

Photocatalytic Degradation of Nitrogen Oxides on Titania under UV and Visible Light Irradiation and Application in Outdoor Air Purification

Yao-Hsuan Tseng^{*,a}, Chien-Chih Chen^b, Jia-Hung Huang^a, and Yu-Ming Lin^a

a Center for Environmental, Safety and Health Technology, Industrial Technology Research Institute, Taiwan

b Department of Chemical Engineering, National Tsing-Hua University, Taiwan

Email: yaohsuanTseng@itri.org.tw

ABSTRACT

The ultraviolet and visible light activated titanium dioxide was synthesized and employed in the photocatalytic oxidation of NO. Sol-gel process by using tetra-n-butyl orthotitanate and ethanol to synthesize mixed-crystal (anatase and brookite) titanium dioxide were carried out under acid catalyzed condition. Platinum was loaded with impregnation method on the surface of titanium dioxide to modify the property. The prepared photocatalysts were activated in the degradation of NO_x under ultraviolet and visible light, respectively. The experimental results showed that near 40% removal of NO could be obtained in a flow type reaction system under irradiation of visible light. Furthermore, an outdoor air purification device with photocatalyst was developed under the sunlight irradiation. The result of outdoor test showed high potential application of photocatalyst in the removal of NO_x contaminants.

INTRODUCTION

The nano-size and anatase-type TiO₂ is widely used as photocatalyst. The TiO₂ photocatalyst act by UV irradiation at around 388 nm due to its energy gap. The energy distribution of UV region (280-400 nm) in solar light is only 4%, and 45% belongs to visible light region (400-700 nm). Under UV irradiation, TiO₂ photocatalyst is effective in air purification, water purification, self-cleaning, antifogging, and so on^[1]. Thus, visible-light-activated photocatalyst attracts many chemists to increase the application of photocatalyst. In the former, sputtering^[2], plasma^[3], and metal ion-implantation^[4] are used to modify TiO₂ for visible-light activity. In this investigation, the simple synthesis methods of photocatalyst are developed and the synthesized photocatalysts are active in degradation of NO_x under illumination of visible light.

Sol-gel and impregnation methods were employed to produce visible-light-activated TiO₂. Four types of photocatalysts were successfully synthesized. The particle size, crystallinity, and UV-visible absorption spectrum of these photocatalysts were detected. Further, these photocatalysts were used in the degradation of NO_x under ultraviolet and visible light to

examine their activity. The high visible-light-activated TiO₂ with small selectivity of NO₂ is obtained. Furthermore, photocatalytic degradation of NO_x under illumination of fluorescent lamps and outdoor air purification experiment were developed to prove the practicability of TiO₂.

EXPERIMENT

(1) Synthesis the visible-light-activated TiO₂

a. Sol-gel method: Measured quality of tetrabutyl orthotitanate was dropped in the ethanol solution. After complete dissolution, nitric acid was added to catalyze the hydrolysis and condensation reactions. Then, the precipitate of titanium hydroxide was produced. After drying at 120°C, the dried powder was calcined at 250°C to obtain the photocatalyst—Cs.

b. Sol-gel method with platinum salt: The platinum-contented titanium dioxide—Csp was synthesized in the same reaction conditions as in the previous section, except that the tetraammineplatinum nitrate solution was added to participate in the reaction before adding nitric acid. The amount of Pt added was 1 mol% versus Ti.

c. Impregnation method: The TiO₂ powders, Cs and Hombikat UV100, were used in this experiment, respectively. The 10g of powder were added to 100mL of tetraammineplatinum nitrate solution and stirred at 500 rpm for 1 hr in the ambient condition. The amount of Pt added was 1 mol% versus Ti. The mixed slurry was dried at 120°C for 4 hrs, and calcined at 250°C for 10 hrs. After calcination, the platinum-loaded photocatalysts—Cis (modified Cs) and Ciu (modified UV100) were obtained by the impregnation method.

(2) Photocatalytic degradation of NO_x by TiO₂

The degradation of NO_x was analyzed using the continuous system was shown in [Figure 1](#). The both side of outer tube of reactor were sealed by silicone plugs with a gas inlet. 0.3g of photocatalyst was spread on the glass plate (internal diameter: 9 cm), which was placed in the round shape reactor (internal diameter: 14 cm, height: 3.6 cm). 1 ppm of NO gas in the controlled humid air was introduced into the single pass reactor at the flow rate of 1 L/min while the controlled light was irradiated to the photocatalyst. The light source was 100W mercury lamp with lens of 365 nm, 400 nm, 435 nm, 500 nm, and 546 nm.

