

Recent Advances in Titania-based Composites for Photocatalytic Degradation of Indoor Volatile Organic Compounds

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ABSTRACT

Indoor air pollutants can cause severe health problems, specifically in terms of toxicological impacts on human. Every day, a complex mixture of many air pollutants is emitted from various sources and subject to atmospheric processes that can create varied classes of pollutants such as carboxylic acids, aldehydes, ketones, peroxyacetyl nitrate, and hydrocarbons. To adhere to indoor air quality standards, a number of techniques such as photocatalytic oxidation of various volatile organic compounds (VOCs) have been employed. Among these techniques, titania (TiO₂) based photocatalytic reactions have proven to be the best benchmark standard approach in the field of environmental applications. Over the last 45 years, TiO₂-based photocatalytic reactions have been explored for the degradation of various pollutants. This review discusses the indoor air quality profile, types of indoor pollutants, available indoor air cleaning approaches, and performance of TiO₂-based catalysts. Finally, we have presented the perspectives on the progress of TiO₂ induced photocatalysis for the purification of indoor air.

Key words: Indoor air, VOCs, Photocatalysts, Titanium dioxide, UV/Vis light, Purification, Degradation, Reactor design

1. INTRODUCTION

Due to rapid industrialization in the late 18th century, pollution levels have been increased in cities, causing to form solid particulate matter, aerosols, and acid rain

(Malley *et al.*, 2016; Seto *et al.*, 2012) which reflects the ever increasing effect of anthropogenic activities on outdoor air quality. In first world countries, emissions of pollutants into the atmosphere have drastically decreased since the 1980's due to the implementation of effective emissions abatement devices (Malley *et al.*, 2016; Shaheen and Lipman, 2007). However, the quality of indoor air is generally worse than outdoor air (USEPA, 2017). The outdoor air can be polluted by emission of various pollutants from industry and road vehicles while poor indoor air quality can be the result of polluted outdoor air in flow, low building air exchange rate, and emission of varied compounds from candles, decorative stoves, cooking, decaying food, furniture emissions, moulds, building materials, and human exhaled breath (Nath *et al.*, 2016). Among various hazardous compounds, volatile organic compounds (VOCs), being one of the important class of anthropogenic pollutants, are emitted from different industrial and urban sources (Wang *et al.*, 2007; Augugliaro *et al.*, 1999). Generally, in confined places VOCs come from wall finishings (Lee *et al.*, 2003), nearby vehicular emissions (Baek *et al.*, 1997), and human activities. The presence of VOCs in indoor environments reflects the poor indoor air quality (IAQ) which can make people more susceptible to allergies, respiratory infections, and cancers (Butterworth, 2006).

The use of insulating and building materials has been identified as one of the important sources for the emission of VOC, leading to the exceedance of VOC guidelines in confined spaces (e.g., buildings, cars, buses, and aeroplanes) (Chin *et al.*, 2014; USEPA, 2017). Since people often spend most of the time in confined spaces, e.g., buildings (87%) and in vehicles

(6%), so are suffered from the extended exposures of VOCs (Klepeis *et al.*, 2001) compared to outdoor air. As a result, indoor air pollution has shown higher order effects on human health, indicating that human activities were greatly affected by environmental exposure, which presents a compelling economic case for investment to achieve good indoor environmental quality (Fisk and Rosenfeld, 1997).

Several efforts have been made on the reduction of indoor air pollutants specifically VOCs, allowing to attain good indoor air with little or no production of toxic side products. A few of these approaches are given below:

- a) Increasing the air exchange rate
- b) Reducing VOC emissions
- c) Proper use of hazard analysis critical control points (HACCPs) and control of substances hazardous to health (COSHH) standards
- d) Minimization of VOC levels using various indoor air treatment methods

The first three strategies are based on the preventive measures to reduce VOCs levels in confined places. Furthermore, the controlling of indoor air pollutants in confined spaces may not be feasible due to the poor air exchange rates. Similarly, indoor air may become more polluted by air exchange procedure because of the high levels of air pollutants in outdoor air (USEPA, 2017). Moreover, internal circulation of air (inside automobiles) is not generally capable of reducing the levels of pollutants (Sattar *et al.*, 2016).

The most ideal option would be to prevent the entrance of VOCs in confined spaces and that is often not feasible. In the alternative, various strategies (thermal degradation, bioremediation, mechanical and electrical filtration, absorption, adsorption, membrane separation, ozonation, condensation and photocatalytic oxidation) have been used for the minimization of air pollutants in indoor air, however each approach has its own merits and demerits (Luengas *et al.*, 2015). For examples, thermal degradation of organic compounds requires high thermal energy and while bioremediation processes usually requires long time spans to degrade pollutants. In very confined spaces such as submarines, purification of air from hazardous compounds is carried out by air revitalization technique managed through different modern technologies (Clark, 1990). To maintain the oxygen contents inside the cabins, O₂ is generated through electrolysis and is controlled by computer systems. At the same time, polluted air is scrubbed for removal of CO₂, particulate matter, oxidation of some organic compounds, and dehumidification. Moreover, particulates and VOCs were greatly minimized by installing high efficiency particulate

arrestance filters (HEPA-filter) in the ventilation system (Severs, 2006). However, condensation, filtration, and sorption approaches may not be viable when indoor air contains substantial amounts of pollutants.

Hence, photocatalytic oxidation of organic compounds may be one of the most desirable approach for the minimization or removal of pollutants in indoor air (Reddy and Kim, 2015). In this method, organic compounds are degraded by photochemical reactions using various inorganic substances as photocatalysts. Photocatalytic oxidation of volatile organic compounds can only lead to partial decomposition of pollutants and are difficult to prevent CO₂ evolution since it is based on the chemical composition and toxic nature of VOCs. Several studies have used various kinds of photocatalysts for the degradation of indoor VOCs with high degree of removal efficiencies (Luengas *et al.*, 2015; Bianchi *et al.*, 2014; Cai *et al.*, 2014; Kartheuser *et al.*, 2012; Mo *et al.*, 2009; Arzac *et al.*, 2008; Auvinen and Wirtanen, 2008; Arana *et al.*, 2004; Jimmy and Chan, 1998).

In view of the seriousness of poor IAQ, it is desirable to review recent developments made especially in photocatalytic oxidation for the remediation of VOCs in indoor environments using TiO₂ based catalysts. This review also describes the further developments on air purification techniques, especially in terms of practicality and performance efficiencies in the practical applications. After review of literature reveals that all the works have been focused on the removal of pollutants only at lab-scale, and very few researchers have made their efforts in the removing of VOCs from indoor air using TiO₂ as photocatalyst.

