Studies on the titanium dioxide nanoparticles: biosynthesis, applications and remediation

Meghmala S. Waghmode¹ · Aparna B. Gunjal² · Javed A. Mulla¹ · Neha N. Patil¹ · Neelu N. Nawani³

© Springer Nature Switzerland AG 2019

Abstract

Nanoparticles have wide applications in various fields due to their small size. Titanium dioxide nanoparticles are bright with high refractive index ($n = 2.4$) which makes them suitable for industry dealing with toothpaste, pharmaceuticals, coatings, papers, inks, plastics, food products, cosmetics and textile. Three crystalline phases of titanium dioxide, are anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) in which brookite has no commercial value. Due to their self cleaning and antifogging property, they are used in the preparation of cloths, windows, tiles and anti-fogging car mirrors. Titanium dioxide nanoparticles also serve as environment sanitizing agent. Sol–gel route, flame hydrolysis, co-precipitation, impregnation and chemical vapor deposition like techniques are used for the synthesis of TiO_2 nanoparticles. Biosynthesis of titanium dioxide nanoparticles has gained wide interest among researchers due to its cost effective, eco-friendly and reproducible approach. The sol–gel route remediation of the titanium dioxide from the environment is an important step and it can be achieved by using physical processes like sedimentation and filtration. The biosynthesis of titanium dioxide nanoparticles can be used in comparison to chemical synthesis. The titanium dioxide nanoparticles have wide applications, viz., reducing toxicity of dyes and pharmaceutical drugs; waste water treatment; reproduction of silkworm; space applications; food industries; etc., and so have immense industrial importance. The applications of nanoparticles synthesized by biological approach will be advantageous for the industries; environment and agriculture.

Keywords Sedimentation · Filtration · Antifogging · Refractive index · Titanium dioxide nanoparticles

1 Introduction

India is the reservoir of two chief minerals of titanium viz., Ilmenite ($\text{FeO} \cdot \text{TiO}_2$) and rutile (TiO_2). Titanium dioxide (TiO_2) exists in rutile, anatase (octahedrite) and brookite form. Brookite is not found in abundance, it is an altered product of some titanium minerals. The reservoirs of TiO_2 in different states are shown in Table 1. The TiO_2 nanoparticles have many merits viz., high specific-surface area, proper electronic band structure, high quantum efficiency, chemical innerness and stability [1]. The research is gaining immense interest for the synthesis of TiO_2 on a large-scale by biological way which will be cost-effective.

There is report on TiO_2 nanoparticles synthesized using microbes viz., *Lactobacillus* sp. and *Sachharomyces cerevisiae* which is low-cost [3, 4]; using *Aspergillus flavus* TFR7 [5, 6], *Chromohalobacter salexigens* strain PMT-1 [7]. There is a report on biologically synthesized of TiO_2 nanoparticles using *Bacillus subtilis* (FJ460362) for the study of photo catalytic activity in controlling aquatic biofilm [8]. Nanoparticles have wide applications specially the TiO_2 particles viz., cosmaceutical, pharmaceutical, optical, commercial applications [9].

There are reports on applications of TiO_2 nanoparticles. Cyanide annual world production is 1.4 million tons and is mainly used for gold mining. But, most of the cyanide from

✉ Aparna B. Gunjal, aparnavsi@yahoo.com | ¹Department of Microbiology, Annasaheb Magar Mahavidyalaya, Hadapsar, Pune, Maharashtra, India. ²Asian Agri Food Consultancy Services Ltd, Pune, Maharashtra, India. ³Dr. D.Y. Patil's Vidyapeeth Dr. D.Y. Patil Biotechnology & Bioinformatics Institute, Tathawade, Pune, Maharashtra, India.

Table 1 Reservoirs of TiO₂. Source: (Indian Minerals Yearbook [2])

States of India	Resources of ilmenite minerals (million tonnes)	Resources of rutile minerals (million tonnes)
Odisha	96.44	4.47
Tamil Nadu	179.02	8.00
West Bengal	2.05	0.19
Andhra Pradesh	163.05	10.25
Jharkhand/Bihar	0.73	0.01
Gujarat	2.77	0.02
Kerala	145.70	8.41
Maharashtra	3.74	23.00

the industry enters the environment and is very toxic. There are various approaches to remove cyanide which is time consuming and costly. Photo catalytic properties of titanium dioxide nanoparticles helps in removal of cyanide from the waste water using the hydrolysis technique [10]. Similarly, there is a report where TiO₂-activated carbon composites have application in photo catalytic degradation of β -naphthol from the waste water [11]. The photo catalytic behavior of TiO₂ has been studied for the degradation of beta-naphthol using x-ray diffraction and TEM [12].

There are many methods of the synthesis of TiO₂ nanoparticles viz., sol–gel technique, solvothermal, hydrothermal, electrochemical process, precipitation method; etc. But they have disadvantages e.g. sol–gel takes hours to days for the formation of TiO₂ nanoparticles; hydrothermal method is synthetic method and involves chemical reactions; precipitation method involves difficulty in control of particle size as fast precipitation causes formation of larger particles. Microbial nanoparticle synthesis based method is eco-friendly and cheap as it get operated under mild conditions.

