



Removal of Ammonia Gas *via* Conducting Polymer-Assisted Titania Under Visible-Light or UV Exposure†

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Conducting polyaniline (PANI)-assisted titania (PANI-TiO₂) composite was synthesized using a facile hydrothermal-chemisorption method. Its surface characteristics were determined using UV-visible, scanning electron microscopy and Fourier transform infrared techniques. In addition, its application for photocatalytic removal of airborne ammonia under visible- or UV-light exposure was evaluated. Scanning electron microscopy images confirmed that both the PANI-TiO₂ composite and unmodified TiO₂ were composed of polydispersed microsphere-shaped particulates, while P25 TiO₂ displayed much smaller particle shapes. Fourier transform infrared results for the PANI-TiO₂ composite indicated that polyaniline could be embedded into TiO₂. The PANI-TiO₂ composite and two reference photocatalysts (unmodified TiO₂ and P25 TiO₂) had a similar variation in the adsorption efficiencies of ammonia over time. However, the photocatalytic removal efficiencies for ammonia obtained using the PANI-TiO₂ composite under visible-light exposure were higher than the results obtained from the two reference photocatalysts. The photocatalytic removal efficiencies for ammonia with all three photocatalysts were about 100 % under UV exposure conditions, which did not allow for a comparison of the photocatalytic removal efficiencies of the three photocatalysts. The average photocatalytic removal efficiency over the PANI-TiO₂ composite decreased from 83 to 39 %, as the reaction time increased from 2.5 to 15.2 s. Overall, PANI-TiO₂ composites can be utilized to remove ammonia gas under visible-light as well as UV irradiation.

Keywords: Conducting polyaniline, Composite, Reaction time, Ammonia, Removal.

INTRODUCTION

Since pork is one of the most popular meats in the world, the worldwide pork consumption accounts for about 40 % of the total meat consumption¹. The advances in swine production in modern livestock agriculture is highly anticipated. As such, large-scale swine production facilities have emerged over the last several years, resulting in a rapid increase in the swine population in geographically concentrated areas. For instance, the number of pigs in the European Union approached 149 million in 2011 and worldwide pork production was predicted to approach 104 million metric tons in 2012¹. However, swine agriculture produces swine wastes, which can cause a variety of environmental problems². The dramatic growth and consolidation of swine agriculture have led to increased public concerns about environmental impacts such as bad odor and adverse health effects. Specifically, ammonia, a by-product of microbial degradation of organic substrates in manure and

released from wastewater into the atmosphere³, is a concern. Nitrogen loss *via* NH₃ emission from U.S. swine agriculture was calculated⁴ to be 56 %. Moreover, atmospheric ammonia can react to produce ammonium particulates, *e.g.*, ammonium sulfate and ammonium nitrate, which can be transported downwind from the ammonia emission source⁵. The ammonium particulates are associated with human health hazards and upsetting plant nutrient balances^{5,6}. In addition, atmospheric ammonia emitted from swine sheds can result in public odor complaints⁷. Accordingly, the development of ammonia emission control strategies in swine sheds is required to lessen the environmental impact.

Current practices for removal of airborne ammonia from swine sheds are predominantly based on adsorption and activated carbon beds are mainly used because of their large pore volume and high specific surface area⁸. However, the applications of the activated carbon bed is limited in that the chemical species are not removed but simply accumulated on

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a solid phase and the used activated carbon is considered a hazardous waste⁹. Alternatively, a heterogeneous photocatalytic technique using titania (TiO₂) can oxidize most organic species to non-hazardous carbon dioxide and water vapor¹⁰. Nevertheless, TiO₂ can only function under UV irradiation conditions only because of its broad band gap^{10,11} and this is a critical disadvantage. Another disadvantage associated with the use of TiO₂ is the high recombination rate of the photon-induced charge carriers, which lowers the photocatalytic activity¹². A significant number of chemical modification methods, including metal ion doping, nonmetal doping and conducting material supports, have been applied in an attempt to improve the light absorption efficiency and photocatalytic performance of TiO₂ under visible light¹³⁻¹⁷. In particular, conductive polymer materials have been proposed as promising supports that could extend the light absorbance of TiO₂ to the visible range¹⁵⁻¹⁷.

