

# OVERVIEW OF TiO<sub>2</sub> NANOSTRUCTURES, THEIR SYNTHESIS & POTENTIAL APPLICATIONS FOR SUSTAINABLE ENVIRONMENT

## Abstract

With the advent of nanotechnology, TiO<sub>2</sub> based nanostructures are getting eminence and hold an inimitable niche among various other nanomaterials due to their distinct physicochemical properties. Various methodologies have been used to successfully synthesize different morphologies of TiO<sub>2</sub> nanostructures including 0D, 1D, 2D and 3D depending on their dimensions in the range of nanometers. The size, shape and desired properties (i.e. thermal stability, mechanical strength, conductivity, permeability, high surface area and light emission) of nanostructures can be attained by manipulating experimental parameters including precursor solution, temperature, pH and reaction time. This chapter covers the comprehensive updated introduction of TiO<sub>2</sub> nanostructures including their classification, various forms, synthesis processes along with their pivotal significance for sustainable environment in diverse fields including photocatalytic applications in water purification, CO<sub>2</sub> reduction, water splitting, biomedical applications, lithium ion batteries and solar cells. Researchers have been exploring new insights in tailoring these nanostructures for their potential applications in sustainable environmental that will amaze us in the twenty-first century.

**Keywords:** TiO<sub>2</sub> nanostructures, 0D-TiO<sub>2</sub>, 1D-TiO<sub>2</sub>, 2D-TiO<sub>2</sub>, 3D-TiO<sub>2</sub>, Applications, photocatalysis, sustainable environmental.

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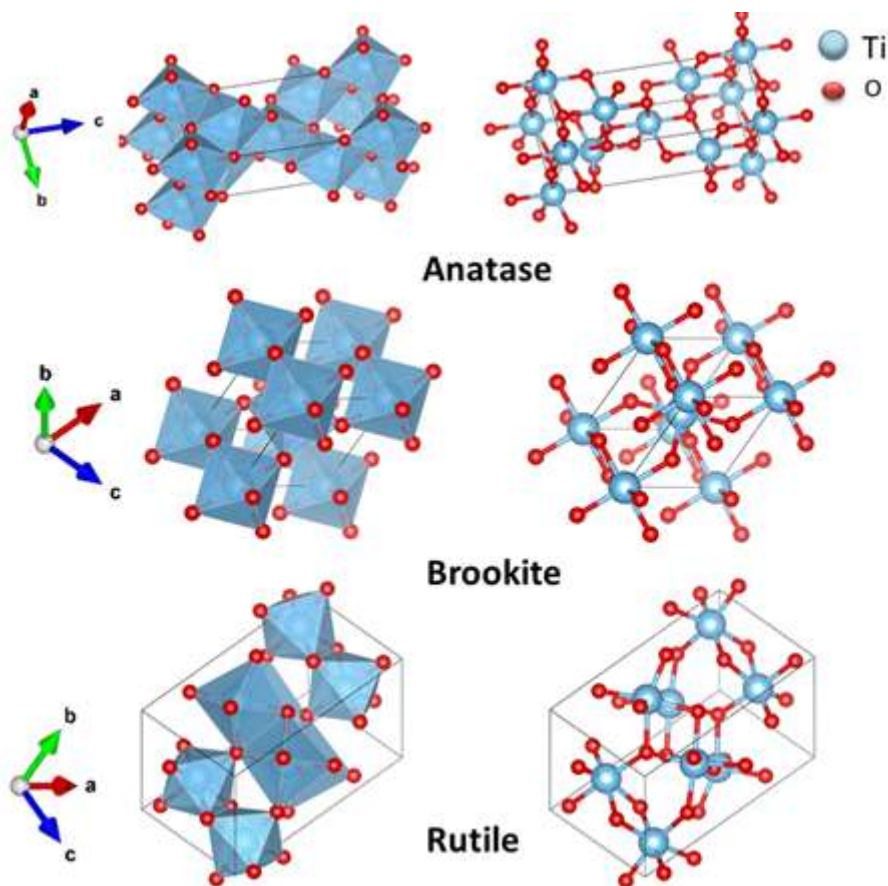
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## I. INTRODUCTION

Nanotechnology, as an innovative and multidisciplinary method, has been widely applied in every aspect of life, including environmental engineering, biology, material science, chemistry, physics and electronics etc. This term is also referred as a "platform technology" since it may easily be combined with other technologies to amend and validate existing scientific notions<sup>1</sup>. In other words, nanotechnology is the manipulation of matter at nanoscale with aim to develop novel procedures and strategies based on scientific knowledge from biomedical and industrial applications<sup>2</sup>. It allows scientists to build, manipulate, and use materials on the nanoscale scale. Various nanostructures having anticipated properties have been extensively used in several environmental applications, among them, nano-sized titanium dioxide (TiO<sub>2</sub>) has gained special interest. As science and technology advance, the semiconductor TiO<sub>2</sub>, as a representation of photocatalytic technology, appears on the horizon. William Gregor discovered titanium for the first time in 1791. Titanium (Ti), a transition metal having atomic number 22, is a light, glossy, robust, and corrosion-resistant metal having several applications in cosmetics, pharmaceutical, agriculture and sustainable environment<sup>3</sup>. TiO<sub>2</sub> based nanomaterials have advantage compared to other nanomaterials due to easy availability, less toxicity, chemical stability, economical and their competency to mineralize pollutants<sup>4-5</sup>. It can be produced in a variety of shapes, including nanotubes, nanorods, nanowires, nanofibers and nanoparticles by using various fabrication processes.

