Liquid-phase non-thermal plasma-prepared N-doped TiO₂ for azo dye degradation with the catalyst separation system by ceramic membranes

Hsu-Hui Cheng, Shiao-Shing Chen, Yi-Wen Cheng, Wei-Lun Tseng and Yi-Hui Wang

ABSTRACT

This study strived to improve the photocatalytic activity by using liquid-phase non-thermal plasma (LPNTP) technology for preparing N-doping TiO₂ as well as to separate/recover the N-dope TiO₂ particles by using ceramic ultrafiltration membrane process. The yellow color N-doped TiO₂ photocatalysts, obtained through the LPNTP process, were characterized with UV–Vis spectroscopy, X-ray diffraction (XRD), and electron spectroscopy for chemical analysis (ESCA). The UV–Vis spectrum of N-doped TiO₂ showed that the absorption band was shifted to 439 nm and the band gap was reduced to 2.82 eV. The structure analysis of XRD spectra showed that the peak positions and the crystal structure remained unchanged as anatase after plasma-treating at 13.5 W for 40 min. The photocatalytic activity of N-doped TiO₂ was evaluated by azo dyes under visible light, and 63% of them was degraded after 16 hours in a continuous-flow photocatalytic system. For membrane separation/recover system, the recovery efficiency reached 99.5% after the ultrafiltration had been carried out for 90 min, and the result indicated that the photocatalyst was able to be separated/recovered completely.

Key words | Azo dyes, ceramic membranes, liquid-phase non-thermal plasma, N-doping TiO₂, visible light

INTRODUCTION

The textile industry contributed 11.8 billion US dollars of Taiwan’s output in 2007, but its dyeing process consumes a huge amount of water. The wastewater from textile dyeing has been known to exhibit strong color, high chemical oxygen demand, and a large amount of suspended solids (Lu et al. 2009). The azo dyes are synthetic compounds characterized by the presence of one or more azo group (-N=N-) bound to aromatic rings (Liu et al. 2005). The release of azo dyes into the environment leads to a great concern due to the coloration of natural waters, their toxicity, mutagenicity, and carcinogenicity. Since the discovery of its photocatalytic activity in the early 1970s, the interest in applying titanium dioxide (TiO₂) for degradation of harmful organic substances in water has been rapidly increased. However, the light absorbed by anatase TiO₂ is only UV light with wavelength shorter than 390 nm, and only a small fraction (~5%) of the solar energy can be utilized in practical applications (Sato et al. 2005; Wang et al. 2006). Therefore, TiO₂ photocatalysts having high efficiency under visible light irradiation are greatly needed for practical and widespread use.

A plenty of researches have been conducted to enhance the visible light sensitization of TiO₂, which has been the most promising photocatalyst for its photocatalytic activity, high stability, low cost, and non-environmental impact (Wang et al. 2006; Hsu et al. 2009). Among the viable doping elements or compounds for TiO₂, the substitutional doping of nitrogen has been recognized to be one of the
most effective means for producing visible light irradiation effect (Chen et al. 2007; Hsu et al. 2007). A number of researches have doped nitrogen into TiO₂ using different preparation methods and N-doped precursors. However, few papers focused on the plasma treatment for preparation of TiO₂, which has numerous advantages such as high purity, good step coverage, and precise control of operating parameters (Maeda & Watanabe 2006). Plasma, a high-energy rapid-heating power source, is produced by the high-voltage discharge processes. Although several investigations on the plasma treatment for preparing N-doped TiO₂ were conducted with thermal plasma such as gas-phase plasma, and thin films methods (Wang et al. 2006; Chen et al. 2007), there are no reports focused on the liquid-phase non-thermal plasma (LPNTP) technique.

