Overview of TiO_2 nanostructures & their potential applications for sustainable environment

Zunaira Habib[a,c], 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

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.

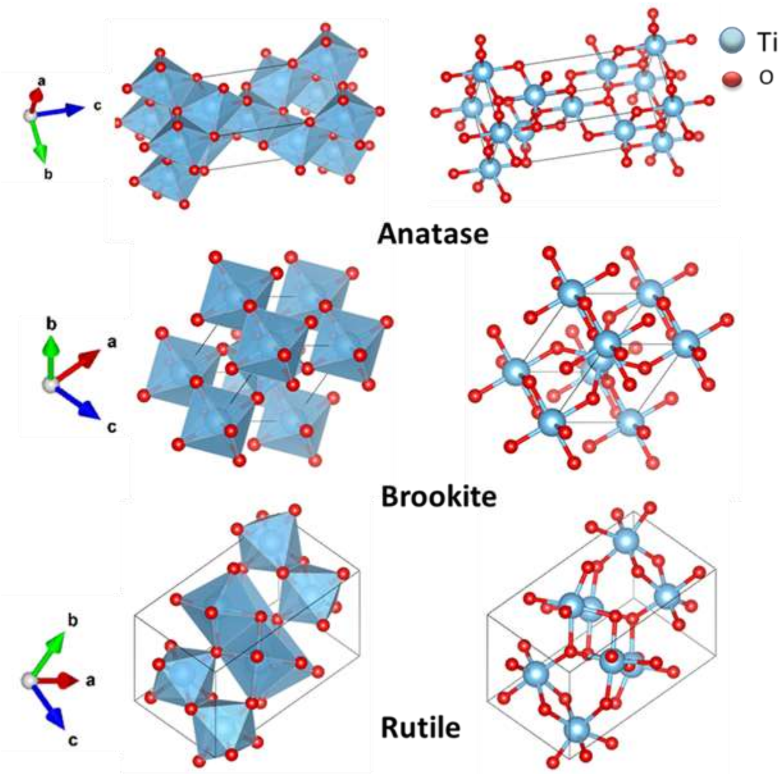

Figure 1: Different crystal forms of TiO_2

Table1: 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 nanomaterials 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].

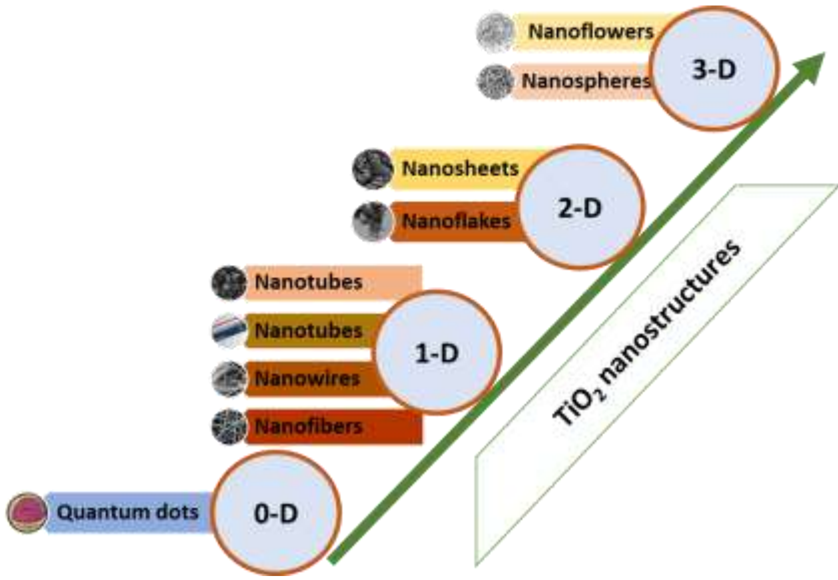

Figure 2: Classification of TiO_2 nanostructures

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].

1.5 Synthesis of TiO_2 Nanostructures

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

1.5.1 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].

