IJARSCT
ISSN (Online) 2581-9429
IJARSCT
Impact Factor: 5.731
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 12, Issue 4, December 2021

Potential of Titanium Dioxide and its Application

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Abstract: *Now a day's metal and metal Oxides including titanium dioxide have been widely studied, due to their importance in recent medical therapies, catalysis, photocatalysis, antibacterial agent and also as nano paints. It is an inorganic compound with attractive physical and chemical characteristics based on the size, crystal phase and shape of particle. Utilization of titanium dioxide is natural amicable because of some electrical, optical and morphological properties,TiO_2 nanoparticles were concentrated as photosensitizing specialist in the treatment of harmful growth just as in photodynamic inactivation of anti-microbial opposition microscopic organisms. TiO_2 is also used to mineralized organic compound such as alcohol, carboxylic acid, phenolic derivatives using oxygen as primary oxidant.TiO_2 has been also used as bleaching, opacifying agent and as U.V protector in cosmetics, paints and enamel.*

Keywords: Titanium Dioxide

I. Introduction

Titanium Dioxide is a naturally occurring substance, chemical formula TiO_2, known as titania [1]. It is a common material which has been widely used for many years, Naturally occurring titanium dioxide forms when titanium reacts with the oxygen in the air. Titanium oxide is found in minerals in the earth's crust. It also found with other elements, including calcium and iron. Commercially titanium dioxide was first introduced in 1923,no health concerns and no cases of problems have been detected associated with it. Recently it has been studied that thousands of workers in manufacturing industry or working with titanium dioxide, do not have any health hazards[2]

1.1 Source

Titanium is mainly sourced from ilmenite ore, which is the most widespread form of titanium dioxide containing ore around the world. Rutile is the next most abundant and contains around 98 percent titanium dioxide in the ore. The metastable anatase and brookite phases convert to the equilibrium phase rutile irreversiblyby heating above temperatures in the range of 600to 800°C (1,112 to 1,472°F).

1.2 Process of Formation

There are two main processes for TiO_2: Sulphate process and Chloride process but Chloride process is predominat over sulphate process.

Sulphate process[3]

$FeTiO_3 + 2H2SO_4 \rightarrow FeSO_4 + TiOSO_4 + 2H_2O$

$TiOSO_4 + (n+1)H2O \rightarrow TiO_2{\bullet}nH_2O + H_2SO_4$

$TiO_2{\bullet}nH2O \rightarrow TiO_2 + nH_2O$ [3]

1.3 Advantages of Sulfate process

The raw material i.e. ilmenite and sulfuric acid used for the above process are low in price and easily available this process requires simple process and it is a well known technology. The equipment used for the sulfate process are simple and made up of anti-corrosion material.

1.4 Disadvantages of Sulfate process

1. The process is very short and works on harsh operation, high consumption of sulfuric acid and water, and many wastes and by-products are formed, which are harmful to the environment.

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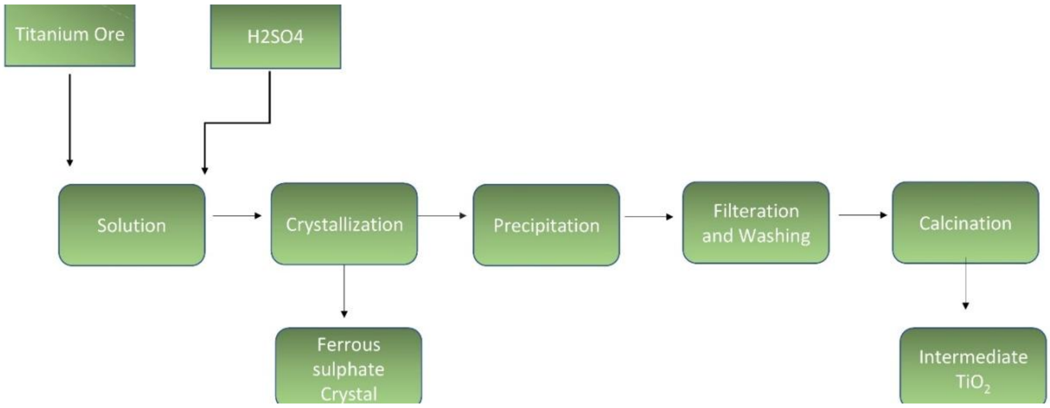

