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Highly Efficient Photocatalytic Degradation of NO for Indoor Air Purification by Using Ceramic Foam Air Filters Coated with Mesoporous TiO_2 Thin Films

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***Abstract*:** Ceramic foam air filters with three-dimensional (3D) porous structure and high surface area were coated with mesoporous TiO_2 thin films via reverse micellar method. The mesoporous TiO_2 thin films demonstrated a highly efficient photocatalytic degradation of nitrogen oxide (NO). More than 92.5% of NO can be degraded in a single pass for air filter samples with different pore densities. The 3D porous structure of ceramic air filters enhances flow turbulence and mixing and therefore provides the catalytic system with excellent gas-dynamic properties and sufficient contact between the gaseous reactants and the surface of the catalysts. The higher pore density of the ceramic foam filters results in higher photocatalytic rate. The presence of more adsorption sites on the surface for water vapor, gaseous reactants, and gaseous products in photocatalytic reactions improves photocatalytic activity. The porous ceramic air filters coated with mesoporous TiO_2 have large surface area and high photocatalytic activity and overcomes the disadvantages of using powdered TiO_2 photocatalysts on substrates. Thus, we confirmed that the 3D porous ceramic foam filters coated with mesoporous TiO_2 thin films have a higher photocatalytic degradation rate of NO in air than that in flat ceramic tiles. No deactivation was observed, and a consistently high degradation rate of NO was obtained in all reaction cycles for the TiO_2-coated 3D porous ceramic filters.

Keywords: Photocatalyst, TiO_2, Air purification, filter

1. Introduction

Photocatalysis provides a promising solution for removing indoor air pollutants. TiO_2 is an effective photocatalysts because of its strong oxidizing power, non-toxicity, and long-term photostability [1–7]. Generally, the widely reported forms of TiO_2 photocatalysts are highly dispersed or suspended fine particles/powders in liquid medium. However, powdered TiO_2 photocatalysts are unsuitable for air purification because these particles may become respirable and thus cause adverse human health problems. Therefore, several studies have been performed to immobilize TiO_2 particles as thin films on different rigid supports, such as glass, stainless steel, and aluminum plates.

Coating a substrate significantly affects the surface adsorption of reactants for photocatalysis. Traditionally, photocatalytic thin films are usually coated on flat surfaces, such as honeycomb air filters. In this study, we selected a three-dimensional (3D) and porous ceramic foam as the coating substrate because of its excellent hydrodynamic properties for gas passing. The ceramic foam exhibits a 3D porous structure with versatile pore density, surface area, and chemistry. The 3D porous ceramic foam air filters have high bed porosity, which results in a low pressure drop required by such filters. Unlike honeycomb air filters, the 3D porous ceramic foam filters have convoluted pore structures that enhance intense turbulence and mixing. The open porous and reticulate structure of the 3D ceramic filters provides the catalytic system with an excellent gas-dynamic

properties and sufficient contact between the gaseous reactants and the surface of the catalysts. Porous materials have significant advantages in liquid or gas phase-based catalytic reactions.

In addition, depending on the methods of depositing and fixing TiO_2, the formation of TiO_2 films on a solid substrate may reduce the effective surface area of TiO_2 photocatalysts and thus results in a decreased photocatalytic activity. However, the TiO_2 thin films with a mesoporous structure have a high photocatalytic activity because the structure possesses a high specific area with more active sites for catalytic reactions. This research is the first to report the photocatalytic degradation of NO by using mesoporous TiO_2 thin films coated on 3D porous ceramic foam air filters prepared via reverse micellar method. NO is selected as the target air pollutant for degradation because this gas is a major indoor air pollutant with deleterious health effects. The level of NO and NO_2 in indoor environments is normally within the range of several hundred ppb and less than a hundred ppb, respectively.

