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# A review on different method of preparation of $TiO_2$ nanoparticles

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## ABSTRACT

Titanium dioxide ($TiO_2$) is a material with excellent merits in solar energy transferring and photo catalysis of passion compounds in environment. $TiO_2$ used as a pigment in paints, cosmetics etc. $TiO_2$ nanoparticles are much effective as a photo catalyst than in bulk powder. With this view an exhaustive literature review was carried out for preparation $TiO_2$ nanoparticles by different methods and its applications. The various methods of preparation of nanoparticles include sol-gel, hydrothermal, precipitation, microemulsion, biological methods etc. $TiO_2$ nanoparticles; then scale up studies may be carried out for feasible production of $TiO_2$ nanoparticles for various purposes. In most of the research work reported the liquid titanium is used as a precursor for $TiO_2$ nanoparticles in sol-gel method. It may be economical.

**KEYWORDS:** Titanium dioxide ($TiO_2$), Nanoparticles, Sol-gel method, Microemulsion.

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## INTRODUCTION

Nanoparticles are of a great scientific interest because they are a bridge between bulk materials and molecular structure. Bulk materials have constant physical properties regardless of its size; the properties of materials change as their size approaches the nano-scale. The percentage of atoms at the surface of a material becomes significant. Nanoparticles have a very high surface to volume ratio. Due to these changes of properties the nanoparticles are used for various applications.

### *Need of $TiO_2$ nanoparticles*

- As the size of the $TiO_2$ particles decreases, the fraction of the atoms located at the surface increases with higher surface area to volume ratios, which can further enhance the catalytic activity.
- The increase in the band gap energy with decreasing the nanoparticles size can potentially enhance the redox potential of the valence band holes and the conduction band electrons, allowing photo redox reactions, which might not otherwise proceed in bulk materials, to occur readily.
- By a decrease in particle size below a certain limit, surface recombination process become dominant. Since most of the electrons and holes were generated close to the surface and surface recombination was faster than interfacial charge carrier transfer process.

### 1.4. *Importance of present study*

Titanium dioxide ($TiO_2$) is a material with excellent merits in solar energy transferring and photo catalysis of poison compounds in environment. $TiO_2$ used as a pigment in paints, cosmetics etc. It is used for beam splitters, optical coating and anti reflection coating because of its high dielectric constant and refractive index. It is also used in humidity sensor and high temp. oxygen sensor. The properties of $TiO_2$ nanoparticles materials are a function of the crystal structure nanoparticle size and morphology and it is also strongly dependent of method of preparation. When the diameter of the crystals of semiconductor particles falls below a critical radius about 10 nm, each charge carrier appears to be having quantum mechanically as simple particles in a box.

As a result of this confinement the band gap increases band edge shift to larger redox potentials. However the solvent reorganization free energy for charge transfer to a substrate remains unchanged because of the increased driving force and the unchanged solvent reorganization free energy the rate constant of charge transfer in the normal Marcus region increases using size quantized semiconductors particles increases the photo efficiency of system in which the the rate limiting step is charge transfer.

***Mill and Le Hunt*: -** Because the absorption edge blue shifts with decreasing particle size the redox potential of the photo generated electrons and holes in quantized semiconductor particle increased. In other words, quantized particle shows higher photo activity than microcrystalline semiconductor.

Recently $TiO_2$ has been prepared in the form of powder, crystals, thin films, nanotubes & nanorods. Phase processing is one of the most convenient and commonly used methods in chemical synthesis. This method provides the advantages of controlling the stoichiometry, homogeneous product and allowing the formation of complex shapes and preparation of composite materials. However same disadvantages exist including expensive precursors, long processing times and present of carbon as an impurity.

Dowsson et al subjected mixed phase $TiO_2$ powders with different compositions and particle sizes to hydrothermal reaction with NaOH. The anatase phase component of the starting material was easily converted to trititanate nanotubes at 140°C. The rutle phase reacted to form trititanate plates & belts at 170 °C. If the reaction time was increased to 7 day then all of the rutile phase converted in to trititanate and morphology of resulting products was exclusively nanoplates and belts with nanotubes.

## *$Tio_2$ chemical structure:-*

TiO2 belongs to the transition metal oxides family. There are four polymorphs of $TiO_2$.

