An Innovative Measurement for Testing the Nanocatalyst Degradation Efficiency of NH$_3$

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Abstract. This study develops a low-cost, fast and innovative measurement method for testing the efficiency of photocatalysts in the degradation of gaseous concentrations. In the past, photocatalyst tests of catalyst response to gases mainly relied on measurement with either GC/MS (Gas Chromatography/Mass Spectrometer) or FTIR (Fourier Transform Infrared Spectroscopy), to monitor the reaction process. However, these two instruments are very expensive, and the processes are complicated and time-consuming. The major devices of the measurement method developed by this study are UV/VIS spectrophotometer and quartz cuvettes. The experimental procedures are not only simple but fast. In the experiment, a gas of a specific concentration is first injected into an enclosed quartz cuvette. The cuvette is then placed in the UV/VIS spectrophotometer to carry out tests to obtain an absorption spectrum. Thus, a calibration curve of UV light absorbance intensity vs. various gaseous concentrations can also be obtained using the same method. The degradation efficiency of the different photocatalysts is to be measured. Quartz plates are coated with two different types of TiO$_2$ nanocatalysts. The coated plates are then placed in separate cuvettes. After injecting NH$_3$ into a quartz cuvette, the cuvette is then put under the UV light irradiation to perform the degradation experiment. Afterwards, the cuvette is transferred to the UV/VIS spectrophotometer for testing. The absorbance intensity of the absorption spectra is then compared with the calibration curves. Based on the change of the gaseous concentration, the degradation efficiency of the photocatalyst is determined. The experimental results reveal that the self-made TiO$_2$ nanocatalyst has excellent degradation efficiency towards NH$_3$. When NH$_3$ is exposed to UV irradiation for 60 minutes, the gaseous concentration can be reduced to 10.35% of the original concentration. However, the commercial TiO$_2$ nanocatalyst can only reduce the gaseous concentration to 50.2% of the original concentration. In addition, the degradation reaction rate constant of the self-made TiO$_2$ nanocatalyst towards NH$_3$ is as high as 0.029 min$^{-1}$.

1. Introduction

At present, air and water pollution is problem many countries need to solve as the pollution can directly affect the quality of life. There are two types of air pollution, namely indoor and outdoor.
Indoor air pollution mainly comes from the vapors or fumes emitted from materials used in construction, furniture, bathrooms and kitchens. Formaldehyde (Formalin) and ammonia are the most common vapors emitted that can be noxious and harmful. Even at very low concentrations, they are easily noticeable. For example, the smell threshold value of ammonia is 5.3 ppm. Although it may not be harmful at that concentration, it will cause odor problems in closed public spaces. Traditionally, the common materials using to treat noxious odor molecules in the air are activated carbon and Zeolite. However, these absorbents cannot be regenerated and need to be changed constantly. Therefore, mild and long-lasting photocatalysts are very suitable for the removal of low concentrations of noxious molecules and at the same time can refresh the air. The theory of photocatalyst decomposition VOC is: By the activation of light, moisture and oxygen molecules which are in contact with the photocatalyst are converted to hydroxide radicals, extra-oxygen ions and hydrogen peroxide. When organic pollutants in the vapor phase come in contact with the active substances, they are oxidized to 

