Indoor air purification using heterogeneous photocatalytic oxidation

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**INDOOR AIR PURIFICATION USING
HETEROGENEOUS PHOTOCATALYTIC
OXIDATION**

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2013

INDOOR AIR PURIFICATION USING HETEROGENEOUS PHOTOCATALYTIC OXIDATION

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ABSTRACT

Heterogeneous photocatalytic oxidation (PCO) is a very promising technology for mineralization of gaseous contaminants such as formaldehyde and other volatile organic compounds (VOCs) existing in the typical indoor environment. Current problems encountered when implementing PCO for indoor air purification include ineffective immobilization, low degradation efficiency and lack of UV light source indoors. This project experimentally investigated the photocatalyst immobilization method as well as visible-light induced PCO of gaseous formaldehyde. An easy and cost-effective spray-coating method was established through optimizing the substrate material, stabilization temperature, binder types and binder dosages. The effects from different limiting factors for the visible-light PCO reaction, such as volumetric flow rate, contaminant initial concentration, relative humidity, visible light intensity and photocatalyst loading amount, were carefully tested in a fix-bed PCO reaction system. The possible mechanisms of visible-light PCO of gaseous formaldehyde were explored by using two visible-light active photocatalysts and comparing between UV-PCO and visible-light PCO processes. A prototype indoor air cleaner equipped with visible-light PCO component was designed based on the scientific findings of the lab scale experiment. Its cleaning effectiveness was evaluated through environmental chamber test. The result shows considerable removal efficiency for both formaldehyde and other existing VOCs such as toluene. Relatively high clean air delivery rate (CADR), in comparing with other commercialized PCO air cleaners, was achieved for gaseous contaminants indoors with energy-efficient LED light source. This study provides a better understanding of visible-light induced PCO of gaseous contaminants, which might be used for design and preparation of high-performance indoor air cleaning devices. The spray-coating method is effective, economical and can be easily applied for large-scale photocatalyst immobilization.

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CHAPTER 1

Introduction

1.1. Problem Statement

1.1.1. Indoor air pollution (IAP) and its health effects

Prior to 1970s, air pollutions in outdoor environment had been considered as the major risk for human health, generally due to the occurrences of several major air pollution events such as the London smog and the L.A. photochemical smog, etc (Stolwijk 1992). Comparing to outdoor air pollutions, problems raised by IAP during this period were occasionally investigated with less interest (Harrison 1997). In recent years, although outdoor air pollution which is particularly associated with vehicle exhausts still remains great concerns, there has been increasing recognition that IAP is of equal or greater significance to human health (Schwartz 2004). As early as in 1995, the US Environmental Protection Agency (EPA) considered IAP as one of the top environmental risks (U.S.EPA 1995). More and more researches have confirmed that IAP contributes significantly to human exposure to hazardous pollutants both in industrialized or developing countries (Bruce, Perez-Padilla et al. 2000; Rojas-Bracho, Suh et al. 2000; Sarnat, Koutrakis et al. 2000; Bardana 2001; Jaakkola 2002; Hodgson and Levin 2003).

Reasons for this include: the majority of their time people spend indoors; the wide and varied range of indoor emission sources; and the higher concentration of certain pollutants indoors compared with outdoors, for example, formaldehyde, and other pollutants from environmental tobacco smoke (ETS). According to a survey of the

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human activity pattern of US residents conducted by Klepeis *et al.* (Klepeis, Nelson et al. 2001), people spend an average of 87% of their time in enclosed buildings and about 6% of their time in enclosed vehicles, totally over 90% of their time in an enclosed environment. The exposure to IAP can be even worse in developing countries where the burning of biomass indoors for cooking and heating contributes to extremely high levels of particulates and combustion related pollutants (Smith 2000; Ezzati and Kammen 2002; Briggs 2003; Franklin 2007).

In Table 1-1, the major indoor air pollutants and their corresponding sources are identified. In general, indoor air pollutants are emitted by the fabric of buildings, and may also be a by-product of the activities that are undertaken within them (Jones 1999). Despite the possible outdoor contributions to IAP, many air pollutants have considerably higher concentrations indoor than outdoors. In particular, some important indoor air pollutants such as formaldehyde and other VOCs (xylenes, toluene, trichloroethylene, e.g.) are consistently found to be higher indoor than outdoors (Jurvelin, Vartiainen et al. 2001; Adgate, Church et al. 2004; Jung, Artigas et al. 2011). In a review by Wallace (Wallace 1996) of indoor particle levels in U.S. homes, indoor PM concentrations can be twice those measured outdoors, where cigarette smoking and cooking activity are two major emission sources.

Although the likelihood that an individual will get sick from exposure to certain contaminant depends on several factors such as personal sensitivity to that contaminant, concentration of the contaminant, current health condition of the individual, as well as exposure frequency and duration, indoor air pollutants have been confirmed to have the potential to cause and exacerbate a variety of adverse health effects in humans, ranging from acute and chronic respiratory symptoms and diseases to cancers (Berglund, Brunekreef et al. 1992; Bascom, Kesavanathan et al. 1995; Žuškin, Schachter et al. 2009). Since early 1980s, a series of symptoms that may be experienced by building occupants, such as irritation of eyes, nose and neck, dry mucous membranes, skin rashes, tiredness, headache, and nausea, have been described as the ‘Sick Building Syndrome’ (SBS). In comparing to the naturally ventilated buildings, SBS are more commonly observed in modern energy-efficient

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tight buildings, particularly buildings installed with mechanical heating, ventilation, and air-conditioning (HVAC) systems, which to some extent verified that SBS is associated with poor indoor air quality (IAQ).

Table 1-1 Major indoor air pollutants and their main emission sources

Pollutants	Emission sources
Volatile Organic Compounds (VOCs)	
<i>Formaldehyde (HCHO)</i>	Composite wood products (e.g. particleboard), furnishings, insulations, ETS, paints, detergents, cosmetics
<i>Aromatic hydrocarbons</i>	Fuel combustion, building materials,
<i>Halogenated hydrocarbons</i>	cleaning products, aerosol sprays,
<i>Terpenes</i>	paints, adhesives, solvents, pesticides, ETS, outdoors
Environmental Tobacco Smoke (ETS)	Cigarettes, cigars, pipes
Particulate matter (PM)	Fuel combustion, ETS, general activities, outdoors
Allergens (Biological)	
<i>House dust mite</i>	Dust, bedding, carpeting
<i>Animal dander</i>	Pets
<i>Fungi (moulds)</i>	Dampness/moisture
<i>Pollens</i>	Plants
<i>Cockroaches</i>	Pests
Nitrogen dioxide (NO ₂)	Unvented gas/kerosene appliances, fuel combustion, vehicle emission in garage, outdoors
Carbon monoxide (CO)	Fuel combustion, unvented gas/kerosene appliances, ETS
Carbon dioxide (CO ₂)	Metabolic activity, combustions
Ozone (O ₃)	Ozone generator, ionizer, outdoors

1.1.2. Current indoor air purification technologies and limitations

Despite the commonsense IAQ control strategies, such as source control and effective ventilation to keep adequate fresh air supply, air purification techniques have been steadily growing up over the past two decades aiming to provide improved IAQ to building residents. According to a survey of homes across the U.S. which was conducted by the Association of Home Appliance Manufacturers (AHAM) in 2002, 3 out of 10 households in the States own at least one type of air cleaning devices (Shaughnessy and Sextro 2006). Reasons for this are: source control, in most circumstances, is relatively “uncontrollable” due to different activity patterns and life styles such as ways of cooking, preferences in choosing building materials and household products, smoking and/or other general activities at home, etc; while increasing ventilation might also result in introducing more outdoor pollutants into indoors.

Based on the physical and chemical properties of different kinds of indoor air pollutants, indoor air purification techniques can be classified as particle removal, gaseous pollutant removal and biological pollutant elimination. Technically, air purification techniques are usually classified according to their cleaning mechanisms as filtration based, adsorption based and reaction based cleaning techniques. Table 1-2 presents the classification of current available indoor air purification technologies. Most of the listed technologies are now used in commercialized indoor air cleaners; however, the performances are varied a lot due to the limitations of the technologies.

The high-efficiency particulate air filter (HEPA) is usually used in the mechanical filtration based air cleaners to remove 99.97% of particles greater than 0.3 μm from the air that passes through. However, the use of HEPA filter will increase airflow

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resistance and require high capacity fan or motor to accommodate with. Usually a typical residential air cleaning system adopted with HEPA filter will be very noisy due to the high capacity motor used. Most importantly, HEPA filtration itself has no effect on removal of gaseous pollutants such as VOCs.

Table 1-2 Classification of current indoor air purification technologies

Category	Technology	Target pollutant	Mechanism
Filtration based	Mechanical air filter	Particle matters (PM), dust, pollen	Particles captured on filter materials such as HEPA
	Electrostatic precipitator	Airborne particles	Charged particles accumulated on collector with opposite charge
Adsorption based	Gas-phase adsorber	Gaseous pollutants	Gaseous pollutants adsorbed on sorbent like active carbon, zeolite, e.g.
	Bio-scrubber	NO _x , CO, CO ₂ , hydrocarbons	Pollutants digested by certain microbes
	Ion generator (ionizer)	Airborne particles	Charged particles deposited/adsorbed on nearby indoor surfaces
Reaction based	Ozone generator	Gases, biologicals	Pollutants oxidized by ozone
	Ultraviolet germicide	Biologicals	Bacterial/mold spores killed by UV irradiation
	Photocatalytic oxidation (PCO)	Gases, biologicals	Pollutants oxidized by oxidative species generated through photocatalysis

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The adsorption based gas-phase filters, such as active carbon filled, can adsorb gaseous pollutants like VOCs to some extent, but usually have a short lifetime. Refill or exchange will increase the operation cost. And the most important fact is that the sorbent only adsorbs, not decomposes, the gaseous pollutants. The adsorbed pollutants then have a chance to be desorbed into the air again. The UV germicide technology usually requires high UV intensity and long irradiation time to kill bacterial and mold spores. While for the electrostatic precipitator, ionizer and ozone generator, no matter how effective they are, they would generate ozone, either as operation byproduct or intentional emission, which can cause adverse health effect, such as lung irritation, to building residents at very low concentrations (> 0.05 ppm) (U.S.EPA 2007).

Commercialized photocatalytic oxidation (PCO) air purifier has been introduced to the market quite recently. It basically uses UV + TiO_2 photocatalyst to generate hydroxyl radical to oxidize gaseous pollutants and sterilize microorganism. Despite the potential risk of UV exposure, its efficiency is limited by effective coating method and various reaction parameters, which have not been well explored.

1.2. Hypothesis

Based on the above reviews of current scientific knowledge in the research area of heterogeneous PCO of indoor air pollutants, the following hypotheses were formulated:

H1. Low temperature direct coating method can achieve satisfactory result for photocatalyst immobilization.

A convenient and cost-effective spray-coating method is expected to provide

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uniform coatings on different kinds of substrate. This immobilization technique uses catalyst suspension for direct coating at room temperature. No further heat treatment is needed for the coating stabilization. By adding a binding agent in the coating suspension, stable and durable coating can be achieved. It is expected that the amount of binding agent may affect the coating structure and further influence the PCO efficiency.

To verify the performance of this spray-coating method, a conventional dip-coating method will be employed for comparison in terms of coating stability and PCO degradation efficiency of gaseous formaldehyde. The effect of binding agent amount will be evaluated through different coatings with the same photocatalyst loading.

H2. Visible-light PCO of formaldehyde might follow different mechanisms as comparing to UV-PCO process, thus make it less important for the presence of water vapor.

Water vapor is usually considered as an essential factor in UV-PCO process as its content affects the population of hydroxyl radical, which is the dominant oxidative species, as well as the number of effective reaction site. In visible-light PCO process, it is expected that changing of water vapor content can not affect the generation of hydroxyl radicals and so that the PCO degradation efficiency.

A modified fix-bed photo-reactor is used to evaluate the visible-light PCO degradation efficiency of gaseous formaldehyde. Degradation efficiencies on different commercial and lab-synthesized visible-light active photocatalysts will be compared. The influential factors including volumetric flow rate, relative humidity, pollutant initial concentration, visible-light intensity, photocatalyst loading amount will be discussed in details to provide a better understanding of the visible-light PCO of gaseous formaldehyde. By comparing with the UV-PCO of formaldehyde

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under the same reaction system, the mechanism of visible-light PCO of formaldehyde can be explored.

1.3. Objectives

The objectives of this study were

- (1) To design and fabricate a low pressure drop fix-bed photo-reactor that can easily control different kinetic parameters during PCO test,
- (2) To develop new immobilization method and optimize the coating via selecting high surface area substrate material and changing the content of binding agent in coating suspension,
- (3) To evaluate the effects of volumetric flow rate, relative humidity, pollutant initial concentration, visible-light intensity, and photocatalyst loading amount on the visible-light PCO degradation efficiency of gaseous formaldehyde; Understand the degradation mechanism,
- (4) To scale up the visible-light PCO unit to a practical indoor air purifier design; test the performance of the purifier.

1.4. Dissertation overview

This dissertation is presented in seven chapters and one appendix. Material in chapter 4, 5 and 6 is being prepared for publication in peer-reviewed technical journals. The remaining chapters include an introduction to this dissertation including the problem statement, hypothesis and objectives in Chapter 1; the extensive literature review in Chapter 2; the methodology in Chapter 3; and a conclusion section that summarizes the major findings of this work, their significance to the environmental engineering field, and proposed future research in Chapter 7. Brief description of Chapter 4, 5, and 6 are as follow:

Chapter 4 evaluates the stability and reliability of the simple and economical spray

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coating method used for effective photocatalyst immobilization. Effect of binding agent amount on the PCO degradation efficiency of gaseous formaldehyde is evaluated.

Chapter 5 discusses different influential factors of the visible-light PCO of gaseous formaldehyde. The effect of water vapor in visible-light PCO which is different from UV-PCO process is discussed in details. Reaction mechanism of visible-light PCO of gaseous formaldehyde is proposed.

Chapter 6 describes the scale-up design of the visible-light PCO unit. An indoor air purifier prototype is fabricated according to this design. The performance of the air purifier prototype is examined in real indoor environment for elimination of existing common indoor air VOCs. The feasibility of application of PCO for indoor air purification is discussed.

CHAPTER 2

Literature Review

2.1. Volatile organic compounds (VOCs) in the indoor environment

Indoor concentrations of Volatile organic compounds (VOCs) in non-occupational buildings (residential and office buildings, eg.) have been extensively studied since the late 1980s with the development of sampling and measurement methods and the increasing concern of indoor air quality (Salthammer 1999). Table 2-1 lists an overview of several recent studies on concentration levels of typical indoor VOCs detected in different kinds of buildings worldwide.

In general, individual VOC concentration is on sub-ppm level. Total VOC concentration (TVOC) is typically smaller than 10 mg/m³ inside all kinds of non-occupational buildings. However, if ETS involved as an indoor emission source, concentrations of formaldehyde, benzene and other toxic VOCs can reach to extremely high level (Crump, Squire et al. 1997; Singer, Hodgson et al. 2002).

Some most detected VOCs indoors include formaldehyde, toluene, *m.p*-xylenes, α -pinene, and benzene. Concentrations of individual VOCs and TVOC have a decline trend through the past decade, but still can reach high level in newly constructed/furnished indoor environments. Outdoor sources can significantly affect the indoor concentration of certain VOCs, such as benzene, varied to some extent according to outdoor pollution situation and weather conditions.

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Table 2-1 Typical volatile organic compounds (VOCs) indoors and their concentration levels

Source (Time)	Countries (area)	Sample (N)	Most abundant VOCs/TVOC ^a	Concentration Levels/Average
Chan et al. (2011) (Chi Sing, Shun Cheng et al. 2011)	China (southern)	Hotel (13)	formaldehyde toluene <i>m,p</i> -xylenes acetone acetaldehyde	114±84 µg/m ³ 101±133 µg/m ³ 13±9 µg/m ³ 54±24 µg/m ³ 41±42 µg/m ³
Chikara et al. (2009) (Chikara, Iwamoto et al. 2009)	Japan (Fukuoka)	Home (12)	benzene toluene <i>m,p</i> -xylenes α -pinene <i>p</i> -dichlorobenzene	1.1 µg/m ³ 8.9 µg/m ³ 0.9 µg/m ³ 2.1 µg/m ³ 3.6 µg/m ³
Jia et al. (2008) (Jia, Batterman et al. 2008)	USA (Michigan)	Home (159) ^b	benzene toluene <i>m,p</i> -xylenes α -pinene <i>d</i> -limonene TVOC	2.84 ^c µg/m ³ 15.56 ^c µg/m ³ 7.93 ^c µg/m ³ 9.04 ^c µg/m ³ 25.74 ^c µg/m ³ 123.11 ^c µg/m ³
Hippelein (2004) (Hippelein 2004b)	Germany (Schleswig -Holstein)	Home (79)	toluene 2-propanol α -pinene TVOC	19 µg/m ³ 32 µg/m ³ 29 µg/m ³ 373 µg/m ³
Sekhar et al. (2003) (Sekhar, Tham et al. 2003)	Singapore	Office building (5) ^d	formaldehyde TVOC ^e	0.004-0.15 ppm 0.35-2.25 ppm
Ilgen et al. (2001) (Ilgen, Karfich et al. 2001)	Germany (northern)	Home (59/56) ^f	benzene toluene <i>m,p</i> -xylenes	2.38/3.46 µg/m ³ 30.82/25.28 µg/m ³ 7.15/7.11 µg/m ³
Crump et al. (1997) (Crump, Squire et al. 1997)	UK (Garston)	Test house (4) ^g	formaldehyde benzene toluene xylenes undecane TVOC	48 ^h /41 ⁱ µg/m ³ 12 ^h /5 ⁱ µg/m ³ 13 ^h /14 ⁱ µg/m ³ 52 ^h /28 ⁱ µg/m ³ 71 ^h /22 ⁱ µg/m ³ 1731 ^h /484 ⁱ µg/m ³

^aSum of total detected individual concentration, ^bincluding residences in industrial, urban and suburban area, ^cannual mean, ^dtypical office buildings with HVAC system, ^etoluene equivalent, ^f59 homes in rural and 56 in urban area, ^ghighly-insulated non-occupied, ^haverage of 1st year after construction, ⁱaverage of 2nd year after construction.

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Different from other VOCs, formaldehyde usually is separated from the main VOCs stream due to it is not detected by the conventional gas chromatographic methods which are commonly applied to VOC analysis (Maroni, Seifert et al. 1995). At room temperature, formaldehyde is a colorless gas with a pungent, irritating odor. It is largely used as precursor to many other chemicals used in building materials and in its liquid form called ‘formalin’ as disinfectants for preservation of biological specimens. Several adverse health effects can be raised from exposure to formaldehyde through inhalation and/or direct contact (Table 2-2). Since early 1980s, numbers of occupational exposure studies have been carried out to address the potential carcinogenicity of formaldehyde in humans (Jones 1999). It was confirmed that residential exposure to formaldehyde has significant correlation to the happening of nasopharyngeal cancer (Vaughan, Strader et al. 1986). In June 2011, the National Toxicology Program Report on Carcinogens (RoC 12th edition) by the U.S. Department of Health and Human Services changed the listing status of formaldehyde from “reasonably anticipated to be a human carcinogen” to “known to be a human carcinogen” (DHHS 2011).

Table 2-2 Health effects from formaldehyde exposure ^a

Concentration level (ppm)	Observed health effects
<0.05	None reported
0.05-1.0	Odor threshold limit
0.05-1.5	Neurophysiologic effects
0.01-2.0	Irritation of eyes
0.10-25	Irritation of upper airway
5-30	Irritation of lower airway and pulmonary effects
50-100	Pulmonary edema, inflammation, pneumonia
>100	Coma, death

^a Source: Hines *et al.* (Hines, Ghosh et al. 1993)

2.2. Heterogeneous photocatalytic oxidation (PCO) and its application in indoor air purification

2.2.1. Development of PCO technology

The systematic research about photocatalytic reaction started in the late 1960s in Japan, when Fujishima (Fujishima, Honda et al. 1969; Fujishima and Honda 1972) and his colleagues chose UV-illuminated TiO_2 as the positive electrode in their research on photoelectrochemical solar cells to split water into hydrogen and oxygen. Nevertheless, TiO_2 had persistently been concerned for its photo-sensitivity property ever since 1930s. In 1938, Doodeve et al. (Doodeve and Kitchener 1938) first used TiO_2 (rutile) as a photo-sensitizer to bleach dyes under UV irradiation with and without the presence of oxygen. The followed studies focused on the mechanisms of photoadsorption and photodesorption of oxygen and water molecules on TiO_2 and the surface kinetics (Kennedy, Ritchie et al. 1958; Primet, Pichat et al. 1971; Bickley and Stone 1973).

Research on photo-oxidation using TiO_2 as a photocatalyst was first carried out by testing the auto-oxidation of TiO_2 under UV light as well by dispersing the powder particles into alcohols and hydrocarbons solutions (Kato and Mashio 1956). Other earlier works regarding to decomposition through photocatalysis reactions included the photo-oxidation of ammonia using TiO_2 (McLean and Ritchie 1965), and heterogeneous photo-oxidation of isopropyl alcohol on zinc oxide (Ikekawa, Kamiya et al. 1965).

The extensive knowledge accumulated from the development of semiconductor photoelectrochemistry during 1970s had greatly assisted the development of photocatalysis (Heller 1981). Particularly, it finally turned out that TiO_2 performs more excellent for photocatalytically breaking down organic compounds (Fujishima, Rao et al. 2000). Since 1977, when Fank and Bard (Frank and Bard 1977b; Frank and Bard 1977a) first studied the possibility to decompose cyanide and sulfide in TiO_2 aqueous suspension, the interest of applying heterogeneous photocatalytic

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oxidation (PCO) on degradation of environmental pollutants has been greatly enhanced. Up to present, heterogeneous PCO technology has been widely used in environmental protection field such as pollutant decomposition, sterilization, anti-contamination, and self-cleaning surface, etc. Table 2-3 shows some commercialized TiO₂-based photocatalytic products in Japan. It is noted that a significant application of PCO products is in the air-cleaning field.

Table 2-3 Commercialized TiO₂-based photocatalytic products on Japan market (up to 2006)^a

Category	Product	Application
Exterior construction materials	Tiles, glass, tents, plastic films, aluminum panels, coatings	Self-cleaning
Interior furnishing materials	Tiles, wallpapers, window blinds	Self-cleaning, antibacterial
Road-construction materials	Soundproof walls, tunnel walls, road-blocks, coatings, traffic signs and reflectors, lamp covers	Self-cleaning, air-cleaning
Purification facilities	Air cleaners, air conditioners, purification system for wastewater and sewage, purification system for pools	Air-cleaning, water-cleaning, antibacterial
Household products	Fibers, clothes, leathers, lightings, sprays	Self-cleaning, antibacterial
Others	Facilities for agricultural uses	Air-cleaning, antibacterial

^asource from Fujishima and Zhang (Fujishima and Zhang 2006).

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Air purification technique of heterogeneous PCO commonly uses nano-sized photocatalyst powder coated/deposited on certain substrate surface and ultraviolet/visible light to convert organic compounds in indoor air into non-toxic minerals as carbon dioxide (CO_2) and water vapor (H_2O) (Dunnill, Aiken et al. 2009). Taken UV- TiO_2 system as an example, the schematic of the UV-PCO process on VOCs decomposition is illustrated in Fig. 2-1.

Figure 2-1 Schematic diagram of UV- TiO_2 PCO process of VOCs

The reaction mechanism can be easily expressed as follow: When UV light irradiates on TiO_2 surface, an electron (e^-) on the valance band (VB) will be excited by absorbing energy of the incident photons and be ejected to the conduction band (CB), leaving a hole (h^+) on the VB – eq. (2-1); at the same time, the photo-generated e^- and h^+ can be recombined together – eq. (2-2); when contacting with other attached compounds, the photo-generated e^- and h^+ will lead to a series of redox reactions on the CB and VB, respectively – eq. (2-3 to 2-7).

Reduction on CB:

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Oxidation on VB:

When organic compounds are transferred to TiO₂ surface, all the oxidative species, including hydroxyl radical ($\bullet OH$), hole (h^{+}), superoxide radical ($O_2^{\bullet -}$), and hydrogen peroxide (H_2O_2), etc., generated during PCO process will contribute together to the oxidation of the adsorbed organic compounds on TiO₂ surface (Legrini, Oliveros et al. 1993; Hoffmann, Martin et al. 1995; De Lasa, Serrano et al. 2005). However, in UV-TiO₂ system, $\bullet OH$, which has strong oxidative potency, is believed to be the dominant species that oxidize the adsorbed organic pollutants into CO₂ and H₂O (Dunnill, Aiken et al. 2009).

