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Investigation of the performance of TiO₂ photocatalytic coatings

Nan Yao, King Lun Yeung∗

Department of Chemical and Biomolecular Engineering, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China

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ABSTRACT
TiO₂ photocatalysts were prepared and coated on surfaces. Ultrathin TiO₂ coatings were obtained by wash-coating and screen-printing techniques. The latter provides films of excellent adhesion that could tolerate washing under water jet. The scratch-proof coatings were characterized, and X-ray diffraction (XRD), atomic force microscopy (AFM) and N₂ physisorption indicated that the addition of polyethylene glycol (PEG) not only improved the coating properties of TiO₂ but also served as poragen to produce high surface area, mesoporous TiO₂. The coated TiO₂ displayed better activity than the commercial P25 TiO₂ for photocatalytic oxidation of ethylene, ethanol, acetaldehyde, isopropanol and acetone. The catalyst also exhibited excellent bactericidal, fungicidal and virucidal activities against a wide variety of Gram-positive and Gram-negative bacteria, fungal spores and T2 bacterial phage. A simple photoreactor with tangential air flow was designed and tested in a chamber, before incorporating in a prototype air purifier. The study showed that there is good agreement between laboratory catalyst reaction data (i.e., 110 mmol h⁻¹ for acetone) and the prototype test results (69 mmol h⁻¹).

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1. Introduction

People often spent more than eighty percent of their time indoor and the indoor environment has an important impact on people's health and well-being [1]. There are extensive reports on the exposures and health impacts of various indoor air pollutants [2–5]. Studies have shown that human exposures to indoor pollutants that exceed outdoor level by 2–5 times are not uncommon and in some situation, indoor pollution level can reach 100 times that of the outdoor [6]. A single exposure to high level indoor air pollution can cause headache and nausea, skin and eye irritations, respiratory difficulty, fatigue and even death for the case of carbon monoxide [6], while chronic exposure to indoor pollutants such as radon, environmental tobacco smoke (ETS), VOCs, particulates and bioaerosols can result in asthma, cancer, developmental defects and delays in children and weakening of the cardiovascular system in the elderly [7]. Thus, poor indoor air quality poses a greater risk to pregnant women, young children and elderly person.

Poor indoor air quality costs the state of California an estimated US$ 45 billion a year from medical expenses, health valuation on premature death and loss of productivity [8]. An improvement of US$ 7 million people living on less than 1100 km² of land. The narrow pollution is reported to cost AUD$ 12 billion annually [10]. Hong Kong, like most Asian cities is densely populated with more than 7 million people living on less than 1100 km² of land. The narrow roads and tall, high-rise buildings trap pollution resulting in poor air quality. This directly affects the indoor air quality, which is far more complex and dynamics due to its sensitivity to human habit. A recent study by Chau et al. [11] investigated the health benefit from indoor air quality improvements in Hong Kong residence and concluded that the use of air cleaners provided the greatest annual health benefit.

A majority of air purifiers is based on filtration and adsorption technologies to remove airborne particulates, bioaerosols and malodor. Heterogeneous photocatalytic oxidation (PCO) has been investigated for decades and is considered an attractive technology for treatment of organic air pollutants (i.e., VOCs and malodors) and disinfection of airborne microorganisms at room conditions [12–18]. Ultraviolet (UV) light is generally used as the light source in the PCO processes, but new generation of visible-light active TiO₂ are also showing great promise [19,20]. The most common approach is to coat the catalytic materials (usually nano-TiO₂) on substrates to increase the irradiated area [21–25]. TiO₂ coating is therefore important to PCO performance. Coating delamination also poses a risk to environment and health [26–29]. This work reports the preparation of nanostructured TiO₂ coating by screen-printing method to obtain scratch-proof photocatalytic TiO₂ coatings on surface. Tests on VOC removal and antimicrobial properties (bacteria and fungi) of the coatings made by screen-printing and wash-coating methods were performed in both laboratory and prototype air purifier.
2. Experimental methods