## II. NANOSTRUCTURED TITANIUM DIOXIDE

Titanium dioxide having formula TiO<sub>2</sub> is a significant binary metal oxide and it occurs naturally in three solid phases: anatase, rutile, and brookite. Anatase is a main phase of commercial TiO<sub>2</sub> and is commonly employed in various applications. Degussa P25 is a common commercial TiO<sub>2</sub> with a 4:1 anatase to rutile ratio. TiO<sub>2</sub> based nanomaterials are superior over other nanomaterials due to their mechanical robustness, low cost, chemical stability and non-toxic nature<sup>6</sup>. Overall, as per global market analysis, TiO<sub>2</sub> market is predicted to upsurge from USD 15,405.5 million (2017) to USD 20,530.1 million (2024), with 4.2% of compound annual growth rate (CAGR). Nearly 4 million tons of TiO<sub>2</sub> manufactured globally in one year, out of which 3000 tons is in the range of nano size materials<sup>7</sup>. Figure-1 shows crystal structure and Table-1 depicts the crystal arrangement and characteristics of all TiO<sub>2</sub> forms.



**Figure 1:** Different crystal forms of TiO<sub>2</sub>

**Table 1:** Different crystal structures of TiO<sub>2</sub>

Properties	Anatase	Rutile	Brookite
Crystal Structure	Tetragonal	Tetragonal	Orthorhombic
Bond angle (O-Ti-O)	81.2°-90.0°	77.7°-92.6°	77.0°-105°
Bond length (Å) Ti-O	1.93387 1.97955	- 1.94624	1.47462 - 1.93657
Lattice Constant (Å)	$a=4.5936$ $c=2.9587$	$a = 3.784$ $c = 9.515$	$a = 9.184$ $b = 5.447$ $c = 5.154$
Molecule	2	2	4
Volume/molecule (Å <sup>3</sup> )	31.2160	34.061	32.172
Density (g/cm <sup>3</sup> )	4.13	3.79	3.99

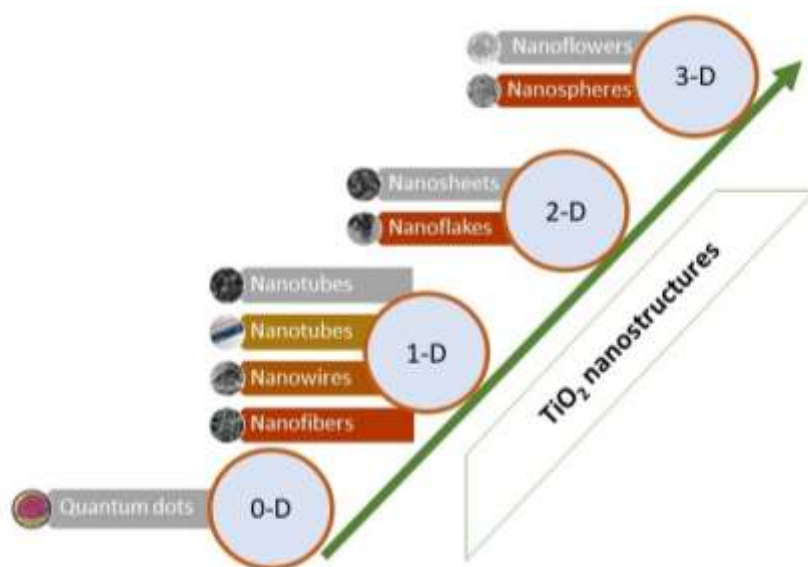
Source: <sup>8</sup>

In recent years, it's been a hot issue to accomplish the synthesis of high crystalline TiO<sub>2</sub> nanostructure with tunable properties by controlling its morphology. In this perspective, mesocrystal TiO<sub>2</sub> having incredible properties in several applications has gained attraction of many researchers<sup>7</sup>. In last few decades, research on efficient nanomaterials have been

conducted in attempt to increase their efficiency for real world problems. In this regard, TiO<sub>2</sub>-based nanostructures with efficient performance have been produced in order to minimize pollutants load. Traditional treatment technologies typically have low efficiency and high prices. However, the specific benefits of using nanoparticles (low-cost, non-toxic, reusability and stability) emerged as a potential way to save the environment from pollution. This chapter provides a comprehensive updated introduction to TiO<sub>2</sub> nanostructures, including their classification, various forms, and synthesis processes, as well as their critical role in solving numerous challenging environmental issues that humanity has faced in recent years.

### III. CLASSIFICATION OF NANOSTRUCTURED MATERIALS

Hierarchical TiO<sub>2</sub> based nanomaterials have elicited the interest of many scientists and engineers over the last few decades due to their unusual features, which have resulted in numerous breakthroughs in the field of science and technology. Various methodologies have been used to successfully synthesize TiO<sub>2</sub> nanostructures in a range of numerous morphologies such as 0D (quantum dots), 1D (nanowire, nanofibers, nanotubes, nanorods etc.), 2D (nanosheets, nanoflakes, etc.), and 3D (nanospheres, nanoflowers, etc.) as shown in Figure 2. The term one-dimensional (1D) nanostructure refers to nanocrystals with elongation over the threshold (approximately 10 nm) limited to only one direction. The characteristics of crystalline solids or even bidimensional formations vary considerably when the diameter of the nanotube, nanowire and nanorods decreases<sup>9</sup>.



**Figure 2:** Classification of TiO<sub>2</sub> nanostructures

- 1. 0-D Nanostructures:** 0-D nanostructures have all dimensions in the range of nanometer. Nanoparticles nanodots and quantum dots are some examples. Over the last few decade, a substantial progress has been attained in the synthesis of 0-D nanostructures with various innovations in chemical and physical fabrication methods (Wang et al., 2020).
- 2. Quantum Dots:** Quantum dots (QDs) are nanoscale semiconductor structures with unique quantum mechanics features. With their large surface area and extraordinary

performance, QDs have received a lot of attention for a variety of applications. When compared to bulk materials, QDs have different physical and chemical properties. The surface features of QDs have a positive impact on various applications, including solar cells, fuel cells, photocatalyst and antimicrobial activity<sup>9</sup>). For TiO<sub>2</sub> QDs synthesis, many complex technologies such as chemical vapor deposition (CVD) and ultra-high vacuum (UHV) etc. have been used. However, a simple and low-cost sol-gel approach was also reported in literature where, under visible light, the synthesized QDs were evaluated for photocatalytic degradation of different model dyes<sup>10</sup>.