The nanotechnology is gaining immense importance and the researchers are focusing for the new applications of nanoparticles in industries; agriculture; pharmaceuticals; etc. There is a need to study large scale biosynthesis of TiO₂ nanoparticles and their applications in unexplored fields.

The novelty of the review here is it mentions specifically the synthesis and applications of TiO₂ nanoparticles. Although, there are research papers on TiO₂ nanoparticles, but still more work needs to be done and the review gives the detail idea of various applications of TiO₂ nanoparticles which can be the scope for further research studies on TiO₂ nanoparticles.

With this view, the objective of the review here is to focus on the aspects of biosynthesis of TiO₂ nanoparticles and also their utility in pharmaceutical, construction,

textile, food industries; etc. The applications of TiO₂ nanoparticles in aerospace; solar cells and agriculture is also described. The review also highlights the application of TiO₂ nanoparticles in waste water treatment dependent on the photo catalytic behavior. The remediation and recycling of TiO₂ is also mentioned in the review.

2 Biosynthesis of TiO₂ nanoparticles

Living systems are involved in the production of nanoparticles which are more stable as compared with chemically synthesized nanoparticles. Nanoparticles synthesized using microorganisms are found to have less aggregation behavior due to presence of more repulsive forces. Utility of nanoparticles is mainly dependent upon its size, shape as well as stability. Hence, researchers focus on the biogenic synthesis of nanoparticles which can fulfill the criteria. TiO₂ nanoparticles which naturally exists in three different crystalline forms anatase, rutile and brookite can be produced using biological agent. Extensive research is carried on the biosynthesis of nanoparticles. Biosynthesis of nanoparticles is one of the growing areas in the field of nanotechnology. Various reports are available on the utilization of bacteria, fungi, algae, plant material and enzymes for the biosynthesis of nanoparticles. The mechanisms involved in the microbial synthesis of nanoparticles are bio absorption, extracellular complexation or precipitation of metals, bioaccumulation, efflux systems, and alteration of solubility and toxicity via reduction or oxidation and lack of specific metal transport systems [13]. Negative electrokinetic potential, bio sorption and bio reduction ability of the microorganisms makes them suitable candidate to synthesize nanoparticles [3, 4]. There is information on synthesis of TiO₂ nanoparticles using fungal pathogen *Fusarium oxysporum*. *Saccharomyces cerevisiae* and *Lactobacillus* sp. have been reported to produce 30 and 18 nm TiO₂ nanoparticles using TiO (OH)₂. Energy source, pH and overall oxidation reduction potential were found to be important factors in the synthesis of TiO₂ nanoparticles, while in the case of *Saccharomyces cerevisiae*, oxidase enzyme plays an important role [3, 4]. TiO₂ nanoparticles in anatase form were synthesized using *Curcuma longa* plant extract due to its content of terpenoids, flavonoids and proteins [14]. Fenugreek (*Trigonella foenum graecum* (L.)) has been studied to synthesize TiO₂ nanoparticles with antimicrobial property [15]. There is a report on the synthesis of rutile TiO₂ nanoparticles using custard apple peel extract and precursor TiO (OH)₂ [16]. The presence of OH group in the chemical constituents of *Annona squamosa* was found to be responsible to dehydrate titanyl hydroxide to TiO₂ and stabilize the nanoparticles [16]. TiO₂ nanoparticles produced using *Vigna radiata* (green gram)

legumes showed antibacterial, antioxidant and cytotoxicity activity against Mg 63 osteosarcoma cell lines [17]. Titanium dioxide nanoparticles due to *Lactobacillus crispatus* has been found to reduce biofilm formation; hemolysin and also urease which are responsible to develop multidrug resistance ability in the pathogens [18]. Electrostatic interaction between *Lactobacillus* sp. and metal clusters are responsible for the metal nanoparticles synthesis [19]. The production of anatase TiO₂ nanoparticles mediated by *Bacillus subtilis* has been studied [20].

Guava (*Psidium guajava*) leaf extract mediated TiO₂ nanoparticles showed antioxidant and antimicrobial activities [21]. Guava leaf extract contains alcohol, primary and aromatic amines which assists in the synthesis of TiO₂ nanoparticles [21]. TiO₂ nanoparticles made by using *Aspergillus flavus* TFR7 and bulk TiO₂, was used as foliar spray (10 mg/l)

on mung bean (*Vigna radiata* L.). This fungal mediated TiO₂ found to enhance the vigor index of mung bean [5, 6]. Fungi secrete capping proteins which play the role of encapsulation of nanoparticles while associated proteins contributes in the mineralization of precursor salt [22, 23]. *Aspergillus niger* and *Aspergillus tubingensis* TFR-5 have also been reported to have the capability to produce TiO₂ nanoparticles [24, 25].

3 Application of titanium dioxide nanoparticles

The applications of titanium dioxide nanoparticles are shown in Fig. 1.

Fig. 1 Applications of TiO₂ nanoparticles

3.1 Industrial applications of titanium dioxide nanoparticles

TiO₂ nanoparticles have wide applications in industry; some of them are given in Table 2.

