

# Nano Titanium Dioxide -An Effective Photocatalyst for Emerging Applications



Ragavi Priyadharshani Raja, Geetha Kathiresan, R. Ilavarasi

**Abstract:** Titanium dioxide ( $TiO_2$ ) is a widely studied material and exists in three major crystal structures: rutile, brookite and anatase. Due to its advantages in high chemical and thermal stability, non-toxicity, high catalytic activity, resistance to corrosion, and high reactivity under ultraviolet light (<387 nm), it can be used in many applications such as photo catalysis, photovoltaics, sensors, hydrogen generators batteries, self-cleaning, electrochromic devices and also used in some biomedical application for site specific drug delivery. These applications in various fields depends not only on the properties of the  $TiO_2$  material but also it involves in modifying  $TiO_2$  structure and doping of other element on it which will show adverse impact in application of  $TiO_2$  with the surrounding environment. In this review, we are discussing about the synthesis, properties, and applications of titanium dioxide nanoparticle ( $TiO_2$  NP) in various fields.

**Keywords:**  $TiO_2$  Synthesis, Properties, Photocatalyst, Photo Electrochemical detection.

## I. INTRODUCTION

Titanium dioxide ( $TiO_2$ ) is a well-known semiconductor nanomaterial has been proved to be an excellent basic material in many other applications. Nowadays, its application has been considerably increased in the field of nanoscience and nanotechnology, because of its enhanced chemical and physical properties in the nanoscale level. Based on its synthesis and properties, many other reviews and reports have been done. Those researches has been done with the promising chemical and physical properties which includes photoelectric activity, large surface area, high stability[1], adsorption edge energy, efficient separation of the charge carriers, crystallite size[2], high sensitivity, selectivity in the field of photo electrochemistry detection[3], high reactivity under ultraviolet light (<387 nm)[4], biological inert nature and high electronic mobility [5].

Here, in this review we are mainly concentrating in synthesis, properties, modification and applications of titanium dioxide ( $TiO_2$ ) nanomaterials. At nanometre scale, the synthesis of titanium dioxide ( $TiO_2$ ) could be in the form of nanoparticles, Nano rods, nanowires, nanocomposites and nanotubes which are well categorized with the appropriate preparation method and also the synthesis of mesoporous/nanoporous  $TiO_2$ , and photonic materials are

well defined. Those preparatory methods are discussed in this review with proper procedures and prepared respective materials are in a nanoscale, could be properly characterized with some major techniques which are transmission electron microscopy (TEM) or scanning electron microscopy (SEM). The crystallographic structure of  $TiO_2$ , can be identified with the help of X-ray diffraction(XRD) techniques and the X-ray Photoelectron Spectroscopy (XPS) techniques gives the information about chemical compositions and oxidation states of the surface species of the respective materials in the research fields [6]. To reveal the elemental composition on some nanocomposites based researches, Energy-dispersive X-ray spectroscopy EDS was carried out. The major properties of titanium dioxide such as thermal, structural, electronic and optical are discussed in this review. Of which above mentioned properties, titanium dioxide has wide application with its optical properties. As it is transparent in visible light region, it should be doped or sensitized with some other materials for enhancing optical property and activities of  $TiO_2$  nanomaterials, thereby increasing its application as a photocatalyst and sensing, photovoltaics, water splitting, photo-/electrochromic, and hydrogen storage and hydrogen generated batteries. As a promising photo catalyst,  $TiO_2$  nanoparticles playing an important role in toxic molecule detection based researches in the environmental pollution challenges. Also the preparation and the properties of titanium dioxide nanomaterials based researches are discussed in this review. The flow chart for the types of nanomaterials as shown in the Figure.1.

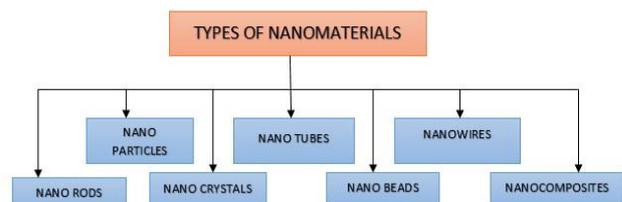


Fig. 1: The flow chart for the types of nanomaterials.

## II. SYNTHESIS METHODS

The synthesis of nanomaterials, nanotubes, nanorods, nano composites by sol-gel method is explained here. In this process, a sol (colloidal substance) is obtained from the hydrolysis and polymerization reaction of the precursors. At the end of polymerization state, conversion of liquid phase to solid gel phase occur. There are numerous method available for synthesizing nanomaterials like emulsion techniques, spray pyrolysis, precipitations, wet chemical synthesis[7,8], and production of thin films based on nanomaterials were produced by spin coating or dip coating.