- 3. 1-D Nanostructures:** 1-D nanostructures are generally the nanostructures having one dimension dominant over the others. Nanotubes, nanoneedles, nanorods and nanowires are examples of 1-D nanostructures. It is renowned that 1D nanostructures are an excellent system for studying the effect of thermal and electrical transport or mechanical properties on quantum confinement including size reduction and dimensionality. 1-D nanostructures also play a substantial role in both functional units and interconnection in the formation of nanoscale electronic, electrochemical, optoelectronic and electromechanical devices<sup>11</sup>.
- 4. Nanofibers:** Nanofibers having diameter lower than 1 μm have shown their worth in various environmental applications. There are diverse methods to produce nanofibers including nanolithography, melt blowing, self-assembly, electrospinning and template synthesis<sup>12</sup>. Among the prevailing strategies for synthesis of 1D nanofibers, electrospinning is a versatile and vastly accepted method due to its economical setup. Furthermore it is chosen over solvent casting and phase separation techniques due to larger surface to volume ratio and intra/inter fibrous pores. The morphology of synthesized nanofibers can be controlled by several parameters including solution limitations, electrospinning and ambient conditions<sup>13</sup>.
- 5. Nanowires:** Like nanorods, nanowires are cylindrical solid having circular base but with extended than nanorods. Nanowires are distinguished from nanorods by their substantially greater aspect ratio, or larger length to diameter ratio. Although nanorod and nanowire morphologies do not often have layered interior structures, their aspect ratios are comparable to nanotubes. Usually, nanowires are found in the samples of nanotubes when synthesized at higher temperature i.e. 400 °C<sup>14</sup>.
- 6. Nanotubes:** Nanotubes have different shapes, such as elongated cylinders with hollow spaces running through the middle length. Nanotubes have an aspect ratio that is normally larger than ten and sometimes can surpass several thousand. TiO<sub>2</sub> nanotube walls are frequently stacked, with layers ranging from two to ten. Nanotubes can be architecturally formed into "onion," or concentric circles. The same nanotube can also have a variable number of layers even within the two independent walls. Nanotubes are typically linear, having a relatively constant diameter. Usually, nanotubes are linear having constant diameter. However, sometimes, nanotubes with closed ends and irregular internal diameter are also found<sup>9</sup>.
- 7. Nanorods:** Nanorods are tightly packed, behaving as a single crystal that can participate in rapid electron transit, lowering the possibility of electron recombination. TiO<sub>2</sub>

nanorods have a strong quantum confinement effect, an extremely ordered structure having large surface area, which improves the charge carrier separation and increases charge transport efficacy. As a result, it is required in diverse applications in energy, environmental, and biomedical domains. Mostly for photocatalytic practices such as photocatalytic removal of organic contaminants and antimicrobial activity<sup>15</sup>.

8. **2-D Nanostructures:** The 2-D nanostructures usually have two dimensions beyond the nanometric range and therefore exhibit plane-like arrangements. They involve nanocoatings, thin films and nanolayers<sup>16</sup>.
9. **Nanosheets:** These are flake like materials with 1 to 100 nm thickness and flat surface having improved aspect ratios to reduce turbidity, providing good adherence to substrates, and improved smoothness. Fabricating TiO<sub>2</sub> nanosheets has been demonstrated an effective approach to lower the band gap in order to enhance the light harvesting which ultimately reduce the energy consumption<sup>17</sup>.
10. **Nanoflakes:** Nanoflakes or films are more porous, providing higher surface area and much more active sites as compared to nanosheets. The conventional sol-gel process is the most frequently used method for fabricating TiO<sub>2</sub> thin films using various ionic and non-ionic surfactants<sup>17</sup>.
11. **3-D Nanostructures:** The 3-D nanostructures have usually three dimensions beyond the nanometric size range. A diverse distribution of nanocrystallites, nanotubes, nanolayers, nanoparticles and group of nanowires are included in a common 3-D nanostructure. 3D nanostructures offer a wide range of uses for magnetic materials, battery electrode material and catalysis. Because the behavior of 3-D nanostructures depend on their sizes, forms, dimensions, and morphologies (the crucial variables in their performance and applications), it is essential to synthesize them in a regulated structure morphology<sup>18</sup>.
12. **Nanoflowers:** Many researchers have been intrigued by 3-D hierarchical nanostructures due to their extraordinary and uncommon features, which lead to potential applications in environment and energy fields. Titania nanoflowers (TNFL) have several advantages over typical nanoparticles, including improved charge separation, easy recovery and higher UV absorption. The TNFL's features, such as high surface area, pore structure, increased photocatalytic efficacy and optimal refractive index etc. have a wide range of applications in environmental management, air purification, sterilization, and a variety of energy applications. The self-assembly of various titania nanostructures, including nanoparticles, nanowires and nanofilms etc. results in the development of hierarchical TNFL. In general, production and relocation of photocarriers happen efficiently on a material having high surface area, resulting in better adsorption of pollutants on active sites<sup>9</sup>.
13. **Nanospheres:** Hollow spheres are emerging research areas for the development of effective photocatalysts. The porous shells of TiO<sub>2</sub> hollow structures contain high surface areas and more active sites, as well as a smaller diffusion distance of photogenerated load carriers and enhanced contact to reactants. That is why, the main factors in the development of superior TiO<sub>2</sub> hollow photocatalysts are accurate control over various properties and structure<sup>9</sup>.

#### IV. SYNTHESIS OF TiO<sub>2</sub> NANOSTRUCTURES

Some of the major techniques for the synthesis of various nanostructures have been discussed here.