1. Anatase (tetragonal)
2. Rutile (tetragonal)
3. Brookite (orthorhombic)
4. $TiO_2$ (B) (monoclinic)

**Table 1 Crystal structure data**

| **Properties** | **Rutile** | **Anatase** | **Brookite** |
|---|---|---|---|
| Crystal structure | Tetragonal | Tetragonal | Orthorhombic |
| Lattice constant ( ) | a = 4.5936<br>c = 2.9587 | a = 3.784<br>c = 9.515 | a = 9.185<br>b = 5.447<br>c = 5.154 |
| Space Group | $Pu_2/mnm$ | $I4_1/amd$ | Pbca |
| Molecule (cell) | 2 | 2 | 4 |
| Volume / molecule ( ) | 31.2160 | 34.061 | 32.172 |
| Density (g cm3) | 4.13 | 3.79 | 3.99 |
| Ti-O bond length ( ) | 1.949(4)<br>1.980(2) | 1.937(4)<br>1.965(2) | 1.87-2.04 |

## PREPARATION

$TiO_2$ exists in three phases.

i. Anatase
ii. Brookite
iii. Rutile

Rutile is the stable phase as a bulk material generally preparation methods for $TiO_2$ favour the anatase structure.

These observations are attributed to two main effects.

1. Surface energy of particles
2. Precursor chemistry

Very small particle dimensions surface energy is an important part of the total energy and it has been found that the surface energy of anatase is lower than these of rutile and brookite phases. The surface energy of nanoparticles describes the observation of a crossover size of about 30 nm where anatase nanoparticles transform in rutile phase.

The crystal structure stability of nanoparticles has been explained on the basis of a molecular picture. Where the nucleation and growth of the different polymorphs of $TiO_2$ are determined by the precursor chemistry which is depends on the reactant used in method of synthesis of naoparticles.
Phase pure anatase nanoparticles with diameter ranging from 6-30 nm are generally prepared from titanium (IV) isopropoxide and acetic acid. When we use stronger acids than the fraction of product usually consists of brookite nanoparticles. Larger anatase particles are difficult to synthesis due to transformation to rutile upon increasing treatment times and for temperature.

Phase pure brookite particles (0.3-1µm) have been prepared by using amorphous titania as a starting material and hydrothermal treatment with NaOH the preparation of brookite nanoparticles of dia 5-10 nm has been reported by thermolysis of $TiCl_4$ in aqueous HCL solution. The composition of the reaction product was found to be dependent on the Ti:Cl concentration at Ti:Cl = 17-35. Different types of methods are used for synthesis of $TiO_2$ nanoparticles like sol gel, hydrothermal, microemulsion,gas phase detonation method, hydrolysis method, thermolysis, vapour condensation, self templating methods.

**SOL- GEL METHOD –** This method based on inorganic polymerization reaction. In sol-gel method 4 steps are takes place.

1. Hydrolysis of precursors.
2. Condensation. (gel formation )
3. Drying.

4. Thermal decomposition.

In hydrolysis step precursors dissolved in water or alcohol. Acid or base also also helps in the hydrolysis of the precursor.

In condensation steps it form a gel and the solvent is removed this step. After condensation step calcinations take place, in this step higher temperature decompose the organic precursors. The size of nanoparticles can be control by the controlling the solution composition, pH and temperature. Mesoporous nanoparticles synthesized by this method. These nanoparticles can be used as a ceramic membrane top layer absorbent and catalyst support. The advantages of sol-gel process are ambient temperature used for sol preparation and gel processing. Product homogeneity, low temperature sintering, ease of making multi component and good control over size and shape as well as size distribution.

In 2002 Sugimato et.al have reported the preparation of $TiO_2$ nanoparticles via sol- gel method (shape control). In this paper Triethanalamine (TEOA) act as a shape controller of anatase $TiO_2$ nanoparticles the shape of particles are ellipsoidal and the pH is about 11.

Hussain et al reported that the sol-gel process in vortex reactor. In this paper size of nanoparticles was about 10- 20 nm and little porosity & good crystalline anatase with rutile phase was found. In this process large amount of nanoparticles are prepared.

Behajady et al reported that methanol used as a solvent and titanium IV isopropoxide used as a precursor and calcinations temperature was 450 oC.

Heller et al reported that titanium isopropoxide is hydrolyzed and it is coated on a glass base , which is previously treated with $H_2SO_4$ to produce a sodium depleted layer and than calcined at $500^oC$ for 20 min. The thickness of such film not wears when scribed with pencil of hardness or softer and cannot remove by using scotch tape or rubbing with paper. The diameter of nanoparticles were about 3-6 nm.

Chau et al reported well dispersed surface modified nanoparticles by this method and incorporated then in to epoxy matrix to form hybrid nanocomposites with high refractive index than pure epoxy system.

Loryuenyong et al used titanium isopropoxide as a precursor and ethanol isopropanol as a solvent. The anatase and rutile phase was found at 300 and 700 $^oC$ respectively.