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Some of those synthesis method are explained here as follows.

### A. Nano Powders

For the synthesis  $\text{TiO}_2$  nanomaterial, Titanium tetra isopropoxide  $[\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4]$ , SigmaAldrich, 97%, iso-propanol  $[(\text{CH}_3)_2\text{CHOH}]$ , Sigma-Aldrich, 99.7% and nitric acid  $[\text{HNO}_3]$  were used. Here, they have added Titanium tetra isopropoxide into the solution containing iso-propanol and deionized water under constant stirring at  $80^\circ\text{C}$  into the round bottom beaker. After 1 h, concentrated  $\text{HNO}_3$  mixed with deionized water was added into the TTIP solution and keep it under constant stirring at  $60^\circ\text{C}$  for 6 h highly viscous sol gel was obtained. These prepared sol gel, undergone annealing process to form a powdered form of  $\text{TiO}_2$  nanocrystalline. Further preparation of  $\text{TiO}_2$  film, the prepared powder was added to the solution of iso-propanol in the ratio of 1:10. The  $\text{TiO}_2$  nanoparticles deposited on titanium substrate using the dip coating method. Further optical studies, The  $\text{TiO}_2$  film were prepared on the two glass substrates. Its crystalline nature is observed by XRD techniques and it was found to be rutile and anatase [9]. The FE SEM image of the  $\text{TiO}_2$  nano powder as shown in the Fig. 2, which reveals that they are spherical in shape and clustered on the glass substrate and Fig. 3 represents the XRD image of  $\text{TiO}_2$  nanoparticles. By dissolving the titanium tetrachloride in the mixture of solutions containing ethanol and acetic acid. Final mixture was kept under autoclave at  $180^\circ\text{C}$ , after this process it was cool down to room temperature. A fine powder of  $\text{TiO}_2$  was obtained after drying the rinsed product for 2h [10].

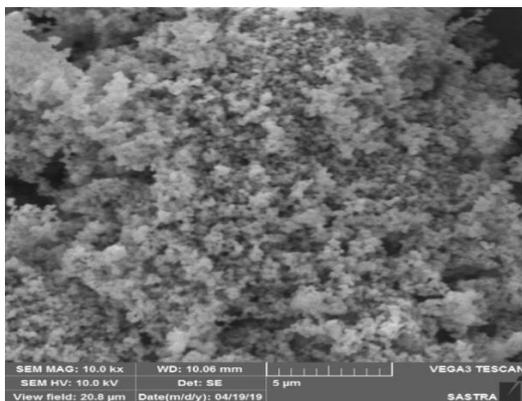


Fig. 2: FE SEM image of  $\text{TiO}_2$  Nanopowders.

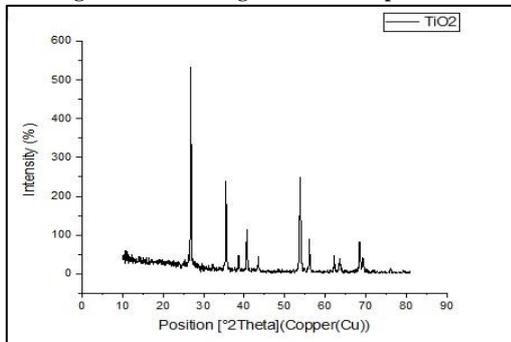


Fig.3: XRD image of  $\text{TiO}_2$  Nanopowders.

### B. Nano Tubes

For the preparation of  $\text{TiO}_2$  nanotubes and nanorods, the preparatory methods were almost same. Titanium isopropoxide (TI) was used as a precursor which was

dissolved in ethanol to synthesize TI solution. This TI solution should be added with the mixture of ethanol, acetylacetone and water to yield  $\text{TiO}_2$  sol with different molar concentrations at room temperature. After that anodic alumina template membrane having pores with the uniform diameter ranging from 200-250 nm, is dipped frequently in to this  $\text{TiO}_2$  sol. After drying this template for 1 day and allowed to heated in air at  $400^\circ\text{C}$ , it could give nanorods and nanotubes in the pores of AA template membrane [11].

### C. Nano Wires

$\text{TiO}_2$  nanowires have been prepared by electrophoretic deposition of  $\text{TiO}_2$  sol in to the pores of an AA membrane template maintaining at  $500^\circ\text{C}$  for 24 h. To isolate  $\text{TiO}_2$  nanowires, AAM template is dissolved in a 5 wt % NaOH solution [12].  $\text{TiO}_2$  nanorod array could be synthesized by dropwise adding the mixture of ethanol and deionized water in to the solution of tetrabutylorthotitanate under magnetic stirring. Finally it was deposited on the ZnO Nano rod and allow it to dry ( $100^\circ\text{C}$  for 10 min) and heated in air ( $550^\circ\text{C}$  for 1 h) to obtain  $\text{TiO}_2$  nanorod array [13].