Polyaniline (PANI) is an excellent conductive polymer that has outstanding conductivity, chemical stability and low cost compared to other polymers, *e.g.*, polythiophene and polypyrrole^{18,19}. Therefore, some researchers^{15,19,20} have combined TiO₂ with polyaniline to improve the photocatalytic functions of the TiO₂ photocatalyst. The coupling of TiO₂ to conductive polyaniline can lower electron-hole recombination and enhance photocatalytic activity and this is likely because of the charge separation of photon-induced carriers at the heterojunction formed between the two substrate¹⁵. Moreover, the aforementioned researchers found that PANI-supported TiO₂ photocatalysts had elevated photocatalytic performances for the degradation of water pollutants, *e.g.*, aqueous phenol and chlorophenol, compared to unmodified TiO₂. However, the application of PANI-supported TiO₂ to the degradation of air pollutants is rarely found in scientific literature. It is known that the light absorbance and photocatalytic degradation mechanisms of chemical molecules differ between water-solid and air-solid boundaries²¹, implying that the photocatalytic activity obtained at the water-solid base may not be the same as that at the air-solid base. Accordingly, this study was conducted to examine the feasibility of a PANI-supported TiO₂ (PANI-TiO₂) composite for the degradation of airborne ammonia under visible-light or UV exposure. In addition, the photocatalytic activities of two reference photocatalysts (undoped and P25 TiO₂ nanoparticles) were investigated and compared with those of the PANI-TiO₂ composite.

EXPERIMENTAL

Photocatalysis of airborne ammonia: The photocatalytic degradations of airborne ammonia activities over the PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂ were investigated using a cylindrical plug-flow type reactor with an inside wall coated with a thin film of PANI-TiO₂ composite, unmodified TiO₂, or P25 TiO₂. For the coating process, the photocatalyst powder was ground and then mixed with an ethylenediaminetetraacetic acid solution (0.1 M). Distilled water and Triton X-100 were added to this solution and the sol-type product was coated on the inside surface of the Pyrex tube. The coated tube was then dried in an oven at 110 °C for 1 h and heated in a furnace at 450 °C for 1 h. A cylindrical fluorescent black light lamp (F8T5BLB, Youngwha Lamp Co.) or fluorescent

day light lamp (F8T5DL, Youngwha Lamp Co.) was placed inside the Pyrex tube and served as the inner surface boundary layer in the Pyrex tube. A clean dried air stream, supplied from a compressed air cylinder, was additionally purified by flowing it through a carbon purifier. A standard gas stream (10 ppm ammonia) was synthesized by mixing ammonia in a mixing glass device *via* an auto-programmed syringe pump (Model Legato 100, KdScientific Inc.) with air supplied at a specified flow rate. The generated standard gas was flown into a buffering chamber to stabilize the input airstream and transferred into the Pyrex tube. The air stream flow rate (AFR) was determined using mass flow controllers (Defender 510, Bios International Co.).

The removal efficiency of airborne ammonia over the PANI-TiO₂ composite was investigated under different experimental conditions by varying the reaction time and light source type. The reaction time was adjusted to 15.2, 7.6, 3.8, or 2.5 s by varying the air stream flow rate to 0.5, 1, 2, or 3 L min⁻¹, respectively. To test one parameter, the other parameter was fixed to a representative value: reaction time at 7.6 s and light source a fluorescent day light lamp. In addition, the hydraulic diameter of the Pyrex reactor, which is denoted as the inside diameter of the Pyrex reactor minus the outside diameter of the lamp, was 1 cm. The light intensity supplied by the fluorescent black light lamp and fluorescent day light lamp were 0.4 and 2.3 mW cm⁻², respectively, at the distance from the lamp to the inside wall of the Pyrex reactor. Gaseous chemical species in the effluent air were measured at the inlet and outlet ports of the photocatalytic reactor. Gas sampling was carried out by filling an empty Teflon bag and then, drawing gas from this bag through an ammonia gas detection tube using a gas sampling pump.

