Review of TiO_2 Nanoparticles

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Abstract - Study of Titanium dioxides, have been done extensively,owing to its enthuasiastic normal properties in a field having wider domain . These fields include antibacterial agents,catalysis,photocatalysis and in civil field as nano-paints by which life quality is influenced .Hence doped TiO2 by noble metals and TiO2 are good choices in the application of performance of photocatalysis .Attractive chemical and physical features of TiO2 depends to a large extent on size, crystal phase, and particles shape. For instance, various crystalline phases of Titanium Dioxide have energy band gaps, which are distinct, rutile phase of TiO2 having 3.0 eV and anatase phase of TiO2 having band gap of 3.2 eV, actually decide the photocatalsis performance of Titanium Dioxide . Present review paper deals exhaustively with theoretical concepts and few applications pertaining to TiO2 nanoparticles structure. For environmental applications, Optical, electrical and morphological properties are making Titanium Dioxide, an ideal choice .

Keywords : **Anatase, Rutile, TiO2, paint, photocatalysis, self-cleansing**

1.Introduction

TiO2, also called as Titanium(IV)oxide or titania or Titanium (IV) oxide also called as Titania, which is a member of Transition metal oxides family, is the natural oxide of titanium, having chemical formula TiO2 [1]. TiO2 which is white in colour is found in all kinds of plastics, rubber, synthetic fibres, papers, capacitors, painting colors, printing ink, crayons, cosmetics and food alongwith ceramics and electronic components[2] .

As a pigment, when Titanium Dioxide is used as a pigment, it is called Pigment White 6 or titanium white, or CI 77891.

There are three naturally existing crystalline phases of TiO2,namely rutile phase, brookite phase and anatase phase [3].

Maximum endeavour done to carry out research on Titanium Dioxide material, generated several challenging applications in areas ranging from sensors, photocatalysis, photovoltaics and photo-electrochromics[4].

These applications can be normally categorized into "energy" and "environmental" types, many types of which are not dependent only on the properties pertaining to Titanium Dioxide material itself but also on the variations in the host of Titanium Dioxide material (For example,with organic and inorganic dyes) .

In the past decades,the skyrocketing growth of research activities has been seen in nanotechnology and nanoscience [5, 6]. When the material size gets reduced smaller up to the nanometer ,there is exhibition of new chemical and physical properties. There are variations in properties in forms of the shapes in the nano-materials shrinkage variation amongst nanomaterials unique properties, the dynamics of holes and electrons in semiconductor nanomaterial is basically controllable by quantum confinements and transport property pertinent to photons and phonons are greatly impacted by geometry and size of crease by significant amounts with reduction in size of material [7] . Surface area of size of small particles is very much beneficial for several device, which are Titanium Dioxide-based, making interactions simple amongst device and interacting medium, which mainly occurs at surfaces or on interface and depend to large extent upon surface of materials[8]. Hence, Titanium Dioxide is one amongst most famous nanosize material which is commercially available and has applications in various fields owing to it's biocompatibility, wider availability, little cost and very high chemical stability and non-toxicity[9].

1.1 Detailed Mechanism of TiO2 as Photocatalysis

Photo-catalysis comprises catalysis and photochemistry with both catalyst and light being required to precipitate or onset a conversion, which is chemical [10] .Commencement of the photo-catalysis process takes place by the electromagnetic radiation,absorption exciting electrons from valence bands to conduction bands, leaving holes in valence bands .This process has been schematically represented in (Fig. 1) .Under the process, irradiation by Ultraviolet light, is used by photons having energy equal to or larger than Titanium Dioxide band gap energies ($h\nu \geq 3.2$ electron Volts at $\lambda \leq 380$ nanometers); generating pairs of electron-hole (Charge carrier) [11] .Negatively charged electron moving from valance band to conduction band thereby leaving behind hole,which is charged positively. After that, holes and electrons participate in oxidation reduction reaction with species which are adsorbed on TiO2 surface, such as hydroxide (OH-) ions, water, oxygen or organic compounds. Valence band hole (h+) is highly oxidizing and highly reducing is electron (e-) of conduction band [12]. H2O or OH- ion is oxidized by the charge carrier h+ to the hydroxyl radical (OH•), which is non-selective oxidant and is highly powerful. It very easily attacks on pollutants, which are adsorbed on surface of TiO2 or in aqueous solutions decomposing to CO2 and H2O [13].On conduction bands, electrons reduce adsorbed oxygen species to superoxides (O2•), after that goes under series of reaction to generate OH• radicals. Reactions of radical with organic substances, harmful microorganisms or environment pollutants eventually decomposes the latter [14]. In case where the above mentioned process does not take place, charge carriers recombination takes place and energy is liberated thermally . Due to this,there is significant drop in photocatalytic efficiency of TiO2 [15, 16] . Recombination of electron-hole is a reaction competing with electron-acceptor and hole-donor, electron-transfer reactions. There is occurance of recombination in the bulk of semiconductor or on the surface eventually in the liberation of heat (or light) and harmful for the photocatalysis activity because of quenching of redox property of the semiconductors [17,18].

