Plant-Mediated Green Synthesis of Titanium Dioxide Nanoparticles: Mechanisms, Characterization Strategies, and Emerging Applications in Sustainable Nanotechnology

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Abstract

Due to their unique properties, titanium dioxide nanoparticles (TiO_2 NPs) have been widely used in many fields, such as the medical, electrical, chemical, and membrane industries. The self-cleaning property, photocatalytic effect, appropriate band gap, high antibacterial performance, and remarkable physical and chemical stability contribute to this great potential. However, the conventional chemical synthesis of TiO_2 NPs employs toxic reducing agents which cause environmental and health problems. Recent investigations, however, have tended to lean towards biosynthesis employing plant-based extracts containing high levels of natural biomolecules including polyphenols. These complexes not only function as a reducing agent for titanium precursors but can also act as capping and produce NPs with different morphologies, sizes and greater surface reactivity.

Green synthesis is increasingly used as an efficient, cost-effective, and eco-friendly technology. This review is aimed to discuss the biosynthesis of TiO_2 NPs, based on plant extracts, focusing on experimental conditions and the immense plant diversity available for the synthesis of such NPs. The article also discusses the physico-chemical characteristics of resultant NPs, rendering them suitable for numerous applications (biomedical applications in particular) due to their biocompatibility and functional uses. The results are expected to stimulate further studies on green nanotechnology and to design new synthesis methods for safe and multifunctional nanomaterials.

Keywords: Green Synthesis, Titanium Dioxide NPs, Plant Extracts, Nanoparticle Characterization, Phytochemical Reduction, Biomedical Applications

1. Introduction

The question of stability and convergence of continuum models that approximate discrete crack surfaces has been of interest for decades. Membranes have employed NPs in a variety of applications, such as water purification [1–4], gas separation [5], and with medical applications such as wound healing [6, 7]. The nanosize effect on BuOH was able to significantly increase the surface area, leading to superior performance, such as antimicrobial, antifouling, and photocatalytic properties. However, there are health and environmental concerns about the use of synthetic ingredients [4].

The novel concept of green synthesis provides a considerable relief in this direction. Biologically synthesized NPs—synthesized using biological routes have stimulated attention for their extra beneficial characteristics, such as antibiotic resistance [8, 9] and biocompatibility [10], which are not better detected in chemically and physically synthesized NPs. These biomimetic NPs, once embedded in the membrane, are beneficial for performance and safety. Several review articles have overviewed the development of biosynthesized NPs and their possible applications [11–14].

Although physic-chemical methods for synthesis are fairly developed, both suffer from such problems as particle size, morphology, stability and aggregation control. Furthermore, there is an extra dimension added in purifying the NPs for further use [15]. The 'green synthesis' process utilizes natural sources, like microorganisms, fungi, algae, and notably plant extracts, to overcome many of these challenges. In addition, this technique requires no hazardous chemicals, and is economic, flexible and energy-saving even without high pressure and temperature [15, 16].

Traditional approaches often contain the usage of strong reducing agents such as sodium borohydride ($NaBH_4$), DMF, Tollen's reagent, hydrazine hydrate, etc. [17]. These reagents are very dangerous for the environment and for biology [11]. Therefore, there is an urgent requirement to prepare the highly efficient, green, and benign synthesis route of the goal photo-responsive materials.

Green biosynthesis can provide an opportunity to bypass this. It is particularly attractive for biomedical applications as one of its greatest merits is to be nontoxic [13]. The sustainability of synthesis process which includes the economic practicability, ecological responsibility and adaptation to social acceptability, becomes a critical criterion [11, 18-20]. Normally we have a "top-down" or "bottom-up" procedure for the synthesis of NPs (see Fig. 2). Bulk materials are subjected to top-down approach methods like milling or sputtering to form NPs. In contrast, the bottom-up approach structures atoms or molecules to build nanosized devices.

However, these tactics are well-established but with limitations which biosynthesis can overcome. Of importance is that the biosynthesis eliminates the pollution of the nanoparticle surfaces commonly formed during the chemical procedures due to the presence of the residual by-products [21]. That is especially useful for applications such as medicine which require purity.