Synthesis of photocatalysts: The PANI-TiO₂ composite was synthesized using a hydrothermal process, followed by a chemisorption method. For this process, 2 mL titanium(IV) chloride (98 %, Aldrich Inc.) was mixed with 23 mL distilled water in a flask immersed in an ice-water bath and this solution was mixed with 2.5 g of ammonium sulfate (99.5 %, Aldrich Inc.) and 20 g of urea (100 %, Aldrich Inc.). Subsequently, this solution was stirred for 2 h and 25 mL of ethanol (99.9 %, Aldrich Inc.) was added. The transparent solution was transferred to a 120 mL Teflon-lined stainless steel autoclave and heated at 90 °C for 18 h and cooled down over 24 h. This treated product was then filtered to give precipitate and this precipitate was cleaned with ethanol and distilled water. Finally, the filtered precipitate was heat-treated at 450 °C for 2 h to obtain the TiO₂ powder.

The prepared TiO₂ powder (2.5 g) was mixed with 13 mg of polyaniline and 110 mL of tetrahydrofuran (99.9 %, Aldrich Inc.) to synthesize the PANI-TiO₂ composite. This solution was sonicated for 40 min, stirred for 20 h and then filtered to give the precipitate. This precipitate was cleaned with ethanol and distilled water and then dried at 90 °C for 10 h to obtain the final PANI-TiO₂ composite.

The surface natures of the prepared PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂ were examined by UV-visible, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) techniques. Visible and UV light absorption

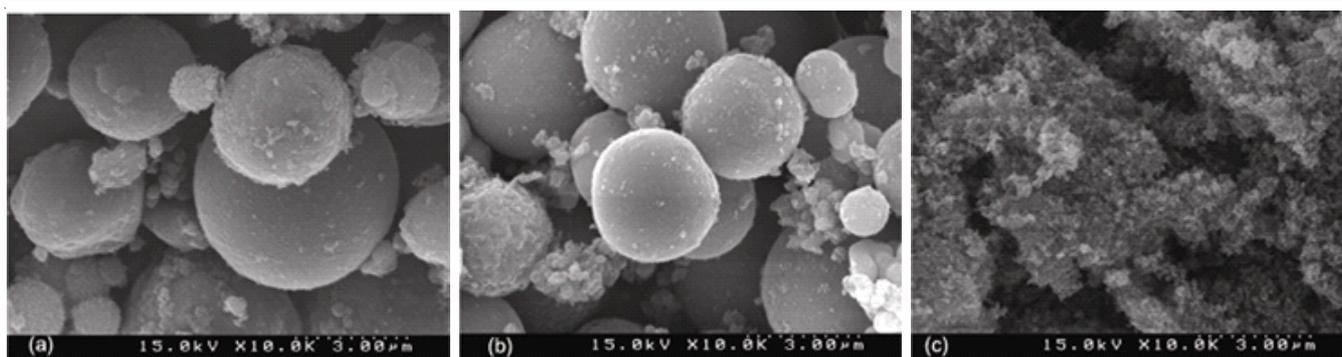


Fig. 1. Scanning electron microscopy of PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂

characteristics were investigated using a ultraviolet-visible-near infrared Varian CARY 5G spectrophotometer. The particle morphology was determined using an FE-SEM S-4300 (Hitachi Co.). Structural information was obtained from an FTIR spectrophotometer (Spectrum GX, Perkin Elmer Inc.) in the spectral range of 4000-400 cm⁻¹.