1.2 Diagramatic representation of mechanism of TiO2 as Photocatalysis

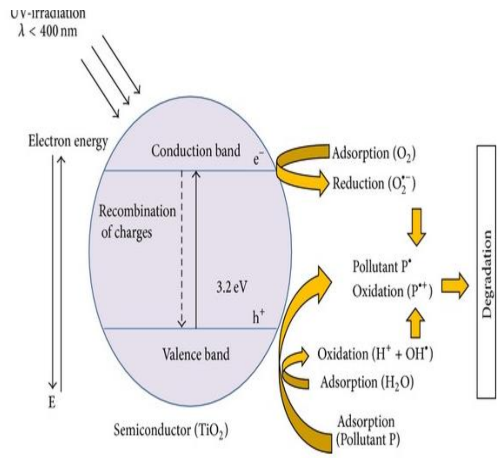

Fig.1. In Titanium Dioxide particles, principal photocatalytic process

There are various parameters,mass/concentration,light intensity, wavelength, Ph and temperature, the nature of a photocatalyst impacting photocatalytic performances [19] .Other parameters include particle size, surface area, the adsorption nature and concentration of the substrate [20, 21] .TiO2 nanoparticles, have diverse applications owing to properties,which are perfect including water purification, of air,antibacterial, decontamination, UV protection, tooth paste, photocatalysis, paint and sensing applications. (Fig. 2) shows diverse applications of Titanium Dioxide . Present review, concentrates on few of applications owing to its importance in routine lives [22, 23] .

Fig . 2. High building coated with Self-cleaning TiO2 [2]

Stable thermally, easy to cleanse surfaces, anti-fogging, anti-skids anti-fouling and anti-graffiti characteristic, perfect electrical and thermal conductivities, complete retentions of gloss and other mechanical characteristic like scratch resistances, chromate and lead free, anti-reflectionin in nature, very good adherences on several kinds of material. self-cleaning, painting is related to nano-coating, as shown in (Fig. 2).

1.3. Self – Cleaning Technology Coating

There is significant improvement in previous few years, in self-cleaning technology coating .Owing to wider applicability from textiles and glass windows to cement, labour –saving device may become significant by self-cleaning coating. Potential of self-cleaning technology are many and self-cleaning technology has really global market . Few of these potentials are being achieved :amongst them are self-cleaning paint which, in Europe, is widely available [24].Many national glazing companies are offering products : self-cleaning windows . In terms of maintenance, environment and the cost, which are interrelated to each other, the ability of a surface to cleanse itself is nodal point of cynosure. There`are various costs involved among them are related cost with cleansing solvents, in scrubbing roofs, a time cost, along with a replacement cost involved from use of solvent .When all these costs are eliminated, whole society gets benefitted by elimination of dissolvent vapor in the environments, while also, from the surface, the harmful effects of bacterias are eliminated .

