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Experimental study on visible-light induced photocatalytic oxidation of gaseous formaldehyde by polyester fiber supported photocatalysts

**Zhenan Han ^a, Victor-Weichung Chang ^{a*}, Xiaoping Wang ^a, Teik-Thye Lim ^a,
Lynn Hildemann ^b**

^a *Division of Environmental and Water Resources Engineering, School of Civil and Environmental Engineering, Nanyang Technological University, Block N1, 50 Nanyang Avenue, Singapore 639798, Singapore.*

^b *Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305-4020, USA*

Corresponding authors: Tel: +65 6790-4773; Fax: +65 6791-0676; Email:

hanz0006@ntu.edu.sg

ABSTRACT

Heterogeneous photocatalytic oxidation (PCO) has shown large potentials in controlling airborne gaseous pollutants such as volatile organic compounds (VOCs). This article addresses PCO of gaseous formaldehyde (HCHO) by VIS-active photocatalysts which were immobilized on polyester fiber filter through a spray coating method under room temperature. The coatings showed good dispersion and strong adhesion on the fiber surface as supported by the SEM images and the stability test result. High PCO efficiency was achieved by the spray-coated filter under typical room light illumination. The effects from various reaction parameters, such as volumetric flow rate, pollutant initial concentration, relative humidity, illumination strength, as well as photocatalyst loading amount, on the PCO efficiency were also evaluated systematically. A Langmuir-Hinshelwood model was used to examine the kinetics of VIS-PCO of HCHO. One of the important findings was that changes of relative humidity had little influence on the PCO efficiency at either low or high HCHO concentrations. Different from the UV-PCO process where hydroxyl radical ($\text{OH}^\bullet$) is the major oxidative species, the VIS-generated holes, $\text{h}^+_{(\text{VIS})}$, as well as the superoxide radical ($\text{O}_2^{\bullet-}$) were considered to contribute predominantly to the degradation of HCHO under visible

light illumination.

Keywords: Photocatalytic oxidation, visible light, formaldehyde, spray coating

1. Introduction

Heterogeneous photocatalytic oxidation (PCO) technology has been considered as an effective way for water and air cleaning in the past two decades [1]. 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 [2, 3], NO [4, 5], BETX (benzene, ethylbenzene, toluene and xylene) [6-8], and TCE (trichloroethylene) [9, 10], due to the fact that air pollutants indoors put greater risks on human health than those outdoors [11].

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 [12]. 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 valence band edges, which allows the adsorption of visible light at sub-band gap energies of less than 3.2 eV [13]. 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 [14]. 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 [15-20]. 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 [21-23]. 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 [24-27], volumetric flow rate [13, 25, 28]. 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. [29], the photo-generated hole (h^+) was supposed to play an important role in the degradation process of room-light-induced PCO on various gaseous pollutants by Pt/N-TiO₂ photocatalysts; while in Liu et al. [30] 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 ($OH^\bullet$). 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.

2. Material and methods

2.1 Materials 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. Another carbon and nitrogen co-doped TiO₂ (TiO₂-CN) was prepared following Wang and Lim's method [31]. 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. 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 TiO₂:SiO₂ 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 mm × 50 mm × 3 mm (W × L × 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 h to stabilize the coatings.

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 Cu Kα radiation ($\lambda = 1.5418 \text{ \AA}$) in a 2θ range of 5-80°. X-ray photoelectron spectroscopy (XPS) evaluation were performed by a Kratos Axis Ultra spectrometer (Kratos, Japan) with a monochromatic Al Kα 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). BET surface areas of the spray-coated filter samples were measured by nitrogen physisorption on an Autosorb-1 system (Quantachrome, USA). SEM images of the spray-coated filter samples were captured on a JSM-7600F (JEOL, Japan) Field Emission Scanning Electron Microscopy (FE-SEM). To evaluate the mechanical stability of the coatings, a 120 h 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.

2.2 PCO experiment

The fix-bed photoreactor was designed following the ISO standard 22197-1 [32] with specific modification. The reactor body was made of 316 L 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 shown in Fig. 1. 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 sampling and analytical method was developed with the NIOSH recommended method 2541 as a reference [33]. 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.

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 h 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:

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

Possible degradation by-product, HCOOH, was also monitored in the outlet using GC-TCD method. No detectable HCOOH was found throughout the experiment. As to the degradation end products, CO₂ concentration in the outlet was monitored using commercial CO₂ sensor. As the HCHO concentrations used in this study were mostly in several ppm range, the resulting increase in CO₂ concentration was almost non-detectable because the error range of most CO₂ sensors was about ± 25 ppm. Given the normal CO₂ concentration at 380 ppm in typical ambient air, the results from the CO₂ sensors can only provide the general trend instead of the exact concentration changes.

