Overview of TiO_2 nanostructures, their synthesis & potential applications for sustainable environment

Zunaira Habib[a], **Sadaf Ikram**[b,c]

[a]*Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Islamabad*

[b]*Quaid-i-Azam University Islamabad, Pakistan*

[c] *Rawalpindi Women University, Rawalpindi*

Abstract: With the advent of nanotechnology, TiO_2 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_2 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_2 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_2 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_2 nanostructures, 0D-TiO_2, 1D-TiO_2, 2D-TiO_2, 3D-TiO_2, Applications, photocatalysis, sustainable environmental.

Table of Contents

Introduction 3

Nanostructured titanium dioxide 3

Classification of Nanostructured Materials 5

1.1 0-D nanostructures 6

1.1.1 Quantum Dots 6

1.2 1-D nanostructures 7

1.2.1 Nanofibers 7

1.2.2 Nanowires 7

1.2.3 Nanotubes 8

1.2.4 Nanorods 8

1.3 2-D nanostructures 8

1.3.1 Nanosheets 8

1.3.2 Nanoflakes 9

1.4 3-D nanostructures 9

1.4.1 Nanoflowers 9

1.4.2 Nanospheres 9

Synthesis of TiO_2 Nanostructures 10

1.5 Hydrothermal Synthesis 10

1.6 Solvothermal Synthesis 11

1.7 Chemical vapor deposition 11

1.8 Anodic oxidation synthesis 11

1.9 Electrospinning Synthesis 12

1.10 Template assisted method 13

Fundamentals of TiO_2 and associated drawbacks 13

Applications of TiO_2 nanostructures 14

1.11 Water/wastewater treatment using TiO_2 15

1.12 Lithium-ion batteries 18

Table 3: Different TiO_2 nanostructures/composites and their storage capacities for lithium ion batteries 21

Conclusions and Future Perspectives 21

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[1]. 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[2]. It allows scientists to build, manipulate, and use materials on the nanoscale scale. Various nanostructures having anticipated properies have been extensively used in several environmental applications, among them, nano-sized titanium dioxide (TiO_2) has gained special interest. As science and technology advance, the semiconductor TiO_2, 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[3]. TiO_2 based nanomaterials have advantage compared to other nanomaterials due to easy availability, less toxicity, chemical stability, economical and their competency to mineralize pollutants[4-5]. It can be produced in a variety of shapes, including nanotubes, nanorods, nanowires, nanofibers and nanoparticles by using various fabrication processes.

Nanostructured titanium dioxide

Titanium dioxide having formula TiO_2 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_2 and is commonly employed in various applications. Degussa P25 is a common commercial TiO_2 with a 4:1 anatase to rutile ratio. TiO_2 based nanomaterials are superior over other nanomaterials due to their mechanical robustness, low cost, chemical stability and non-toxic nature[6]. Overall, as per global market analysis, TiO_2 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). Nearby 4 million tons of TiO_2 manufactured globally in one year, out of which 3000 tons is in the range of nano size materials[7]. Figure-1 shows crystal structure and Table-1 depicts the crystal arrangement and characteristics of all TiO_2 forms.

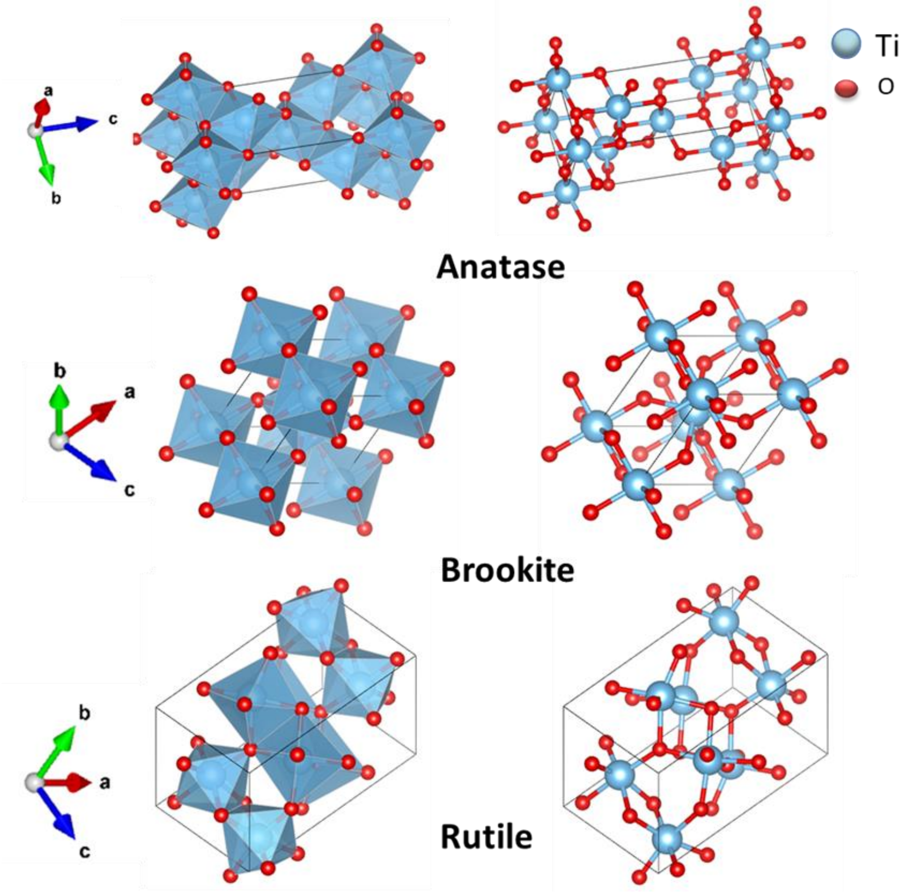

Figure 1: Different crystal forms of TiO_2

Table 1: Different crystal structures of TiO_2

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 (Å3)	31.2160	34.061	32.172
Density (g/cm^3)	4.13	3.79	3.99

Source: [8]

In recent years, it's been a hot issue to accomplish the synthesis of high crystalline TiO_2 nanostructure with tunable properties by controlling its morphology. In this perspective, mesocrystal TiO_2 having incredible properties in several applications has gained attraction of many researchers [7]. In last few decades, research on efficient nanomaterilas have been conducted in attempt to increase their efficiency for real world problems. In this regard, TiO_2-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_2 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.

