# Review on Recent Advances in Synthesis of Black $TiO_2$

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**Abstract:- Nanomaterials made of titanium dioxide ($TiO_2$) are commonly regarded as state-of-the-art photocatalysts for environmental remediation and energy conversion. Due of its unique electrical and optical characteristics, several attempts have been made to manufacture $TiO_2$ materials using various techniques. The electrical and optical characteristics of $TiO_2$ materials have long been investigated. The development of oxygen vacancies and $Ti^{3+}$ defects in black $TiO_2$ has increased solar light absorption, promoted the separation of photo-generated charge carriers, and therefore improved photocatalytic activity in $H_2$ generation and pollutant degradation. A lattice disorder on the surface, as well as the presence of oxygen vacancies, $Ti^{3+}$ ions, Ti-OH, and Ti-H groups, contribute to black $TiO_2$'s improved photocatalytic activity. Enhancing the optical absorption characteristics of $TiO_2$.In this article, we summarize the synthesis pathways, morphology and photocatalytic properties of Black titanium dioxide ($TiO_2$).**

***Keywords:-*** *Synthesis pathways, Morphology, Photocatalysis.*

## I. INTRODUCTION

Water covers 70% of the Earth, therefore it is reasonable to assume that it will always be plenty. Even still, potable water, which is utilized to irrigate our farm crops, is extremely scarce. Only 3% of the total available water on our planet is fresh water, and two-thirds of that is tucked away in glaciers or otherwise unavailable for humans to utilize. As a result, over 2.7 billion people face water scarcity for at least one month each year, and 1.1 billion people lack access to water globally.[1]

For 2.4 billion people, poor sanitation is a major worry, putting them at risk of diseases like cholera and typhoid fever, as well as other water-borne illnesses. Diarrhea kills two million people per year, the majority of them are children.. [2] All these are the negative impact of water because of its unavailability in many or the areas. If we focus now there are many ways to save water from wasting.

Water contamination is on the rise these days, thanks to rising population, industrialization, and urbanization. Chemical, petrochemical, pharmaceutical, and mining industries all demand enormous amounts of water. Ultrapure water is required in the pharmaceutical, microelectronics, and semiconductor sectors. Unfortunately, hazardous organic and inorganic substances contaminate the water discharged by these companies. [3]Toxic organic compounds such as chlorinated and non chlorinated aliphatic and aromatic compounds, dyes, detergents, and surfactants, agro wastes such as insecticides, pesticides, and herbicides, volatile organic compounds, plastics, inorganic compounds such as toxic metals, and pathogens such as bacteria, fungi, and virus are among the most common pollutants. All of this is wreaking havoc on the environment as well as living organisms. [4]

Water shortage is one of the world's most critical problems, and it will become more so in the future as the world's population and industry develop. Pollutants from diverse industries have recently been projected to have contaminated water to unsafe levels all around the world in the last two decades. These disrupt the environment's balance and inflict substantial harm to living organisms. Water is no longer an infinite resource, as people have realized.[5]. As a result, the necessity for innovative and effective water treatment processes for companies is clear. Today's fast increasing businesses produce a massive amount of chemical waste and effluent, much of which is illegally discharged into sea water or is treated in the CETP to some extent (Common Effluent Treatment Plant) [3] This treatment needs high amount of capital for investment and huge amount of land for equipment. It is necessary to use them because we can't let this much amount of water untreated and not to be transferred in sea or rivers as well. [5]

### *A. Toxicity in the Effluent Water*

The full response of test organisms to all substances in wastewater is provided through toxicity evaluation, which is an important metric in wastewater quality monitoring.

Table 1 Toxicity evaluation [6]

| Particulars | $P^H$ | BOD (mg/L) | COD (mg/L) | TSS (mg/L) | Nitrate (mg/L) | P (mg/L) |
|---|---|---|---|---|---|---|
| **Untreated Waste Water** | 7.6 | 32 | 650 | 275 | 76 | 8 |
| **Treated Waste Water** | 8.01 | 20 | $40 \pm 1$ | 15 | 13 | 2.5 |
| **Approved standards for discharge to surface water** | 6.5 | 30 | 60 | 40 | 50 | 6 |

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*B. Different Treatment Methods to treat Effluent*

Mainly there are Four methods used for treatment of waste water

- ➢ Physical Treatment
- ➢ Biological Treatment
- ➢ Chemical Treatment
- ➢ Sludge Treatment

➢ *Physical Waste Water Treatment:-*

Physical methods are used to clean wastewater. Solids are removed through methods such as screening, sedimentation, and skimming, without chemicals. With sedimentation, insoluble/heavy particles are suspended from the waste water, and it is one of the most used physical wastewater treatment processes. [7]

Once the insoluble matter has gone to the bottom, you can separate the clear water. Another good physical water treatment method is aeration. This process includes pushing air through the water to supply oxygen. To eliminate all contaminants, the final stage, filtration is used. The most popular type of filter is the sand filter, Which can be applied to separate contaminants and insoluble particles from waste water. Sand filters are easily employed to remove oil from the surfaces of wastes.[8]

➢ *Biological Water Treatment:-*

This treatment involves various biological processes to break down the organic material present in wastewater, such as soap, human waste, oils and food. [9]Microorganisms metabolize organic matter in the wastewater in biological treatment. It can be divided into three categories: -

- Aerobic Process
- Anaerobic Process
- Composting

- *Aerobic process*

This process take place in presence of oxygen in which bacteria decomposes the organic matter and converts it into carbon dioxide that can be used by plants.

- *Anaerobic process*

The process take place in absence of oxygen. And in this Fermentation is used for fermenting the waste at specific temperature.

- *Composting*

This method involves mixing wastewater with sawdust or other carbon sources and it is a aerobic treatment. Although secondary treatment removes the majority of particles in wastewater, certain dissolved nutrients like nitrogen and phosphorus may remain.

➢ *Chemical Water Treatment:-*

According to its name, this treatment uses chemicals in water to kill microorganisms that degrade water. Chloride is a typical oxidizing agent used to kill these microorganisms [10] Chemicals prevent bacteria from growing in water, resulting in pure water. If an acid or base is used to bring water to its neutral PH of 7, it is called neutralization.

➢ *Sludge Treatment:-*

Separation of solid and liquid phases is a solid-liquid process in which the solid phase must have minimum moisture, while the liquid phase separated must have minimal solid particles.

Dewatering of sludge from industrial wastewater or sewage plants is an example of this, where the residual moisture in the dewatered solid determines disposal costs and the pollution load returned to the treatment facility is determined by the cent rate quality.[11]

To remove the solids from the wastewater, a solid-liquid separation device such as a centrifuge is utilised. Wastewater has a big impact on the environment, so it's crucial to treat it properly. You not only safeguard the organisms that live on it, but you also protect the earth as a whole by cleaning wastewater. [12]

*C. What is Photocatalysis?*

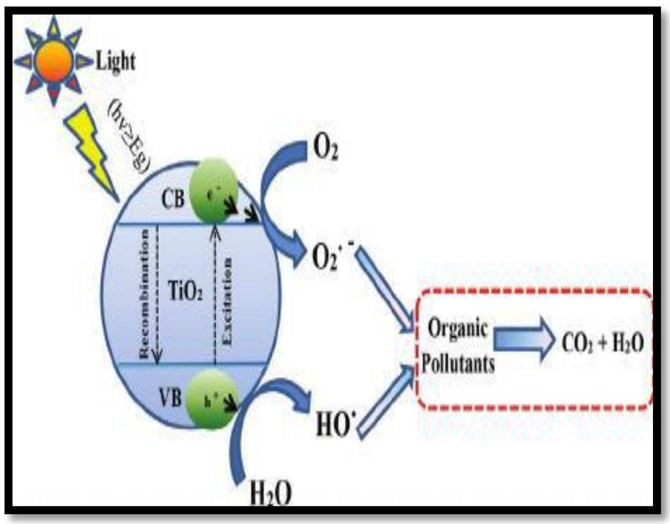


Fig 1 Schematic diagram of Photocatalysis [13]

When a light source interacts with the surface of semiconductor materials, referred to as photocatalysts, photocatalysis occurs.[2] During this process, there must be at least two simultaneous reactions occurring, oxidation from photogenerated holes, and reduction from photogenerated electrons.

