Effect of Nitrogen Doping on Optical and Photocatalytic Properties of TiO₂ Thin Film Prepared by Spin Coating Process

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Abstract

Nitrogen-doped TiO₂ thin films were prepared by spin coating on glass substrate. Different amount of nitrogen doped in TiO₂ matrix was 0, 3 and 10%. As-obtained films were annealed at 400°C for 2 h. The optical and photocatalytic properties of N-doped TiO₂ thin films were analyzed via UV-Vis spectrophotometry. The chemical properties were investigated by Fourier transform infrared spectrometer and Raman spectroscopy. When doping TiO₂ with nitrogen, its absorption spectrum is shifted to visible region resulting to the enhancement of photocatalyst properties in dye photodegradation. Raman and FTIR patterns show that N-doped TiO₂ pattern is still identical to undoped TiO₂ pattern resulting to unsubstitutution of nitrogen atom in Ti-O bonding.

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1. Introduction

Photocatalytic reactions at the surface of metal oxide photocatalyst have been attracting much attention over last decade. Titanium dioxide ($\text{TiO}_2$) is one of functional metal oxide semiconductor that performs high efficiency in photocatalytic activities because of non-toxicity, excellent energy conversion efficiency and long-term chemical stability [1]-[3]. The applications of $\text{TiO}_2$ photocatalyst have been reported in various environmental applications such as hydrogen generation, bacteria inactivation and photocatalytic degradation [4]. However, $\text{TiO}_2$ can absorb under UV illumination due to its wide band gap energy. Due to only 3-5% of UV in solar spectrum, the efficiency of $\text{TiO}_2$ under natural sunlight is limited by its drawback. Therefore the researches of activated $\text{TiO}_2$ under solar irradiation have been proposed in recent years by incorporating with metal, non-metal, organic materials [5]-[7]. Among them, non-metallic dopant such as carbon (C), sulfur (S) and nitrogen (N) has been considered to one of effective methods for visible-light-active in $\text{TiO}_2$.

Nitrogen is one of material that was acknowledged for enhancing the photoresponding range into visible light in $\text{TiO}_2$ because of leading to a narrowing band gap in $\text{TiO}_2$ according to the research of Asahi and coworker [8]. Y. Cong and colleague proved that the significant visible light response and the improvement of photocatalytic degradation were obtained by N-doped $\text{TiO}_2$ [9]. S. Bangkedphol and coworker reported on the improvement of photocatalytic degradation of tributyltin under natural light by using N-doped $\text{TiO}_2$ [10]. J. Senthilnathan and L. Philip successfully enhanced photocatalytic activity of lindane under visible light irradiation by the presence of O-Ti-N bonding of N-doped $\text{TiO}_2$ [11].

A number of N-doped $\text{TiO}_2$ syntheses have been proposed, for example, wet method, hydrolysis precipitation, thermal treatment with nitrogen gas system and sol-gel process [12]-[15]. For thin film technology, sol-gel method has attracted special interest due to high dielectric constant and good homogeneity at low cost. The main objective is to investigate the effect of the different content of N doping in $\text{TiO}_2$ thin film on its chemical bonding, optical property, and response under visible range. The efficiency of N-doped $\text{TiO}_2$ photocatalysts were proved by the photocatalytic degradation of Rhodamine B ($\text{RhB}$) under visible illumination.

Experimental Procedure

For the preparation of N-doped $\text{TiO}_2$ thin film, a mixture solution of 3.4 ml titanium (IV) butoxide, 10 ml acetylacetone, 20 ml absolute ethanol and 0.5 ml hydrochloric acid was stirred. 1 ml of ammonium acetate ($\text{NH}_4\text{COOH}$) in deionized water was dropped in the mixture, while stirring the solution for 2 h. The ratio of doping nitrogen was fixed at 0, 3 and 10 wt.% in $\text{TiO}_2$ matrix. After that, the yellowish solution was aged for 6 h at room temperature. The precursor solution was then coated on glass substrate by spin coating process at speed 2,500 rpm and followed by heating at 100 °C for 10 min to evaporate the solvent. The coating was repeated for 7 times. Finally, as-prepared of N-doped $\text{TiO}_2$ films were obtained by annealing at 400 °C for 2 h. The optical properties in transmittance mode were analysed by UV-Vis spectroscopy (PG Instrument). The chemical properties were investigated by Fourier transform infrared spectrometer (FTIR, Thermo Scientific) and Raman spectroscopy (Thermo Scientific; DXR Raman microscope).

The photocatalyst of N-doped $\text{TiO}_2$ thin film was carried out by dye photodegradation of Rhodamine B ($\text{RhB}$) under sunlight comparing to pure $\text{TiO}_2$ film. N-doped $\text{TiO}_2$ thin film was dipped in 3 mM $\text{RhB}$. The solution was irradiated in sunlight for 4 h. $\text{RhB}$ degradation was investigated each 2 h by the decrease of its absorbance at maximum wavelength ($\lambda_{\text{max}}$) via Helios UV-Vis spectrometer.

