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Carbon Based Titania Photocatalysts†

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Photocatalytic degradation has always been an active field of research interest for scientific studies, which started almost three decades ago. Photocatalysis, not only is considered to be a promising method to revert the detrimental effects of organic pollutants, dyestuff and various other pollutants in air and water, but also has emerged as a promising way for the fabrication of semiconductor devices, solar cells, *etc*. So far photocatalytic purification of water by irradiation of titanium dioxide (TiO_2) particles has proven to be an effective way of mineralization of pollutants. Carbon based titania photocatalyst demonstrated its excellent photocatalytic activity and has been increasingly investigated for further improvement. This review highlights the photocatalytic effect of TiO_2 as well as the use of carbon based substances like, activated carbon, activated carbon fiber, fullerenes (C_{60}), carbon nanotubes, graphene as support materials for TiO_2 photocatalysis.

Key Words: Carbon, Titanium dioxide, Photocatalyst.

INTRODUCTION

In recent times, environmental pollution and ways to mitigate it, has become one of the biggest investigating concerns for many scientists all over the world. Numerous industrial effluents for example dyestuff from textile and paint industries, various inorganic and organic wastage from petroleum industries, chemical industries, *etc*., are been carelessly released into the natural water sources and air, that are causing severe environmental degradation and taking a toll on nature and humans alike. Various methods have been suggested to handle the removal of the effluents from water *viz*., biodegradation, coagulation, adsorption, advanced oxidation methods and the membrane process[1-6]. In the last decade, advanced oxidation methods have been widely used in the treatment of wastewater since they are able to handle the problem of organic pollutant destruction in aqueous solutions[7-9]. The most attractive feature of advanced oxidation methods is that this highly potent and strongly oxidizing radical allows the destruction of a wide range of organic chemical substrate with no selectivity. Titanium dioxide (TiO_2), has emerged to be an popular choice for heterogeneous catalysis in environmental purification treatments.

Photocatalysis is defined as an acceleration of a photochemical reaction in the presence of a catalyst. The photocatalytic activity of a photocatalyst greatly depends on its ability to create electron hole pairs, which generates free radicals that undergoes further reactions to degrade various organic, inorganic effluent. An ideal photocatalytic material should be an amalgamation of the following properties: (i) high efficiency in solar energy conversion; (ii) high activity regarding the relevant process of interest; (iii) biologically and chemically non-toxic, inert and stable over long periods; (iv) easily processable and available.

Photocatalytic degradation assisted by TiO_2: Titanium oxide absorbs light having an energy level higher than that of the band gap energy (3.0 eV for rutile type; 3.2 eV for anatase type), the electrons in the valence band (referred as excitation) to the conduction band. Consequently, a number of electron holes are created in the valence band due to this excitation, inducing strong oxidative and reductive processes. The electron holes act as powerful oxidants and electrons act as powerful reductants and initiate a wide range of chemical redox reactions, which can lead to complete mineralization of dyes, organic contaminants and other harmful and toxic substances (Fig. 1).

Need of support materials for photocatalyst: TiO_2 powder has the authoritative ability to photodegrade the pollutant molecules when radiated with UV radiation. If titania powder is dispersed in a pool of polluted water under sunlight conditions, it will degrade the pollutant in the water[10]. However,

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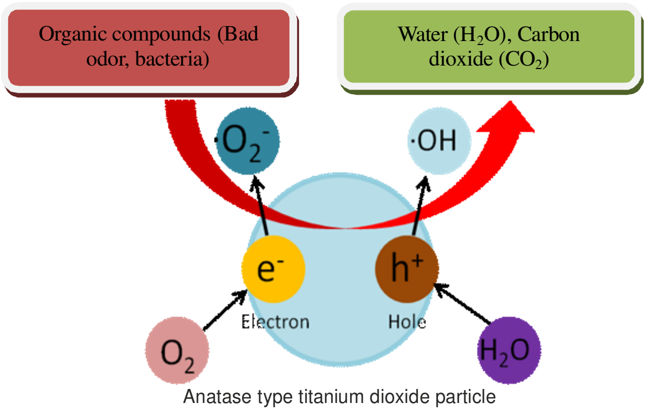

