



# A Review of Photocatalytic Treatment for Various Air Pollutants

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## ABSTRACT

Photocatalysis is a photochemical catalytic reaction which is a highly promising tool for the environmental cleanup process. It is very effective in treatment of environmental pollutants by its unique redox property. It has wide applications in the treatment of atmospheric pollutants (e.g., nitrogen dioxide, trichloroethylene, volatile organics, hydrogen sulfide, benzene, etc) through oxidative removal and by disinfection (aeromicro flora). In this research, the fundamental aspects of photocatalysis are described with respect to the composition of catalysts, experimental conditions (e.g., temperature, duration, etc), and interfering factors (e.g., catalyst deactivation).

**Key words:** Treatment of air, Pollution control, Photocatalysis, Oxidation of air pollutants

## 1. INTRODUCTION

Photocatalysis is a rapidly expanding technology for the treatment of air pollutants. It can be defined as the mechanism leading to “acceleration of photoreaction with the aid of a catalyst”. The initial recognition on the heterogeneous photocatalysis was made when Fujishima and his colleagues discovered photolysis of water (Fujishima *et al.*, 1972). In recent years, the use of semiconductor materials gained interests as photocatalytic medium for the removal of organic and inorganic species. This method has been suggested as a potent tool for environmental protection due to its great oxidation capacity (Robert and Malato, 2002). The photocatalysis is a very effective tool to process the environmental pollution. However, its application toward the treatment of the air pollutants is open widely. Hence, in this article, emphasis is given to describe its treatment efficiency in a number of aspects by surveying the uptodated knowledge in this field of research.

The catalyst can be used to induce oxidation and re-

duction of substrates simultaneously. UV light with higher energy band of  $< 390$  nm (or sunlight 390-700 nm) can be used as excitation energy. Heterogeneous photocatalysis using semiconductors (such as titanium dioxide ( $\text{TiO}_2$ )) can be more effective than conventional waste treatment methods for removing organic species in the environment. The redox capacity of such media promotes the conversion of substrate to carbon dioxide and water. This process is also called mineralization. Carbon dioxide is formed as the end product due to the oxidation of carbon atom of the reactant molecule. However, depending on the composition of reactant, the end product of the reaction can differ to a degree (Denny *et al.*, 2007).

Photocatalysis with a semiconductor oxide (such as  $\text{TiO}_2$ ) is initiated by the absorption of a photon with energy equivalent to or greater than the band gap of the semiconductor (c.a. 3.2 eV for anatase). It then produces electrons and holes ( $e^-/h^+$ ) in conduction band and valence band, respectively (Wilke and Breuer, 1999). Following the irradiation, the  $\text{TiO}_2$  particle can act either as an electron donor or acceptor for molecules in the surrounding medium. The electron and hole can also be recombined to release the absorbed light energy in the form of heat. When this recombination takes place,  $\text{TiO}_2$  cannot act as catalyst. Under such circumstances, both the redox process cannot take place. The valence band hole is strongly oxidizing due to the presence of OH radical, while the conduction band electron is strongly reducing due to the presence of  $\text{O}_2^-$  radical (Bahruji *et al.*, 2010).

At the external surface, the excited electron on the conduction band and the hole on the valence band can take part in redox reactions. As the electron is excited from valence band to conduction band by absorption of energy, an empty positive hole is formed at valence band. When  $\text{TiO}_2$  comes in contact with water, the hydroxylation of hole takes place to form hydroxyl radical. The  $\text{OH}^-$  radical adsorbed on valence band is anion form. As it has negative electrical charge, it is strongly attracted to positive hole. After being combined with hole, its negative charge is neutralized to form

hydroxyl radical ( $\cdot\text{OH}$ ). This neutralized hydroxyl radical is very reactive in nature with strong affinity for electrons which facilitates the oxidation of other compounds. This hydroxyl radical (2.08) is the strongest oxidizing agent only after fluorine (3.06) (Datta *et al.*, 2004).

