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An Overview on Green Titanium Nanoparticles Based on Plants: Synthesis, Potential Applications and Eco-Friendly Approach.

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Abstract: Nanotechnology is generating a lot of buzz across the world because of its fascinating applications in various disciplines. Due to recent breakthroughs in the nanotechnology sector, metal oxide nanoparticles (NPs) have found a number of uses in a variety of industrial, medicinal, and environmental fields. Titanium dioxide (TiO_2) nanoparticles have been widely utilized in everyday life and maybe manufactured using a variety of physical, chemical, and green approaches. Green synthesis is a non-toxic, cost-effective, and environmentally responsible way to make NPs. The green, chemical, physical, and biological production of TiO_2 NPs has received a lot of attention, and these NPs may be analyzed using high-tech tools. The current study contains extensive information on the comparative synthesis of TiO_2 NPs with various properties and their wide range of applications. Because of the decreased usage of precursors, time-effectiveness, and energy efficiency during green synthesis processes, green approaches have been proved to be more efficient than chemical synthesis methods for TiO_2 NPs production. The relevance of green manufacturing of TiO_2 nanoparticles using plant extract is discussed in this review study. Recent breakthroughs in the manufacture of TiO_2 nanoparticles, from plants have shown promise in various scientific and technological domains. The physical features, crystal properties, antibacterial, anticancer, and photo catalytic activity of TiO_2 are summarised in this review. The many components of the green synthesis strategy for TiO_2 NPs and medicinal applications were discussed. Nanoparticle stability and toxicity, as well as surface engineering strategies for ensuring biocompatibility, are also reviewed. Furthermore, the obstacles and concerns surrounding using green product TiO_2 NPs in water and wastewater treatment were explored. Hence, this review article condenses TiO_2 NPs physicochemical properties, green synthesis, toxic exposure, bio-distribution, and applications.

Keywords: Green synthesis, Nanoparticles, TiO_2, wastewater treatment, photo catalytic activity

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1. INTRODUCTION

Nowadays nanotechnology is one of the fastest growing areas of science and technology. The metallic nanoparticles show different properties viz. chemical, physical, optical and thermal as compared to the metallic elements in bulk state due to their high surface area to volume ratio 1. Therefore, these unique properties make nanoparticles (with diameter smaller than 100 nm) favourable for many different applications[2].Because of this unique physicochemical characteristic of nanoparticles including catalytic activity, antimicrobial properties, they are gaining the interest of many scientists for their novel method of synthesis[3].The remarkable changes were observed in the physical and chemical properties, and enhancements in the surface-to-volume ratios (increase in surface reactivity) of materials are obtained when they are prepared in Nano scales (1–100 nm). Nanoparticles can be categorized into metals (Pt, Au, Cu, Pd, etc.), metal oxides (SiO_2, Al_2O_3, TiO_2, ZrO_2, Fe_2O_3, etc.) and semiconductors (ZnS, CdS, CdSe, etc.). The various Ag, ZnO, TiO_2 nanoparticles have been an interest for many authors[4-10]. Among various nanoparticles Titanium dioxide TiO_2 NPs are manufactured worldwide in large quantities for use in a wide range of applications[11-15]. It is widely used as pigment because of its brightness and very high refractive index. Approximately four million tons of this pigment is consumed annually worldwide[36]. These TiO_2 nanoparticles have been used in paints, coatings, plastics, papers, inks, medicines, pharmaceuticals, food products, cosmetics, sunscreens, toothpaste, and also used as a component for articulating prosthetic implants for the hip and knee[16-21]. Surprisingly, new developed TiO_2 nanocomposite membranes have recently shown the properties of both, anti-adhesion via imparting hydrophilicity and anti-microbial (under Irradiation)[22] approaches. Due to their fascinating properties, TiO_2 nanoparticles have found vast array of applications such as in nanobiotechnology[23], nanomedicine[24], energy devices[25], soil remediation[26], food[27], healthcare and cosmetic products[28], wastewater treatment[29], and paint[30], paper[31], and plastics productions[32].

1. Physical Properties of TiO_2

Titanium dioxide is extensively used as a white pigment in outside paintings for being chemically inert, and for its great coating power and as a bleaching and pacifying agent in porcelain enamels, giving high brightness, hardness and acid resistance. The titanium oxide is also known as titanium (IV) oxide, titanic acid anhydride, titania, titanic anhydride, The physical properties of TiO_2 have been summarized in Table1.

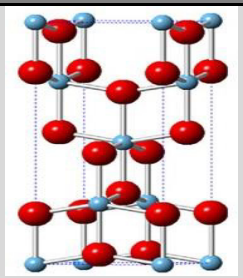
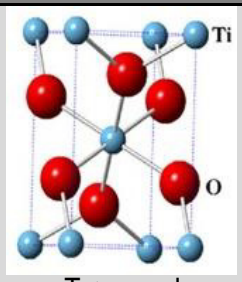
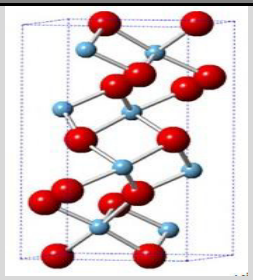
Table 1. Physical Properties of TiO_2

Chemical formula	TiO_2
Molar mass	79.866 g/mol
Appearance	White solid
Odour	Odourless
Molecular weight	79.9 g/mol
Density	4.23g/cm^3 (rutile)
	3.78 g/cm^3 (anatase
Boiling point	2972°C
Melting point	1843°C
Density	4.26 g/cm3 at 25°C
Magnetic susceptibility (χ)	$+5.9 \cdot 10^{-6}$ cm^3/mol
Refractive index	2.488 (anatase), 2.583 (brookite), 2.609 (rutile)
Bandgap energy (eV)	3.03
optimum size	11 – 25 nm
Zeta potential in nano pure water (pH 5.6) (mV)	32.7 ± 0.5

2. CRYSTAL PROPERTIES

There are three types of TiO_2 polymorph minerals viz. Anatase, rutile and Brukite available in nature which have been shown in Fig.1 and their crystal properties have been incorporated in Table2. Both anatase and rutile have tetragonal structure and are vastly used in the different fields of science but Brukite has orthorhombic structure[33]. The crystal properties of all three phase viz., anatase, rutile and brookite have been incorporated in Table2.

