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Chapter

Mechanistic Understanding of Stability and Photocatalytic Efficiency of Titanium Dioxide Nanomaterials in Aquatic Media: A Sol-Gel Approach

Saptarshi Ghosh and Manoranjan Sahu

Abstract

Titanium dioxide (TiO_2) nanoparticles enhance the intrinsic value of commercial products like various cosmetics, paints, self-cleaning products, etc. Several research on the fabrication of TiO_2, stabilization of TiO_2 to retain its nanometric scale and increasing the inherent property of the material (i.e., photocatalytic) is ongoing for the last few decades. Still, the synthesis of highly efficient, stable, reproducible and cost-effective TiO_2 nanoparticles remains a grand challenge for the researchers and scientific community. Further research is needed to develop an in-depth understanding of synthesis, aggregation kinetics and efficiency to improve the performance of TiO_2 nanomaterial for the degradation of persistent organic pollutants (POPs). In this book chapter, we have summarized the synthesis process using the sol-gel pathway followed by its stability behavior and photocatalytic activity in the aqueous solutions. This study also highlighted the effects of various process variables such as pH, catalyst concentration, inorganic species etc. in the photocatalytic performance of TiO_2 nanoparticles. Finally, we have reviewed various strategies that have been performed for increasing the photocatalytic efficiency of TiO_2 by overcoming its limitations.

Keywords: doping, DLVO theory, photocatalysis, sol-gel process, TiO_2 nanoparticles

1. Introduction

Titanium is a transition metals having electronic configuration $3d^2 4S^2$. In nature, it is mainly available in the form of ilmenite ($FeTiO_3$) and binary metal oxides [1]. In a binary metal oxide form, Titania has three phases: anatase, brookite and rutile [2]. For the commercial purposes, anatase phase of titanium dioxide is largely used. It was found that, at high temperatures brookite and anatase phases transform to rutile, which is the most stable form of TiO_2. Now, as compared to bulk material, nano-structured TiO_2 has showed unique optical [3], electronic [4] and catalytic properties [5]. Due to these special properties, the interest for nanostructured titanium dioxide

has grown to use it in various applications such as photocatalysis, paint pigments [6], cosmetics, personal care products [7], sensors, water and air purification, etc.

1.1 Processes for synthesis of nanomaterials

Nanomaterials synthesis processes can be broadly classified into top-down and bottom-up processes. In the bottom-up synthesis process, nanomaterials are synthesized from basic building units like, atoms or molecules. Whereas, in top-down approach, bulk materials are broken down into smaller counter parts. Top-down synthesis includes processes such as laser ablation, sputtering and grinding, ball milling, etc. In last few decades, use of nanomaterials have tremendously increased in several industries such as paint, cosmetics, catalyst, etc. In this regard, various synthesis process has been implemented and followed for fulfilling the industrial demand for nanomaterials. The commonly used nanomaterials synthesis processes are as follows:

a. Condensation process: it is a bottom-up synthesis process in which nanoparticles are synthesized through flame pyrolysis.

b. Chemical vapor deposition: a process in which thin film is deposited onto a substrate through chemical reactions of the gaseous precursors.

c. Mechanical milling: it is a top-down process where nanoparticles are synthesized by breaking down of larger molecules into smaller units of nanometer range by the effect of mechanical device called mill.

1.2 Sol gel process for TiO$_2$ synthesis

At laboratory scale, sol-gel is the most commonly used process for nanomaterials synthesis. It is a bottom-up process in which a colloidal suspension is formed by dispersing solid particles in a liquid called a Sol and agglomerate together to form a continuous three-dimensional network extending throughout the liquid called a gel. Generally, a sol-gel process is based on following steps [8]:

i. Hydrolytic polycondensation: it is the first step in a sol-gel process in which a sol is formed by the hydrolysis of alkoxide precursors.

ii. Gelation: at gel point, uniform suspension starts forming by deposition of substrate into the sol known as gel and the process is gelation.

iii. Drying: drying is performed to remove the liquids from the gel and a major change to the network structure may occur. The gel structure is maintained by forming aerogel in which air is replacing the liquid. Similarly, a xerogel is formed by normal drying in which gel structure collapses because capillary forces drawing the walls of the pores together and reducing the pore size. Cracking may occur when the tension in the gel is so large that it cannot shrink anymore.

iv. Calcination: it is a thermal treatment in which very high temperature is employed to crystallize the nanomaterials by removing organics and volatile substances.