Biosynthesized TiO_2 NPs have attracted attention mainly owing to their interesting properties, such as photocatalytic performance, self-cleaning property, antimicrobial action, and good stability. The natural components have become the treasure chests for green synthesis, the exploitation of which is expected to usher in a new era in the preparation of functional nanomaterials. This review work is to provide a full perspective of TiO_2 biosynthesis via plant sources with emphasis on sustainable processes and in the context of the material's performance and applications in diverse systems.

2. Biogenic production Using Plant Extracts

Indeed, there is substantial evidence to suggest that the TiO_2 NPs can demonstrate excellent oxidative ability as well as extraordinary chemical, optical stability, and photodegradation and antimicrobial activity that makes it very beneficial in areas such as catalysis, pigments, purification of water, and biomedicine [13,22]. An important characteristic of green-synthesized TiO_2 is the participation of biomolecules of the plant extracts that act as reducing and capping agents. This has a dual effect as it not only promotes the formation of NPs but also increases their stability and compatibility to a variety of environments [23].

Using extracts from plants (leaf, root, bark, or flower) is very helpful as most of the plants were already known for their medicinal or aromatic uses [24]. Plant extracts are easier to use and process than bacteria or fungi they react faster and do not need to be cultured under sterile conditions for production, the write in the journal Laboratory Investigation, and are easily scalable. Extraction is often performed at low temperatures and with solvents such as water or ethanol in order to preserve the active phytochemicals [15].

The concentration and species of the plant extract have a big influence on the shape, size and dispersity of NPs [25]. These effects were attributed to the presence of bioactive moieties including alkaloids, flavonoids, terpenoids, phenolic, saponins, and tannins, which have functional groups (e.g., hydroxyl, carbonyl, amine) that can reduce and stabilize Ti precursor [26,27, 29]. This renders green synthesis desirable not only in terms of the sustainabil ity of the method, but also for generating NPs with possible medical applications, as a dual advantage that cannot be achieved with the chemical based methods [12,19].

Several researches have already been conducted to optimize the various parameters of the synthesis like the solvent nature, the concentration of plant material, drying, the reaction temperature and many others [30, 31]. Usual preparation Fresh plant material is cleaned, dried, often in the shade for about 15 days, and then powdered. This is boiled in solvent, filtered and the extracts rich in phytochemicals are then used to reduce the titanium precursor. The reaction product is filtered, washed (usually with ethanol), and dried or calcined at temperatures from 450 to 600 C to eliminate residual organics.

It was, for instance, reported that well-crystallized spherical TiO_2 NPs of size < 100 nm were obtained by treatment of Nyctanthes arbortristis leaves in ethanol at 50°C followed by calcination at 500°C for 3 h [28]. For Moringa oleifera leaves, NPs of 12 nm mean size of tetragonal TiO 2 were obtained using Ti (isopropoxide) and ethanol under similar conditions [32]. Such examples strongly indicate that through green synthesis, it becomes feasible to achieve particles with desired shapes and phases.

The color of reaction solutions due to surface plasmon resonance (SPR) under synthesis conditions is usually used for monitoring the NPs [33]. Plant-mediated syntheses do not always exhibit a clear impact, as observed in the process of Psidium guajava extract with the pristine $TiO(OH)_2$ [34, 35].

Extraction method, in particular the solvent used, has a major impact on the quantity and type of phytochemicals extracted. More polar solvents such as ethyl alcohol and methyl alcohol are effective in the extraction of antioxidants [36, 37]. For instance, Koffi et al. ethanolic extracts of Ivorian plants provided more phenols content than methanol, acetone, and water [38].

Another consideration is pH. Under basic conditions, NPs are usually more easily formed owing to the increase in ionization of biomolecules [29, 42]. It has been reported that tetragonal rutile phase TiO_2 NPs with a diameter of ca. 19 nm can be synthesized from the peels of Citrus sinensis by the pH value adjustment to pH=7 [42]. Also, Hibiscus rosa sinensis extract synthesized perfectly spherical TiO_2 NPs (~7 nm) with excellent crystallinity and very low presence of aggregated particles [47].

Similarly, various NPs were formed and aggregation behaviors were modified from 20 to 50 nm in addition to the pH values (due to phytochemical activity) with Aloe barbadensis and Jatropha curcas [39,40,41]. As a general rule, high pH encourages the formation of monodispersed smaller particles, now if you go for a low pH it may tend to agglomerate.

