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TiO_2 Based Photo-Catalysis for Virus Disinfection ⋆

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Abstract

This review considers the current literature that is focused on the interface nanostructure/cell-wall microorganism to understand the annihilation mechanism. In this report, photocatalysis is discussed for viral disinfection including TiO_2 photocatalysis and other metal-containing photocatalysis. TiO_2 based materials and its composites, metal-TiO_2 systems, TiO_2 heterojunction systems with other semiconductors, and TiO_2 systems with graphene and other carbonaceous materials are discussed in detail. Some practical uses of titanium dioxide for photocatalytic disinfection processes for the effective prevention/eradication of microorganisms, considering the resistance that the microorganism could develop without the appropriate regulatory aspects for human and ecosystem safety are also discussed.

Keywords: Nanostructure; Microorganism; Photocatalysis; TiO_2; Heterojunction; Composites

1 Introduction

Many illnesses including fever, heart problems, hepatitis, paralysis, respiratory infections are caused by viruses. Viruses have a less infectious quantity of < 10–10^3 particles in comparison with bacterial pathogens and a significant high illness risk of 10-10 000 times under a similar level of exposure [1]. Unfortunately, viruses are difficult to be physically removed due to their small sizes and unique surface properties [2]. Following section describes some disinfection techniques.

Free chlorine is the most commonly used for water treatment and has good viral inactivation properties. The main drawback of chlorination is the formation of mutagenic and carcinogenic disinfection byproducts (DBPs). These DBPs contribute to the recontamination and salting of fresh water sources [3]. Another commonly used disinfection method is the ozonation. It is also unstable in water and undertakes reactions with some water matrix components. The main advantage of ozone is that it decomposes into hydroxyl radicals (·OH), which are strong

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oxidants in water [4], that make the ozonation more effective than Cl_2 against bacterial cells and viruses [5]. Like chlorination, ozonation can also produce DBPs in the presence of organic matter e.g. aldehydes, carboxylic acids and ketones [6]. In recent years, germicidal UV has gained more attraction for water disinfection, as low-pressure UV creates practically no disinfection byproducts [7]. UV according to irradiation wavelengths are divided into UVA (315-400 nm), UVB (280-315 nm), UVC (200-280 nm) and vacuum UV (VUV) (100-200 nm). For microorganism inactivation, UVC is the most effective one. UVC light destroys irradiated DNA, directly inducing pyrimidine and purine dimers and pyrimidine adducts. UVC intensity of 7 mJ/cm^2 inactivates bacteria cells by 99% for water disinfection. The susceptibility of protozoa to UVC damage is similar to that of bacteria; thus, 99% inactivation for Cryptosporidium can be achieved at 5 mJ/cm^2 [8].

2 Photocatalysis for Viral Disinfection

According to general description of thermal catalysis, photocatalysis is a process in which speeding up of a photoreaction takes place by the presence of a catalyst, which shows that both light and a catalyst are needed to cause or to accelerate a chemical transformation [8]. As the photoreaction takes place in more than one homogeneous medium, it is usually called "heterogeneous photocatalysis".

Semiconductor photocatalysis has been used for inactivation of organic pollutants and has gained attraction by the researchers [9]. Among the first developers of photocatalytic viral disinfection were Sjogren and Sierka, who carried out TiO_2 based photocatalysis to inactivate Escherichia virus MS2 [10]. Subsequently many researchers has carried out disinfection of water by TiO_2 and TiO_2 based photocatalysis [8]. In order to achieve more antiviral effects, metal based photocatalysts are also being used. Metal-free photocatalysts are also gaining interest from researchers as these are found ample in nature and are low cost, sustainable and safe.

Cho et al. [10] discovered different inactivation kinetics of bacteria and viruses and observed that the virus MS2 was stronger than the bacterium E. coli due to the difference in the surface structures of both. It was learned that intensive oxidation was required to denature the virus structure. Fujishima and Honda [11] carried out the photocatalytic splitting of water on TiO_2 electrodes and this led to the beginning of heterogeneous photocatalysis [8] subsequently leading to the marvelous research activities to understand the fundamental process of heterogeneous photocatalysis [12]. Many researchers have observed the effectiveness of TiO_2 photocatalysis for water disinfection [13].

