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*MINI REVIEW*

# Titanium Dioxide Nanomaterials: Synthesis and Applications

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The emergence of nanomaterials as an exciting class of materials is the main reason for the high demand for nanoparticle utility and practical applications in the modern era. At present, the green synthesis process has proved to be the most advanced method in the production of nanoparticles. In green synthetic method, plant or its part is used for bioreduction of metal ions to their elemental form. Nanoparticles manufactured by this method are simple, accessible, eco-friendly and available at low cost and can be easily scaled up for larger operations. For this reason, in the modern era, their application is being done in areas like biosensors, lithium ion batteries, water purification, electrocatalysis, coating, photo-thermal therapies, drug delivery, *etc*. Among the different metal and metal oxide nanoparticles $TiO_2$ is one of the most promising nanoparticles due to their unique structural chemical and morphological properties. Green synthesis of $TiO_2$ nanoparticles by using extract of different biological agent is one of the most growing areas of research. Phytochemicals, enzymes, and proteins, all bioactive components, play an essential role in the production of nanoparticles. The potentiality of titania ($TiO_2$) to operate as an antibacterial and photocatalytic agent is one of the topics that has garnered the most interest from the scientific community. This review provides an overview of different available green synthesis method for the fabrication of $TiO_2$ nanoparticles and also highlighted the different industrial applications of $TiO_2$.

**Keywords: Green synthesis, Plant extract, Nanoparticles, $TiO_2$ nanoparticles.**

## INTRODUCTION

Nanotechnology was developed as a result of researchers seeing potential in the many properties of nanoparticles, which led to the development of the field. Due to its microscopic size, durability and unmatched strength, it has immense potential in many fields such as medicine, electronics, automobiles, petroleum, bioscience, forensics, *etc*. [1,2]. Nanoparticles are a broad category of substances that include particular matter, with a particle size less than at least 100 nm. Thus, the content can be 0D, 1D, 2D or 3D depending on the size [3,4]. Scientists realized the importance of these findings after learning that a substance's shape can alter its physical and chemical characteristics [4,5].

**Synthetic methods of nanoparticles:** The procedures for the formation of nanoparticles are decided upon completely on the basis of the requirements. Every strategy has a number of advantages, in addition to a number of disadvantages. The production procedures are selected with care and taking into account the efficiency of the infrastructure as much as possible [6]. Physical approaches are better suited for the small scale production than other approaches (*i.e.* chemical approaches), as the price of the manufacturing is a concerned in the selection of chemical methods [7], whereas the biological methods have different importance.

### Physical methods

**Ball milling:** Planetary mills, vibratory mills, tumbler mills, rod mills and mills made of carbide and steel rigid spheres are all employed in the production of nanoparticles. The nanocrystalline forms of Ti, Cr, Co, W and Ag-Fe are produced in this procedure. The gas or air inside the vessels spins rapidly around the axis of rotation [8] as the vessels spin in the ratio of 2:1 of balls to ingredients. The material is squeezed between the sides of the receptacles and the balls. For the purpose of creating nanoparticles of a particular size, it is crucial to mill them at the optimum duration and speed [9,10].

**Melt mixing:** Nanoparticles are formed by mixing fusion metal fluxes with high-speed disturbances. The nanoparticles are taken out of a glass. Glass is an amorphous solid, an incomplete symmetrical arrangement of atoms and molecules [11]. The metal forms an amorphous solid-metallic glasses when cooled to great cooling ratios. For example: hot stream of Ti and molten stream of Cu-B form $TiB_2$ nanoparticles [12].

**Pulse laser ablation:** The objective sample is first moved to the vacuum chamber. Plasma is then created by focusing a highly pulsed laser beam on the sample. which is converted to a colloidal solution of the nanoparticle. Lasers of the second type of harmonic group are widely used in the production of nanoparticles. The components influencing the final composition are as follows laser, few pulses, type of solvent and pulsation time [13].

**Pulsed wire discharge method:** The pulsed wire discharge method is another physical method technique for preparing nanoparticles [14]. This technique is completely different as compared to the physical techniques as discussed above. In this technique, vaporization of a metallic cable through a pulsed current is performed to generate vapour and then the vapour is passed through an ambient gas to cool, after cooling to form nanoparticles. This technology is rarely employed in industry, since it is both prohibitively expensive and at first glance, manifestly impractical for many metals [15]. However, for metals with strong electric conductivity, its radial availability in the form of thin wire is particularly advantageous [16].