Figure 1: Sulfate process

Chloride Process[4]

"Titanium is separated by using chloride process from its ore. In this process, the feedstock is treated at 1000 °C with carbon and chlorine gas, giving titanium tetrachloride. Typical is the conversion starting from the ore ilmenite" [1]

$$2\ FeTiO_3 + 7\ Cl_2 + 6\ C \rightarrow 2\ TiCl_4 + 2\ FeCl_3 + 6\ CO$$

$$TiCl_4 + O_2 + heat \rightarrow TiO_2 + 2Cl_2$$

1.5 Applications of Titanium dioxide

TiO_2 is a white color found in all kinds of paints, printing ink, plastics, paper, synthetic fibers, rubber, condensers, painting colors and crayons, ceramics, electronic components along with food and cosmetics. NPs of titanium dioxide have been reported helpful in field of photodynamic therapy for drug delivery at specific site [5].

Titanium dioxides (TiO_2) have been widely studied, due to its interesting general properties in a wide range of fields including catalysis, photocatalysis, and antibacterial agents and in civil as nano-paint (self-cleaning) that affect the quality of life. [6]

When used as a pigment, it is called titanium white, Pigment White 6, or CI 77891. The great efforts devoted to the research on TiO_2 material produced many promising uses in areas which range from photovoltaics and photocatalysis to photo-electrochromic and sensors. These uses can be generally classified into "energy" and "environmental" types, many of types rely not only on the properties of the TiO_2 material itself but also on the changes in the TiO_2 material host.

Titanium dioxide single-crystal can also be studied under Independence spectroscopy photoelectron spectroscopy and Kelvin probe measurement which shows that the Fermi level and conduction band depend on sample environment [7]. Titanium dioxide has been use as bleaching and opacifying agent in porcelain enamels it gives brightness, hardness and acid resistance. It is also used in cosmetics that charge in screen lotions, skin care products, as UV protector because it's property to absorb UV light [8].

Colour and brightness of food products TiO_2 is enhance by using TiO_2.It is also used as white pigment in toothpaste. TiO_2 nanostructure have been employed in photoelectrochemical biosensing application which enhance detection of target. these are excellent additive materials for Titanium implants deficiencies and use coating for the where surface of Titanium implants [9]. Titanium dioxide NPS are very important as these particles have positive use in new medical therapies. The application of heat Titanium NPS in photodynamic therapy are limited by the necessity to use UV light of very low tissue sanitation and harmful effect on the human body [10].

TiO_2 pigments have many important properties like scattering power, brightness, hiding power, mass tone, gloss formation, gloss haze, dispersibility, lightfastness and weather resistance; these properties are a function of chemical purity, lattice stabilization, primary particle size, particle size distribution and the coating.

Theoretically the size of TiO_2particle is in between 0.2 and 0.3 µm, but due to the formation of agglomerates this pigmenthave considerably larger size, these agglomerates affect hiding power, tinting strength and other end-use properties of the coating. [11]

TiO_2 is recently used in biocompatibility of bone implants and an insulator in MOSEFETS [12]TiO_2 nanostructures are used for coatings of the bare surface of titanium implants, which are excellent additive materials to recompense titanium implants deficiencies—like poor surface interaction with surrounding tissues—by providing nano porous surfaces and hierarchical structures.[13] In the surface science of metal oxides titanium dioxide (TiO2) is the most studied crystalline oxide. Its physical and chemical properties are dominantly determined by its surface condition. Ti3+ surface defect (TSD) is one of the most important surface defects in TiO2.

