

TITANIA NANOTUBES FABRICATION BY ELECTROCHEMICAL ANODIZATION AND DYE DEGRADATION PROCESS

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Abstract

The potential of photocatalysis applications rapidly expands, offering energy-efficient solutions across various industries. Titanium dioxide nanotubes (TiO₂ NTs/TNTs) are emerging as effective catalysts for water filtration techniques. Electrochemical anodization is the preferred method for producing suitable TNTs on a titanium plate. The key challenge lies in fabricating these desired TNTs efficiently in terms of time, cost, and energy. These effective nanotubes can achieve optimal photocatalytic dye degradation by modifying their optical and morphological properties. This paper explores the fabrication of NTs by manipulating different parameters and the successful application of Titania in dye degradation through appropriate doping.

Keywords: Anodization; Doped TiO₂; Parameters; Photocatalyst; Water purification

Introduction

Nanotechnology is increasingly becoming the foundation of modern progress. Every application is in the hands of nanotechnology to an infinite extent. It progresses in several areas, including fuel production, effective power sources, healthcare, natural preservation, security, and privacy. Depending on their shape, physical, chemical, and size, we are surrounded by several types of nanoparticles: ceramic, carbon-based, metallic, semiconductor, polymeric, etc. However, the nanotubes, a one-dimensional nanoscale material, are particularly intriguing. Their unique properties, such as their high surface area and unique electronic and ionic properties, make them very useful in many fields, including magnetism, electronics, and catalysis. The current level of activity in

nanotechnology, particularly in nanotubes, is a testament to their potential and the eagerness to explore their applications further, leaving us all fascinated and curious about their possibilities.

Carbon nanotubes were the foundation of early research. Over time, new materials for creating nanotubes started to appear. Such a substance with a variety of qualities is TiO₂. These are widely used in H-generation (Pathinettam Padiyan and Henry Raja, 2011), solar cells (Yan and Zhou, 2011), water treatment (Lee and Park, 2013), CO₂ reduction (Qu *et al.*, 2005), etc., because of their capabilities such as: nontoxicity, wide bandgap, biocompatibility, photocatalytic ability, unique electronic and ionic properties, and high surface area. Titania NTs can be fabricated by using different methods like sol-gel

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(Takahashi, 2018), hydrothermal (Bilgin *et al.*, 2015), physical vapour deposition (Gholami *et al.*, 2020), and chemical vapour deposition (Wang *et al.*, 2014). Electrochemical anodization can also be considered a low-cost, effective, and facile method for developing TNTs. The self-ordered TiO₂ NTs were initially discovered in 1999 by Zwilling *et al.* (Zwilling *et al.*, 1999), by electrochemical anodization. He adopted fluoride-containing electrolytes for the formation of these nanotubes. Various electrolytes, such as: HF, NH₄F, NaF, formamide, Na₂SO₄, etc., are currently used for nanotube formation. These electrolytes determine pore size, spacing, length, thickness, and diameter for NTs. Many other anodization parameters also affect Titania's morphology, such as: time, voltage, electrodes, temperature, pH value, etc.

These efficient TNTs can be used in a variety of nanotechnology fields. TNT, which plays a significant role in waste-water treatment applications, is the subject of intensive research today. The scarcity of drinking water is one of the critical problems we are currently facing. Millions of people perish each year as a result of drinking water shortages. In many areas of India, drinking water is still in short supply. Water can be purified in several ways, including boiling, filtration, distillation, chlorination, and water purification by photocatalysis, which offers a cheap, helpful, and engaging one (Sharma and Bhattacharya, 2017). A more exciting research field today is the retention of nanomaterials in photocatalysis.

Numerous nanostructures, including spheres, particles, wires, rods, sheets, and tubes, have been developed for this application. Several investigations have been gathered to demonstrate the results of materials with improved photocatalytic capacity to aid in selecting better photocatalysts. Titania NTs, a photocatalyst that absorbs light and raises energy, can be employed in photocatalysis. This energy is delivered to the substance that will undergo a chemical reaction. The role of photocatalytic activity in producing pure water is acceptable. Titanium dioxide nanoparticles (TNP) make an efficient photocatalyst for photocatalytic water purification. The main drawback of Titania is its bandgap, which is only activated under UV light. These demerits can be overcome by doping the Titania with metal/non-metal, reducing bandgap, and working effectively in the visible region (Xue *et al.*, 2020).

Dyes and Water Pollution

Water contamination is a challenge in both wealthy and low-income nations. Numerous elements,

including precipitation, climate, soil type, vegetation, geology, flow conditions, groundwater, and human activities, impact the water's condition. The point sources from companies and local governments pose the most significant risk to water quality. Agriculture, urban development, and mining all have an impact on the quality of water (Camara *et al.*, 2019).

Pollutants are materials that, when discharged into the environment, have negative consequences or deplete resources and may result in long- or short-term damage. Pollutants can be of several forms and include a variety of characteristics, such as: Industrial pollutants, which include heavy metals with a low or low ability for absorption, synthetic compounds, and non-biodegradable polymers. With time, these contaminants build up in the ecosystem. Likewise, too, some environmental contaminants from funds have absorptive qualities. When their quantity exceeds the environment's capacity to absorb them, they pose an issue. Only recycling these contaminants into harmless forms or diluting them to lessen their toxicity are other options (Priya *et al.*, 2023). Point source pollution (Zhang *et al.*, 2019), is defined as pollution that has a known source or enters the water from a location that can be identified, such as: a ditch, industry, storm drain, sewage treatment plant, etc.

In the case of water pollution, the industry's dye emissions are significant (Figure 1). Since 1,000,000 tons of dyes are produced worldwide, they are used by small- to large-scale companies in the food, cosmetic, textile, and pharmaceutical industries, among others. Considering the reports of the Water Pollution Growth Rate (2015-2020), industrial wastewater discharge increased to +20%, +15% increase in agricultural runoff, and municipal wastewater effluent rose to +10% and +5% increase in oil spills and leaks. Water usage in dyeing technology is relatively substantial since water is used as a medium and is frequently washed one or more times. Fibber type, dye, and slurry wastewater released from distinct processes have very different water quality characteristics (Liu, 2020). Cleaning agents like enzymes and soaps based on caustic soda are utilized. This clears the substrate of extra colour and paste. Water is also required to clean the printing equipment and remove the loose colour paste from the printing blankets, printing screens, and dyeing containers (Patel, 2011).