3.2 Role of TiO₂ nanoparticles in reducing toxicity of dyes and pharmaceutical drugs

TiO₂ work as a nanocatalyst in the degradation of methyl orange dye. TiO₂ nanoparticles synthesized using *Citrus paradisi* peel extract exhibited 72% degradation of methyl orange using sunlight [37]. Antiseptic commonly used in pharmaceutical industry chlorhexidine digluconate (CHD) affects aquatic environment by inducing resistance in microorganisms and also affects human health. Using optimum conditions of UV light intensity of 50 $\mu\text{W cm}^{-2}$, pH 10.5, 2.5:1 of substrate-to-catalyst ratio 68.2% degradation of chlorhexidine digluconate (CHD) was achieved using titanium dioxide as a photo catalyst. In future, it is possible to reduce the toxic effects of waste water generated from pharmaceutical industry [38]. Researchers tried nanocomposites for the removal of antibiotics from the environment. G-TiO₂ composites were found to have 97% removal efficiency of levofloxacin (for 1 mg/l) using 300 W UV power and 45 min irradiation time [39]. Use of TiO₂ as a sorbent is limited due to its low surface area which is able to remove contaminants in low concentration. To reduce its agglomeration ability and to increase its surface area along with photo catalytic activity, TiO₂ has been supported on zeolite, alumina, activated carbon and stainless steel. Composites of TiO₂ with coconut shell powder were prepared using sol–gel method with heat treatment. These composites were reported to remove 98% carbamazepine, antiepileptic drug which is an important organic pollutant [40].

Table 2 Industrial applications of TiO₂ nanoparticles

Uses of TiO ₂ nanoparticles	References
Cosmetics	[26, 27]
Dye sensitized solar cells	[28]
Paper, plastic and rubber industry	[29]
Food additive	[30]
Construction material	[31]
Coating to building	[32]
Pigment	[33]
Medical devices	[34]
Gas sensing	[35]
Sunscreens	[36]

TiO₂ nanoparticles can be used for the photo degradation of toxic dyes and other pharmaceutical drugs, thus avoid harmful effects on environment.

3.3 TiO₂ nanoparticles in the reproduction of silk worm

It has been reported that low concentrations of TiO₂ nanoparticles shows significant changes in the reproduction rate of *Bombyx mori*. There is a report where feeding *Bombyx mori* with TiO₂ nanoparticles resulted in a rapid development of sex organs and up regulation of reproduction-related genes [41]. After feeding of *Bombyx mori* average increase was found to be 51 eggs/insect and 0.34×10^{-4} g/egg [41].

Reproduction efficiency of silkworm can be increased by mixing low concentration of TiO₂ nanoparticles in their feed.

3.4 Waste water treatment

Low cost, resistance to corrosion and overall stability makes TiO₂ nanoparticles suitable for the waste water treatment [42]. Remediation of surface water can be achieved using TiO₂ nanoparticles as solid phase extraction (SPE) packing material to preconcentrate and extraction of heavy metals from water [43]. Ultraviolet light and titanium dioxide (TiO₂) nanoparticles doped with iron showed 98.58% diazinon removal efficiency, diazinon is one of organophosphate pesticides which it is classified as a relatively dangerous substance (Class II by World Health Organization), found in ground water [44]. Decolorization of waste water is the primary treatment considered in waste water treatment. Dyes like Rhodamine B, methylene blue and malachite green are primary dyes found in the effluent. Dye Rhodamine B is found to degrade up to 95% due to hybrid system combining UV/TiO₂ nanoparticles and polyvinylidene fluoride (PVDF) membrane [45].

TiO₂ nanoparticles play important role in the removal of the xenobiotic compounds like pesticides; dyes; toxic compounds from the waste water, thus having wide application in waste water treatment.

3.5 Role of TiO₂ nanoparticles in agriculture

According to the report given by Chao and Choi, TiO₂ nanoparticles increases the photosynthetic rate, immunity of the plant which results in 30% increase in the crop yield [46]. Increased photosynthetic rate was observed in spinach [47]. *Zea mays* sprayed with nano TiO₂ in the reproductive stages of the crop was found to have more pigmentation [48] which is responsible to increase crop yield [49]. TiO₂ nanoparticles can be applied either as soil

amendment or foliar spray. The nanoparticles get bio distributed through the vascular network. Distribution of nanoparticles is varying among crops. In case of tomato plants, application of TiO_2 nanoparticles in aerosol format was found to be more effective to increase photosynthesis and lycopene content as compared with TiO_2 nanoparticles as soil amendment [5, 6].

TiO_2 nanoparticles can be used to speed the photosynthetic rate of various crops and also enhance the crop yield.

3.5.1 Use of TiO_2 nanoparticles in nanomedicine

TiO_2 nanoparticles are used in nanotherapeutics [50]; photodynamic therapy (PDT) [51] and for articulating prosthetic implants [52]. TiO_2 nanoparticles are also used in cosmetics and in treatment of hyper pigmented skin and other nondermatologic diseases [53].

TiO_2 nanoparticles due to their special physical properties have useful applications in nanomedicine.

3.6 In purification of air

Titanium dioxide (TiO_2) photo catalyst could oxidize and mineralize compounds in the vapor or liquid phase. Hence, researchers created various filters to get rid of the indoor pollutants. Cigarette smoke (principal indoor air pollutant) can be removed by TiO_2 -impregnated titanium mesh filter (TMiP) by electrochemical anodization of the titanium mesh, and dip coating into TiO_2 anatase solution. This filters can remove volatile and nonvolatile compounds of cigarette smoke like ammonium, nicotine, 3-ethenylpyridine and tar [54]. TiO_2 has been employed in Japan as photochemical deodorizer [55]. When TiO_2 nanoparticles are stimulated by sunlight, they convert the pollutants and oxides to environmental less toxic products like carbon dioxide and calcium nitrate. Volatile organic compounds (VOC) pose various adverse effects on the health. Toluene is one of the VOC which can be decomposed by coating activated carbon with TiO_2 [56].

