Chapter 9
Photocatalysts for Indoor Air Pollution: A Brief Review

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Contents

Abstract Photocatalysis is one of the fastest growing technologies for the treatment of pollutants, utilizing the mechanism of reaction with the help of light (photo

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emissions). Photocatalysis has captured broad academic and research interest during the past three decades for its potential of controlling pollution in air and water. Its qualities, such as low cost and high efficiency, have caused researchers all over the world to focus on it and also promoted many industrial applications and much research. Photocatalysis has been used to remove major air pollutants, disinfect water, and oxidize various organic chemicals. In this connection, this chapter considers the properties of the ideal photocatalyst, available photocatalytic materials for air pollution control, common indoor air pollutants and their severe health effects, and purification techniques for indoor air pollution. Furthermore, photocatalytic oxidation techniques for the removal of volatile organic compounds are discussed in detail.

Keywords Photocatalyst · Indoor air pollution · Titanium dioxide · Photocatalytic oxidation

9.1 Introduction

Today the entire world is struggling with the severe effects of environmental pollution and researchers all over the world are looking to provide solutions for this problem (Anpo 2000; Naushad 2014). In 2012, one in eight of all deaths, around 7 million people, died because of bad air quality, which has a vast negative impact around the worldwide (Naushad 2014; Lelieveld et al. 2015). To have more yield and more profits, chemical industries provide products with more favourable usage although they have hazardous impacts on the human health and environment. Compounds such as phenol, pesticides from wastewater sewage, polymeric surfactants, and herbicides release dangerous chemical substances that are not easily biodegradable (Hoffmann et al. 1995; Alshehri et al. 2014; Al-Othman et al. 2011; Al-Kahtani et al. 2018).

People think that pollutants occur more in the outdoor environment compared to indoors because of heavy traffic pollutes the air. But, although this may be shocking, an urban area with average traffic might be cleaner than indoor air. Some of the studies reported that the concentration of air pollution indoors is five times higher than in the outdoor environment (Zhang and Smith 2003; Bernstein et al. 2008; Kolarik et al. 2010). Factors such as smoke, electronic equipment, inadequate ventilation, mould damage, and furniture increase air pollution in schools, homes, and public places. Sick building syndrome is a disorder found to occur in a group of people who spent time in a certain building with indoor air pollution (Wolkoff and Nielsen 2001; Crook and Burton 2010; Norhidayah et al. 2013). Some pollutants may cause diseases such as respiratory infections or cancer that are diagnosed later (Zhang and Smith 2003). From the foregoing facts and the literature, it is evident that the people spend 90% of their time in an indoor environment, which is a key factor to be considered for human health and comfort (Li 2016). Also, some of the studies state that compared to the outdoor environment there is a lag in public health awareness in indoor air pollution (Challoner and Gill 2014; Rohra and Taneja 2016).

The quality of the indoor air can be improved by eliminating or reducing contaminants by ventilation, by controlling indoor source pollutant emission, and by using low emission materials. Adequate ventilation and effective infiltration are the traditional methods to improve indoor air quality (IAQ) in which indoor air pollution can be reduced by introducing outside air into the building. As ventilation is inadequate (Bennett 2009) in modernized buildings, the only way to achieve air quality is to purify the air.

Photocatalysis is one of the fastest growing technologies for the treatment of air pollutants, utilizing the mechanism of reaction with the help of light (photo emissions). Fujishima and Honda 1972, while working on the photolysis of water, initially recognized this as a heterogeneous photocatalyst. Much research was put forward in their work towards the development and growth of photocatalysis techniques, and in recent years researchers have explored and reported the use of semiconductor materials as photocatalysts for elimination of organic and inorganic species. It has been considered an effective tool for the protection of the environment because of its large oxidation capacity (Robert and Malato 2002). Still, applications towards the improvement of indoor air by reducing the contaminants are open to wide usages. Hence, this chapter discusses photocatalysis for efficient indoor air pollution remediation, techniques and methods available for the elimination of pollutants, and the perspectives.

9.2 Ideal Catalyst

Fujishima et al. have reported that a photocatalyst to be considered as an ideal candidate should possess such characteristics as these (Fujishima et al. 2000):

1. Photo-activity, nontoxic nature, low cost
2. Inert to chemical and biological activity
3. Photo-corrosion stability
4. Active towards visible light

The various steps involved in photocatalysis activities (Shan et al. 2010) are diffusion, adsorption, reaction, desorption, and diffusion of the final products from the surface of the catalyst (Serpone and Emeline 2012). Figure 9.1 represents the steps involved in photocatalytic activities.

9.3 Photocatalytic Materials for Air Pollution

Semiconductors such as TiO_2, Fe_2O_3, ZnO, CdS, WO_3, and SnO_2 (Vinu and Madras 2010) have major roles in photocatalytic activity. Compared to TiO_2, all the other candidates have some limitations: for example, ZnO is unstable at low pH values, CdS, iron oxides, and ZnS suffer from corrosion, and WO_3 is less active. Among these, TiO_2 is considered to be a potential candidate for photocatalytic activities

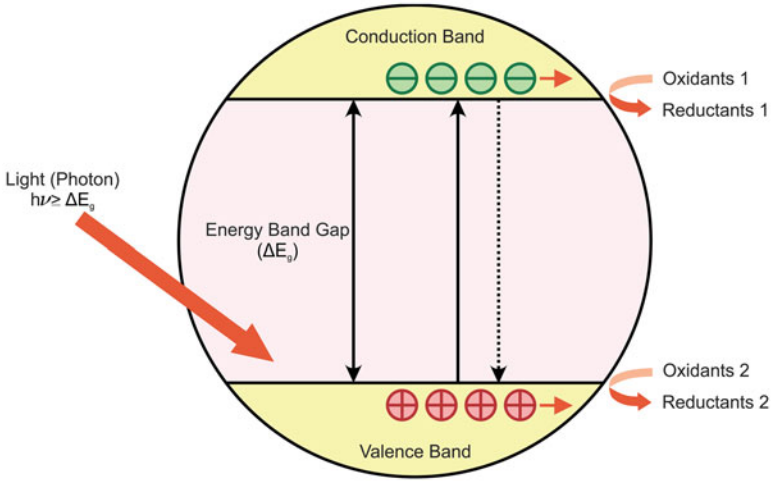

Fig. 9.1 Schematic representation of photocatalysis scheme (Demeestere et al. 2007)