Rapid recombination of charge carriers is the main disadvantage of TiO_2 which lowers its photocatalytic behavior. To overcome this, many techniques such as the morphological control and the formation of heterojunction systems with other components like metals, semiconductors and carbonaceous materials have been adopted [9]. Several studies indicated the alteration means such as single doping, co-doping and impregnation with different metal and non-metal ions to increase TiO_2 photocatalytic performance and photoactivity in the visible light region [14, 15].

3 Fundamental Mechanism for TiO_2 Photocatalysis

Titanium dioxide (TiO_2) in heterogeneous photocatalysis has been gaining interest from researchers in recent years [16]. Nanocrystalline TiO_2 is found in three major polymeric forms

including rutile, anatase and brookite [17]. Whereas anatase and rutile have tetragonal crystal structures even though they do not belong to the same phase groups, on the other hand brookite has an orthorhombic structure and the uncommon TiO_2 phase is monoclinic [18]. In pure TiO_2, anatase phase shows higher catalytic ability and electron mobility than either the rutile or brookite phases and hence more beneficial for photovoltaic and photocatalytic applications [17]. The semiconductor TiO_2 is being used as a photocatalyst for creating a number of reductive and oxidative reactions on its surface. Photocatalytic reaction mainly depends on wavelength or light energy and the catalyst. When the light falls on the surface of a semiconductor TiO_2 and if the photon energy (hv) is equivalent or greater than the band gap energy of semiconductor usually 3.2 eV (anatase) or 3.0 eV (rutile) [19], lone electron will be excited to the empty conduction band in femtoseconds [19] thus forming a positively charged electron hole. The electron holes induce oxidation process and electrons condition the reduction process. The electron holes react water molecules or hydroxide ions (OH^-) forming hydrogen peroxide (H_2O_2) molecules or hydroxyl radicals ($\cdot OH$). Electrons react with molecular oxygen (O_2) forming superoxide anion radicals ($\cdot O_2^-$). The Reactive Oxygen Species (ROS) destroy the organic pollutants, bacteria and viruses and convert organic matter to CO_2 and H_2O. Fig. 1 shows the mechanism of TiO_2 irradiation process.

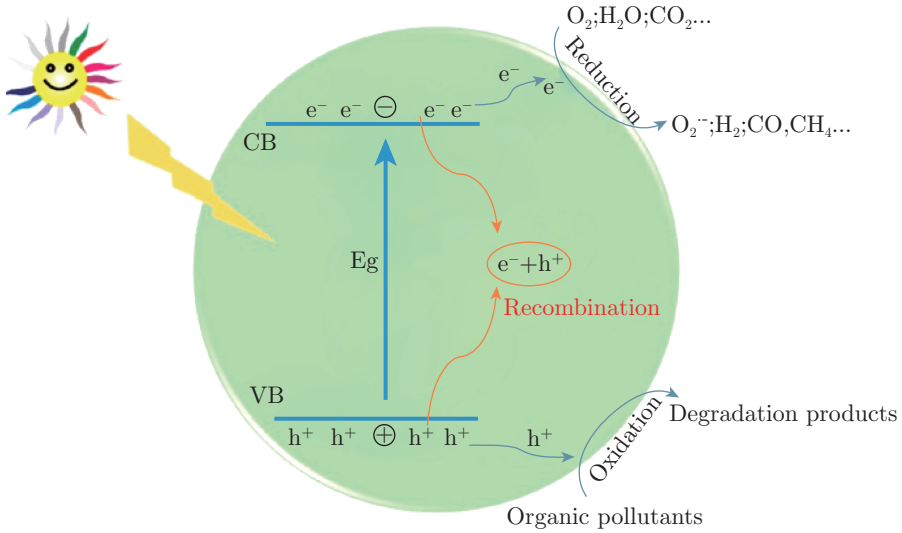

Fig. 1: Schematic diagram of photocatalysis process [20]