Regarding the environment, the discharge of dye waste from dye production or consuming units into water bodies presents prospective risks to water quality. It causes significant health problems for individuals, animals, and plants, mainly aquatic life. To add colour or alter the colour of something, dyes are compounds that can be obtained naturally or

synthetically. These have their colours due to the absorption of distinct light wavelengths. The chemical substance that gives a colour is referred to as a colourant. They absorb into the fabrics and chemically modify them to produce colour that lasts a long time. The substrate on which this coloured material is applied is chemically attached. Dye is typically used in the aqueous solution and may require a mordant to improve the fastness of the dye on it. Natural dyes are regarded as the early-stage source of dyes (Patel, 2011). They are typically more dependable, affordable, and readily available. Synthetic dyes are those made from organic or inorganic chemicals. Traditional natural dyes quickly replace synthetic dyes (Figure 2) (Chavan, 2011).



Figure 1. Shows water pollution caused by textile effluents (Source: <http://www.catchnews.com/environment-news>)

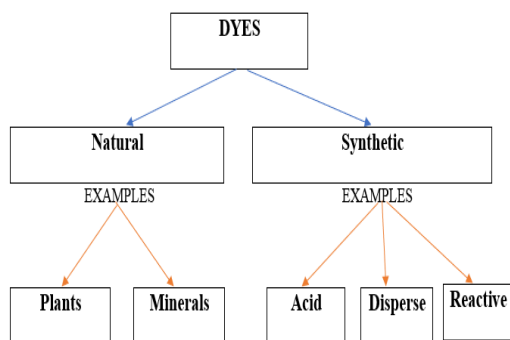


Figure 2. Shows types of Dyes

Due to the complex structures and synthetic origins, dyes are created to withstand deterioration through time, exposure to sunshine, water, soap, and oxidizing agents, and are difficult to eliminate by traditional wastewater treatment techniques. These dyes can be degraded using various techniques, including physical, chemical, and biological. Physical methods and adsorption techniques are frequently employed to remove colours from water. Due to its sludge-free, clean operation, it is a cost-efficient and successful procedure for eliminating

colours. Silica gel (Samiey and Toosi, 2010), sawdust (Chikri *et al.*, 2020), clay (Almeida *et al.*, 2009), and plant wastes (Weng *et al.*, 2009). Other substances have all been tested as adsorbents for removing colour from aquatic media. From both the standpoints of water purification and its reusability, removing colourants from water is extremely important. However, adsorption also entails the phase transfer of contaminants to other tertiary wastes, which necessitates further treatment or proper disposal. One of the methods for removing impurities from wastewater is membrane filtering (Zulkefli *et al.*, 2022). Significant drawbacks of membrane-filtration processes include the fact that they can only be used at low wastewater flow rates, that producing new membranes is more expensive than replacing old ones regularly, that high working pressure is needed to force wastewater through membrane filtration, and that they cannot lower the content of suspended solids. Fungi, bacteria, yeasts, and algae are some microorganisms that may be employed to biodegrade colours (Jamee and Siddique, 2019). Practical limitations, however, frequently place limits on this technique's capabilities. Coagulation and flocculation are two chemical processes used to separate the colours (Badawi *et al.*, 2023). The main drawbacks of these methods are their cost and the secondary contamination problems resulting from excessive use of chemicals. Fewer active organisms may be involved in the aerobic biological process and a long hydraulic retention period due to the highly toxic nature of particular substances. Environmental chemists have become increasingly concerned about dye pollution, particularly in developed nations like the United States, the United Kingdom, Germany, China, Japan, etc., which have rapidly industrialised and are more susceptible to dye pollution.

The photocatalytic oxidation process has attracted a lot of attention. It has been extensively explored as one of the most promising technologies for degrading organic contaminants in a water environment under a catalyst (Wang *et al.*, 2016). There were so many parameters that influenced the dye degradation application through photocatalysis, such as: light intensity, time, presence of oxidants, catalyst type, dye concentrations and types, etc (Kumari *et al.*, 2023). Higher light intensities give more photodegradation results. In the case of photosensitive dyes and pigments, light intensity should be kept at low levels when studying the photodegradation to avoid inappropriately relating the exposure doses of standard and accelerated ageing. Increasing exposure time will raise the degradation rates (Groeneveld *et al.*, 2023). The presence and absence of oxygen molecules play an essential role in dye degradation application.

Multiple studies have shown that in most cases of organic colourants, a decrease in oxygen concentration leads to lower photodegradation rates. However, a complete halt to the fading process has not been observed (Shabil Sha *et al.*, 2024).

Photocatalysis

Catalysis can be divided into 1) homogeneous and 2) heterogeneous. If catalysis happens when the reactant and the catalyst are in the same phase, it is called homogeneous. Suppose the reactant and catalyst are in different phases called heterogeneous. The semiconductor used as the catalyst is a heterogeneous process, and the reaction occurs between these phases. The method of capturing light energy and transforming it to generate charge carriers is called photocatalysis. A photocatalyst is a compound used to perform photocatalysis. As a result, reacting compounds receive energy from reacting substances, which causes the chemical reaction. This absorbs light energy and raises it to higher energy states. The catalyst's capacity to produce the electron and hole pairs necessary for the secondary response is a significant determinant of photocatalytic activity (Ameta *et al.*, 2018). As a photocatalyst, today can access a variety of materials. In this field, n-type semiconductors are primarily used. Materials employed in this field include TiO_2 , InO_3 , SrO_2 , ZnO , SnO_2 , ZnS , Fe_2O_3 , and WO_3 due to their excellent charge transmission properties, photochemical stability, and photocatalytic abilities. Due to the advantageous band gaps and band edge positions, semiconducting metal oxides are mainly employed for photocatalysis (Ishchenko *et al.*, 2016). Titania exhibits excellent stability, photocatalytic activity, widespread availability, non-toxicity, and strong oxidative power compared to other materials. Because of this, Titania is more effective in the field of photocatalysis. The failure of the photocatalytic system was indicated by the photocatalytic system's poor migration ability, rapid charge carrier recombination rate, and minimal use of visible light in industrial applications. We must increase the effectiveness of Titania to prevent these issues. For instance, narrowing Titania's band gap can be effective in the visible spectrum. The band gap can be decreased by doping or co-doping the photocatalyst with metals or non-metals, which also minimizes the rapid recombination of charge carriers (Thambiliyagodage and Usgodaarachchi, 2021).