RESULTS AND DISCUSSION

Characteristics of PANI-TiO₂ composite: The surface properties of the PANI-TiO₂ composite and two reference photocatalysts (unmodified TiO₂ and P25 TiO₂) were obtained from spectral analyses. The SEM images (Fig. 1) indicated that both the PANI-TiO₂ composite and unmodified TiO₂ were composed of polydispersed microsphere-shaped particulates, while the P25 TiO₂ displayed significantly smaller particle shapes. These results are consistent with those observed by other researchers^{20,22}. However, the particle sizes of the PANI-TiO₂ composite were larger than those of the unmodified TiO₂ and this was ascribed to the interaction between polyaniline and the TiO₂ photocatalysts. Overall, the SEM results demonstrated that the PANI-TiO₂ composite can be synthesized *via* the combined method of hydrothermal and chemisorption processes utilized in the current study.

Fig. 2 shows the UV-visible absorption images of the PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂. The unmodified TiO₂ and P25 TiO₂ photocatalysts showed absorption wavelength edges about 420 and 410 nm, respectively. However, the light absorption region for the PANI-TiO₂ composite extended well into the visible range and this was attributed to the hetero-junction formed between polyaniline¹⁵ and TiO₂. These results were similar to those reported by Li *et al.*¹⁹.

Fourier transform infrared for the PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂ are shown in Fig. 3. The FTIR spectra of the PANI-TiO₂ composite were similar to each other, although the transmittance intensity differed to some extent. For the PANI-TiO₂ composite, the major absorption peak appearing at 3376 cm⁻¹ was ascribed to N-H stretching¹⁹. In addition, the band at 1299 cm⁻¹ was attributed to C-N stretching of polyaniline¹⁵. The low frequency bands around 733 cm⁻¹ for all three photocatalysts (PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂) were likely due to the Ti-O-Ti vibration of anatase²³. Therefore, the FTIR spectra for the PANI-TiO₂ composite indicate that polyaniline could be embedded into TiO₂.

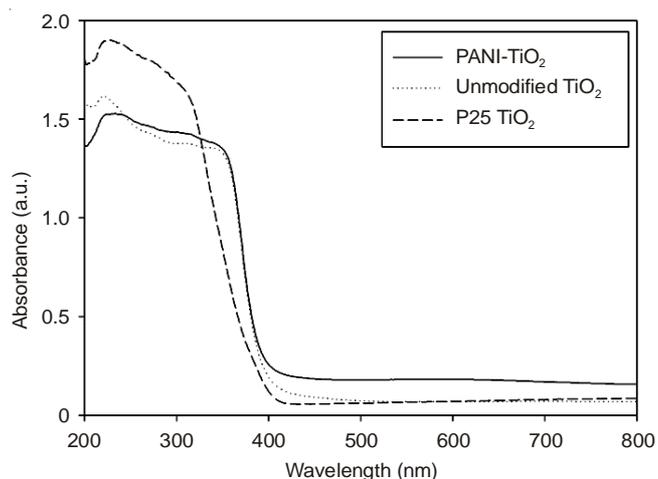


Fig. 2. UV-visible absorption spectra of PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂

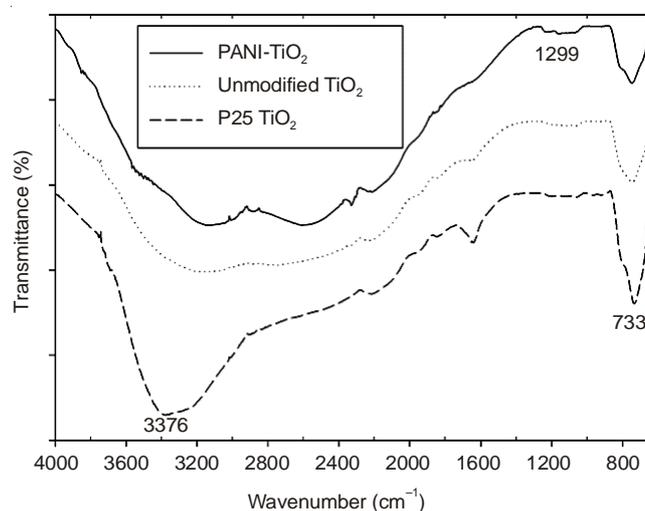


Fig. 3. Fourier transform infrared spectra of PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂

Photocatalytic removal efficiency for airborne ammonia:

Adsorption and photocatalytic removal efficiencies for airborne ammonia over the PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂ under visible-light or UV exposure were determined. As shown in Fig. 4, the three photocatalysts displayed similar variations in the adsorption efficiencies of ammonia over time. Specifically, the adsorption efficiencies for ammonia decreased over time. The adsorption efficiencies

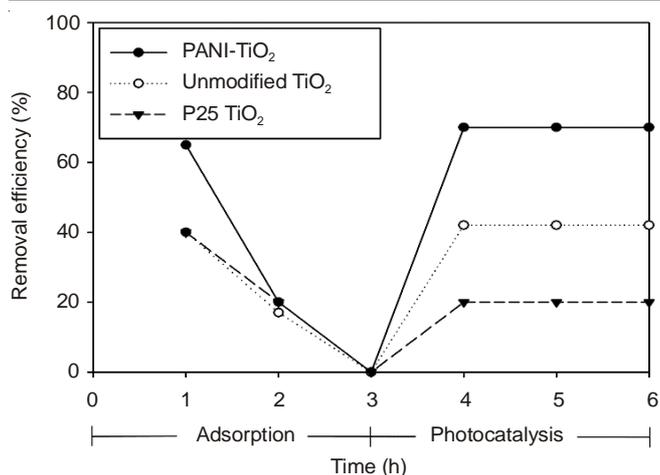


Fig. 4. Removal efficiencies (REs) of ammonia over PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂ under visible-light exposure

were 62 and ~0% 1 and 3 h, respectively, since the start of the adsorption processes. However, the photocatalytic removal efficiencies for ammonia obtained using the PANI-TiO₂ composite under visible-light exposure were higher than the results obtained for the two reference photocatalysts. For instance, the time-series average removal efficiency for the PANI-TiO₂ composite was 73%, while the values for the unmodified TiO₂ and P25 TiO₂ were 42 and 19%, respectively. The higher removal efficiency of the PANI-TiO₂ composite under visible-light exposure is likely because of the synergistic interaction of conductive polyaniline with TiO₂, which results in reduced electron-hole recombination and extends the light absorption to the visible region. Therefore, it is suggested that PANI-TiO₂ composites can be utilized efficiently to remove airborne ammonia. Moreover, the removal efficiency did not decrease trend over the specified photocatalytic period, suggesting that the PANI-TiO₂ composite was not deactivated over the study period. In contrast, previous researchers^{15,22} observed the deactivation of PANI-TiO₂ composites synthesized at certain PANI-to-TiO₂ ratios when the composites were applied to the photocatalytic degradation of airborne aromatic hydrocarbons or aqueous rhodamine B under visible-light. Specifically, Jo and Kang²² reported that the PANI-TiO₂ composite prepared with a PANI-to-TiO₂ ratio of five displayed a gradual decrease in catalytic activity during a 3 h photocatalytic degradation of aromatic hydrocarbons and this was ascribed to deactivation of the TiO₂. When considered together, these results indicate that the PANI-TiO₂ composite prepared in the present study was synthesized with a proper PANI-to-TiO₂ ratio. In addition, the photocatalytic removal efficiencies for ammonia over all three photocatalysts (PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂) were about 100% under UV exposure conditions (Fig. 5), making it impossible to compare the photocatalytic removal efficiencies of the three photocatalysts.