2.1. Material preparation and coating

The TiO₂ preparation and coating are summarized in Scheme 1. A 28 ml solution of 1 M titanium isopropoxide (TIP, 98%, ACROS) in 2-propanol (IPA, 99.8%, BDH) was added dropwise to a 72 ml of deionized and distilled water under vigorous mixing. The resulting suspension was stirred for an hour at room temperature for complete hydrolysis of TIP (step 1, Scheme 1). The solution was slowly heated to 343 K and 1 M HNO₃ was added to give a [H⁺]/[Ti⁴⁺] = 0.4. The peptization was carried out for 2 h, before cooling to room temperature to obtain a clear TiO₂ sol (step 2, Scheme 1) [30,31]. Polyethylene glycol (PEG, ACROS, a.m.u. = 400) was added to the sol under vigorous mixing to obtain a coating sol sample (Sol A). A coating paste (Paste A) was obtained by evaporating the solvents (i.e., H₂O and trace IPA) at 338 K. Coating precursor (Sol B) was also prepared by suspending commercial Degussa TiO₂-P25 powder and HNO₃ (1.6 M) in a 50 ml of deionized and distilled water with [H⁺]/[Ti⁴⁺] ratio of 1 via ultrasonication. Powders of TiO₂ sol (steps 2′ and 2′′, Scheme 1) and Paste A (step 5′, Scheme 1) were prepared for analysis.

Stainless steel (SS-304BA) and aluminum (Al-6061) plates were cut into 210 mm × 300 mm rectangular pieces. The plates were cleaned with detergent and rinsed with water followed by ethanol and acetone to remove dirt and contaminants. The TiO₂ was coated on the plates by wash-coating and screen-printing methods. The plate was placed horizontally in enough Sol A solution to cover its surface. The deposited layer of TiO₂ was dried and then calcined in air at 723 K for an hour (wash-coating method, step 4′, Scheme 1). Sol B was also wash-coated on the plates, dried and heated to 473 K for an hour. A thin layer of paste was coated on the plates by screen-printing (step 5, Scheme 1). A scraper controlled by an automated system was positioned at the upper edge of the paste and a constant force was applied as the scraper was dragged from the top edge to the lower edge of the surface. The coated plates were calcined in air at 723 K for an hour.

2.2. Material characterization

The powder and coated samples were examined by atomic force microscope (AFM, Nanoscope III) and scanning electron microscope (SEM, JEOL 6300F), and analyzed by X-ray diffraction (XRD, Philips PW1830), micro-Raman spectroscopy (Renishaw RM3000) and nitrogen physisorption (Coulter SA3100). The size, morphology and aggregation of deposited TiO₂ sol was investigated by AFM. The TiO₂ sol was deposited on a freshly cleaved mica and dried at room temperature. The sample was imaged by Nanoscope III AFM under tapping mode and using a 130 μm J-scanner and silicon cantilever tips (nanosensors). The greater roughness of the stainless steel and aluminum substrates used for the coated samples preclude the use of AFM and the samples were examined by SEM. Samples were cut from the coated plate, mounted on aluminum holders using conducting adhesive, sputter-coated with a thin layer of gold (Edwards Scancoat Six), and imaged at an accelerating voltage of 10 keV.

The X-ray diffraction of the powder and coated samples was conducted at a scan rate of 0.05° using a CuKα X-ray source with a graphite monochromator. The weight fraction of the different TiO₂ phases was calculated from the integrated peak intensity and the crystal size was estimated from Scherrer equation. The Raman spectra of the samples were recorded using a Renishaw RM3000 micro-Raman system equipped with an Olympus BH-2 microscope. The spectral resolution was set approximately at 1.0 cm⁻¹ and the spot size at about two micrometer in diameter. The excitation source used was an Argon laser operating at 514.5 nm with an output power of 25 mW. The nitrogen physisorption of the powder samples was carried out in a Coulter SA 3100 to determine the specific surface area, pore size distribution and pore volume. The sample's specific surface area was calculated based on the Brunauer, Emmett, and Teller (BET) theory and the mesopore vol-
ume and its distribution were calculated using the Barrett, Joyner, and Halenda (BJH) theory from the desorption isotherm.

