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A Novel Multifunctional Photocatalytic Oxidation (PCO) Gel Preventing Mold/Mildew Growth and Volatile Organic Compound (VOC) Emission

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UNIVERSITY OF MIAMI

A NOVEL MULTIFUNCTIONAL PHOTOCATALYTIC OXIDATION (PCO) GEL PREVENTING MOLD/MILDEW GROWTH AND VOLATILE ORGANIC COMPOUND (VOC) EMISSION

By

Yao Gao

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A NOVEL MULTIFUNCTIONAL PHOTOCATALYTIC OXIDATION (PCO) GEL PREVENTING MOLD/MILDEW GROWTH AND VOLATILE ORGANIC COMPOUND (VOC) EMISSION

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With the increasing time people spend indoors, the indoor environment quality draws more and more attention. The concentration of indoor pollutants is usually much higher than outdoors, in which volatile organic compounds (VOCs) and mold/mildew are both major pollutants and cause many health problems to residents. Efforts devoted from academy and industry to protecting people from indoor environment problems are apparently not sufficient.

Photocatalysts, such as TiO_2, WO and ZnO, can absorb light photons and react with O_2 and H_2O to generate highly oxidative radicals, which can oxidize VOCs and disinfect microorganisms. Recently, this photocatalytic oxidation (PCO) technology has been intensively studied to reduce VOCs and disinfect bacteria in the indoor environment. Few papers address the indoor mold/mildew problem, and this research therefore endeavors to do so. The objectives are to evaluate the effectiveness of PCO technology to resist mold/mildew growth and prevent VOC emission from building materials under either UV or visible light irradiation. The models, including linear regression, logistic regression, and numerical model, are also built for interpreting experimental results and for predicting performance in application.

The mold/mildew resistance of different PCO gels was examined using accelerated mold/mildew growth agar plate tests. These gels included TiO_2 only and TiO_2 in combination with H_2O_2 and with Ag. Without the application of PCO gels, no mold/mildew inhibition was observed from UV (365 nm) or visible light. Under UV light irradiation, the TiO_2 gel achieved complete mold/mildew inhibition. Without light, a 12-day delay of mold growth was obtained using the Ag-TiO_2/H_2O_2 gel. Under visible light irradiation, the Ag-TiO_2/H_2O_2 gel was also the most effective PCO gel with a 8-day delay of mold growth, which, however, was shorter than the same gel in the condition of no light with a 10-day delay due to the light-induced deterioration of the Ag-TiO_2. The reduction of VOC emission from PCO gel (TiO_2 gel and Ag-TiO_2/H_2O_2 gel) coated building materials under UV or visible light irradiation was also confirmed by small chamber tests (the Ag-TiO_2/H_2O_2 gel with above 50% reduction of total VOC emission).

A linear model was obtained for the Ag-TiO_2/H_2O_2 gel in the condition of no light, with respect to the correlation between the delay of mold growth and the gel ingredients. A logistic model was created for predicting the probability of mold growth on different TiO_2 gels with different UV light exposure time at different intensities. A numerical model was developed with better accuracy than the previous one for VOC emission from PCO gel coated building materials.

This study showed that the PCO gel might be a promising multifunctional material in resisting mold/mildew growth and preventing VOC emission in the indoor environment (The TiO_2 gel for complete mold/mildew inhibition and the Ag-TiO_2/H_2O_2 gel for delay of mold growth in emergency situations and reduction of VOC emission from building materials). More stable Ag-TiO_2 or other visible-light-driven photocatalysts are needed in future research because of the deterioration of the current one.

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INTRODUCTION

1.1. Indoor Air Pollution

In recent years, indoor air quality has obtained increasing attention, due to the high percentage-90% of time people spend indoors (U.S. EPA, 1987a; 1989; 1998; Leech et al, 2002). Comparative risk studies performed by the U.S. Environmental Protection Agency (EPA) have consistently ranked indoor air pollution among the top five environmental risks to public health (U.S. EPA, 1987b; 1990). U.S. EPA also reported that indoor levels of pollutants might be 2 to 5 times-and occasionally more than 100 times-higher than outdoor levels (U.S. EPA, 1987a). People's exposure to indoor air pollutants may be 10 to 50 times more than outdoor exposure (U.S. EPA, 1998).

There are two major types of indoor pollutants: chemical pollutants and microbiological pollutants. One of the major microbiological pollutants in the indoor environment is mold/mildew. The spore concentration of *Cladosporium sp.*, *Penicillium sp.*, *and Aspergillus sp.* was found predominating the indoor environment (Hunter et al., 1988; Andersson et al., 1997; Seltzer and Baxter, 1998; Gravesen et al., 1999; Miller et al., 2000; Lee et al., 2006; Haas et al., 2007; Dassonville et al., 2008; Rabito et al., 2008; Aringoli et al., 2008; Codina et al., 2008; Bogomolova and Kirtsideli, 2009). Suspended fungal spores are transported by air, which can grow on any indoor surface with sufficient organic supply, oxygen and humidity, causing many related human health problems. Mold/mildew growth in the indoor environment affects the health of residents in two combined mechanisms. Fungal spores and mold/mildew fragments spread in the indoor air can act as allergen causing allergy or allergy-like symptoms to human, some of which are lethal. Also, some toxic chemicals called mycotoxin can be attached to dusts or fungal components releasing to indoor air (Wicklow and Shotwell, 1983; Palmgren and Lee, 1986). The inhalation of those toxins may cause human illness or even potentially cancer. The most famous indoor mold is *Stachybotrys chartarum* also called “black mold” causing severe human health problems in water-damaged buildings (CDC report, 1995; Montana et al., 1997; Etzel et al., 1998). A comprehensive review of the scientific literature was conducted by the Institute of Medicine of the National Academies (2004). Sufficient evidence for an association between mold or dampness in the indoor environment and upper respiratory tract symptoms, wheeze, cough, asthma symptoms in sensitized persons & hypersensitivity pneumonitis in susceptible persons was concluded. Also, limited or suggestive evidence for an association between dampness in the indoor environment and lower respiratory illness in otherwise healthy children & shortness of breath (dyspnea) was found (Institute of Medicine, 2004).

In 2005, Hurricanes Katrina and Rita ripped through the Golf coast in August and September, respectively. Approximately 80% of the city-New Orleans was flooded for more than 2 weeks, and it ultimately took the city’s pumping system 43 days to remove the flooding waters from lower-lying areas (Knabb et al., 2005; CDC, 2006). The big flooding created ideal conditions for mold growth. Water damaged buildings became the very suitable habitat for mold growth. More than 100,000 homes in the flooded areas were estimated to experience significant mold growth (Riggs et al., 2005). Personal property as well as personal health was compromised by mold growth in water-damaged houses.

Volatile organic compounds (VOCs) are a group of chemical compounds with a boiling temperature less than 250 ℃. So, VOCs can easily vaporize at room temperature. Thus, they are well-known indoor chemical pollutants, most of which are known to be toxic and considered to be carcinogenic, mutagenic, or teratogenic (Alberici and Jardim, 1997). Adverse health effects potentially caused by exposure to VOCs in indoor air include: (1) irritant effects, including perception of unpleasant odors, mucous membrane irritation, and exacerbation of asthma, (2) systemic effects, such as fatigue and difficulty concentrating, and (3) toxic, chronic effects, such as carcinogenicity (Spengler and Sexton, 1983; WHO, 1989; Girman et al., 1989). Sick Building Syndrome (SBS) is also attributed to indoor VOC concentration in some cases.

1.2. Nature of the Problem

Building materials, furnishing and furniture are the main habitats for mold/mildew growth and a major VOC source in the indoor environment. The traditional control method for mold/mildew growth is to control the humidity level by heating, ventilation and air conditioning (HVAC) system, which has three major defects:

a) It onsumes extra energy and becomes ineffective when losing the power.
b) It generates unequaled humidity condition, leading to outbreak of mold/mildew on some spots with higher humidity level.
c) It cannot control or respond to the water damage.

A variety of organic or metallic (e.g., Ag and Cu series) biocides have been used for mold inhibition in building materials. Such biocides are only effective for short-term antifungal purposes, and can, themselves, be toxic (Chen et al., 2009). So, a non-toxic, long-lasting coating material which can resist mold growth for long term or for emergency period (such as the flooding period during hurricane) even under high humidity condition is needed.

The traditional control method for VOCs is to reduce the VOC concentration in the indoor air using ventilation system and/or air clean system, which have three major defects:

a) They consume extra energy and become ineffective when losing the power.
b) They generate unequaled VOC concentration, leading to some spots with extremely high VOC concentration.
c) They are not as effective as source control method, since they are just removing VOCs which are already present in indoor air.

In recent years, “green” building materials, as a source control method, have been applied to create a healthier indoor environment for occupants. However, their application is limited by:

a) Their high Price.
b) Their limited variety of products.
c) Their use in old buildings is restricted.

So, a long-lasting coating material which can be applied to and reduce the VOC emission from any indoor surfaces under general indoor condition is needed.

A promising technology-photocatalytic oxidation (PCO) technology has been intensively studied for several decades, since Fujishima and Honda (1972) discovered the water photo splitting in a TiO_2 anode photochemical cell. Instead of thermo-activation for conventional catalysis, heterogeneous photocatalysis only require photonic energy to activate the chemical reaction, which means that it can have a broader range of application (Chen and Poon, 2009). The catalysts (the conventional catalysts or photocatalysts) are not consumed in the chemical reaction, which have a potential to be sustainable materials (Wang, 2011). In the presence of oxygen and water, the photocatalysts, such as TiO_2, ZnO and so on, can be activated by ultra violet (UV) light or visible light and generate electron-hole pairs by overcoming the band gap between valence band (VB) and conduction band (CB). Then, electron-hole pairs, either directly or indirectly by further producing oxidative radicals (O_2^- and OH*) and H_2O_2, react with organic compounds or bio-structures. Many studies on PCO technology have contributed to the VOC degradation in air and microbiological resistance.

1.3. Objective

The objectives are to evaluate the effectiveness of PCO technology to resist mold/mildew growth and prevent VOC emission from building materials under either UV or visible light irradiation. The models, including linear regression, logistic regression, and numerical model, are also built for interpreting experimental results and for predicting performance in application.This coating material has the potential to be an energy-efficient control method for indoor mold/mildew growth and VOC emission, tolerating unequaled indoor environment conditions and reducing risk for accidental conditions.

1.4. Dissertation Outline

The dissertation is divided into seven chapters:

a) Introduction: background information on indoor air quality, VOC & mold/mildew problems, and proposed solution using PCO technology.

b) Review of visible-light-driven modified TiO_2: history of PCO technology & TiO_2 and methods to modify TiO_2 for visible light activity.

c) Preliminary mold/mildew growth test on TiO_2 and H_2O_2: research on the synergy between TiO_2 & H_2O_2 on mold/mildew resistance and preliminary result on the mold/mildew resistance of PCO gels.

d) Mold/mildew growth test on PCO gels: research on the optimal mold/mildew resistance of PCO gels loaded with different photocatalysts including TiO_2 & Ag-TiO_2 with & without H_2O_2 and factory experiment on the optimized PCO gels.

e) VOC test on PCO gel coated building materials: confirmation of the reduction of VOC emission from the PCO gel coated building materials.

f) Mold/Mildew growth model: regression model on the result from mold/mildew growth tests.

g) VOC emission model: new VOC emission model considering the PCO reaction on the surface of building materials using new PCO reaction model.

Chapter 2

REVIEW OF VISIBLE-LIGHT-DRIVEN MODIFIED TiO_2

2.1. **Background of TiO_2**

To obtain the optimal formulation and preparation method of the PCO gel that even works under visible light irradiation, a review for visible-light-driven photocatalysts was done before any experiments were performed.

In the PCO application, titanium dioxide (TiO_2) is the most widely used photocatalyst. TiO_2 is a common semi-conductor material that has been used as a white pigment in paints, cosmetics and foodstuff since ancient time (Fujishima et al., 1999). There are three crystal structures of TiO_2: anatase, rutile and brookite. Anatase is more widely used due to its higher photoactivity than other types. TiO_2 has its superior characteristics (Zhao and Yang, 2003): a) Relatively inexpensive, safe, chemically stable; b) High photocatalytic activity compared with other metal oxides; c) Oxidation of the major classes of pollutants at ambient temperature; d) Capable of completely degrading a large range of pollutants in certain reaction condition; e) No chemical additives are required. Based on its photocatalytic oxidizing power, its application includes water purification, air purification, microbial disinfection, and self-cleaning material, etc.

Generally, the PCO reaction can be divided into four steps:

a) Adsorption of pollutants. In PCO reaction, the contaminants are first adsorbed onto the active sites on the surface of photocatalyst. So as water and oxygen (other reactants).

b) Formation of electron-hole pairs. This is the most important step for PCO reaction. Photo-energy is needed to overcome the band gap between valence band (VB) and conduction band (CB). When the energy provided (photon) is larger than the band gap, the electron-hole pairs are created in the semiconductors for the following pollutant oxidation reaction. The common light source is ultra-violet (UV) light. In the case of TiO_2, UV light will activate TiO_2 to generate pairs of electron-hole: $TiO_2 + hv \rightarrow h^+ + e^-$. h^+ and e^- are powerful oxidizing and reductive agents, respectively.

c) Oxidation of pollutants. The charge will transfer between electron-hole pairs and adsorbed reactants on the semiconductor surface. On the surface of TiO_2, oxidative reaction is (OH^- is from adsorbed water) $OH^- + h^+ \rightarrow OH$; while, reductive reaction is $O_2 + e^- \rightarrow O_2^-$. The hydroxyl radical (OH*) coming from the oxidation of adsorbed water or adsorbed OH^- is the primary oxidant; and the presence of oxygen can prevent the re-combination of hole-electron pairs. Then, OH* further oxidizes the adsorbed pollutants into the final products-CO_2 and H_2O. $OH^* + \text{pollutant} + O_2 \rightarrow \text{products} (CO_2, H_2O, \text{etc})$.

d) Desorption of products. Final products such as CO_2 and H_2O will emit back to ambience through desorption.

According to the principles of semiconductor TiO_2 photocatalysis, the photocatalytic activity is mainly dependent on three factors: a) electron-hole generation capacity; b) electron transfer route and efficiency; c) separation efficiency of photogenerated charge pairs (Xie et al., 2005). Currently, two major limiting factors impede the progress of PCO technology. Firstly, because of the relative big bandgap (above 3eV), most of widely used photocatalysts can only absorb the ultra-violet portion of the solar energy. Secondly, fast recombination between photogenerated electron-hole pairs takes place in photocatalysis, lowering the photocatalytic efficiency and wasting energy in unproductive ways (Dozzi et al., 2009). The review will take a look at the history of TiO_2 in PCO application (Table 2.1) and the development of visible-light-driven photocatalysts based on the modified TiO_2 (Table 2.2). Much effort was made in the development of more efficient photocatalyst and the application of the photo-purification of water & air.

2.2. 1972-1980

In the late 1960s, Fujishima, Akira began to study oxide semiconductor which would respond to light, while he was still a graduate student at the University of Tokyo (Fujishima and Zhang, 2006). In 1972, Fujishima and Honda discovered the water photo splitting on TiO_2 electrode, after which many researches were conducted on the photoactivity of TiO_2. As early as 1971, Formenti et al. (1971) observed the partial oxidation of paraffins by heterogeneous photocatalysis. The oxidation of organic compounds over TiO_2 under the irradiation of UV light was also noticed by Sullivan (1972) due to the photo-degradation of polymer containing TiO_2. After that, Bickley and Stone (1973) and Bickley et al. (1973) studied the gas-solid heterogeneous photocatalysis using isopropanol vapor and TiO_2. In 1977, Frank and Brad (1977) first studied the photocatalytic oxidation of CN^- and SO_3^{2-} over TiO_2 under UV light irradiation. Their research aroused the interest of photocatalytic oxidation over TiO_2 in environmental application. During that period of time, metal ions such as Cr (Ghosh and Maruska, 1977; Maruska and Ghosh, 1979; Houlihan et al., 1978), Cd (Monnier and Augustynski, 1980), and Co (Matsumoto et al., 1980) were studied to extend the spectral reponse of TiO_2 into the visible light region. Dye sensitization for spectral extension of TiO_2 to visible light was intensively examined in water splitting and solar cell (Hauffe and Bode, 1974; Memming, 1974; Osa and Fujihira, 1976; Spitler and Calvin, 1977). Dye molecules are adsorbed on the surface of TiO_2 particles, forming chemical complexes that can absorb visible light and inject the exited electrons into the conduction band of TiO_2, leading to the photocatalysis under visible light irradiation.

2.3. 1981-1990

Researchers continued studying the application of photocatalysts in the degradation of environmental contaminants. Most of efforts were contributed to the water purification. Many kinds of water contaminants were intensively studied for photocatalytic oxidation over TiO_2 under UV light irradiation including sulphides (Davidson and Pratt, 1983), phenol (Matthews, 1987; Augugliaro et al., 1988b), chloroform (Pruden and Oilis, 1983), 2-propanol (Harvey et al., 1983), 2-chlorophenol (Matthews, 1987), 4-chlorophenol (Barbeni et al., 1984; Matthews, 1987), chlorobenzene (Matthews, 1986), salicylic acid (Matthews, 1987), benzoic acid (Matthews, 1987), 2-naphtho1 (Matthews, 1987), naphthalene (Matthews, 1987), and fluorescein (Matthews, 1987), potassium iodide

(Draper and Fox, 1990b), 2,4,5-trichlorophenol (Draper and Fox, 1990b), methyl viologen dichloride (Draper and Fox, 1990b), potassium tetrachloroplatinum(II) (Draper and Fox, 1990b), tris(1,10-phenanthroline)-iron(II) perchlorate (Draper and Fox, 1990b), N,N,N',N'-tetramethyl-p-phenylenediaminem (Draper and Fox, 1990b), thianthrene (Draper and Fox, 1990b), Thiocyanate (Draper and Fox, 1990a), p-Nonylphenyl poly(oxyethylene) ethers (Hidaka et al., 1988a), sodium dodecylbenzene sulphonate (Hidaka et al., 1988b). The photocatalytic oxidation of air pollutants, especially some volatile organic compounds, was also drawing the attention of the researchers, though there were fewer papers published for gaseous contaminants than that for aqueous contaminants. Toluene (Ibusuki and Takeuchi, 1986) as the largest component of environmental aromatic hydrocarbons, 2-ethoxyethanol (Yamagata et al., 1989) as a volatile organic solvent and trichloroethylene (Dibble and Raupp, 1990) as a major vapor contaminant of water treatment facility effluents were confirmed being oxidized by the photocatalytic oxidation over TiO_2 under UV light. The addition of H_2O_2 into TiO_2 was found to promote the rate of photocatalytic reaction under UV light irradiation (Augugliaro et al., 1988a and 1990, Wei et al., 1990).

In 1985, Matsunaga drew the interest of photocatalyst to the disinfection of microorganisms. He found the bactericidal effect of TiO_2 against several species of microorganisms such as *Escherichia coli* (*E. coli*) and postulated the oxidation of enzyme inside the microbial cells due to the photocatalytic reaction causing the death of the cells (Matsunaga, 1985). Then, Matsunaga et al. (1988) built a continuous-sterilization system using TiO_2 powders in which *E. coli* cells were continuously sterilized. It was a big step for the real application of photocatalyst in microbial disinfection.

Chromium ion was kept being used for the sensitizer of TiO_2 to obtain the visible light photo-activity. Borgarello et al. (1982) observed visible light induced water cleavage on chromium-doped TiO_2 particles. To increase the light harvesting and the absorption of visible light, chromophores were adopted as a dye sensitizer because of highest photon to current conversion efficiency among other dyes. This new dye sensitization system was developed in which Ru(bpy) complexes were used as a sensitizer on TiO_2 (Desilvestro et al., 1985; Furlong et al., 1986; Vlachopoulos et al., 1988). Enea et al. (1989) screened systematically a number of other chromophores suitable for sensitization of TiO_2. They reported the laser dye coumarin 343 had the highest efficiency. Amadelli et al. (1990) further developed the cyano-bridged trinuclear complex based on Ru(bpy) complexes adsorbed on the surface of TiO_2 for the better light absorption of the dye sensitization process. Another dye sensitization system using transition metal cyanide complexes as charge transfer dyes for TiO_2 was developed by Vrachnou et al. (1989).

2.4. 1991-2000

Within this period, a considerable amount of research was carried out in both water (Al-Sayyed et al., 1991; Augugliaro et al., 1991; Kormann et al., 1991; Matthews, 1991; Ollis et al., 1991; Davis et al., 1994; Lakshmi et al., 1995; Wang et al., 1999a; Gouvea et al., 2000) and air (Peral and Ollis, 1992; Obee and Brown, 1995; Luo and Ollis, 1996; d'Hennezel et al., 1998; Kwon et al., 2000) purification. In order to increase the efficiency of the photocatalysts, the mechanism of photocatalytic reaction was studied

(Mills and Hoffmann, 1993; Pelizzetti and Minero, 1993; d'Hennezel et al., 1998; Wang et al., 1999b). There are many factors that can influence the rate of photocatalytic reaction such as light intensity (Kormann et al., 1991; Chen and Ray, 1999), oxygen (Augugliaro et al., 1991; Augugliaro et al., 1999; Chen and Ray, 1999), water (Peral and Ollis, 1992; Obee and Brown, 1995; Sitkiewitz and Heller, 1996), dopants (Al-Sayyed et al., 1991; Sclafani et al., 1991; Litter, 1999; Wilke and Breuer, 1999), additives (Do et al., 1994; Zhao et al., 1998; Wang et al., 1999b; Kwon et al., 2000), etc. The photocatalysis of TiO_2 was also studied for real applications (Bahnemann et al., 1991; Matthews, 1991; Ollis et al., 1991; Venkatadri and Pete, 1993; Davis et al., 1994; Sauer and Ollis, 1994 and 1996; Alfano et al., 2000).

Metal ion doping for TiO_2 photocatalysis system had been examined since 1980s. Litter (1999) summarized the previous research result of many kinds of transition metal ions for their influence of photocatalytic reaction. Some metal ions such as Fe^{3+}, Ag^{+}, and Cu^{2+} with low level of concentration have positive effect on the photocatalytic reaction acting as an electron deliverer to O_2; however, with high concentration of those ions and some other metal ions such as Mn^{2+} Co^{2+} and Cr^{3+}, the photocatalytic reaction would be inhibited or even stopped mainly due to their recombination center roles for the photocatalytic electrons and holes. The loading of noble metal on TiO_2 powders such as Au (Albert et al., 1992; Gao et al., 1992), Ag (Sclafani et al., 1991; Lee et al., 1992), and Pd (Papp et al., 1993), which also acts as an electron deliverer for fast reduction of O_2, can be an effective way to improve the photo-activity of TiO_2. Using binary metal oxides as photocatalysts are another way to promote the photocatalytic efficiency, Lin and Yu (1998) first conducted an experiment on gaseous phase photocatalytic degradation using mixed TiO_2-rare earth oxides. They found that photoactivity the mixture of TiO_2 with La_2O_3 (0.5 wt.%) or Y_2O_3 (0.5 wt.%) exhibit higher photoactivity than pure TiO_2 (P25) for the oxidation of acetone. On the other hand, the mixtures of TiO_2 with CeO_2 had lower photoactivity than pure TiO_2. Later, Kwon et al. (2000) used WO_3/TiO_2 binary metal oxides system to study the role of WO_3 in enhancing the photocatalytic activity of TiO_2. The increase of photo-activity with the addition of WO_3 was confirmed by the degradation of benzene and 2-propanol.

Venkatadri and Pete (1993) stated that TiO_2 assisted photocatalytic oxidation is more suitable for ground water treatment with low concentration of contaminants instead of waste water treatment with high concentration of contaminants and the possible application of solar irradiation would facilitate the economics of its application. Sauer and Ollis (1994) summarized all the previous researches on photocatalytic degradation of major air contaminants such as alkanes, 1-butanol, toluene, trichloroethylene & odor compounds using the honeycomb monolith reactor and proposed the honeycomb monolith as an effective configuration for removal of all major classes of air contaminants. With the knowledge accumulation from over two-decade research, many review papers were also published regarding to each aspects of the photocatalysis (Fox and Dulay, 1993; Pelizzetti and Minero, 1993; Wold, 1993; Hagfeldt and Gratzel, 1995; Hoffmann et al., 1995; Mills and Le Hunte, 1997; Peral et al., 1997; Blake et al., 1999; Litter, 1999; Alfano et al., 2000). It is realized that compared to the water purification, photocatalytic reaction may be more applicable for air contaminants; for there is relatively small concentration of pollutants in the air (usually below 500 ppm and sometimes in ppb level) and relatively abundant oxygen (21% of air is oxygen) acting as an electron acceptor in the photocatalytic reaction. So, the photocatalytic reaction would be more efficient in air purification. Many researches were conducted on TiO_2 photocatalysis for major air contaminants including nitrogen oxides (Ibusuki and Takeuchi, 1994; Nakamura et al., 2000), ethanol (Sauer and Ollis, 1996), 2-propanol (Kwon et al., 2000), acetaldehyde (Sopyan et al., 1994 and 1996; Ohko et al., 1998; Sauer and Ollis, 1996), formaldehyde (Peral and Ollis, 1992; Obee and Brown, 1995), benzene (Sitkiewitz and Heller, 1996; d'Hennezel et al., 1998; Kwon et al., 2000), toluene (Obee and Brown, 1995; Luo and Ollis, 1996; d'Hennezel et al., 1998; Augugliaro et al., 1999; Cao et al., 2000), m-xylene (Peral and Ollis, 1992), 1-butanol (Peral and Ollis, 1992), butyraldehyde (Peral and Ollis, 1992), 1,3-butadiene (Obee and Brown, 1995), acetone (Peral and Ollis, 1992; Sauer and Ollis, 1994), TCE (Jacoby et al., 1995; Luo and Ollis, 1996), and stearic acid (Sitkiewitz and Heller, 1996). Alberici and Jardim (1997) demonstrated the capacity of TiO_2 photocatalysis process to destroy different classes of VOCs present in air using 17 VOCs in the feed air to a plug flow reactor with UV light illuminated TiO_2. At the steady state, high conversion yields were obtained for most of VOCs (above 60% and some above 95%); however, the photodegradation of isopropylbenzene (30.3%), methyl chloroform (20.5%) and pyridine (15.8%) was not so efficient.

Due to the non-toxicity of TiO_2, strong oxidizing power, and possible use of sunlight, the microbial disinfection over TiO_2 was continually evaluated with different kinds of bacteria (Saito et al., 1992; Watts et al., 1995; Kikuchi et al., 1997; Sunada et al., 1998), viruses (Watts et al., 1995), and real application (Ireland et al., 1993; Wei, et al., 1994; Watts et al., 1995). Ireland et al. (1993) first developed a TiO_2 photocatalytic reactor to study the use of TiO_2 for microbial inactivation. In 1995, Watts et al., (1995) first documented the inactivation of virus (poliovirus 1) using TiO_2 under UV light and sunlight. The modification of its surface structures by TiO_2 photocatalytic process may be the cause of the inactivation. The mechanism of this disinfection process by photocatalysis was also intensively examined (Saito et al., 1992; Kikuchi et al., 1997; Wamer et al., 1997; Maness et al., 1999). Saito et al., (1992) confirmed the bactericidal action of TiO_2 on the mutans group of streptococci. They found that bacterial death appears to be caused by a significant disorder in cell membranes and finally the cell walls were decomposed. Kikuchi et al. (1997) found that the long-range bactericidal effect is attributed mainly from hydrogen peroxide produced by the photocatalysis, together with a cooperative effect due to other oxygen species. H_2O_2 and O_2^- produced by photocatalysis of TiO_2 are less toxic to the microorganisms due to the presence of superoxide dismutase and catalase enzyme in all aerobic microbial to convert those toxic active oxygen radicals into non-toxic substances. OH* also produced by the photocatalysis is more toxic compared to H_2O_2 and O_2^-; however it cannot sustain long, compared to H_2O_2 with longer life. The major mechanism of disinfection by the photocatalysis of TiO_2 involves that H_2O_2 penetrates of cells and reacts with Fe^{2+} ions which are present significantly inside the cells to produce more OH* which damages the cells: $Fe^{2+} + H_2O_2 \rightarrow OH^* + OH^- + Fe^{3+}$ (Blake et al., 1999).

It is worth of pointing out that Fujishima and his colleagues performed a series of researches (Sopyan et al., 1994 and 1996; Matsubara et al., 1995; Negishi et al., 1995; Ohko et al., 1997 and 1998) on highly efficient TiO_2 film they developed (pure anatase form) under weak UV light irradiation ranging from 1 uW/cm^2 to 1 mW/cm^2, some of which was at ordinary indoor UV level. They found that with weak UV light of 1 uW/cm^2 was sufficient to decompose some air contaminants such as 2-propanol (Ohko et al., 1997) and acetaldehyde (Ohko et al., 1997). Under weak UV light of 1 mW/cm2, *E.coli* was efficiently killed on a TiO_2-coated glass plate (Kikuchi et al., 1997). Those series of researches extend the practical application of TiO_2.

In the development of visible-light-driven photocatalyst, the system of TiO_2 with dye sensitization under visible light irradiation was continually studied (Zhao et al., 1998). Anpo et al. (1997 and 1998) prepared a TiO_2 photocatalyst with the implantation of Cr ion which was able to absorb visible light. NO reduction of photocatalytic efficiency was found compared the NO decomposition into N_2, O_2, and N_2O in oxygen free environment under visible light irradiation with that under UV light irradiation. In 2000, Nakamura and his colleagues (Nakamura et al., 2000) developed a visible-light-driven TiO_2 photocatalyst by plasma-treating. The photocatalytic oxidation of plasma-treated TiO_2 was confirmed by NO removal under visible light irradiation, which is attributed from the oxygen vacancies formed inside the crystal structure for the formation of the oxygen vacancy state located between the valence and the conduction bands.

2.5. 2001-Present

The development of photocatalysts entered a new stage in 21st century. As palmisano and his colleagues stated in their review paper (Palmisano et al., 2007), photocatalysis is a promising route for 21st century organic chemistry to potentially contribute to replacing environmentally hazardous processes with energy efficient routes allowing to totally avoid the use and production of harmful chemicals and to maximize the quantity of raw material that ends up in the final product. During almost 4 decades of study on photocatalysis, the basic structure of photocatalysis is almost built up (Thompson and Yates et al., 2006; Wang et al., 2007a; Mo et al., 2009). The gap between still needs to be filled up. Some photocatalytic products were going into the real market, even though some of them still needed to be improved.

In Japan, the commercialized TiO_2-based photocatalytic products include exterior construction materials, interior furnishing materials, road construction materials, purification facilities and household goods, etc. Self-cleaning exterior construction materials are widely applied in Japan, which uses the action of sunlight and rainwater to keep the exterior surface of building clean by the photocatalytic and superhydrophilic properties of TiO_2. Another important application of TiO_2 photocatalysis is in the purification of indoor air, due to the low concentration of contaminants in the indoor air. TiO_2-based air filters can operate with UV lamps to decompose the adsorbed pollutants instead of accumulating them by active carbon filters. So, it has longer operating life and is easy to regenerate by washing with water. It can also kill the microorganisms in indoor air, which is very important for the applications in hospitals, institutions for the elderly, and schools, etc. TiO_2-based antibacterial products such as tiles, fibers, and sprays, etc., are also applied to hospitals in Japan (Fujishima and Zhang, 2006). As we stated above, the direction of the development of photocatalysis would be conquering two limiting factors-light absorption and photocatalytic efficiency to create and engineer high-efficient, visible-light-driven photocatalyst and photocatalytic process. More and more researches carried on after 2000 turned their direction to develop photocatalysts with visible light photoactivity by modifying TiO_2.

Table 2.1 Brief History of Photocatalysts (TiO_2 and Modified TiO_2)

Period	Year	Significant Events
1972-1980	1972	Fujishima and Honda discovered the photoactivity of TiO_2 and its mechanism
	1973-	Dye sensitization for spectral extension of TiO_2 to visible light was intensively examined in water splitting and solar cell
	1977	Frank and Brad aroused the interest of photocatalytic oxidation over TiO_2 in environmental application
	1977-	Research of photocatalysis on water purification
	1977-	Transition metal ions such as Cr, Cd, and Co were used for the extension of spectral response of TiO_2 into visible region
1981-1990	1985	Matsunaga drew the interest of photocatalyst to the disinfection of microorganisms.
	1985	New dye sensitization system for visible-light-driven photocatalysts used Ru(bpy) complex
	1986	Ibusuki and Takeuchi used the photocatalytic technology in degradation of VOCs
	1986	Sato reported the preparation of N-TiO_2
1991-2000	1991-	Noble metal was noticed to greatly improve the photocatalytic activity
	1992-	The disinfection process by photocatalysis is attributed to the disorder in cell membranes
	1993-	Many review papers were published
	1994-	Fujishima and his colleagues performed a series of researches on highly efficient TiO_2 film under weak UV light irradiation
	1995	Watts et al. first documented the inactivation of virus (poliovirus 1) using TiO_2 under UV light and sunlight
	1997	Alberici and Jardim demonstrated the capacity of TiO_2 photocatalysis process to destroy different classes of VOCs present in air
	1998	Lin and Yu first used binary metal oxides on gaseous phase photocatalytic degradation
	2000	Nakamura and his colleagues developed a visible-light-driven TiO_2 photocatalyst by plasma-treating.
2001-present	2001-	Increasing application of photocatalysis in the real environmental application
	2001-	More interest in developing visible-light-driven photocatalyst with high photocatalytic efficiency

2.6. Modified TiO_2

2.6.1. Background

The application of most of the popular photocatalysts is restricted by their soly absorption of UV light, i.e. TiO_2. To extend the application of the conventional photocatalysts as well as to maintan their superior property and low price, those photocatalysts, originally active in UV light, are modified to achieve visible light activity. The varieties of modified TiO2 are the most intensively studied visible-light-driven photocatalysts. There are several methods that can be used to modify TiO_2 for visible light activity:

a) Non-metal doping;

b) Metal doping;

c) Both non-metal and metal co-doping;

d) Oxides, sulfides, bromides, and chlorides mixing;

e) H_2O_2 addition;

f) Dye sensitizing; and others.

2.6.2. Non-metal Doping

TiO_2 doping with non-metallic impurities such as boron (Zaleska et al., 2008; Portjanskaja et al., 2009), carbon (Kuo et al., 2007; Irie et al., 2006; Wong et al., 2007; Gu et al., 2008; Dong et al., 2009a), sulfur (Ohno et al., 2003; Umebayashi et al. 2003a; Ohno, 2004; Ohno et al., 2004; Takeshita et al., 2006; Portjanskaja et al., 2009), phosphorus (Lin et al., 2007; Zheng et al., 2008; Natori et al., 2009), fluorine (Yu et al., 2002; Li et al., 2005a; Serpone, 2006; Yang et al., 2007a), Iodine (Hong et al., 2005; Long et al., 2006; Liu et al., 2009a), nitrogen is the most promising technology to extend the photoactivity into visible light region. Those non-metallic impurities doped into the crystal lattice, usually substituting for O, can create a smaller band gap, which, then, can absorb the visible light photon and start the photocatalytic reaction. The O vacancies are also generated through the doping process, which can contribute to the visible light photoactivity of the doped catalyst. However, whether the O vacancies enhance the visible light photoactivity of non-metal doped photocatalysts via stabilizing the doping impurities or directly absorbing the visible light photon is still under debate. Nakamura et al. (2004) and Livraghi et al. (2006), and Wu et al. (2008) considered that visible-light response of N-TiO_2 arise from an N-induced midgap level, which is formed slightly above the top of the valence band. Batzill et al. (2006) admitted that the introduction of N-centers favors the formation of oxygen vacancies, but the oxygen vacancies just act as dopant stabilizing entities. On the other hand, it has also been argued that it is the oxygen vacancies or associated defects contribute to the visible light activity, and the N-centers just serve to enhance the stabilization of these defects (Emeline et al., 2007; Wendt et al., 2008). Nambu et al. (2006) and Graciani et al. (2008) suggested that there is a relationship between implanted nitrogen atoms and oxygen vacancies summarized in the following two facts. The presence of vacancies of oxygen lowers the implantation energy of nitrogen and stabilizes them; whereas, the presence of implanted N lowers the energy of formation of oxygen vacancy. Anyway, the electron-hole pairs can be generated in non-metal doped TiO_2 by either non-metalic impurities or oxygen vancancies under visible light irradiation. Then, TiO_2 will trap the excited electrons and transport them to the adsorbed O_2 on the surface of the photocatalysts. The photo-excited holes will spontaneously oxidize OH^- into OH. Therefore, the non-metallic doping improves the photoactivity of TiO_2 under visible light irradiation.

Other factors than the visible light absorption, which are changed simultaneously by the doping element, can also influence the photocatalytic activity and the practical application of the modified TiO_2. Turbidity of the slurry solution decreases with the increase of carbon content, which increases the possibilities of practical application of TiO_2 as a photocatalyst in water-treatment systems under visible light (Janus et al., 2006 and Morawski et al., 2006). P-doped species can increase the surface area of the materials and retard the phase transition of anatase to rutile. The excellent photocatalytic activity of P-TiO_2 compared with pure TiO_2 could be explained by its high surface area and small crystallite size (Lin et al., 2007; Zheng et al., 2008).

