Research Article

Preparation of N-Doped TiO_2 - ZrO_2 Composite Films under Electric Field and Heat Treatment and Assessment of Their Removal of Methylene Blue from Solution

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TiO_2 - ZrO_2 composite film with the grain size of 50 nm was synthesized by electric field and heat (EF&H) treatments. Portions of O atoms in the TiO_2 network structure were replaced by N atoms as revealed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses, suggesting formation of a nonstoichiometric compound $\text{TiO}_{2-x}\text{N}_x$ on the composite film. The UV-Vis spectra of the film suggested that the visible light with wavelength of 550 nm could be absorbed for the N-doped composite film after EF&H treatment in comparison to a cutoff wavelength of 400 nm for the composite film without EF treatment. Photocatalytic experiments showed that the degradation rate of methylene blue by N-doped composite films increased significantly under visible light irradiation. The partial replacement of O by doped N played a very important role in narrowing the band gap and improving the visible light photocatalytic reactivity.

1. Introduction

TiO_2 films are widely used in many fields, ranging from transforming solar energy into chemical energy and electric energy to environmental remediation, including photocatalytic degradation of pollutants in atmosphere and water, sterilization, and self-cleaning, and so forth [1–3]. The TiO_2 has low thermal expansion coefficient making it inferior to metal materials that have high thermal expansion. This drawback results in a lower TiO_2 film efficacy compared to metal surfaces, and thus, limited its practical applications. TiO_2 - ZrO_2 composite film has the advantages of adjustable thermal expansion rate. It can be applied to a variety of metal surface modifications. But the photocatalytic reactivity of TiO_2 under visible light condition (wavelength greater than 387.5 nm) still remains low after the addition of ZrO_2 to TiO_2 . In order to utilize the visible part of the solar spectrum, or under general illumination conditions, two approaches could be undertaken with one being doping transition metals into TiO_2 [4, 5], and the other being forming defects of

TiO_x catalyst compounds [6, 7]. Although doping transition metals can improve the reactivity of TiO_2 under visible light, the TiO_2 reactivity under ultraviolet light would decrease correspondingly. In addition, the reactivity under visible light was much lower than that under UV because of the metal ions becoming the recombination centers. In addition, stability of TiO_2 would be reduced due to doping [8]. The TiO_2 reactivity under visible light condition could be increased by incorporation of nitrogen atoms into TiO_2 [9]. But, it was not until 2001, when Sato et al. [8] reported in science that substitution of a small quantity of lattice O by N could narrow the TiO_2 band gap, thus increasing the TiO_2 reactivity under visible light condition, while maintaining its UV light reactivity. This discovery attracted great attention for nonmetallic elements doped TiO_2 [10, 11].

In this paper, the N-doped TiO_2 - ZrO_2 composite film with relatively high photocatalytic reactivity under visible light was prepared by a sol-gel method followed by treating the products under electric field and heat in nonequilibrium state. It is anticipated that this simple process could gain wide

popularity in the field of surface treatment of various daily use.

2. Experimental Methods

2.1. Sol Preparation. The TiO_2 sol was prepared through hydrolyzing the tetrabutyl titanate ($\text{Ti}(\text{OBU})_4$) under acidic condition. To do so, 10 mL tetrabutyl titanate (98%) was dissolved in 40 mL absolute alcohol (99.7%) and 10 mL acetyl acetone (99.9%) was added to inhibit premature hydrolyses of tetrabutyl titanate. The mixture was stirred for 30 min using a magnetic stirrer. Then, 10 mL deionized (DI) water was added slowly and the mixture stirred vigorously to form a uniform dispersion. During this process, dilute hydrochloric acid (3.6%) was continuously added to maintain the pH value of the solution at 1.8.

Similarly, the ZrO_2 sol was prepared using a molar ratio of $\text{Zr}(\text{OPr})_4$ (99%): n-propyl alcohol (99.8%): acetyl acetone: water at 1:4:2:2. A period of 12 h aging is needed for the ZrO_2 sol, before it was fully mixed with the prepared TiO_2 sol at a ratio of 1:4 (ZrO_2 sol: TiO_2 sol). Then, 1 g NH_4NO_3 (99%) was added to the mixture. The mixture was stirred for 2 h and allowed to stand for 12 hours, before being used for coating film.

2.2. Film Preparation. Sillex glass with a diameter of 1.5 cm was used as the substrate for film coating at a thickness of 1 mm. The substrate was washed in ether under ultrasound and then rinsed with DI water. The cleaned substrate was dried at 80°C for 1 h in an oven. A dip-coating method with a pulling speed of 0.5 mm/s was adopted. After dip-coating the substrate was dried in an oven at 80°C for 4 h. The dried sample was placed in electric furnace (Figure 1) and treated under external direct current electric field with voltages of 0 or 600 V, respectively (the calculated electric field strength was 0 or 6000 V/cm). Heat treatment was carried out in N_2 atmosphere at 500°C for 1 h.