2. Stability of nanomaterials

To retain the properties of nanomaterials, one of the biggest challenges is the agglomeration of nanoparticles. The stability of nanomaterials depends on two opposite forces; one being the electrostatic repulsive force and second is van der Waals forces of attraction. Deryaguin-Landau-Verwey-Overbeek (DLVO) theory first gave this concept of opposite forces in a suspension. According to DLVO theory, particle stability depends on particle to particle and surface to particle interactions but, it varies for nanomaterials of different structures and heterogeneity. The DLVO theory does not consider all these factors, which make the calculation of nanomaterials stability more challenging. The potential energy of interaction due to the Van Der Waals force is given by the expression

$$V_a = \frac{-A}{6}\left[\frac{2a^2}{S(S+4a)} + \frac{2a^2}{S(S+2a)^2} + \ln\frac{S(S+4a)}{S(S+2a)^2}\right]$$

where A is the Hamaker constant, a is the particle radius, and s is the separation distance between the particle surfaces [9]. The Hamaker constant indicates the strength of mutual attraction between two colloidal particles and depends on material properties, and was 4×10^{-20} J for TiO_2 [10]. Similarly, potential energy between particles due to electrostatic repulsion is expressed as follow

$$V_r = 2\pi\varepsilon_0\varepsilon_r a\zeta^2 \ln\left(1 + e^{-ks}\right)$$

where $\varepsilon_0\varepsilon_r$ is the dielectric permittivity of the medium, ζ is the potential at the surface of the particle, and k is the Debye length (reciprocal of double layer thickness). Now, the total potential energy is calculated as $V_t = V_\alpha + V_r$. Another drawback of DLVO theory is that it did not considered hydration and Born forces in calculation [9].

Now, when nanoparticles are entered into the environment, due to influence of various physicochemical factors and environmental conditions, they got agglomerated and with time these agglomerates might transformed into strong aggregates or rather loose agglomerates. Various studies reported that mobility of TiO_2 in porous media is affected by various factors such as pH of the medium, ionic strength, presence of Natural Organic matters (NOMs), etc. [11, 12]. It was observed that with rise in pH, the mobility of TiO_2 nanoparticles increases whereas ionic strength promotes the retention of nanoparticles in porous media. The reason for the retention at higher ionic concentration is because of enhanced agglomeration resulting into greater retention.

Similarly, Brownian motion is another important factor of colloids or nanoparticles for collisions with each other. The reasons for such collisions might be due to attractive forces or repulsive forces. In the colloidal systems, the dominant attractive force is Van Der Waals forces and to maintain the stability, an adequately strong repulsive force is required to neutralize the van der Waals attractions. In general, in a colloidal systems stability was achieved by the addition of surfactants [13], polymers [14] and/or electrostatically.

2.1 Stability of TiO_2 suspensions

One of the major limitations of TiO_2 nanoparticles in the suspension was its agglomeration because it reduces the surface area of nanoparticles resulting into
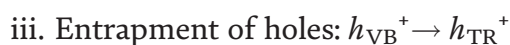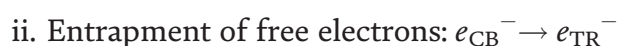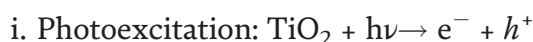
reduction in catalytic performance [15]. Thus, it is important to identify and study the role of different parameters which significantly contributes towards agglomeration of TiO_2 nanoparticles. Various parameters influence the stability of nanoparticles such as, ionic strength, pH, concentration of NPs, sticking coefficient, etc. But, predominantly it is the surface charge which controls the stability of nanoparticles. In particular, if the particles have a zeta potential more than ±30 mV, they are considered stable [16]. However, addition of salts in a solution increases the ionic strength and promotes the attraction with opposite charge particles hence, their sticking efficiency increases. Basically, salt ions will reduce the thickness of electrostatic double layer and allows particles to come closer to each other by attractive forces and forms agglomerates [17]. In addition, collisions between particles also promotes aggregation and the Brownian motion is the driving force to bring collisions among nanoparticles in the aqueous medium. Another parameter affecting the stability of nanoparticles is the pH of the medium. Now, depending on the pH value, surface ionization happens and it controls the surface charge of metal oxides present in water, including TiO_2.

