



Titanium Dioxide Nanoparticles: Advances in Synthesis Strategies, Multifunctional Applications, and Environmental Risk Assessment

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Abstract:

Nanotechnology is a rapidly growing field globally as a versatile technology in various disciplines. From all nano-materials, titanium dioxide nanoparticles (TiO₂ NPs) are considered the one of the most used in the day to day commodity products. These are produced by diverse physical, chemical, and biological approaches. Particularly, green synthesis has come to light as an ecofriendly, economically efficient and nontoxic technique.

TiO₂ NPs have exhibited enormous potential in agriculture, particularly in ameliorating plant growth under stress (biotic and abiotic) depending upon size, concentration, and exposure time. Besides agricultural use, they find application in nanopertilizers, wastewater treatment for heavy metal scavenging and in antibacterial applications.

However, the possibility of their genotoxic potential due to mal-handling and exposure cannot altogether be ruled out. These double-edged findings call for further studies. This review presents and discusses the state of the art literature findings on the synthesis, functionalization, and possible environmental and human health risks associated with TiO₂ NPs, notably eco-compatible production and safe disposal.

Keywords: Titanium Dioxide Nanoparticles (TiO₂ NPs), Green Synthesis, Photocatalysis, Antimicrobial Activity, Environmental Toxicity, Nanomaterial Applications

1. Introduction

Nanotechnology is an emerging field based on the manipulation of matter at the dimensions of 1 to 100 nanometres and it is attracting global attention for potential applications in various fields such as agriculture, medicine, energy and electronics [1]. Particles on the nanometer scale, particularly ones composed of metals such as copper, silver, zinc, iron and titanium dioxide, can have both beneficial and harmful effects on plant growth. However, further intense studies are still required to reveal their environmental and biological influences [2].

Plants are essential protagonists of these interactions, being the base of the food chain and terminals for entrance of engineered nanomaterials (ENMs). These products can even cause damage to ecosystems in cases of excessive application, polluting soil, water, and air [3]. In ENMs, titanium dioxide nanoparticles (TiO₂ NPs) are one of the commonly used nanomaterials commercially, because of their wide spread uses e.g., in paints, cosmetics, solar cells, and waste water treatment [4].

The United States, for example, produced just under 1.31 million tonnes of TiO₂ pigment in 2014, with global consumption of its nanoparticle counterpart approaching around 10,000 tonnes each year. By 2021, this number increased sharply, particularly in countries such as China and the U.S. which demonstrates the global demand and use-case of this product. Such popularity is due to the good chemical stability, high refractive index, low cost, and strong oxidation ability of TiO₂. These nanoparticles are available in three naturally occurring crystalline phases (anatase, rutile, and brookite), each of which has unique applications in several sectors including optics, electronics, food products, cosmetics, etc [5].

Daily exposure to TiO₂ NPs is frequent since they are formulated in substances such as toothpaste, sunscreens, shampoos, and some foods to improve brightness and flavor [6]. But their ubiquity raises environmental and health concerns, due to their propensity to end up in the air, water and soil [7]. For example, studies have indicated that TiO₂ NPs can have either beneficial or adverse effects on plant and aquatic life, depending on concentration, size, and length of exposure. For example, In *Vicia faba*, *Spinacia oleracea* and *Vigna radiata* the compounds promoted growth while they were toxic to the marine alga *Nitzschia closterium* [8–12].

The capability of these NPs to scavenge ROS and the induction of antioxidant enzymes makes TiO₂ NPs especially appealing in agriculture. It was found that these nanoparticles could possibly be used to mitigate plant stress and improve plant yield through modification of oxidative stress mechanism [13]. This review attempts to bring into understanding the synthesis techniques of TiO₂ NPs, prospects of applications and its environmental implications such as toxicities and disposal.