2. INDOOR AIR QUALITY PROFILE AND PHOTOCATALYSIS

Due to high levels of pollutants in air, indoor air quality (IAQ) is considered as an important task for health and safety concern. Currently, IAQ is tied to symptoms such as fatigue, headaches, and irritation of the eyes, nose, and throat. To address the several health issues, it is vital to have a clear picture about the approximate composition of contaminants and their sources in indoor air along with the nature of contaminants (Table 1). Three types of parameters (physical, chemical, and biological) are needed to be measured to maintain good IAQ. Physical parameters involve air temperature, relative humidity, and air movement while chemical parameters involve chemical species such as inorganic and VOCs. The biological parameters involve total fungal counts and airborne counts. Table 1 illustrate an overview of physico-chemical and

Table 1. Indoor air quality parameters with standard values for 8 hours average working in work and public zones.

| Order order | Parameter | Unit | Excellent class | Good class | Limit for IAQ |
|-------------|--|--------------------|-----------------|------------|---------------|
| 1 | Air temperature | °C | 20 to < 25.5 | < 25.5 | 22.5-25.5 |
| 2 | Airborne bacteria | cfu/m ³ | < 500 | < 1000 | 500 |
| 3 | Relative humidity | % | 40 to < 70 | < 70 | < - 70 |
| 4 | Respirable suspended particles (PM ₁₀) | µg/m ³ | < 20 | < 180 | 150 |
| 5 | Carbon dioxide | ppmv | < 800 | < 1000 | 1000 |
| 6 | Carbon monoxide | ppmv | < 1.7 | < 8.7 | 9 |
| 7 | Formaldehyde | ppbv | < 24 | < 81 | 100 |
| 8 | Toluene | ppbv | | 290 | |
| 9 | Xylene | ppbv | | 333 | |
| 10 | Benzene | ppbv | | 5 | |

Source: https://www.bca.gov.sg/greenmark/others/NEA_Office_IAQ_Guidelines.pdf, <http://www.iaq.gov.hk/tables.html> and <http://greenguard.org/files/IAQ%20Management%20Plan.pdf> (Access date 07-01-2017)

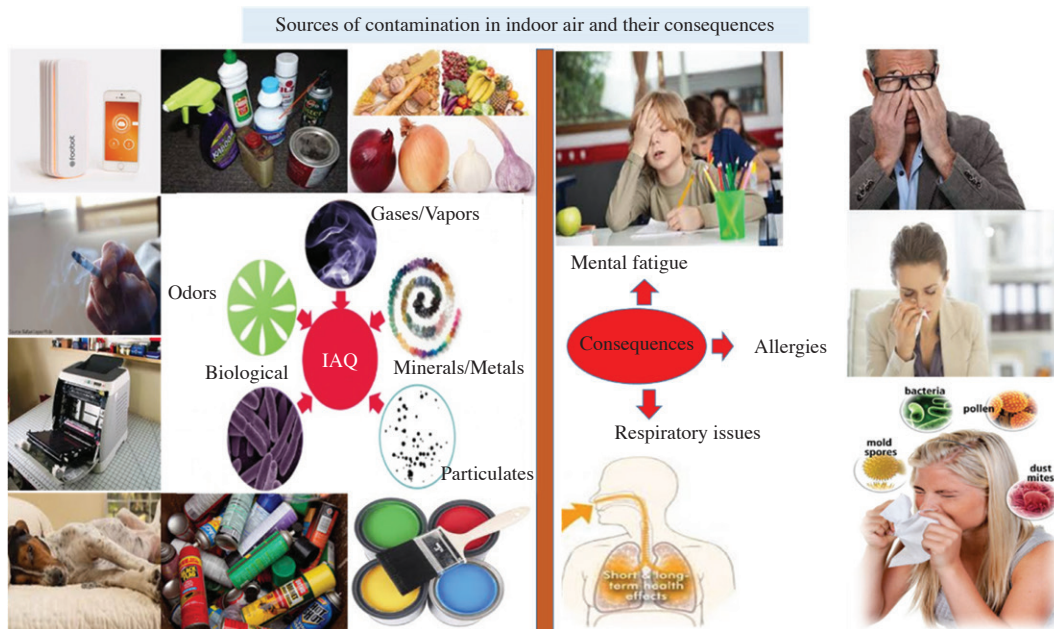


Fig. 1. Sources of contamination in indoor air and their consequences on human health.

biological parameters that can be used for measuring of IAQ. To ensure the quality standards of indoor air for occupation health and safety, various legislation had been introduced at international, national and regional scales. The main objectives of these programs (occupational safety and health administration (OSHA), health hazard evaluations (HHEs), institution of occupational safety and health (IOSH), and national examination board in occupational safety and health (NEBOSH) are to provide guidelines to protect the health and comfort of workers and other residents.

2.1 Sources and Health Concerns of Polluted Indoor Environment

Generally, VOCs are released from various sources

such as solvents, paints, workplace cleansers, pesticides, glues, disinfectants, and perfumes. As a result, VOCs are easily entered into the indoor environment and their possible consequences are shown in Fig. 1. It is well established that IAQ is responsible for building related illnesses (da Costa Filho *et al.*, 2017), and multiple chemical reactivity (MCR) (Lan *et al.*, 2011), directly or indirectly causes 4.3 million premature deaths in 2012 (WHO, 2014). Sick building syndrome (SBS) one of the various diseases in humans caused due to air contamination shows how poor air quality in confined spaces imparts serious health effects on humans (Redlich *et al.*, 1997). Among air pollutants, volatile organic compounds are suspected to be one of the major components that can cause SBS and related

illnesses. As IAQ degrades, prolonged exposure may make the symptoms more serious possibly due to decrease in immunity. For example, prolonged exposure of higher concentrations of VOCs can affect the central nervous system and respiratory tract, which lead to cancer, because numerous VOCs are carcinogenic and teratogenic (Butterworth, 2006). Similarly, low concentrations of VOCs are also suspected to cause asthma, irritation to eyes and sensitization to skin (Nath *et al.*, 2016).

2.2 Indoor Air Pollution: Treatment Techniques and Selection Criteria for Photocatalysts

The removal of VOCs from indoor air can be achieved through many techniques such as thermal treatment, filtration, bioremediation, chemical oxidation, and ozonation each having its own limitations. For example, thermal destruction of VOCs efficiently degrades VOCs but it requires high energy inputs and also generates by-products (CO, CO₂, and NO₂) that may cause another source of contaminants. To overcome these difficulties, the chemical methods have proven to be the promising approaches for the removal of VOCs from indoor air, however these methods are also not free from flaws because these require specific and selective inorganic compounds to oxidize organic pollutants, which limits their usage for the oxidation of wide range of organic compounds. In such cases, the use of photocatalysts would be one of the promising options for the degradation of VOCs in indoor air due to their reusability, low-cost, simplicity, and efficiency (Megahed, 2013).

Criteria that govern the effectiveness of a photocatalyst include: its photoactivity, biological/chemical inertness, photo stability (i.e., not liable to photo anodic corrosion), reusability, cost, and non-toxicity (Paulauskas *et al.*, 2013; Oliveira *et al.*, 2012; Shrivastava, 2012; Litter, 1999). A good photocatalyst must be photo activated that generate the relevant electron-hole charge carriers necessary for the degradation of air pollutants. It must not deteriorate during the photocatalytic reaction and be reusable over several cycles. Specific surface area of the material is of utmost importance in the photocatalytic reactions that are generally used in the purification of water and air (Fang *et al.*, 2009). Since large surface area provides many active sites for the degradation of organic compounds via photocatalytic reaction. Further, larger surface area generates more surface states that can act as surface traps to enhance carrier separation and to improve photocatalytic efficiency. In particular, fine crystalline and porous nanostructures of different morphologies are found to be the best photocatalysts for the degrada-

tion of wide variety compounds.

