pollutants in the aquatic environment. The study achieved limit of detection (LOD) in the ppt level and showed how TiO<sub>2</sub> nanotubes enhanced the electrocatalytic activity of the composite via acting as a template to minimize the agglomeration of RGO, making use of its low band gap character.<sup>122</sup> TiO<sub>2</sub> nanotubes have been also employed to enhance the detection of other metals such as Fe(III) and La(III) by promoting the sensitivity and the ion uptake of the sensors' adsorption sites.<sup>123,124</sup> Additionally, pharmaceutical analyses have utilized TiO<sub>2</sub> nanotubes in composites to electrochemically determine the concentration of certain drugs such as metformin and benzocaine.<sup>125</sup> The LODs of both studies were as low as 3 nM each, which indicates the distinctive electrochemical properties of TiO<sub>2</sub> nanotubes for such application. Furthermore, TiO<sub>2</sub> nanotubes powder have been widely used for gas sensing applications. This includes a variety of gases such as hydrogen, acetone, and hydrogen peroxide, either using pristine or metal loaded TiO<sub>2</sub> nanotubes powder.<sup>126</sup> Recently, a study by David et al has proved the enhanced H<sub>2</sub>O<sub>2</sub> sensing properties of TiO<sub>2</sub> nanotubes powder especially when loaded with Pt. This granted the feasible pathways for electron transfer and enhanced the irreversible nature of the electrochemical reaction.<sup>126</sup> This would pave the way for further functionalization of TiO<sub>2</sub> nanotubes powder using more cost-effective and earth-abundant metals in the near future.



**Figure 12.** Schematic representation of sensing mechanism on TNTP platforms.

### TNTP for Pollutants Degradation Application:

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Due to their unique properties, TNTs have been used extensively in solid phase extraction and degradation of various pollutants in environmental and industrial applications. To be more specific, residual dyes resulting from several industries are perceived as highly undesirable organic pollutant that produce huge quantities of wastewater.<sup>127</sup> In the time being, it is very crucial to turn such wastewater into more usable resources for drinking or irrigation after either degradation or removal of pollutants. For example, **Table 2** shows contribution of reactive dyes to wastewater production due to their low fixation rates in textile industry.<sup>128</sup>

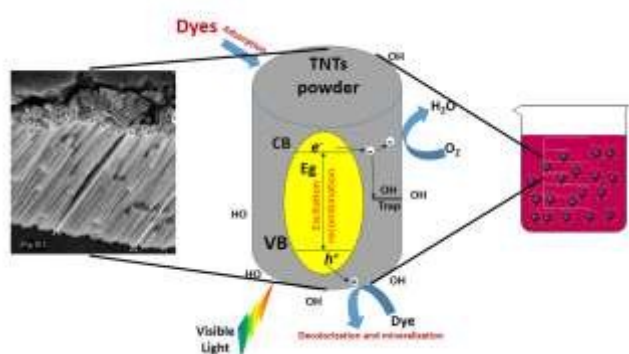
**Table 2.** Mass of dye wastewater from different types of textile dye.

Types of textile dyes	Acid	Reactive	Disperse	Direct	Vat	Basic	Sulfur
Mass of dye water (1000 tons)	20	58	18	20	8	3	40

