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FACILE TECHNIQUE FOR THE IMMOBILISATION OF TIO_2 NANOPARTICLES ON GLASS SUBSTRATES FOR APPLICATIONS IN THE PHOTOCATALYTIC SELF-CLEANING OF INDOOR AIR POLLUTANTS

(Salutan nanopartikel TiO_2 ke atas Substrat Kaca Melalui Teknik Mudah untuk Penyingkiran Bahan Pencemar Udara dalaman Melalui Proses Fotokatalisis)

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Abstract

Self-cleaning technology employing titania (TiO_2) photocatalysts has major applications in the removal of indoor air pollutants. Pollutant removal efficiency significantly depends on the properties of the photocatalyst thin film, which is deposited on substrates. The present work developed a facile immobilisation technique that is based on simple sol–gel process. In this technique, TiO_2 nanoparticles are spray-coated onto a porous glass substrate. The uniformity of the TiO_2 coating on the glass surface was studied using a dynamic flowsense charge-coupled device camera. The influence of different TiO_2 nanoparticle concentrations in the ethanol phase was identified through rheological analysis, which showed that nanoparticle concentration is a crucial factor that affects the uniformity of the coating layer. The ability of the obtained material to catalyse formaldehyde photodegradation in presence of artificial UV light was investigated. Results demonstrated that >15.0 g/L TiO_2 is required to activate formaldehyde photodegradation and that uniform surface coatings with sufficient surface thickness can be obtained by spraying TiO_2 nanoparticles on glass substrates at concentrations of more than 15.0 g/L. This study demonstrated that uniformly coated photocatalysts for the efficient self-cleaning of indoor air pollutants can be fabricated through a facile technique.

Keywords: self-cleaning, TiO_2, sol-gel, formaldehyde, photocatalysis

Abstrak

Teknologi pembersihan menggunakan TiO_2 sebagai fotokatalis yang memainkan peranan penting terutamanya dalam menyingkirkan bahan pencemar udara dalaman. Pembersihan bahan pencemar ini sangat bergantung kepada ketebalan filem salutan terbentuk pada substrat. Dalam kajian ini teknik mudah dapat dicapai melalui proses sol-gel dan diikuti dengan salutan semburan TiO_2 berliang nanopartikel ke atas substrat kaca. Keseragaman pembentukan titania bersalut pada permukaan kaca dikaji menggunakan kamera “gabungan cas dinamik flowsense. Pengaruh kepekatan nanopartikle TiO_2 yang berbeza-beza dalam fasa etanol membawa kepada analisis reologi. Kajian reologi menunjukkan keberkesanan kepekatan nanopartikel bagi mendapatkan lapisan salutan yang seragam. Keberkesanan salutan dinilai dengan penyingkiran formaldehid dalam kehadiran cahaya UV tiruan. Keputusan penyingkiran menunjukkan bahawa kepekatan TiO_2 yang tinggi dengan melebihi 15.0 g/L menunjukkan penyingkiran formaldehid pada tahap yang ketara disebabkan oleh keseragaman salutan pada permukaan kaca serta ketebalan permukaan yang mencukupi. Kajian ini menunjukkan prestasi yang baik dalam mengesahkan salutan fotokatalis yang seragam untuk meningkat keberkesanan penyingkiran bahan pencemar udara dalaman.

Kata kunci: penyingkiran, TiO_2, sol-gel, formaldehid, fotokatalisis

Introduction

Indoor air pollution is a growing concern and has emerged as a major health threat in numerous countries. Thus, indoor air pollution requires immediate resolution. On average, every human being spends approximately 90% of their daily life indoors. Therefore, humans are constantly exposed to indoor air pollutants. Exposure to indoor air pollutants can cause health issues, such as sick building syndrome. The most ubiquitous indoor air pollutants include CO_2, NO_2, formaldehyde and volatile organic compounds (VOCs) [1]. These pollutants can be found easily in any commercial or industrial building. Among these pollutants, formaldehyde is most common. The major sources of formaldehyde pollutants include formaldehyde-emitting building materials and consumer products, such as furniture and other wooden products. Combustion processes, such as smoking, cooking and incense burning, are also sources of formaldehyde emissions. The secondary formation of formaldehyde is triggered by the oxidation of VOCs and the reactions between ozone and terpenes. Researchers have only recently considered photocatalyst-based self-cleaning technology as a feasible solution to indoor air pollution [2].

