

Single-step synthesis of visible-light $\text{TiO}_{2-x}\text{N}_x$ photocatalyst nanopowder by thermal plasma

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ABSTRACT

TiO_2 photocatalyst has been shown to effectively decompose various pollutants in gaseous or aqueous phases. The major defect of TiO_2 , however, appears to be the large band-gap energy of 3.2 eV that makes the TiO_2 only being excited by UV light. Furthermore, the manufacturing process of TiO_2 strongly influences the purity and surface properties of resulting nanoparticles which subsequently affect the characteristics of TiO_2 photocatalytic reactions. Therefore, there is a need to produce visible-light photocatalyst via novel processes. In this study, nitrogen-doped TiO_2 (i.e., $\text{TiO}_{2-x}\text{N}_x$) nanopowders, which have been recognized as effective photocatalysts for band gap narrowing, were synthesized using a transferred DC plasma torch as the heating source. The $\text{TiO}_{2-x}\text{N}_x$ nanopowders were formed via a single-step thermal process. The formed $\text{TiO}_{2-x}\text{N}_x$ samples were characterized with TEM, XRD and UV-Vis. The experimental results indicated that the formed $\text{TiO}_{2-x}\text{N}_x$ nanopowders had a particle size within 5–20 nm. Furthermore, the formed nanopowders were a mixture of the anatase and rutile phase. An evident red-shift in wavelength absorption was also observed. These results revealed that the proposed thermal plasma method successfully fabricated N-doped TiO_2 in a single-step process.

Keywords: nitrogen doped, titanium dioxide, evaporation condensation, plasma torch

1 INTRODUCTION

TiO_2 nanoparticles have been widely demonstrated to photocatalyze and photodegrade various gaseous or aqueous pollutants, such as volatile organic compounds, NO_x , SO_x , and dioxin/furan. However, the large band-gap energy of 3.2 eV makes the pure TiO_2 only being excited by ultraviolet light ($\lambda < 365$ nm) source only. Several studies have indicated that an improved TiO_2 photocatalyst excited by visible light source can be prepared by substitute doping with nonmetal atoms, such as carbon [1], sulfur [2] and nitrogen [3-5]. These nonmetal atoms in TiO_2 lattice shift the absorption edge of TiO_2 to lower energies through band gap narrowing. Nitrogen doping has been presented as one of the most effective processes for band gap narrowing to visible light. Asahi et al. [3] performed theoretical

computing for the substitution of oxygen in TiO_2 lattice with several anionic materials and suggested that the substitute doping of N was the most efficient for the visible light ($\lambda=436$ nm) activity of TiO_2 photocatalysts. Based on this calculation, they manufactured $\text{TiO}_{2-x}\text{N}_x$ films by sputtering a TiO_2 target with a 40% N_2/Ar gas mixture. After annealing the films in N_2 gas at 550°C for 4 hours, an increase in photocatalytic activity in the resulting films was observed. Ihara et al. [4] synthesized anatase powders containing trace amounts of nitrogen by calcining the hydrolysis product of $\text{Ti}(\text{SO}_4)_2$ with NH_3 using an ordinary electric furnace in dry air at 400°C for 1 hour. The resulting powders possessed highly visible activity and vivid yellow color. It was also found that the visible activity could be realized on polycrystalline particles and the grain-boundaries (GBs) were thought to be important because oxygen vacancies were easily created in GBs that could form a GB state. Therefore, they concluded that oxygen-deficient sites formed in GBs were important to emerge visible activity, and nitrogen doped in the part of oxygen-deficient sites was important as a blocker for reoxidation.

Several methods have been reported to successfully fabricate N-doped TiO_2 films or particles, including surface treatment of TiO_2 target by sputtering [3, 6] or plasma [7-11], chemical vapor deposition [12], pulse laser deposition [5, 13], electron beam evaporation [14, 15], or through aqueous phase reactions such as the sol-gel method [16]. The sources of nitrogen doping can be N_2 gas [8], ammonia gas [4, 17, 18], or other N-containing compounds. Among the aforementioned processes, solution syntheses were extensively used for the production of TiO_2 photocatalysts. However, solution concentration of reagent, reaction time and temperature strongly affected the growth of TiO_2 photocatalyst. In addition, N-doped TiO_2 can also be developed by further modifying raw TiO_2 materials; a multi-step synthetic process, however, was needed. Few studies have shown to produce $\text{TiO}_{2-x}\text{N}_x$ in a single-step process.