In addition, several investigations have attempted to separate TiO₂ particles in wastewater. Because the fine TiO₂ particles could be liberated into the effluent of a suspended TiO₂ system, the thin film was typically used. However, thin film has a disadvantage due to its smaller contact area with contaminant in wastewater (Cui et al. 2006). Consequently, the ceramic UF membrane separation process was utilized for recovering the TiO₂ particles in a suspended system to prevent the liberation of the TiO₂ particles. The advantage of using ceramic UF membrane over the traditional polymeric UF membranes is that the polymeric UF membranes cannot be used to separate TiO₂ particles in acidic wastewater (Zhao et al. 2002). Besides, the ceramic UF membranes have inherently superior physical integrity, chemical resistance, and thermal stability compared to polymeric membranes. Zhao et al. (2002) successfully used 30 µm pore-size tubular ceramic and Al₂O₃ composite MF membranes for the recovery of fine TiO₂ particles in acid wastewater. Cui et al. (2006) also used 0.2 µm pore-size a tubular ceramic MF membranes for the recovery of TiO₂ particles from degradation of methyl orange under UV light irradiation, which the rejection rate of N-doped TiO₂ particles achieved 99%. Although the previous researches focused on the use of ceramic MF membranes for treating wastewater containing micron and submicron particles (Zhao et al. 2002; Cui et al. 2006), there are no reports focused on the photocatalytic of N-doped TiO₂ by photocatalysis combined with ceramic UF membranes (pore diameter 20 nm) to recover catalysts under visible light so far.

Therefore, this study strived to improve the photocatalytic activity by LPNTP-prepared N-doping TiO₂ and to develop a new photocatalytic reactor. The study further attempted to recycle/separate N-dope TiO₂ particles by ceramic membranes. The correlation between the photocatalytic activity of N-doped TiO₂ and their properties, such as band gap energy, crystal phase composition, and the separation/recovery rate for N-doped TiO₂ particles studies was also elucidated.

**MATERIALS AND METHODS**

**LPNTP system**

N-doped TiO₂ was prepared by using the LPNTP system, as shown in Figure 1a. The bipolar pulsed power supply was used to provide pulsed irradiation of 0–30 kV and the pulsed repetition frequency rate of 60 Hz with the high voltage discharge electrode. The pulsed output voltage and current were measured with a high-voltage probe (Tektronix P6015A) and a pulsed current probe (Pearson Electronics M411), respectively. The discharge parameters were also monitored by a digital oscilloscope (Qmax UM2202). The needle-plate electrode was placed in the center of a cylindrical quartz tube (60/55 mm OD/ID) for generating a corona discharge in water. A stainless-steel hollow needle was used as the discharge electrode. The point electrode of hollow needle, ca. 3.2 cm, was installed in the center of cylindrical reactor above the bottom of the vessel. Only the conical tip of the point electrode was in direct contact with the water. Additionally, the stainless-steel round plate with 40 mm in diameter, used as the ground electrode, was installed at the top of reactor opposite to the needle discharge electrode. The distance between the ground plate and needle electrode was adjusted. The reactions temperatures were set from 273 to 323 K, and the air flow rate was controlled to 150 mL/min.

**Preparation of N-doped TiO₂**

The N-doping TiO₂ photocatalysts were prepared by using LPNTP technology. 0.6 g of Degussa P-25 TiO₂, a commercial TiO₂ in nanometre size with anatase and rutile phases,
and NH₄Cl powder with various dosages (0.6, 1.8, and 3.6 g) were mixed with 70 mL distilled water in a glass tube at 300 K for 10 min. The pH value of NH₄Cl solution was adjusted to 5. The suspended mixture of TiO₂ in NH₄Cl solution was transferred to the LPNTP reactor and the discharge was operated at 13.5 W for 40 min. The suspended solution was washed with water 3 times and moved to an oven for the continuous desiccations at 573 K for 3 h. The synthesis conditions are listed in Table 1. After the mixture was cooled down to the room temperature, N-doped TiO₂ was obtained. The band gap of the N-doped TiO₂ was measured by UV–Vis spectrophotometer (Cary 300 Bio) equipped with the integrating sphere accessory for diffuse reflectance spectra. The chemical composition of the N-doped TiO₂ was verified using the electron spectroscopy for chemical analysis (ESCA; VG Scientific ESCALAB 250). Crystal structures were analyzed by X-ray diffraction (XRD, Rigaku DMAX 2200VK). All peaks measured by the XRD analysis were assigned by comparing with those of Joint Committee on Powder Diffraction Standards (JCPDS) data.