2.3. Photocatalytic and antimicrobial properties of TiO2-coated plates

The photocatalytic oxidation (PCO) of hydrocarbon (i.e., ethylene (99.9%)) and volatile organic compounds (i.e., ethanol (99.9%, Merck), acetaldehyde (99.5%, Aldrich), isopropanol (99.8%, Mallinckrodt) and acetone (99.5%, Labscan)) were carried out in a stainless steel photoreactor described in prior works [32,33]. The flat, rectangular photoreactor measured 578 mm × 113 mm and contained inlet and outlet ports, a recess for the catalytic plate (25 mm × 25 mm) and two sets of machined baffles. A 6.25 mm thick Pyrex glass top-cover creates a narrow rectangular channel (2 mm deep x 112 mm wide) for gas flow. Hydrocarbon gas was metered by an electronic mass flow controller and mixed with synthetic air to give a 400 sccm reactant mixture containing 240 ppm hydrocarbon. Liquid VOC was delivered by a syringe pump (kdScientific 1000) at a 0.01 ml h⁻¹ to a constant temperature heat exchanger and mixed with 400 sccm synthetic air before entering the photoreactor. The 25 mm², TiO2-coated plate was placed 322 mm downstream from the gas inlet and after steady-state, the catalyst plate was illuminated by five fluorescent black lamps (6 W, BLB Sankio Denki) placed 10 mm above the reactor window. The outlet gas composition was monitored by a gas chromatograph (HP 6890) equipped with thermal conductivity and flame ionization detectors and a GS-GASPRO capillary column (0.32 mm x 30 m). The gases used in the GC are helium (UHP, CW), hydrogen (UHP, HKO) and synthetic air (HP, HKSP).

Antimicrobial tests were carried out for bacteria, fungi and bacterial phage in a class II biological safety cabinet. The “antibacterial-drop test” [34] was adopted and modified for the bactericidal, fungicidal and virucidal tests. Bacteria including Bacillus cereus, Bacillus subtilis, Escherichia coli, Neisseria sicca, Pseudomonas aerugiosa, Sarretia marcescens and Staphylococcus epidermidis were cultivated in standard nutrient broth at 310 K to their exponential growth phase. The bacteria were harvested and the concentration was adjusted to 10³–10⁴ ml⁻¹. A 500 μl of the bacteria suspension was placed on the 25 mm × 25 mm, TiO2-coated plate and air dried in a Class II biological safety cabinet to reduce the water content and increase the area of contact between the bacteria and coated plate surface. After drying for an hour, the plates were irradiated with UV lamp for a total dosage of 5 J cm⁻². Triplicate samples were tested and two sets of controls (i.e., dark and uncoated plate) were used. Viable bacteria were recovered by gently washing the plate with 500 μl sterile nutrient broth and an aliquot was inoculated onto a fresh nutrient agar plate. The number of viable bacteria colonies were enumerated after the plate was incubated at 310 K for 24 h.

Fungi colonies, including Penicillum chrysogenum, Cladosporium sp. and Aspergilus niger, were cultivated on the malt extract agar plates for a week and the spores were harvested by slight agitation in sterilized distilled water. The spores were counted with a hemacytometer and the initial spore concentration for testing was adjusted to 10⁴–10⁵ ml⁻¹. The plates were challenged with 500 μl fungal spores and irradiated with UV dosage of 5 J cm⁻². The viable fungi were recovered by washing with sterile water. An aliquot was inoculated onto a malt extract agar plate and cultured for 5 days at 301 K. The stock of T2 phage was maintained by culturing the phage with its host, E. coli cells. The phage was recovered after the virucidal test by washing the plate with E. coli cell suspension. The washing was placed in an agar plate, cultured at 310 K for 24 h and the plaque counts were counted and the final concentration calculated.