The photocatalytic activity of the non-metal doped TiO_2 will be increased with the increase of non-metallic doping elements. However, the excessive doping will result in the decrease of photoactivity, since the doping impurities can also act as the recombination centers of photo-generated holes and electrons (Chen et al., 2007c; Ozaki et al., 2008; Zaleska et al., 2008; Portjanskaja et al., 2009). Let's take N-TiO_2 as an example. With the increase of N doping, the visible light activity of N-TiO_2 will slightly increase at first and after a certain optimal percentage of the N doping, it will then decrease. The optimal amounts of N doping in TiO_2 were N_y-TiO_2 at $y = 6$ (Chen et al., 2007c), 0.15–0.17 wt.% of nitrogen (Yin et al., 2005), 1.61 at% (Buzby et al., 2006), 3.4% (Shen et al., 2007), 6.0% (Kitano et al., 2006), and N/Ti ratio of 2.0 (Xing et al., 2009a).

Since Sato (1986) reported the preparation of a yellow material obtained by calcination of titanium hydroxide in the presence of ammonium chloride, causing the photocatalytic sensitization of TiO_2 into the visible light region, N-TiO_2 has been most intensively studied among all the modified TiO_2. Many kinds of organic substrates were confirmed to be oxidized by N-TiO_2 in both aqueous solution and gas phase under visible light irradiation and their visible light photo-degradation efficiencies were much higher than the undoped TiO_2: methyl orange (Lei et al., 2005; Shao et al., 2008), propane (Zhang et al., 2008a), phenol (Kosowska et al., 2005; Wang et al., 2005; Zhang et al., 2009), formaldehyde (Qu et al., 2009), methylene blue (Cao et al., 2007; Sathish et al., Shen et al., 2007; Wan et al., 2007; Li et al., 2009a), trichloroethylene (TCE) (Yokosuka et al., 2009), CO (Sato et al., 2005; Kang et al., 2007), NO (Yin et al., 2003; Yin et al., 2005), NO_x (Zhou et al., 2007; Kang et al., 2008), azo dyes (Kosowska et al., 2005; Wawrzyniak and Morawski, 2006), ethylene glycol (EG) (Tachikawa et al., 2006), gaseous isopropanol (Tokudome and Miyauchi, 2004), 2-chlorophenol (2-CP) (Buzby et al., 2006; Ananpattarachai et al., 2009), ethylene, (Chen et al., 2008), herbicides RS-2-(4-chloro-o-tolyloxy)propionic acid (mecoprop) & (4-chloro-2-methylphenoxy)acetic acid (MCPA) (Abramovic et al., 2009), 4-CP (Fu et al., 2006), an azo dye Orange G (OG) (Sun et al., 2008a), gaseous formaldehyde & toluene (Aoki et al., 2006), toluene in gas phase (Irokawa et al., 2006; Wu et al., 2008; Dong et al., 2009b), formic acid (Balcerski et al., 2007), 2-propanol (Irie et al., 2003; Kitano et al., 2006; Prabakar et al., 2008), 2,4-dichlorophenol (Xing et al., 2009a), rhodamine B (Shao et al., 2008), and benzoic acid (Wang et al., 2007b). . Many reported the reduction of UV light activity for N doping (Balcerski et al., 2007; Abramovic et al., 2009). Balcerski et al. (2007) and Yates et al.

(2006) found that the visible-light-active N-TiO_2 has defect sites in the form of Ti-N triple bonds. The increase of these sites leads to a loss of crystallinity that accounts for the reduced photocatalytic activity under UV irradiation.

Other non-metal dopings such as C (Dong et al., 2009a), S (Nishijima et al., 2007a), F (Wu and Chen, 2008), and P (Natori et al., 2009) were also found to improve the photocatalytic activity of TiO_2 under visible light.

Codoping two or three non-metal species into TiO_2 aroused the interest from the researchers who were trying to find the synergy between different sorts of non-metal ions such as B & F (Reyes-Garcia et al., 2007), B & N (Gombac et al., 2007; Ling et al., 2008; Yan et al., 2008), N & C (Noguchi et al., 2005; Chen et al., 2007d; Yin et al., 2007), N & S (Liu and Gao, 2004; Yu et al., 2006; Xu et al., 2008; Sathish et al., 2009; Rengifo-Herrera et al., 2009), N & F (Li et al., 2005b; Yamada et al., 2008; Meng et al., 2009; Wang et al., 2009), N & Si (Ozaki et al., 2007 and 2008), C, N & Cl (Li et al., 2006), C, N & S (Hupka et al., 2006; Zhou and Yu, 2008; Bengtsson et al., 2009; Nadtochenko et al., 2009). The result was controversial, some of which showed the increase of photocatalytic activity of two or three non-metal elements codoped TiO_2 compared to one non-metal element doping (Chen et al., 2007d) and some else exhibited no difference (Sathish et al., 2009). Chen et al., 2007 observed that C, N-TiO_2 nanomaterials exhibited the highest photocatalytic activity among C-TiO_2, N-TiO_2, and C, N-TiO_2, which could be assigned to the synergistic effect of doped C and N atoms. Also, Li et al. (2005b) observed that the highest visible-light activity of N, F-TiO_2 for decompositions of both acetaldehyde and trichloroethylene among N-TiO_2, F-TiO_2, and TiO_2. However, Sathish et al. (2009) hardly found the enhanced photocatalytic activity of N, S-TiO_2 by S species compared to N-TiO_2, Neither, Wang et al. (2009) found the N, F−TiO_2 exhibited lower photocatalytic activity for the oxidative degradation of Methylene Blue under visible light irradiation than N-TiO_2, though the former has much stronger visible-light absorption than the latter. It could be the different reaction substrates in the experiment that caused the controversial result. Hupka et al. (2006) observed that N, C, S-TiO_2 had higher phenol degradation under visible light than N, C-TiO_2. However, in the degradation of 4-chlorophenol, N, C-TiO_2 was better than that of N, C, S-TiO_2. The mechanism of codoping non-metal elements is still not very clear. For N and C codoped TiO_2, Chen et al (2007d) thought that N atoms can incorporate into the lattice of anatase through substituting the sites of oxygen atoms, while most C atoms can form a mixed layer of deposited active carbon and complex carbonate species at the surface of TiO_2 nanoparticles. For N, F-TiO_2, N-doping into TiO_2 results in not only the improvement in visible-light absorption but also the creation of surface oxygen vacancies. F-doping produces several beneficial effects including the creation of surface oxygen vacancies, the enhancement of surface acidity and the increase of Ti^{3+} ions (Li et al., 2005b). Ozaki et al (2008) considered the stabilization of N doping by Si doping is the synergy present in N, Si-TiO_2.

Some of the studies showed a promising potential for using non-metal doped TiO_2 in degradation of VOCs. S-TiO_2 showed fairly high photocatalytic activity under visible light irradiation in oxidation of acetaldehyde (Nishijima et al., 2007b) and 2-propanol (Ohno, 2004; Ohno et al., 2004) in gas phase. F doped TiO_2 prepared by Li et al. (2005a) had high photocatalytic activity for the decomposition of gas-phase acetaldehyde under both UV and visible light irradiation. For the photocatalytic oxidation of acetone and formaldehyde, the daylight-induced photocatalytic activities of the as-prepared N, S-TiO_2 powders were about ten times greater than that of Degussa P25 (Yu et al., 2006). Jo and kim (2009) observed that the degradation efficiency by an annular reactor coated with N-TiO_2 was well above 90% for four target compounds (ethyl benzene, o,m,p-xylenes) under visible light irradiation, suggesting that this photocatalytic system can be effectively employed to cleanse these pollutants at indoor air quality levels. Dong et al. (2009a) reported that the reaction rate constant of mesoporous C-TiO_2 in degradation of gaseous toluene under visible light irradiation was 17.6 times higher than that of TiO_2 (P25).

The disinfection of microbes using non-metal doped TiO_2 in the indoor environment was also examined. Cao et al. (2007) prepared the photocatalytic paint by adding N-doped nanocrystalline anatase TiO_2 powders into self-engineered oxidation resistance latex paint system. The sterilization of *E.coli* by the N-TiO_2 modified paint could exceed more than 99% after 2 to 4 hours visible light irradiation. Vacaroiu et al. (2009) also concluded that N-TiO_2 could be used in disinfection of *E. coli* under visible light irradiation. Rengifo-Herrera et al. (2009) found that N, S-TiO_2 (P25) showed a high photocatalytic activity in *E. coli* inactivation under visible light.

Other similar method used sulfate species adsorbed on TiO_2 to promote the absorption of visible light. The sulfate species are incorporated into the TiO_2 network, resulting in the narrowing of band gap. Thus, the SO_4^{2-}/TiO_2 exhibited much higher activity under visible light (Yang et al., 2005; Parida et al., 2008). With further configuration of non-metal doped TiO_2, Liu et al. (2007a) and Kang et al. (2008) mixed N-TiO_2 with TiO_2 for the efficient prevention of recombination between photoexcited electron and hole. N-TiO_2 supplies electrons and holes under visible light irradiation and acts as a hole acceptor, while TiO_2 acts only as an electron acceptor. Cojocaru et al. (2009) developed a photocatalyst-N-TiO_2 loaded with active carbon (AC). Under visible light irradiation, N-TiO_2-AC photocatalysts exhibited a remarkable activity, due to the high adsorption capability of AC.

Some negative result of non-metal doped TiO_2 was also present. Tachikawa et al. (2004) observed no oxidation reaction with S, C-TiO_2 powders, although charge carriers were sufficiently generated under excitation by visible light. Two mechanisms were proposed to explain the controversial findings. The photoproduced holes under visible light irradiation in the S, C-TiO_2 are quickly trapped in the doping sites that are located deep in the photocatalyst instead on the surface where the organic substrates are adsorbed. Furthermore, the photoproduced holes should have poor oxidizing power because of using photons with low energy. The mobility and potential energy of photoproduced holes trapped at the doping sites have significant influences on the photocatalytic efficiency of the S, C-TiO_2 powders (Tachikawa et al., 2004). Rengifo-Herrera et al. (2009) observed no phenol degradation on both doped and undoped Degussa P-25 powders illuminated by visible light. Under visible light irradiation, the photogenerated holes in N, S-TiO_2 (P25), due to the N and S localized states, have a lower oxidative potential, which is probably innocuous to phenol. No visible light-induced photocatalytic activity was observed, though N-TiO_2 possesses features extending towards the visible light region (Yates et al., 2006).

2.6.3. Metal Doping

Transition metal doping can improve the visible light photoactivity of TiO_2 in two mechanisms: (a) Transition metal ion doping is responsible for extending light absorption of TiO_2 into visible region; (b) Transition metal ion can act as an electron trapper to enhance the separation of photo-induced holes and electrons. In general, Metal ions (Mn^+) capture photogenerated electrons and pass them to O_2 during the photocatalysis of metal-doped TiO_2 (Eq. 2.1 and Eq. 2.2).

$$Mn^+ + e^- \rightarrow M^{(n-1)+} \qquad 2.1$$

$$M^{(n-1)+} + O_2 \rightarrow Mn^+ + O_2^- \qquad 2.2$$

The dopant effectiveness lies not only in trapping the charge carriers to prevent recombination reactions but it should also detrap the charge carriers at a faster rate to facilitate the generation of highly reactive oxidative radicals such as hydroxyl and super oxide radicals. The detrapping of the trapped charge carriers depends mainly on the electronic configuration and stable oxidation state of the dopants (Devi et al., 2009b). Sn, not a transition metal, was also studied in modifying TiO_2, which has similar mechanisms to improve the visible light photocatalytic activity (Sayılkan et al., 2007; Yao et al., 2007).

The doping metal for increasing the photocatalytic activity also influenced other aspects of the photocatalysts. Cui et al. (2008) found that the recombination rate of photogenerated electron-hole pairs on Cu^{2+}-TiO_2/Ti film was decreased because of the increase of the surface roughness and restrain of crystal growth on TiO_2 film by Cu^{2+}, leading to successful photodegradation of phenol in aqueous solution under visible light irradiation. Also, the presence of cerium retards TiO_2 transition from amorphous to crystalline anatase form, which contributes to the increased photocatalytic performance under visible light irradiation (Silva et al., 2009).

Transition metals such as Fe (Carneiro et al., 2005; Wang et al., 2006a; Wang et al., 2006b; Zhu et al., 2007; Yu et al., 2009), Cu (Maeda and Yamada, 2007; Cui et al. 2008), Co (Shi et al., 2006), V (Izumi et al., 2007; Lu et al., 2007; Masih et al., 2007), Cr (Umebayashi et al. 2003b; Bae et al., 2007; Lam et al., 2007; Wan et al., 2008, Noble metal (Pt (Li and Li, 2002; Kim et al., 2005; Sun et al., 2005; Chen et al., 2007a; Ishibai et al., 2007; Yi et al., 2007; Egerton and Mattinson, 2008), Pd (Grandcolas et al., 2008), Ag (Rupa et al., 2007; Hou et al., 2009; Menesi et al., 2008 and 2009; Li et al., 2009b), Au (Jakob et al., 2003; Subramanian et al., 2003; Mrowetz et al., 2007; Kowalska et al., 2009; Wu et al., 2009a; Zhao et al., 2009) and Ru (Houskova et al., 2009)), and Lanthanide metal (Ce (Xu et al., 2006; Yan et al., 2006; Ma et al., 2009; Silva et al., 2009), Nd (Xie and Yuan, 2004; Xie et al., 2005), Th (Devi et al., 2009a and 2009b), and Eu (Xie and Yuan, 2005)) were reported to improve the visible light photoactivity of TiO_2 in above two mechanisms. However, some researchers also obtained some controversial results. Ha et al. (2006) found that Co-doped TiO_2 showed no visible light photoactitity for CH_3Cl degradation. Maeda and Yamada (2007) observed that Fe-doped TiO_2 with 2 at% of Fe hardly showed visible light photocatalytic activity due to its quick Recombination of the photogenerated electron/hole pairs. Dozzi et al. (2009) challenged the positive effect of Au loading on TiO_2. They obtained the opposite results from the photo-degradation of the different organic chemicals over Au-TiO_2 compared to unmodified TiO_2 and stated that the effect of Au nanoparticles on the oxidation of organic substrates may appear controversial, because a) Au deposition may greatly change the surface property of photocatalyts, causing an intrinsic decrease in photocatalytic activity; b) the photocatalytic oxidation rate over Au-TiO_2 under visible light irradiation depends on the reaction track of chemical substrates during the photocatalysis. Whether the organic substrate preferentially undergoes the direct oxidation by photoproduced holes or by the highly oxidative radical generated through photocatalysis has dramatical difference in photocatalytic efficiency. In this second case, gold nanoparticles on TiO_2 may act as the recombination centers of photogenerated charge carriers.

Noble metals mainly comprised of Pt, Pd, Ag, Au and Ru as a doping metal to TiO_2 have been gained much attention from the researchers. The relative big ion sphere makes them scavenge photogenerated electrons more efficiently. Kafizas et al. (2009) found that Nano Au-TiO_2 and Ag-TiO_2 exhibited significantly higher rates of photocatalysis under visible light irradiation, despite its relatively high band-gap (3.10 eV) that should only be activeated by UV light. They suggested that as no direct correlation between calculated band-gap and photoactivity was seen in the experiment with different wavelength irradiation, a charge separation model was used to describe the mechanism by which this enhanced photoactivity was achieved. However, the mechanism of photoinduced reactions of noble metal doped TiO_2 under visible-light irradiation has not yet been clarified. There was a debate on the influence of the Au particle size on photocatalytic activities. The smaller size of Au particle leads to higher acitivity (Haruta et al., 1997; Orlov et al., 2004 and 2007). Whereas, an opposite dependence, higher degradation efficiency under visible light irradiation along with large Au particle size has also been reported (Kowalska et al., 2009).

Hou and Liu (2008) compared the photoactivity of the 4 different noble metal-modified TiO_2 films. They found that the order of optimum reaction rate for the degradation of Methyl Oragne (MO) is $k_{Pt}>k_{Pd}>k_{Ag}>k_{Au}$ when noble metal modified TiO_2 films were under visible light irradiation. The reason of higher enhanced photocatalytic efficiency of Pd/TiO_2 films than Ag/TiO_2 films irradiated under visible light must be that Pd/TiO_2 films can use more visible light for catalytic activity than Ag/TiO_2 films. The worst enhanced photocatalytic efficiency of Au/TiO_2 films under both UV and visible light must be associated with its largest particle size. However, Au and Ag doping were also found to have superior photocatalytic activity, as stated above.

Metal doping has an optimal amount in the modified photocatalyst, but the values are different from the different metal ions and different experiment conditions. The photocatalytic activity of metal-doped TiO_2 usually increases with the increase of metal dopant in the photocatalyst at small doping level. However, the photocatalytic activity will decrease with excessive metal doping, which can become recombination center of photo-induced holes and electrons (Li and Li, 2002; Lam et al., 2007; Yi et al., 2007; Zhu et al., 2007a; Hou and Liu, 2008; Hou et al., 2009). It was also reported that the metal doped TiO_2 under visible excitation having less redox power at the expense of utilizing low energy photons limits the range of chemical substrates that can be photocatalytically oxidized (Kim et al., 2005).

Not as in non-metal doping, there were few researchers who tried examining the synergy in two or three metal elements codoped TiO_2. Grandcolas et al. (2008) found that the decoration of platinum by palladium in Pt, Pd codoped TiO_2 could further limit the charge recombinations by involving the palladium mainly in the photogenerated charge transfer process in CO removal under visible light irradiation. More researches will be needed on the modified TiO_2 with different metal elements co-doping.

Some of the studies showed a promising potential for using metal-doped TiO_2 in degradation of VOCs. Bae et al. (2007) obtained the high oxidation potential of Cr-TiO_2 for CH_3OH degradation to CO_2 under visible light irradiation. Lam et al. (2007) confirmed that the visible-light-driven photocatalytic activity of Cr-TiO_2 by the degradation of formaldehyde gas using single-plate and parallel-plate photoreactor. Sidheswaran and Tavlarides (2008) achieved up to 90 mol% conversion in degradation of toluene gas over Ce-TiO_2 under constant visible light irradiation for the residence time greater than 15 seconds. Kowalska et al. (2009) speculated that upon the excitation of Au-TiO_2 under visible light irradiation, Au particles inject the photogenerated electrons into the conduction band of TiO_2 and thus reduce oxygen adsorbed on the surface of TiO_2. The resultant electron-deficient Au could, then, oxidize 2-propanol. Yu et al. (2009) observed that at the optimum Fe/Ti = 0.5%, the photocatalytic activity of Fe-TiO_2 nanorods exceeded that of Degussa P25 by a factor of more than two times in the photocatalytic oxidation of acetone in air under visible light irradiation.

The disinfection of microbes in the indoor environment using metal-doped TiO_2 was also studied. Hu et al. (2007) observed that over AgI/TiO_2 under visible light irradiation, the concentration of 4.7×10^6 CFU/mL of *E. coli* was completely inactivated within 15 min, while 6.9×10^7 CFU/mL was completely killed at 60 min of irradiation. With the initial concentration increasing, the inactivation rate decreased. However, the initial concentration of 1.2×10^9 CFU/mL was also completely removed at 120 min of irradiation. He et al. (2008a) found that using Fe-doped TiO_2 modified photocatalytic paint, the sterilization ratio of *E. coli* could exceed more than 99% in less than 4 hours under 400-lux-visible light irradiation. Wu et al. (2010) synthesized a Montmorillonite (MMT)-supported Ag/TiO_2 composite, which could maintain antibacterial effect in long-term operation. At the initial level of 3.2×10^8 CFU/mL, with Ag/TiO_2/MMT, *E. coli* was almost completely killed after illumination under visible light for approximately 3h, which was much higher than Ag/AgBr/TiO_2 system.

2.6.4. Both Non-metal and Metal Co-doping

Non-metal doping can introduce a new local band in doped TiO_2 which can be excited by visible light photons. While, metal doping can mainly improve the charge separation between electrons and holes. Metallic, non-metallic co-doped TiO_2 under visible light irradiation shows combined effects of both metal and nonmetal doping: not only improve the visible light absorption but also reduce the chance of recombination of photoinduced electron-hole pairs, which is responsible for the higher photocataltic activity. The synergy was found in many studies. Liu et al. (2007b) found that the decomposition of methylene blue (MB) solution under visible light irradiation was higher on Ag/N-TiO_2 than N-TiO_2. The photocatalytic activity of as-prepared Ag/N-TiO_2 was obviously enhanced due to the decreasing recombination of a photoexcited electron-hole pair by Ag. Li et al. (2008) obtained the higher conversion and mineralization of many VOCs over Pt, N-TiO_2 than those over N-TiO_2. The Au, N-TiO_2 samples prepared by Wu et al. (2009b) presented much higher photocatalytic activity than N-TiO_2 under visible light irradiation. However, the superior photocatalytic activity of metallic, non-metallic co-doped TiO_2 to either metallic or non-metallic doped TiO_2 has not been confirmed, due to the relative small number of researches.

Many kinds of combination of metal and non-metal dopants were studied such as N-TiO_2 with Ag (Liu et al., 2007b), Cu (Morikawa et al., 2006 and 2008); Fe (Ohno, 2006; Ohno et al., 2006; Xing et al., 2009b), Pt (. Morikawa et al., 2006; Zhou et al., 2007; Li et al., 2008; Zhang et al., 2009), Au (Wu et al., 2009a), V (Higashimoto et al., 2008), Ni (Zhang and Liu, 2008), W (Li et al., 2008b; Shen et al., 2008), Ta (Obata et al., 2007), & Er & La (Ling et al., 2009), S-TiO_2 with Fe (Ohno, 2006; Ohno et al., 2006 and 2008), & La & Y (Gao et al., 2005) and I-TiO_2 with Ce (Song et al., 2008), & La (He et al., 2008b), Some controversial results were also obtained. Zhang and Liu (2008) observed an enhancement of 200% in photoactivity for the decomposition of formaldehyde under visible light for the N-Ni co-doped photocatalyst. However Morikawa et al. (2006) found no improvement of photocatalytic activity over N-TiO_2 by loading Ni.

Different metal ions may have different effects on different organic substrates. Morikawa et al. (2008) compared the visible-light-driven photo-degradation of several kinds of organic compounds over N-doped TiO_2 loaded with Fe, Cu or Pt. Although the loading of Fe, Cu or Pt resulted in similar rates of enhancement of acetaldehyde oxidation, and that Cu and Pt gave the highest rates of acetic acid and toluene oxidation, respectively.

Some of the researches showed a promising potential for using metallic, non-metallic co-doped TiO_2 in degradation of VOCs. Morikawa et al. (2006) found that the photo-degradation of acetaldehyde into CO_2 over N-TiO_2 was markedly enhanced by Pt loading under visible light. Ohno (2006) and Ohno et al. (2006) found that the Fe^{3+} adsorbed on the surfaces of S- or N-TiO_2 photocatalysts were highly efficient in degradation of 2-propanol under visible light. Ohno et al. (2008) synthesized rutile S-doped TiO_2 photocatalysts loaded with Fe^{3+}, which showed high level of photocatalytic activity in the oxidation of acetaldehyde in gas phase. Morikawa et al. (2008) found that the N-doped TiO_2 loaded with Pt gave high rates of acetaldehyde and toluene oxidation in gas phase. Li et al. (2008a) observed 46% conversion of ethylene over Pt/N-TiO_2 under visible light and the stabilized 100% mineralization after 4h test run. The conversion and mineralization of benzene were 18 and 80%, respectively. The photocatalytic conversions of toluene and ethylbenzene on Pt/N-TiO_2 were 20 and 23%, respectively, accompanied by a similar mineralization of 84%.

The disinfection of microbes using metallic, non-metallic co-doped TiO_2 in the indoor environment was also studied. Hamal et al. (2010) synthesized a photocatalyst based on TiO_2 codoped with Ag, S, and C. This photocatalyst even exhibited very strong antimicrobial properties without light activation against both *E. coli* (log kill > 8) and *Bacillus. subtilis* spores (log kill > 5) for 30 min exposures, compared with TiO_2 (P25).

2.6.5. Oxides, Sulfides, Bromides, and Chlorides Mixing

The bandgap of TiO_2 determines its most absorption of UV light. However, there are many other oxides (Cu_2O (Bessekhouad et al., 2005; Zhang et al., 2007; Han et al., 2009), Bi_2O_3 (Bessekhouad et al., 2005), WO_3 (Bosc et al., 2006; Gomez et al., 2006; Georgieva et al., 2007; Keller et al., 2007), Sr_2CeO_4 (Zhong et al. 2007), SrO (Han et al., 2007), ZnO & CdO (Suarez-Parra et al., 2003), CeO_2 (Liu et al., 2005), Cr_2O_3 (Miyazaki et al., 2008), Fe_2O_3 (Liu and Gao, 2006; Nishijima et al., 2007b and 2008; Kuang et al., 2009), FeO (Mazille et al., 2009a and 2009b), and SnO_x (Maeda and Hirota, 2006)), Sulfides (CdS (Srinivasan et al., 2006; Wu et al., 2006; Sun et al., 2008b; Banerjee et al., 2008; Li et al., 2009c) and MoS_2 (Pourabbas and Jamshidi, 2008)), Bromides (AgBr (Hu et al., 2006; Zang and Farnood, 2008)), and Metal chloride complexes ($Na_2[PtCl_6]$, $AuCl_3$, $RuCl_3$, and $H_2[PtCl_6]$) (Macyk and kisch, 2001; Hashimoto et al., 2009), which can absorb visible light and generate photo-induced holes and electrons. Most of the oxides, sulfides, bromides, and metal chloride complexes (we will call them sensitizers) do not have good property in charge separation between visible-light-induced holes and electrons, though they can utilize visible light photons. In the mixture of those sensitizers and TiO_2, the sensitizers are responsible for the visible light absorption. Coupling with TiO_2, those sensitizers can transfer the photo-induced electrons to TiO_2 for charge carrier separation, increasing the photocatalytic activity. However, those sensitizers are not very stable during the photocatalysis (Proudfoot, 1997; Wu et al., 2006). If the photogenerated holes cannot induce an oxidation process, the photocorrosion of the sensitizer is thought highly likely to occur (Bessekhouad et al., 2004; Serpone et al., 1995). So, when the organic substrates are hard to be oxidized by the holes or oxidative radicals generated by the holes, the sensitizer will lose its photocatalytic activity under visible light irradiation and so will the mixture photocatalyst. This situation occurred when benzamide and 4-hydroxybenzoic acid were used as pollutants (Bessekhouad et al., 2005). Also, the mechanism of the mixture photocatalysts is still under study and not clarified. Zhang et al. (2007) observed that TiO_2/Cu_2O composite film needed the assistance of $FeSO_4$ and ethylenediaminetetraacetic acid (EDTA) for the degradation of MB under visible light irradiation. Without the presence of $FeSO_4$ and EDTA, there was no degradation for methylene blue. They suggested that TiO_2/Cu_2O composite film generated H_2O_2, and Fenton regent formed with Fe^{2+} and EDTA is responsible for the degradation of MB.

Generally speaking, the photocatalytic efficiency increases with increases of the sensitizer amount. However, either the photocatalytic activity reaches saturation at certain amount of sensitizer (Bessekhouad et al., 2005); or excessively loaded sensitizer can act as recombination centers for electron-hole pairs, decreasing the photocatalytic performance of the mixture photocatalysts (Bosc et al., 2006; Gao et al., 2006; Georgieva et al., 2007). There was a great difference on the ratio of components in Cu_2O/TiO_2 utilized in the degradation of organics. Han et al. (2009) reported that 5 mol% TiO_2 dispersed in Cu_2O displayed higher activity in the degradation of dodecyl-benzenesulfonate (DBS) in visible light. Whereas, Bessekhouad et al. (2005) obtained the highest photocatalyic activity at 30 wt.% Cu_2O in Cu_2O/TiO_2 in the degradation of dye Orange II in visible light.

Some innovative thoughts came from the combination of non-metal doping and sensitizer addition. Gao et al. (2006) synthesized the WO_3/N-TiO_2 composite photocatalysts and studied the N doping coupling with WO_3 mixing. WO_3 coupling increases the active nitrogen species, which in turn coordinats with tungsten and disperses on TiO_2 surface to form N-W-O linkages, contributing to visible light responses. Thus, the visible light activity of the composite photocatalysts was enhanced. Nishijima et al. (2007b) found that S-TiO_2 loaded with Fe_2O_3 nanoparticles (1.0 wt%) had the strongest visible light response among the photocatalysts examined (S-doped TiO2 and N-TiO_2 with or without Fe_2O_3 loading). Wang et al. (2006c) observed the stronger visible light absorption of ZrO_2/N-TiO_2 samples compared to N-TiO_2 samples. The addition of

ZrO_2 restrains undesirable crystal growth, preserving nitrogen species in the composite photocatalyst, which leads to the increase of visible light activity. Li et al. (2009d) found that PdO/N-TiO_2 had an enhanced photocatalytic activity under visible light illumination than nitrogen doped titanium oxide.

Some of the researches showed a promising potential for using the mixture of visible light sensitizers and TiO_2 in degradation of VOCs. Keller et al. (2007) observed that the promotion of TiO_2 with WO_3 strongly increased the toluene removal efficiency compared to the WO_3-free analogues. WO_3/rutile TiO_2 achieved a toluene removal of 98% under visible light irradiation. Zhong et al. (2007) found that the maximum 65% conversion rate of gaseous benzene on TiO_2/Sr_2CeO_4 under visible light irradiation in 4h. Nishijima et al. (2008) also found that Loading of Fe_2O_3 on S-TiO2 nanotube (TNT) remarkably improved the photocatalytic activity of S-doped TNT for oxidation of acetaldehyde under visible light irradiation.

The disinfection of microbes in the indoor environment using the mixture of visible light sensitizers and TiO_2 was also examined. Hu et al. (2006) prepared the catalyst Ag/AgBr/TiO_2 and confirmed the killing of *Staphylococcus aureus* (*S. aureus*) and *E. coli* under visible light irradiation. Wu et al. (2009c) reported that in 30 min of visible light irradiation, the *E. coli* survived $<10^{-7}$ on PdO/N-TiO_2, which was beyond detection limit. Disinfection data indicated that PdO/N-TiO_2 composite photocatalysts had a much better photocatalytic activity than either palladium-doped (PdO/TiO_2) or nitrogen-doped titanium oxide under visible-light illumination.

It is worth to point out SiO_2 which belongs to the oxide, though no absorption of visible light is found on it. Many researchers used SiO_2 as a support material for TiO_2 and other metal dopants. The presence of a second phase with good adsorptive capabilities (like the SiO_2 support) led to better photocatalytic results. The increased oxidizing potential of the Ti cations are due to the formation of Ti-O-Si bonds (Neatu et al., 2009). The visible light response of TiO_2-SiO_2 is mainly attributed to the metal ions incorporated. TiO_2-SiO_2 is used as a matrix for the metal ions and interacts with those metal ions to improve the photocatalytic activity. There is a significant interaction between the incorporated transition metal ions and titania (Li et al., 2008c). Silica-titania based framework and MCM-41 & MCM-48 molecular sieves (Silica based with the loading of TiO_2) were usually adopted for the metal ion impregnation.

The metal ion Cr was intensively studied with TiO_2/MCM-41 or TiO_2/MCM-48 for the photocatalytic activity in visible light (Reddy et al., 2002 and 2004; Sun et al., 2006; Marques et al., 2008; Portela et al., 2008). The VOC degradation over those photocatalysts was also obtained. Marques et al. (2008) found that photocatalytic tests using visible light showed that 20%TiO_2/Cr-MCM-41 converted 40% of the thiophene in gas phase, whereas TiO_2 (P25) converted only 20%. Rodrigues et al. (2005) synthesized a highly active, titania-loaded, chromium-incorporated MCM-48 visible-light photocatalyst. The high photocatalytic degradation of acetaldehyde was confirmed on this photocatalyst.

The Co–TiO_2–SiO_2 system was also studied (Matsuoka et al., 2003; Wang et al., 2004a and 2004b; Zhang et al., 2005; Li et al., 2008c). It is even better than TiO_2/Co-MCM-41 catalyst (Matsuoka et al., 2003; Li et al., 2008c), Co-MCM-41(Li et al., 2008c), and Co–TiO_2 (Li et al., 2008c). The incorporations of Co into the SiO_2 and TiO_2/SiO_2 aerogels were found active for photodegradation of acetaldehyde under visible light irradiation (Wang et al., 2004a and 2004b).

Some other metal ions were also examined including Pt (doped in TiO_2-SiO_2) (Mohammed et al., 2009), Mn & V (doped in TiO_2-SiO_2) (Neatu et al., 2009), and Ce (doped in TiO_2/MCM-41) (Yang et al., 2009).

2.6.6. H_2O_2 Addition

The chemisorptions of H_2O_2 on the surface of TiO_2 can result in the formation of yellow complex “Titanium peroxide” (Boonstra and Mutsaers, 1975). Titanium peroxide complex formed on the TiO_2 surface could extend the photoresponse to the visible region. The excited surface complex injects an electron to the conduction band of TiO_2. The photoexcited electron-hole pairs on the catalyst surface will, then, further initiate the decomposition of H_2O_2 to produce hydroxyl radicals (Yu et al., 1997; Ohno et al., 2001; Li et al., 2001; Sioi et al., 2006; Rao and Chu, 2009). The stronger withdrawing effect of surface complex groups to electrons can increase the charge of Ti surface species, which can stabilize the photoexcited electron-hole pairs and hinder recombination of photogenerated electrons and holes (Tsai and Cheng, 1997; Barraud et al., 2005; Yang et al., 2005). The addition of hydrogen peroxide into the Ag–TiO_2 catalyst improves the photodegradation rate of Reactive Yellow-17 (RY-17) under visible light irradiation. However, quenching of the hydroxyl radicals was observed with high concentration of H_2O_2, which, therefore, decrease in photodegradation of dyes (Rupa et al., 2007).

The previous research carried on in our lab developed a novel PCO gel with H_2O_2 added to achieve the maximum photocatalytic oxidation of VOCs emitted from the building materials in UV and visible light. More than 60% total VOC emission from tested pressure treated wood and oil based paint were reduced in both UV and visible light. 35% H_2O_2 was found to be the most effective concentration for the novel PCO gel (James, 2005).

2.6.7. Dye Sensitizing

Under visible light irradiation, the exited dye molecule will inject an electron to the conduction band of TiO_2; meanwhile, the dye is converted to cationic dye radical. The injected electron can reduce surface chemisorbed oxygen molecule to form the oxidizing species that bring about photodegradation. (Dieckmann and Gray, 1996; Qu et al., 1998; Liu et al., 2000; Liu and Zhao, 2000; Epling and Lin, 2002; Stylidi et al., 2004; Yang et al., 2006; Li et al., 2008d; Zhang et al., 2008b). The adsorption of the dye onto TiO_2 plays an important role in the photocatalytic activity of the dye sensitized TiO_2 under visible light irradiation. The additives were put into the dye/TiO_2 system to enhance the adsorption of dye onto TiO_2 such as Dodecylbenzene sulfonate surfactant (DBS) (Wu et al., 1998; Liu et al., 2000), Cu^{2+} (Mahmood et al., 2009), and Zn^{2+} (Mahmood et al., 2009). Sonication increases the amount of reactive radical species, resulting in faster oxidation of the substrate and degradation of intermediates and also the disaggregation of the photocatalyst. The accelerated sonophotocatalytic degradation of Reactive Red (RR) 198 dye under visible light using dye sensitized TiO_2 activated by ultrasound was confirmed. Further, the photocatalytic activity of RR 198 dye sensitized TiO_2 was demonstrated by the degradation of phenol under visible light and ultrasound (Kaur and Singh, 2007). The drawbacks of the dye/ TiO_2 system were also reported. In most cases of dyes sensitization, dyes are easily escaped from the surface of TiO_2 due to the physical combination of dyes and TiO_2, which would result in the environmental pollution again.

Moreover, most photosensitizer dyes with low molecular weight are unstable under UV or solar light irradiation (Zhu et al., 2007b). The photocatalytic oxidation reaction will cease, when the solution is bleached and the dye sensitizer is degraded. No active oxidative species will be formed and the concentrations of the dye intermediates remain practically stable upon further exposure to visible light irradiation (Stylidi et al., 2004).