Classification of Nanostructured Materials

Hierarchical TiO_2 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_2 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[9].

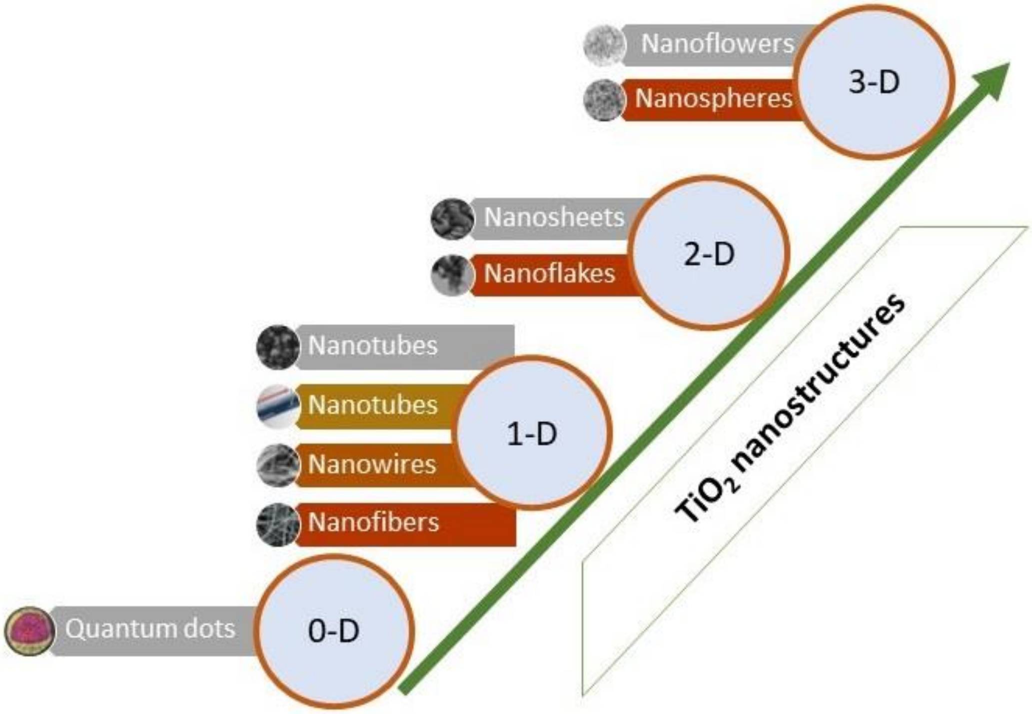

Figure 2: Classification of TiO_2 nanostructures

1.1 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).

1.1.1 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 [9]). For TiO_2 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 [10].

1.2 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 [11].

1.2.1 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[12]. 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 [13].

1.2.2 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 [14].

1.2.3 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_2 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 [9].

1.2.4 Nanorods

Nanorods are tightly packed, behaving as a single crystal that can participate in rapid electron transit, lowering the possibility of electron recombination. TiO_2 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[15].

1.3 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 [16].

1.3.1 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_2 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 [17].

1.3.2 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_2 thin films using various ionic and non-ionic surfactants[17].

1.4 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[18].

1.4.1 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[9].

1.4.2 Nanospheres

Hollow spheres are emerging research areas for the development of effective photocatalysts. The porous shells of TiO_2 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_2 hollow photocatalysts are accurate control over various properties and structure[9].

Synthesis of TiO_2 Nanostructures

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

1.5 Hydrothermal Synthesis

Hydrotthermal method is a widely used synthesis method for creating different nanostructurs. 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_2 nanosrtuctures. 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_2 QDs based nanostructures are the least investigated for energy as well as environmental applications [19].Recently, few techniques have been investigated to synthesize TiO_2 QDs and its different heterostructures after the innovative work by [20] for synthesis of TiO_2 nanosheets decorated with QDs through hydrothermal strategy. It resulted in higherphotocatalytic efficiency associated with larger band gap of QDs and its heterostructures.

In the preparation of 1D TiO_2 nanostructures, different precursors including tetrabutyl titanate, titanium alkoxides, titanium ethoxide, titanium isopropoxide and titanium halides (TiF_4, $TiCl_4$) 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 [21]. 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_2 crystals having various shapes including elongated rhombic, truncated, spherical, rhombic, dog bone and truncated rhombic by a revised hydrothermal method using $TiCl_4$ and TiF_4 as capping agents [19].

1.6 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 [22]. 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[21].

1.7 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 [23]. 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_2 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_2 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 [21].

1.8 Anodic oxidation synthesis

Another significant method for production of 1D TiO_2 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 oxides the Ti metal for generating an oxide layer, or liquefies in the electrolyte, resulting in the production of TiO_2 nanostructures. Whereas, H_2 gas is generated at the cathode. The same mechanism was explained by [24]. 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. [21].

1.9 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 [25].