- 1. Hydrothermal Synthesis:** Hydrothermal method is a widely used synthesis method for creating different nanostructures. It harnesses the precipitation and chemical reaction that occurs in a closed system under high temperature and pressure. However by manipulating various parameters including pH, temperature and precursor solution, one can get the controlled growth of TiO<sub>2</sub> nanostructures. The hydrothermal method is one of the most extensively used methods for growing shape-tailored nanostructures due to its adaptability, repeatability, controllability, large scale industrial production and low cost. Among the various nano-heterostructures (1D, 2D, and 3D), TiO<sub>2</sub> QDs based nanostructures are the least investigated for energy as well as environmental applications<sup>19</sup>. Recently, few techniques have been investigated to synthesize TiO<sub>2</sub> QDs and its different heterostructures after the innovative work by<sup>20</sup> for synthesis of TiO<sub>2</sub> nanosheets decorated with QDs through hydrothermal strategy. It resulted in higher photocatalytic efficiency associated with larger band gap of QDs and its heterostructures.

In the preparation of 1D TiO<sub>2</sub> nanostructures, different precursors including tetrabutyl titanate, titanium alkoxides, titanium ethoxide, titanium isopropoxide and titanium halides (TiF<sub>4</sub>, TiCl<sub>4</sub>) etc are used in a closed stainless steel vessel. These precursors are dissolved in alkaline or concentrated aqueous (particularly alkaline) solutions in first step and then stirred before being placed into an autoclave which is ultimately placed in a furnace at a high temperature or pressure for calcination to produce final product. It is relatively simple and economical process and different parameters including pH, pressure, temperature and solvent concentration etc. play a vital role in the synthesis and tailored properties (viscosity, thermal conductivity, heat capacity and dielectric constant etc.) of final product<sup>21</sup>. In recent times, various studies are focused on the synthesis of 2D crystals with (001) facets owing to its high reactivity by simple hydrothermal technique. By this method TiO<sub>2</sub> crystals having various shapes including elongated rhombic, truncated, spherical, rhombic, dog bone and truncated rhombic by a revised hydrothermal method using TiCl<sub>4</sub> and TiF<sub>4</sub> as capping agents<sup>19</sup>.

- 2. Solvothermal Synthesis:** The solvothermal synthesis is comparable to the previously mentioned hydrothermal technique. The main distinction is in the solvents utilized in the synthesis procedure e.g. aqueous solution in hydrothermal and organic solvents in the solvothermal synthesis<sup>22</sup>. It entails the usage of nonaqueous solvents and stainless steel autoclaves in the same manner, along with the control of numerous parameters for the production of various nanostructures. In solvothermal synthesis, Ti salt is reacted with alkaline solution yielding layered nanosheets of sodium titanate that are transformed into 1D sodium titanates in various organic solvents. The other steps are similar to hydrothermal process, followed by calcination at elevated temperature to achieve the highly crystalline and retained structure<sup>21</sup>.
- 3. Chemical Vapor Deposition:** Chemical vapor deposition (CVD) is another effective technique for the production of various nanostructures having larger surface area with uniformity and good quality. It includes the reaction between a heated substrate and a

gaseous precursor which resulted in desired product in the form of thin film on substrate<sup>23</sup>. In recent years, various advanced and modified CVD procedures have been developed. Recent advances in this sector indicate tremendous promise for large-scale production of controlled size, shape and phases of 1D TiO<sub>2</sub> nanostructures on the surface of substrate. Basically it depends on catalyzed growth employing a metal itself or its precursor via the mechanism of vapor-solid growth. For example, Ti metal or its precursors are typically used in the production of TiO<sub>2</sub> nanostructures. No doubt, CVD is an effective approach having various benefits, however, it is expensive and entails few complex experimental conditions. Nevertheless, this technique still requires some extra efforts on exploring innovative ideas in this research<sup>21</sup>.

- 4. Anodic Oxidation Synthesis:** Another significant method for production of 1D TiO<sub>2</sub> is anodic oxidation, commonly employed to produce vertically aligned doped or undoped nanostructures. Titanium alloy or foil is used as precursor material whose anodization is conducted at a constant potential in an electrochemical cell followed by a challenging cleaning step. In the process of synthesis, high voltage either oxidizes the Ti metal for generating an oxide layer, or liquefies in the electrolyte, resulting in the production of TiO<sub>2</sub> nanostructures. Whereas, H<sub>2</sub> gas is generated at the cathode. The same mechanism was explained by<sup>24</sup>. It was stated that generated oxide layer reacts with the fluorinated electrolyte, resulting in etching and the production of pores followed by methanol rinsing, drying, and calcination at a high temperature for subsequent development of vertically aligned nanostructures. The structural properties and morphology are influenced by different parameters including applied potential, temperature, anodizing time, electrolyte concentration and pH etc.<sup>21</sup>.
- 5. Electrospinning Synthesis:** Out of the other 1D nanostructures, electrospinning is a significant and unique approach for nanofibers synthesis. This approach has been used to produce nanofibers from a number of materials, including polymeric materials, nanocomposites, metals and semiconductors etc. for a variety of applications spanning from energy, biomedical sensing and environmental applications<sup>25</sup>.

This technique did not gain popularity until 1990s, after that some researchers worked on it<sup>26</sup>. This technology has now opened up new possibilities for the creation of multifunctional, large-scale and economical nanofibers for environment and energy sectors. Electrospinning was used for the first time to synthesize silica nanofibers<sup>27</sup>. Following that, variety of inorganic nanofibers (TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, ZnO, CeO<sub>2</sub> and SnO<sub>2</sub>) were electrospun for application in photocatalysis. In last few decades, various researchers have keen to fabricate and characterize electrospun nanofibers where polymer (precursor) solution consists of amorphous TiO<sub>2</sub>. After calcination at 500 °C, the synthesized nanofibers are converted into crystal forms (anatase and rutile) for effective photocatalytic activity. tetrabutyl titanate (Ti(OBu)<sub>4</sub>) and titanium-tetraisopropoxide (TTIP) can be used as TiO<sub>2</sub> precursors<sup>28</sup>. The electrospinning lab scale setup is simple and easy. To collect the nanofibers, a syringe pump, a high electric current source, and a collector made of stainless steel and connected to ground are required. By applying high electric field, an electrostatic force overcomes surface tension and results in the emission of a liquid jet that approaches to the collector in form of a Taylor cone<sup>29</sup>.