Evaporation condensation has been shown to possess advantages to develop nanoparticles and film with clean surface and a narrow particle size distribution. In this study, N-doped TiO_2 nanoparticles were prepared using a thermal plasma torch evaporation condensation system. The morphology and crystal phase of the resulting nanoparticles were then examined. The main goal of this study was to create a single step procedure for production of $\text{TiO}_{2-x}\text{N}_x$

photocatalyst with a broad absorption spectrum in visible-light range.

2 EXPERIMENTAL

2.1 Preparation of $\text{TiO}_{2-x}\text{N}_x$ nanoparticles

The $\text{TiO}_{2-x}\text{N}_x$ nanoparticles were prepared using a transferred DC plasma torch assembled by Taiwan Plasma Corp. (Kaohsiung, Taiwan). The details of the thermal plasma torch are presented in Figure 1. Titanium metal (99.8%) was used as the target and applied by 2.50 ± 0.15 KW target power. The distance between the titanium target and plasma torch was 4 mm and the operating current was 110 A, which was shown to be the optimum operating current according to our preliminary tests operated between 90 and 150 A. The base pressure was 20 kPa. O_2 (2 L min^{-1}) was used as both the reacting gas and the shelter gas and fed via passage B in Figure 1. Nitrogen, argon and helium were mixed as the plasma gas and fed via passage A in Figure 1. The gas composition was adjusted with various N_2 flow rate (F_{N_2}) at a fixed flow rate of Ar (F_{Ar}) at 1.5 L min^{-1} and He (F_{He}) at 0.5 L min^{-1} . The N_2 concentration ($\text{N}_2\%$) was presented as:

$$\text{N}_2\% = \frac{F_{\text{N}_2}}{(F_{\text{Ar}} + F_{\text{He}})} \times 100\% \quad (1)$$

The tail gas containing the formed $\text{TiO}_{2-x}\text{N}_x$ nanoparticles was passed through a stainless steel powder filter and a buffer tank induced by a vacuum pump. These samples were then collected and stored for subsequent analyses.

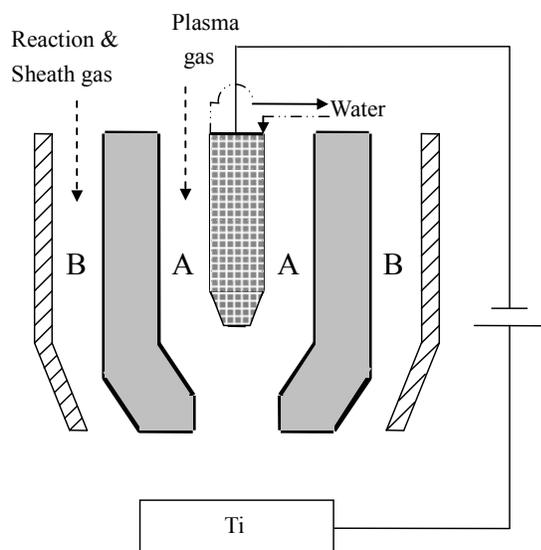


Figure 1: Schematic diagram of transferred DC plasma torch for producing N-doped TiO_2 photocatalysts.

2.2 Nanoparticles characterization

The size of formed $\text{TiO}_{2-x}\text{N}_x$ nanoparticles sizes was analyzed with a transmission electron microscope (TEM, Philips CM-200). The structure and crystallinity of collected nanoparticles were characterized by X-ray diffraction (XRD, Shimadzu XRD-600). The UV-visible diffuse reflection spectra were measured by a spectrophotometer (Hitachi, U-3010).