1.5.2 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 [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].

1.5.3 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 [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].

1.5.4 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].

1.5.5 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 [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].

1.5.6 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].

1.6 Applications of TiO_2 nanostructured materials

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 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).

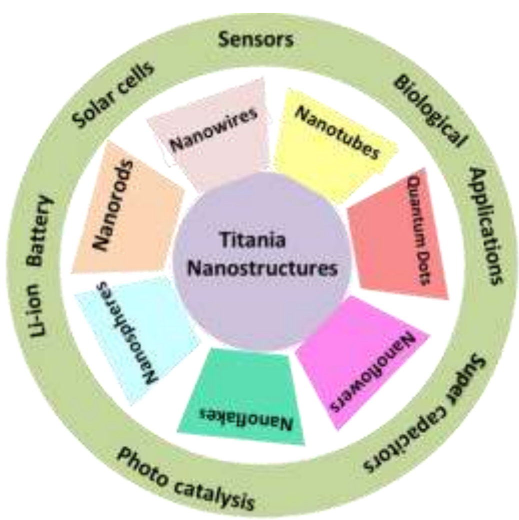

Figure 3: Applications of different TiO_2 nanostructures

1.6.1 Photocatalytic Applications

Photocatalytic technology is thought to be one of the most promising advanced oxidation-reduction processe for improving air quality by decomposing organic and inorganic air 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.

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.

1.6.1.1 Photo/photoelectron-catalytic degradation of aqueous pollutants

Because of TiO_2 inexpensive cost, physical and chemical stability, large specific surface area, and minimal electron/hole recombination, it is the most extensively employed metal oxide in photocatalytic destruction of air pollutants. The different TiO_2 nanostructures synthesized and modified for their application in photocatalytic degradation of aqueous pollutants are summarized in the tale 2.

Table 2: Differently modified titania nanostructures for photodegradation of aqueous pollutants

Precursors	Synthesis	Applications	Reference
TiO_2 nanotube arrays	Heterogeneous solvothermal synthesis	Photocatalytic activity under UV light	[31-32]
Cellulose acetate/TiO_2 ultrafine fiber	Electrospinning	Water treatment under UV light	[33]
Ag/TiO_2 nanotubes composite	Hydrothermal method	Photocatalytic activity of rhodamine B	[34]
TiO_2@carbon core/shell nanofibers (TiO_2@C NFs)	Electrospinning technique and hydrothermal method	Photodegradation of RhB	[35]
p-n Cu_2O/TiO_2 NTAs	Electrodeposition method	Photodegradation of methyl orange	[36]
Titanate nanotubes	Annealing	Reduction of Cr(VI) to Cr(III) in contaminated water	[37-38]
TiO_2 nanosheets with Mn_xO_y nanoparticles	One-pot hydrothermal method.	Photocatalytic degradation of Cr in the presence of visible light	[39].
TiO_2 nanomaterials coupled with Au, N, CdS etc.	Electrochemical anodization	Photocatalytic and photoelectrocatalytic activity	[40-42]

1.6.1.2 Photocatalytic CO_2 reduction into energy fuels

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. Examples of different TiO_2 nanostructures and composites produced for photocatalytic reduction of CO_2 are summarized in the table 3.

Table 3: Titania nanoparticles and composites for photocatalytic applications

Precursors	Synthesis	Applications	Reference
Cu/TiO_2 nanoparticles composites	Sol-gel method	Methanol yield of Cu/TiO_2 was 20 µmol·g-1·h-1	[43]
Pt/TiO_2 nanoparticles composites	Electrospinning	Photoreduction of CO_2 into methane	[44]
Noble metal (Pd, Pt, Au and Ag) modified reduced graphene oxide/TiO_2 nanoparticle	Solvothermal method	Photoreduction of CO_2 into methane	[45]
TiO_2 single crystals coated with ultrafine Pt nanoparticles	Gas-phase deposition methods	Photoreduction of CO_2	**[46]**
TiO_2 nanotube arrays	Electrochemical anodization	Photoreduction	[47]
Pt/TiO_2 nanotube composite	Microwave-assisted solvothermal approach	Photocatalytic conversion of carbon dioxide and water vapor into methane	[48]
nitrogen/TiO_2 nanotube arrays loaded with both Cu and Pt nanoparticles composites	Annealing	Carbon dioxide and water vapor conversion to methane and other hydrocarbons	[49,50]