Table 2 The crystal properties of most three common phases of TiO_2 [34-38]

Properties	Anatase	Rutile	Brookite
Crystal structure	 Tetragonal	 Tetragonal	 Orthorhombic
Heating converts to	Rutile	-	Anatase
Stability	Stable	most stable	least stable
Density (g/cm^2)	3.894	4.250	4.120
Space group	$I4_1/amd$	$P4_2/mnm$	Pbca
Molecule (cell)	2	2	4
Lattice constant (A)	*a* = 3.784 *b* = 9.515	*a* =4.594 *b* = 2.959	*a* = 9.184 *b* = 5.447 *c* = 5.154
Ti—O bond length (A)	1.937(4) 1.965(2)	1.949(4) 1.980(2)	1.87–2.04
O—Ti—O bond angle	77.7° 92.6°	81.2° 90.0°	77.0°–105.0°
Volume/molecule (A^3)	34.061	31.216	32.172
Main property and Refractive index	The most photoactive form of used as a catalyst or catalyst support	Highest refractive index(2.65-2.95) mostly used as pigment and in optical device	The largest cell volume (8 TiO_2 groups per unit cell. 4 from anatase and 2 from rutile), mixing with anatase form for catalytic applications.
Mohs Hardness	5.5-6	6-6.5	5.5-6
Melting Point	1200C)	1825^0C	brookite n/a (converts to rutile)

Anatase has the most significant use as a photocatalyst due to mobility of charge carriers of Anatase ($80cm^2V\text{-}1s\text{-}1$) is 89 times faster than rutile[39]. Both phases have same tetragonal crystal structures even though they do not belong to the same phase groups, while brookite has an orthorhombic structure and the uncommon TiO_2 (B) phase is monoclinic[40-42]. It has been reported that even though the rutile phase is less stable than the anatase phase at 0K, the corresponding energy difference between these phases is rather small (about 2–10 kJ/mol). Gupta *et al.*[43]discussed that anatase phase TiO_2 can be chosen over other phases due its low density, high electron mobility, and low dielectric constant consequently the anatase phase low density, it easily undergoes transition to the rutile phase at high temperatures (usually around 450–1200^0 C)[44]. They also concluded that both the brookite and anatase phases usually transform to the rutile phase. A. O *Araoyinbo I* etal.[45] studied the XRD patterns of titanium dioxide nanoparticles, shown in Fig. 2.

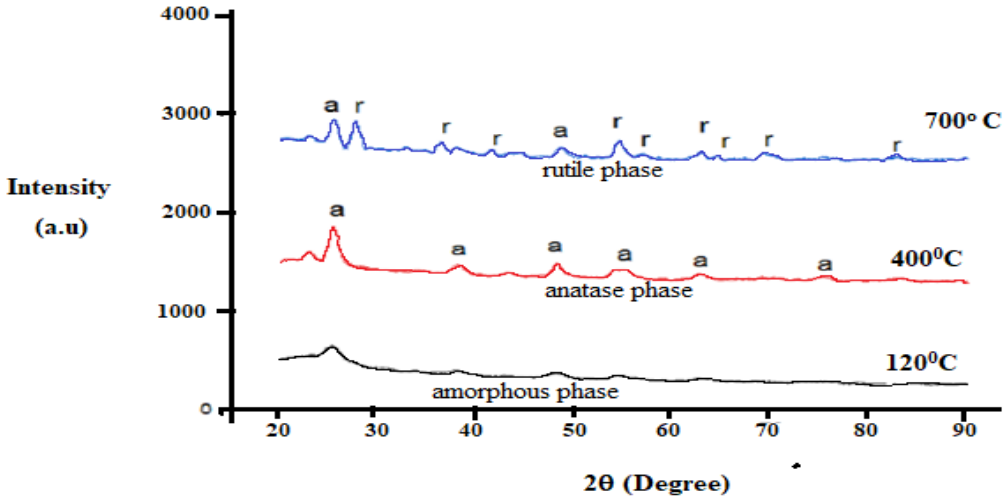


Fig 1. XRD pattern of TiO_2 NPs[45]

The 120°C dried titanium dioxide exhibits an amorphous phase where no distinct peak is identified. The 400°C titanium dioxide exhibits anatase phase and the significant peaks were observed. This result confirmed the width of the anatase peak

diffraction from XRD indicating the smaller crystalline size at 400°C. Phase transformation occurred from anatase phase to thermodynamically more stable rutile phase when calcination temperature increases to 700°C.

3. APPLICATIONS OF TiO_2 NANOPARTICLES

Recently, environmental purification with TiO_2 nanoparticles has also attracted great attention by many authors due to their chemical stability, low pollutant loading, low toxicity, self-cleaning ability, hydrophilicity, and availability at low cost[46-47]. Thus green synthesis by using plants is more beneficial than production by chemical methods. Literature survey revealed that in future, the most probability the study of Nano-size particles, devices, and composites, which find the ways to make stronger materials, generate light and energy, and purify water. The most important applications of TiO_2 nanoparticles have been shown in Fig.2.