2. Results and Discussion

The chemical composition of the TiO_2 thin film coated on ceramic foam filter was analyzed via XPS. The high-resolution XPS spectra (Fig. 1) indicate that Ti $2p_{3/2}$ at 458.7 eV and $Ti2p_{1/2}$ at 464.3.8 eV in the sample confirm the existence of the TiO_2 photocatalyst. A significant amount of Ti can be found after TiO_2 coating.

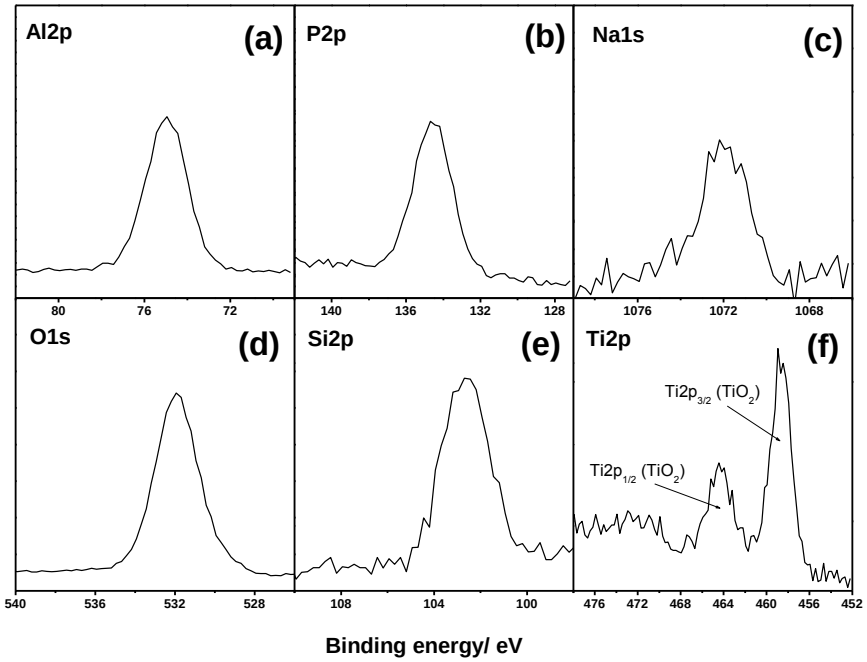

Fig. 1: High-resolution XPS spectra of (a) Al 2p, (b) P 2p, (c) Na 1s, (d) O 1s, (e) Si 2p, and (f) Ti 2p regions for the TiO_2-coated ceramic foam air filter

The photocatalytic performance of the TiO_2-coated porous ceramic air filters with different pore densities was evaluated based on the degradation of NO under UV irradiation. Fig. 2 shows that the NO concentration sharply decreased when the UV light was switched on for all air filters with different pore densities. Thus, a higher pore density, i.e., 30 ppi, results in a higher photocatalytic efficiency. The TiO_2-coated porous ceramic filters with 30 and 20 ppi can degrade 79% and 76% of NO in a single pass, respectively. Moreover, the air filter with a lower pore density, i.e., 10 ppi, can degrade 65% of NO in a single pass. This finding indicates that the pore density of the filter is crucial to photocatalytic efficiency. In addition, a low pollutant concentration was maintained in this study. The effect of the adsorption of pollutants and water vapor is more vital at ppb level concentration of pollutants than at ppm level concentrations. In this study, the NO concentration was maintained

at levels lower than 1000 ppb. The ceramic foam filters with a high pore density have more adsorption sites for water vapor and pollutants and hence enhance the photocatalytic efficiency. Remarkably, more than 95% of NO can be degraded in a single pass for all air filter samples with different pore densities when two TiO_2 coated foam ceramic filters, instead of one filter, were used.