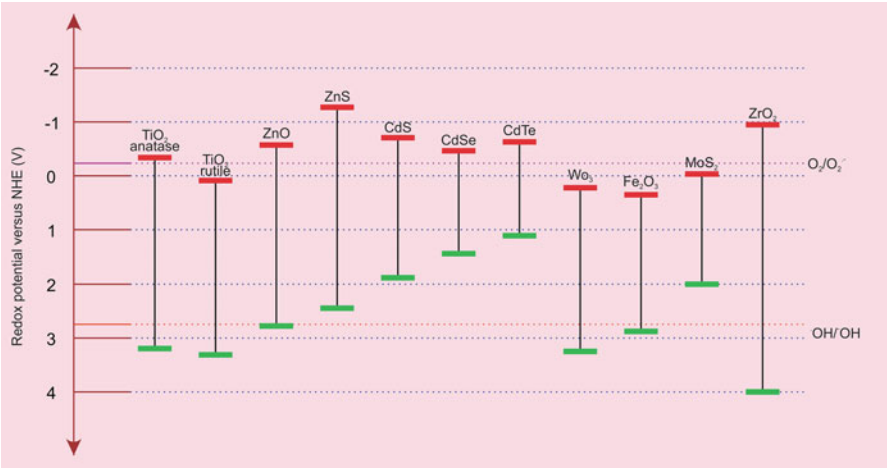

Fig. 9.2 Energy bandgap diagram of various semiconductor oxides (Demeestere et al. 2007)

because of its numerous advantages: chemical stability, low cost, expected electronic and optical properties, and nontoxicity (Litter 1999). Figure 9.2 represents the energy bandgap diagram of various semiconductor oxides.

Generally, TiO_2 is available in three forms: anatase, rutile, and brookite. Of these the third is an uncommon form and stable only at high temperatures. Figure 9.3 represents the structures of TiO_2 in three different forms. Although TiO_2 has several merits towards photocatalytic activities, it is also restricted because of the wide bandgap (3.2 eV), which requires an excitation source of ultraviolet (UV) wavelength

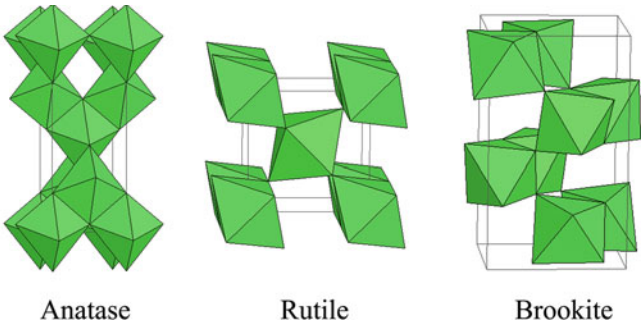

Fig. 9.3 Various TiO_2 phases (Smyth 2010)

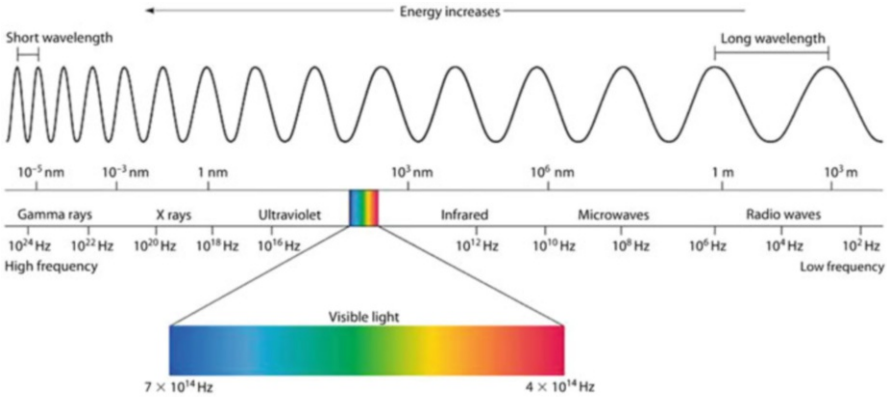

Fig. 9.4 Electromagnetic spectrum representing the entire wavelength region (www.miniphysics.com)

at 387 nm. The availability of this excitation energy is only 5% (Fig. 9.4). The photocatalytic oxidation (PCO) of volatile organic compounds (VOC) and inorganic pollutants are mostly treated by using wide bandgap semiconductor materials. The surface reactants on the semiconductors are the main reason for the foundation of the PCO air purification process (Bickley and Stone 1973; Spanhel et al. 1987; Cant and Cole 1992; Linsebigler et al. 1996; Khan and Ghoshal 2000; Shen and Ku 2002). The properties such as catalyzing, adsorbing, deodorizing, and disinfection of TiO_2 project it as a potential candidate for air pollution treatments.

Serious studies were put forward by researchers all over the world to improve the photocatalytic activity of existing materials or to find an alternate to enhance photocatalytic activity. Li et al. (2005) stated that shifting the optical absorption point of TiO_2 near to the lower energy can improve photocatalytic activities in the visible wavelength. It is a renewable energy source and can be used for large-scale operations. Photocatalysis can be achieved by doping anions (such as sulfur, fluorine, nitrogen, boron, and carbon) in TiO_2 to achieve high efficiency. Several

modification techniques are used for producing highly active TiO_2 for photocatalytic activities, such as doped TiO_2 (e.g., self-doping, non-metal doping, co-doping, metal doping), mesoporous TiO_2, shape-controlled TiO_2, supported TiO_2, surface-modified TiO_2, and dye-sensitized TiO_2 (Sun et al. 2010).

Nitrides, metal sulfides, and oxynitrides are also proposed as candidates for photocatalytic activity using visible light (Inoue 2009). Researchers have proposed a surface plasmonic effect-based plasmonic photocatalyst (Kale et al. 2014). Very recently, graphitic carbon nitride-based metal-free photocatalysts have also been used as a photocatalyst using visible light (Sun et al. 2014; Cao et al. 2015). Although the technique and the enactment of PCO for purification of air pollutants are customized, the difficult aspect is the advances in photocatalytic material and reactors for this application.

Machado et al. 2006 reported that photocatalytic activities can be enhanced by increasing the surface area of the catalyst. A high interaction of reactant with catalyst takes place when the surface area is large. Doping of materials helps reduce the energy bandgap between the valence and conduction bands, which in turn requires low energy (visible light source) for the excitation of electrons from the lower to the higher band (Juanru et al. 2007).

9.4 Biological and Chemical Contaminants

People spend most of their time in an indoor air environment, which determines the health and well-being of a person. Perilous substances emanating from construction materials and indoor tools cause a wide range of health problems and even may be fatal. Around 4.3 million people died in 2012 because of illnesses produced by household air pollution (WHO 2014). Indoor contaminants can be classified into two major categories: chemical and biological.