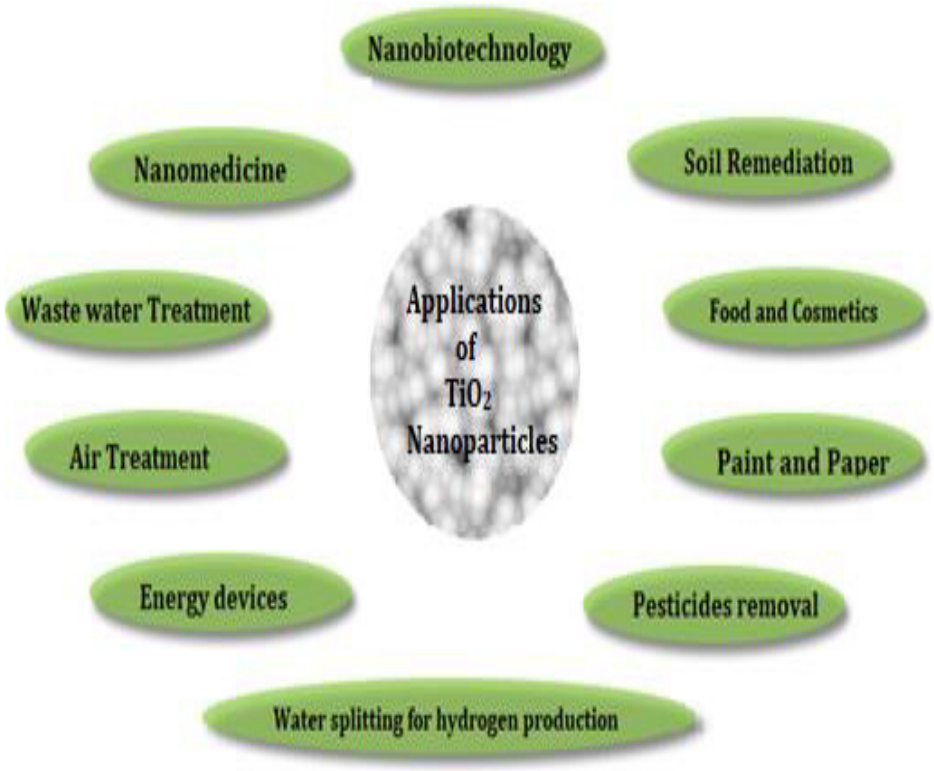


Fig 2. Applications of TiO_2 Nanoparticles

3.1 Wastewater Treatment

For any water body to function adequately in satisfying drinking water must have corresponding degree of purity. Drinking water should be free of carcinogenic substances, harmful bacteria, and toxic chemicals[48]. In Future the high demand for clean water will be increased by about one-third of its present state[49].This is due to its crucial role for the production of electronic devices, pharmaceuticals, paints, foods, and other beverages[50-52]. Recent advances in nanotechnology and Nano engineering by use of non-absorbents, promising in achieving good quality of water[53], nanoparticle-enhanced filtration[54], Nano catalysts[55] and bioactive nanomaterials[56]. Various nanoparticles have been successfully reported for water and wastewater treatment, such as zerovalent metal nanoparticles (silver nanoparticles, iron nanoparticles, zinc nanoparticles), metal oxide nanoparticles (titanium dioxide nanoparticles, iron oxide nanoparticles, zinc oxide nanoparticles), carbon nanotubes, and nanocomposites[57]. NPs, especially the chemically synthesized titanium dioxide (TiO_2), have been extensively applied in the photo-catalytic treatment of industrial wastewaters. Ray and Lu *et al.* 2015[59]studied Nano-sized TiO_2-based photo-catalytic treatment and concluded,that, it is a highly effective method for the degradation and detoxification of recalcitrant organic and inorganic pollutants from industrial wastewaters. In past decade various photo catalytic nanomaterials, such as nanoparticles of zinc oxide[60-61], nanocubes of silver chloride[62-63]nanoparticles of bismuth vanadate, quantum dots and[64], and cadmium sulfide[65]have been investigated for their water treatment abilities., but purification with TiO_2 nanoparticles as a photo-catalyst has attracted great attention due to their chemical stability, low pollutant loading, low toxicity, self-cleaning ability, hydrophilicity, and availability at lowcost[66].Oyekale, A.S. *et al.* (2017) reported that sustainable and effective treatment of the wastewater from hospitals is often challenging to environmental and wastewater engineer worldwide[67]. The effective treatment of the wastewater from hospitals usually contains pharmaceutical, radioactive, and chemical substances, alongside numerous pathogenic microorganisms[68-69]. Chong and Jin[70]studied the use of TiO_2 nanofibers for the treatment and biodegradability enhancement of a pharmaceutical compound (carbamazepine) in a hospital wastewater mimic, and observed that the TiO_2 nanofibers removed 78% of the carbamazepine, 23% phosphate, and 40% chemical oxygen demand (COD) within four hours. The current interest in the researchers for the TiO_2 nanoparticles is also due to the growing microbial resistance against antibiotics, and the development of resistant strains. TiO_2 nanoparticles have demonstrated significant antibacterial activity[71-74]

3.2 *Titanium dioxide is a photo catalyst*

TiO_2 is a great invention in 1972 for using as photo-catalyst extensively during "Honda-Fujishima Effect", was described by Honda and Fujishima[75].Fujishima *et al*[72] describe photo-catalysis as a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself. Fatimah Al Qarni[19] prepared green NPs which exhibited improved photo-catalytic activity[76]. Xiaolan Kang *et al*.[77], Malakootian and Mansuri[78]studied photo-catalytic reduction of inorganic contaminants (Cr^{+6} to Cr^{+3}) from wastewater along with photo-oxidation of organic pollutants. They proposed the schematic diagram of operation of a photo-chemically excited TiO_2 particle shown in fig.3 with the following mechanism. The characteristics of some TiO_2 compounds as photo-catalysts are presented in Table3.

$$TiO_2\,(catalyst) + hv \rightarrow h^+ + e^-$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$
$$H_2O + h^+ \rightarrow OH + H^+$$
$$OH + Organics \rightarrow CO_2 + H_2O$$
$$H^+ + Organics \rightarrow CO_2 + H_2O$$

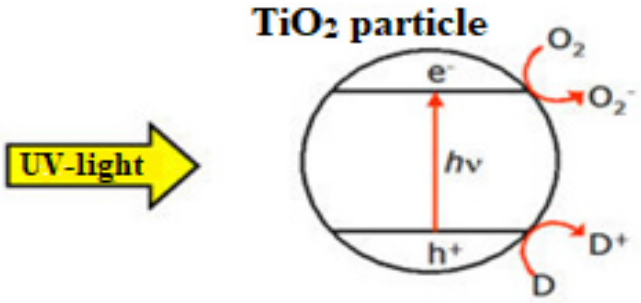


Fig 3. Schematic diagram of operation of a photo-chemically excited TiO_2 particle

Table 3. Characteristics of photo-catalysts obtained based on non-structured TiO_2[79]

Photo-catalysts	Average size (nm)	Synthesis method
TiO_2/Ti	150	Alkaline treatment, followed by oxidation with acetone
Fe_3O_4/SiO_2/ TiO_2	90	Hydrothermal method
TiO_2	45	Sol-gel Method

4. SYNTHESIS OF TIO_2 NANOPARTICLES

Recently numerous types of TiO_2 nanoparticles have been synthesized in the form of nanotubes, nanosheets, nanofibers, nanorods, and interconnected architectures[80-81]. The regularly employed synthesis methods are the hydrothermal, sol–gel, solvothermal, vapour deposition, oxidation, and the thermal decomposition methods. The Green synthesis of TiO_2 nanoparticles is done by various methods viz., the Hydrothermal Method, Sol–Gel Method, Solvothermal Method etc. The other various methods have been shown in Fig.3 and Fig 4.