The series of chain oxidative-reductive reactions that occur at the photon activated surface was widely postulated as follows [19]:

$$\text{Photoexcitation: } TiO_2 + hv \rightarrow e^- + h^+ \tag{1}$$

$$\text{Charge-carrier trapping of } e^- : e^-_{CB} \rightarrow e^-_{TR} \tag{2}$$

$$\text{Charge-carrier trapping of } h^+ : h^+_{VB} \rightarrow h^+_{TR} \tag{3}$$

$$\text{Electron-hole recombination: } e^-_{TR} + h^+_{VB}(h^+_{TR}) \rightarrow e^-_{CB} + \text{heat} \tag{4}$$

$$\text{Photoexcited } e^- \text{ scavenging: } (O_2)_{ads} + e^- \rightarrow OH\cdot \tag{5}$$

$$\text{Oxidation of hydroxyls: } OH^- + h^+ \rightarrow OH\cdot \tag{6}$$

$$\text{Photodegradation by } OH\cdot : R - H + OH\cdot \rightarrow R^{/} + H_2O \tag{7}$$

$$\text{Direct photoholes: } R + h^+ \rightarrow R^+ \rightarrow \frac{\text{Intermediate(s)}}{\text{Final}} \text{Degredation Products} \tag{8}$$

$$\text{Protonation of superoxides: } O_2^{\cdot -} + OH\cdot \rightarrow HOO\cdot \quad (9)$$

$$\text{Co-scavenging of } e^- : HOO\cdot + e^- \rightarrow H_2O^- \quad (10)$$

$$\text{Formation of } H_2O_2 : HOO^- + H^+ \rightarrow H_2O_2 \quad (11)$$

The e^-_{TR} and h^+_{TR} in (Eq. (4)) represent the surface trapped valence band electron and conduction-band hole respectively. It was reported that these trapped carriers are usually TiO_2 surface bounded and do not recombine immediately after photon excitation [19]. In the absence of electron scavengers (Eq. (4)), the photo excited electron recombines with the valence band hole in nanoseconds with simultaneous dissipation of heat energy. Thus, the presence of electron scavengers is vital for prolonging the recombination and successful functioning of photocatalysis. (Eq. (5)) depicts how the presence of oxygen in prevents the recombination of electron-hole pair, while allowing the formation of superoxides radical ($O_2^{\cdot -}$). This $O_2^{\cdot -}$ radical can be further protonated to form the hydroperoxyl radical ($HO_2^{\cdot}$) and subsequently H_2O_2 as shown in (Eqs. (9) and (10)), respectively. The $HO_2^{\cdot}$ radical formed was also reported to have scavenging property and thus, the co-existence of these radical species can doubly prolong the recombination time of the h^+_{TR} in the entire photocatalysis reaction. However it should be noted that all these occurrences in photocatalysis were attributed to the presence of both dissolved oxygen (DO) and water molecules. Without the presence of water molecules, the highly reactive hydroxyl radicals ($OH^{\cdot}$) could not be formed and delay the photo degradation of liquid phase organics. This was evidenced from a few reports that the photocatalysis reaction did not proceed in the absence of water molecules [19].

4 Other Metal-containing Photocatalysts

Despite TiO_2 based photocatalysts, there have been a number of metal containing visible light photocatalysts including plasmon induced viral inactivation by Ag-AgI/Al_2O_3 [21] And Pt-WO_3 [22]. Giannnakis et al. found three types of iron oxides namely Wustite, Maghemite, and nano-Maghemite for photocatalytic antiviral activity under visible light irradiation [23].

5 TiO_2 Based Materials and Its Composites

There have been a number of studies on photovoltaic disinfection based on TiO_2, including bacteria, viruses, fungi, algae and others [24]. However, the biggest disadvantage of TiO_2 is the rapid restoration of its charge carriers, which considerably confines photocatalytic behavior. In this regard, a number of strategies have been proposed to enhance the photoactivity, such as morphological control and the formation of heterojunction systems with other components such as metal, semiconductors and carbonaceous materials.

6 TiO_2 Based Materials and 0D-3D Systems

It is notable that the photocatalytic execution of TiO_2 relies strongly on its size and morphology. Other précised morphologies have indicated extraordinary exhibitions for the photocatalytic eradication of pathogenic microorganisms. For example, the nanotube architecture shows good

performance in the destruction of microorganisms because of its inherent features such as huge surface to volume ratio and improved light harvesting [25]. The arrangement of self-organized TiO_2 nanotube arrays is typically brought out through a traditional anodization measure utilizing titanium foil as substrate [9]. Hierarchical structures, for example, nanorod spheres have been accounted for the destruction of Escherichia coli and Staphylococcus aureus [26]. Complex hierarchical structures like 3D dendritic microspheres based on rutile TiO_2 nanoribbons as well have been studied for antibacterial applications [27].