It is confirmed that visible-light-induced photocatalytic oxidation takes place on many kinds of organic dyes sensitized TiO_2: dye alizarin red (AR) (Liu et al., 2000), tetraethylated rhodamine (RhB) (Qu et al., 1998; Wu et al., 1998), Reactive Red (RR) 198 (Kaur and Singh, 2007), Chicago Sky Blue 6B and Benzopurpurin 4B (Mohammed and Mckenzie, 2005), crystal violet (CV) (Li et al., 1999; Li et al., 2008d), textile dye X3B (Xu and Langford, 2001), fuchsin basic (FB) (Li et al., 1999), Sulforhodamine B dye (SRB) (Liu and Zhao, 2000; Chen et al., 2002), methylene blue (MB) (Chen et al., 2003), acid orange 7 (AO7) (Stylidi et al., 2004; Wang et al., 2004), acid chrome blue K (ACBK) (Mahmood et al., 2009), porphyrin (Li et al., 2008d; Chang et al., 2009), polyaniline (Wang et al., 2006d and 2007c; Feng et al., 2008), phthalocyanine (Hodak et al., 1996; Iliev, 2002; Iliev and Tomova, 2002; Iliev et al., 2003; Chen et al., 2005; Wang et al., 2006d; Wang et al., 2006e; Sun and Xu, 2009), Mn(II)-terpy complexes (Abuabara et al., 2007; McNamara et al., 2008) and $Ru(bpy)_3]^{2+}$ (Bossmann et al., 2001).

Some innovative methods combined dye/TiO_2 system with other technologies to improve the photocatalytic activity under visible light irradiation. Bae and Choi (2003) developed a new photocatalyst-Pt/TiO_2/$RullL_3$, incorporating noble metal doping and dye sensitizer. Platinum nanoparticles on dyesensitized TiO_2 (Pt/TiO_2/$RullL_3$) drastically enhanced the degradation rate of TCA and CCl_4, which ascribed to the fast electron trapping in Pt competing with the back electron transfer. Li et al. (2008d) synthesized a photostable 3D-ordered TiO_2 hybrid photocatalyst with the core/shell structure of dye-containing polymer/titania. The nanostructured TiO_2 hybrid photocatalyst exhibited efficient and stable photocatalytic activity for the photodegradation of crystal violet (CV) under visible light irradiation.

2.6.8. Others

There were a few modified TiO_2 systems that could not be sorted into the above five categories, but possessed a potential to be used under visible light irradiation.

The $InVO_4$-TiO_2 based thin films with Ag (Ge et al., 2006) and Pd (Ge and Xu, 2006) dopings were developed. Metal/$InVO_4$-TiO_2 exhibited photo activity under visible light irradiation, which can ascribed to the simultaneous effects of doped noble metal by acting as electron traps and $InVO_4$ as a narrow band gap sensitizer (Ge et al., 2006 and Ge and Xu, 2006).

Rayalu et al. (2007) synthesized a zeolite-based composite photocatalysts with incorporation of Heteropolyacids (HPA), semiconductor TiO_2 and transition metal cobalt on zeolite. HPAs can be used as photocatalysts active in visible light. Zeolite plays the most significant role to provide a high surface area for incorporation of TiO_2 and HPA, and ion exchange properties for incorporation of Co^{2+}. The Co^{2+} ion present not only acts as an electron acceptor for separation of electron-hole pairs, but also acts as a chromophore, which absorbs visible light.

The upconversion luminescence agent can absorb visible light and then emit UV light. When the upconversion luminescence agent is doped into TiO_2, it can transform visible light which cannot be used by TiO_2 into UV light which can activate the photocatalysis of TiO_2 (Wang et al., 2006f and 2007d; Feng et al., 2008).

2.7. Conclusion

With nearly 4 decades research on the photocatalysis of TiO_2, the mechanism of photocatalytic reaction, the influencing environmental factors, and the application of the photocatalysts were understood well, especially under UV light irradiation. The degradation of VOCs in air and the disinfection of microorganisms are two of the major application of the photocatlaysts. The commercial products in the market and the applications in the real project based on the photocatalytic technology predict a bright future for the photocatalysts. However, compared to some mature technologies, the photocatalysts are still undergoing a development phase. The photocatalytic efficiency and the limitation of using UV light are two big challenges for the photocatalysts.

Entering the 21st century, more and more studies have been under developing the visible-light-driven photocatalysts for extending the use of photocatalysts and improving the photocatalytic efficiency under visible light irradiation. There are generally 6 methods to modify TiO_2, the most widely used photocatalyst, for obtaining the photocatalytic activity under visible light irradiation (Table 2.2): a) non-metal doping; b) metal doping; c) both non-metal and metal doping; d) Oxides, Sulfides, Bromides, and Chlorides Mixing; e) H_2O_2 addition; f) dye sensitizing. Many of the visible-light-driven photocatalysts developed exhibited fairly good photocatalytic activity under visible light irradiation in the degradation of the substrate chemicals or the disinfection of microorganisms in the specific experiments. However, some controversial results were reported. The drawbacks of the visible-light-driven photocatalysts were also stated such as the instability, the reduction of the UV light photocatalytic activity, and the low redox power which is not enough for oxidizing some chemicals. The mechanism of the photocatalysis under visible light irradiation is still not very clear. Many aspects of the visible-light-driven photocatalysts still needs future research such as the mechanism of the visible light photocatalysis, the preparation process of the visible-light-driven photocatalysts, and the substrate chemicals and target microorganisms.

From this review, the modified TiO_2 exhibits the photocatalytic activity under visible light irradiation on the degradation of VOCs and the disinfection of microorganisms, which are the main purpose of this research. They have a potential to be applied to the reduction of VOC pollutants and the resistance of mold growth in the indoor environment. Among all the modified TiO_2, Ag doped TiO_2 (Ag ions are inserted into the crystal lattice of TiO_2 in chemical preparation) was found very effective on bacteria, yeast and Bacillus spore control under visible light irradiation (Hu et al., 2007; Liu et al., 2009b; Wu et al., 2010; Hamal et al., 2010) for Ag, itself, possesses a great biocide effect. Besides, H_2O_2 is a powerful disinfectant, which can even kill fungal spores and is widely used in water disinfection and mold/mildew remediation process. By adding Ag or/and H_2O_2, not only can the photocatalytic activity of TiO_2 on VOC oxidation under visible light be improved, but also its biocide effects are expected to be enhanced. The modified TiO_2 potentially allows for the mold/mildew resistance and VOC oxidation in the indoor environment under interior lighting.

Table 2.2 The Modified TiO_2 in Degradation of VOCs and Disinfection of Microorganisms under Visible Light Irradiation

Modifying Method	Mechanism	Modified TiO_2	Substrates	Significant Publication
Non-metal Doping	Non-metal impurities and oxygen vacancies induce visible light absorption	S-TiO_2	2-propanol	Ohno, 2004; Ohno et al., 2004
		F-TiO_2	acetaldehyde	Li et al., 2005a
		N,S-TiO_2	acetone, formaldehyde	Yu et al., 2006
		S-TiO_2	acetaldehyde	Nishijima et al., 2007a
		N-TiO_2	ethyl benzene, o,m,p-xylenes	Jo and kim, 2009
		C-TiO_2	toluene	Dong et al., 2009a
		N-TiO_2	*E.coli*	Cao et al., 2007; Vacaroiu et al., 2009
		N,S-TiO_2	*E.coli*	Rengifo-Herrera et al., 2009
Metal Doping	Metal impurities induce visible light absorption and improve the seperation of photogenerated electrons and holes	Cr-TiO_2	Methanol	Bae et al., 2007
		Cr-TiO_2	formaldehyde	Lam et al., 2007
		Ce-TiO_2	toluene	Sidheswaran and Tavlarides, 2008
		Au-TiO_2	2-propanol	Kowalska et al., 2009
		Fe-TiO_2	acetone	Yu et al., 2009
		AgI/TiO_2	*E. coli*	Hu et al., 2007
		Fe-TiO_2	*E. coli*	He et al., 2008a
		Ag-TiO_2/MMT	*E. coli*	Wu et al., 2010
Metal, Non-metal co-doping	Both benefits from metal and non-metal dopants	Pt,N-TiO_2	acetaldehyde	Morikawa et al., 2006
		Fe,S or N-TiO_2	2-propanol	Ohno, 2006; Ohno et al., 2006
		Fe,S-TiO_2	acetaldehyde	Ohno et al., 2008
		Pt,N-TiO_2	ethylene, benzene, ethylbenzene	Li et al., 2008a
		Ag,S,C-TiO_2	*E. coli*	Hamal et al., 2010
Oxides, sulfides, bromides, and chlorides mixing	Oxides, sulfides, bromides, and chlorides are used as a sensitizer to absorbe visible light and TiO_2 acts as an electron scavenger	WO3/TiO2	toluene	Keller et al., 2007
		Sr_2CeO_4/TiO_2	benzene	Zhong et al., 2007
		Fe_2O_3/S-TiO_2	acetaldehyde	Nishijima et al., 2008
		Ag/AgBr/TiO_2	*S. aureus*, *E. coli*	Hu et al., 2006
		PdO/N-TiO_2	*E. coli*	Wu et al., 2009c
H_2O_2 Addition	H_2O_2 forms "Titanium peroxide" on the surface of TiO_2 for visible light absorption	TIO_2/H_2O_2	Various VOCs	James, 2005
Dye Sensitizing	Dye molecules adsorbed on the surface of TiO_2 can be activated by visible light	TiO_2/Dye	NA	NA

Chapter 3

PRELIMINARY MOLD/MILDEW GROWTH TEST ON TiO_2 AND H_2O_2

3.1. Background

Most of the research on the antimicrobial performance of TiO_2 was conducted on bacteria. There are not many papers regarding its antifungal performance (Sichel et al., 2007). Chen et al. (2009) found that TiO_2 coating could deactivate the fungal spores on wood surface under UV light irradiation, but there is no antifungal effect under visible light irradiation. Also, mold growth can be expected in unlit areas.

H_2O_2 is widely used for microbial control, and it can kill fungal spores. When TiO_2 particles are used as a photocatalyst with the addition of H_2O_2, the photocatalytic reaction occurs even under irradiation of visible light (Yu et al., 1997; Ohno et al., 2001; Li et al., 2001; Sioi et al., 2006; Rao and Chu, 2009). It is known that the chemisorptions of H_2O_2 on the surface of TiO_2 can result in the formation of the yellow complex "Titanium peroxide" (Boonstra and Mutsaers, 1975). The titanium peroxide complex formed on the TiO_2 surface could extend the photoresponse to the visible region and can be excited by visible light.

This study was conducted to investigate the possible synergy between TiO_2 and H_2O_2 for mold/mildew resistance, compared to TiO_2 or H_2O_2 alone. The effects of different light sources (no light, UV light, and visible light) and different H_2O_2 concentrations on the mixture of TiO_2 and H_2O_2 were also evaluated.

3.2. Materials and Preparation

The fungal species used in this experiment was *Aspergillus niger*, which is a common mold species in the indoor environment (Codina et al., 2008). The three kinds of test coating samples were H_2O_2, TiO_2 gel and TiO_2/H_2O_2 gel:

a) H_2O_2 with 3% and 35% concentration was chosen in this experiment. The average volume of the H_2O_2 coating coated on the filter papers was 0.2 mg/cm^2.

b) The TiO_2 gel was prepared by adding excessive TiO_2 (P25) powders in polyethylene glycol gels (PEG) water solution (the mixing ratio of PEG and H_2O is 1:2 weight ratio) under sonication. The average volume of the TiO_2 coating coated on the filter papers was 3.5 mg/cm^2.

c) The TiO_2/H_2O_2 gel was prepared by vigorously mixing H_2O_2 (3% and 35%) with TiO_2 gel (the mixing ratio of the TiO_2 gel and H_2O_2 is 3:2 volume ratio). The average volume of the TiO_2/H_2O_2 coating coated on the filter papers was 1.7 mg/cm^2.

3.3. Experiment

The test procedure was mainly based on ASTM D5590-00-Determining the Resistance of Paint Films and Related Coatings to Fungal Defacement by Accelerated Four-Week Agar Plate Assay. Some modifications of this standard test method were done for the specific need of the experiment.

The fungal spores were purchased and cultured on the Petri dishes with Potato Dextrose Agar. After the full development of mold and maturation of spores, those Petri dishes were placed and stored in a refrigerator at approximately 3 to 10℃. Prior to each experiment, mold was subcultured onto agar plates and incubated until the maturation of spores. These subcultures were then used in preparing a spore suspension (SS).

The preparation of spore suspension began with a sterile 10-mL portion of water pipetted into one subculture with a sterile Pasteur pipette. After swirling and gently agitating the subculture plate to loosen the spores, the spore suspension was collected and carefully aspirated. The collected spore suspension was checked under the microscope for mycelial contamination, and a note of the relative populations of spores versus mycelial forms was made. Then, the spore suspension was diluted with sterile water so that the resultant spore suspension contained 0.8 to 1.2 by 10^4 spores/mL as determined with a counting chamber.

The three kinds of coating samples to be tested were applied to glass fiber filter paper disks (Glass fiber, Grade 391, 9 cm supplied by VWR) by dipping the filter papers into coating samples for 2 min. The loadings of H_2O_2, TiO_2 gel and TiO_2/H_2O_2 gel samples on the filter paper were approximately 0.4 mg/cm^2, 1.7 mg/cm^2, and 3.5 mg/cm^2, respectively. Then, the sample disks were suspended on drying racks and allowed to air dry for 48 hours at room temperature.

At the beginning of each experiment, these filter paper disks were placed onto agar plates. Next, a thin coat of spore suspension (0.5 mL) was applied to each specimen using a sterile pipette. The sterile plastic rods were used to evenly spread the inoculum over the surface of each test sample. The spore suspension (0.5 mL) was periodically reapplied to the specimen every two days (it may take two days to show the trace of mold/mildew growth under the experiment condition) to investigate periodically antifungal effect of coating samples. All the plates were incubated at 28 ℃ and >90 % relative humidity for 4 weeks or until full coverage of mold growth on plate surface. Different kinds of lamps (UV light or visible light) were hung over the tested agar plates in case certain light irradiation was needed for the test. The general experiment setting is illustrated in Fig. 3.1.

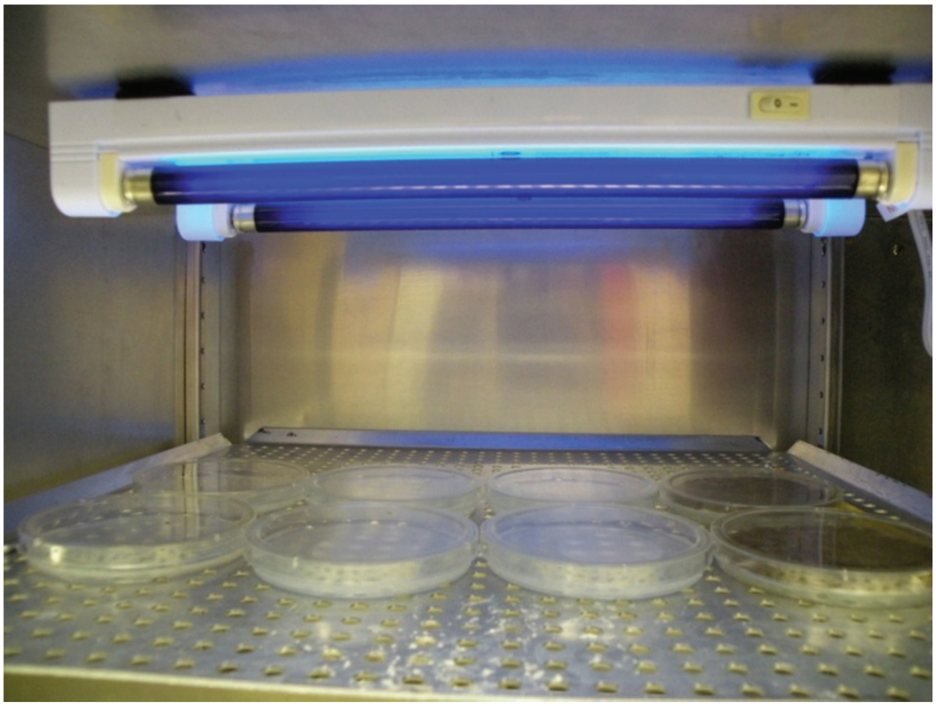


Figure 3.1 Mold/mildew resistance experiment setting.

The mold growth experiment on the 3 kinds of prepared coating samples was conducted in three major conditions:

a) Without light,

b) With UV light irradiation (at 365 nm average 0.5 mw/cm^2),

c) With visible light irradiation (average 1500 lux).

The responses of the coating samples to the different light sources were investigated. Each test had two negative controls, two positive controls and three test groups: filter papers coated with H_2O_2 alone, filter papers coated with the TiO_2 gel alone, and filter papers coated with the TiO_2/H_2O_2 gel. Each test group was repeated at least three times. Each time the spore suspension was reapplied, a positive control was added. The mold growth was rated every day during the four-week experiment.

After the exposure of UV or visible light irradiation, the inoculated Petri dishes with no mold growth were, then, be put without light. If there is mold growth during one-week dark treatment, the previously inoculated fungal spores are just inactivated by the photocatalytic process. If no mold growth showing, the fungal spores are killed (Chen et al., 2009).

3.4. Results and Discussion

3.4.1. Mold Growth without Light.

Without light, it took two days for mold to fully cover all the surface of the Petri dish. The coating samples with TiO_2 or H_2O_2 alone (both 3% and 35% concentration) did not show the resistant effect on mold growth. Without light, TiO_2 as a photocatalyst cannot be exited, generating highly oxidative radicals which are believed to destroy microorganisms. H_2O_2 alone is too unstable to adhere to the filter paper, and it evaporates and decomposes very fast. However, with TiO_2/35% H_2O_2 samples, the mold growth was not observed in the first four days. In other words, the mold growth started after the third inoculation of mold spore suspension. TiO_2 with a porous surface can adsorb and stabilize H_2O_2 by forming “Titanium peroxide” (Boonstra and Mutsaers, 1975). So, the H_2O_2 can prevent the mold growth in the first four days. However, with time passing, TiO_2/35% H_2O_2 samples seemed lose their effect on prevention of mold growth, which were seen from the start of mold growth after the third inoculation. During this period, H_2O_2 is gradually used up in the destruction of mold spores and some also evaporates. After four days, the H_2O_2 left is not enough to prevent the mold growth. In addition, there was no mold resistance found in TiO_2/3% H_2O_2 samples, probably due to low oxidative power with low concentration of H_2O_2 (concentration would be even lower when mixing with TiO_2 gel).

Another test was performed to investigate if TiO_2/35% H_2O_2 samples delayed the growth of spores from the first two inoculations, or if they kill them but lose their effect on the third inoculation. The third inoculation was not conducted on some of Petri dishes that had no mold growth after two inoculations. No mold growth was, then, found on those Petri dishes for four weeks. Therefore, spores from the first two inoculations were killed by TiO_2/35% H_2O_2 samples because of the strong oxidative power of 35% H_2O_2.

3.4.2. Mold Growth under UV Light.

Under UV light irradiation at 365 nm peak, the time that took for mold to fully cover all the surface of the Petri dish remained similar to that without light. UV light irradiation at 365 nm peak has little effect on mold growth. The only difference was that under UV light, mold developed spores later than without light. H_2O_2 samples (both 3% and 35% concentration) still showed little delay effect on mold growth. However, both TiO_2 and

TiO_2/H_2O_2 (both 3% H_2O_2 and 35% H_2O_2) samples completely inhibited the mold growth under UV light irradiation for four weeks, even though the Petri dishes were periodically applied with mold spores every two days. The H_2O_2 and highly oxidative radicals produced by TiO_2 with UV light activation are considered to be responsible for the prevention of mold growth (Fujishima and Honda, 1972; Kikuchi et al., 1997; Cho et al., 2004). The damage of the membrane structure and membrane functions by highly oxidative radicals is the root cause of cell death when photocatalytic TiO_2 particles are outside the cell (Maness et al, 1999). The oxidative radicals can be produced continually on the surface of TiO_2 particles under UV light irradiation. So, the TiO_2 and TiO_2/H_2O_2 samples showed the long-term prevention of mold growth.

As Chen et al. (2009)'s study, the Petri dishes without any mold growth after four weeks incubation were placed in darkness. The mold growth was checked every day during one-week dark treatment. Unlike Chen et al. (2009)'s result, there was no mold growth found on any TiO_2 or TiO_2/H_2O_2 samples after the one-week dark treatment. Based on this result, the mold spores in our experiment were killed, not just deactivated, with TiO_2 or TiO_2/H_2O_2 samples under UV light irradiation. There are two possible reasons for the controversial results:

a) The concentration of spore suspension used in Chen et al. (2009)'s experiment was 100 times larger than that in our experiment. It might be hard to completely kill all the spores, some of which might already germinate and just be suppressed by the photocatalysis.

b) Not as Chen et al. (2009) only used the TiO_2 water suspension for coating the wood, PEG, as a matrix for the TiO_2 gel, was added. The large pore size resulted from PEG improves the contact between substrates and photocatalysts, enhancing the photocatalytic efficiency (Guo et al., 2004). The possible promotion effect of PEG may cause the difference of these results.

3.4.3. Mold Growth under Visible Light.

Under visible light irradiation, the normal mold growth rate was the same as that without light. Visible light at 1500 lux has no effect on mold growth. H_2O_2 (both 3% and 35% concentration) and TiO_2 samples also did not show any delay effect on mold growth. So, visible light does not improve the unstable property of H_2O_2; either, TiO_2 cannot be activated by visible light. However, with TiO_2/35% H_2O_2 samples, the mold growth was observed to start on the seventh or eighth day from the first inoculation. In other words, it prevented mold growth from the first three inoculations. The longer period of mold prevention under visible light irradiation than that without light on TiO_2/35% H_2O_2 samples is considered to be attributed to the titanium peroxide complex produced by the chemisorptions of H_2O_2 on the surface of TiO_2, which responds to visible light (Yu et al., 1997; Ohno et al., 2001; Li et al., 2001; Sioi et al., 2006; Rao and Chu, 2009). In this way, like the photocatalytic reaction of TiO_2 under UV light, TiO_2/35% H_2O_2 samples can continually produce H_2O_2 and highly oxidative radicals under visible light, which is toxic to mold spores. However, H_2O_2 will also decompose gradually into hydroxyl radicals during the photocatalytic process (Li et al., 2001). Even though more H_2O_2 and oxidative radicals were produced on TiO_2/35% H_2O_2 samples, which could last for more days under visible light, the samples still lost the effect after six or seven days and after the forth inoculation with the loss of titanium peroxide complex. There was also no mold resistance found in TiO_2/3% H_2O_2 samples under visible light, which suggests that less formation of titanium peroxide complex due to lower concentration of H_2O_2 leads to little photocatalytic efficiency in visible light.

The same dark treatment was performed on TiO_2/35% H_2O_2 samples before the forth inoculation when there was no mold growth. Still, no mold growth was observed after the one-week dark treatment, which indicated that mold spores from the first three inoculations were killed by TiO_2/35% H_2O_2 samples under visible light. The addition of H_2O_2 not only activates TiO_2 under visible light irradiation, but also increases the photocatalytic efficiency for killing the fungal spores.

The detailed result is contained in Table 3.1, and photo result is illustrated in Fig. 3.2.

3.5. Conclusion

Under UV light irradiation, it was observed that TiO_2 and TiO_2/ (3% and 35%) H_2O_2 could both completely prevent mold/mildew growth during the experiment period (four weeks). Without light, TiO_2/35% H_2O_2 showed some delay effect on mold growth. Under visible light irradiation, TiO_2/35% H_2O_2 inhibited mold growth for longer time than that without light because of the visible light activity. 3% H_2O_2 had little effect on improving photocatalytic efficiency of TiO_2 under either visible light or without light. In addition, TiO_2/H_2O_2 samples were found to kill mold spores without light, under UV light, or under visible light; meanwhile, TiO_2 can also kill mold spores under UV light.

The mold/mildew resistance of TiO_2 under UV light was verified by the periodical exposure of fungal spores. TiO_2 with UV light would be an effective way to prevent mold/mildew growth. This study showed that the modified TiO_2 might be a promising material in resisting indoor mold/mildew growth under interior lighting. The delay effect on mold growth found with TiO_2/H_2O_2 without light or under visible light irradiation may contribute to the mold/mildew resistance in the indoor environment when the conventional methods for mold/mildew resistance temporarily fail such as the situations during a power failure, flood, or hurricane. Even though it was found that TiO_2/H_2O_2 has longer mold resistant time in visible light than expected, H_2O_2 is so unstable and may decompose quickly in the indoor environment. H_2O_2 may need to be periodically sprayed on the surface of the coating material for maintaining the photocatalytic activity under visible light (cleaning the surfaces every few days with H_2O_2). Further research is required to find a way to stabilize H_2O_2 in the coating material, or more stable substitutes for H_2O_2 need to be explored. The gel made in this research should be applied as a coating material on any surfaces in the indoor environment. Modification of the gel is necessary for the real application.

Table 3.1 Mold Growth Test Results for TiO_2 and H_2O_2

Samples	Light Sources	Incubation Time					
		2 days	4 days	5 days	6 days	7 days	28 days
Blank	Without Light	*	*	*	*	*	*
H_2O_2 (3% and 35%)		*	*	*	*	*	*
TiO_2		*	*	*	*	*	*
TiO_2/3% H_2O_2		*	*	*	*	*	*
TiO_2/35% H_2O_2				*	*	*	*
Blank	UV Light	*	*	*	*	*	*
H_2O_2 (3% and 35%)		*	*	*	*	*	*
TiO_2							
TiO_2/3% H_2O_2							
TiO_2/35% H_2O_2							
Blank	Visible Light	*	*	*	*	*	*
H_2O_2 (3% and 35%)		*	*	*	*	*	*
TiO_2		*	*	*	*	*	*
TiO_2/3% H_2O_2		*	*	*	*	*	*
TiO_2/35% H_2O_2						*	*

*Showing Mold Growth

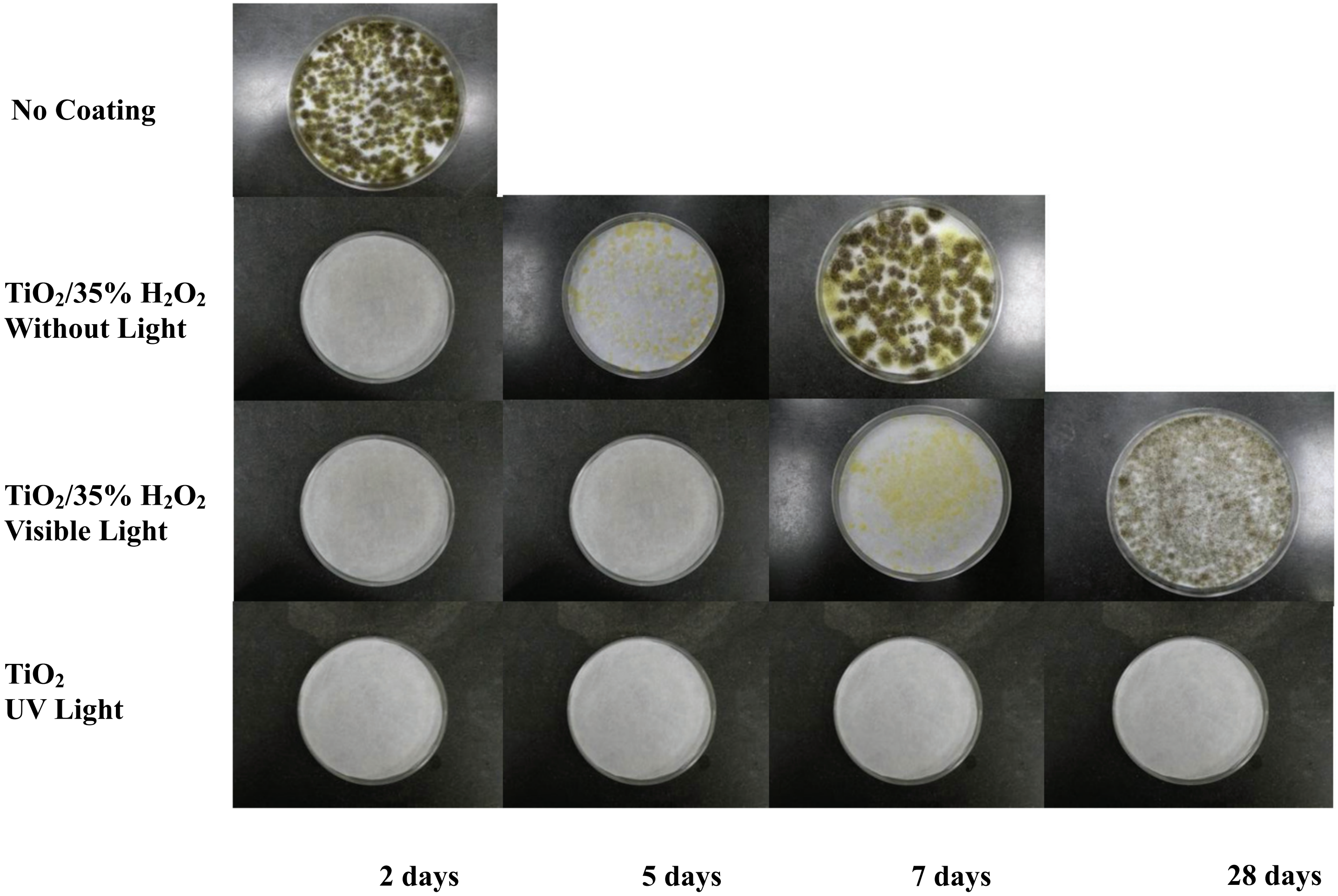


Figure 3.2 The picture result of mold growth test on TiO_2 and H_2O_2 at different incubation time

Chapter 4

MOLD/MILDEW GROWTH TEST ON PCO GELS

4.1. Background

A previous study performed in the Building Environmental System Laboratory (BESL) at the University of Miami developed a novel PCO gel for reducing VOC emission from building materials under UV or visible light irradiation (Fig. 4.1). This PCO gel is composed of polyethylene glycol gel (PEG) matrix (framework), semiconductor nanoparticles (TiO_2), a light sensitizing catalyst, and a supplemental oxide (H_2O_2). The excellent efficiency of VOC removal by this novel PCO gel was verified (James, 2005). However, the microbiological resistant property of the PCO gel has not been examined. Based on the preliminary result of mold growth experiment on TiO_2 with H_2O_2, it is promising that the modified TiO_2 has potential to be a mold/mildew resistant coating material.

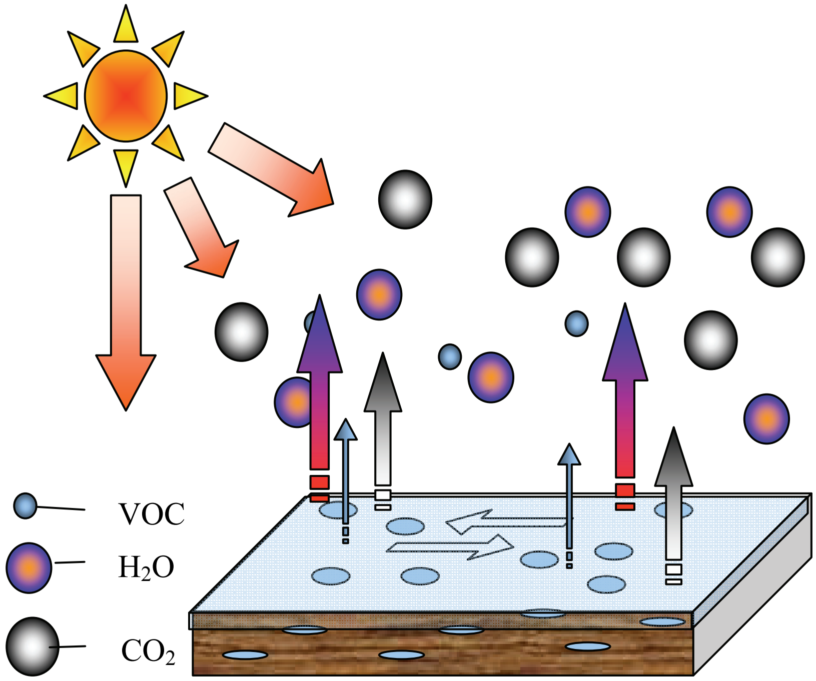


Figure 4.1 The PCO gel and the prevention of pollution (James, 2005).

In this research, the formulation of the previously developed PCO gel was changed. Due to the high cost and toxicity of fluorocarbon used as a visible light sensitizer in the previous PCO gel, Ag was doped into TiO_2 (developed by Lifeline Technologies, India), instead, to increase the visible light photoactivity and the microbiological resistance. H_2O_2 was also mixed in PCO gels to check the synergy between Ag doping and H_2O_2 on mold/mildew resistance. The Ag only sample was not developed, because the main purpose of this research is not to evaluate Ag as a biocide.

Furthermore, Eco-paint samples (also developed by Lifeline Technologies, India) added with TiO_2 or Ag-TiO_2 with or without H_2O_2 were also tested for mold/mildew resistance. Compared to the PCO gel, the paint with additives may be more practical for real application.

4.2. Materials and Preparation

The fungal species used in the experiment was still *Aspergillus niger*. The three kinds of tested gel samples were TiO_2 gel, Ag-TiO_2 gel & Ag-TiO_2/H_2O_2 gel, and the three kinds of tested paint samples were TiO_2 paint, Ag-TiO_2 paint & Ag-TiO_2/H_2O_2 paint. These samples were prepared in the following methods:

a) The TiO_2 gel was prepared by adding different amounts of TiO_2 (P25) powder in polyethylene glycol gel (PEG) water solution (the mixing ratio of PEG and H_2O is 1:2 weight ratio) under sonication. The average volume of the TiO_2 coating coated on the filter papers was 3.5 mg/cm^2.

b) The Ag-TiO_2 gel was prepared by adding different amounts of Ag-TiO_2 paste in polyethylene glycol gel (PEG) water solution (the mixing ratio of PEG and H_2O is 1:2 weight ratio) under sonication. The average volume of the Ag-TiO_2 coating coated on the filter papers was 4.5 mg/cm^2.

c) The Ag-TiO_2/H_2O_2 gel was prepared by vigorously mixing H_2O_2 (35%) with the Ag-TiO_2 gel at different ratios. The average volume of the Ag-TiO_2/H_2O_2 coating coated on the filter papers was 2.6 mg/cm^2.

d) The TiO_2 paint was prepared by adding TiO_2 (P25) powder into Eco-paints (with biocide or without biocide) at certain percentage and then vigorously mixed. The average volume of the TiO_2 paint coating coated on the filter papers was 9.6 mg/cm^2.

e) The Ag-TiO_2 paint was prepared by adding Ag-TiO_2 paste into Eco-paints (with biocide or without biocide) at certain percentage and then vigorously mixed. The average volume of the Ag-TiO_2 paint coating coated on the filter papers was 10.3 mg/cm^2.

f) The Ag-TiO_2/H_2O_2 paint was prepared by vigorously mixing H_2O_2 (35%) with Ag-TiO_2 paint at certain ratios. The average volume of the Ag-TiO_2/H_2O_2 paint coating coated on the filter papers was 6.1 mg/cm^2.

4.3. Experiment

The mold/mildew resistance experiment followed a similar procedure based on ASTM D5590-00 as the preliminary mold/mildew growth test. The paint samples were brushed on the filter papers instead of dipping the filter paper into the paint.

The mold growth experiment on the prepared coating samples, and paint samples were also conducted in three major conditions:

a) Without light,

b) With UV light irradiation,

c) With visible light irradiation.

The whole experiment was divided into two major stages. In the first stage, all different kinds of samples made by different materials and combinations were screened to find the best materials and combinations for mold/mildew resistance, respectively, in these three major conditions: without light, with UV light irradiation (at 365nm average 0.5 mw/cm^2), and with visible light irradiation (average 1500 lux). In the second stage, some factors, which can influence the mold/mildew resistance of the best samples such as the loading percentage of photocatalysts, the H_2O_2 mixing ratio, the light intensity, and the light exposure time, were analyzed on the best materials and combinations found in the first stage.

4.4. The First Stage Result and Discussion

4.4.1. The First Stage Specification

The same amount of TiO_2 and Ag-TiO_2 was, respectively, added into the PCO gels for TiO_2 gel and Ag-TiO_2 gel samples (1g TiO_2 or Ag-TiO_2 was added into 25g PEG and 50g water). For Ag-TiO_2/H_2O_2 gel samples, the volume ratio of Ag-TiO_2 gel to H_2O_2 was fixed at 3:2. In the paint samples, the same amount of TiO_2 and Ag-TiO_2 was, respectively, added into the Eco-paint for TiO_2 paint and Ag-TiO_2 paint samples (1g TiO_2 or Ag-TiO_2 was added into 100g Eco-paint). For Ag-TiO_2/H_2O_2 paint samples, the volume ratio of Ag-TiO_2 paint to H_2O_2 was fixed at 6:1, which is the minimum ratio that does not affect the appearance of the paint application. All of those prepared samples were subjected to the mold growth test without light, under UV light, and under visible light, respectively.

4.4.2. Paint Samples

The paint sample result will be first presented and discussed, because of its irregularity. All the paint samples made from the paint with biocide showed no mold growth for 28 days (the whole period of the mold growth experiment), no matter what kind of photocatalytic additives (TiO_2, Ag-TiO_2, or Ag-TiO_2/H_2O_2) were put into the paint samples. The biocide completely disguised the effect of the photocatalytic additives on mold/mildew resistance that was of most interest.