2. Synthesis of TiO₂ NPs

TiO₂ NPs can be synthesized by two general strategies such as top-down and bottom-up route. Top-down approaches first disassemble bulks materials into particles in the nanosize regimen through physical methods such as etching, milling, pulsed laser ablation, or sputtering [14, 15]. On the other hand, the bottom-up approach fabricates nanoparticles based on atomic or molecular level assembly by methods like chemical vapor deposition, sol-gel technique, flame spraying, hydrothermal reaction, sonochemistry and green synthesis.

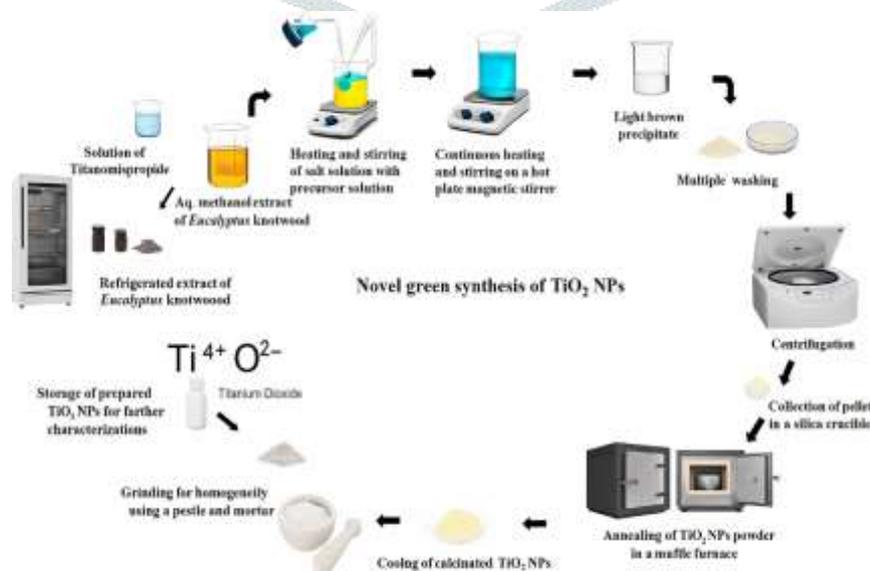


Figure 1: Schematic illustration of the novel green synthesis of TiO₂ NPs

Although the bottom-up mechanisms provide better regulation of the particle size and shape, but in the traditional chemical methods, they often use the toxic solvent, high temperature and energy consumption for the preparation of composites to some degree, bringing about the safety problems and also resulting in the environmental pollution. These limitations have steered researchers towards biological or “green” synthesis, which is safer, cheaper and more environmentally friendly (Figure 1).

2.1 Chemical Synthesis

TiO₂ NPs can be prepared through chemical methods like co-precipitation [16], sol–gel [17], solvothermal [18], and hydrothermal synthesis [19]. These methods enable precise control of nanoparticle morphology, but they are not without limitations – most of them involve high energy, high temperature, and high pressure inputs, and toxic materials [20].

For instance autoclaves under harsh conditions are used in hydrothermal and solvothermal techniques. Organic solvent OBB is used in solvothermal synthesis, which is less harmful but requires expensive equipment and long reaction time. In addition, impurities may be introduced during these processes by surfactants, which can also be harmful to the environment, particularly to aquatic systems [21–23].

In addition, other techniques such as spray pyrolysis have been used for film and powder uniformity production; however, they are energy consuming and expensive methods which restrict their carrying out at the industrial scale [24]. The electrophoretic deposition is a convenient and fast process, but is limited by the solvent—that is mainly water—and also will release volatile organic pollutants to the air [25,26].

PA synthesis enables a one-step process, but without uniform microwave heating; PA and gel synthesis generally lead to products with particles, but small and uniform in size [27,33]. Although sol-gel has been researched quite maturely, the processing is expensive because of high pure raw material, along with problems, such as cracking and volume reduction during drying [28].