### Evaluation of photocatalytic activity with separation of catalyst

In this section, the optimum N-doped TiO₂ condition of particles was selected for photocatalytic activity tested by decolorization of organic compound Acid Orange 7 (C₁₅H₁₁N₂NaO₄S) which is one of the most commonly-used azo dyes. AO7 with purity greater than 99% was obtained from Tokyo Kasei Kogyo (Japan). The initial concentration of AO7 solution 10 mg/L, the natural pH of AO7 solution was 5.0, and N-doped TiO₂ catalysts concentration ranged from 0.1 to 0.5 g/L. The photodegradation experiments were observed in a continuous-flow photocatalytic reactor, and N-doped TiO₂ particles were separated/recycled using ceramic membranes. The main element of the photocatalysis–membrane separation system

### Table 1 | Experimental conditions for preparation of N-doped TiO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO₂ powder (g)</th>
<th>NH₄Cl powder (g)</th>
<th>DI water (mL)</th>
<th>Concentration [TiO₂]/[NH₄Cl] (g/mL)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP-25</td>
<td>0.6</td>
<td>0.0</td>
<td>70</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TiO₂·NH₄Cl = 1:1 (40 min)</td>
<td>0.6</td>
<td>0.6</td>
<td>70</td>
<td>0.6/0.6</td>
<td>1:1</td>
</tr>
<tr>
<td>TiO₂·NH₄Cl = 1:3 (40 min)</td>
<td>0.6</td>
<td>1.8</td>
<td>70</td>
<td>0.6/1.8</td>
<td>1:3</td>
</tr>
<tr>
<td>TiO₂·NH₄Cl = 1:6 (40 min)</td>
<td>0.6</td>
<td>3.2</td>
<td>70</td>
<td>0.6/3.2</td>
<td>1:6</td>
</tr>
</tbody>
</table>
(PMSS) was shown in Figure 1b. The photoreactor was open to atmosphere and the quartz reactor was surrounded by 12 light tubes in total. The visible light tubes were germicidal lamps with wavelength 419 nm (Sankyo Denki Co., Ltd.). The light power, ca. 10 mW/cm², located at the center position of the reactor in the air was measured by a power meter (Model 840-C Handheld). The pretreatment procedure, AO7 solution was stirred in the dark for at least 30 min to ensure the complete equilibration of AO7 adsorption onto the samples. The absorbance of the AO7 after illumination was determined by using a UV–Vis spectrophotometer at the wavelength 484 nm. Finally, the photodegradation of AO7 solutions after treatment was poured into the 3 L feed tank by the ceramic membrane tube to separate catalyst in the suspension system. The ceramic membrane tube was manufactured by Pall Membrane Co., USA, with length of 250 mm, outer diameter 10 mm, and inner diameter of 7 mm. The pore size of the membrane was 10 nm on a zirconia (ZrO₂) porous support, and the membrane total surface area was 0.005 m². The transmembrane pressure (TMP) was 2.8 bar, the temperature was 25°C and the cross-flow velocity was 0.0001 m/s.