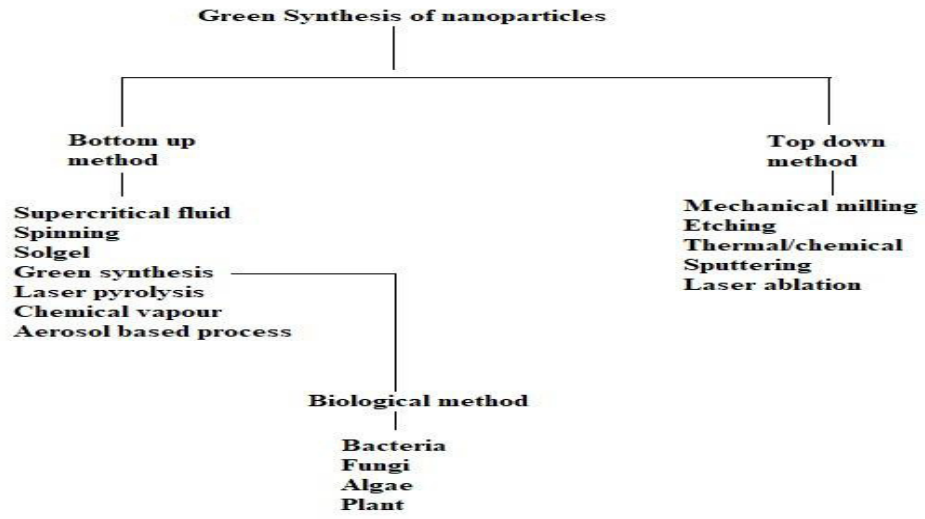


Fig 4. Green synthesis of nanoparticles by different methods

The synthesis of nanoparticles of TiO_2 in the laboratory is mainly carried out by sol–gel method. This method is generally employed to synthesize crystalline or amorphous structure of organic and inorganic materials which requires low temperature [82]Hydrothermalmethod has been utilized by many researchers for the synthesis of TiO_2 nanoparticles[83-89]. In this regard, Dawson *et al*. synthesized TiO_2 nanoparticles by the hydrothermal method, wherein they subjected various compositions and particle sizes of TiO_2 mixed powders to hydrothermal reaction in the presence of NaOH[91] Hussain *et al*. also synthesized novel nano- TiO_2 whose size ranged from 10 to 20nm by the sol–gel technique[92]. In another study, Chong *et al*. synthesized TiO_2 nanoparticles by the sol–gel method[93]. TiO_2. Arami *et al* (2007) reported that sol-gel process, emulsion and pyrolysis have been used to prepare mono dispersed spherical TiO_2 nano-particle, although sol-gel method for TiO_2 nano-particle has another disadvantage of the use of costly organic solvents. The solvothermal synthetic strategy is closely related to the hydrothermal technique but for the use of non-aqueous solvents in the former[94]. Moreover, the solvothermal method offers intriguing advantages including an improved tuning of morphology, particle size, crystallinity of the synthesized nanoparticles, and temperature and pressure controls of the solvents used for the synthesis[95]. Furthermore, TiO_2 nanoparticles can be synthesized by either the wet or dry processes. In the dry process, the vapour phase oxidation of $TiCl_4$ is conducted, which leads to formation of amorphous TiO_2 nanoparticles as shown below:

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g)$$

Recently TiO_2 nanoparticles have been synthesised by various sources (Shown in Figure 4) using TiO_2 nanoparticles have been synthesized using natural products like *Nyctanthes arbortristis* extract[9], *Catharanthus roseus*[10] aqueous leaf extract, *Eclipta prostrata* aqueous leafextract[11] and *Annona squamosa L.* peel extract[96-99].

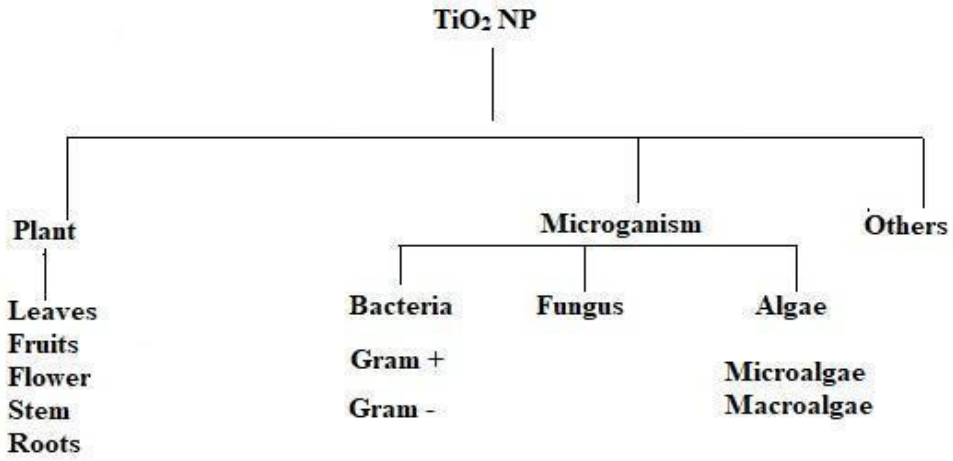


Fig 5. TiO_2 Nanoparticles synthesis by different sources

The synthesis of nanoparticles by using plants is less complex and a single step process unlike microbial isolation. Generally, the prepared TiO_2 NPs have been characterized by using characterized by UV-Vis spectroscopy, X-ray Diffraction (XRD), Fourier transforms infra-Red spectroscopy (FT-IR), atomic force microscopy (AFM), and scanning electron microscopy (SEM), thermo gravimetric analysis (TGA). The morphology and applications of various plants have been incorporated in Table4.

Table 4. Study of TiO_2 NPs biosynthesis using plants

Sl No.	Plant (family)	Part taken for extraction	Size (nm)	Shape	Applications	Ref.
1	*Catharanthus roseus*	Leaf	25-110	Irregular	Antiparasitic activity	[100]
2	*Eclipta*	Leaf	49.5	Spherical		[101]
3	*Jatropha curcas*	Latex	25-100	Spherical		[102]
4	*Oryza sativa*	Straw	10-16		Photocatalyst	[103]
5	*Cassia fistula*	Whole Plant	-	Spherical	Antibacterial	[104]
6	*NyctanthesArbortristis*	Leaf	100 to 50.	Spherical	Antimicrobial	[105]
	P. domestica L.(Plum), P. Persia L.(Peach) and A. deliciosa (Kiwi))	Fruits peel	47-63	Cylindrical	antibacterial, antioxidant activities	[106]
5	*Nyctanthes leaves extract (Night-flowering Jasmine)*		100–150	Spherical	Biomedical systems	[107]
6	*Annona squamosa*	Fruit peel	23 ± 2	Poly dispersed and Spherical	Bio therapeutics, bioengineering and electronics	[108]
7	*0.3% aqueous extract of latex of Jatropha curcasL. (physic nut)*	Latex	25–100	Mostly spherical and Uneven	Biotechnology, environmental, Biomedical and electronic systems	[109]
8	*Aloe vera gel extract*		80–90	Almost spherical	Photocatalytic activity	[110]
9	*Aqueous flower extract of Calotropis gigantea*	Flower	160–220	Spherical and aggregated	Acaricidal activity	[111]
10	*Aqueous leaf extract of Solanum trilobatum (Purple fruited pea eggplant)*	Leaf		Uneven spherical and Oval	Larvacidal and pediculocidal Activities	[112]
11	*Leaf aqueous extract of Psidium guajava (Guava)*	Fruits	32.58	Spherical shape and Clusters	Antibacterial and antioxidant Activity	[113]
12	*Trigonella foenum-graecum L.*	Leaves	20–90	Spherical	Antibacterial	[114]
13	*Cicer arietinum L.*	Seeds	14	Spherical	Antibacterial	[115]
14	*Azadirachta indica*	leaf extract	15 to 42	Spherical	Antimicrobial	[116]
15	*Psidium guajava*		32.58	spherical	Antibacterial and antioxidant	[117]
16	*Trigonella foenum-graecum*	Leaves	20–90	Spherical	antimicrobial activity	[118]
17	*Psidium guajavaextract*	Leaves	32.58	spherical clusters	antibacterial and antioxidant activities	[119]
18	*Ocimumbasilicum*	Leaf	100-120	Spherical	Antibacterial	[120]
19	*Echinacea purpurea Herba*	Whole plant	120	spherical clusters	Bioreductant	[121]
20	*oscimum sanctum herba*	Leaf	90-100	spherical clusters	Bioreductant	[122]