\[ \text{H}_2\text{O} \text{ and } \text{CO}_2, \text{ or in to smaller organic molecules, which can be readily further decomposed by microorganisms. The degradation theory of inorganic pollutants is: when inorganic pollutants (NOx, NH}_3, \text{ etc.) in the vapor phase come in contact with active substances, they are oxidized into water-soluble molecules and temporally adsorbed into the surface of the photocatalyst. These molecules can then be washed away with water, which can be later absorbed by microbes and plants, or neutralized by weak aqueous alkaline solutions and discharged into the environment. Photocatalysts can be liquid or solid. Liquid photocatalysts are organic compounds, while solid photocatalysts are largely TiO}_2. Titanium dioxide is a powerful oxidizing and reducing agent. It is a very stable compound, harmless to the environment and cheap. Besides the nano-scale Anatase type TiO}_2, there are other types of photocatalysts. These include various types of nano-scale inorganic semi-conducting compounds that were recently discovered, such as ZnO, SrTiO}_3, Fe}_2O}_3, SnO}_2 and CdS. In fact, many photocatalyst products, besides containing TiO}_2 photocatalyst, may also contain other photo-activated inorganic and nonphoto-activated inorganic compounds, and other components to improve product properties. The purpose for using multiple property-changing techniques of photocatalysts is to inhibit the re-combination process. Basically, only when the forbidden energy gap expands, which can then increase the pairing efficiency of negative electron and electron – hole pairs, can the oxidation/reduction rate and the photocatalytic activity of photocatalysts increase. The \( r \) kinetics of the Langmuir Hinshelwood model [1] is as below:

\[
\ln \frac{C_0}{c} + K(c_o - c) = K_r t \tag{1}
\]

Where, \( K_r \) is the reaction constant, \( K \) is the absorption constant, \( C_0 \) is the initial reaction concentration, and \( c \) is the testing concentration. Substituting the experimental results into the above equation and plotting the reaction rate vs. concentration can we obtain the reaction rate constant. The equation can be simplified as:

\[
\ln \frac{C_0}{c} = K_o t \tag{2}
\]

Where "\( K_o \)" is the reaction rate constant.

For systems of CdS/ TiO}_2 [2], TiO}_2/CdSe [3], ZnO/ TiO}_2 [4], TiO}_2/SnO}_2 [5], TiO}_2/PbS [6] and TiO}_2WO}_3 [6], it can be shown that composite compound semiconductors have higher catalytic activity than single semiconductors. Of course, if the photocatalyst product is a mixture, the activity of a photocatalyst cannot be ascertained by only determining particle diameter and surface area. At present, photocatalytic activity can be evaluated by the following methods: 1. Determining the color fading behavior of red and blue organic pigments; 2. Determining the photodecomposition of organics and the degradation behavior of inorganics; 3. Performing germ resistance tests; 4. Testing for the amount of UV absorption; 5. Testing for deodoring ability; and 6. Performing an anti-stain test.

There are many ways to determine the concentration of gaseous compounds in the air. The test method can be selected depending on the properties of the compound. At present, many detection techniques require large and expensive apparatus, such as: GC/ MS (Gas Chromatography/Mass
Spectrometer), FTIR (Fourier Transform Infrared Spectroscopy), Raman spectra instruments, chemoluminescence instruments, tunable diode laser absorption spectroscopy/NIR TDLAS/NIR techniques. The principles of each type of instrument are also different. Usually, the commercial products can be briefly classified as: electrochemical, optical, resisting and potentiometric. In the past, reaction processes using photocatalysts for gaseous catalysis reactions was usually measured by GC/MS and FTIR. GC/MS is the most common method used commercially. Mass Spectrometers use potentiometric gas detection and can be used for both organic and inorganic structural determination and quantitative analysis. The integrated technique of GC/MS is rather mature, has and with excellent GC analysis capability, can separate trace amounts of individual compounds from a complex gas sample, but without destroying them. Chemical types and structures of the individual identified compounds can be obtained by comparison of the chromatography retention times with a mass spectrograph. Low-volatile or thermally unstable compounds must first use a different method to convert them into vapor and thermally stable compounds before analysis by GC/MS can be done. However, the cost of the above equipment is high and testing process is very complicated. The FTIR method uses an optical gas analyzer. The principle of operation of optical gas analyzers is the measurement of the absorption of light at specific wavelengths by the gas, i.e. comparing the absorbance intensity of light entering the sample cell and a reference cell to measure the gaseous concentration for quantitative analysis. Optical gas analyzers can also use the reflectance of different gases for detection. The greatest advantage of an optical gas analyzer is its better selectivity. The drawbacks of the high precision instrument are high costs, complicated designs, and large size.