The oxidation reactions are hence observed due to the presence of hydroxyl radical at valence band as well as other oxidizing agents, which are present in solution of reactants. An important reaction of the conduction band electron is the reduction of the adsorbed  $\text{O}_2$  to  $\text{O}_2^-$ . Thus, a redox environment is created by the presence of hydroxyl (oxidizing) and superoxide (reducing) radical over  $\text{TiO}_2$  surface. Upon the creation of the redox environment, the mineralization of desired component is observed, i.e., conversion of initial compound to final end product which is mainly carbon dioxide, water, and organic acids (Liu *et al.*, 2006) (Latasree *et al.*, 2004).

### 1. 1 Characteristics of an Ideal Photocatalyst, Advantages of This Method

According to Fujishima *et al.* (2000), the ideal photocatalyst should possess the following properties.

- Photo activity, low cost, and non-toxic nature: For large scale environmental clean up operations, the photocatalyst has to be available at low cost without toxic properties to flora and fauna when used at large concentrations.
- Biological and chemical inertness: The catalyst used in the process of substrate treatment must not promote the formation of other complex and undesired substrates.
- Stability towards photocorrosion: The catalyst must not undergo corrosion under prolonged light

exposure; it has to be stable to tolerate the long light exposure which will be persistent throughout the process.

- Suitability towards visible or near UV light: An excitation source which is essential for the initiation of reaction must be of low energy in the visible or near UV region so that the high radiation energy is not required.

### 1. 2 Various Steps in Photocatalysis Process

Heterogeneous photocatalysis is type of interaction where the reactant and catalyst exist in different phases. This type of reaction generally involves the following five steps (Shan *et al.*, 2010): (i) diffusion of reactants to the surface of catalyst, (ii) adsorption of reactants onto the surface, (iii) reaction on the surface, (iv) desorption of products from the surface, and (v) diffusion of products from the surface (Devilliers, 2006) (Fig. 1).

## 2. PHOTOCATALYTIC MATERIALS

A wide range of semiconductors may be used for photocatalysis such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CdS}$  (Vinu and Madras, 2010). Among these semiconductor oxides,  $\text{ZnO}$  is generally unstable in illuminated conditions, especially at low pH values.  $\text{WO}_3$ , although useful in the visible range, is less active photocatalytically than  $\text{TiO}_2$ . Among others, the possibilities of  $\text{CdS}$ ,  $\text{ZnS}$ , and iron oxides have been also tested. However, all of those materials have suffered from corrosive properties. Hence,  $\text{TiO}_2$  is yet the most useful material for photocatalytic purposes, owing to a number of advantages: exceptional optical and electronic properties, chemical stability, non-toxicity and low

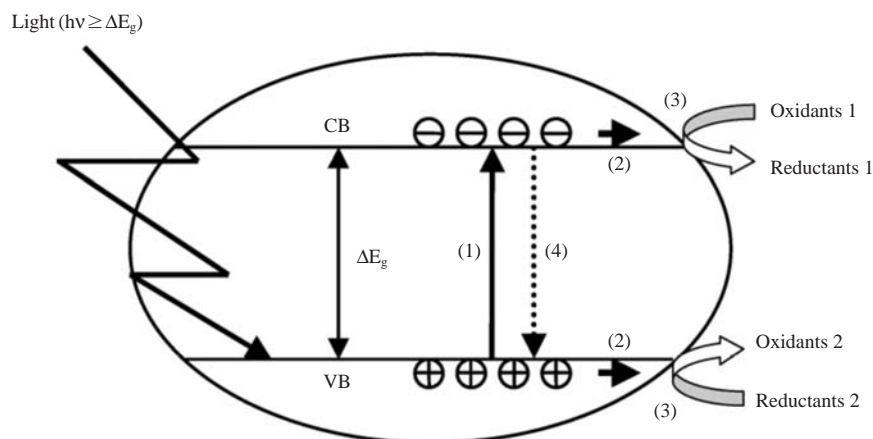
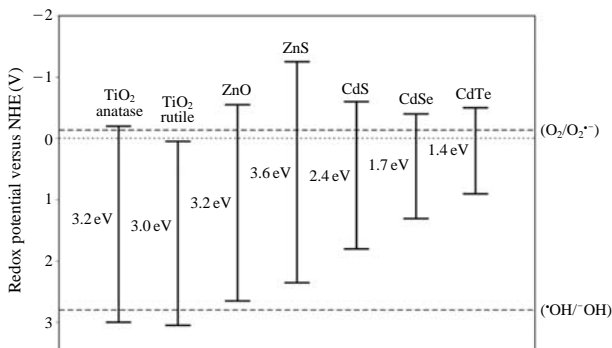