2.2.2. Application of PCO in indoor air purification

2.2.2.1. Using PCO for improving IAQ

Using PCO to decompose gaseous pollutants, such as VOCs, in the indoor air has the following advantages: (1) Energy-efficient (using UV and/or visible light as energy source); (2) Non-selectivity of different kinds of organic pollutants; (3) Complete mineralization (finally oxidized into H_2O and CO_2); (4) Persistent treatment (throughout the lifetime of photocatalysts).

So far, many researches have evaluated whether air purification approaches using the principle of PCO can be applied for improving indoor air quality. Yu et al. (Yu, Lee et al. 2006) studied the correlation between photocatalytic oxidation result and chemical/physical properties of different species of indoor VOCs. For aromatic VOCs, degradation rates had strong relation with their Henry's Law constants, but

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not for other kind of VOCs such as n-hexane and iso-butanol. Hodgson et al. (Hodgson, Destailats et al. 2007) studied UV-PCO of different mixtures of indoor VOCs and concluded that the conversion efficiency generally followed the order: alcohols and glycol ethers > aldehydes, ketones, and terpene hydrocarbons > aromatic and alkane hydrocarbons > halogenated aliphatic hydrocarbons. Aldehydes were found to be produced as byproduct due to incomplete mineralization. Chen and Zhang (Chen and Zhang 2008) also found interference effect among different VOC mixtures during UV-PCO. The more the mixture size, the stronger the interference effect would be. This may due to the incomplete oxidation of certain species, such as aromatics, during PCO process where their intermediates hindered oxidation of other species such as aldehydes and alcohols.

Tompkins et al. (Tompkins, Lawnicki et al. 2005) evaluated the process, technical, and sizing considerations of PCO to treat low-level indoor air contaminants and pointed out the challenges that limit PCO application for air purification were to design PCO device with low pressure drop, make efficient use of light, and employ a stable and durable catalytic system. Kolarik and Wargocki (Kolarik and Wargocki 2010) found PCO device could improve IAQ in rooms polluted by common building materials and appliances (building related sources). However, when pollution sources were human bioeffluents and household products like detergents, the examined PCO device would even worsen the air quality probably due to incomplete oxidation of alcohols.

2.2.2.2. Development of visible-light active photocatalyst

Basically, different kinds of metal oxide semiconductors such as TiO_2 , ZnO , Fe_2O_3 , ZrO_2 , WO_3 , SnO_2 , Al_2O_3 , CeO_2 , ZnS and CdS etc, can be used as photocatalyst (Mo, Zhang et al. 2009). Among the above common photocatalysts, the most used one are TiO_2 , ZnO and WO_3 . TiO_2 , a cheap, chemically stable and highly active photocatalyst under UV irradiation, was used mostly in previously published works (Fujishima and Zhang 2006). Degussa P25 which is a commercialized TiO_2 photocatalyst powder with a crystal distribution of 70% anatase and 30% rutile was

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widely used in the field of air purification (Kirchnerova, Herrera Cohen et al. 2005; Mo, Zhang et al. 2009). However, as in the typical indoor environment there is less UV source to activate TiO_2 , many attempts have been carried out to synthesize visible-light active photocatalyst.

Different modification methods, such as doping transition metal ions, nitrogen and carbon into TiO_2 , as well as applying sensitizing species coupled with TiO_2 , can be used to generate visible-light active photocatalyst. Bosc et al. (Bosc, Edwards et al. 2006) reported mesoporous anatase TiO_2 coupled with WO_3 at low concentration (4 wt.%) led to high PCO degradation efficiency of toluene in gas phase using both UV and visible light. Zhang et al. (Zhang, Chen et al. 2013) synthesized novel porous $\text{CuO}_x/\text{CeO}_2$ co-loaded $\text{ZrO}_2\text{-TiO}_2$ nanocomposite with high surface area to remove soot under NO/O_2 . The composite structure could be well controlled by adjusting the ratio of ethanol to water during the solvothermal process.

Synthesized $\text{TiO}_{2-x}\text{N}_x$ photocatalysts have been proved to have better activity than common TiO_2 under visible light irradiation for PCO of 2-propanol (Irie 2003), acetaldehyde, and toluene (Irokawa 2006). Carbon (Hamal 2007; Li, Gu et al. 2007; Wu 2007) can also be used as dopant to modify TiO_2 into visible-light active $\text{TiO}_{2-x}\text{C}_x$ photocatalysts (thin film or powder). Either nitrogen-doped or carbon-doped TiO_2 materials will have adsorption in visible-light wavelength ($> 400\text{ nm}$) by substituting some of the lattice oxygen atoms with nitrogen and/or carbon atoms so that lowering the band-gap energy.

2.2.3. Current problems encountered by PCO application in indoor air purification

2.2.3.1. Immobilization of photocatalysts for practical application

The prerequisite for successful implementation of heterogeneous PCO in indoor air purification is to develop stable and reliable photocatalysts in an integrated form that can be easily used in practical engineering. The common way is to immobilize

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synthesized photocatalyst onto a solid substrate surface by coating or physical/chemical deposition. Generally, there are two kinds of immobilization methods. One is to form photocatalyst thin film on the supporting materials through chemical solution deposition (such as sol-gel), chemical vapor deposition (CVD), atmospheric pressure CVD (APCVD) or hydrothermal process; the other method is direct coating of photocatalyst powder onto supporting materials through dip-coating (also known as wash-coating), sputtering or spray-coating. Table 2-4 summarizes some typical coating methods employed in previous publications.

Table 2-4 Summary of immobilization methods of various photocatalysts

Immobilization method	Catalyst	Substrate	Calcination/stabilization	Coating circle	Source
Dip-coating/ Wash-coating	TiO ₂ (anatase)	Ceramic honeycomb	105 °C for 3-4 hr	11	Sauer & Ollis (1994) (Sauer and Ollis 1994)
	P25 (Degussa)	Alumina honeycomb	—	—	Obee & Brown (1995) (Obee, T. N. and Brown, R. T. 1995)
	P25 (Degussa)	Glass plate	70 °C till dry	Several ^a	Obee & Hay (1997) (Obee and Hay 1997)
	P25 (Degussa)	Glass beads	104 °C for 1 hr	3-4	Wang et al. (1999) (Wang, Hsieh et al. 1999)
	P25 (Degussa)	Glass fiber filter	120 °C for 1 hr	—	Ao et al. (2004) (Ao, Lee et al. 2004)
Sol-gel + dip-coating	M ⁿ⁺ /TiO ₂	Glass fiber fabric	450 °C for 1 hr	Single	Brezová et al. (1997) (Brezová, Blažková et al. 1997)

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Table 2-4 (continue)

	TiO ₂ , Pt/TiO ₂	Glass slide	350 °C for 4 hr	–	Cao et al. (2000) (Cao, Gao et al. 2000)
	TiO ₂ (anatase)	Porous stainless steel plate	200 °C for 3 hr	Single	Maria et al. (2000) (Maira, Yeung et al. 2000)
	TiO ₂	Adsorbent s ^b	300 °C for 1 hr	Single	Bhattachar yya et al.(2004) (Bhattacha ryya, Kawi et al. 2004)
	WO ₃ /TiO ₂	Lime-silic a glass slide	350 °C for 2 hr	–	Bosc et al. (2006) (Bosc, Edwards et al. 2006)
	TiO _{2-x} N _x , TiO _{2-x} N _x /Zr O ₂	–	400-600 °C for 4 hr	–	Wang et al. (2006) (Wang, Yu et al. 2006)
Hydrotherma l	TiO _{2-x} N _x	Pyrex glass plate	400 °C for 1 hr	–	Ihara et al. (2003) (Ihara, Miyoshi et al. 2003)
	Pd-TiO ₂	Pyrex tube	500 °C for 4 hr	Single	Belver et al. (2003) (Belver, López-Mu ñoz et al. 2003)
CVD ^c	TiO _{2-x} N _x	Pyrex glass plate	500 °C for 0.5 hr	6	Miyauchi et al. (2004) (Miyauchi, Ikezawa et al. 2004)
APCVD ^d	TiO _{2-x} N _x	Glass sheet	500 °C	–	Dunnill et al. (2009) (Dunnill, Aiken et

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Table 2-4 (*continue*)

PLD ^e	TiO _{2-x} N _x	Quartz glass	600 °C	Single	al. 2009) Zhao et al. (2008) (Zhao, Jiang et al. 2008)
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^atill a 0.74 mg/cm² film was achieved; ^bincluding MCM-41, β -zeolite and montmorillonite;

^cchemical vapor deposition; ^datmospheric pressure CVD; ^epulsed laser deposition.

Among various preparation methods, sol-gel + dip-coating is one of the most widely used technique due to the forming of more uniformly distributed catalyst thin film and the effective control of particle size, shape and properties (Tseng, Lin et al. 2010). To stabilize the coatings, an annealing process, usually a heat treatment, is also required in order to favor further poly-condensation and to enhance the mechanical properties and structural stability via high temperature calcination, densification and grain growth (Byrne, Eggins et al. 1998; Tseng, Lin et al. 2010). For the direct coating method, although considerable degradation efficiencies were reported on direct dip-coated solid substrates (Sauer and Ollis 1994; Obee and Hay 1997), the stability and durability of the coatings are seldom discussed. In addition, although the calcination process afterward sol-gel dipping is usually considered to provide stable coatings, significant detachment of the coated photocatalysts was found by Lim et al. (Lim, Lynch et al. 2009) when studying PCO of methylene blue in liquid phase with various immobilization/substrate combinations which were all heat-treated at 500 °C to stabilize the coatings.

The selection of different types of substrates also imposes a boundary when choosing the proper immobilization methods. Sol-gel dipping method is particularly favored when using solid form substrates such as glass, aluminum, stainless steel in a shape of monolith, sheets or plate which can maintain their inherent physical/chemical properties and integrity during heat treatment. In recent years, more and more attentions have been drawn on fibrous or textile-structured surfaces, such as cellulose acetate (Coronado, Suárez et al. 2008), cotton textiles (Yuranova, Mosteo et al. 2006), wool-polyamide (Bozzi, Yuranova et al. 2005) and polyester (Mejía, Marín et al. 2010) etc., which can provide much larger surface area and

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are flexible and low-cost for scaling up in practical application. For those kinds of material, direct coating using the current available commercialized photocatalysts, such as Degussa P25, may be a more cost-effective way. The key is to develop a simple, economical and reliable immobilization process which can provide stable and durable coatings while guarantees a satisfactory PCO performance.

2.2.3.2. PCO reactor design

PCO degradation of gaseous pollutants is a surface reaction process which basically consists of two steps: firstly, pollutant molecules have to be transferred and adsorbed onto photocatalyst surface; secondly, the adsorbed pollutants are decomposed by the PCO process. Therefore, the mass transfer effect, the reaction surface area as well as the reaction rate that is influenced by different kinetic parameters such as flow rate and pollutant concentration are all essential factors that affect the performance of a PCO reactor (Dunnill, Aiken et al. 2009). Ideally, the design of the PCO reactor should provide large reaction surface area, support small pass-through channels and low air velocity for a high mass transfer and have the incident light irradiate directly on the reaction surface. Nevertheless, when used for indoor air purification, the design of PCO reactor should be capable of treating fairly high gas feed rate with low pressure drop.

According to the configuration of the light sources with respect to the reaction area, different types of PCO reactor have been designed and employed for VOCs removal in previous studies, such as the monolith honeycomb reactor (Obee, T. N. and Brown, R. T. 1995; Obee and Hay 1997; Hossain, Raupp et al. 1999), the plate-type fix-bed reactor (Sauer and Ollis 1994; Mo, Zhang et al. 2005; Yang, Zhang et al. 2007), the annular reactor (Jacoby, Blake et al. 1995; Doucet, Bocquillon et al. 2006; Mo, Zhang et al. 2008), the fluidized-bed reactor (Chang, Chen et al. 2003), the packed-bed reactor (Arabatzis, Spyrellis et al. 2005) and the mop fan type reactor (Riffat and Zhao 2007) etc. Among different types of photo-reactors, the monolith honeycomb, annular, fluidized-bed and fix-bed reactor are four representatives.

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(1) Monolith honeycomb reactor

Honeycomb monolith reactors have been utilized for the automobile exhaust emission control and NO_x reduction in power plant exhaust. A honeycomb monolith reactor contains certain number of channel; each single channel typically has an internal dimension of the order of 1 mm. The cross-sectional shapes of channels are square or circular. The catalyst is coated onto the walls of channels in a very thin wash coat (Hayes, Kolaczkowski et al. 1992). The advantages of monolith configuration are low pressure drop and high surface-area-to-volume ratio. Figure 2-2 shows an example of the monolith honeycomb reactor design.

Figure 2-2 Schematic diagram of the monolith reactor used by Hossain (Hossain, Raupp et al. 1999)

To promote the energy efficiency of the monolith design, several researches focusing on the mathematical modeling of air flow, photon flux field as well as mass transfer for photocatalytic monolith reactors had been carried out (Hossain, Raupp et al. 1999). Sauer (Sauer, Hale et al. 1995) et al. studied the PCO of gaseous acetone with a concentration of 70 to 400 ppm by using near-UV illuminated TiO₂ coated on the surface of a ceramic honeycomb monolith. They used a reticular system to show that the monolith reactor can treat single and multiple contaminated air feed streams. However, as the incident light is parallel to the reaction area in this design, the PCO reaction rate is also limited.

(2) Annular reactor

The annular reactor (Figure 2-3) is generally composed of two concentric cylinders that form an annular region with a certain gap. The catalyst is coated on the interior

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wall of the outer cylinder when the light source locates at the center, and the thickness of the catalyst film coated on the surface of reactor is thin enough to let all the catalyst be illuminated by UV light. When light source locates outside the reactor, the catalyst is coated on the surface of two centric cylinders. The cross section of annular reactor is small so that high gas flow velocity can be obtained to ensure that products desorbed from surface could be removed quickly (Larson, Widegren et al. 1995).

Figure 2-3 Schematic diagram of the annular reactor used by Larson (Larson, Widegren et al. 1995) et al.

Different structures of the annular reactor include concentric annular tube flow reactor with catalyst thin film on the inner surface (Lichtin, Avudaithai et al. 1996) and continuous quartz glass tubes annular reactor (Lim, Jeong et al. 2000). Although the configuration of the annular reactor provides direct light illumination on the reaction surface which can improve the PCO reaction rate comparing to the honeycomb type, the small convective mass transfer rate and the reaction area are the limiting factors for its PCO performance (Dunnill, Aiken et al. 2009).

(3) Fluidized-bed reactor

Fluidized-bed reactor allows the feed gas flow directly passing through the catalyst

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bed. An typical design of the fluidized-bed reactor used by Dibble (Dibble and Raupp 1990) et al. is shown in Figure 2-4. TiO_2 was supported on Davisil 646 silica gel and formed the TiO_2 -silica gel. The cross-sectional area at the top of reactor was 125% larger than that of lower portion. This feature was helpful to reduce the momentum of catalyst particle and prevent the catalyst particles from flowing with the gas. The glass frit in the overhead effluent tube was another important part to prevent the catalyst from mixing in the effluent gas.

Figure 2-4 Schematic diagram of the fluidized-bed reactor used by Dibble (Dibble and Raupp 1990)

One obvious drawback of this design is that light can not uniformly reach the effective reaction surface which decreases the efficiency of the light source and the photocatalyst. In addition, the uniform fluidization of the photocatalyst inside the catalyst bed is usually hard to achieve. Thus, in other researches, some new features have been added to improve the design of fluidized-bed reactors. Lim (Lim, Jeong et al. 2000) et al. combined the features of an annular and a fluidized-bed reactor to design a modified fluidized-bed reactor, where the catalyst formed an annular bed with UV light in the center. In order to provide a uniform fluidization of the catalyst, a quartz filter was used as a distributor. Meanwhile, a square mirror box surrounded

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the reactor to minimize the loss of light irradiation and to improve the utilization of reflected and deflected light. Nam (Nam, Kim et al. 2002) et al. fixed the light source at the center of catalyst bed which was applied to the entire volume of the reactor. Six nozzles as air distributors were also installed at the bottom of the reactor to get the uniform air distribution in the catalyst bed. Nevertheless, the relatively large resistance to the feed air flow restricts the use of fluidized-bed reactor in treating high flow rate streams.

(4) Fix-bed plate type reactor

Fix-bed reactor is designed to be capable of treating relatively high gas feed rates. The reactor configuration provides low pressure drop and simultaneously efficient contact of incident photons, photocatalysts and gaseous pollutants. Another advantage of this design is that the irradiation/illumination on the reaction surface is uniform and can be easily adjusted by varying the distance between the light source and the reaction surface (Yang, Zhang et al. 2007). One of the typical plate type designs is illustrated in Figure 2-5.

Figure 2-5 Schematic diagram of the fix-bed plate type reactor used by Mo (Mo, Zhang et al. 2005)

Although large convective mass transfer rate and high reaction rate can be achieved on the photocatalyst thin film coated on plate type reactor, the effective reaction area, restricting by the dimension of the plate substrate, is usually much smaller than other types of reactor designs (Dunnill, Aiken et al. 2009).

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2.2.3.3. Influential factors of PCO reaction

The performance of PCO degradation of VOCs is influenced by various kinetic parameters such as relative humidity, light intensity, pollutant initial concentration, volumetric flow rate, resident time, temperature, oxygen content, catalyst loading amount, as well as different kinds of pollutant. Although great progress has been achieved on the effects of different kinetic parameters on UV or Visible-light PCO degradation efficiency, there are still considerable differences or conflicts in the findings or conclusions among previous studies.

For instance, in one of the early researches by Ibusuki and Takeuchi (Ibusuki and Takeuchi 1986), it was found that addition of H₂O brought about remarkable enhancement of toluene (of 80 ppm) photo-oxidation on TiO₂, which was pointed out by the author, due to the increase of active species ($\bullet$ OH) on TiO₂ surface caused by h^+ oxidation of the adsorbed hydroxyl group from water molecules. Similar results were reported by Weedon (Weedon 1994) et al., who found enhanced oxidation rates for several organic gaseous contaminants including toluene with concentrations above 50 ppm; and by Suzuki (Suzuki 1993) who reported enhanced toluene photo-oxidation rate with concentration well above 1 ppm as humidity level increased. However, Luo (Luo and Ollis 1996) and Ollis reported a conflicting result for PCO of toluene with concentrations from 80-550 mg/m³ (about 19-132 ppm), where they found that toluene photo-oxidation rate decreased with the relative humidity higher than 20%.

A competitive adsorption between water molecule and the reactants on the surface of TiO₂ was reported by Obee (Obee, T. N. and Brown, R. T. 1995; Obee 1996; Obee and Hay 1997) et al. when studying PCO of sub-ppm level gaseous contaminants such as toluene, formaldehyde, ethylene and 1,3-Butadiene. The bimolecular Langmuir-Hinshelwood (BLH) model was therefore proposed in those studies to evaluate the interacting between water vapor and pollutant concentration on the PCO efficiency. Theoretically, at high concentrations, the PCO reaction rate increased with increasing relative humidity (above 7.5%), while at low concentrations, such as sub-ppm level, the PCO reaction rate decreased with

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increasing relative humidity level due to the competitive adsorption from water vapor over contaminants on the photocatalyst surface. Although this finding was also proved by other experimental results (Nam, Kim et al. 2002; Chang, Chen et al. 2003), a recent work by Guo (Guo, Bai et al. 2008) et al. pointed out that even at the minus 1 ppm toluene concentration level (about 0.4 ppm), the PCO conversion rate of toluene increased with increasing relative humidity from 15% to 60%. Jo (Jo and Park 2004) et al. also reported that for VOCs at low-ppb levels, the destruction of VOCs was independent of humidity, but dependent on face velocity, inlet ports size and light intensity. They also pointed out that the inconsistency from previous researches might be due to the difference in the inlet VOC concentrations.

Interesting result was found in Wang (Wang, Tsai et al. 1998) et al. study about PCO of TCE on a relatively high concentration level of 788 ppm, where the experimental data showed that the increasing of water vapor concentration lowered the reaction rate of TCE. The author also attributed this effect to the competitive adsorption between TCE and water molecules on the catalyst surface. However, to the author's knowledge, competitive adsorption from water vapor is hardly observed in such a high pollutant concentration.

In sum, the influences from different kinetic parameters on the reaction rate of PCO for indoor air purification are still unclear. The correlation and interacting between different influential factors make this issue become complex. In addition, due to the shortage of UV light in the typical indoor environment, further studies on visible-light PCO of indoor air pollutants are essentially needed. The effects from different reaction parameters as well as the reaction mechanism of pollutants under visible-light PCO are all challenging topics.

CHAPTER 3

Development of Convenient and Cost-Effective Catalyst Immobilization Technique and Establishing of PCO Experimental Methodology

3.1. Introduction

Photocatalyst immobilization is the key for successful implementation of heterogeneous photocatalytic oxidation (PCO) for indoor air purification. Selecting the proper substrate material and effective coating method are two essential factors in catalyst immobilization. Suitable substrates should have stable physical and chemical properties and also can provide large surface area for catalyst to attach on. The selection of coating method should meet the following requirements: providing stable and durable coating; providing effective and sufficient contact between the coating and the pollutant stream; non-selective of different substrates; easy and energy-efficient; economical and suitable for large-scale application.

The conventional sol-gel dipping method is particularly favored when using solid form substrates such as glass, aluminum, stainless steel in a shape of monolith, sheets or plate which can maintain their inherent physical/chemical properties and integrity during the high temperature heat treatment process (Brezová, Blažková et al. 1997; Cao, Gao et al. 2000; Maira, Yeung et al. 2000; Belver, López-Muñoz et al. 2003; Ihara, Miyoshi et al. 2003; Bhattacharyya, Kawi et al. 2004; Miyauchi, Ikezawa et al. 2004; Bosc, Edwards et al. 2006; See, Wang et al. 2007; Zhao, Jiang et al. 2008; Dunnill, Aiken et al. 2009). Materials with much larger surface area in comparing to the plate form solid substrates, such as polymers and fibrous substances, usually are not resistant to the high temperature heat treatment.

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Large-scale application of PCO for indoor air purification can be realized by using the fabric and textile materials prepared through direct coating of commercialized photocatalysts (Paz 2010). However, some critical issues such as coating stability are still needed to solve.

When immobilizing photocatalysts, such as commercial TiO_2 nano-powder, onto substrate surface by direct coating, one important issue is the adhesion between TiO_2 particle and the substrate. Poor adhesion has been reported on glass substrate by dip coating or spin coating (Mills, Elliott et al. 2002; Keshmiri, Mohseni et al. 2004), where even slight mechanical abrasion may remove TiO_2 particles from the substrate surface. Thus, a binding agent is usually necessary for direct coating in order to form reliable adhesion between catalyst and the substrate (Du, Carneiro et al. 2008; Lim, Lynch et al. 2009; Plantard, Goetz et al. 2011). Either organic or inorganic binding materials have been used for photocatalyst immobilization (Thevenet, Guaiella et al. 2005; Henderson 2011); however, discussions on binder type, amount on the performance of the coatings as well as the coating stability are seldom reported.

In this section, immobilization of TiO_2 nano-powder onto different kinds of substrate was conducted by a novel spray coating method under low temperature. Two different binders were used in the coating suspensions. The effects of different binders as well as coating stabilization temperature on the coating structures and their PCO degradation efficiency of gaseous formaldehyde were evaluated. With the same catalyst loading amount, the PCO activities of different kinds of substrate were compared.

The PCO experiment was carried out on a fix-bed photo-reactor. Details of the reactor and overall experimental setup design were introduced. Sampling and analytical methods for gaseous formaldehyde were established. A series of preliminary test were taken in order to evaluate the detection reliability and the experimental system stability.

3.2. Experimental methods

3.2.1. Preparation of different coating combinations by novel spray coating method

Two kinds of binding agent, commercial polyurethane (PU, Stahl, Netherlands) and colloidal silica Ludox-AS40 (Sigma-Aldrich, USA), are selected and compared in this study for spray coating of Degussa P25 TiO₂ nano-powder (70% anatase, 30% rutile with effective surface area of roughly 50 m²/g) on to different substrates. PU, a curable organic polymer, has been reported to be used as binder for coating of TiO₂ on plate type substrates (Kasanen, Suvanto et al. 2009; Kasanen, Suvanto et al. 2011). By changing the PU dispersion/H₂O ratio, stable coating can be obtained (Kasanen, Suvanto et al. 2011). Colloidal silica, usually used as surfactant and high temperature binder in the industry, is seldom reported being used as binding agent for photocatalyst coating in literature (Holland 2007).

Another important step that may affect the coating structure is the final stabilization step. Different from the high temperature heat-treatment step adopted in conventional sol-gel dip coating, we suppose high temperature will not be favored by the direct spray coating.

Three kinds of substrate, JGS1 quartz glass (Sunful, China), anodized aluminum (Exel, Singapore) and polyester fiber filter (BioFit, Singapore) were used with a dimension of 100×50×3 mm. Different coating combinations are shown in Table 3-1.