3. Titanium dioxide nanoparticles as photocatalyst

TiO_2 nanoparticles have been considered and studied widely as one of the most effective photocatalyst for the oxidation of organic pollutants [18]. It is because of its thermodynamic stability, nontoxicity, economically cheap and have higher photocatalytic performance comparing to other semiconductors [19]. The crystalline phases of TiO_2 are anatase, rutile and brookite. Among these three, the most active form of TiO_2 is anatase because of its high adsorptive rate (active sites), high hole trapping capacity and most thermally stable crystal phase of TiO_2. TiO_2 has an energy gap (E_{bg}) of 3.2 eV for anatase type and it performs both oxidation as well as reduction. However, TiO_2 is active only under UV region ($\lambda < 390$ nm) and the earth's solar spectrum have around 5% of that. Thus, it performs limited photocatalysis in the visible regions.

3.1 Mechanisms of photocatalysis

The photocatalysis by TiO_2 favors both oxidation (valence band) and reduction (conduction band) on its surface, typically in the band edges. In a TiO_2 or in other semiconductor, the highest occupied molecular orbital is separated from the lowest unoccupied molecular orbital by an energy band gap (E_{bg}). When the photocatalyst comes under the light irradiation that have the energy greater than or equal to the band gap, the photoexcitation takes place as illustrated in **Figure 1**. It transfers the electron from the valence band of a semiconductor to the conduction band of a semiconductor, leaving behind a hole in the valence band [20]. This ultimately forms a positively charged hole and an electron i.e., electron-hole pairs or exciton. These photogenerated charged pairs have a strong tendency to recombine, it may be a surface recombination or volume recombination. Thus, if we can reduce the recombination of these electron-hole pairs, it can create a chain of photochemical reactions as stated below [21]:
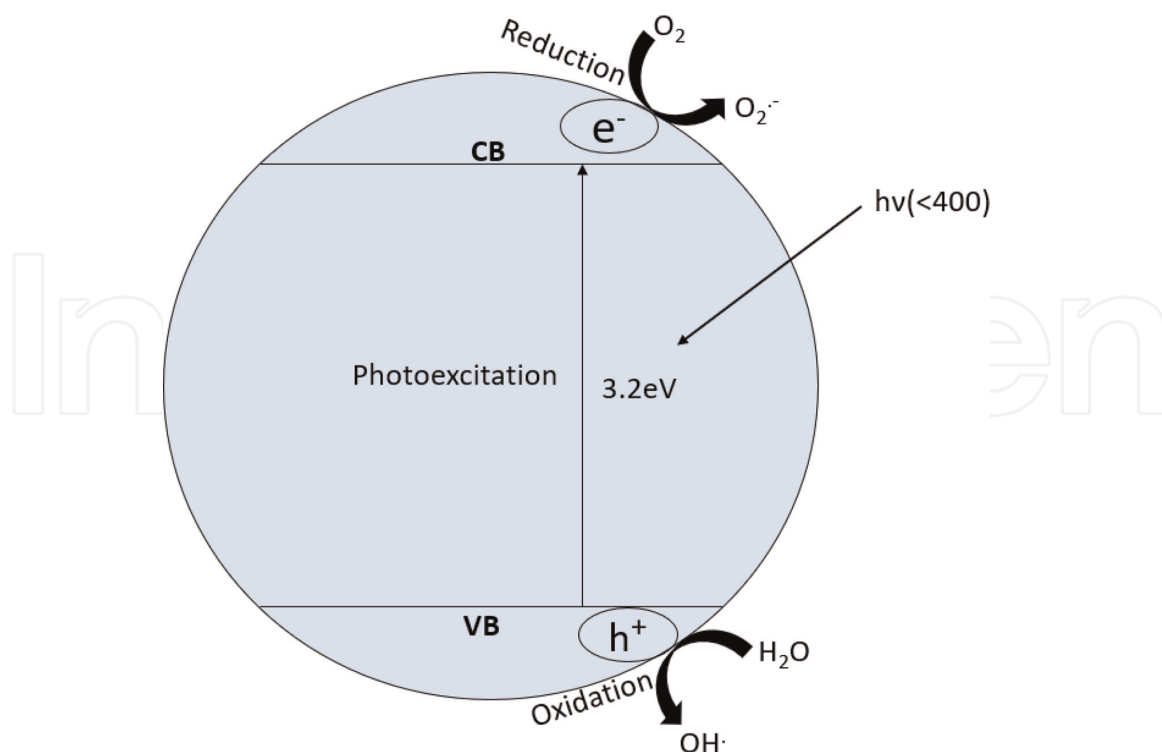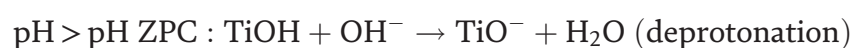
i. Photoexcitation: $TiO_2 + h\nu \rightarrow e^- + h^+$