A material that is capable of absorbing light, producing electron-hole pairs undergo chemical transformation is known as Photocatalyst. There are Many Photocatalysts reported in literature such as $TiO_2$, $CeO_2$, $SnO_2$ etc. Among all these $TiO_2$ is extensively used Photocatalyst. [3], [4]

The photocatalyst itself should not undergo change and therefore a precise synchronization of the two processes needs to take place. In 1972 Fujishima and Honda were the first to demonstrate water electrochemical photocatalysis at a semiconductor electrode. [5]Later it was discovered that $TiO_2$ aids in decomposing cyanide in water, rising interest towards the material's environmental applications. $TiO_2$ is suitable for photocatalysis for several reasons, some of which are its common availability, relatively low cost, and high chemical stability. [14]

Photocatalysis can be used to degrade contaminants and improve the quality of the atmosphere's air in a real-world setting. As a result, photocatalysis can be employed in the construction industry to improve indoor air quality. It's a chemical reaction triggered by photo absorption in a Photocatalyst that doesn't alter during the reaction. It is a "green" technology that operates at room temperature and pressure and uses a light source and oxygen from the air. [15] The capacity of the catalyst to make electron-hole pairs, which generate free radicals capable of subsequent reactions, is essential for photocatalytic activity.

*D. Mechanism of Photocatalysis*

The basic photocatalytic mechanism is as shown in figure 3. It includes the following steps.

[1] When absorption of energy (Photons) having energy greater than the band gap of photocatalyst then transfer of electrons takes place from valence band to conduction band. These leads to creation of holes ($h^+$) in valence band. [16]

**Photocatalyst + hν → $hVB^+ + eCB^-$ ………….. (1)**

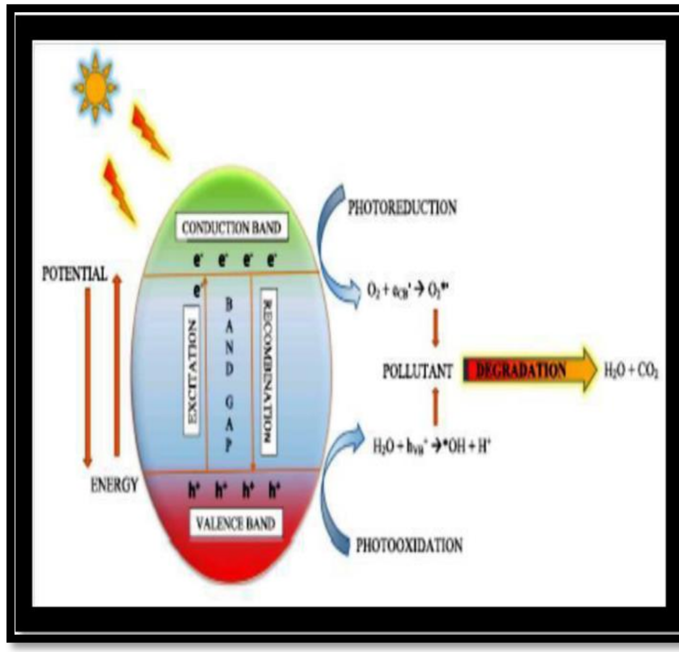


Fig 2 Schematic of Mechanism of Photocatalysis[13]

[2] These holes and electrons can recombine and release the absorbed energy in the form of heat.

**$hVB^+ + eCB^- \rightarrow$ energy (heat) …..………………. (2)**

[3] These electrons and holes then react with available oxidants and reductants to form powerful and unstable radicals.[16]

**$H_2O + hVB^+ \rightarrow$ *OH (hydroxyl radical) + $H^+$………(3)**

**$O_2 + eCB^- \rightarrow O_2$*− (superoxide radical) ………… (4)**

[4] Then these free radicals react with pollutants and degraded into carbon dioxide and water.

***OH + pollutant → Intermediates → $H_2O + CO_2$………….. (5)**

**$O_2$*− + pollutant → Intermediates → $H_2O + CO_2$ …………(6)**

*E. Titanium Dioxide ($TiO_2$)*

Titanium dioxide is widely used photocatalyst because of its superior optical and electronic properties. It has a melting point of **1,843ºC** and a boiling point of **2,972ºC**, so it occurs as a solid in nature and, even in its particle form, it is insoluble in water. Titanium dioxide ($TiO_2$) is a naturally occurring oxide of titanium. It is also referred to as titanium (IV) oxide or titania. $TiO_2$ is a cheap and widely available white oxide material having a molecular mass of 79.86 g/mol, a density of 3.9–4.2 g/cm$^3$, a refractive index in the range of 2.5–2.75, and Mohs hardness of 5.5–7 [17]. There are three naturally occurring crystalline phases of $TiO_2$: anatase, rutile, and brookite. Anatase and rutile have a tetragonal structure, whereas brookite has an orthorhombic structure. For industrial applications, the anatase and rutile phases are the only ones commonly used. [18]. $TiO_2$ is a semiconductor, with a band gap of 3.2 eV for anatase and

3.0 eV for rutile. $TiO_2$ is a non-toxic, chemically stable, non-flammable, and biocompatible material. It can also be used as a white pigment During the past few decades, exploration of nanomaterials has grown rapidly since nanosized materials demonstrate completely different properties from their bulk counterparts. As a result, $TiO_2$ is one of the most widely used nanomaterials and is useful in a wide range of applications [19].

Titania ($TiO_2$) is a white oxide ceramic having three crystalline forms: rutile, which has a tetragonal structure, anatase, which has a tetragonal structure as well, and brookite, which has an orthorhombic structure. Although most $TiO_2$ on the market is white in colour, it has another feature that is synthesised from the white $TiO_2$. [17]

*F. Limitations of TiO2 Photocatalyst:-*

- It is not sufficient to utilize maximum visible light.
- High e-h recombination rate.
- Low adsorption of 0rganic pollutants.
- Aggregation of NPs.
- Difficulties in recovering of NPs.
- Poor thermal stability (Anatase).

*G. White TiO2*

- It is the most promising Sunlight Harvester.
- It have band gap of 3.2 eV.
- It is cheap, non-toxic, photolytically and chemically stable also reusable with high turnover rate.
- Its physical and chemical modification is simple and easy to understand.

## II. LITERATURE REVIEW

*A. Hydrogenation Method*

Mao and his co-workers [6] described a new method for making disordered nanophase $TiO_2$ by hydrogenating $TiO_2$ and adding a dopant. They made nanophase $TiO_2$ by heating a precursor solution including Titanium tetraisopropoxide, ethanol, HCl, and Pluronic F127 at 480°C for one day, then evaporating and drying it at 110°C for 24 hours, and finally calcining it at 500°C for 6 hours.

They claimed that hydrogenation of $TiO_2$ at 20 bars and 200ºC for 5 days produced a disordered surface layer that shifted optical absorption from ultraviolet to near infrared. Furthermore, the band gap of hydrogenated black $TiO_2$ was around 1.0 eV, which was significantly lower than the 3.3 eV. They discovered that hydrogenated black $TiO_2$ has high activity and stability for photocatalytic hydrogen generation from water. The rate of hydrogen production was double that of previous semiconductor photocatalysts.