The spray coating method used in this study follows a standard procedure: All substrates were first washed with 0.5% nonionic washing agent Felosan RG-N (Bezema, Switzerland) at liquid-to-fabric ratio of 50:1 in an ultrasonic washer (Kudos, China) for 15 min and rinsed with Milli-Q water followed by sonication for 15 min for three times. The substrates were then washed with pure acetone and dried in pure nitrogen gas flow at room temperature. The coating suspensions were prepared using P25 TiO₂ nano-powder, Milli-Q water and the binders. A suspension

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of 5 g/L of P25 TiO₂ nano-powder was firstly prepared with Milli-Q water under magnetic stirring for 30min, followed by dripping certain amount of binder liquid slowly into the TiO₂ suspension at a speed of 1 mL/min with stirring. The mixed suspension was then further stirred for several hours till the uniform TiO₂ slurry was observed.

Table 3-1 Different spray coating combinations

Substrate	Sample code	Binder	Binder dosage	Stabilization temperature
Quartz glass	G-1	Polyurethane	PU dispersion/H ₂ O	60 °C
	G-2	(PU)	mass ratio of 1:4 ^a	120 °C
	G-3	Colloidal	SiO ₂	60 °C
	G-4	silica (SiO ₂)	equivalent/TiO ₂ mass ratio of 2:1	120 °C
Anodized aluminum	A-1	Polyurethane	PU dispersion/H ₂ O	60 °C
	A-2	(PU)	mass ratio of 1:4 ^a	120 °C
	A-3	Colloidal	SiO ₂	60 °C
	A-4	silica (SiO ₂)	equivalent/TiO ₂ mass ratio of 2:1	120 °C
Polyester fiber filter	P-1	Polyurethane	PU dispersion/H ₂ O	60 °C
	P-2	(PU)	mass ratio of 1:4 ^a	120 °C
	P-3	Colloidal	SiO ₂	60 °C
	P-4	silica (SiO ₂)	equivalent/TiO ₂ mass ratio of 2:1	120 °C

^aaccording to the reported result by Kasanen et al. (Kasanen, Suvanto et al. 2011)

After the coating suspensions were prepared, a Navite F-75G spray gun (Navite, China) was used for spray coating, with nitrogen as the carrier gas under a high pressure of 65 psi. The spray distance from the nozzle exit to the substrate surface was optimized at 150 mm to minimize the waste of coating suspensions. To achieve uniform coating on the bulk body of the substrate, the substrates were spray-coated for several rounds until the coating suspensions were finished. An interval of 15 min

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was taken every two rounds using a blow drier to evaporate water vapor. The coatings were further stabilized at different temperatures. The substrates were all weighed by a digital ultra-balance (Mettler-Toledo, Switzerland) before and after coating.

The coating surface characterization was carried out using an EOVS (Carl Zeiss, Germany) scanning electron microscopy (SEM). BET surface area measurements of the spray-coated samples were taken on an Autosorb-1 system (Quantachrome, USA).

3.2.2. Design of fix-bed photo-reactor and integrated PCO experimental setup

The photocatalytic oxidation (PCO) of gaseous formaldehyde was performed on a fix-bed photo-reactor which was designed according to the ISO standard 22197-1:2007 (ISO 2007b) with special modifications based on the application in this study (Figure 3-1). The primary reason for choosing this design in this study is because the modified fix-bed reactor allows testing and comparison of different kinds of substrate materials; and by adopting high surface area materials, the PCO performance of the fix-bed reactor will be very competitive in comparing to other types of reactor design. In addition, the influential factors, such as light intensity, relative humidity and pollutant inlet concentration, etc., can be easily adjusted and controlled in this modified fix-bed reactor design.

Figure 3-1 Schematic diagram of photo-reactor: a. cross-section view; b. top view. (1) Testing gas flow. (2) Top cover. (3) Optical window. (4) Testing substrate samples. (5) Height-adjusting plate.

Figure 3-2 Image of finalized fix-bed photo-reactor

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The reactor body (including the main body and the top cover) is made of well polished stainless steel 316L (Exel-Mitsui, Singapore). An optical window for UV/Vis illumination with almost no resistance, which is made of GE214 fused quartz glass (General Electric, USA), is installed on the top cover with silicon rubber seals along the rim. A height-adjusting plate is placed inside the main body of the reactor, which is used to adjust the air layer thickness in between the substrate sample surface and the optical window. After the substrate sample is placed on top of the height-adjusting plate, the top cover will be tightened to the main body by screws, also with silicon rubber seals along the rim to make sure the whole body in air-tight condition. The image of the finalized reactor design is shown in Figure 3-2.

A cover frame is used to fix the optimal window onto the top cover of the reactor body. By adopting this design, the optimal window can be easily exchanged and the possible leakage in the rim of the optimal window will be eliminated. Leakage checkup is performed every time before and after each experimental test using a Snoop (Swagelok, USA) liquid leak detector on all the connections and rims of the reactor.

Figure 3-3 Schematic diagram of PCO experimental setup. (1) Purified air cylinder. (2) Flow meter. (3) Humidifier. (4) Source tank. (5) Formaldehyde solution. (6) Mixing chamber. (7) 8 v DC fan. (8) Hygro-thermometer. (9) Photo-reactor. (10) UV light lamp. (11) Three-port control valve. (12) Sampling tube. (13) Sampling pump. (14) Mass flow controller. (15) Vent.

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Three parallel photo reactors are adopted in order to test different substrate samples simultaneously. The schematic diagram of the PCO experimental setup is shown in Figure 3-3. The light sources are positioned above each reactor in the center line and are installed on a height-adjusting frame which can easily adjust the distance between the light source and the reactor surface in order to change the incident light intensity. Certain amount of 37% (wt.%) formaldehyde solution (Sigma-Aldrich, USA) is injected into a 5 L stainless steel source tank to generate gaseous formaldehyde by vaporizing. Purified synthetic air, with about 20% O₂ and 80% N₂ (v/v %), is used as carrier gas to take gaseous formaldehyde and water vapor into 21 L stainless steel mixing chamber where they will be well mixed at different ratios controlled by volumetric flow meter in each flow path. A 8 V DC fan is placed inside the mixing chamber and operate all time to accelerate the mixing of formaldehyde and water vapor in the carrier gas and help the mixed gas to reach steady state before it enter the photo-reactors. An EA-25-NIST hygro-thermal meter (Extech, USA) is installed on the mixing chamber with the probe inside to monitor relative humidity and temperature inside the mixing chamber. The well-mixed feed gas then will enter the photo-reactors for the PCO reaction. There are four mass flow controllers (Omega, UK) used in four pass routes in controlling the flow rate of the feed gas. Formaldehyde sampling is carried out by active sorbent tube sampler coupled with sampling pump (SKC, USA). Before sampling starts, the three-port control valves will be switch to the bypass route. Four sampling sections are used each test to catch three outlet concentration (C_{Out}) on the outlet of the three reactors and one inlet concentration (C_{In}) on the inlet of the reactors.

In this study, three FPX9BLB 9 W UV light lamps (USHIO, Japan) with light centered at 368 nm (UVA) are used as light source. Before the UV light lamps were turned on, the well-mixed testing gas flow was continuously passing through the reactors until the substrate samples reached saturation, which was marked by $C_{In} = C_{Out}$. This step avoids the influence from adsorption/desorption process of formaldehyde molecules on the substrates before the PCO reaction takes place. The stabilization process usually took several hours regarding to different pollutant

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concentrations. The initial formaldehyde concentration (C_{In}) would also reach the steady state during this process. The UV light lamps were then turned on for the PCO reaction. For certain reaction time, C_{In} and C_{Out} were taken simultaneously. The PCO degradation efficiency of formaldehyde was calculated by:

$$\eta_{HCHO}(\%) = \frac{C_{In} - C_{Out}}{C_{In}} \times 100 \quad (3-1)$$

3.2.3. Establishing of testing and sampling method for determination of gaseous formaldehyde concentration

Due to the high toxicity and volatility as well as low stability of formaldehyde in gas phase, direct sampling and testing of gaseous formaldehyde is hard to realize. The common way for sampling gaseous formaldehyde is by using liquid/solid sorbent materials to capture formaldehyde molecules and derivatize it into more stable HCHO-derivatives. There are two sampling strategies: active sampling, in which gas flow containing formaldehyde is forced to passing through the samplers; and passive diffusion sampling, in which formaldehyde in the air diffuses naturally onto the sampler surface. The passive diffusion method is usually used for long-time (one day or more) sampling to measure the average formaldehyde levels in the indoor air, during which the normal living/working conditions will not be affected (Crump, Squire et al. 1997). While active methods, which usually take 30 – 60 min, are faster and easier for personal sampling and are commonly used for quick determination of exposure levels (Akbar-Khanzadeh and Park 1997).

There are several active sampling and testing methods for gaseous formaldehyde recommended by the National Institute for Occupational Safety and Health (NIOSH, USA) and the Occupational Safety and Health Administration (OSHA, USA) such as the NIOSH-3500, 3501 and 2541 and the OSHA-52. Those methods using gas chromatography (GC) or high performance liquid chromatography (HPLC) detections to determine the equivalent HCHO-derivatives usually have high sensitivity and accuracy. High sensitive commercial gas detectors have been used

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for monitoring gaseous formaldehyde concentration in some literatures (Obee, T. N. and Brown, R. T. 1995; Kuo, Tseng et al. 2007). However, the data reliability of those kinds of gas detector is still not clear.

In this study, an active sampling + GC-FID testing method was developed based on the NIOSH recommended method 2541 (NIOSH 1994). The reason for choosing the NIOSH-2541 method is because it provides high sample stability. By changing different sampling sorbent tube and adopting high sensitive GC-FID testing apparatus, the sensitivity and accuracy of this method were significantly improved.

The active sampler used here is the commercial SKC 226-117 (SKC, USA) sorbent sampling tube. It consists of a 12 cm long glass tube with 6 mm OD and 4 mm ID and with flame-sealed ends and plastic caps. Inside the sorbent tube, two sections of 2-(hydroxymethyl) piperidine-coated XAD-2 sorbent are packed with 150 mg in the front section and 75 mg in the back section which are retained and separated by plugs of silanized glass wool. The sorbent tubes are stored in refrigerator at 4 °C before use. The ends of the sorbent tube will be broken immediately before sampling and attached to the sampling route in the experimental setup and the sampling pump. The four sampling pumps were calibrated with a bubble flow meter (Gilian, USA) in line before use.

During sampling, formaldehyde will react with 2-(hydroxymethyl) piperidine on the sorbent bed. The sampling rate is limited by the speed of this reaction. Sampling rate above 0.10 L/min may cause appreciable breakthrough owing to incomplete reaction which possibly may invalidate the samples (1994). The NIOSH-2541 method recommends a maximum sampling rate of 0.10 L/min. When using the 226-117 sorbent tube in our method, no breakthrough was observed at a sampling rate of 100 mL/min regardless of the difference in formaldehyde concentrations.

After sampling, the sorbent tube will be capped and stored in refrigerator (4 °C). During sample preparation, the HCHO-derivatives will be washed out from the sorbent. A standard desorption procedure is followed: Firstly, the front glass wool

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plug and the sorbent in the front section are removed into a 4 mL vial and added with 1 mL toluene. The sorbent in the back section with the remaining glass wool plugs will be removed to the second 4 mL vial and added with 1 mL toluene. The vials are then capped and agitated in ultrasonic water bath for 60 min. The formaldehyde derivatives are dissolved in the toluene solution during ultrasonic agitation. The solutions in the 4 mL vials are then filtrated by 0.2 μm nylon syringe filter (Target, USA) and collected in 2 mL GC testing vials.

Table 3-2 GC-FID test conditions for formaldehyde derivatives.

Parameters	Conditions
Analyte	Oxazolidine derivative of formaldehyde
Injection Volume	1 μL splitless, split vent time 30 sec
Temperature – Injector	300 $^{\circ}\text{C}$
Detector	300 $^{\circ}\text{C}$
Column	70 $^{\circ}\text{C}$ for 1 min, 15 $^{\circ}\text{C}/\text{min}$, hold at 240 $^{\circ}\text{C}$ for 3 min
Carrier Gas	Helium at 1.3 mL/min, makeup flow of 29 mL/min in nitrogen
Column	DB-WAX 123-7033, 30 m $\times$ 0.32 mm, 0.50 μm film thickness

An Agilent 6890 gas chromatography (GC) system coupled with a flame ionization detector (FID) are used for detection. A DB-WAX 123-7033 capillary column (Agilent, USA) is chosen for effective separation of formaldehyde derivative from other contents. Details of the GC-FID test conditions are listed in Table 3-2.

A standardized formaldehyde stock solution with concentration of 1.014 mg/mL was prepared for calibration and method evaluation use. Detailed procedures of preparation and standardization of this stock solution are as follow: Firstly, 2.7 mL of 37% aqueous formaldehyde solution was diluted to 1 L with Mili-Q water. To standardize the stock solution, place 5 mL freshly prepared 1.13 mol/L sodium sulfite solution in a 50 mL beaker and magnetically stirred. Adjust its pH value

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between 8.5 to 10 using 0.01 mol/L sulfuric acid and/or 0.01 mol/L sodium hydroxide and record the final pH value. Then add 10 mL prepared formaldehyde stock solution into the sodium sulfite solution. The pH value then should be higher than 11. Titrate the solution back to its original pH value (before formaldehyde added) with 0.01 mol/L sulfuric acid. Once if the endpoint pH value is overrun, then back-titrate to the endpoint with 0.01 mol/L sodium hydroxide. The concentration C_{stock} (mg/mL) of the formaldehyde stock solution can be calculated at:

$$C_{stock} = \frac{30 \times (0.01 \times V_a - 0.01 \times V_b)}{10} \quad (3-2)$$

where V_a is the volume of sulfuric acid used for titration, V_b is the volume of sodium hydroxide used for back-titration. The stock solution was kept in amber container and stored in refrigerator (4 °C). This solution is stable for at least 1 year according to the author's experience.

Fresh analytical standards were prepared daily by injecting appropriate amounts of the diluted formaldehyde stock solutions onto 150 mg of the sorbents in a 4 mL amber vial and sealed with Teflon-lined cap. Serial dilutions of the calibration stock solutions were used to spike the sorbent in the range of interest. The calibration standards were kept at room temperature (24 °C) for 12 hrs before the desorption step (stated above) took place. Six working standards together with the blank spikes were analyzed to generate the calibration graph of peak area vs. amount of formaldehyde in the desorption volume ($\mu\text{g/mL}$). Correlation coefficients of the three calibration curves are all ≥ 0.998 (See Appendix). With the calibration curves, formaldehyde amount in the desorption solution ($\mu\text{g/mL}$) of a particular sample can be determined by comparing its peak area response to the calibration curve. It is noted that if any response is found on the back sorbent section, it should be added to the amount found on the front section. Possible breakthrough will happen when the amount found on the back section is higher than 1/10 of the amount found on the front section. The corresponding concentration of formaldehyde (mg/m^3) in a particular gas sample can be calculated as:

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$$C_{gas} (mg / m^3) = \frac{C_{dsp} \times V_{dsp}}{r \times t} \quad (3-3)$$

where C_{dsp} ($\mu\text{g/mL}$) is the concentration in the desorption solution; V_{dsp} (mL) is the volume of the desorption solution; r (L/min) is the sampling rate; and t (min) is the sampling time. Here in this study, the concentration of gaseous formaldehyde is converted into v/v% in parts per million (ppm) which will be easier to compare with the results of other researches through the equation:

$$C_{gas} (ppm) = \frac{C_{gas} (mg / m^3) \times 24.4}{M_{HCHO}} \quad (3-4)$$

where 24.4 is the molar volume (L/mol) of the ideal gas at 1 atm and 24 °C; M_{HCHO} (g/mol) is the molecular weight of formaldehyde.

3.3. Results and discussion

3.3.1. Preliminary test on detection reliability and system stability

In order to verify the reliability of the overall detection procedure, a series of preliminary tests were carried out to determine the method detection limit, recovery rate, sensitivity and precision, as well as the experimental setup stability.

3.3.1.1. Detection limit of the overall detection procedure

The analyte concentrations reported here are based on a desorption volume of 1 mL (of toluene solution). The amounts are presented as formaldehyde, even though the derivatives are the actual species analyzed.

The detection limit of the analytical method (GC-FID) was determined as 358 pg

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per injection (1 μ l). This was the amount of analyte which gave a peak whose height was about 3 times the height of the peak given by the residual formaldehyde derivative in a typical blank front section of the sampling tube.

Six samples were used to determine the detection limit of the overall procedure. Individual samples were prepared by spiking 358 ng of formaldehyde onto 150 mg of sorbent (equivalent to the amount of sorbent in the front section of the sampling tube). The samples were allowed to sit overnight before desorbed with 1 mL of toluene by sonication and analyzed by GC-FID. An average recovery of the six samples was about $93.8 \% \pm 2.4 \%$, which was very satisfactory and approximately equivalent to the detection limits of the analytical method. Thus, the detection limits of the overall detection procedure (derivatization + desorption + analysis) for gaseous formaldehyde were about 358 ng per sample (amount in 1 mL desorption solution), which were equivalent to 0.058 ppm in a 5 L gas sample at 24 °C.

3.3.1.2. Sensitivity

The sensitivity of the analytical method over three concentration ranges was determined from the slope of the calibration curves. From Figure A-1 (a-c), the sensitivities for gaseous formaldehyde concentration range of 0.07-3.58 ppm, 11.92-84.24 ppm and 95.36-226.87 ppm were 204, 175 and 217 area unit per μ g/mL of formaldehyde. There is no significant difference in sensitivities for different target formaldehyde concentration levels.

3.3.1.3. Recovery

The recovery of formaldehyde of the overall procedure was also evaluated by testing of several analyte spikes in different concentrations which were stored at 4 °C for 1 day, 7 days and 14 days. The result is shown in Table 3-3.

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Table 3-3 Recovery of formaldehyde of the overall procedure

Analyte spikes	Level-1			Level-2			Level-3		
	Stored for 1 day	Stored for 7 days	Stored for 14 days	Stored for 1 day	Stored for 7 days	Stored for 14 days	Stored for 1 day	Stored for 7 days	Stored for 14 days
Authentic amount ($\mu\text{g/mL}$)	15.24	15.24	15.24	168.53	168.53	168.53	1065.44	1065.44	1065.44
Tested amount ($\mu\text{g/mL}$)	14.64 $\pm$ 0.012	15.46 $\pm$ 0.036	13.78 $\pm$ 0.053	165.67 $\pm$ 0.8	166.73 $\pm$ 0.4	160.66 $\pm$ 1.03	1134.58 $\pm$ 3	1058.37 $\pm$ 2	969.61 $\pm$ 1.2
Recovery rate (%)	96.06	101.44	90.42	98.30	98.93	95.33	106.49	99.34	91.01

The result indicates that long-term storage, like 14 days, may have minor negative effect on the recovery of formaldehyde. The overall recovery rate of formaldehyde in a large concentration range is very satisfactory with the average value from 90.42% to 106.46%. Thus, in the following experiments, the storage time of all samples was less than 14 days.

3.3.1.4. Precision and system stability

To determine the precision of the overall procedure and the system stability of the experimental setup, formaldehyde was sampled on the outlet of the mixing chamber as well as on the reaction sampling ports in the setup. Three different concentration levels that are covered in the ranges of the three calibration curves were tested.

For each concentration level, four samples were taken on the outlet of the mixing chamber simultaneously after formaldehyde reached steady state inside the mixing chamber. Each sample was analyzed for three times in duplicate. Totally 12 analyte data were collected and compared for each concentration level. The coefficient of

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variation (CV) values for three concentration levels in 1.67 ± 0.05 ppm, 26.89 ± 0.50 ppm and 127.48 ± 1.96 ppm are 2.97%, 1.86% and 1.54%, respectively, indicating that the overall procedure is more precise when sampling and testing formaldehyde concentration higher than 2 ppm. The detected gaseous formaldehyde concentrations using the sampling and analytical procedure in this study have high precision and reliability.

The system stability test was carried out under dark condition with no catalyst loading (blank reactor). Samples were taken on the sampling ports in the experimental setup, with one formaldehyde inlet concentration (C_{in}) and three outlet concentrations (C_{out}). Three concentration levels were also considered. Each sample was also tested for three times in duplicate. The coefficient of variation (CV) of the one C_{in} and three C_{out} in three concentration levels of 3.46 ± 0.12 ppm, 38.43 ± 0.88 ppm and 110.54 ± 2.03 ppm are 3.37%, 2.29%, and 1.84%, respectively. For each concentration level, there is no significant difference between C_{in} and C_{out} under dark condition when formaldehyde reached steady state and continuously passed through the photo reactors, which indicates that the overall PCO experimental setup has very high stability.

3.3.2. Effect of different binders on the PCO degradation efficiency of gaseous formaldehyde

The SEM images of the spray-coated samples with polyurethane or colloidal silica binders on different kinds of substrate materials are shown in Figure 3-4. Both of the two kinds of binder used here can help to form solid TiO_2 active layer on the aluminum, quartz glass and polyester fiber substrate surfaces by the spray coating method developed in this study.

All of the coatings are stable enough to resist to slight abrasion with tissue paper or to wind blowing by a dry blower. No obvious detached catalyst particle was observed.

Figure 3-4 SEM images of different spray-coated substrate samples with polyurethane as binder (A1, G1, P1) and colloidal silica as binder (A3, G3, P3).

Comparing between the two kinds of binder, polyurethane leads to much heavier coagulation effect on the coatings than colloidal silica does. For all three kinds of substrate material, it is clearly observed that immobilized catalyst particles coagulate into big cluster by using the polyurethane binder (sample A1, G1, P1). While for samples using the colloidal silica binder (sample A3, G3, P3), the immobilized catalyst particles are more uniformly dispersed on the substrate

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surfaces with less coagulation. In Figure 3-5, the catalyst agglomerate sizes between samples using polyurethane binder and colloidal silica binder are compared on the aluminum substrate. The typical catalyst agglomerate size of sample using polyurethane binder is much bigger, about 5 times, than that of sample using colloidal silica binder.

Figure 3-5 Comparison of catalyst agglomerate sizes between sample using polyurethane binder (A1) and sample using colloidal silica binder (A3).

The heavy coagulation formed by using the polyurethane binder will definitely affect the effective surface area of the coatings and limit the contact between the photocatalyst and the pollutant. BET surface area measurement result of the above six samples is shown in Table 3-4. For samples using polyurethane as binder (sample A1, G1, P1), their BET surface areas are all smaller than the corresponding sample A3, G3, P3 which use colloidal silica as binder. For sample A1 and G1, as heavy coagulation resulted in big catalyst agglomerate size, their BET surface areas are even smaller than that of the uncoated TiO_2 in powder phase ($48.6 \text{ m}^2/\text{g}$). For samples coated on polyester fiber substrate (P1 and P3), as the substrate provides much bigger surface area for catalyst to attach on comparing to the plate-form aluminum and quartz glass substrates, their BET surface areas are relatively higher than the other samples. Moreover, coatings on the polyester fiber surface have more uniform dispersion and smaller catalyst agglomerate size in comparing with other coatings on the plate-form substrates.

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Table 3-4 BET surface area measurement of different spray-coated samples

Sample	A1 ^a	A3 ^a	G1 ^a	G3 ^a	P1 ^b	P3 ^b	TiO ₂ powder
Surface area (m ² /g)	40.3	47.3	42.2	53.1	68.6	93.2	48.6

^a Samples used for BET test were coatings removed from the substrates with the amount of 0.2864 ± 0.0021 g; ^b Samples used for BET test were coated fiber cut from the sample bulk with the amount of 0.2794 ± 0.0017 g.

Photocatalytic oxidation of gaseous formaldehyde was carried out on the above mentioned spray-coated samples under UV irradiation. The result is shown in Figure 3-6. For each tested substrate sample, four repeatable PCO cycles were taken. System uncertainties (represented by STDEV) are given as error bars. No degradation was observed in the absence of either photocatalyst or light source. UV light intensity was measured by a XRP-3000 radiometer (Accumax, USA).

Figure 3-6 PCO of gaseous formaldehyde by different spray-coated substrate samples ($C_{in} = 42.19 \pm 2.50$ ppm, RH = 60%, volumetric flow rate = 1 L/min, UV light intensity = 3.8 mW/cm^2 , temperature = 24°C).

For each kind of substrate material, PCO efficiency of formaldehyde is higher on

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sample using colloidal silica binder than on the corresponding sample using polyurethane binder. Difference in PCO efficiency can be partially attributed to the heavy coagulation and big catalyst agglomerate size introduced by using the polyurethane binder. On the other hand, Kasanen et al. (Kasanen, Suvanto et al. 2011) reported that cured waterborne polyurethane dispersion could be degraded by UV-PCO using TiO_2 photocatalyst. Therefore, for samples prepared using polyurethane as binder, their PCO degradation efficiency of formaldehyde might be affected by the competitive PCO process of the organic polymer additive itself.