ii. Entrapment of free electrons: $e_{CB}^- \rightarrow e_{TR}^-$

iii. Entrapment of holes: $h_{VB}^+ \rightarrow h_{TR}^+$

Figure 1.
Mechanisms of reactive oxygen species (ROS) generation by TiO$_2$ under illumination.

    iv. Charge carrier recombination: $e_{TR}^{-} + h_{VB}^{+} \rightarrow e_{CB}^{-} + \text{heat}$

    v. Photoexcited electro scavenging: $(O_2)_{ads} + e^{-} \rightarrow O_2^{-}$

    vi. Oxidation of hydroxyls: $OH^{-} + h^{+} \rightarrow OH^{\cdot}$

    vii. Photodegradation by OH$^{\cdot}$ radicals: $\text{R-H} + OH^{\cdot} \rightarrow R'^{\cdot} + H_2O$

3.2 Factors influencing photocatalysis

3.2.1 Effect of pH

For the metal oxide like TiO$_2$ the surface charge may be positive or negative due to amphoteric behavior. Zero Point Charge (ZPC) represents the pH in which the catalyst does not have any charge on the surface. Various literature concluded that the ZPC of TiO$_2$ comes around 6–8 [22]. If the system is acidic (pH < pH ZPC), the catalyst protonated to gain positive charge on the surface and consecutively attracts negatively charged pollutants, but for alkaline conditions (pH > pH ZPC), the catalyst deprotonated to gain negative charge on the surface and favors the attraction of positively charged contaminants. The chemical transformation of TiO$_2$ with pH is as follows:

$$\text{pH} < \text{pH ZPC} : \text{TiOH} + H^{+} \rightarrow \text{TiOH}_2^{+} \ (\text{protonation})$$

$$\text{pH} > \text{pH ZPC} : \text{TiOH} + OH^{-} \rightarrow \text{TiO}^{-} + H_2O \ (\text{deprotonation})$$

Hence, pH is one of the important factors that controls photocatalysis.

3.2.2 Effect of catalyst concentration

The efficiency of photocatalysis was depends on the concentration of the photocatalyst used, but the performance rates was independent of the concentration above a certain limit because of the complete absorption of light energy by the photocatalyst [23]. Adding catalyst more than its optimum concentration causes excessive scattering of irradiating radiation. Similarly, if the photocatalyst concentration is less than its optimum level then the generation of charged species was inadequate due to lack of availability of active sites.

3.2.3 Effect of inorganic species

Presence of inorganic species can alter the photocatalytic process in various ways. Species like H_2O_2, $S_2O_8^{2-}$, etc. can improve the photocatalytic removal of pollutants by acting as electron trappers, thus enhancing the synthesis of $OH^{\cdot}$ and other reactive oxygen species. But, the excessive loadings of inorganic species can reduce the photocatalytic process by taking up the $OH^{\cdot}$ from the system. The photocatalytic efficiency of TiO_2 decreases with the availability of inorganic species like, $FeCl_2$, $Fe_2(SO_4)_3$, Na_2SO_4 and Na_2CO_3 because they alter the pH of the solution and also the active sites of the catalyst blocked by adsorption of ionic species. Ions that represent color in a solution can prevent the entry of light into the solution and decreases the photocatalytic process. Hence, ionic strength of a solution plays a prominent role in controlling the photocatalytic activity and pre-treatment was needed to achieve optimum photocatalytic treatment.

3.2.4 Effect of morphology of photocatalyst

Photocatalyst with various shape and size do not shows the exact photocatalytic behavior because of the dissimilarity in surface areas, charge transfer capacity and associated properties of the catalyst. It was reported that the photocatalytic performance is highly dependent on the morphologies and dimensions of the photocatalyst. The varied structure of the catalyst includes nanosphere, nanotubes, and nanosheets. All these structures show some peculiar properties that can enhance the photocatalysis. The zero-dimensional nanosphere have the high surface area where as the interconnected pore structure and shorter carrier-diffusion paths in three dimensional nanocubes and nanotubes helps in the movement of charged species. Hence, the morphology of the nanomaterial has a fascinating role in the photocatalytic processes and it is better to perform the experiment after modifying its shape. Future research work is needed to study the performance by changing the shape of the photocatalyst.