Self-cleaning surface coatings that employ metal oxides are used as alternative approaches for the remediation of indoor air pollutants [3]. Self-cleaning coatings can be classified in two different categories, namely, superhydrophilic and superhydrophobic coatings [4–11]. Superhydrophilic coatings are progressive and are based on suitable metal oxides. They chemically degrade complex pollutants through a photon energy-assisted cleaning mechanism [4]. Superhydrophilic TiO_2-coated glass substrates provide a new way to clean indoor air pollutants. TiO_2 is a popular and widely studied semiconductor photocatalyst given its various superior advantages [12–14]. It exhibits excellent photocatalytic activity in the photodegradation of harmful and toxic organic aquatic pollutants [15–20]. Developed or modified TiO_2 composites have been used in water and energy-related applications, including the removal of toxic aquatic pollutants, the photoreduction of CO_2 and the production of hydrogen through hydrolysis.

Nevertheless, the application of TiO_2 to remediate air pollution, particularly indoor air pollution, has not been extensively studied. The use of TiO_2 as an immediate remedy for indoor air pollutants has attracted increased attention because of its superior photostability, photoactivity and superhydrophilicity compared with other photocatalysts [21, 22]. These unique qualities set a strong foundation for the effective removal of indoor air pollutants. However, the removal of air pollutants is a gas-phase reaction. Thus, the TiO_2 suspension technique used in water treatment is inappropriate for air pollution treatment because it will not facilitate the photocatalytic reaction in air. TiO_2 nanoparticles must be immobilised onto substrates, such as glass and walls, before they can be used to remove air pollutants. However, immobilising TiO_2 nanoparticles onto surfaces is difficult. Thus, an appropriate and cost-effective technique for the immobilisation of TiO_2 is needed. Coating has emerged as a facile approach for the immobilisation of TiO_2 nanoparticles on substrates.

Various coating techniques have been adopted by many researchers. These coating techniques include sputtering, chemical vapour deposition and thermal spraying [23–29]. However, all these methods have their own drawbacks, such as high temperature requirements that can change the TiO_2 microstructure. Moreover, all of these coating techniques are economically nonviable [23,30]. Hence, the present work demonstrates the deposition of a uniform, transparent, photocatalytic and superhydrophilic TiO_2 coating on a glass substrate through a simple spraying technique. The TiO_2-coated glass substrates have potential applications in the removal of indoor air pollutants, particularly formaldehyde.

Materials and Methods

Materials

Titania (TiO_2) powder (P25 Degussa), ethanol, acetone and isopropanol were purchased from R & M Chemicals. Deionised water was used in all experiments. All chemicals were of analytical grade and used without any further purification.

Spray coating

TiO_2 solutions with concentrations of 2.5, 5.0, 10.0, 15.0 and 20.0 g/L were prepared by mixing 0.5, 1, 2, 3 or 4 g of P-25 TiO_2 powder with 200 mL of ethanol, respectively. The solutions were stirred vigorously until homogenous and white in colour. Soda lime glass plates (20 mm × 20 mm × 2 mm) were first cleaned and washed several times with deionised water, then washed with acetone, ethanol and isopropanol in a sonicator. Then, the cleaned glass plates were dried in an oven at 80 °C to ensure that all surface contaminants were removed. Each prepared TiO_2 nanoparticle solution was loaded into a controlled pneumatic spray gun and carefully sprayed onto the cleaned soda lime glass for 10 s. Spraying was repeated five times to ensure that the coating solution was uniformly coated onto the glass surface. Then, the coated glass substrates were sintered.