There must be two processes going on simultaneously during the photocatalysis process. 1) The oxidation of holes produced by light (Equation

1,b), and 2) the reduction of electrons produced by light (Equation 1, c) (Figure 3). Oxidation kills the microbes and organic molecules in the air and water. Hydroxyl radicals ($\text{OH}^\cdot$) are generated when an electron and a hole oxidize water. The bacterial cell structure may be destroyed by hydroxyl radicals, which can also transform oxygen molecules into small amounts of CO_2 and water (Zakir *et al.*, 2020). In the same way that photogenerated holes can oxidize the electron donor, photogenerated electrons can decrease an electron acceptor. In other words, water molecules create a hydroxyl radical after losing an electron to a positively charged electron hole in the valance band. A water molecule reacts with an oxygen molecule to produce superoxide ions, which then combine with water molecules to form hydroxide ions (OH^-) and peroxide radicals ($\text{OOH}^\cdot$). This process is called superoxide reduction. When holes oxidize OH^- to OH , peroxide radicals and H^+ ions interact to generate OH and OH^- (Equations 1) (Pavel *et al.*, 2023).

Equations. (1)

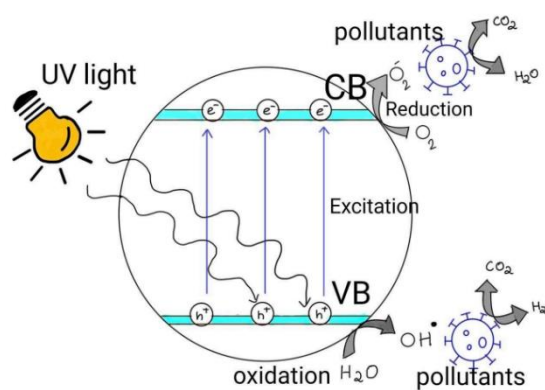
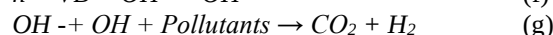
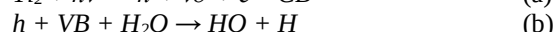
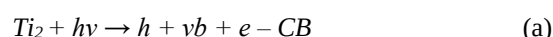


Figure 3. Shows photocatalysis process (Oxidation and Reduction)

Why Titanium Dioxide NTs?

Today's preferred effective photocatalyst is titanium dioxide, an n-type metal oxide semiconductor. Compared to metals and insulators,

semiconductors have a medium band gap. In insulators, a large amount of energy is needed to excitation charge carriers, and in metals, the conduction and valence bands overlap. So, either oxidation or reduction happened due to these band positions. That is why semiconductors are preferred for photocatalysis applications. Titanium is white, has an atomic number of 22, and is considered the most prevalent transition metal on Earth, which does not naturally exist in elemental form and frequently reacts with gases like nitrogen and oxygen. When compared to oxygen in the atmosphere, titanium dioxide/Titania appears in nature as an elemental form (Ren, 2018). Titania is used in many applications, such as: a photocatalyst in hydrogen generation, antibacterial activity, dye-sensitized solar cells, CO₂ reduction, air and water purification, used in supercapacitors and also applied in the medical industry, according to its non-toxicity, corrosion resistance, eco-friendly, biocompatibility, distinctive electronic and ionic properties, durability over time, high oxidative power, widespread availability, cost-effective, high photocatalytic ability (Wang *et al.*, 2015). The white colour of Titania is utilized as a bleaching agent as well as in cosmetics, paintings, sunscreen lotions, toothpaste, papers, inks, and food colouring (Dudefoi *et al.*, 2017). ZnO can work effectively in photocatalysis like Titania but easily dissolves in an acidic solution, so it cannot be applied technically.

Titania can take a lot of different natural forms; three primary phases of Titania naturally exist anatase, rutile, and brookite (Figure 4). Other Titania compounds, such as: ramsdalite, columbite, and hollandite, can be created in a lab under high pressure by processing rutile with anatase. Only at low temperatures does the brookite phase exist because it is unstable at ambient temperature. Due to its high stability, rutile is the most common type of Titania. However, the anatase phase has been used for photocatalytic activity. It has higher photocatalytic activity, excellent photochemical stability, and better oxidative power than other forms. Raising the temperature can convert the anatase phase into the rutile phase. In recent years, anatase and rutile mixtures have demonstrated higher photocatalytic activity than pure anatase phases (Ishigaki *et al.*, 2020). However, the anatase forms with better crystalline size and morphology provide practical photocatalytic applications.

The band gaps of these phases are more significant; for example, Titania's band gap only allows UV light to activate it. Rutile's bandgap value is approximately 3 eV, while anatase's is roughly 3.2 eV (Nagaraj *et al.*, 2019). Rutile and anatase can be a limitation when using these

materials for specific applications, which can be an inconvenience in various ways:

1. Limited visible light absorption: The material is not responsive to visible light, which is a significant portion of sunlight. This reduces its efficiency in applications like photocatalysis, solar cells, or photovoltaics.
2. UV light requirement: The need for UV light to activate the material can be a challenge, especially in applications where UV light is not readily available or is difficult to harness.
3. Higher energy thresholds: The wide bandgap requires higher energy inputs to excite electrons, which can lead to increased energy costs or reduced efficiency in specific applications.

However, the unique properties of Titania, such as: its high photocatalytic activity, chemical stability, and non-toxicity, still make it a valuable material for various applications, including photocatalysis, water splitting, and self-cleaning surfaces. The wide band gap also brings advantages, such as: high stability and resistance to corrosion, suitable for applications requiring high energy thresholds, like: UV protection, self-cleaning surfaces, air and water purification, etc. However, less bandgap should be needed for water purification under sunlight to effectively absorb visible light. Researchers continue to explore strategies to overcome the limitations of the wide bandgap-the difference between the two forms of TiO₂ results in different specific gravities and electrical band topologies. Therefore, Titania needs some dopants to lower its band gap and make it suited for absorbing visible light to activate in the visible range. Tetragonal structures comprise the anatase and rutile crystal systems, and the brookite structure is orthorhombic (Table 1).