Other TiO_2 based nanostructures like titanate nanotubes have been utilized for disinfection purposes [28, 29]. Generally, these protonated nanotubes are set up through hydrothermal technique under alkaline conditions and utilizing TiO_2 as precursor [30].

7 Metal Doped TiO_2 Systems

Different metal ions are doped in TiO_2 in order to increase its photocatalytic activity [31, 32]. Metal ions when doped with TiO_2 change the corresponding energy level structure as the metals are more active, and electrons can be excited easily thus resulting in a broader range of absorption in a TiO_2 system [33-35]. Electrons generated by TiO_2 excitation can be captured by the metals as it is shown in figure. Furthermore, electrons inside TiO_2 can not return to the original state as metal ions act as a carrier trapping center. Metal ions higher than tetravalent are more effective to capture electrons than titanium ions and metal ions lower than tetravalent trap holes. In this way, metal doping improves TiO_2 photocatalytic efficiency [36, 37].

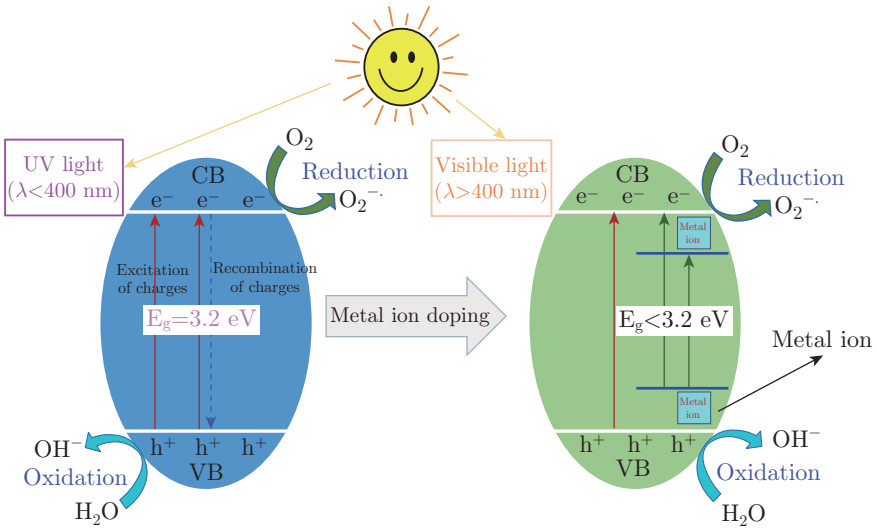

Fig. 2: Schematic diagram of metal ion doping TiO_2 [38]

Various studies have stated the adjustment of TiO_2 by methods for single doping, co-doping and impregnation with different metal and nonmetal ions to increase its photocatalytic execution as well as to exhibit photoactivity in the visible light region [14, 30]. In this sense, doping with cations/anions in the crystal structure of TiO_2 is utilized to make intra band gap states close to the edges of the conduction (CB) and valence (VB) bands causing absorption in the visible light area [39]. N-doped TiO_2 has been accounted for in the photocatalytic elimination of microorganisms such as Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, Shigella flexneri,

Listeria monocytogenes, Vibrio parahaemolyticus and Acinetobacter baumannii [40, 41]. On the other hand, the deposition of metal nanoparticles on the surface of TiO_2 additionally represents an efficient approach in the photocatalytic improvement of this metal. The contact between the metal nanoparticles and the surface of a semiconductor can make an electric field encouraging an interfacial process of electron transfer from the photo-excited semiconductor to the deposited metal [9].

Precious metal materials having large radius can be easily deposited on the surface of TiO_2 particles and can serve active trap for electrons with a certain amount of precious metals deposited [42-44]. Figure 3 shows the transfer of electrons from the surface of $TiO_2$with a higher Fermi level to the surface of the precious metal with a lower Fermi level. With the two surfaces Fermi levels equal, the electrons will no more be transferred thus forming a Schottky barrier. This barrier excellently separate photogenerated electron hole pairs and improve the photocatalytic activity of TiO_2 [45-47].