Characterization

Film thickness was measured using a surface profilometer. Dynamics FlowSense Charge-coupled Device (CCD) camera (Dantech Dynamics, Denmark) was used to capture images of the TiO_2-coated glass substrates under cold light sources. Surroundings were kept dark to ensure that cold light passed through the glass surfaces coated with various TiO_2 concentrations at the same intensity. Image processing was performed for the analysis of surface properties. Images were converted to greyscale mode for surface plot and three-dimensional (3D) surface analysis. The intensity of images varied from 0 to 255 on the basis of the coated properties. Rheological experiments were performed with Anton Paar Physica MCR 302 with suitable geometry.

Photocatalytic experiment

The schematic of the experimental setup used in this study is shown in Figure 1. A compressor (MACO) with a capacity of 0 CFM to 6.3 CFM was used to provide steady-flow conditions. The air stream from the compressor was filtered using a filter regulator (SHAKO) and a 5 µm air filter (SMC) to filter out any dust particulates and excessive water vapour. The flow rate was manually adjusted by using a flowmeter (Dwyer, USA). Formaldehyde was aerosolised by forcing a stream of air through an aerating unit containing 37% formaldehyde solution (R & M Chemicals). UV-A light (HPMV 400V, NIKKON) was used as the radiation source for the photoreactor. Photocatalytic experiments were performed under a fume chamber with proper closure to prevent the dispersion of airborne formaldehyde and UV light radiation to the surroundings. Formaldehyde concentration was measured by using a Formaldemeter™ htV-m (PPM Technology, UK) every 15 minutes for 3 hours. Removal efficiency was calculated in accordance with the following equation 1:

$$\text{Removal} = \frac{(\text{Initial Concentration } (C_i) - \text{Final Concentration } (C_f) \times \text{Air flow rate } (Q)}{\text{Coating Surface Area } (A) \times \text{Removal Time } (t)} \quad (1)$$

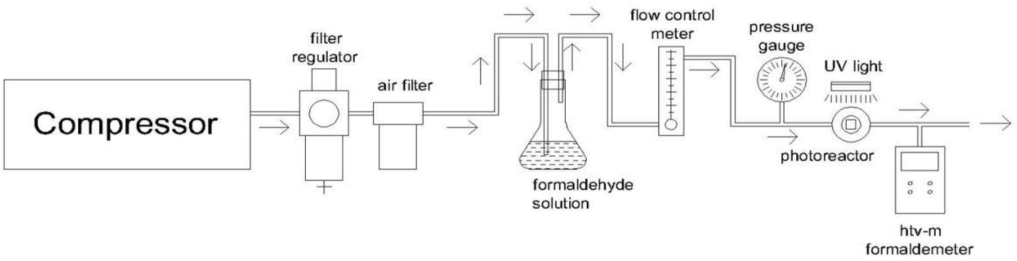

Figure 1. Photocatalysis experimental setup

Results and Discussion

Surface coating

Coating uniformity is an important criterion in the present study. The optimal TiO_2 concentration required to produce a uniform coating on the substrate was identified by depositing different concentrations of TiO_2 nanoparticles on glass substrates and by analysing the properties of the TiO_2-coated substrates. Analytical results indicated that the optimal TiO_2 concentration is >15.0 g/L. Figure 2 shows glass substrates coated with different TiO_2 concentrations, and Figure 3 shows the CCD camera images of these samples. As shown in these images, the surfaces of the substrates coated with less than 15.0 g/L TiO_2 appear rough and uneven. The substrate coated with 2.5 g/L TiO_2 exhibits a small pothole defect, as shown in Figure 3a. These defects decrease photocatalytic efficiency. The roughness of the coating surface decreases as TiO_2 concentration increases.