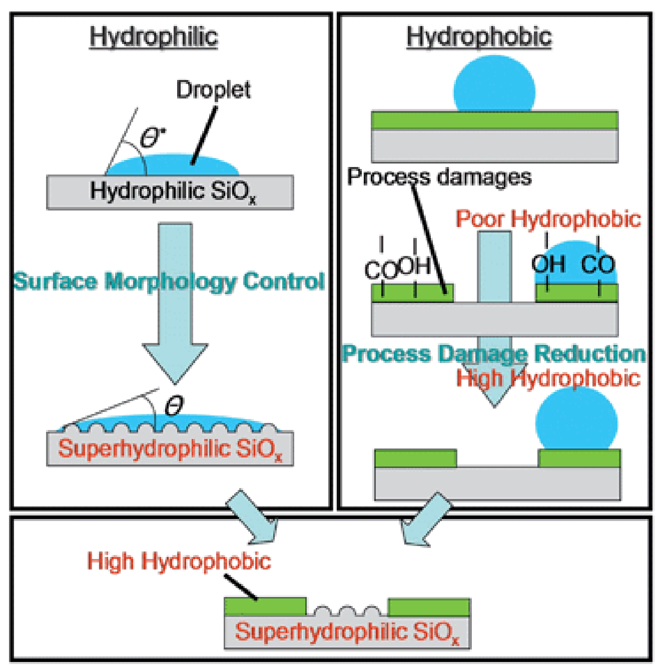

Fig. 3. Various categories of self-cleaning surface [26]

Wettability and water repellence are the main properties of solid surfaces .both are directly dependent on roughness of surface and surface energy . However, surface energy, is inherent property of material used, so that wettability of surface is very difficult in controlling when surface is having exposure to Ultra-Violet light over longer time span [26]. Classification of self-cleaning coating field may be done in two categories: hydrophilic and hydrophobic as shown in (Fig. 5) .These hydrophobic and hydrophilic type of coatings cleanse themselves by the water work , firstly through rolling droplets formulations and latter by the sheeting water, by which, dirt is carried away .There is an additional characteristic of Hydrophilic coatings, which is this, that this coating can break down chemically adsorbed dirt in Ultra-Violet light or sun light [26]. There is existence of. surfaces and interfacial tension when there is one or more condensed phase measured in energy of a unit area. In the Surface tensions, there occurs only one condensed phase, but in interfacial tension, there is occurrence of two short phases in mutual contact .At interchanges of three phases, normally solid phase, liquid phase and vapour phase, Contact angle is one of few quantities, measurable in surface science. Contact angle is defined as a measure of competing tendency of drops to spread, in order to entirely do coverage of solid surfaces or to round up in order to reduce its self area. Wetting gradient of liquid droplets on solid, is computed by the contact angle . Contact angle also imposes the boundary conditions for computing shapes of meniscuses from Young-Laplace equation . Angle of Contact may be utilized for computation of surface tensions of liquid drop and solid surfaces [27]. For drops, which are small, hydrostatic effects are assumed to be negligible where contact angle is determined from measured height, h, and radius of contact [28] .

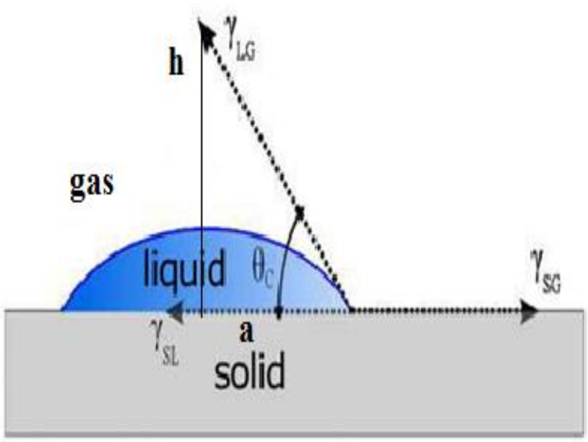

Fig. 4. On a flat substrate, Contact angle between solid-liquid-gas phase of a liquid drop [29].

$$Tan\ (\theta c\ /2) = h/a \qquad (1)$$

Thomas Young was first to study Contact angle of water droplet . He modelled the static angle of contact . In general, Young’s equation is total of force vector on equilibrium and may be used to evaluate surface tensions of solid substrates having been given three known liquid surface tension,coupled with three angles of contact [30] .

$$\gamma sg = \gamma sl + \gamma lg\ cos(\theta c\ ) \qquad (2)$$

1.4. Impact of Surface Roughness Wenzel Equation

In addition to chemical composition, governing the wettability of solid surface, geometrical micro/nanostructure of the surface, also governs wettability of surface of solid as per observation in (Fig. 5) [31] .