2.4. Performance of a prototype PCO-based air purifier system

Two pieces of 210 mm × 300 mm TiO2-coated stainless steel plates (Paste A, screen-printed) were machined to form mating halves of a cylinder with a diameter of 134 mm and length of 300 mm. A single UV lamp (8 W, 30 cm long) was inserted in the center of the cylinder and irradiated a TiO2-coated area of about 1100 cm². A slot was cut near one end of the cylinder and a fan was mounted to circulate the air through the assembly as shown in Fig. 1a. A total VOC sensor (pbp RAE) monitors the VOC level in the chamber along with the electrochemical VOC gas sensors (Figaro TGS 2620) and temperature/humidity sensors (Honeywell HIH-3605-A) placed in the chamber and at the inlet and outlet of the assembly. The chamber was first cleaned and then purged with compressed air for at least an hour. Baseline measurements were made before introducing VOC into the chamber. The VOC was fed to the chamber by bubbling a sidestream of air into a series of three bubblers kept in a constant temperature bath, two containing the liquid VOC (i.e., acetone) and the last packed with glass beads. This ensures that the air is saturated with the organic vapor before dilution into the main air stream entering the chamber to give a VOC level of 4–10 ppm. After equilibration, the fan and UV lamp were turned on, and the temperature, humidity and VOC concentration were monitored with time. The experimental run often lasted for sixteen hours and the VOC removal rate was calculated from the data. The quantum efficiency is calculated as the number of VOC removed via photochemical process divided by the number of photons absorbed in the same interval.

The chamber tested PCO assembly unit shown in Fig. 1a was incorporated in a prototype air purifier unit provided by Chiaphua Industries Ltd. HK as shown in Fig. 1b. The VOC remediation was tested for ethanol and acetone at ambient temperatures (ca. 298 K) and humidity (ca. 60% R.H.). The VOC liquid was evaporated and mixed with air inside the air duct before entering the prototype air purifier at an air flow of 120 m³ h⁻¹. The temperature (National Semiconductor LM35 DZ), humidity (Honeywell HIH-3605-A) and VOC (Figaro TGS 2620) sensors were strategically located at the entrance and exit of the air purifier and the air temperature, humidity and VOC concentration were collected each second using PICO software. A digital multi-gas monitor (Bruel & Kjaer 1302) measured the outlet and ambient CO₂ level. The VOC removal rate was calculated from the difference in VOC concentration at the inlet and outlet of the air purifier.

The bioaerosol removal rate was measured for natural bioaerosol (i.e., airborne bacteria and fungi). The measurements were made at the University student canteen during the peak lunch hours when the average bioaerosol loading reaches 800 CFU m⁻³. The bioaerosol consists mostly of environmental microorganisms such as Micrococcus sp., S. epidermidis, Cladosporium sp., Penicillum sp. and yeast. Two bioaerosol impactors (single-stage) with pump (Model 1631-107B-G557X) were used in the experiment. TSA and MEA plates were used for sampling of airborne bacteria and fungi, respectively. One bioaerosol impactor was located near the air inlet of the air purifier and the other at the exit. The sampling of the inlet and outlet air was conducted simultaneously at a sampling rate of 28.3 L min⁻¹ for 10 min, and three sampling runs were performed for bacteria and three for fungi.