Li et. [20] reported on the effects of hydrogen treatment on the photocatalytic activities of rutile $TiO_2$ nanowire arrays with diameters of 100-200 nm. They discovered that as the temperature increased, the colour of hydrogen-treated $TiO_2$ nanowire films changed from white to yellowish green at 350ºC and black at 450ºC. Photocurrent densities were also two times higher in hydrogenated $TiO_2$ nanowire samples than in pure $TiO_2$. They stated that the density of photocurrent increases as the temperature of hydrogen annealing rises.

Huang et.al [21] reported effect of hydrogen treatment on the activity of anatase $TiO_2$.They discovered that hydrogen production rates were 3.2 to 3.8 times greater with hydrogenated $TiO_2$ than with air-treated $TiO_2$ and commercial P25. Mullins et al. [40] recently observed a synergistic effect after co-treating $TiO_2$ nanowire arrays with $H_2$ and $NH_3$, significantly improving water photo-oxidation performance under visible light illumination.

Fig 3 Unmodified White and Hydrogenated black TiO2

*B. Chemical Reduction Methods*

➢ *$NaBH_4$ Reduction*

Wenzhang Fang et.al [22] reported $NaBH_4$ reduction that was used to prepare $Ti^{+3}$ self-doped $TiO_2$. They created a series of $TiO_2$ nanoparticles called m-$TiO_2$ (Where m denotes the amount of $NaBH_4$ added). The synthesized material was then calcined for 3 hours at 500°C in a muffle furnace. They discovered that the photocatalytic activity of self-doped $TiO_2$ with $Ti^{+3}$ is proportional to the doped $Ti^{+3}$. Because of the increased BET surface area after HCL washing, the produced catalyst demonstrated stronger visible light photocatalytic activity than before.

➢ *$CaH_2$ Reduction method*

Guilian Zhu et. al [23] reported $CaH_2$ reduction method for black $TiO_2$ synthesis with increased photocatalytic decontamination and water splitting performances at low temperatures. They demonstrated that $TiO_2$ was reduced to

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$Ti_2O_3$ using the reducing agent $CaH_2$. The use of metal hydride to reduce transition metal oxides at low temperatures to generate oxygen shortages has become more useful than traditional approaches. At low temperatures, $CaH_2$ decomposes and releases highly active hydrogen atoms. The reduced nanoparticles have a crystalline core/amorphous shell structure and outperform commercial P25 $TiO_2$ in photocatalytic water purification and photo electrochemical water splitting by 2.4 times and 4.5 times, respectively.

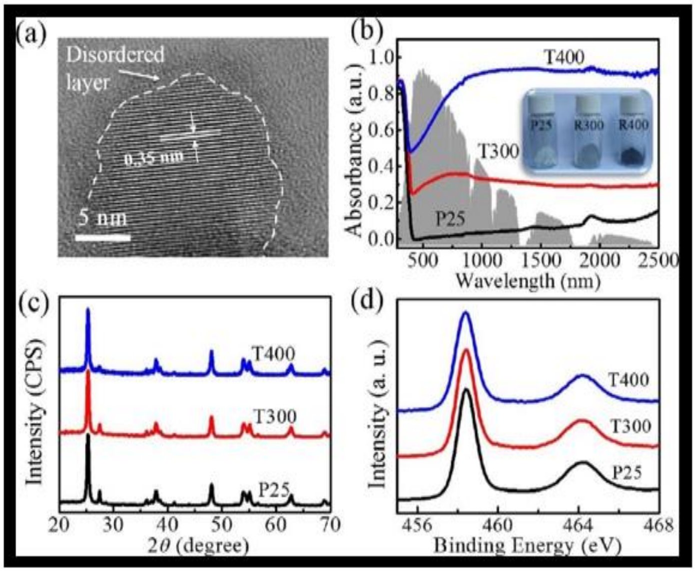

Fig 4: Photographs of synthesize P25, T300 and T400[24]

They found that Reduction at 300ºC result in grey colour $TiO_2$, denoted as T300 and reduction at 400ºC result in black colour $TiO_2$, denoted as T400.The band gap of pristine $TiO_2$was approximately 3.2 ev but after $CaH_2$ reduction it exhibit enhanced visible light absorption of visible light and corresponding band gap was 3.05 eV. They also claim that T400 absorbs 81 percent of solar radiation, which is significantly more than pristine $TiO_2$. They discovered that treating $TiO_2$ with $CaH_2$ lowers the Rutile ratio and causes flaws and an amorphous shell. The low temperature decreased samples' photocatalytic organic degradation and water-splitting capabilities are both superior to those of P25. In addition, $CaH_2$ reduction improves electron concentration and photo electrochemical water-splitting capabilities significantly.

➢ *Magnesium Reduction Method*

Miaomiao Ye et.al [25] reported synthesis of Black $TiO_2$ by magnesium (Mg) reduction of white pristine P25 $TiO_2$ nanocrystals followed by removal of excess Mg with aqueous HCl and Distilled water.

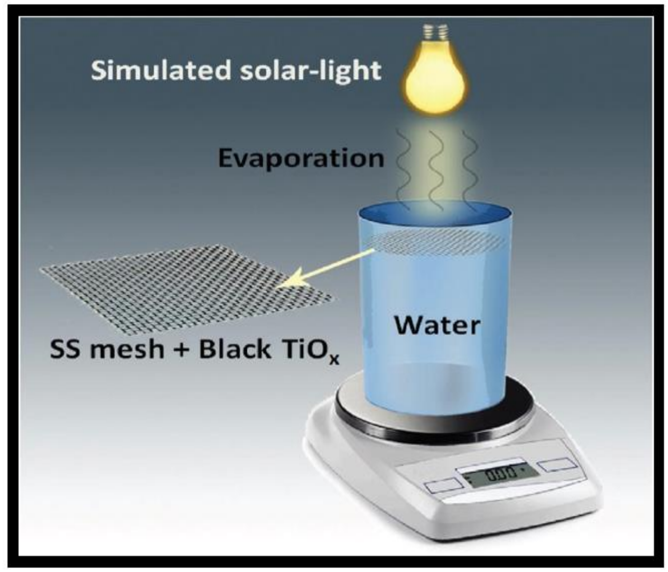

Fig 5: Schematic diagram of Solar water evaporator[21]

They discovered that as the amount of magnesium in $TiO_2$ grows, the oxygen concentration falls, increasing liquid absorption and darkening the contaminant's colour from white to black. They discovered that black $TiO_2$ efficiently generates water vapour with solar thermal conversion as high as 50% under solar simulated light irradiation of $1000 Wm^{-2}$ when tested in a solar water evaporator. [21]

They demonstrated the applicability of black $TiO_2$ for water evaporation by coating and super hydrophilizing it on an SS mesh. The degree of $TiO_2$ reduction affects the efficiency of converting solar light energy to heat. They discovered that the higher the $TiO_2$ reduction, the higher the Ti/O ratio, the blacker the $TiO_2$, and the better the solar energy to water evaporation conversion efficiency, the higher the $TiO_2$ reduction, the higher the Ti/O ratio, the blacker the $TiO_2$, and the better the solar energy to water evaporation conversion efficiency.