4.1 Physicochemical Properties of TiO_2 Nps

Titanium has an average content of 4400 mg/kg in the earth's crust. Ti does not exist in the metallic state in nature due to its high affinity for oxygen and other elements. Ti's most common oxidation state is +4; however, there are also +3 and +2 states. The most often utilized compounds in the industry are metallic Ti, TiO_2, and $TiCl_4$. TiO_2 (CAS: 13463-67-7) is the naturally occurring oxide of titanium, commonly known as titanium (IV) oxide, titanic acid anhydride, titania, titanic anhydride, or Ti white. TiO_2 is a non-combustible, odourless white powder with a molecular weight of 79.9 g/mol, a melting point of 1843°C, and a relative density of 4.26 g/cm3 at 25°C. TiO_2 is a poorly soluble particle that has been used as a white pigment for a long time. The crystal structures of TiO_2 are anatase and rutile, with anatase being more chemically reactive[123]. Sayes *et al*[124] found that after UV irradiation, NPs (80/20; anatase/rutile, 3–5 nm; 100 g/ml) created six times more reactive oxygen species (ROS) than rutile. When anatase is exposed to UV radiation, it produces reactive oxygen species (ROS)[124]. TiO_2 anatase is thought to have a higher hazardous potential than TiO_2 rutile[125-126]. Under ambient light circumstances, however, anatase-generated ROS does not occur. In most cases, TiO_2 NPs are a combination of anatase and rutile crystal forms. Shape, size, surface characteristics, and interior structure are the most critical parameters impacting particle physicochemical attributes. Chemically, TiO_2 FPs (the rutile form) is thought to be inert. However, as the particles get smaller, their surface areas grow greater, and researchers are concerned about the detrimental consequences of TiO_2 NPs on human health as a result of the increased size[126]. The activity of TiO_2 NPs is influenced by surface modification, such as coating. In summary, TiO_2 NPs and TiO_2 FPs have different physicochemical properties. These characteristics are likely to have an impact on bioactivity. Even though TiO_2 FPs have been shown to have minimal toxicity, adverse health impacts and environmental bio-safety of TiO_2 NPs should be carefully examined based on this fact. Researchers should thoroughly analyze the physicochemical properties of TiO_2 NPs in bulk and supplied to the test system.

4. Toxicity and Biocompatibility—an in Vitro and in Vivo Study of Titanium Dioxide Toxicity

The low toxicity of titanium dioxide explains its widespread use. Numerous investigations using TiO_2 of various nanoparticle and micro particle sizes and crystal shapes were conducted to assess skin, lung, immune system, and hematotoxicity. Although titania is a prominent ingredient in many cosmetic formulas, particularly sunscreens, powders, and eye shadows, its size and crystal forms (anatase and rutile) appear to impact its safety.The in vitro and in vivo research on TiO_2 NPs' skin-related toxicity raised two issues: skin toxicity and systemic toxicity connected with skin penetration. After sub chronic dermal exposure, Wu *et al*. investigated the toxicity and penetration of TiO_2 NPs in hairless mice and porcine skin[127]. According to the findings, nanosized TiO_2 may offer a health risk to people following chronic cutaneous contact over a lengthy period, owing to deeper tissue distribution. Crosera *et al*. investigated TiO_2 NPs' penetration into Franz cells for 24 hours using intact and needle-abraded human skin and cytotoxicity on HaCaT keratinocytes in another investigation. The presence of TiO_2 NPs was found to be limited to the epidermal layer, while their concentration in the dermal layer was below the detection limit. A minor cytotoxic effect on human HaCaT keratinocytes was observed, implying that TiO_2 NPs may pose a concern only after long-term exposure[128]. Yin *et al*. investigated the photo-toxicity of TiO_2 NPs with various molecular sizes and crystal morphologies (anatase and rutile) in HaCaT human skin keratinocytes in related work[129]. The findings showed that TiO_2 NPs are phototoxic to human skin keratinocytes due to reactive oxygen species (ROS,) production during UVA irradiation. It's worth noting that the rutile form of nano- TiO_2 was shown to have lower photo-toxicity than anatase[129]. Much research has been conducted on the possible risk of TiO_2 inhalation exposure. The toxicology investigation revealed mostly titania-related side effects and trials that could indicate severe "overload." Lee *et al*. did a study that can be used as an example[130]. Bronchioloalveolar adenomas and cystic keratinizing squamous cell carcinomas were observed in rats after long-term inhalation exposure to bulk TiO_2 dust at high concentrations (up to 250 mg/m3 for 2 years, 6 h/day for 5 days/week). The researchers determined that the observed cancers formed from excessive dust loading in the lungs, so-called TiO_2 "overload," due to the unique nature of the relevant pre-malignant tumours, which were uncommon for human lung cancer, and the lack of tumour metastases to other organs. Vandebriel *et al*[131], who researched TiO_2 NPs, a popular ingredient used in paints during their manufacturing or applications, recently published an interesting study on the possible risk of inhalation exposure. TiO_2 NPs were investigated in vitro and in vivo for their immunological activities. The first phase of the study focused on the in vitro effects of TiO_2 NPs on the development of dendritic cells, which are a crucial component of the lung immune system. In contrast, the nod piece examined their adjuvant action in mice in vivo. A group of fourteen TiO_2 NPs was chosen for the study, each with different crystal shapes and coatings. In vitro, anatase and anatase/rutile TiO_2 NPs caused higher expression of CD83 and CD86 and higher production of IL-12p40 than rutile NPs, indicating that rutile NPs are safer than anatase NPs. Anatase and anatase/rutile NPs stimulated dendritic cell maturation larger than rutile NPs in this approach. This conclusion is significant for future titanium dioxide crystal structure selection for industrial applications, particularly in areas where inhalation exposure during product production or application must be considered[131]. Dendritic cell maturation activation has been shown to cause a cascade of physiological events, including a detailed immunological response and indirect inflammation[132]. Continuous exposure to TiO_2 may thus result in an overactive immune system and persistent inflammation. Chronic inflammation is thought to be a detrimental state that leads to tissue loss and the development of other disorders[133]. Madhubala *et al*. did complementary research on the function of inflammatory processes by studying the in vitro cytotoxic and immunomodulatory effects of low concentration TiO_2 NPs on diverse human cell lines[133]. In a dose-dependent manner, the immunomodulatory effects of TiO_2 NPs were investigated on human monocytic leukemia (THP-1) and human mast (HMC-1) cell lines. In the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay, the viability of THP-1 cells treated with titania NPs was considerably reduced at higher dosages. In conclusion, the acute toxicity of TiO_2 NPs has been extensively examined in rat and mouse models using a variety of exposure various research focusing on the respiratory system outnumbers those focusing on other exposure modes. According to studies, exposure of the pulmonary system to TiO_2 NPs resulted in both local and systemic symptoms and aggravation of pre-existing symptoms. TiO_2 NPs delivered through the lungs cause higher inflammation than FPs with the same