Sol-gel method is a very good method for the synthesis of the doped nanomaterials with very high surface area to volume ratio. The photocatalytic activity is improved by varying the metals which was used for doping like $Cu^{2+}$, $Ca^{2+}$, $Sr^{2+}$ , $Ba^{2+}$ etc.

Wang et al prepared nitrogen doped $TiO_2$ nanoparticle by to step hydrolysis calcinations method.

Moon et al synthesized boron doped $TiO_2$ nanoparticles by this method which enhanced the photocatalytic activity for splitting of water.

Last decade many researches have been carried out to produce nanotube using this method.

Venkataraman et al reported that use of ionic liquid $Ti(t\text{-}OBu)_4$ as a solvent in a surface. Sol-gel process to form $TiO_2$ coated cellulose fibers anatase nanoparticles were produce.

Gu et al prepared fabricated nanotubes /hallow sphere hybrid structured functional anatase $TiO_2$ by sol-gel using commercial filter paper as nanotubes template and silica / poly styrene colloidal microsphere and cellulose templates were removed by calcinations / alkali treatment.

## MICRO EMULSION TECHNIQUE

This technique is thermodynamically stable. Optically isotropic solution of two immiscible liquid consisting of micro domains of one or both liquids are stabilized by an interfacial film of surfactant. This method is use for the production of nanoparticles and the production of nanoparticles can be control by the reactant distribution in the droplets and by the dynamics of inter droplet exchange of reactants. A cage like structure provides by the surfactant stabilized micro cavities. Because of this effect, it controlled the particles nucleation growth and agglomeration. In this process two forms were occurs O/W (oil in water) and W/O (water in oil) which is in aqueous and non aqueous in mediums respectively.

Emulsion depends upon the particle size, particle- particle interaction, particle water interaction. The size of the particles are depends upon the ratio of surfactant to water this is the major advantage of micro emulsion process. The particle size is same as that of the water droplet in the reverse micro emulsion.

Deorsola et al reported that water in oil microemulsion is used to produce ultra fine nanoparticles.

Chahabra et al reported that ultrafine $TiO_2$ nanoparticles were produced by using water in oil microemulsion as a micro reactor to precipitate the precursor hydroxide of titanium IV and then it calcined at different temperature. They found that if the calcined temperature decreases the surface area of particles decreases and therefore particle size increases and when the particle size decreases, the attenuation of ultra violet radiation increases. They found only anatase $TiO_2$ nanoparticles which is act as photocatalyst for photo degradation of phenol.

Wu et al reported that both anatase and rutile phase nanoparticles were produced by hydrothermal treatment of micro emulsion at 120 $^{o}$C.

Geo et al reported that in water in oil micro emulsion, the diameter of nanoparticles controlled by the separation of the nucleation stage from the crystal growth stage. They used micro emulsion system as a reactors to control the crystal growth of particles of similar size.

Zubieta et al reported that $TiO_2$ nanoparticles were prepared by an aerosol OT /hexane/ water reverse micro emulsion system to degradation of methylene blue dye. The crystalline composition, size of particles and porosity were depends on the water content in the reverse micells.

Cong et al prepared nitrogen doped $TiO_2$ nanoparticles by this method under nitric or hydrochloric acid environment. In the paper, no high temperature was required for calcinations and thus prevents the agglomeration and sintering of the $TiO_2$ particles. Cong et al found that the particles were produced by this method is useful for decomposition of rhodamine B.

Adan et al synthesized an iron doped nanoparticles. In this paer anatse phase were prepared and this particles has good quality as a photocatalyst for photodegradation of phenol.

According to Zori et al $TiO_2$ nanoparticles prepared by hydrolysis of titanium tetraisopropoxide (TTIP) in water in oil microemulsion and than calcined at 350 $^{o}C$ the particles phase were anatase which is highly photoactive.

## PRECIPITATION METHOD

The precipitation form from a homogeneous liquid phase is because of physical change in temperature, pH, solvent of evaporation, reactant concentration etc. Chemical process can also be participating for precipitation (addition of bases or acids use of complex forming agents). Two processes occur in precipitation. 1. Nucleation 2. Growth and agglomeration of particles

In nucleation process, smallest elementary particles of the new phase were formed that particles are stable under the precipitation conditions.

### *Growth or agglomeration of the particles*

The controlling of release anions & cations can be adjust the kinetics of nucleation and particles growth because of this we find the monodisperse nanoparticles. The composition of precipitate depends on the differences in solubility between component and reaction. Slow precipitation form small particles in size and fast precipitation form large particles in size.