(3) Outdoor air purification experiment

The photocatalyst sheets were used in the air purification experiment. The composition of photocatalyst sheet (20 mg/cm² of TiO₂) was TiO₂, SiO₂, and nonwoven fabric (PE/coPET). A flat reactor (1 m²) covered with Pyrex glass was used for outdoor air purification experiment. The air was introduced into the reactor at the flow rate of 4.5 L/min while the solar light was irradiated to the photocatalyst.

Results and discussion

1. Characterization of the TiO₂

The results of XRD, TEM, and UV-Visible absorption were shown in [Figure 2, 3, and 4](#), respectively. The XRD pattern depicts the crystal structure of Cs and Cis are anatase and brookite, but Csp, Ciu, and UV100 are only anatase. The brookite structure is probably due to the existence of carbon atom in the crystal. The crystal structure and particle size are not changed with impregnation due to calcinations at low temperature (250 °C)^[5]. The particle sizes of Cs, Cis, and Csp are distributed around 5-10 nm, which are close to the most reactive particle size-7 nm^[6]. The order of visible-light absorption of these photocatalysts is: Csp > Cis > Cs ≈ Ciu > UV100. Therefore, the PtO deposited on the TiO₂ surface and impurities (C and PtO) contained in the TiO₂ enhance the visible-light absorption.

2. Reaction behavior of photocatalytic degradation of NO with TiO₂

At the beginning, 1 ppm of NO gas was introduced to reactor under dark condition. After few adsorption of NO on TiO₂, the concentration of NO was kept at 1 ppm. The mercury lamp was turned on to start the photocatalytic reaction. The distribution of NO and NO₂ during the reaction period was shown in [Figure 5](#). The steady state, 0.58 ppm of NO and 0.02 ppm of NO₂, was achieved after 5 min. The total concentration of NO_x keeps at 0.60 ppm during 2 hrs, so it depicts that the activity of photocatalyst is not decreased with time. 40% of NO_x were oxidized to NO³⁻ and NO²⁻ under irradiation of 500 nm and TiO₂-catalysis. The reaction behavior of Cis under irradiation of different wavelength was similar to [Figure 5](#), in which the photocatalytic reactions achieved steady state quickly. The same phenomenon was also observed with using other photocatalysts.

3. Activity of variant photocatalysts under UV and visible light irradiation

In this work, the synthesized photocatalysts and three commercial photocatalysts were employed in the degradation reaction of NO_x. The removal rates of NO_x with using variant photocatalysts under irradiation of UV and visible light were shown as [Table 1](#). The reactivity of all photocatalysts under irradiation of 365 and 400 nm are very similar to each other. However, the reactivities of three commercial photocatalysts under visible light (435~546 nm) are much less than the synthesized photocatalysts. The order of the visible-light activity of these photocatalysts is: Cis > Ciu > Cs > Csp >> UV100 (ST01 and P25). However, the results of UV-visible light absorption does not consist with the results of visible-light activity. The results also indicate that the photocatalytic reactivity of Csp and Cs under irradiation of 546 nm is decreased about 50% than under irradiation of UV light. The main loss of reaction

rate of Csp and Cs is because that the oxidation rate of NO₂ is decreased, and oxidation of NO is still proceeded well under visible light. With using Csp and Cs, the conversion of NO is less dependent on light wavelength, and the conversion of NO₂ is decreased by increasing the light wavelength. The photocatalysts, Cis and Ciu, which are synthesized by impregnating PtO on the TiO₂, show good visible-light activities in the degradation reaction of NO. The reason of visible-light activity is the existence of trace impurities of the TiO₂. The impurities, carbon, nitrogen, and platinum oxide, created intra-bandgap states close to the conduction or valence band edges which induce visible-light absorption at the sub-bandgap energy^[7]. During the synthesis steps of Csp, the platinum salt is added in the sol-gel step, so only small ratio of PtO is dispersed on TiO₂ surface. Hence, with same added amount of PtO, the visible-light activity of catalyst Csp is much less than Cis and Ciu, especially under irradiation of 500 nm and 546 nm. The excellent visible-light activated photocatalyst is obtained by combination of sol-gel and impregnation methods. Furthermore, the fluorescent lamp was used to simulate the indoor illuminative conditions. The light wavelength of fluorescent lamp is mainly located between 420 nm and 670 nm, except a small peak at 365 nm. The order of the removal rate of photocatalysts under irradiation of fluorescent lamp is same as visible-light reactivity.