Table 1. Shows crystallographic data of Titania structures

Phases	Anatase	Rutile	Brookite
Systems	Tetragonal	Tetragonal	Orthorhombic
a (Å)	3.789	4.594	9.184
b (Å)	3.789	4.594	5.447
c (Å)	9.537	2.959	5.145
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å ³)	136.93	62.45	257.38
E.g. (eV)	~3.2	~3.0	~3.4

a, b, and c- Cell dimensions; α , β , and γ - Crystal angles; V- Volume; E.g. -Energy gap

The characteristics and nanostructure of Titania influenced how the application was built. The fabrication process and the intended uses

determine how distinct Titania nanostructures, such as: nanoparticles, nanotubes, nanofibers, nanoflowers, nanorods, nanowires, and nanosheets, are synthesized (Khan *et al.*, 2018). For instance, nanotubes on titanium plates are a more practical nanostructure than nanopowder in the photocatalytic application. The nanotubes provide large specific areas with longer nanotubes, reduce recombination of charge carriers, and make the total recovery of nanoparticles after water treatment frequently tricky because of their small size (Lu *et al.*, 2016). It has been noted that TiO_2 powders have negative consequences, including oxidative stress in human cells and genetic instability in animals. Recovery and ethical disposal of the nanoparticles are now top priorities. TiO_2 on a solid base has a high degree of degradation in wastewater treatment and a high specific area. This is the reason why picked here as TNTs on titanium thin film for the research application as photocatalysts for dye degradation. Shown in Figure 4.

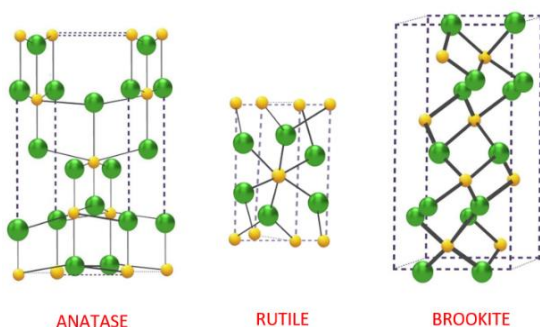


Figure 4. Shows different crystalline structures of Titania

Methods for the Fabrication of TNTs

There was an abundance of techniques accessible for the synthesis of TNTs. Sol-gel (Bazli *et al.*, 2019), hydrothermal (Ángel López Zavala *et al.*, 2017), electrochemical anodization (Sunija, 2018), physical-chemical vapour deposition (Lee *et al.*, 2011), etc., are examples of processes that can be used.

Physical vapour deposition creates metal vapour thinly coated with an electrically conductive metal (1981). This procedure is completed in a high-pressure vacuum chamber (10⁻⁶ torr) (Shang and Zeng, 2013). Instead of being isolated, the coating is simultaneous over the whole object. The fundamental distinction between these depositions is the coating material; whereas chemical vapour deposition uses a gaseous coating substance, physical vapour deposition uses a solid one. Another distinction is that the coated atoms

interact physically and chemically with the substrate as they move and are deposited there. One of the chemical vapour deposition benefits is the capacity to produce homogenous films with minimal porosity, high purity, and stability. It does have some drawbacks, though, as the process creates hazardous gaseous byproducts and expensive monitoring is needed (Karfa *et al.*, 2019).

Among other nanostructures, metal oxide nanoparticles are produced via the “sol-gel process” chemical method (1991). In this method, the precursor to the molecule dissolves in water or alcohol and becomes the gel. Given that the gel produced by hydrolysis is wet, it must be dried appropriately, considering the gel’s desirable qualities and intended use (Bokov *et al.*, 2021). Low processing temperature, remarkable homogeneity, and simplicity characterize this substance. Various optical, electrical, energy, surface engineering, biosensors, and medicinal utilize the materials made using the sol-gel process (Sobczyk-Guzenda *et al.*, 2013). Long deposition times, expensive production expenses, the need for high temperatures to create anatase nanocrystals, and the inability to adhere a thick coating of nanoparticles to the substrate are all drawbacks of this method (Varshney *et al.*, 2016).

Electrochemical anodization is one of the better processes for creating well-ordered nanotubes (1999). It is a straightforward, long-lasting, corrosion-resistant, and free technique. The entire system is simple to use. Two electrodes and an electrolyte are used in anodization. An easy electrolytic procedure creates a metal oxide on the material’s surface (Souza *et al.*, 2018). This method, among others, allows easy control over the dimensions of the porous structures by only modifying the anodization conditions (Masuda *et al.*, 2018). Supercapacitors, biomedical areas, photocatalysis applications, and other uses for anodized material are all possible. According to several studies, the electrochemical anodized nanotube architecture has unique mechanical, photovoltaic, biological, and semiconducting properties that other methods cannot produce (Shi *et al.*, 2022). This method was introduced in 1999 and modified as advanced electrochemical anodization in 2020 (Table 2).

The hydrothermal process is a frequently employed approach for producing Titania nanomaterial (2004). It follows a solution-reaction model, which works well in various temperatures as it starts at average and rises to a high temperature. Because of this, nanomaterials created via a hydrothermal technique are not heat-resistant (Gan *et al.*, 2020). The process is a crucial method that includes forming materials under high pressure and temperature in an autoclave, known as hydrothermal

and solvothermal synthesis. Several applications, including bone regeneration, proton conduction, photoinduced hydrophilicity, photocatalysts, and dye-sensitizing solar batteries, are anticipated for TiO₂-derived nanotubes that are produced by hydrothermal treatment of TiO₂ particles in a concentrated NaOH aqueous solution (Muniyappan *et al.*, 2017). The fundamental benefit of this method is that it can be tightly controlled through liquid-phase or multiphase chemical processes, with high vapour pressures and little loss of nanomaterials. High temperatures and the need for pricey equipment are some of its drawbacks.

Table 2. Shows chronology of Fabrication Methods for Electrochemical Anodized Titanium Oxide

Year	Fabrication methods
1999	Zwilling <i>et al.</i> discovered the formation of titanium oxide nanotubes using electrochemical anodization in sulfuric acid.
2001	Grimes <i>et al.</i> report the fabrication of TiO ₂ nanotubes using anodization in hydrofluoric acid.
2004	Mor <i>et al.</i> developed a method for growing TiO ₂ nanotubes using anodization in a sulfuric acid and hydrofluoric acid mixture.
2005	Paulose <i>et al.</i> demonstrate the control of nanotube diameter and length using varying anodization voltages.
2007	Varghese <i>et al.</i> report the fabrication of TiO ₂ nanotubes with improved morphology using anodization in ethylene glycol.
2010	Allam <i>et al.</i> develop a method for growing TiO ₂ nanotubes using anodization in a sulfuric acid and oxalic acid mixture.
2012	Roy <i>et al.</i> demonstrate the fabrication of TiO ₂ nanotubes with enhanced photocatalytic activity using anodization in a mixture of sulfuric acid and hydrogen peroxide.
2015	Alivov <i>et al.</i> report the growth of TiO ₂ nanotubes using anodization in a mixture of sulfuric acid and potassium sulfate.
2018	Wang <i>et al.</i> develop a method for fabricating TiO ₂ nanotubes using anodization in a mixture of sulfuric acid and sodium sulfate.
2020	Liu <i>et al.</i> demonstrate the fabrication of TiO ₂ nanotubes with improved morphology and photocatalytic activity using anodization in a mixture of sulfuric acid and ammonium fluoride.