2.2.1 Biological (Green) Synthesis

Because of concerns about the environment arising from chemical approaches, green synthesis offers a more viable option. The method employs naturally available reducing agents in plants, microorganisms, food waste, and other biological resources for a safe, cost effective and scale up preparation of TiO₂ NPs [29,30]. These bio-based processes are low energy consuming and free of toxic chemicals which generally are suitable for industrial applications [20, 31].

2.2.1 Plant-Based Synthesis

Green synthesis of the nanoparticles using plant extracts is the perfectly available and non-toxic source of natural reducing and stabilizing agents which are rich in such as alkaloids, phenolics, terpenoids and flavonoids [32]. Leaves, flowers, stems, roots, and seeds have been used. Leaf extracts are particularly preferred because they can be easily collected and have abundant metabolites [14].

For instance, anatase-phase TiO₂ photocatalyst with oxygen vacancy was obtained from cinnamon extract, which may be used in the solar light harvesting [33]. Nanoparticles were obtained from leaf extracts of *Syzygium cumini* and *Moringa oleifera*, which were exploited for wastewater lead removal and for eco-friendly antimicrobial purposes [34,14]. Other plant-based precursors such as orange peels, *Cucurbita pepo* seeds, *Cynodon dactylon*, *Trigonella foenum-graecum*, and pomegranate peel have also been used in the development of functionalized TiO₂ NPs for sensing, antimicrobial coatings and water purification [31,36–38]. Recently, watermelon rind waste-derived TiO₂ NPs with size of ~7 nm has been biosynthesized. These particles showed high antioxidant, antibacterial and anticancer activities [39].

2.2.2 Microbial Synthesis

TiO₂ NPs can also be produced by microorganisms such as bacteria, fungi, and yeast. Species-dependent intracellular (inside the cell) or extracellular (outside the cells, in the culture medium) bioproduction of nanoparticles. The extracellular synthesis can be more suitable for the scalability and purification of the metabolites [49].

But there are problems with microbe-based approaches: not all strains do a good job of generating nanoparticles, and NPs are difficult to tune in terms of size and shape. For example anatase-phase TiO₂ with good antibacterial activity was synthesized by baker's yeast [50]. Streptomyces sp. non-toxic TiO₂ NPs prepared for antibiofilm applications [51]. Acinetobacter, Bacillus and Planomicrobium were shown to be successful for scalable cost effective production of TiO₂ NPs with environmental and antimicrobial applications.

2.2.3 Other Biologic Sources

Other biological sources have been employed in addition to plants and microorganisms. Green synthesis with starch, egg albumin, and the egg shell has been exploited for simple, low-cost and low impact on the environment [52, 53]. Biopolymers, such as gelatin and cellulose, rice straw, arginine, and protamine were also used for the synthesis of certain structured TiO₂ with porous structure, biocompatibility and photocatalytic activity [54–56]. These new sources further widen the toolkit for green nanoparticle synthesis.

3. Uses of Titanium Dioxide Nanoparticles

3.1 Improving Crop Resilience to Environmental Stress

This environmental stress including drought, temperature, salt and nutrient limiting stress are major threats to agricultural productivity which are normally more damaging than biotic or mechanical damages. Plants in turn mobilize a range of defensive strategies, such as the synthesis of phenolic compounds that boost their radical scavenging power [57].

The influence of titanium dioxide nanoparticles (TiO₂ NPs) on plant performance is contradictory and depends upon various factors such as concentration, size, and ecological parameters. For instance, in *Nitzschia closterium*, TiO₂ NPs induced oxidative stress and growth inhibition [58,59]. However, in cotton, *Dracocephalum*, and *Vitex* crops, these nanoparticles increased the antioxidant content, the essential oil yield and the stress resistance [60]. Likewise, there was a decrease in membrane damage in chickpea plants following TiO₂ NP exposure [61–63].

In *Nigella sativa*, TiO₂ NPs promoted thymoquinone biosynthesis by stimulating the key metabolic pathways [64]. High irradiance with TiO₂ NP exposure increased flowering, fruit yield and antioxidant enzyme activity in tomatoes, indicating that stress-mediated signals might be influencing plant reproduction [65].