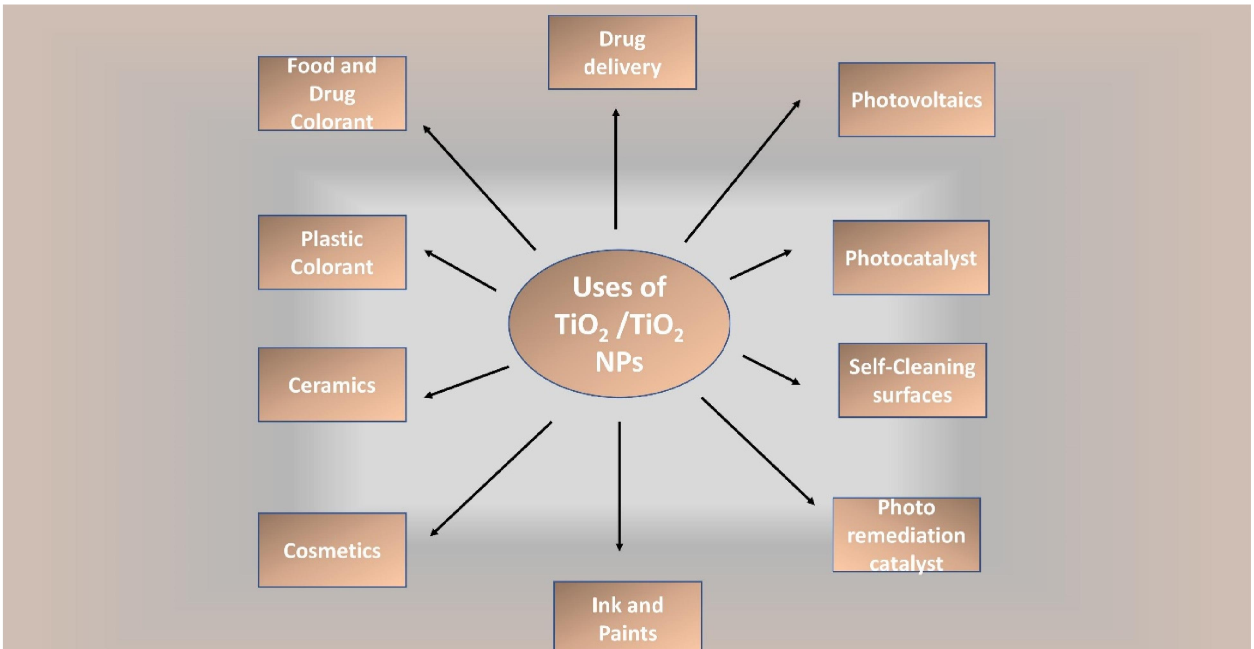

Figure 2: Uses of Titanium Oxide

"Titanium dioxide (TiO2) photocatalysis is an oxidation method that has found wide use in self-cleaning materials and water purification, where the general aim is to completely mineralize and detoxify the organic pollutants"[16] "TiO2 photocatalysis can generate the same reactive oxygen species as in biological systems, namely hydroxyl radicals (•OH) and superoxide anions (O2•–)UV light with higher energy than that of the band gap of TiO2 excites electrons to the conduction band under TiO2 photocatalysis, which leaves holes on the valence band. The electrons on the conduction band can reduce molecular oxygen to superoxide. Reactions of valence band holes with water produce hydroxyl radicals. A hole can also accept an electron directly from an organic molecule adsorbed onto the TiO2 surface" [16]. "Photocatalytic degradation of carbamazepine takes place by UVC-assisted Nd-doped Sb2O3/TiO2 photocatalyst" [17]

TiO2 used as photocatalyst inphotocatalytic degradation of atenolol (ATL) which was investigated in aqueous suspensions using. "Complete degradation of 37.6 µM ATL was obtained after 60 min irradiation in pH 6.8 Milli-Q water in the presence of 2.0 g L−1 Degussa P25 TiO2".[18]. The rate of the photocatalytic oxidation of cyanide in aqueous TiO2 suspensions (0.1–5.0 g l−1), was investigated as a function of catalyst loading air-flow rate (0.2–1.1 l min−1), and the concentration of ethylenediaminetetraacetate, EDTA (0.4–40 mM) at pH 13.0. The cyanide oxidation rate did not vary with the TiO2 loading while a slight increase in the degradation rate with an increase in the air-flow rate was found.[19]. TiO_2 NPs revealed attractive potential as photocatalysts for anti-inflammatory, analgesic drugs [20] "In addition, TiO2-coated glass slides were applied for the study of a variety of oxidation reactions, including drug candidates and their oxidation products"[21]