The main instrument used for this study is a VU/VIS spectrophotometer quipped with a quartz cuvette. The experimental procedures are simple and fast. Our results of ammonia measurement is in agreement with those of Thompson [8] et al, which prove that our simple and convenient methods are new techniques for sample pre-treatment and the measurement of TiO$_2$ photocatalyst photo-degradation efficiency.

2. Experimental methods

For detection, a fixed-gas analysis device equipped UV/VIS spectrophotometer (brand-Thermo) with a wavelength range of 190~1100 nm was used. Quartz cuvettes (Hellma), volume 3 mL; UV lux gauge: (UVP MS-100), measuring range: 0.00 to 19.99 mW/cm$^2$; Ammonia sensor (BG), measuring range: 0~100 ppm; UV light tube for irradiation of quartz cuvette was a Japanese-made 254 nm tube, luminance 0.30mW/cm$^2$; Sample treatment technique: 0.001 mL samples of various concentrations of liquid ammonia, were injected into separate quartz colorimetric troughs, then heated to 100$^\circ$C to vaporize the ammonia. Then each quartz colorimetric trough was transferred to the spectrophotometer for UV exposure. The concentration of ammonia was determined (in the range of 1~40 ppm) with electrochemical theory. At the same time, the spectrophotometer was heated to 70$^\circ$C in a thermostat tank to avoid condensation of ammonia in the quartz cuvettes. After the measurement, the absorption spectra diagram of ammonia at various concentrations was obtained. These results were then compared with reference data to evaluate the feasibility of this analytic method. The first photocatalyst used in this experiment was a nanofluid TiO$_2$, which was prepared by us with the Submerged Arc Nano particle Synthesis System, SANS. The second nanofluid TiO$_2$ was prepared by diluting a commercial Ti-1125A photocatalyst powder. Quartz glass substrates were coated with the two types of nanofluid TiO$_2$, and then baked three times at 60$^\circ$C. This process was repeated three times in order to fix the TiO$_2$ onto the quartz glass substrates. Then the different photocatalyst-coated quartz glass substrates were inserted into separate quartz cuvettes. Each quartz cuvette was then transferred to the UV/VIS spectrophotometer to investigate the influence of various operational parameters on the efficacy of ammonia decomposition by photocatalyst under UVA for 60 min. The parameters were feed concentration and contact time. The reaction condition of ammonia degradation is shown in Table1. The experiment device is shown in Figure 1.

The test results of this measurement analysis method contains, measurement calibration curve, substrate effect, the efficiency of ammonia degradation by the photocatalysts, concentration limits,
sample storage stability, etc. A statistic analysis of the experimental data of the various measurements is presented by mean value ± standard deviation.

### Table 1. The reaction condition of the ammonia degradation tests.

| Test conditions       | Values                                      |
|-----------------------|---------------------------------------------|
| Feed conc.            | 1, 5, 10, 20, 30, 40 ppm                    |
| Volume of gas tested  | 0.001mL                                     |
| Property of UVA       | Wave length 254nm, luminance 0.30mW/cm²    |
| Test substrates       | TiO₂ coated on quartz glass                 |
| Operation time        | 60min                                       |