This technique did not gain popularity until 1990s, after that some researchers worked on it [26]. 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 [27]. Following that, variety of inorganic nanofibers (TiO_2, Fe_2O_3, WO_3, ZnO, CeO_2 and SnO_2) 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_2. After calcination at 500 ^{o}C, the synthesized nanofibers are converted into crystal forms (anatase and rutile) for effective photocatalytic activity. tetrabutyl titanate ($Ti(OBu)_4$) and titanium-tetraisopropoxide (TTIP) can be used as TiO_2 precursors [28]. 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 steainless stell 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[29].

1.10 Template assisted method

Another auspicious and widely used method for producing 1D TiO_2 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_2-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 [30].

Fundamentals of TiO_2 and associated drawbacks

From past few decades, photocatalytic degradation of organic pollutants from aqueous solutions has been widely studied [31]. The process of degradation starts with a photon absorption that have band gap energy greater than TiO2 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 [32] . The electrons generated from this process produce (O_2•-) anion after reaction with O_2 followed by the formation of H_2O_2. However, in the presence of electron scavenger, recombination delays which is an advantage in this process. It is assumed that HO_2• radicals have competency to scavenge electron which eventually contribute in delaying recombination time. Conclusively, we can say that photogenerated holes along with reactive O_2 play a vital role in photocatalytic degradation of organic pollutants[33]. Figure 4 illustrates the whole phenomenon of photocatalytic degradation.

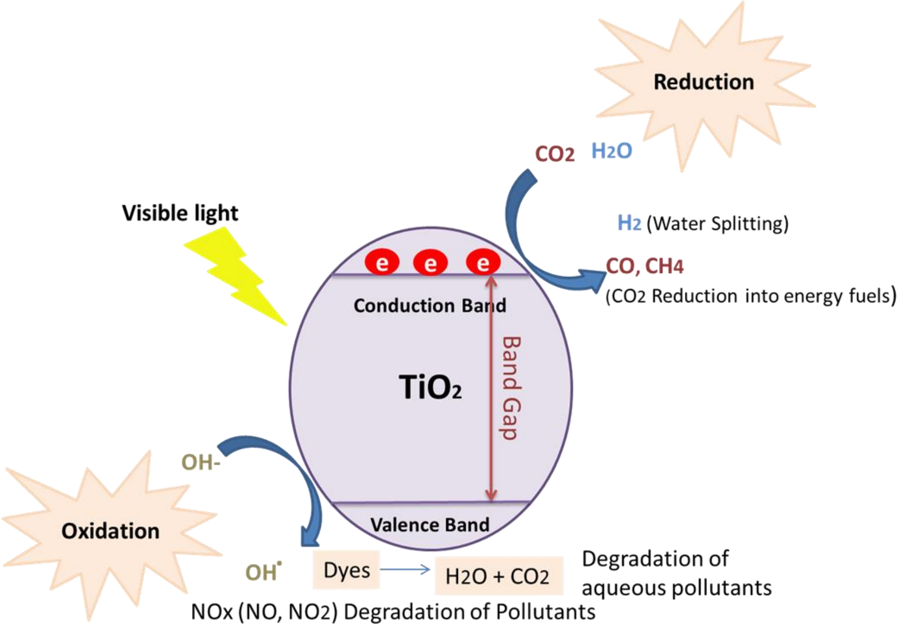

Figure 3: Schematic illustration of TiO_2 mechanism

No doubt that TiO_2 nanostructures have advantage over other semiconductors such as Cds, ZnO, ZnS and Fe_2O_3 [34]. 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.

Applications of TiO_2 nanostructures

TiO_2 nanomaterials due to their distinctive features have been used extensively in numerous photocatalytic applications including pollutants degradation, water splitting, CO_2 reduction into energy fuels, supercapacitors, solar cells as well as lithium ion batteries as shown in Figure 3. TiO_2'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_2 atmospheric concentration causes global warming that has drawn attention of researchers to develop solutions for CO_2 reduction.

The photocatalytic transformation of CO_2 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_2 because of its high reduction ability, enormous surface area, high porosity, and chemical stability has been extensively used in photoreduction of CO_2 into energy fuels such as CH_4, CO, CH_3OH 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[35-37]. TiO_2 nanoparticles have also find its applications in solar cells, predominantly quantum dots sensitized, dye-sensitized and perovskite solar cells. Among 0D, 2D TiO_2 nanostructures, 1D TiO_2 nanostructures display high energy transformation efficacy due to facile transfer of electrons and high aspect ratio[38].

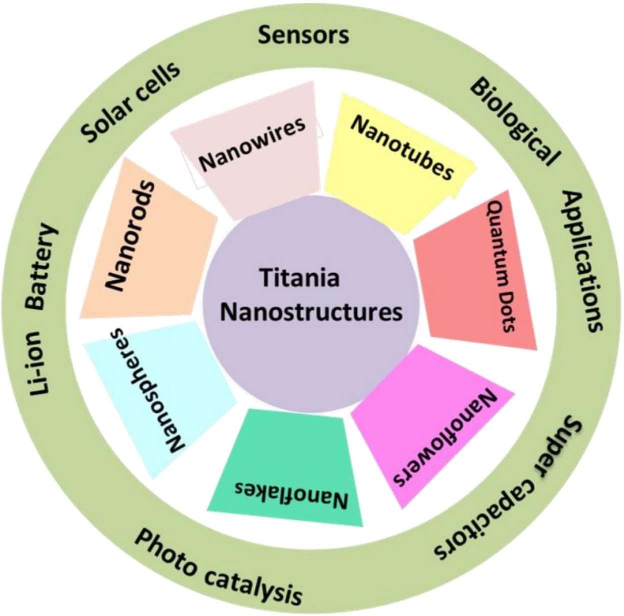

Figure 4: Applications of different TiO_2 nanostructures

1.11 Water/wastewater treatment using TiO_2

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 [39]. 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_2 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[40] .