The oxidation of indoor air pollutants by TiO_2 nanoparticles helps in the purification of air, which is very important for all the living beings.

3.7 Use of photo catalytic nano TiO_2 for photo catalyst coating

A film of photo catalytic titanium dioxide is a super oxidative, hydrophilic and antistatic material used for self-cleaning of buildings. The film also oxidizes the hydrocarbon emitted as automotive exhaust and rain water washes the dirt and helps the building exterior to remain clean. Nano TiO_2 photo catalyst coating will act as an invisible

film and can be applied on ceiling, floor carpets, curtains, car interior, toilet seats etc. Due to this nano TiO_2 film, the microorganisms can be removed. TiO_2 nanoparticles are used in the anti-fogging car mirrors [57].

The photocatalytic film of TiO_2 can help to keep the buildings clean.

3.8 TiO_2 nanoparticles in treatment of osteosarcoma and chondrosarcoma

Osteosarcoma and chondrosarcoma are malignant bone tumors found in patients of all ages. Surgical amputation of the malignant lesion is generally carried out. Recently, it has been shown that TiO_2 nanoparticles kill HeLa cells via photo catalysis in vitro [58]. This indicates the TiO_2 nanoparticles induces cytotoxicity to bone tumor cells which will be helpful in minimization of the recurrence of osteosarcoma and chondrosarcoma.

The TiO_2 nanoparticles can be used to treat the bone tumors, thus having application in the medical field.

3.9 For dye-sensitized solar cells

TiO_2 nanoparticles have applications as semiconductor for dye-sensitized solar cells because it is non-toxic, easily available and cheap [59].

TiO_2 nanoparticles have photovoltaic effect and therefore used in solar cells.

3.10 TiO_2 in food products

Food products containing TiO_2 include white-colored sauces, confectioneries nondairy creamers and cheese. In foods, it restores whiteness of creamy products (e.g. salad dressings) and in confectionery; it forms a blockade for colors (e.g. soft-centered sweets with a crisp shell). India sets the limit on the use of TiO_2 nanoparticles up to 1% (w/w) in chewing gum and 0.01% (w/w) in beverages (Food Safety and Standards India [60].

TiO_2 nanoparticles has applications in food industries.

3.11 Remediation of nanoparticles

TiO_2 nanoparticles have the potential to work as tracer of nanoparticles of similar size and aggregate like TiO_2 [61].

4 Maintenance of historical architecture

Various historically important forts and monuments get dirty over the period of time. Maintenance of cultural heritage from getting dirty is the primary requisite. Strategies applied for the consolidation of restoration

materials include application of alkaline earth metal hydroxide nanoparticles or nanostructured SiO_2 , Al_2O_3 , TiO_2 in low and high molecular weight matrices [62, 63]. Self cleaning, depolluting and biocide activity of titania makes them suitable to use in the construction or maintenance of stone surfaces [64]. Photo catalytic activity of TiO_2 nanoparticles can exist in the presence of UV light to modify these TiO_2 nanoparticles to retain anatase form and photo catalytic potential in the presence of sunlight also. To retain the potential of TiO_2 nanoparticles, various approaches like synthesis of TiO_2 in benzyl alcohol, water and ethylene glycol dispersions of benzyl-capped anatase nanoparticles have been studied for the retention of photocatalytic activity in presence of sunlight [65]. Spray coating of TiO_2 nanoparticles as colloidal suspension on travertine limestone found to be effective to maintain the stone surface [64]. Water and ethylene glycol dispersions of benzyl-capped anatase nanoparticles of TiO_2 were applied onto Noto stone and Carrara marble specimens found to retain photo catalytic activity [65].

The photo catalytic potential of TiO_2 nanoparticles is very important for the maintenance of historical monuments.

4.1 Titanium for aerospace industry

The application of titanium alloys in the aerospace sector includes airframe, engine, helicopter, and space applications. Light weight, high strength, compatibility with CFRP and external corrosion resistance of titanium and its alloys enables them to be used in aircraft [66]. Broad research has been carried out on the preparation of titanium alloys like Ti–6Al–4V at low cost and its use in aerospace industry. Titanium alloys have an excellent strength-to-weight ratio.

TiO_2 nanoparticles has application in the making of aircraft and aircraft engines.

4.2 Toxic effects of TiO_2 on human

Information is available on the toxic effects of TiO_2 on human as they can bio concentrate, bio accumulate, and bio magnify in the tissues of mammals and other vertebrates [67]. Microparticles of TiO_2 get accumulated in macrophages of human gut-associated lymphoid tissue [68]. There is a report on the in silico study of TiO_2 spherical nanoparticles using twenty standard amino acids in aqueous solution [69]. Basic amino acids tend to have direct interaction with TiO_2 , while acidic amino acids have indirect interaction with TiO_2 spherical nanoparticles [69].