The morphology of nanostructures can be tuned to different morphologies such as nano spheres, wires, and plates by optimizing various parameters (concentration, temperature, pH and template) during their synthesis. These different morphologies arguably play key role in improving the performance of catalyst with improved oxidation rates. For example, nanostructures have been synthesized with various morphologies including 0 D (nano-dots (Yu *et al.*, 2009), 1 D (nanotubes, nano-rods, nano-wires, nano-belts, and nano-needles (Sun *et al.*, 2014)), 2 D (nano-wells (Hoang *et al.*, 2013), and 3 D (Platelets of perovskite, organic frameworks, and various metallic oxides (Li and Liu, 2016)). These nanostructured materials exhibit excellent conductive scaffolds that improves photo electrochemical water splitting and overall photocatalytic degradation of pollutants in air or water. Furthermore, an ideal photocatalyst must possess reasonable band gap active in the visible region, which can capture the UV light for the activation of photocatalytic reactions. Band gap of materials increases as their dimensions are reduced to the nanometer scale. Hence, nanostructures would produce wide band gaps relative to their bulk form. Therefore, nanostructured semi-conductors exhibit higher oxidizing and reducing potentials than their bulk form because of their unique physico-chemical and optical properties. In a typical photocatalysis process, photocatalyst generates reactive oxygen species by absorption of UV light via electron-hole recombination events. As a result, an effective electron hole pair is generated and must be quickly separated, which leads to undergo redox reaction at the photocatalyst-adsorbate interface without electron-hole recombination. To act as the best photocatalyst, the conduction band edge of photocatalyst must be more negative than the redox potential of H⁺/H₂ (0 V) vs. normal hydrogen electrode (NHE). Similarly, the top edge of the valence band must be more positive than the redox potential of O₂/H₂O (1.23 V) (Coronado *et al.*, 2013). In photocatalysis, the reduction/oxidation of species can be initiated by the adsorption of chemical species on the surfaces of catalyst through the photogenerated charge carriers, depending on the relative positions of their redox potentials. It was observed that the redox potential of the hole on TiO₂ is +2.53 V at neutral pH, whereas that of the excited electron is -0.52 V (both versus standard hydrogen electrode (SHE)). Therefore, reduction reactions can be occurred only when the redox potential of the excited electron is negative enough to reduce the oxidant, while the oxidation reactions can be taken place when the redox potential of the h⁺ is more positive than that of the reductant. Importantly, the redox reactions are easily taken place

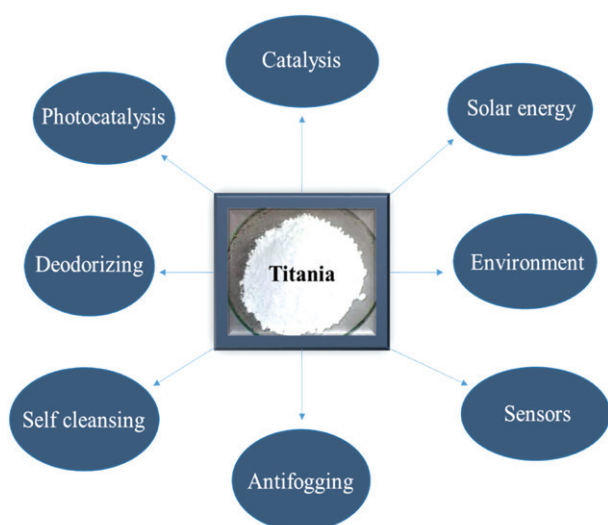


Fig. 2. Various applications of titanium dioxide.

using TiO_2 as a photocatalyst since the photogenerated electrons and holes are strong enough reducing agents ($-0.52 \text{ V} < -0.413 \text{ V}$) and oxidizing agents ($2.53 \text{ V} > 0.83 \text{ V}$), respectively. Therefore, TiO_2 has gained much attention because of moderate band gap, high photoactivity, nontoxicity, cost efficiency, chemical/photochemical stability, and reusability (Fiorenza *et al.*, 2016; Ireland and Ducati, 2015; Cai *et al.*, 2014; Nishijima *et al.*, 2007; Zuo *et al.*, 2006; Arana *et al.*, 2004; Noorjahan *et al.*, 2004). Amongst semiconductor photocatalysts, TiO_2 has found to be an ideal material for UV induced photocatalysis because of its abundance, physico-chemical properties, and low cost. Since the first photocatalytic water splitting was demonstrated using TiO_2 electrodes under ultraviolet light in 1972 (Fujishima and Honda, 1972), there has been significant progress on the use of TiO_2 as photocatalyst for the degradation of various chemical species. Thus, to date, a number of studies has been explored on the various types of TiO_2 materials as photocatalysts in multidisciplinary research areas such as energy, health, and environmental applications. Furthermore, TiO_2 -based photocatalytic reactions have become a hot research field in the purification of air and water. Fig. 2 shows the applications of TiO_2 in multidisciplinary research areas.

3. DEGRADATION OF HAZARDOUS COMPONENTS IN AIR

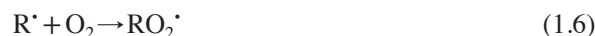
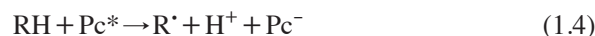
Numerous organic compounds (aliphatic and aromatic) can be found in indoor air ranging from ppb to ppm as given in Table 1. The photocatalytic activity of

various TiO_2 -based photocatalysts was mainly based on the generation of hydroxyl and peroxide radicals, which in turn are capable to oxidize and reduce various species present in the reaction environment. In a comparative study, Nagarajan *et al.* (2017) quantified the hydroxyl radicals that were generated from various photocatalysts with a chemical probe-coumarin. In this approach, coumarin is converted into 7-hydroxycoumarin as a fluorescent compound which enables the amount of hydroxyl radicals to be determined. It was shown that photocatalysts absorb UV/Vis light for the photocatalytic oxidation of chemical species via OH radical production. Various approaches have been utilized to increase catalytic activity of TiO_2 based photocatalysts to cover whole visible region. In this concern, significant efforts have been devoted on the design and synthesis of photocatalysts which are more efficient in visible region as the solar spectrum consists of more than 40% of visible light and around 4% of UV radiation. To understand the performance of photocatalysts, it becomes vital to consider the primary contributing factor; electronic structure, which governs the initial photo-excitation of electrons to higher energy levels (valence to conduction bands) (Nagarajan *et al.*, 2017).

3.1 Theoretical Aspects of Photo-degradation Reaction

Generally, photocatalysis involves two processes: photochemistry and catalysis. Catalysis involves the use of catalyst to reduce activation energy and to enhance rate of chemical reaction without being consumed at the end of reaction. In a photochemical reaction, reactant species absorb photons and generate products of excited molecules, radicals, or ions. Hence, photocatalysis is the acceleration of a chemical transformation by catalyst in the presence of ultraviolet, visible, or infrared light quanta (Haque *et al.*, 2012).