Nanoparticle crystallinity is also affected by thermal processing, in particular calcination. In most green syntheses, the tetragonal crystal phase is obtained, with cubic phase formation being an exception that has been reported [28, 32, 40–43]. Here, these results indicate that the biosynthetic origin of TiO_2 NPs not only do they got immediate screening compared to chemically synthesized materials but also the exclusion of toxic residues by using biological agents in general [23,44–46].

3. Characterization of Biosynthesized TiO_2 NPs – Size and Shape Regulation

Nanoparticle biosynthesis's characterization is a key issue for application acceptability and performance prediction. In recent years, efforts have been made to develop reactors for a controlled synthesis of most proteinogenic amino acids in general and α-amino-■-nitroalkanoic acids in particular with a high degree of reliability, especially for environmental and biomedically-related applications where precision is critical [44].

Physical properties of the greenly synthesized plant-mediated TiO_2 NPs The plant-extracted green-synthesized TiO_2 NPs possess a number of physical properties (particle size, surface morphology, surface area, thermal stability, and optical behavior) that have the exclusive effect in the successful application of plant-mediated TiO_2 NPs [28, 60–64]. Different methods of characterizations exist to analyze such features, which are appropriate for different types of data. Some important characteristics and its related analytical techniques are as follow:

Size and Structure: Formulations size and dimensions can be determined via methods such as XRD, particle size analyzer (PSA), dynamic light scattering (DLS), atomic force microscopy (AFM), and TEM. Crystallography and structure XRD enables one to deduce crystal structure, crystalline phase, and diffraction patterns, and average crystallite sizes are calculated from the Debye–Scherrer formula [32,40]. DLS is appropriate for characterization of particle size in colloidal solutions, and PSA is applied with ultrasound dispersion to achieve the measurement of histograms of size distribution. On the other hand, AFM is applied to visually inspect surface topography and textures [40,65,66].

Surface Functional Groups: FTIR is one of an important tool for looking on the chemical bonding and functional groups attached on the surface of the nanoparticle. This method is used to confirm the existence of organic compounds such as C–C, C=C, C–O, O–H and N–H bonds—confirming that biomolecules from the plant extract are bound on to the NPs [34, 35, 46].

Morphology and composition: Scanning electron microscopy (SEM), field emissionSEM (FESEM), and transmission electron microscopy (TEM) are used to study the shape and surface of the nano-particles. FESEM provides surface imaging with high resolution, whereas TEM can give access to internal structures. Complementing methods such as energy-dispersive X-ray spectroscopy (EDS/EDX) are used to examine the elemental composition and purity of the samples [28, 35,5 1].

Optical properties: The interaction of light by NPs is studied by UV–Vis spectroscopy. This is crucial under applications such as the photocatalysis. The absorption edge of biosynthesized TiO_2 are usually around 380 nm and can be shifted to the visible region by the surface modifications or doping [31, 49, 60, 65, 70]. Similarly, this technique identifies the existence of phyto-antioxidants, i.e., phenolics and flavonoids, as indirect proof of plant-based bio-coatings [71–73].

Colloidal stability: Suspended NPs may coagulate, inhibiting their surface activity. it is known that measuring the zeta potential can be used to estimate surface charge and to predict colloidal stability. Generally, particles with either a positive or negative zeta potential beyond 30 mV are thought to be stable because of electrostatic repulsion. The values of zeta potential are markedly influenced by ionic strength and solution pH [67,74–76].

Thermal performance: The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) are operated to evaluate the thermal stability of biosynthesized NPs and to determine the decay temperature of organic compounds [60].

The significance of zeta potential, for instance, is well illustrated by Sankar et al. [46] prepared the TiO_2 NPs with leaf extract of Azadirachta indica (neem). Their particles were negatively charged −24 mV) and of an average size of approximately 124 nm. The particle surface electric charge, zeta potential, which was found to be negative, contributed to the colloidal suspensions stability prepared conditions at pH 1.5 and 50°C, using titanium isopropoxide as precursor.