Nonbiodegradable organic Dyes may cause wastewater to have high toxicity to humans, aquatic life and environment. Their high colour intensity may block the sun light from passing through water which creates restriction for aquatic diversity. It is widely acknowledged that the some of the released aromatic compounds in wastewater are considered toxic, carcinogenic, or mutagenic.<sup>129–131</sup> Hence, the use of such contaminated wastewater may cause humans different dermal and respiratory diseases.<sup>132</sup> The obstreperous nature of dye wastewater treatment rises from the fact that its organic compounds cannot be digested aerobically nor naturally degraded by light.<sup>133</sup> However, photocatalytic degradation of organic dye by TNTs has been of an interest due to their high photon absorption through high number of active sites.<sup>134–136</sup> In addition, the unique one-dimensional aligned structure helps in increasing photocatalytic efficiency through vertical charge transport by little losses at grain boundaries by recombination.<sup>137–139</sup> The degradation mechanism depends on the electrons and holes production upon TNT exposure to light. The produced electrons and holes help reduce O<sub>2</sub> and oxidize H<sub>2</sub>O molecules, respectively. The formed species, typically oxide ions and hydroxyl radicals, are of a powerful effect toward organic pollutants, degrading them into their primary molecules such as CO<sub>2</sub>.<sup>66</sup> A similar mechanism is proposed for the antibacterial effect of TNTP which will be discussed later on. **Figure 13** describes the principal mechanism for using TNTP in the process of environmental disinfection. In 2005, Quan et al explained the higher photo-electrochemical degradation of pentachlorophenol by TNTs in comparison with ordinary TiO<sub>2</sub> nanoparticles due to larger kinetics constant.<sup>140</sup> In addition, TNTs also proved to exhibit twice degradation efficiency as TiO<sub>2</sub> nanoparticles for acid orange dye.<sup>141</sup>



In order to reduce some of the common limitations of TNTs such as wide band gap and effectiveness to function only under UV region; significant efforts have been made to enhance TNTs photocatalytic activity by anionic/cationic doping or other techniques.<sup>142,143</sup> Different researchers proposed binary systems since it can diminish recombination while accumulating both holes and electrons in two dissimilar layers to endorse charge carriers separation.<sup>144,145</sup>



**Figure 13.** The principal mechanism for using TNTP in the process of environmental disinfection.

Although introducing impurity levels by cationic dopants might restrict migration of charge carriers if exceeded optimum value,<sup>126</sup> it can also enhance response at visible light spectrum. This can be ascribed to the decrease in the lifetime of the electron-hole pair which was explained through doped sites that may act as recombination sites for charge carrier. Similarly, anion-doped  $\text{TiO}_2$  shows a smaller bandgap than ordinary  $\text{TiO}_2$  which is attributed to the higher potential energy of nanometals that form a new VB closer to CB. It is believed that anion doping can enhance photocatalytic activity of TNTs than cationic doping in visible region, due to the impurity states close to VB reducing recombination.<sup>127</sup>

Compared to the TNTs array that is directly attached to the metal substrate, TNTP can exhibit a superior photocatalytic performance in degradation of organic pollutants. This enhancement was ascribed to the higher surface area of the later. As annealing at high temperatures of the TNT arrays attached to the Ti metal substrate leads to crystallite growth in the TNTs walls resulting in increased tube wall thickness and subsequently decreased surface area.<sup>14</sup> Another drawback that can lower the photocatalytic activity of TNT arrays attached to the Ti substrate is that the transformation from the anatase phase to the rutile one upon annealing above  $550^\circ\text{C}$ .<sup>148,149</sup> Destabilizing the anatase phase of the TNTs results in shrinking their photocatalytic activity.<sup>150,151</sup>

Jia et. al.<sup>14</sup> studied the effect of annealing temperature on the crystal structure and the photocatalytic performance of the TNTP. The TNTs was prepared via anodization technique followed by sonication in ethanol in order to remove the nanotube layer then the as prepared TNTP was subjected to different annealing temperatures ( $450$ ,  $550$ ,  $650$  and  $750$ )  $^\circ\text{C}$  for 2h in air. The SEM and XRD patterns showed that all the samples conserved the tubular