9.4.1 Biological Contaminants

Biological contaminants are living entities that can be transported via air and are often invisible. Bacteria, viruses, animal dander, moulds, and pollen are some of the common biological impurities which can cause dangerous effects in humans (Nelson et al. 1988). Nutrients and poor moisture content are the two important reasons for the growth of these pollutants (US Department of Health and Human Services 2006). The amount of contaminant that is needed to cause infection in the human being is unknown but will vary from one person to other.

Among the contaminants, airborne bacteria and fungi are considered to be major pollutants that cause challenging health issues. These pollutants will grow under high humidity conditions in materials such as grease, soap scum, dirt, textiles, and paper. Once the mould colony has been formed, it will start floating on the air

(Dallongeville et al. 2015) and fall on land or surfaces, which leads to symptoms such as eye and skin irritation, nasal stuffiness, and wheezing (Taskinen et al. 1997). Madureira et al. (2015) proposed a brief investigation of biological pollutants by accumulating air samples from homes, primary schools, childcare centres, and elderly care centres in the area of North Portugal, and reported that the pollutants are high in childcare centres and schools because of lack of ventilation and different density of occupants. Dust mines are another source causing biological pollutants (Calderón et al. 2015).

9.4.2 Chemical Contaminants

Among chemical contaminants, gases such as nitrogen dioxide (NO_2), carbon monoxide (CO), sulfur dioxide (SO_2), particulate matter ($PM_{2.5}$ and PM_{10}), and chemical and microbial volatile organic compounds (VOCs) are the most serious candidates causing air pollution (Bernstein et al. 2008). One second-most candidate is radon, a colourless radioactive gas that causes lung cancer in most countries (Environmental Protection Agency 2017).

Possible health problems caused by some of the most significant indoor air pollutants, their effects, and the indoor sources are listed in Table 9.1. The first step to reduce or avoid problems from these materials is to know their impact.

Stranger et al. (2009) reported a brief investigation on particulate matter in which the collected samples revealed that 90% of indoor and 85% of outdoor particles are smaller than 2.5 μg. The approximate indoor mass density of $PM_{2.5}$ was found to be 46.6 $\mu g/m^3$ and 29.5 $\mu g/m^3$ in a smoker's and non-smoker's house, respectively, which are above the normal $PM_{2.5}$ EU norm of 25 $\mu g/m^3$. The indoor $PM_{2.5}$ concentrations of ten various buildings in Dublin, Ireland, were analyzed and reported by Challoner and Gill 2014. The concentration of $PM_{2.5}$ was found to be greater during working hours when compared to non-working hours, of which five locations exceeded the EU norm.

The concentration of PM_{10} is approximately equal to 49.4 $\mu g/m^3$ in a smoker's house and 33.8 $\mu g/m^3$ in a non-smoker's house (Stranger et al. 2009). The obtained PM_{10} concentration is found to be more or less equal with the WHO indoor air guidelines value and in good agreement with the mass concentration ranges published by the US Environmental Protection Agency (USEPA 2004a, b).

Concentrations of NO_2 for personal exposure, indoor and outdoor, were 41.4, 32.6, and 38.9 $\mu g/m^3$, respectively. The concentrations of NO_2 were in the range 25–43 $\mu g/m^3$ for personal exposure, 13–62 $\mu g/m^3$ indoors, 24–61 $\mu g/m^3$ outdoors, and 27–36 $\mu g/m^3$ in the workplace, as reported in the INDEX report by the European Commission (EC). In European homes, the maximum associated levels for the use of gas appliances are in the range 180–2500 $\mu g/m^3$ (Koistinen et al. 2008). Rivas et al. (2014) recently examined the concentrations of NO_2 in Barcelona schools and reported that the mean concentration of NO_2 (30 $\mu g/m^3$) is below the guideline level. The concentration of SO_2 both indoors and outdoors was investigated by

Table 9.1 Common chemical indoor air pollutants: their health effects and sources

References	Potential health effects	Compound	Source
Environmental Protection Agency (2017), European Commission. Air Quality Standards (2015), National Ambient Air Quality Standards (NAAQS) (2014), WHO. Technical report (2005), Leung (2015), WHO (2000)	Respiratory and cardiovascular effects	Fine particles (PM2.5)	Furnaces, cleaning and cooking sprays, heaters, fireplaces, and outdoor air
European Commission. Air Quality Standards (2015), National Ambient Air Quality Standards (NAAQS) (2014), WHO. Technical report, World Health Organization (2005), Leung (2015), WHO (2000)	Respiratory and cardiovascular effects	Particulate matter (PM10)	Outdoor air and combustion sources
European Commission. Air Quality Standards (2015), WHO (2005), WHO. Technical report (2010), Leung (2015), WHO (2000)	Asthma, inflammation, reduced resistance to respiratory contagions, broncho-constriction	Nitrogen dioxide (NO_2)	Tobacco, outdoor air, smoke, heating equipment, coal or wood stoves
Leung (2015), WHO. Technical report (2010), WHO (2000)	Highly toxic and fatal	Carbon monoxide (CO)	Tobacco, outdoor air, smoke, heating equipment, coal or wood stoves
European Commission. Air Quality Standards (2015), WHO. Technical report, (2005)	Asthma and respiratory symptoms	Sulfur dioxide (SO_2)	Tobacco, outdoor air, smoke, heating equipment, coal or wood stoves
Bahri and Haghighat (2014), European Commission, Air Quality Standards (2015), WHO Regional Office for Europe. Technical report (2010), WHO (2000)	Leukemia, bone marrow damage, cancer, genotoxic, respiratory problems	Benzene (C_6H_6)	Paints, tobacco, lubricants, stored fuel, detergents, and pesticides
Bahri and Haghighat (2014), WHO Regional Office for	Eye irritation, throat and nose infections,	Formaldehyde (CH_2O)	Combustion sources, detergents, wood products, solvents,

(continued)

Table 9.1 (continued)