TiO_2 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_2 nanoparticles. In a previous study, the effect of shape and size of 0-D and 1-D TiO_2 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[41]. In another study, TiO_2 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 degaration 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[42].

The oxidative mineralization of textile effluent coming from industry was also examined under UV radiation using TiO_2 in slurry. In a result, 40-90% COD removal was observed after 4hrs. Other crystalline form of TiO_2 (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_2O_2 presence. Besides this, TiO_2 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 [43].

TiO_2 can be used as thin films or in suspension in photocatalytic degradation. No doubt, that TiO_2 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 [44]. It is reported that UV-TiO_2 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_2 exhibited efficient results as compared to one without coating. That is why the reactors coated with TiO_2 films have gained attention to many researchers [45]. Some of the studies on different TiO_2 nanostructures synthesized and modified for their application in photocatalytic degradation of aqueous pollutants are summarized in the below.

Table 2: Overview of several TiO_2 based photocatalysts, their synthesis approach and application in water treatment

Precursors	Synthesis	Applications	Reference
TiO_2 nanotube arrays	Heterogeneous solvothermal synthesis	Photocatalytic activity under UV light	[46-47]
Cellulose acetate/TiO_2 ultrafine fiber	Electrospinning	Water treatment under UV light	[48]
Ag/TiO_2 nanotubes composite	Hydrothermal method	Photocatalytic activity of rhodamine B	[49]
TiO_2@carbon core/shell nanofibers (TiO_2@C NFs)	Electrospinning technique and hydrothermal method	Photodegradation of RhB	[50]
p-n Cu_2O/TiO_2 NTAs	Electrodeposition method	Photodegradation of methyl orange	[51]
Titanate nanotubes	Annealing	Reduction of Cr(VI) to Cr(III) in contaminated water	[52-53]
TiO_2 nanosheets with Mn_xO_y nanoparticles	One-pot hydrothermal method.	Photocatalytic degradation of Cr in the presence of visible light	[54].
TiO_2 nanomaterials coupled with Au, N, CdS etc.	Electrochemical anodization	Photocatalytic and photoelectrocatalytic activity	[55-57]

1.12 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[58]. A number of materials, notably lithium-metal alloys (Li_xM 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_2-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_2 a safe anode material suitable for a variety of applications[59]. 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_2 (335 mAh g^{-1}) 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_2 nanostructures have good safety and mesoporous structure which leads to effective transport of lithium ions[60]. Particularly 1D TiO_2 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_2 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[61]. Extrinsic engineering strategies for TiO_2 to achieve high performance LIBs include carbon coating, conductive network design, conductive agent hybrid strategy and mechanical support such as preparation of TiO_2(B) nanowires by Armstrong et al displayed initial discharge capacities of 230 $mA\cdot h\cdot g^{-1}$ at current densities of 50 $mA\cdot g^{-1}$[61-62].

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 [63]. The 1D TiO_2 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[64].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_2 nanoflake core-branch arrays with significantly greater charge and discharge capabilities than the standard SnO_2 powder electrode. Specifically, the core-branch array-based electrode retained a high capacity of roughly 580 mA h g^{-1} (at a current density of 1.6 A g^{-1}) after 50 cycles, but the commercial SnO_2 powder electrode nearly dropped to zero capacity[65]. The same group also developed TNT@Fe_2O_3 nanospikes core-shell nanoarrays for LIBs applications. Fe_2O_3 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_2@Fe_2O_3-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 g1 was achieved after 200 cycles. Furthermore, to improve the Li-ion diffusivity and electronic conductivity, heteroatom doping and coupling of TiO_2 with other materials (MoS_2, MoO_3 , MnO_2 , SnO_2 etc.) to prepare TiO_2 hybrid nanostructures has proven effective strategies for the facile transportation of Li ions and electrons[66-71]. TiO_2 has low conductivity and slow Li^+ 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[72]. Mn^{3+} ions replace Ti^{4+} ions to generate $Ti_{1-x}Mn_xO_2$ solid solutions with an extend lattice. $Ti_{0.95}Mn_{0.05}O_2$ demonstrated the best lithium storage behavior in LIBs, with a capacity of around 113 mAh g^{-1} after 118 charge/discharge cycles at 1C. Even at a rate of 2C, the $Ti_{0.95}Mn_{0.05}O_2$ electrode provided a reversible capacity of around 121 mAh g^{-1}. This improved battery performance could be due to increased Li^+ diffusion, improved electron transport, and improved anatase lattice stability during lithiation/delithiation[72]. 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_2 nanostructures/composites and their storage capacities for lithium ion batteries

Materials	**Storage capacities**	**Reference**
TiO_2 without CNTs TiO_2/CNTs	62 mAh g^{-1} at the current density of 5,000 mA g^{-1} 238 mAh g^{-1} at current density of 5,000 mA g^{-1}	[73]
TiO_2/graphene composites	130 mAh g-1 at 12 C	[59]
TiO_2 hollow nanofibers (HNFs) TiO_2 HNF-400	152 mA h g^{-1} at the current density of 185 mA g^{-1}	[74]
Hydrogen titanate nanowires and nanotubes electrodes	296.6 and 282 mA h g^{-1} at current densities of 0.3 and 0.24 A g^{-1}	[75]
TiO_2(B) nanowires	305 mA h g^{-1} at a current density of 0.5 A g^{-1},	[75]
Co-doped TiO_2 nanoparticles	167 mAh g^{-1} at the 0.5C current density	[76]
bicontinuous titania scaffold	254 mAh·g^{-1} at the current density of 1 A·g^{-1}	[77]
TiO_2/Fe_2O_3 composite	686 mAh g^{-1} at a current rate of 100 mA g^{-1}	[78]

Conclusions and Future Perspectives

In the past few years, TiO_2 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_2 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_2 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_2 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_2 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.