RESULTS AND DISCUSSION

Characterization of N-doped TiO₂

Figure 2a shows the UV-visible spectra of the TiO₂ and the N-doped TiO₂ from 200 to 800 nm. Samples A–D indicate typical UV–visible spectra of semiconductor materials with band gap absorption onset at 427, 437, 439 and 388 nm, which correspond to energy band gaps 2.90, 2.84, 2.82 and 3.20 eV, respectively. The UV-visible observation indicates that the red shift of optical energy gaps is resulted from increase of nitrogen doping into TiO₂. The red shift in optical energy band gap by N-doping occurs due to the following factors: (1) the energy level of N 2p state lies below the conduction band and valence band edge of TiO₂; (2) and interrelation of such energy levels in the band gap.
makes the red shift rise in the band gap transition and visible light absorption through the charge of transferring between a dopant and a conduction or valence band (Hong et al. 2006). It was elucidated that the liquid-phase method enhanced by the NTP at atmospheric pressure can incorporate nitrogen atoms into TiO2. Figure 2b shows the ESCA spectra of N 1s, Ti 2p and O 1s. TiO2 was characterized with peaks appearing at around 458–459 eV for Ti 2p3/2 and 464 eV for Ti 2p1/2. The Ti 2p peaks of the N-doped TiO2, however, shift to a lower binding energy. Obviously, the presence of N-doping in the TiO2 particles is substantiated by the N 1s spectra, where significant peaks around 402 eV, 400 eV, and 396 eV were also observed for the N-doped TiO2. N-doped TiO2 observed three N 1s peaks with the binding energy of 402, 400, and 396 eV, corresponding to atomic β-N (396 eV) and molecularly chemisorbed γ-N2 (400 and 402 eV) (Asahi et al. 2001). When the N-doped TiO2 was prepared using nitrogen carrier gas in atmospheric pressure plasma treatment, N 1s peaks exist at 402 eV and 400 eV, not at 396 eV (Chen et al. 2007). In the case of samples C the N-doped TiO2, N 1s peak at 402 eV assigned to Ti-N bond was observed. However, N 1s peak at 402 eV assigned as molecular nitrogen did not exist.

The XRD powder diffraction patterns for the samples A–D are shown in Figure 2c. Since the peak positions of XRD spectra were barely changed, the crystal structure was maintained as anatase even after plasma-treatment. This result suggests that the plasma-treatment at a low temperature does not affect the crystal structure. In general, the high temperature treatment by traditional preparation methods such as calcination and sol-gel causes the transformation of the crystal from anatase phase to rutile phase. Since the rutile phase is thermodynamically stable at all temperatures, while the anatase phase is metastable, the anatase phase of pure TiO2 starts to be transformed irreversibly into the rutile phase at ca. 673 K (Wang et al. 2007). By using the plasma treatment at a low temperature, band gap values of N-doped TiO2 was altered without a change of crystal structure.

Decolorization of AO7 in continuous-flow photocatalytic reactor

In this section, the optimum N-doped TiO2 condition of particles (TiO2:NH4Cl = 1:6) was selected for photocatalytic activity tested by decolorization of AO7. The relative decreases of AO7 concentration, C/C0, with the
illumination time for various initial concentrations are shown in Figure 3a. As the initial concentration of AO7 increased, the reaction rates decreased. It is believed that the increased concentration affects light penetration in the AO7 solution. Therefore, at a higher initial concentration, the light penetration was reduced and less photons reached the catalyst surface. Others also reported similar results (Kiriakidou et al. 1999). In addition, the slope of decay of \( C / C_0 \) appeared in a good agreement with pseudo-first-order kinetics (not shown). Moreover, the capacity of photocatalyst for azo dye (q, mg azo dye/mg N-TiO2) followed the Langmuir adsorption model. This proposed mechanism was confirmed by the linear plots of 1/q vs. 1/C, as shown as a straight line in Figure 3b. Hence, the photocatalytic degradation of AO7 using the Langmuir adsorption model describes the effect of initial concentration and the capacity of photocatalyst for azo dye fairly well.