Fig. 1. Schematic representation of the oxidation process of titanium dioxide

researchers[11] have discovered that during the photodegradation process, interaction by certain pollutant molecules or their intermediates could cause the TiO_2 powder to coagulate, thereby reducing the amount of UV radiation from reaching the TiO_2 active centers (due to reduction of its surface area) and thus reducing its catalytic effectiveness. In order to overcome this coagulation problem, some researchers have used different materials as a support for the titania photocatalyst. Various substrates have been used as a catalyst support for the photocatalytic degradation of polluted water. For example glass mesh, glass fabric, glass wool[12], glass beads[13] and glass reactors[14-17] were commonly used as a support for titania. Other uncommon materials such as microporous cellulosic membranes[18] *e.g.*, alumina clays[19], ceramic membranes[20,21], monoliths[22,23], zeolites[24] and even stainless steel[25] were also experimented as a support for TiO_2. Many more materials were investigated to be used as a support for titania, but only some were mentioned above. The necessary criterions for the selection of catalyst support material are as follows:

(i) The supporting material must have the capability of being transparent or at least allow UV radiation to pass through it; (ii) It should be chemically inert and non reactive to pollutant materials, its intermediates and the surrounding aqueous system; (iii) It should have a high surface area and a strong adsorption affinity towards the pollutants (organic or inorganic compounds) to be degraded. This criterion reduces or eliminates the intermediates produced during the photocatalytic degradation while further increasing mass transfer rates and processes for an efficient photodegradation; (iv) It should allow for fast and easy photocatalyst recovery and reuse with or without regeneration[10].

Carbon based titania photocatalyst: TiO_2, although having excellent photocatalytic activity, but due to some operational limitations it has low adsorption capabilities. Carbon and TiO_2 combine to produce a composite material possessing the cooperated properties of good adsorption and photocatalytic activity leading to an enhanced effect[10]. Based on these criterions of catalyst support for photocatalysis, activated carbons, activated carbon fibers and nano carbons have also been extensively researched and used as a support material for TiO_2. Porous carbon materials such as activated carbons and activated carbon fibers made for it are undoubtedly versatile, as demonstrated by the variety of structures and the wide range of applications in which they are found. Indeed they can be used for everything from gas storage to catalyst supports, molecular sieves, absorbents, electrodes in electrical devices, environmental pollutant filters and medical derivatives[26-28]. The introduction of a second component in such a composite structure can stabilize the textural properties upon thermal treatment, which modifies the distributions of active sites and generally enhances the catalytic activity of the pure oxides[29]. These composites have specialized properties as the materials of which they are composed, exhibit cooperative or synergistic effects.

Basic principle of the synergism: The basic photophysical and photochemical principles underlying photocatalysis are already established and have been reported in many literatures[30,31]. Only the molecules that are in direct contact with the catalyst surface undergo photocatalytic degradation. Photocatalytic reaction is initiated when a photoexcited electron is promoted from the filled valence band of semiconductor photocatalyst (SC) to the empty conduction band as the absorbed photon energy, hν, equals or exceeds the band gap of the semiconductor leaving behind a hole in the valence band. Thus electron and hole pair (e^- - h^+) is generated. The following chain reactions have been widely postulated.

$$\text{Photoexcitation}: TiO_2/SC + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$\text{Oxygen ionosorption}: (O_2)ads + e^- \rightarrow O_2^{\cdot -} \quad (2)$$

$$\text{Ionization of water}: H_2O \rightarrow OH^- + H^+ \quad (3)$$

$$\text{Protonation of superoxides}: O_2^{\cdot -} + H^+ \rightarrow HOO^{\cdot} \quad (4)$$

The hydroperoxyl radical formed in (4) also has scavenging property as O_2 thus doubly.

Prolonging the lifetime of photohole:

$$HOO^{\cdot} + e^- \rightarrow HO_2^- \quad (5)$$

$$HOO^- + H^+ \rightarrow H_2O_2 \quad (6)$$

Both the oxidation and reduction can take place at the surface of the photoexcited semiconductor photocatalyst (Fig. 2). Recombination between electron and hole occurs unless oxygen is available to scavenge the electrons to form superoxides ($O_2^{\cdot -}$), its protonated form generates the hydroperoxyl radical (HO_2) and subsequently H_2O_2[10].

Activated carbon supported TiO_2 photocatalyst: Activated carbon synonymous as activated charcoal or active carbon is a porous, amorphous solid carbon material. It has been extensively researched as an support material that can increase the photodegradation rate by increasing the quantity of the substrate that comes in contact with TiO_2 by means of adsorption. The synergistic effect can be explained as an enhanced adsorption of the target pollutant onto the activated carbon phase followed closely by a transfer through an interphase to the TiO_2 phase, giving a complete photodegradation process. The photodegradation process was evident by going through experimental methods of photodegradation of organic dyes (like methylene blue) which shows positive results[32].