"Photodegradation is recently drawing much attention due to its potential to oxidize such contaminating compounds and its large-scale deployment is still being evaluated. In order to optimize these processes, quantifying and developing new kinetics models are an essential step. Photodegradation kinetics of caffeine was evaluated under different UV-C doses (1.9–15.2 mJ cm–2 s–1 and λ = 254 nm) and in the presence of two degradation agents, hydrogen peroxide (H_2O_2) and commercial titanium dioxide (TiO_2) nano powder" [22].

In this study, ALD was chosen to deposit a biologically inspired nanoscale thin film coating on structural Mg-Zn binary alloys. Tetrakis (dimethylamido) titanium (TDMATi) was chosen as the ALD precursor to deposit titanium dioxide (TiO_2) on the alloys. Nano-sized TiO_2 is used widely in a variety of daily products, such as antifouling paints, plastic goods, sunscreens, pharmaceutical additive agents and food colorants.[23] To Enhance Cytocompatibility for Bioresorbable Vascular Stents Atomic Layer of TiO_2 Nano-Thin Films on Magnesium-Zinc Alloys have been deposited.[24]

Titanium dioxide scaffolds are manufacture through various techniques using collagen, polyvinyl alcohol, sodium chloride [25].The pharmacokinetics of metal NPs, including TiO_2, depends on many factors, including particle type, surface charge, surface coating, size, dose, and exposure route[26],[27]

"The combination of the electroporation and the conjugation of the TiO_2 nanoparticles with the monoclonal antibody improves the photokilling selectivity and efficiency of photoexcited TiO_2 on cancer cells in the photodynamic therapy(PDT) as the conjugation of the TiO_2 nanoparticles with monoclonal antibodies increases the photokilling selectivity of TiO_2 nanoparticles to cancer cells and the electroporation could accelerate the delivery speed of the TiO_2 nanoparticles to cancer cells".[28] Analogous studies using even higher doses of TiO_2 gave similar results confirming that orally administered TiO_2 does not penetrate the gastrointestinal tract and that penetration is medically insignificant[29]

Iron (III) doping of TiO_2 NPs has been synthesized from unknown catalytic role of Iron(III) nano hydrated (Fe(NO3)3.9H2O) and TiO2 in the ratio 1:1 these powder are treated hydrothermally.This Fe-doped TiO2 NPs have so many applications in photovoltaic and photocatalytic in new technologies. [30]

By M. WaseemAkram etal Au-TiO_2 nanoparticles conjugated with doxorubicin are used for photodynamic therapy applications[31].Muhammad Atif etal. Studied TiO2-NPs on wheat rust against antifungal activity against toxic plant pathogens these TiO2-NPs have best antifungal activity against wheat rust especially NPs synthesized from C.quinoa [32]. TiO_2 has been found useful in numerous technological application, also used for photocatalytic degradation of organic pollutants, water splitting for hydrogen formation and energy storage devices [33].

Gercuts et al observe that go to NPS has been excreted by the kidney in rats [34] Xie et al studied that TiO_2 NPs level in rats, is higher in urine than in feces, indicating renal excretion as the primary route of TiO_2 elimination [35]

Ti-H_2O_2 treated at 800c for 72 hours, with various additive to form TiO_2nanorods, nanoflowers and nanotubes were precipitated. This study is used to enhance the photocatalytic activity of TiO_2 [36].

Study on TiO_2 NPS penetration on franz cell for 24 hours using intact and needle aborded human skin as well as evaluation cytotoxicity on HacaTkaratinocytes, it was demonstrated that the presence of TiO_2 NPs was coronavirus limited to epidermal layer,and the concentration of dermal layer was below the detection limit[37]

Due to high use of nanoparticles it is of great interest to study the health effect caused due to exposure of nanomaterials.Gerard vales etal. carried out experiment on human bronchial epiththelium cell and BEAS-2B cell using chronic exposure,experiment showing no genetoxic effect in coment and in MN assay [38].