### D. Other Form Of $\text{TiO}_2$

Potassium titanium oxide oxalate dehydrate (PTO) was used as an precursor element in the synthesis of anatase hierarchically cactus like  $\text{TiO}_2$  array. This element was added to a ultrapure water followed by adding diethylene glycol. This mixture was kept in an autoclave where the cleaned FTO substrate was introduced and the entire setup was maintained at a temperature of  $160^\circ\text{C}$  for 3-12h. At the end of the reaction, FTO substrate was taken out, rinsed well with ultrapure water and dried with ambient air at  $80^\circ\text{C}$ , annealing at  $450^\circ\text{C}$  for 2 hr [14]. Hydrothermal synthesis of nano particles were developed nowadays because it could yield nanocrystals directly as compared to other processes such as sol gel and co precipitation methods because it would need calcination and milling, it could leads agglomeration and degradation of the particle surface. For the synthesis of  $\text{TiO}_2$  nanoparticles, titanium isopropoxide  $(\text{Ti}(\text{OC}_3\text{H}_7)_4)$ , was hydrolyzed with deionized water under vigorous stirring at room temperature. The resulting suspension was filtered and purified. Remaining sediment was again added to distilled water and the mixture was kept in a closed container under sonification for few mins. The aqueous solution of erbium nitrate pentahydrate  $(\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O})$ , Acros) was added dropwise to that mixture. The final mixture was allowed to centrifugation process, two types of samples, a wet sediment, and a nanoparticle suspension were obtained. The process of centrifugation and sonication was repeated three times. Finally, films were formed by casting the suspension on glass substrates [15]. The hierarchical yolk shell  $\text{TiO}_2$  beads were synthesized from the solution containing the mixture of  $\text{NH}_4\text{F}$ , urea, titanium tetrachloride,  $\text{H}_2\text{O}$  and water under hydrothermal synthesis method at varying temperatures of  $100^\circ\text{C}$ ,  $120^\circ\text{C}$ ,  $140^\circ\text{C}$ ,  $160^\circ\text{C}$  and  $180^\circ\text{C}$  for 12 h respectively. Final gained product was rinsed, dried and annealed for  $500^\circ\text{C}$  for 3 h [16].

### E. Modification Process

By modifying the surface structure of anatase  $\text{TiO}_2$  particles, the photocatalytic property could be greatly improved which is explained as follows: this process undergone irradiation reaction in a aqueous solution of NaOH and TBAOH solution. With the help of sona assisted exfoliation process the highly reactive exposed anatase 001 facets became delaminated from the outer surface of the mother  $\text{TiO}_2$ . This delaminated layer could be stabilized by the formation of Ti-O-TBA [17]. Also, the MIP(molecularly imprinted polymer) modification on the branched titanium dioxide nanorods was prepared to detect some molecules. Hereby, hydrothermal method was also used to prepare branched  $\text{TiO}_2$  NRs on fluorine doped tin oxide substrate. Here the mixture of ultrapure water and hydrochloric acid was prepared after that titanium butoxide solution was added to that mixture. After stirring, an ultrasonically cleaned FTO (fluorine doped tin oxide) was placed in a sealed Teflon lined stainless steel autoclave containing mixed solution at an angle against the wall of the container. The hydrothermal synthesis was performed at  $150^\circ\text{C}$  for 4 h in an electric oven. Finally an  $\text{TiO}_2$  NRs modified FTO was then purified and it were rinsed with the mixture containing ultra pure water and concentrated HCl then the FTO substrate was removed and rinsed well with ultrapure water. Titanium dioxide nanorods modification with molecularly imprinted polymer (MIP) was synthesized by surface molecular self assembly strategy[3]. Another method for improving the photocatalytic property of  $\text{TiO}_2$  was doping or adding an element to the  $\text{TiO}_2$  particles. In such cases, Tungsten-doped  $\text{TiO}_2$  (W-  $\text{TiO}_2$ ) has a better photo catalytic activity and it could be prepared via the sol-gel method. Titanium butoxide was used as a precursor and tungstic acid as a dopant material. The procedure to synthesis W-  $\text{TiO}_2$  was adding tungstic acid dissolved in  $\text{H}_2\text{O}_2$  to the mixture of Titanium butoxide and deionized water under vigorous stirring at a particular temperature. Finally an orange viscous solution was obtained which was kept at room temperature to turn into a gel. It should be dried and grinded in to a fine powder [18,19].  $\text{Cr}^{3+}$  was also used as dopant material as it improves the surface activity of the  $\text{TiO}_2$  material.  $\text{Cr}^{3+}$ -doped  $\text{TiO}_2$  nanoparticles (Ti-Cr) was also prepared by the same sol gel method. Titanium isopropoxide as a source element for the synthesis of  $\text{TiO}_2$  and chromium (III) nitrate nonahydrate and the prepared  $\text{TiO}_2$  were used for the synthesis of (Ti-Cr) NCs [4]. With the source element of titanium butoxide and uncalcined ceria we could prepare  $\text{TiO}_2/\text{CeO}_2$  nanocomposites were prepared and it was prepared with common method of wet chemical synthesis [20]. Graphene/  $\text{TiO}_2$  nanocomposites were prepared by the hydrothermal process. Here graphene was reduced from graphene oxide [21,5], later  $\text{TiO}_2$  nanoparticles were deposited on the graphene sheet with glucose as the facet controlling agent [21]. For the synthesis of  $\text{TiO}_2$  nanofiber, it should be added with some specific polymer. Here, polyacrylonitrile (PAN) and polyurethane (PU) were dissolved in DMAc (dimethylacetamide), to that mixture  $\text{TiO}_2$  nanoparticle was added. Finally, PAN/ PU/  $\text{TiO}_2$  nanofibrous membrane was obtained using the electrospinning process [22].