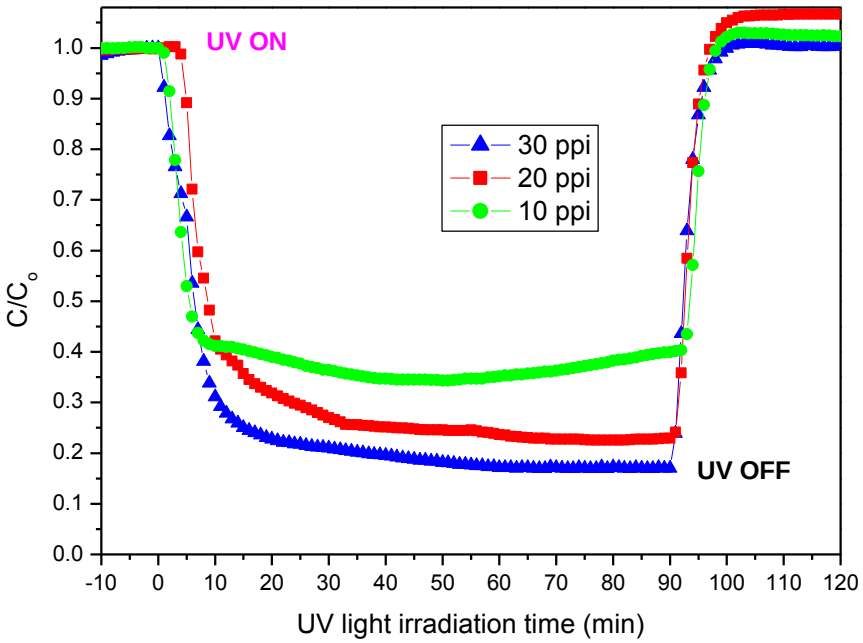

Fig. 2: Photocatalytic degradation of NO for the TiO_2-coated ceramic foam air filters with different pore densities (pores per inch (ppi)) under UV light irradiation. Dimension of air filter used = 30 cm (L) × 30 cm (W) × 1 cm (H); integrated UV intensity within the range of 310 nm to 400 nm = 540 ± 10 □W/cm^2; RH = 65 ± 5%; Temp = 22 ± 2°C; initial NO concentration = 1,000 ppb.

Fig. 3 shows the photocatalytic oxidation of NO and the conversion of NO_2 from NO for the TiO_2-coated ceramic foam air filter with 30 ppi under UV light irradiation. The background concentration inside the test chamber was 16 ppb. After UV light was switched on, NO_2 functioned as the intermediate from the photocatalytic degradation of NO. The amount of generated NO_2 evidently increases with reaction time and then reaches a constant concentration of 58 ppb. Moreover, NO_2 was continuously formed and further transferred into HNO_3 during irradiation. Nitrogen oxides (NO and NO_2) are major pollution sources in our environment and are harmful to human health. Therefore, evaluating the photocatalytic activity of the TiO_2-coated filters based on the NO removal rate is insufficient. More attention should be given to the conversion of NO_2 to HNO_3 because the latter can be easily removed. Previous studies [4–6] have shown that NO_2 is the intermediate generated from the photocatalytic degradation of NO, which is supported by the following reactions:

$NO + HO_2\bullet \rightarrow NO_2 + OH\bullet$

$NO_2 + OH\bullet \rightarrow HNO_3$

NO_2 functions as the intermediate during the photocatalytic oxidation of NO and can further react with OH• to form HNO_3. Thus, the NO_2 generated from the photodegradation of NO is adsorbed on the ceramic foam air filters because of their large adsorption capacities. The adsorbed NO_2 is photodegraded to HNO_3, which reduces the amount of NO_2 exiting in the system. This result further confirms that the TiO_2 thin film coated on ceramic foam filters can efficiently remove NO and NO_2.