Biosynthesized (anatase) TiO_2 NPs are usually in the range of 7–150 nm and are generally spherical or near spherical in shape; however, oval, irregular, agglomerated, or individually dispersed shapes are also reported, which could be attributed to the nature of biomolecules used as capping agents [28, 39, 40, 47]. An anatase-phase XRD peaks is observed in plant-derived TiO_2, suggesting successful preparation of the material (in contrast to plant extract alone, for which XRD features were not observed, since no titanium precursor was present, as expected) [45]. The size of TiO_2 NPs was 7 nm for Hibiscus rosa-sinensis synthesised compared to those chemically synthesized (24 nm) with wider XRD peaks indicating phytochemical mediated strain and less agglomeration [47]. Singh et al. [78] reported that the shape and crystal size of nanoparticles can be controlled by changing the type of precursor, type of functional group and synthesis condition. Hudlikar et al. [58] observed that free SDS treatment, under heating at 85°C, causes aggregation of NPs and their FTIR signal disappearance, important for application where uncapped NP are needed such as for thin films, or coatings.

4. Mechanism of Biosynthesized TiO_2NPs

Although the identification and characterization of the biomolecules accountable for the green synthesis of TiO_2 NPs have significantly achieved, the exact mechanistic pathway is yet to be revealed. However, increasing amounts of evidence suggest that certain plant metabolites, in particular phenolics, alkaloids, polysaccharides, alcohols, and other organic molecules are also involved in the development, stabilization, and reduction of these titanium precursors during biosynthesis [11, 20].

The mechanism may be quite different depending on the type of the plant species because each species has different biomolecules profiles capable of modulating nanoparticle formation [21]. In general, the reduction potentials of metal ions as well as the actual reducing abilities of plant extracts contribute to nanoparticle synthesis.

For example, a potential bioreduction mechanism was supposed for titanyl hydroxide [$TiO(OH)_2$], responsible for the plant root extract reduction by Researchers [56]. Their FTIR evidence revealed the existence of hydroxyl groups, mainly originating from phenolic compounds, participating in the reduction on Ti (IV) to TiO_2 and also working as capping agents. These molecules were grafted onto the particle surface, thereby preventing their agglomeration. The changes in peak positions of FTIR also suggested that phytochemicals were interacting with metal ions, during the synthesis.

This dual role as a bioreductant and a capping agent is not the only one. The same conclusion was found in studies of flavonoids, terpenoids, and polyphenolic compounds of other plants [47]. These biomolecules can act as not only the shape/body-determining agent of the particles but also protect the aggregation-free stability by covering the nanoparticle surfaces, to well distribute and biocompatible with living organisms.

For example, Rajkumari et al. ra leaf extract spectrum in FTIR showed band's broad OH stretching, meaning the existence of acids (carboxylic), flavonoids, terpenoids and proteins [39]. These chemicals were directly involved in the development and stabilization of TiO_2 NPs. Likewise, Sankar et al. [46] was that active compounds in Azadirachta indica extract fulfilled similar roles.

Pratap et al. [41] reported that hydroxyl groups of Jatropha curcas L. leaf extract served as reducing as well as capping agents. Their UV-Vis spectroscopy spectra showed a high absorbance peak at 336 nm, which is characteristic of TiO_2 formation, thus supporting the possibility that phenols and polyphenolic tannins played a role in the synthesis and stabilization of the NPs.

Nithya et al. [61] confirmed further this by examining FTIR spectra that indicated the existence of stretching vibrations of hydroxyl and amino groups for alcohols, phenols and amines. The presence of such biologically active functional groups proved that the green synthesis of TiO_2 NPs was possible through phytochemical participation in the synthesis.

Roopan et al. [33] have proposed a stepwise mode of action from Annona squamosa (sugar apple) peel extract. TiO_2 NPs are nucleated and grown when hydroxyl groups of phytochemicals are present; they play an important role in the reduction of titanium ions by phytochemicals. During further process, the same or more biomolecules would stabilize the NPs for the fact that they can coat on the surface of NPs by forming an organic shell to increase the monodispersity and homogeneous distribution [6].

A synergy is evident in most of these biosynthetic pathways: phytochemicals are involved through multiple roles: as reducing agents, as nucleation promoters and as capping agents. Moreover, this dual utility alleviates the requirement for extraneous toxic chemicals and provides better surface chemistries for nanomaterials used in biomedical, environmental, and catalytic applications.

5. Applications of Biosynthesized TiO_2 NPs

Biologically synthesized TiO_2 NPs have gained attention and great potential for diverse applications, from environmental methods to healthcare. The green synthesized-TiO_2 is different from its chemical- based one due to the existence of the surface-bound phytochemicals (generated from plant extract) that contribute to its biocompatibility and catalytic activity.