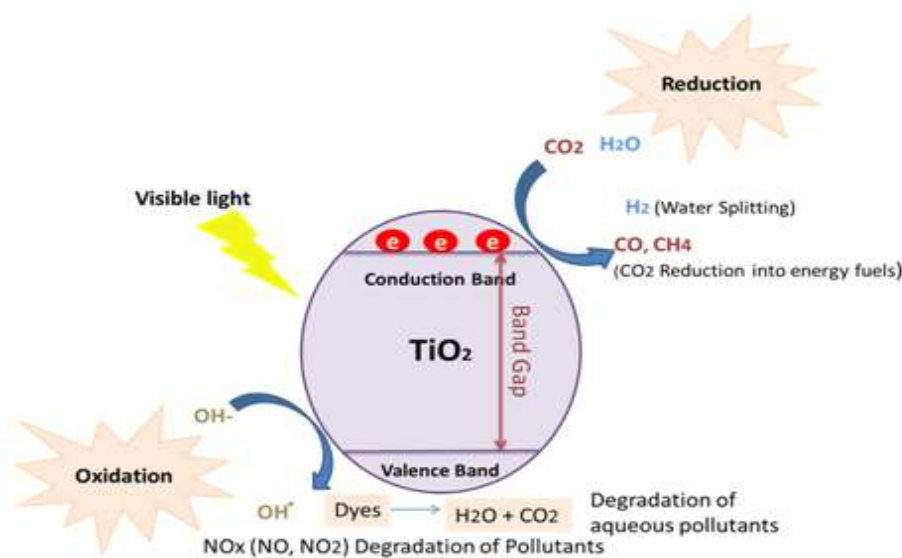
- 6. Template Assisted Method:** Another auspicious and widely used method for producing 1D TiO<sub>2</sub> nanostructures is the template assisted method. As previously discussed, the



template-assisted approach, like hydrothermal synthesis, mixes sol-gel along with pre-prepared templates. In this process, known templates can be used to synthesize nanostructures of known morphologies. The TiO<sub>2</sub>-sol is either poured into the pre-prepared templates or direct template is dipped into it. The nanostructures with controlled morphologies can be prepared with this method depending upon composition and concentration of sol, size and shape of template, deposition temperature as well as duration time. The templates can be prepared by nanoporous materials including zinc oxide, zeolite, silica and alumina. Some processes like combustion and chemical etching can be used to remove template after the completion of experiment and nanostructures like template duplicate are obtained as final product. However, atomic layer deposition is considered as best choice to control the size and shape of nanostructures in this method<sup>30</sup>.

## V. FUNDAMENTALS OF TiO<sub>2</sub> AND ASSOCIATED DRAWBACKS

From past few decades, photocatalytic degradation of organic pollutants from aqueous solutions has been widely studied<sup>31</sup>. The process of degradation starts with a photon absorption that have band gap energy greater than TiO<sub>2</sub> nanostructures having wavelength below 380 nm. This absorption resulted in the translocation of electron from valence band (VB) to conduction band (CB) followed by formation of a hole where electron-hole pair is produced. These hole-pairs can be lost promptly due to phenomenon of recombination. Only the hole-pair who is strictly trapped to surface of catalyst could be able to participate in photo-oxidation<sup>32</sup>. The electrons generated from this process produce (O<sub>2</sub>•-) anion after reaction with O<sub>2</sub> followed by the formation of H<sub>2</sub>O<sub>2</sub>. However, in the presence of electron scavenger, recombination delays which is an advantage in this process. It is assumed that HO<sub>2</sub>• radicals have competency to scavenge electron which eventually contribute in delaying recombination time. Conclusively, we can say that photogenerated holes along with reactive O<sub>2</sub> play a vital role in photocatalytic degradation of organic pollutants<sup>33</sup>. Figure 4 illustrates the whole phenomenon of photocatalytic degradation.



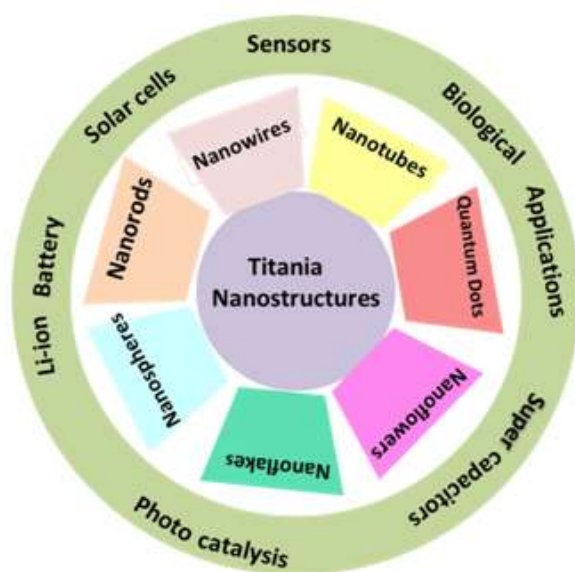
**Figure 3:** Schematic illustration of TiO<sub>2</sub> mechanism

No doubt that TiO<sub>2</sub> nanostructures have advantage over other semiconductors such as CdS, ZnO, ZnS and Fe<sub>2</sub>O<sub>3</sub><sup>34</sup>. However, various drawbacks including larger band-gap, lower photon utilization and lower quantum efficacy make it difficult to use in practical applications of wastewater treatment. Several strategies (i.e. doping and composites formation) have been utilized by researchers to overcome these issues.