References

1. Hanif, M. A.; Nadeem, F.; Zahid, M.; Khan, F. G.; Hanif, A.; Akhtar, M. N., Applications of coagulation-flocculation and nanotechnology in water treatment. In *Aquananotechnology*, Elsevier: 2021; pp 533-558.
2. Jeevanandam, J.; Barhoum, A.; Chan, Y. S.; Dufresne, A.; Danquah, M. K., Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. *Beilstein journal of nanotechnology* **2018,** *9* (1), 1050-1074.
3. Jafari, S.; Mahyad, B.; Hashemzadeh, H.; Janfaza, S.; Gholikhani, T.; Tayebi, L., Biomedical applications of TiO2 nanostructures: recent advances. *International journal of nanomedicine* **2020**, 3447-3470.
4. Durgalakshmi, D.; Ajay Rakkesh, R.; Rajendran, S.; Naushad, M., Principles and mechanisms of green photocatalysis. *Green Photocatalysts* **2020**, 1-24.
5. Gusain, R.; Gupta, K.; Joshi, P.; Khatri, O. P., Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Advances in colloid and interface science* **2019,** *272*, 102009.
6. Habib, Z.; Lee, C.-G.; Li, Q.; Khan, S. J.; Ahmad, N. M.; Jamal, Y.; Huang, X.; Javed, H., Bi-Polymer electrospun nanofibers embedding Ag3PO4/P25 composite for efficient photocatalytic degradation and anti-microbial activity. *Catalysts* **2020,** *10* (7), 784.
7. Zahra, Z.; Habib, Z.; Chung, S.; Badshah, M. A., Exposure route of TiO2 NPs from industrial applications to wastewater treatment and their impacts on the agro-environment. *Nanomaterials* **2020,** *10* (8), 1469.
8. Siroha, P.; Singh, D.; Soni, R.; Gangwar, J. In *Comparative study on crystallographic representation of transition metal oxides polymorphs nanomaterials using VESTA software: Case study on Fe2O3 and TiO2*, AIP Conference Proceedings, AIP Publishing: 2018.
9. Reghunath, S.; Pinheiro, D.; KR, S. D., A review of hierarchical nanostructures of TiO2: Advances and applications. *Applied Surface Science Advances* **2021,** *3*, 100063.
10. Gnanasekaran, L.; Hemamalini, R.; Ravichandran, K., Synthesis and characterization of TiO2 quantum dots for photocatalytic application. *Journal of Saudi Chemical Society* **2015,** *19* (5), 589-594.
11. Machín, A.; Fontánez, K.; Arango, J. C.; Ortiz, D.; De León, J.; Pinilla, S.; Nicolosi, V.; Petrescu, F. I.; Morant, C.; Márquez, F., One-dimensional (1D) nanostructured materials for energy applications. *Materials* **2021,** *14* (10), 2609.
12. Tijing, L. D.; Yao, M.; Ren, J.; Park, C.-H.; Kim, C. S.; Shon, H. K., Nanofibers for water and wastewater treatment: recent advances and developments. *Water and Wastewater Treatment Technologies* **2019**, 431-468.
13. Lim, C. T., Nanofiber technology: current status and emerging developments. *Progress in polymer science* **2017,** *70*, 1-17.
14. Ha, H.; Amicucci, C.; Matteini, P.; Hwang, B., Mini review of synthesis strategies of silver nanowires and their applications. *Colloid and Interface Science Communications* **2022,** *50*, 100663.
15. Gupta, T.; Cho, J.; Prakash, J., Hydrothermal synthesis of TiO2 nanorods: formation chemistry, growth mechanism, and tailoring of surface properties for photocatalytic activities. *Materials Today Chemistry* **2021,** *20*, 100428.
16. Show, P. L.; Chai, W. S.; Ling, T. C., *Microalgae for Environmental Biotechnology: Smart Manufacturing and Industry 4.0 Applications*. CRC Press: 2022.
17. Wang, C.; Ghazzal, M. N., Nanostructured TiO2 for improving the solar-to-hydrogen conversion efficiency. *Energy Advances* **2023**.
18. Wang, K.; Ma, Q.; Qu, C.-X.; Zhou, H.-T.; Cao, M.; Wang, S.-D., Review on 3D fabrication at nanoscale. *Autex Research Journal* **2022,** (0).

19. Paul, K. K.; Giri12, P., Shape Tailored TiO. *Nanoscience and Nanotechnology* **2019,** *19*, 307-331.

20. Pan, L.; Zou, J.-J.; Wang, S.; Huang, Z.-F.; Yu, A.; Wang, L.; Zhang, X., Quantum dot self-decorated TiO 2 nanosheets. *Chemical communications* **2013,** *49* (59), 6593-6595.

21. Prakash, J.; Kumar, A.; Dai, H.; Janegitz, B. C.; Krishnan, V.; Swart, H. C.; Sun, S., Novel rare earth metal–doped one-dimensional TiO2 nanostructures: Fundamentals and multifunctional applications. *Materials Today Sustainability* **2021,** *13*, 100066.

22. Selmani, A.; Kovačević, D.; Bohinc, K., Nanoparticles: From synthesis to applications and beyond. *Advances in Colloid and Interface Science* **2022,** *303*, 102640.