In contaminated soil, NPs of TiO₂ Equipment purchases also have a contributing impact on lowering the shelter of heavy metal absorption by crops. This is especially important in cadmium, arsenic, and lead decontamination [66,67]. However, their efficacy relies on the soil type, exposure pathway (foliar, hydroponic, or seed priming), and characteristics of nanoparticle such as size and concentration [68–71].

For example, TiO₂ NPs seed priming increased salt stress tolerance in comparison to *Origanum majorana* and up-regulated phenolic pathways and ABC transporter as detoxification agents ([72,73]). In coriander, TiO₂ NPs elevated proline synthesis and enhanced yield under cadmium stress [74]. Cucumber plants under drought and Ni stress gained favorable redox balance, sulfur forming, and K retention by TiO₂ treatment [75]. In tomatoes, TiO₂ enhanced water content but diminished drought-induced stress responses to drought like MDA and proline [76]. TiO₂ mitigated arsenic-induced oxidative stress in *Vigna radiata* [77].

The gene-level alterations instigated by TiO₂ NPs have been highlighted in a number of studies. The transcripts of heat shock protein genes were overexpressed by salt stress in *Vicia faba* [78]. The expression of flavonoid related genes, *pal* and *ras* [79] was up-regulated in *Dracocephalum* roots. In *Arabidopsis* genes implicated in sulphur metabolism and detoxification of ROS were upregulated (=either encoded or activated?), which helped to protect *Arabidopsis* against the toxic effects of tetracycline [80, 83]. Expression of auxin pathway genes promoted root development in *Arabidopsis* [81] and expression of metal transporter genes was suppressed in the presence of lead in rice [82]. Other investigations also reported up-regulated stress enzyme activity and nutrient uptake in a variety of crops [84–88].

3.2 Decontamination of Waste Water from Heavy Metals

As generally non-biodegradable heavy metals (e.g., arsenic, cadmium, chromium, mercury, lead) are a severe danger to both human health and environment. Those pollutants are wide spread in the industrial and domestic effluent and can last in the ecosystems for years [59,101,102].

Nanomaterials, in particular, TiO₂ NPs, represent an excellent option for this purpose. Due to their large surface area, good photocatalytic and powerful oxidative properties, they have also been regarded as efficient adsorbents. Under the action of UV or visible light, the bioavailability and toxicity of Cd (the heavy metal) can be changed by TiO₂ NPs, thereby reducing their harm [103–107].

3.3 Photocatalytic Disposition of Pollutants

TiO₂ NPs are also superior in degrading organic pollutants such as dyes and nitroarene compounds in wastewater. The pollutants are frequently recalcitrant and toxic; however, the photocatalytic nature of TiO₂ makes it capable of degrading the pollutants under UV or sometimes under visible light [52].

Plant-mediated TiO₂ NPs using *Prunus yedoensis* and *Jatropha curcas* have proved to be efficient photocatalysts. The presence of functional groups, such as hydroxyls and phenolics, found by FTIR spectroscopy, has been shown to increase light absorption and the degradation capabilities [108,109].

An application example in practice was the field testing of a solar photocatalytic parabolic trough reactor with green-synthesized TiO₂ that reached a chromium removal of >75% and a substantial chemical oxygen demand (COD) decrease [109]. The working principle is that the hole (h⁺) and the electron (e) generated after the irradiation of a band gap can then degrade organic molecules by means of ROS such as OH⁻ and O₂⁻ [110].

3.4 Antimicrobial Activity

TiO₂ NP are powerful antibacterial and antifungal agents, due to their capacity to produce ROS upon interacting with microbial cells. These ROS attack the cell membrane, inactivate enzymes and block the nutrients intake resulting in the death of the microorganism [6].