3. Results and discussion

Indoor air pollutants consist of particulates, bioaerosols and gaseous pollutants (i.e., VOCs, CO, CO₂) and are known to adversely impact health and comfort [35]. An on-site survey of forty-four residential households in Hong Kong was conducted during the
summer (June–August) and winter (November–December) periods of 2003 immediately after the outbreak of the severe acute respiratory syndrome (SARS) coronavirus. The surveyed homes are apartment flats with floor areas ranging from 35 to 170 m² and are located in high-rise public and private residential buildings that are typical for Hong Kong. Several of the air contaminants listed in Table 1 was monitored on a 24-h basis and the mean results were reported. The concentrations of VOCs were determined in accordance to USEPA TO-17 method and the airborne bacteria were measured according to the ACGIH guidelines for bioaerosol assessment.

The mean total VOC level exceeds 100 µg m⁻³ for both summer and winter, but the composition of the pollutant varies. An inordinate high level of formaldehyde was detected during the summer months and was attributed to the more frequent use of commercial disinfectants and cleanser in households following the SARS outbreak. This could explain the low bacteria count of the bioaerosol samples obtained during this period. The formaldehyde returned to normal level during the winter months when anxiety about SARS abated. This is also reflected by an increase in the mean level of airborne bacteria during the winter, however lower ventilation and frequent indoor activities (i.e., higher CO₂) also contribute to the overall increase in indoor bioaerosol. The results of the winter survey is more in-line with the earlier study conducted in 1999 by Lee et al. [36]. The particulate (RSP), formaldehyde and bacteria levels in both 1999 and 2003 winter surveys exceed the Hong Kong Environmental Protection Department IAQ Excellent Class Standard of 20 µg m⁻³, 30 µg m⁻³ and 500 CFU m⁻³, respectively. Prior works by the authors showed that various nanostructured TiO₂ photocatalyst is effective against a wide range of organic pollutants including aromatic and chlorinated hydrocarbons and could be optimized to curtail the formation of undesired byproducts.

### Table 1

| Pollutants                  | IAQ° excellent class | July–October | Summer | Winter |
|----------------------------|----------------------|--------------|--------|--------|
| RSP (µg/m³)                | <20                  | 150          | 67     | 76     |
| Carbon dioxide (ppm)       | <2000                | 580          | 461    | 567    |
| Formaldehyde (µg/m³)       | <30                  | 14           | 77     | 14     |
| Benzene (µg/m³)            | 4.7                  | 0.3          | 4.8    |        |
| Ethyl benzene (µg/m³)      | 2.6                  | 1.8          | 6.5    |        |
| Toluene (µg/m³)            | 52.1                 | 19.7         | 17.4   |        |
| Xylenes (µg/m³)            | 8.4                  | 6.4          | 12.5   |        |
| Tetrachloroethylene (µg/m³)| 2.5                  | 5.4          | 9.8    |        |
| Bacteria                   | <500                 | 730          | 134    | 796    |

° IAQ was conducted by Acron International Technology Ltd. under innovation technology fund contract.

Guidance notes for the management of indoor air quality in offices and public places, Hong Kong Environmental Protection Department, The Government of HKSAR.

Living room data from Ref. [36].
The nanostructured TiO$_2$ can also inactivate Gram-positive and Gram-negative bacteria [41–44].

3.1. Nanostructured TiO$_2$ and coatings

The titania powder obtained from vacuum drying of the TiO$_2$ sol (step 2', Scheme 1) consisted of 3 nm anatase TiO$_2$ according to X-ray diffraction. This indicates that acid peptization did not only produce smaller sol, but also transformed the titanium hydroxide [$\text{TiO}_x(\text{OH})_y$, $x = 2-0, y = 4 - 2x$] into 3 nm-sized, anatase TiO$_2$. The particle size obtained from the diffraction peak broadening is consistent with the AFM result shown in Fig. 2a. The sol deposited on the atomically smooth surface of the freshly cleaved mica appears as round clusters embedded in larger aggregates. The addition of PEG polymer to the sol (Sol A) prevented aggregation as shown in Fig. 2b and improved the particle dispersion through steric stabilization [45], but did not affect the particle size. Fig. 2c compares the nitrogen sorption isotherms for the TiO$_2$ powders obtained from TiO$_2$ sol (step 2'') and Paste A (step 5', Scheme 1). Both samples display a type IV isotherm that indicates the presence of framework-confined mesopores. The absence of a sharp rise in nitrogen uptake near the saturation pressure (i.e., $P/P_0 = 1$) means that there are few macropores in the samples [46]. In addition to being a stabilizer, the PEG also acted as porogen and the TiO$_2$ prepared from Paste A displayed larger surface area (235.7 m$^2$ g$^{-1}$) and pore volume (0.3 cm$^3$ g$^{-1}$) than sample obtained from the titania sol without PEG. The latter had a surface area and pore volume of 105.9 m$^2$ g$^{-1}$ and 0.1 cm$^3$ g$^{-1}$, respectively.