They proposed using this low-cost, low-toxic, high-thermal-conversion-efficiency, chemically stable Black $TiO_2$ to convert solar energy to thermal energy for evaporation of sea or brackish water in areas where drinking water is scarce.[8]

➢ *Aluminium reduction*

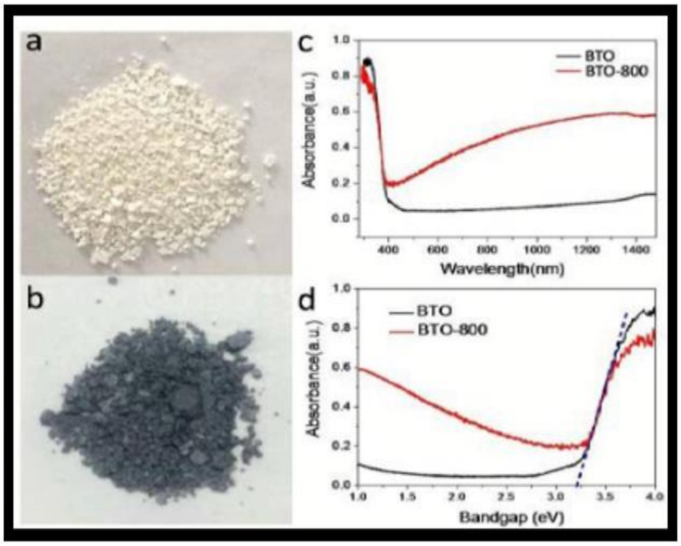


Fig 6: Photograph of $BaTiO_3$ and black BTO-800[26]

Wang et. al [26] described a method for producing black $TiO_2$ nanoparticles from molten aluminium using an evacuated two-zone vacuum furnace. They demonstrated that the absorption of visible light and near infrared light is improved by their crystalline core amorphous structure. By reducing aluminium at various temperatures, Zhu et al. created black brookite $TiO_2$. They discovered that deforming the shell and adding oxygen vacancies and $Ti^{+3}$ states increased photocatalytic activity and light absorption.

*C. One step reduction reduction/crystallization process*

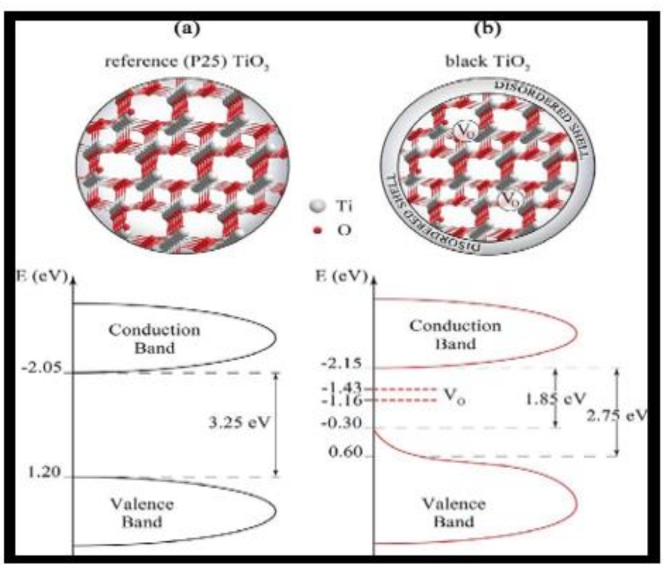


Fig 7: Schematic structure of P25 and black $TiO_2$[27]

Alberto Naldoni et. al [27] reported one step reduction process for synthesis of Black $TiO_2$. Black $TiO_2$ powder was obtained by heating of titanium precursor under hydrogen stream followed by fast cooling in inert environment until room temperature. They proved that process exhibit a bandgap of only 1.85 ev which matches well with visible light absorption.

*D. Argon Treatment*

Zhang et. al [28]reported synthesis of Black $TiO_2$ by argon treatment of sol gel derived Ni doped $TiO_2$. The Ni doped $TiO_2$ was mixed with $NaBH_4$ and heated at 350°C under atmosphere for 1 h followed by cooling at room temperature. The various samples based on amount of Ni such as 0, 1.0 ,2.0,3.0,4.0 mol% were denoted as MO,M1,M2,M3 and M4. These materials turned black when treated under Argon atmosphere and were denoted as b-MO,b-M1,b-M2,b-M3,b-M4 respectively. Grabstanowicz et. al [29] prepared black $TiO_2$ powders using two step strategy. The titanium precursor $TiH_2$ was mixed with $H_2O_2$ to get slurry. The slurry turned yellow on vacuum desiccation followed by drying at 110°C.Finally yellow powder turns black when heated at 630°C for 3 h in argon atmosphere. They found that synthesize material exhibited larger absorption in the visible and near infrared regions compared to normal $TiO_2$.

*E. High/Low pressure Hydrogen treatment*

Chen et. al [30] described the synthesis of black $TiO_2$ by hydrogenating crystalline $TiO_2$ at a high pressure of 20 bar for 5 days at 200°C in an $H_2$ environment. They discovered that the creation of a disordered layer on the surface of black $TiO_2$ lowered the band gap, which was favourable for carrier trapping. Sun et al. reported synthesis of hydrogenated Black $TiO_2$ from anatase $TiO_2$ nanocrystals under high hydrogen pressure. They used an automated sievert's setup to examine the hydrogen adsorption and desorption properties.

Leshuk et. al [30]reported hydrogenation of pristine $TiO_2$ at different temperatures. They observed the color change and wavelength absorption for a sample which was hydrogenated at 450°C under 20 bar pressure for 24 h. Lu et. al synthesize black titanium dioxide at ambient temperature under high pressure by $H_2$ treatment on commercial P25.They found that color of P25 turned black after 20 days of hydrogenation also the optical absorption of synthesize material was about 1.0 ev which was lower compared to P25.

*F. One Pot Gel Combustion method*

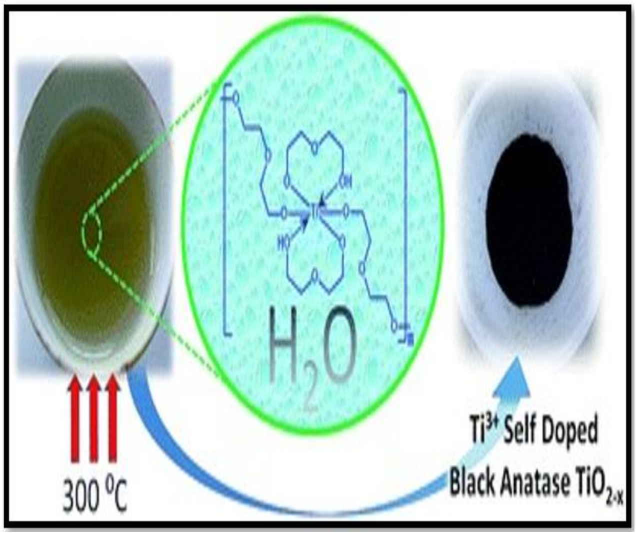


Fig 8: Schematic illustration of one pot gel combustion method [31]

Ullatil and Periyat et.al [31] reported synthesis of black $TiO_2$ via one pot gel combustion method. They synthesize self doped black anatase titanium dioxide using hydroxylation of titanium glycolate gel followed by Calcination at 300ºC for 2 hours. They proved that the defective anatase $TiO_2$ were comprised of $Ti^{+3}$ and oxygen vacancy sites. Thus synthesized material is 33% more photo catalytically active than Degussa-P25

*G. Modified Sol gel method*

Ting Wang et. al [32] reported facile synthesis of Black TiO2 with modified sol gel method assisted with CTAB template agent. In this synthesis 5 ml of tetrabutyl titanate were added into 20 ml anhydrous ethanol and light yellow solution was formed. Then 0.5 g CTAB were dissolved into 10 ml of ethanol. The solution was added into light yellow solution under continuous stirring to form a yellow sol. It heated at 180OC for 4 h. The powder obtained was designated as TiO2-CTAB. In order to eliminate the residual CTAB molecules, TiO2-CTAB was further calcined at 300 °C for 1 h, and black TiO2 powders were obtained and designated as TiO2CTAB-300°C.

They suggested that CTAB played versatile role of not only altering morphology and structure of TiO2 nanoparticles but also promoting the generation of Vo and improving the visible light absorption. There are large amounts of Vo in the TiO2CTAB-300°C nanoparticles, which lead to its strong visible absorption. TiO2CTAB-300°C catalyst showed efficient photocatalytic activity under visible light irradiation, and giving a H2 generation of 620 µmol/g, which was three times higher than control TiO2 (210 µmol/g).