According to Namin et al,, $TiO_2$ nanoparticles by the reaction between aqueous $TiCl_4$ solutions with ammonium hydroxide. Ammonium hydroxide uses a precipitation agent. Then after freshly prepared $TiO_2$ gel was allowed to crystallize under refluxing and stirring condition for 6 hr over $90^{\circ}C$ and oven dried high in temperature above $100^{\circ}C$.

Shchipunov et al reported that ethylene glycol used as a reaction medium. Bit dissolved with polysaccharide xanthan because of this reaction formed $TiO_2$ nanoparticles on the carbohydrate macromolecules like the biomineralization in living organism are formed. In this synthesis polysaccharide served as a template.

To manipulate the metal oxide morphology to fibriller and plate like structures by varying the concentration of xanthan and water and also the synthesizing conditions. After reaction prepared $TiO_2$ calcined at temperature between 300°C and 900 °C. Crystalline anatase and rutile were found at 300°C and 700°C.

According to Sato et al. Nitrogen ion doped $TiO_2$ nanopaticles prepared by the homogenous precipitation in hexamethylenetetramine titanium trichloride mixed solution followed by heat treatment in the solution at desired temperatures.

According to the Kostedt et al., ZnO doped $TiO_2$ nanoparticles prepared by precipitation of zinc nitrate and titanium tetrachloride as precursors. The pH 8.5 was adjusted by slowly adding and ammonium hydroxide solution and continuing stir for 2 hr., white $Zn(OH)_2/Ti(OH)_4$ were formed.
Wang et al reported $Al_2O_3$ doped $TiO_2$ nanoparticles with high specific surface area and large pore diameter with the help of using ultrasound assisted precipitation. Because of ultrasound effect it produces the strong chemical & mechanical effects which were enhance the growth of nanoparticles. In his paper, using ethanol instead of water which support could hinder the particles growth and then increased the specific surface area and pore diameter.

## HYDROTHERMAL METHOD

Synthesis of crystal or crystal growth under high temperature & high pressure water conditions from substances which are insoluble in ordinary temperature and pressure (<100°C & 1 atm.) are prepared by hydrothermal method. The critical temperature and pressure of water are 374°C & 22.1 mpa respectively. Hydrothermal synthesis of $TiO_2$ nanoparticles are influence of various parameter like temperature , experimental duration , pressure, solvent type, pH and the starting charge on the resultant product. The synthesis of $TiO_2$ is usually carried out in small autoclaves of the morey type, provided with Teflon liners. The condition selected for the synthesis of $TiO_2$ nanoparticles are $T \leq 200°C$, $P < 100$ bars. The use of Teflon liners helps to obtained pure and homogenous $TiO_2$ particles. Solutions of NaOH, KOH, HCl, $HNO_3$ , HCOOH and $H_2SO_4$ are treated as mineralisers and it is found that $HNO_3$ is a better mineraliser for obtaining mono – dispersed nanoparticles of $TiO_2$ with homogeneous composition under the present experimental conditions.

According to Qian et al,$TiO_2$ nanoparticles prepared by this method. In this paper two steps were done. In first step oxidation of titanium with an aqueous solution of $H_2O_2$ and ammonia to form a gel and in second step hydrothermal treatment of gel under various conditions.

Kim et al reported that the reaction between Degussa P-25 powder and 10 M NaOH at 150$^{o}$C temperature and reaction time of 48 h. resulting product did not contain any remaining Degussa P-25 nanoparticles and the morphology of nanotubes is very smooth without the presence of any bundle like structure.

Xan et al prepared rutile $TiO_2$ nanotubes without using molds or templates for replication. In this paper facial ethanol induced hydrothermal method were used. In this method the phase transformation from anatase to rutile was promoted through the chelating role of ethanol to the water ethanol ratio and the type of alcohol have important influence on the shape and phase structure of the products.

According to Xu et al, H- titanate nanotube prepared by dispersed in an acid medium during hydrothermal process. The sizes of nanotubes were about 3nm and shape was rhombic. Anatase nanorods found at 1pH value but if anatase phase nanotubes turn in to the rutile phase the pH value should be less than or equal to 0.5.

Zhao et al synthesized $TiO_2$ nanoparticles by this method using cetyltrimethyl ammonium bromide as a template.

According to Wang et al, $TiO_2$ nanoparticles was synthesized by this method for photo degradation of methyl orange.

Pavasupree et al reported that anatase $TiO_2$ nanoparticles prepared by this method and this nanoparticles used for oxidation reaction for I to $I_2$ in excess of I conditions.