Figure 3-7 SEM images of sample G1, (a) freshly prepared; (b) after four repeatable PCO cycles.

Figure 3-7 (a) shows the SEM image of freshly prepared sample G1, where before PCO reaction carried out the quartz glass substrate (appears as darker image) was fully covered by polyurethane- TiO_2 clusters (appears as brighter image). After the four repeatable PCO cycles, certain amount of polyurethane binder disappeared in Figure 3-7 (b) which shows more darker images associated to the quartz glass substrate, indicating that some of the polyurethane binder have been degraded during the PCO process. While for samples prepared by using the colloidal silica binder, despite the better coating dispersion and smaller catalyst agglomerate size, the inorganic constituent of the binder remains stable during the PCO of formaldehyde, which also contributes to the higher PCO degradation efficiency. Consequently, comparing to polyurethane, colloidal silica appears to be a better binding agent for preparing immobilized photocatalyst using the spray coating

method.

3.3.3. Effect of stabilization temperature on the PCO degradation efficiency of gaseous formaldehyde

Figure 3-8 SEM images of different spray-coated substrate samples stabilized at 60 °C (sample A3, G3, P3) and 120 °C (sample A4, G4, P4) using colloidal silica as binder.

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To determine the effect of stabilization temperature on the coating surface structures and their PCO activities, six spray-coated samples were prepared accordingly on three different substrate materials, with sample A3, G3, P3 stabilized at 60 °C and sample A4, G4, P4 stabilized at 120 °C using colloidal silica as binder. The SEM images of the above samples are shown in Figure 3-8. For all three kinds of substrate materials, coatings stabilized at 60 °C have more homogeneous TiO₂ film and lower film delamination; while coatings stabilized at 120 °C have larger film delamination as well as heavy cracking.

Delamination and cracking of the coated photocatalyst thin film might lead to loss of active reaction site, and more important, to unstable immobilization due to the weak adhesion between catalyst and the substrate caused by delamination. PCO of formaldehyde was carried out on the spray-coated polyester substrate sample P3 (stabilized at 60 °C) and P4 (stabilized at 120 °C) for four repeatable cycles. The result is shown in Figure 3-9.

Figure 3-9 PCO of gaseous formaldehyde on polyester sample P3 (stabilized at 60 °C) and P4 (stabilized at 120 °C) for four repeatable cycles ($C_{in} = 27.74 \pm 4.64$ ppm, RH = 60%, volumetric flow rate = 1 L/min, UV light intensity = 3.8 mW/cm², temperature = 24 °C)

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Due to the more homogeneous photocatalyst coating film on the substrate surface, sample P3 has higher PCO degradation efficiency than sample P4 in all the four PCO cycles. According to the gravimetric measurement of sample P3 and P4 during the four repeatable PCO cycles, sample P3 has no obvious loss of catalyst coating layer; while sample P4 has about 10 % loss of the catalyst coating layer, which explains the continuous decrease in PCO degradation efficiency of sample P4 through cycle 1 to cycle 4.

3.3.4. Comparison of the performances of different kinds of substrate materials

From the above optimization of the spray coating protocol, the ideal spray coating conditions are established by using colloidal silica as binding agent in the coating suspension and 60 °C for coating final stabilization step. In order to compare the performances of different spray-coated substrate materials, PCO degradation efficiency of formaldehyde is normalized into Δ_{HCHO} (ppm) per g of photocatalyst. Under the same experimental conditions, PCO performances of the spray-coated substrate sample A3, G3 and P3 are compared in Figure 3-10.

From Figure 3-10, with the same photocatalyst active layer loading amount, the PCO efficiency of the spray-coated polyester fiber substrate is almost twice that of the aluminum and quartz glass substrates. This is because the fibrous structure of the polyester substrate provides much larger surface area for the photocatalyst to attach on which helps to generate more uniform catalyst dispersion and less overlapping. While for the plate-form aluminum and quartz glass substrates, photocatalyst particles overlaps and coagulates with each other on the limited substrate surface during spray coating, resulting in uneven catalyst dispersion and larger agglomerate size. In addition, the porous skeleton of the polyester substrate also provides a three-dimension environment for the PCO reaction, which significantly enhances the contact between the photocatalyst thin film and the pollutant.

Figure 3-10 PCO performance of different substrate materials ($C_{\text{in}} = 42.19 \pm 2.80$ ppm, RH = 60%, volumetric flow rate = 1 L/min, UV light intensity = 3.8 mW/cm^2 , temperature = 24°C).

3.4. Conclusion

Highly sensitive and precise sampling and analytical method of gaseous formaldehyde was established using active-sampling + GC-FID detection of formaldehyde derivative. The detection limit of the overall procedure (sampling + analysis) was 358 ng per desorption solution (1mL) which is much more sensitive than that of the reference method NIOSH 2541. The overall procedure has very high recovery rate at an average value between 90.42% to 106.46% for samples stored up to 14 days. The precision (coefficient of variation, CV) of the overall procedure for 36 replicate samples in three concentration levels ranges from 1.54% to 2.97%, indicating the detected formaldehyde concentration has high reliability.

High performance fix-bed photo-reactor and the overall experimental setup for PCO reaction were designed and fabricated. The reactor allows comparing of different substrate materials under the same experimental conditions. The limiting factors that affect the PCO efficiency can be easily adjusted in the experimental setup. The

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overall PCO reaction system has very high stability for long time continuous running.

A simple and economical photocatalyst immobilization method was developed and optimized. This method using spray coating can provide stable and effective photocatalyst thin film on different kinds of substrate material without high temperature heat-treatment process. According to the optimization results and discussion, the inorganic colloidal silica is a better binding agent against the polyurethane gel. Samples prepared with colloidal silica as binder have more uniform catalyst dispersion, less coagulation and smaller catalyst agglomerate size. Samples prepared with polyurethane have heavy coagulation, larger catalyst agglomerate size and low stability during UV-PCO process due to the degradation of the binder itself. PCO degradation efficiencies of gaseous formaldehyde on samples with colloidal silica binder are all higher than samples with polyurethane binder.

The evaluation of the stabilization temperature shows that more homogeneous photocatalyst thin films are formed at 60 °C rather than at 120 °C. Heavy film delamination and cracking were observed on samples stabilized at 120 °C, which results in lower PCO efficiency comparing to samples stabilized at 60 °C. The delamination and cracking also lead to poor adhesion of photocatalyst on the substrate surface, resulting in unstable PCO performance of the samples.

For the same amount of photocatalyst coating, the spray-coated polyester fiber substrate sample has almost double the efficiency over the aluminum and quartz glass substrate samples. High surface area of the fibrous structure enables catalyst particles to disperse more homogeneously on the substrate surface with less overlapping. The 3-D structure also enhances the contact between photocatalyst thin film and the pollutant.

In general, PCO of gaseous formaldehyde can be successfully performed on the experimental system used in this study with high stability. The sampling and

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analytical protocol of gaseous formaldehyde has high sensitivity and precision. Effective photocatalyst immobilization can be achieved through the spray coating method by using colloidal silica as binder. Stable and high performance coating can be obtained on the polyester fiber substrate with a final stabilization step at 60 °C. The following works will focus on the combination of colloidal silica + polyester fiber substrate to further investigate their application in indoor air purification.

CHAPTER 4

Indoor Air Purification Using TiO₂-coated Polyester Fiber Filter: Effect of Binder Dosages on the Degradation of Gaseous Formaldehyde

4.1. Introduction

Indoor air pollution has become one of the top environmental risks to human health due to its significant contribution to human exposure to hazardous contaminants (Bruce, Perez-Padilla et al. 2000; Bardana 2001; Franklin 2007). The reasons for this include: people spend the majority of their time indoors; there is a wide and varied range of emission sources indoors; and for certain kinds of pollutant, e.g. formaldehyde and environmental tobacco smoke (ETS), the concentration levels are always higher in indoors compared with outdoors. Despite controlling the emission source and increasing ventilation, various of control technologies, such as filtration (Klimov, Serdyuk et al. 2009), adsorption (Jee, Lee et al. 2005), ionization (Nishikawa and Nojima 2001), ozone oxidation (Huang, Lee et al. 2012), etc., have been used for indoor air purification of different pollutants.

The application of heterogeneous photocatalytic oxidation (PCO) for air purification has been investigated intensively in the past two decades, particularly in converting indoor air volatile organic compounds (VOCs) into less toxic minerals, carbon dioxide and water (Zhao and Yang 2003; Hodgson, Destailats et al. 2007). This technique carries certain advantages such as: utilizing UV and/or visible light as initialization energy; non-selectivity of organic pollutants; potential to complete mineralization into CO₂ and H₂O; and persistent effectiveness throughout the lifetime of the photocatalyst under ambient temperature.

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As one of the best known carcinogenic VOCs, formaldehyde has been commonly identified in the typical indoor environment for its wide application in building materials and household products. It is also a by-product from cigarette smoking and fuel-burning (Daisey, Hodgson et al. 1994; Crump, Squire et al. 1997; Hodgson, Rudd et al. 2000; Hippelein 2004a). Using heterogeneous PCO for the degradation of formaldehyde has been considered as a promising technique. Many previous studies focused on the degradation mechanism and limiting factors, such as relative humidity, initial pollutant concentration, light intensity, etc. (Peral and Ollis 1992; Obee, Timothy N. and Brown, Robert T. 1995; Obee 1996; Noguchi, Fujishima et al. 1998). In the past decade, more concerns have been raised on the effectiveness of photocatalyst immobilization for its potential on large scale application (Paschoalino, Kiwi et al. 2006; Žabová and Dvořák 2009; Paz 2010).

Catalyst immobilization is the key for successful implementation of heterogeneous photocatalytic oxidation (PCO) of indoor air pollutants. Substrate selection and effective coating method are two crucial factors in catalyst immobilization. Suitable substrates should not only have stable physical and chemical properties but also can provide large surface area for the catalyst to attach on. A desirable coating method should meet the following requirements: provides stable and durable coating; provides effective and sufficient contact between the coating and the pollutants; non-selective of different substrates; easy and energy-efficient; economical and suitable for large-scale application.

Some commonly used substrates such as glass, aluminum, and stainless steel etc. are suitable for high temperature annealing treatment after coating. However, the stiffness and weight of the materials impose limitations for large-scale implementation. Textile-structured polymer materials, such as polyester (Meji'a, Mari'n et al. 2010), cellulose acetate (Coronado, Suárez et al. 2008), cotton textiles (Yuranova, Mosteo et al. 2006), and wool-polyamide (Bozzi, Yuranova et al. 2005), have also been studied in recent years for their low cost, flexibility and large surface area. Polyester, commonly referring to polyethylene terephthalate (PET), is one of the most stable and widely used artificial fabrics in the industry. In recent years,

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TiO₂ coated polyester materials have been studied for the application on indoor air purification (Dong, Bai et al. 2007; Park and Na 2008), disinfection and anti-bacteria (Paschoalino and Jardim 2008; Mihailovic, Saponjic et al. 2010), as well as self-cleaning surface (Sawada, Sugimoto et al. 2003). Most of the previous works were focusing on the degradation/elimination efficiency rather than on the stability and durability of the coatings.

Sol-gel dip coating is a widely used immobilization method for fix-bed photocatalysis (McMurray, Byrne et al. 2004). Although the performance of sol-gel dip coating is satisfactory in terms of coating stability, the high temperature (typically higher than 400 °C) heat treatment step for annealing after coating is not applicable to the textile-structured substrates without losing their physical and chemical integrity (Lim, Lynch et al. 2009). Other coating methods, such as spin coating, electrochemical deposition, electrophoretic coating, and sputtering etc., usually have complicated steps to achieve the preferable film thickness and are also costly and difficult for practical application (Byrne, Eggins et al. 1998; Kasanen, Suvanto et al. 2011).

Large-scale application of PCO for air purification can be achieved through direct coating of commercial photocatalysts such as Degussa P25 TiO₂ (Paz 2010). When using direct coating, the primary issue of interest is the stability of the coating. Poor adhesions have been reported on glass substrate by direct coating method such as dip coating or spin coating (Mills, Elliott et al. 2002; Keshmiri, Mohseni et al. 2004), where even slight mechanical abrasion may remove the photocatalyst from the substrate surface. Thus, a binding agent is usually necessary for direct coating in order to form solid adhesion between catalyst and substrate. Either organic polymer or inorganic binding materials have been used for photocatalyst immobilization (Du, Carneiro et al. 2008; Lim, Lynch et al. 2009; Henderson 2011). However, the effect of binder amount on the PCO activity and stability of the coating is seldom discussed.

The present study attempts to develop a simple and economical spray coating

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method to effectively immobilize P25 TiO₂ (Degussa) nanoparticle onto polyester fiber substrate. Colloidal silica (Ludox AS-40), which is a typical industrial binder but seldom be reported for being used as binder in direct coating of photocatalyst, was added into the coating suspension as a binding agent to increase the adherence between TiO₂ and the substrate. Without high temperature heat treatment, the coatings were finally cured at 60 °C for stabilization. PCO of gaseous formaldehyde was carried out on the spray-coated samples. The effect of binder dosages on the PCO efficiency of the coatings was evaluated and discussed in details. One sample prepared by dip coating was also evaluated for comparison purpose. Mechanical stability test was taken to evaluate the effects of different methods (spray coating vs. dip coating) on the stability and durability of the coating.

4.2. Experimental methods

4.2.1. Materials

The polyester substrates used in this study are non-woven dry polyester fabrics, with a typical filter thickness of 10 mm and overall packing density of 0.055 g/cm³. The polyester fiber has diameter of about 25-40 μm and fiber density of about 0.24-0.38 dtex. They are usually used as air filter media in the HVAC system for particle filtration and are provided by a local supplier (BioFit, Singapore). Titanium dioxide TiO₂ (Degussa P25) was purchased from Evonik Degussa (Germany). Ludox AS-40 colloidal silica was purchased from Sigma-Aldrich (USA). All other chemicals used for the preparation of spray/dip-coated samples as well as for photocatalytic activity test were chromatography grade and used without further purification as received (Sigma-Aldrich, USA). Milli-Q water was used as solvent at all time.

4.2.2. Preparation of spray-coated polyester samples

The spray-coating method used here are similar to that developed in Chapter 3, but different binder dosages will be evaluated to figure out the best coating conditions. The polyester substrates were cut into the size of roughly 100×50×3 mm. All the substrates were washed with 0.5% nonionic washing agent Felosan RG-N (Bezema, Switzerland) at liquid-to-fabric ratio of 45:1 in an ultrasonic washer (Kudos, China) for 15 min and rinsed with Milli-Q water followed by sonication for 15 min for three times. Pure acetone was used in the final washing stage, and the substrates were dried in pure nitrogen gas flow at room temperature.

The coating suspensions were prepared using P25 TiO₂ nano-powder, Milli-Q water and Ludox AS-40 (binder). Four different coating suspensions with TiO₂:binder (SiO₂ equivalent) mass ratio of 2:1, 1:1, 1:2, 1:4 were prepared (identified hereafter as sample S-1, S-2, S-3 and S-4, respectively). Certain amount of P25 TiO₂ nano-powder was firstly suspended in Milli-Q water under magnetic stirring for 30min, followed by dripping Ludox AS-40 slowly into the TiO₂ suspension at a speed of 1 mL/min with stirring. The mixed suspension (5 g of TiO₂ per liter) was then further stirred for 1 hr.

A Navite F-75G spray gun (Navite, China) was used for spray coating, with nitrogen as the carrier gas under a pressure of 65 psi. The spray distance from the nozzle exit to the substrate surface was 150 mm. To achieve uniform coating on the bulk body of the substrate, the substrate was spray-coated on both sides. Each side was sprayed evenly for 10 rounds. An interval of 15 min was taken every two rounds using a blow drier to evaporate water. The spray-coated substrates were finally cured at 60 °C for 3 hr to stabilize the coatings. The substrate was weighed by a digital analytical balance (readability of 0.0001 g, Mettler-Toledo, Switzerland) before and after coating.

4.2.3. Preparation of dip-coated polyester sample

One dip-coated polyester sample (identified hereafter as sample D-2) with TiO₂:binder (SiO₂ equivalent) mass ratio of 1:1 was also prepared. The substrate pre-treatment and preparation of coating suspension are identical to those used in preparing the spray coating samples. The substrate was dipped into the coating solution for 30 min with stirring and then dried by a blow drier for 15 min. Several rounds of dipping-drying process were taken until the amount of coating reached the same value as that of the spray-coated sample S-2. The coating was then also stabilized at 60 °C for 3 hr.

4.2.4. Sample characterization

Surface characterization of the spray/dip-coated samples was carried out by a JEOL JSM-5410LV (JEOL, Japan) scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS) analysis. The amounts of TiO₂ and SiO₂ contents on the substrates were derived by gravimetric measurement together with X-ray fluorescence (XRF) analysis on a Bruker AXS SRS 3400 (Bruker, Germany) X-ray fluorescence spectrometer with Rh source. Infrared spectroscopy was performed on a Perkin Elmer 100 Optica (Perkin Elmer, USA) Fourier Transform Infrared Spectrometer (FTIR). The spectrum was taken in the range of 500-4000 cm⁻¹. BET surface areas of the samples were determined by nitrogen physisorption on an Autosorb-1 system (Quantachrome, USA).

4.2.5. Evaluation of photocatalytic activity

The photocatalytic oxidation (PCO) of gaseous formaldehyde was performed on a fix-bed photo-reactor which was designed according to the ISO standard 22197-1:2007 (ISO 2007a) with special modifications based on the application in this study. The schematic diagram of the fix-bed photo-reactor design is similar with

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Figure 3-1.

The reactor body is made of polished stainless steel 316L (Exel-Mitsui, Singapore). An optical window made of GE214 fused quartz glass (General Electric, USA) is installed on the top cover to allow UV irradiation. Three parallel photo-reactors were used simultaneously. The schematic diagram of the PCO experimental setup is similar with Figure 3-3.

Three FPX9BLB 9 W UV light lamps (USHIO, Japan) with light centered at 368 nm were positioned above each photo-reactor in the center line. The PCO experiments were carried out using a standard procedure as follows. Certain amount of 37 wt. % formaldehyde solution was added into the source tank and sealed. The polyester samples were placed into the photo-reactors. The carrier gas (purified air) firstly flowed through the source tank and the humidifier, carrying the formaldehyde vapor and water vapor into the mixing chamber. The well-mixed testing gas then passed through the three photo-reactors in a parallel order. Volumetric flow rate was controlled by mass flow controllers connected at the end of each photo-reactor. Formaldehyde was sampled by sorbent tube (226-117, SKC, USA) at 100 mL/min every 15 min. After sampling, formaldehyde derivatives captured by the sorbent were dissolved out with 1 mL toluene by sonication and analyzed by an Agilent 6890 GC-FID system (Agilent, USA). Details of the GC test conditions are shown in Table 4-1.

The detection limit of the analytical procedure (GC-FID) was about 358 pg/injection (1 μ L). This was the amount of the analyte which gave a peak whose height was about 3 times the height of the peak given by the residual formaldehyde derivative in a typical blank front section of the sampling tube. The detection limit of the overall procedure (derivatization + desorption + analysis) then was determined as 358 ng per sample, which was equivalent to approximately 0.2 ppm in a 1.5 L gas sample at 24 °C. This was the smallest quantitated amounts of analyte spiked on the front section of the sampling tube, with an average recovery of 95.8 % $\pm$ 2.4% (n = 6).

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Table 4-1 GC test conditions for formaldehyde derivative.

Parameters	Conditions
Analyte	Oxazolidine derivative of formaldehyde
Injection Volume	1 μ L splitless, split vent time 30 sec
Temperature – Injector	300 $^{\circ}$ C
Detector	300 $^{\circ}$ C
Column	70 $^{\circ}$ C for 1 min, 15 $^{\circ}$ C/min, hold at 240 $^{\circ}$ C for 3 min
Carrier Gas	Helium at 1.3 mL/min, makeup flow of 29 mL/min
Column	DB-WAX 123-7033, 30 m $\times$ 0.32 mm, 0.50 μ m film thickness

Before switching on the UV light lamps, the testing gas flow would continuously pass through the photo-reactors to reach the steady state, which was indicated by reaching the same values in inlet (C_{In}) and outlet (C_{Out}) concentrations. According to the preliminary test result, this process usually took about 1.5 to 2 hr in our current system. Therefore, in the present study, UV light lamps were turned on after 2 hr of system stabilization. The PCO removal rate of formaldehyde, η (%), was calculated as:

$$\eta(\%) = \frac{C_{In} - C_{Out}}{C_{In}} \times 100 \quad (4-1)$$

The PCO experimental conditions are shown in Table 4-2. Four repeatable PCO experimental cycles were taken for each tested sample. The initial concentrations of formaldehyde averaged at 24.6 ± 2.8 ppm for all PCO tests, although the typical formaldehyde concentrations in a problem building range from 0.5 to 2 ppm. Since the baseline concentration of formaldehyde in the testing environment is typically 0.2-0.3 ppm, a concentration that is about 100 times higher than the environmental baseline was chosen to avoid the noise impact. In addition, higher concentration

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also help to shorten the sampling time needed in our analytical process so that a higher temporal resolution can be obtained.

Table 4-2 PCO experimental conditions.

Parameters	Values
Initial HCHO concentration (ppm)	24.6±2.8
Relative humidity (%)	60±4
Temperature (°C)	24±1 ^a
UV light intensity E ($\mu\text{W}/\text{cm}^2$)	3692
Volumetric flow rate (mL/min)	1000
Facing velocity (m/s)	0.067
Retention time (s)	1.5 ^b

^aReaction temperature was consistently maintained at 24±1 °C in a temperature-control environmental chamber.

^bRetention time was calculated by flow rate/cross-section area of air stream in the reactor.

4.2.6. Mechanical stability test of spray/dip-coated polyester samples

The mechanical stability test then was taken for each sample. An OS-20 Orbital Shaker (Boeco, Germany) was used for testing the mechanical stability of the coatings on the substrates by circle shaking. Shaking speed was set at the maximum rate of 200 rpm and continuously ran for 72 hr. The loss of TiO₂ and SiO₂ loadings after shaking were measured. Photocatalytic activities of all five samples after stability test were further examined for four successive cycles.

4.3. Results and discussion

4.3.1. Gravimetric and X-ray fluorescence (XRF) measurements of TiO₂ and SiO₂ contents on freshly prepared polyester samples

To compare the photocatalytic activities of the coated polyester samples, TiO₂ and SiO₂ (binder) loading amounts on the overall bulk of the substrates should be confirmed in the first place by gravimetric measurement and X-ray fluorescence spectroscopy (XRF). The overall substrate was first weighted by an analytical balance and then scanned in XRF to obtain the composition weight percentages of TiO₂ and SiO₂ component. The loading amount of each component then can be calculated by substrate weight $\times$ composition weight percentage. The results are shown in Table 4-3. For each tested sample, the values of the weight percentages (%) of TiO₂ and SiO₂ are the average of four repeatable XRF measurements taken on the whole substrate. All five samples have comparable TiO₂ loading amount, with average of 0.2542 ± 0.0194 g. For the spray-coated samples, loading amount of SiO₂ increases from S-1 to S-4, which corresponds to the different binder dosages in the coating suspensions. The measured mass ratios of TiO₂:SiO₂ for all five samples are approximately consistent with the theoretical values as 2:1, 1:1, 1:2 and 1:4 through S-1 to S-4. Consequently, the comparison of photocatalytic activities of all the five freshly prepared (before stability test) samples was based on equivalent photocatalyst loading amount.

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Table 4-3 Loading amounts of TiO₂ and SiO₂ on different samples before/after stability test.

Samples	Filter weight before coating ^c (g)	Total filter weight after coating ^c (g)	Composition weight percentages ^f (%)				Composition loading amount ^g (g)				Mass ratio of TiO ₂ :SiO ₂ ^h		
			B/ST ^d		A/ST ^e		B/ST ^d		A/ST ^e				
			TiO ₂	SiO ₂	TiO ₂	SiO ₂	TiO ₂	SiO ₂	TiO ₂	SiO ₂			
S-1 ^a	0.89	1.346	1.312	19.2 ±0.3	8.9 ±0.4	16.5 ±0.3	9.7 ±0.2	0.259 ±0.003	0.128 ±0.003	0.216 ±0.004	0.120 ±0.005	1:0.5	1:0.6
S-3 ^a	0.97	2.466	2.443	9.5 ±0.3	19.4 ±0.3	9.3 ±0.3	18.9 ±0.2	0.234 ±0.006	0.479 ±0.006	0.228 ±0.007	0.462 ±0.005	1:2.0	1:2.0
S-4 ^a	1.34	3.271	3.233	7.3 ±0.3	23.7 ±0.5	7.1 ±0.3	23.0 ±0.3	0.237 ±0.011	0.775 ±0.015	0.230 ±0.008	0.744 ±0.011	1:3.3	1:3.2
S-2 ^a	0.86	1.720	1.680	14.1 ±0.2	13.7 ±0.4	13.9±0.3	12.2 ±0.2	0.242 ±0.004	0.236 ±0.006	0.234 ±0.006	0.205 ±0.003	1:1.0	1:0.9
D-2 ^b	0.78	1.510	1.377	16.6 ±0.2	15.5 ±0.3	12.1 ±0.4	13.4 ±0.3	0.250 ±0.003	0.234 ±0.004	0.166 ±0.005	0.184 ±0.004	1:0.9	1:1.1

^a spray-coated. ^b dip-coated. ^c measured by analytical balance. ^d B/ST – Before stability test. ^e A/ST – After stability test.