chemistry at equal mass concentrations. On a similar particle surface area basis, however, pulmonary inflammation induced by TiO_2 NPs was comparable to that caused by TiO_2 FPs. The outcomes of the other exposure methods must be considered. For example, research shows that TiO_2 NPs can enter the systemic circulation via the lungs or the gastrointestinal tract (GIT) and then be disseminated throughout the body, including the liver, kidneys, spleen, and even the brain[134]. Organ damage and inflammatory responses could be induced by the distribution and accumulation of TiO_2 NPs in the organs. However, most of the doses used are far too high to be practical in the workplace. TiO_2 NPs have also been shown to affect the blood circulation system in vitro[134]. Fourth, thorough toxic kinetics investigations of TiO_2 NPs absorption, distribution, metabolism, accumulation, and excretion through various routes of exposure into the human body are required[134]. Future research should also look at systemic reactions that are separate from the organ of exposure and biomarkers that represent TiO_2 NP exposure and deleterious repercussions. Finally, the chemical mechanisms by which TiO_2 NPs could induce cancer remain unknown. Limited evidence suggests that ROS production and signalling changes in cancer-related genes may play a role in TiO_2 NP carcinogenicity. As a result, more research is needed to understand the molecular pathways of carcinogenicity in TiO_2 NPs.

4.4 Titanium Dioxide's Pharmacokinetics, Bio-distribution, and Biological Fate

Only a few studies have looked into the pharmacokinetic properties of TiO_2 NPs thus far. In addition, some of the accounts in the literature are conflicting or imprecise. Particle type, surface charge, surface coating, size, dose, and exposure route all affect the pharmacokinetics of metal NPs, including TiO_2 [135-136]. Orally, transdermally, or via injection, titanium dioxide can enter the body in three ways. The bioavailability of TiO_2 from the gastrointestinal tract is constantly being researched and discussed. There are numerous indicators that titania does not or only partially permeate the gastrointestinal tract. There was no significant increase in NP concentration in any of the studied tissues 24 hours following oral administration of TiO_2 NPs at a dose of 100 mg per kilogram of body weight in animal tests[137]. Comparative investigations with greater doses of TiO_2 produced similar results, demonstrating that orally administered TiO_2 does not penetrate the gastrointestinal tract and that penetration is medically unimportant[138]. High quantities of TiO_2 NPs, on the other hand, have been shown to cause agglomeration and so boost their uptake by macrophages in experiments utilizing the physiologically based pharmacokinetic modelling technique. According to Bachler *et al.*[139], TiO_2 NPs can be bio distributed in two ways: by their ability to permeate blood arteries and into organs and through phagocytosis of NPs by the mononuclear phagocyte system. However, it should be noted that the pharmacokinetics of NPs following intravenous injection varies[139]. Because NPs' bioavailability is complete in this scenario, their dispersal in the body must be carefully examined. In a study by Fabian *et al.*[140], rats were given 5 mg TiO_2 NPs per kg of body weight intravenously and then monitored for 28 days. Throughout the experiment, the animals were healthy and acted as usual. TiO_2 did not accumulate at measurable levels in blood cells, plasma, brain, or lymph nodes, according to a histopathological examination. On the other hand, the liver had the greatest titania levels, while the spleen, lungs, and kidneys had lower but still elevated levels[140]. Geraets *et al.*[141] made an important observation about rats' TiO_2 NPs excretion by the kidneys. They observed that TiO_2 is slowly excreted from the body, indicating that it could accumulate in tissues. This is not a severe problem because the photosensitizer is only used once or several times during photodynamic therapy[141]. Furthermore, a study conducted on rats by Xie *et al*[142] revealed that TiO_2 NPs in urine were higher than in faeces, implying that renal excretion is the predominant route of TiO_2 NP elimination[142].

4.4 Synthesis of TiO_2 NP

Despite the material's promising features for photodynamic treatment, work is currently being done to change the NPs' surface in motor connection efficiency and physicochemical properties, including visible light absorption. PDT has the potential to be enabled by surface-modified TiO_2 NPs with photosensitizing characteristics[143]. Many investigations aimed at extending the spectral sensitivity of TiO_2 have shown effective photosensitization with the use of a broad band-gap semiconductor. As a result, titanium dioxide may be doped with various metal ions and non-metal dopants[144-145] or dyes[146-148]. Transition metal ions with inorganic or organic ligands are commonly found in surface complexes that operate as TiO_2 photosensitizers. The organic ligands are covalently bonded to the titanium dioxide surface and are coordinatively bound to the central ion. Surface titanium may also be linked to metal centres via inorganic ligands, including CN–, F–, and PO43–. Photosensitization results from photo-induced electron injection from the complex's surface into the semiconducting support's conduction band or whole injection into the valence band. Direct or indirect photosensitization procedures can be used to produce photo-induced charge injection. Due to the presence of anchoring groups in the structure of organic molecules, the complexes produced at the titanium dioxide surface can be generated through chemisorptions in some situations[143]. Titanium dioxide[154] is a semiconductor-based material having an energy gap of 3.23 eV for anatase and 3.06 eV for rutile polymorph. When a molecule absorbs a photon with energy greater than or equal to that amount, it is stimulated. It can create negative electrons in the conduction band while leaving positively charged holes in the valence band. ROS, including superoxide (O2•-), hydrogen peroxide (H2O2), and hydroxyl radical (•OH), are formed when free electrons attack nearby oxygen and water molecules[149]. In biological systems, these forms of oxygen are precarious and react with cell components, resulting in apoptotic or necrotic cell death. TiO_2 NPs have also been shown to prevent efflux-mediated multidrug resistance[149-150]. When titania NPs are disseminated in aqueous solutions, they tend to form agglomerates in most situations[151-152]. Because these shapes have a smaller surface area, they have lesser photo-activity. In addition to TiO_2 NPs' biological activity, sedimentation can diminish their concentration, causing problems with repeatability and preventing consistent dose. As a result, stable formulations of NPs with functionalized surfaces on their surfaces were designed to avoid or remove this unwanted feature. The modification of NPs, for example, relies on the application of a charge for electrostatic repulsion or the adsorption of stabilizers to create stearic hindrance[153].