To study the influences from different experimental parameters on the degradation efficiency of VIS-PCO of HCHO, the parameters (volumetric flow rate, initial 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 1. 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 [24]. Under each experimental condition, four repeated circles were taken in order to minimize the experimental uncertainty and further verify the stability of the coatings.

3. Results and discussion

3.1 Characterization of the modified photocatalysts

Fig. 2 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.

Fig. 3 shows the XPS spectra of N 1s, C 1s, Ti 2P and O 1s for the two modified TiO₂ photocatalysts. In Fig. 3a, the peak centered at about 399.4 eV is present in the TiO₂-CN sample which indicates the formation of Ti-N-O and/or Ti-O-N bonding [34]. As for the

TiO₂–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 Fig. 3b. The peaks at about 284.8 eV can be assigned to the adventitious elemental carbon in both samples [35]. For TiO₂–CN, the peak at about 288.5 eV indicates the presence of C–O bond [35]; while the other weak peak at about 281.5 eV can be assigned to the Ti–C bond formed during doping [36]. For TiO₂–C, the peaks at about 289 and 286 eV can be assigned to the formation of C=O and C–O bonds, respectively, signifying the incorporation of carbon species into the TiO₂ lattice [31]. In Fig. 3c, 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 TiO₂–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 [34]. The O 1s spectra in Fig. 3d 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 TiO₂ lattice of the two modified photocatalysts. The introduction of these lattice defects may induce to absorption in the visible light wavelength range.

The DRS of the two modified photocatalysts are shown in Fig. 4a 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 $(\text{ah}\nu)^{1/2}$ vs. the energy of absorbed light (Fig. 4b). 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).

3.2 Evaluation of the coatings and their VIS-PCO of HCHO

BET surface area test was taken on the spray-coated filters. For each filter sample, four pieces of small identical parts (10 × 10 × 3 mm) were taken for BET measurement to obtain an average specific surface area value of the coating. The average BET surface areas of

TiO₂–C and TiO₂–CN coatings were measured as 128.6 m²/g and 102.3 m²/g, respectively, showing that the TiO₂–C coating has preferable surface microstructure than that of the TiO₂–CN coating. SEM images of the spray-coated polyester fiber filters are shown in Fig. 5. 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 Fig. 5, the TiO₂–C coating has smaller agglomerate size than that of the 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.

The photocatalysts and binder contents on the spray-coated polyester fiber filters, before and after the shaking test, are shown in Table 2. 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.

VIS-PCO of HCHO was carried out on the spray-coated samples for four repeated circles both before and after the shaking test. The result is shown in Fig. 6. It can be seen from Fig. 6 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.

3.3. Evaluation on the effects of different reaction parameters

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, four 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 Fig. 7a, 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. [37] where they found a 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 Fig. 7a, 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. [28] 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.

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

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

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 (AHAMs) to evaluate the performance of an air cleaning device.

Fig. 7b 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 [24, 38] on UV-PCO of HCHO and also agreed by Wang et al. [39] and Devahasdin et al. [26] when studying on PCO of NO. Similar finding was also reported by Yu and Brouwers [13] where they found that the lower the flow rate was, the faster the conversion increase speed was obtained.

As can be seen from Fig. 7b, 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}) [24]. 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.

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 Fig. 8a, where $\eta_{(\text{HCHO})}$ drops continuously with increasing HCHO initial concentration. This is parallel with the result in Qi et al study [37], where the HCHO initial concentration increased from 1.84 to 24 mg/m^3 (about 1.50-19.52 ppm at 20 °C) and the HCHO degradation efficiency decreased from 72% to 43.4% with a flow rate of 5 L/min.

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

$$\gamma = \frac{kK_a C_{in}}{1 + K_a C_{in}} \Leftrightarrow \frac{1}{\gamma} = \frac{1}{kK_a C_{in}} + \frac{1}{k} \quad (3)$$

where k is the reaction rate constant and K_a is the adsorption equilibrium constant. Using the data from Fig. 8a, the measured oxidation rate can be calculated by Eq. (2). The reaction rate constant k (0.3842 $\mu\text{-mole}/\text{cm}^3/\text{h}$) and the adsorption equilibrium constant K_a (0.4391 ppm^{-1}) then can be obtained through the least square regression. The dependence of oxidation rate γ on the HCHO initial concentration C_{in} is illustrated in Fig. 8b. 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 Laugmuir-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 [24] when they studied UV-PCO of HCHO. The relationship between HCHO initial concentration and the oxidation rate is also coherent with Liu et al. [40] 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.