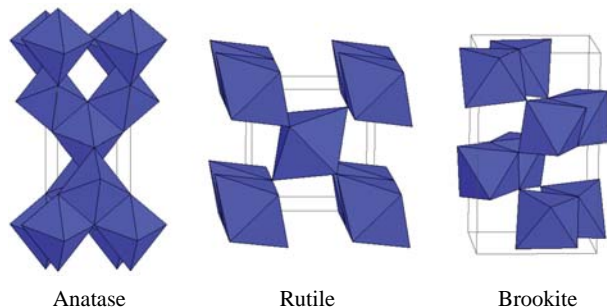
Fig. 1. Diagrammatic representation of Photocatalysis mechanism (Demeestere *et al.*, 2007).

cost (Litter, 1999) (Fig. 2).

The commonest crystalline forms of TiO<sub>2</sub> are anatase and rutile. The third form is brookite. Whose form is uncommon and unstable (It is stable only at high temperature). The structures of anatase, rutile, and brookite are presented in Fig. 3. However, the usage of TiO<sub>2</sub> as a photocatalyst can also be limited by several factors.



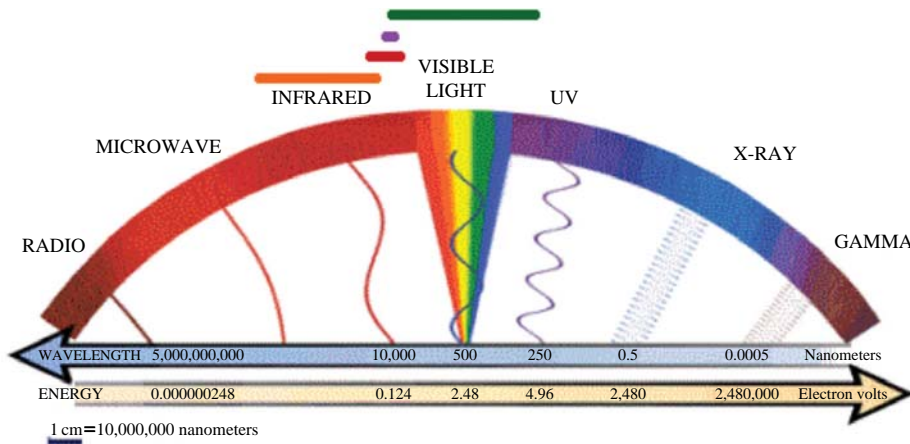
**Fig. 2.** Band gaps of various semiconductor oxides (Demeestere *et al.*, 2007).



**Fig. 3.** Different phases of TiO<sub>2</sub> (Smyth, 2010).

The most restrictive factor has been the need of UV (wavelength of < 387 nm) as an excitation source due to its wide band gap (3.2 eV). Only 5 percent of visible radiation is available for this required excitation energy (Fig. 4). The photocatalytic method has wide applications in the waste water treatment, due to high availability of OH in water (Blanco *et al.*, 2009). Although different in nature, its application to the treatment of various range of air pollutants is also reported. The catalyzing, deodorizing, adsorbing, and disinfection property of the TiO<sub>2</sub> makes it a potential photocatalyst for the treatment of air pollutants.

Intensive studies are in progress to develop the existing materials or to prepare alternate materials for improved photocatalytic behaviour, which can be used under solar energy. To this end, the absorption of radiation must be shifted from UV to visible light region; it is active in UV region and is usually doped with a metal to structurally modify and increase the absorption capacity in the visible region. Visible light is renewable source with high potential, when employed at large scale treatment operations. The other demanding research area includes the modifications to increase the surface area of catalyst. The greater the surface area of the catalyst, the higher the extent of interaction takes place between the catalyst and reactant (Machado and Charles, 2006). As a result, a greater efficiency in reaction can be achieved. Several studies reported that doping TiO<sub>2</sub> with anions (such as carbon, nitrogen, sulfur, boron, and fluorine) can help shift the optical absorption edge of TiO<sub>2</sub> towards lower energy (Li *et al.*, 2005). Through such modification, one may increase the photocatalytic activity in visible light region. By the process of doping, the gap between valence and conduction band can be reduced with the formation of interbands between them (Juanru *et al.*, 2007). Hence, less



**Fig. 4.** Electromagnetic spectrum showing visible and UV region (www.spacetoday.org).

energy source (like visible radiation) can be sufficient for the excitation of electron from valence band to conduction band.