Furthermore, the result obtained from the paint samples without biocide appeared inconsistent with the repeated experiments. In the condition of no light or visible light, a few test agar plates with paint samples, with or without photocatalytic additives and regardless of additive types, showed the first sign of mold growth after 12 days; whereas, most of others showed the mold growth after 15 days. For example, in the first set of experiment under visible light irradiation, one of the agar plates with the TiO_2 paint first exhibited the sign of mold on the 13th day. Another agar plate with the Ag-TiO_2/H_2O_2 paint displayed the mold growth on the 14th day. Others gradually developed the mold growth after 15 days. However, in the second set of experiment under visible light irradiation, one of agar plates with the Ag-TiO_2 paint was the first one showing the mold growth on the 14th day. All of others developed the mold growth after 15 days. In those two sets of experiments with paint samples, no regulation or conclusion related to the photocatalytic additives could be obtained from the results, because the result did not depend on what photocatalytic additives were added in the paint. Even without any photocatalytic additives or biocides, the paint-only samples exhibited a long delay of mold growth. Here, the paint barrier effect for mold growth seemed to take the most credit for influencing the mold growth on the paint samples. The eco-paint does not contain much organic substance, resulting in an unfavorable habitat for mold growth (D'Orazio et al., 2009). The variation of the paint thicknesses on the filter papers was relatively small, but the application of the paint on the filter papers might not be completely homogeneous, leaving thin paint spots on the surface that might provide the very habitat for mold growth. As observed in the experiment, the mold growth on the paint samples always started with some spots on the surface of the plates. Generally, the paint samples without photocatalytic additives (the mold growth mostly started after 19 days) seemed to have a longer inhibition period than the paint samples with photocatalytic additives (the mold growth mostly started after 15 days) under visible light irradiation and without light. Similar result was found by Chen et al. (2009) when they used paint with TiO_2 coating under visible light or natural light for testing the mold growth on the paint. They observed more serious mold growth on the paint sample with TiO_2 coating than the paint-only samples. Chen et al. (2009) speculated that water adsorbed on the surface of TiO_2 due to its hydrophilicity would facilitate the mold growth if the photocatalyst cannot produce enough H_2O_2 and oxidative radicals to interfere with the mold growth process. Conservatively, the similar conclusion cannot be made from the result of our experiment for two reasons:

a) The substrate used in our experiment was Potato Dextrose Agar, which contains abundant water. Instead, Chen et al. (2009) used wood which is not comparable to the agar even soaked with water. So, the hydrophilicity of TiO_2 may not be so important in our experiment.

b) The paint barrier effect for mold growth could not be eliminated from the experiment. The mold inhibition period for the paint-only samples varied from sample to sample. It is hard to find the exact mold inhibition period attributed to the paint barrier effect. So, the different results between the paint samples with and without photocatalytic additives may be caused by the variance of paint barrier effect with different samples, not by the photocatalytic additives.

Under UV light irradiation, all the paint samples with TiO_2 (P25) showed no mold growth for 28 days. However, the result from other samples exhibited the similar irregularity as with visible light or without light. Some of them developed mold within 28 days; others did not show any mold sign for 28 days. In general, under UV light irradiation, the resistance of all the paint samples for mold growth seemed better than that under visible light irradiation or without light. It is not safe to make any conclusion due to the paint barrier effect. It is only recommended that TiO_2 (P25) may be the effective additive for the paint to resist mold/mildew growth under UV light irradiation.

The irregularity results from the paint samples indicate strong interfere from other factors than the photocatalytic additives such as the biocide, the paint barrier effect, and the heterogeneous application of paint samples on the filter papers. Therefore, the result obtained from the paint samples can not be used to examine the mold/mildew resistant effect of the photocatalytic additives, even though it is a practical way for the application of the photocatalysts with paint.

4.4.3. Gel Samples

Much more consistency and regularity was observed on the result of the gel samples. Some of the gel samples tested in the preliminary mold experiment were retested. The loading of the photocatalytic additives and the mixing ratio of H_2O_2 were kept consistent in those samples too (the TiO_2 gel prepared using 1 g TiO_2 was mixed with 35% H_2O_2 at 3:2 volume ratio of the TiO_2 gel to H_2O_2). The summary of the result is shown in Table

4.1. The repeated experiments had at most 1 or 2 days difference. The shortest time with the first sign of mold growth is chosen for conservativeness.

Table 4.1 The First Stage Mold Experiment Result for the Gel Samples

Gel Samples	Light Source	The Shortest Time with the First Sign of Mold Growth (Day)
Blank	without Light	2
H_2O_2		2
TiO_2		2
TiO_2/H_2O_2		5
Ag-TiO_2		5
Ag-TiO_2/H_2O_2		11
Blank	UV Light	2
H_2O_2		2
TiO_2		Complete Mold Inhibition
TiO_2/H_2O_2		Complete Mold Inhibition
Ag-TiO_2		3
Ag-TiO_2/H_2O_2		7
Blank	Visible Light	2
H_2O_2		2
TiO_2		2
TiO_2/H_2O_2		7
Ag-TiO_2		3
Ag-TiO_2/H_2O_2		9

4.4.3.1. Without Light

Without Light, the Ag-TiO_2 gel exhibited the similar mold resistance as the TiO_2/H_2O_2 gel. Ag ions were considered to be the cause of the delay of the mold growth, which could interfere with the metabolisms by combining with thiol groups (Morato et al., 2003). However, Ag ions in the Ag-TiO_2 gel were not enough to have complete prevention of mold growth; also, the main purpose of the research was not to use Ag as a biocide. When combining the Ag-TiO_2 with H_2O_2, the mold inhibition period was the longest (11 days) among all the gel samples in the condition of no light. Besides the individual mold resistant effects of Ag ions and the adsorbed H_2O_2, the Fenton-type reaction can take place between metal and H_2O_2 to produce OH* (Fujihira et al., 1981; Sclafani et al., 1992) which is a stronger oxidizer and more toxic to the fungal spores than H_2O_2 (Eq. 4.1).

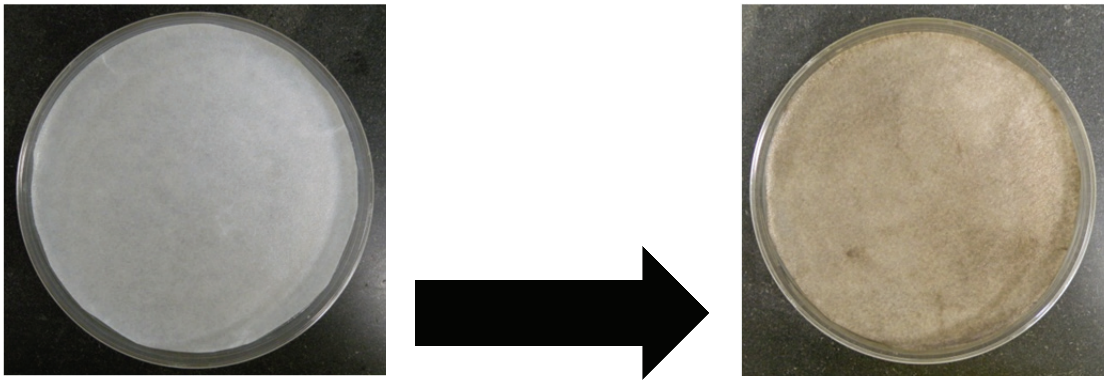
$$Ag + H_2O_2 + H+ \rightarrow Ag+ + OH^* + H_2O \qquad 4.1$$

Therefore, as the most effective sample without light, the Ag-TiO_2/H_2O_2 gel would be taken into the second stage of the mold experiment.

Some of the Ag-TiO_2/H_2O_2 gel samples without light were not inoculated with spores after 9 days of the mold experiment for checking whether the previously inoculated spores were killed or deactivated. No mold growth was observed for the following 19 days of the mold experiment, which confirmed the killing effect of the Ag-TiO_2/H_2O_2 gel on the mold spores, the same effect found in the preliminary mold experiment for TiO_2/H_2O_2 without light. The killing effect on the spores was also found in the Ag-TiO_2 gel.

4.4.3.2. UV Light

Under UV light irradiation, TiO_2 with or without H_2O_2 could completely prevent the mold growth for 28 days. It confirmed the result obtained from the preliminary mold experiment. Because of the continuous production of highly oxidative radicals, TiO_2 (P25) is very effective for the prevention of mold/mildew growth under UV light irradiation. However, Ag-TiO_2 did not show good photocatalytic activity under UV light irradiation. The decrease of the photocatalytic activity of the visible-light-driven photocatalysts was reported by Yates et al. (2006) and Balcerski et al. (2007). Even, the result of Ag-TiO_2 without light was better than that under UV light irradiation. The possible reason would be the chemical change of Ag-TiO_2 under UV light irradiation, leading to the reduction of the photocatalytic activity of Ag-TiO_2 and even worsening the discharge of Ag ions. The Ag-TiO_2/H_2O_2 gel showed the same deterioration under UV light irradiation compared to the result obtained from the condition of no light. The color of the samples with Ag-TiO_2 or Ag-TiO_2/H_2O_2 was changed from white (after preparation) to brown (after 2 days UV light irradiation), which indicates the instability of Ag-TiO_2 under UV light irradiation (Fig. 4.2). Therefore, TiO_2 (P25) would be taken into the second stage of the mold experiment under UV light irradiation, due to its high photocatalytic activity and superior stability under UV light irradiation.



(a) (b)

Figure 4.2 The color change of Ag-TiO_2 after UV light irradiation or visible light irradiation: (a) before light irradiation; (b) after light irradiation.

The Ag-TiO_2/H_2O_2 gel samples under UV light irradiation was placed into the dark after 5 days of the mold experiment for checking whether the previously inoculated spores were killed or deactivated. No mold growth was observed during the one-week dark test, confirming the killing effect of the Ag-TiO_2/H_2O_2 gel on the mold spores, the same effect found in the preliminary mold experiment for TiO_2 or TiO_2/H_2O_2. No dark test was performed on the Ag-TiO_2 gel samples due to the shortness of its mold inhibition period under UV light irradiation.

4.4.3.3. Visible Light

Under visible light irradiation, TiO_2 (P25) showed no photocatalytic activity as expected. Though the result of the Ag-TiO_2 gel (2 days mold inhibition period) was better than that of the TiO_2 gel and the result of the Ag-TiO_2/H_2O_2 gel (8 days) was better than that of the TiO_2/H_2O_2 gel (6 days), both the results of the Ag-TiO_2 and Ag-TiO_2/H_2O_2 gel under visible light irradiation were worse than that without light. Whereas, the TiO_2/H_2O_2 gel showed a better result under visible light irradiation than that without light. With the addition of H_2O_2, TiO_2 develops the photocatalytic activity under visible light irradiation, resulting in a longer mold inhibition period than that without light. However, both Ag-TiO_2 and Ag-TiO_2/H_2O_2 exhibited worse mold resistance under visible light irradiation than that without light. Visible light deteriorates the mold/mildew resistance of Ag-TiO_2, instead of activating it as the visible-light-driven photocatalyst as observed on the TiO_2/H_2O_2 gel. The same deterioration effect of Ag-TiO_2 found under UV light was also found under visible light with the same color change of Ag-TiO_2 from white to brown (Fig. 4.2). Even though the Ag-TiO_2/H_2O_2 gel was found to be the most effective sample under visible light irradiation with an 8-day mold inhibition period, the mold/mildew resistance of Ag-TiO_2/H_2O_2 was worsened under visible light irradiation by comparing the result of the Ag-TiO_2/H_2O_2 gel obtained in the condition of no light. The deterioration of Ag-TiO$_2$ under visible light irradiation is considered to be the major reason. Therefore, in the second stage of the mold experiment, no experiment would be performed on any samples under visible light irradiation. More stable visible-light-driven photocatalysts would be needed for future research.

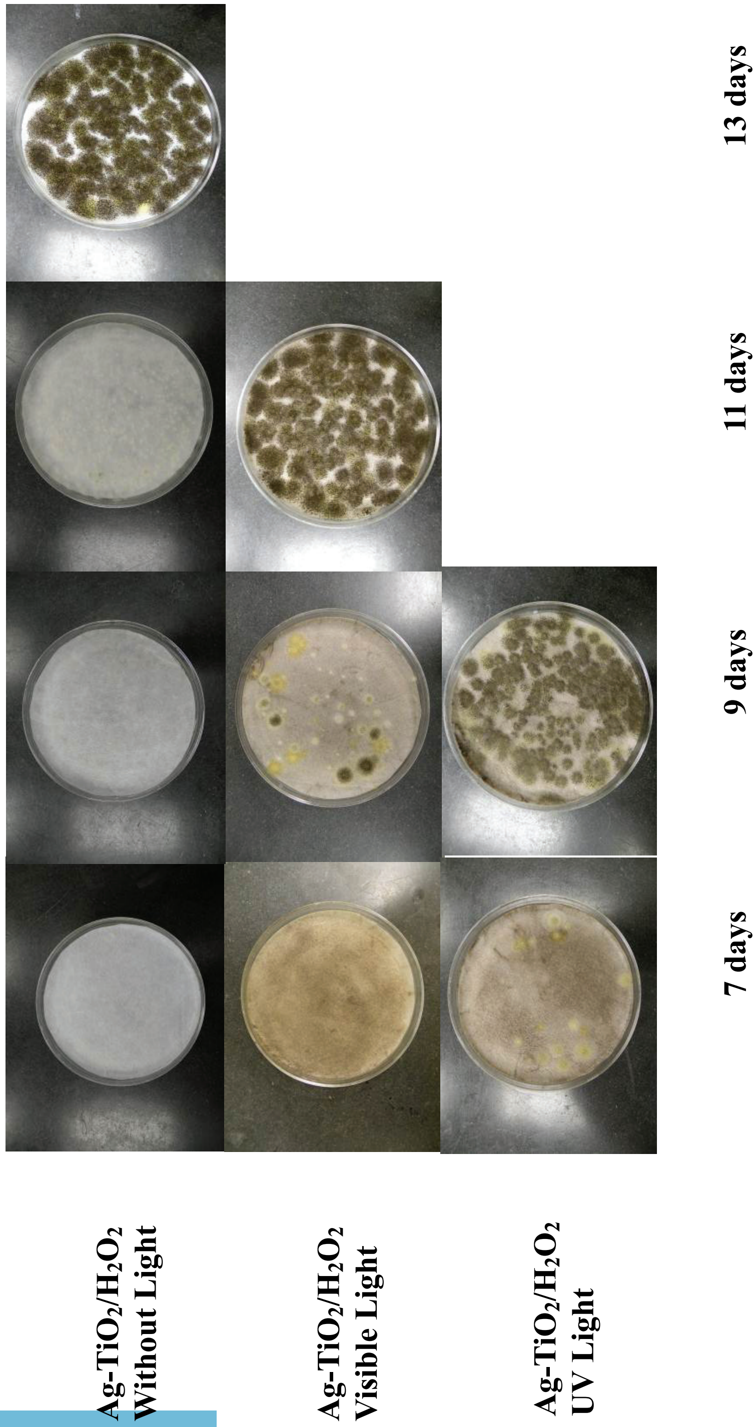


Figure 4.3 The picture result of mold growth test for the Ag-TiO$_2$/H$_2$O$_2$ gel at different incubation time

The Ag-TiO_2/H_2O_2 gel samples under visible light irradiation also underwent the one-week dark test after 7 days of the mold experiment. It was confirmed that the previously inoculated mold spores were killed by the Ag-TiO_2/H_2O_2 gel under visible light irradiation. No dark test was performed on the Ag-TiO_2 gel samples due to the shortness of its mold inhibition period under visible light irradiation.

4.5. The Second Stage Result and Discussion

4.5.1. The Second Stage Specification

The paint samples were not suitable for the research on the effect of the photocatalytic additives. So, no paint samples participated in the second stage. Even though the Ag-TiO_2/H_2O_2 gel showed the best mold/mildew resistance among all of the gel samples, the delay effect on the mold growth over the Ag-TiO_2/H_2O_2 gel was even worse under visible light irradiation than that without light. From the visible light experiment result, the visible light photo-activity of Ag-TiO_2 on mold/mildew resistance was deteriorated under visible light irradiation, which unqualified it for the second stage experiment. Therefore, no samples would be subjected to the factory analysis under visible light irradiation in the second stage. Due to the instability of the visible light photocatalyst (Ag-TiO_2) under visible light irradiation in the mold growth test condition, more stable Ag-TiO_2 or other visible-light-driven photocatalysts are needed in future mold/mildew resistance research. The second stage experiment was only performed in the condition of no light or UV light.

4.5.2. Without Light

4.5.2.1. Result

Without light, the Ag-TiO_2/H_2O_2 gel had the longest delay time for mold growth. Two factors were analyzed for Ag-TiO_2/H_2O_2 gels: the loading of Ag-TiO_2 in the gel and the ratio of H_2O_2 to the Ag-TiO_2 gel. The Ag/TiO_2 gel was prepared by adding 0.125g, 0.5g, 1g, and 2g Ag-TiO_2, respectively into 25g PEG and 50g water. Then, the prepared Ag/TiO_2 gel was mixed with 35% H_2O_2 at different volume ratios of H_2O_2 to the Ag-TiO_2 gel: 1:12, 1:3, 2:3, and 1:1. The total 16 kinds of Ag-TiO_2/H_2O_2 gels were developed. The first sign of mold growth on those samples was recorded. The mold growth test result without light is shown in Table 4.2.

Table 4.2 The Mold Growth Result on Ag-TiO_2/H_2O_2 without Light

The Weight of Ag-TiO_2 Added in the PCO Gel (g)	The Ratio of H_2O_2 to Ag-TiO_2 Gel in the PCO Gel (Volume Ratio)	Average Time with the First Sign of Mold Growth (days)
0.125	1:12	4
	1:3	4
	2:3	3
	1:1	2.3
0.5	1:12	5.7
	1:3	6
	2:3	5.3
	1:1	4
1	1:12	7.7
	1:3	9.7
	2:3	10.3
	1:1	9.7
2	1:12	11.7
	1:3	11.3
	2:3	13
	1:1	13.3

Combining this result with the result of only Ag-TiO_2 and only H_2O_2, the significance was obtained for Ag-TiO_2, H_2O_2 and interaction between them from a two-way ANOVA test (Table 4.3).

Table 4.3 Two-Way ANOVA Test on the Mold Growth Result without Light

Source	df	SS	MS	F	Significance (P=0.05)
TiO_2	4	833.2533333	208.3133333	679.2826087	6.3882
H_2O_2	4	109.7866667	27.44666667	89.5	
Interaction	16	111.0133333	6.938333333	22.625	
Within Error	50	15.33333333	0.306666667		
Total Error	74	1069.386667			

4.5.2.2. The Effect of Ag-TiO_2

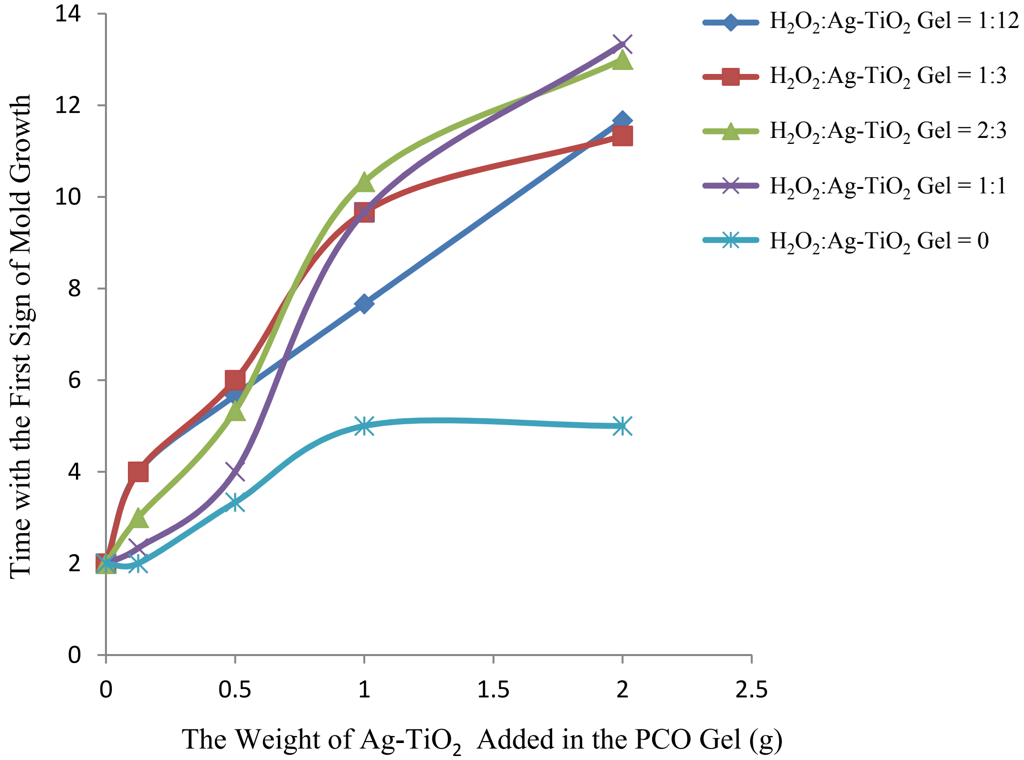


Figure 4.4 The effect of Ag-TiO_2 in the Ag-TiO_2/H_2O_2 gel sample on mold/mildew resistance without light.

From the ANOVA test, Ag-TiO_2 is the most important influencing factors for the Ag-TiO_2/H_2O_2 gel. With the increase of the amount of Ag-TiO_2 added in the preparation process, the mold/mildew resistance of Ag-TiO_2/H_2O_2 enhanced dramatically, no matter at what H_2O_2 level (Fig. 4.4). More Ag-TiO_2 generally means more Ag ions present, which act as biocide for resisting mold growth. Furthermore, with the addition of H_2O_2, more Ag-TiO_2 means more H_2O_2 adsorption on the surface of Ag-TiO_2, which can be preserved after the drying period of the filter papers and is effective to prevent the sporulation. In all the tested Ag-TiO_2/H_2O_2 gels, the delay effect of mold growth rose approximately linearly with the increase of Ag-TiO_2 at any tested levels of H_2O_2. However, without H_2O_2, the delay effect of mold growth on Ag-TiO_2 alone quickly reached the stable with the increase of Ag-TiO_2 addition to the gel. Also, the relatively low delay effect was observed with the Ag-TiO_2 only gels compared to the Ag-TiO_2/H_2O_2 gels. No addition of H_2O_2 would greatly reduce the mold/mildew resistance. In general, the promotion effect on Ag-TiO_2 from H_2O_2 was confirmed from the logistical increase to the linear increase of the mold/mildew resistance with the increase of Ag-TiO_2. This promotion effect can be attributed from the antifungal property of H_2O_2 itself and the Fenton-type reaction between Ag and H_2O_2. Expectedly, the mold/mildew resistance of Ag-TiO_2/H_2O_2 gels will intensify with the further increase of Ag-TiO_2 in the gel. Then, it will either reach the constant because of the saturation of the promotion effect or drop because of the relative lack of H_2O_2. Besides, the PEG used in the preparation of the gel samples has its maximum holding capability for Ag-TiO_2. 2 g Ag-TiO_2 seemed to nearly reach the maximum holding capability of the PEG with a small amount of precipitation. The improvement of the preparation method for the gel samples would be needed to further increase the mold/mildew resistance of the Ag-TiO_2/H_2O_2 gels.

4.5.2.3. The Effect of H_2O_2

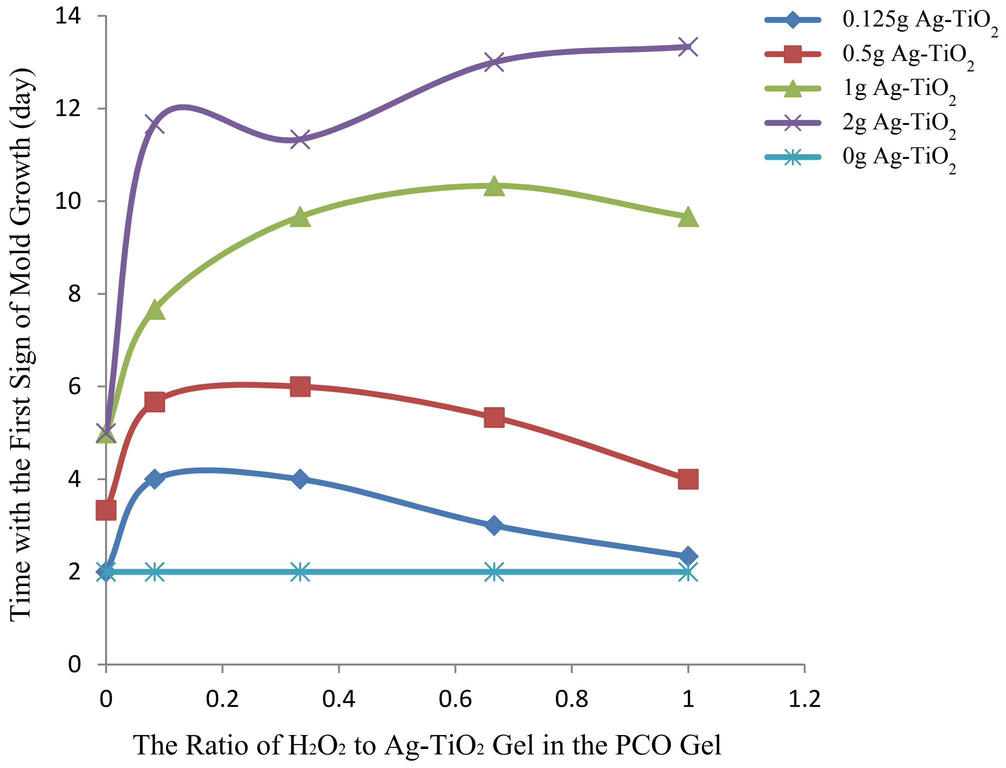


Figure 4.5 The effect of H_2O_2 and the interaction between Ag-TiO_2 & H_2O_2 in the Ag-TiO_2/H_2O_2 gel sample on mold/mildew resistance without light.

H_2O_2 has less effect on mold/mildew resistance than Ag-TiO_2 in the Ag-TiO_2/H_2O_2 gel. A large difference of the mold/mildew resistance is observed between the different levels of Ag-TiO_2, illustrated in Fig. 4.5. Within the same level of Ag-TiO_2, the influence of H_2O_2 on the mold/mildew resistance of the Ag-TiO_2/H_2O_2 gel is relatively small compared to the big difference found with Ag-TiO_2. H_2O_2, itself, can kill fungal spores, which easily results in an incorrect expectation that the more H_2O_2, the higher mold/mildew resistance of the Ag-TiO_2/H_2O_2 gel in our case. If the antifungal effect of Ag ions is excluded, the mold/mildew resistance of the Ag-TiO_2/H_2O_2 gel mainly depends on the adsorbed H_2O_2, which can be preserved through the drying period of filter papers (most of unadsorbed H_2O_2 evaporated during the drying period). The evaporation of H_2O_2 is largely restricted by Ag-TiO_2 in the Ag-TiO_2/H_2O_2 gel. Therefore, Ag-TiO_2 not only directly contributes to the mold/mildew resistance by Ag ions, but also affects the performance of H_2O_2. That's why H_2O_2 showed relatively small influence than Ag-TiO_2 in the mold/mildew resistance of the Ag-TiO_2/H_2O_2 gel.

Comparing the result of Ag-TiO_2 only gels and the result of Ag-TiO_2/H_2O_2 gels with 1:12 of H_2O_2 to the Ag-TiO_2 gel, the enhance of the delay effect on mold growth was observed by adding H_2O_2 to the Ag-TiO_2 gel. However, H_2O_2 does not always have a positive effect on mold/mildew resistance in the Ag-TiO_2/H_2O_2 gels. Excluding the promotion effect by adding H_2O_2, at the low levels of Ag-TiO_2 (0.125 g and 0.5 g), more H_2O_2 resulted in the decrease of the delay effect on mold growth over the Ag-TiO_2/H_2O_2 gels; whereas, at the high level of Ag-TiO_2 (1 g and 2 g), more H_2O_2 led to a small increase of the delay effect on mold growth over the Ag-TiO_2/H_2O_2 gels. The mold/mildew resistance of Ag-TiO_2 gels depends on the amount of Ag-TiO_2, the amount of H_2O_2 left after the drying process of the filter papers and the optimal mixing ratio between them. When the amount of Ag-TiO_2 is relatively small in the gel, more H_2O_2 means a dilution of Ag-TiO_2 in the final Ag-TiO_2/H_2O_2 gels; in the meantime, H_2O_2 adsorbed on the surface of Ag-TiO_2, which can survive during the drying process, also declines with the decrease of Ag-TiO_2. Most of H_2O_2 evaporates after the drying period of the filter papers, resulting in the low mold/mildew resistance of Ag-TiO_2/H_2O_2 gel samples. The extreme example of this dilution effect was the H_2O_2 only sample in which no mold/mildew resistance was found. However, not like at the low level of Ag-TiO_2 in which the dilution effect from H_2O_2 dominates, at the high level of Ag-TiO_2, more H_2O_2 means more promotion effect on the Ag-TiO_2/H_2O_2 gels. Instead, less H_2O_2 does not provide enough promotion effect on mold/mildew resistance. A small increase of the delay effect on mold growth over Ag-TiO_2/H_2O_2 gels was found with the volume ratio of H_2O_2 to the Ag-TiO_2 gel from 1:12 to 1:1 at the levels of 1 g and 2 g Ag-TiO_2. It is estimated that with more H_2O_2 added, the mold/mildew resistance of Ag-TiO_2/H_2O_2 gels would decline eventually when the dilution effect regains the control. In fact, a slight drop of the mold/mildew resistance from 2:3 to 1:1 volume ratio of H_2O_2 to the Ag-TiO_2 gel, though not significant, was observed on the Ag-TiO_2/H_2O_2 gels with 1 g Ag-TiO_2 added. Also, the Ag-TiO_2/H_2O_2 gels with 2 g Ag-TiO_2 almost reached the constant for the delay effect on mold growth, because there was a very small difference of the delay effect on mold growth for the gels with 2:3 and 1:1 volume ratio of H_2O_2 to the Ag-TiO_2 gel.

4.5.2.4. The Recommended Gel Sample without Light

Among all kinds of PCO gels tested in the first stage of the mold experiment, the Ag-TiO_2/H_2O_2 gel was the most effective sample for delaying the mold growth without light. Among all kinds of the combination of Ag-TiO_2 and H_2O_2 in the Ag-TiO_2/H_2O_2 gels, the Ag-TiO_2/H_2O_2 gel with 2 g Ag-TiO_2 and 2:3 or 1:1 volume ratio of H_2O_2 to the Ag-TiO_2 gel had the longest delay time for mold growth. Due to the very slight difference (no significance found between those two samples) of the 2:3 and 1:1 samples and the optimum ratio-2:3 found in the previous study on the reduction of VOC emission from the building materials, the Ag-TiO_2/H_2O_2 gel with 2 g Ag-TiO_2 and 2:3 volume ratio of H_2O_2 to the Ag-TiO_2 gel is recommended to be the ideal gel sample for resisting mold/mildew growth without light in the scope of this research.

4.5.3. UV Light

4.5.3.1. Result

Under UV light irradiation, TiO_2 gels can completely prevent mold growth for 28 days with 0.5 mW/cm^2 light intensity and 24 hours exposure time per day in the first stage experiment. The three influencing factors were analyzed for the TiO_2 gel samples: the loading of TiO_2 in the gel (Li et al., 2008e), the light intensity (Benabbou et al., 2007), and the exposure time (Rincon and Pulgarin, 2003). The TiO_2 gels were prepared by adding 0.125g, 0.5g, 1g, and 2g TiO_2, respectively into 25g PEG and 50g water. Then, the prepared TiO_2 gels were subjected to UV light irradiation at 0.3, 0.4, 0.5, and 0.6 mW/cm^2 light intensity and 4 hours, 8 hours, 12 hours and 24 hours exposure time per day. The total 64 kinds of tests on the TiO_2 gels were developed. The TiO_2 gel was found to completely prevent the mold growth for the whole period of the experiment under UV light irradiation in the first stage of the mold experiment. Thus, the complete inhibition of mold growth on the TiO_2 gels under UV light irradiation was still the objective, and the mold growth test result showed mold growth or no mold growth. The mold growth test result under UV light irradiation is shown in Table 4.4.

Table 4.4 The Mold Growth Result on TiO_2 (P25) Gel under UV Light Irradiation

TiO_2 (g)	UV Intensity (mW/cm^2)	UV Exposure Time (h/day)	Mold Growth
0.125	0.3, 0.4, 0.5, 0.6	4, 8, 12, 24	*
0.5	0.3	4, 8, 12, 24	*
	0.4	4	*
		8	*
		12	*
		24	
	0.5	4	*
		8	*
		12	
		24	
	0.6	4	*
		8	*
		12	
		24	
1	0.3	4, 8, 12, 24	*
	0.4	4	*
		8	*
		12	*
		24	
	0.5	4	*
		8	
		12	
		24	
	0.6	4	*
		8	
		12	
		24	
2	0.3	4, 8, 12, 24	*
	0.4	4	*
		8	*
		12	*
		24	
	0.5	4	*
		8	
		12	
		24	
	0.6	4	*
		8	
		12	
		24	

*Showing mold growth

4.5.3.2. The TiO_2 Loading in the TiO_2 Gel

In the scope of this experiment, all the TiO_2 gels with 0.125 g loading of TiO_2 showed mold growth, no matter at what light intensity and light exposure time. The concentration of the H_2O_2 and oxidative radicals (Rincon and Pulgarin, 2003; Cho et al., 2004) generated by the photocatalysis of TiO_2 under UV light irradiation is directly related to the mold/mildew resistance of the TiO_2 gel. Insufficient H_2O_2 and oxidative radicals, toxic to the fungal spores, were produced due to the low loading of TiO_2 in the TiO_2 gel (with the loading of 0.125 g TiO_2). With the increase of TiO_2 loading (Li et al., 2008e) in the TiO_2 gels, the TiO_2 gels started to show mold growth inhibition in some experiment condition. More TiO_2 in the TiO_2 gel generally means more active sites on the surfaces to absorbe more UV light and to produce more contacts between the substrates & TiO_2, leading to the enhancement of photocatalytic activity. With the loading of 0.5 g TiO_2, the TiO_2 gel was able to generate a sufficient concentration of H_2O_2 and oxidative radicals by photocatalysis when other conditions were also satisfied such as sufficient UV light intensity and exposure time. From the Fig. 4.6, the TiO_2 gels with 1 g or 2 g TiO_2 loading has larger “no mold” area than that with 0.5 TiO_2 loading, which means that the TiO_2 gels with 1 g or 2 g TiO_2 loading can prevent the mold growth in more unfavorable condition than that with 0.5 TiO_2 loading. The increase of TiO_2 loading benefits the mold/mildew resistance of the TiO_2 gel. No difference was observed between 1 g and 2 g TiO_2 loading. The effect of TiO_2 loading on the mold/mildew resistance of the TiO_2 gel reached the constant. The excessive loading of TiO_2, more than 1 g, does not gain any credit for the inhibition of mold growth in the scope of this experiment. The excessive TiO_2 overlaping in the TiO_2 gel exhibits no improvement in the active sites on the surface.

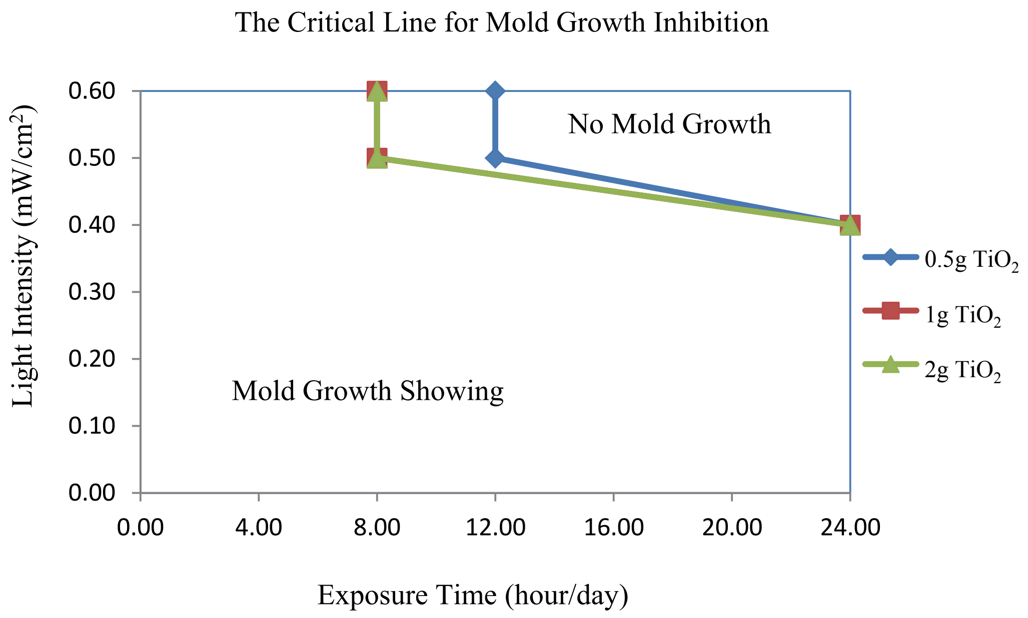


Figure 4.6 The critical line for mold growth influenced by TiO_2 added in TiO_2 gels.