In Fig. 3, the synergistic degradation mechanism has been demonstrated on a pollutant dye. The main properties of titania and activated carbon (AC/TiO_2 complex) attributing to the photocatalytic activity are homogeneous distribution between titania complexes and porosity of the external surface, resulting in complete photodegradation.

Activated carbon fiber supported TiO_2 photocatalyst: Activated carbon fiber, a new formulation of activated carbon remains in the form of a felt or cloth. It is a popular choice of support material owing to its numerous advantageous properties

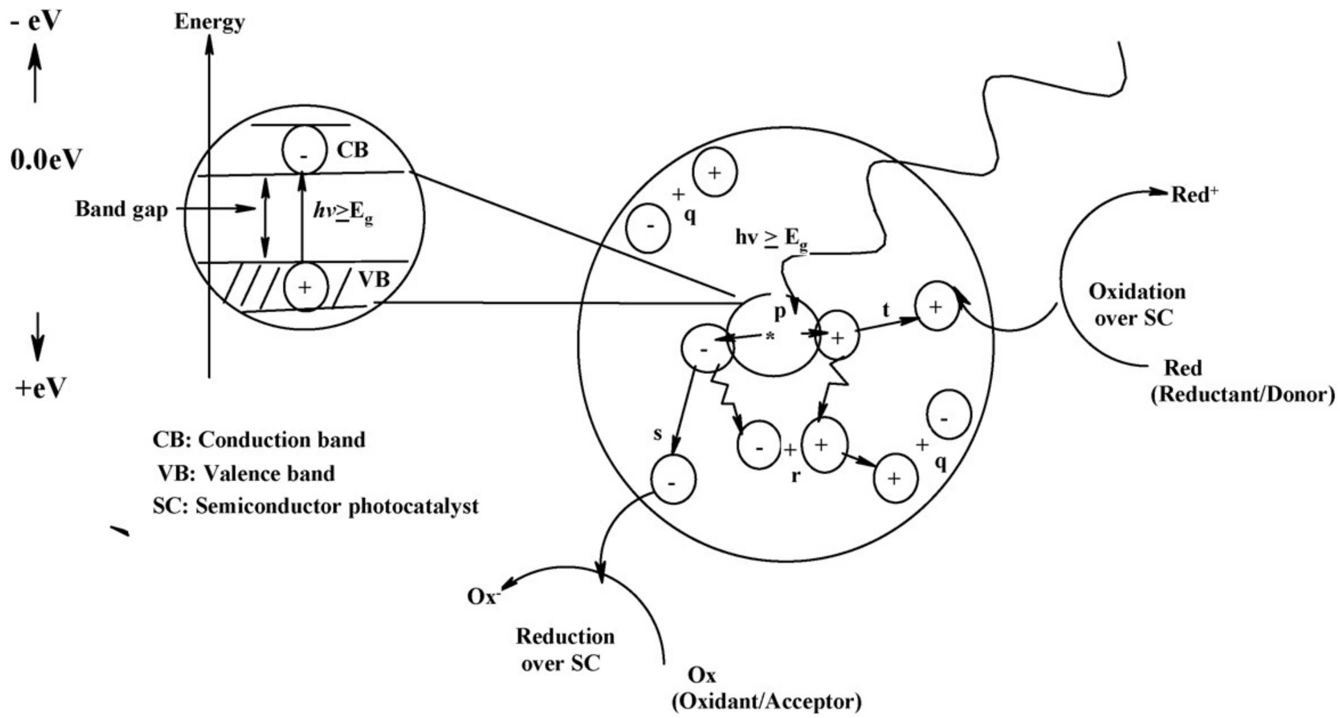

Fig. 2. Schematic photophysical and photochemical processes over photon activated semiconductor cluster (p) photogeneration of electron/hole pair, (q) surface recombination, (r) recombination in the bulk, (s) diffusion of acceptor and reduction on the surface of semiconductor and (t) oxidation of donor on the surface of semiconductor particle