4.3 Toxic effects of TiO_2 on ecosystem

Wide use of TiO_2 nanoparticles in personal care products viz., shaving creams ($< 0.01 \mu\text{g}/\text{mg}$), toothpastes and sunscreens (1% to $> 10\%$ titanium by weight), foods and household products leads to its release through human excreta, washed off of surfaces, or disposed of to sewage that enters wastewater treatment plants and in bio solids which will be further applied to soil as fertilizer. As per report on WWTP, raw sewage contained 100 to nearly $3000 \mu\text{g Ti}/\text{l}$ [61]. Treated effluent was found to contain TiO_2 particles with 4 and 30 nm particle size [30]. After waste water treatment, effluent was found to contain from less than $5 \mu\text{g}$ up to $15 \mu\text{g}$ of nano- TiO_2/l [61]. Presence of TiO_2 nanoparticles into the environment affects phytoplankton and coastal ecosystems that support fishing and recreational activities. Algae are primarily used as biological marker in aquatic system to study biological toxicity of pollutants. TiO_2 nanoparticles inhibit algae by causing membrane structure deformation due to increased lipid peroxidation [70]. TiO_2 nanoparticles exhibit more cellular toxicity in anatase due to increased amount of intracellular reactive oxygen species (ROS) [71]. The nano bio interfacial interaction of anatase TiO_2 -NPs with EPS of algae showed higher algal toxicity than that of rutile TiO_2 -NPs [71]. Growth rate of freshwater green algae predominant in North America viz., *Scenedesmus quadricauda*, *Chlamydomonas moewusii* and *Chlorella vulgaris*, was found to be inhibited due to the presence of TiO_2 nanoparticles in freshwater microcosms [72]. Combination of anatase and rutile showed more toxicity and antagonistic effect on freshwater algae *Chlorella* [73].

4.4 Recycling of TiO_2

Disposal of sludge is very important to avoid its sequential effects. Land filling is one of the methods which are primarily used. But leaching of the heavy metals into the environment limits its use. Another alternative to land filling is restoration or recycling of the sludge. It is possible to prepare TiO_2 nanoparticles using sludge. Treatment of the sludge with coagulant TiCl_4 and aiding chemicals like $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 and $\text{Ca}(\text{OH})_2$, resulting flocculated sludge after incineration at 600°C yield TiO_2 doped with Fe, Al and Ca [74].

5 Conclusion

Broad spectrum use of titanium dioxide nanoparticles has gained attention among researchers. Extensive research is ongoing on the chemical and biological synthesis of nanoparticles. Rutile TiO_2 pigment is generally preferred