*H. $ZnCl_2$/KCl molten salt assisted synthesis*

Jijian Xu et. al [28] reported facile high yield $ZnCl_2$/KCl molten salt route for synthesis of black titania hexagonal nanosheets by oxidizing $TiH_2$ in $ZnCl_2$/KCl salt melt under atmospheric pressure and low temperature 400ºC .They suggested that Black titania possesses a tunable phase composition and enhance visible light photocatalytic activity accompanied with a controllable morphology transformation from hexagonal nanosheets to nanorods.

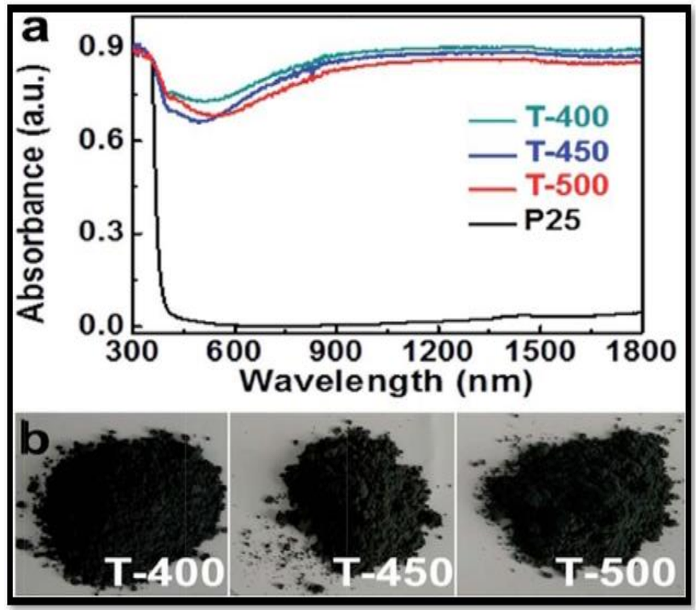


Fig 9: Photograph of black TiO2 synthesized at various temperatures [28]

*I. Hydrogen plasma assisted Chemical Vapor Deposition*

Feng Teng et. al [33] reported Preparation of black $TiO_2$ by hydrogen plasma assisted chemical vapor deposition. 2 g of P25 powder (Degussa) was stirred for 10 min with 50 ml of sodium hydroxide solution in beaker. The obtained solution was transferred into Teflon lined stainless steel autoclave with an inner volume of 40 ml and the autoclave has been sealed and placed in an oven before the oven was heated to 120ºC for 12 h. The resultant precipitate was washed with HCl followed by washing using deionized water to attain a PH between 6 and 7. Prepared powder was dried at 110ºC.

*J. TiO2 coated plastic sheets*

Sutisnaa , Edy Wibowoa ,[34] carried out experiment based on , ***TiO2 coated plastic sheets***. Which have been used to degrade batik wastewater under solar exposure. They have mainly focussed on and experimented on (BOD, COD, TSS), Total of 8 pieces of catalyst sheets are added on 1000 ml of the waste, and managed to degrade 50.41% of the initial concentration during 5-days irradiation respectively.

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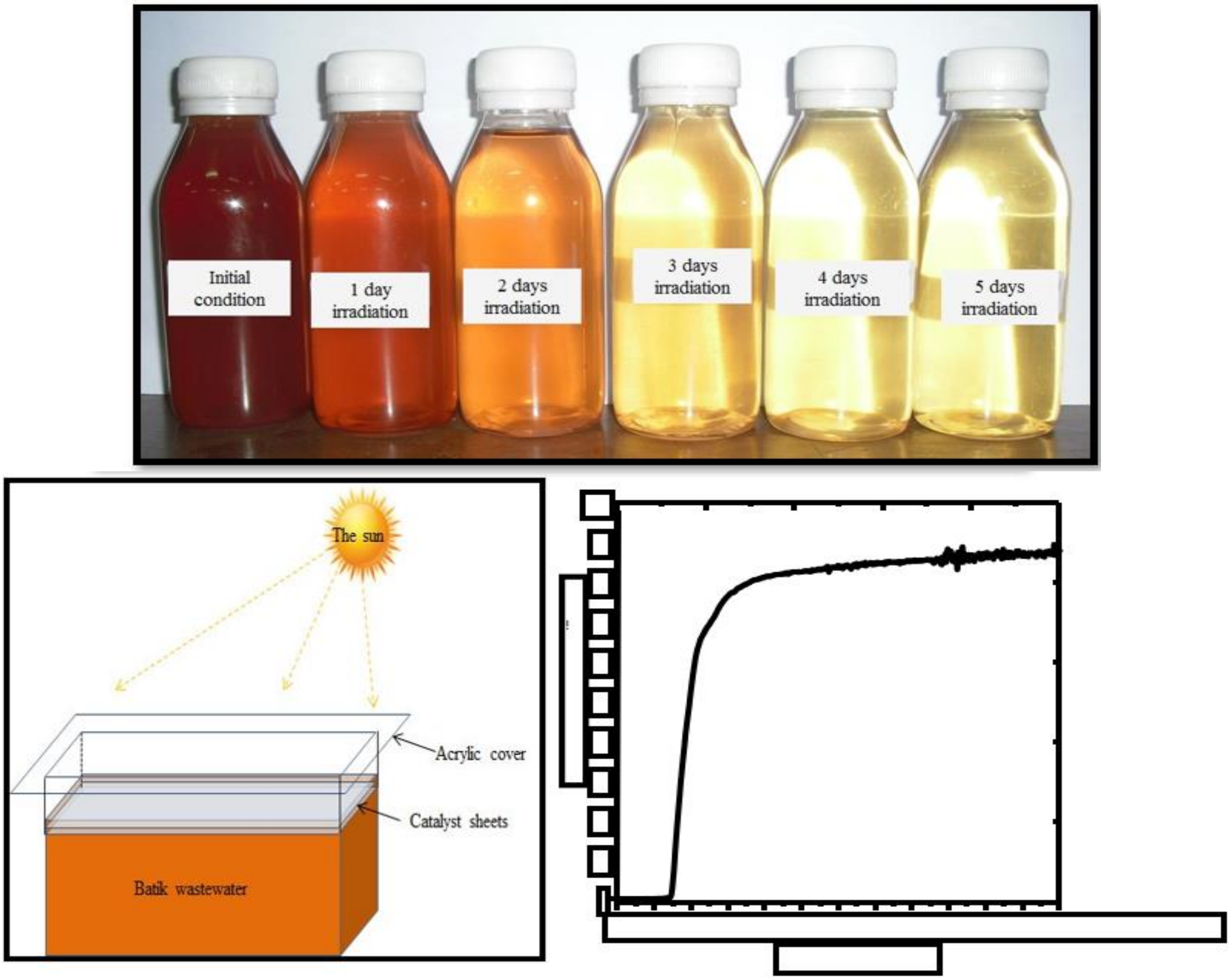


Fig 10: Experimental setup of Batik waste water treatment. [35]

*K. Treatment of waste water using $TiO_2$ photocatalyst*

Suman Dutta , [36](ISM) DHANBAD, INDIA has conducted a detailed study on topics such as waste water treatment utilising TiO2 based photo catalysts, photocatalyst mechanism, reaction mechanism, and types of photoreactors that can be used. Our main focus, however, is on ( Modification of photocatalyst ).