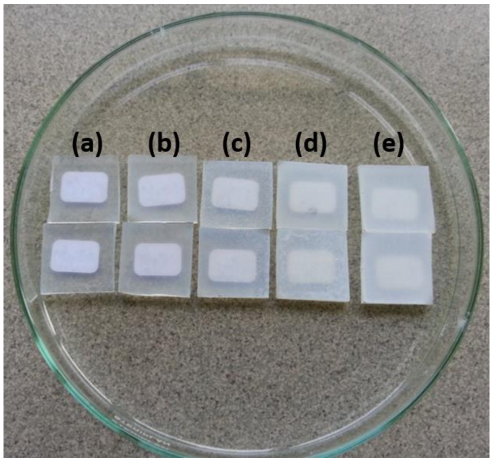

Figure 2. Images of glass surface coated with TiO_2 at different concentration (a) 2.5 g/L, (b) 5.0 g/L, (c) 10.0 g/L, (d) 15.0 g/L and (e) 20.0g/L

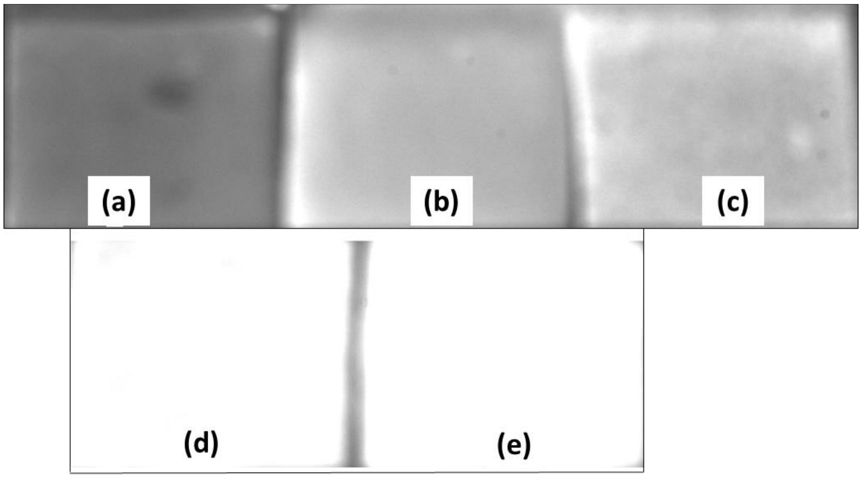

Figure 3. CCD images of different concentration coated on glass surface (a) 2.5 g/L, (b) 5.0 g/L, (c) 10.0 g/L, (d) 15.0 g/L and (e) 20.0 g/L

Figure 4 shows the two-dimensional (2D) perspective of coating thickness obtained by plotting the surfaces of substrates coated with different TiO_2 concentrations. The plot shows that surface coating intensity increases as TiO_2

concentration increases. In contrast to the surface of the glass substrate coated with <15.0 g/L TiO_2, that of the glass substrate coated with 15.0 g/L TiO_2 is highly uniform without any observable surface defects. The uniformity of the surface coatings is further verified by the 3D surface plot shown in Figure 5. Similar to the 2D plot, the 3D plot indicates that rough coatings are obtained when TiO_2 is deposited at low concentrations, whereas smooth, even coatings without defects are obtained when TiO_2 is deposited at concentrations greater than 15.0 g/L. These results prove the robustness of the simple spraying technique adopted in this study.