for the materials which is exposed to outdoor conditions like paints, plastics and inks due to its high resistance to UV light. Anatase TiO₂ pigment is the choice for paper, ceramics, rubber and fibers manufacturing industries due to its less abrasive power [75]. Biogenic synthesis is the method of choice due to its cost effectiveness, reproducibility and less time requirement. Microorganisms and plant extracts are used for the biosynthesis of TiO₂ nanoparticles. Compared to microorganisms, plant extracts are more feasible to use for nanoparticles synthesis due to less requirement of aseptic conditions [21]. Plants contain flavonoids, citric acid, ascorbic acids, reductases, dehydrogenase and external electron shuttlers which makes them suitable for the nanoparticles synthesis [76]. Biogenic synthesis of nanoparticles requires alcohol, amines, enzymes and proteins for the stabilization and reduction of precursor salts. Titanium can be applied as foliar spray and found to have significant effect on growth, photosynthesis rate and carbohydrate synthesis [5, 6]. TiO₂ can sustain in the environment for long period and its antimicrobial activity makes them strong disinfectant which will be 3 times stronger than chlorine, and 1.5 times stronger than ozone. Air purifiers containing TiO₂ avoid smoke, pollen, virus, bacteria and harmful gas and grab the free bacteria present in the air by filtering percentage of 99.9% due to the highly oxidizing effect of photo catalyst (TiO₂). Protection of lamp houses, walls in tunneling and white tents from becoming sooty and dark, can be achieved due to the self-cleaning and high photo catalytic potential of TiO₂.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Lai Y, Wang L, Liu D, Chen Z, Lin C (2015) TiO₂-based nanomaterials: design, synthesis and applications. *J Nanomater* 2015:1–3
- Indian Minerals Yearbook, Part- III: Mineral Reviews (2013) 52nd edn
- Jha A, Prasad K, Kulkarni A (2009) Synthesis of TiO₂ nanoparticles using microorganisms. *Coll Surf B: Biointerfaces* 71:226–229
- Jha A, Prasad K, Kulkarni A (2009) Synthesis of TiO₂ nanoparticles using microorganisms. *Colloids Surf B* 71:226–229
- Raliya R, Biswas P, Tarafdar J (2015) TiO₂ nanoparticle biosynthesis and its physiological effect on mung bean (*Vigna radiata* L.). *Biotechnol Rep* 5:22–26
- Raliya R, Nair R, Chavalmane S, Wang W, Biswas P (2015) Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (*Solanum lycopersicum* L.) plant. *Metallomics* 7:1584–1594
- Tharanya P, Vadakkan K, Hemapriya J, Kannan V, Vijayanand S (2015) Biogenic approach for the synthesis of titanium dioxide nanoparticles using a halophilic bacterial isolate- *Chromohalobacter salexigens* strain PMT-1. *Int J Curr Res Acad Rev* 3:334–342
- Dhandapani P, Maruthamuthu S, Rajagopal G (2012) Bio-mediated synthesis of TiO₂ nanoparticles and its photocatalytic effect on aquatic biofilm. *J Phytochem Photobiol* 110:43–49
- Banerjee K, Thiagarajan P (2014) A review of titanium dioxide nanoparticles-synthesis, applications and toxicity concerns. *Nanosci Nanotechnol Asia* 4:132–143
- Ijadpanah-Saravi H, Safari M, Khodadadi-Darban A, Rezaei A (2014) Synthesis of titanium dioxide nanoparticles for photocatalytic degradation of cyanide in waste water. *Anal Lett* 47:1772–1782
- Ijadpanah-Saravi H, Dehestaniathar Khodadadi A, Safari M (2016) Optimization of photocatalytic degradation of β -naphthol using nano TiO₂-activated carbon composite. *Desalin Water Treat* 57:4708–4719
- Ijadpanah-Saravi H, Sarafi M, Noruzi-Masir B, Darban AK, Bakhshi P (2017) Intelligent tools to model photo-catalytic degradation of titanium dioxide nanoparticles. *J Chemom* 31:e2907–e2909
- Beveridge TJ, Hughes MN, Lee H, Leung KT, Poole RK, Savvaidis I (1997) Metal–microbe interactions: contemporary approaches. *Adv Microb Physiol* 38:177–243
- Abdul R, Nuaman R, Abd A (2016) Biological synthesis of titanium dioxide nanoparticles by *Curcuma longa* plant extract and study its biological properties. *World Sci News* 49:204–222
- Subhapiya, Gomathipriya (2018) Green synthesis of titaniumdioxide (TiO₂) nanoparticles by *Trigonella foenum-graecum* extract and its antimicrobial properties. *Microb Pathog* 116:215–220
- Roopan SM, Bharathi A, Prabhakaran A, Rahuman A, Velayutham K, Rajakumar G (2012) Efficient phytosynthesis and structural characterization of rutile TiO₂ nanoparticles using *Annona squamosa* peel extract. *Spectrochim Acta A Mol Biomol Spectrosc* 98:86–90
- Chatterjee N, Yang J, Atluri R, Lee W, Hong J, Choi J (2016) Amorphous silica nanoparticle-induced perturbation of cholesterol homeostasis as a function of surface area highlights safe-by-design implementation: an integrated multi-OMICS analysis. *RSC Adv* 6:68606–68614
- Ibrahim KH, Salman JA, Ali FA (2014) Effect of titanium nanoparticles biosynthesis by *Lactobacillus crispatus* on urease, hemolysin and biofilm forming by some bacteria causing recurrent UTI in Iraqi women. *Eur Sci J* 10:324–338
- Nair B, Pradeep T (2002) Coalescence of nanoclusters and formation of submicron crystallites assisted by *Lactobacillus* strains. *Cryst Growth Des* 2:293–298
- Kirthi AV, Rahuman AA, Rajakumar G, Marimuthu S, Santhoshkumar T, Jayaseelan C, Elango G, Zahir A, Kamaraj C, Bagavan A (2011) Biosynthesis of titanium dioxide nanoparticles using bacterium *Bacillus subtilis*. *Mater Lett* 65:2745–2747
- Santosh M, Sirin C, Philipp S, Andreas H, Carsten S, Marialore S (2016) The role of halide ions in the anisotropic growth of gold nanoparticles: a microscopic, atomistic perspective. *Phys Chem Chem Phys* 18:13246–13254
- Raliya R, Tarafdar J (2012) Novel approach for silver nanoparticle synthesis using *Aspergillus terreus* CZR-1: mechanism perspective. *J Bionanosci* 6:12–16
- Raliya R, Rathore I, Tarafdar J (2013) Development of microbial nanofactory for zinc, magnesium, and titanium nanoparticles production using soil fungi. *J Bionanosci* 7:590–596
- Durairaj B, Muthu S, Xavier T (2015) Antimicrobial activity of *Aspergillus niger* synthesized titanium dioxide nanoparticles. *Adv Appl Sci Res* 6:45–48
- Tarafdar A, Raliya R, Wei-Ning W, Pratim B, Tarafdar J (2013) Green synthesis of TiO₂ nanoparticle using *Aspergillus tubingensis*. *Adv Sci Eng Med* 5:943–949