For instance, TiO₂ NPs synthesized with *Psidium guajava* leaves demonstrated notable antibacterial activity on *Staphylococcus aureus* and *Escherichia coli*, and inhibition zones as great as 25 mm were recorded. The active functional groups responsible for nanoparticle stability and activity were verified by FTIR analysis [111].

According to the investigations, green-fabricated TiO₂ NPs possess higher biocidal potential when compared to chemically fabricated TiO₂ NPs because of the smaller particle size and bioactive capping components [112]. For example, the TiO₂ extracted from *Bacillus subtilis* showed strong effects on dental use [113]. Biologically prepared TiO₂ NPs exhibited even better antimicrobial activity compared to that of standard antibiotics in most of the cases [114].

3.5 Nano-Fertilizers

Traditional fertilizers such as nitrogen (N), phosphorus (P), and potassium (K) (commonly known as NPK fertilizers) are frequently inefficient, with only 25–30% of the nutrients applied being absorbed by plants. To overcome this waste of input, the value of nanotechnology in agriculture is being realised. Nanotechnology employs scale of materials in the range of 1 to 100 nm to increase nutrient delivery and uptake, while providing higher reactivity, greater surface area, and improved plant interaction [115,116].

After application, these nanoparticles can be absorbed by leaves and roots. Leaf absorbed nanoparticles penetrate through the cuticle, epidermis, and mesophyll covering into the vascular tissues, whereas the root absorbed particles penetrate through root hairs, epidermis, and cortex, crossing both symplastic and apoplastic pathways [117].

Of all types of nanomaterials that have been employed to date as fertilizers, bio-fabricated titanium dioxide nanoparticles (TiO₂ NPs) are the most promising with respect to their photocatalytic activity, morphological stability, adjustable hydrophilicity, and biocompatibility [118,119]. Unlike metal nanoparticles that are not stable in water, TiO₂NPs are highly soluble and are optimal for plant use [120,121].

These nanoparticles can induce plant defence mechanisms, making them better equipped to face abiotic stress such as drought, cold and heavy metal toxicity. Their efficiency is a function of the size and shape of the particles and dose as well as crop and environment.

For example, In red bean (*Vigna angularis*), the TiO₂ NPs were able to enhance the root growth, chl synthesis, and nutrient accumulation with no or little physiological damage postexposure [122–124]. Compared with ZnO NPs, the positive effects of TiO₂ NPs on enhancement of photosynthesis and reduction of oxidative stress was more prominent [125]. As well, a fungus *Aspergillus flavus* TFR 7 was employed for the biogenesis of TiO₂ NPs which showed positive impact on the growth and nutrient uptake, including phosphorus of mung bean even in absence of P fertilizers [126].

TiO₂ NPs also promoted shoot growth and essential oil content of crops such as *Mentha arvensis* and preserved cell membranes from oxidative damages under drought stress [127]. In case of *Glycyrrhiza glabra* (licorice) such NPs enhanced the cold stress tolerance and reduced the toxic compounds such as MDA and H₂O₂ [128].

In addition, TiO₂ NPs are considered to be effective to ameliorate antibiotic toxicity. In *Oryza sativa* and *Arabidopsis thaliana*, they detoxified tetracycline by uptake and rendering nutrient again available [129]. Cowpea plants treated with TiO₂ NPs under cadmium stress exhibited a decrease in metal content and an increase in activity capacity of antioxidant enzymes and the chlorophyll concentration, indicating a reduced stress and an improved nutrient uptake [130]. In tomatoes, the use of TiO₂ NPs resulted in improved stress tolerance as well as fruit yield and biomass, and was proposed as an alternative to chemical nematicides [131,132].

Due to their multifunctional properties (improvement of photosynthesis and protection of plants against biotic and abiotic stress) NP-TiO₂ are also being applied beyond agricultural applications to other fields including medicine (drug delivery, phototherapy, imaging), environmental remediation and biotechnology [121].