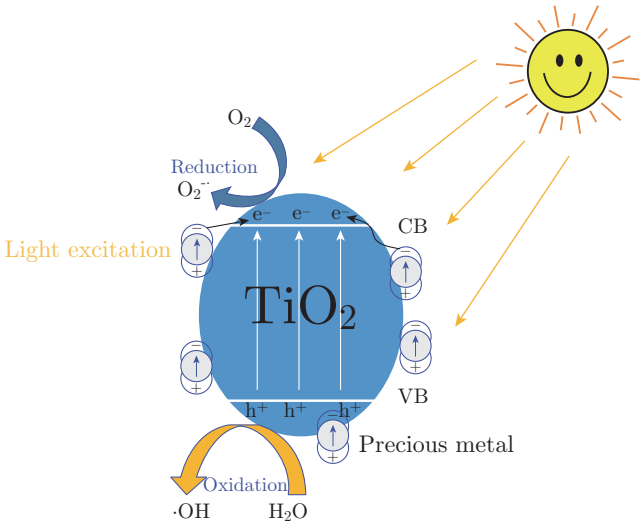

Fig. 3: Diagram of precious metal materials deposition [38]

Among the metals put down in TiO_2, silver is one of the attractive metals. Keeping in view the interesting properties of the silver, the Ag-TiO_2 composites have been utilized in the removal of a large number of microorganisms [48-52]. Copper is another metal broadly utilized in combination with Titanium Dioxide for antimicrobial purposes. This metal alone exhibits good antibacterial and antiviral properties since copper ions can penetrate across their cell membrane [53, 54]. Other metal-TiO_2 systems utilizing Au, Pt and Pd have been studied for the photocatalytic destruction of microorganisms [55-58].

8 TiO_2 Heterojunctions with Semiconductors

The arrangement of heterojunction systems is normally completed to give the spatial separation of the photogenerated charge carriers in the catalysts, considerably improving the photocatalytic execution compared with photoactivity shown with the pristine semiconductors. In an overall manner, two semiconductors display a nearby contact shaping heterostructures dependent on the physical junction of their particles. In this sense, as indicated by the valence (VB) and conduction

(CB) band capacities of the semiconductors, there are three kinds of heterojunction systems which are shown in Figure 4.