3.3 Modification of TiO_2 nanoparticles

TiO_2 has certain limitations and to improve the photocatalytic performance of TiO_2 various doping and nanocomposite strategies have been used. Recently, modifications of TiO_2 with carbon-based materials such as activated carbon, carbon nanotubes (CNT), [60]-fullerene and Graphene have received much attention to overcome the limitations of limited surface area. The mechanisms and strategies behind different

doping patterns and nanocarbon-TiO_2 systems such as AC-TiO_2, CNT-TiO_2 and Graphene-TiO_2 nanocomposites are discussed in the below sections.

3.3.1 Doping

Doping means addition of impurities within the crystal lattice to extend its absorption to a longer wavelength. Doping may be cationic or anionic that can replace the atoms within the crystal lattice and creates structural defects. It also restricts the recombination of photo-induced charged carriers. Anionic dopants are considered to be useful for modification of TiO_2 because the p-orbitals of oxygen will interact with the p-orbitals of other anions and ultimately narrows down the band gap. Similarly, metal doping can stop the recombination of electron and hole pairs because the photo-excited charged species tends to move to the metals (electron traps). For cationic doping transition metals are generally preferred because they have a range of oxidation states. Thus, doping of TiO_2 by metal or non-metal brings reduction in the recombination rate of the excitons and promotes the absorption to longer wavelength. TiO_2 can be made visible light-active either by introducing structural defects such as Ti^{3+} and oxygen vacancies or by incorporation of non-metals such as N, C, and S, and transition metal ions. The various strategies of band gap modification are represented as follows:

3.3.2 Formation of localized energy states

Doping with non-metal, such as N, C, F, S and B extends the light adsorption of TiO_2 towards the visible light region and thus enhances the photocatalytic activity. Among all the non-metal doped TiO_2, nitrogen doped TiO_2 has been found to exhibit superior photocatalytic activity under visible light irradiation. As shown in **Figure 2**,
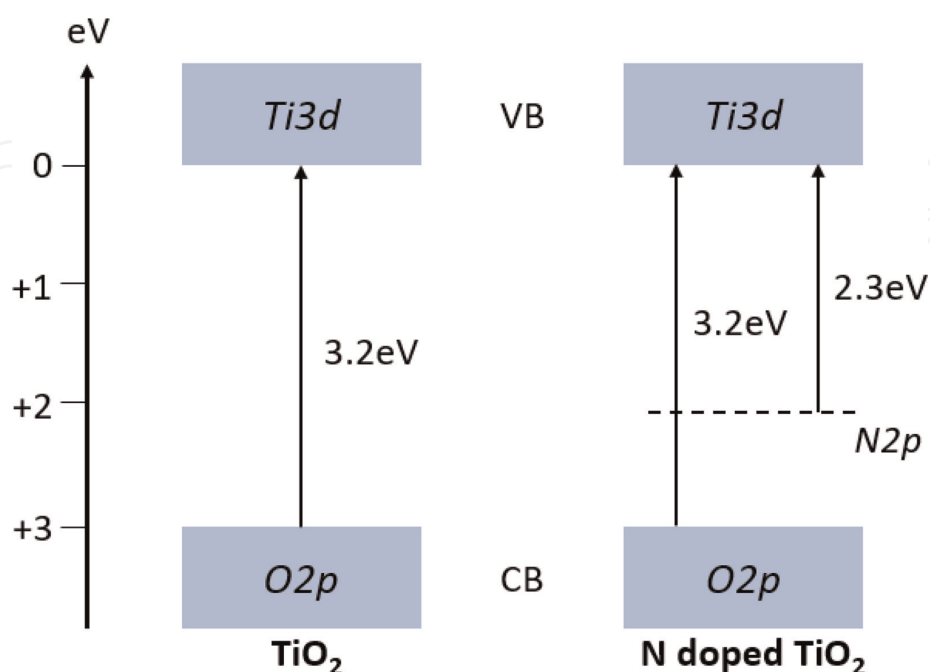

Figure 2.
Mechanism of band gap modification in nitrogen doped TiO_2. Modified and adapted from Ref. [24].

the ionic size of nitrogen was quite similar with the size of oxygen so that the orbital interactions (O2p orbital and N2p orbital) happens smoothly. And as the energy level for nitrogen was less than the oxygen, it forms a localized dopant state above the valence band of TiO_2 and helps in the shifting of the absorption range from UV to visible [24].