## VI. APPLICATIONS OF TiO<sub>2</sub> NANOSTRUCTURES

TiO<sub>2</sub> nanomaterials due to their distinctive features have been used extensively in numerous photocatalytic applications including pollutants degradation, water splitting, CO<sub>2</sub> reduction into energy fuels, supercapacitors, solar cells as well as lithium ion batteries as shown in Figure 3. TiO<sub>2</sub>'s mechanical and photochemical qualities also mark it more appealing for usage in cosmetics (i.e. sunscreens), electronics (i.e. solar cells), and medicine (i.e. vascular stents, bone implants and dental). The increased CO<sub>2</sub> atmospheric concentration causes global warming that has drawn attention of researchers to develop solutions for CO<sub>2</sub> reduction.

The photocatalytic transformation of CO<sub>2</sub> into energy fuels can not only reduces its concentration in the atmosphere but also aids in the alleviation of energy scarcity. In this respect TiO<sub>2</sub> because of its high reduction ability, enormous surface area, high porosity, and chemical stability has been extensively used in photoreduction of CO<sub>2</sub> into energy fuels such as CH<sub>4</sub>, CO, CH<sub>3</sub>OH etc. Nanostructure titanium are potential biosensor candidates due to their moderate conductivity, high surface area, and affinity for positive metal ions in aqueous solutions. These nanostructures can also be employed as bioscaffolds for cell cultures, as they have sufficient stiffness and a large macroporous structure for cell growth and nutrition<sup>35-37</sup>. TiO<sub>2</sub> nanoparticles have also find its applications in solar cells, predominantly quantum dots sensitized, dye-sensitized and perovskite solar cells. Among 0D, 2D TiO<sub>2</sub> nanostructures, 1D TiO<sub>2</sub> nanostructures display high energy transformation efficacy due to facile transfer of electrons and high aspect ratio<sup>38</sup>.



**Figure 4:** Applications of different TiO<sub>2</sub> nanostructures

**1. Water/Wastewater Treatment using TiO<sub>2</sub>:** In recent era, how to efficiently deal with prevailing environment related challenges is the matter of great concern. Access to potable water is a major issue that must be resolve efficiently before it's too late. Among various water/wastewater treatment techniques, Advanced Oxidation Processes (AOPs) have appeared as most promising technique to eliminate water pollutants by several redox processes. The stubborn organic pollutants are removed by utilizing OH· radicals (a strong oxidizing factor) and effective oxidants through direct or indirect approaches<sup>39</sup>. The generation of hydroxyl radicals is initiated in the presence of power sources such as ultrasonic, heat and ultraviolet radiations. Conclusively, among various AOPs (electrochemistry, Fenton, ultrasound and ozonation etc.), Photocatalysis is thought to be one of the most promising advanced oxidation-reduction processes for improving water quality by decomposing organic and inorganic contaminants. 1D TiO<sub>2</sub> nanostructures in comparison to 0D and 2D have efficient electronic charge properties and higher surface area that is why widely used in nanodevices, water splitting and photocatalysis<sup>40</sup>.

TiO<sub>2</sub> nanoparticles have a long history of use in photocatalysis. However, their efficiency depends on surface area, type of crystal structure, band gap and doping of different metals. A number of strategies are being developed to optimize these properties of TiO<sub>2</sub> nanoparticles. In a previous study, the effect of shape and size of 0-D and 1-D TiO<sub>2</sub> nanorods for photocatalytic degradation of red amaranth toxic dye was investigated. According to research findings, the crystal structure of nanorods was improved followed by enhanced efficiency through sodium elimination. It was concluded that this kind of nanomaterials are appropriate candidates with little modification of dye solution with acid<sup>41</sup>. In another study, TiO<sub>2</sub> suspension was used for photocatalytic degradation of three different types of textile dyes under mercury lamp. Different dyes behave different degradation behavior under the same experimental conditions. It was expected that various factors are responsible for this kind of degradation including pH, oxygen flux, temperature, dye concentration, inorganic ions, irradiation time and catalyst dose. The reduction in chemical oxygen demand (COD) was indication of complete mineralization<sup>42</sup>.

The oxidative mineralization of textile effluent coming from industry was also examined under UV radiation using TiO<sub>2</sub> in slurry. In a result, 40-90% COD removal was observed after 4hrs. Other crystalline form of TiO<sub>2</sub> (rutile and anatase) were also investigated and anatase exhibited more pronounced photocatalytic efficiency as compared to rutile. Also the acidic conditions exhibited efficient degradation rate in H<sub>2</sub>O<sub>2</sub> presence. Besides this, TiO<sub>2</sub> does not lost its catalytic efficiency even after three consecutive runs. Finally, this photocatalyst was used to estimate the ecotoxicity of marine bacteria named *Vibrio fischeri* which was reduced completely followed by photocatalytic oxidation<sup>43</sup>.

TiO<sub>2</sub> can be used as thin films or in suspension in photocatalytic degradation. No doubt, that TiO<sub>2</sub> in the presence of UV irradiation is an effective approach for mixed wastewater (textile and municipal effluent) in terms of color removal, antimicrobial efficiency and mineralization of organic compounds<sup>44</sup>. It is reported that UV-TiO<sub>2</sub> in a batch reactor can effectively remove dye color and COD from textile wastewater prepared in lab having wetting agents, sodium chloride (NaCl) and sodium hydroxide (NaOH). However, a reactor coated with thin films of TiO<sub>2</sub> exhibited efficient results as compared

to one without coating. That is why the reactors coated with TiO<sub>2</sub> films have gained attention to many researchers<sup>45</sup>. Some of the studies on different TiO<sub>2</sub> nanostructures synthesized and modified for their application in photocatalytic degradation of aqueous pollutants are summarized in the below.