Fig. 3a shows a high magnification picture of TiO$_2$-coated plate prepared from Sol A by wash-coating method. It is clear that a thin uniform layer of TiO$_2$ was obtained following air calcination. The X-ray diffraction in Fig. 3c detects only the support indicating that wash-coating produced an ultrathin coating on the plate. The micro-Raman spectroscopy is a sensitive surface technique and Fig. 4 shows the sample displays three weak bands at 400 cm$^{-1}$, 500 cm$^{-1}$ and 630 cm$^{-1}$ corresponding to anatase [47]. An aver-
age TiO₂ crystal size of ~8 nm was estimated from the Raman peak broadening (14 cm⁻¹) according to the procedure described by Iida et al. [48]. The commercial Degussa P25 TiO₂ was used for comparison. Although the primary particles of P25 are smaller than 100 nm, they form large agglomerate [49] resulting in thick and uneven coating on the plate surface as shown in Fig. 3b. The thick coating displays X-ray diffraction peaks corresponding to anatase and rutile TiO₂ [50] as shown in Fig. 3c. Diffraction peaks from the substrate are not detected, a further indication of thick coating. Unlike the plate coated from Sol A (Fig. 3a), the adhesion of the coating is poor and the deposited TiO₂ are easily delaminated.

TiO₂-coated plates were prepared from Paste A by screen-printing method are shown in Fig. 5. The method is simple and easy to automate, and could coat large area of plates with uniform layer of TiO₂. Fig. 5a shows a piece of stainless steel plate coated with TiO₂ following air calcination. The Raman analysis indicates pure anatase TiO₂ phase with crystal size of ~7 nm (Fig. 4). A high magnification picture of the TiO₂-coated stainless steel in Fig. 5b shows that TiO₂ are uniformly deposited on the surface and form a dense surface coating layer as shown in Fig. 5b inset. The adhesion of TiO₂ prepared by the wash-coating and screen-printing methods were examined by subjecting the coated plates to a water jet (0.25 L/s, 10 min). No detectable loss in mass was observed for by the screen-printed samples and 10–20% loss was detected for the wash-coated samples. Table 2 summarizes the properties of TiO₂ coating prepared by different methods. In fact, the PEG polymer in Sol A and Paste A prevented aggregation and improved surface coating allowing deposition of an ultrathin and strongly adhered layer of TiO₂.

### 3.2. Photocatalytic and antimicrobial properties of TiO₂-coated plates

The photocatalytic activity of TiO₂-coated plates prepared from Sol A and Sol B by wash-coating method was investigated in the laboratory photoreactor. The reaction rate was determined for ethylene, ethanol, acetaldehyde, 2-propanol and acetone at room temperature under flow conditions. Fig. 6a plots the steady-state conversion rates of the hydrocarbon and VOCs in dry synthetic air. The reaction rates obtained for samples coated from Sol A are higher than Sol B (P25-TiO₂) coated plates, and varies depending on the organic pollutants. The TiO₂-coated plate from Sol A is effective against ethylene, ethanol, acetaldehyde and acetone. The gas chromatograph did not detect any byproducts and complete mineralization was obtained, except for 2-propanol from which a 10–20% is converted to acetone. The P25-TiO₂ coated plate display low conversion rates and aldehydes were detected in reactor exit. These data indicate that the prepared TiO₂ has better PCO performance than that of commercial P25-TiO₂ sample.