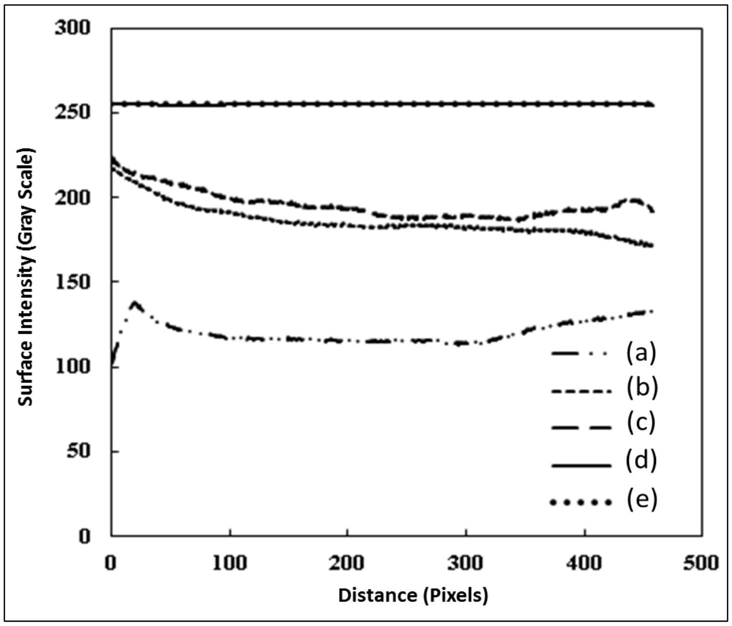

Figure 4. 2-D surface plotting for coating of different concentration (a) 2.5 g/L, (b) 5.0 g/L, (c) 10.0 g/L, (d) 15.0 g/L and (e) 20.0 g/L

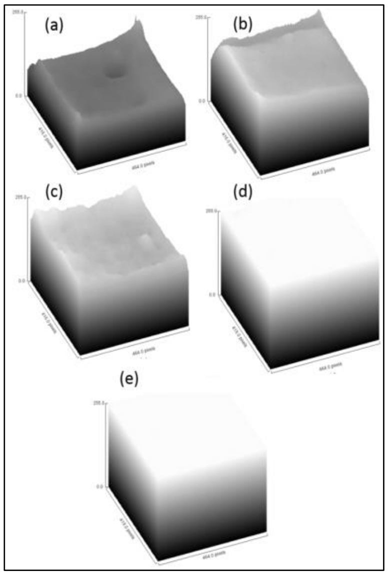

Figure 5. 3-D surface plotting for coating of different concentration (a) 2.5 g/L, (b) 5.0 g/L, (c) 10.0 g/L, (d) 15.0 g/L and (e) 20.0 g/L

The rheological behaviour of the suspension was inferred from the plot of shear stress versus shear rate shown in Figure 6a. As shown in the figure, all concentrations follow a linear trend, indicating Newtonian behaviour. Figure 6b shows the viscosity versus shear rate of different TiO_2 concentrations. Viscosity marginally increases as TiO_2 concentration increases, and the coating solution concentration of 20.0 g/L exhibits the highest viscosity. This phenomenon indicates that the increase in the degree of nanoparticle interaction in the colloidal suspension increases solvent immobilisation [31, 32]. Therefore, coating uniformity will be improved by increasing viscosity, as proven by the 2D and 3D surface plots.