4. Outdoor air purification experiment

In this work, an outdoor test was set up near the Taipei train station where the heavily air-polluted region is. The experiment results were as shown in **Figure 6**. The main composition of outdoor pollutants is NO_x, SO_x, VOC, and PM, so it is reasonable to get lower efficiency of NO_x degradation in the outdoor test than in the laboratory. After 24 hrs of reaction, the color of photocatalyst sheet was converted from white to slight yellow, but it still keeps a good reactivity. The periods of heavy pollution are distributed around working hours (6-18 o'clock). The average conversion of NO_x is 68% during 24 hrs of reaction, and the conversion is over 90% with solar light irradiation (7-18 o'clock). The result also indicates that the solar light irradiation is effective to excite TiO₂ for the outdoor air purification. The removal rate of NO_x is 36.0 μmol/day under TiO₂-catalysis and solar light.

References

1. Fujishima, A.; Tata, N. R.; Donald, A. T., *J. Photoch. Photobio. C*, 2000, 1, 1
2. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y., *Science*, 2001, 293, 269
3. Nakamura, I.; Negishi, N.; Kutsuna, S.; Ihara, T.; Sugihara, S.; Takeuchi, K., *J. Mol. Catal. A-Chem.*, 2000, 161, 205
4. Yamashita, H.; Harada, M.; Misaka, J.; Takeuchi, M.; Ikeue, K.; Anpo, M., *J. Photoch. Photobio. A*, 148, 2002, 257

5. Li, Y.; Lim, S. H.; White, T., Withers, R.; Liu, B. H., 2003, 44, 1328
6. Anpo, M.; Shima, T.; Kodama, S.; Kubokawa, Y., J. Phy. Chem., 1987, 91, 4305
7. Kisch, H.; Wojciech Macyk, W., Chemphyschem, 2002, 3, 399