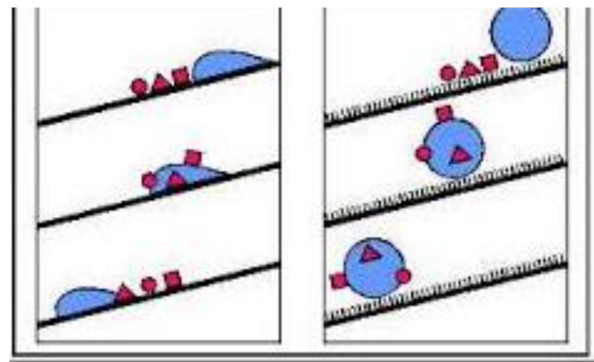

Fig. 5. Rolling droplet of water on a roughened hydrophobic surface versus sliding water droplet on an ordinary Hydrophobic surface [31]

In contact angle science, surface roughness has a significant role, when water droplets put on micron strong hydrophilic surface due to water passing into the grooves, therefore there is decrease in angle of contact .The impact, however, is having a negative impact on a hydrophobic surface where Guo *et. al.* explaining a relationship between roughness of surface and angle of contact, where more roughness of surface of hydrophobic paint, increases the angle of contact .This may be attributed to increase in surface energies by roughening, doing a maximum energy polymorphism between droplet of water and surface, causing droplets to recede, thereby formation of larger angles of contact [32] .. Surfaces which are heterogeneous and rough at scales over molecular sizes,while within scale where optical technique can well be used, roughness of surface is explainable by Wenzel equation [33].

$$cos\theta\ app = R\ rough\ cos\theta \qquad (3)$$

Where θ app is the obvious angle of contact as observed or as seen by optical microscope or eye,and R rough is ratio of effective surface area to expected surface area and is always greater than or equal to unity .This equation therefore explains that for $\theta < 90^{\circ}$, roughness of surface reduces the obvious angle of contact but for $\theta > 90^{\circ}$ roughness of surface increases obvious angle of contact . Majority of solid surfaces are not uniform chemically, where the obvious angle of contact is dependent on binary chemical types within the surface or on the surface. Cassie [34] assumed bi-components surface, which is smooth , where two distinct areas with angles of contact θ1 and θ2 taking surface rates f1 and f2, giving rate of obvious angle of contact as [34]:

$$\cos\theta\ app = f1 \cos\theta 1 + f2 \cos\theta 2 \quad (4)$$

2. Experimental Method:

2.1. Pint Applications

There are various method for improvement of self-cleansing property of nano-crystallines film . Few strategy for improving the coating may involve increase in surface areas of films by addition of nanoparticle such as Titanium Dioxide nanoparticles having a significant impact both on cost and quality[35] .
Furthermore, increase in the number of generated electron–hole pair increases the lifetime of the pair in material by reduction in rate of recombination or creation of coatings which are activated by low energy light,
thus high proportion of solar spectrum is utilized[36] .

2.2 Incorporation of a Mixture of the two Phases of Nanoparticles into the Local Paint

Titanium Dioxide nanoparticles having binary phases (anatase and rutile) and having various concentration was mixed under the magnetic stirring at 50˚C till two hours nearly, till homogenous mixtures having pH within ranges of (6-7) was attained .Thereafter,polyethylene glycol was added as dispersing agent [37] with molecular mass of 6000, and mass which is four time of mixtures of nano Titanium Dioxide catalysts. Ultimately,using magnetic stirrer this suspension was mixed till 15 minutes at 60˚C. Final mixture of nano–TiO2 having two phase and Polyethylene glycol was added in local paint which is based on water and mixed till two hour by use of electrical mixer for modification of properties of local paints..Variation in quantity of Titanium Dioxide was done as 1%, 1.5% and 2% from weight of the paint . Table 2 exhibits compositions of nano-Titanium Dioxide and ratio of anatase phase and rutile phases of Titanium Dioxide nanoparticles.

Table 2. Respective anatase/rutile phases ratio and the concentrations ratio of TiO2 nanoparticles.