3 RESULTS AND DISCUSSION

3.1 Morphology of $\text{TiO}_{2-x}\text{N}_x$

Figure 2 shows the TEM images of the nanoparticles produced under various nitrogen doping concentrations. It was observed that all the formed nanoparticles were spherical or hexagonal. The nanoparticles synthesized in a plasma environment without N_2 , however appeared to have a smaller particle size as compared to those produced under 5–10% N_2 plasma environment. When Ar and He were used as the only plasma gas, the sizes of resulting nanoparticle were between 5 to 10 nm. When N_2 was mixed with the Ar and He as the plasma gas, the sizes of $\text{TiO}_{2-x}\text{N}_x$ nanoparticles were around 5 to 20 nm. The particle sizes of samples synthesized at various N_2 concentrations (i.e., between 5–10%) were approximately the same, indicating that the amount of N_2 mixed to plasma gas had an insignificant effect on the shape and size of the particles. The aforementioned observations were somewhat expected because the flame temperature of transferred plasma torch was markedly influenced by the type of plasma gases [19]. The size of nanoparticles appeared to increase at a $\text{N}_2/\text{Ar}/\text{He}$ environment may be attributed to the greater thermal conductivity of N_2 (1.0). When N_2 was added to the plasma gas, the plasma power was observed to increase from 2.28 KW to 2.50 ± 0.15 KW, which was expected to increase the plasma temperature and cause the growth of $\text{TiO}_{2-x}\text{N}_x$ nuclei.

3.2 XRD analysis

The data in figure 3 show the XRD powder patterns for the samples synthesized at various nitrogen concentrations. Because the TiO_2 nanoparticles were laid on a silver membrane filter paper, Ag with four peaks were shown in the XRD powder patterns. The XRD results indicated that all of the $\text{TiO}_{2-x}\text{N}_x$ nanoparticles were in anatase and rutile phases and had better crystallization than the TiO_2 nanoparticles without N-doping. These results suggested that the N_2 addition increased the plasma temperature, which caused the observed phase transformation of the nanocrystal from anatase to rutile. It is important to note that the nitrogen addition amount in this study was not enough to create TiN . N_2 addition in excess amounts could cause a negative effect on the crystallinity of $\text{TiO}_{2-x}\text{N}_x$. Wong et al. [6] indicated that the excess N_2 fraction created

TiN, which increased the nitrogen incorporation and destroyed the anatase TiO₂ phase in the TiO_{2-x}N_x nanoparticles. As a result, the XRD patterns of the TiO_{2-x}N_x nanoparticles became weak and broad, and shifted to lower angle of (101) peak. The phenomena exhibited that the N incorporation induced decreasing crystallinity and increasing lattice parameters, strain or defects, as found by Gole et al. and Yang et al. [15, 20].