### III. PROPERTIES OF $\text{TiO}_2$

On reviewing about the properties of titanium dioxide, we should know about the structural, thermodynamic, optical, electronic and photon induced electron- hole properties.

#### A. Thermodynamic Properties

On discussing about the thermodynamic property of  $\text{TiO}_2$ , each polymorphs have different surface enthalpies at different thermodynamic stability. On applying temperatures the transformation of phases occurs as, anatase to brookite to rutile, brookite to anatase to rutile, anatase to rutile and brookite to rutile and all are based on energetic strategies of  $\text{TiO}_2$  particles [12]. In isothermal reaction, At  $723\text{K}$ , transformation of anatase to brookite occur, further it can be transferred to rutile phase. However, it implies that there was no direct transformation to rutile phase at that temperature. At  $853\text{K}$ , formation of rutile phase occur. The transformation rate depends upon the amount of rutile, if the amount of rutile decreases, the transformation of brookite from anatase could be readily observed. With the lower amount of anatase and at  $973\text{K}$ , the transformation of anatase to both brookite and rutile could be possible at longer reaction time. In isochronal reaction, at  $598\text{K}$  there should be increase in brookite concentration when transformation occurring from anatase to brookite. Above  $850\text{K}$ , there would be rutile concentration increases which implies rutile transformation. On this thermodynamic and kinetic analyses at isothermal and isochronal condition, there will be reverse transformation occurs below  $623\text{K}$  and at higher temperature above  $623\text{K}$ , anatase could be transformed to brookite or rutile and then brookite transforms to rutile [23].

#### B. Structural Properties

In the case of discussing the structural properties of  $\text{TiO}_2$ , we should discuss about the different polymorphic phases such as anatase, rutile and brookite. Of which the rutile phase is common and anatase, brookite and newly discovered  $\text{TiO}_2$  B were all synthesized by the wet chemical synthesis. Consider an tetrahedral rutile structure of  $\text{TiO}_2$ , the two  $\text{TiO}_2$  atoms are located at the primitive cell. Each Ti atom is surrounded by slightly twisted octahedron of O atoms. All those polymorphic phases have been analyzed with the same octahedral  $\text{TiO}_2$  as a primitive structural unit. The only difference among all the structures are the edge sharing octahedra. There could be two in rutile phase, three in brookite and four in anatase[24].

#### C. Electronic Properties

If we discuss about the electronic properties Of  $\text{TiO}_2$  we should probably know the band structure, density of states and electron density. The direct way of studying the conduction band structure has been done through optical experiments by exciting across the optical gap. Hence, in the study of band structure analyses with absorption and wavelength modulated transmission spectroscopic studies reveals that the  $\text{TiO}_2$  is a direct forbidden gap semiconductor which means that it possess direct transition is so called dipole forbidden.