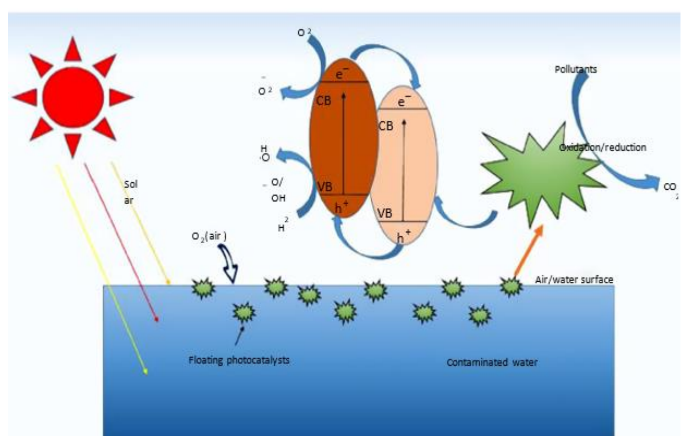


Fig 11:Schematic depiction of the floating photocatalyst[36]

*L. Coating of TiO2 on plastic sheets using spray method*

F D Utami , D Y Rahman [37] has prepared TiO2 coated on transparent plastic sheet using (Spray method). The method was employed to degrade organic wastewater (Methylene Blue) under solar exposure. And they have achieved 98% of result in 16 hours of irradiation for A total of 300 blue

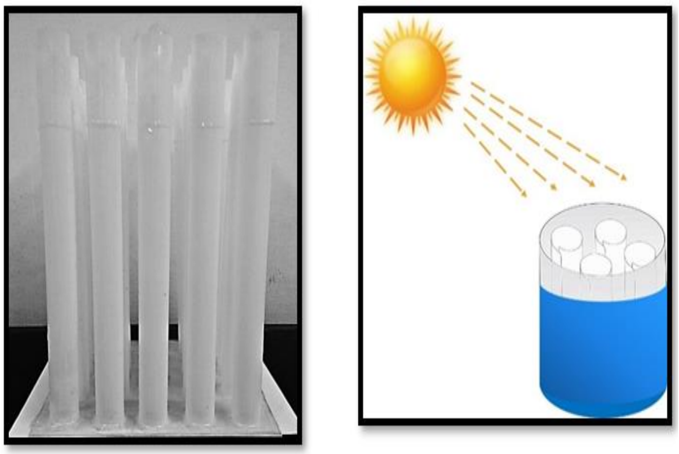

Fig 12; TiO2/Plastic cylinder catalysts (left) and Photocatalyst test (right) [37]

*M. Titration co-precipitation*

Mike Agbesi Acheampong and Duke Mensah Bonsu Antwi [38] worked on a titration co-precipitation approach followed by Titanium dioxide coating using the sol-gel method. Magnetic $Fe_3O_4$ nanomagnetic particles must be synthesized. By reducing phosphate, nitrate, and decolorizing methyl blue solutions, they tested numerous different produced $TiO_2/Fe_3O_4$ nanomagnetic particles with varied molar ratios of $TiO_2$ to $Fe_3O_4$. They discovered that $TiO_2/Fe_3O_4$ particles are good at removing phosphate, nitrate, and methyl blue from wastewater.

*N. Sol gel Method*

YONGFA ZHU, LI ZHANG[39] experimented on SOL-GEL method and found that Nanosized TiO2 powder with anatase structure is synthesized using TiCl4 ethanol solution as a precursor. And they also found that the formation of inorganic gel and anatase TiO2 nano particles can be promoted by increasing the gelatinizing time.

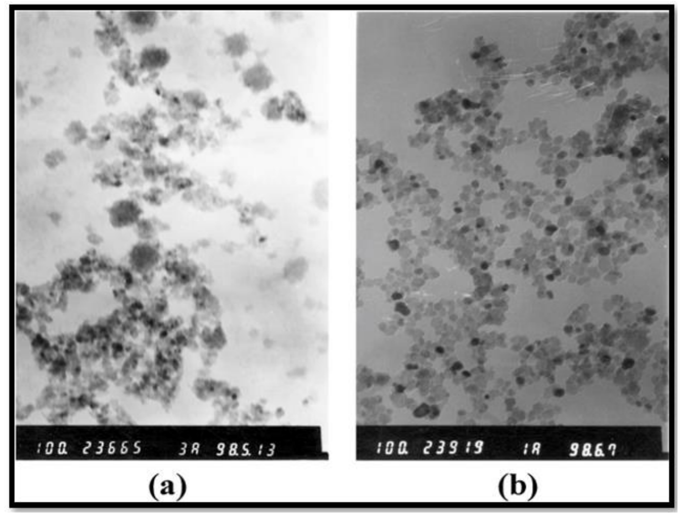


Fig 13 : The typical TEM photographs of TiO2 powder gelatinizing for various time and calcined for 1 hour at 400◦C.[39]

*O. Modified sol gel method*

Sanjay Gopal Ullattil and Pradeepan Periyat[40] explicitly stated about the basic principles of sol–gel processing and their advantages / disadvantages, concentrating on the synthesis of nanocrystalline $TiO_2$. And they also found that from the , three different crystal forms of $TiO_2$, anatase, rutile and brookite, more photo catalytically active anatase phase is usually converted into rutile phase at low temperature, limiting the high-temperature applications of anatase. And they found that anatase possesses high temperature stability compared to others forms.

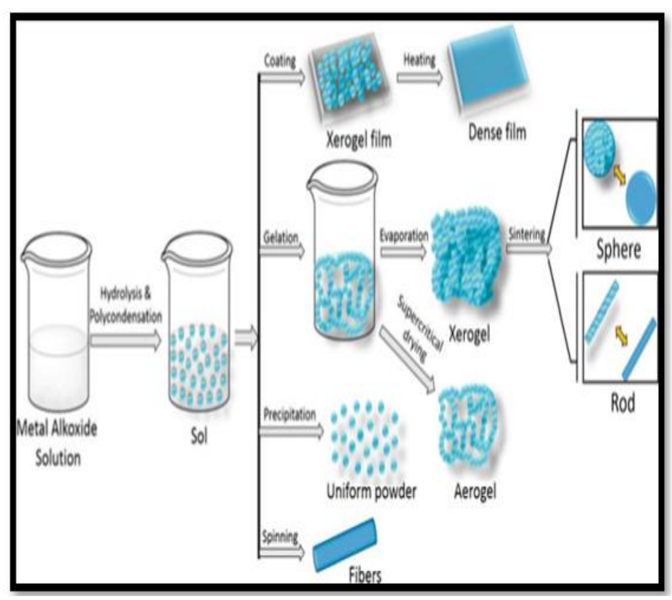


Fig 14: Schematic representation of sol–gel processing / Various Steps in Sol–Gel [40]Processing