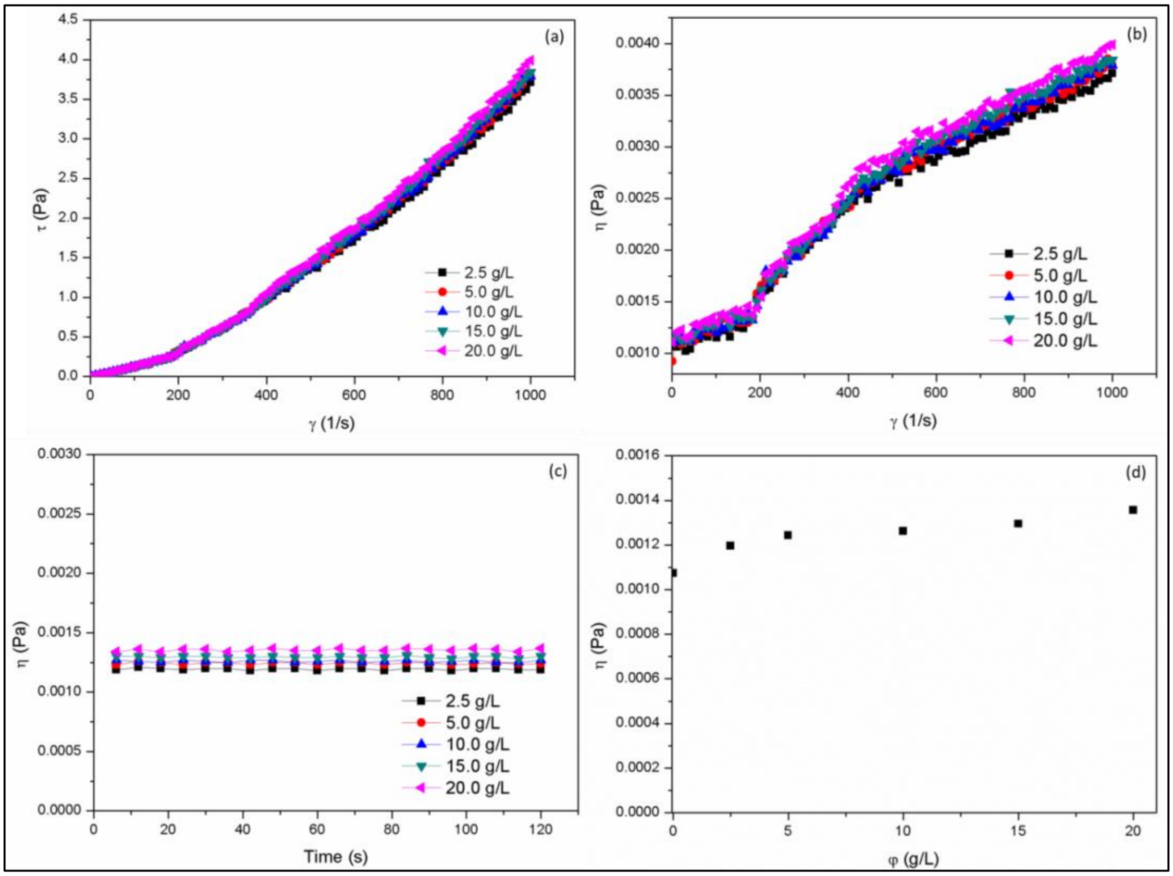

Figure 6. Rheological study (a) Shear stress versus shear rate, (b) Viscosity versus shear rate, (c) Viscosity versus time and (d) Viscosity versus TiO_2 concentration

Effect of Concentration on Formaldehyde Photocatalysis Efficiency

Figure 7 shows the photodegradation of formaldehyde over 3 hours of irradiation with artificial UV light. Formaldehyde concentration was recorded immediately once the airborne formaldehyde concentration had stabilised. As shown in the figure, coatings fabricated with TiO_2 concentrations of less than 15.0 g/L do not successfully remove formaldehyde and instead contribute to the overall level of airborne formaldehyde. Airborne formaldehyde levels have increased because nondegraded formaldehyde evaporates under heat emitted by UV light and becomes airborne once photon energy is activated. This phenomenon indicates that low amounts of TiO_2 cannot effectively photocatalyse formaldehyde degradation even after 3 hours of photodegradation and instead increases the levels of nondegraded formaldehyde in the chamber.

Meanwhile, coatings fabricated with TiO_2 concentrations of >15.0 g/L significantly decrease airborne formaldehyde levels after 3 h. On average, coatings prepared with 15.0 and 20.0 g/L TiO_2 decrease airborne formaldehyde levels to 0.15 and 0.30 ppm, respectively. This significant decrease may be attributed to photodegradation in the reaction chamber. Formaldehyde levels stabilise at the initial stage of photocatalysis induced by coatings containing 15.0 g/L TiO_2 because photodegradation capacity offsets the constant increase in airborne formaldehyde level attributed to evaporation. An overdosage of 20.0 g/L TiO_2 improves removal rate and overcomes the ongoing formaldehyde flow. The outperformance of formaldehyde increases the humidity level inside the reaction chamber. Humidity improves photodegradation. Sun et al. observed similar results [33]. The increase in humidity is attributed to water evaporation in the reaction chamber. The residual water that has not evaporated forms $^{\bullet}OH$ on the coated surfaces. The hydroxyl radical is a powerful oxidant given its high redox potential, and its presence increases the photodegradation rate. However, some of the residual water will evaporate because of the strong heat radiation from the light source, thus causing the degradation rate to fluctuate (Figure 7).