Typically, an excited photocatalyst (Pc^*) initiates chemical transformations of reactants (R) into products (P) and return into their ground state after performing each cycle of chemical transformations (Dionysiou *et al.*, 2016). A typical photocatalytic reaction mechanism for the degradation of air pollutants can be written as (Dionysiou *et al.*, 2016):



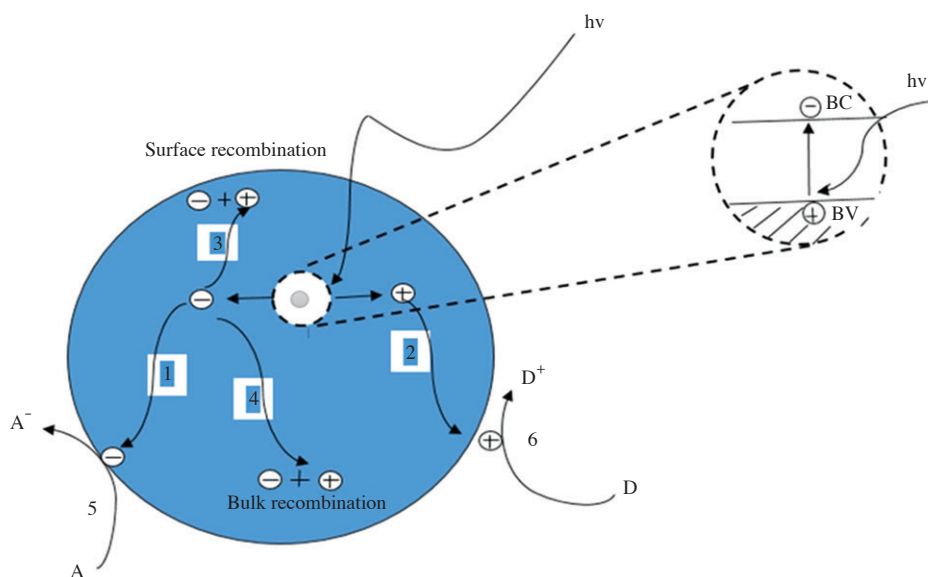


Fig. 3. Schematic diagram showing charge carrier dynamic upon irradiation of a semiconductor: 1 electron transport to the surface, 2 hole transport to the surface, 3 surface recombination, 4 bulk recombination, 5 electron transference to an acceptor molecule and 6 hole trapping by a donor molecule-Adapted from (Coronado *et al.*, 2013).



Peroxy radicals (RO_2^*) can be formed by the oxidation of alkyl radical (R') in the presence of oxygen in air (Eq. 1.6). Alternatively, hydroperoxide (ROOH) may be formed (Eq. 1.7), with participation of superoxide radical (HO_2^*). As a result, CO_2 and H_2O were generated as end products in the photocatalytic destruction of any organic compounds (Eq. 1.8) (Dionysiou *et al.*, 2016). Upon irradiation of catalysts with light, the charge carrier interface dynamics take different forms, which facilitates to form photogenerated holes that are strong enough to oxidize various organic compounds via photochemical reactions (Fig. 3). For example, the semiconductor can donate electrons to acceptors (pathway 1) to reduce the acceptor), whilst holes migrate to the surface to oxidize the donor species (pathway 2). The generated electron-hole pairs can recombine, dissipating the input energy in the form of heat (surface recombination) (pathway 3). Moreover, the carriers can also combine within the photocatalyst surface to generate alkyl radicals (pathway 4).

To enhance absorption abilities of photocatalysts in visible region of the electromagnetic spectrum, it is vital to design the metal oxides (TiO_2 and ZnO) with various heteroatom doping for effective absorption of UV-visible light, which leads to low electron-hole charge recombination events. Modification can be achieved by doping through various components like

non-metals (Asahi *et al.*, 2001), metals (St. John *et al.*, 1983), dye sensitisation (Gurunathan *et al.*, 1997), and semiconductor coupling (Li *et al.*, 2015). Various research groups have explored the use of non-metals like N, S, C, and F as dopants in TiO_2 nanomaterials for efficient absorption of UV-visible light (Umebayashi *et al.*, 2002). Particularly, the doping of nitrogen in semiconductor materials has gained much interest due to its high stability and its similarity in atomic size to oxygen, allowing to achieve low ionization potentials with enhanced visible light absorption (Pelaez *et al.*, 2013).

Noble metals (such as Pt, Au, Pd, Rh, Ni, Cu, and Ag) are effective for improving efficiencies of photocatalysis due to their tendency to act as electron sink (Wu and Lee, 2004). Specifically, electrons are conducted via these metals to prevent recombination with holes. Electron spin resonance (ESR) spectroscopy is a very useful tool for investigating electron transfer dynamics between conduction band and the metal particles. This technique has been employed to confirm electron transfer between Pt nanoparticles and TiO_2 (Anpo and Takeuchi, 2003). They proposed a direct relation between irradiation time and Ti^{3+} signals. As Pt loading increased, it led to the reduction of electron transfer. The accumulation of electrons on the metal particles lowered the fermi levels towards the conduction band of TiO_2 , resulting in enhanced reduction potential of photocatalyst (Subramanian *et al.*, 2003).

Metals have also been used to increase the absorption range in the visible region through their plasmonic resonance nature. The collective oscillations of the elec-

tronic cloud of metal nanoparticles can sensitize TiO₂ photocatalysts to absorb in the visible spectral range. This has been observed for Ag, Au, and Cu where they exhibited plasmonic resonance in the visible spectral range (Kaur and Pal, 2015; Sakthivel *et al.*, 2004). Another common strategy for ensuring visible light absorption is to use chemical chromophores. This strategy is commonly called as dye sensitization and is well exploited in the well-known dye sensitized solar cells (DSSC) (Cost, 1991). Chromophores are similar to light harvesting light pigments as present in algae and higher green plants.

Coupling two or more semiconductor photocatalysts with different band-gaps have also been investigated to achieve visible light active photocatalysis (Gurunathan *et al.*, 1997). Typically, TiO₂ has a wide band gap that can help to couple with a narrow band gap semiconductor (CdS), which improves the photocatalytic efficiency (Kang *et al.*, 1999). In such nano architecture, conduction band (da Costa Filho *et al.*, 2017) electrons are injected from CdS to the conduction band of TiO₂ (Fig. 4), whilst the corresponding valence band (VB) holes of TiO₂ are injected into VB of CdS. This hetero structure arrangement promotes high electron-

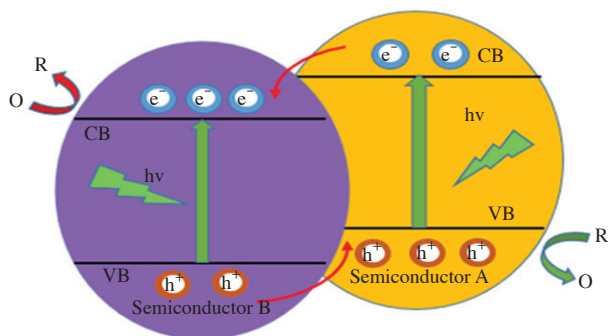


Fig. 4. Semiconductor coupling, adapted from (Wang *et al.*, 2014).

hole separation in photocatalytic reactions, which improves the rate of photochemical reactions with high degree. Fig. 5 depicts the basic features of the complete mechanism of TiO₂-based photocatalysts, photocatalytic decomposition of VOCs, and mitigation of ultimate mineralized product (CO₂). Moreover, the reaction setup (in Fig. 5) can also be employed for the mineralization of VOCs contained in newly built and/or furnished houses.

3.2 Optimization of Photo Induced Degradation of VOCs in Indoor Air

Noticeably, the efficiency and performance of catalyst are strongly affected by applied reaction parameters. Hence, it is essential to describe all the affecting parameters in photocatalytic reactivity. It was noticed that several factors such as reaction temperature, humidity, particle size of the catalysts, reactor design, velocity of air, and the time span strongly affect the photocatalytic degradation of VOCs in indoor air (Hager and Bauer, 1999). A number of research studies have investigated the optimum parameters for efficient photocatalytic degradation of various organic compounds in indoor air (Lin *et al.*, 2013; Liu *et al.*, 2006; Obee and Hay, 1997).