**Chemical vapour deposition:** When it comes to producing nanomaterials based on carbon, this technique is significant. In this method, vapour phase precursors film is formed through a chemical reaction on the substrate surface. A precursor for all intents and purposed is considered suitable for CVD only if it has high definitely chemical purity, sufficient volatility, generally low cost, pretty food stability (during evaporation), a non-hazardous nature and a really long self-life and there would be no remaining wastes after its decomposition. For example, for carbon nanotube fabrication (by the CVD method. A gas is slowly introduced into the system after the substance is heating at high temperature in the furnace. At higher temperatures, the gas decomposed and carbon atoms are released. These atoms then come back together on the substrate to form carbon nanotubes [17]. However, the choice of catalyst is important for the type and morphology of material. Overall, CVD is a reliable method for producing nanoparticles of high quality and it has gained recognition in the context of 2D nanomaterials [18,19].

**Laser pyrolysis:** Carrier gas is used to introduce the gaseous phase precursors into a chamber, where the laser beam and the precursors meet there. The excessive strength laser beam has to generate an excessive nearby temperature to boost up the nucleation and increase of nanoparticles. The catcher equipment collects the particles from the filter. This process is also known as the gaseous phase process [20].

**Laser cluster beam deposition:** In this method, the deposited material is heated in a closed crucival to generate steam and the resulting vapour is then discharged into a vacuum through a nozzle [21,22]. Usually, the nozzle is about 1 to 2 mm in diameter. Some of the material that is ejected is sent towards the substrate because this material is turned into ions by being hit with electrons where it comes with a neutral beam component. The rapidly expanding vapour is believed to produce supersonic jets in which the condensation process produces clusters of 100 and 1000 of atoms. This type of process occurs at low temperatures that would resemble the well-established production of an atomic group of gas in a supersonic jet [23]. Depositing thin layers with ionized instead of ion groups solves many of the problems associated with depositing low-energy ions. The ideal strength should be on the order of the number of ions arriving on the subtract to the atoms binding strength at the surface of the film and shouldn't exceed the sputtering threshold [24].

### Chemical methods

**Sol-gel method:** The sol gel method is a wet chemical procedure widely used in industry to synthesize nanomaterials. High-grade metallic oxide nanomaterials are generally synthesized by sol-gel techniques [25]. This process takes place at a low temperature, so the process consumes less energy and causes less pollution. Sol liquids consist of a single solid particle, which is a subclass of colloids, while the gel exists as a continuous network of porous particles present in the fluid. In sol gel process, the sol is first formed in liquid, then the sol particles are joined to form a network. Powder and thin film of liquids are possible only when the liquids are dried [26].

**Sonochemical synthesis:** During this procedure, intense ultrasonic radiation is irradiated at the molecules, which in turn causes a chemical reaction to take place. Advantages of this method are that its operating conditions, simplicity and can easily control nanoparticle size by changing the concentration of precursors in the solution [27]. In sonolysis technique, a metal is first carefully selected, a circle of precursors of that complex metal is passed through waves of sound of a certain frequency. In this, two types of materials are used in the preparation of volatile and non-volatile precursor nanomaterials. There are some conditions in this method which are as follows: (i) the speed limit of sound in liquid should be between 1000 to 1500 m/s; (ii) the ultrasonic wavelength range should be from 10 cm to 100 μm; and (iii) the frequency range should be from 20 kHz to 15 MHz [28].

**Co-precipitation method:** This method is useful for synthesizing high quality nanoparticles at low temperatures and cheaply without the need for special environments because the method not only requires high pressure but also does not require high temperatures. In this method, by the filtration and washing the impure materials are eliminated [29].

**Inert gas condensation method:** Buhrman & Granqvist constructed an inert gas condensation system and used to prepare the ultrafine-particle metal [30]. It is a technique for synthesizing nanostructured materials using bottom-up method. The process consists of two main steps *viz.* (i) allowing the material to evaporate and then rapidly cooling it to produce nanoparticles that have right size [31].