4.5.3.3. The UV Light Intensity

All the TiO_2 gels under 0.3 mW/cm^2 UV light irradiation showed mold growth, regardless of what loading of TiO_2 and light exposure time. The low UV light intensity can not fully activate TiO_2 for resisting mold growth. The energy for the photocatalysis is originated from the photons. Low intensity of UV light results in the low energy input for the photocatalytic reaction. So, not all the active sites on the surface of TiO_2 are excited. The photoproduced electron-holes pairs are not sufficient to maintain a high concentration of H_2O_2 and oxidative radicals for mold/mildew resistance. Higher UV light intensity (Benabbou et al., 2007) than 0.3 mW/cm^2 is required to activate the mold/mildew resistance of the TiO_2 gel by producing more H_2O_2 and oxidative radicals. The critical UV light intensity found in this research was 0.4 mW/cm^2 for the TiO_2 gel, at which UV light intensity the TiO_2 gel with 0.5 g, 1 g, and 2 g TiO_2 loading could completely inhibit the mold growth with 24 hours per day UV light exposure. The higher UV light (0.5 and 0.6 mW/cm^2) intensity also possesses the larger "no mold" area, illustrated in Fig. 4.7. UV light at 0.5 and 0.6 mW/cm^2 was more favorable to the photocatalysis of the TiO_2 gel. No difference was observed between 0.5 and 0.6 mW/cm^2 UV light intensity for resisting mold growth, which implies that 0.5 mW/cm^2 UV light intensity achieves the maximum effect on mold/mildew resistance. Further increase of UV light intensity would have no benefit on mold/mildew resistance, only leading to an energy waste by the lighting. With certain UV light intensity, all the active sites on the surface of TiO_2 are fully excited and adsorbed with highly oxidative radicals, achieving the highest photocatalytic efficiency. Extra UV light photons will not be absorbed by TiO_2, except that extra active sites are introduced.

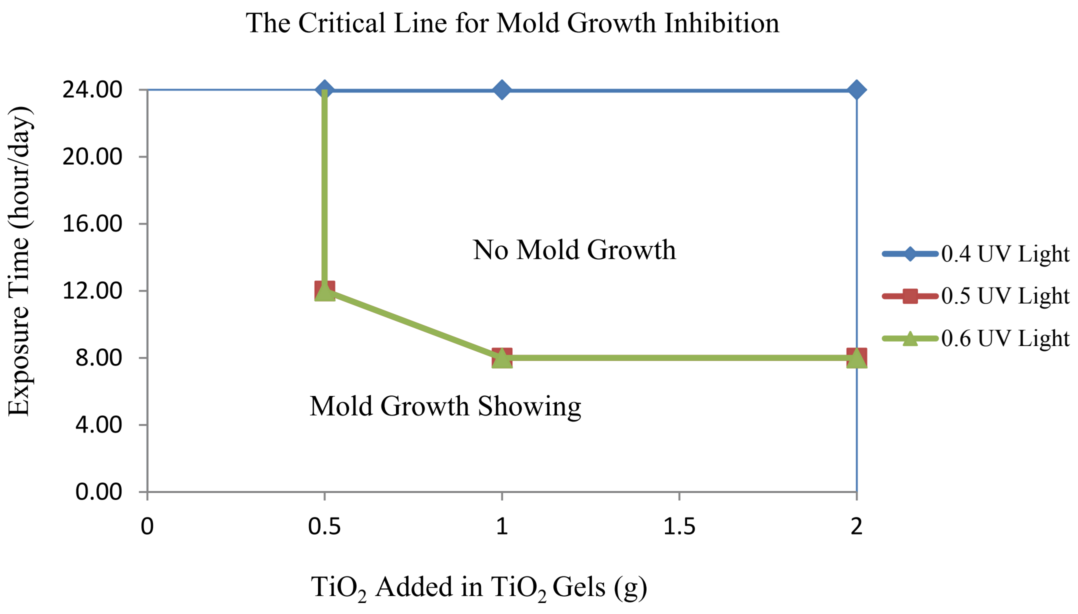


Figure 4.7 The critical line for mold growth influenced by UV light intensity.

4.5.3.4. The UV Light Exposure Time

All the TiO_2 gels with 4 hours per day UV light exposure time showed mold growth, no matter with what loading of TiO_2 and UV light intensity. Even though the TiO_2 gel can be fully activated and is able to generate a sufficient concentration of H_2O_2 and oxidative radicals for resisting mold growth, the sufficient H_2O_2 and oxidative radicals would not last long enough to kill the mold spores. The concentration of H_2O_2 and oxidative radicals decreases when the UV light is turned off. Longer UV light exposure time (Rincon and Pulgarin, 2003) definitely benefits on the mold/mildew resistance of the TiO_2 gel, corresponding with the larger “no mold” area illustrated in Fig. 4.8. In this research, 8 hours per day was the minimum UV light exposure time enough for some TiO_2 gel samples to completely prevent mold growth. Different concentrations of H_2O_2 and oxidative radicals were generated by different combination of the TiO_2 gel samples and UV light intensity, judged from the result. For instance, the TiO_2 gel with 1 g TiO_2 loading at 0.4 mW/cm^2 UV light intensity demanded 24 hours per day UV light exposure time to completely prevent mold growth; whereas, under 0.5 mW/cm^2 UV light irradiation, 8 hours per day were only required on the same TiO_2 gel. The high concentration of H_2O_2 and oxidative radicals created by the TiO_2 gel with 1 g TiO_2 loading under 0.5 mW/cm^2 UV light irradiation can kill the mold spores after 8 hours. The H_2O_2 and oxidative radicals would diminish without UV light. However, it can still maintain a certain level, when dropping from the high concentration, keeping certain mold/mildew resistance. Also, the rest of the day is not enough for the development of mold. Then, the high concentration of H_2O_2 and oxidative radicals will be resumed by UV light irradiation on the next day. The continuous UV light exposure for 24 hours per day would be favorable for mold/mildew inhibition, which, however, may not be practical or economical. 8 hours exposure time per day may be more practical for the real application of the TiO_2 gel in the indoor environment. When there is no resident in the building, UV light can be turned on for mold/mildew growth inhibition on the TiO_2 gel.

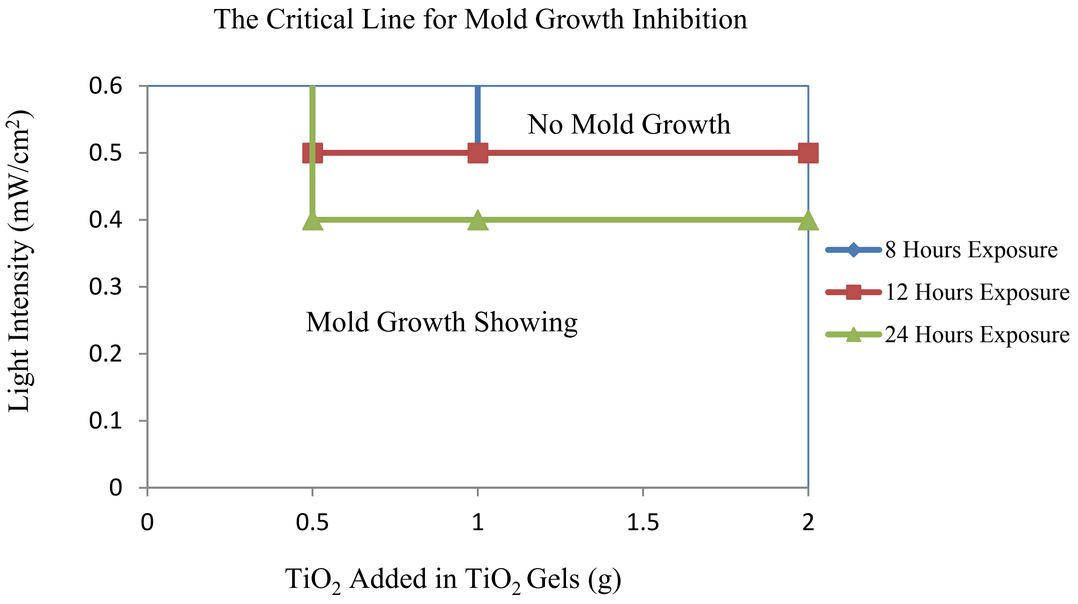


Figure 4.8 The critical line for mold growth influenced by UV light exposure time.

4.5.3.5. The Recommended Gel Sample and UV Light Condition

Among all the combinations of the TiO_2 gels, UV light intensities and exposure time which can completely inhibit mold growth, 0.4 mW/cm^2 UV light intensity seems a little weak, for all the TiO_2 gels working at this UV light intensity needs 24 hours UV light exposure per day. Furthermore, 0.6 mW/cm^2 UV light intensity does not improve the mold/mildew resistance of the TiO_2 gel from 0.5 mW/cm^2 UV light intensity and consumes extra lighting energy. 0.5 mW/cm^2 UV light intensity would be chosen for the application of the TiO_2 gel. Under 0.5 mW/cm^2 UV light irradiation, 2 g TiO_2 loading does not increase the mold/mildew resistance of the TiO_2 gel compared to 1 g TiO_2 loading; meanwhile, 0.5 g TiO_2 loading requires at least 12 hour UV light exposure per day for mold growth inhibition, which is less practical than 8 hours exposure per day demanded by 1 g TiO_2 loading. Therefore, the TiO_2 gel with 1 g TiO_2 loading is recommended for the complete prevention of mold growth, operating under 0.5 mW/cm^2 UV light irradiation with at least 8 hours UV light exposure per day.

4.6. Conclusion

To find and optimize the most effective PCO gel for resisting mold/mildew, the mold experiment was divided into two stages.

First, the mold growth tests were conducted on all kinds of PCO gel and paint samples in three major conditions: without light, under UV light irradiation, and under visible light irradiation. The result of paint samples appeared to be irregular because of the interfering factors, which is not suitable for the study of the photocatalytic effect on mold/mildew resistance. Further investigation should be performed on the paint samples, since it is thought to be a practical way in real application. The TiO_2 gel could completely prevent mold growth for the whole period of the experiment-28 days under UV light irradiation. The Ag-TiO_2/H_2O_2 gel was found with the longest delay period of mold growth without light or with visible light. However, visible light worsened the mold/mildew resistance of the Ag-TiO_2/H_2O_2 gel due to the deterioration of Ag-TiO_2 under light irradiation. In the experiment of the Ag-TiO_2/H_2O_2 gel, the shorter mold growth inhibition period was observed under visible light than that without light. Thus, there was no PCO gel entering the second optimization stage under visible light irradiation, even though the Ag-TiO_2/H_2O_2 gel was found to be the most effective under visible light irradiation for resisting mold/mildew (even better than the TiO_2/H_2O_2 gel).

Second, the TiO_2 gel and the Ag-TiO_2/H_2O_2 gel were optimized under UV light irradiation and without light, respectively. The factors considered in the TiO_2 gel included the loading of TiO_2, UV light intensity and UV light exposure time. The loading of Ag-TiO_2 and the addition of 35% H_2O_2 were analyzed for the Ag-TiO_2/H_2O_2 gel without light. The influence of temperature and humidity to mold/mildew was eliminated by offering the most mold-favored temperature and humidity. The optimum components in the gel and the optimum operating conditions (light condition) are summarized in Table 4.5.

The TiO_2 gel is able to completely inhibit mold growth under UV light irradiation even in the most favorable temperature and humidity for mold growth. The low UV light intensity-0.5 mW/cm^2 (lower than regular sunlight 1 or 2 mW/cm^2) with 8 hours per day exposure time is needed for the complete prevention of mold growth. 365 nm UV light instead of 264 nm (affecting DNA in the cell) was used for the TiO_2 gel at low light intensity, which reduces the biohazard for human health. So, the TiO_2 gel would have a potential to be used in the indoor environment for preventing mold growth in warm, humid climates. When the TiO_2 gel is coated on the indoor surfaces, the UV light bulb can be installed and turned on for the total 8 hours per day if there are no people in the room such as during the night of office buildings, during the day of residential buildings, and anytime of non-occupancy.

Table 4.5 The PCO Gels with Optimized Components and Operating Condition

PCO Gel	Optimized Components	Optimized Operating Conditions	The First Sign of Mold Growth
TiO_2 Gel	1 g TiO_2 (P25) added into the solution of 25 g PEG and 50 g water	0.5 mW/cm^2 UV light irradiation 8 hours UV light exposure per day	No Mold Growth
Ag-TiO_2/H_2O_2 Gel	2 g Ag-TiO_2 added into the solution of 25 g PEG and 50 g water for Ag-TiO_2 gel; 35% H_2O_2 mixed with Ag-TiO_2 gel at 2:3 volume ratio of H_2O_2 to Ag-TiO_2 gel	Without Light	13 days

The Ag-TiO_2/H_2O_2 gel in this mold experiment had longer mold inhibition time than the TiO_2/H_2O_2 gel found in the preliminary experiment without light or under visible light. Thus, the Ag-TiO_2/H_2O_2 gel may be a better choice for resisting mold/mildew. The Ag-TiO_2/H_2O_2 gel is also a promising solution for resisting mold growth during some emergency situations such as a power failure, flood or hurricane. The longer mold inhibition time will give people more time to clean and dry out their houses and belongings without mold growth. The periodic spraying 35% H_2O_2 on the Ag-TiO_2/H_2O_2 every 12 days may sustain the mold/mildew resistance property. H_2O_2 in the Ag-TiO_2/H_2O_2 gel still needs to be stabilized, or more stable substitute for H_2O_2 can be found.

The deterioration of Ag-TiO_2 under light irradiation leads to the short-term mold/mildew resistance. More stable Ag-TiO_2 or other visible-light-driven photocatalysts are demanded for future research under visible light irradiation. It is worth investigating the solution of the deterioration under visible light irradiation for long-term mold/mildew resistance of visible-light-driven photocatalysts since visible light is more practical than UV light in the indoor environment.

Chapter 5

VOC TEST ON PCO GEL COATED BUILDING MATERIALS

5.1. Background

UV or visible light, themselves, can not destroy VOCs. However, when they work with photocatalysts, the PCO reaction can reduce VOCs in the indoor air. The two kinds of PCO gels, TiO_2 gel with 1 g TiO_2 loading and $AgTiO_2/H_2O_2$ gel with 2 g Ag-TiO_2 loading & 35% H_2O_2 added at 2:3 volume ratio of H_2O_2 to Ag-TiO_2 gel, obtained from the mold growth experiment are most effective for resisting mold/mildew growth, respectively, under UV light and without light. The followed-up VOC emission experiment was performed to examine the reduction efficiency of VOC emission on those PCO gel coated building materials.

The building materials chosen for this study were pressure treated wood and oil-based paint, representing dry material and wet material, respectively. The pressure treated wood is widely used in residential, commercial and industrial building structures. It is treated by chemical preservatives to be protected from decay, fungi, insects and marine borers; however, the treating process will contribute to more VOC emission from the pressure treated wood than that from untreated wood. Oil-based paint is also commonly used in building construction and found to emit high rates and large concentrations of VOCs, even much more than pressure treated wood.

5.2. Experiment

The PCO gel was coated on the surface of pressure treated wood or oil-based paint as a coating material. The PCO gel coated building materials were subjected to VOC emission test under UV light or visible light irradiation. The results were then compared with the blank raw materials.

For "dry" material samples, 1.5 inches thick pressure treated wood was cut into 5.5×4 inches. For "wet" material samples, 0.75 inches thick red oak with very low VOC emission was cut into 3.5×4 inches and used as a substrate for oil-based paint. 3±0.5 g paint was coated on the surface of red oak at the beginning of the test (average 33.2 mg/cm^2). The whole VOC emission experiment can be divided into the following tests:

a) Pressure treated wood without any treatment and oil-based paint without any treatment.
b) Pressure treated wood and oil-based paint with the TiO_2 gel under UV light and visible light irradiation, respectively.
c) Pressure treated wood and oil-based paint with the Ag-TiO_2/H_2O_2 gel under UV light and visible light irradiation, respectively.

VOC emission experiment was mainly based on ASTM D 5116-06 Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products. The procedure of VOC emission experiment will be briefly addressed. More detailed procedure can be found in James (2005).

The small-scale chamber experiment system was set up as illustrated in Fig. 5.1. The chamber was ventilated with clean and conditioned air. The air conditioning process included particle removal, VOC oxidization, and temperature & humidity control. The ventilation rate was adjusted as 1 ACH (air change per hour). Data monitoring and analysis equipment (Campbell R23 datalogger) was also attached to the small chambers for temperature and humidity monitoring.

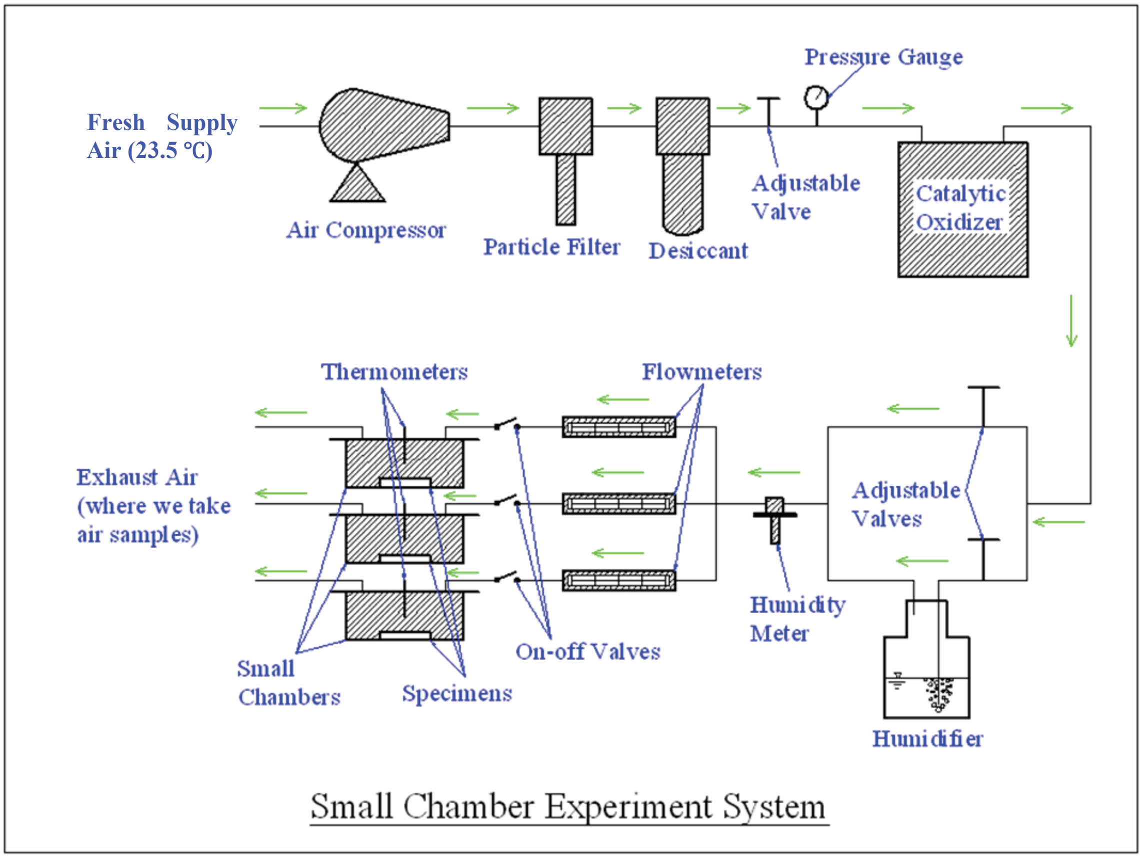


Figure 5.1 The small chamber experiment system.

Before each small chamber test, the chamber needed to be cleaned with laboratory detergent and deionized water. Then, the chamber was flushed with conditioned air to obtain the required and stabilized environment inside the chamber. The temperature and humidity were 23±0.5 ℃ and 50±5%, respectively. The chamber background VOC concentration was measured, ensuring it less than 0.02 mg/m^3 (Zhu et al., 1999) before the real test. The maximum background concentrations detected in both pressure treated wood and oil-based paint are illustrated in Fig. 5.2.

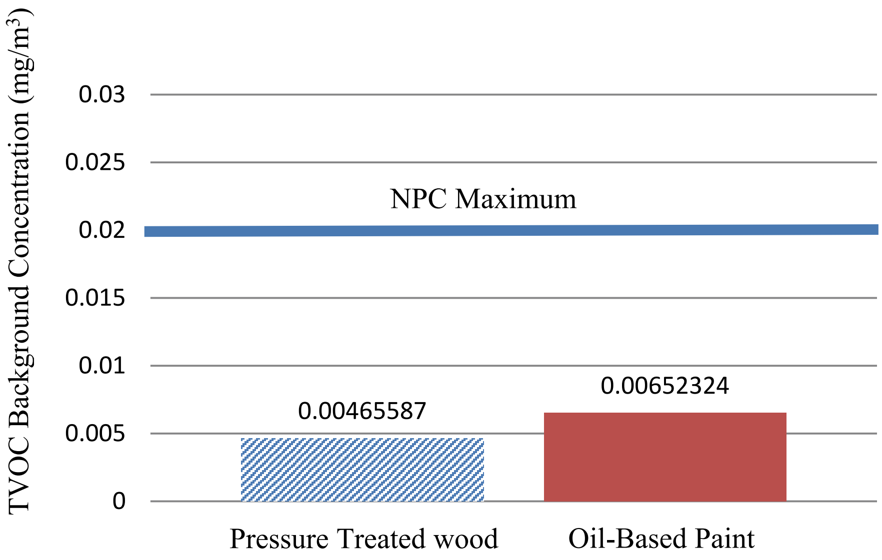


Figure 5.2 The chamber background VOC concentration

At the beginning of each test, the fresh material with or without the PCO gel coating were placed into a specimen holder and then put into the chamber. 5±0.5 g PCO gel, either TiO_2 gel or $AgTiO_2/H_2O_2$ gel, was coated on pressure treated wood (average 34.5 mg/cm^2), and 1±0.2 g was coated over oil-based paint (average 11.1 mg/cm^2). The chamber was set up as seen in Fig. 5.3. During the test under UV light or visible light irradiation, an 8W black-light lamp or an 8W florescent lamp was hung over the material, respectively. Both of them were kept at the same distance from the materials, and light intensity of UV light and visible light was measured to ensure the consistency. The UV light intensity was average 0.5 mW/cm^2 at 365 nm peak wavelength, and the visible light intensity was average 1500 lux. The air samples were taken at the air exhaust of the chamber, assuming air inside the chamber was completely mixed and the VOC concentration in the exhaust air represented the VOC concentration inside the chamber. Generally, the VOC concentration for the wet materials is much higher than the dry materials and the wet materials have their faster decaying emission rate of VOC concentration than that of the dry materials. The experiment for dry material lasted for 5 days; whereas the experiment for wet material lasted for 4 days. The air samples were taken at certain time intervals during the whole period of the experiment. The dry materials were treated differently to the wet materials in the sampling process. The dry material air samples were taken at the following intervals; t= 0.25h, 0.5h, 1h, 1.5h, 2h, 3h, 4h, 5h, 6h, 7h, 8h, 9h, 10h, 12h, 16h, 20h, 24h, 28h, 36h, 48h, 72h, 96h and 120h. For the wet materials, the air samples were taken at t= 0.1 h, 0.3 h, 0.6 h, 1h, 1.5h, 2 h, 2.5h 3 h, 3.5h, 4 h, 5h, 6h, 7h, 8h, 10h, 12h, 24h, 4h, 72h and 96 h. With the sampling flow rate of 200 mL/min, for the dry materials, the volume of air samples taken were 3 min within 1 hour, 5 min from 1 to 12 hours, 10 min from 12 to 24 hours, and 15 min after 1 day; whereas, for the wet materials, the volume of air samples taken were 2 min within 8 hours, 5 min from 8 to 12 hours, 15 min from 12 to 48 hours, and 30 min from 48 to 96 hours.

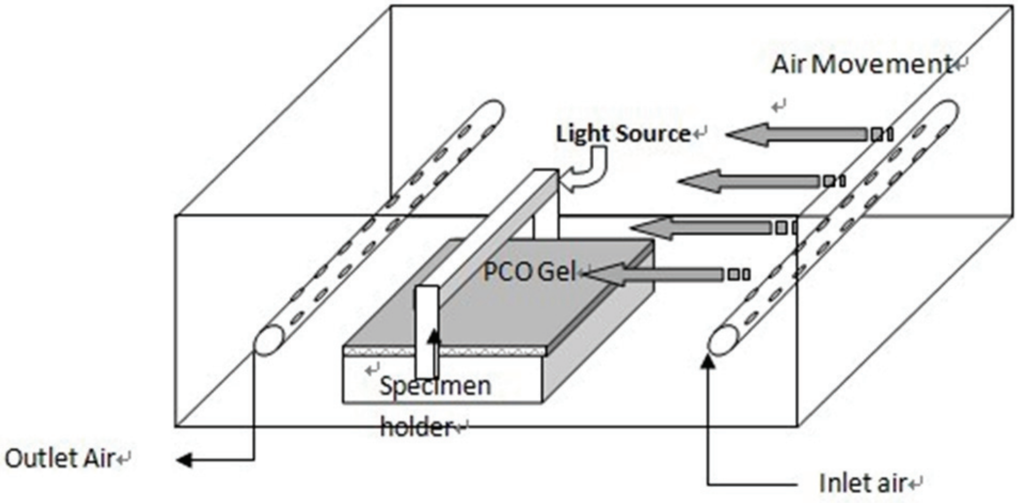


Figure 5.3 Illustration of setup inside the small scale chamber (James, 2005).

The air samples taken from the chamber were then analyzed by Automatic Thermal Desorber (ATD) and Gas Chromatographer/Mass Spectrometer (GC/MS) system (Fig. 5.4), and the TVOC concentration in the small-scale environmental chamber was quantified. The TVOC concentrations in the small chamber at different time intervals were obtained for calculating the emission data from the building materials with or without the PCO gels. The photocatalytic efficiency of the PCO gels was evaluated by the reduction of VOC emission from the building materials by comparing the PCO gel coated materials with the blank materials.

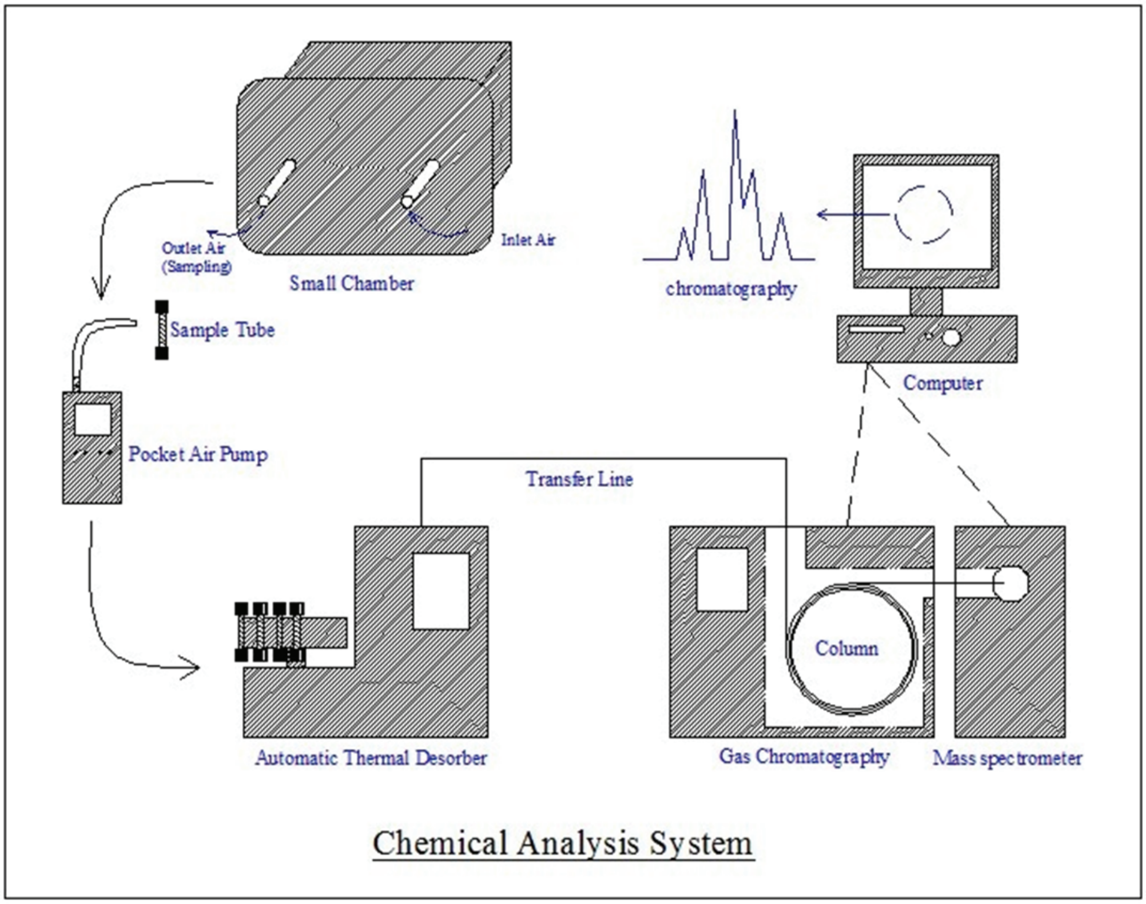


Figure 5.4 The VOC analysis system

5.3. Result and Discussion

5.3.1. General Description

From all the results of the different gel samples, VOC emission from the building materials (pressure treated wood and oil-based paint) was reduced by the PCO reaction and/or H_2O_2 oxidation (Fig. 5.5, 5.6, 5.7, 5.8, 5.9, 5.10, 5.11, 5.12). UV in the figures means under UV light irradiation; meanwhile, VI means under visible light irradiation. VOCs were diffused from the materials into the gel layer. In the gel, the photocatalysts adsorbed the reactants on the surface and degraded them with the oxidative radicals generated under light irradiation. Meanwhile, H_2O_2, if present, also oxidized VOCs inside the gel. The products of those reactions (CO_2 and H_2O) and the unreacted VOCs were then emitted from the gel layer into the air.

The previous study (James, 2005) in our lab showed that H_2O_2 was greatly effective within the first 6 hours in the destruction of VOCs, after which H_2O_2 would lose its effect. H_2O_2 is either evaporated or consumed by VOC degradation. In the case of oil-based paint, H_2O_2 inside the PCO gel will degrade even faster due to the high VOC emission. The PCO reaction would continue being effective on the degradation of VOCs with hydroxyl radicals and super-oxide ions formed after the initial production of highly reactive electron and hole pairs or by the chain reaction of hydrogen peroxide for the whole period of the experiment; whereas, at the beginning of the experiment, the PCO reaction will be overwhelmed by the high concentration of VOCs, especially in the case of oil-based paint. With high VOC concentration, the VOC molecules occupy a large number of active sites on the surface of photocatalysts, blocking the adsorption of other important reactants such as oxygen and water, which decreases the photocatalytic activity of photocatalysts.

5.3.2. Pressure Treated Wood

Pressure treated wood has a relatively small VOC emission and emission rate at the beginning. The TVOC concentration in the chamber increased after the pressure treated wood placed in and reached the highest after 7 or 8 hours experiment. Then, the concentration decreased gradually with time, and the emission was relatively low after 5 days. Under UV light irradiation, both the TiO_2 gel and Ag-TiO_2/H_2O_2 gel managed to degrade the VOCs significantly, with the reduction of TVOC emission-33.2% and 54.4%, respectively (Fig 5.5). With the aid of H_2O_2, the Ag-TiO_2/H_2O_2 gel showed better efficiency in the degradation of VOCs under UV light irradiation. The benefit from H_2O_2 not only showed on greater reduction of VOC emission, but also exhibited the lowering of the peak concentration (H_2O_2 targeted on the beginning period when the VOC emission rate was relatively high). However, the previous study found that H_2O_2 alone can have almost 30% reduction of VOC emission from pressure treated wood under UV light irradiation (James, 2005). If the H_2O_2 effect is taken off from the result of the Ag-TiO_2/H_2O_2 gel (the benefit of the peak concentration reduction is neglected), Ag-TiO_2 may have lower photocatalystic efficiency than TiO_2 under UV light irradiation. This was also found in the mold experiment where in the same condition the TiO_2 gel could completely prevent mold growth but the Ag-TiO_2 gel could not due to the deterioration of Ag-TiO_2 under light irradiation. Even the deteriorated Ag-TiO_2 showed the photocatalytic activity under UV light in VOC degradation, it was not sufficient to prevent mold growth. With the addition of H_2O_2, the Ag-TiO_2/H_2O_2 maintained a high photocatalytic efficiency of VOC degradation in the period of the small chamber experiment (5 days). The difference of photocatalytic efficiency between Ag-TiO_2/H_2O_2 and TiO_2 gradually diminished with the evaporation and consumption of H_2O_2 in the gel as well as the deterioaration of Ag-TiO_2. The Ag-TiO_2/H_2O_2 gel lost its mold inhibition property on the 7th day under UV light irradiation, beyond the whole period of the small chamber experiment. So, the severe deterioration effect of Ag-TiO_2 was not seen in VOC emission test.

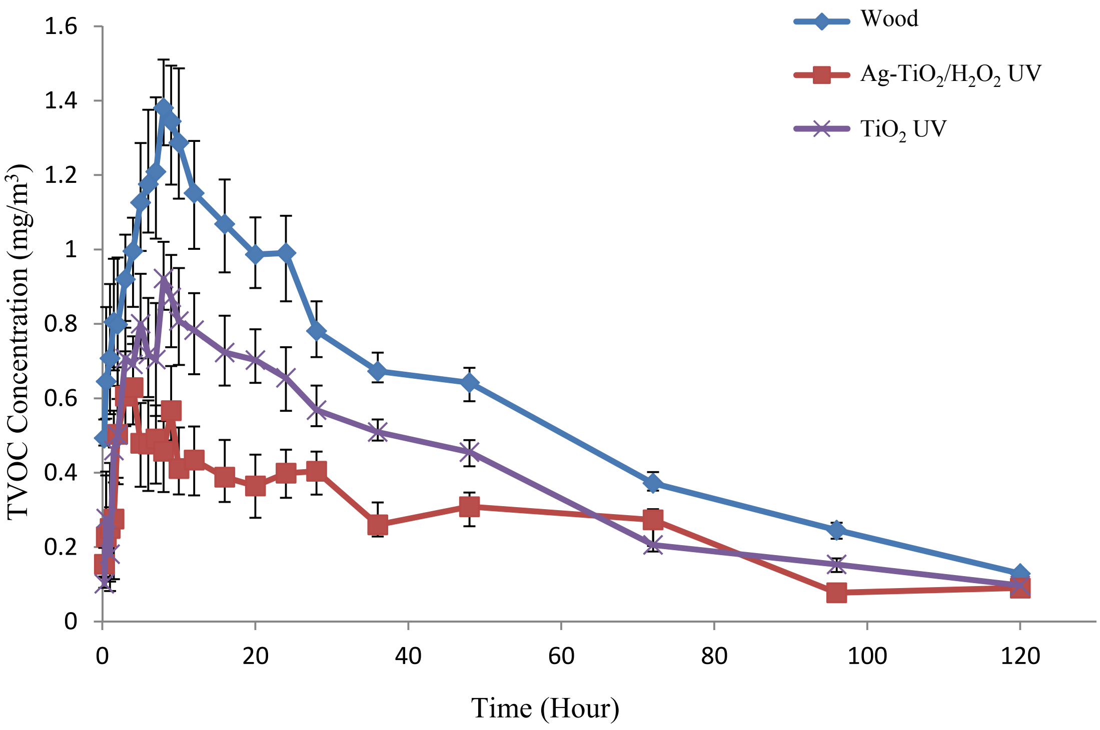


Figure 5.5 VOC emission from pressure treated wood under UV light irradiation

Under visible light irradiation (Fig. 5.6), TiO_2 barely had photocatalytic activity (10.9% reduction of VOC emission). There was a big difference between the photocatalytic activity of TiO_2 under UV and visible light irradiation for pressure treated wood (Fig. 5.8). Whereas, the Ag-TiO_2/H_2O_2 gel kept the similar photocatalytic efficiency (52.3% reduction of VOC emission) under visible light irradiation (Fig. 5.7) as under UV light irradiation. The Ag-doping seemed to increase the photocatalytic activity of TiO_2 under visible light irradiation in spite of the deterioration of Ag-TiO_2. On the other hand, H_2O_2 could also cause the visible light response, and, itself, oxidize VOCs. In mold growth tests, neither Ag-doping nor H_2O_2 was enough to impove the visible light activity for the complete mold inhibition, which would be even worsened by the deterioration of Ag-TiO_2. The VOC degradation over the Ag-TiO_2/H_2O_2 gel under visible light irradiation may be attributed to the H_2O_2 oxidation, the H_2O_2 induced photocatalytic reaction, and remaining visible light activity of Ag-TiO_2.