Results and Discussion

UV-visible absorbance spectra of N-doped $\text{TiO}_2$ at different amount of nitrogen are illustrated in Fig.1. The strong absorption of $\text{TiO}_2$ in a range of 270-350 nm is originated from typical band gap energy of $\text{TiO}_2$ corresponding to high absorption in UV region. Meanwhile, the enhancement of absorption in visible region of $\text{TiO}_2$ was obtained by increasing nitrogen ratio. This result suggests that $\text{NH}_4\text{COOH}$ can be used as nitrogen source in $\text{TiO}_2$ matrix for improving its visible absorption. The highest red shifting was at 10% nitrogen doping but its decreasing UV absorption was obtained. The significant increase of red shift in absorption edge is resulting from the narrow band gap by the additional electronic states of nitrogen above the valence band edge of nitrogen in $\text{TiO}_2$ band energy [16]. For small amount of nitrogen in $\text{TiO}_2$, the absorption in visible region was decreased due to the insufficient nitrogen from precursor.
Fig. 1. Absorbance spectra of different amount of N doping in TiO_2 matrix.

Fig. 2. Raman spectra of N-doped TiO_2 with different amount of N doping (a) 0, (b) 3 and (c) 10 wt.%.

Fig. 3. FTIR spectra of N-doped TiO_2 with different amount of N doping at 0 and 10 wt.%. 

Fig. 4. Photocatalytic degradation of RhB under sunlight by N-doped TiO₂ thin film with different amount of N doping (a) 0, (b) 3 and (c) 10 wt.%.

The Raman spectra of undoped TiO₂ and N-doped TiO₂ in range of 200-2000 cm⁻¹ are illustrated in Fig. 2. For undoped TiO₂, wavenumber at 515 cm⁻¹ is attributable to Ti-O bonding in anatase phase which related to Raman-active mode with the symmetries of B₁g [17]. The peak in range of 1080-1100 cm⁻¹ is corresponding to C-H bonding due to the residual organic material in precursor. Meanwhile, Raman shift patterns of all N-doped TiO₂ are identical to undoped TiO₂ patterns without noticeable peaks. This result indicates that nitrogen doping insignificantly affects the structure of TiO₂ by the substitution of nitrogen atom in TiO₂. FTIR spectra of undoped TiO₂ and N-doped TiO₂ at 10 wt.% are shown in Fig. 3 for confirming chemical bonding in the films. The peaks in range of 750 - 900 cm⁻¹ are belonging to Ti-O-Ti bonding resulting to the formation of TiO₂ on thin film at 400 °C. While wavenumber of 1050-1070 cm⁻¹ is related to O-C-C bonding that indicated the organic remainder in material [18]. However, the corresponding result of 3 wt.% N-doped TiO₂ sample exhibits insignificant change in peak position due to close doping content (data not shown).

The photocatalytic efficiency of undoped TiO₂ and N-doped TiO₂ at different nitrogen loading were scrutinized by the photodegradation of aqueous RhB under solar light in 4 h as shown in Fig.4. It is clearly observed that the photocatalytic activity of N-doped TiO₂ photocatalyst is more effective especially nitrogen doping at 3 wt.% shown faster reaction comparing to other conditions. This phenomenon was originated from the incomplete decomposition of large doping nitrogen precursor content in TiO₂ matrix. The constant rate of RhB degradation with TiO₂ P25 1.25 mm min⁻¹ whereas N-doped TiO₂ photocatalyst at 3 and 10 wt.% shows the constant rate of the activity of about 13.75 and 7.50 mm min⁻¹. This result implies that nitrogen doping in TiO₂ can significantly enhance the photocatalytic degradation comparing to undoped TiO₂ due to narrowing band gap energy of TiO₂ leading to the enhancement of optical absorption of photocatalyst under visible illumination [19]. Whereas the large amount of nitrogen doping was effect on decreasing light absorption in visible region. In addition, the decrease of absorption intensity of RhB under solar light was caused by de-ethylation of RhB occurred by the attacking of active oxygen species from TiO₂ photocatalyst on N-ethyl group of RhB. This mechanism was related to the change of RhB structure [20].

Conclusion

Thin films of N-doped TiO₂ with different loading nitrogen on TiO₂ have been prepared by sol-gel method and spin coating process. The obtained thin films were investigated on the application of photocatalysts in dye photodegradation. Accompanying optical absorption properties, TiO₂ absorbance is improved and shifted to visible region with the existence of nitrogen due to the narrowing band gap of TiO₂. From Raman and FTIR spectra suggest that nitrogen dopant has inconsiderable influence on the chemical bonding of Ti-O. Good efficiency of photocatalytic activity under solar light was obtained by N-doped TiO₂ comparing to undoped TiO₂. The optimum ratio of N doping in TiO₂ for RhB decolorization is 3 wt.% under irradiation 4 h. These results suggest that good performance of TiO₂ photocatalyst in visible region is improved by nitrogen doping.
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References