23. Abid, N.; Khan, A. M.; Shujait, S.; Chaudhary, K.; Ikram, M.; Imran, M.; Haider, J.; Khan, M.; Khan, Q.; Maqbool, M., Synthesis of nanomaterials using various top-down and bottom-up approaches, influencing factors, advantages, and disadvantages: A review. *Advances in Colloid and Interface Science* **2022,** *300*, 102597.

24. Li, R.; Yang, J.; Xu, S.; Zhou, Y.; Wang, X.; Peng, H.; Du, J., Preparation of Gd-doped TiO2 nanotube arrays by anodization method and its photocatalytic activity for methyl orange degradation. *Catalysts* **2020,** *10* (3), 298.

25. Xue, J.; Wu, T.; Dai, Y.; Xia, Y., Electrospinning and electrospun nanofibers: Methods, materials, and applications. *Chemical reviews* **2019,** *119* (8), 5298-5415.

26. Reneker, D. H.; Chun, I., Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology* **1996,** *7* (3), 216.

27. Shao, C.; Kim, H.; Gong, J.; Lee, D., A novel method for making silica nanofibres by using electrospun fibres of polyvinylalcohol/silica composite as precursor. *Nanotechnology* **2002,** *13* (5), 635.

28. Solcova, O.; Balkan, T.; Guler, Z.; Morozova, M.; Dytrych, P.; Sarac, A. S., New preparation route of TiO2 nanofibers by electrospinning: spectroscopic and thermal characterizations. *Science of Advanced Materials* **2014,** *6* (12), 2618-2624.

29. Kalantari, M.; Du, R.; Ayranci, C.; Boluk, Y., Effects of interfacial interactions and interpenetrating brushes on the electrospinning of cellulose nanocrystals-polystyrene fibers. *Journal of colloid and interface science* **2018,** *528*, 419-430.

30. Ge, M.; Li, Q.; Cao, C.; Huang, J.; Li, S.; Zhang, S.; Chen, Z.; Zhang, K.; Al-Deyab, S. S.; Lai, Y., One-dimensional TiO2 nanotube photocatalysts for solar water splitting. *Advanced science* **2017,** *4* (1), 1600152.

31. Ahn, K.; Pham-Cong, D.; Choi, H. S.; Jeong, S.-Y.; Cho, J. H.; Kim, J.; Kim, J.-P.; Bae, J.-S.; Cho, C.-R., Bandgap-designed TiO2/SnO2 hollow hierarchical nanofibers: Synthesis, properties, and their photocatalytic mechanism. *Current applied physics* **2016,** *16* (3), 251-260.

32. Qian, R.; Zong, H.; Schneider, J.; Zhou, G.; Zhao, T.; Li, Y.; Yang, J.; Bahnemann, D. W.; Pan, J. H., Charge carrier trapping, recombination and transfer during TiO2 photocatalysis: An overview. *Catalysis Today* **2019,** *335*, 78-90.

33. Banerjee, S.; Dionysiou, D. D.; Pillai, S. C., Self-cleaning applications of TiO2 by photo-induced hydrophilicity and photocatalysis. *Applied Catalysis B: Environmental* **2015,** *176*, 396-428.

34. Sharon, M.; Modi, F.; Sharon, M., Titania based nanocomposites as a photocatalyst: A review. *Mater. Sci* **2016,** *3*, 1236-1254.

35. Benčina, M.; Iglič, A.; Mozetič, M.; Junkar, I., Crystallized TiO2 nanosurfaces in biomedical applications. *Nanomaterials* **2020,** *10* (6), 1121.

36. Ilyas, M.; Waris, A.; Khan, A. U.; Zamel, D.; Yar, L.; Baset, A.; Muhaymin, A.; Khan, S.; Ali, A.; Ahmad, A., Biological synthesis of titanium dioxide nanoparticles from plants and microorganisms and their potential biomedical applications. *Inorganic Chemistry Communications* **2021,** *133*, 108968.

37. Sagadevan, S.; Imteyaz, S.; Murugan, B.; Anita Lett, J.; Sridewi, N.; Weldegebrieal, G. K.; Fatimah, I.; Oh, W.-C., A comprehensive review on green synthesis of titanium dioxide nanoparticles and their diverse biomedical applications. *Green Processing and Synthesis* **2022,** *11* (1), 44-63.

38. Shankar, K.; Mor, G. K.; Prakasam, H. E.; Yoriya, S.; Paulose, M.; Varghese, O. K.; Grimes, C. A., Highly-ordered TiO2 nanotube arrays up to 220 µm in length: use in water photoelectrolysis and dye-sensitized solar cells. *Nanotechnology* **2007,** *18* (6), 065707.

39. Reddy, P. A. K.; Reddy, P. V. L.; Kwon, E.; Kim, K.-H.; Akter, T.; Kalagara, S., Recent advances in photocatalytic treatment of pollutants in aqueous media. *Environment international* **2016,** *91*, 94-103.

40. Mohadesi, M.; Sanavi Fard, M.; Shokri, A., The application of modified nano-TiO2 photocatalyst for wastewater treatment: A review. *International Journal of Environmental Analytical Chemistry* **2022**, 1-22.

41. de León, J. D.; Rojas, J.; Dominguez, D.; Esqueda-Barrón, Y.; Romo-Herrera, J.; Fuentes-Moyado, S., The effect of shape and size of 1D and 0D titanium oxide nanorods in the photocatalytic degradation of red amaranth toxic dye. *Nano-Structures & Nano-Objects* **2021,** *26*, 100738.

42. Ahirwar, D.; Bano, M.; Khan, F., Synthesis of mesoporous TiO 2 and its role as a photocatalyst in degradation of indigo carmine dye. *Journal of Sol-Gel Science and Technology* **2016,** *79*, 228-237.