The effects of coating process on TiO₂ adhesion and PCO performance were investigated. Fig. 6b plots the PCO reaction rates of acetone on TiO₂-coated plates prepared by wash-coating of Sol A and screen-printing of Paste A. After each reaction runs that lasted

### Table 2

| Coating method       | Coating precursor | Weight added (g cm⁻²) | Thickness | Surface morphology |
|----------------------|-------------------|-----------------------|-----------|-------------------|
| Wash-coating         | P25               | 2.2 × 10⁻⁴            | Thick     | Uneven           |
| Wash-coating         | Sol A             | 4.8 × 10⁻⁵            | Thin      | Uniform          |
| Screen-printing      | Paste A           | 3.2 × 10⁻⁵            | Thin      | Dense and uniform|

**Fig. 4.** Raman spectra of TiO₂ coatings prepared by wash-coating and screen-printing methods.

**Fig. 5.** (a) Optical microscope and (b) scanning electron microscope pictures of TiO₂ coating prepared by the screen-printing method.
for 8 h, the plates were removed from the reactor and subjected to a jet of compressed water (0.25 L/s) for 10 min. The plate was dried and returned to the photoreactor and its photocatalytic activity was re-measured. The TiO₂-plate prepared by wash-coating suffered an immediate loss in activity after the first washing (Fig. 6b), while the screen-printed plate maintained its activity even after the third wash. It is generally accepted that the hydroxyl radicals (•OH) and superoxide (O₂•⁻) species generated by UV light react and convert adsorbed organic molecules into CO₂ and H₂O [12]. Therefore, the loss of TiO₂ catalyst from poor adhesion (i.e., wash-coated TiO₂) led to eventual decrease in PCO activity (Fig. 6b). The release of TiO₂ adsorbed organic molecules into CO₂ and H₂O [12].

The antimicrobial activity of screen-printed TiO₂ plates was tested for bacteria, fungi and bacteriophage. Gram-positive bacteria including B. cereus, B. subtilis and S. epidermidis and Gram-negative bacteria including E. coli, N. sicca, P. aeruginosa and S. marcescens were tested. Table 3 shows that except for N. sicca, better than ninety eight percent reduction in viable cells were obtained for the rest of the test bacteria under 5 J cm⁻² UV dosage. The TiO₂-coated plates kept in the dark are inactive as shown in Table 3, so are the uncoated plates irradiated by UV. The UV-irradiated TiO₂-coated plates were also effective against P. chrysogenum and Cladosporium sp. with better than 98% reduction, while a more modest reduction of 83% was obtained for A. niger. The 4 log reduction or 99.99% inactivation of bacteria phage T2 is obtained over the irradiated TiO₂-coated plates. These data showed that current TiO₂-coated plates have marked germicidal function under UV illumination. Hydroxyl radicals (•OH) and superoxide (O₂•⁻) are also believed to be responsible for the germicidal activity of UV irradiated TiO₂ photocatalyst [51,52]. Cho et al. [51] reported a strong correlation between the inactivation of E. coli and the amount of generated •OH radical. Kashiige et al. [52] were able to show that for bacterial phage inactivation starts with the denaturing of the capsid protein by the •OH radical followed by the damage of the phage DNA within.