3.3.3 Broadening of valence band

The broadening of valence band mainly happens through the co-doping. TiO_2 co-doped with different elements, has attracted tremendous attention in the field of photocatalysis. Some studies reported that TiO_2 co-doped with appropriate elements could exhibit a much higher photocatalytic activity than any singly doped photocatalyst, because of the existence of synergistic effects between the doping elements. As soon as two different doping elements will be present in the TiO_2 matrix, their respective 2p orbital energy levels will both contribute to the creation of new energy states within the TiO_2 band gap in a synergetic manner. As compared to other non-metal elements, the co-doping of titanium dioxide with carbon and nitrogen (**Figure 3**) has been found to exhibit synergistic effect in a most pronounced manner resulting in a considerable visible light response of the respective co-doped materials [25].

3.3.4 Formation of color centres

Color centres give rise to formation of intra band gap energy states due to partial reduction of TiO_2. Color centres forms due to oxygen vacancy as well as electron vacancy in a metal oxide like TiO_2. Due to the loss of an O atom in a metal oxide the electron pair that remains trapped in the cavity V_O (reaction 1) left behind gives rise to an F centre (reaction 2), whereas a positively charged F^+ centre is equivalent to a
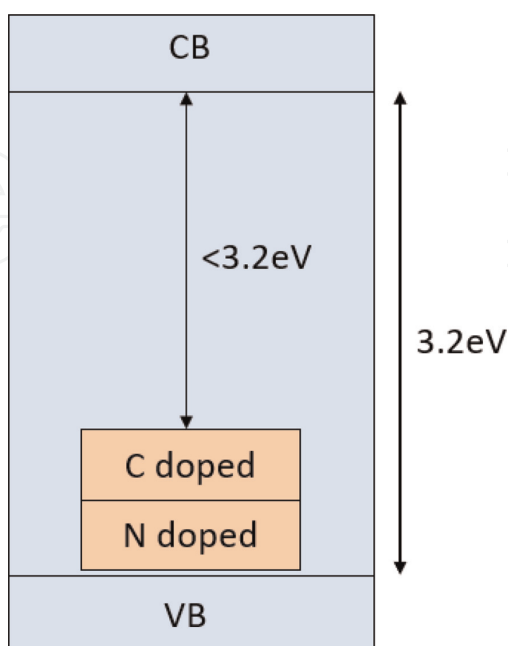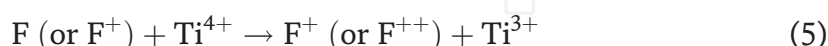

Figure 3.
Formation of new energy bands leading to thickening of VB in C—N co-doped TiO_2 Photocatalysts. Modified and adapted from Ref. [25].

single electron associated with the O vacancy (reaction 3). The electron-pair deficient oxygen vacancy, also known as an anion vacancy V_A, is referred to as a doubly charged F^{++} centre (reaction 4). Hence, the Color centres associated with oxygen vacancies are the F, F^+, and F^{++} centres in TiO_2. The electrons left in the V_O cavity can also interact with adjacent Ti^{4+} ions to give Ti^{3+} centres (reaction 5).

$$O^{2-} \rightarrow O + V_o + 2e^- \tag{1}$$

$$V_o + 2e^- \rightarrow F \tag{2}$$

$$V_o + e^- \rightarrow F^+ \tag{3}$$

$$V_o \rightarrow \{V_A \text{ or } F^{++}\} \tag{4}$$

$$F \text{ (or } F^+) + Ti^{4+} \rightarrow F^+ \text{ (or } F^{++}) + Ti^{3+} \tag{5}$$

And, this Ti^{3+} (d^1) centres has a tendency to create a distortion within the crystal lattice called Jahn-Teller distortion that brings the electronic transition ($^2T_2 \rightarrow {}^2E$) in the crystal lattice as demonstrated in **Figure 4** and shifts the absorption into visible range [26].