References	Potential health effects	Compound	Source
Europe, Technical report (2010), WHO (2000)	headaches, asthma, cancer symptoms		waxes, nail polish removers, tobacco smoke and glues
Bahri and Haghighat (2014), WHO (2000), WHO, Regional Office for Europe, Technical report (2010)	Risk of cancer, reproductive risks, central nervous system (CNS) damage	Trichloroethylene (TCE, C_2HCl_3)	Paint removers, printing ink, solvents, etc.
WHO, Regional Office for Europe, Technical report (2010)	Airway tumours, respiratory tract lesions	Naphthalene ($C_{10}H_8$)	Biomass combustion, mothballs
Bahri and Haghighat (2014), WHO (2000), WHO, Regional Office for Europe, Technical report (2010)	Narcosis, cumulative liver, menstrual disorders, altered sperm structure and reduced fertility, CNS damage	Tetrachloroethylene (C_2Cl_4)	Solvents, printing ink, paint removers, etc.
The US Environmental Protection Agency website (2016), WHO, Regional Office for Europe, Technical report (2010), WHO (2000)	Leukemia, lung cancer and cancers of extrathoracic airways	Radon (Rn)	Groundwater, some earth-derived building materials, earth and rock under buildings and tobacco smoke
European Commission. Air Quality Standards (2015), WHO (2000)	Brain damage, problems in kidney and nervous system, death, and anemia	Lead (Pb)	Soil near highway, water from lead pipes, and dust from lead paints
EPA. Ground Level Ozone – Health effects (2014a), European Commission. Air Quality Standards (2015), WHO, Technical report, (2005), WHO (2000)	Lung infections and respiratory symptoms	Ozone (O_3)	From photochemical reactions in the presence of sunlight and pollutants
European Commission. Air Quality Standards (2015), United States Environmental Protection Agency. Benzo(*a*)pyrene (BaP). TEACH Chemical Summary (2007), WHO Regional Office for Europe. Technical report (2010)	Lung cancer	Benzo[*a*]pyrene (C20H12)	Fireplaces, stoves, tobacco smoke and wood

Stranger et al. (2009), who reported that the levels found were much lower than the guidelines level.

The indoor air quality in ten energy-efficient French schools was examined for 4.5 days (Verriele et al. 2016), and about 150 VOC species were characterized. Measured VOC level varied from 100 μg/m^3 to 680 μg/m^3, depending on occupancy level. At most, 40–85% of ketones and aldehydes are detected from the overall VOC. Acetone, formaldehyde, pentanal, acetaldehyde, 2-butanone, heptane, hexaldehyde, and toluene are present in major concentrations. Aromatic compounds and formaldehyde have concentrations of 8–50 μg/m^3 and 14.8 μg/m^3, respectively, and terpenes are always a minor compound (Verriele et al. 2016). VOC concentration varies sharply in various indoor environments.

9.5 Methods to Control the Mobilization of TiO_2

For the development of photo-reactors for the purification of air contaminants, the controlling of TiO_2 is a tedious process. To control the mobilization of TiO_2, techniques such as fabrication of TiO_2 as a film and depositing TiO_2 on the supported materials are followed. Thevenet et al. (2014) reported that the mobilization of TiO_2 can be controlled by depositing P25-loaded TiO_2 in glass fibers and using these for PCO removal of acetylene. Colloidal silica at 50% and 50% TiO_2 by weight are suspended in water for coating on silica glass fibers. Materials such as PVC sheets (Tejasvi et al. 2015), monoliths (Monteiro et al. 2015), optical fibers (Hou and Ku 2013), and graphene oxides (Andryushina and Stroyuk 2014) were also used for controlling the mobilization of photocatalytic materials.

Compared to the deposition of TiO_2 on supported materials, the synthesis of TiO_2 film is the most powerful method for controlling the mobilization of the photocatalyst materials. Antonello et al. (2014) proposed a novel method for the fabrication of transparent TiO_2 with high mechanical strength using an electrochemical technique. The fabricated film was then used for the PCO removal of volatile oxidation compounds as well as a self-cleaning material. TiO_2 thin films for application to glass windows were suggested by Xie et al. (2016), using a polyvinylpyrrolidone (PVP) modified sol-gel route.

Chemical vapour deposition (CVD), electrophoretic deposition, sol-gel, layer-by-layer method, and thermal methods are important methods proposed for controlling TiO_2 mobilization. In CVD techniques, at high temperature the supporting material is exposed to the gaseous form of the catalyst, which decomposes at the support surface (Shan et al. 2010; Robert et al. 2013). These methods can be used for the synthesis of N-doped TiO_2 from various mixtures (Dunnill et al. 2009), in situ crystallization of TiO_2 (Nizard et al. 2008; Sun et al. 2008), and for controlling film thickness (Nolan et al. 2006).

The sol-gel is a very simple method, in which the support materials are dipped into a solution of TiO_2 mixture heated at high temperature above 450 °C at a controlled rate. Flexibility, simplicity, and low cost make this method the one

most used (Shan et al. 2010; Lopez et al. 2013; Sampaio et al. 2013). For substrates such as stainless steel, Al_2O_3 monoliths, and aluminum and glass fibers, a low-temperature sol-gel method is proposed to fabricate thick, robust, and stable photocatalytic layers for various commercial applications (Kete et al. 2014).

In thermal techniques, the catalyst mixture is directly interspersed on the supporting substrate and then thermally treated to form desired characteristics (Tennakone et al. 1995; Shan et al. 2010). However, performance and characteristics of the deposited catalyst hinge on the calcination temperature (Yu et al. 2000). In the layer-by-layer method, the support material that is to be coated is dipped or sprayed using a catalyst solution for the required thickness. The thickness of the catalyst can be easily controlled and hence a large surface area can be obtained (Yu et al. 2000; Nolan et al. 2006; Krogman et al. 2008; Nizard et al. 2008; Sun et al. 2008; Nakajima et al. 2009; Priya et al. 2009). In the electrophoretic deposition method, under the influence of an electric field, the charge particles are moved in a stable support material. This method is found to be most environmentally safe for the complex shapes and provides uniform film thickness. It can be used to deposit TiO_2 composites on the metal (Raddaha et al. 2014) or plastic (Chen et al. 2011) substrates, TiO_2 nanotube arrays (Bavykin et al. 2013), and perhaps used for coating biological molecules in future (Chávez-Valdez et al. 2012).

9.6 Purification Techniques for Indoor Air Pollution

Various measures should be taken to provide a healthy and comfortable indoor environment by limiting the concentration levels of pollutants and improving indoor air quality (IAQ). Various methods for prevention of air pollution are indoor source control, ventilation, and indoor air purification. Both destructive and nondestructive methods are explained briefly in the following sections.

9.6.1 Indoor Source Control

As said by the modern hygiene and preventive medicine pioneer Max Von Pettenkoffer (1958), "*If there is a pile of manure in a space, do not try to remove the odor by ventilation. Remove the pile of manure.*" (Paunović et al. 2005). This quote explains the significance of controlling the source in an indoor environment as a primary approach. To improve IAQ, the most inexpensive operative method is to eradicate or decrease the indoor air pollution sources (Guo et al. 2003).