### Table 3

| Microorganisms | Inactivation |
|---------------|-------------|
|               | Darkb       | UV-irradiatedc |
| **Bacteria (10⁴ CFU ml⁻¹)** |             |               |
| Bacillus cereus | 3.9         | 99.9          |
| Bacillus subtilis | 8.7         | 99.4          |
| Escherichia coli | 15.0        | 99.9          |
| Neisseria sicca | 13.2        | 62.6          |
| Pseudomonas aeruginosa | 99.9 |               |
| Serratia marcescens | 98.8 |               |
| Staphylococcus epidermidis | 99.9 |               |
| **Fungi (10⁴ CFU ml⁻¹)** |             |               |
| Penicillium chrysogenum | 13.0       | 98.1          |
| Cladosporium sp. | 23.6        | 99.9          |
| Aspergillus niger | 83.5        | 99.9          |
| **Bacteria phage (10⁴ CFU ml⁻¹)** |             |               |
| Bacteria phage T2 (DNA virus) | Nil         | 99.9          |

* Samples prepared from Paste A by screen-printing method.
* The number of P. aeruginosa, S. marcescens and A. niger was higher than the control. No experiment was done on phages for coated sample in the dark.
* The inactivation data were measured at a UV dosage of 5 J cm⁻².

3.3. Performance of a prototype PCO-based air purifier system

The majority of commercial air purifies uses adsorbent materials that require routine replacements to treat gaseous pollutants and malodors, thus incurring additional cost and generating adsorbent wastes. Heterogeneous photocatalytic oxidation has been studied for decades and is considered to be an attractive technology for treatment of organic pollutants in air [12,39]. The TiO₂ is a widely used photocatalyst, being highly efficient and stable as well as safe and inexpensive. The TiO₂-coated plate assembly shown in Fig. 1a was tested in a closed chamber to verify the PCO performance of large TiO₂ coating. A tangential air flow was used to achieve a higher mass transfer rate, but at an increased pressure drop as shown by the 3-dimensional, computational fluid dynamics model in Fig. 7a. The VOC concentration (i.e., acetone) in the chamber was monitored with time and plotted in Fig. 7b. The chamber displays a leak rate (i.e., natural decay) of ca. 30 ppb h⁻¹ from an initial acetone concentration of ca. 9000 ppb. The leaks occurred at the chamber seals, which were replace after every ten runs. The chamber was allowed to equilibrate before the UV lamp is turned on. The tests performed on TiO₂-coated plates prepared by wash-coating of Sol A and screen-printing of Paste A show both assemblies have similar high PCO activities (ca. 4000 ppb h⁻¹ or 69 mmol h⁻¹) and quantum efficiencies (79%). The experimental results were less than the theoretical conversion rate of 110 mmol h⁻¹ from model calculation assuming ideal reactor conditions due to a lower mass transfer rate. However, the removal rate of 69 mmol h⁻¹ from tangential flow was significantly higher compared to straight flow that had a measured conversion rate of 25 mmol h⁻¹ (and quantum efficiency is 29%). The screen-printed plates were able to maintain a reaction rate of 55–78 mmol h⁻¹ even after repeated washing.

The screen-printed TiO₂-coated plate assembly (Fig. 1a) was incorporated in a prototype air purifier shown in Fig. 1b and tested for VOC and bioaerosol removal. The tests were carried out at ambient temperature and conditions. Acetone and ethanol were evaporated and guided to the inlet of the air purifier using an air
The coating process is solvent-free, clean and applicable to most surfaces. A more quantitative measurement of film adhesion would be important for coating optimization. The PCO reaction study showed that the new TiO$_2$ coatings are generally more active than the commercial P25 TiO$_2$, however the reaction rates vary depending on the organic molecules. Reactions for pollutant mixture at environmentally relevant concentrations level (i.e., <1 ppm) and humidity would provide better measure of the catalyst performance in indoor air. An unconventional approach was adopted in the design of the air purifier. Unlike traditional air purifiers that are designed to accommodate air purification technologies around an air handling system, the PCO reaction chamber was designed first and tested, before the air handling system was designed around the chamber. Thus, allowing us to optimize the PCO performance of the air purifier. This general approach is applicable to other environmental catalysts [53–57].

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