Sample Number	Percentage of TiO2 (wt %)	Anatase : Rutile ratio
1	1.0	10:90
2	1.0	50:50
3	1.0	90:10
4	1.5	10:90
5	1.5	50:50
6	1.5	90:10
7	2.0	10:90
8	2.0	50:50
9	2.0	90:10

3. Results and Discussion:

3.1. Morphological Properties of TiO2 Nanoparticles

It is indicating that sizes of anatase nanoparticles ranges between 3-30 nanometer having almost uniform spherical shapes, which is in complete agreement to result reported [38]. Size homogeneity and the shape of Titanium Dioxide nanoparticles would impact characteristic of local paints when addition takes place..The anatase phase nanoparticles can be used in paints owing to photocatalysis property of Titanium Dioxide which leads to self-cleansing surface and material. However, it has been witnessed that sometimes, particles aggregation occurs in both the phases .For preventing this,Polyethylene glycol is added in mixture of two phases as dispersing material .

3.2. Contrast properties and Washability of TiO2 Nanoparticles

Main purpose of testing the local paints after adding the synthesized Titanium Dioxide nanoparticles, has purpose of the washability tests which is the one of significant measurement extensively used in the paint applications for testing resistances offered by several material to abrasion, scrubbing and washing . In addition to this , the local paint prior to and post- adding the mixture of Titanium Dioxide nanoparticles in the anatase phase and the rutile phase including Polyethylene glycol as the dispersing materials. All these result shows that coated film stands 3000 blow brush in the washability instruments with the mixture of nanoparticles, It may be worthnoting that Standard having number 985 for same local paints has 500 blow brushes. Film with added mixture of nanoparticles has increased washability at the rate of 2500 blow brush .In other words,in contrast measurement, Opacity reflectometer instrument, is used for measuring opacity or the luminous reflectances of the gray scale samples. This is appropriate for growth of coatings hiding power .Investigation of contrast result was done for local paint sample mixed withTitanium Dioxide nanoparticles and Polyethylene glycol by installation of a Morris plate for the hiding power horizontally,coating samples to uniform thickness of 50 microns, leaving it settling till 2 hours and again coating by same amount by movement of brush perpendicularly to first direction of movement. After keeping samples to dry horizontally till 24 hours,calculation of the luminous reflectance is done for black and the white part for Morris plate to hiding power,by making use of reflectance device when receiving angle is zero and angle of incidence is 45 degree. Result for contrast tests for sample are in domain of 0.97-0.99. It may be noted that for Standard having number 985 for same local paints, as say contrasts for white color is 0.90. The result demonstrate explicit enhancements of the local paints contrast property after addition of mixture of Titanium Dioxide nanoparticle [2] .

3.3. Hydrophobic & Hydrophilic Surfaces (contact angle) properties of Titanium Dioxide

There has been a significant quantum of work for development of coatings,which are resistant to contamination .

Their potential is enormous as a commercial product and market is truly global. Owing to their extensive range of probable applications,from cement to textiles and window glass, self-cleansing coating may be a significant labour saving devices. Classification of Self-cleansing coating can be done in two types: super- hydrophobic; super - hydrophilic.Through the work of water, both are clean themselves .Hydrophobic coatings cleanse themselves by water droplets, which are rolling and that carries away any dirt, while hydrophilic coatings cleanse themselves by the sheeting water for removal of the dirt from the surfaces .Still, Hydrophilic coating has ability for chemically break down of the absorbed organics in sunlight or Ultraviolet [39] .The surface is hydrophobic, when angles of contact is greater than 90˚ and surfaces are hydrophilic,when angles of contact is lesser than 90˚, In present work, with TiO2 nanoparticles, and UV irradiation, there is conversion of the surface angle of contact from the hydrophobic to hydrophilic .This is very significant for removal of contaminants and organics There was an enhancement in angles of contact up to 104±2, which results in hydrophobicity .Owing to lower surface energies, hydrophobicity depend to a large extent on both the chemical composition and the surface roughness which can reduce the surface energy considerably[40]. For self-cleaning, the hydrophilic surface is excellent ..