3.2.1 Temperature and Humidity

Various studies have been reported the influence of reaction temperature and humidity on photocatalytic degradation of volatile organic compounds in indoor air (Lin *et al.*, 2013; Hussain *et al.*, 2011; Liu *et al.*, 2006; Jo and Park, 2004; Hager and Bauer, 1999; Herrmann, 1995). The effect of temperature on photodegradation of organic compounds is mainly related to sorption characteristics. The low temperature controls the desorption of products while high temperature limits the adsorption phenomena of reactants (Herrmann, 1995). In order to attain equilibrium between the adsorption and desorption of reactants and products, the

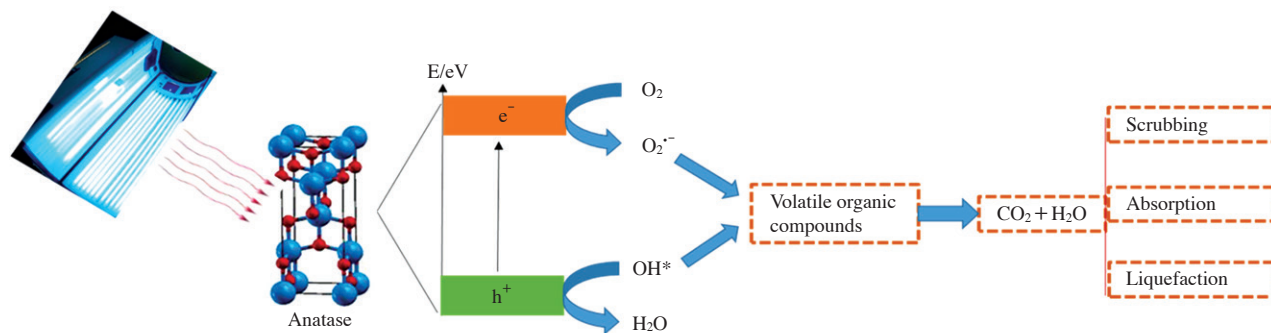


Fig. 5. The photocatalytic mechanism of TiO₂ based catalysts, photocatalytic decomposition of VOCs and mechanism to mitigate CO₂.

reaction temperature is to be maximized.

In a study of the photodegradation of inlet air poisoned with 2-propanol, acetone, and toluene, it was described that the degradation of aforementioned organic compounds is maximum in ambient conditions without the need of heating (Hager and Bauer, 1999). However, according to Liu *et al.* (Liu *et al.*, 2006), reaction temperature and photocatalytic degradation of organic compounds in indoor environments are directly related to each other. In their study, photocatalytic decomposition of ethanol, acetone, and acetaldehyde was carried out at three different reaction temperatures (14, 31, and 43°C). It was further evaluated that at higher temperature, the photodegradation of these compounds occurred more rapidly than at low temperature and thus reduced the reaction time required for the complete decomposition. This finding is in agreement with the fact that solar devices which use light concentrators instead of light collectors generally require circulating water jackets to maintain ambient temperature (Mehos and Turchi, 1993). Similar observations were noticed in a study carried out by Hussain *et al.* (Hussain *et al.*, 2011) in determining the effect of reaction temperature on photocatalytic degradation of ethylene, propylene, and toluene.

Because the photocatalytic reaction involves the generation of hydroxyl radicals, it necessitates the presence of a minimum amount of water in contaminated air to achieve optimum degradation of VOCs. It was also suggested that the optimum amount of water is necessary for the degradation of toluene and 2-propanol although the presence of water inhibited the mineralization of acetone in the applied reaction conditions (Hager and Bauer, 1999). They observed that in the presence of water, adsorption efficiency of acetone decreased because of its competition for active sites. Consequently, it can be evaluated that the influence of relative humidity is related to the nature of contamination. For instance, the total mineralization of toluene and formaldehyde into CO₂ by a photocatalyst is retarded in the absence of water. According to Phillip and Raupp (Phillips and Raupp, 1992), higher degradation efficiencies can be achieved if equilibrium is established between consumption of water, adsorption of reactants, and desorption of products. Nonetheless, higher quantities of water vapor may shift this equilibrium and this may reduce the reaction efficiency. In the photocatalytic oxidation (PCO) of benzene, ethyl benzene, and o-, m-, p-xylenes, trichloroethylene, and perchloroethylene, it was evaluated that the influence of relative humidity was small and PCO efficiencies were close to 100% for four different humidity ranges from 18 to 78% (Jo and Park, 2004).

3.2.2 Velocity of Air, Mass and Nature of VOCs

The velocity of indoor air may also affect the photocatalytic degradation of VOCs because it controls the degree of adsorption of contaminants on the surface of catalyst. It is a common observation that lower flow rates cause more degradation of organic compounds in contrast to higher flow rates. Such a phenomenon may be attributed to the fact that low flow rates enhance the residence time of the contaminants around the adsorbents, thus more adsorption yielding better efficiencies. Similar observations were made in a study carried out by (Hager and Bauer, 1999). They pointed out that the photocatalytic degradation of 2-propanol, acetone, and toluene was occurred more swiftly when low flow rates of inlet air were maintained. Contrary to this observation, the flow rate of contaminated air in the photocatalytic reaction chamber was suggested to have little effect on the degradation of ethanol, acetone, and acetaldehyde (Liu *et al.*, 2006). Whilst, a high velocity of inlet air increases the circling times of the contaminants around the catalytic surface, poor adsorption efficiency would cause negative impact. Hence, slow flow rates of contaminated air may yield better efficiencies.

Photocatalytic oxidation reactions of VOCs also depend on their concentrations in inlet air. It has been reported that low masses of VOCs results in remarkable changes in the degradation rate compared to higher masses (Lin *et al.*, 2013). Similar observations were made in the study of the photodegradation of ethylene, formaldehyde, and 1-butene (Cao *et al.*, 1999; Noguchi *et al.*, 1998; Obee and Hay, 1997). It was also seen that the degradation rate of formaldehyde was decreased as its concentration increased to 600 ppmv in air (Noguchi *et al.*, 1998). Moreover, in a mixture of formaldehyde and acetaldehyde having a concentration less than 1200 ppmv in inlet air, photocatalytic oxidation (PCO) rate of formaldehyde is higher than that of acetaldehyde due to its higher adsorption efficiency in contrast to acetaldehyde (Noguchi *et al.*, 1998). Similarly, the number of contaminants in inlet air also affects their relative rate of photocatalytic degradation. The photolytic disintegration of ethanol and acetone was investigated (Liu *et al.*, 2006), and it was observed that the initial degradation rate of acetone was reduced in the presence of ethanol and that this retardation in catalytic activity of acetone continued with increasing concentration of ethanol in the mixture. They also described that the rate of generation and consumption of acetaldehyde (an intermediate in the degradation of ethanol) was influenced by the quantity of ethanol and acetone in inlet air.

3.2.3 Intensity of UV/Vis Radiation and Mass of Catalyst

Light intensity also controls the catalytic activity of the reactions which are induced by light. Intensity of light is the number of quanta which are responsible for the excitation efficiency of valence electrons from valence bond to conduction band. The dependence of degradation efficiency was investigated in relation to intensity light (Hager and Bauer, 1999). They varied intensity of light from 9.1 to 20.4 mW/cm² and achieved a change in percentage conversion from 1.6-9.1. As such, conversion was directly proportional to the radiant flux of UV lamp. In another study, it was concluded that photo-induced nature of the catalytic reaction needs a minimum radiation flux (Lin *et al.*, 2013).