**Hydrothermal synthesis:** This method is counted among the most robust processes, as it not only has easy conduction but also plays an important role in the preparation of the high-quality nanomaterials. Researchers report that hydrothermal synthesis is a chemical approach that produces nano-crystalline powders without any firing step due to its low crystallization temperature [32]. Metal ion content is typically limited in the industrial applications due to the high degree of difficulties associated with managing the chemical process during synthesis and preventing agglomeration [33].

## Biological methods

**Synthesis using microorganisms:** The size and shape of the nanoparticles depends on the pH, temperature and substance concentration on the organism employed and the conditions employed during synthesis. Different types of microorganisms have different methods for manufacturing nanoparticles [34]. Microbes use enzymes to break down metal ions stuck inside their cells into smaller, more manageable nanoparticles. There are two ways in which bacteria influence mineral formation. In the first place, at a specific point in time, the composition of the solution changes, making it more supersaturated than it was before. Another possibility is the manufacture of organic polymers, also known as biodegradable polymers. The nucleation may be affected by the first inhibition of the minerals [35]. Secondly, in the intracellular approach, the unique ion transport found in every single microbial cell is utilized. In this method, the cell wall is involved in the synthesis of nanostructured particles of intracellular and this cell wall is part of microorganism. There is an electrostatic interaction between the negative charge of the cell wall and the positive charge of metal ions. The enzymes reduce the ions (which are present inside of cell wall) to the nanoparticles and thus the cell wall dispersed by the nanoparticles. There is a stepwise process where verticillium makes nanoparticles inside cells. The mechanism of this synthesis involves bioreduction, trapping and capping, where the surface of the fungal cells interacts with the metallic ions to trap the ions by electrostatic interaction. This cell wall contains enzymes that work to convert the metal ions into metal nanoparticles. Nitrate reductase is an enzyme secreted by the fungus that plays a key role in bioreduction and, by extension, the formation of nanoparticles. For all these reasons, many researchers supported nitrate reductase [36]. Different metal nanoparticles have been synthesized from various kinds of microorganisms (bacteria, fungi, algae, *etc*.) are listed in Table-1.

TABLE-1
SYNTHESIS OF $TiO_2$ NANOPARTICLES BY USING DIFFERENT MICROORGANISMS

| Microorganism | Shape | Size (nm) | Ref. |
|---|---|---|---|
| *Lactobacillus sp.* | Spherical | 26.35 | [37] |
| *Saccharomyces cerevisiae* | Spherical | 8-35 | [37] |
| *Staphylococcus aureus* | Spherical | 20 | [38] |
| *Bacillus subtilis* | Spherical | 66-77 | [39] |
| *Bacillus mycoides* | Spherical | 40-60 | [40] |
| *Lactobacillus johnsonii* | Oval | 4-9 | [41] |
| *Halomonas elongata* | Spherical | 20-25 | [42] |
| *Aspergillus flavus* | Spherical | 62-74 | [43] |
| *Aspergillus niger* | Irregular | 200-800 | [44] |
| *Aeromonas hydrophilli* | Spherical | 28-54 | [45] |
| *Acorus calamu* | Irregular | 15-40 | [46] |
| *Parmotrema austrosinense* | Irregular | 10-80 | [47] |

## Synthesis using plant extracts

**Plant:** Several different parts of the various plants are capable of gathering small quantities of heavy metals. Hence, biosynthesis methods by employing extracts of plant have given rise to an efficient, simple and cost-effective method as well as a new technology as an excellent alternative means for the production of nanoparticles. Many researchers used plant leaf extracts through the green synthesis process to explore the applications of nanoparticles [48-50]. Plants contain different types of biomolecules like carbs, polypeptides, coenzymes, *etc*. and these are capable of reducing metallic salts to respective metal nanoparticles. $TiO_2$ nanoparticles can be synthesized using a wide variety of plants, including aloe vera, guava, basil, lemon, neem, coriander, lemongrass, mustard, *etc*. [51-54].