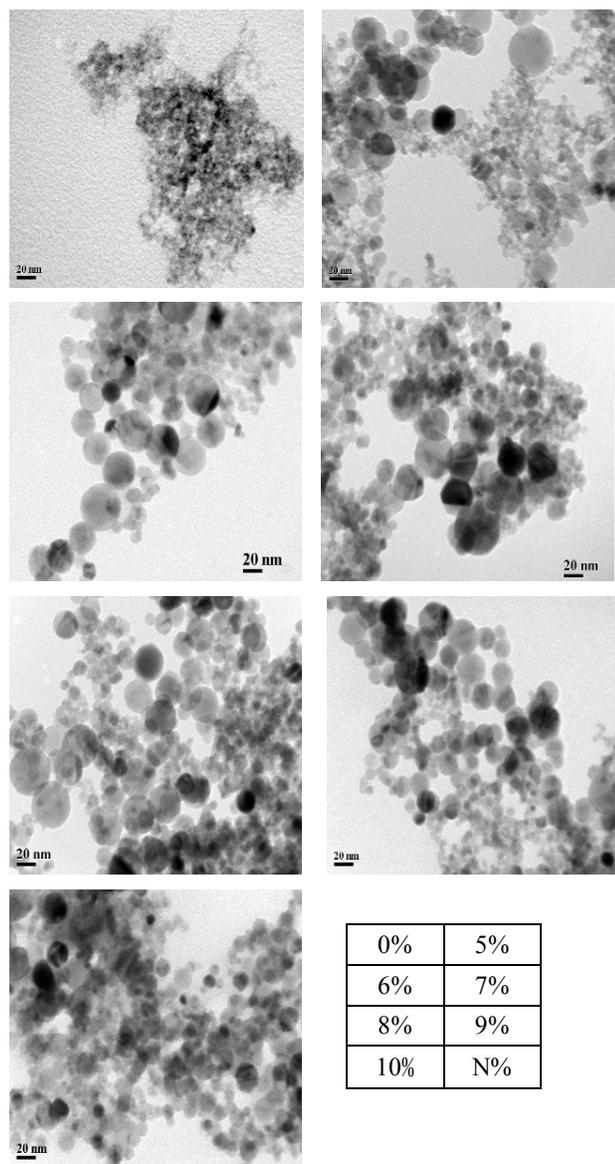


Figure 2: TEM images of TiO₂ nanoparticles.

3.3 UV-Vis Spectra

Figure 4 shows the UV-visible spectra of the nanoparticles synthesized at various nitrogen concentrations and Degussa P25 over the wavelength range of 300–800 nm. For P25, the absorption edge was observed to be at

~400 nm. The nanoparticles of TiO₂ synthesized by thermal plasma without N₂ supply showed an absorption edge at 390 nm. This absorption edge corresponded to the band gap of TiO₂ at 3.18 eV and was similar to that of P25. The N-doped TiO₂ nanoparticles, however, had a clear red shift into the visible light absorption range. Additionally, a significant red shift of the absorption edges at around 490 and 590 nm regions, respectively, were observed for the sample produced at the 7% N₂ environment. These new absorption bands were thus attributed to the doped N atoms.

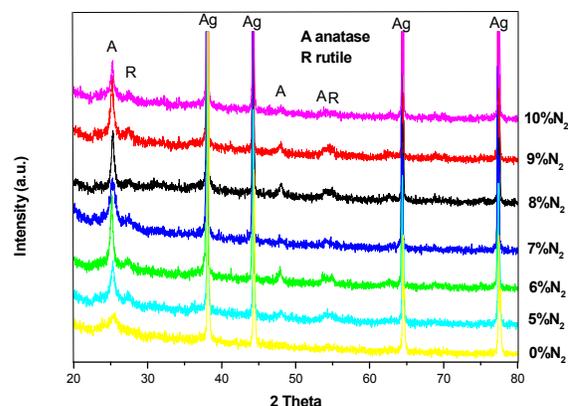


Figure 3: XRD patterns of TiO₂ nanoparticles.

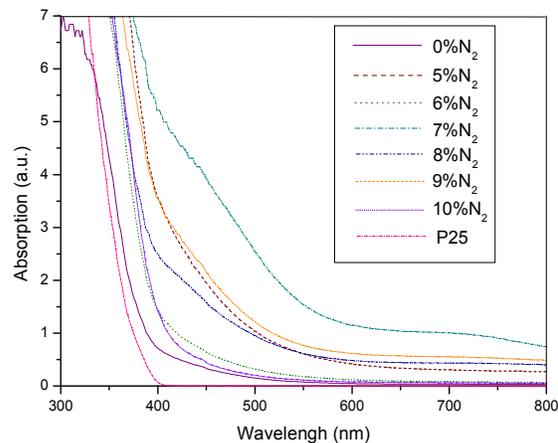


Figure 4: Optical absorption spectra of the commercial photocatalysts (P-25) and the synthesized TiO₂ nanoparticles.

4 CONCLUSION

TiO₂ photocatalysts doped with nitrogen were successfully prepared by evaporation condensation using a thermal plasma system. Results indicated that the nanoparticles had a size within 5–20 nm. The crystal phases

of the $\text{TiO}_{2-x}\text{N}_x$ nanoparticles were mainly in anatase and rutile forms. The substitution of nitrogen was found to cause a significant red shift in the absorption edge to lower energy due to band gap narrowing. The significant red shift of the absorption edges at around 490 and 590 nm respectively were observed for the sample developed at 7% N_2 . These results demonstrated that the proposed thermal plasma method successfully fabricated N-doped visible-light TiO_2 in a single step.

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