1.6.1.3 Photo/photoelectron-catalytic water splitting

For ecological energy economy, hydrogen is considered as clean and renewable energy source. Photocatalysis for water splitting is an effective technique for production of hydrogen. The mechanism of titania nanoparticles for photocatlytic degradation of pollutants is similar to water splitting and hence they can be employed as photocatalysts for water splitting as well. In this regard, 1D nanostructured materials are thought to be auspicious candidates for photocatalytic and photoelectrocatalytic water splitting under UV light. A large number of strategies have been developed to further improve the photocatalytic efficiencies of titania such as *Dang et al* prepared TiO_2 nanotube/graphene (TNT/GR) via one-step hydrothermal method and a significantly higher photocatalytic hydrogen production was observed[51]. Furthermore, TNTs composites with Ag[52] and multiply heteroatom doped TiO_2 also exhibited enhanced photocatalytic activities for hydrogen production.

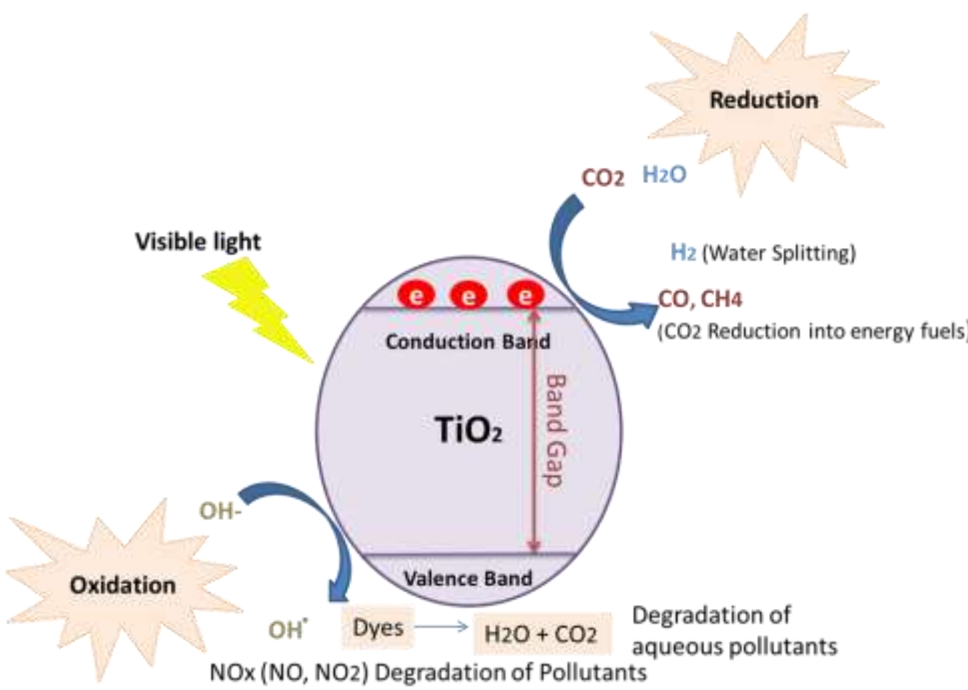

Figure 4: Photocatalytic applications of TiO_2 nanostructures

1.6.2 Biomedical Applications

The use of nanostructured inorganic materials in diverse biological applications, such as controlled drug delivery, labeling of biological objects, and the construction of artificial tissues from nanostructured composite materials, has recently become an important topic of research[53]. Nanostructure titanates 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[54-56].