The dependence of photocatalytic activity on the amount of catalyst was investigated by Hermann *et al.* (2016). In that study, it was observed that rate of photocatalytic reaction was directly proportional to the mass of catalyst. This regime was due to the fact that higher catalytic mass has possessed greater surface area, which allows high degree of reactant species adsorption on the surfaces of catalyst, leading to better catalytic conversion. However, at certain range of catalyst concentration, the degradation rate becomes independent of

catalyst mass because of lower reactant mass transfer and penetration of light. Therefore, it is important to optimize the amount of catalyst to ensure the absorption of maximum amount of photons. Moreover, surplus amount of catalyst in the form of multilayers may mask the exposed surface area for light absorption, thus reducing the rate of disintegration of organic compounds (Lin *et al.*, 2013).

3.2.4 Photocatalytic Reactor Designs for VOCs Degradation in Indoor Spaces

Reactor design also significantly contributes in the catalytic efficiency for the degradation of VOCs due to two reasons: firstly it helps in gathering radiation flux from the radiation source and secondly it provides a mechanism for proper deployment of photocatalytic materials for close interaction between catalyst, VOC and radiation, hence achieving better performance. The laboratory scale photocatalytic reactors have been designed in many ways such as flat plate, multi-plate, paper-based immobilized TiO₂, annular, corrugated plate, multi-annular, monolith, packed bed, foam packed bed, and fluidized bed each having its own benefits and limitations. Some simplified representations of photo-reactors are shown in Fig. 6. In plate type and

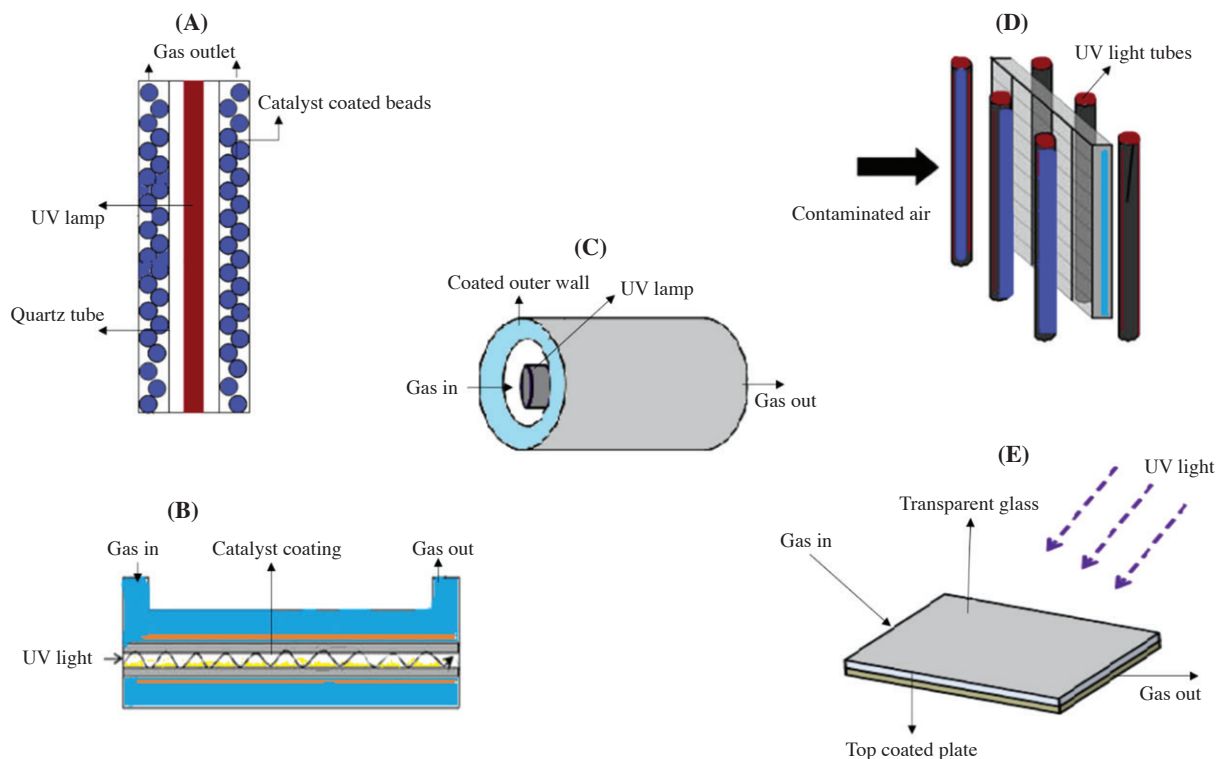


Fig. 6. Schematic of various photocatalytic oxidation reactors. (A) Packed bed, (B) Optical fiber (C) Annular (D) Honeycomb (E) Catalytic coated plate (Hossain *et al.*, 1999; Choi *et al.*, 2001; Mo *et al.*, 2009; Boyjoo *et al.*, 2017).

annular reactors inner surfaces are coated with photocatalysts. These reactors are very helpful in optimizing the reaction parameters but cannot be commercialized due to their low air throughput (Boyjoo *et al.*, 2017). Annular reactors, packed bed or fluidized bed reactors are free of pressure drops along the reactor end and are easy to construct. But the major draw backs of these reactors are their requirement of high amounts of catalysts to be packed and losses of catalyst contents during the exit of air, thus requiring extra traps for catalyst recovery. In such cases monolith based reactors are more promising but they require fiber optic type light source to reduce the light intensity drop-off through the monoliths. In view of all these limitations and to enhance catalytic efficiencies, the designing and deployment of new reactors are important breakthroughs in the research on TiO₂ photocatalysis that have led to significant beneficial for many practical applications to environmental remediation.

4. TITANIUM DIOXIDE BASED PHOTOCATALYSTS FOR VOCs DEGRADATION IN INDOOR SPACES

Titania, being a good photocatalyst especially in UV region, has been utilized extensively in the past decades for the degradation of various kinds of pollutants (organic and inorganic) in air. Titania exists in three different crystalline polymorphs (anatase, rutile and brookite) which consist of a number of TiO₆ octahedrons arranged in well-defined patterns (Hu *et al.*, 2014). The variation in linking patterns of TiO₆ is responsible for a particular crystal structure, crystalline nature, surface structure and electronic properties and photocatalytic nature of TiO₂. It is well established that anatase based TiO₂ are potentially more active towards photocatalytic characteristics relative to rutile and brookite forms (Khataee *et al.*, 2009). However, the mixture of anatase and rutile also sometimes exhibit more photocatalytic activity than alone anatase (Tiwari *et al.*, 2016). The photocatalytic properties of titania are also governed by the adopted morphologies, particle sizes, and ultimate surface area exposed for specific applications. Generally, TiO₂ is prepared in the form of tablets (Stroyuk *et al.*, 2017), dispersed powders in fixed bed reactors (Huang *et al.*, 2017), immobilized (da Costa Filho *et al.*, 2017; Ireland and Ducati, 2015) on various kinds of supports (Silica, cellulosic paper, glass plates) and also is synthesized in different morphologies (nano-powders, nanowires, nano-belts, nano-spheres, and nano-fibers) exhibiting variations in degrees of photocatalytic properties (Shi *et al.*, 2017). These variations are attributed towards variations in

exposed surface area available for adsorption of contaminants and their subsequent degradation.

On account of peak absorption of pristine titanium dioxide in the UV region due to its wider band gap of 3.2 eV, it is active at 200-370 nm. In order to cover the entire solar spectrum, different strategies have been adopted; morphological modification (enhanced specific surface area, porosity and active sites) and chemical modifications such as metal doping, non-metal doping, dye sensitization, semiconductor coupling (Pelaez *et al.*, 2012) and reductive hydrogen plasma have been explored (Palmer *et al.*, 2002). These alterations generally result in improved photocatalytic efficiencies.