**Plant leaf extract-based mechanism:** Th extracts of plant leaves are not only a source of synthesis of metal nanoparticles but also an excellent source of synthesis of metal oxide nanoparticles. Moreover, the plant leaf extracts serve a dual role in the manufacture of nanoparticles acting as both stabilizing and reducing agents to facilitate the synthesis process [55]. An important factor in the synthesis of nanoparticles is the composition of the leaf extract of the studied plant. For example, different plant phytochemicals have different concentration levels [56,57]. The various functional groups existing in flavonoids having the capability to reduce metallic ion [58]. Flavonoids undergo tautomerization reactions that liberate reactive hydrogen atoms; these atoms convert the enol-form to the keto-form, which in turn decreases the number of cations in metallic nanparticles [59]. Plant extracts may also contain the sugars glucose and fructose, both of which have been linked to the formation of metal nanoparticles; however, it is important to observe that glucose can produce nanoparticles of varying morphology and size, whereas fructose's mediated nature is monodispersed in $TiO_2$ nanoparticles [60,61].

**$TiO_2$ nanoparticles and their applications:** Titania, which is an inorganic material, has important applications in many technical fields due to its commercial importance, it is commonly used as a pigment in paints, dielectrics and plays an important role in the field of photocatalytic applications [62]. Titania is a biocompatible, non-toxic, inorganic substance that can be used for photoelectrochemical energy generation [63]. Titania nanoparticles is also used in biomedical sciences such as pharmaceutical industries as well as bone tissue engineering [64] and the details of some applications are given in Table-2. The significance and multiplicity of these applications have pushed immense concern and significant advances in the manufacturing, classification and fundamentally understood of $TiO_2$ nanomaterials in the preceding decades. Bulk modification of positive ion and negative ion-doping is studied as a means of addressing the drawbacks of electron-hole combining and a relatively small surface zone in commercially-relevant $TiO_2$ nanomaterials [65].

## Conclusion

This mini-review focused on the several options for producing nanoscale materials with practical industrial applications, such as titanium dioxide. During the last few decades, a large

TABLE-2
SUMMARY OF THE SYNTHESIS OF $TiO_2$ NANOPARTICLES BY USING PLANT EXTRACT

| Name of the plant | Characterization | Size (nm) | Morphology | Applications | Ref. |
|---|---|---|---|---|---|
| *Jatropha curcas* L. latex | XRD, SAED TEM, EDX, FTIR | 25-100 | Spherical | Biomedical, bioengineering, electronic and environmental systems | [66] |
| *Aloe vera* | XTD, PSA, TEM, TG/DTA | 32 | Tetragonal irregular | Detoxifier, antiseptic, tonic for the nervous system, immune boosting, harbal medicine | [67] |
| *Cucurbita pepo* seeds | XRD, (UV-VIS), FTIR | | Tetragonal | Treat problems of the urinary system, hyper-tension, prevents the formation of kidney stones | [68] |
| *Moringa oleifera* | XRD, (UV-VIS) | 12.22 | Tetragonal | Antibacterial, antiseptics, antifungal, anti-inflammatory activities | [69] |
| *Trigonella foenum-graecum* | FTIR, UV, XRD, HR-TEM, HR-SEM | 20-90 | Spherical | Antimicrobial activities | [70] |
| *Syzygiu-m cumini* | HR-SEM, HR-TEM, EDS, FT-IR, XRD, DLS, BET | 10 | Spherical | Photocatalytic removal of lead form industrial wastewater | [71] |
| *Mentha arvensi* | XRD, UV-VIS, FTIR, SEM | 20-70 | Spherical | Antibacterial and antifungal activities | [72] |
| Orange peel | XRD, FE-SEM, FTIR, UV-VIS, PL, EDX | 21.61-17.30 | Triangular | Antibacterial, cyto toxicity and humidity sensor | [73] |
| *Carica papaya* | XRD, FE-SEM, TEM, FTIR, BET, UV-VIS | < 20 | Spherical | Photocatalytic efficiency | [74] |
| Cinnamon | XRD, SEM, EDX, UV-VIS, PL | 70.1 | Spherical | Photocatalytic property | [75] |

number of researches have been carried out in the field of the green synthesis of $TiO_2$ nanoparticles. However, there is a need for more investigation into the potential usage of phyto-synthesized $TiO_2$ nanoparticles beyond their current use in biomedicine and environmental remediation.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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