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*P. Critical Review table*

**Table 2Different Methods for synthesis of Black TiO2 and their precursors and Performance**

| Name | Synthetic Route | Precursors | Performance | Ref |
|---|---|---|---|---|
| **Black $TiO_2$** | One pot gel combustion method | Titanium Butoxide and Diethylene glycol | The black $TiO_2$ is 33%more Photoactive than Degussa P-25 | |
| **$Ti^{+3}$ self doped $TiO_2$** | $NaBH_4$ Reduction | Tetra butyl titanate, $NaBH_4$, Ethanol and Nitric acid | For enhanced visible light absorption, $Ti^{+3}$ generation is responsible | [22] |
| **Black $TiO_2$** | Sol gel method | Tetra butyl titanate, CTAB ,Ethanol | $H_2$ generation of 620 μmol/g, which was three times higher than control $TiO_2$ (210 μmol/g), seen to be given by Black $TiO_2$ photocatalyst | [32] |
| **Reduced Black $TiO_2$** | Magnesiothermic reduction | Titanium chloride , Magnesium | The Black $TiO_2$ shows remarkable hydrogen production ability in the presence of Pt as a co-catalyst. And as compared to precious reported black this values are superior | [33] |
| **Hydrogenated Black $TiO_2$** | Hydrogenation | Titanium tetraisopropoxide, ethane, deionized water | As solar energy increased Hydrogen production increases. | [38] |
| **Black $TiO_2$** | Oxidation and calcination | $TiH_2$, $ZnCl_2$/KCl, ethanol | The Black titanium shows better photocatalytic activity than P25 | [22] |
| **Black $TiO_2$** | Anodization method | Titanium foils, Acetone, Ethanol | The black $TiO_2$ is 33%more Photoactive than Degussa P-25 | [24] |
| **Laser modified black $TiO_2$** | Ultrasonic treatment | Anatase $TiO_2$, distilled water | It absorb full visible light spectrum and thus exhibit good photocatalytic activity | [39] |
| **Black $TiO_2$** | Flame aerosol process | Titanium isopropoxide,silver acetate, 2-ethyl hexanoic acid, acetonitrile | Crystalline Ti-suboxide onto Ag nanoparticles supported on nano-structured exhibit strong activity under visible light | [28] |
| **Black $TiO_2$** | Hydrogenation | $TiH_2$, Ethanol | | [13] |
| **Ordered Mesoporous Black $TiO_2$** | Evaporation induced self assembly method | Tetrabutyl titanate, Ethanol ,HCl, Ethylenediamine | Ordered mesoporous Black $TiO_2$ has wide pore size and Surface area compared to Mesoporous white $TiO_2$ | [10] |
| **Coper doped $TiO_2$** | Complex Precipitation method | Copper nitrate trihydrate, Glycerol, Anatase $TiO_2$ | Catalyst prepared by 10% copper loading shows better activity than Wet impregnation method | [21] |
| **Black $TiO_2$** | Chemical vapor deposition assisted by Hydrogen plasma | P25 powder (Degussa),NaOH, HCl | Disordered layer is formed after hydrogen plasma treatment, in black $TiO_2$ which may be caused by numerous oxygen vacancies and Ti-H bonds | [33] |
| **Reduced Black $TiO_2$** | Facile hydrothermal Approach | $TiCl_3$, L- ascorbic acid, NaOH | When compared to the white (20.6 mol $g^1$ h1) and brown $TiO_2$ (38.9 mol $g^{-1}$ $h^{-1}$), the black $TiO_2$ has a far higher activity with a hydrogen evolution rate of 116 mol $g^{-1}$ $h^{-1}$. | [34] |
| **N doped yellow $TiO_2$** | Hydrolysis and Calcination | Titanium tetraisopropaxide, Urea | N-doped $TiO_2$ powders obtained by heating $Ti(OH)_4$ with urea exhibit similar activity to $TiO_2$ powders prepared by heating $TiO_2$ with Urea. which also responds on visible light. | [21] |

| | | | | |
|---|---|---|---|---|
| **Carbon modified $TiO_2$** | Hydrolysis, aging, drying and Calcination | Titanium tetrachloride, Tetra butyl ammonium hydroxide, Sodium hydroxide and Glucose | A good activity for degradation of 4-chlorophenol is exhibited by these photocatalyst which get well absorbed into visible to infrared region up to 800 nm. | [22] |
| **Black $TiO_2$** | Ultrasonication process | Titanium sulfate ,ammonia | $TiO_2$ prepared by this method with applying changes in structure and DOS of amorphous hydroxylated shows both activities such as solar driven and visible light driven | [23] |

## III. CONCLUSIONS

The synthesis, characteristics, alterations, and applications of $TiO_2$ nanoparticles have all been extensively studied in recent decades, yielding a large database. New features and applications with increased performance have been introduced thanks to advancements in $TiO_2$ nanomaterial production. We infer from our evaluation of studies that each synthesis method has its own unique and particular requirements that distinguish it from the others. as an example, The major benefits of the sol-gel method include the ability to prepare sols and gels at room temperature, high purity of precursors, product homogeneity, low sintering temperatures, and good control over powder particle size and form. Chemical reduction methods include reducing $TiO_2$ with active hydrogen species like hydrogen ions or hydrogen atoms with $H_2$ or $H_2$/Ar or hydrogen atoms with $N_2$, using high temperatures with active metals like aluminium, magnesium, and zinc powder, or reducing $TiO_2$ in solution with $NaBH_4$ and organic molecules like imidazole and ascorbic acid. It has been created a one-pot gel combustion of black anatase $TiO_2$-x self-doped with $Ti^{3+}$. Anatase $TiO_2$ nanocrystals include large $Ti^{3+}$ and oxygen vacancy sites, which have been thought to be important components for photocatalysis. According to the findings, black anatase $TiO_2$ had 33 percent more photoactivity than Degussa-P25, a widely available photocatalyst. The photocatalytic features of white $TiO_2$ include the fact that it cannot absorb visible light and so has a lower photo conversion efficiency. It has poor charge separation ability due to its short light response range and low efficiency.

## REFERENCES

[1]. R. Vinu and G. Madras, “Environmental remediation by photocatalysis,” Journal of the Indian Institute of Science, vol. 90, no. 2, pp. 189–230, 2010.
[2]. M. Schiavello and T. Scwe, “Photocatalysis Applications”.
[3]. A. Mills and S. le Hunte, “An overview of semiconductor photocatalysis,” vol. 108, no. 1997, pp. 1–35, 2000.
[4]. D. Chen, M. Sivakumar, and A. K. Ray, “Heterogeneous photocatalysis in environmental remediation,” Developments in Chemical Engineering and Mineral Processing, vol. 8, no. 5–6, pp. 505–550, 2000, doi: 10.1002/apj.5500080507.
[5]. K. Nakata and A. Fujishima, “Journal of Photochemistry and Photobiology C : Photochemistry Reviews TiO 2 photocatalysis : Design and applications,” vol. 13, pp. 169–189, 2012, doi: 10.1016/j.jphotochemrev.2012.06.001.
[6]. X. Chen, L. Liu, P. Y. Yu, and S. S. Mao, “Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals,” Science, vol. 331, no. 6018, pp. 746–750, 2011, doi: 10.1126/science.1200448.
[7]. A. Aguedach, S. Brosillon, J. Morvan, and E. Kbir, “Photocatalytic degradation of azo-dyes reactive black 5 and reactive yellow 145 in water over a newly deposited titanium dioxide,” vol. 57, pp. 55–62, 2005, doi: 10.1016/j.apcatb.2004.10.009.
[8]. P. Taylor and U. G. Akpan, “Desalination and Water Treatment Photocatalytic degradation of wastewater containing acid red 1 dye by titanium dioxide : effect of calcination temperature,” no. October 2012, pp. 37–41, doi: 10.1080/19443994.2012.672209.
[9]. Y. C. Chung and C. Y. Chen, “Degradation of Di-(2-ethylhexyl) phthalate (DEHP) by TiO2 photocatalysis,” Water, Air, and Soil Pollution, vol. 200, no. 1–4, pp. 191–198, 2009, doi: 10.1007/s11270-008-9903-9.
[10]. M. A. Lazar, S. Varghese, and S. S. Nair, “Photocatalytic water treatment by titanium dioxide: Recent updates,” Catalysts, vol. 2, no. 4, pp. 572–601, 2012, doi: 10.3390/catal2040572.
[11]. G. Ghasemzadeh, M. Momenpour, and F. Omidi, “Applications of nanomaterials in water treatment and environmental remediation,” 2014, doi: 10.1007/s11783-014-0654-0.
[12]. D. Suryaman and K. Hasegawa, “Biological and photocatalytic treatment integrated with separation and reuse of titanium dioxide on the removal of chlorophenols in tap water,” Journal of Hazardous Materials, vol. 183, no. 1–3, pp. 490–496, 2010, doi: 10.1016/j.jhazmat.2010.07.050.
[13]. C. Byrne, G. Subramanian, and S. C. Pillai, “Recent advances in photocatalysis for environmental applications,” Journal of Environmental Chemical Engineering, vol. 6, no. 3, pp. 3531–3555, 2018, doi: 10.1016/j.jece.2017.07.080.