43. Abbas, M.; Adil, M.; Ehtisham-ul-Haque, S.; Munir, B.; Yameen, M.; Ghaffar, A.; Shar, G. A.; Tahir, M. A.; Iqbal, M., Vibrio fischeri bioluminescence inhibition assay for ecotoxicity assessment: a review. *Science of the Total Environment* **2018,** *626*, 1295-1309.

44. Habib, Z.; Khan, S. J.; Ahmad, N. M.; Shahzad, H. M. A.; Jamal, Y.; Hashmi, I., Antibacterial behaviour of surface modified composite polyamide nanofiltration (NF) membrane by immobilizing Ag-doped TiO2 nanoparticles. *Environmental Technology* **2020,** *41* (28), 3657-3669.

45. Al-Mamun, M.; Kader, S.; Islam, M.; Khan, M., Photocatalytic activity improvement and application of UV-TiO2 photocatalysis in textile wastewater treatment: A review. *Journal of Environmental Chemical Engineering* **2019,** *7* (5), 103248.

46. Shao, Z.; Li, H.; Li, M.; Li, C.; Qu, C.; Yang, B., Fabrication of polyaniline nanowire/TiO2 nanotube array electrode for supercapacitors. *Energy* **2015,** *87*, 578-585.

47. Jia, Q.; Que, W.; Zhang, J., Heterogeneous solvothermal synthesis of one-dimensional titania nanostructures on transparent conductive glasses. *physica status solidi (a)* **2011,** *208* (10), 2313-2316.

48. Wang, S.-D.; Ma, Q.; Liu, H.; Wang, K.; Ling, L.-Z.; Zhang, K.-Q., Robust electrospinning cellulose acetate@ TiO 2 ultrafine fibers for dyeing water treatment by photocatalytic reactions. *RSC Advances* **2015,** *5* (51), 40521-40530.

49. Yang, D.; Sun, Y.; Tong, Z.; Tian, Y.; Li, Y.; Jiang, Z., Synthesis of Ag/TiO2 nanotube heterojunction with improved visible-light photocatalytic performance inspired by bioadhesion. *The Journal of Physical Chemistry C* **2015,** *119* (11), 5827-5835.

50. Zhang, P.; Shao, C.; Zhang, Z.; Zhang, M.; Mu, J.; Guo, Z.; Liu, Y., TiO2@ carbon core/shell nanofibers: controllable preparation and enhanced visible photocatalytic properties. *Nanoscale* **2011,** *3* (7), 2943-2949.

51. Zhang, J.; Wang, Y.; Yu, C.; Shu, X.; Jiang, L.; Cui, J.; Chen, Z.; Xie, T.; Wu, Y., Enhanced visible-light photoelectrochemical behaviour of heterojunction composite with Cu 2 O nanoparticles-decorated TiO 2 nanotube arrays. *New Journal of Chemistry* **2014,** *38* (10), 4975-4984.

52. Liu, W.; Ni, J.; Yin, X., Synergy of photocatalysis and adsorption for simultaneous removal of Cr (VI) and Cr (III) with TiO2 and titanate nanotubes. *Water research* **2014,** *53*, 12-25.

53. Zheng, P.; Zhou, W.; Wang, Y.; Ren, D.; Zhao, J.; Guo, S., N-doped graphene-wrapped TiO2 nanotubes with stable surface Ti3+ for visible-light photocatalysis. *Applied Surface Science* **2020,** *512*, 144549.

54. Lu, D.; Fang, P.; Liu, X.; Zhai, S.; Li, C.; Zhao, X.; Ding, J.; Xiong, R., A facile one-pot synthesis of TiO2-based nanosheets loaded with MnxOy nanoparticles with enhanced visible light–driven photocatalytic performance for removal of Cr (VI) or RhB. *Applied Catalysis B: Environmental* **2015,** *179*, 558-573.

55. Wang, M.; Ioccozia, J.; Sun, L.; Lin, C.; Lin, Z., Inorganic-modified semiconductor TiO 2 nanotube arrays for photocatalysis. *Energy & Environmental Science* **2014,** *7* (7), 2182-2202.

56. Wu, L.; Li, F.; Xu, Y.; Zhang, J. W.; Zhang, D.; Li, G.; Li, H., Plasmon-induced photoelectrocatalytic activity of Au nanoparticles enhanced TiO2 nanotube arrays electrodes for environmental remediation. *Applied catalysis B: environmental* **2015,** *164*, 217-224.

57. Lai, Y.-K.; Huang, J.-Y.; Zhang, H.-F.; Subramaniam, V.-P.; Tang, Y.-X.; Gong, D.-G.; Sundar, L.; Sun, L.; Chen, Z.; Lin, C.-J., Nitrogen-doped TiO2 nanotube array films with enhanced photocatalytic activity under various light sources. *Journal of Hazardous Materials* **2010,** *184* (1-3), 855-863.

58. Madian, M.; Eychmüller, A.; Giebeler, L., Current advances in TiO2-based nanostructure electrodes for high performance lithium ion batteries. *Batteries* **2018,** *4* (1), 7.

59. Su, X.; Wu, Q.; Zhan, X.; Wu, J.; Wei, S.; Guo, Z., Advanced titania nanostructures and composites for lithium ion battery. *Journal of Materials Science* **2012,** *47*, 2519-2534.

60. Zhang, M.-M.; Chen, J.-Y.; Li, H.; Wang, C.-R., Recent progress in Li-ion batteries with TiO 2 nanotube anodes grown by electrochemical anodization. *Rare Metals* **2021,** *40*, 249-271.