Safety measures are essential as new nanoparticle enter the market and there relative toxicities is scarce, as this maybe in head by workers while working in paint industries and TiO_2 to NPS have allergic reaction in by Vandebraj et al[39] continuous exposure to TiO_2 leads to chronic inflammation which is responsible for destruction of body tissues leads to other diseases [40]

II. Physicochemical Property and Characterization

Naturally occurring Titanium dioxide is named after two abudant minerals tetragonal crystallographic polymorphs of TiO_2, antase and rutile another orthorhombic crystal is brookite. TiO_2 is mostly prepared by the purification of rutile mineral, aur by chlorination or sulphonation of ilmenite, after thermal treatment amorphous TiO_2 may be transformed

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into anatase or brookite in a process called calcination [41] “Sol-gel synthesis and hydrothermal method are synthetic method to prepare titania NPs two particles can be modified by the addition of various surfactants on dopants or by post synthetic modification such as doping surface functionalization or binding with organic molecule[42].It has been observed that the absorbance of dye moleculestakes place on the surface of catalyst ,which absorbs UV light, no absorption by TiO2 is observed, this reduces formation of OH radical which blocks the active sites of photocatalyst by using dye molecules[43]. NPs are modified to improve the photosensitization property including the visible light absorption bracket [44] Titanium dioxide can be doctor with various metal and nonmetals dopants for effective photo sensitisation of wide band gap semiconductor of TiO_2”[45,46]

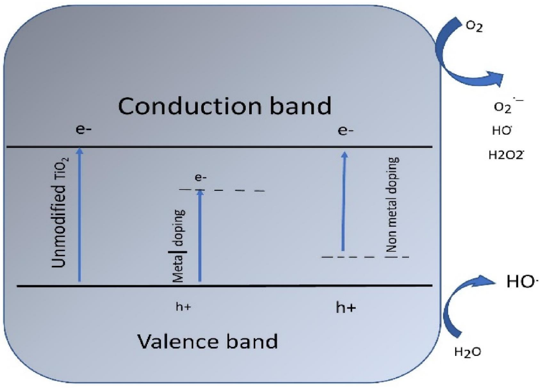

Figure 3: **Mechanism of reactive oxygen species generation by TiO2**

Table 1: Applications of someTiO_2.NPs combined in medicine.

Sr.no	Shapes of NPs	Method of Synthesis	Photosensitizer	Uses	Ref.no.
1	anatase (23 nm)	Subphthalocyanine derivative	TiCl4 and benzyl alcohol; macrocycle deposition overnight in THF	Clinical trial against S. aureus, E. coli	54
2	anatase (23 nm)	Zinc(II) phthalocyanine derivatives	from TiCl4 and benzyl alcohol; macrocycle deposition overnight in THF	Clinical trial against: S. aureus	55
3	anatase (25 nm)	Zinc(II) tetrakis(3- dodecylpyridyloxy)phthalocyanine (mixture of isomers)	deposition in pyridine/ethanol mixture	Cilinical trial MRSA, Salmonella enteritidis	56
4	anatase/rutile (thickness- 600 nm , size-100 nm)	Copper tetracarboxyphthalocyanines (mixture of isomers)	Anodization	Activity against MRSA	57
5	P25 TiO2 (75% anatase and 25% rutile, size 25 nm)	5,10,15,20-tetrakis(2,6- difluorosulfonylophenyl)porphyrin and its zinc(II) complex	commercial distribution	Activity against S. aureus, E. coli	58
6	N-TiO2 -NH2 (size: 20–30 nm)	Aluminum(III) phthalocyanine chloride tetrasulfonate	N-doping by calcination of commercially available anatase TiO2 NPs in ammonia atmosphere	Photodynamic theory against cancer (HeLa and KB cell lines)	59
7	N-TiO2 -NH2 (size: 20–30 nm)	Aluminum(III) phthalocyanine chloride tetrasulfonate	N-doping by calcination of commercially available anatase TiO2 NPs in ammonia atmosphere	In photodynamic therapy of cancer	60
8	TiO2 nanowhiskers (size < 100 nm)	tetrasulphonatophenyl porphyrin	undefined deposition in H_2O	In photodynamic therapy of rheumatoid arthritis	61
9	TiO2 nanowhiskers	tetrasulphonatophenyl porphyrin	undefined; deposition in H_2O	In photodynamic therapy of diabetes mellitus	62
10	P25 TiO2 (75% anatase and 25% rutile, size—21 nm)	Chlorin e6	silylation with or without PEgylation	In photodynamic therapy against glioblastoma cell	63
11	TiO_2(100 nm)	methylene blue used in mixture but without grafting the NPs	commercial distribution	Activity against: S. aureus, E. coli, and Candida albicans	64