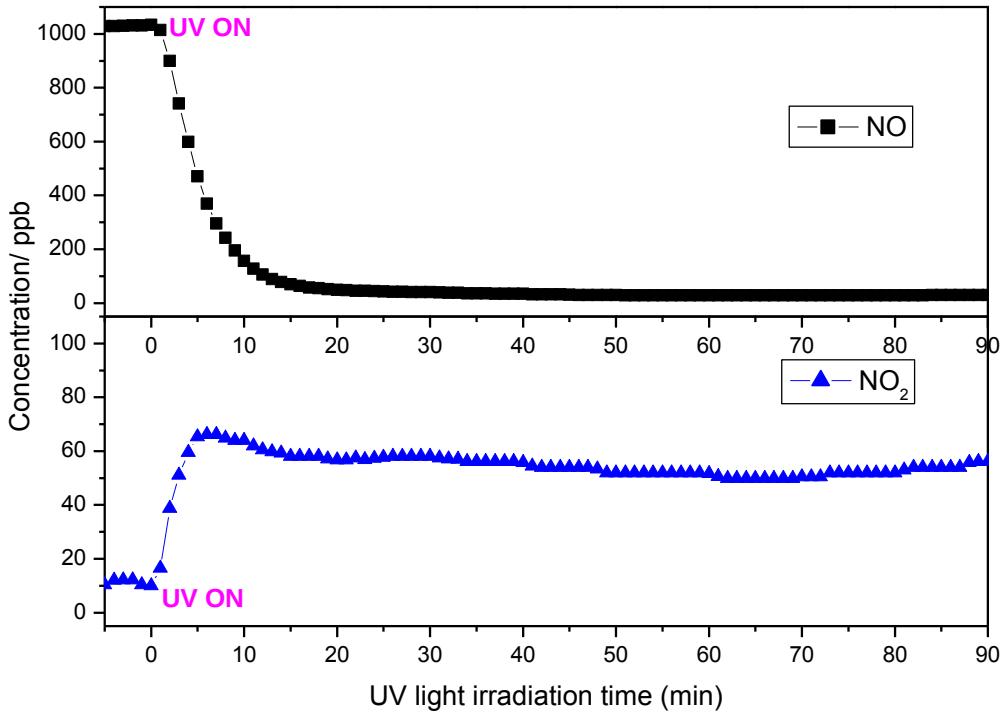

Fig. 3: Photocatalytic oxidation of NO and the conversion of NO_2 from NO for the TiO_2-coated ceramic foam air filter with 30 ppi under UV light irradiation. Dimension of the air filter used = 60 cm (L) × 30 cm (W) × 1 cm (H); integrated UV intensity within the range of 310 nm to 400 nm = 540 ± 10 □W/cm^2; RH = 65 ± 5%; Temp = 22 ± 2 °C; initial NO concentration = 1000 ppb.

Maintaining repeatability and long lifetime in terms of photocatalytic activity is also important for photocatalysis to minimize air filter replacements. Fig. 4 shows the effect of reaction cycles on the photocatalytic activity of the TiO_2-coated ceramic filters for the photocatalytic degradation of NO with an initial concentration of 400 ppb. After adsorption and desorption reached equilibrium, the UV light was turned on for more than 1 h and then turned off for more than 1 h to recover the equilibrium status between adsorption and desorption. This process was repeated for three times to evaluate the effect of reaction cycles on the photocatalytic activity of the TiO_2-coated porous ceramic filters. Moreover, the NO concentration rapidly decreases and reaches a very low level when the UV lamp is switched on. In addition, the NO concentration gradually decreases with prolonged UV irradiation time. About 92.5% to 97.5% of NO can be degraded for all air filter samples with different pore densities. The photocatalytic oxidation of NO is similar in all reaction cycles. The previous reaction cycles have no evident effect on the photocatalytic reactions of the TiO_2-coated filters in subsequent reaction cycles.