3.4. Antibacterial activity of Photocatalytic TiO2 NP's

The antimicrobial effect reaction was firstlydiscovered [41]. Efficacy of photocatalysis oxidations under irradiation by Ultra-violet irradiations against several microorganism of Gram-positive bacterias , yeast , the Gram- negative bacterias and the green algae were investigated by them.. From there onwards, a series of investigation on photocatalysis disinfections have been thoroughly carried out on a wider ranges of microorganism such as viruses,fungis and several species of the bacteria [42,43, 44] . Irradiation of Titanium Dioxide by Ultraviolet light activate valence band electrons to get transferred in conduction band thereby leaving a hole, which is positively charged charge carriers,which are activated, react with water molecules and the atmospheric oxygen to generate the reactive oxygen species .The biocidal actions of Titanium Dioxide photocatalyst is often attributed to OH• radical and the other reacting oxygen species [45,46] which is positively driving force for antibacterial activity of Titanium Dioxide [47,48]. Particularly, there are few studies,which proves that membrane of cell is basic site to get attack by the reacting photogenerated species of O2, which leads towards lipid per-oxidation [48,49]. Combining more oxidative attack of intracellular component and damage of cell membrane caused death of cell . It has been proposed by other studies that photo oxidation of the co-enzyme A (A coenzyme, which is extracted from the pantothenic acid, (Very significant in the respirations and many biochemical reaction) would lead to inhibition of the respirations of the cell and ultimately death of cells [48] . Normally,disinfection by TiO2 is 3 time higher than the Cl and (3/2) times higher than O3[50] .

Thin layer of Titanium Dioxide with higher photocatalysis activity and antibacterial property, have been prepared for using as self cleansing transparent coating for windows in outdoor application .TiO2 nanoparticles were prepared by sol-gel method by use of TiCl4 as precursor .It has been prepared thin layers of Titanium Dioxide with high photocatalysis activity and antibacterial properties for using as self- cleansing transparent coating for windows in outdoor application. In this study Titanium dioxide nanoparticles were prepared by sol-gel method using TitaniumT etrachloride as precursor,and calcinated at various calcination temperature (400, 600, 800, and 1000)

0C [51]. Synthesized nanoparticle was characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Atomic Force Microscopy (AFM), Ultraviolet spectroscopy .Study of Self-cleaning properties was carried out by two significant tests; hydrophilicity by measurement of the Water Contact Angle and photocatalysis activity, by use of KMnO4 as model organic pollutants .Secondly, by spin coating, coating of thin films of Titanium Dioxide nanoparticle was deposited. Assessment of antimicrobial activities of Titanium Dioxide nanoparticle was done against two types of bacterias[52]. Different phases of crystalline TiO2 have different band gap, rutile Titanium Dioxide, having 3 electron Volts and anatase phase of Titanium Dioxide having 3.2 electronVolts, actually determine photocatalytic performances of Titanium Dioxide . This is explaining few application and the theoretical concept of nanostructures of Titanium Dioxide nanoparticle .This also demonstrates optical,electrical and the morphological property making Titanium Dioxide an ideal choice for application pertaining to environment [53] .

4. Conclusion and future direction of research

Although plenty of research has been carried out worldwide regarding application of TiO2 nanoparticles, Yet, more is to be done .Photocatalytic activity of TiO2 nanoparticles,could be exploited fully for production of prospective fuel H2 gas. For doing this,initially TiO2 miniplants should be set up at the banks of rivers . In India, there are many rivers containing substantial quantity of water. Depending upon the successful outcome of these miniplants, major plants should be established to overcome problem of fuel crisis. Because masses are incurring a lot of expenditure on petrols and diesels to ply automobiles . Use of petrol and diesel in automobiles, is increasing pollution in environment, considerably .Which is eventually causing health problems to masses .This is need of hour, that H2 gas, which is very lighter gas, must be used as fuel.

This would greatly reduce environmental pollution .This H2 gas may be obtained by photocatalytic decomposition of water by TiO2 nanoparticles . In addition to this,fuel H2 gas is very much cheaper therby impacting the economy little. Not only in India, use of H2 gas as a fuel would impact global economy also . A lot of expenditure,which is being incurred on use of other fuels,would also be significantly reduced .

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