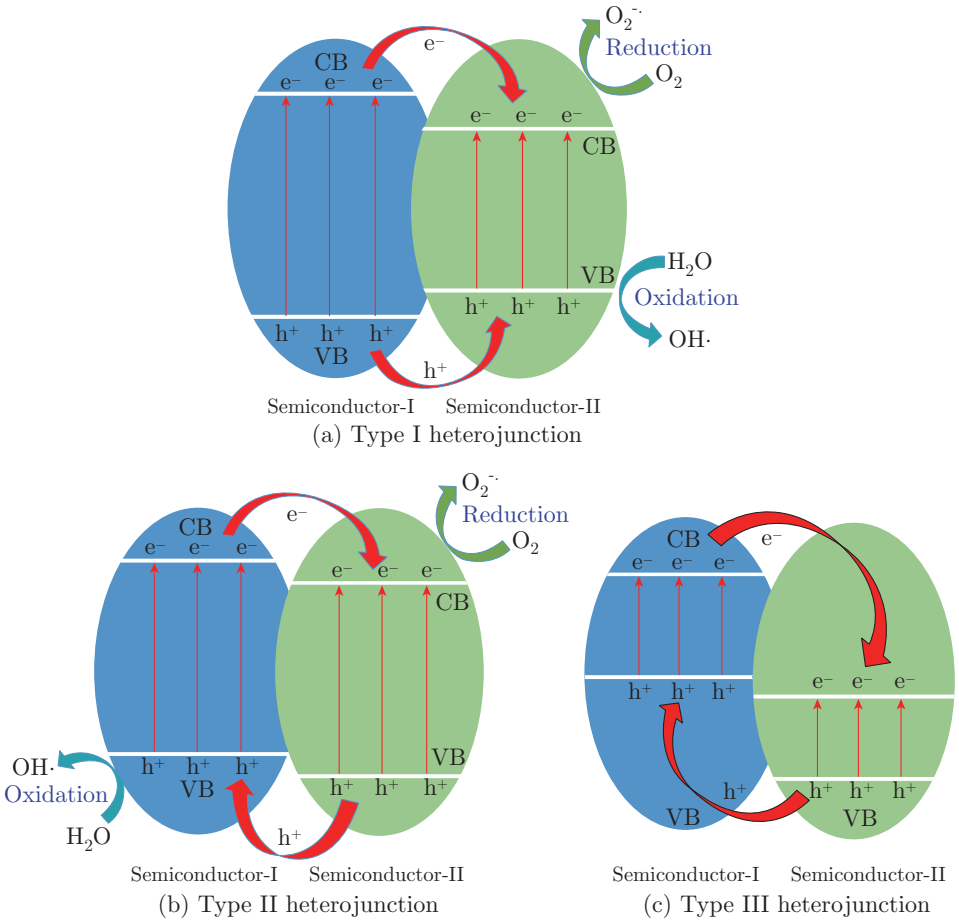

Fig. 4: Two semiconductors based heterojuction systems [38]

A type-1 heterpjunction consists of two semiconductors with semiconductor A having higher conduction band edge than that of semiconductor B. Likewise, the top of the VB of semiconductor A displays a lower value than the top edge of the VB of semiconductor B. Under this arrangement, the hole-electron pairs photogenerated in the semiconductor B move to the semiconductor A which serves as a recombination point for these charge carriers. Thus the heterojunction type I usually displays a poor photocatalytic performance. In type II heterojunction, the bottom edge of the conduction band of the semiconductor A is more negative in comparison with the bottom of the CB of the semiconductor B. Conversely, the top edge of the VB of semiconductor B has a more positive potential than the VB of semiconductor A. These differences are responsible for providing the efficient transfer of the photogenerated charge carriers between the semiconductors thus decreasing their recombination and increasing the photocatalytic performance of the joined system. Type III heterojunction displays a band formation similar to that of type II, however, the difference in the potentials of the VB and CB is more prominent. This formation is usually known as Z-scheme heterojunction, where a Z-shaped transport path is carried out [59]. Moreover, a photocatalytic Z-scheme system can be sought out either directly or indirectly depending upon how an electron mediator is necessary to achieve the transfer mechanism.

TiO_2 has been generally studied in the formation of heterogeneous systems with different semi-

conductors for the destruction of organic pollutants, hydrogen production from water splitting and for CO_2 photo-reduction [60, 61]. Nevertheless, only a few TiO_2 coupled systems have been studied for photocatalytic didinfection of microorganisms. The graphitic carbon nitride (g-C_3N_4) is a polymer semiconductor having good photocatalytic abilities with its use for hydrogen production through the water splitting process reported in last decade [62]. In recent times, the g-C_3N_4/TiO_2 hybrid system has been reported for the photocatalytic disinfection of E. coli bacteria under visible light irradiation [63]. The dose of the hybrid system was 0.6 g/L [63]. In this study, the concentration of the potassium ions (K^+) gradually increased with the increase of photocatalytic treatment time. Since the outflow of potassium ions is connected with the permeability of the cell membrane, this phenomenon shows the effective annihilation of the E. coli bacteria in g-C_3N_4/TiO_2 heterojunction system. Other coupled systems between TiO_2 and ZnAl layered double hydroxide (LDH), NiO, WO_3, Cu_xO_y, In_2O_3, Fe_2O_3, and $NiFe_2O_4$ have been studied as well for the photocatalytic inactivation of microorganisms [64-68].

There have been some ternary systems that have been reported as well for the destruction of pathogenic microorganisms. Usually these systems consist of two photoactive materials shaping a binary heterojunction and a third component that is responsible for the efficient charge transfer between both semiconductors like zero-valent metals (Ag, Cu) as well as layered materials with high electron mobility [69]. In this sense, the Cu-ZnO/TiO_2 system has been studied for the degradation of bacterial colonies of E. coli and S. aureus under visible light irradiation. The ternary Ag/AgX/TiO_2 system (X=Cl, Br, I) has also been used in photocatalytic disinfection process [69, 70]. Besides, other more complex systems have been reported, where every component assumes a specific role in the hybrid composite, thus expanding the photocatalytic performance of the overall system [71-73].