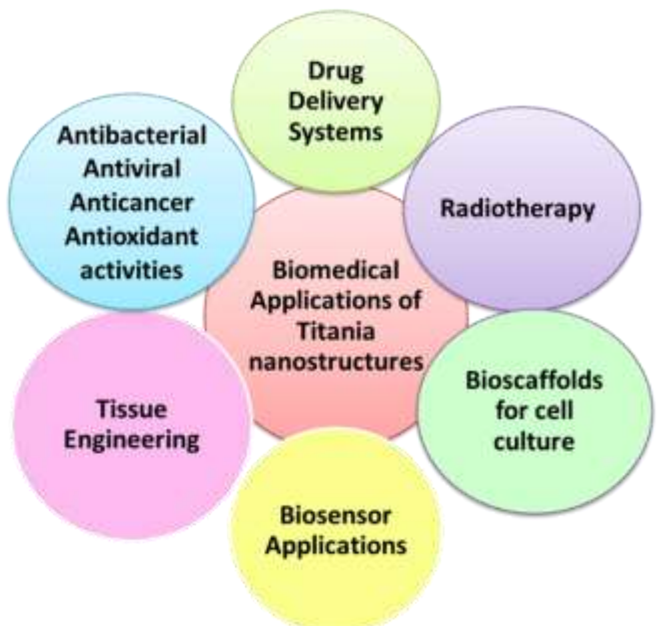

Figure 5: Biomedical Applications of TiO_2 Nanostructures

1.6.3 Solar cells

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. However, the presence of wide band and less absorption of solar light results in low photoelectric conversion efficiency. To counter this problem one of the strategy is the formation of composites with semiconductors having low energy band. TiO_2 nanostructures differently modified for solar cell applications by various scientists are listed in

Table 4: Modified titania nanostructures for solar cells applications

Photoanode	Synthesis	Applications	Reference
vertically aligned TiO_2 nanotubes arrays	Electrochemical anodization method	Power conversion efficiency of 6.89%.	[57]
TiO nanotubes	Hydrothermal method	Energy conversion efficiency (6.4%)	[58]
Ag and Au decorate TiO_2 nanofibers		6.13% and 7.7% Conversion efficiency	[59-60]
TiO_2 nanotubes coupled with TiO_2 nanoparticles		Conversion efficiency at more than 7.0%,	[44, 61]
porous rutile TiO_2 nanorod arrays (NRAs)	Two-step hydrothermal treatment	Efficiency of 7.91%	[62-63]
1D TiO_2 nanostructures with carbon, ZnO			[64]

1.6.4 Lithium-ion batteries

Rechargeable lithium ion batteries are in rising demand because of sustainability, consumption in household electronics and vehicles. Therefore, to meet increasing demands various transition metal oxides are explored to obtain outstanding electrochemical features. Amongst these metal oxides, TiO_2 nanostructures have been identified as suitable applicant due to effective transport of lithium ions, good safety and mesoporous structure (Figure 6). 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 such as preparation of TiO_2(B) nanowires by Armstrong et al displayed initial discharge capacities of 230 mA·h·g-1 at current densities of 50 $mA·g^{-1}$[65]. 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].

Figure 6: Titania based nanostructures as electrodes in lithium ion batteries

1.6.5 Supercapacitors

Among energy storage devices, Supercapacitors have gained much interest because of long cycling life, fast rates of charge/discharge, high power density, and safety. TiO_2 nanostructures have also been explored for their use in supercapacitors. However, the low conductivity of TiO_2 hampered their charge storage ability. To increase the conductivity of TiO_2 nanostructures, they are coupled with metal oxides (RuO_2, MnO_2, NiO, and so on)[8-10], carbon materials[11], and conducting polymers[12] such as preparation of polyaniline nanowire/TiO_2 nanotube array electrode by Shao et al[31].

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