**Table 2: Overview of several TiO<sub>2</sub> based photocatalysts, their synthesis approach and application in water treatment**

Precursors	Synthesis	Applications	Reference
TiO <sub>2</sub> nanotube arrays	Heterogeneous solvothermal synthesis	Photocatalytic activity under UV light	[ <sup>46-47</sup> ]
Cellulose acetate/TiO <sub>2</sub> ultrafine fiber	Electrospinning	Water treatment under UV light	[ <sup>48</sup> ]
Ag/TiO <sub>2</sub> nanotubes composite	Hydrothermal method	Photocatalytic activity of rhodamine B	[ <sup>49</sup> ]
TiO <sub>2</sub> @carbon core/shell nanofibers (TiO <sub>2</sub> @C NFs)	Electrospinning technique and hydrothermal method	Photodegradation of RhB	[ <sup>50</sup> ]
p-n Cu <sub>2</sub> O/TiO <sub>2</sub> NTAs	Electrodeposition method	Photodegradation of methyl orange	[ <sup>51</sup> ]
Titanate nanotubes	Annealing	Reduction of Cr(VI) to Cr(III) in contaminated water	[ <sup>52-53</sup> ]
TiO <sub>2</sub> nanosheets with Mn <sub>x</sub> O <sub>y</sub> nanoparticles	One-pot hydrothermal method.	Photocatalytic degradation of Cr in the presence of visible light	[ <sup>54</sup> ].
TiO <sub>2</sub> nanomaterials coupled with Au, N, CdS etc.	Electrochemical anodization	Photocatalytic and photoelectrocatalytic activity	[ <sup>55-57</sup> ]

- 2. Lithium-ion Batteries:** Rechargeable lithium ion batteries are in rising demand because of sustainability, consumption in household electronics and vehicles. As a result, in order to meet rising demand, various transition metal oxides are being investigated in order to obtain outstanding electrochemical properties, as graphite, a traditional anode material, has several drawbacks. The drawbacks of graphite include low operating voltage, which leads to lithium dendrite formation, which can result in an internal short circuit. Moreover, problems of structure collapse and exfoliation arises with cycling that leads to rapid capacity fading<sup>58</sup>. A number of materials, notably lithium-metal alloys (Li<sub>x</sub>M where, M = Sn, Al, Ga, Ge, Pb, Sb, etc.) and transition metal oxides (MO, M = Ti, Sn, etc.) have been offered as promising candidate for the negative electrode in lithium ion batteries. Because of their immense structural stability, TiO<sub>2</sub>-based materials are being pioneered as negative electrodes capable of overcoming the shortcomings of graphite (Figure 6). Furthermore, because of the higher delithiation potential (1.7 V vs. Li/Li+), the production of lithium dendrites is successfully prevented, making TiO<sub>2</sub> a safe anode material suitable for a variety of applications<sup>59</sup>. These features are highly required in order to mass-produce LIBs suited for mobile and stationary storage applications.



**Figure 5:** Titania based nanostructures as electrodes in lithium ion batteries

Nevertheless, the poor electrical conductivity, low ionic diffusivity, and low theoretical capacity of TiO<sub>2</sub> (335 mAh g<sup>-1</sup>) are the main obstacles hindering the production of high-performance LIBs with titania anodes. Furthermore, they are plentiful, environmentally benign, and obtained through cost-effective production ways. Moreover, TiO<sub>2</sub> nanostructures have good safety and mesoporous structure which leads to effective transport of lithium ions<sup>60</sup>. Particularly 1D TiO<sub>2</sub> nanowires and nanotubes possess an open layered assembly with a significantly greater interlayer spacing, which makes them excellent aspirants to deliver rapid diffusion channels for reversible lithium ion intercalation and deintercalation, hence high value of charge/discharge capacity. There have been an ongoing effort by the scientists to improve the specific capacity, rate capability and safety for TiO<sub>2</sub> based anode materials. For this purpose various materials engineering strategies both intrinsic and extrinsic have been used to achieve high performance LIBs. For the alleviation of poor electronic and Li ion diffusion kinetics intrinsic tuning of properties and extrinsically hybridization with other compounds are the different approaches that are being applied. Intrinsic engineering strategies include size tailoring, morphology optimization, facet control and electronic structure manipulation<sup>61</sup>. Extrinsic engineering strategies for TiO<sub>2</sub> to achieve high performance LIBs include carbon coating, conductive network design, conductive agent hybrid strategy and mechanical support such as preparation of TiO<sub>2</sub>(B) nanowires by Armstrong et al displayed initial discharge capacities of 230 mA·h·g<sup>-1</sup> at current densities of 50 mA·g<sup>-1</sup><sup>61-62</sup>.

To address these constraints, one viable technique is to reasonably integrate two or more components, i.e., decorate the 1D backbone with additional metal oxide to produce branched arrays. A study investigated various 3D branched titania nanostructures (BTNs) for energy storage applications. The hybrid construction is advantageous in that it can play synergistic functions of reducing volume expansion and increasing capacity<sup>63</sup>. The 1D TiO<sub>2</sub> backbones not only accelerates lithium ion transport but also increases electrode/electrolyte interfacial contact. Crystal S. Lewis and colleagues investigated the influence of different hydrothermally produced titania morphologies on anode material performance<sup>64</sup>. The surface area of 0D commercial nanoparticles (Degussa P25) was