The density of states (DOS) of rutile  $\text{TiO}_2$  has been evaluated/ characterized by the linear analytic tetrahedron method because its offering the constant energy surfaces. The prominent features of the valence band have been determined to be comparatively insensitive to the surface effects and the calculations has been done through tight binding calculations where we could found the differences between the bulk and surface DOSs were found to be negligible. On accounting the electronic properties of  $\text{TiO}_2$ , the participation of d-orbitals in the e-properties of transition metal oxides gives a better covalent character and a deformation of the atomic like charge density surrounding the transition metal ion and it reveals positive deformation along and perpendicular to the Ti-O bonds in 110 plane of the tetragonal units. The negative deformation along the 001 direction. Ti-O bonds shows prominent covalent bonding character which could be predicted by differencing the electro negativities of the Ti-O bonds. By using the pseudo charge density analyses we could analyze the charge densities in the band level. Its shown that in  $\text{TiO}_2$  structure significant quantity of charge occupying on the O atoms in the conduction band states as well as the Ti charge in the valence band [24]. The electronic structure of brookite is almost similar to the anatase because there is a slight differences between the local crystal structure of two phases and the brookite phase also have direct band gap which is comparatively larger than both the rutile and anatase. [25].

#### D. Optical Properties

To know the optical properties of  $\text{TiO}_2$ , we should characterize it for the three polymorphic phases (rutile, brookite, anatase) by using reflectance spectroscopic techniques. For rutile and anatase phase, consider the imaginary part of dielectric functions possess tetragonal unit cells and for brookite which is orthorhombic. From the study, it is known that anatase and brookite possess similar properties compared to the rutile. As declared in previous researches and studies, the threshold energies of anatase and brookite were 2.27 and 2.22 eV respectively which are related to the direct band gap values. We should predict the values of the respective phases by comparing the imaginary values and the experimental values. Here, approximately concluded that the reflectance value of anatase(6.33), anatase(5.62) and brookite(7.89) [25] and those fundamental theoretical calculations based on the LDA theory [24,25]. The optical transitions property of  $\text{TiO}_2$  have been investigated by applying at higher photon energy. Those plasmonic peak obtained at 12.7 and 19.5 eV for anatase and brookite respectively in comparison to the rutile obtained within the 20eV range, as confirmed in previous studies [25]. There are so many interesting and wide application arise with the photon induced activity of the  $\text{TiO}_2$  nanomaterials(i.e, could be in the form of nanotube, nanoparticles, nanocomposites, nanorods etc.). All those principles are mainly based on the redox reaction. The process involving in this photon derived techniques were named as photovoltaic cell, photocatalysis and photon induced hydrophilicity. The photon which is induced to excite the electron to produce electricity gives application in the field of photovoltaic cell or it can be derived to a chemical reaction in the case of photocatalytic reaction and also holding the holes on the  $\text{TiO}_2$

surface causes a high wettability which provides application in photo induced super hydrophilicity (PSH) [26].

#### IV. APPLICATION OF $\text{TiO}_2$

As we known that the application of  $\text{TiO}_2$  is strongly based on its peculiar properties, with that we can review those applications of titanium dioxide in the field of energy and environment. of those properties, the photocatalytic and sensing properties of  $\text{TiO}_2$  has been used in many applications which include degradation of toxic/ harmful dye molecule such as reactive black 5(RB5) dye from aqueous solution by coating ( $\text{TiO}_2$ ) titanium dioxide with ( $\text{Fe}^0$ ) zero valent iron ( $\text{Fe}^0/\text{TiO}_2$  NCs) [6] and (010) plane of anatase  $\text{TiO}_2$  provides high photocatalytic activity in the adsorption of N719 dye [27]. The photocatalytic degradation of toluene was optimized by tungsten doped nanoparticles (W-  $\text{TiO}_2$  NPs) under visible light irradiation. The photocatalytic activity of  $\text{TiO}_2$  was greatly improved by the addition of tungsten element thereby it reduces the electron hole recombination rate [18]. Similarly, for the degradation of (4-chloro-2-methylphenoxy) acid acetic (MCPA) was done by the photocatalytic degradation of  $\text{Cr}^{3+}$ -doped  $\text{TiO}_2$  nanoparticles (Ti-Cr)[4]. With the properties of hydrophilicity, photocatalytic, antibacterial activity and also the coating stability of  $\text{TiO}_2$ /graphene oxide modified polyacrylic coating, having application in photo decolorization efficiency of organic dye contaminants [28]. By using UV/  $\text{TiO}_2\text{NP}/\text{H}_2\text{O}_2$  as a photocatalyst, the breakdown of gemifloxacin was done as this residuals in hospital waste water and in industries could cause genotoxicity and antibiotic resistance [29]. Similarly, with the  $\text{TiO}_2$  thin film as a electrode in a photo electrochemical method, which offers a photocatalytic degradation of oxalic acid and 4-chlorophenol(4-CP) under UV light (monochromatic, 365nm) irradiation[30]. Also, the enhanced catalytic activity of  $\text{TiO}_2/\text{CeO}_2$  nanocomposites for the oxidation of benzene under Xe irradiation was due to the synergetic effects between photocatalysis of  $\text{TiO}_2$  and thermocatalysis of  $\text{CeO}_2$ [20]. Compared to  $\text{TiO}_2$  photocatalytic colloids, the enhanced photocatalytic degradation of organic pollutants such as methyl orange (MO) have been obtained by using  $\text{CeO}_2/\text{TiO}_2$  nanobelt heterojunctions under the same UV/ visible light irradiation [31]. Similarly hydrothermally synthesized  $\text{TiO}_2$  nanoparticles assisted on the nanofibers of poly(methyl methacrylate) has showed efficient degradation of methyl orange[32]. The photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) and bisphenol A (BPA) has been done by using the nanocomposites  $\text{TiO}_2/\text{g-C}_3\text{N}_4(\text{CN})$  decorated by Au assisted under visible light irradiation[33]. In the field of sensing hazardous elements with  $\text{TiO}_2$  as a photocatalyst, the photoelectrochemistry detection of ochratoxin A was done with the nano composites  $\text{TiO}_2/\text{S-BiVO}_4@\text{Ag}_2\text{S}$  as it provide high photocurrent intensity under visible light irradiation as  $\text{TiO}_2$  posses photoelectric activity. Since Bismuth vendate ( $\text{BiVO}_4$ ) with porous surface offers a adsorption of  $\text{TiO}_2$  on to the pores and it also provides the insitu growth of  $\text{Ag}_2\text{S}$ [1],