Wu et al prepared uniform size anatase $TiO_2$ nanoparticles. The shape of nanoparticles was spherical. In this paper alkaline hydrothermal treatment of metallic Ti and hydrogen peroxide and their subsequent proton exchange followed by calcinations in air. This nanoparticles use for photodegradation of rhodamine B in water.

Troung et al synthesized crystalline structure nanoparticles by this method. Anatase, rutile, brookite were easily obtained by controlling the pH of the solution. In this paper using novel titanium oxalate complex so that because of oxalic acid flower like rutile phase obtained.

Thapa et al synthesized 12 nm size nanoparticles. The indirect and direct band gap of these nanoparticles was about 3.09eV and 3.75 eV respectively. This nanoparticle is useful for photo degradation of methyl orange and rhodium B.

## BIOLOGICAL METHOD

In this method we learn about interaction between inorganic nanoparticles and biological structures. In this method many organism can produce inorganic materials. This method is very eco friendly for the synthesis of nanoparticles. Bacteria- derived poly dispersed nanoparticles are affected by cell growth of the bacteria, composition of the incubation solution and growth conditions of the minerals but properly controlling the synthesis parameter (concentration, pH, temperature etc). Jha et al synthesized $TiO_2$ nanoparticles by *lactobacillus sp*. The average particle size were 30 nm and and shape was hollow sphere. Different types of bacteria like *spirillum* , *vibirio* , *bacillus* , *square bacteria* , *fusiferm* bacteria, star shape bacteria can lead to hollow nanorods, nanocables , nanohelixes , twinspheres , chain sphere etc.

Kirthi et al reported that $TiO_2$ nanoparticles prepared by using bacterium *bacillus subtilis*. Pure forms of nanoparticles were produce by abundantly available micro-organism. The sizes of nanoparticles were 66-77 nm and shape was spherical. In this paper bacterium, fungi and yeasts are also capable for producing nanoparticles.

According to Bnsal et al $TiO_2$ nanoparticles prepared from aqueous anionic complex $TiF_{62}$ by using *fusarium oxysporum*. This facial hydrolysis done at room temperature.

According to Sundrarayan et al, spherical $TiO_2$ nanoparticles prepared by using Nyctanthes leaves extract. Powder of these leaves was mixed with ethanol and extracted under reflux condition at $50^{\circ}C$. This extract reacted with titanium tetraisopropoxide and stir at $50^{o}C$ for 4 h. $TiO_2$ separated with the help of centrifugation and than calcinated at $500^{o}C$. The size of nanoparticles was 100-500 nm.

## CONCLUSION

In this review paper we have described many types of method for the synthesis of $TiO_2$ nanoparticles like sol-gel , microemulsion, precipitation , hydrothermal and biological process. Each method has its own importance like sol-gel method is very easy, low cost method hydrothermal is very simple method and biological method is ecofriendly. A different type of method has different terms and condition, like in sol-gel method ambient temperature, high purity precursor's product homogeneity and low temperature sintering are important. Hydrothermal method provides excellent chemical homogeneity for deriving metastable structures at low temperature. In microemulsion method size and shape of $TiO_2$ nanoparticles is affected by the ratio of surfactant to water . in biological method using toxic chemicals are avoided .