Electrochemical Anodization

Electrochemical anodization is regarded as an electrolytic process. Utilizing this technique, titanium's surface could produce oxide (Figure 5 (a)). Pore initiation, growth, and propagation are three processes during anodization. Two electrodes, a DC power source, and an appropriate electrolyte comprise an electrochemical cell. The electrode was positioned face-to-face and at least 2 cm apart after being dipped into the electrolyte. The electrode's other end is attached to the DC power source.

This approach uses a suitable counter electrode and titanium as the working electrode (Sun *et al.*, 2021).

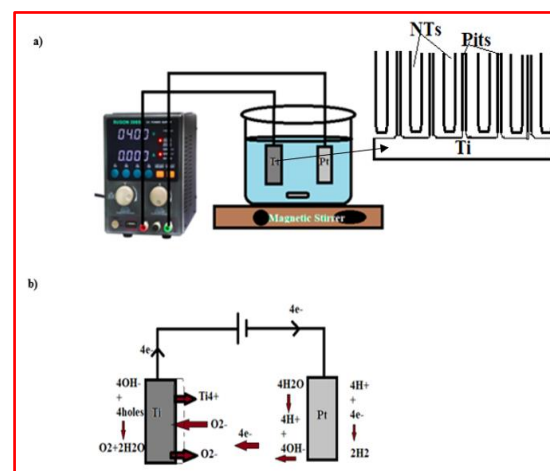
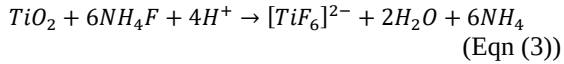
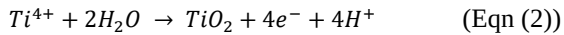


Figure 5. Shows a) Anodization process and Nanotubes formation, b) Chemical reaction

The electrolyte's electrons travel toward the anode/electrolyte interface when the power is turned on (Figure 5 (b)). By doing this, titanium releases Ti ions into the electrolyte, interacting with the oxygen ions to form an oxide layer on its surface (Equation 2). In addition, the titanium ions interact with the fluoride ions in the electrolyte to create titanium hexafluoride (TiF₆²⁻) (Equation 3). The growth rate of TNTs is also related to the diffusion of [TiF₆]²⁻ and fluoride concentration in the electrolyte. The [TiF₆]²⁻ complexes are the primary species responsible for the growth of TNTs, as they facilitate the transportation of Ti⁴⁺ ions. The diffusion rate of [TiF₆]²⁻ complexes towards the electrode surface controls the growth rate of TNTs. This soluble molecule merely aids in forming pores on the surface of titanium dioxide (Dou *et al.*, 2019). For this reason, fluoride-based electrolytes are typically employed to create TNTs. The optimal fluoride concentrations (usually 0.1-1.0 wt%) promote the growth of TNTs with the desired morphology and structure (Arsha and Henry Raja, 2024). The relationship between growth rate and fluoride concentration is nonlinear, with optimal fluoride levels maximizing growth rate. Therefore, the growth rate of TNTs is directly tied to the diffusion of [TiF₆]²⁻ complexes and fluoride concentration in the electrolyte, with optimal conditions leading to the formation of high-quality TNTs (Safwat *et al.*, 2024). First, Gong and co-workers reported using fluoride-based electrolytes to produce TNTs by anodization in 2001 (Varghese *et al.*, 2003).

At the initial stage of anodization,



Any electrolyte will partially dissolve metal oxide. Only solutions for which oxide acquires faster than it dissolves must be applied. No additional current flow results from increasing the applied potential before a threshold level is achieved. Therefore, the barrier's electric field is sufficiently robust to drive the diffusion of oxygen ions through it. The metal and oxygen ions interact, increasing the oxide barrier's thickness or density. Consequently, the chemical reaction occurs as,

- 1) The oxide growth at the surface of the metal with the contact of Ti metal with O_2^-/OH^+ ions.
- 2) After the formation of the initial oxide layer, these anions migrate through the oxide layer and reach the metal oxide interface, where they react with metals (Brudzisz *et al.*, 2021).

According to the anodization process, titanium is anodized in an electrolyte solution, forming a thin oxide layer on its surface. The presence of $[TiF_6]^{2-}$ helped to form pits or pores on this layer, and these randomly distributed pits or defects on the titanium surface are considered nucleation sites for pore formation. Electrochemical reactions at the pore bottom drive the growth of pores into the titanium substrate and accelerate the dissolution of titanium ions at these bottom to enhance pore growth. Titanium ions react with oxygen and water to form titanium oxide, which deposits on these pore walls. Continued pore growth and oxide deposition lead to the formation of nanotubes with a hollow interior, and further anodization increases the tube wall thickness and modifies the tube morphology. Due to repulsive forces between neighbouring pores, the tubes self-organize into a hexagonal array.

There are four processes of anodization, chemical dissolution, field-assisted oxidation, field-assisted migration, and field-assisted dissolution (Shahzad *et al.*, 2015). Chemical dissolution first takes a backseat to field-assisted dissolution due to the strong electric field over the electrode. As the anodization develops and the oxide thickness increases, field-assisted dissolution will be replaced by chemical dissolution. The pores' size and density will grow due to chemical dissolution (Kim *et al.*, 2018). The attack rate would increase if anodization occurred in the electrolyte with the highest fluoride concentration. The bottom of the tube grows thinner as a result, increasing the length of the NTs

(Muzakir *et al.*, 2020). The oxide/electrolyte interface will etch chemically more quickly and produce shorter NTs if the solution is engineered to be sufficiently acidic (low pH) (Lim *et al.*, 2012).

The current-time graph (Figure 6) shows that current increases during the early oxidation stages and declines due to the rapidly expanding oxide layer. Creating pits with a diameter of less than a nanometer causes the maximum oxide layer current to increase significantly afterwards, which are designed as a result of fluoride ions-the current drops again when the tubular structure below the pits starts to form. The current converges when the oxide production and dissolution reactions achieve an equilibrium (Ribeiro *et al.*, 2021). The pore density rises as these pits are transformed into larger pores. The pits start to separate when the oxide growth and dissolution rates are equal, forming compact NTs.