61. Zhang, Y.; Tang, Y.; Li, W.; Chen, X., Nanostructured TiO2-Based Anode Materials for High-Performance Rechargeable Lithium-Ion Batteries. *ChemNanoMat* **2016,** *2* (8), 764-775.

62. Armstrong, A. R.; Armstrong, G.; Canales, J.; García, R.; Bruce, P. G., Lithium-ion intercalation into TiO2-B nanowires. *Advanced Materials* **2005,** *17* (7), 862-865.

63. Wu, W.-Q.; Xu, Y.-F.; Liao, J.-F.; Wang, L.; Kuang, D.-B., Branched titania nanostructures for efficient energy conversion and storage: A review on design strategies, structural merits and multifunctionalities. *Nano Energy* **2019,** *62*, 791-809.

64. Lewis, C. S.; Li, Y. R.; Wang, L.; Li, J.; Stach, E. A.; Takeuchi, K. J.; Marschilok, A. C.; Takeuchi, E. S.; Wong, S. S., Correlating titania nanostructured morphologies with performance as anode materials for lithium-ion batteries. *ACS Sustainable Chemistry & Engineering* **2016,** *4* (12), 6299-6312.

65. Zhu, C.; Xia, X.; Liu, J.; Fan, Z.; Chao, D.; Zhang, H.; Fan, H. J., TiO2 nanotube@ SnO2 nanoflake core–branch arrays for lithium-ion battery anode. *Nano Energy* **2014,** *4*, 105-112.

66. Armstrong, G.; Armstrong, A. R.; Bruce, P. G.; Reale, P.; Scrosati, B., TiO2 (B) nanowires as an improved anode material for lithium-ion batteries containing LiFePO4 or LiNi0. 5Mn1. 5O4 cathodes and a polymer electrolyte. *Advanced Materials* **2006,** *18* (19), 2597-2600.

67. Liao, J. Y.; Manthiram, A., Mesoporous TiO2-Sn/C Core-Shell Nanowire Arrays as High-Performance 3D Anodes for Li-Ion Batteries. *Advanced Energy Materials* **2014,** *4* (14), 1400403.

68. Wang, W.; Tian, M.; Abdulagatov, A.; George, S. M.; Lee, Y.-C.; Yang, R., Three-dimensional Ni/TiO2 nanowire network for high areal capacity lithium ion microbattery applications. *Nano letters* **2012,** *12* (2), 655-660.

69. Wang, B.; Chen, Q.; Hu, J.; Li, H.; Hu, Y.; Peng, L.-M., Synthesis and characterization of large scale potassium titanate nanowires with good Li-intercalation performance. *Chemical physics letters* **2005,** *406* (1-3), 95-100.

70. Li, J.; Wan, W.; Zhou, H.; Li, J.; Xu, D., Hydrothermal synthesis of TiO 2 (B) nanowires with ultrahigh surface area and their fast charging and discharging properties in Li-ion batteries. *Chemical Communications* **2011,** *47* (12), 3439-3441.

71. Li, J.; Tang, Z.; Zhang, Z., Layered hydrogen titanate nanowires with novel lithium intercalation properties. *Chemistry of Materials* **2005,** *17* (23), 5848-5855.

72. Opra, D.; Gnedenkov, S.; Sinebryukhov, S.; Podgorbunsky, A.; Sokolov, A.; Ustinov, A. Y.; Kuryavyi, V.; Mayorov, V. Y.; Zheleznov, V., Doping of titania with manganese for improving cycling and rate performances in lithium-ion batteries. *Chemical Physics* **2020,** *538*, 110864.

73. Cao, F.-F.; Guo, Y.-G.; Zheng, S.-F.; Wu, X.-L.; Jiang, L.-Y.; Bi, R.-R.; Wan, L.-J.; Maier, J., Symbiotic coaxial nanocables: Facile synthesis and an efficient and elegant morphological solution to the lithium storage problem. *Chemistry of Materials* **2010,** *22* (5), 1908-1914.

74. Oh, S.-I.; Kim, J.-C.; Dar, M. A.; Kim, D.-W., Synthesis and characterization of uniform hollow TiO2 nanofibers using electrospun fibrous cellulosic templates for lithium-ion battery electrodes. *Journal of Alloys and Compounds* **2019,** *800*, 483-489.
75. Zhang, Y.; Jiang, Z.; Huang, J.; Lim, L. Y.; Li, W.; Deng, J.; Gong, D.; Tang, Y.; Lai, Y.; Chen, Z., Titanate and titania nanostructured materials for environmental and energy applications: a review. *RSC advances* **2015,** *5* (97), 79479-79510.
76. Kashale, A. A.; Rasal, A. S.; Kamble, G. P.; Ingole, V. H.; Dwivedi, P. K.; Rajoba, S. J.; Jadhav, L. D.; Ling, Y.-C.; Chang, J.-Y.; Ghule, A. V., Biosynthesized Co-doped TiO2 nanoparticles based anode for lithium-ion battery application and investigating the influence of dopant concentrations on its performance. *Composites Part B: Engineering* **2019,** *167*, 44-50.
77. Sheng, Q.; Li, Q.; Xiang, L.; Huang, T.; Mai, Y.; Han, L., Double diamond structured bicontinuous mesoporous titania templated by a block copolymer for anode material of lithium-ion battery. *Nano Research* **2021,** *14*, 992-997.
78. Li, S.; Zhang, Y.; Huang, J., Three-dimensional TiO2 nanotubes immobilized with Fe2O3 nanoparticles as an anode material for lithium-ion batteries. *Journal of Alloys and Compounds* **2019,** *783*, 793-800.