Figure 4 shows the AO7 removal efficiency and \( k_{\text{obs}} \) as a function of TiO\(_x\)N\(_y\) dosages at pH of 5.0 and hydraulic retention time (HRT) of 10 hr. The AO7 removal efficiency increases from 41% for TiO\(_x\)N\(_y\) of 0.1 g to more than 96% for TiO\(_x\)N\(_y\) of 0.5 g. In addition, the photocatalytic decolorization of the AO7 was found to follow pseudo-first-order kinetics model, \( \ln([\text{AO7}]_0/\text{[AO7]}) = k_{\text{obs}}t \), where \([\text{AO7}]_0\) is the initial concentration, and \([\text{AO7}]\) is the concentration at any time, \( t \). Furthermore, the increase of catalyst did not affect the light penetration and absorption of photons for the AO7 removal in the continuous-flow photocatalytic reactor; therefore, the screening effect of excess particles did not significantly occur.

### Photocatalyst separation from effluent of the photocatalytic reactor

This section deals with the photocatalyst separation from effluent of the photocatalytic reactor, which is vital for the operation of PMSS. From Figure 5a, the flux increases as the pressure increases; however, no limiting flux is found.
from this membrane separation system. Therefore, the transmembrane pressure of 2.8 bar was chosen for investigating the effect of addition of TiO$_2$N$_x$ particles to a feed on a permeate flux during the determination of PMSS. It was found (Figure 5b) that the presence of the TiO$_2$N$_x$ catalyst in a concentration of 0.15 g/L did not affect the permeate flux in membrane separation process. This result indicated that the permeate flux does not significantly differ between the PMSS of the catalyst suspension in distilled water and in dye solution.

The separation/recovery efficiency of ceramic membrane for the TiO$_2$N$_x$ catalyst is shown in Figure 6a. Before 60 min, the recovery efficiency of TiO$_2$N$_x$ particles was more than 64%, and the recovery efficiency of TiO$_2$N$_x$ particles reached 83% after 80 min. When the ultrafiltration had been carried out for 90 min, the recovery efficiency reached 99.5%. Meanwhile, no TiO$_2$N$_x$ particles could be detected in the permeate. This result indicated that the photocatalyst was able to separate/recover completely. On the other hand, the effect of the filtration time on the permeation flux of the ceramic membrane was shown in Figure 6b. The permeation flux did not decline and remained at 280 L/m$^2$ h. This result indicated that the fouling did not occur on the membrane surface for the PMSS.

**CONCLUSIONS**

The N-doped TiO$_2$ was successfully prepared by the LPNTP technology under low temperature and normal pressure and band gap values of TiO$_2$ were changed without a change of crystal structure. Furthermore, the N-doped TiO$_2$ photocatalyst was superior for AO7 decomposition, compared with commercial DP-25 photocatalyst under visible light irradiation, especially for the N-doped TiO$_2$/NH$_4$Cl mass ratio of 1.6. For the continuous-flow photocatalytic experiments, 63% of AO7 concentration was degraded under visible light irradiation for 16 hours and the screening effect of excess particles did not significantly occur. The TiO$_2$N$_x$ catalyst did not affect the permeate flux in membrane separation. For membrane separation/recovery system, the recovery efficiency reached 99.5% after the ultrafiltration had been carried out for 90 min, and this result indicated that the photocatalyst was able to be separated/recovered completely.

**REFERENCES**

Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. & Taga, Y. 2001
Visible-light photocatalysis in nitrogen-doped titanium oxides.


Photocatalysis membrane separation coupling reactor and its application.


Hsu, B. C., Chen, S. S., Su, C. C. & Liu, Y. T. 2007

Hsu, B. C., Chen, S. S., Su, C. C. & Li, Y. C. 2009


Liu, Y., Chen, X., Li, J. & Burda, C. 2005

Lu, X., Yang, B., Chen, J. & Sun, R. 2009

Maeda, M. & Watanabe, T. 2006

Sato, S., Nakamura, R. & Abe, S. 2005


Zhao, Y., Zhong, J., Li, H., Xu, N. & Shi, J. 2002