Fig. 6 shows the photocatalytic removal efficiency of ammonia over the PANI-TiO₂ composite under visible-light irradiation according to reaction time. The photocatalytic removal efficiency of ammonia over the PANI-TiO₂ composite increased as the reaction time increased. For instance, the average photocatalytic removal efficiency over the PANI-TiO₂ composite decreased from 83 to 39%, as the reaction time increased

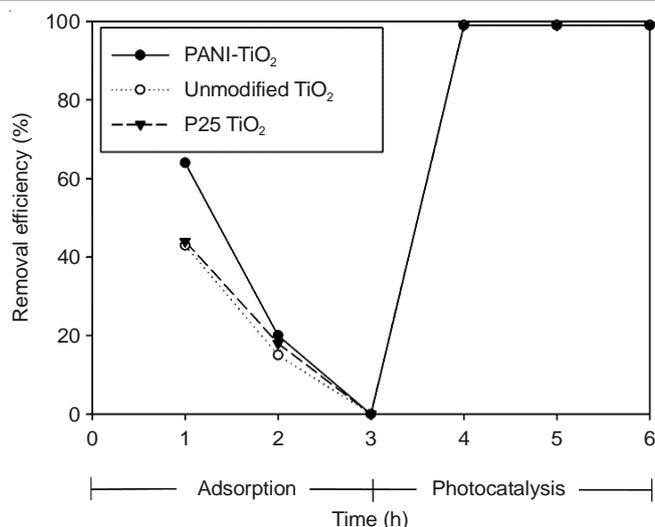


Fig. 5. Removal efficiencies (REs) of ammonia over PANI-TiO₂ composite, unmodified TiO₂ and P25 TiO₂ under UV exposure

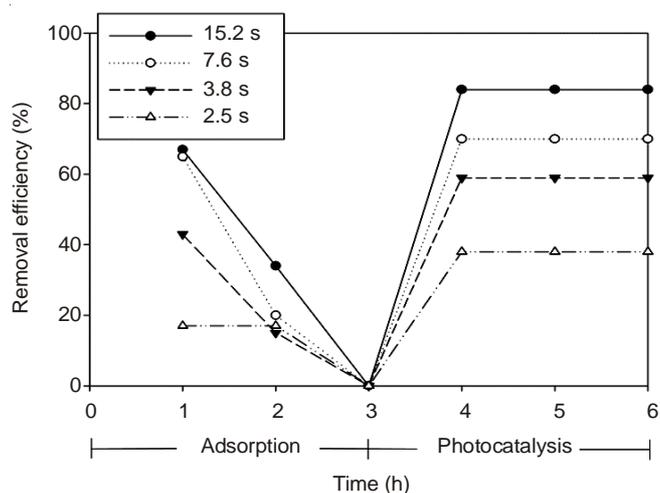


Fig. 6. Removal efficiencies (REs) of ammonia over PANI-TiO₂ composite under visible-light exposure according to reaction time

from 2.5 to 15.2 s. Similarly, Yu and Brouwers²⁴ observed that the photocatalytic removal efficiency of gas-phase nitrogen oxide over the P25 TiO₂ powder under UV-light exposure increased as the reaction time increased. The photocatalytic removal efficiency of gas-phase chemical species can, however, increase as the reaction time decreases (air flow rate increases) because of increased mass transfer at high air flow conditions^{25,26}. Therefore, the low photocatalytic removal efficiency of ammonia at short reaction times indicates that the effects of a short residence time in the reactor may outweigh the mass transport effects on the photocatalytic removal efficiency of ammonia.

Conclusion

In this study, the feasibility of using PANI-TiO₂ composite for the degradation of airborne ammonia under visible-light or UV exposure was examined. Spectral investigations on the surface and morphological characteristics of the PANI-TiO₂ composite suggested that conductive polymer and semi-conducting TiO₂ could be successfully combined to form the PANI-TiO₂ composite and this composite could be functioned under visible-light exposure. The removal efficiencies for

ammonia obtained using the PANI-TiO₂ composite under visible light exposure were higher than the results obtained from the two reference photocatalysts. Unfortunately, the photocatalytic removal efficiencies for ammonia with all three photocatalysts were about 100 % under UV exposure conditions, which did not allow for a comparison of the photocatalytic removal efficiencies of the three photocatalysts. The photocatalytic removal efficiency over the PANI-TiO₂ composite decreased as the reaction time decreased. Taken together, these results suggest that PANI-TiO₂ composites can be employed to remove odorous ammonia gas under visible-light and UV irradiation.

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