**Table 2: Literature review of different methods and applications**

| Sr. No | Method of preparation | Application | Author 's name and year | Title | Remarks |
|---|---|---|---|---|---|
| 1 | Sol – gel Method (shape control) | Design of smart organic hybrid materials | Sugimato et al.(2002) | Synthesis of uniform anatase $TiO_2$ nanoparticles sol-gel method shape control[1] | Triethanalamine (TEOA) act as a shape controller of anatase $TiO_2$. It produce ellipsoidal particles above pH 11. |
| 2 | Sol gel method. | Removing pollutants from air and water, solar cells | Uekawa et al. (2002) | Low temperature synthesis and characterization of porous anatase $TiO_2$ nanoparticles[2]. | The particle size of anatase nanoparticles increased from 9 to 15 nm with increasing the heating time from 6 to 48 hr. Particle size almost uniform. The nanoparticles had micropores and Surface area was in the range of 254 to 438 $m^2/g$. |
| 3 | Anatase & rutile $TiO_2$ nano particles were prepared by heating the Ti-peroxy ompound diluted with a polyol aqueous solution at 368°K for 24 hr. | Removal of pollutants from air and water, solar cell and photo electrochemical system | Uekawa et al. (2003) | Synthesis of rutile and anatase $TiO_2$ nano particles from Ti-peroxy compound aqueous solution with polyols[3]. | Ethylene glycol, glycerine were used to diluting solution. The sp. Surface area increase with an increasing the polyol concentration of diluting solution. |
| 4 | Facial gas flame combustion method . | Metal oxide semiconductors materials | Zhao et al (2007 | Synthesis and optical properties of $TiO_2$ nanoparticles[4]. | Ultrafine particles. Single anatase crystalline phase is about 9 nm were produced. |
| 5 | Detonation method | Photocatalyst ,solar cell | Xin et al (2008) | Synthesis of $TiO_2$ nanoparticles from sprayed droplets of titanium tetrachloride by gas phase detonation method[5] | It is a cheap synthesis method. High temperature and pressure during detonation and high cooling after the detonation to prevent nano particles from growing to larger size. |
| 6 | Ionic liquid assisted method. | Photo degradation of pollutants in waste water, organic contaminants | Zengh et al. (2009) | Ionic liquid assisted synthesis of large scale $TiO_2$ nanoparticles with controllable phase by pH hydrolysis of $TiCl_4$[6] | Pure rutile and rutile-anatase composite $TiO_2$ nanoparticles successfully synthesized by this method. Diameter of anatase phase are 4-6nm and rutile nanorodes are about 3-6nm in diameter and 20-60 nm in length. |
| 7 | Synthesis of $TiO_2$ nano particles by the oxidation of titanium tetrachloride in high strength propane /air turbulent flame for mass production. | Photocatalysis materials for the purification of polluted water and air | Xie et al. (2009) | Synthesis of $TiO_2$ nanoparticles by propane / air turbulent flame CVD process[7]. | Used for mass production of $TiO_2$ nanoparticles. The mean size 30-80 nm. |
| 8 | Polyol– mediated synthesis technique. | Photocatalytic degradation of acetaldehyde | Tripathy et al. (2009) | Polyol-assisted synthesis of $TiO_2$ nanoparticles in a semi aqueous solvent[8]. | Nanoparticle with crystallite size 20-40 nm prepared in room temperature. |

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| | | | | | Anatase and rutile phases have average BET surface areas of 86 and 71 $m^2g^{-1}$, respectively. |
| 9 | Dissolving TiI4 in DMSO (dimethyle sulfoxide ) and then add 0.1mol NaOH $TiI4+4NaOH \rightarrow TiO_2+H2O+4NaI$ | UV irradiated aqueous degradation of the bis – 4 nitrophenyl phosphate (BNPP) as well as the 4-nitrophenyl phosphate (4-NNP) and 4 nitro phenol (4-NP) | Zumeta.et al. (2010) | Synthesis of $TiO_2$ nanoparticles with narrow size distribution and their evaluation in the photocatalytic oxidative degradation Bis (4-nitrophenyl phosphate )[9] | Average size 2.1 ± 0.3 nm is reported. It is fast ,inexpensive, one pot and one step method. |
| 10 | A new turbulent premixed stagnation swirl flame (SSF) is used to synthesize $TiO_2$ nanoparticles. | Photo catalyst, semiconductors | Wang et al. (2010) | Synthesis of $TiO_2$ nanoparticles by premixed stagnation swirl flames[10]. | High anatase purity with mean diameters of 5-10 nm. |
| 11 | Micro emulsion / heat treated method. | Photo catalyst decomposition of methylene blue | Zori et al. (2011) | Synthesis of $TiO_2$ nanoparticles emulsion/heat treated method and photo degradation of methylene blue[11]. | Spherical shape produced by this method. |
| 12 | Plasma treated carbon nanotubes method | Photo anodes of dye sensitized solar cell | Zhang et al (2011) | Synthesis of $TiO_2$ nanoparticles on plasma treated carbon nanotubes and its application in photoanodes of dye sensitized solar cells[12] | Effective method to improve the disper- sion property of CNTs by introducing oxygen containing groups using the $O_2$ plasma technique. The plasma technique is a useful method to improve the Conversion efficiency of DSSCs is about 75%. |
| 13 | Hydrolysis method. | Aqueous hybrid electrochemical capacitors | Yir et al. (2011) | Polyoxometalate-Assisted Synthesis of $TiO_2$ Nanoparticles and Their Applications in Aqueous Hybrid Electrochemical Capacitors[13] | Polyoxometalate adjusted the hydrolyzation reaction rate and controlled the size of $TiO_2$. Nanoparticle possessed higher energy density than others. |
| 14 | Thermolysis process. | Thin film solar cell. | Bhakat et al. (2012) | Uniform $TiO_2$ nano particles synthesis and characterization by thermolysis process[14] | The size of particles is in the range of 100 to 300 nm spherical in shape and having nanorods like structure on the surface of nanoparticles. Shape,size and structure depend upon the heating time and quantity of titanium tetra chloride in the reaction. |
| 15 | Titanium isopropoxide and benzyl alcohol reacted in to a stainless steel double walled reactor heated at 175°C for 48 hr. | Dye sensitized solar cell. | Zimmermann et al. (2012) | Spontaneous water release inducing nucleation during the non-aqueous synthesis of $TiO_2$ nanoparticles[15] | Reaction to $TiCl_4$ via alkyl halide elimination Cubic shaped anatase nanoparticles are obtained only after an induction period of almost 24 hr. Suddenly pressure increase was found to occur being |