### 3. PHOTOCATALYSIS AND ITS APPLICATION TO THE TREATMENT OF AIR POLLUTANTS

Photocatalysis can be used as a very effective tool to treat air pollutants. It is also proved that this process is applicable in ambient environments, especially less humidified indoor environments (Jo and Kim, 2009). It has various advantages in comparison to the other conventional methods (Table 1). It has also been proven to deal with a wide range of air pollutants (Table 2). Here some pollutants and their treatment efficiency are taken as a reference to indicate its efficiency against different types pollutants released from various sources.

#### 3.1 Purification of Indoor Air and Gaseous Effluents

There are various indoor pollutants which can be responsible to cause various chronic health problems. Radons, formaldehyde, and VOC are common examples of indoor air pollutants. The number of aromatic VOC including benzene, toluene, and xylene (commonly called BTX) has been treated by the photocatalytic method (Pichat *et al.*, 2000). The TiO<sub>2</sub> photocatalytic treatment of toluene is known to yield benzaldehyde, with high applications in synthetic industry (Sleiman *et al.*, 2009). TiO<sub>2</sub> also has high capacity to deodorize the indoor air. The deodorization may be considered as the outcome of oxidation of the pollutant (Wei *et al.*, 2010). A photo-reactor coated with TiO<sub>2</sub> fiber glass mesh in the presence of artificial radiation light at approximately 365 nm (UV) is found to be very efficient in the mineralization of BTX compounds (Pichat *et al.*, 2000). This oxidation can be further enhanced under the presence of strong oxidants (like ozone) in the in-

**Table 1.** Comparison of various treatment methods for airborne pollutants.

Treatment methods	Advantages	Disadvantages
Biological treatment	Efficient in treatment of pollutants, with low cost	Very slow and needs large area
Photocatalysis	Stable, cheap, reusable high activity, chemically and biologically inert, works at ambient environment	External source is required
Electrostatic separation	Treats particle matter than gaseous pollutants	High cost, can treat only dry emission
Ozonation	Efficiency in treatment of recalcitrants and also disinfection of air can be done	Increased ozone in air causes problems, Formation of ozonated pollutants
Photolysis	Very fast removal	Highly harmful because of high UV radiation
Adsorption	Very useful with volatile compounds Hazardous compounds and unreactive compounds can be observed	Most of adsorbents are specific, Disposal of adsorbents is serious problem

**Table 2.** Examples of photocatalytic treatment for the treatment of air pollutants.

Catalyst employed	Target compound	Catalyst and reaction features	References
TiO <sub>2</sub> Ti/SiO <sub>2</sub>	BTX	Very efficient in treatment adsorbing as well as catalytic agent	(Pichat <i>et al.</i> , 2000) (Zou <i>et al.</i> , 2006)
TiO <sub>2</sub> TiO <sub>2</sub> on Si support	TCE	DCAC (dichloroacetyl chloride) and various other products DCAC is not formed, others are formed as TiO <sub>2</sub>	(Wang <i>et al.</i> , 2002) (Park <i>et al.</i> , 2004)
Cu/TiO <sub>2</sub>	NO <sub>2</sub>	Efficiency decreased by accumulation of HNO <sub>3</sub>	(Ohko <i>et al.</i> , 2009)
Cr-MCM-TiO <sub>2</sub> CdS	H <sub>2</sub> S	SO <sub>2</sub> is not formed, but sulphates are formed Hydrogen production and efficiency	(Portela <i>et al.</i> , 2008) (Bai <i>et al.</i> , 2010)
TiO <sub>2</sub> Pd-TiO <sub>2</sub>	Gaseous benzene	Good efficiency in mineralization 2.32 higher activity than TiO <sub>2</sub>	(Zhong <i>et al.</i> , 2007) (Zhong <i>et al.</i> , 2009)
TiO <sub>2</sub>	Chloramines	Chlorobenzene and phenols are formed	(An <i>et al.</i> , 2011)
Ag-TiO <sub>2</sub>	Disinfection	Effective in disinfection of B. aereus, E. coli, S. auerus, A. niger	(Vohra <i>et al.</i> , 2006)