**Figure 1.** Diagram of the Experiment device.

### 3. Results and Discussion

3.1. The establishment of an analytic method for ammonia detection

3.1.1. *The influence of the type of substrate gas.* Figures 2–4 are the respective plots for nitrogen, oxygen and argon passing through a quartz colorimetric trough filled with 1 mL de-ionized water at a flow rate of 60 mL/min under the same conditions to yield the absorbance value of each gas in water. The comparison analysis of the substrate effect was done by covariance analysis. The absorption spectra of nitrogen resulted in different absorption values in multi-time tests, and show that N₂ and H₂O combine to form different molecular structures because the molar absorptivity (or extinction coefficient) of any absorption peak of a compound in an absorption spectra has a specific value based on its molecular structure. Thus, if nitrogen is used as pipeline cleansing and mixing gas, it may form another kind of molecule with moisture in the experimental circuit pipes and cause experiment deviation. The absorption spectra of oxygen in many tests showed very stable absorption values thus can be used as an experimental gas. The disadvantage is that oxygen is not an inert gas and can easily combine with other molecules in the air and cause complicated ions for quantitative gas analysis. The absorption spectra of argon resembles that of de-ionized water and is an inert gas, which does not react with other molecules in the air. Thus, argon is an ideal gas for pipeline cleansing and mixing. Therefore, we used argon as the substrate for pipeline cleansing, vaporization of the liquid ammonia, and dilution of the ammonia vapor.
3.1.2. The influence of ammonia generation technique. To insure the quality of the feed ammonia in the second stage of the experiment, the TiO₂ nanocatalyst degradation efficiency of NH₃, the sample pre-treatment employed three (3) techniques to generate NH₃. (1) Different concentrations of NH₄OH were prepared and argon was bubbled through the NH₄OH solution to generate NH₃; (2) Concentrated NH₃ was mixed with argon to generate different concentrations of NH₃; (3) 0.001 ml of various concentrations of NH₄OH were prepared and injected into separate quartz cuvettes, then heated to 100°C to vaporize the NH₃. Each cuvette was then mounted on the experimental apparatus to determine the concentration of the feed gas. As this was a quantitative instead of a continuous feeding experiment, the feeding method used for the NH₃ calibration curves and TiO₂ nanocatalyst degradation efficiency of NH₃ determination was method (3). Figure 5 shows the experiment data obtained by using feeding method (1). To generate 100 ppm of a specific concentration NH₄OH with argon and vaporize it to various concentrations of NH₃. However, this method was not suitable for this experiment, because when the feed is delivered into the quartz cuvette, the amount of NH₃ need to be controlled by a flowmeter. Figure 6 shows the experiment data using method (2). It was found that when pure ammonia mixed with argon passing through the quartz colorimetric trough at 60 mL/min, the overlap of absorption spectra will affect the quantitative analysis of compounds. This was probably due to the ε value of the molecular structure peak. Thus, this method was also unsuitable because of the interference. Figure 7 shows the results of method (3). The concentration of the generated ammonia can be quantified as the gas sample was tested in situ. That is why it is more suitable for feeding. The absorption wavelengths absorbed for all three methods ranged from 190 to 220 nm. The wavelength range is very close to the Thompson report, (absorption range from 1850 to 2200 Å). Thus, this proves this method is correct and feasible.

From Figure 7 we can see that the absorbance changes with concentration. This is because the intensity of the peak can be quantitatively expressed. The intensity of a waveband is related to the specific molecular structure and the molecular number absorbed in light ray-length. Absorbance is a logarithmic value of the ratio of intensity of light entering the sample and the intensity of light leaving the sample, as shown in Equation (3):

\[ A = εcl \]  \hspace{1cm} (Beer’s law)

Where ε is the molar absorptivity, c is the solution concentration (mol/l), and l is the light ray-length (cm) of the sample passed. Under the same light ray-length and molar absorptivity, when feed concentration (c) increases, the absorbance (A) increases, too. Therefore, the absorbance of ammonia increases with concentration, this is in agreement with Beer’s Law.
3.2. Establishment of measuring method

3.2.1. Preparation of calibration curve. After the completion of the investigation of the efficiency factors for ammonia extraction, an ammonia calibration curve was established with optimal ammonia pre-treatment conditions. First, the pH value of a liquid ammonia mixture was adjusted to approximately pH7; then this liquid was used to prepare samples of NH₃ of various concentrations. The 0.001 mL of each sample solution was injected into the quartz colorimetric trough, then heated to 100°C to vaporize the ammonia. The concentration of ammonia gas was in the range of 1~40 ppm. Due to the narrow linear range of the quartz cuvettes and the low ammonia gas concentration used for TiO₂ photodecomposition, the samples were analyzed by quartz cuvette and UV/VIS spectrophotometer. The calibration curve was obtained by using the mean value of the peak area, at concentrations of 1, 5, 10, 20, 30 and 40 ppm. As shown in Figure 8, samples of each concentration were analyzed five times in order to evaluate the accuracy of the measurements. The mean value of the peak area ratio represents the intensities of the five analyses and the intensity of inner standard peak area. From Figure 7, we can see that the accuracy of the calibration curve. Below 20 ppm, the deviation is 13%. Although this deviation is large, it is still in the tolerable range (15%). However, above 30ppm, it is less than 1%. A theoretical value can be obtained using the calibration curve with a regression equation; this equation can be used as the reference for ammonia concentration conversion for later experiments. The formula is as shown below:

\[ Y = 2.365 - 2.202 \times X + 0.370 \times X^2 - 0.008 \times X^3 \]  

(4)

Where Y is the concentration, X is the integration value of ammonia absorption spectra at 190~218 nm.

![Figure 5. The absorption spectra of liquid ammonia vaporization with argon stream.](image)

![Figure 6. The absorption spectra of pure ammonia in argon.](image)

![Figure 7. The absorption spectra of NH₃ vaporization by heating.](image)

![Figure 8. Calibration curves of NH₃.](image)
3.2.2. Detection limit. This measuring method measured six blank gas samples consecutively with internal standard to get the detection limit. The detection limit was calculated as follows: first calculate the mean ratio value of ammonia and internal standard peak area, after adding three times the standard deviation, then divide by the slope of low concentration calibration curves which were produced at the same day. The detection limit calculated this way was 0.63 ppm. Therefore, the lowest standard concentration of this measurement was 1.89 ppm (the limit of the three-fold method). The highest testing sample concentration was 32 ppm (80% of the highest concentration of standards).

3.3. The influence of NH₃ degradation by TiO₂ nanocatalyst

3.3.1. The influence of feed concentration. Figures 9 to 14 show the influence of changing feed concentration to light absorption under the same conditions of illumination intensity, amount of catalyst and feed volume. It can be seen that in order to reach stable light absorption conditions, the contact time must increase with the increase of feed concentration. This phenomenon is more obvious when the concentration is higher. The reason for light absorption to show transient fluctuation is the influence of the change of ammonia concentration during the photocatalytic degradation reaction. Because this method employs fixed injection quantity, based on reaction kinetics, the photocatalytic degradation reaction is mass transfer control. Due to the thickness of the boundary and that the reaction rate cannot be changed by the flow rate of the feed, it is possible that under these operational conditions, the reaction rate is determined by reactant transfer control instead of rate control. Thus, the reaction is diffusion controlled. Based on the change in light absorption, it can be concluded that the photocatalyst reaction is proceeding in the direction of degradation.

Due to the need for semiconductor-mediated photocatalytic reactions of proper light illumination, the absorption must be equal to or greater than the energy gap in order for the valence electrons to gain enough energy and activate it to leap to a conduction band and leave holes in the valence band, which forms separate electron-hole (e⁻-h⁺) pairs. These are the initial steps of the process of heterogeneous catalysis of ordinary semiconductors, which then further induces oxidation or reduction. So for the reaction to proceed, there must be enough energy and correct orientation for at least one collision in order for bond cleavage. The energy needed for this process (activation energy) is the energy barrier of their reaction; the higher the energy barrier and the number of barriers the slower the reaction. Of course, the barrier changes with the concentration. Therefore, with the increase of ammonia concentration, the energy barrier will increase, too. This is probably because at high concentration, ammonia saturates the active sites of the catalyst surface, and is strongly adsorbed onto it, and at the same time reduces the number of active sites on the surface of the catalyst, thus the photocatalytic degradation time increases with the increase of concentration.