^f measured by XRF in oxide testing mode for 4 repeatable measurements on the whole filter substrate.

^g calculated by total filter weight × weight percentage. ^h ratio of the average loading amount for each component.

4.3.2. Scanning electron microscopy (SEM)

Figure 4-1 SEM images of spray-coated samples with $\text{TiO}_2\text{:SiO}_2$ mass ratio of (a) 2:1, (b) 1:1, (c) 1:2, (d) 1:4 and dip-coated sample (e) with $\text{TiO}_2\text{:SiO}_2$ mass ratio of 1:1.

Figure 4-1 show the scanning electron microscopy of the four spray-coated samples (Figure 4-3, a-d) and the one dip-coated sample (Figure 4-1, e). Spray-coated sample S-2 (Figure 4-1, b) has the most uniform TiO_2 dispersion and less

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coagulation. The agglomerate size of TiO_2 attached on the polyester fiber increases with increasing binder loading amount. Spray-coated sample S-4 (Figure 4-1, d), which has the highest binder loading amount, shows heavy coagulation which might limit the contact between TiO_2 and the reactant species and further affect the PCO efficiency. For the dip-coated sample D-2 (Figure 4-1, e), a large agglomerate size can also be observed due to the coagulation formed in the dip-coating process, which affects the effective surface area of the coating and will further reduces its PCO activity. The following BET and PCO tests will verify the above observations.

4.3.3. Energy dispersive spectroscopy (EDS) analysis

EDS test was carried out simultaneously with SEM analysis in order to obtain the relative content of elemental compositions on the microstructure of the coating. Both Ti and Si signals were observed on the spectroscopy. The presence of TiO_2 and SiO_2 on the fiber surface was confirmed again. The average elemental percentages of Ti, Si are 3.97%, 6.50% on sample S-2, and 4.19%, 4.66% on sample D-2, respectively, which are correlated to the TiO_2 and SiO_2 loading amount in the whole bulk of the substrates measured by XRF. This surface elemental analysis may be used as an alternative when XRF is not available.

4.3.4. Infrared spectroscopy of the spray/dip-coated samples

FTIR analysis was carried out in order to obtain a better understanding of the coating structure. The IR spectra of the spray-coated sample S-2 and the dip-coated sample D-2 are shown in Figure 4-2 (a) and (b), respectively. In Figure 4-2 (a), TiO_2 bands are observed in the range of $500 - 800 \text{ cm}^{-1}$ with strong adsorption band appearing at 600 cm^{-1} representing of TiO_2 matrixes in six-fold coordination (Mohamed, Salama et al. 2002). The bands at 1060 cm^{-1} and 1080 cm^{-1} can be assigned to the asymmetric stretching and bending mode of the Si-O-Si banding (El Shafei and M. Mokhtar 1995; Mohamed, Salama et al. 2002).

Figure 4-2 FTIR spectra of (a) spray-coated sample S-2, and (b) dip-coated sample D-2.

A band at 950 cm^{-1} can be assigned to the stretching of Si-O species of the Ti-O-Si linkage which is formed by the inclusion of Ti^{4+} into the SiO_2 matrixes (Yamashita, Kawasaki et al. 1998). Combining all the information provided, it implies that TiO_2 species were embedded into SiO_2 matrixes through the high pressure spray coating approach. The bands at $1150 - 1240$ are associated to the ester group vibrations in the polyester structure.

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The IR spectrum of the dip-coated sample D-2 is presented in Figure 4-2 (b). TiO_2 bands between 500 and 800 cm^{-1} , as well as the asymmetric stretching band of Si-O-Si at 1060 cm^{-1} are also observed (El Shafei and M. Mokhtar 1995; Mohamed, Salama et al. 2002). However, there is no strong adsorption band which can represent the formation of Ti-O-Si linkage observed in Figure 4-2 (b), indicating that the immobilization of TiO_2 on the substrate through SiO_2 binder by the dip coating method is not as strong as those using the spray coating method in this study.

4.3.5. Stability of the spray/dip-coated samples

The coating amounts on all five polyester samples were measured and compared before and after the stability test. The result is shown in Table 4-3. The immobilized TiO_2 by spray coating has very good adhesion on the polyester fiber surface. After continuous shaking for 72 hr, the losses of TiO_2 content on the spray-coated sample S-2, S-3 and S-4 are all less than 3.6 %. Sample S-1 has a relatively higher loss at 16.7 %, which might mainly due to the insufficient binder as it has the lowest binder amount. The dip-coated sample D-2 has lost its TiO_2 significantly at 33.4 % after the stability test, which indicates the poor adhesion of the coating on the polyester fiber surface using dip coating. This result again verifies the observation in the IR spectra that strong bond between photocatalyst and the binder was formed by spray coating, but not by dip coating.

4.3.6. Surface area measurement by BET

BET measurements of the spray/dip-coated samples are shown in Table 4-4. Each coating sample was measured for four times (four small parts taken from different sites on the sample) to get an average BET value. Spray-coated sample S-2 has the highest BET area of 95.10 m^2/g . BET areas of spray-coated sample S-3 and S-4 dropped significantly to 64.56 m^2/g and 47.30 m^2/g , respectively. This result also

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confirms the observation on the SEM images that the excessive amount of binder causes larger agglomerate size which in turn leads to smaller effective surface area. Spray-coated sample S-1, which has the smallest binder loading, has a smaller BET area compared to sample S-2, indicating that certain amount of binder is preferred to generate uniform coating.

All the spray-coated samples have larger BET surface area than that of the dip-coated sample D-2 (49.97 m²/g), except for sample S-4 (47.30 m²/g) which has the largest binder loading. After the stability test, dip-coated sample D-2 has big decrease (about 14.9 %) in surface area due to the significant loss of TiO₂ content; while spray-coated sample S-2 has only a small decrease in surface area (about 2.5 %).

Table 4-4 BET surface area of different spray/dip-coated samples.

Samples	TiO ₂ :SiO ₂ mass ratio	BET area (m ² /g)	
		Before stability test	After stability test
S-1 ^a	2:1	56.23	
S-2 ^a	1:1	95.10	92.68
S-3 ^a	1:2	64.56	
S-4 ^a	1:4	47.30	
D-2 ^b	1:1	49.97	42.52

^a spray-coated, ^b dip-coated.

4.3.7. Photocatalytic oxidation (PCO) of gaseous formaldehyde

Figure 4-3 shows the variation of formaldehyde PCO removal rate within 105 min reaction (irradiation) time by sample S-2. The purpose of this test was to figure out when the system would provide a stable degradation after light turned on. Four repeatable experimental cycles were taken under the same conditions. Within the first 15 min after light turned on, as the substrate sample had already adsorbed HCHO and reached saturation during dark condition, the difference between inlet

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and outlet concentrations was not obvious when HCHO continuously flowing through the substrate sample. From 15 to 60 min, the removal rate increased progressively when more active sites were available and slowed down when the reaction process approaching the stable state. After 90 min, the removal rate did not change further. Therefore, in this continuous flow system, removal efficiencies of different samples were compared after light turned on for 90 min. No evident degradation was observed in either the absence of TiO₂ coating (non-loaded substrate) or UV irradiation.

Figure 4-3 Variation of PCO removal rate of formaldehyde within 105 min reaction time by sample S-2.

The PCO degradation efficiencies of formaldehyde by different spray/dip-coated samples before and after the stability test are shown in Figure 4-4. The spray-coated sample S-2 has the highest formaldehyde removal rate both before ($92.86\% \pm 2.58\%$) and after ($91.96\% \pm 2.42\%$) the stability test. For all spray-coated samples, there is no obvious loss of photocatalytic activity after the stability test, except for sample S-1, which is mainly due to the loss of TiO₂ loading on sample S-1 after stability test (see Table 4-3), indicating that small binder dosage can not provide satisfactory adherence of TiO₂ on the polyester substrate.

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For the dip-coated sample D-2, significant reduction of removal rate, from $75.28\% \pm 3.13\%$ to $40.93\% \pm 3.64\%$, is observed after stability test due to the significant loss of TiO_2 loading (shown in Table 4-3). It is worth to note that although there is a slightly higher TiO_2 loading on sample D-2 than that on sample S-2 before the stability test, the large agglomerate size formed during the dip coating process restricts its photocatalytic activity, resulting in the lower PCO efficiency than that of sample S-2.

Figure 4-4 PCO removal rate of formaldehyde by different spray/dip-coated samples before and after stability test.

One of the important findings in this study is the effect of binder dosage on the PCO activities of the spray-coated samples, which is clearly illustrated in Figure 4-4. For the freshly prepared spray-coated samples with equivalent TiO_2 loading amount, formaldehyde removal rate increases in the beginning and then decreases accordingly when the binder dosage rises from sample S-1 to S-4. Formaldehyde removal rate of sample S-2 is higher than that of sample S-1 due to the more uniform dispersion of TiO_2 coating and smaller agglomerate size. Further increasing the binder dosage in sample S-3 and S-4 leads to large agglomerate size thus decreases the effective surface area as seen in SEM images and BET test results. In

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addition, large amounts of binder might also wrap TiO_2 and limit the contact between TiO_2 and formaldehyde molecules. Small surface area combined with less contact lead to the decreasing photocatalytic activities of sample S-3 and S-4. With respect to the coating methods, the spray coating method developed in the present study shows great advantage over dip coating method in providing more stable and durable immobilized photocatalysts on the polyester fiber surface.

4.4. Conclusions

Effective immobilization of TiO_2 photocatalyst onto polyester fiber filter substrate was successfully conducted via spray coating approach. A strong dependence between the binder (SiO_2) dosage and the coating structure was observed. The optimal coating was achieved for $\text{TiO}_2\text{:SiO}_2$ mass ratio of 1:1, which shows the most uniform TiO_2 dispersion, the smallest coating agglomerate size and the highest PCO removal rate of gaseous formaldehyde. Certain amount of binder provides strong adherence of TiO_2 on the polyester fiber surface and also improves the formation and dispersion of small coating agglomerate. Higher binder dosage increases the coating agglomerate size and further limits the contact between TiO_2 and formaldehyde molecules.

Another sample prepared by conventional dip coating method with $\text{TiO}_2\text{:SiO}_2$ mass ratio of 1:1 shows bigger agglomerate size, smaller surface area and lower photocatalytic activity in comparing with the corresponding spray-coated sample.

The immobilization of TiO_2 on polyester substrates by spray coating is stable and durable, with only little loss of TiO_2 loading and no obvious decline on PCO efficiency after a 72 hr mechanical stability test. The stability of the dip-coated sample is not satisfactory with significant loss of TiO_2 loading and according decrease of photocatalytic. The spray coating method developed in this study is cost-effective and can be easily scaled up for the practical application of heterogeneous photocatalytic oxidation in indoor air purification.

CHAPTER 5

Experimental study on visible-light photocatalytic oxidation of gaseous formaldehyde by polyester fiber supported photocatalysts: effect of reaction parameters

5.1. Introduction

Heterogeneous photocatalytic oxidation (PCO) technology has been considered as an effective way for water and air cleaning in the past two decades (Dunnill, Aiken et al. 2009). Compared to other purification technologies, PCO has several advantages, such as clean, safe, energy efficient, and allowing complete mineralization of organic compounds into CO₂ and H₂O. There are increasing interests in recent years on PCO for indoor air purification of typical gaseous pollutants, such as HCHO (Akbarzadeh, Umbarkar et al. 2010; Fu, Zhang et al. 2011), NO (Huang, Ho et al. 2009; Mitsionis, Vaimakis et al. 2011), BETX (benzene, ethylbenzene, toluene and xylene) (Strini, Cassese et al. 2005; Boulamanti, Korologos et al. 2008; Tang and Yang 2012), TCE (trichloroethylene) (Cao, Yeung et al. 2007; Young, Lim et al. 2008), etc., due to the fact that air pollutants indoors put greater risks on human health than those outdoors (Jones 1999).

One of the inherent disadvantages of the commonly used photocatalysis approach, UV-TiO₂, is that only light in the UV wavelength range ($\lambda < 400$ nm) can be used to initiate the PCO reaction (Kuo, Tseng et al. 2007). This greatly limits the application in the typical indoor environment. The conventional attempt to extend the adsorption of TiO₂ to visible light range (400 - 700 nm) is to narrow its band gap (3.2 eV) by creating intra-band gap states that are close to the conduction or

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valence band edges, which allows the adsorption of visible light at sub-band gap energies of less than 3.2 eV (Yu and Brouwers 2009). Doping with non-metal species, such as N, C, S and F has been proved to be an effective way to generate visible light photoactivity (Fujishima and Zhang 2006). Some VIS-active photocatalysts modified by the doping method have been commercialized.

Studies on VIS-PCO of indoor air pollutants have been carried out extensively in recent years (Aoki, Morikawa et al. 2006; Ge, Xu et al. 2006; Li, Xu et al. 2009; Zhou, Li et al. 2009; Yu, Ballari et al. 2010; Wellia, Xu et al. 2011). Most of the current studies are focusing on the synthesis of VIS-active photocatalysts rather than on the immobilization of catalyst and the effects of reaction parameters that will help to promote practical application and to better understand the VIS-PCO process. Unlike the application in the liquid solutions, photocatalysts in powder form cannot be used directly for the gas phase oxidation without prior immobilization onto the proper substrate. The conventional sol-gel dipping and various chemical deposition methods usually required high temperature heat treatment for stabilizing the coatings (McMurray, Byrne et al. 2004; Yates, Nolan et al. 2006; Lim, Lynch et al. 2009). These methods are costly and inconvenient for large-scale application and have inherent limitation when selecting substrate materials. Thus, simple and cost-effective immobilization methods are essentially needed for VIS-PCO application to indoor environment.

Although significant progresses have been achieved on PCO of gaseous pollutants, there are still considerable differences in the results of the previous studies regarding to the effects of reaction parameters such as relative humidity (Obee, T. N. and Brown, R. T. 1995; Ao and Lee 2003; Devahasdin, Fan Jr et al. 2003; Daniel Vildoza 2011), volumetric flow rate (Ao and Lee 2003; Yu, Zhang et al. 2007; Yu and Brouwers 2009), etc. In addition, the degradation mechanisms of VIS-PCO of gaseous pollutants such as HCHO are seldom discussed. There are also discrepancies in the findings on the VIS-PCO mechanism. For instance, in a study by Sun et al. (Sun, Hongqi, Ullah, Ruh et al. 2011), the photo-generated hole (h^+) was supposed to play an important role in the degradation process of

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room-light-induced PCO on various gaseous pollutants by Pt/N-TiO₂ photocatalysts; while in Liu et al. (Liu, Wei et al. 2011) study of Fe and N-doped VIS-active TiO₂, high degradation of HCHO under visible light illumination was attributed to enhanced generation of hydroxyl radical (OH[•]). Therefore, more research efforts are necessary to acquire a clear comprehension of the VIS-PCO process.

In this study, a convenient spray-coating method was developed to effectively immobilize photocatalysts onto polyester fiber filter. Surface characterization and stability evaluation of the spray-coated polyester filters were conducted. Heterogeneous PCO of gaseous HCHO was then carried out by the spray-coated polyester filter under visible light illumination in a fix-bed photoreactor. The reaction parameters, such as volumetric flow rate, initial pollutant concentration, relative humidity level, visible light illumination intensity, as well as the loading amount of photocatalyst, that influence the VIS-PCO efficiency were investigated systematically. The degradation mechanism of VIS-PCO of HCHO was also proposed.

5.2. Experimental methods

5.2.1. Material preparation and characterization

Two non-metal-doped TiO₂ photocatalysts were used in this study. One commercialized carbon-doped TiO₂ (TiO₂-C, Kronos, Germany) was obtained from a local supplier. Detailed properties of this commercialized TiO₂-C photocatalyst are shown in Table 5-1. Another carbon and nitrogen co-doped TiO₂ (TiO₂-CN) was prepared following Wang and Lim's method (Wang and Lim 2011). Degussa P25 TiO₂ (Degussa, Germany) was also used for comparison purpose.

The substrates used in this study are non-woven dry polyester fabrics, with a typical filter thickness of 10 mm and overall packing density of 0.055 g/cm³. The polyester fiber has a diameter of about 25-40 μm and fiber density of about 0.24-0.38 dtex.

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This fiber material is commonly used as air filter media in the HVAC system for particle filtration and is provided by a local supplier. Ludox AS-40 colloidal silica (Sigma-Aldrich, USA) was used as a binding agent to immobilize the photocatalyst on the polyester fiber surface. Photocatalyst and binder were mixed with equivalent $\text{TiO}_2\text{:SiO}_2$ mass ratio of 1:1 and then dissolved with Milli-Q water while magnetically stirred to form the coating suspension. The coating suspension was then spray-coated onto the polyester filter with a size of roughly $100\text{ mm} \times 50\text{ mm} \times 3\text{ mm}$ ($W \times L \times T$), using a Navite F-75G spray gun (Navite, China) with nitrogen as carrier gas under a high pressure of 65 psi. The spray distance from the nozzle exit to the substrate surface was controlled at 150 mm. To achieve uniform coating on the bulk body of the filter, multiple coatings were performed on both sides. The coated filters were then dried at 60°C for 3 hr to stabilize the coatings.

Table 5-1 Properties of the Kronos vlp 7000 photocatalyst ($\text{TiO}_2\text{-C}$) provided by manufacturer.

Parameters	Values
TiO_2 content	Approx. 95% in Anatase
Crystallite size (anatase)	Approx. 15 nm
BET surface area	$>250\text{ m}^2/\text{g}$
Density (ISO 787, Part 10)	$3.9\text{ g}/\text{cm}^3$
Bulk density	Approx. $350\text{ kg}/\text{m}^3$
Max. processing temperature	150°C

X-ray diffraction (XRD) patterns of the two photocatalysts were obtained using a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) with monochromated high-intensity $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) in a 2θ range of $5\text{-}80^\circ$. X-ray photoelectron spectroscopy (XPS) evaluation were performed by a Kratos Axis Ultra spectrometer (Kratos, Japan) with a monochromatic $\text{Al K}\alpha$ excitation source ($h\nu = 1486.71\text{ eV}$). A UV-vis spectrometer (Lambda 35, Perkin-Elmer, USA) equipped with an integrating sphere assembly was used to obtain the UV-vis diffuse reflectance spectra (DRS). SEM images of the spray-coated filter samples were captured on a JEOL JSM-5410LV (JEOL, Japan) scanning electron microscopy. To

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evaluate the mechanical stability of the coatings, a 72-hr continuous shaking test was conducted on an OS-20 Orbital Shaker (Boeco, Germany) at the maximum shaking rate of 200 rpm on the spray-coated samples. The amounts of TiO₂ and SiO₂ contents on the substrate surface were analyzed before and after the shaking test by X-ray fluorescence (XRF) measurement on a Bruker AXS SRS 3400 (Bruker, Germany) X-ray fluorescence spectrometer with Rh source.

5.2.2. PCO experiment

The schematic diagram of the fix-bed photo-reactor used in this study is similar with that of Figure 3-1. The reactor body was made of 316L polished stainless steel (Exel-Mitsui, Singapore) which minimized the adsorption of pollutant inside the reactor. An optical window (GE 214 quartz glass) with ultra low resistance for UV and/or visible light was installed on the top cover of the reactor with inert sealing along the rim. Leak test was performed before and after each experimental circle.

The schematic diagram of the PCO experimental set-up is similar with that of Figure 3-3, but only different light source. Three parallel reactors were used in order to test different samples simultaneously under the same reaction conditions. The light source used were three 30 W fluorescence light tubes (Philips, Netherlands), which are commonly used as home lighting with a visible light range of 400-700 nm. Each light tube was installed on a height-adjustable frame that can adjust the distance between the light tube and the reactor surface. Purified synthetic air, with 20% O₂ and 80% N₂ (v/v%), was used as carrier gas to transfer gaseous formaldehyde and water vapor into the mixing chamber where different mixing ratios were controlled by the volumetric flow meter in each flow path. The temperature and relative humidity in the mixing chamber were monitored by a hygro-thermometer. Gaseous HCHO was generated by evaporating of 37% HCHO solution. SKC sorbent tube 226-117 (SKC, USA) is used for sampling gaseous formaldehyde through 2-hydroxymethyl-piperidine coated XAD-2 sorbent. The sampling rate was controlled by a sampling pump (SKC, USA). An Agilent-6890 GC-FID system (Agilent, USA) was used for concentration determination. The

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sampling and analytical method was developed with the NIOSH recommended method 2541 as a reference (NIOSH 1994). The GC testing conditions are shown in Figure 5-2. The detection limit of the overall procedure was 358 ng per sample, which was equivalent to approximately 0.2 ppm in a 1.5 L gas sample at 20 °C.

Table 5-2 GC-FID testing conditions for analysis of formaldehyde derivatives.

Parameters	Conditions
Analyte	Oxazolidine derivative of formaldehyde
Injection Volume	1 µL splitless, split vent time 30 sec
Temperature – Injector	300 °C
Detector	300 °C
Column	70 °C for 1 min, 15 °C/min, hold at 240 °C for 3 min
Carrier Gas	Helium at 1.3 mL/min, makeup flow of 29 mL/min
Column	DB-WAX 123-7033, 30 m × 0.32 mm, 0.50 µm film thickness

The PCO experiments were carried out following a standard procedure. Firstly, before the light tubes were turned on, the well-mixed testing gas was continuously flowing through the reactor until the filter sample inside reached steady state, which was determined by reaching identical HCHO concentrations at both inlet (C_{In}) and outlet (C_{Out}) of the reactor. This stabilization process usually took 1.5-3 hr depending on the experimental conditions. The sampling rate was set at 100 mL/min and sampled for 15 min, which is equivalent to a 1.5 L gas sample. The degradation efficiency of VIS-PCO of HCHO, $\eta_{(HCHO)}$ (%), was calculated by:

$$\eta_{(HCHO)} (\%) = \frac{C_{In} - C_{Out}}{C_{In}} \times 100 \quad (5-1)$$

To study the influences from different experimental parameters on the degradation efficiency of VIS-PCO of HCHO, the parameters (volumetric flow rate, initial

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concentration, relative humidity, visible light intensity and the amount of photocatalyst) were adjusted accordingly in the following PCO tests. The detailed experimental conditions are shown in Table 5-3. The initial formaldehyde concentrations tested in this study were all above 2 ppm in order to avoid the background noises and to ensure high confidence level from the analytical protocols, although HCHO levels found in the problem buildings are typically about 0.5-2 ppm. Under each experimental condition, four repeatable tests were taken in order to minimize the experimental uncertainty.

Table 5-3 VIS-PCO experimental conditions.

Parameter	Varying range
Volumetric flow rate (L/min)	0.1 - 1.2
Initial HCHO concentration (ppm)	3.4 - 35.4
Relative humidity (%)	20 - 90
Visible light intensity (lux)	4000 - 14000
Photocatalyst loading amount ^a (g)	0.1349 - 0.2890

^aequivalent TiO₂ content on the 100 mm × 50 mm × 3 mm (W × L × T) polyester filter.

5.3. Results and discussion

5.3.1. Characterization of the modified photocatalysts

Figure 5-1 shows the XRD patterns of the TiO₂-CN and TiO₂-C photocatalysts. Both of them are exhibiting peaks assigned to the pure anatase phase with high crystallinity, although the commercialized TiO₂-C shows lower intensities than those of the synthesized TiO₂-CN sample. The mean crystallite sizes of the TiO₂-CN and TiO₂-C nanoparticles are derived by the Scherrer's equation using the full-width at half maximum of the anatase (101) peak and are calculated to be 14 nm and 9 nm respectively. The BET specific surface areas of the TiO₂-CN and TiO₂-C photocatalysts were measured as 102.3 m²/g and 128.6 m²/g respectively.

The $\text{TiO}_2\text{-C}$ nanoparticles inherently have a more preferable microstructure and morphology than that of the $\text{TiO}_2\text{-CN}$.

Figure 5-1 XRD patterns of the two modified photocatalysts.