door environmental conditions. Doping of  $\text{TiO}_2$  can further increase its catalytic efficiency (Park *et al.*, 2004). VOCs in urban atmosphere are produced mainly by automobile exhausts. The majority of them are very stable recalcitrant compounds.  $\text{TiO}_2$ - $\text{SiO}_2$  based photocatalysis was thus employed for the removal of VOC (Zou *et al.*, 2006). The catalyst can act as adsorbing as well as catalyzing agent. The amounts of hydrocarbons and carbon dioxide are observed as the end products by such photocatalytic treatment of VOC. The presence of NO (along with VOC) showed some interfering effects (Ao *et al.*, 2003). In addition, it is also reported that humidity as well reactive nature of NO with VOCs had huge influence on the progress of reaction.

### 3.2 Removal of Trichloroethylene (TCE)

TCE is a very harmful widespread gaseous air pollutant, being carcinogenic in nature. When gas phase TCE is subjected to photodegradation in packed bed continuous flow reactor, it yielded many intermediate products like phosgene, dichloroacetyl chloride (DCAC), chloroform, hexachloroethane, alcohols, esters, aldehydes, carbon monoxide, and carbon dioxide (Wang *et al.*, 2002). Phosgene emission can be reduced by using allopane clay suspended  $\text{TiO}_2$ . Here, phosgene is adsorbed on to surface of allopane clay catalyst, and it can be degraded gradually (Nishikiori *et al.*, 2011). TCE degradation mechanisms usually begin with the  $\text{Cl}^-$  subtraction by the attack of hydroxyl radical of water present in air (Amama *et al.*, 2001). TCE has also been removed by employing degussa titania coated reactor wall deposited on silica based support (Mohseni, 2005). A large amount of TCE can be removed by this process. The removal efficiency of TCE is very high due to the addition of silica support on degussa, as it provides higher interactive surface area for catalyst and reactant. The intermediates formed in the presence of silica-based support and in its absence can exhibit huge variations. Pure degussa titania interaction with TCE resulted in phosgene and dichloro acetyl chloride (DCAC) as end product (Mohseni, 2005). However, in the presence of silica based support, the DCAC was not formed. Instead, a very little amounts of carbon tetrachloride and chloroform were formed. As such, the efficiency of TCE photodegradation is very high, when  $\text{TiO}_2$  is doped with high valency cations (Park *et al.*, 2004).

### 3.3 Photocatalytic Reduction of $\text{NO}_2$

$\text{NO}_2$  is harmful and reactive compound and is emitted from various industrial sources (Latza *et al.*, 2009). For removal of  $\text{NO}_2$ , its photocatalytic reduction to NO by cupric ion loaded thin  $\text{TiO}_2$  films was studied

(Ohko *et al.*, 2009). As cupric ion can induce photocatalytic reduction of  $\text{NO}_2$  to NO in air, it can also act as oxidizing agent to yield  $\text{HNO}_3$  from NO. As such, cupric ion can be used to provide delicate redox conditions. However, oxidation efficiency of NO to  $\text{HNO}_3$  decreased, as the accumulation of  $\text{HNO}_3$  proceeds. In an alternative method, the photocatalytic oxidation of NO can take place under some specified hydrothermal conditions. The P25 degussa titania, commercially produced by a German company (Anatase and Rutile in ratio of 3 : 1), showed best oxidation of NO, if the catalyst is calcined at temperature of 200 degree for the duration of 24 hrs (Wu *et al.*, 2008). The application of photocatalytic concrete material in urban places has also been very effective in the treatment of  $\text{NO}_2$  at highly polluted urban areas (Ballari *et al.*, 2010).