3.3.2. The influence of the special properties of the photocatalytic nano materials. In the experiment to analyze the properties of photocatalytic nano materials, changing the catalyst medium, comparing the influence of various catalysts on conversion rate, using various feed concentrations and contact time were used to observe their reaction relationship. From Figures 10, 13 and 11, 14, it can be seen that under the same feed concentration, the ability of Ti-1125A in the degradation of NH₃ is obviously lower than the SANSS. Ti-1125A has no degradation efficiency at 30 ppm. This is due to the influence of the TiO₂ structure on degradation efficiency. It is obvious that the self-made SANSS-TiO₂ was a successful high-activity TiO₂ nanocatalyst preparation. Many references have mentioned that the photocatalyst reaction obeys the Langmu-Hinshelwood model as Figures 15 and 16 show. Substituting the results in Figure 15 (10 ppm degradations of NH₃) into Equation (2), gives the $k_a$ values of ammonia degradation by SANSS-TiO₂ and Ti-1125A as 0.039 and 0.027 min⁻¹, respectively. When the ammonia concentration is 20 ppm (in Figure 16), the $k_a$ values of SANSS-TiO₂ and Ti-1125A are 0.029 and 0.018 min⁻¹, respectively. When the concentration is 30 ppm (Figure 17) the $k_a$ value of SANSS-TiO₂ is 0.057 min⁻¹, and of Ti-1125A, 0.0104 min⁻¹. Thus, when it is required to compare the ammonia degrading efficiency of two different types of TiO₂ photocatalysts, it can be done by
comparing their $k_a$ values. The higher the $k_a$ value, the lower the activation energy required, which would provide a good condition for the semiconductor photocatalyst process, and thus, a faster reaction. After UV exposure for 60 minutes, the self-made SANSS-TiO$_2$ photocatalyst can reduce the ammonia to 10.35% of the original concentration, while for the commercial nano TiO$_2$, the reduction was only to 50.2% of the original concentration. From the $k_a$ values, it can be seen that the self-made SANSS-TiO$_2$ is better than the commercial product for ammonia degradation.

**4. Conclusion**

This study is aimed at low-concentration NH$_3$ in indoor air; to test nanocatalyst degradation efficiency. The measurement was performed by injecting samples with specific concentrations (in the...
concentration range of the calibration curve) into an enclosed quartz cuvette containing the photocatalyst material, then transferring the cuvette to a UV/MIS spectrophotometer for UV irradiation and quantitative testing. The experimental results show that the self-made TiO₂ nanocatalyst is excellent in the degradation of NH₃. When NH₃ receives UV irradiation for 60 minutes, the gaseous concentration can be reduced to 10.35% of the original concentration. But the commercial TiO₂ nanocatalyst can only reduce the concentration to 50.2% of the original. In addition, the degradation reaction rate constant of the self-made TiO₂ nanocatalyst towards NH₃ can reach as high as 0.029 min⁻¹.

The newly-developed method can provide a simple, fast, and reliable technique for testing the photocatalyst degradation efficiency towards NH₃. This is different from prior methods by using GC/MS or FTIR. This new method does not need many testing instruments and complicated operational procedures, and can not only lower costs, but also decrease the danger to personnel of exposure and increase the safety of personnel under hazardous conditions. Tests of animal wastes show that this method can be used in efficiency tests of photocatalyst in the degradation of low concentration ammonia.

References
[1] Kohl A.L. and Nielsen R.B. 1997 Gas Purification 5th Ed. gulf (Houston TX)
[2] Vogel R, Hoyer P, Weller H and J. Phys. Chem 1994 98 3183–88.
[3] Liu D, Kamat P V and J. Electroanal. Chem 1993 Interfacial Electrochem 347 451–456
[4] Sukharev V, Kershaw R, J. Photochem 1996 Photobiol. A: Chem 98 165–169.
[5] Bedja I, Kamat P V and J. Phys. Chem 1995 99 9182–88.
[6] Do Y R, Lee W and Dwight K et al 1994 J. Solid State Chem 108 198–201.
[7] Thompson B.A., Harteeck P., Reeves and R.R. J. Geophys Res. 68 6431–36
[8] H, Hart. L, E. Craine. D and J. Hart 2003 Organic Chemistry 11th (U.S.A) Ed. Houghton Mufflin pp91–93 p395