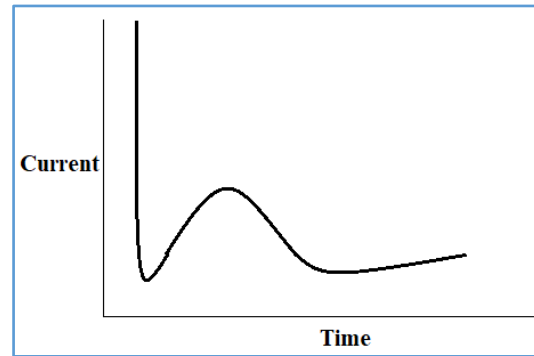


Figure 6. Shows current-time plot

Parameters Affecting TNT Formation

Different variables impacted the synthesis of TNTs. Examples include anodization potential, temperature, the kind of electrolyte, the length of anodization, pH of the electrolyte, annealing temperature, electrolyte concentration, electrolyte temperature, electrodes, etc. TNT manufacture by anodization can be characterized in two ways: first, it is a delicate technique, and second, it can generate the desired dimension by altering these factors. As a result, the groundwork for making TNTs is thought to be the anodization parameters and annealing temperature. However, this control has significant limitations. Similar to the above limit, changing anodization parameters is disobeyed by the dimension change of TNTs. That implies that the oxide dissolution and synthesis rate enter an equilibrium state.

Anodization Duration

The length of the anodization process greatly influences TNT dimensions; this results in longer TNTs. But as time went on, the average growth rate

shrank (Chernozem *et al.*, 2016). TNT creation is thought to take 15 minutes, at the very least. It will create short NTs if the anodization process is sped up too quickly. The quickest anodization time makes a homogeneous and spotless NT coating possible. After three hours of anodization, organized tubes with distinct walls were present on all studied surfaces; nevertheless, some particles covered the NT tip. The literature claims that nanotubes need time to self-organize and improve their uniformity and level of organization. Several authors have covered the impact of anodizing time on NT length (Regonini and Clemens, 2015).

The diameter change is also influenced by the anodization period. Except for when an HF-based aqueous solution is exposed to a relatively low voltage (10 V), an increase in diameter is proportionate to lengthening the anodizing time. The 24-hour anodizing process, in this instance, governs the switching of the etching-dissolution operations and the shortening of the NTs. More specifically, once nanotubes have been formed, the etching operation stops while the dissolution process continues, leading to the cleaving of the tubes at their upper levels. Because tubes don't have a perfectly cylindrical interior, a secondary impact of height shortening reduces the diameter length (Portan *et al.*, 2012).

Anodization Potential

The diameter of the NTs has a significant impact on the anodization potential or voltage. About 20V is the bare minimum potential needed to create an NT. At this voltage range, self-organized tubes with predictable patterns have been seen. At the same time, the self-organized tubes start to behave irregularly at 50 V and suffer structural damage at 60 V, respectively. As a result, it was decided that 50 V was the maximum potential for steady anodization for the electrolyte in use. With increasing anodizing voltage (Sreekantan *et al.*, 2011), the NTs' outer diameter and length steadily grew more significantly. The relationship between inter-pore distance and anodization voltage for materials like oxides is nonlinear at high voltages, with a linear dependence only observed at lower voltages. At lower voltages, the inter-pore distance increases linearly with the anodization voltage. As the oxide grows, the electric field strength increases with voltage, leading to a greater distance between pores. The inter-pore distance may even saturate or decrease with further increases in voltage. This is attributed to various factors, including increased electric field: higher voltages lead to stronger electric fields, which can cause more rapid oxide growth and altered pore morphology; oxide thickening; thicker oxides form

at higher voltages, reducing the effective electric field and changing the pore spacing, pore competition: pores may compete for growth at higher voltages, leading to non-uniform spacing and diameter, surface roughening: higher voltages can cause surface roughening, disrupting the regular pore arrangement, and electrochemical reactions: more complex electrochemical reactions occur at higher voltages, influencing pore growth and spacing. These factors contribute to the non-linear dependence of inter-pore distance on anodization voltage at higher voltages. Researchers often use intermediate voltages (20-40 V) to balance pore size, spacing, and oxide thickness for specific applications.

The applied potential difference across the oxide layer affects how strong the electric field is. A low driving field over the bottom oxide caused the tube development for anodization at low applied voltage to proceed slowly. This allowed the growth process to continue. With a rise in average tube diameter, the NTs transformed anodization voltages of 20 to 40 V into highly organized nanotubular structures with circular nanopores and thick walls (Muzakir *et al.*, 2020). When the interface film substrate was over 30 V, large broken patches of a porous oxide film with a micrometre-scale diameter appeared. These areas can be connected to breakdown events at high potentials.

Additionally, it was discovered that the voltage ramp that came before the constant voltage of 20 V during anodization could regulate the length of TNT. A voltage ramp could create a desired pH gradient between the tube bottom and mouth. As a result, this will produce an environment more favorable for developing long tubes. After the abrupt voltage drop, current oscillations during voltage ramping could be seen. These fluctuations are attributed to field-assisted oxidation, which increases the resistance of the oxide layer, and field-assisted dissolution, which is encouraged by fluoride ions. Causing pore development to start (Lim *et al.*, 2012).

Electrolytes Nature

The primary component, the electrolyte, plays a crucial role in the creation of titanium. The four generations of TNTs exemplify this, each explained using different electrolytes. In 1999, Zwilling and colleagues made a significant discovery, reporting that anodizing Ti in an electrolyte containing F-produced organized nanopores oxide structures. They utilized chromic acid, either with or without hydrofluoric acid, to create Titania. In the chromic acid electrolyte, a thin oxide compact film develops. In the fluorinated electrolyte, a duplex film consists of a compact layer covered by a columnar porous

layer form. Their findings revealed that dissolution and oxide production compete to drive growth in fluorinated electrolytes, a significant insight in materials science and nanotechnology.

Gong and colleagues meticulously reported creating the first generation of TNTs using anodization in 2001, which involved rigorous experimentation and analysis (Gong *et al.*, 2001). Gong and Colleagues discovered that the NT structure is significantly compromised at anodizing voltages exceeding 40 V. This leads to creating a sponge-like randomly porous structure when using fluoride-containing electrolytes to produce TNTs. Their findings indicate that the shape of the porous film is similar to that of porous (sponge-like) alumina at low anodizing voltage. They concluded that titanium anodization in HF solution had produced arrays that resembled well-aligned titanium oxide NTs. The resultant nanotubes contain a barrier layer at their base, are straight, and have adjustable pore sizes that range from 25 to 65 nm.