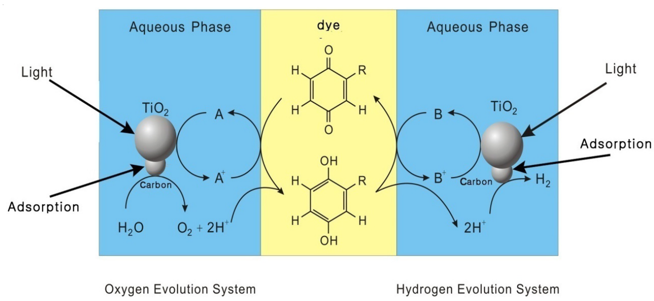

Fig. 3. Schematic diagram of synergitic degradation mechanism between dye and activated carbon/TiO_2 photocatalyst

like large adsorption volume, fast adsorption speed, heat-resistance, acid and alkaline resistance. Its absorption property is nearly unperturbed after several regeneration. The organic pollutants gets selectively adsorbed by the activated carbon fibers and offered to TiO_2, loaded on the activated carbon fibers *via* diffusion for decomposition. The rate of decomposition depends on the adsorption strength. The adsorption and photocatalysis of activated carbon fiber/TiO_2 system were regenerated after the migration of the photocatalytic products from TiO_2 surface.

Nanocarbon supported TiO_2 photocatalyst: In recent times, nanocarbon based TiO_2 composites have been attracting a lot of attention and has become a very active field of research due to their unique and promising applications, to solve the big problem of pollution. Carbon nanotube/TiO_2 composites, C_{60} /TiO_2 composites, metal supported carbon nanotube titania additionally have photoxidation property on harmful bacteria resulting in anti bacterial effect that can be advantageous for the purification of water and air sources.

Fullerene (C_{60}) as carbon support for TiO_2 photocatalyst: Carbon material fullerene (C_{60}) has attracted extensive attentions for their various interesting properties like delocalized conjugated structures and electron-accepting ability. One of the most remarkable properties of fullerene in electron-transfer processes is its efficiency in arousal of a rapid photoinduced charge separation and a relatively slow charge recombination[33]. Thus, the combination of photocatalyst and fullerene may endow with an ideal system to achieve a superior charge separation by photoinduced electron transfer. For the intention of enhanced photocatalysis, the use of fullerene in synergy with TiO_2 is a very popular subject of interest to be investigated.

Mechanism: Fullerene can accept or donate electron to TiO_2 semiconductor depending on different conditions. Basically, UV excitation of TiO_2 colloids leads to trapping of holes and electrons, which can be suppressed by C_{60} meanwhile, C_{60} could also donate electron to TiO_2 semiconductor (Fig. 4). In case of visible laser excitation, electrons get injected from C_{60} to TiO_2 through a biphotonic electron ejection mechanism[34].

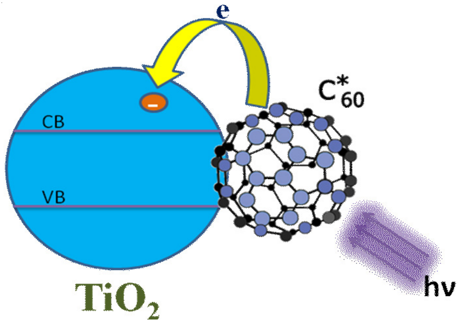

Fig. 4. Photoinduced charge transfer between TiO_2 and C_{60}[14]

Carbon nanotubes supported TiO_2 photocatalyst: Carbon nanotube (CNT) supported TiO_2 composites are grabbing much attention, admiringly because of its cooperative and synergistic effects. Moreover, carbon nanotube possesses favourable electronic, adsorption, mechanical and thermal properties. Thus carbon nanotube is more attractive support catalyst comparative to activated carbon.

Mechanism: In carbon nanotube/TiO_2 composites the carbon nanotube acts as an electron sensitizer and donor in the photocatalysis process. The semiconductor properties of carbon nanotube owe to its ability to accept photo-induced electron by UV irradiation and transfer it to the conduction band of TiO_2 particles. Consequently the electrons in the conduction band react with oxygen (O_2) and trigger the formation of superoxide radical ion (O_2^-). Simultaneously, the positive charge hole created in the valence band in TiO_2 particles derives the H^+ electron from the water molecules (H_2O_2), leaving the (OH^-) hydroxyl radical. Thereafter, the superoxide and hydroxyl radicals are responsible for the decomposition effect of organic compounds into less harmful substances. This property of carbon nanotube/TiO_2 composites can be proven by the experimental results of the degradation of organic dyes (like for instance methylene blue) when irradiated with UV radiation[35].