26. Wolf R, Matz H, Orion E, Lipozencic J (2003) Sunscreens-the ultimate cosmetic. *Acta Dermatovenerol Croat* 11:158–162
27. Shi H, Magaye R, Castranova V, Zhao J (2013) Titanium dioxide nanoparticles: a review of current toxicological data. *Part Fibre Toxicol* 10:1–33
28. Fan J, Li Z, Zhou W, Miao Y, Zhang Y, Hu J, Shao S (2014) Dye-sensitized solar cells based on TiO₂ nanoparticles/nanobelts double layered film with improved photovoltaic performance. *Appl Surf Sci* 319:75–82
29. Zhang W, Zhu Z, Cheng C (2011) A literature review of titanium metallurgical processes. *Hydrometallurgy* 108:177–188
30. Weir A, Westerhoff P, Fabricius L, Hristovski K, von Goetz N (2012) Titanium dioxide nanoparticles in food and personal care products. *Environ Sci Technol* 46:2242–2250
31. Guo S, Wu Z, Zhao W (2009) TiO₂-based building materials: above and beyond traditional applications. *Chin Sci Bull* 54:1137–1142
32. Mills A, Hodgson S, Lee S (2005) Self-cleaning titania films: an overview of direct, lateral and remote photo-oxidation processes. *Res Chem Intermed* 31:295–308
33. Feldman C (2001) Preparation of nano scale pigment particles. *Adv Mater* 13:1301–1303
34. Visai L, de Nardo L, Punta C, Melone L, Cigada A, Imbriani M, Arciola C (2011) Titanium oxide antibacterial surfaces in biomedical devices. *Int J Artif Organs* 34:929–946
35. Fergus JW (2003) Doping and defect association in oxides for use in oxygen sensors. *J Mater Sci* 38:4259–4270
36. Trouiller B, Reliene R, Westbrook A, Solaimani P, Schiestl RH (2009) Titanium dioxide nanoparticles induce DNA damage and genetic instability in vivo in mice. *Cancer Res* 69:8784–8789
37. Kumar B, Cumbal L (2014) Light harvesting titanium nanocatalyst for remediation of methyl orange. *Int J Chem Mol Nucl Mater Metall Eng* 8:196–199
38. Das R, Sarkar S, Chakraborty S, Choi H, Bhattacharjee C (2014) Remediation of antiseptic components in wastewater by photocatalysis using TiO₂ nanoparticles. *Ind Eng Chem Res* 53:3012–3020
39. Alicanoglu P, Sponza D (2017) Photodegradation of levofloxacin antibiotic via graphene/TiO₂ and its reusability. *Int J Waste Resour* 3(Suppl):7
40. Khraisheh M, Kim J, Campos L, Al-Muhtaseb A, Walker G, AlGhouti M (2013) Removal of carbamazepine from water by a novel TiO₂-coconut shell powder/Uv process: composite preparation and photocatalytic activity. *Environ Eng Sci* 30:515–526
41. Ni M, Li F, Wang B, Xu K, Zhang H, Hu J, Tian J, Shen W, Li B (2015) Effect of TiO₂ nanoparticles on the reproduction of silkworm. *Biol Trace Elem Res* 164:106–113
42. Theron J, Walker J, Cloete T (2008) Nanotechnology and water treatment: applications and emerging opportunities. *Crit Rev Microbiol* 34:43–69
43. Quétel C, Vassileva E, Petrov I, Chakarova K, Hadjiivanov K (2010) First results on Fe solid-phase extraction from coastal seawater using anatase TiO₂ nano particles. *Anal Bioanal Chem* 396:2349–2361
44. Baneshi M, Rezaei S, Sadat A, Mousavizadeh A, Barafrashtehpour M, Hekmatmanesh H (2017) Investigation of photocatalytic degradation of diazinon using titanium dioxide (TiO₂) nanoparticles doped with iron in the presence of ultraviolet rays from the aqueous solution. *Biosci Biotech Res Comm* 10:60–67
45. Vatanpour V, Karami Asma, Sheydaei Mohsen (2017) Central composite design optimization of Rhodamine B degradation using TiO₂ nanoparticles/UV/PVDF process in continuous submerged membrane photoreactor. *Chem Eng Process: Process Intensif* 116:68–75
46. Chao SL, Choi HS (2005) Method for providing enhanced photosynthesis. *Korea Res Inst Chem Technol S Korea Bull* 11:1–34
47. Lei Z, Mingyu S, Chao L, Liang C, Hao H, Xiao W, Xiaoqing L, Fan Y, Fengqing G, Fashui H (2007) Effects of nanonotase TiO₂ on photosynthesis of spinach chloroplasts under different light illumination. *Biol Trace Elem Res J* 119:68–76
48. Morteza E, Moaveni P, Farahani H, Kiyani M (2013) Study of photosynthetic pigments changes of maize (*Zea mays* L.) under nano TiO₂ spraying at various growth stages. *Springerplus* 2:1–5
49. Yang F, Hong FS (2006) Influence of nano-anatase TiO₂ on the nitrogen metabolism of growing spinach. *Biol Trace Elem Res* 110:179–190
50. Yuan Y, Ding J, Xu J, Deng J, Guo J (2010) TiO₂ nanoparticles co-doped with silver and nitrogen for antibacterial application. *J Nanosci Nanotechnol* 10:4868–4874
51. Szacilowski K, Macyk W, Drzewiecka-Matuszek A, Brindell M, Stochel G (2005) Bioinorganic photochemistry: frontiers and mechanisms. *Chem Rev* 105:2647–2694
52. Jacobs JJ, Skipor AK, Black J, Urban R, Galante JO (1991) Release and excretion of metal in patients who have a total hip-replacement component made of titanium-base alloy. *J Bone Joint Surg Am* 73:1475–1486
53. Wiesenthal A, Hunter L, Wang S, Wickliffe J, Wilkerson M (2011) Nanoparticles: small and mighty. *Int J Dermatol* 50:247–254
54. Slimen H, Ochiai T, Nakata K, Murakami T, Houas A, Morito Y, Fujishima A (2012) Photocatalytic decomposition of cigarette smoke using a TiO₂-impregnated titanium mesh filter. *Ind Eng Chem Res* 51:587–590
55. Fukuyama J (2004) Odor pollution control for various odor emission sources in Japan, East Asia. In: *Odor measurement and control review workshop (Environmental Management Bureau, Ministry of the Environment, Government of Japan)*, pp 67–77
56. Rezaee A, Pourtaghi G, Khavanin A, Mamoori R, Ghaneian M, Godini H (2008) Photocatalytic decomposition of gaseous toluene by TiO₂ nanoparticles coated on activated carbon. *Iran J Environ Health Sci Eng* 5:305–310
57. Montazer M, Seifollahzadeh S (2011) Enhanced self-cleaning, antibacterial and UV protection properties of nano TiO₂ treated textile through enzymatic pretreatment. *Photochem Photobiol* 87:877–883
58. Sha B, Gao W, Han Y, Wang S, Wu J, Xu F, Lu T (2013) Potential application of titanium dioxide nanoparticles in the prevention of osteosarcoma and chondrosarcoma recurrence. *J Nanosci Nanotechnol* 13:1208–1211
59. Mbonyirivuze A, Zongo S, Diallo A, Bertrand S, Minani E, Yadav L, Mwakikunga B, Dhlamini S, Maaza M (2015) Titanium dioxide nanoparticle biosynthesis for dye sensitized solar cells: review. *Phys Mater Chem* 3:12–17
60. Food Safety and Standards [FSS] India (2011) Food safety and standards (food product standards and food additives) regulation. 4:449–529
61. Kiser M, Westerhoff P, Benn T, Wang Y, Pérez-Rivera J, Hristovski K (2009) Titanium nanomaterial removal and release from wastewater treatment plants. *Environ Sci Technol* 43:6757–6763
62. Chelazzi D, Poggi G, Jaidar Y, Toccafondi N, Giorgi R, Baglioni P (2013) Hydroxide nanoparticles for cultural heritage: consolidation and protection of wall paintings and carbonate materials. *J Colloids Interf Sci* 392:42–49
63. Miliani C, Velo-Simpson M, Scherer G (2007) Particle-modified consolidants: a study on the effect of particles on sol-gel properties and consolidation effectiveness. *J Cult Herit* 8:1–6
64. Goffredo G, Munafo P (2015) Preservation of historical stone surfaces by TiO₂ nanocoatings. *Coatings* 5:222–231
65. Gherardi F, Colombo A, Goidanich S, Simonutti R, Toniolo L (2014) Innovative nano-TiO₂ particles for self-cleaning treatments of historic architecture and sculptures. *Restor Build Monum* 20:423–432