Free oxygen may attack surrounding O_2 and H_2O to form Arrow ROS, including superoxides ($O2^{\cdot -}$), hydrogen peroxide (H_2O) and hydroxyl radical ($^{\cdot}OH$) [48] TiO_2 NPS inhibit efflux multidrug-resistance.

Titania NPS forms agglomerates due to its nature which decreases the surface area and also lowers photo activity, sedimentation of TiO_2 NPs lowers concentration and interfere with the reproducibility of result so to prevent this unexpected property stable formulation NPs is essential [49]

Titanium dioxide NPs have high energy for excitation reserves in white band gap which is possible only with UV light. Agglomerates reduces this photo reactivity as well as functional surface area[50] Archana et al studied blends of Chitosan, poly(N-Vinyl pyrrolidone) and TiO_2 by IR spectroscopy, thermo gravimetric analysis, transmission electron microscopy and scanning electron microscopy[51]

TiO_2 NPS combines with various other inorganic element and compound to improve the photo chemical properties. Cerium- doped(Ce-doped) TiO_2 thin films synthesized by the sol-gel dip coating route studied by Kalyani et al[52]

Nitrogen doped TiO_2-TSAlClPc system have capacity to kills 85% of the cancer cells at 420 -800 nm. Similarly photo killing of Hella cells on absorption of visible radiation of different region from 420- 800 and 420—575nm [65] TiO_2 where used as bactericide on various bacteria including both gram positive and Gram Negative strengths [66] this property can be improved by exposure to UV light. Tuncle et al show that in the application of antimicrobial photodynamic therapy Zn(II) phthalocyanine with(4-carboxyphenyl) ethynyl moieties alone or after integration with TiO_2 NPS which lead to photo cytotoxicity[67] Titanium nanoparticles have significant advantages in chemotherapy which enable efficient drug molecules and thus better pharmacokinetics and their targeteddelivery[68,69]

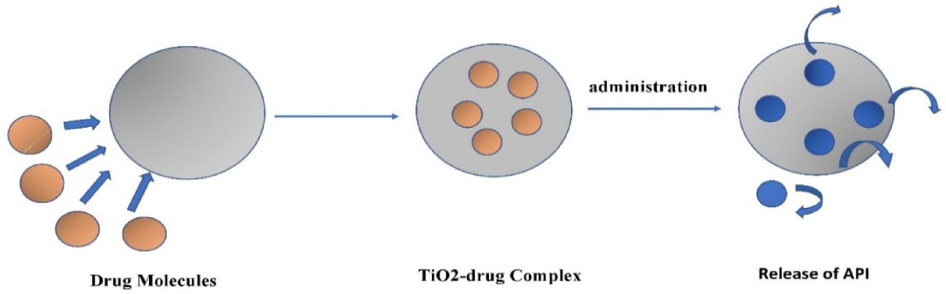

Figure 4 : Titanium Oxide as drug delivery agent

Table 2: Applications of selected TiO2 NPs in combination with doxorubicin in medicine