4. Toxicity of TiO₂ NPs

Despite various benefits of titanium dioxide nanoparticles (TiO₂ NPs), their impact on plants is not universally favorable. The likely occurrence of a phenomenon, that is, hormesis, when low-concentration application of nanoparticles stimulates plant growth and high dosages can cause growth retardation [133].

With an increasing application of TiO₂ NPs in agriculture, medicine, and industry there is a potential threat for environmental accumulation. These NPs may infiltrate into soil systems with the irrigation water,

nominous fertilizers or sludge, leading to long-term effects on ecosystems, especially on the plants which are the base of the food chain [134].

Several studies have evaluated the toxicity of NPs finding that particle size, crystal phase, surface coating, environmental conditions and plant species affect toxicity results [121].

New emerging evidence indicates that TiO₂ NPs can induce genetic instability in plants. For instance, In *Allium cepa* (onion), TiO₂ induced DNA damage, which in turn resulted in disorganization of root meristematic cells [135,136].

Onion roots treated with extract exhibited enhanced level of malondialdehyde (MDA, a lipid peroxidation marker) and repressed root elongation, which are the signs of oxidative stress [137]. In *A. thaliana*, chromosomal abnormalities and changes in microtubule array organisation and dynamics directly affect root development [138].

Dose-related whiteness porting responses were also reported. Toxic signs (root growth inhibition, and a changed pollen–mother cell division pattern) were observed in *A. cepa* at concentrations of 12.5–100 µg/mL [139].

Cellular effects TiO₂ NPs shave the capacity to interfere with important cellular processes. The oxidative stress caused by TiO₂ leads to the damage of membranes and enzyme function. Alterations in gene expression including genes involved in antioxidant protection--are widespread under high exposure.

Some studies also report adverse effects on photosynthesis, nutrient uptakes or water balance, particularly when TiO₂ reaches levels in leaf tissues or roots beyond safe levels. The toxicity of TiO₂ NPs is not the same. The dominant factors that affect the transmission of each record are properties of the particles (such as size, shape, and surface area); environmental conditions (light, pH, temperature) and as well as the route and concentration, and

The organization-level controllable factors were the plant-specific physiological and anatomical features (i.e., root structure, metabolic rate). These differences highlight the importance of careful dose optimization and risk evaluation for the applications of TiO₂ NPs in agriculture or environmental applications.

5. Conclusion and Future outlook

Titanium dioxide nanoparticles (TiO₂ NPs) are one of the most extensively studied and used nanomaterials in various fields, including agriculture, environmental remediation, medicine, and materials science. Due to their distinctive characteristics such as high surface area, photocatalytic activity, chemical stability, and biocompatibility, they are highly appreciated.

For agriculture, TiO₂ NPs have also shown a significant performance on increased crop yield, stress resistance, and degradation of pollutants, for heavy metal and antibiotics. Their use as nanofertilizers, antimicrobial agents, and photocatalysts have placed them as interesting tools for environmental management as well as sustainable farming.

The advent of green synthesis approaches incorporating plants, microbes and other biological materials presents the additional benefit of safer cost-effective, and eco-friendly nanoparticle production. With these approaches, the whole world movement to greener, circular bioeconomy is supported.

Nevertheless, the growing occurrence of TiO₂ NPs in the environment also raises legitimate questions about their toxicity, bioaccumulation, and genetic effects on plants and other biota. The dose-dependent effects, in particular genotoxicity and oxidative damage in high concentration, point toward the requirement for standardized protocols and regulatory policies for their safe uses.

Future areas to research for TiO₂ NPs are long-term environmental effect of TiO₂ NPs, optimization of the biosynthesis methods to ensure reproducible quality, investigating targeted delivery systems in agriculture and medical fields, nanoparticle – plant - soil interactions at molecular scales and deploying green production techniques to an industrial scale. Redressing innovation and environmental safety, TiO₂ NPs can be a keystone of future sustainable nanotechnologies.

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