Photocatalysis represents the most promising application of these NPs. TiO_2 is considered as a photocatalyst when activated under ultraviolet (UV) light and it can decompose organic pollutants present in air and water. Biosynthesized TiO_2, in particular, has exhibited a superior activity in these applications as a result of their improved surface reactivity and the suppression of particle agglomeration, all of which can be utilized for increasing the numbers of the active sites through photocatalytic action [42, 52, 53]. Biodegradable TiO_2, for instance, has been applied to wastewater treatment to degrade dye pollutants and phenolic compounds.

Also the biomedical applications are an important field for antibacterial, antimicrobial, wound healing, drug delivery, and biosensors by using green TiO_2 NPs. The antibacterial efficacy of TiO_2 NPs was synthesized from different plant extracts has well been confirmed in several studies. The phytochemical coatings cause them to bind more effectively to bacterial versus human membranes, and decrease cytotoxicity of human cells, such as endothelial cells, which is important for medical applications [28, 39, 47, 54].

In addition, agriculture and pest management is another area that has cushion against the effect of TiO_2 NPs. Larvicidal, insecticidal, antifungal activity of these NPs has been recorded and are effective especially when plants extracts viz: Mangifera indica, Calotropis gigantea were used to synthesize [54,55,59]. These nanomaterials, which are also used in conjunction with plant extracts, represent eco-friendly products for controlling pests and diseases, which threaten agricultural productivity.

Biosynthesized TiO_2 is investigated for its UV blocking activity in the cosmetic and personal care sector. Because TiO_2 is non-hazardous and has ability to reflect UV light, it is widely used in sunscreens, skin creams, and protective coatings. The use of green synthesis guarantees that the product is devoid of noxious byproducts which are usually accompanied with chemical methods [12].

Energy and electronics applications also are beginning to incorporate such TiO_2 NPs in dye-sensitized solar cells and sensor technology. The biosynthesized TiO_2 possesses customized band gaps and a superior charge transfer capability, being essential to the enhanced photovoltaic efficiency and sensor sensitivity [60].

The application scenario becomes even more complex taking into consideration the catalysis role of TiO_2 in chemistry and the chemical synthetisys, serving as a supporting material for other catalysts or acting as a catalyst itself. Due to its huge surface area, stability and tunable surface chemistry, bio-TiO_2 is an excellent participant for organic transformations and for the detoxification of the environment [53].

In the light of these achievements, it is evident that plant-based TiO_2 NPs are eco friendly as well as having performance advantages in numerous sectors. As a result of their increased bioavailability, stability, and low toxicity, they represent a viable alternative for future demands in material science throughout green technologies.

6. Conclusion

It is possible to eliminate the burden on the environment by synthesising TiO_2 NPs from plant sources in a greener manner. In disparity to common physic-chemical procedures, bio synthesis, especially with plant extracts, offers a more eco-friendly, cost-effective, and suitable approach to synthesize TiO_2 NPs possessing the required physicochemical properties.

The great advantage of biosynthesis is that phytochemicals are multifunctional. These bio-nature agents, as modifiers, not only reduce metal ion, but also cap and stabilize the as-synthesized NPs, which greatly improves the dispersity, biocompatibility, and reduce toxicity of the NPs. Furthermore, the versatility of green synthesis in modifying particle size, shape, and crystalline phase creates countless possibilities for custom-made applications—ranging from photocatalysis to water purification, biomedicine, and agriculture.

The mechanism of formation of the NPs is evolving, although it is obvious that general biomolecules such as phenolics, contain flavonoid and terpenoid are also responsible for the formation of NPs. As described in this review, experimental parameters, e.g., pH, temperature, solvent, and extract concentrations, significantly influence the properties of the TiO_2 NPs obtained.

That there is also not a limited selection of species to be used as plants. The application of this enormous botanical resource, based on relatively simple laboratory setups, (far from the sophisticated setup of a reference university), is feasible both for advanced research institutions and for growing new laboratories worldwide.

In an era of increasing popularity of green chemistry and circular economy concepts, biologically-synthesized TiO_2 NPs are set to become a foundation of eco-friendly materials science. However, developing the extraction and synthesis techniques, disclosing the detail reaction behaviors and mechanisms and developing in an industrial scale are still tasks that need to be done. By tapping further into nature's potential, scientists can establish a foundation for new, safer materials that return to the productivity levels of the past.

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