4.5 Photo-catalyst section

In vitro and in vivo biological research has often revealed the photodynamic activity of metallic nanoparticles made of gold, silver, and titanium. PDT experiments using nanoparticles or quantum dots in conjunction with photosensitizers such as

phthalocyanines, porphyrins, and other dyes are becoming increasingly popular. NPs appear to be suitable carriers for targeted treatment as well. PDT may be performed in particular tissues with the use of convenient drug delivery methods for photosensitizers[155-156]. Because of their drawbacks, such as their absorption of only short UV wavelengths and aggregation in aqueous environments, plain titania NPs have been modified using a variety of inorganic and organic dopants. Porphyrins and phthalocyanines are two chemical colours that are frequently combined with TiO_2. Using such hybrid materials as catalysts for visible-light biomedical and environmental photocatalysis in photovoltaics to manufacture dye-sensitized solar cells (DSSC) and photosensitizers for PDT has been extensively used[157-160]. Pan *et al*. offered an outstanding example of a TiO_2 NPs and phthalocyanine combination when they used electrostatic interactions to link aluminum(III) tetrasulfonated phthalocyanine chloride (TSAlClPc) to nitrogen-doped anatase TiO_2 NPs[161-162]. TSAlClPc alone had just a mild photo killing impact, with more than 83 percent of cells surviving, whereas NPs were less active, slightly killing more than 70% of HeLa cells. Furthermore, nitrogen-doping of NPs has been shown to promote photodynamic activity by enhancing the creation of singlet oxygen ($1O_2$) and superoxide anion radicals while suppressing the development of hydroxyl radicals[162]. The continued growth of TiO_2 applications in photodynamic treatment can be shown by a work in which phthalocyanine was deposited on TiO_2 nanopore thin films. This approach was employed by Perillo *et al*. to make a possible photosensitizer using copper tetracarboxyphthalocyanines (TcPcCu) that was effective against MRSA[163]. A visible light source was used to irradiate the bacteria and photosensitizer solution. A sample comprising solely TiO_2 thin film revealed no variations compared to the control. The TiO_2/PcTcCu thin film sample, on the other hand, inhibited MRSA development by 81.5 percent[163]. Tuchina *et al*. conducted a photo cytotoxicity investigation using methylene blue (MB)[164], one of the earliest photosensitizers utilized in the laboratory and medical practice. They tested a combination of two individuals—MB and TiO_2 NPs—against *S. aureus*, *E. coli*, and *Candida albicans* for antibacterial photodynamic activity. Suspensions of bacteria or fungus were cultured in the dark for 10 minutes before being treated with two LED lights simultaneously (405 and 625 nm). The combination of both PSs and simultaneous irradiation with red and blue light decreased the number of *S. aureus* cells by up to 90%. Using a mixture of photosensitizers against *C. albicans*, very similar results were obtained. Surprisingly, there was practically no action against *E. coli*.

4.6 TiO_2 NPs for Cancer

Every day, cancer becomes a growing concern worldwide, and no cure eliminates cancer. As a result, it was thought that nanoparticles, in addition to radiation, chemotherapy, and other treatments, may be a novel strategy in cancer treatment investigations. Titanium dioxide (TiO_2) and zinc oxide (ZnO) nanoparticles employed in photodynamic therapy (PDT) are ROS-producing agents, according to the research. Reactive oxygen species (ROS) have a high oxidative potential and damage DNA and cell membrane in cancer cells, resulting in necrosis. Damage to the nucleus and mitochondria causes apoptosis, whereas damage to the endoplasmic reticulum causes autophagy. In research by Youkhana *et al*., titanium dioxide nanoparticles were utilized as radiosensitizers on two cultivated cell lines, human keratinocytes (HaCaT) and prostate cancer (DU145) cells; experiment using anatase TiO_2 nanoparticles, the correct radiation dosage was calculated. Cell viability and clonogenic assays were used to measure cell survival rates. According to the cytotoxicity test, TiO_2 nanoparticles were non-toxic up to 4 mM, and cell viability remained stable at doses higher than 4 mM. Finally, they discovered that TiO_2 nanoparticles positively affect dose delivery and that Ti_2O_3 nanoparticles are suitable for imaging; thus, titanium nanoparticles could be used as theranostic agents, which define a molecule's ability to be used for both therapy and diagnostic purposes[165]. Nanoparticles employed in Photodynamic Therapy (PDT) are classed as passive or active nanoparticles and potentially reduce Pc toxicity. Passive nanoparticles carry photosensitive compounds, whereas active nanoparticles are involved in the light stimulation process. Passive nanoparticles include gold, silica, and polyacrylamide, whereas active nanoparticles include titanium dioxide (TiO_2). TiO_2 is a photocatalyst that releases oxidizing radicals by interacting with water when exposed to UV light, which can harm adjacent cells[166]. Titanium dioxide and zinc oxide are two of the most effective photosensitizers for PDT applications, and their efficacy in PDT has been proven to be identical[167]. Yurt *et al*.[168] created ZnPc molecules and incorporated them into titanium dioxide nanoparticles, then investigated the PDT potencies of these molecules in breast and cervical tumors. They discovered that ZnPc- TiO_2 had a substantially higher photodynamic activity than ZnPc alone and that ZnPc- TiO_2 tagged with 1311 had a high cellular uptake in breast and cervical tumors, suggesting that it may be employed as a PDT agent[168]. Yurt *et al*. discovered that ZnPc- TiO_2 had a more substantial phototoxic impact in colon tumors than ZnPc[169]. Because of the challenges with PDT, there is a greater demand for innovative cancer treatment options. Sonodynamic treatment (SDT) is one of these approaches involving sonosensitizers and ultrasound (US). By triggering sonosensitizer particles, US are more efficient than UV radiation in reaching deeper into tumour cells. As a result, activated sonosensitizers produce reactive oxygen species (ROS) in target cells. Nanoparticles, namely TiO_2 NPs, may be used as sonosensitizers when coupled with metals or antibodies. After ultrasonic stimulation, TiO_2 nanoparticles have been shown to destroy nanoparticle-impregnated glioma cells [170] The cytotoxicity of TiO_2 NPs to HepG2 cells was investigated by Ogino *et al*. (2014). TiO_2 NPs were coupled with the PreS1/S2 antibody, which hepatocytes recognize. This conjugation was found to boost the cytotoxic impact of NPs[171]. In their study, you *et al*. evaluated the use of long-circulating hydrophilized titanium dioxide nanoparticles ($HTiO_2$ NPs) in sonodynamic treatment. $HTiO_2$ NPs are more resistant to degradation than traditional sonosensitizers because ROS does not destroy titanium dioxide. Additionally, a hydrophilic polymer called Carboxymethyl dextran (CMD) was employed to coat the NPs, improving their stability and increasing blood circulation time. CMD's flexible shape also facilitates extravasations from the tumor vascular. According to in vivo O_2 mapping in tumors, ROS levels have risen. H TiO_2 nanoparticles in ultrasonically treated cells It has also been discovered that ROS are detected in blood arteries far more than in deeper places[172]. According to Ninomiya *et al*., ultrasound therapy may distinguish cancer cells using avidin modified TiO_2 NPs, and these cells prefer to take avidin TiO_2 NPs[173]. Titanium dioxide nanoparticles were studied as an enhancing agent for computed tomography imaging (CT) and radiation treatment in research by Smith *et al*. Ionising radiation is used in radiation treatment to target tumors and cause DNA damage in tumor cells resulting in cell death. Another use of nanoparticles is dual-mode image contrast and