Sr.no	Shapes Of NP's	Synthesis	Uses	Ref.
1	TiO2 (anatase, 10 nm) Au-TiO2 (1–30 nm)	TiO2 from butyl titanate by solvothermal method; Au-TiO2 by solvothermal method using mixture of butyl titanate and HAuCl4 ; both were followed by calcination.	PDT and doxorubicin delivery tested on breast cancer cells	70
2	UCNPs@mSiO2 /TiO2 (30 nm of silica/titania shell thickness)	silica coating was synthesized on UCNPs with tetraethylorthosilicate, silylated and reacted with tetrabutyl titanate followed by calcination to yield anatase phase	PDT mixed with doxorubicin delivery against HeLa cells)	71
3	NaYF4 :Yb/Tm-TiO2 (sphere-shaped) (20–40 nm)	TiO2 NPs prepared by solvothermal method from tetrabutyl titanate; trifluoroacetates of lantanides were mixed with TiO2 NPs and thermally treated; further functionalization included PEGylation, silylation and conjugation of folic acid	PDT with doxorubicin delivery tested on drug-resistant breast cancers	72
4	ZnPc@TiO2_CHCl3 (20 nm) ZnPc@TiO2_THF (125 nm) ZnPc@TiO2_CHCl3 /THF (13 nm); mostly anatase with small addition of rutile	NPs—commercially; nanotubes—from titanium(IV) isopropoxide in a sol-gel method followed by hydrothermal treatment; deposition of ZnPc in CHCl3 , THF or 1:1 v/v CHCl3 /THF	PDT, bioimaging and doxorubicin delivery (tested on HeLa cells)	73
5	UCNPs@SiO2@TiO2	crystalline structure was prepared from titanium diisopropoxide bis(acetylacetonate)by hydrothermal treatment which was grown on UCNPs@SiO2 -NH2 NPs	PDT in cancer treatment mixed with doxorubicin (tested on HeLa cells)	74
6	diamond-shaped mesoporous TiO2 (220 nm in width, 250 nm in length, 40 nm thick, pore size—4.1 nm)	tanium isopropoxide at 28 ◦C, followed by silylation and PEGylation	drug delivery vehicles for cancer therapy	75
7	0.3 µm TiO2 nanotube (single nanotube diameter—90 nm)	glycerol/water/NH_4F is used to grow TiO2	Visible-light-triggered release of ampicillin	76

TiO_2 has many application in medical and drug delivery system and chemotherapeutics, TiO_2 NPS have been applied in pharmacy TiO_2 Ag NPs were is synthesized by mixing TiO_2 with silver nitrate, at 300°C, which reduces the toxicity of teeth whitening gel[77]. Onwobu et al synthesised eggshell-TiO_2 composite commercial in ground mill with egg shell powder and TiO_2[78] which is used for occluding open dentine tubules.

TiO_2 (anatase),TiO_2(rutile) and TiO_2 mixed phase (anatase,rutile) use for photocatalytic degradation of atenolol[79] P25 (21nm) used to improve endoprosthesis biocompatibility[80] Cuppine et al observe time necessary for tooth bleaching decreases upto half an hour by the combination of TiO_2 with H_2O_2gel [81]

Modified TiO_2 composite with shear bond strength 13.9 mpa found suitable for safe the bonding of orthodontic brackets studied by Sharma et al[82] TiO_2 nanoparticles have antibacterial and antifungal property, Co-Cr alloy coated with TiO_2 under UV irradiation show significant antifungal activity [83]

III. Summary

Titanium has vast application in medical, solar cell photodynamic therapy cosmetics acceptor because of excellent photochemical properties and biocompatibility .These particles have low cost and easily usable. The number of active sites on the surface decides the photosensitization property and manufacturing cost .TiO_2nano an micro particles are widely used in photodynamic therapy TiO_2 have occasion as a drug carrier without any harm effect on health issue, TiO_2 NPS are used for so many diseases. TiO_2 have many application in food and drug, colorant , ink and paints, cosmetics sunscreen components batteries etc. No data is available forTiO_2 toxicity but it is necessary to develop this area extensively.

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