Figure 5-2 shows the XPS spectra of N 1s, C 1s, Ti 2P and O 1s for the two modified TiO_2 photocatalysts. In Figure 5-2(a), the peak centered at about 399.4 eV is present in the $\text{TiO}_2\text{-CN}$ sample which indicates the formation of Ti-N-O and/or Ti-O-N bonding (Chen, Bai et al. 2007). As for the $\text{TiO}_2\text{-C}$ sample, no peak assigned to the nitrogen content is observed. The spectra of C 1s core levels of the two samples are shown in Figure 5-2(b). The peaks at about 284.8 eV can be assigned to the adventitious elemental carbon in both samples (Ren, Ai et al. 2007). For $\text{TiO}_2\text{-CN}$, the peak at about 288.5 eV indicates the presence of C-O bond (Ren, Ai et al. 2007); while the other weak peak at about 281.5 eV can be assigned to the Ti-C bond formed during doping (Irie, Watanabe et al. 2003). For $\text{TiO}_2\text{-C}$, the peaks at about 289 and 286 eV can be assigned to the formation of C=O and C-O bonds,

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respectively, signifying the incorporation of carbon species into the TiO_2 lattice (Wang and Lim 2011). In Figure 5-2(c), signals of the core levels of Ti 2p in the two samples are observed with binding energies of around 458 eV for Ti $2p_{3/2}$ and around 464 eV for Ti $2p_{1/2}$. In addition, for the $\text{TiO}_2\text{-CN}$ sample, the peak with binding energy of about 455.6 eV might be associated to the presence of Ti-C and Ti-N bonds formed when doped with carbon and nitrogen species (Chen, Bai et al. 2007). The O 1s spectra in Figure 5-2(d) also confirm the presence of O-Ti, O-C and/or O-N bonds. In sum, it is well justified that carbon and/or nitrogen dopants are present in the TiO_2 lattice of the two modified photocatalysts. The introduction of these lattice defects may induce to absorption in the visible light wavelength range.

Figure 5-2 XPS spectra of (a) N 1s; (b) C 1s; (c) Ti 2p; and (d) O 1s for the two modified photocatalysts.

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The DRS of the two modified photocatalysts are shown in Figure 5-3(a) and compared with Degussa P25. It is obvious that both TiO₂-C and TiO₂-CN samples have significant absorbance of visible light in the range of 400-600 nm. The TiO₂-C sample shows a larger red-shift of the visible light absorption edge in comparison with the TiO₂-CN sample, which may be owing to the difference in their band gap energies. This result is in line with the above XPS analysis that the lattice defects on TiO₂ surface formed by doping with carbon and/or nitrogen species are responsible for the visible light activity. According to the DRS plot, the band gap energy (E_g) of the photocatalysts can be derived with the transformed Kubelka-Munk function by plotting the $(ah\nu)^{1/2}$ versus the energy of absorbed light in Figure 5-3(b). The calculated band gap energy of the TiO₂-C and TiO₂-CN samples are 2.47 eV and 2.84 eV respectively, which are all lower than that of the P25 TiO₂ (3.2 eV).

Figure 5-3 (a) UV-vis absorption spectra; and (b) transformed diffuse reflectance spectra of the two modified photocatalysts.

5.3.2. Evaluation of the coatings and their VIS-PCO of HCHO

SEM images of the spray-coated polyester fiber filters are shown in Figure 5-4. The photocatalyst clusters were formed during spray-coating and uniformly covered the polyester fiber surface. Both of the samples show relatively high agglomerate size due to the use of binder that induced coagulation. The homogeneity of the surfaces was well controlled by the spray coating process. As can be seen from Figure 5-4, the TiO₂-C coating has smaller agglomerate size than that of the

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TiO₂-CN coating due to its smaller particle size, which may create larger surface area for the pollutant to attach on. As the inter-spaces between the neighboring fibers are unfilled and allow both light and pollutant to enter, a three-dimension environment for the PCO reaction were formed, thereby enhancing the contact between the pollutant and the photocatalyst when comparing to the plate-form coatings.

Figure 5-4 SEM images of the spray-coated polyester filters with (a) TiO₂-CN; and (b) TiO₂-C.

The photocatalysts and binder contents on the spray-coated polyester fiber filters, before and after the shaking test, are shown in Table 5-4. The loading amount of the photocatalysts and binder contents did not change much after the shaking test, indicating strong immobilization of photocatalysts on the fiber surface formed by the spray-coating method in this study. During the high pressure spray-coating process, the photocatalyst molecules were strongly bonded to the SiO₂ binder on the polyester fiber surface. Since the process does not require high-temperature heat treatment to stabilize the coatings, it can be applied to large-scale coating on different textile materials and building surfaces.

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Table 5-4 Photocatalysts and binder contents on the spray-coated polyester fiber filters.

Sample	Total filter		Weight		Weigh		Loading		Loading	
	weight after		percentage of		percentage of		amount of		amount of	
	coating (g) ^c		TiO ₂ (wt/wt		SiO ₂ (wt/wt		TiO ₂ (g) ^g		SiO ₂ (g) ^g	
			%) ^f		%) ^f					
	B/ST ^d	A/ST ^e	B/ST ^d	A/ST ^e	B/ST ^d	A/ST ^e	B/ST ^d	A/ST ^e	B/ST ^d	A/ST ^e
#1 ^a	2.403	2.382	11.83	11.68	12.49	12.16	0.284	0.278	0.300	0.290
#2 ^b	2.231	2.198	12.64	12.76	13.36	12.11	0.282	0.280	0.298	0.266

^aSpray-coated with TiO₂-CN.

^bspray-coated with TiO₂-C.

^cWeighted by analytical balance.

^dBefore shaking test.

^eAfter shaking test.

^fmeasured by XRF on the whole bulk of the spray-coated filter samples.

^gcalculated by filter weight × weight percentage.

VIS-PCO of HCHO was carried out on the spray-coated samples for four repeatable circles both before and after the shaking test. No degradation was observed in the absence of either photocatalysts or light source. The result is shown in Figure 5-5. It can be seen from Figure 5-5 that both TiO₂-C coated and TiO₂-CN coated samples have much higher degradation efficiency than that of P25 TiO₂ under visible light illumination. The TiO₂-C coated sample shows higher visible light activity than that of the TiO₂-CN coated sample. This is due to its lower band gap energy, which gives rise to high utilization of the incident visible light; and its higher specific surface area, which generates more active reaction sites. Comparing all three samples before and after the shaking test, no obvious decrease of degradation efficiency is observed. This result again reaffirms that the spray-coating method can generate very stable immobilization of photocatalysts. Considering the preferable PCO performance of the TiO₂-C coated sample under visible light illumination, it was used for the following studies on the evaluation of the effects of different reaction parameters during VIS-PCO of HCHO.

Figure 5-5 VIS-PCO degradation efficiency of HCHO by different spray-coated samples ($C_{in} = 8.7 \pm 0.3$ ppm, $Q = 1$ L/min; $I = 10000$ Lux; $RH = 60\%$).

5.3.3. Evaluation on the effects of different reaction parameters

5.3.3.1. Effect of volumetric flow rate

Changes in volumetric flow rate will affect the PCO reaction rate by changing the convection mass transfer and the adsorption of HCHO molecules onto the photocatalyst surface. To verify the effect of volumetric flow rate on the VIS-PCO of HCHO, 4 different flow rates from 0.1 L/min to 1.2 L/min were evaluated with initial HCHO concentration (C_{in}) at 12.7 ± 2.2 ppm, relative humidity (RH) at 60% and visible-light intensity (I) at 10000 lux. The result is shown in Figure 5-6(a), where HCHO degradation efficiency decreased consistently when increasing flow rate from 0.1 L/min to 1 L/min and became stable when flow rate increased further. This is in line with the result of Qi et al. (Qi, Sun et al. 2007) where they found a

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steady decrease of PCO degradation efficiency of HCHO as the flow rate increased in both UV-TiO₂ and UV-TiO₂/O₃ processes with a HCHO initial concentration of 10 mg/m³ (about 8.1 ppm at 20 °C). In Figure 5-6(a), it is clear that low flow rates are favored by the degradation of HCHO under visible light illumination due to the longer residence time that forces more HCHO molecules to be adsorbed on the photocatalyst surface. Yu et al. (Yu, Zhang et al. 2007) also found that too high a flow rate resulted in shorter residence time and reduced the amount of formaldehyde degraded. However, the low convection mass transfer rate in low flow rates may slow down the PCO reaction.

Figure 5-6 Effect of volumetric flow rate Q on (a) VIS-PCO degradation efficiency of HCHO; and (b) HCHO oxidation rate ($C_{In} = 12.7 \pm 2.2$ ppm, RH = 60%, I = 10000 lux).

To verify the effect of volumetric flow rate on the reaction rate, the HCHO oxidation rate in the VIS-PCO process, γ ($\mu\text{-mole}/\text{cm}^3/\text{hr}$), is defined as:

$$\gamma = (C_{In} - C_{Out}) \times \frac{Q}{V} = C_{In} \times \frac{\eta Q}{V} \quad (5-2)$$

in which C_{In} and C_{Out} are the inlet and outlet HCHO concentration, Q is the volumetric flow rate, V is the flow region (illuminated reaction region), η is the single pass efficiency. Here γ is normalized by the flow region V (volume of the fiber filter, $10 \times 5 \times 0.3 \text{ cm}^3$) as the real reaction area is unknown. It is noted that the value (ηQ) is defined as the clean air delivery rate (CADR) which is used by the American Association of Home Appliance Manufacturers (AHAM) to evaluate the

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performance of an air cleaning device.

Figure 5-6(b) shows the dependence of HCHO oxidation rate on the volumetric flow rate. As the flow rate increases, the HCHO oxidation rate increases accordingly and becomes stable with flow rate higher than 1 L/min. This is in line with Obee and Brown's studies (Obee, T. N. and Brown, R. T. 1995; Obee 1996) on UV-PCO of HCHO and also agreed by Wang et al. (Wang, Wu et al. 2007) and Devahasdin et al. (Devahasdin, Fan Jr et al. 2003) when studying on PCO of NO. Different finding was also reported by Yu et al. (Yu and Brouwers 2009) where they found that the lower the flow rate was, the faster the conversion rate was obtained.

As can be seen from Figure 5-6(b), in the range of $Q > 1$ L/min, the effect from mass transfer on the oxidation rate becomes negligible as the high flow rates enhance the convective mass transfer rate from the bulk to the photocatalyst surface and reduce the difference between the concentration in the bulk (C_{bulk}) and the concentration adjacent to the photocatalyst surface (C_{surface}) (Obee, T. N. and Brown, R. T. 1995). Although the PCO reaction becomes faster in high flow rates, the single pass efficiency (η) decreases with increasing flow rate and become too small to measure when $Q > 1.2$ L/min (indicating by the increasing uncertainty bars) due to the shorter residence time. It is noted that the difference between C_{bulk} and C_{surface} should be as small as possible in order to scientifically interpret the measured kinetic data. From the above result, the 1 L/min flow rate in our system seems reasonable to achieve a balance between generating kinetic data and obtaining considerable degradation efficiency. The volumetric flow rates in the following experiments were all set at 1 L/min thereafter.

5.3.3.2. Effect of HCHO initial concentration

To evaluate the effect of initial concentration on the degradation efficiency of HCHO, VIS-PCO of HCHO by the $\text{TiO}_2\text{-C}$ coated sample was carried out with different HCHO initial concentration ranging from 3.4 ± 0.4 ppm to 35.4 ± 1.2 ppm. The result is shown in Figure 5-7(a), where $\eta_{\text{(HCHO)}}$ drops continuously with

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increasing HCHO initial concentration. This is parallel with the result in Qi et al.'s study (Qi, Sun et al. 2007), where the HCHO initial concentration increased from 1.84 to 24 mg/m³ (about 1.50 to 19.52 ppm at 20 °C) and the HCHO degradation efficiency decreased from 72% to 43.4% with a flow rate of 5 L/min.

Figure 5-7 Effect of HCHO initial concentration on (a) VIS-PCO degradation efficiency of HCHO; and (b) HCHO oxidation rate ($Q = 1$ L/min, $\text{RH} = 60\%$, $I = 10000$ lux).

A Langmuir-Hinshelwood model is used here to express the VIS-PCO of HCHO by the $\text{TiO}_2\text{-C}$ coated sample:

$$\gamma = \frac{kK_a C}{1 + K_a C} \Leftrightarrow \frac{1}{\gamma} = \frac{1}{kK_a C} + \frac{1}{k} \quad (5-3)$$

where k is the reaction rate constant and K_a is the adsorption equilibrium constant. Using the data from Figure 5-7(a), the measured oxidation rate can be calculated by Eq. (5-2). The reaction rate constant k ($0.3842 \mu\text{-mole}/\text{cm}^3/\text{hr}$) and the adsorption equilibrium constant K_a (0.4391 ppm^{-1}) then can be obtained through the least square regression. The dependence of initial oxidation rate γ on the HCHO initial concentration C_{in} is illustrated in Figure 5-7(b). The oxidation rate increases steadily with increasing HCHO initial concentration; and the increasing trend slows down in higher concentration level. The correspondence between the measured data and the Langmuir-Hinshelwood model is satisfactory, revealing that the oxidation rate is first-order at lower concentration level and becomes zero-order at higher concentration level. This kinetic model is confirmed by Obee and Brown (Obee, T. N. and Brown, R. T. 1995) when they studied UV-PCO of HCHO. The relationship

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between HCHO initial concentration and the oxidation rate is also coherent with Liu et al. (Liu, Li et al. 2008) study where they reported that the reaction rate of the HCHO decomposition increased with initial HCHO concentration increasing from 0.8-5.3 ppm. In general, the VIS-PCO of HCHO can achieve higher efficiency for low initial concentration, but at the expense of a longer reaction time. The VIS-PCO of HCHO happens more rapidly for high initial concentration; however, the degradation efficiency is not desirable.

5.3.3.3. Effect of relative humidity

Water vapor (H_2O) is usually considered a key factor that influences the UV- TiO_2 process based on the widely accepted mechanism that hydroxyl radical ($\text{OH}^\bullet$), formed through $\text{H}_2\text{O}/\text{OH}^-$ oxidation by the photo-generated h^+ , is the primary oxidative species that oxidizes the pollutants adsorbed on TiO_2 surface. As H_2O content changes, the $\text{OH}^\bullet$ population will alter accordingly. Besides, as the surface of TiO_2 will be hydroxylated when exposed to H_2O where hydroxyls are formed as a result of dissociative chemisorption of H_2O onto the Ti^{4+} sites (Primet, Pichat et al. 1971; Turchi and Ollis 1990), H_2O molecule will adsorbed on the surface hydroxyl groups via hydrogen bonding (Raupp and Dumesic 1985). As hydrogen bonding is normally stronger than other chemical bonding between the pollutant molecules and the hydroxyl groups (active sites), water vapor is likely to compete with the pollutant molecules in adsorbing on the photocatalyst surface and consequently inhibit the PCO reaction rate (Obee, Timothy N. and Brown, Robert T. 1995).

To investigate the effect of water vapor on the VIS-PCO of HCHO by the TiO_2 -C coated sample, three RH levels, 20%, 60% and 90%, were evaluated at two initial concentration levels of 8.6 ± 0.5 ppm and 3.3 ± 0.3 ppm, respectively. The result is shown in Figure 5-8(a), where the effect of RH on degradation efficiency is negligible at lower concentration level; while at higher concentration level, the degradation efficiency drops with RH up to 90%. Although under high concentration level, a possible competitive adsorption between H_2O and HCHO is observed when RH reaches 90%. The degradation efficiency of HCHO is not

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affected by increasing RH from 20% to 60%. This result is different from the previous studies on UV-TiO₂ photocatalysis. For example, Liu et al. (Liu, Li et al. 2008) found that the HCHO removal peaked at RH of 55% then declined when RH rose to 80% at an initial concentration of 5.5 ± 0.2 ppm. Similar result was also reported by Qi et al. (Qi, Sun et al. 2007) in their study on UV-PCO of HCHO, in which the HCHO degradation first increased and then decreased with RH increasing from approximately 25% to 70% at HCHO concentration of 22.2-24.0 mg/m³ (about 18.1-19.5 ppm at 20 °C).

Figure 5-8 Effect of relative humidity on the VIS-PCO degradation efficiency of HCHO by (a) TiO₂-C coated sample; and (b) TiO₂-CN coated sample ($Q = 1$ L/min, $I = 10000$ lux).

The result in Figure 5-8(a) indicates that increasing the amount of water vapor might not induce an increase in the population of OH[•] during the VIS-PCO process. To verify this finding, the TiO₂-CN coated sample was also adopted to evaluate the effect of RH during VIS-PCO of HCHO. Similar trend was obtained and shown in Figure 5-8(b). The possible competitive adsorption between H₂O and HCHO was observed for the high concentration level when RH reached 90% or higher. At low RH level, for either high or low concentrations, it is supposed that there were enough active sites for both H₂O and HCHO to attach, which means that the PCO process was not limited by adsorption but by the surface reaction. Varying the amount of H₂O did not inflict changes in degradation efficiency suggesting that the number of the oxidative species did not change. The VIS-PCO process might follow different reaction mechanism in comparison to the UV-PCO process.

5.3.3.4 Effect of visible light intensity

Influence from light intensity in UV irradiated photocatalysis has been well studied. The pollutant oxidation rate increases with increasing UV light intensity which follows a first order correlation at intensity below one sun equivalent (about 1–2 mW/cm² for wavelengths below 350 and 400 nm, respectively); For intensity well above one sun equivalent, the correlation changes to half order (Obee, Timothy N. and Brown, Robert T. 1995; Jean-Marie 1999). The reason is that for the first scenario, i.e. intensity below one sun equivalent, the PCO process will consume most of the photo-generated e^-/h^+ pairs; while for the second scenario, the recombination process will dominate, leaving less photo-generated e^-/h^+ pairs for the PCO process.

For visible light illuminated PCO reaction, the influence from light intensity is seldom discussed. Qu et al. (Qu, Liu et al. 2009) studied the effect of visible light illumination on the photo-degradation of HCHO by a nitrogen doped TiO₂ photocatalyst. With HCHO initial concentration at 0.98 mg/m³ (about 0.8 ppm at 20 °C), the degradation increased linearly from 25.5% to 59.6% alongside an incrementing illumination intensity of 0 to 30000 lux and stabilized thereafter. Yu et al. (Yu and Brouwers 2009) found an increasing NO_x conversion rate with visible light intensity increasing from 1.0 to 13.0 W/m² according to a logarithmic relation.

To the authors' knowledge, the energy expression in describing visible light intensity can only be adopted when the portions of different wavelength ranges of the light source are clearly identified. In this study, the visible light intensity of the fluorescence light tube used was measured by an illuminometer in lux. The effect of visible light intensity on PCO efficiency of HCHO is shown in Figure 5-9. The PCO efficiency of HCHO increases linearly with increasing light intensity from 4000 to 14000 lux. It should be noted that higher light intensity (>14000 lux) range was not studied as the temperature inside the photo-reactor will increase significantly under strong illumination and it is not favored by the PCO reaction on the current design.

Figure 5-9 Effect of visible light intensity on the PCO degradation efficiency of HCHO ($C_{\text{in}} = 9.6 \pm 0.8$ ppm, $Q = 1$ L/min, RH = 60%).

5.3.3.5 Effect of photocatalyst loading amount

The amount of photocatalyst will affect the PCO process by changing the population of the photo-generated e^-/h^+ pair as well as the numbers of active site for pollutants to attach. Qu et al. (Qu, Liu et al. 2009) reported that the degradation of HCHO increased from 0 to 82.9% when the amounts of N-TiO₂ powder increased from 0 to 5 g, with HCHO initial concentration at 0.98 mg/m³ (about 0.8 ppm at 20 °C), relative humidity at $33 \pm 5\%$, and illumination intensity at 10000 lux. Liu et al. (Liu, Li et al. 2008) studied the PCO of HCHO by TiO₂ coated glass plate, where they reported an increase in reaction rate with TiO₂ solid loading from 0 to 2 mg/cm², but the increase was not significant when TiO₂ loading was more than 2 mg/cm².

The effect of photocatalyst loading amount on the VIS-PCO degradation efficiency of HCHO by the TiO₂-C coated sample was also evaluated in the present study. The

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amounts of the loaded photocatalyst on the polyester filter were determined by gravimetric measurement and X-ray fluorescence (XRF) analysis as previously stated. The influence from photocatalyst amount is shown in Figure 5-10. For two different HCHO initial concentration levels, it is noticeably observed that the VIS-PCO degradation efficiency of HCHO increases significantly with increasing photocatalyst loading amount. More elaborately, the degradation efficiency improved three times over when photocatalyst loading amount increased from 0.1349 to 0.2890 g per substrate for both high and low HCHO initial concentrations. At lower initial concentration, the effect of photocatalyst loading amount on the VIS-PCO degradation efficiency of HCHO is greater than that at higher initial concentration.

Figure 5-10 Effect of photocatalyst loading amount (per substrate) on the VIS-PCO degradation efficiency of HCHO at two initial concentration levels ($Q = 1 \text{ L/min}$, $\text{RH} = 60\%$, $I = 10000 \text{ lux}$).

5.3.4. Possible reaction mechanism of visible-light PCO

The reaction mechanism of UV-TiO₂ photocatalysis has been proposed as following.

Generation of e^-/h^+ pairs:

On the valance band:

On the conduction band:

Theoretically, all the active species, such as holes (h^+), hydroxyl radical ($OH^\bullet$), superoxide radical ($O_2^{\bullet -}$), and hydrogen peroxide (H_2O_2), etc., generated during the photocatalysis process will be the potential oxidant to a specific pollutant. Currently, there are still different opinions regarding the UV induced PCO mechanism. Some authors agree that the direct oxidation mechanism by the photo-generated holes (h^+) on the valance band (Ishibashi, Fujishima et al. 2000); while the more prevailing opinion stands by hydroxyl radical ($OH^\bullet$) as the dominating oxidant (Obee, Timothy N. and Brown, Robert T. 1995). Indisputably, the role of $OH^\bullet$, generating from H_2O/OH^- oxidation by the photo-generated h^+ , are undoubtedly considered to be very important during UV-PCO process (Fujishima, Rao et al. 2000).

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For the non-metal-doped TiO₂ photocatalysts used in this study, as the doping of carbon and/or nitrogen forms intra-gap state of C 2p and/or N 2p locating above the valence band edge (O 2p) of TiO₂, the band gap of TiO₂ is then narrowed from 3.20 eV to 2.47 eV (TiO₂-C) and 2.84 eV (TiO₂-CN), allowing certain portion in visible light wavelength being absorbed to initiate the PCO process. According to the above detailed evaluation of VIS-PCO of HCHO by the two modified photocatalysts, H₂O has little influence on HCHO degradation in RH level from 20% to 60%. The increase of H₂O content did not result in enhanced generation of OH[•]. Even at extremely low RH level, e.g. 20% or less, the degradation of HCHO under visible light illumination is still quite considerable. In other words, OH[•] may not be the dominant oxidative species during VIS-PCO of HCHO. Similar result was reported by Wang et al. (Wang and Lim 2011) on the VIS-PCO of bisphenol-A in liquid phase by the C-N co-doped TiO₂, where they determined the roles of different oxidative species and concluded that the superoxide radical (O₂^{•-}), the singlet oxygen (¹O₂), and the hole (h⁺), rather than OH[•], are the predominant oxidative species.

In this study, the generation of OH[•] was also very limited on the TiO₂-C and TiO₂-CN photocatalysts under visible light illumination. The reason is because although visible light can be absorbed by the modified TiO₂ to generate electron/hole pairs, the redox potential of the VIS-generated holes, h⁺_(VIS) are smaller than that of the UV-generated holes, h⁺_(UV). As the redox potential of OH[•]/H₂O pair and h⁺_(UV) is about 2.27 and 2.53 V (vs. SHE) (Fujishima and Zhang 2006) respectively, H₂O (OH⁻) can be oxidize by h⁺_(UV) to generate OH[•]. While for h⁺_(VIS), its redox potential on TiO₂-C and TiO₂-CN used in this study is derived as about 1.80 and 2.17 V (vs. SHE) respectively, inferring that the oxidation of H₂O (OH⁻) to generate OH[•] by h⁺_(VIS) is thermodynamically unfeasible. On the other hand, as the position of the conduction band does not change after doping, the generation of O₂^{•-}, which also has relatively high oxidative activity (Nosaka, Nakamura et al. 2002), will not be affected. O₂^{•-} and the h⁺_(VIS) will then together mineralize the adsorbed HCHO molecules. The possible mechanism of VIS-PCO of HCHO is proposed as following:

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Under the experimental conditions employed in this study, no HCOOH as a byproduct was detected, indicating that HCHO was completely mineralized into CO₂ and H₂O by the current VIS-PCO process. The illustration of the VIS-PCO mechanism is shown in Figure 5-11.

Figure 5-11 Proposed mechanism of VIS-PCO of HCHO by C and/or N doped TiO₂ photocatalysts.