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| | | | | | attributable to the formation of water. |
| 16 | Facial hydrothermal method. | Photocatalytic reduction of $CO_2$ to $CH_3OH$ | Truong et al. (2012) | Synthesis of $TiO_2$ nanoparticles using novel titanium oxalate complex towards visible light-driven photocatalytic reduction of $CO_2$ to $CH_3OH$[16] | $TiO_2$ nanoparticles with controlled crystalline structure and morphology were synthesized by this method. Anatase , rutile and brookite are easily obtained by controlling the pH of the solution.Flower like rutile phase obtained by using oxalic acid. |
| 17 | Simple hydrothermal method. | Degradation of orange II, methyl orange and rhodamine B. | Thapa et al. (2012) | Anatase $TiO_2$ nanoparticles synthesis via simple hydrothermal route: Degradation of Orange II, Methyl Orange and Rhodamine B[17]. | 12 nm size anatase nanoparticles are obtained by this method. Indirect and direct band gap of nanoparticles were measured to be about 3.09 eV & 3.75 eV respectively After UV exposure orange II (20min), methyl orange (25 min), and rhodamine B (155 min) concentration were found to degrade more than 99%, 98%, 99%, respectively. |
| 18 | Polyacrylamide gel method. | Photo degradation of AO7 (acid orange 7) | Xian et al. (2012) | Polyacrylamide gel synthesis and photocatalytic properties of $TiO_2$ nanoparticles[18]. | Uniform shaped like sphere nanoparticles were prepared by this method. Ethanol was used as a hydroxide scavenger to investigate its effect on the photo catalytic efficiency as well as the OH radical yield. |
| 19 | Vapour condensation method. | Photocatalytic activity to killing microorganism, used as a antibacterial substance | Kim et al. (2011) | Antibacterial performance of $TiO_2$ ultrafine nanopowder synthesized by a chemical vapour condensation method: Effect of synthesis temperature and precursor vapour concentration[19] | Specific surface area and crystallinity of CVC- $TiO_2$ were varied depending on synthesis temperature and precursor vapour concentration. CVC- $TiO_2$ show better specific area & crystallinity than P25 $TiO_2$. CVC- $TiO_2$ generated larger amount of hydroxyl radicals than P25 $TiO_2$. |
| 20 | Hydrolysis of $TiCl_4$ method. | Photocatalysis, purification of water, solar cells. | Abbas et al. (2011) | Synthesis, characterization and particle size distribution of $TiO_2$ colloidal nanoparticles[20] | In this process synthesized $TiO_2$ particles were found to be predominantly of anatase and narrow particle size distribution were obtained.Particle size produced about 4-5 nm and free from organic compounds. |
| 21 | Modified polymeric precursor method. | Photocatalyst and solar cells and sensor. | Soares et al. (2011) | Facile synthesis of N-doped $TiO_2$ nano | This simple method is used to produced N-doped $TiO_2$ |