With branched TiO<sub>2</sub> nanorods (B-TiO<sub>2</sub> NRs) modified with imprinted polymer (MIP), the detection of chlropyris (CPF) was done efficiently based on photo electrochemistry detection and sensing strategy. The reactive sites of MIP was highly increased by branched TiO<sub>2</sub> NRs as its offers high surface area than TiO<sub>2</sub> NRs [3]. Similarly with the same hierarchically branched TiO<sub>2</sub> nanorods, the maximum photocurrent density was attained under Xenon lamp illumination [19]. For the photocatalytic reduction of CO<sub>2</sub> and N<sub>2</sub>O, TiO<sub>2</sub> as it is being possess the synergetic properties of high surface area, crystallite size of rutile, absorption band energy and mainly the separation of charge carriers, was used as a dopant element to the pure g-C<sub>3</sub>N<sub>4</sub> for improving its photocatalytic property [2]. The molecularly imprinted polymer modified anatase hierarchically cactus like TiO<sub>2</sub> arrays have been used in a photo electrochemical detection and visualized sensing platform. However, this AHCT arrays were synthesized with RNase B layer which acts as an insulator for the reaction and it is connected to the electrode. For the de-colourization of RNase B layer which could be connected to the PB electrode. Under light illumination, there could be de-colourization occur from PB to Prussian white which implies the de-colourization of RNase B [14]. In the application of assaying galic acid (GA) in red wine by using photo electrochemistry method with polyaniline reduced graphene oxide titanium dioxide. As TiO<sub>2</sub> is a good photocatalyst and graphene is considered as an electron acceptor and transporter in photocatalysis and reduces the rate of charge recombination further polyaniline gave a better stability, corrosion protection and high mobility of charge carriers. These combination of TiO<sub>2</sub>/PANI/graphene gave a good photocatalytic activity in a novel photo electrochemistry platform [5]. Also, developing a non-enzymatic glucose sensor was done by fabricating Ag & Pt hollow nanoparticles supported on TiO<sub>2</sub> nanotubes which was used as an electrode in that reaction [34]. On discussing about the application of TiO<sub>2</sub> in a photovoltaic cell or solar cell and in batteries is mainly based on the excellent optoelectronic properties, photocurrent conversion efficiency and readily manufacturing process. In the case of dye sensitized solar cells (DSC), TiO<sub>2</sub> anatase possess optoelectronic properties, shows a better photocurrent conversion efficiency and used as a photoanodic material in a DSC. Of these TiO<sub>2</sub> nanoparticles are having decreased surface area which could affect the DSCs efficiency, hence hierarchically TiO<sub>2</sub> structures with large surface area consisting of TiO<sub>2</sub> nanoparticles and hierarchical yolk shell anatase TiO<sub>2</sub> beads [16] have been used because it holds a maximum dye loading and efficient scattering [2,35,36], similarly with mesoporous anatase TiO<sub>2</sub> microspheres showed an enhanced scattering and photoelectrical conversion efficiency [36]. Also, perovskite solar cell have been also made by fabricating it with Au@TiO<sub>2</sub> core shell nanoparticles in to a porous TiO<sub>2</sub> or with perovskite (calcium titanate) semiconductor capping layers [37] and in graphene quantum dots solar cell, TiO<sub>2</sub>/CdS/GQDs was used as a photoanode [38]. In the case of increasing the electrochemical performance efficiency of lithium ion batteries and sodium ion batteries (LIBs and SIBs), the mixed phase of both TiO<sub>2</sub> anatase and TiO<sub>2</sub>-B (TiO<sub>2</sub> nanobelt) on Co<sub>9</sub>S<sub>8</sub> composites has been employed as an anode material and its provides better specific capacity of batteries and greater stability [39]. A nano crystallites anatase TiO<sub>2</sub> has also been used as a buffering element which covers the