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When exposed to UV irradiation, $h^+_{(UV)}$ with stronger oxidative potential can be generated on the valance band edge of O 2p, which will promote the formation of $OH^\bullet$. Figure 5-12 shows the comparison of PCO degradation of HCHO under UV and visible light by the TiO_2 -C coated sample. When light source changed from 30 W fluorescence light tube to 9 W black UV light lamp (centered at 368 nm, intensity of 3.7 mW/cm^2), the degradation of HCHO increased more than one time for both the low and high initial concentrations. The increased amount of $OH^\bullet$ under UV irradiation contributed to the enhanced degradation efficiency. This again verified that $OH^\bullet$ is not the primary oxidant in VIS-PCO of HCHO but dominates during UV-PCO of HCHO.

Figure 5-12 Comparison between UV-PCO and VIS-PCO of HCHO at two initial concentration levels ($Q = 1 \text{ L/min}$, $RH = 60\%$, $I_{VIS} = 10000 \text{ lux}$, $I_{UV} = 3.7 \text{ mW/cm}^2$).

5.4. Conclusions

VIS-PCO of gaseous HCHO was carried out by non-metal-doped TiO₂ photocatalysts which was immobilized on polyester fiber filter through spray coating at room temperature. SEM images confirm that the photocatalysts were uniformly dispersed on the fiber surface with small agglomerate size. The coatings show good stability through a 72-hr mechanical shaking test, with almost no loss in photocatalyst content and PCO activity.

Reaction parameters that affect the degradation efficiency of HCHO under visible light illumination were evaluated and discussed in detail. According to the experimental result, small volumetric flow rate leads to higher degradation of HCHO due to the long residence time which results in large adsorption of HCHO molecules on the photocatalyst surface. High flow rates induce high convection mass transfer and then accelerate the PCO process. However, the shorter residence time affects the degradation efficiency. The degradation efficiency decreases with increasing HCHO initial concentration. The oxidation rate of HCHO increases rapidly with initial concentration increases within the low value range, and becomes stable when the initial concentration continue to increase to high value range. The result successfully correlates to a Langmuir-Hinshelwood model which indicates that the VIS-PCO of HCHO in this study is first order at low initial concentration level and zero order at high initial concentration level. Changes in relative humidity from low to high level does not affect the VIS-PCO degradation efficiency of HCHO for low pollutant concentration and only causes a little decrease in degradation when RH reaches 90% for high pollutant concentration. This result differs from the previous findings on the influence of water vapor in the UV-TiO₂ process, where the increase of RH usually result in higher degradation efficiency with the increase of OH[•] population. Degradation efficiency increases linearly with increasing visible illumination intensity. Under the same experimental conditions, the degradation efficiency increases significantly with increasing photocatalyst loading amount at either high or low pollutant concentrations. Changing the light source into UVA (368 nm), while keeping other parameters unchanged, the

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degradation of HCHO increases more than one time compared to the VIS-PCO process, indicating that $O_2^{\bullet-}$ and $h^+_{(VIS)}$, not $OH^{\bullet}$, may be the dominant oxidative species that contribute to the VIS-PCO of HCHO.

CHAPTER 6

Design, Preparation and Test of an Air Cleaner Prototype for Elimination of Gaseous Pollutants Indoors

6.1. Introduction

6.1.1. Research Interest on PCO Application

Early scientific findings about the phenomenon of photocatalytic effects on titanium dioxide can be dated back to 1930s – 1960s, during which most of the studies carried out were trying to understand the “chalking behavior” (Jacobsen 1949) and the degradation of colorants (Goodeve and Kitchener 1938) by using the “titanium white” pigment in the paints. Rather than the current popular term “photocatalysis” used since the early 1980s, the early workers in this area often used the term “photosensitization”. Few of the early works studied reactions on titanium dioxide, such as the photo-oxidation of ammonia (McLean and Ritchie 1965), however, those works were sporadic and did not produce a significant scientific impact or commercial interest in the utilization of titanium dioxide as a photoactive material (Paz 2010).

Ever since the publication of Fujishima and Honda’s (Fujishima and Honda 1972) pioneering paper on water splitting, heterogeneous photocatalysis has witnessed the beginning of an exponential growth on scientific manuscripts and patents with particular emphasis on the utilization of titanium dioxide for environmental applications such as water splitting, water and air treatment, sterilization and self-cleaning surfaces (Serpone, Emeline et al. 2012). The number of publications has kept on booming for the pass two decades as the awareness to environmental

issues being extremely increased.

Figure 6-1 Numbers of scientific manuscripts on titanium dioxide photocatalysis per year in three categories: water treatment (filled diamonds), air treatment (filled triangles) and self-cleaning surfaces (filled circles).

Figure 6-1 presents the number of scientific manuscripts (including journal articles and reviews) on titanium dioxide photocatalysis per year from 1990 to 2011, categorized according to application on: water treatment, air treatment, and self-cleaning surfaces. The results in Figure 6-1 were obtained by using SciVerse Scopus (2012) as a search engine, having “Titanium dioxide”, “Photocatalysis”, and “Water treatment” / “Air treatment” / “Self-cleaning” as searching hints in the Article Title, Abstract, Keywords field. It is a fact that the total number of publications on titanium dioxide photocatalysis is larger than the sum of manuscripts in these three categories each year, as these three categories can not cover all the applications in this field. Also, there is a chance that some authors used synonyms, e.g. “titania” and/or “TiO₂” instead of “titanium dioxide”, in their titles, abstracts and keywords. Nevertheless, the information provided by Figure 6-1 reveals the facts that: water treatment is still the subject with the most concerns on photocatalysis application; there is a lag in the scientific research on air treatment using photocatalysis; and there is a monotonically increase in the number of

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publications in each of the categories, particularly in the past decade. The possible reasons for the lag in the potential application of photocatalysis on air treatment are: lack of standardized gas-phase PCO reaction apparatus; the relatively lower efficiency of gas-phase PCO in comparison with liquid-phase PCO due to the inadequate contact between the photocatalyst and the target pollutant in the feeding gas flow; and no less important, more concerns on water pollution than on air pollution due to the increasingly severe water resource crisis worldwide.

6.1.2. Market Interest

In terms of practical use of photocatalysis technology, it seems to be by far less popular than the scientific interest, which can be easily reflected by the large number of published scientific manuscripts in comparison with the small number of commercialized products that appear in the market (Paz 2010). For almost three decades after the first “modern” manuscript on photocatalysis published, and despite the expectations from industrial and public side, photocatalysis has not become an indispensable technology that affects people’s daily life worldwide. However, regionally, especially in Japan, the commercial activities in the application of heterogeneous photocatalysis have been growing strongly for the past two decades. According to an overview by Mills and Lee (Mills and Lee 2002) in 2002, where they reviewed the major commercial applications of semiconductor photochemistry promoted on the world wide web, the majority of patents in semiconductor photocatalysis was assigned to Japanese companies including Fuji Electric Co. Ltd, Hitachi Ltd., Mitsubishi Ltd., Toyota Ltd., Nippon Muki Co. Ltd., etc., in the areas of photo-mineralizing organics, photo-sterilizing and photo-demist. Interestingly, according to the authors’ review, the biggest commercial application of semiconductor photocatalysis was not the destruction of organics in water but rather the destruction of organics in the gas phase. Particular interests were found in the areas of destruction of toxic volatile organic compounds (VOCs) and deodorization in either domestic or industrial scale.

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Similar trend was found by Paz (Paz 2009) in a review of patents on photocatalysis applications from 1990 to 2007, where the author pointed out that it seemed the scientific community was much less aware to the growing interest of the industrial and the commercial community, manifested, for example, by the large number of patents in air treatment using heterogeneous photocatalysis. The fact that since the year of 1997, the number of patents on air treatment using photocatalysis has surpassed that of water treatment is quite striking, especially if one takes into account that the number of scientific publications on water treatment is much larger than that of air treatment which is illustrated in Figure 6-1. The distribution of patents between the three above-mentioned categories on a cumulative basis from 1990 to 2007 is shown in Figure 6-2. It is evident that the number of patents on air treatment is larger than the sum of patents on water treatment and on self-cleaning surfaces.

Figure 6-2 Distribution of patents accumulated from 1990 to 2007 between three major categories in air treatment, water treatment and self-cleaning (Paz 2009).

Although there is evidently a growing interest in the implementation of photocatalysis for air treatment purpose, there are still some main challenges, such as mass transport, effective contact between photocatalyst and the pollutants, quantum efficiency, deactivation caused by potential byproducts and the long-term

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stability of the immobilized photocatalyst, that are still being faced by the industry in way to manufacturing practical, working devices that can be sold successfully in the market. Moreover, almost all of the available patents are utilizing TiO_2 photocatalysis, which require a UV light source to initiate the PCO reaction (Paz 2010). This might be due to the fact that the quantum efficiency of modified TiO_2 under visible light illumination is by far lower than the quantum efficiency of unmodified TiO_2 under UV irradiation (Zaleska 2008; Lim, Zhou et al. 2009; Rehman, Ullah et al. 2009; Sun, H., Ullah, R. et al. 2011), which has also been proved in this study (Chapter 5). Inevitably, the use of air purifier equipped with UV-PCO component in the indoor environment will pose potential exposure of harmful UV radiation to human beings. Therefore, the demand of utilizing visible-light/room-light induced PCO component that can provide effective elimination of gaseous pollutants on indoor concentration levels is essential for either industry or the public.

6.1.3. Experimental Purposes

The primary purpose of this study is to verify the validity of the scientific findings in this dissertation regarding visible-light initiated PCO degradation of gaseous formaldehyde and to explore the feasibility of implementing Vis-PCO for large-scale indoor air purification. The result will help us to better understand the Vis-PCO process and provide supporting data for optimizing the design of the air cleaner.

Based on the research on Vis-PCO of gaseous formaldehyde in this dissertation, the fix-bed photo-reactor and the immobilized photocatalyst developed earlier were scaled up into a portable air cleaner prototype which is intended to be used for indoor air purification of gaseous pollutants. To examine the “effectiveness” of the prototype, environmental chamber test was carried out in a 50 m^3 closed office room with the prototype working inside. The tested chamber was operated under static condition without mechanical ventilation and air conditioning. Another

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similar office room (50 m^3) was also used as a control chamber with no air cleaning device inside and operated simultaneously with the tested chamber. The decays in concentrations of formaldehyde and several other typical VOCs existing in the rooms were measured over a period of 4 hr. The effectiveness of the air cleaner prototype for each single compound was expressed in the value of clean air delivery rate (CADR) which is commonly used to evaluate the performance of portable air cleaners by the U.S. Association of Home Appliance Manufacturers (AHAM).

6.2. Experimental Methods

6.2.1. Preparation of large-scale immobilized photocatalyst

Nine pieces of $400\times 255\times 2\text{ mm}$ ($L\times W\times T$) polyester fiber filter were used as substrate for supporting the Kronos vlp 7000 (Kronos, Germany) visible-active photocatalyst ($\text{TiO}_2\text{-C}$). The photocatalyst was immobilized onto polyester fiber filter through spray coating method established earlier in Chapter 5. Certain amount of $\text{TiO}_2\text{-C}$ photocatalyst and binder were mixed at a converted $\text{TiO}_2\text{:SiO}_2$ mass ratio of 1:1 and then dissolved with Milli-Q water while magnetic stirred to form the coating suspension. The coating suspension was then spray-coated onto the polyester fiber filter using a spray gun with nitrogen as the carrier gas under a pressure of 65 psi. Several circles of spray coating were performed to form uniformly distributed $\text{TiO}_2\text{-C}$ thin film. The coated filter substrate was further dried at 60°C for 3 hr to stabilize the coating. The photocatalyst loading amount on the nine substrates after stabilization was about $2.0\pm 0.2\text{ g}$.

6.2.2. Prototype design and configuration

The prototype is constituted by a PCO reaction matrix (Figure 6-3, a) and a shell body (Figure 6-3, b) made of acrylic glass. The PCO reaction matrix, which has 9 tubular photocatalyst cells, can be fit into the shell body with air-tight sealing. Two

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DC exhaust fans (12 v, 2.28 W) are installed on the bottom of the shell body to provide a maximum 258 m³/h air flow rate.

(a)

(b)

Figure 6-3 Schematic diagrams of the PCO reaction matrix (a) and the shell body (b) of the air cleaner prototype.

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Figure 6-4 shows the schematic diagram of the structure of a single photocatalyst cell. In each cell, one piece of the photocatalyst-coated polyester fiber filter is fitted onto the tubular aluminum supporting mesh from inside. The light source used inside each cell is 6 LED light strips (5050 SMD, 30 pcs/m, 7.5 W/m) evenly distributed on the surface of a columnar aluminum support. This design can provide uniformly distributed incident light on the polyester fiber filter surface and enhance the utilization of the visible light illumination during PCO reaction. According to the spectrum of the light source, these white LED show strong blue light emitted at about 470 nm and more broadband Stokes-shift light emitted at around 500 – 600 nm. There is approximately a 2-mm thick air layer in between the LED strips and the polyester fiber filter. The measured light intensity on the filter surface is roughly 5000 lux.

The forced air flow will enter the cell from the inlet along the axial direction and then pass through the filter along the radial direction. The face velocity can be effectively reduced by increasing the face area on this configuration, so that a longer retention time and lower pressure drop will be achieved.

Figure 6-4 Schematic diagram of a single photocatalyst cell

6.2.3. Protocols for environmental chamber tests

The environmental chamber tests were conducted in two identical office rooms with a volume of 50 m³ and interior dimensions of 5.16 × 3.18 × 3.05 m (L × W × H). There are several typical furniture and office appliances inside each room: one desk, four chairs, two bookshelves, one computer table, one desktop, one printer. Before used for the chamber tests, the rooms were out of use for approximately a week, with the windows, doors, interior seams and the HVAC supply-air inlet and outlet all sealed. Background tests were taken before the chamber tests took place. Six kinds of VOCs, toluene, benzene, xylene (m, p), styrene, benzaldehyde and trichloroethylene (TCE) were detected, among which toluene has a relatively high concentration of about 103.2 ± 4.8 ppb while other compounds all have concentrations < 10 ppb. Background concentrations of formaldehyde in the two rooms are about 0.12 ± 0.013 ppm, slightly higher than the 0.1 ppm threshold limit.

To evaluate the performance of the air cleaner prototype in the typical problem building with formaldehyde exposure (usually 0.5 – 2 ppm), a source of formaldehyde was introduced into the control and tested rooms to generate a concentration around 2 ppm under steady state. A stand fan was placed in the corner of each room and operated after the sources were introduced and through out the chamber tests in order to create a well-mixed indoor environment. VOCs sources were not introduced into the rooms in this preliminary experiment due to the limit of time and the safety concerns. However, as high background level of toluene was confirmed in the rooms, it was supposed that the effect of the air cleaner prototype on degradation of typical indoor VOCs existing in the rooms could be evaluated under the current indoor conditions. The formaldehyde sources were removed before the chamber tests started. During the tests, temperature and relative humidity in the control and tested room were averaged at 28±3 °C, 63±11 % and 27±3 °C, 63±9 % respectively. Due to resources limitation, the environmental chamber tests were only repeated for twice. However, repeatable results were observed to represent the performance of the air cleaner prototype.

6.2.4. Sampling and Analysis

Figure 6-5 Tested room floor plan with instruments and sample locations.

The air cleaner prototype was placed in the center of the tested room on the desk (about 70 cm above the ground). There are two sampling ports located in the center of the tested room for formaldehyde and VOCs sampling. Another two sampling

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ports are located on the outlet of the air cleaner in order to measure the single pass efficiency of the air cleaner (see Figure 6-5). In the control room, there are two sampling ports located in the center of the room for formaldehyde and VOCs sampling. The chamber tests were conducted for 4 hr. Totally 7 samples for each of the detected compounds were collected.

For formaldehyde, the sampling and analysis procedures followed the methods established in Chapter 4, using SKC sorbent tube 226-117 at a sampling rate of 100 ml/min for 30 min and analyzed by GC-FID. For VOCs, Carbograph 2TD thermal desorption sampling tubes were used at a sampling rate of 100 ml/min for 30 min. Before sampling, the tubes were pre-cleaned at 320 °C for 30 min at a flow rate of 50 ml/min. After sampling, the tubes were capped tightly and stored in 4 °C fridge before analyzing. A Markes TD-100 thermal desorber (Markes International, UK) combined along with an Agilent 7890A gas chromatography/5975C mass spectrometry (Agilent, USA) was used for VOCs detection. The TD + GC/MS analysis follows a standard procedure:

The tubes were de-capped and installed into the thermal desorber. In the primary desorption stage, the parameters of the desorber were with the coldtrap maintained at 0 °C. The tubes were desorbed for 10 min at 250 °C with a desorption flow rate of 100 ml/min and split ratio of 2. In the secondary desorption stage, the coldtrap temperature was ramped to 250 °C immediately after the GC/MS was ready for injection, with a desorption flow rate of 10 ml/min and split ratio of 5. Therefore, during the overall thermal desorption stage, the gross split ratio was 10. One DB-5MS column (30 m × 0.25 mm × 0.25 μm) was used for separating the compounds. A temperature program was set: initially 40 °C for 10 min, then increased to 250 °C at 5 °C/min and hold for 5 min. The solvent delay time was 2 min. The MS was running with EI source in full scan model. Calibration curves of individual compounds were developed using EPA 624 standard on the concentration levels of interest. The linearity for each of the calibration curves was all above 0.990.

6.2.5. Evaluation of Cleaning Performance

According to the performance evaluation methodology of portable room air cleaners published by the AHAM, the term “clean air delivery rate” (CADR) is defined as “the rate of contaminant reduction in the test chamber when the unit is turned on, minus the rate of natural decay when the unit is not running, multiplied by the volume of the test chamber as measured in cubic feet” (AHAM 2006). In other word, the CADR value describes the equivalent volume of clean air provided to the room by operation of an air cleaner. Although AHAM initially uses the CADR methodology to evaluate the performance of air cleaners in reducing particulate matter concentrations, this approach is by no means restricted to particulate matter as an analyte (Shaughnessy and Sextro 2006). It has been proved in many published works that the CADR approach which utilizes a well-mixed box model and the assumption of first-order decay can be extended to the removal of gaseous pollutants (Daisey and Hodgson 1989; Axley 1994; VanOsdell 1994; Niu, Tung et al. 1998; Chen, Zhang et al. 2005).

The well-mixed box model can be expressed by a simple mass balance equation:

$$\frac{dC}{dt} = P\lambda_v C_o + \frac{S}{V} - \lambda_v C - \lambda_d C - \lambda_{ac} C \quad (6-1)$$

where C is the indoor contaminant concentration, P is the penetration factor, λ_v is the air exchange rate, C_o is the outdoor contaminant concentration, S is the contaminant emission rate (mass per unit time), V is the indoor volume, λ_d is the removal rate due to natural decay indoors (deposition, adsorption, reaction, e.g.), and λ_{ac} is the removal rate due to the operation of air cleaner.

In our environmental chamber tests, the emission sources were removed before the tests began, which means $S = 0$. Assuming the outdoor concentration of the target contaminants can be neglected. Eq. 6-1 then reduces to:

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$$\frac{dC}{dt} = -(\lambda_v + \lambda_d + \lambda_{ac})C \quad (6-2)$$

Eq. 6-2 describes the experimental removal rate of the target contaminants in the tested room with the air cleaner in operation. The solution to Eq. 6-2 is:

$$C(t) = C(0) \exp[-(\lambda_v + \lambda_d + \lambda_{ac})t] \quad (6-3)$$

$$\ln C(t) = -(\lambda_v + \lambda_d + \lambda_{ac})t + \ln C(0) \quad (6-4)$$

Then, by plotting $\ln C(t)$ vs time, the slope, which equals to $(\lambda_v + \lambda_d + \lambda_{ac})$, can be obtained by least square regression. As the CADR value is defined as $V\lambda_{ac}$, which equals to $V(\lambda_{AC} - \lambda_{noAC}) = V(\lambda_v + \lambda_d + \lambda_{ac}) - V(\lambda_v + \lambda_d)$, the CADR of individual contaminant can be determined as the difference between the removal in the tested room and the control room in this study.

6.3. Results and Discussion

6.3.1. Removal of formaldehyde

Figure 6-6 shows the removal of formaldehyde in the control room and the tested room during the 4 hr experimental period. The source introduced an initial concentration about 1.8 ppm inside the rooms, which represents heavy formaldehyde contamination problem. In the end of the testing period, there is no obvious decay of formaldehyde in the control room, while over 98 % of formaldehyde was removed from the tested room.

Figure 6-6 Formaldehyde removal in the control room, and the tested room with the air cleaner prototype in operation.

Using the CADR approach to evaluate the performance of the air cleaner prototype, formaldehyde removal rate due to filtration and natural decay ($\lambda_v + \lambda_d$) is obtained of about 0.08 h^{-1} in the control room; the removal rate in the tested room with the air cleaner in operation is about 1.03 hr^{-1} . So formaldehyde removal rate due to the operation of the air cleaner is about 0.95 hr^{-1} , and a corresponding CADR value of $47.5 \text{ m}^3/\text{h}$.

To evaluate the PCO experimental kinetics of the air cleaner during the environmental chamber test, the single pass degradation efficiency of formaldehyde was also measured. Assuming the indoor environment of the tested room was under well-mix condition at all times, the short-circuiting effect, i.e. the “cleaned” air from the outlet re-circled into the inlet of the air cleaner, can be neglected. So the detected indoor concentration C was used as the air cleaner inlet concentration C_{in} . The single pass degradation efficiency was calculated by:

$$\eta(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (6-5)$$

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Figure 6-7 presents the dependence of single pass degradation efficiency on the formaldehyde inlet concentration. As C_{in} decreased along the experimental time from 2254 to 103 $\mu\text{g}/\text{m}^3$ (about 1.83 to 0.16 ppm), η increased from 37% to 74%. The last sample point (sample number 7) is not included in Figure 6-7 as the outlet concentration is not detectable.

Figure 6-7 Dependence of single pass degradation efficiency on formaldehyde inlet concentration of the air cleaner.

As the real active area of the PCO component inside the air cleaner is not precisely known, formaldehyde reaction rate can be normalized by the flow face area of the PCO component. The normalized reaction rate γ ($\mu\text{g}/\text{m}^2/\text{s}$) can be calculated by:

$$\gamma = (C_{in} - C_{out}) \times \frac{Q_{ac}}{A} \quad (6-6)$$

where Q_{ac} (m^3/h) is the flow rate of air through the air cleaner, A (m^2) is the face area of the PCO filters. Here Q_{ac} was measured as 97.2 m^3/h . Using a Langmuir-Hinshelwood model to express the PCO reaction rate of formaldehyde by the air cleaner:

$$\gamma = \frac{kK_a C_{in}}{1 + K_a C} \Leftrightarrow \frac{1}{\gamma} = \frac{1}{kK_a C_{in}} + \frac{1}{k} \quad (6-7)$$

The reaction rate constant k and the adsorption equilibrium constant K_a can be obtained by least square regression (Figure 6-8).

Figure 6-8 Langmuir-Hinshelwood correlation coefficients.

The dependence of formaldehyde reaction rate γ on the inlet concentration C_{in} is expressed in Figure 6-9. The correspondence between the measured data and the Laugmuir-Hinshelwood model is good, indicating that the PCO reaction is first-order at lower concentration level and becomes zero-order at higher concentration level.

Figure 6-9 Formaldehyde reaction rate dependence on the air cleaner inlet concentration.

This result agrees with the conclusion in Chapter 5 when studying VIS-PCO of formaldehyde with the fix-bed photo-reactor in the laboratory using the same photocatalyst. Comparing to the laboratory scale experiments, the most significant changes in the PCO component in the air cleaner prototype are the increased number of active reaction site (photocatalyst loading amount + effective surface area) and the inlet flow rate. In the laboratory scale experiments, with initial concentration at 3.4 ± 0.4 ppm, flow rate of $0.06 \text{ m}^3/\text{h}$ (1 L/min), the single pass degradation efficiency is about $62 \pm 3 \%$; in the environmental chamber tests with the air cleaner prototype, initial concentration at 1.83 ppm ($2254.57 \mu\text{g}/\text{m}^3$) and inlet flow rate of $97.2 \text{ m}^3/\text{h}$, the single pass degradation efficiency can still reach to about 37 %. Considering the tremendous increase in inlet air flow rate, the single pass degradation efficiency of the air cleaner prototype is very satisfactory at lower initial concentration levels. The tubular filter design effectively reduced the face velocity of the flow passing through the filters, which induced in increasing retention time of contaminants. The convection mass transfer was also enhanced when the contaminants passing through the filter by reducing the diffusion distance from the bulk to the catalyst surface. In addition, the greatly increased number of active reaction site on the filters also contributed to maintain considerable

degradation efficiency with high treatment capacity.

6.3.2. Removal of VOCs

The removal of 6 detected VOCs in the control and tested room is shown in Figure 6-10.

(a)

(b)

Figure 6-10 Removal of 6 detected VOCs in the control room (a) and the tested room (b).