4.1 Pure Titania

Notably, wide band gap of TiO₂ restricts its use in UV region for environmental applications. In an attempt to achieve improved photocatalytic activity and absorption in the visible region by increasing surface area and reducing particle size, numerous morphological modifications in titania have been explored (Ola and Maroto-Valer, 2015). One dimensional TiO₂ nanostructures such as nanotubes, nano-rods, nanowires, nano-belts, and nano-needles have been synthesized by various methods such as hydrothermal and self-assembly, particularly nano sized tubular films deposited by electrochemical anodization on titanium metal foils (Nah *et al.*, 2010; Lee *et al.*, 2016). These films possess many benefits such as controlled porosity, vectorial charge transfer, tailored morphology, and a low chance of electron hole recombination at grain boundaries. On account of these characteristics, these films exhibit enhanced performance in photo-induced oxidation of various chemical species (Nah *et al.*, 2010).

Another commonly investigated morphology of titania is monodispersed nanoparticles possessing small crystal size, high surface area, high density of surface coordination unsaturated sites, and reduced bulk recombination, offering improved catalytic performance over microscale catalysts (Hernández-Alonso *et al.*, 2009; Eiden-Assmann *et al.*, 2004). Moreover, TiO₂ nanoparticles with optimized physico-chemical and optical properties exhibit better performance than commercially available photocatalytic materials (e.g. Degussa P25) to disintegrate VOCs (aldehydes, alcohols, aromatic and aliphatic compounds) in indoor environments, when introduced alone to the photocatalytic chambers (Abbas *et al.*, 2011). TiO₂ nanoparticles undergo deactivation with increasing reaction cycles due to accumulation and strong adsorption of intractable carbonaceous intermediates at the catalyst active sites (Ren *et al.*, 2016; Hay *et al.*, 2015).

In such cases, the use of titania nanotubes (TNT) with open channels may facilitate the diffusion of oxy-

gen molecules to the active sites and offer resistance to the deactivation of photocatalyst (Weon *et al.*, 2017). Single ended TiO₂ nanotubes may also exhibit the problem of less diffusion of oxygen molecules and may also lead to deactivation. To avoid this issue, more attention is being focused on freestanding doubly open-ended TiO₂ nanotubes (DNT) film due to their property of double ended openings (Wong *et al.*, 2016). In this regard, DNTs are more helpful in facilitating the mass diffusion of oxygen and contaminants to their active sites, leading to enhanced photocatalytic activity. Additionally, they are more resistant towards deactivation and can be used in many cycles without any loss in efficiency.

4.2 Titania Modified with Metals

Since UV covers a small part of solar spectrum, there is a great desire to find more viable photo-catalysts, which work in visible spectral region and especially are more active between 380-500 nm. In this context, substantial efforts were made to improve the photocatalytic efficiency of TiO₂ activated in visible region by doping with metals in TiO₂ nanocomposites, allowing to control the size, morphology with high surface area and to adjust energy band gap, which improves the adsorption capability for the degradation of VOCs in indoor environments (Reddy and Kim, 2015).

Metal doping is considered as the oldest one and extensively explored with many positive outcomes in various environmental and synthetic applications (Choi *et al.*, 1994). Metal doping can indeed facilitate the formation of electron capture centers in the band structure of semiconductor such as TiO₂ which result in reduction of electron hole pair recombination processes. Moreover, metal doping may also result in photocatalytic oxidation induced by visible region. A range of metals from the periodic table are in use for doping of TiO₂ but doping with d and f block metallic elements is widely explored (Marchelek *et al.*, 2017; Wang *et al.*, 2014; Ismail and Bahnemann, 2012). The chemical modification of TiO₂ by Ni²⁺ may result in the extension of absorption edges of TiO₂ films from UV region to visible light region and this doping may prevent effectively the injection of photogenerated electrons from TiO₂ films to metallic nickel. Further extension of working of TiO₂ from UV to visible region (Bathochromic effect) can be executed by using the plasmonic effect of coinage and noble metals (Deng *et al.*, 2016; Wang *et al.*, 2014). Doping of TiO₂ with Au nanoparticles is believed to engineer a promising visible light induced photocatalyst due to its strong visible-light absorption via local surface plasmon resonance (LSPR) of Au nanoparticles (Wang *et al.*, 2014). Moreover, it has been observed that Au/TiO₂ nano-catalysts are ac-

tivated by atmospheric-pressure oxygen plasma rather than calcination approaches, higher catalytic performance for disintegration of VOCs in air can be achieved (Deng *et al.*, 2016). The introduction of noble metals such as Pt in TiO₂ material was made possible in making worm like Pt-TiO₂ network (Ismail and Bahnemann, 2012). The addition of colloidal Pt nanoparticles in TiO₂ not only enhanced the photocatalytic efficiency of mesoporous TiO₂ by two times for commercially available TiO₂ but also made it resistant towards deactivation. Moreover, these semiconductor catalysts are stable and can be recycled without loss of the photochemical activity up to five-folds (Ismail and Bahnemann, 2012).

Similarly, doping of TiO₂ with strontium by alkali hydrothermal method to form SrTiO₃ microspheres also proved as a good catalyst especially in longer wavelengths (Zheng *et al.*, 2011). In another study, this semiconductor was further modified with CdTe quantum dots for inducing low powered LED lights (465 nm) (Marchelek *et al.*, 2017). Apart from doping, other extensively pursued modifications are composites. These composite based materials are prepared primarily through coupling of TiO₂ with light absorbing materials such as dyes or other materials (chromophores).

4.3 Titania Modified with Non-metals

Chemical modification of titania with different non-metallic elements of the periodic table such as nitrogen (Wang *et al.*, 2006), carbon (Kuo *et al.*, 2007), and sulfur (Yu *et al.*, 2005) has displayed promising results in visible light (>400 nm) induced photocatalysis. The non-metals are substituted on the oxygen atoms in TiO₂ lattice, which leads to a band gap narrowing, resulting in absorption in the Vis region. In this respect, doping of nitrogen in semiconductors nanomaterials is considered as to be activated more effectively by longer wavelength radiations because valence band of nitrogen (N2p) is higher energy level than that of oxygen (O2p) thus presenting a bathochromic shift (Huang *et al.*, 2016).

Similarly, doping carbon in titania may introduces new states close to the valence band edge of TiO₂ narrowing the photocatalyst band gap, making the catalysts to be optically active in visible region (Ballari *et al.*, 2016). Moreover, carbonaceous species located at the surface of the photocatalyst may facilitate the sorption phenomena and thus promotes the photocatalytic performance in the abatement of pollutants contained in confined places. The presence of porous adsorbent surfaces such as nano silica (SBA-15) and zeolites (HZSM-5) with TiO₂ increases the concentration of substrate near the photocatalyst and protects the organic support against the photodegradation (Noorjahan *et*

al., 2004). Moreover, the surface modification of TiO₂ with silica and zeolites has significantly enhanced the catalytic performance of TiO₂ as compared to commercially available TiO₂. Additionally, thin film of TiO₂ with zeolites are flexible and exhibited good abrasion resistance on prolonged reaction spans for the photodegradation of organic compounds.