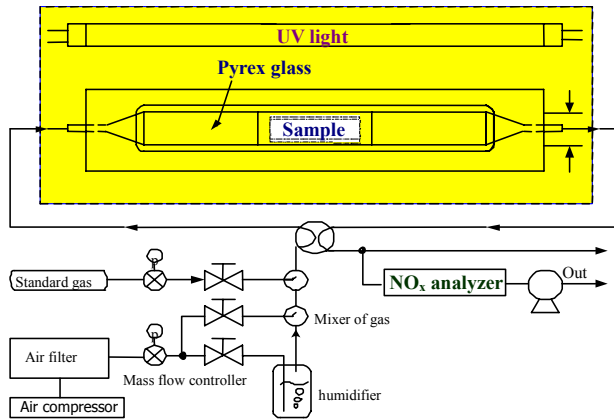


Figure 1. Photocatalytic deNO_x reaction system

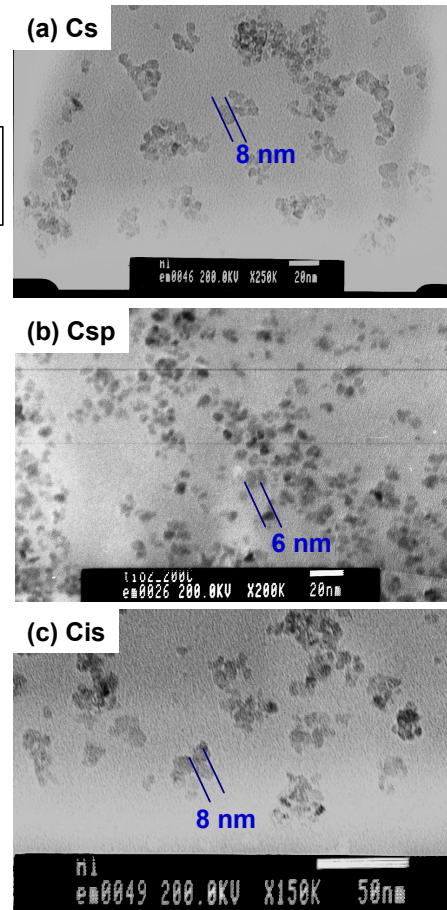


Figure 3. TEM image of the photocatalysts

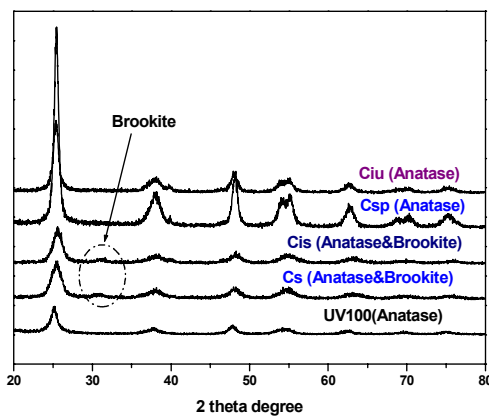


Figure 2. XRD patterns of the photocatalysts

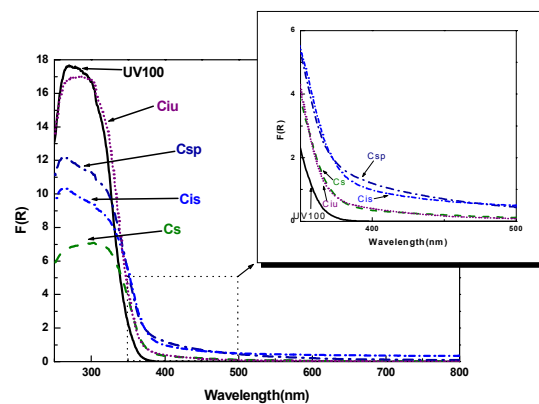


Figure 4. UV-visible absorption spectra

of the photocatalysts

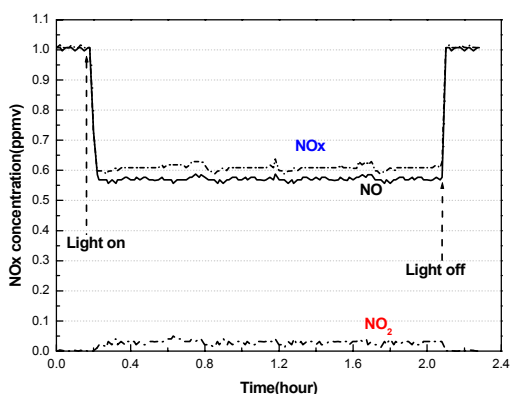


Figure 5. Transient behavior of the photocatalysts during 2 hours of reaction; Cs: 0.3 g, irradiation intensity of 500 nm: 1 mW/cm², relative humidity: 52%, inlet concentration of NO: 1 ppm, flow rate: 1 L/min, 27°C

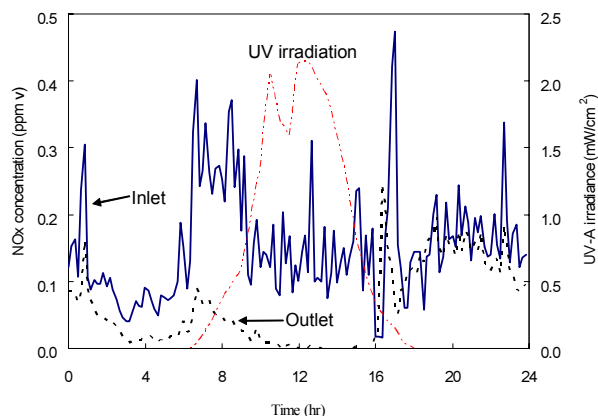


Figure 6. Concentration of NOx and UV light irradiation versus time during the outdoor air purification experiment; area of TiO₂ sheet: 200cm², TiO₂ contain: 20 mg/cm², relative humidity: 55–80%, flow rate: 4.5 L/min, temperature: 17–26°C, date: 2004/02/19

| Wavelength photocatalyst | 365 nm | 400 nm | 435 nm | 500 nm | 546 nm | Fluorescent lamp ^a |
|-----------------------------|--------|--------|--------|--------|--------|-------------------------------|
| Cs | 1.05 | 0.88 | 0.86 | 0.61 | 0.51 | 0.91 |
| Csp | 0.93 | 0.88 | 0.86 | 0.47 | 0.47 | 0.85 |
| Cis | 0.96 | 0.96 | 0.93 | 0.88 | 0.85 | 1.00 |
| Ciu | 0.99 | 0.94 | 0.93 | 0.84 | 0.83 | 0.97 |
| UV 100 | 0.92 | 0.81 | 0.61 | 0 | 0 | 0.47 |
| ST01 | 0.93 | 0.93 | 0.54 | 0 | 0 | 0.45 |
| P25 | 0.96 | 0.86 | 0.61 | 0 | 0 | 0.42 |

Table 1. The average removal rate of deNOx with variant photocatalysts versus irradiation of wavelength; amount of photocatalyst: 0.3g, irradiation intensity: 1 mW/cm², relative humidity: 50%, inlet concentration of NO: 1 ppm, flow rate: 1 L/min, 27°C, NOx removal rate: μmol/hr