### 3.4 $\text{H}_2\text{S}$ Photo Degradation

Hydrogen sulphide is a colorless, poisonous, flammable gas with the characteristic foul odor of rotten egg (Kourtidis *et al.*, 2008; Lambert *et al.*, 2006). It often results from the bacterial breakdown of organic matter in the absence of oxygen, such as in swamps and sewers (anaerobic digestion) (Chairapat *et al.*, 2011). It also occurs in volcanic gases, natural gas, and some well waters.  $\text{H}_2\text{S}$  can also be subject to photodegradation by chromium doped molecular sieves in the presence of  $\text{TiO}_2$  (Portela *et al.*, 2008). The chromium doped mesoporous crystalline molecular (Cr-MCM) sieves, prepared by hydrothermal method, are impregnated with  $\text{TiO}_2$ . During the photodegradation, there was no oxidation of  $\text{H}_2\text{S}$  to sulfur dioxide. However, the accumulation of sulphates deactivated the catalytic property of chromium. As another approach of  $\text{H}_2\text{S}$  treatment, its photocatalytic decomposition was carried out in the presence of CdS catalyst. It allows the decomposition and photodegradation simultaneously with the production of  $\text{H}_2$  (Bai *et al.*, 2010).

### 3.5 Oxidation of Gaseous Benzene

Benzene is a flammable, colorless and carcinogenic compound (Bird *et al.*, 2005). It is naturally produced, when wood is completely burned (during forest fires) or volcanic eruptions (Capaccioni *et al.*, 2004). The commonest exposure to benzene is through the inhalation of cigarette smoke or car exhaust (Edwards and Jhantunen, 2001) (Weisel, 2010). This extremely toxic compound was discovered in the gas emitted by burning coal (The Lancet, 1904).

The photocatalytic oxidation of benzene can be carried out utilization of doped  $\text{TiO}_2$  catalysts (Zhong *et al.*, 2007; Fu *et al.*, 1995). The doped catalyst exhibited high decomposition of benzene than bare  $\text{TiO}_2$ . It is highly reactive in the presence of sunlight, indica-

tive of high potential in solar photocatalysis. The addition of Pd in to TiO<sub>2</sub> increases photocatalytic activity by more than 2.3 times than pure TiO<sub>2</sub> (Zhong *et al.*, 2009).

### 3. 6 Photo Degradation and Detoxification of Chloranilines

Chloroaniline is a typical semi-volatile aromatic amine (Kataoka, 1996). It is precursor for various anti-bacterial products. It is strong irritant with the potential for tissue damage. The photocatalytic degradation of chloramines containing gases can be achieved very rapidly by TiO<sub>2</sub> catalyst (An *et al.*, 2011). Chlorobenzene and phenols are formed as intermediates of this degradation. Here the degradation as well as detoxification of the gaseous aromatic amines is simultaneously observed by this method.

### 3. 7 Microbial Disinfection in Air by Photocatalysis

Air usually contains high amount of micro-organisms. There are various airborne diseases which are transmitted through air (like tuberculosis, whooping cough, etc) (Martinez *et al.*, 2008). The application of photocatalysis for the disinfection of microbes has been exercised. The Ag doped TiO<sub>2</sub> acts as a very good disinfecting agent (Akhavan, 2009). The catalyst coated filters when passed over recirculation air, can induce disinfection of various microorganisms (e.g., *Bacillus cereus*, *Staphylococcus aureus*, *Escherichia coli*, and *Aspergillus niger*) which are used as indices for disinfecting property (Vohra *et al.*, 2006). Photocatalysis is also very efficient in the inactivation of microbial growth. The principle of disinfection of photocatalyst can be expressed as the disintegration of cells by the activity of OH radical which oxidizes the intracellular components of micro-organisms (Cheng *et al.*, 2007). Thus, this method can be very beneficial under rapidly infectious conditions.

## 4. CONCLUSIONS

This article is written to review basic principle and concept of photocatalysis and its application toward the treatment of air pollutants. A wide variety of air pollutants and photocatalytic methods that have been successful in their treatment was briefly described here. Although the application of photocatalysis was has been extended to cover many field conditions, the progress in this field of research is yet insufficient. However, based on the realization of its potential, a lot of photocatalytic applications and material modifications have been made for pollution control on a

large scale. Yet a vast variety of atmospheric gases are not subjected to this method of treatment. In the near future, one needs to find a more favorable means to extend its applicability for the abatement of various air pollutants.

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