Source control includes different principles and applications based on the properties of the particular contaminants, preventing contaminants from entering the buildings, and exchanging emitting sources with low-emitting or non-emitting sources (Nazaroff 2013). Also, indoor environment factors such as climate and

humidity can be controlled to decrease the emission rate or to avoid conditions that can lead to the generation of contaminants (Clements-Croome et al. 2008).

Several combinations are proposed to improve IAQ. Hult et al. (2015) have carried out examinations of new US residences to determine the extent to which formaldehyde exposure can be reduced by controlling indoor sources (building materials). Homes built with low-VOC materials were compared for formaldehyde concentration with buildings with conventional materials. At an air exchange rate of 0.35 per hour, the formaldehyde concentration in conventionally built homes (46 μg/m^3) was found to be higher than in homes with low-emitting materials (34 μg/m^3), that is, 27% reduction was found in buildings with low-emitting materials. This investigation proves the merits and importance of source control.

9.6.2 Ventilation

The second most useful approach for maintaining good IAQ is by providing ventilation by either natural or mechanical methods (Technical 2008). By ventilation, indoor pollutants can be reduced by mixing with conditioned outdoor air, dispensing this conditioned air throughout the building, and exhausting indoor air to the outside environment.

The difference in air pressure of indoor and outdoor environments provides ventilation by passing the air through leaks in the building shell. However, this is not possible in recently built new buildings, which are constructed to be more airtight and use insulation to reduce loss of energy. Fresh air is reduced in mechanical ventilation systems to exchange indoor air with a supply of relatively clean outdoor air (Yu et al. 2009).

Lyng et al. (2015) has studied the effect of concentrations of polychlorinated biphenyl (PCB) in air by employing mechanically balanced ventilation units. Air exchange rates were increased from 0.2 to 5.5 per hour with mechanical ventilation, and PCB concentrations were decreased to 30%. Hence, it is evident that indoor air pollution can be significantly reduced by installing ventilation in buildings.

9.6.3 Filtration

Filtering is one of the most important techniques in which contaminants responsible for air pollution can be removed and contaminants in the environment can be reduced significantly. Mechanical and electronic air filters are the two basic types of filters employed to remove pollutants and airborne microbes. Mechanical filters simply capture the pollutant particles passing through them. High-efficiency particulate air (HEPA) filters are examples of such mechanical filters, with the filtering efficiency of 99.97% for larger particles (0.3 μm airborne particles). In spite of its advantages, HEPA has disadvantages such as low filtering efficiency for smaller

particles: these may be a source of infection from microorganisms harmful to human health and act as a source of pollution when they have not been used properly. Deposition of organic and inorganic matter on the filter leads to microbial growth that decreases filter efficiency and finally causes filter deterioration (Yu et al. 2009). Also, and at the same time, the reaction of deposited particles in the filter with ozone results in formation of by-products such as formic acid, formaldehyde, ultra-fine particles, and carbonyls (Hyttinen et al. 2006; Waring et al. 2008; Yu et al. 2009). Hence, use of mechanical filters for prevention of air pollution requires constant monitoring, cleaning, and replacing of filters (Zhang et al. 2011).

Electronic air filters such as electrostatic precipitators (ESP), which follow the principle of electrostatic attraction to catch air particles, can be used to remove contaminants from the air. The air is passed through an ionization section of the filter where the particles are charged. The ionized particles then pass through the collector plates of opposite charge where they are attracted and trapped by the plates. For the efficient use of filters, the particles must be cleaned frequently from the collector plates. In wet ESP, water is used to clean off the particles whereas in dry ESP rappers are used. A demerit of the ESP is the rapping re-entrainment. While cleaning the dust from the filters, some dust must remain in the filter itself, which causes filter efficiency to decrease. In another method to remove particles from the air, a large quantity of charged particles is passed through a room using an ionizer. Instead of collecting the charged particles as in ESP, here the airborne particles mingle with the ions and seem to be become charged particles. These particles in turn become attached to the nearby surface or attract each other and go out of the air (Environmental Protection Agency 2014b).

Compared to the filters (HEPA or ESP), ionizers seem to have less efficiency in filtering particles such as pollen, tobacco, fungal spores, smoke, and dust (Shaughnessy et al. 1994; Pierce et al. 1996). Regrettably, a few of the electronic filters emit ozone as a secondary product of their operation (Poppendieck et al. 2014). In a comparative study of different ionizers the ozone generation rates range from 56 μg/h to 2757 μg/h (Niu et al. 2001). Berry et al. (2007) examined the consequences of indoor ozone level with a commercially available ionic air cleaner. The measured ozone level was found to be very high in front of the ionic cleaner (77 ppb) when compared to the same room without an ionic cleaner (13–19 ppb). The obtained ozone level was found to be close to EC guidelines.

9.6.4 Adsorption

Electronic and mechanical air filters remove only particulate matter, whereas adsorption units can remove VOC. In the adsorption process, the gasses are attracted towards the surface of a solid such as zeolite, activated carbon, or activated alumina and subsequently removed from the air stream (Yu et al. 2009). Adsorption can occur as physical adsorption or chemical adsorption. If adsorption is induced by Van der Waals forces (intermolecular attractive force), it is then called physical

adsorption in which there is no modification in the properties of either the adsorbent or the gas. Chemical adsorption, also called chemisorption, includes the formation of new chemical bonds (Zhong and Haghighat 2015; WHO 2000). It is a vital reaction in which electron or ion exchange occurs among gas and adsorbent. Particles that have a greater attraction towards the adsorbent will be adsorbed and the remaining molecules will be retained in air. Hence, this method is only efficient for a limited quantity of pollutants. It is also reported that the accretion of pollutants will provide a path for the growth of bacteria and moulds (Van Durme et al. 2008). Schleibinger and Rüden 1999 reported growth of VOC before and after the use of filter pieces. They also proved the presence of VOCs such as esters, alcohols, aldehydes, and ketones in the used filter. Another major demerit is that adsorption will be easily carried out at humidity and lower temperatures, which has a negative impact on targeted indoor pollutants. Similar to filters, absorbents also have limited capacity in reducing air pollution. Hence, these should be frequently maintained for better results (Ge et al. 2015).