crystallite Si nanoparticles in lithium ion batteries, improving the specific capacity of a battery thereby increase the ion polarization of the battery [40]. Non porous TiO<sub>2</sub> nanoparticle has been using as an supporting element to synthesize cobalt catalyst for enhance the oxidation of (MgSO<sub>3</sub>) magnesium sulphite (desulphurization) thereby lowering the effect of secondary pollution [41]. In the field of marketing, for the need of waterproof, UV resistance, thermal moisture controllability and breathability, an super hydrophobic electrospun polyacrylonitrile (PAN)/polyurethane (PU)/titanium dioxide (TiO<sub>2</sub>) nano fibrous membranes has been fabricated by coating with 2-hydroxy-4-n-octoxybenzophenone (UV531) and fluorinated acrylic copolymer (FAC). Here, TiO<sub>2</sub> employed as an organic blocker and UV531 act as an organic absorber to provide better UV protection for the modified Nano fibrous membranes [42]. For improving the functional sustainability of periphytic biofilms, its surface was exposed to titanium dioxide nanoparticles, hence it provides greater removal of organic matter and Cu<sup>2+</sup> [43]. In the field of biomedical field, TiO<sub>2</sub> have wide application because of its property of good biocompatibility, low toxicity and employed as an efficient photosensitizers. With that, the black TiO<sub>2</sub> nanoparticle synthesized through a facile calcination method combined with an in situ controllable solid state reaction approach shows narrow bandgap of ~2.32 eV which enhance the photo response to visible light and near infrared region. At 808 nm, more reactive oxygen species were induced to provide phototherapy to kill the bladder cancer cells [44]. In the case of site specific drug delivery, TiO<sub>2</sub> has been employed to increase the effectiveness of the drugs. Here curcumin incorporated titanium dioxide nanoparticles (CTNPs) has showed efficient cell viability, improved stability and less toxicity at maximum exposure [45]. An overall outline of titanium dioxide (TiO<sub>2</sub>) application and its preparatory method are aligned in a tabular way as given in the Table 1 below.

## V. CONCLUSION

In this overall review of Titanium dioxide, we can probably know the synthesis of TiO<sub>2</sub> nanomaterials as in the form nanoparticles, nanocomposites, nano rods, nanotubes and nanoarrays by sol-gel and hydrothermal synthesis methods and also we can slightly know the modifications done so far, either on the TiO<sub>2</sub> surface or doping some elements to improve its properties for better availability in the energy and environmental applications. Also the properties of titanium dioxide such as structural, thermodynamic, optical, electronic and photon induced activities have been said theoretically. Most of the applications of TiO<sub>2</sub> was mainly employed in the field of photocatalytic degradation of organic pollutants, dye molecules and some hazardous elements and also it was significantly used in photo electrochemical detection and sensing of chemical and biological elements. As an excellent photoanode, it has been widely enrolled in the application of photovoltaic solar cells and in lithium ion batteries. Furthermore, it has found application in CO<sub>2</sub> reduction, site specific drug delivery and in some commercial markets to attain product stability.

## Review on Titanium Dioxide Synthesis and Its Application on Prospecting Photocatalysis

The above mentioned all applications have been discussed. entire titanium dioxide (TiO<sub>2</sub>) nanostructures. Based on this review, we can get an overall idea about the