9 TiO_2 Systems with Graphene and Other Carbonaceous Materials

Graphene as a photocatalytic material has gained great interest since it was first reported by Novoselov in 2004 [74]. Grapheme is composed of one atom thick layer of sp^2 hybridized carbon atoms forming six member rings arranged in a two dimensional hexagonal lattice [75]. Graphene exhibits ballistic transport and this characteristic makes it suitable for coupling with TiO_2 thus increasing photocatalytic properties of the semiconductor and reducing the recombination rate of the photogenerated charge carriers. In this sense, grapheme/TiO_2 and reduced grapheme oxide/TiO_2 have been used in cleansing process of water polluted with pathogenic microorganisms [76-79]. As indicated by the mechanism revealed, the photoexicited electrons in TiO_2 can be transported to the π-π conjugated network of the grapheme, thus increasing the efficiency of the photocatalytic process.

For disinfection process, single-walled (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) in conjunction with TiO_2 forming composites have also been reported [80]. According to Kongkan and Kamat, SWCNTs in contact with photoirradiated TiO_2 can store up to one electron per 32 carbon atoms [81]. Thus the photogenerated electrons in TiO_2 can be transferred and stored in the CNTs. Because of CNTs high electron accepting properties, they can delocalize these charge carriers and increasing the photocatalytic performance of TiO_2. Other carbon based materials like carbon quantum dots (CQDs), have also been combined with TiO_2 for the destruc-

tion of microorganisms. The CQDs display intriguing properties such as photoinduced electron transfer, up and down conversion photoluminescence and electron storage [82, 83].

For the photocatalytic inhibition of E. coli bacteria, activated carbon supported TiO_2 nanoparticles (TiO_2/AC) have been reported [84, 85]. The chitosan, another carbonaceous material, has also been utilized in the preparation of TiO_2 nanocomposites for the inactivation of E. coli and S. aureus [86]. The assimilation of carbon atoms within the crystal structure of TiO_2 gives a prolonged absorption to the visible light range and an efficient separation of the photogenerated charge carriers [87]. The least complex method for doing the preparation of C-doped TiO_2 is the use of carbohydrates, such as glucose and sucrose as carbon precursors [88]. Thus, the incorporation of the carbonaceous species in TiO_2 happens during the calcination process of the organic precursors.

10 Applications of TiO_2 Based Photocatalysis

In recent years, the use of TiO_2 for photocatalytic decontamination has been extended for commercial applications. The most common use is the exclusion of bacteria in aqueous systems [89]. Photocatalytic treatment technology uses the hydroxyl radical (·OH) that deeply oxidize and decompose organic pollutants into non toxic inorganic small molecules [90]. Simultaneously, it also successfully eradicates heavy metal ions. TiO_2 thin films have been utilized in many everyday commodities from industries like food, construction, environmental, medical etc. Coating of textile materials with photoactive materials in order to clean and remove pathogenic microorganisms is another eco friendly application that can be exploited commercially. Numerous textiles, for example, cotton, rayon and polyester can be coated or grafted with TiO_2 with the help of sol-gel, reflux, dip-coating, spin-coating methods. The strong oxidative ability of TiO_2 can damage the textile fibers if both TiO_2 and textile fibers are in direct contact. To escape this problem, spatial hindrances that prevent decomposition of fibers are created by blending photocatalysts with materials such as silica (SiO_2) and apatite [91].

11 Conclusion

Photocatalysis with the ability of forming electron hole pairs and creating band gap excitation makes it favorable for disinfection purposes. In this regard, TiO_2 is one of the most promising. The main problem of photocatalysis is the rapid charge recombination and back reaction and difficulty in using visible light efficiently. During the previous years, attention has been given to the development of modified TiO_2 with the aim of achieving new properties and improved performance. This review gives an overview of the fundamental mechanism of TiO_2 based photocatalysis, and its modification with other materials. Metal doped TiO_2 systems, TiO_2 heterojunction with other semiconductors and TiO_2 systems with grapheme and other carbonaceous materials have described briefly.

Acknowledgement

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