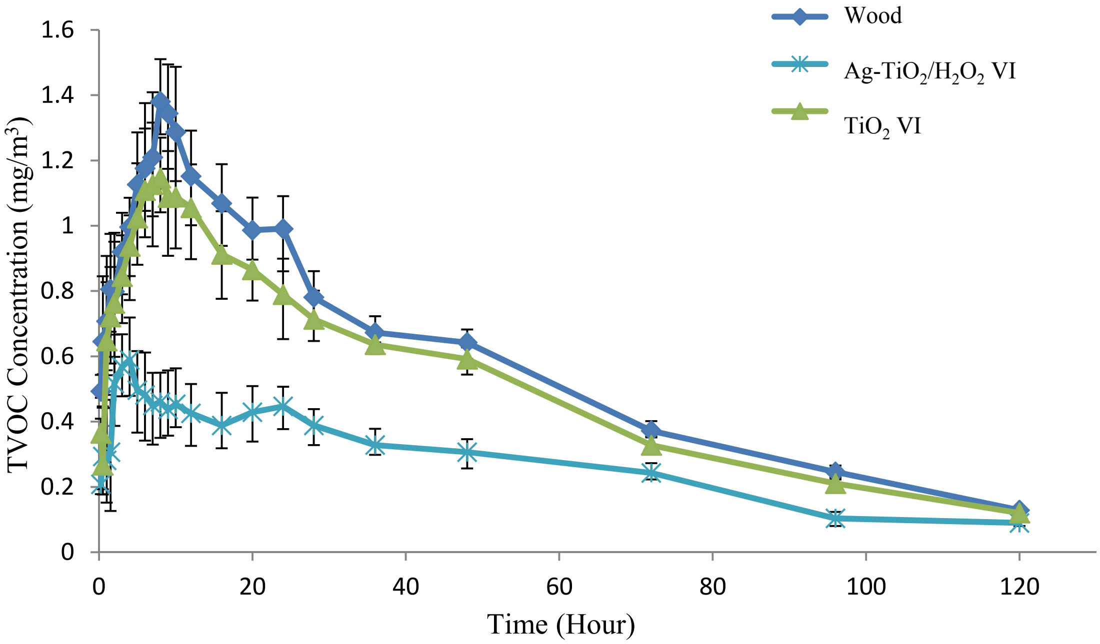


Figure 5.6 VOC emission from pressure treated wood under visible light irradiation

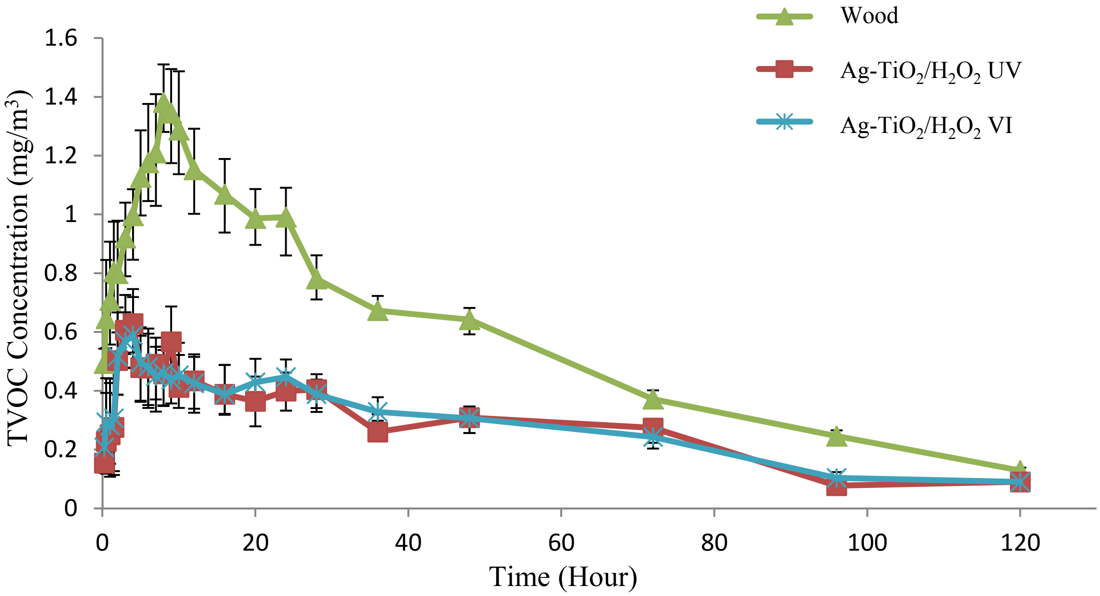


Figure 5.7 Comparison of the Ag-TiO_2/H_2O_2 gel coated pressure treated wood under UV and visible light irradiation

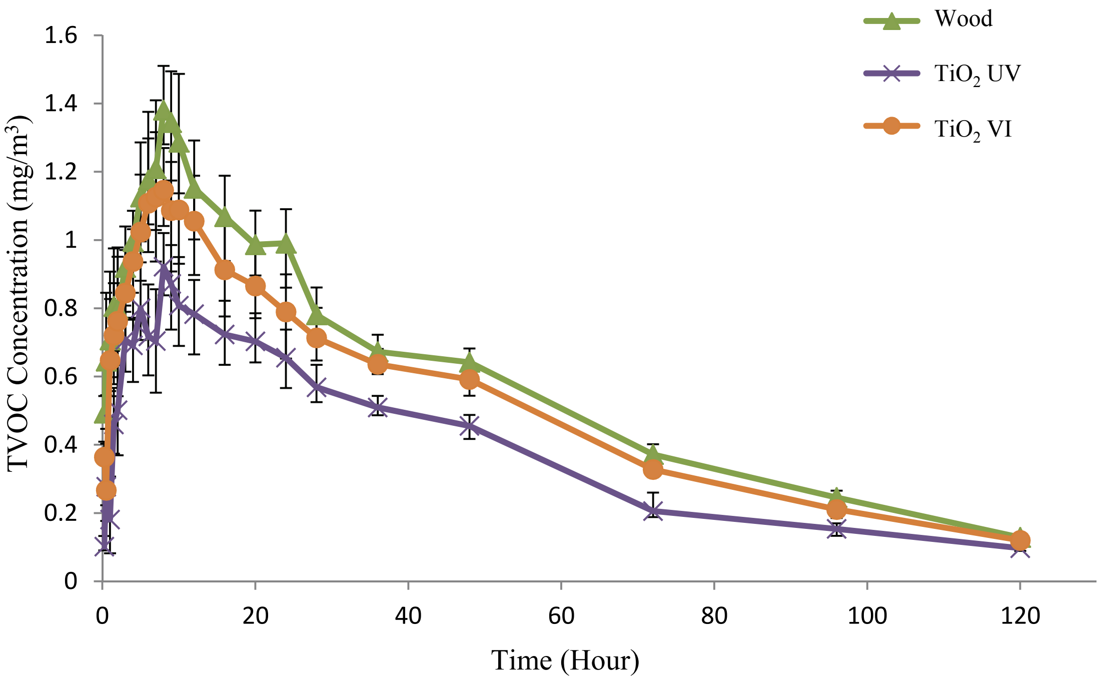
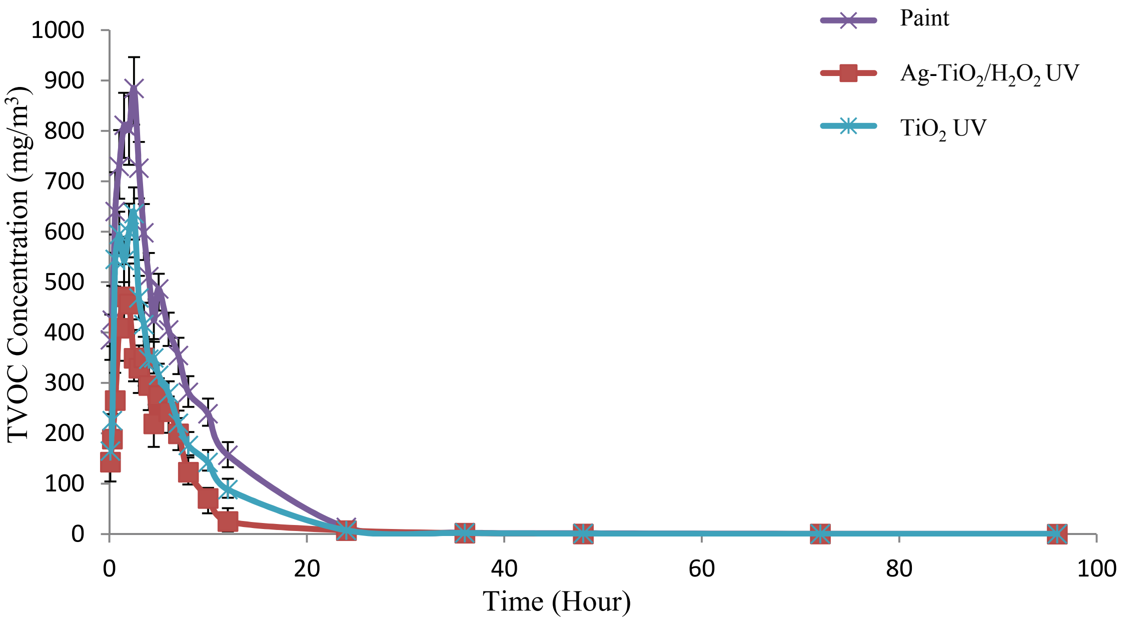


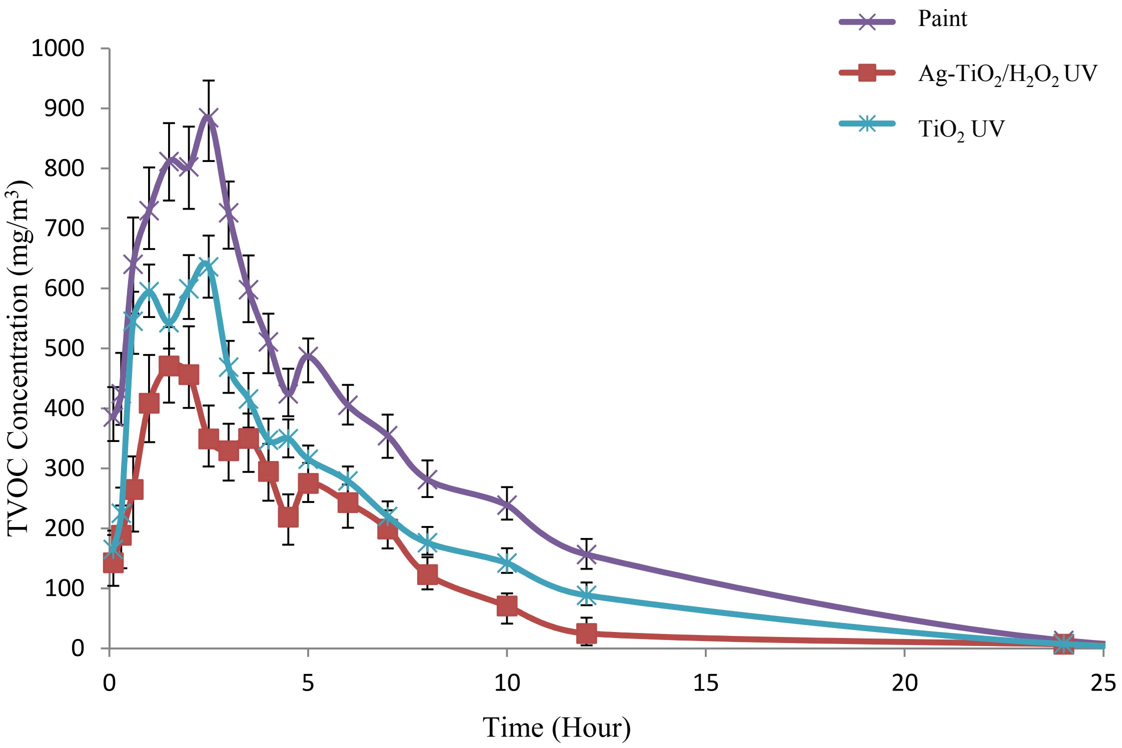
Figure 5.8 Comparison of the TiO_2 gel coated pressure treated wood under UV and visible light irradiation

5.3.3. Oil-based Paint

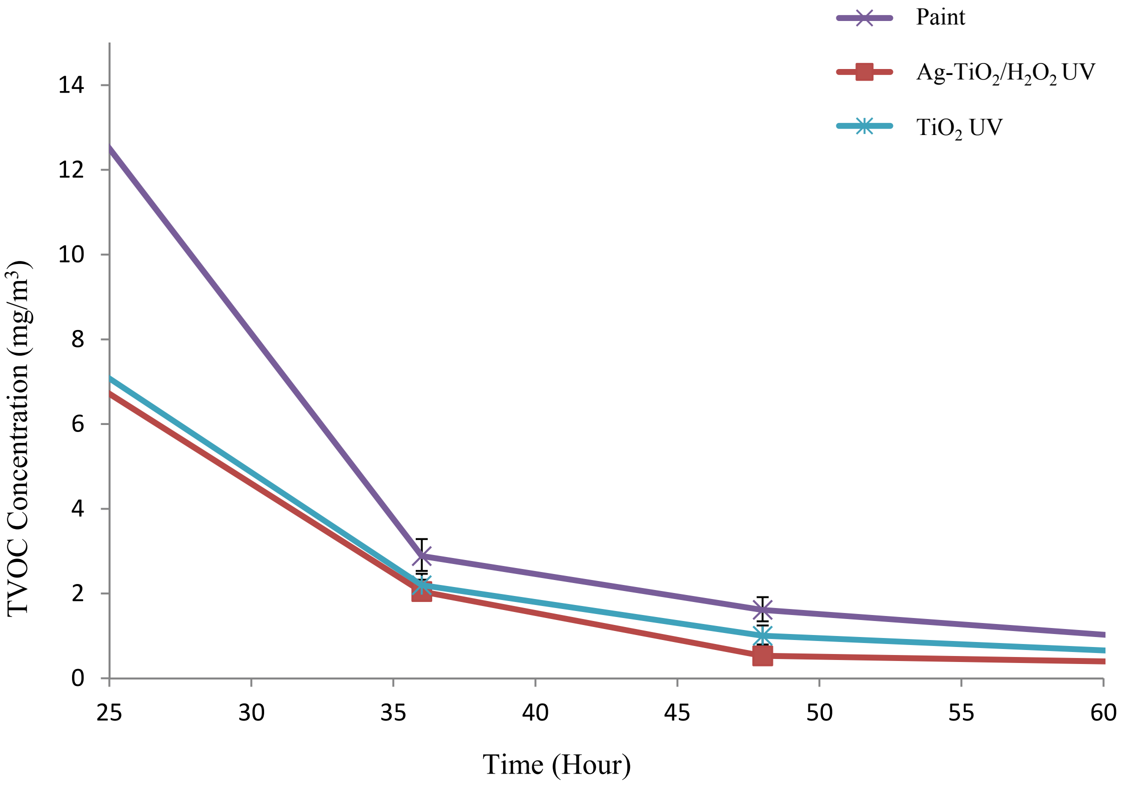
Oil-based paint has a higher VOC emission and emission rate at the beginning than pressure treated wood. After oil-based paint samples were placed in the chamber, the TVOC concentration increased dramatically and reached the highest at 2 or 2.5 hours after the experiment began. Then, the concentration decreased remarkably and became relatively low after 24 hours. To better show the change of TVOC concentration of oil-based paint samples, the whole process is divided into several sections with different time frames illustrated in Fig. 5.9 and 5.10. Under UV light irradiation, the similar reduction of VOC emission of oil-based paint was achieved as in the case of pressure treated wood-33.9% with the TiO_2 gel and 55.7% with the Ag-TiO_2/H_2O_2. Compared to the TiO_2 gel, the Ag-TiO_2/H_2O_2 gel still had better photocatalytic efficiency under UV light irradiation for reducing VOC emission from oil-based paint. H_2O_2 also contributed a lot to the reduction of VOC emission at the beginning of the experiment; however, the peak concentration was not lowered as much as in the case of pressure treated wood due to the concentrated emission from oil-based paint, even though H_2O_2 was very active at the beginning phase. H_2O_2 was consumed fast by the high concentration of VOCs. The difference of VOC chamber concentration between the Ag-TiO_2/H_2O_2 gel and the TiO_2 gel coated oil based paint under UV light irradiation decreased very fast, and the chamber concentrations became very similar after 24 hours. Similar to the case of pressure treated wood, the Ag-TiO_2/H_2O_2 gel maintained UV light activity, though it may not be enough or long enough to completely prevent mold growth with the deterioration of Ag-TiO_2. Or, the severe deterioration of Ag-TiO_2 did not take place within the short period of VOC emission test time.



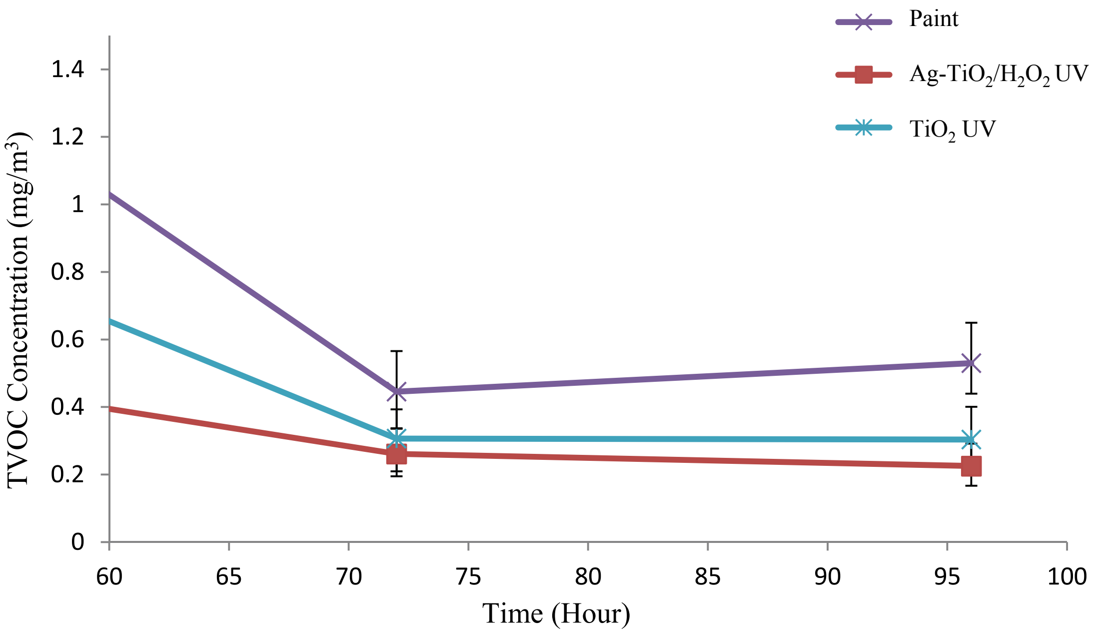
(a)


Paint
Ag-TiO$_2$/H$_2$O$_2$ UV
TiO$_2$ UV
1000
900
800
700
600
500
400
300
200
100
0
TVOC Concentration (mg/m^3)
0
5
10
15
20
25
Time (Hour)

(b)


Paint
Ag-TiO$_2$/H$_2$O$_2$ UV
TiO$_2$ UV
14
12
10
8
6
4
2
0
TVOC Concentration (mg/m^3)
25
30
35
40
45
50
55
60
Time (Hour)

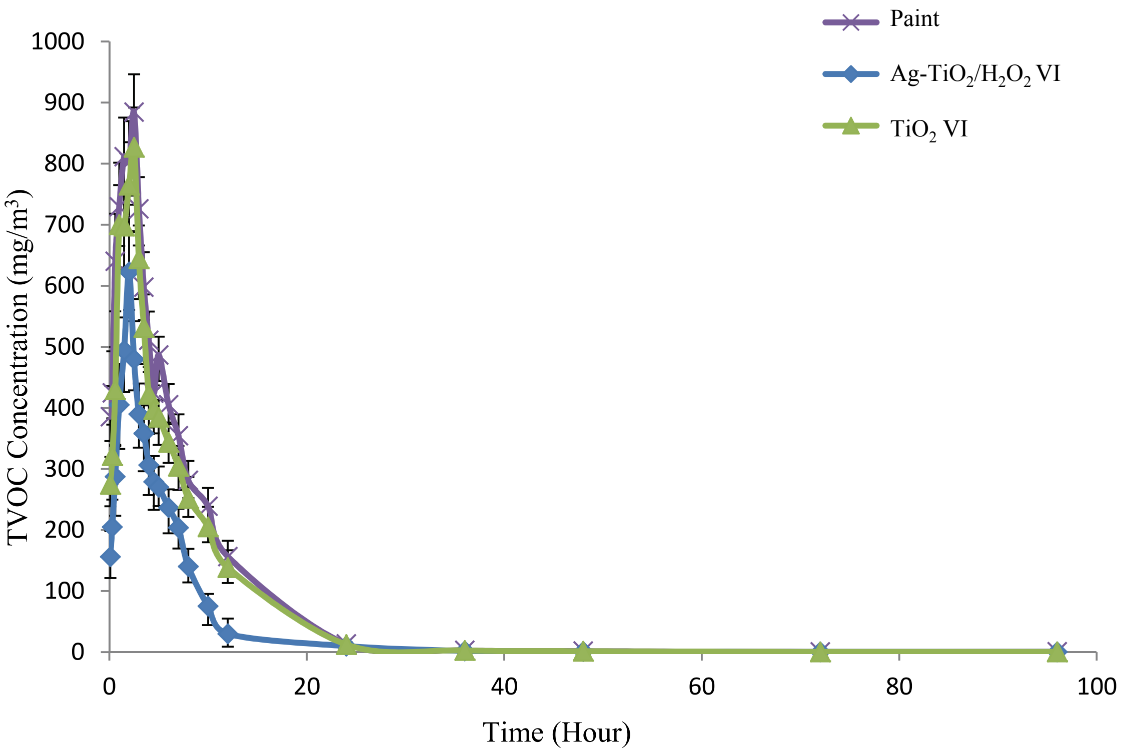
(c)



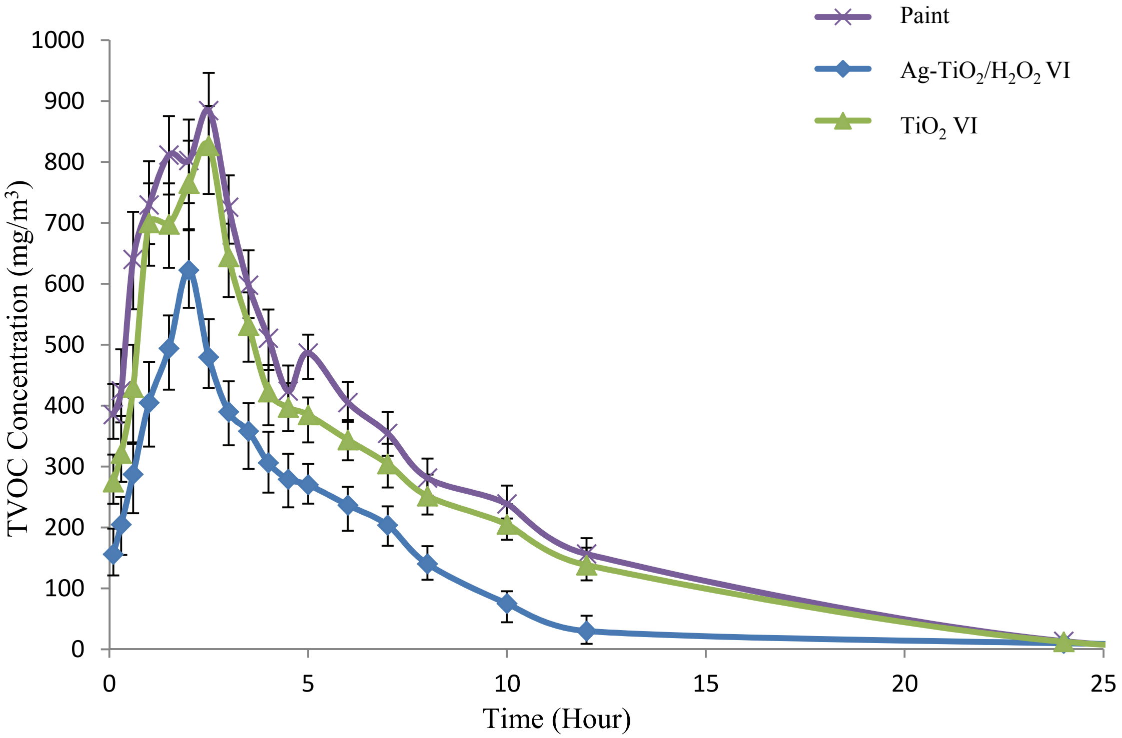
(d)

Figure 5.9 VOC emission from oil-based paint under UV light irradiation: (a) the whole period of the experiment; (b) 0-25 hours; (c) 25-60 hours; (d) 60-96 hours.

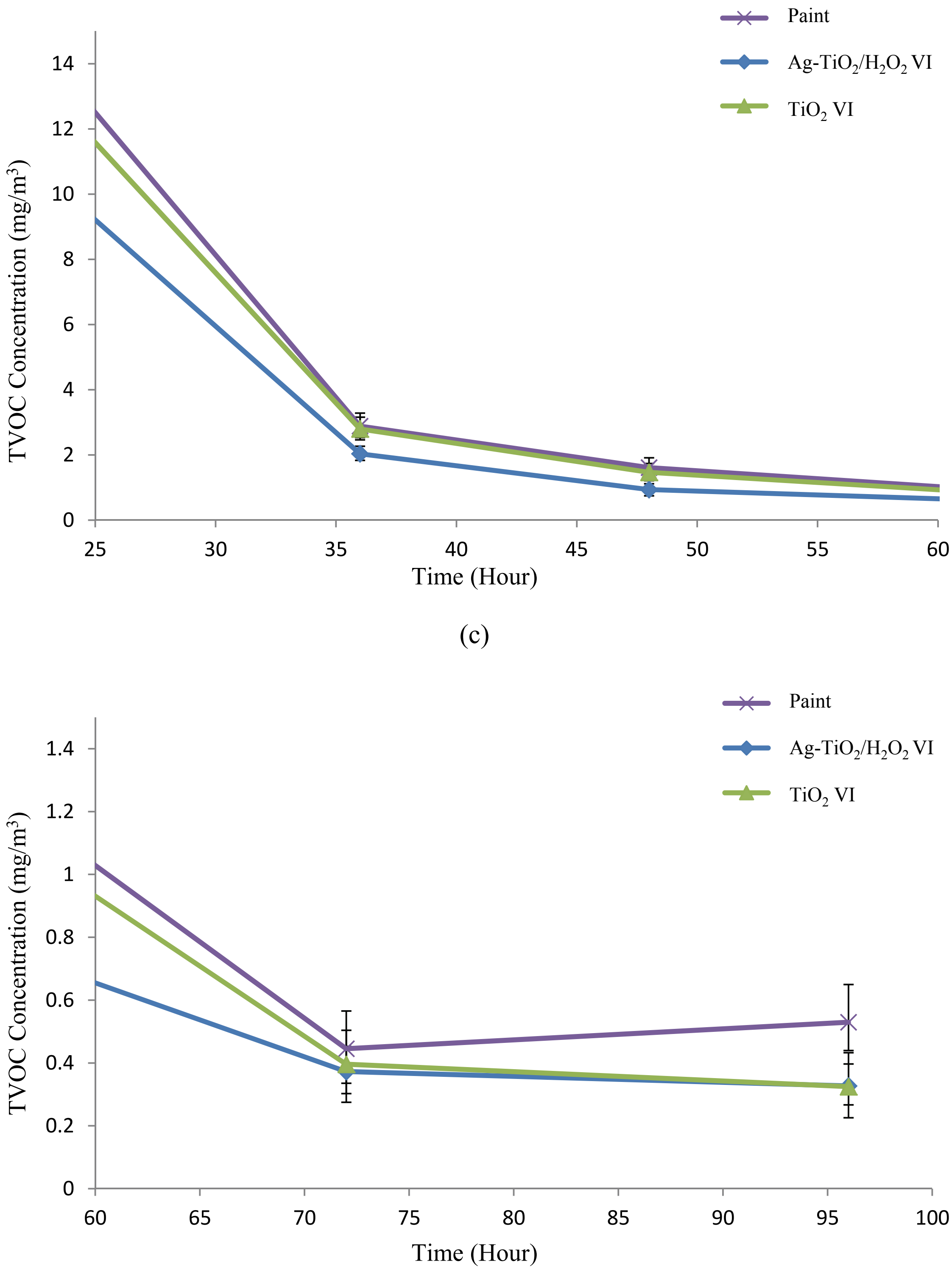
Under visible light irradiation, the TiO_2 gel, which can not be fully activated by visible light, had little photocatalytic efficiency with 12.5 % reduction of VOC emission from oil-based paint, compared to the efficiency under UV light irradiation (Fig. 5.12). Whereas, the Ag-TiO_2/H_2O_2 gel maintained high photocatalytic efficiency with 50.3% reduction of VOC emission from oil-based paint under visible light irradiation similar to under UV light irradiation (Fig. 5.11). Under UV light irradiation or visible light irradiation, the similar photocatalytic activity between the cases of pressure treated wood and oil-based paint was also found on the Ag-TiO_2/H_2O_2 gel. With the aid of H_2O_2, better VOC degradation efficiency was also achieved under visible light irradiation. All the results obtained from the oil-based paint experiment confirmed the same trend that was found in the pressure treated wood experiment.


Paint
Ag-TiO2/H2O2 VI
TiO2 VI
TVOC Concentration (mg/m3)
1000
900
800
700
600
500
400
300
200
100
0
0
20
40
60
80
100
Time (Hour)

(a)


Paint
Ag-TiO2/H2O2 VI
TiO2 VI
TVOC Concentration (mg/m3)
1000
900
800
700
600
500
400
300
200
100
0
0
5
10
15
20
25
Time (Hour)

(b)



(c)

(d)

Figure 5.10 VOC emission from oil-based paint under visible light irradiation: (a) the whole period of the experiment; (b) 0-25 hours; (c) 25-60 hours; (d) 60-96 hours.

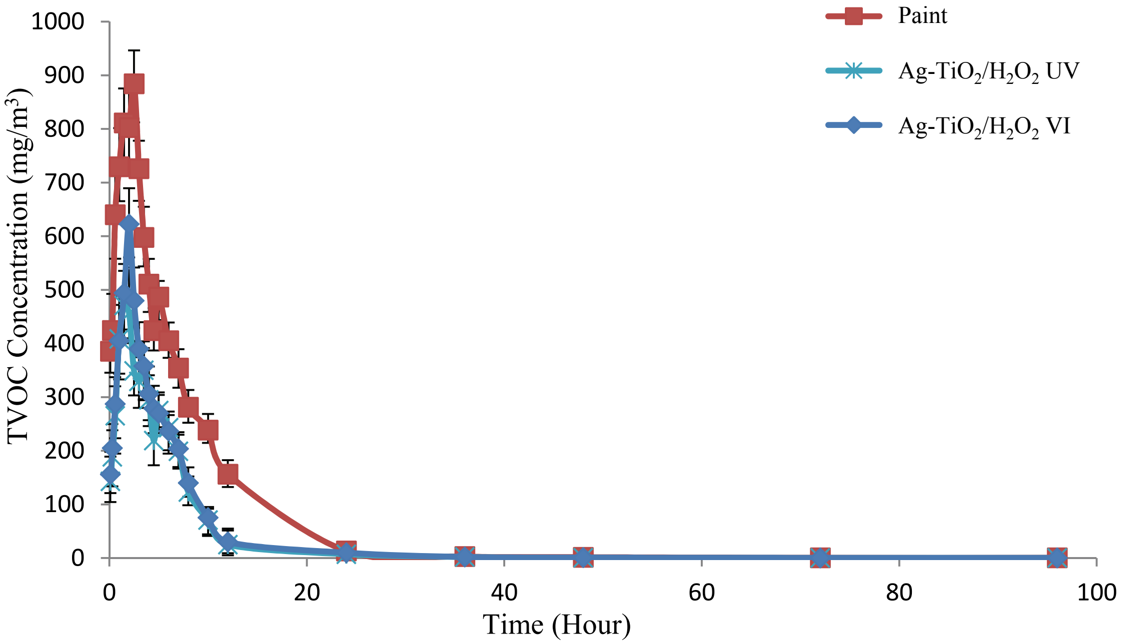


Figure 5.11 Comparison of the Ag-TiO_2/H_2O_2 gel coated oil-based paint under UV and visible light irradiation

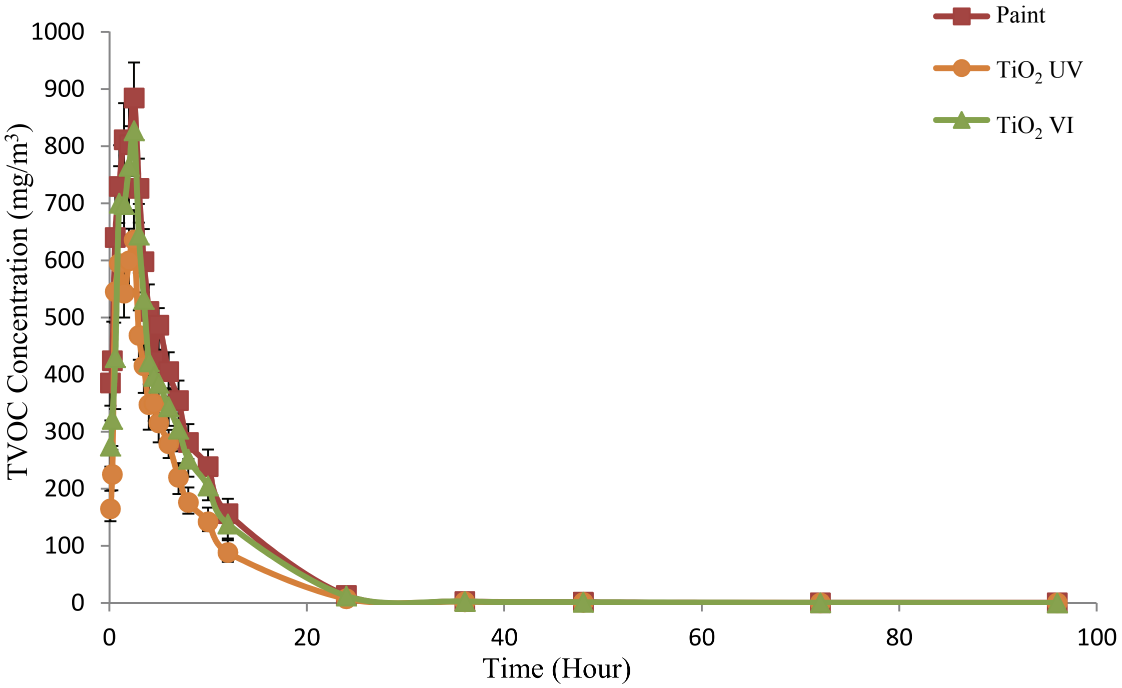


Figure 5.12 Comparison of the TiO_2 gel coated oil-based paint under UV and visible light irradiation

5.4. Conclusion

Table 5.1 The Reduction of TVOC Emission from Building Materials by the PCO Gel

Building Materials	PCO Gel	Light Source	TVOC Reduction (%)
Pressure Treated Wood	TiO_2	UV	33.2
		Visible	10.9
	$Ag\text{-}TiO_2/H_2O_2$	UV	54.4
		Visible	52.3
Oil-based Piant	TiO_2	UV	33.9
		Visible	12.5
	$Ag\text{-}TiO_2/H_2O_2$	UV	55.7
		Visible	50.3

The two kinds of PCO gels-the TiO_2 gel and $Ag\text{-}TiO_2/H_2O_2$ gel were studied for their reduction of VOC emission from building materials under UV or visible light irradiation. The TiO_2 gel was found to be only effective under UV light irradiation with above 30% reduction of VOC emission from both pressure treated wood and oil-based paint. With the aid of H_2O_2, the $Ag\text{-}TiO_2/H_2O_2$ gel was more efficient for the reduction of VOC emission with above 50% reduction on both pressure treated wood and oil-based paint than the TiO_2 gel (Table 5.1). Even though the deterioration of $Ag\text{-}TiO_2$ observed in the mold experiment under light irradiation could still happen in the VOC emission experiment, $Ag\text{-}TiO_2$ still maintained some photocatalytic activity on VOC degradation under either UV or visible light irradiation. In the mold experiment, the addition of 35% H_2O_2 into $Ag\text{-}TiO_2$ extended the mold inhibition period to more than 7 days. Also, H_2O_2 benefited the reduction of VOC emission from building materials by aiming at the oxidation of VOCs at the beginning phase of VOC emission from building materials, in which the highest emission rate and chamber concentration were observed. The most effective PCO gel obtained for the reduction of VOC emission from building materials was the Ag-TiO_2/H_2O_2 gel, which, due to the deterioration of Ag-TiO_2, was not so efficient as the PCO gel studied in the previous research (James, 2005) with above 60% reduction of VOC emission. However, the use of fluorocarbon in the previous one is considered not economical or environment-friendly because of the extremely high price and toxicity. Therefore, the Ag-TiO_2/H_2O_2 gel applied as a coating material in this research is a potential solution for the reduction of VOC emission from building materials even under visible light irradiation. More stable Ag-TiO_2 or other visible-light-driven photocatalysts under light irradiation are recommended in future research. The addition of 35% H_2O_2 is also recommended for the application for reducing the VOC emission from building materials. The development of multifunctional coating material based on the PCO technology for both mold/mildew resistance and VOC emission reduction from building materials is feasible and promising.