**Table 1: Overall outline of titanium dioxide (TiO<sub>2</sub>) application and its preparatory method.**

MAIN ELEMENT	ADDITIONAL ELEMENT	MODIFICATION	METHOD	APPLICATION	REFERE-NCES
Titanium dioxide (TiO <sub>2</sub> ) anatase	Zero valent iron (Fe <sup>0</sup> )	-	Coating of Fe <sup>0</sup> on TiO <sub>2</sub> surface.	Catalytic degradation of Reactive Black 5 in aqueous solutions enhanced by ultrasound assistant	6
Layered titanate nanosheet colloidal solution	-	Titanium dioxide (TiO <sub>2</sub> ) Nano crystal.	Hydro-Thermal synthesis	Enhancing the photo catalytic reaction on adsorption of N719 dye.	27
Titanium dioxide (TiO <sub>2</sub> )	Tungsten (tungstic acid)	-	Doping	Photo-catalytic degradation of toluene under visible light irradiation	18
Titanium dioxide (TiO <sub>2</sub> )	Chromium	-	Wet synthesis	MCPA Degradation under visible light irradiation.	4
Titanium dioxide (TiO <sub>2</sub> ) anatase and rutile	Graphene oxide	Polyacrylic coatings	Wet synthesis	Photo de- colourization efficiency of organic dye contaminants	28
Titanium dioxide (TiO <sub>2</sub> )	Hydrogen peroxide(H <sub>2</sub> O <sub>2</sub> )	-	Wet chemical synthesis	photocatalytic degradation kinetics of gemifloxacin	29
Titanium dioxide (TiO <sub>2</sub> )	-	TiO <sub>2</sub> thin film	fabrication	photocatalytic degradation of oxalic acid and 4-chlrrophenol (4-CP) under UV light	30
Titanium dioxide (TiO <sub>2</sub> ) anatase	CeO <sub>2</sub> (TiO <sub>2</sub> / CeO <sub>2</sub> nanocomposites)	-	Hydrothermal synthesis	oxidation of benzene under Xe irradiation	20
Titanium dioxide (TiO <sub>2</sub> )	CeO <sub>2</sub> (CeO <sub>2</sub> / TiO <sub>2</sub> nanobelt)	-	Hydrothermal method	photocatalytic degradation of methyl orange (MO) UV/ visible light irradiation	31

Titanium dioxide (TiO <sub>2</sub> )	poly(methyl methacrylate)	-	Hydrothermal method	degradation of methyl orange	32
Titanium dioxide (TiO <sub>2</sub> )	g-C <sub>3</sub> N <sub>4</sub> (CN) & Au	-	Hydrothermal method	photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) and bisphenol A (BPA) under visible light irradiation	33
Titanium dioxide (TiO <sub>2</sub> )	S-Bivo4@Ag2S	-	Hydrothermal method	photoelectrochemistry detection of ochratoxin A under visible light irradiation	1
Branched TiO <sub>2</sub> nanorods(B-TiO <sub>2</sub> NRs)	-	Imprinted polymer	Hydrothermal method	Photoelectrochemistry detection of chlropyris (CPF)	3
Titanium dioxide (TiO <sub>2</sub> )	-	Hierarchically branched TiO <sub>2</sub> nanorods	Hydrothermal method	Photoelectrochemical Hydrogen Production	19
g-C <sub>3</sub> N <sub>4</sub>	Titanium dioxide (TiO <sub>2</sub> )	-	simple mechanical mixing	photocatalytic reduction of CO <sub>2</sub> and N <sub>2</sub> O	2
Titanium dioxide (TiO <sub>2</sub> )	-	anatase hierarchically cactus like TiO <sub>2</sub> arrays	molecular imprinting technique,	decolourization of RNase B Under light illumination	14
Titanium dioxide (TiO <sub>2</sub> )	Graphene oxide	Polyaniline	TiO <sub>2</sub> /PANI/graphene by one-step method.	Assaying galic acid (GA) in red wine by using photoelectrochemistry method	5
Titanium dioxide (TiO <sub>2</sub> )	Ag & Pt hollow nanoparticles	Titanium dioxide (TiO <sub>2</sub> ) nanotubes	Fabrication	Nonenzymatic glucose sensor	35
Titanium dioxide (TiO <sub>2</sub> )		Mesoporous anatase TiO <sub>2</sub> microspheres	Hydrothermal method	Dye sensitized solar cells (DSC)	36
Titanium dioxide (TiO <sub>2</sub> )	Gold nanoparticle	Au @ Titanium dioxide (TiO <sub>2</sub> ) core shell	Fabrication method	Perovskite solar cell	37
Titanium dioxide (TiO <sub>2</sub> )	CdS	GQDs	chemical oxidation and an acidic treatment	Quantum dots solar cell	38
Titanium dioxide (TiO <sub>2</sub> )	Cobalt pentlandite(Co <sub>9</sub> S <sub>8</sub> )	TiO <sub>2</sub> anatase and TiO <sub>2</sub> -B (TiO <sub>2</sub> nanobelt)	solvothermal reaction	An anode material in lithium ion batteries and sodium ion batteries(LIBs and SIBs)	39

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