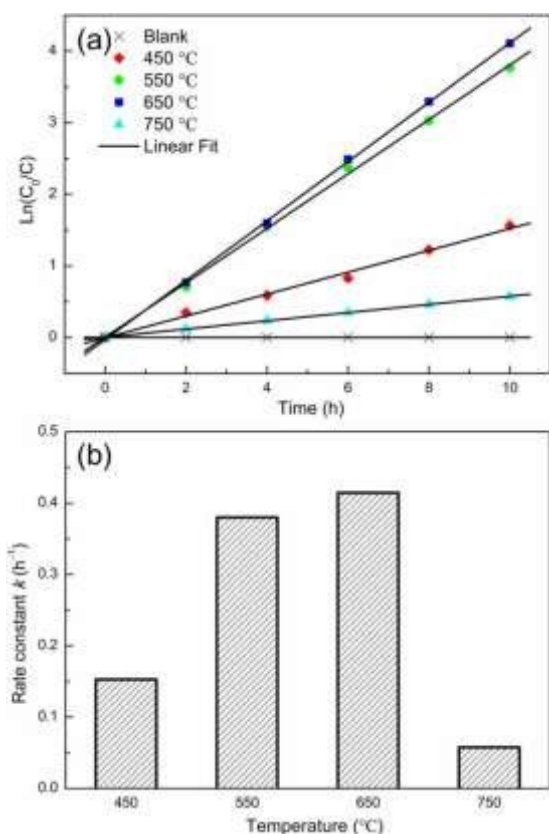
morphology and the anatase crystal structure upon annealing up to  $750^\circ\text{C}$ , respectively. Despite off the decreased specific surface area of the TNTs upon increasing the annealing temperature up to  $750^\circ\text{C}$ , the samples showed enhanced photocatalytic degradation of methylene blue upon increasing the annealing temperature up to  $650^\circ\text{C}$ . This indicates the superior effect of the enhanced crystallinity compared to the effect of the specific surface area as shown in **Figure 14**.<sup>14</sup>

Liang et al.<sup>93</sup> demonstrated the effect of doping TNTP with cobalt ions on the photocatalytic degradation of methylene blue under the UV irradiation. The co-precipitation method followed by the hydrothermal treatment was used to fabricate un-doped and Co- doped TNTP. The as-prepared samples were annealed at  $450^\circ\text{C}$  for 3h. The XRD patterns was indexed to the anatase phase and confirmed that doping with cobalt ions at low concentrations does not affect the crystal structure of the TNTs. Doping TNTs with Co ions at concentrations up to 1.3% has increased the photocatalytic degradation rate of methylene blue up to 97.2% compared to the un-doped TNTs 80.6% under the UV irradiation.<sup>93</sup>

## Conclusions & Future Perspectives

TNTP are a type of semiconducting materials that can offer a feasibly synthesis, low cost, and promising performance for a variety of applications. This review recapitulates the cutting-edge of the knowledge about TNTP developed and experimentally tested. Fabrication methods of ultra-sonication, the hydrothermal, and the rapid break down anodization have been summarized and the properties of the produced TNTP were further discussed. Effects of synthesis technique and defect structure on TNTP for biological application were reviewed. More investigation is needed to evaluate how TNTP can be better utilized as drug carriers and sensing substrates where  $\text{TiO}_2$  is currently a predominant platform. Based on the biological advantages of TNTP, using them for antibacterial approaches has been discussed. The review also demonstrated the auspicious performance of TNTP for energy conversion applications. This is expected to be more effective upon better fundamental understanding and control of TNTP structural parameters such as anchoring, sensitization, decoration and functionalization. The effect of TNTP preparation conditions on their capacitance and organic degradation applications has been also overviewed. Comparative studies between TNTP and TNT array would be useful to assess the former's efficiency under other fabrication techniques and treatment conditions such as annealing parameters, defect formation, and phase change. One of the important future insights is to synthesize mixed oxide nanotube powders to enhance the optical, electrical, and electrochemical performance of  $\text{TiO}_2$  nanotubes. Another future trend could be the development of various protocols to dope the  $\text{TiO}_2$  nanotube powders with foreign elements for various applications.





**Figure 14.** (a) Time dependent MB concentration showing the photocatalytic decomposition kinetic behaviour of the NT powders obtained at various annealing temperatures, (b) The photocatalytic rate constant. Reproduced from Ref. 14 with permission from Springer Publishing group under Creative Commons Attribution 4.0 International License.

## Conflicts of interest

The authors declare no conflict of interest.

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