Cai and associates described the second generation (Cai *et al.*, 2005). NT arrays of many microns in length can be produced using variable pH KF (or NaF with identical results) electrolytes. The necessary pH is then attained by adding NaOH. The pH of the electrolyte affects the behaviour of the electrochemical etches and chemical dissolution because titanium ions are hydrolyzed. As the pH rises, hydrolysis increases, reducing the pace of chemical dissolution. For a specific pH, the duration increases with the applied potential. In highly acidic circumstances (pH 1), longer anodization times do not extend tubes. NT length in weak acid electrolytes is time-dependent. As the anodization duration extends from 23 to 90 hours, the nanotube length increases from 0.8 μm to 2.3 μm . With rising pH levels, the hydrolysis content increases, causing a significant amount of hydrous titanic oxide to precipitate on its surface. Using less potent fluoride salt solutions in place of the HF acid decreased the rate of Titania disintegration in the first generation of NTs, resulting in a maximum thickness of 2-3 μm . The rapid rate of TiO_2 dissolution by an acid solution in the water limits the shape, structure, and maximum feasible NT length to around 0.5 μm in the first-generation approach of tube array production. By mixing ethylene with weak acids like KF or NaF in the electrolyte, this problem can be overcome. The resulting self-organized nanoporous TiO_2 has 500 nm long and 90-110 nm wide pores. The cross-sectional image clearly shows the tubes' cylindrical shape, and the tubes' wall thickness is determined to be 50 nm. These findings open up new possibilities for applying TNTs in materials science and nanotechnology, inspiring

hope for the future (Pathinettam Padiyan and Henry Raja, 2011).

Reducing the water concentration in the anodization bath to less than 5% is critical to producing exceedingly long NT arrays. The ability to produce oxide is constrained because the donation of oxygen is more challenging with organic electrolytes than with water. The longer NT can be made because the decreased water concentration slows down the chemical breakdown of the oxide in fluorine-containing electrolytes. These tubes had an average outer diameter of 180 nm, a wall thickness of 24 nm, and an aspect ratio of 390. Due to reduced anodization potentials, shorter tubes with smaller diameters are produced. The longer tubes result from the increased driving force for ionic transport across the barrier layer at the bottom of the pore, which causes the Ti/TiO_2 interface to migrate into the Ti metal more quickly. The amount of water in the aqueous electrolytes is one of the elements that help generate oxide by quick chemical dissolution. The water concentration in the electrolyte needs to be as low as possible to extend the length of the TNT arrays. This is the primary idea behind our decision to use a polar organic solvent, ethylene glycol with NH_4F , as the electrolyte composition for the third generation of TiO_2 NT synthesis. The incredibly dense third-generation TNT array was created, with a pore diameter of 180 nm and a length of 1000 μm . The wall of the NTs is about 25 nanometers thick. Comparing the third generation to the first and second, the tube length has increased twice. Paulose and colleagues used polar chemical electrolytes to introduce the third generation (Paulose *et al.*, 2006).

Allem *et al.* produced Titania NTs using fluoride-free electrolytes, and they observed a baleen-like structure in a FEG-SEM image of a sample made at 18 V, 0.5 M HCl, and 0.4 M H_2O_2 for 10 minutes. The top and cross-view FEG-SEM images of the fourth-generation TNT array film show bundles of tubes and many vacancies.

The typical lengths and inner diameters are 900 nm and 15 nm, respectively. The fourth generation of TNT tubes has a much smaller diameter, implying a larger surface area. Over a voltage range of 5 to 60 V, they failed to produce NT arrays at either lower or higher HCl concentrations. We increased the anodization voltage to 20 V and the length of the NT up to 600 nm using a stepwise anodization voltage increase; nevertheless, the resulting NTs are not well-organized (Allam and Grimes, 2007). Nanoporous and nanotubular films are nanostructured materials but differ distinctly (Table 3).

If a thin oxide layer with low fluorine content forms on the surface of anodized Titania films, it's likely a nanoporous structure and not the nanotubes. If the fluorine-enriched layer between nanotubes is partially dissolved and the remaining structure maintains its cylindrical shape and hollow interior, it's still considered nanotubular and is called low dissolution. If the dissolution leads to a loss of tubular structure and the formation of pores or voids, it's more accurately described as nanoporous and is called high dissolution. The tube walls may thin or become irregular if the fluorine-enriched layer is significantly dissolved. The sample may exhibit a mix of nanotubular and nanoporous characteristics called moderate dissolution.

Table 3. Shows nanoporous and nanotubular films

Nanoporous films	Nanotubular films
Have a porous structure with tiny holes/voids	Consist of arrays of hollow tubes or cylinders
Pores are typically isolated and not interconnected	Tubes are generally aligned perpendicular to the substrate
Surface area is increased due to the porous nature	Have a high aspect ratio (length vs. diameter)
It may have a sponge-like or foam-like structure	May have open or closed ends

Annealing Temperature

The annealing temperature is a primary factor in the post-anodization processing and depends on the formation of effective NTs. That is utilized to change TNTs' amorphous structure into its crystalline counterpart. In addition to the crystalline phase, factors affecting the photocatalytic performance of nanostructured TiO_2 include the degree of crystallization, crystallite size, morphological changes, thermal stability, and surface characteristics (Albu *et al.*, 2010). When created, the Peroxo group containing titanite (PTNTs) NTs had a tubular structure. Above 200°C of annealing, this tubular structure appears to be "dismantled," at around 200°C, the end portion of the tube seems to reopen by forming a cleavage that seems to extend further. The re-opening of PTNTs may produce "stacked bamboo leaf-like nanosheets" at temperatures 300 and 400°C (Park *et al.*, 2020). The anatase phase will occur as the temperature rises above 250°C. Anatase underwent a complete transformation at about 420°C (Zanoxolo Mbese and Madikizela, 2019). A rise in heat conditions causes the rutile structure to form. The combined form of rutile and anatase demonstrates a more substantial photocatalytic effect than pure anatase (Park *et al.*, 2020).