9.6.5 Ultraviolet Germicidal Irradiation

The aforementioned techniques will change the phase of the molecules from one form to another instead of destroying them. To destroy pollutants in the air, numerous innovative methods have been proposed, named advanced oxidation processes (AOP). These methods eliminate a broad range of VOCs by producing such agents as atomic oxygen and ozone. Ozone generators, photocatalytic oxidation, plasma reactors, and UV lamps are some examples of AOP. Ultraviolet germicidal irradiation (UVGI) kills biological pollutants by flouting the molecular bonds in their DNA using ultraviolet radiation (Zhang et al. 2015). The replication of the pollutants can be completely limited by breaking their DNA, which in turn causes cell death (Bennett 2009). The UVGI cleaners can be used for the timely purpose but not as an effective replacement technique for filtration systems (Zhang et al. 2011). The efficiency of the UVGI has been limited because of the devastation of moulds and bacteria requires high radiation, which in turn became harmful (Environmental Protection Agency 2009; Wang et al. 2009).

9.6.6 Ozonation

Ozonisers as mostly used for indoor air purification purposefully emit ozone by utilizing electrical discharge or UV lamps to clean the environment. The ozone generators are considered to be an effective purification tool that is highly oxidative and destroys most of the unsaturated VOCs in the indoor air environment. The ozone vendors generally state that ozone generators are effective and safe devices for reducing indoor air pollution. They also claim that the ozone, also called energized oxygen, activated oxygen, or super oxygen, can kill all the contaminants and provide

a pollutant-free indoor air environment by destroying all airborne particles, viruses, moulds, chemicals, odors, and bacteria and produce secondary products such as water, carbon dioxide, and oxygen. In spite of all the advantages just mentioned, the ozone purifiers have many demerits (Environmental Protection Agency 2009, 2014b).

In principle, ozone generators are not an efficient method for destroying pollutants at low ozone levels, being an effective approach only at unsafe, high ozone levels. The emitted levels of ozone generators are approximately 500 ppb (Hubbard et al. 2005), which is five times higher than the maximum ozone exposure reported by the World Health Organization (WHO). Boeniger 1995 also reported that the reaction time for ozone with air pollutants is very high and may last for several months or even years. Contrary to claims by ozone vendors, ozone generators are not efficient in removing formaldehyde (Esswein and Boeniger 1994) or carbon monoxide (Shaughnessy et al. 1994) from the air. Some researchers also report that the reaction of ozone with pollutants may result in harmful secondary products (Weschler et al. 1992a, b; Weschler and Shields 1996).

9.7 Photocatalytic Oxidation

Photocatalytic oxidation (PCO) is an inventive and encouraging technique for removing contaminants from indoor air. With the help of light energy, enactment of the semiconductor is improved and thus can eradicate a wide range of indoor pollutants into CO_2 and H_2O (Demeestere et al. 2007; Nakata and Fujishima 2012; Chen et al. 2015a). Based on band structure, the semiconductors are characterized and the energy bandgap is defined as the bandgap (Eg) between the valence band and conduction band. The semiconductor material is activated by UV light that has energy equal to or greater than the bandgap. The electron in the valence band absorbs the energy from a photon and shifts to the higher valence band (conduction band), creating a hole in the conduction band. This pair is called an electron–hole pair.

9.7.1 Photocatalyst Oxidation Removal of Volatile Organic Compounds

Compared to outdoor air quality, indoor air quality is a cause of major anxiety and many problems to humans. VOCs, important contaminants in indoor air pollution, have become the most widespread PCO targets (Zhao and Yang 2003; Wang et al. 2007). Some studies related to TiO_2-based PCO for VOCs are tabulated in Table 9.2. The PCO confiscation of VOCs together with toluene, acetone, benzene, acetaldehyde, etc. are removed using continuous reactors rather than aqueous degradation. The reproducibility of pure TiO_2 depends on parameters such as shape control (Le Bechec et al. 2015), size dependence (Bianchi et al. 2014), preferentially

Table 9.2 Photocatalytic oxidation of VOCs using TiO_2-based photocatalyst

Authors	Photocatalyst	Source	Pollutant	Performance
Bianchi et al. (2014)	Nano- and micro-sized TiO_2	UVA at 30 W/m^2	Acetone, acetaldehyde, toluene	PC105 (Cristal) > P25 (Evonik) > 1077 (Kronos) > AT-1 (Cristal)
Le Bechec et al. (2015)	TiO_2 microfibers	UV-365 from LEDs	Acetone, heptane, toluene	For acetone, toluene, and heptane on TiO_2 fibers the quantum efficiencies of 0.0106, 0.0024, and 0.0027 is obtained
He et al. (2014)	Mesoporous TiO_2	UVA of 0.19 mW/cm^2	Benzene	Conversion efficiency of 80% is achieved on TS-400 (the best prepared sample)
Ren et al. (2016)	Anatase (F-doped) TiO_2 nano sheets with exposed 0 0 1 facets	UV-A of 4.97 mW/cm^2 and visible light (400–1000 nm) 15.04 mW/cm^2	Acetone, benzene, toluene	High efficiency is obtained using UV and visible light
Liu et al. (2013)	TiO_2/SiO_2 nano composites	160 W high-pressure mercury lamp	Benzene	When Ti/Si = 30: 1, 92.3% conversion in 120 min, 6.8 times higher than P25
Huang et al. (2015)	Transition metal modified TiO_2	Vacuum ultraviolet (VUV)	Benzene	Highest conversion of about 58% is obtained for Mn/TiO_2
Murcia et al. (2013)	Pt/TiO_2	UV-365 from LEDs (90 mW/cm^2)	Cyclohexane	Conversion efficiency of 100% is obtained and the $C0_2$ is promoted by platinum
Chen et al. (2013)	N-doped and O-deficient TiO_2	Visible light (>400 nm)	Benzene	72% conversion of benzene and CO_2 yield is obtained
Thevenet et al. (2014)	Silica glass fibers supported P25-Degussa TiO_2	UV-365 (8–10 mW/ cm^2)	Acetylene	Intermediates such as formaldehyde, formic acid and glyoxal are obtained with mineralization rate of 85%
Monteiro et al. (2015)	A monolithic catalytic bed coated with P25 and PC500	A solar simulator	Perchloroethylene (PCE) and *n*-decane	69% mineralization rate for PCE and 100% for *n*-decane
Andryushina and Stroyuk (2014)	Graphene oxide supported P25	UV at 25 mW/cm^2	Ethanol and benzene	95% conversion is achieved

(continued)

Table 9.2 (continued)