Chapter 6

MOLD/MILDEW GROWTH MODEL

6.1. Background

For the evaluation of the response of humidity, temperature, and exposure time for mold growth on wood materials, several mold growth models (Viitanen 1997; Hukka and Viitanen 1999; Viitanen et al. 2000) have been developed, based on the comprehensive laboratory studies with Northern wood species (Viitanen and Ritschkoff 1991). Viitanen (1997) created three groups of models based on the regression analysis of the critical time required for the growth of mold on pine and spruce sapwood. These models mainly addressed the effect of critical humidity and temperature for mold growth.

In this study, the mold growth model was developed based on the regression analysis of the critical time required for the growth of mold on the agar plates with the PCO gel coated filter papers (the results of mold growth experiment). The resistant effect of the PCO gel on mold growth was included in the models. The effects of humidity and temperature for mold growth were eliminated by providing the most mold-favored humidity and temperature in the mold growth experiment.

There are two mold growth models for two kinds of PCO gels, the Ag-TiO_2/H_2O_2 gel without light and the TiO_2 gel under UV light irradiation.

6.2. "Without Light" Model

In the "without light" model, the loading of Ag-TiO_2 in the Ag-TiO_2 gel and the volume ratio of 35% H_2O_2 to Ag-TiO_2 gel were considered to be two major factors for the Ag-TiO_2/H_2O_2 gel to influence the delay of the mold growth on the agar plates with the Ag-TiO_2/H_2O_2 gel coated filter papers. The linear regression model was obtained for the "without light" model with consideration of the interaction between those two factors.

In statistics, linear regression is the first type of regression analysis, being rigorously studied and widely used in research and practices. Linear regression is an approach to study the relationship between the dependent variable Y and one or many independent variables X. Data is modeled using the linear function and parameters are calculated in the linear model, which can be written in the following form (Eq. 6.1):

$$Y_i = \beta_1 x_{i1} + \cdots + \beta_p x_{ip} + \varepsilon_i = x_i'\beta + \varepsilon_i, \qquad i = 1, \ldots, n, \qquad 6.1$$

Where, Y_i is dependent variables;

x_i are independent variables;

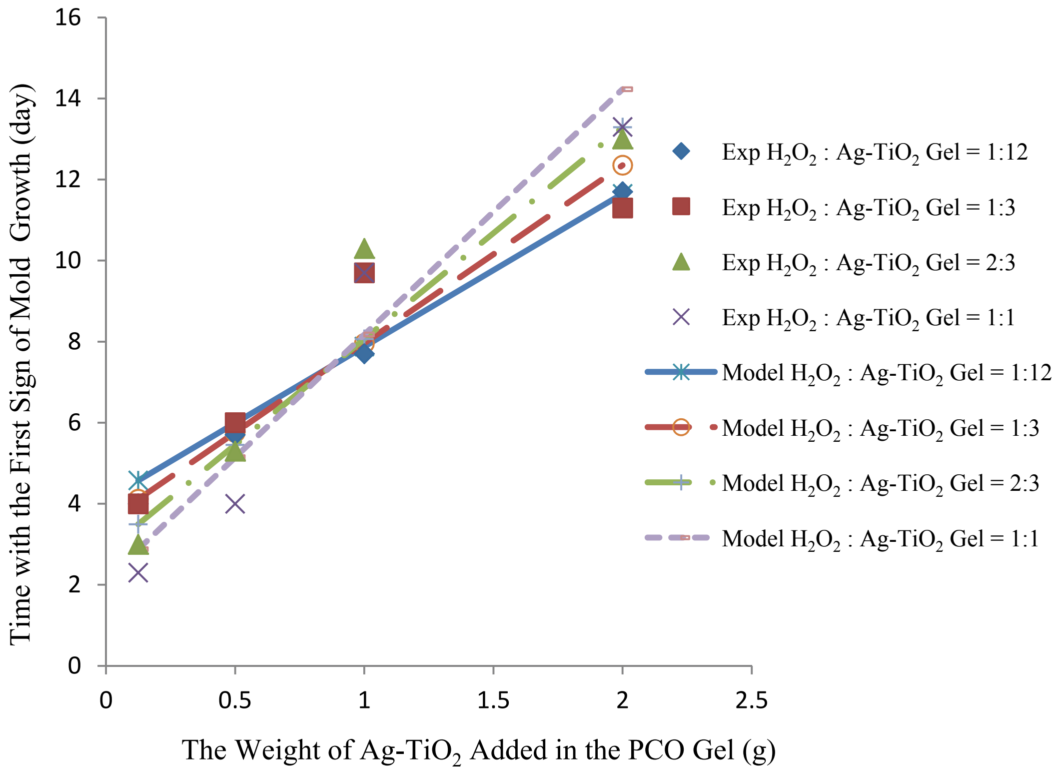
β_i are regression coefficients for each x_i;

ε_i is error term.

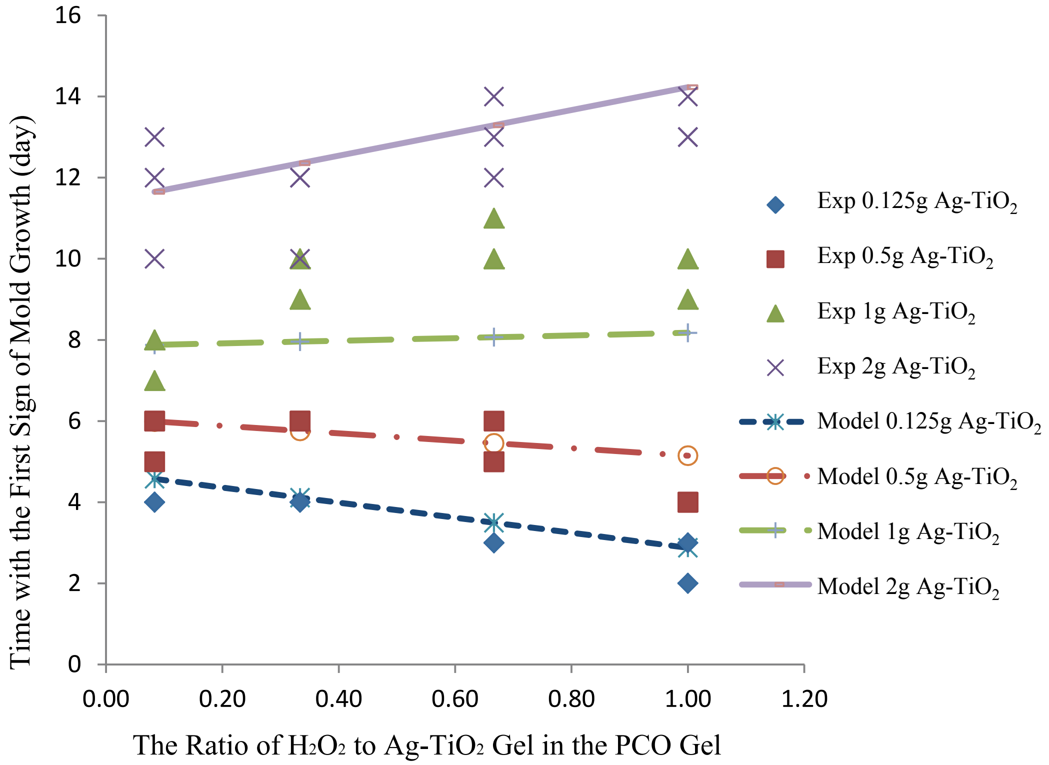
Particular to our case, two major factors are the loading of Ag-TiO_2 in the Ag-TiO_2 gel and the ratio of 35% H_2O_2 to Ag-TiO_2 gel, represented by x_{Ag} (g) and x_h (mL/mL) in Eq. 6.2, respectively. The interaction term between the loading of Ag-TiO_2 and the addition of 35% H_2O_2 is also introduced in the form of $x_{Ag}x_h$ due to the significance found in ANOVA test for the interaction effect. The independent variable Y is the mold inhibition days for the Ag-TiO_2/H_2O_2 gel. The linear regression model for the mold inhibition days of the Ag-TiO_2/H_2O_2 gel without light is described in Eq. 6.2.

$$Y = 3.565\, x_{Ag} - 2.164\, x_h + 2.489\, x_{Ag}\, x_h + 4.284 \qquad 6.2$$

The R square test indicates that the linear regression model fits 93% of the experimental data, which means the linear model would be enough to interpret the experimental data and predict the trend. The comparison of the modeling result and the experimental data is shown in Fig. 6.1.



(a)



(b)

Figure 6.1 Model result vs experimental data-the time of the first sign of mold growth on the Ag-TiO$_2$/H$_2$O$_2$ gel without light: (a) result with Ag-TiO$_2$ increase; (b) result with H$_2$O$_2$ increase.

In general, the linear regression model accurately fits for the experimental data of the Ag-TiO$_2$/H$_2$O$_2$ gel without light, especially when addressing the effect of the increase of Ag-TiO$_2$ on the mold/mildew resistance. The biggest error is found when the model tryed to simulate the effect of the increase of H$_2$O$_2$ on the mold/mildew resistance in the Ag-TiO$_2$/H$_2$O$_2$ gel with 1 g loading of Ag-TiO$_2$. The reason for this error probably comes from the intension to catch the transition of the slope from negative to positive with the increase of Ag-TiO$_2$. This error is still acceptable, because the influence of H$_2$O$_2$ is relatively small causing a small change of the mold/mildew resistance when compared to the influence of Ag-TiO_2.

6.3. "UV Light" Model

In the "UV light" model, the loading of TiO_2 in the TiO_2 gel, the UV light intensity and the UV light exposure time are considered to be three major factors to decide whether or not the TiO_2 gel can completely inhibit the mold growth on the agar plates with the TiO_2 gel coated filter papers. The logistic regression is adopted for the "UV light" model, for the result of the experiment on the TiO_2 gel is either the mold growth would appear or not, which is not quantitative but qualitative result.

In statistics, logistic regression is usually used to predict the occurrence probability of an event from the influence of one or many independent (predictor) variables by fitting data to a logit function. The most interesting feature of the logistic regression is the predictor variables which can be either numerical or categorical. In the logistic regression, The 100% occurrence is represented as f(z) = 1, and 100% non-occurrence is represented as f(z) = 0, complying with the function of the logistic curve (Fig. 6.2):

$$f\ (z) = \frac{e^z}{e^z+1} = \frac{1}{1+e^{-z}} \qquad 6.3$$

Where, z represents the total exposure to all the independent variables.

Here, the linear regression is usually used for binomial regression:

$$z = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \cdots + \beta_k x_k, \qquad 6.4$$

Where, x_i are independent variables;

β_0 is called "intercept" and other β_i are regression coefficients.

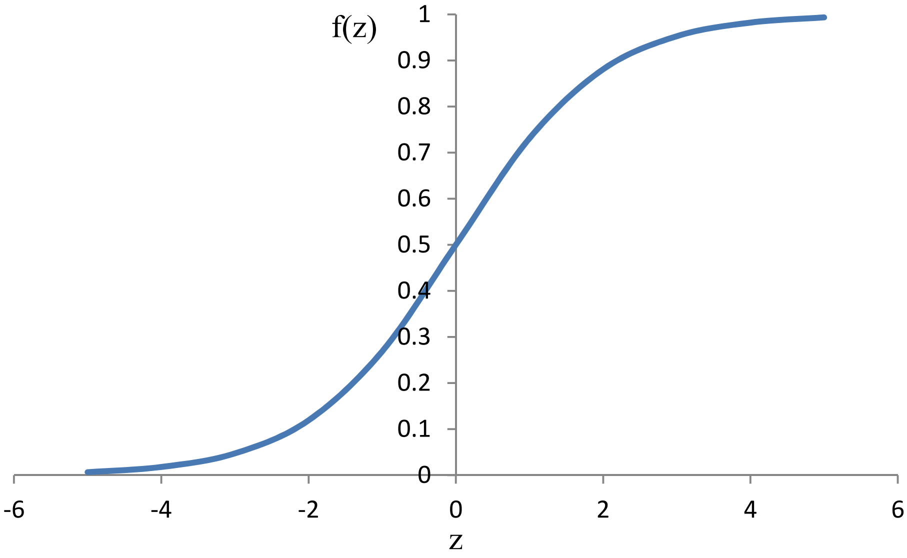


Figure 6.2 The logistic curve.

Before the logistic model is applied to estimate the probability of mold growth on the TiO_2 gel coated filter papers, the step function can be used for the situation obtained from the mold experiment in which the mold growth will definitely show. When the addition of TiO_2 in the TiO_2 gel was equal or less than 0.125g, the UV light intensity was equal or less than 0.3 mW/cm^2, or the UV light exposure time per day was equal or less than 4 hours, the mold grew normally on all the test agar plates (Eq. 6.5).,

$$f(x) = 1, \qquad x_{Ti} \leq 0.125, \text{ or } x_I \leq 0.3, \text{ or } x_t \leq 4 \qquad 6.5$$

Where, x_{Ti} is the weight of TiO_2 added in the TiO_2 gel, g;

x_I is the UV light intensity coated on the TiO_2 gel, mW/cm^2;

x_t is the UV light exposure time for the TiO_2 gel per day, hour.

f(z) = 1 is specified as the showing of mold growth and f(z) = 0 means no sing of mold growth in the model.

Furthermore, the logistical model is utilized to estimate the occurrence probability of mold growth from 0.125 g to 2 g TiO_2 addition, from 0.3 to 0.6 mW/cm^2 UV light intensity, and from 4 to 24 hours UV light exposure time per day. The logistical regression was obtained from the mold experimental data on the TiO_2 gel under UV light irradiation (Eq. 6.6).

$$f(z) = \frac{1}{1+e^z} \qquad 0.125 \leq x_{Ti} \leq 2, 0.3 \leq x_I \leq 0.6, 4 \leq x_t \leq 24 \qquad 6.6$$

Where, $z = 6.3577 - 23.7848\, x_{Ti} - 13.473\, x_I - 0.5931\, x_t + 13.5902\, x_{Ti}\, x^2_I\, x_t$

The interaction of those three factors is found in the form of $x_{Ti}\, x_I^2\, x_t$, which has the best precision. The good agreement of the logistic regression is found by Hosmer–Lemeshow test (Hosmer and Lemeshow, 2000) in which the significance is observed for this model. When assuming above 60% predicted probability of mold growth means mold growth and below 40% means no mold growth, the accuracy percentage of prediction by this model is 96.9% in the 64 cases tested in the mold experiment. Only 2 cases of all, locating in the transition zone of logistic model from 1 to 0, indicate error prediction by this model (Fig. 6.3). The overall correctness of this logistic model is highly acceptable. The whole model can be written as Eq. 6.7.

$$f(z) = \begin{cases} 1 & x_{Ti} \leq 0.125, \text{or } x_I \leq 0.3, \text{or } x_t \leq 4 \\ \frac{1}{1+e^z} & 0.125 \leq x_{Ti} \leq 2,\ 0.3 \leq x_I \leq 0.6,\ 4 \leq x_t \leq 24 \\ z = 6.3577 - 23.7848x_{Ti} - 13.473x_I - 0.5931x_t + 13.5902x_{Ti}x_I^2x_t & \end{cases} \qquad 6.7$$

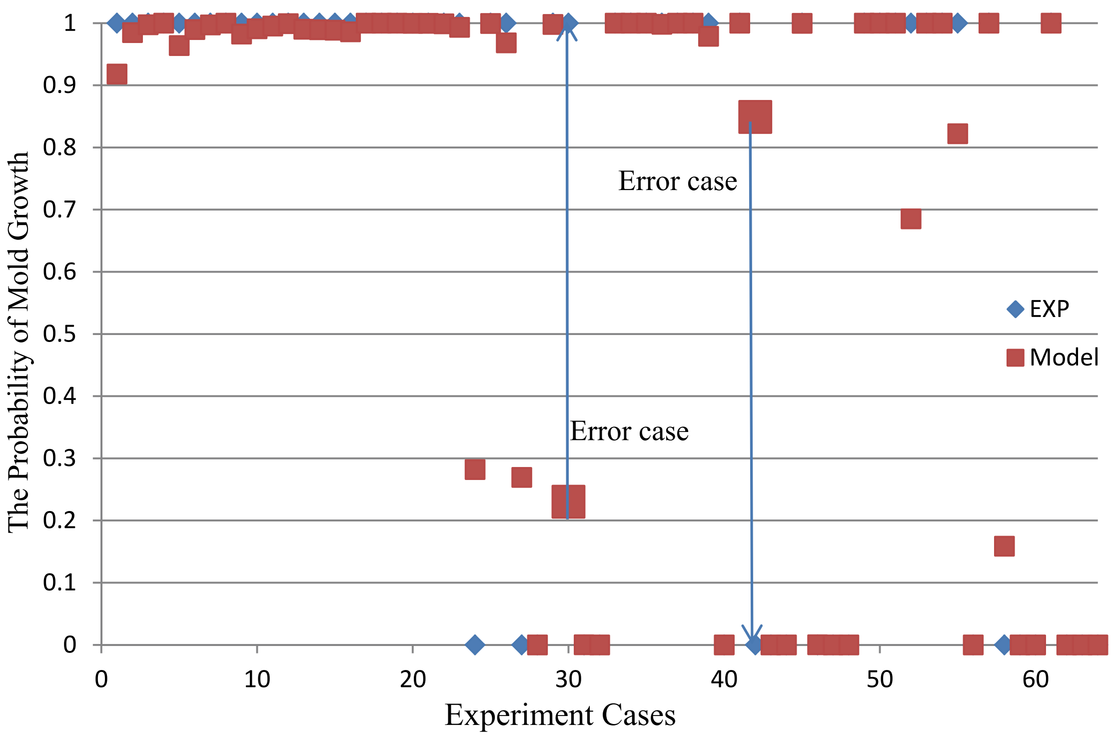
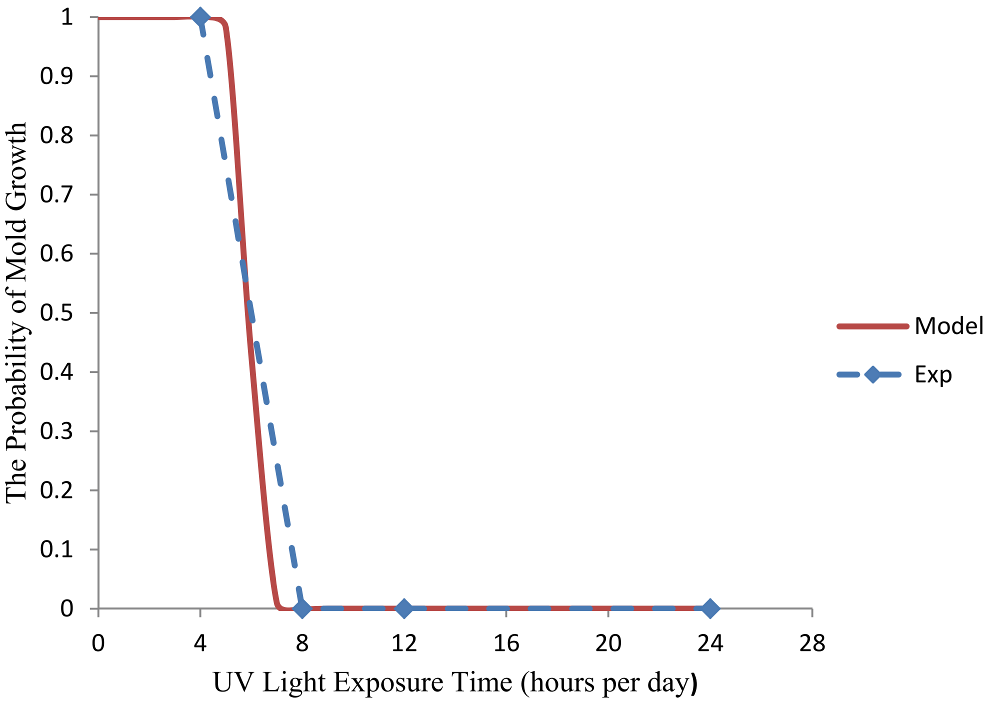


Figure 6.3 The prediction of the logistic model in the experiment cases

Some examples for the comparison between experimental data and logistic model simulation are illustrated in Fig. 6.4.


1
0.9
0.8
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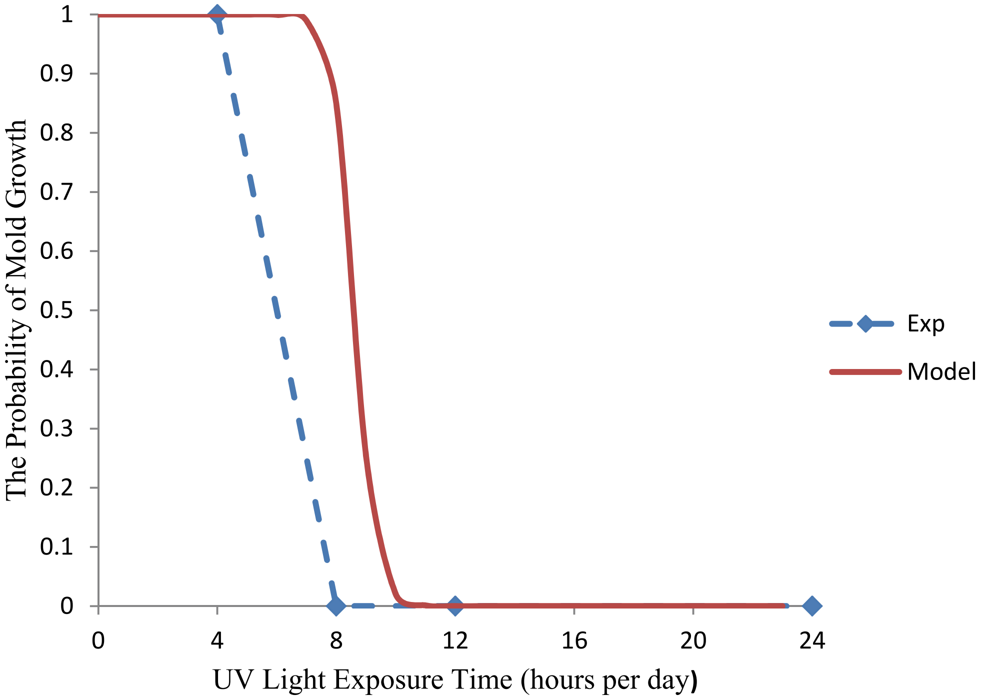
0.6
0.5
0.4
0.3
0.2
0.1
0
The Probability of Mold Growth
0
4
8
12
16
20
24
28
UV Light Exposure Time (hours per day)
Model
Exp

(a)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The Probability of Mold Growth
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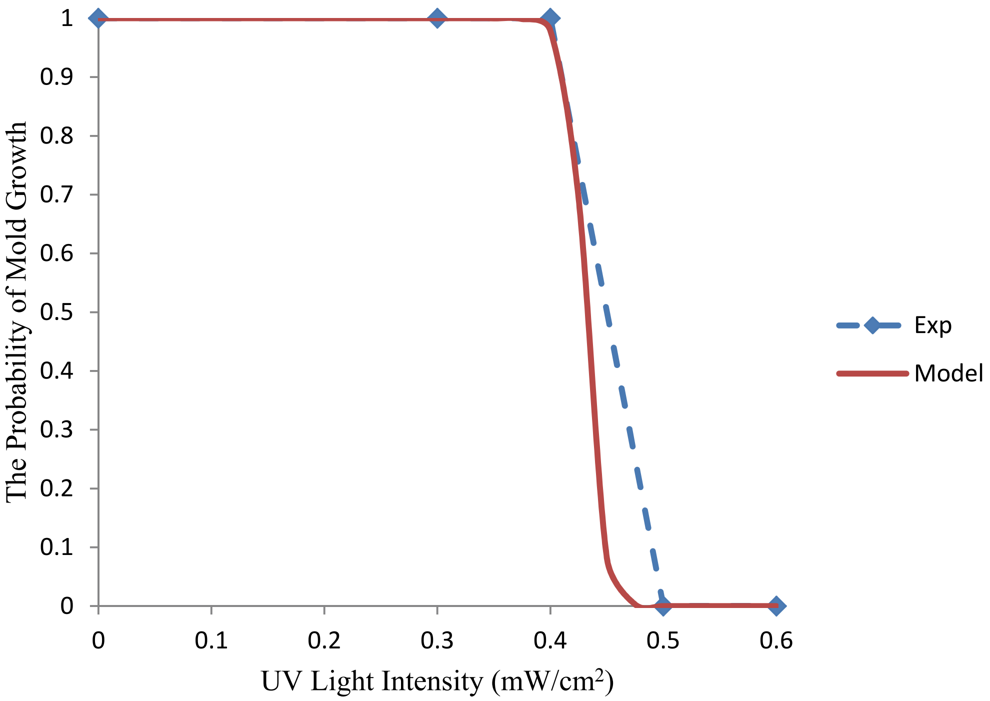
UV Light Exposure Time (hours per day)
Exp
Model

(b)


1
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0.3
0.2
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The Probability of Mold Growth
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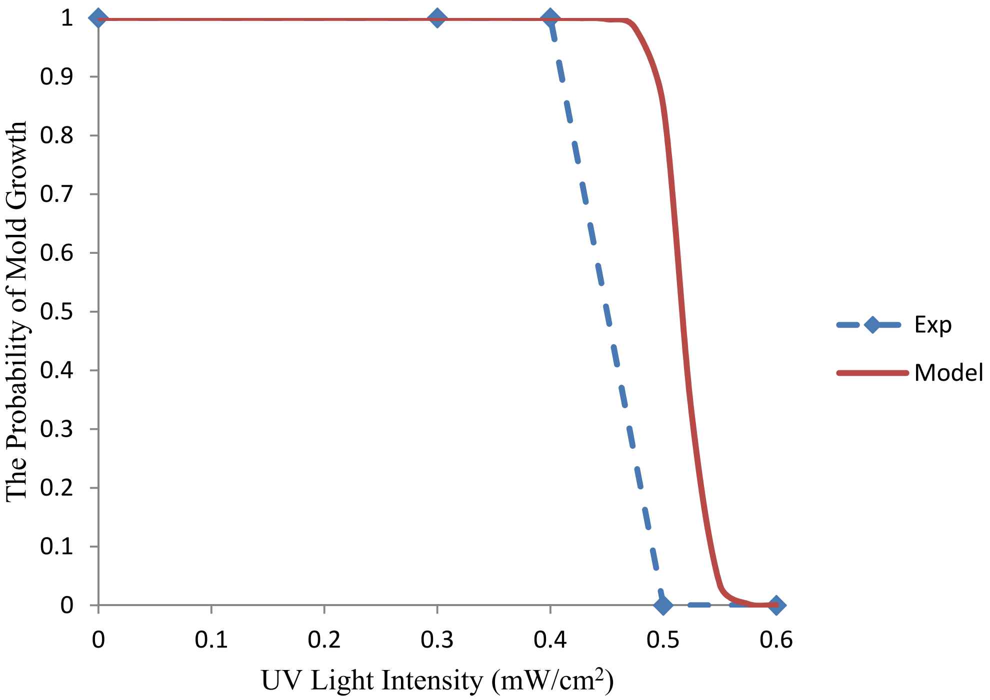
0.3
0.4
0.5
0.6
UV Light Intensity (mW/cm^2)
Exp
Model

(c)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0
The Probability of Mold Growth
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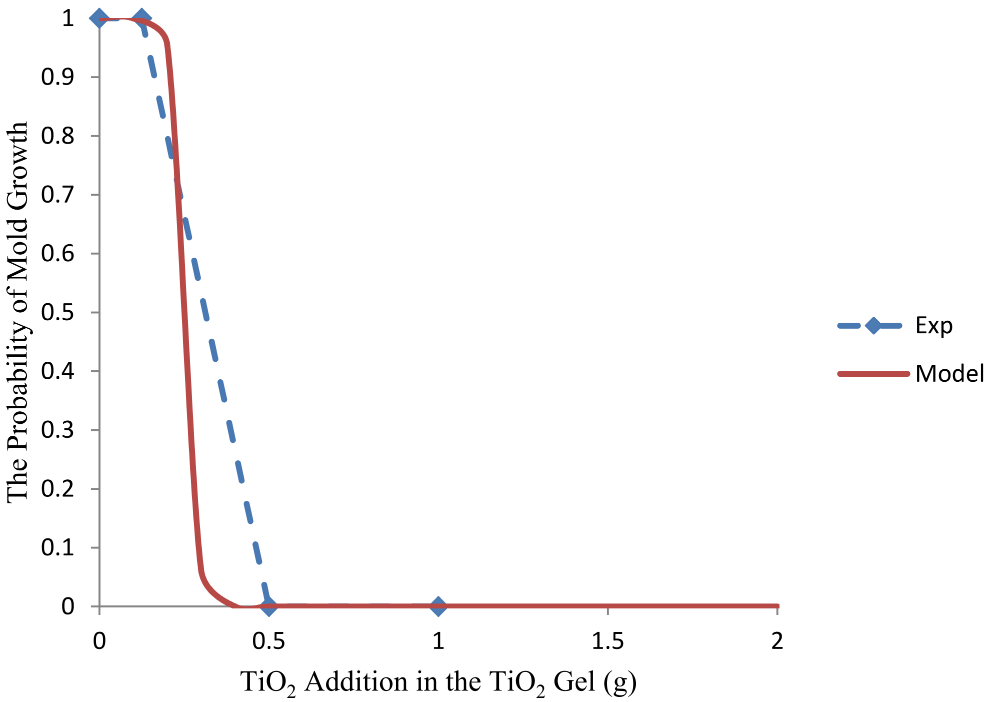
0.1
0.2
0.3
0.4
0.5
0.6
UV Light Intensity (mW/cm^2)
Exp
Model

(d)


1
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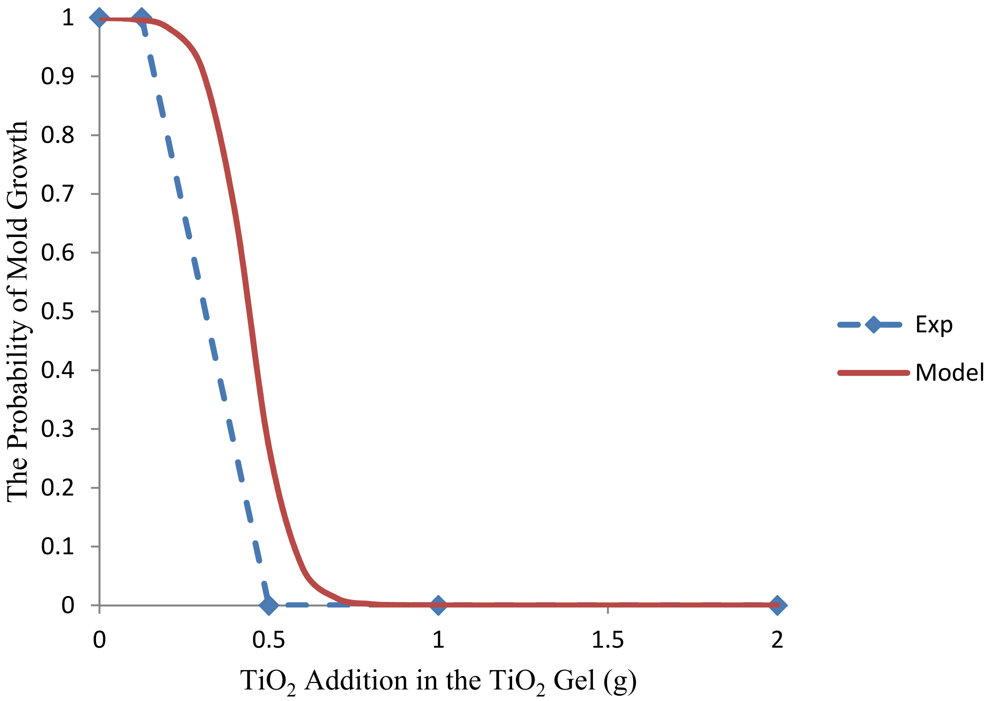
0.3
0.2
0.1
0
The Probability of Mold Growth
0
0.5
1
1.5
2
TiO$_2$ Addition in the TiO$_2$ Gel (g)
Exp
Model

\

(e)


1
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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
The Probability of Mold Growth
0
0.5
1
1.5
2
TiO$_2$ Addition in the TiO$_2$ Gel (g)
Exp
Model

(f)

Figure 6.4 The examples of the comparison between experimental data and logistic model: (a) The effect of UV light exposure time at 1 g TiO_2 addition and 0.5 mW/cm^2 UV light intensity; (b) The effect of UV light exposure time at 1 g TiO_2 addition and 0.6 mW/cm^2 UV light intensity; (c) The effect of UV light intensity at 1 g TiO_2 addition and 12 hours per day UV light exposure time; (d) The effect of UV light intensity at 1 g TiO_2 addition and 8 hours per day UV light exposure time; (e) The effect of TiO_2 addition at 0.5 mW/cm^2 UV light intensity and 24 hours per day UV light exposure time; (f) The effect of TiO_2 addition at 0.5 mW/cm^2 UV light intensity and 12 hours per day UV light exposure time.

Generally, the logistic model for the TiO_2 gel under UV light irradiation achieves good accuracy with the analysis of the effects of 3 major factors considered in the model. From the Fig. 6.4, some prediction errors appear in Fig. 6.4 (b) and (d). Through the examination of the experimental data, there is no change in the mold experiment result from 1 g to 2 g TiO_2 addition and from 0.5 to 0.6 mW/cm^2 UV light intensity. However, the model tries to predict the difference, according to the trend obtained in other data, which probably causes the prediction error. The insufficient of data sets may be another reason of this biased prediction. More experiments can be performed in future to refine this model.

6.4. Conclusion

Two statistic models are created for the Ag-TiO_2/H_2O_2 gel without light and the TiO_2 gel under UV light irradiation, respectively. The factors analyzed in the mold growth experiment and the interactions between were considered. In the linear regression model for the Ag-TiO_2/H_2O_2 gel and the logistic regression model for the TiO_2 gel, factors are useful for predicting gel performance with the resultant model showing a good agreement with the experimental data. Those two mold growth models can be used to interpret the experiment result and predict, in the scope of the experiment, the time required for the initial sign of mold growth in the application of the Ag-TiO_2/H_2O_2 gel without light and whether or not the TiO_2 gel can completely prevent the mold growth under UV light irradiation.

Thus, the critical time for the initial sign of mold growth in the application of the Ag-TiO_2/H_2O_2 gel without light will be used to predict the critical time for recovering the mold-unfavored temperature and humidity without showing any mold growth when temperature and humidity is very suitable for the mold growth (such as the situations during a power failure, flood, and hurricane). Furthermore, the model for the TiO_2 gel under UV light irradiation can be used to plan the application of the TiO_2 gel, the installation of UV light bulb and the lighting schedule, or predict the showing of mold growth on the TiO_2 gel. More experiments may be performed to obtain more data for improving the regression models.

Chapter 7

VOC EMISSION MODEL

7.1. Background

The VOC emission data of different building materials can be obtained through the experiment described in Chapter 5, which, however, is expensive and cannot be performed in all situations. Therefore, the VOC emission model is developed for estimating and predicting the VOC emission from building materials.

VOC emission models can be divided into two classes: empirical models and physical models. Empirical models are usually based on the regression of experimental data. There were first order decay models, second order decay models, power law equation models, constant emission models, and instant emission models (Dunn et al., 1987; Tichenor et al., 1991; Chang and Guo, 1992; Clausen et al., 1993; Guo, 2002). Generally, empirical models possessed a good agreement with the experiment result, but they are not correlative with the physical process. Physical models were developed to specify and evaluate the different physical steps in the emission process. In 1993, Tichenor et al (1993) proposed a VOC emission model for wet material called Vapor Pressure and Boundary Layer (VB) model, considering emission as a pure evaporation process and neglecting the diffusion process in the materials. VB model is usually accurate for the beginning few hours of the emission process, because the evaporation dominates during this period. Little et al. (1994) developed a VOC emission model for a dry material-new carpet, simulating diffusion process inside the material and mass transfer process on the surface of material. The method to find the diffusion parameters was also presented. Yang et al. (1999) created a model based on VOC diffusion within the materials including both dry and wet materials. The diffusion coefficient is associated with the VOC concentration in the wet materials. Computed Fluid Dynamics (CFD) was also applied to obtain the parameters for mass transfer process between material and chamber air.