4.4 Titanium Dioxide Modified with Novel Materials

Modification of titania with novel materials such as organic frameworks, graphenes, and quantum dots have revolutionized the performance of photocatalysts in various fields such as hydrogen generation, solar cells, and environmental applications (Lian and Yan, 2016; Dan-Hardi *et al.*, 2009). Metal-organic frameworks (MOFs) as heterogeneous catalysts have been explored extensively in varied applications such as energy and water splitting (Fu *et al.*, 2012) since they are free from the problems such as adsorbent saturation or their behavior as secondary emitters but there are still few reports in which the catalytic activity of MOF materials has been applied for the purification of contamination in indoor environments. Notably, charge transfer can occur between photo-excited inorganic semiconductors and MOFs, supplying long-lifetime electrons for the reduction of gas molecules adsorbed on the MOF for their degradation. By applying this concept, a new highly porous MOF (Ti₈O₈(OH)₄(O₂C-C₆H₄-CO₂)₆) also called MIL-125 engineered from titanium-oxo-hydroxo clusters and dicarboxylate linkers were synthesized and applied for the disintegration of different alcohols such as methanol, ethanol, and benzyl alcohol under UV irradiation (Dan-Hardi *et al.*, 2009). They observed that MIL-125 exhibits high photonic sensitivity, inherent to the titanium-oxo component. It was also described that a reversible photochromic behavior induced by alcohol adsorption occurs which results in simultaneous reduction of titanium centers and oxidation of adsorbed alcohol molecules.

In order to tune the photocatalytic properties of MOF (MIL-125), benzene dicarboxylate can be replaced by O-aminoterephthalate. In an attempt to reduce the band gap of MIL-125, the effect of substitution of terephthalic acid with diamino terephthalic acid linking unit was explored (Hendon *et al.*, 2013). The authors indicated that the modification of MIL-125 with diamino terephthalic acid lowered the band gap from 3.6 to 1.28 eV thus shifting absorption spectrum from UV to visible region. Similarly, the Eu was doped in the MIL-125 for the synthesis of MIL-125(Ti)-amino-Eu and investigated its catalytic efficiency for the photochemical oxidation of α -phenethyl alcohol to acetophenone in UV light (Lian and Yan, 2016). They also indicated

that the composite (MIL-125(Ti)-AM-Eu) material is promising for developing a new turn-off fluorescence sensor for α -phenethyl alcohol.

In another study, photocatalytic degradation of spiked concentrations of formaldehyde and O-xylene were investigated using TiO₂/MIL-101 (chromium terephthalate is called MIL-101) as photocatalyst under UV irradiation (Hu *et al.*, 2014). They were successful in achieving 80% degradation of analytes in 200 min, showing great potentiality for effective adsorption and photocatalytic degradation for the chemical species.

Modifications in metal organic frameworks can not only be achieved by doping with other metals but also with incorporation of some other materials such as graphene. In this context, the MIL-125 was functionalized on the surfaces of graphene oxide (GO) to form MOF-GO nano-composites (Barea *et al.*, 2014). As a result, a new pore space was generated in the interface between the carbon layer and the MOF units due to strong coordination between functional groups of GO and MOFs' metallic centers. The generation of this structural characteristic in MOF-GO may enhance their physical adsorption capacity towards organic vapors in gas streams relative to the parent MOFs (Barea *et al.*, 2014). Despite many improvements in characteristics (chemical, thermal, and mechanical) of MOFs, there are still challenges regarding their performance in the typical working conditions (*i.e.* moisture, strong oxidizing/reducing agents, acidic/basic environments, high temperature/pressure) for practical applications.

The deployment of titania-based photocatalysts for the removal of VOCs in indoor spaces is still a scientific challenge. A such, no device has been successfully commercialized to date. This issue can be ascribed to the complexity of VOCs and compromising performance of photocatalysts. Numerous efforts have been devoted to enhance photocatalytic activities for complete mineralization of VOCs and to develop a marketable product. However, the installation of different techniques along with photocatalytic methods can contribute to the reduction of pollutants in indoor spaces, especially in the newly furnished and/or painted buildings. Recently, photocatalytic paints have been introduced to reduce the levels of VOCs. Nonetheless, the decomposition of VOCs on the surface of photocatalysts is not obvious so that the further improvements are needed (Petronella *et al.*, 2017; Auvinen *et al.*, 2008).

5. CONCLUSION

Confined spaces provide working environments and

home for the population but at the same time may pose serious health concerns due to air contaminants. These contaminants may include microbial pathogens, VOCs, and inorganic oxides, and have potentials to cause serious threats ranging from various kinds of allergies to cancers. Therefore, indoor air quality is currently a public intensive concern. The volatile organic compounds are important indoor air pollutions. A number of techniques such as mechanical and electrical filtration, ozonation, photolysis, bio-filtration processes, and advanced oxidation approaches have been employed for the degradation of volatile organic compounds. Among all these purification techniques, the most promising approach of improving the indoor quality is the photocatalytic oxidation using semiconductor materials as photocatalysts. Among various photocatalysts TiO_2 is more preferable because of its high efficiency and cost effectiveness. In order to improve the photocatalytic activity of TiO_2 nanomaterials, significant efforts have been made to tune electronic and physicochemical properties of TiO_2 which can also improve charge separation through formation of composite structures, allowing them to act as effective photocatalyst for the degradation of various organic compounds with high degree. As a result, visible light activated TiO_2 has become a hot topic in environmental applications because of its significance as a photocatalyst for environmental applications under solar irradiation.

Photocatalytic activity of TiO_2 was greatly improved by doping of various metal oxides, metals, non-metals, carbon nanomaterials and MOFs, suggesting that TiO_2 -based photocatalytic approaches are the most promising technologies for eliminating VOCs due to its high efficiency and stability. However, traditional photocatalytic materials such as TiO_2 can only respond to UV irradiation, limiting the light utilization efficiency. Most of the studies have focused hetero-junction semiconductor interfaces but recently promising results have been obtained from a novel approach of constructing homo-junctions of TiO_2 interfaces. In order to achieve maximum photocatalytic degradation efficiencies, further improvements in optimizing reaction conditions and development in synthetic methods for highly efficient photocatalysts, active in UV and especially in Vis region to make the overall process economical, are highly desirable. Moreover, high rate of charge carrier recombination, low quantum efficiency, long term chemical and physical stability, and the generation of poisonous intermediates are still challenges.

Furthermore, the development of new single or photocatalytic composite materials which can be irradiated with conventional visible or solar light is thus a

need. Currently most studies demonstrate their VOCs removal efficiency in a high concentration level (e.g., ppmv), however, much efforts should be focused on the VOCs removal efficiency at low level and more on-site demonstrations should be conducted in order to prove the efficiency in removal of indoor VOCs in realistic environments (e.g., residential and work spaces). Keeping in view the serious health concerns and productivity losses caused from VOCs in indoor air, it is unrealistic to rely upon the purification techniques to solve these problems. In such scenario, it is vital to monitor continuously VOCs levels in indoor air and substantial efforts must be made to reduce the sources of contaminants in confined spaces. Moreover, use of personal protective equipment may also work to some extent especially in reducing allergies. Proper protocols for maintaining quality standards of indoor environments must be operated.

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Acronyms

| | |
|--------|--|
| HACCPs | Hazard analysis of critical control points |
| COSHH | Control of substances hazardous to health |
| HHEs | Health hazard evaluations |
| IAQ | Indoor air quality |
| NEBOSH | National examination board in occupational safety and health |
| OSHA | Occupational safety and health administration |
| IOSH | Institution of occupational safety and health |
| RH | Relative humidity |
| SBS | Sick building syndrome |
| PCO | Photocatalytic oxidation |

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