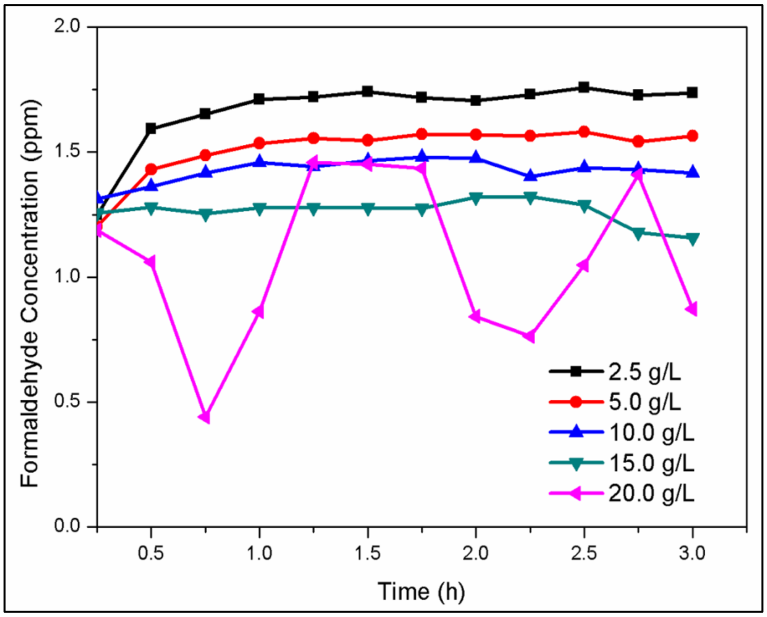

Figure 7. Photodegradation of formaldehyde airborne

Formaldehyde removal rate

As shown in Figure 7, the removal rate obtained with 15.0 g/L TiO_2 is 0.15 ppm, and 1 ppm of formaldehyde is equivalent to 1.23 mg/m^3 at room temperature. Therefore, the concentration of formaldehyde is 0.1845 mg/m^3. By taking airflow into account, where 50 mL/min = 3000 mL/h = 0.003 m^3/h, the amount of formaldehyde oxidised in 1 hour can be calculated as follows:

$$\begin{aligned}\text{Oxidised formaldehyde} &= 0.1845\ \text{mg/m}^3 \times 0.003\ \text{m}^3\text{/h} \\ &= 0.000554\ \text{mg/h} \\ &= 0.554\ \mu\text{g/h}\end{aligned}$$

Given that the area of the coated surface is 0.0004 m^2, the removal rate of the airborne formaldehyde in 1 hour will be as follows:

$$\begin{aligned}\text{Formaldehyde removal rate} &= (0.554\ \mu\text{g/h})/0.004\ \text{m}^2 \\ &= 138.5\ \mu\text{g m}^{-2}\ \text{h}^{-1} \\ &= 1.385\ \text{mg m}^{-2}\ \text{h}^{-1}\end{aligned}$$

Ichiura et al. reported that TiO_2 sheets fabricated by mixing pure TiO_2 with pulp obtained similar average removal rates of 10.0%–15.0% [34]. Yu et al. reported that TiO_2 nanoparticles deposited onto PTFE filters can catalyse formaldehyde photodegradation in the presence of UV light [35]. Liang et al. studied formaldehyde removal by TiO_2-coated thin films [36]. The present results indicate that the significant and rapid removal of formaldehyde will improve air and environmental quality.

Conclusion

Titania (TiO_2) nanoparticles were successfully immobilised on glass substrates through a simple spraying technique. Dynamic flow-sense images showed that highly uniform coatings can be obtained by spraying TiO_2 nanoparticles at concentrations exceeding 15.0 g/L. This result is further supported by 2D and 3D surface plots, wherein no surface defects were observed on coatings prepared with >15.0 g/L TiO_2. This result implies that the simple coating technique adopted in this study can yield TiO_2 coatings with high quality. Higher formaldehyde removal rates were obtained with coatings prepared with higher TiO_2 concentrations than those obtained with coatings prepared with lower TiO_2 concentrations.

Acknowledgement

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