Electrode

The type of counter electrode (CE) used in the anodization process also affects the production of

TNT; different CEs produce nanotubes with varying aspect ratios. TNT produced with a stainless-steel cathode is conical in shape, short, and has thin (5-10 nm) non-uniform walls that appear to fluctuate in diameter at the top and bottom. The walls cannot maintain themselves at this thickness and collapse in unstable spots. The aspect ratio attained when using an aluminium cathode is the same as when using a carbon cathode. However, the TNT made with an aluminium cathode has a top surface comparable to a stainless-steel cathode. The tops of the TNTs tend to fall, but the base walls seem stable. Compared to TNT produced with a carbon cathode, TNT produced with an aluminium cathode is substantially less stable. TNT with high aspect ratios is produced when an iron cathode is used. However, they are not as stable as those produced with a carbon cathode. Compared to NTs made with other cathode materials, those made with carbon have higher aspect ratios, larger tube diameters, and longer tubes. Additionally, the quality and aspect ratios of NTs produced using a carbon cathode are comparable to those produced using a platinum cathode. However, compared to platinum, carbon is significantly less expensive (Sreekantan *et al.*, 2011). The distance between the working electrode (WE) and the common electrode (CE) and the electrodes themselves affects the shape of TNT. The electrode spacing strongly influenced the electrolyte conductivity and titanium concentration, with closer electrode spacings corresponding to higher conductivity and titanium concentration. Electrolyte conductivity and titanium concentration both soar when anode-cathode separation reduces. The resulting TNT tends to grow noticeably when the electrode spacing is decreased from 4.5 to 0.5 cm at a fixed electrolyte condition. The effect of electrolyte composition, the strong field between the electrodes, and the self-enlargement potential is believed to be a driving force for NT separation.

Electrolyte Temperature

The electrolyte temperature significantly impacts the formation of TNTs through anodization. Higher electrolyte temperatures cause longer and thicker NTs due to increased oxidation and viscosity reduction. Considering a non-aqueous electrolyte, the elevated temperature leads to a more organized and crystalline nanotube structure. The higher electrolyte temperature also creates a larger diameter and thicker walls of resultant NTs. The increase in the electrolyte temperature changes the morphology of NTs; for example, the nanorod structure will change to an NT structure (Lazarouk *et al.*, 2012).

Dye Degradation by Titania Nanotubes

The morphology and optical properties of TNTs influenced the photocatalytic activity. That means the longer tubes are highly capable of acting in photocatalysis experiments. Because it shows a high surface area for absorbing light. So, the parameters influenced by anodization are considered the most important for applying TNTs. For example, in the case of electrolytes used in the fabrication method, the ageing of electrolytes reduces photocatalytic activity. The changing of electrolyte composition negatively affects photocatalytic activity. The short pH value of electrolytes was good for well-ordered NT formation (Suhadolnik *et al.*, 2020). The electrolyte temperature also influences the structure of TNTs, limiting Ti foil's structure to be anodized (Sopha *et al.*, 2022). We can also increase the photocatalytic efficiency of TNTs by successful doping, which will reduce the bandgap of Titania and can effectively work in visible regions. The pure Titania is more active in the UV region than the visible one.

Modified TiO₂

The annealing process is essential for Titania tubes generated by anodization. Only the annealing process determines which crystal structure it is. Titanium dioxide can never act as a proper photocatalyst in photocatalysis without annealing. The Anatase form accepts more photocatalytic strength than the rutile one. Without an annealed sample/Titania shows 70% degradation of phenol (Al-Sammarraie *et al.*, 2012.) which allows 87% degradation by anatase and 76% by rutile one.

Photocatalytic efficiency decreases due to the fast recombination rate of electron-hole pairs. To avoid this, coupling, doping, and co-doping methods are required. When we doped Titania with non-metals, noble metals, transition metals, etc. There is an escalation in the specific surface area of Titania. The absorption dimension of the doped catalyst has drifted towards a longer wavelength and can also be active in the visible region (Zhang *et al.*, 1998; Pawar *et al.*, 2018).

Transition metals like iron (Fe), doping into TiO₂ to remove humic acids in drinking water, provide shallow trapping sites for charge carriers. That is, Fe³⁺ traps electrons and holes, which increases photocatalytic activity. The photocurrent of these doped media increased, obviously (Yuan *et al.*, 2013). Copper (Cu) doped Titania is more attractive in photocatalysis than pure Titania (Momeni *et al.*, 2015). It can be fabricated during the anodization process using an HF/HNO₃/H₂O mixture with a ratio of about 1:4:5 in volume. For

methylene blue (MB) degradation, visible light and UV light were used, but the effective degradation only occurs in Cu-TNT with visible light. When we used Cu-TNT, the Fermi level of CuO is placed lower than Titania, which leads the electrons in the valance band to jump up to CuO and disperse to the surface of Titania. Molybdenum (Mo) doping helps with the phase transition and allows the absorption of visible light. This is done using the combined direct current magnetron sputtering and anodization method. Due to increased doping Mo concentration, the bandgap of undoped- Titania is 3.24 eV, becoming 3.16, 3.14, etc. (Xue *et al.*, 2020). Cerium (Ce) is one of the rare earth metals that can be doped with Titania. Ce-TiO₂ activity in 2-mercaptobenzothiazole (MBT) was reported by Li *et al.*, 2005. The 4f electronic configuration of Ce improves the absorption range, which is shifted to the 400-500 nm range. A higher concentration of Ce changes the surface of Titania and converts it to rutile form. Initially, MBT degradation increases with an increase in Ce³⁺ content but will decline beyond the high value of cerium concentration. The result shows that 1.2% Ce³⁺ - Titania gives the best performance in the UV region, and 0.7% Ce³⁺ - Titania performed in the visible region (Li *et al.*, 2005). The non-metal, nitrogen-doped Titania shows high emission of current and excellent field emission stability (Liu *et al.*, 2008). N-doped Titania was obtained using different methods like annealing Titania in a nitrogen atmosphere, N-ion bombardment, plasma treatment, etc. N(2p) states of nitrogen ions are located above the valance band of Titania by substituting oxygen atoms in the Titania lattice. The result of mixing N(2p) with O(2p) states reduces the bandgap of N- N-doped Titania (Wang *et al.*, 2006). The alkaline earth metal Strontium (Sr) doped Titania significantly improves the photoconversion efficiency and is about 0.69%, which is about 0.2% in un-doped Titania (Hamedani *et al.*, 2011). Sr-doped Titania was fabricated during the anodization by using anhydrous strontium hydroxide salt.

Conclusion

This article discusses the efficiency of titanium dioxide in water purification systems and provides information on the optimal anodization parameters used in fabricating these NTs. It reduces the crystal structure's bandgap when we dop Titania with noble metals, non-metals, rare earth metals, etc. It allows the sample surface to be active in the visible region. Therefore, water purification through photocatalysis can be more effective when appropriate anodization parameters and doped Titania are used. This allows

electrons to quickly move from the valence band to the conduction band with the assistance of low-energy photons, and visible light can also serve as the light source for the photocatalysis mechanism.

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