The following reactions occur as shown in Fig. 5:

(1) $CNT^+/TiO_2 \rightarrow CNT/TiO_2^+$

(2) $CNT/TiO_2^+ + (H^+ + OH^- \text{ from } H_2O) \rightarrow CNT/TiO_2 + H^+ + OH^{\hat{}}$

(3) $CNT/TiO_2 \rightarrow CNT/TiO_2^-$

(4) $CNT/TiO_2^- + O_2 \rightarrow CNT/TiO_2 + O_2^-$

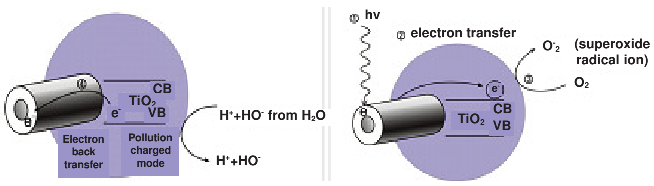

Fig. 5. Photocatalytic activity in carbon nanotube supporting TiO_2 particles

Graphene supported TiO_2 photocatalysis: Graphene is defined as a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice[36]. It possesses many intriguing properties such as extraordinary high thermal conductivity, stiffness and strength, electronic properties[37], *etc*. Graphene has been regarded as an important component for making various functional composite materials. Especially, graphene-based semiconductor photocatalyst have attracted extensive attention because of their usefulness in environmental and energy applications[38].

Photocatalytic mechanism: Graphene particles when subjected to excitation under UV spectrum, the electrons from the π state were injected into the conduction band of the titania (TiO_2)[39].

These electrons transferred to the surface of titania and reacted with oxygen to yield superoxide and hydroxyl radicals as follows[40-43]:

$$O_2 + e^- CB \rightarrow O^-_2$$

$$2O^-_2 + 2H^+ + e^- CB \rightarrow OH^{\hat{}} + OH^- + O_2$$

The radicals thus produced oxidize the dye (in experimentations dyes like Rhodamine B) to yield CO_2, H_2O and other mineralization, as shown in a schematic representation in Fig. 6.

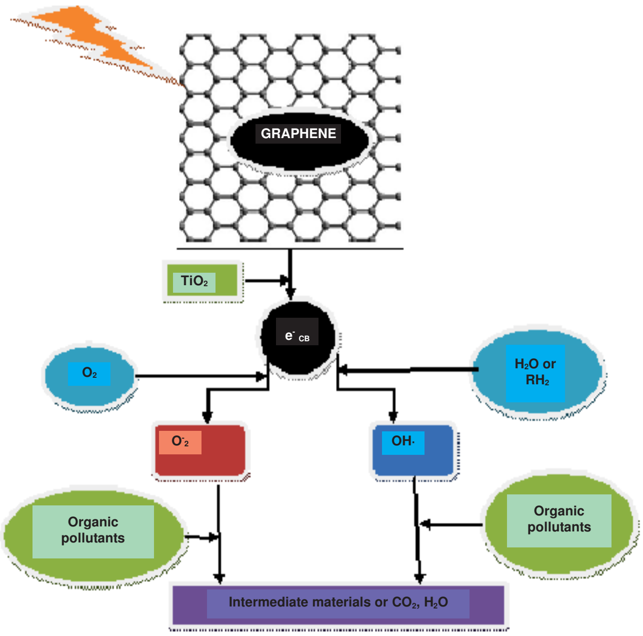

Fig. 6. Photocatalytic mechanism of graphene supported TiO_2

However, novel methods are being developed to amplify the catalytic activity of graphene, one of them being fabrication of graphene with nanoparticles and to form unique hybrid materials with relatively low band gap energy and good photovoltaic activity like for instance, ZnO, CdS, CdSe, *etc*. are very popular nanoparticles that are being investigated nowadays. These methods are particularly helpful in creating more efficient and sensitive solar cells, optoelectric devices, biological labeling, *etc*.

Conclusion

From the above review work, the idea is quiet lucid that carbon based titania material has shown promising results as photocatalyst. After the discovery of novel compound graphene and its impressive activity in the degradation of organic dyes coupled with TiO_2 particles, also indicates its future application in environmental sciences, semiconductor devices, *etc*. However, further insights are needed to explore more into the fascinating area of carbon based photocatalysis. At present the research is at its embryonic stage and hopefully in near future an elaborate knowledge about this shall be obtained and the spaces of improvement may be fulfilled.

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