compared to that of as-prepared 1D and 3D materials. Electrochemical research demonstrated that hydrothermally produced 3D urchin-like motifs outperformed both as-prepared 0D and 1D samples, as well as commercial Degussa P25. This shows that shape, rather than surface area, is more important in determining the efficacy of the Li ion diffusion process. The 3D urchins, in particular, demonstrated consistent rate capabilities, delivering 214, 167, 120, 99, and 52 mAh/g at matching discharge rates of 0.1, 1, 10, 20, and 50 C, respectively. Furthermore, these 3D patterns also showed good cycling performance, with a capacity retention of 90% in cycles 1100 at a discharge rate of 1 C. TNT outperforms its rivals in many 1D topologies due to its hollow nature with inner free space. For example, Fan and colleagues created TNT@SnO<sub>2</sub> nanoflake core-branch arrays with significantly greater charge and discharge capabilities than the standard SnO<sub>2</sub> powder electrode. Specifically, the core-branch array-based electrode retained a high capacity of roughly 580 mA h g<sup>-1</sup> (at a current density of 1.6 A g<sup>-1</sup>) after 50 cycles, but the commercial SnO<sub>2</sub> powder electrode nearly dropped to zero capacity<sup>65</sup>. The same group also developed TNT@Fe<sub>2</sub>O<sub>3</sub> nanospikes core-shell nanoarrays for LIBs applications. Fe<sub>2</sub>O<sub>3</sub> nanospikes were appropriately connected with the TNT backbone, in which case the shell can ensure high capacity while the core can maintain cyclic stability and provide a direct channel for charge transfer. The core-shell branched TiO<sub>2</sub>@Fe<sub>2</sub>O<sub>3</sub>-based LIB anodes demonstrated significant initial discharge and charge capacities due to their combined advantages. At a current density of 200 mA g, an extraordinarily steady capacity retention of 520 mA h g<sup>-1</sup> was achieved after 200 cycles. Furthermore, to improve the Li-ion diffusivity and electronic conductivity, heteroatom doping and coupling of TiO<sub>2</sub> with other materials (MoS<sub>2</sub>, MoO<sub>3</sub>, MnO<sub>2</sub>, SnO<sub>2</sub> etc.) to prepare TiO<sub>2</sub> hybrid nanostructures has proven effective strategies for the facile transportation of Li ions and electrons<sup>66-71</sup>. TiO<sub>2</sub> has low conductivity and slow Li<sup>+</sup> diffusion. To address these problems, particle size reduction and doping are thought to be promising techniques. To manufacture manganese-doped titanium dioxide with an anatase structure (Mn/Ti = 0.05; 0.1; 0.2), a template-assisted sol-gel technique was developed<sup>72</sup>. Mn<sup>3+</sup> ions replace Ti<sup>4+</sup> ions to generate Ti<sub>1-x</sub>Mn<sub>x</sub>O<sub>2</sub> solid solutions with an extend lattice. Ti<sub>0.95</sub>Mn<sub>0.05</sub>O<sub>2</sub> demonstrated the best lithium storage behavior in LIBs, with a capacity of around 113 mAh g<sup>-1</sup> after 118 charge/discharge cycles at 1C. Even at a rate of 2C, the Ti<sub>0.95</sub>Mn<sub>0.05</sub>O<sub>2</sub> electrode provided a reversible capacity of around 121 mAh g<sup>-1</sup>. This improved battery performance could be due to increased Li<sup>+</sup> diffusion, improved electron transport, and improved anatase lattice stability during lithiation/delithiation<sup>72</sup>. Some of the studies reported for titania nanostructures and composites for their applications in lithium ion batteries are summarized in the below table.

**Table 3: Different TiO<sub>2</sub> nanostructures/composites and their storage capacities for lithium ion batteries**

Materials	Storage capacities	Reference
TiO <sub>2</sub> without CNTs TiO <sub>2</sub> /CNTs	62 mAh g <sup>-1</sup> at the current density of 5,000 mA g <sup>-1</sup> 238 mAh g <sup>-1</sup> at current density of 5,000 mA g <sup>-1</sup>	[ <sup>73</sup> ]
TiO <sub>2</sub> /graphene composites	130 mAh g <sup>-1</sup> at 12 C	[ <sup>59</sup> ]

TiO <sub>2</sub> hollow nanofibers (HNFs) TiO <sub>2</sub> HNF-400	152 mA h g <sup>-1</sup> at the current density of 185 mA g <sup>-1</sup>	[ <sup>74</sup> ]
Hydrogen titanate nanowires and nanotubes electrodes	296.6 and 282 mA h g <sup>-1</sup> at current densities of 0.3 and 0.24 A g <sup>-1</sup>	[ <sup>75</sup> ]
TiO <sub>2</sub> (B) nanowires	305 mA h g <sup>-1</sup> at a current density of 0.5 A g <sup>-1</sup> ,	[ <sup>75</sup> ]
Co-doped TiO <sub>2</sub> nanoparticles	167 mAh g <sup>-1</sup> at the 0.5C current density	[ <sup>76</sup> ]
bicontinuous titania scaffold	254 mAh·g <sup>-1</sup> at the current density of 1 A·g <sup>-1</sup>	[ <sup>77</sup> ]
TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub> composite	686 mAh g <sup>-1</sup> at a current rate of 100 mA g <sup>-1</sup>	[ <sup>78</sup> ]

## VII. CONCLUSIONS AND FUTURE PERSPECTIVES

In the past few years, TiO<sub>2</sub> based nanostructures hold a unique place in the arena of nanotechnology over other conventional nanostructures due to their unique properties and superior performance in different fields of science and technology. This chapter is proposed to overview the inclusive information of hierarchical TiO<sub>2</sub> based nanomaterials along with their synthesis approaches and various applications for sustainable environment. Some notable examples of these nanostructures for sustainable environment includes, catalysis, pollutants degradation, smart coatings, fuel cells and plant growth etc. No doubt, the future of these nanostructures seems to be progressing with advancement in nanotechnology both in terms of precision and efficiency. However, the advance study in nanotechnology compels a dynamic power in commercialization and expansion of innovative technologies in future.

TiO<sub>2</sub> nanostructures having a larger band gap, utilize solar radiations in its all applications. This is the main hindrance in the use of these nanostructures. However, the researchers are trying to overcome this issue by making composites, doping with suitable materials and innovative structural designs. These strategies might be helpful in minimizing the limitations associated to these TiO<sub>2</sub> based nanostructures. In this context, various cost effective and innovative synthetic methodologies are expected to step in this platform technology. In other words, we can say that highly stable and cost effective strategies to produce environment friendly nanomaterials with controllable properties in terms of light harvesting are required to fulfill our future demands. Conclusively, the future of TiO<sub>2</sub> based nanomaterials seems bright and researchers from various domains have been trying to find new visions in order to explore their potential applications which will astonish us in this new era.

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