3.3.5 Nanocomposite

TiO_2 based photocatalysis is one of the important catalytic process that can mineralizes the organic pollutant as well as the biological pollutant. But it suffers from low efficiency due to: (i) wide band gap (only activated under UV spectrum), (ii) very high recombination rate of photogenerated charged pairs, (iii) less surface area for the adsorption of pollutants. Now, the idea behind bringing composite of carbonaceous nanomaterials for improving the TiO_2 photocatalysis was to solve the limitations of TiO_2 and to promote forward reaction and adsorption of reactants through provision of adequate quality and quantity of active sites [27]. Various types of carbonaceous
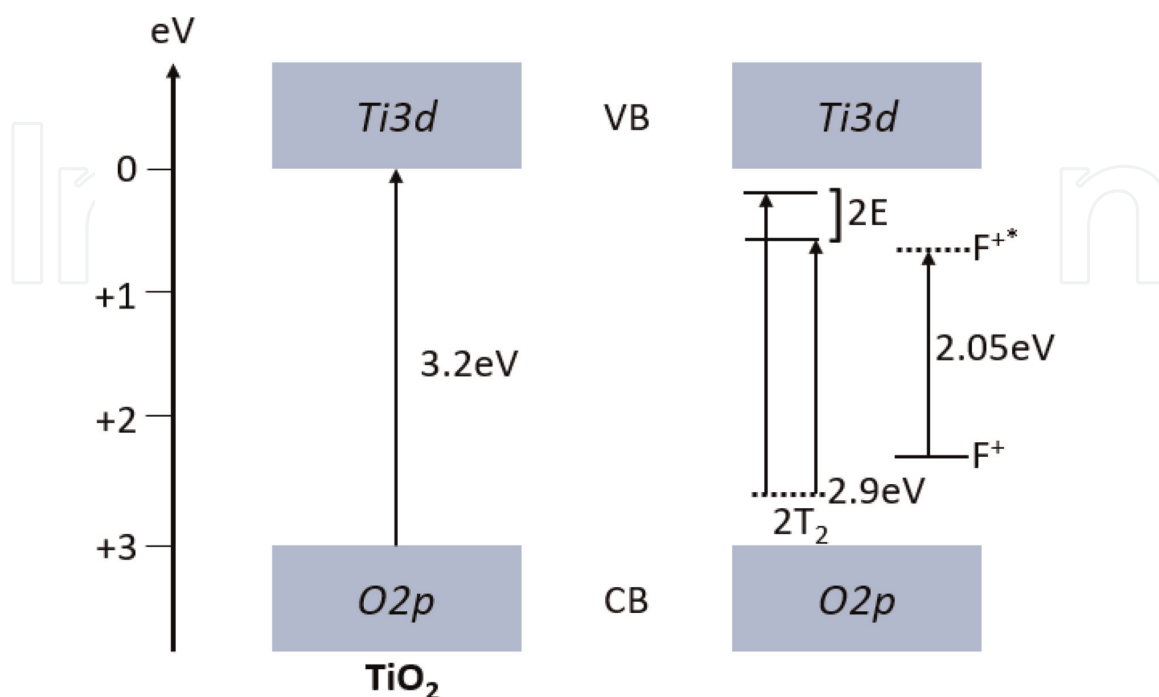

Figure 4.
Formation of color centre in TiO₂. Modified and adapted from Ref. [26].

nanomaterials that are studied to make photocatalytic support (TiO_2-nanocarbon composite) are activated carbon, carbon nanotubes (CNT), and most importantly graphene which are discussed below.

3.3.6 Activated carbon-TiO$_2$ composites

Activated carbon is highly used because it is cheap, inert and easy to manufacture. Activated carbon possesses a porous amorphous structure with porosity spanning macro (>25 nm), meso (1–25 nm) and micro (<1 nm) pore ranges. The fundamental benefit of activated carbon is to provide a high surface area (typically 900–1200 m^2 g^{-1}) over which TiO_2 particles may be distributed and immobilized. The activated carbon support on TiO_2 particles increases the photocatalytic effect by synergistic effect. The synergistically enhanced photocatalytic activity was due to the adsorption of reactants on activated carbon followed by mass transfer to photoactive TiO_2 through the common interface between two. Activated carbon does not chemically interact with TiO_2, unless additional constituents are added to the system. So basically, activated carbon improves the photocatalytic process by adsorbing pollutants [28].