Authors	Photocatalyst	Source	Pollutant	Performance
Hou and Ku (2013)	TiO_2-coated on optical fiber	UV-LED of 126.1 mW/cm^2	Isopropanol	22% IPA removal
Xie et al. (2016)	TiO_2 thin film on window glass	UV with 11.02 mW/cm^2	Acetone and benzene	100% acetone conversion in 25 min and 100% benzene conversion in 110 min
Antonello et al. (2014)	Transparent, mechanically robust TiO_2 films	23 mW/cm^2 UV (280–400 nm) and simulated sunlight	Ethanol and acetaldehyde	Conversion rate of 100% is achieved under UV with 125 and 70 min for acetaldehyde and ethanol respectively
Banisharif et al. (2015)	Fe_2O_3-doped TiO_2	UV and visible light irradiation	Trichloroethylene (TCE)	Conversion rate of 95% is achieved for TCE
Martínez Vargas et al. (2015)	Cu-doped TiO_2	UV365 at 1.0 mW/cm^2	TCE	0.2 wt % Cu content favored the mobility of both TCE and water
Zhuang et al. (2014)	Sn_{2+}-doped TiO_2	Visible light >420 nm	Benzene	TS-40 (Ti/Sn = 40: 1) provided 27% benzene conversion
Han et al. 2013	Spray-coated polyester fiber supported non- metal doped TiO_2	30 W fluorescent lamp at 400–700 nm	Formaldehyde	Highest conversion rate of 38% at C-TiO_2

exposed facets (Ren et al. 2016), and tailored porous structures (He et al. 2014). The larger Brunauer–Emmett–Teller (BET) surface, a more active surface, and pre-adsorption would provide good PCO performance. Figures 9.5 and 9.6 represent the mechanism proposed for the photocatalytic oxidation degradation of benzene and trichloroethylene, respectively.

In PCO air purification, better stability and higher activity can be achieved by the modification of TiO_2 methods of transition metal doping (Park et al. 2004; Huang et al. 2015), non-metal doping (Chen et al. 2013), semiconductor coupling (Liu et al. 2013), and noble metal doping (Murcia et al. 2013). The immobilization technique and material development can be assimilated in practical applications to obtain better outcomes.

Pham and Lee 2015 reported that the V-doped TiO improved photocatalytic activity. The prepared V-doped TiO was then loaded onto polyurethane and then allowed to remove the toluene in a continuous reactor. It is evident from Table 9.2 that the TiO-based photocatalysts are efficient candidates to decompose a vast range of organic contaminants.

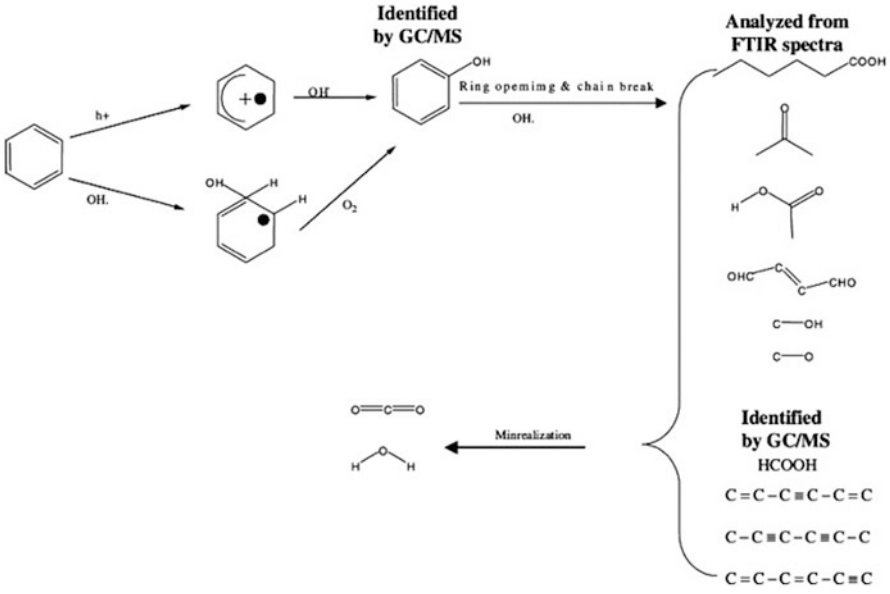

Fig. 9.5 Photocatalytic oxidation of benzene (Ma et al. 2007)

9.7.2 Removal of Inorganic Gas Pollutants Using PCO

Inorganic gas pollutants such as NO_x, CO, H_2S, and SO_x are very hazardous in both the outdoor and indoor environment. In contrast to VOC removal, research on the removal of inorganic gas pollutants is very minor. Continuous reactors are considered to be a best choice for the removal of organic compounds in practice. High mechanical strength can be provided by the TiO_2 film rather than powders. It is also reported that the functionalized polystyrene or polyamide six fibers can be used for the conversion of NO to NO_2 and HNO_3 (Szatmáry et al. 2014). Hence, the TiO_2 (anatase) are coated on the electron-spun polymeric nanofibers. The TiO_2 (pristine) are found to be active only to UV; to make that active in the visible region, oxygen-deficient TiO_2 was prepared for the oxidation of NO in the visible region (Wang et al. 2015). The reduction in the bandgap, increased absorption threshold to visible region, and improved electron–hole pair separation rates are studied and confirmed by the first principle density functional theory calculations.

Metal doping can be used in designing enhanced TiO_2 for photocatalyst oxidation of inorganic gas contaminants. Hu et al. (2015) reported the removal of NO_x can be improved by the synergistic effect of two Pt species together in the catalyst by doping the Pt^{4+} ions in TiO_2 as Pt/TiO_2. Ma et al. (2015) has reported that the UV-visible absorption spectra and TiO_2 photoluminescence activity can be improved by doping the Fe ions. They have used this method in the visible light photocatalytic oxidation of NO_x.