[14]. W. Ren et al., "A Near Infrared Light Triggered Hydrogenated Black TiO2 for Cancer Photothermal Therapy," Advanced Healthcare Materials, vol. 4, no. 10, pp. 1526–1536, 2015, doi: 10.1002/adhm.201500273.

[15]. J. Mou, T. Lin, F. Huang, H. Chen, and J. Shi, "Black titania-based theranostic nanoplatform for single NIR laser induced dual-modal imaging-guided PTT/PDT," Biomaterials, vol. 84, pp. 13–24, 2016, doi: 10.1016/j.biomaterials.2016.01.009.

[16]. "Visible light active photocatalysts recent trends new."

[17]. W. Bahnemann, M. Muneer, and M. M. Haque, "Titanium dioxide-mediated photocatalysed degradation of few selected organic pollutants in aqueous suspensions," Catalysis Today, vol. 124, no. 3–4, pp. 133–148, 2007, doi: 10.1016/j.cattod.2007.03.031.

[18]. T. Dioxide, "Daylight Photocatalysis by Carbon-Modified Titanium Dioxide**," no. Sfb 583, pp. 4908–4911, 2003, doi: 10.1002/anie.200351577.

[19]. R. Baan, K. Straif, Y. Grosse, B. Secretan, F. el Ghissassi, and V. Cogliano, "Carcinogenicity of carbon black, titanium dioxide, and talc," The Lancet Oncology, vol. 7, no. 4, pp. 295–296, 2006, doi: 10.1016/S1470-2045(06)70651-9.

[20]. L. Liu, P. Y. Yu, X. Chen, S. S. Mao, and D. Z. Shen, "Hydrogenation and disorder in engineered black TiO2," Physical Review Letters, vol. 111, no. 6, pp. 1–5, 2013, doi: 10.1103/PhysRevLett.111.065505.

[21]. G. Zhu, J. Xu, W. Zhao, and F. Huang, "Constructing black titania with unique nanocage structure for solar desalination," ACS Applied Materials and Interfaces, vol. 8, no. 46, pp. 31716–31721, 2016, doi: 10.1021/acsami.6b11466.

[22]. W. Fang, M. Xing, and J. Zhang, "Environmental A new approach to prepare Ti 3 + self-doped TiO 2 via NaBH 4 reduction and hydrochloric acid treatment," Applied Catalysis B: Environmental, vol. 161, pp. 240–246, 2014, doi: 10.1016/j.apcatb.2014.05.031.

[23]. G. Zhu et al., "Hydrogenated blue titania with high solar absorption and greatly improved photocatalysis," Nanoscale, vol. 8, no. 8, pp. 4705–4712, 2016, doi: 10.1039/c5nr07953e.

[24]. G. Zhu et al., "Black Titania for Superior Photocatalytic Hydrogen Production and Photoelectrochemical Water Splitting," ChemCatChem, vol. 7, no. 17, pp. 2614–2619, 2015, doi: 10.1002/cctc.201500488.

[25]. M. Ye et al., "Synthesis of Black TiOx Nanoparticles by Mg Reduction of TiO2 Nanocrystals and their Application for Solar Water Evaporation," Advanced Energy Materials, vol. 7, no. 4, pp. 1–7, 2017, doi: 10.1002/aenm.201601811.

[26]. Z. Wang et al., "Visible-light photocatalytic, solar thermal and photoelectrochemical properties of aluminium-reduced black titania," Energy and Environmental Science, vol. 6, no. 10, pp. 3007–3014, 2013, doi: 10.1039/c3ee41817k.

[27]. A. Naldoni et al., "Effect of nature and location of defects on bandgap narrowing in black TiO 2 nanoparticles," Journal of the American Chemical Society, vol. 134, no. 18, pp. 7600–7603, 2012, doi: 10.1021/ja3012676.

[28]. J. Xu, Z. Hong, G. Zhu, T. Lin, F. Huang, and J. Wang, "Molten salt assisted synthesis of black titania hexagonal nanosheets with tuneable phase composition and morphology," RSC Advances, vol. 5, no. 104, pp. 85928–85932, 2015, doi: 10.1039/C5RA17558E.

[29]. C. Fan et al., "Black Hydroxylated Titanium Dioxide Prepared via Ultrasonication with Enhanced Photocatalytic Activity," Scientific Reports, vol. 5, no. 1, pp. 1–10, 2015, doi: 10.1038/srep11712.

[30]. T. Leshuk, S. Linley, and F. Gu, "Hydrogenation processing of TiO2 nanoparticles," Canadian Journal of Chemical Engineering, vol. 91, no. 5, pp. 799–807, 2013, doi: 10.1002/cjce.21745.

[31]. M. Coto et al., "Tuning the properties of a black TiO 2 - Ag visible light photocatalyst produced by a rapid one-pot chemical reduction," Materials Today Chemistry, vol. 4, pp. 142–149, 2017, doi: 10.1016/j.mtchem.2017.03.002.

[32]. T. Wang, W. Li, D. Xu, X. Wu, L. Cao, and J. Meng, "A novel and facile synthesis of black TiO 2 with improved visible-light photocatalytic H 2 generation: Impact of surface modification with CTAB on morphology, structure and property," Applied Surface Science, vol. 426, pp. 325–332, 2017, doi: 10.1016/j.apsusc.2017.07.153.

[33]. F. Teng et al., "Preparation of black TiO 2 by hydrogen plasma assisted chemical vapor deposition and its photocatalytic activity," Applied Catalysis B: Environmental, vol. 148–149, pp. 339–343, 2014, doi: 10.1016/j.apcatb.2013.11.015.

[34]. I. B. Butler, M. A. A. Schoonen, and D. T. Rickard, "Removal of dissolved oxygen from water: A comparison of four common techniques," Talanta, vol. 41, no. 2, pp. 211–215, 1994, doi: 10.1016/0039-9140(94)80110-X.

[35]. E. M. Saggioro et al., "Use of Titanium Dioxide Photocatalysis on the Remediation of Model Textile Wastewaters Containing Azo Dyes," pp. 10370–10386, 2011, doi: 10.3390/molecules161210370.

[36]. L. S. Yoong, F. K. Chong, and B. K. Dutta, "Development of copper-doped TiO2 photocatalyst for hydrogen production under visible light," Energy, vol. 34, no. 10, pp. 1652–1661, 2009, doi: 10.1016/j.energy.2009.07.024.

[37]. N. S. Leyland, J. Podporska-Carroll, J. Browne, S. J. Hinder, B. Quilty, and S. C. Pillai, "Highly Efficient F, Cu doped TiO2 anti-bacterial visible light active photocatalytic coatings to combat hospital-acquired infections," Scientific Reports, vol. 6, no. April, pp. 1–10, 2016, doi: 10.1038/srep24770.

[38]. L. M. S. Colpini, H. J. Alves, O. A. A. dos Santos, and C. M. M. Costa, "Discoloration and degradation of textile dye aqueous solutions with titanium oxide catalysts obtained by the sol-gel method," Dyes and Pigments, vol. 76, no. 2, pp. 525–529, 2008, doi: 10.1016/j.dyepig.2006.10.014.

[39]. P. Dong et al., "Plasmon enhanced photocatalytic and antimicrobial activities of Ag-TiO2 nanocomposites under visible light irradiation prepared by DBD cold plasma treatment," Materials Science & Engineering C, p. #pagerange#, 2018, doi: 10.1016/j.msec.2018.11.005.

[40]. S. G. Ullattil and P. Periyat, "Green microwave switching from oxygen rich yellow anatase to oxygen vacancy rich black anatase TiO2 solar photocatalyst using Mn(II) as 'anatase phase purifier,'" Nanoscale, vol. 7, no. 45, pp. 19184–19192, 2015, doi: 10.1039/c5nr05975e.