66. Inagaki I, Takechi T, Shirai Y, Ariyasu N (2013) Application and features of titanium for aerospace industry. *Nippon Steel Sumitomo Met Tech Rep* 396:23–28
67. Jovanovic B (2014) Critical Review of Public Health Regulations of titanium dioxide, a human food additive. *Integ Environ Assess Manag* 11:10–20
68. Lomer M, Thompson R, Powell J (2002) Fine and ultrafine particles of the diet: influence on the mucosal immune response and association with Crohn's disease. *Proc Nutr Soc* 6:123–130
69. Liu P, Jin H, Guo Z, Ma J, Zhao J, Li D, Wu H, Gu N (2016) Silver nanoparticles outperform in radiosensitizing U251 cells in vitro and in an intracranial mouse model of glioma. *Int Nanomed* 11:5003–5014
70. Ozkaleli M, Erdem A (2018) Biototoxicity of TiO₂ nanoparticles on *Raphidocelis subcapitata* microalgae exemplified by membrane deformation. *Int J Environ Res Public Health* 15:1–12
71. Gao X, Kaijun Z, Luqing Y, Daohui L (2018) Distinct effects of soluble and bound exopolymeric substances on algal bioaccumulation and toxicity of anatase and rutile TiO₂ nanoparticles. *Environ Sci Nano* 5:720–729
72. Cardinale BJ, Bier R, Kwan C (2012) Effects of TiO₂ nanoparticles on the growth and metabolism of three species of freshwater algae. *J Nanopart Res* 14:1–8
73. Iswarya V, Bhuvaneshwari M, Alex S, Iyer S, Chaudhuri G, Chandrasekaran P, Bhalerao G, Chakravarty S, Raichur A, Chandrasekaran N, Mukherjee A (2015) Combined toxicity of two crystalline phases (anatase and rutile) of titania nanoparticles towards freshwater microalgae: *Chlorella* sp. *Aquat Toxicol* 161:154–169
74. Shon H, Vigneswaran S, In Kim, Cho J, Kim GJ, Kim JB, Kim JH (2007) Preparation of titanium dioxide (TiO₂) from sludge produced by titanium tetrachloride (TiCl₄) flocculation of wastewater. *Environ Sci Technol* 41:1372–1377
75. Gazquez M, Bolívar J, Garcia-Tenorio R, Vaca F (2014) A Review of the production cycle of titanium dioxide pigment. *Mater Sci Appl* 5:441–458
76. Pandey S, Oza G, Mewada A, Sharon M (2012) Green synthesis of highly stable gold nanoparticles using *Momordica charantia* as nano fabricator. *Arch Appl Sci Res* 4:1135–1141

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.