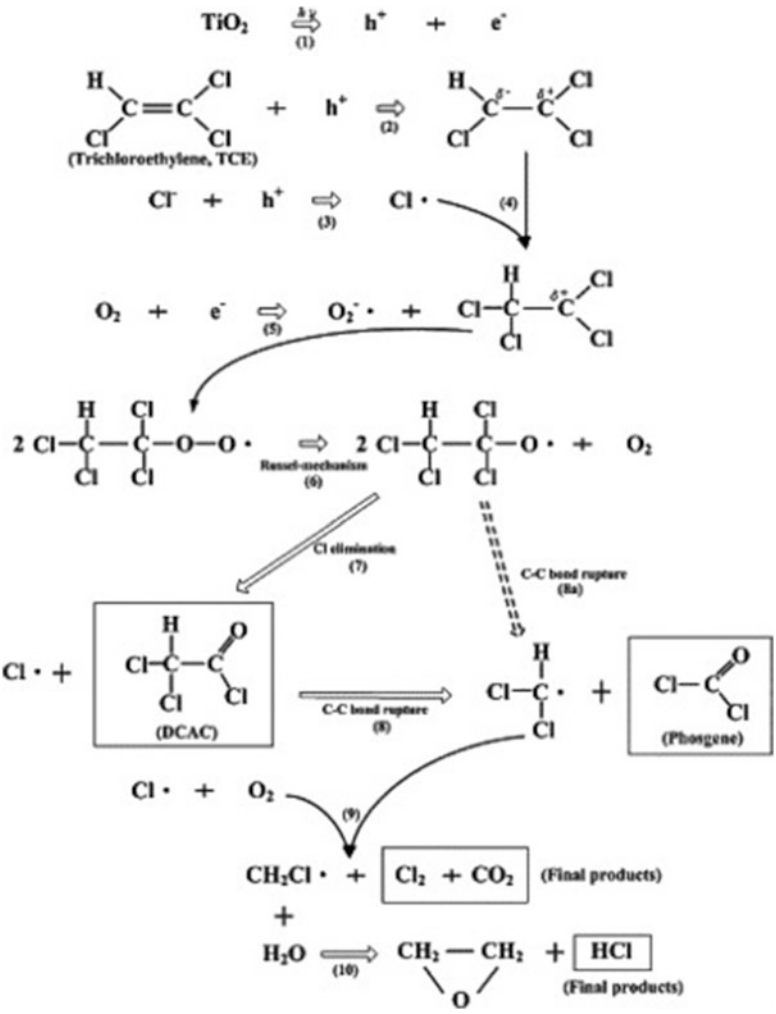

Fig. 9.6 Mechanism for the degradation of trichloroethylene (TCE) (Ou and Lo 2007)

Light absorbance and improved photocatalysis can also be achieved by coupling the TiO_2 to another semiconductor. Alonso-Tellez et al. (2014) reported the new method of coupling in the photocatalytic oxidation of H_2S. The photocatalyst can also be obtained by applying the surface modification method. Jiao et al. reported the preparation of $RuO_2/TiO_2/Pt$ (ternary photocatalyst) with the precise particle size of RuO_2 at about 2 nm, which can be used to remove CO under UV. They have also reported that the finest RuO_2 altered TiO_2 has 20 times greater improved activity than P25, 15 times more than anatase, and 8 times than rutile TiO_2, correspondingly. For the improvement in PCO removal of CO, the noteworthy exposure of RuO_2 (1 1 0) facets are supposed to be the key factor.

9.7.3 Non-Titanium-Based Photocatalyst for Air Purification

Researchers are focusing towards the development of photocatalysts based on TiO_2 rather than other novel photocatalytic materials. Great amounts of other novel photocatalysts are also available for the photocatalytic activities of air purification. Zinc oxide is the next best semiconductor photocatalytic candidate. The photocatalytic activity of ZnO is much higher when compared to TiO_2 in aqueous phase, but the stability of ZnO might be a problem. It has poor stability, but the stability of ZnO can be improved only at high temperatures. Liao et al. (2013) has examined the characteristics of the modified morphology (six prisms of both short and long pyramid shape) and defect-induced ZnO. The modified ZnO has much higher degradation efficiency than the P25 for formaldehyde removal because the modified ZnO polar planes possess higher surface energy, which will result in increased photocatalytic activity.

Y.C. Chen et al. proposed a ZnO/graphene composite by a green one-pot hydrothermal method for the removal of gaseous acetaldehyde (Liao et al. 2013). The photocatalytic activity can be improved by increasing the transfer rate of electrons by introducing rGO (reduced graphene oxide). The degradation rate and CO_2 generation can be drastically improved by controlling the proper rGO content. Sugranez et al. reported that the Fe_2O_3 can be a perfect candidate for the PCO removal of NO_x by retaining HNO_2/NO_3. The Fe_2O_3 is a very stable iron oxide that holds *n*-type semiconductor properties and an energy bandgap of 1.9–2.2 eV.

Bimetal oxides rather than a single metal oxide also can be used as photocatalyst. Huang et al. reported a ZrxTi1xO_2 photocatalyst material which can be used for the decomposition of gaseous HCHO (Chen et al. 2015b). For the removal of formaldehyde using PCO compared to the single Bi_2SiO_5, improved results were observed by using coupled Bi_2SiO_4 and AgI prepared by an in situ preparation method (Wan and Zhang 2015).

Graphitic carbon nitride has considered as a much desired metal-free photocatalyst candidate for air pollution (Sun and Wang 2014; Sun et al. 2014). Sun et al. (2015) reported that the Ag nanoparticle-deposited g-C_3N_4 nano sheets could be used for the PCO removal of NO_x under visible light radiation. Ag nanoparticles not only improve photocatalytic activity but also lead to the selectivity of final products. Katsumata et al. (2013) proposed g-C_3N_4/WO_3 composites for the photo-degradation of acetaldehyde pollution.

9.7.4 Photocatalysis with Ozone

Photocatalysis in combination with ozone (O_3-PCO) has been found to have better efficiency in the destruction of pollutants such as toluene and formaldehyde. To make this method marketable, the stability and efficiency of the same were analyzed and reported by researchers. Haibao Huang in 2010 investigated and reported the

mechanism to improve the stability and performance of the O_3-PCO process under various operating circumstances. The outcome of the process shows that it has admirable stability during the change of initial O_3 concentration and humidity. Compared to the PCO, the O_3-PCO has excellent characteristics for eliminating pollutants. Efficiency in removing toluene and formaldehyde in the ozone-PCO process seemed to be increased from 12% to 96% and from 64% to 97.5%, respectively, when compared to that of PCO. Secondary products for this toluene oxidation were also significantly reduced. It is evident from the foregoing discussion that O_3-PCO is an effective method to reduce the air pollutants compared to the PCO method.

9.8 Summary

In this chapter, we concluded that the basic properties of a photocatalyst, the photocatalyst materials, and their application for the removal of indoor air pollutants clearly indicate that the photocatalyst is an effective method for environmental cleanliness. It is a potential tool for numerous industrial applications such as wastewater treatment, air pollution, and hydrogen generation to maintain a hygienic environment. Although photocatalysts are considered to be suitable for environment pollution remediation, many improvements are still needed to provide a cheap, highly efficient, stable, nontoxic, and highly active photocatalyst in visible regions.

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