enhancement treatment, which is still being explored. Because iodine is routinely employed as a CT image contrast agent, it can be utilized to monitor iodine absorption in tumors[174]. In vivo tests were designed by Harada et colleagues; to assess micelle diffusion across tissues and the effectiveness of ultrasound in suppressing tumor development [175]. In research with CT26 cells, it was discovered that TiO_2 nanoparticles caused oxidative stress without the need for UV light. Ozyüncü *et al*. wanted to make D-Penicillamine (D-PA) conjugated magnetic nanocarrier (nanoparticles) that were radiolabeled with [99m Tc (CO)3] + core and then test the biological activities of the binding complexes on MCF7 human breast cancer cells. They stated that radiolabelled magnetic nanoparticles had good absorption ability on MCF7 cells and that the radiolabeled nanoparticles might be used as novel agents in biomedical applications and cancer therapy [176]. New approaches for medication delivery to cancer cells using nanomaterials and/or nanoparticles might reduce the side effects of pharmaceuticals used in cancer treatment, such as daunorubicin and doxorubicin. Finally, the primary goal of cancer therapy is to destroy cancer cells while also limiting tumor development without harming healthy cells. New medications, chemicals, and materials will be produced in the future as the prevalence of cancer rises. Scientists will continue to look for new ways and approaches for cancer patients until a proper and efficient medication or treatment is discovered. With the advancement of technology, significantly less expensive and more dependable therapies might be used in clinics. Using TiO_2 NPs in various tumors might be a revolutionary method in cancer treatment.

4.7 Toxic exposure to TiO_2 NPs

For many years, scientists have studied the effects of TiO_2 NPs on the human body. Its toxicity and exposure to a human/animal body have been extensively researched and debated. Surface charge, sedimentation, aggregation, and, therefore, the toxicity of TiO_2 NPs are all affected by the crystalline structure, particle size, and coating[177]. Previous in vitro and in vivo studies have confirmed the harmful effects of TiO_2 NPs on the human body, including disrupted cell cycle, nuclear membrane constriction, and apoptosis[178-179]. TiO_2 NPs have also been shown to cause DNA damage [180] and interact with the small intestinal epithelium, crucial for nutrition absorption. TiO_2 NPs can be identified in numerous internal organs after exposure to TiO_2 NPs in various methods, including inhalation, injection, skin contact, and absorption through the alimentary canal. TiO_2 NPs accumulate in the lungs, alimentary tract, liver, heart, spleen, kidneys, and cardiac muscle following inhalation or oral exposure, according to in vivo testing. In mice and rats, they also disrupt glucose and lipid balance [181]. The age might also play a role in the detrimental effects of TiO_2 NPs. Distinct age groups may require different biomarkers for detecting and monitoring the oral toxicity of nanoparticles, as evidenced by the results of experiments on young and adult rats[182]. The existing research is inconclusive, but most of it suggests that when particles are ingested, they are not absorbed into the blood circulation system and are expelled through the gastrointestinal tract[183]. TiO_2NPs were seldom collected from the GIT and transported into systemic circulation in rats and humans, according to recent research [184]. Toxicity following oral treatment to rats was shown to be minimal at NOAEL > 1000 mg/kg bw/24 h (NOAEL—no evident adverse effect threshold) in studies[183]. In their experiments, Amedollia *et al.*[185] found that TiO_2 NPs may penetrate the intestinal mucosa following oral exposure of rats to a level of 2 mg/kg body weight. According to Brun *et al.*[187], TiO_2 NPs are expected to be translocated through the ileac epithelium and Peyer's patches, causing damage to the intestinal epithelium and, most likely, chronic failure. After giving mice TiO_2 NPs (66 nm) via oral gavage at a dosage of 100 mg/kg for 10 days, Nogueira *et al.*[186] discovered inflammations in the small intestine. In another study, it was shown that TiO_2 NPs with varied particle sizes, 15 nm (nanoshell), 100 nm (nanoshell), and 5000 nm (pigments), did not affect enhanced titanium absorption depending on particle size following administration of a single dosage to volunteers (5 mg/kg bw/day)[188]. In a 14-day study, Bu *et al*[189] found that daily oral administration of TiO_2 NPs (160, 400, and 1000 mg/kg) to rats caused disruptions in energy, amino acid metabolism, and intestinal micro biota. They speculated that it might harm the liver and heart in minor ways. TiO_2 NPs in the brain can induce protein oxidation, oxidative damage, antioxidative capability degradation, and increased reactive oxygen species generation[190]. Nuclear envelope shrinkage[191], apoptosis[192], alterations in the concentration of macroelements and macroelements, such as copper (Cu), potassium (K), and zinc (Zn)[193], and disruption of the BBB[194] are some of the other results. The principal mechanisms behind metallic nanoparticle neurotoxicity, according to test results, are oxidative stress (OS), apoptosis, and the inflammatory response[195]. Antioxidants can counteract the neurotoxicity of metallic NPs by lowering the generation of reactive oxygen species (ROS), enhancing the activity of antioxidative enzymes, suppressing inflammation, and reducing the proportion of apoptotic cells[195]. Our direct or indirect exposure to metallic nanoparticles has increased with global economic expansion. Nanoparticles (NPs) are increasingly being used in commercial goods due to the novel features provided by their tiny size. Small concentrations of TiO_2 NPs can impact the intestinal mucosa, the brain, the heart, and other internal organs, increasing the risk of acquiring a variety of illnesses, tumors, and the progression of existing cancer processes. The mechanism underlying NP nanotoxicity has yet to be uncovered. Because several studies link it to oxidative stress, nanotoxicity is a promising subject for further research.

5. CONCLUSION

The plant-based Titanium nanoparticles have huge application in the field of food, pharmaceutical, and cosmetic industries and thus become a major area of research. Biosynthesis of TiO_2 nanoparticles, using an eco-friendly approach has been an interest for many authors in the last decade due to clean and eco- friendly methods, as toxic chemicals are not used. Future prospect of plant-mediated nanoparticle synthesis, need an extension of laboratory-based work to industrial scale. The TiO_2 nanoparticle finds a newer visionary scientific future in green chemistry and green nanotechnology. In order to develop the simple green synthesis, the plant extract mediated process has been considered as a suitable method for the synthesis of titanium nanoparticles.

6. AUTHOR CONTRIBUTION STATEMENT

Mrs. Sneha Olive Dan conducted the literature search and curated the data for designing of the review paper.Mrs. S. H. Khan worked in final refinement of the manuscript with her valuable suggestions to improve the weaker sections.

7. CONFLICT OF INTEREST

Conflict of interest declared none.

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