No significant decay of the VOCs was observed in the control room through the experimental period. In the tested room with the air cleaner in operation, significant decrease of toluene concentration is observed. Correspondingly, increase of benzaldehyde concentration is observed, which is probably as a by-product of PCO degradation of toluene (Blanco, Avila et al. 1996; Mendez-Roman and Cardona-Martinez 1998; Augugliaro, Coluccia et al. 1999; Martra, Coluccia et al. 1999; Marci, Addamo et al. 2003; Van Durme, Dewulf et al. 2007). The concentration of benzene increases during the first hour of the test, and then decreases accordingly, which indicates that benzene is also observed as a by-product during PCO degradation of toluene (Blanco, Avila et al. 1996; Augugliaro, Coluccia et al. 1999; Martra, Coluccia et al. 1999). For other VOCs, different levels of removal are also observed in the tested room.

Figure 6-11 Clean air delivery rate for 5 individual VOCs and formaldehyde.

The CADR values for individual VOCs and formaldehyde are shown in Figure 6-11. Formaldehyde has the highest CADR value, followed by toluene, styrene, xylene and TCE. Benzene as a possible by-product of PCO degradation of toluene has the lowest CADR value. This result is in line with the research by Hodgson et al. (Hodgson, Destailats et al. 2007), where they studied a UV-PCO system for removal of VOCs from air in office buildings. The authors found that conversion

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efficiency generally diminished with increased airflow rate and followed the order: alcohols and glycol ethers > aldehydes, ketones, and terpene hydrocarbons > aromatic and alkane hydrocarbons > halogenerated aliphatic hydrocarbons.

Studies regarding to the evaluation of performance of PCO equipped air cleaners are very limited at present. Chen et al. (Chen, Zhang et al. 2005) evaluated 15 air cleaners using a mixture of representative VOCs. The air cleaners tested covered a wide range of technologies, including sorption, ozone oxidation, air ionization, soil-botanical filtration, and UV-PCO. The UV-PCO device generated a CADR value of approximately 22 m³/h and 23 m³/h for formaldehyde and toluene respectively, which are both lower than the CADR values generated by the air cleaner prototype used in this study. Comparing to other devices, the authors pointed out that the UV-PCO air cleaner did not perform well against the challenge of VOC mixture; while when activated carbon was added to the device, the combined unit shown the best performance, which was attributed by the authors to the sorption on the activated carbon.

When considering the performance of air cleaning for gaseous pollutants, a 80 ft³/min (about 133 m³/h) CADR value is suggested to provide satisfactory cleaning effectiveness for a moderate size room with small losses to surfaces within the room (Shaughnessy and Sextro 2006). However, for the available published results, none of the devices examined by Daisey and Hodgson (Daisey and Hodgson 1989) approached this value; only two devices, which equipped with large amount of carbon in the adsorption bed, examined by Shaughnessy et al. (Shaughnessy, Levetin et al. 1994) exceeded this value for NO₂ removal; three carbon sorption based devices examined by Chen et al. (Chen, Zhang et al. 2005) had CADR above this value for a number of compounds.

Another challenge is how well the air cleaners perform over time. Daisey and Hodgson (Daisey and Hodgson 1989) reported a decrease of 50% or less of the initial CADR values of one carbon sorption based air cleaner after 150 h use in a residence, which was only about 15% of the recommended filter lifetime. For the

PCO air cleaning devices, it is supposed to have a longer working time in comparing to the sorption based devices as no loading saturation will be faced by the PCO device. However, further studies are essentially needed to evaluate the long-term performance of the PCO air cleaning devices.

6.4. Summary and Conclusions

In summary, the air cleaner prototype scaled up based on the scientific findings of the VIS-PCO experimental studies on gaseous formaldehyde in this dissertation shows promising performance in removing gaseous formaldehyde and typical VOCs from air in the office buildings. A relatively high CADR value for formaldehyde and toluene is achieved in comparing with other related studies. Benzaldehyde and benzene are two major by-products during PCO degradation of toluene. CADR values for styrene, xylene, TCE and benzene are all on a considerable level but lower than that of toluene. In terms of energy conservation, the prototype air cleaner has a consumption of 0.611 kWh during the 4 hr experiment, which equals to only 0.013 kWh/CADR values for formaldehyde and 0.020 kWh/CADR values for toluene.

Future research should focus on enhancing the cleaning effectiveness of the VIS-PCO air cleaner on different VOCs by optimizing the reaction structure of the PCO component to further increase the effective contact between the contaminants and the photocatalyst. The treatment capacity should also be improved in order to provide faster cleaning. Possible approaches include add in sorption based element and using more “powerful” UV light source. Studies on the long-term effectiveness of the air cleaner as well as the by-product problem are also essentially needed.

CHAPTER 7

Summary and Conclusions

7.1. Major findings/contributions

The overall objective of this research was to get a clear view on the applicability of heterogeneous photocatalytic oxidation technology for indoor air purification through evaluation of the VIS-PCO degradation of gaseous formaldehyde. A better understanding of the PCO process when used for treating gaseous pollutant was obtained. An immobilization method was developed which can be easily scaled up for practical use.

The major findings of this work are:

- 1) The PCO experiments carried out on the current experimental setup are highly repeatable, with considerable precision. This suggests that our overall experimental method is reliable for a large range of formaldehyde concentration level and our experimental setup works stable. Good agreement has been found between our experimental data and previously published data of PCO degradation of gaseous formaldehyde under typical indoor conditions which also suggest that our findings have substantial applicability to PCO of indoor level gaseous pollutants.
- 2) For the first time, using spray coating + binder to effectively immobilize photocatalyst onto different substrate materials at low temperature. This provides an easy and cost-effective photocatalyst immobilization way for potential large-scale PCO application in indoor air purification. Without high temperature heat treatment process, the flexible, fibrous and/or textile-structured materials can retain their inherent chemical/physical properties while provide high surface area to help in forming more

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uniform catalyst coating. The immobilized photocatalyst can be configured into different size, shape and loading according to the purpose of practical applications.

- 3) Using the optimized immobilized photocatalyst, gaseous formaldehyde with a concentration around 3-4 ppm can be degraded up to 65% under fluorescent illumination in our continuous flow photo-reactor. This is very promising in suggesting that a scaled-up VIS-PCO reaction system with the similar design will be able to purify the enclosed indoor environment under typical indoor conditions. The preliminary experimental result of the environmental chamber tests using our VIS-PCO air cleaner prototype shows promising performance in removing formaldehyde and several typical individual VOCs existing in the office buildings. For formaldehyde and the major target VOCs toluene, a satisfactory CADR value of 48 m³/h and 31 m³/h were achieved. This provides fundamental information for the design and fabricate of PCO-based air cleaning units either in the form of a portable air cleaner or a HVAC air cleaning system.
- 4) It is now much clearer which influential parameters most greatly affect the PCO degradation efficiency of gaseous pollutant, and what different degradation mechanism possessed by the VIS-PCO process in comparing with the UV-PCO process. In general, different from the liquid-phase PCO process where abundant of hydroxyl group providing sufficient amount of hydroxyl radical on and/or near the photocatalyst surface, the PCO reaction in gas-phase is an extreme surface process, any factors that affect the contact between the target compounds and the photocatalyst will lead to changes in PCO efficiency. Mass transfer and the effective contact sites are the major limiting factors. For the VIS-PCO process in gas-phase, water vapor is not an important limiting factors; even high level (90%) of relative humidity will not cause significant changes in PCO efficiency. VIS-PCO of gaseous pollutant has unsatisfactory performance in comparing with UV-TiO₂ PCO due to less generation of highly oxidative hydroxyl radical ($OH^\bullet$). Nevertheless, the results of our lab experiments and the preliminary tests on our air cleaner prototype double confirmed

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that VIS-PCO of gaseous indoor air pollutants can achieve a satisfactory performance under typical indoor environmental conditions.

7.2. Proposed future research

The results presented in this dissertation on the coating optimization and UV/VIS-PCO of gaseous formaldehyde are useful for prioritizing future research efforts. Based on these results, the following topics are suggested for future research:

- 1) Further investigate on the spray coating's stability and durability, and on the applicability of the spray coating method to more different substrate materials. Long-term onsite testing will be needed for evaluating the stability and durability of the spray coating. Materials that constitute the indoor surfaces, such as wall paper, paint-coat and ceiling, e.g., can be chosen for further expand the application of VIS-PCO in the indoor environment.
- 2) Further study on the PCO of other typical indoor air VOCs, including degradation of single species and multiple mixing species. Focusing on the potential loss of activity due to possible byproduct foiling on the coating surfaces.
- 3) For large-scale application, either used in the indoor space or in the HVAC duct, future research should focus on optimizing the reaction structure of the PCO element to further enhance the cleaning effectiveness and treatment capacity. Combination with other cleaning processes and/or with UV light source should be carefully explored. Studies on the long-term effectiveness of the air cleaner as well as the by-product problem are also essentially needed.

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APPENDIX

APPENDIX

Experimental raw data

Table A-1 UV-PCO degradation of HCHO

<i>I</i> ($\mu\text{W}/\text{cm}^2$)	<i>Q</i> (L/min)	<i>RH</i> (%)	<i>C_{in}</i> (ppm)	<i>C_{out}</i> (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3803	1	60	42.0	29.7	29.50	Quartz glass	Polyurethane	P25	4:1	60
3803	1	60	38.1	25.5	32.98	Quartz glass	Polyurethane	P25	4:1	60
3803	1	60	37.5	24.8	33.87	Quartz glass	Polyurethane	P25	4:1	60
3803	1	60	40.6	28.8	29.01	Quartz glass	Polyurethane	P25	4:1	60
3801	1	60	42.0	19.5	53.72	Quartz glass	Colloidal silica	P25	2:1	60
3801	1	60	38.1	16.6	56.46	Quartz glass	Colloidal silica	P25	2:1	60
3801	1	60	37.5	16.0	57.43	Quartz glass	Colloidal silica	P25	2:1	60
3801	1	60	40.6	19.0	53.23	Quartz glass	Colloidal silica	P25	2:1	60

APPENDIX

Table A-1 (continue)

<i>I</i> ($\mu\text{W}/\text{cm}^2$)	$\bar{Q}$ (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3802	1	60	41.0	26.7	34.77	Aluminum	Polyurethane	P25	4:1	60
3801	1	60	39.9	25.8	35.35	Aluminum	Polyurethane	P25	4:1	60
3801	1	60	43.6	29.7	31.82	Aluminum	Polyurethane	P25	4:1	60
3800	1	60	43.2	29.1	32.63	Aluminum	Polyurethane	P25	4:1	60
3801	1	60	40.9	19.3	52.99	Aluminum	Colloidal silica	P25	2:1	60
3803	1	60	39.9	18.1	54.73	Aluminum	Colloidal silica	P25	2:1	60
3801	1	60	43.6	21.9	49.90	Aluminum	Colloidal silica	P25	2:1	60
3802	1	60	43.2	20.8	51.82	Aluminum	Colloidal silica	P25	2:1	60
3800	1	60	42.7	15.7	63.19	Polyester	Polyurethane	P25	4:1	60
3800	1	60	48.7	20.1	58.82	Polyester	Polyurethane	P25	4:1	60
3802	1	60	45.4	18.0	60.41	Polyester	Polyurethane	P25	4:1	60
3801	1	60	43.7	16.5	62.18	Polyester	Polyurethane	P25	4:1	60

APPENDIX

Table A-1 (continue)

<i>I</i> ($\mu\text{W}/\text{cm}^2$)	$\bar{Q}$ (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3803	1	60	42.7	6.4	85.06	Polyester	Colloidal silica	P25	2:1	60
3802	1	60	48.7	9.8	79.81	Polyester	Colloidal silica	P25	2:1	60
3801	1	60	45.4	8.7	80.80	Polyester	Colloidal silica	P25	2:1	60
3801	1	60	43.7	6.7	84.57	Polyester	Colloidal silica	P25	2:1	60
3803	1	60	28.6	4.2	85.48	Polyester	Colloidal silica	P25	2:1	60
3803	1	60	22.3	2.1	88.34	Polyester	Colloidal silica	P25	2:1	60
3801	1	60	26.5	3.6	86.52	Polyester	Colloidal silica	P25	2:1	60
3800	1	60	26.5	3.3	87.44	Polyester	Colloidal silica	P25	2:1	60
3802	1	60	28.6	6.8	76.23	Polyester	Colloidal silica	P25	2:1	120
3800	1	60	22.3	5.9	73.67	Polyester	Colloidal silica	P25	2:1	120
3800	1	60	26.5	8.4	68.22	Polyester	Colloidal silica	P25	2:1	120
3800	1	60	26.5	10.5	60.64	Polyester	Colloidal silica	P25	2:1	120

APPENDIX

Table A-1 (continue)

<i>I</i> ($\mu\text{W}/\text{cm}^2$)	$\bar{Q}$ (L/min)	<i>RH</i> (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3800	1	60	40.1	18.7	53.51	Quartz glass	Colloidal silica	P25	2:1	60
3802	1	60	43.8	20.8	52.66	Quartz glass	Colloidal silica	P25	2:1	60
3801	1	60	41.1	18.5	54.97	Quartz glass	Colloidal silica	P25	2:1	60
3800	1	60	42.6	22.0	48.42	Quartz glass	Colloidal silica	P25	2:1	60
3803	1	60	38.1	17.8	53.31	Aluminum	Colloidal silica	P25	2:1	60
3800	1	60	40.6	17.2	57.64	Aluminum	Colloidal silica	P25	2:1	60
3801	1	60	39.1	17.2	56.09	Aluminum	Colloidal silica	P25	2:1	60
3800	1	60	40.4	18.7	53.71	Aluminum	Colloidal silica	P25	2:1	60
3800	1	60	47.1	7.7	83.72	Polyester	Colloidal silica	P25	2:1	60
3801	1	60	43.2	8.1	81.29	Polyester	Colloidal silica	P25	2:1	60
3800	1	60	44.1	6.3	85.62	Polyester	Colloidal silica	P25	2:1	60
3801	1	60	46.1	9.4	79.63	Polyester	Colloidal silica	P25	2:1	60

APPENDIX

Table A-1 (continue)

<i>I</i> ($\mu\text{W}/\text{cm}^2$)	$\dot{Q}$ (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3803	1	60	21.2	2.2	89.68	Polyester	Colloidal silica	P25	2:1 ^a	60
3802	1	60	28.7	6.0	79.20	Polyester	Colloidal silica	P25	2:1 ^a	60
3803	1	60	26.8	4.3	83.86	Polyester	Colloidal silica	P25	2:1 ^a	60
3802	1	60	24.1	3.3	86.33	Polyester	Colloidal silica	P25	2:1 ^a	60
3803	1	60	21.2	1.0	95.39	Polyester	Colloidal silica	P25	1:1 ^a	60
3801	1	60	28.7	2.9	89.88	Polyester	Colloidal silica	P25	1:1 ^a	60
3800	1	60	26.8	2.1	92.16	Polyester	Colloidal silica	P25	1:1 ^a	60
3800	1	60	24.1	1.5	93.87	Polyester	Colloidal silica	P25	1:1 ^a	60
3801	1	60	24.3	4.3	82.12	Polyester	Colloidal silica	P25	1:2 ^a	60
3800	1	60	20.1	2.0	90.23	Polyester	Colloidal silica	P25	1:2 ^a	60
3802	1	60	22.8	3.3	85.67	Polyester	Colloidal silica	P25	1:2 ^a	60
3800	1	60	21.2	2.6	87.64	Polyester	Colloidal silica	P25	1:2 ^a	60

^aspray-coated sample before stability test.

APPENDIX

Table A-1 (continue)

<i>I</i> ($\mu\text{W}/\text{cm}^2$)	$\dot{Q}$ (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3803	1	60	24.3	8.3	65.64	Polyester	Colloidal silica	P25	1:4 ^a	60
3802	1	60	20.1	5.8	71.10	Polyester	Colloidal silica	P25	1:4 ^a	60
3803	1	60	22.8	7.6	66.76	Polyester	Colloidal silica	P25	1:4 ^a	60
3802	1	60	21.2	6.5	69.38	Polyester	Colloidal silica	P25	1:4 ^a	60
3803	1	60	21.2	4.5	78.69	Polyester	Colloidal silica	P25	1:1 ^b	60
3801	1	60	28.7	8.3	71.22	Polyester	Colloidal silica	P25	1:1 ^b	60
3800	1	60	26.8	6.8	74.75	Polyester	Colloidal silica	P25	1:1 ^b	60
3800	1	60	24.1	5.7	76.51	Polyester	Colloidal silica	P25	1:1 ^b	60
3801	1	60	23.1	5.2	77.34	Polyester	Colloidal silica	P25	2:1 ^c	60
3800	1	60	26.3	7.0	73.43	Polyester	Colloidal silica	P25	2:1 ^c	60
3802	1	60	28.8	8.5	70.56	Polyester	Colloidal silica	P25	2:1 ^c	60
3800	1	60	33.0	10.7	67.68	Polyester	Colloidal silica	P25	2:1 ^c	60

^aspray-coated sample before stability test; ^bdip-coated sample before stability test; ^cspray-coated sample after stability test.

APPENDIX

Table A-1 (continue)

<i>I</i> ($\mu\text{W}/\text{cm}^2$)	$\dot{Q}$ (L/min)	<i>RH</i> (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3801	1	60	23.1	1.1	95.08	Polyester	Colloidal silica	P25	1:1 ^c	60
3800	1	60	26.3	1.8	93.33	Polyester	Colloidal silica	P25	1:1 ^c	60
3801	1	60	28.8	2.7	90.75	Polyester	Colloidal silica	P25	1:1 ^c	60
3801	1	60	33.0	3.8	88.64	Polyester	Colloidal silica	P25	1:1 ^c	60
3800	1	60	19.2	2.4	87.74	Polyester	Colloidal silica	P25	1:2 ^c	60
3800	1	60	22.4	3.2	85.63	Polyester	Colloidal silica	P25	1:2 ^c	60
3801	1	60	24.6	4.3	82.56	Polyester	Colloidal silica	P25	1:2 ^c	60
3801	1	60	27.4	5.3	80.57	Polyester	Colloidal silica	P25	1:2 ^c	60
3800	1	60	19.2	5.7	70.18	Polyester	Colloidal silica	P25	1:4 ^c	60
3800	1	60	22.4	7.1	68.26	Polyester	Colloidal silica	P25	1:4 ^c	60
3801	1	60	24.6	8.3	66.44	Polyester	Colloidal silica	P25	1:4 ^c	60
3800	1	60	27.4	9.5	65.28	Polyester	Colloidal silica	P25	1:4 ^c	60

^cspray-coated sample after stability test.

APPENDIX

Table A-1 (continue)

<i>I</i> (μW/cm ²)	<i>Q</i> (L/min)	<i>RH</i> (%)	<i>C_{in}</i> (ppm)	<i>C_{out}</i> (ppm)	<i>η_(HCHO)</i> (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
3801	1	60	23.1	12.7	45.18	Polyester	Colloidal silica	P25	1:1 ^d	60
3800	1	60	26.3	15.2	42.14	Polyester	Colloidal silica	P25	1:1 ^d	60
3801	1	60	28.8	17.5	39.46	Polyester	Colloidal silica	P25	1:1 ^d	60
3801	1	60	33.0	20.8	36.92	Polyester	Colloidal silica	P25	1:1 ^d	60

^ddip-coated sample after stability test.

APPENDIX

Table A-2 VIS-PCO degradation of HCHO

I (lux)	Q (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
10000	0.1	60	9.1	1.1	88.21%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	0.1	60	9.5	1.4	85.05%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	0.1	60	10.3	1.5	85.23%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	0.1	60	8.2	1.1	87.23%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	0.5	60	13.4	8.3	38.18%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	0.5	60	12.1	7.8	35.88%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	0.5	60	14.3	9.3	34.52%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	0.5	60	13.8	8.6	37.80%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	14.9	11.7	21.19%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	12.6	10.1	19.57%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	14.1	11.5	18.18%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	13.5	10.4	22.58%	Polyester	Colloidal silica	TiO ₂	1:1	60

APPENDIX

Table A-2 (continue)

I (lux)	Q (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
10000	1.2	60	14.5	11.8	18.73%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.2	60	14.2	12.3	13.09%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.2	60	15.2	12.7	16.62%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.2	60	13.1	10.9	17.20%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	3.3	1.1	65.85%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	3.8	1.4	63.17%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	2.8	1.1	61.69%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	3.6	1.5	59.13%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	5.2	2.7	48.19%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	6.4	3.3	49.01%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	5.3	2.8	47.88%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	5.2	2.9	43.92%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60

APPENDIX

Table A-2 (continue)

I (lux)	Q (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
10000	1.0	60	8.8	6.2	29.86%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	8.6	5.6	34.24%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	10.3	7.0	31.62%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	9.4	6.4	31.24%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	15.3	12.1	21.11%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	16.4	13.3	18.86%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	15.1	12.3	18.04%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	16.3	13.2	19.15%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	36.6	33.4	8.69%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	34.8	31.2	10.34%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	34.1	31.0	9.12%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	36.2	32.7	9.69%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60

APPENDIX

Table A-2 (continue)

I (lux)	Q (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
10000	1.0	20	7.4	5.0	32.13%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	20	8.7	6.1	29.85%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	20	8.0	5.6	30.27%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	20	8.2	5.6	31.15%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	9.6	6.5	32.13%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	8.8	5.9	32.48%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	9.1	6.3	30.52%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	9.5	6.5	31.83%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	7.8	6.1	21.62%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	9.1	7.0	23.37%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	8.4	6.5	22.21%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	9.1	6.9	23.52%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60

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Table A-2 (continue)

I (lux)	Q (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
10000	1.0	20	3.1	1.2	62.56%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	20	3.6	1.3	63.78%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	20	2.9	1.0	65.10%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	20	3.4	1.4	59.24%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	3.7	1.3	63.91%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	3.2	1.2	61.76%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	3.2	1.3	59.79%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	3.2	1.1	64.38%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	3.1	1.2	60.22%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	3.3	1.2	62.73%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	3.0	1.2	59.45%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	90	3.5	1.3	63.72%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60

APPENDIX

Table A-2 (continue)

I (lux)	$\bar{Q}$ (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
4000	1.0	60	8.2	7.3	10.55%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
4000	1.0	60	7.4	6.6	11.07%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
4000	1.0	60	8.9	8.0	9.74%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
4000	1.0	60	9.3	8.4	9.86%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
8000	1.0	60	8.7	6.8	22.38%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
8000	1.0	60	8.9	6.9	22.24%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
8000	1.0	60	10.5	8.3	21.03%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
8000	1.0	60	9.7	7.6	21.52%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	11.4	8.3	27.53%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	9.2	6.5	29.13%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	9.6	6.9	28.24%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	11.0	8.0	27.66%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60

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Table A-2 (continue)

I (lux)	Q (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
12000	1.0	60	9.1	6.0	34.09%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
12000	1.0	60	10.7	7.1	33.55%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
12000	1.0	60	9.8	6.5	33.61%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
12000	1.0	60	11.4	7.7	32.64%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
14000	1.0	60	8.4	5.1	39.22%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
14000	1.0	60	11.9	7.4	37.69%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
14000	1.0	60	9.2	5.6	39.06%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
14000	1.0	60	7.6	4.6	39.73%	Polyester	Colloidal silica	TiO ₂ -C	1:1	60
10000	1.0	60	13.3	12.5	6.15%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60
10000	1.0	60	15.1	14.3	5.49%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60
10000	1.0	60	13.9	13.1	5.63%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60
10000	1.0	60	12.8	12.0	6.41%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60

^a catalyst loading amount of 0.1349/substrate.

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Table A-2 (continue)

I (lux)	Q (L/min)	RH (%)	C_{in} (ppm)	C_{out} (ppm)	$\eta_{(HCHO)}$ (%)	Substrate	Binder	Catalyst	Catalyst /binder mass ratio	Coating stabilization temperature (°C)
10000	1.0	60	13.3	10.5	21.19%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60
10000	1.0	60	15.1	12.1	19.57%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60
10000	1.0	60	13.9	11.4	18.18%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60
10000	1.0	60	12.8	9.9	22.58%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60
10000	1.0	60	6.7	6.0	10.87%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60
10000	1.0	60	4.6	4.0	12.51%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60
10000	1.0	60	5.1	4.5	12.43%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60
10000	1.0	60	5.8	5.2	11.15%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^a	60
10000	1.0	60	6.7	3.5	48.19%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60
10000	1.0	60	4.6	2.3	49.01%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60
10000	1.0	60	5.1	2.7	47.88%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60
10000	1.0	60	5.8	3.3	43.92%	Polyester	Colloidal silica	TiO ₂ -C	1:1 ^b	60

^a catalyst loading amount of 0.1349/substrate; ^b catalyst loading amount of 0.2890/substrate.

APPENDIX

(a)

(b)

(c)

Figure A-1 (a-c) Calibration in three target levels using working standards prepared by sorbent spikes with standardized formaldehyde stock solution