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| | | | | particles by a modified polymeric precursor method and its photocatalytic properties[21]. | nano particles using urea as the N source. N doping confirmed by Raman spectroscopy, UV-VIS and XPS. This method does not alter the shape and agglomeration state of nano particles. |
| 22 | Prepared by a two step modification using both propionic acid and n-hexylamine. | Optical materials, fabrication of inorganic/organic nanocomposites. | Nakayama et al. (2007) | Preparation of $TiO_2$ nanoparticles surface-modified by both carboxylic acid and amine: Dispersibility and stabilization in organic solvents[22]. | It is very economical method which is applicable to distribution of a verity of organic solvent without changing the properties of nanoparticles. |
| 23 | Self templating method. | Biological labelling,sensor technology, microarrays and optical computing. | Zhao et al. (2013) | Facile fabrication of fluorescent $TiO_2$ nanoparticles with core-shell structure by a self-templating method[23] | It is simple one step self templating method to synthesize the fluorescent core shell nanoparticle in in an O/W emulsion system. This method effectively reduced the reaction steps and avoided the pollution risk of template. |
| 24 | Synthesis of $TiO_2$ nanoparticles using *lactobacillus sp.* and using yeast. | Bone tissue engineering and pharmaceutical industries. | Jha et al. (2009) | Synthesis of $TiO_2$ nanoparticles using microorganisms[24] | This method is truly green cost effective approach capable of producing $TiO_2$ nanoparticles. 8-35 nm size nano particles were produced. The synthesis of *n*- $TiO_2$ might have resulted due to pH-sensitive membrane bound oxido-reductases and carbon source dependent in the culture solution. |
| 25 | Hydrothermal method. | Dye sensitized solar cells, Photocatayst. | Pavasupree et al. (2006) | Synthesis, characterization, photocatalytic activity and dye-sensitized solar cell performance of nanorods/ nanoparticles $TiO_2$ with mesoporous structure[25]. | The nanorods had diameter about 10- 20 nm and the lengths of 100 – 200 nm the nanoparticles had diameter is about 5-10 nm. The average pore diameter is about 7-12 nm.The mesoporous structure was produced. |
| 26 | Alkaline hydrolysis of metal salt solution followed by its boiling at 100°C for 6 hr. (wet chemical method) | Photocatalytic activity on removal of dye. | Songara et al. (2009) | Synthesis and studies on photochromic properties of vanadium doped $TiO_2$ nanoparticles[26]. | Pure anatase phase and vanadium doped $TiO_2$ nanoparticles were aproduced by this method. Particle size is about 23 nm. |
| 27 | Biological method employing *bacillus subtilis.* | Photocatalytic activity on controlling the bio film. | Dhandapani et al. (2002) | Bio-mediated synthesis of $TiO_2$ nanoparticles and its photocatalytic effect on aquatic biofilm[27]. | In this method spherical shape with an average particle size of 10 -30 nm were produced.It is green cost effective approach. |
| 28 | Sol – gel process in | Photocatalytic | Hussain et al. | Synthesis, | Novel $TiO_2$ nano particles |

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| | vortex reactor. | degradation of ethylene | (2002) | characterization, and photocatalytic application of novel $TiO_2$ nanoparticles[28]. | having high specific surface area were prepared by this method.This method produced 10 -20 nm sizes, little porosity, good crystalline anatase with rutile phase, confined band gap energy and higher OH group nano particles.Large amount of nanoparticles were prepared. |
| 29 | Two step low temperature hydrothermal method | Photocatalysis and photovoltaics. | Souvereyns et al. (2003) | Hydrothermal synthesis of a concentrated and stable dispersion of $TiO_2$ nanoparticles[29] | In this method, 10 wt % aqueous dispersion with prolong stability $TiO_2$ nanoparticles were prepared. Nanoparticles in dispersion have size < 10 nm and contain 80 % anatase 20 % brookite phases. |
| 30 | Gas phase detonation method. | Photocatalyst. | Ouyang et al. (2007) | Synthesis of $TiO_2$ nanoparticles from Sprayed Droplets of Titanium Tetra- chloride by the Gas-Phase Detonation Method[30]. | In this method titanium tetrachloride is used as a precursor and premixed gas ($O_2$ & $H_2$) used as a source of energy.This method produced 80 % anatase and 20 % rutile phase. It is cheap method. |
| 31 | Sol- gel method. | Photocatalyst. | Behnajady et al. (2008) | Investigation of the effect of sol–gel synthesis variables on structural and photocatalytic properties of $TiO_2$ nanoparticle[31] | Methanol as a solvent and titanium IV isopropoxide as a precursor under 3 hr at 80$^{\circ}$C were used to produced $TiO_2$ nanoparticles.Calcinations temperature was about 450 $^{\circ}$C. |
| 32 | Surfactant free solvothermal route. | Dye sensitized solar cells and gas sensing application. | Rao et al. (2009) | Low-temperature synthesis of $TiO_2$ nanoparticles and preparation of $TiO_2$ thin films by spray deposition[32]. | Titanium isopropoxide used as the precursor and toluene used as a solvent at 180 -240 $^{o}$C. Size of nanoparticles varied from 8 – 15 nm. Mixed phase were produced like anatase and rutile. |
| 33 | Tetraethylorthotit anate (TEOT) dissolved in ethanol by using a semi-batch process. | Photocatalytic activity. | Kim et al. (2009) | Optimal conditions for synthesis of $TiO_2$ nanoparticles in semibatch reactor[33]. | In this work, $TiO_2$ nanoparticles were formed from the hydrolysis and condensation of TEOT in the presence of an *in situ* steric stabilizer (HPC) in a semi-batch reactor. 10 nm size were nanoparticels were produced by this method. |

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