This study is to develop a new VOC emission model with a PCO reaction term for PCO gel coated building materials, based on the small chamber experimental data obtained by James (2005). The new PCO reaction model is introduced to acchieve better accuracy than the previous VOC emission model.

7.2. Model Development and Equations

The previous research made efforts to add the photocatalytic reaction component to the existing emission models for the PCO gel coated building materials (James, 2005). The experimental data used for the development of this model was from the small chamber test for VOC emission on the PCO gel coated building materials conducted by James (2005). This PCO gel is composed of polyethylene glycol gel (PEG) matrix (framework), semiconductor nanoparticles (TiO_2), a light sensitizing catalyst, and a supplemental oxide (35% H_2O_2). The total VOC concentrations in the small chamber at different time intervals on both pressure treated wood and oil-based paint with or without PCO gel under UV or visible light irradiation were all evaluated by Gas

Chromatographer and Flame Ionization Detector (GC/FID). This experimental data is used to build the new VOC emission model.

As illustrated in Fig. 7.1, the whole emission process in the model can be divided into three steps (detailed description can be found in (James, 2005)):

a) VOC diffusion within the materials.

b) VOC decomposing in the PCO gel.

c) VOC transferring into the chamber.

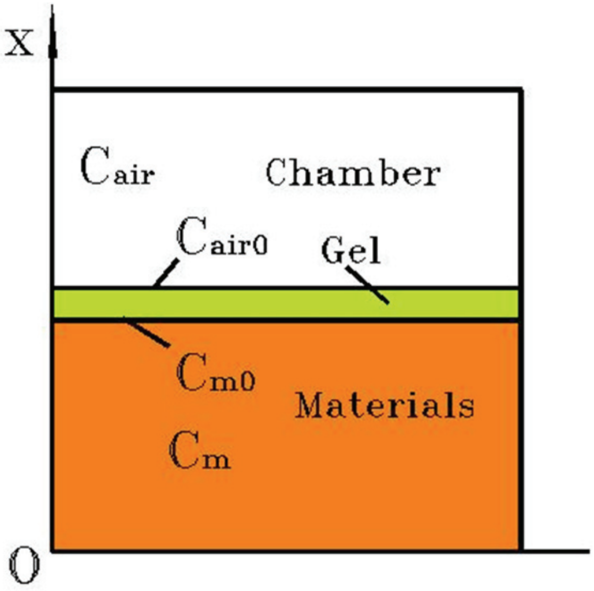

Figure 7.1 The schematic of the building materials coated with the PCO gel.

The step (a) is governed by the second Fick’s law; and the step (c) is governed by the mass transfer coefficient (Little, et al 1994, X. Yang 1999, Hongyu Huang 2002). The step (b) is the most difficult part among the whole modeling process, because the VOC photocatalytic reaction model has not been developed well. For the previous research, the pseudo-first-order reaction model was chosen for describing the VOC photocatalytic reaction process (Eq. 7.1). To simplify the problem, the thickness of the gel is neglected and the reaction is regarded as a surface phenomenon.

$$M_{re} = -K_{re}AC_{m0} \qquad 7.1$$

Where, M_{re}: VOC reaction amount (g)

K_{re}: Reaction coefficient (1/s)

A: Emssion area (m^2)

C_{m0}: VOC concentration at the interface (g/m^3)

The model developed previously for dry materials has an acceptable agreement with the experiment result. However, the modeling result for the PCO gel coated oil-based paint predicts greater reduction of VOC emission than the experiment result, which suggests that the model for wet materials still needs modification for achieving better accuracy (Fig. 7.2 and 7.3).

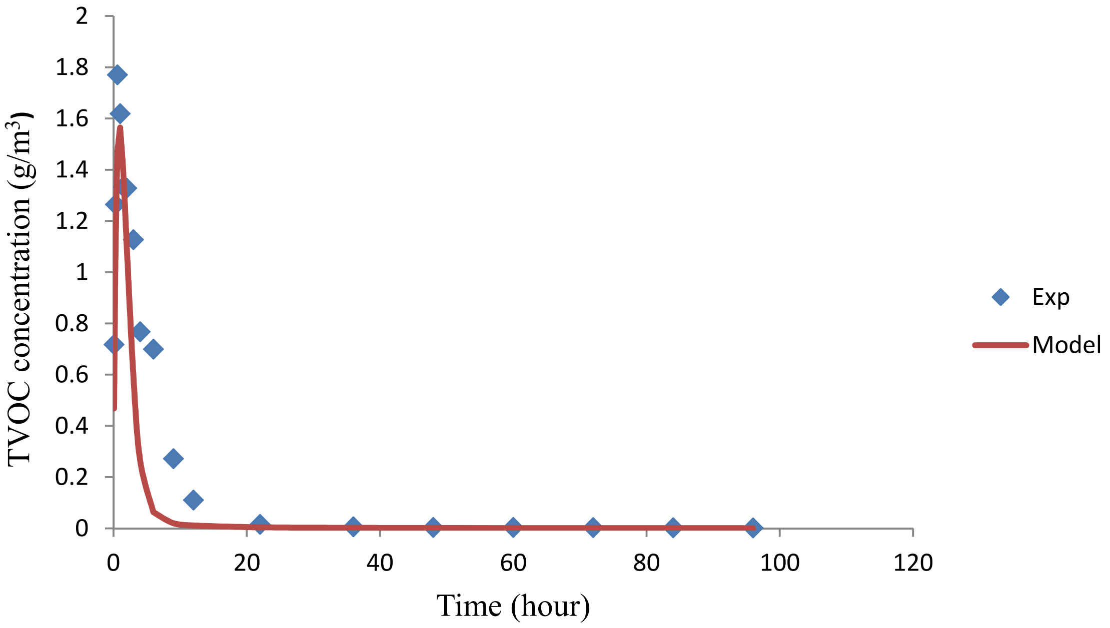

Figure 7.2 Comparison of measure and simulated TVOC emission concentrations from oil-based paint and PCO gel with UV light (James, 2005)

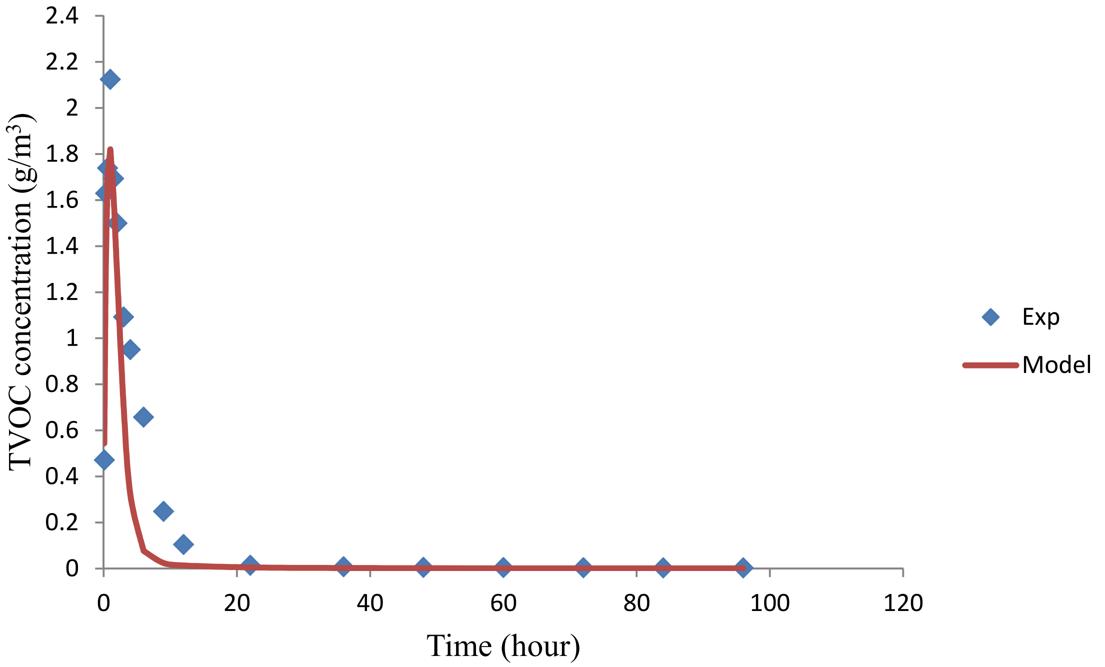

Figure 7.3 Comparison of measure and simulated TVOC emission concentrations from oil-based paint and PCO gel with visible light (James, 2005)

There are two reactions in the previously developed PCO gel: the heterogeneous photocatalytic oxidation reaction by semiconductors and the homogeneous oxidation reaction by hydrogen peroxide. Due to the promotion effect between H_2O_2 and semiconductors, it is difficult to assign different types of reactions (homogeneous and heterogeneous) to both processes. The hydrogen peroxide reaction is dominant at the early stage and diminishes quickly with the consumption of H_2O_2; whereas, the photocatalytic reaction takes place for the whole period of the experiment, which governs the reaction in the late period. Between the early stage and the late stage, there is a transition stage in which both reactions have a similar contribution to VOC reduction. When assuming that the dosage of H_2O_2 is sufficient to maintain a constant concentration and the reactant is more strongly adsorbed on semiconductors than products, the pseudo-first-order reaction model stands for both the hydrogen peroxide reaction and the photocatalytic reaction. However, the pseudo-first-order reaction model is not very accurate for photocatalytic reaction, due to the influencing factors such as pollutant concentration, humidity and temperature. Because the reactions always involve adsorption steps before electron exchange, the adsorption isotherms are expected to play an important role in the kinetic models (Mo et al., 2009). There are many other models for PCO reaction available. The most popular PCO reaction model is Langmuir-Hinshelwood (L-H) model (Eq. 7.2) which considers the equilibrium of adsorption for reactants. The accuracy of this model for the photocatalytic reaction was proved by Peral and Ollis (1992), Sauer and Ollis (1994), Biard et al. (2007), Shiraishi et al. (2007) and Yang et al. (2007).

$$R = K_{re}\frac{K_a C_{m0}}{1+K_a C_{m0}} \qquad 7.2$$

Where, R: reaction rate, (g/m^{2}s)

K_{re}: reaction constant (g/m^{2}s)

K_a: Langmuir adsorption constant (m^3/g)

C_{m0}: VOC concentration of the air adjacent to the reaction surface (g/m^3)

In the early stage, when the hydrogen peroxide reaction is dominant, the whole reaction follows the pseudo-first-order reaction. In the late stage, when the photocatalytic reaction is dominant, the whole reaction fits for the L-H model. In the transition stage, two reaction models are combined with an assumed linear decrease of thr pseudo-first-order reaction constant and an assumed linear increase of the L-H reaction constant. The transition stage is determined by iterations of fitting the experimental data and is found between 0.5 to 3 hours. So, the PCO reaction for the new VOC emission model is shown in Eq. 7.4.

The following assumptions were made in development of this model:

a) The transient VOC diffusion in material can be described by one-dimensional Fick's law equation. VOC gradients are considered the only driving force for mass transfer, and there is no chemical reaction inside the material.

b) The material is homogeneous, and the VOCs in the material are distributed evenly.

c) The parameters of main VOC species are used to represent the parameters of TVOC.

d) Steady state air stream flows over the surface of material in the chamber.

e) The VOC diffusion in the gel layer is neglected.

f) The VOCs at the material-gel interface are in thermodynamic equilibrium.

g) A completely mixing model is assumed in the chamber.

h) At the early stage of VOC emission, a pseudo-first-order equation is used to represent the degradation of VOC in the PCO gel; at the late stage of VOC emission, a L-H model represents the photocatalytic reaction; at the transition stage, a linear correlation is assumed to describe the transition from the pseudo-first-order equation to the L-H model.

Therefore, the governing equations (Eq. 7.3 and Eq. 7.4) for the whole model were developed as follows:

$$\begin{cases} \frac{\partial C_m}{\partial \tau} = \frac{\partial}{\partial x}\left(D_m \frac{\partial C_m}{\partial x}\right) & \mathit{Materials} \\ C_{m0} = K_{ma} C_{air0} & \mathit{Surface} \\ \frac{\partial C_{air}}{\partial \tau} V = N\,(C_{in} - C_{out}) + M_{re} + h_x A\,(C_{air0} - C_{air}) & \mathit{Chamber} \end{cases} \qquad 7.3$$

$$M_{re} = \begin{cases} -K_1 A C_{m0} & 0 \le t \le 0.5 \\ -K_{re1} A C_{m0} - K_{re2} A \frac{K_a C_{m0}}{1+K_a C_{m0}} & 0.5 < t < 3 \\ -K_2 A \frac{K_a C_{m0}}{1+K_a C_{m0}} & t \ge 3 \quad \mathit{Reaction} \\ K_{re1} = (-5.76 \times 10^{-8} t + 1.73 \times 10^{-7}) K_1 & \\ K_{re2} = (1.1904t - 0.5952) K_2 & \end{cases} \qquad 7.4$$

Where, C_m: VOC concentration in the materials (g/m^3)

D_m: VOC diffusion coefficient in the materials (m^2/s)

M_{re}: VOC reaction amount (g)

K_1: Reaction coefficient in the early stage (1/s)

K_2: Reaction coefficient in the late stage (g/m^{2}s)

K_{re1}: Reaction coefficient in the transition stage for pseudo-first-order reaction (1/s)

K_{re2}: Reaction coefficient in the transition stage for L-H model (g/m^{2}s)

K_a: Langmuir adsorption constant (m^3/g)

A: Emssion area (m^2)

C_{m0}: Initial VOC concentration in the materials (g/m^3) or VOC concentration in the gel at the interface (g/m^3)

K_{ma}: Henry law constant

C_{air0}: VOC concentration in the air at the interface (mg/m^3)

C_{air}: VOC concentration in the air (mg/m^3)

V: Volume of the chamber (m^3)

N: Air flow rate (m^3/s)

C_{in}: VOC concentration of inlet (mg/m^3)

C_{out}: VOC concentration of outlet (mg/m^3)

h_x: Mass transfer coefficient (m)

x: Thickness of material (m)

For dry materials, D_m is a constant, but for wet materials, D_m is a function of Cm. The equation for calculating D_m for wet materials is developed by He (2003) in Eq. 7.5.

$$D_m = D_{m0}\left(\frac{C_m}{C_{m0}}\right)^3 + D_s e^{-C_m/C_{m0}} \tag{7.5}$$

D_{m0}: Initial diffusion coefficient in the material (m^2/s)

D_s: VOC diffusion coefficient in the dry film of material (m^2/s)

The following relation (Eq. 7.6) can be used for accounting the effect of temperature (Yang et al., 2001):

$$D_{m0} = D_0 \exp\left(-\frac{E_d}{RT}\right) \tag{7.6}$$

Where, E_d is the activation energy (J/mol)

R is universal gas constant (=8.3145J/mol K).

To determine the coefficient D_{m0}, a diffusion coefficient D_0 at a reference temperature T_0 needs to be known.

In the equations, there are many parameters either determined by experimental data or by model simulation. P-xylene, the largest amount of VOC species present in the oil-based paint, is used to calculate the material properties for TVOC emission. K_{ma} is assumed to be the partition coefficient for pure liquid P-xylene. D_{m0} is obtained using a modified version of J.C. Little's model (Little et al., 1994). The initial concentration C_{m0} is determined by VB model. The mass transfer coefficient is estimated from the CFD simulation (Yang, 1999; Yang et al., 2001). The detailed method to calculate those parameters can be found in James (2005). The reaction constant and Langmuir adsorption constant are obtained by fitting the reaction curve. The curve is generated by the experimental data after 2 hours since the data before that is not stable. The chamber needs 1.5 hours or 2 hours to achieve completely mixing. All the parameters used in the model are displayed in Table 7.1.

Table 7.1 Parameters Used in Developing New VOC Emission Model

Parameters	Values
Initial concentration in the material, C_{m0}	3.613×10^{5} g/m^{3}
Partition coefficient at the material-air interface, K_{ma}	6250
Initial diffusion coefficent in the material, D_{m0}	1.0×10^{-7} m^{2}/s
Diffusion coefficient in dried material, D_s	2.5×10^{-13} m^{2}/s
Mass transfer coefficient, h_x	1.172×10^{-3} m/s
Air exchange rate, N	1 hr^{-1}
Material area, A	0.0056 m^{2}
Material thickness, x	0.000924 m
Chamber volume, V	0.053 m^{3}
Pseudo-first-order reaction constant, K_1	1.44×10^{-7} m/s UV
	1.37×10^{-7} m/s VI
Langmuir reaction constant, K_2	2.98 g/m^{2}s UV
	2.74 g/m^{2}s VI
Langmuir adsorption constant, K_a	2.49×10^{-8} m^{3}/g UV
	2.12×10^{-8} m^{3}/g VI

The initial chamber VOC concentration is assumed to be 0 and the initial material VOC concentration is homogenous in the material and equal to C_{m0}. The initial condition of the model is described in Eq. 7.7.

$$\begin{cases} C_m(x,0) = C_{m0} \\ C_{air}(0) = 0 \end{cases} \qquad 7.7$$

7.3. Model Result and Discussion

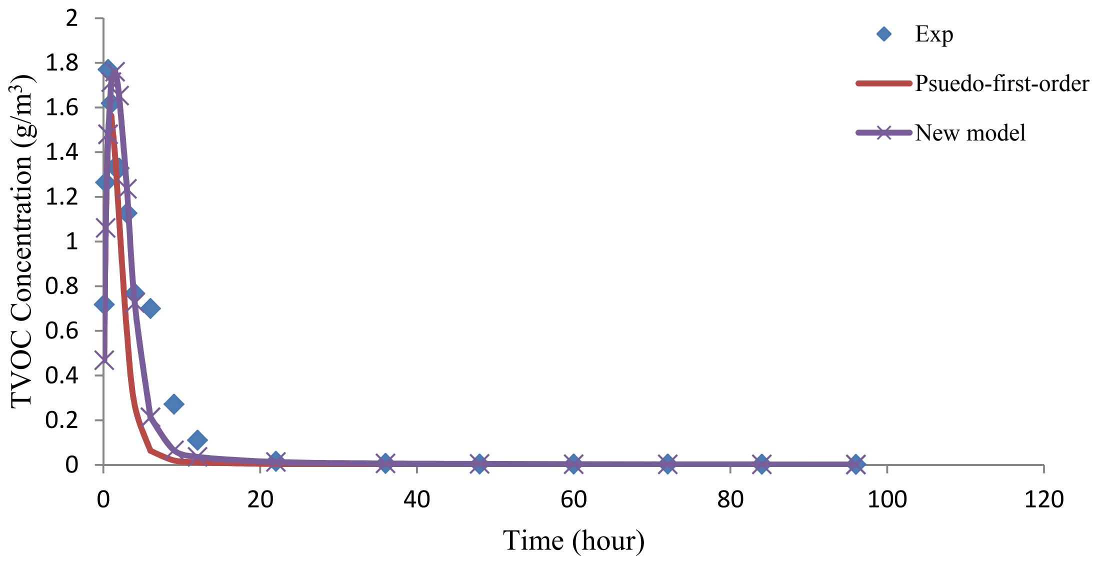

Figure 7.4 Comparison of TVOC emission concentration from oil-based paint with PCO gel under UV light irradiation: experiment, old model and new model.

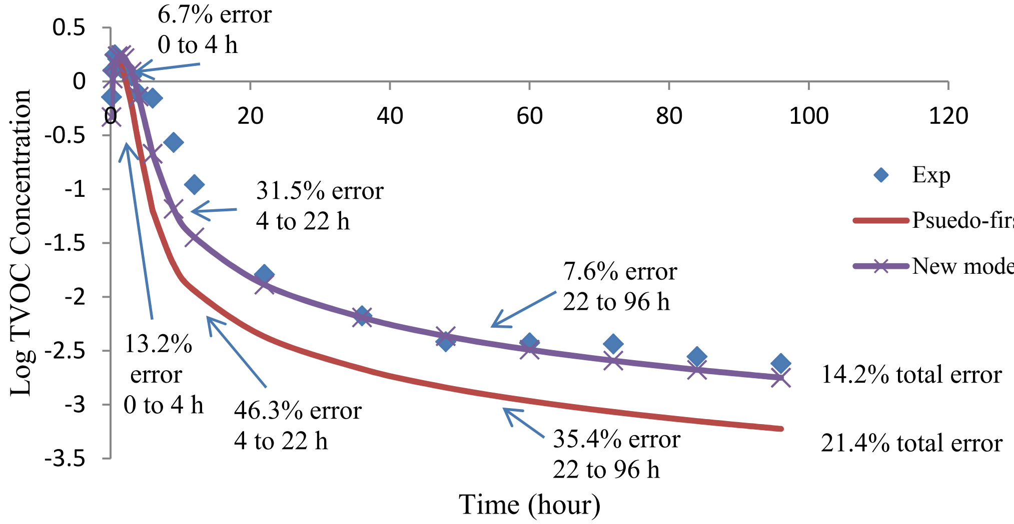

Figure 7.5 Comparison of Log TVOC emission concentration from oil-based paint with PCO gel under UV light irradiation: experiment, old model and new model.

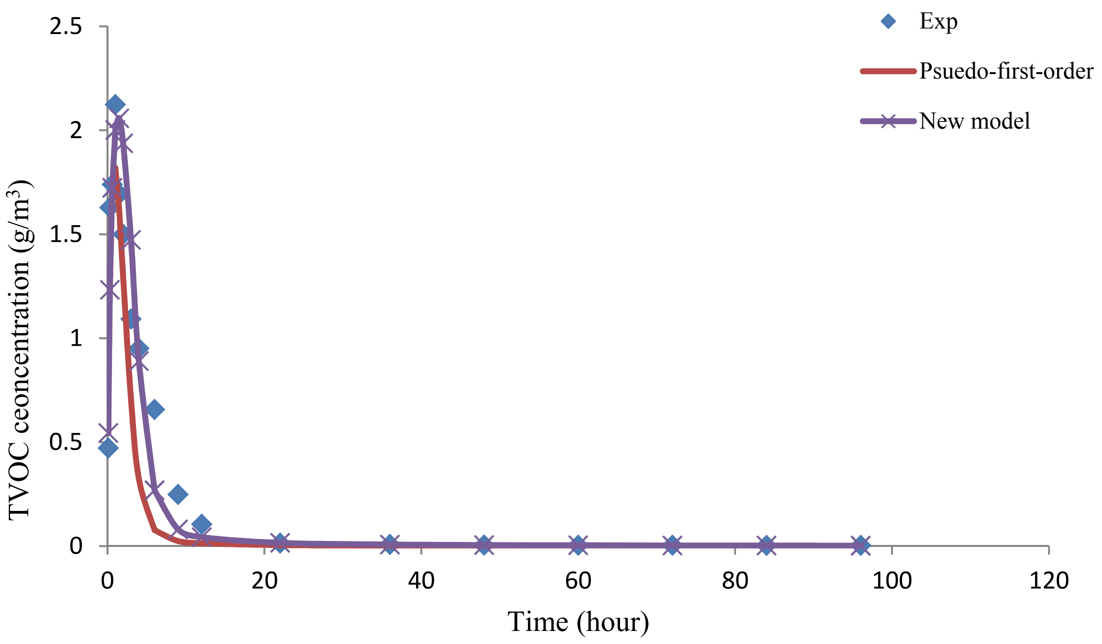

Figure 7.6 Comparison of TVOC emission concentration from oil-based paint with PCO gel under visible light irradiation: experiment, old model and new model.

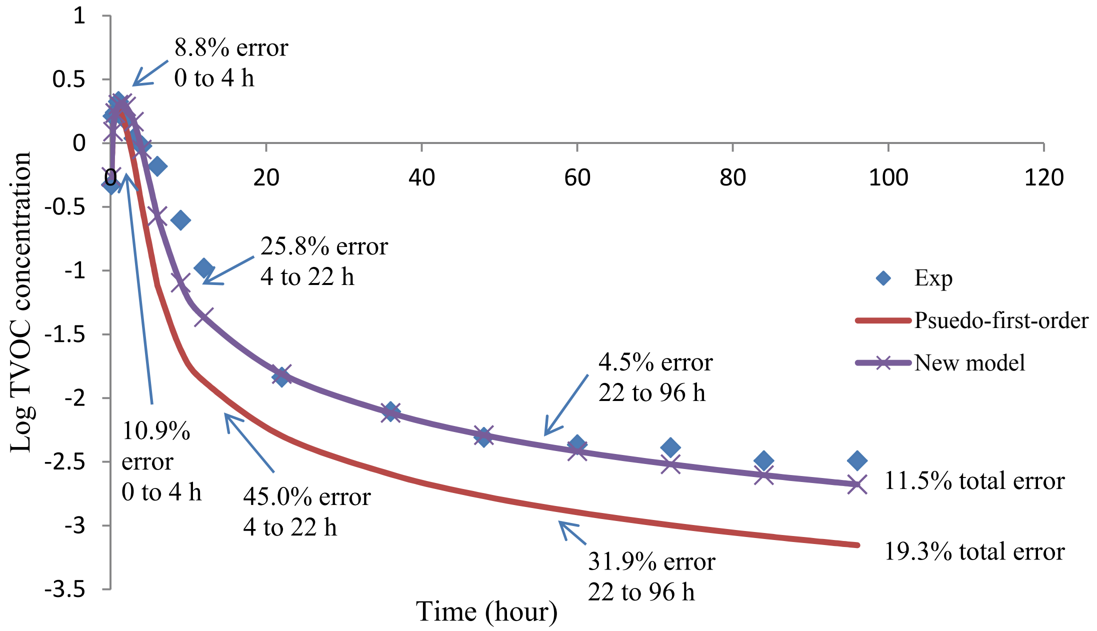

Figure 7.7 Comparison of Log TVOC emission concentration from oil-based paint with PCO gel under visible light irradiation: experiment, old model and new model.

From Fig. 7.4, 7.5, 7.6, and 7.7, the new model has a better agreement with the experimental data than the pseudo-first-order reaction model, especially in long-term prediction. The total root-mean square (RMS) error for the new model is 14.2% with UV light and 11.5% with visible light, which are both smaller than the previous model-21.4% with UV light and 19.3% with visible light. Furthermore, the new model is more suitable for long-term prediction-7.6% with UV light and 4.5% with visible light RMS error after 22 hours, compared to the previous model-35.4% with UV light and 31.9% with visible light. The log value of VOC concentration is used to enlarge the error in small concentrations. There is a big error for the pseudo-first-order reaction model after 6 hours and greater reduction of VOC emission is predicted as shown in Fig. 7.5 and 7.7. In the new model, the L-H model is added for long-term prediction of VOC emission, which is more suitable for the photocatalytic reaction dominated stage. In the early stage of VOC emission, the pseudo-first-order reaction assumes the constant reaction of hydrogen peroxide without decrease. However, H_2O_2 is consumed rapidly by the large amount of VOC emitted from oil-based paint at the beginning. That is why the pseudo-first-order reaction model predicts greater reduction of VOC emission. The transition stage is proposed for the reaction transition from hydrogen peroxide reaction to photocatalytic reaction because of the decrease of H_2O_2 in the PCO gel. Since H_2O_2 has better reaction efficiency than the photocatalytic reaction when VOC concentration is high at the early stage, the new model predicts less reduction of VOC emission and is more suitable for the experimental data at the early and transition stages of VOC emission. Though, there is still a small error for the new model between 4 and 22 hours. The error may be caused by the unstable chamber concentration at the beginning, the unknown hydrogen peroxide diminishing rate, the unverified time for reaction transition process, the assumed linear correlation of reaction constant and time in the transition stage, and/or the deactivation of the photocatalyst under the high VOC concentration.

7.4. Conclusion

In the previously developed VOC emission model for wet materials, the reaction model for the PCO gel used was the pseudo-first-order reaction equation, which did not match the experimental data well, predicting greater reduction of VOC emission from oil-based paint with the PCO gel under either UV or visible light irradiation. The assumption that the hydrogen peroxide oxidation reaction is a constant reaction might not be appropriate due to the rapid decrease of H_2O_2 in the PCO gel, because the high VOC concentration is generated from oil-based paint. Also, the photocatalytic reaction is dominant in the late stage of VOC emission, which is more suitable for the L-H reaction model than the pseudo-first-order reaction model, when considering the adsorption of VOCs on the surface of semiconductors. In the new VOC emission model, the VOC diffusion in wet materials and the VOC mass transfer in the chamber remain the same as the previous one. However, the new reaction model for the PCO gel is introduced including three reaction stages: the hydrogen peroxide reaction stage (the early stage), the transition stage, and the photocatalytic reaction stage (the late stage). In the hydrogen peroxide reaction stage, the pseudo-first-order reaction is assumed. The new model simulates the reduction of H_2O_2 and the reaction transition from hydrogen peroxide dominated reaction to photocatalytic dominated reaction by adding a transition stage with the linear decrease of pseudo-first-order reaction constant and the linear increase of L-H reaction constant. In photocatalytic reaction stage, L-H model is found to be more suitable. Therefore, the new VOC emission model fits better for the experimental data than the old model, even though there is still a small error for the simulated VOC concentration between 4 and 22 hours.

A comprehensive numerical model was developed for VOC emission from building materials with a PCO gel coating. The VOC oxidation reaction was considered in the PCO gel. With physical properties of building materials (initial material VOC concentration, diffusion coefficient, partition coefficient and mass transfer coefficient), reaction parameters of PCO gels and small chamber experimental data, this model can be used to predict VOC emission reduction from different building materials coated with different PCO gels in different indoor environment conditions. The new VOC emission model also provides a way to solve the complicated oxidation process (combining regular oxidation reaction and photocatalytic oxidation reaction) for the PCO gel coated building materials.

Chapter 8

CONCLUSION AND RECOMMENDATIONS

8.1. Conclusion

This research was conducted on the evaluation of PCO technology for mold/mildew resistance and VOC emission reduction from building materials. Many kinds of PCO gels were developed and tested. The potential to create a multifunctional material based on PCO technology for resisting mold/mildew growth and preventing VOC emission was verified. Several conclusions are made.

a) The delay effect on mold growth found with the Ag-TiO_2/H_2O_2 gel without light or under visible light irradiation may contribute to the mold/mildew resistance in the indoor environment when the conventional methods for mold/mildew resistance temporarily fail such as the situations during a power failure, flood, and hurricane. The delay of mold growth will give people more time to clean and dry out their houses and belongings without mold growth. Without light, a 12-day delay of mold growth was obtained using the Ag-TiO_2/H_2O_2 gel with 2g Ag-TiO_2 added and 35% H_2O_2 mixed at 2:3 volume ratio of H_2O_2 to Ag-TiO_2 gel in preparation. Under visible light irradiation, the Ag-TiO_2/H_2O_2 gel was also the most effective PCO gel with a 8-day delay of mold growth, which, however, was shorter than the same Ag-TiO_2/H_2O_2 gel in the condition of no light with a 10-day delay due to the light-induced deterioration of Ag-TiO_2, unlike the enhancement of mold/mildew resistance of the TiO_2/H_2O_2 gel by visible light.

b) The TiO_2 gel would have a potential to be used in the indoor environment for preventing mold growth in warm, humid climates. Under UV light irradiation, the TiO_2 gel achieved complete mold/mildew inhibition. The optimized condition for the complete prevention of mold growth was the TiO_2 gel with 1g TiO_2 (P25) added in preparation and 8 hours per day UV light exposure at 0.5 mW/cm^2 intensity. When the TiO_2 gel is applied to the indoor surfaces, the UV light bulb can be installed and turned on for the total 8 hours per day if there are no people in the room such as during the night of office buildings, during the day of residential buildings, and anytime of non-occupancy.

c) H_2O_2 alone and/or the light irradiation used in the experiment can not resist mold/mildew growth. Without the application of PCO gel and paint samples, no mold/mildew resistance was observed from UV (365 nm) or visible light. H_2O_2 alone could not be preserved on the filter papers after the drying period, also exhibiting no mold/mildew resistance.

d) The addition of 3% H_2O_2 made no difference to the mold/mildew resistance of PCO gels. Whereas, 35% H_2O_2 promoted the mold/mildew resistance of many kinds of PCO gels in the condition of no light or visible light. With the addition of 35% H_2O_2 in PCO gels, the adsorbed H_2O_2 on the surface of semiconductors (TiO_2 or Ag-TiO_2) survived through the drying period of filter papers, resulting in the antifungal effect by H_2O_2 itself and the activation of semiconductors for visible light activity. In the experiment, the addition of 35% H_2O_2 in PCO gels extended the mold/mildew inhibition period. Meanwhile, the longer delay period on mold growth was found with the TiO_2/H_2O_2 gel under visible light than that without light, which can be attributed to the visible light response of the TiO_2/H_2O_2 gel induced by the addition of 35% H_2O_2.

e) The PCO gels, found effective on mold/mildew resistance, can also be used to reduce the VOC emission from building materials under UV or visible light irradiation. The addition of 35% H_2O_2 that could not only increase the photocatalytic efficiency but also lower the peak VOC concentration is recommended for the reduction of VOC emission from building materials. In the VOC emission test, the reduction of VOC emission from PCO gel (TiO_2 gel an Ag-TiO_2/H_2O_2 gel) coated building materials under UV or visible light irradiation was confirmed. With the aid of H_2O_2, the Ag-TiO_2/H_2O_2 gel exhibited better photocatalytic efficiency on VOC degradation-above 50% reduction of the total VOC emission from both "dry" and "wet" building materials than the TiO_2 gel. Even though the deterioration of Ag-TiO_2 observed in the mold experiment under light irradiation could still happen in the VOC emission experiment, Ag-TiO_2 still maintained some photocatalytic activity on VOC degradation under either UV or visible light irradiation.

f) Two mold/mildew growth models were created based on the regression analysis of the mold experimental data. In the linear regression model for the Ag-TiO_2/H_2O_2 gel and the logistic regression model for the TiO_2 gel, factors are useful for predicting gel performance with the resultant model showing a good agreement with the experimental data. The mold/mildew growth model for the Ag-TiO_2/H_2O_2 gel can predict the critical time for mold growth to show on building materials in mold-favored conditions during emergency situations (such as a power failure, flood, and hurricane). Also, the mold/mildew growth model for the TiO_2 gel can be used to plan the application of the TiO_2 gel, the installation of UV light bulb and the lighting schedule in the indoor environment. The new VOC model can predict VOC emission reduction from different building materials coated with different PCO gels in different indoor environment conditions.

g) The new VOC emission model was built based on an existing model, considering the PCO gel on the surface of building materials. The new reaction model in the PCO gel is incorporated to obtain better accuracy than the previous VOC emission model in the case of oil-based paint. Langmuir-Hinshelwood model is introduced to describe the PCO reaction in the PCO gel, leading to a better prediction for the long-term VOC emission. The whole reaction period for the PCO gel is divided into three stages: the hydrogen peroxide reaction stage (the early stage), the transition stage, and the photocatalytic reaction stage (the late stage). It provides a way to solve the complicated oxidation process (combining regular oxidation reaction and photocatalytic oxidation reaction) for the PCO gel coated building materials.

8.2. Recommendations

This research proved the potential for PCO technology to solve both the indoor mold/mildew and VOC problems. Since the PCO gel developed as a coating material can be energy-efficient and sustainable, finding a more applicable and realistic solution to those indoor environmental problems involving PCO technology is important and therefore requires more time and effort. It is highly worth conducting further research for improving PCO gels in resisting mold/mildew growth and preventing VOC emission from building materials.

The following are recommendations for future study.

a) More stable Ag-TiO_2 or other visible-light-driven photocatalysts are needed, since the deterioration of Ag-TiO_2 was observed in the mold/mildew growth tests along with the decline of photocatalytic efficiency under light irradiation. Visible light is more practical than UV light in the indoor environment. It is worth further investigating deterioration of visible-light-driven photocatalysts.

b) Further research is required to find a way to stabilize H_2O_2 in the coating material, or more stable substitutes for H_2O_2 need to be explored. The addition of H_2O_2 into photocatalysts was found effective in resisting mold/mildew growth and preventing VOC emission from building materials. However, H_2O_2 is not very stable, leading to the mold/mildew inhibition loss of the PCO gels, eventually.

c) Modification of the PCO gels is necessary for real applications. Enhancing the holding capacity of the gel for photocatalysts is a way to further increase the mold/mildew resistance. The physical properties of the PCO gels are also required to be improved for better coating and adherance to building materials.

d) More mold/mildew growth experiments should be performed to obtain more experimental data for improving the mold/mildew growth models. More experimental data means better precision and accuracy for regression analysis. The present errors in the mold/mildew growth models may be reduced.

e) The error in the VOC emission model between 4 and 22 hours of the VOC emission tests demands further investigation, even though the total accuracy of the new VOC emission model is much better than the previous one. The possible reasons for this error include the unstable chamber concentration at the beginning, the unknown hydrogen peroxide diminishing rate, the unverified time for reaction transition process, the assumed linear correlation of the reaction constant and time in the transition stage, and/or the deactivation of the photocatalyst under the high VOC concentration.

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