3.3.7 Carbon nanotubes (CNT)-TiO$_2$ composites

Carbon nanotubes may be single walled (SWCNTs) or multi walled (MWCNTs) having specific surface area of 400–900 m^2 g^{-1} and 200–400 m^2 g^{-1} respectively [28]. In addition to the high surface area, the surface chemistry of CNTs may be functionalized (incorporation of alcoholic group, ketonic group, carboxyl group, etc.) to promote specificity towards target pollutant. This represents an advantage over activated carbon, which are basically non-selective and therefore have a lower pollutant degradation rate due to breakdown of both target and neutral species. CNTs are widely reported to synergistically enhance the photocatalytic performance of TiO_2 through the retardation of electron-hole recombination as follows:

I. CNTs are capable of forming Schottky barriers at the CNT-TiO_2 interface, where there is a space charge region. And, TiO_2 is a n-type semiconductor but in the presence of a CNT, the photogenerated electron may move freely towards CNT surface, which may have a lower Fermi level. Thus, CNTs act as an electron sink and the excess holes in the Valence band of TiO_2 migrate to the surface and reacts. The TiO_2 now behaving as a P-type semiconductor. The high electrical conductivity and electron storage capacity (one electron for every 32 carbon atoms) makes CNT as highly effective electron sinks [28].

II. CNTs may enhance the TiO_2 activity by acting as a photosensitizer, transferring electrons to the TiO_2. This may be the reason behind the extending TiO_2 photocatalytic activity to a longer wavelength. In this mechanism the photogenerated electrons in the CNTs is transferred into the conduction band of TiO_2, promoting a reduction process (formation of superoxide anion by the adsorbed molecular oxygen). The positively charged CNTs then remove an electron from the valence band of TiO_2, leaving a hole. The positively charged TiO_2 then takes part in oxidation process with organic pollutants and water to form hydroxyl radicals.

3.3.8 Graphene-TiO$_2$ composites

Graphene is a single layered (one atom thick or thin) with a 2-D hexagonal structure arranged in a honeycomb lattice [29]. The sp^2 hybridized carbon atoms have delocalized π-bonds that improves the structural stability and current conductivity. Graphene has high electron mobility, acts as an adsorbent and promotes ballistic transport, meaning that electrons can travel without scattering, making them electron sinks or ideal electron transfer bridges. These unique properties of the graphene plane are mainly due to its long polyaromatic π-electron systems and coordinative unsaturated terminal carbon atoms. It has an energy band gap of 0 eV because it's filled valence bands touches the empty conduction bands in a certain point called Dirac point, thus giving rise to a new band [30]. Most importantly, graphene is chemically inert and highly stable under conditions where maximum substances would undergo rapid phase transformation and chemical reactions [29, 31, 32].

It was reported that graphene and its derivatives have been successfully used in designing nanocomposite systems for their excellent performance in photocatalysis. These functional nanomaterials have been used in designing photocatalyst systems because of their excellent electron transfer properties, which help to prevent recombination of photoexcited charge carriers in metal oxides (TiO$_2$). These also help in establishing good interaction of target molecules to the surface of the TiO$_2$ nanomaterials due to their adsorption behavior [33]. In summary, adsorption, conductivity, tuning of band gaps and very large planar structure of graphene plays a critical role for photodegradation of various kinds of pollutants over graphene-TiO$_2$ composites.

4. Conclusions

This book chapter covered various nanomaterials synthesis processes specifically sol-gel process, stability of nanomaterials in suspension and the photocatalytic process. Various parameters affecting the photocatalytic efficiency of TiO$_2$ in an aqueous medium is discussed. In addition, the chapter discusses various types of strategies that have been followed to improve the photocatalytic efficiency of TiO$_2$ and also highlighted the current strategies that have been performed. The book chapter clearly indicates that due to distinctive properties like, optical, electronic and catalytic, nanostructured TiO$_2$ becomes fascinating material for research. It is widely used in various environmental applications like disinfection, catalysis, sensing, etc. and for that extensively used in several industries. Thus, it is important to develop cost effective synthesis processes to support the industrial demands. Additionally, TiO$_2$ suffers from certain limitations such as aggregation, wide bandgap, recombination of excitons, etc. which need to be addressed through research and development of technology to enhance its catalytic efficiency so that it can resolve emerging environmental problems.

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Conflict of interest

The authors declare no conflict of interest.

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