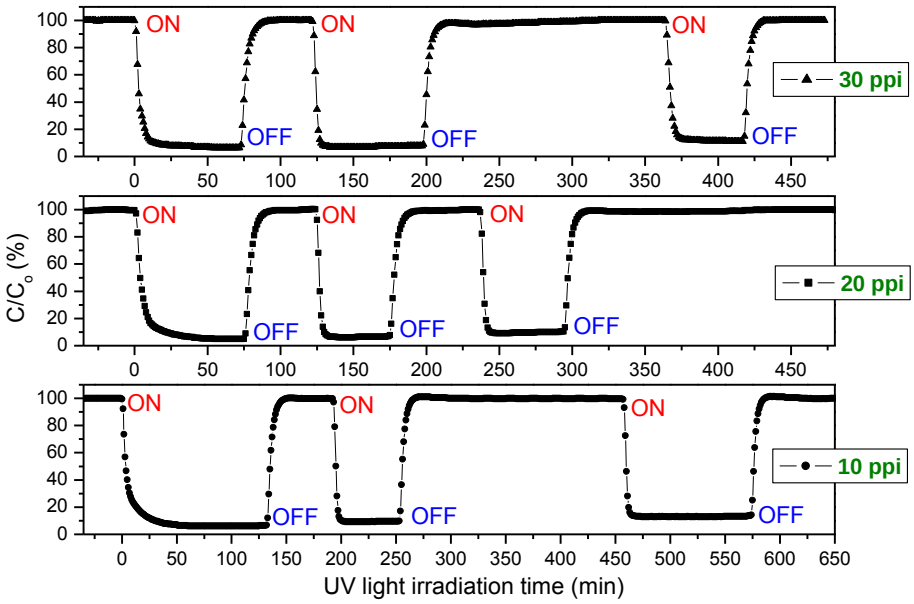

Fig. 4: Photocatalytic degradation of NO in different repeated cycles for the TiO_2-coated ceramic foam air filters with different pore densities (pores per inch (ppi)) under UV light irradiation. Dimension of the air filter used = 30 cm (L) × 30 cm (W) × 1 cm (H); integrated UV intensity within the range of 310 nm to 400 nm = 540 ± 10 □W/cm^2; RH = 65 ± 5%; Temp = 22 ± 2 °C; initial NO concentration = 400 ppb

The NO molecules are photocatalytically degraded into NO_2 and then further oxidized into HNO_3 when the UV lamp is switched on. Fig. 3 shows that the concentration of the NO_2 intermediate in the outlet gas is maintained at a low level. Thus, most NO and NO_2 intermediates are photocatalytically oxidized into HNO_3. The generated HNO_3 could be adsorbed to the active sites of TiO_2 surface. Gradually, HNO_3 occupies these actives sites. This competitive adsorption between HNO_3 and NO decreases the rate of photocatalytic oxidation of NO to NO_2 on the catalyst surface and thus decreases the photocatalytic activity of the TiO_2 thin film. However, in this study, no evident negative effect was observed on the photocatalytic activity of the TiO_2 thin film because of previous photocatalytic reactions. Therefore, the HNO_3 adsorbed on the active sites can transfer to the non-active sites of TiO_2 coating or on the surface of the ceramic foam substrate, which results in the recovery of the active sites on the surface of the TiO_2 photocatalyst. Thus, the NO_2 intermediate may not accumulate on the active sites of the TiO_2 thin film and may not deactivate the TiO_2 photocatalyst.

3. Conclusion

The mesoporous TiO_2 thin films were successfully formed on the 3D porous ceramic air filters with a high surface area via reverse micellar method. The photocatalytic degradation of NO was evaluated on these mesoporous TiO_2-coated porous ceramic air filters. A highly efficient photocatalytic degradation of NO was obtained in this air purification system because of the large effective surface area and high photocatalytic activity of the mesoporous TiO_2 thin film coating. More than 92.5% of NO at 400 ppb can be degraded in a single pass for all TiO_2-coated ceramic foam filters with different pore densities. The 3D porous structure of the ceramic filters enhances flow turbulence and mixing and thus provides a sufficient contact between the gaseous reactants and the photocatalytic surface. The higher pore density of the ceramic foam filters results in a higher photocatalytic rate. The TiO_2-coated 3D porous ceramic filters exhibit a higher photocatalytic degradation rate of NO than the TiO_2-coated flat ceramic tiles. The 3D porous ceramic filters could also maintain a consistent and high degradation rate of NO for all reaction cycles, which indicates that the photocatalyst is not deactivated during NO degradation.

4. Acknowledgements

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