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 [41, 42], H_2O molecule will adsorbed on the surface hydroxyl groups via hydrogen bonding [43]. 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 [24].

To investigate the effect of water vapor on the VIS-PCO of HCHO by the $\text{TiO}_2\text{-C}$

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 Fig. 9a, 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 H₂O and HCHO is observed when RH reaches 90%. The degradation efficiency of HCHO is not 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. [40] 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. [37] in their study on UV-PCO of HCHO, in which the HCHO degradation first increased and then decreased with RH increasing from approximately 25-0% at HCHO concentration of 22.2-24.0 mg/m³ (about 18.1-19.5 ppm at 20 °C).

The result in Fig. 9a 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 Fig. 9b. 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.

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 [24, 44]. 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. [45] studied the effect of visible light illumination on the photo-degradation of HCHO by a nitrogen doped TiO_2 photocatalyst. With HCHO initial concentration at 0.98 mg/m^3 (about 0.8 ppm at $20\text{ }^\circ\text{C}$), the degradation increased linearly from 25.5% to 59.6% alongside an incrementing illumination intensity of 0-30,000 lux and stabilized thereafter. Yu and Brouwers [13] found an increasing NO_x conversion rate with visible light intensity increasing from 1.0 to 13.0 W/m^2 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 Fig. 10. The PCO efficiency of HCHO increases linearly with increasing light intensity from 4000 to 14,000 lux. It should be noted that higher light intensity ($>14,000\text{ lux}$) 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.

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. [45] reported that the degradation of HCHO increased from 0% to 82.9% when the amounts of N- TiO_2 powder increased from 0 to 5 g, with HCHO initial concentration at 0.98 mg/m^3 (about 0.8 ppm at $20\text{ }^\circ\text{C}$), relative humidity at $33\% \pm 5\%$, and illumination intensity at 10,000 lux. Liu et al. [40] studied the PCO of HCHO by TiO_2 coated glass plate, where they reported an increase in reaction rate with TiO_2 solid loading from 0 to 2 mg/cm^2 , but the increase was not significant when TiO_2 loading was more than 2 mg/cm^2 .

The effect of photocatalyst loading amount on the VIS-PCO degradation efficiency of HCHO by the TiO_2 -C coated sample was also evaluated in the present study. The 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 Fig. 11. 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.

3.4 Possible mechanism of VIS-PCO of HCHO

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[•]), superoxide radical (O₂^{•-}), and hydrogen peroxide (H₂O₂), 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 [46]; while the more prevailing opinion stands by hydroxyl radical (OH[•]) as the dominating oxidant [24]. Indisputably, the role of OH[•], generating from H₂O/OH⁻ oxidation by the photo-generated h⁺, are undoubtedly considered to be very important during UV-PCO process [47].

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. [31] 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) [14] 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 [48], 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:

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.

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 $OH^\bullet$. Fig. 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.

4. Conclusion

VIS-PCO of gaseous HCHO was carried out by non-metal-doped TiO_2 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 120 h 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 degradation of HCHO increases more than one time compared to the VIS-PCO process, indicating that O₂⁻ and h_(VIS)⁺, not OH[•], may be the dominant oxidative species that contribute to the VIS-PCO of HCHO.

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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)	4000–14,000
Photocatalyst loading amount ^a (g)	0.1349–0.2890

^a Equivalent TiO₂ content on the 100 mm 50 mm × 3 mm ($W \times L \times T$) polyester filter.

Table 1 VIS-PCO experimental conditions.

Table 2 Photocatalysts and binder contents on the spray-coated polyester fiber filters.

Sample	Total filter weight after coating ^c (g)		Weight percentage of TiO ₂ ^f (wt/wt%)		Weight percentage of SiO ₂ ^f (wt/wt%)		Loading amount of TiO ₂ ^g (g)		Loading amount of SiO ₂ ^g (g)	
	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	2.4026	2.3816	11.83	11.68	12.49	12.16	0.2842	0.2782	0.3001	0.2895
#2 ^b	2.2312	2.1976	12.64	12.76	13.36	12.11	0.2820	0.2804	0.2981	0.2661

^a Spray-coated with TiO₂—CN.
^b Spray-coated with TiO₂—C.
^c Weighted by analytical balance.
^d Before shaking test.
^e After shaking test.
^f Measured by XRF on the whole bulk of the spray-coated filter samples.
^g Calculated by filter weight × weight percentage.

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