2.3. Photocatalytic Performance. The performance of the N-doped TiO_2 - ZrO_2 composite film was evaluated by assessing the photocatalytic degradation of methylene blue (MB) in 10 mg/L. The N-doped TiO_2 - ZrO_2 composite film was added to 100 mL MB solutions of 10 mg/L followed by exposure to different light sources for 3 h. The tests were conducted under a wavelength irradiation of 365 nm created by a high pressure mercury lamp or under continuous wavelength ranging from 400 to 760 nm generated by a 40 W fluorescent lamp. The residual MB concentration in solution was measured at the maximum absorption wavelength of 660 nm using the UV-1901 type UV-Vis spectrophotometer. The MB removal was determined by the differences between the initial and equilibrium MB concentrations.

2.4. Instrumentation Analyses. The XPS was obtained using the PHI5300 type X-ray photoelectron spectrometer; the X-ray diffraction was performed by a D/max-rB X-ray diffractometer; the UV-Vis diffuse reflectance spectrogram was

FIGURE 1: The heating apparatus and specimen arrangement.

FIGURE 2: X-ray diffraction patterns of the composite film annealed at 500°C for 1 h: (a) 0 V and (b) 6000 V/cm.

recorded by the UV-1901 ultraviolet visible spectrophotometer. The surface morphology of the films was observed by the JSM-6301F scanning electron microscope (SEM).

3. Results and Discussion

3.1. Phase Analyses of the Doped Film. Figure 2 showed the XRD patterns of the composite film with heat treatment in the presence and absence of electric field. Without EF treatment, the phase of the film was mainly made of anatase with trace amount of rutile. The rutile phase increased substantially in the composite film after EF&H treatment, suggesting that the external EF promoted crystal transformation on the film. Moreover, the crystallinity of the composite film increases significantly after EF treatment. Meanwhile, no TiN phase was observed in the two XRD patterns (Figure 2).

FIGURE 3: SEM surface micrograph of the samples after EF&H treatment at 6000 V/cm and 500°C for 1 h.

FIGURE 4: XPS of the N1s in composite film treated at 500°C for 1 h: (a) 0 V, (b) 6000 V/cm (no NH_4NO_3) and (c) 6000 V/cm with addition of NH_4NO_3 .

3.2. The Mean Grain Size of the Films. After EF&H treatment the mean grain size of the film surface was about 50 nm as revealed by the SEM micrograph of the composite film (Figure 3).

3.3. XPS Energy Spectrum Analysis. The XPS energy spectra of N1s of the composite film produced in the absence and presence of EF are shown in Figures 4(a) and 4(c). Figure 4(a) shows a peak shoulder at 399.7 eV and Figure 4(c) shows two peak shoulders at 399.7 eV and 396.4 eV, respectively. The binding energy at 399.7 eV indicates the presence of gap state of N element and the binding energy at 396.4 eV corresponded to the Ti-N bond or the O-Ti-N bond [12]. As the XRD analysis did not reveal the TiN phase, the chemical bond corresponding to the peak at 396.4 eV should be assigned to O-Ti-N bond instead of Ti-N bond, which suggested the formation of nonstoichiometric compounds $\text{TiO}_{2-x}\text{N}_x$ in the composite film prepared under EF&H treatment. This suggested that N successfully replaced some of the O atoms near the surface region of the O-Ti-O network under DF&H treatment, forming the N-Ti-O network. Because of the slight difference in electronegativity between

FIGURE 5: UV-Vis DRS of the composite film annealed at 500°C for 1 h: (a) 0 V and (b) 6000 V/cm.

O and N atoms, the electron cloud had a small tendency deflecting towards O atoms, resulting in a slight decrease in the electronic cloud density of N atom. Figure 4(b) is the XPS curve of N1s in the coextruded film prepared under the same EF&H condition without addition of NH_4NO_3 . Only a peak shoulder at 399.7 eV was observed, suggesting the absence of nonstoichiometric compounds $\text{TiO}_{2-x}\text{N}_x$. In comparison to Figures 4(a) and 4(c), the N element in the $\text{TiO}_{2-x}\text{N}_x$ was derived from NH_4NO_3 .

3.4. UV-Vis Spectra of the Thin Film. Figure 5 is the UV-Vis DRS of the composite film without EF and with EF of 6000 V/cm at 500°C heat treatment for 1 h. The composite film prepared without external EF showed no absorption of light whose wavelength was above 400 nm. In comparison, the visible light with wavelength of 550 nm can be absorbed by the composite film prepared with EF&H treatment and contained $\text{TiO}_{2-x}\text{N}_x$, suggesting a red shift in the absorption edge. This red shift of the absorption edge could be attributed to the increased photocatalytic reactivity of the N-doped TiO_2 -ZrO₂ composite film under visible light after EF&H treatment.

3.5. Photocatalytic Performance. Photocatalytic performance test was conducted on the composite film produced in the absence and presence of EF. The degradation rate of MB is listed in Table 1. The degradation rate of composite film prepared under EF of 6000 V/cm was higher than that prepared in the absence of EF. Under the irradiation condition of 365 nm by the high-pressure mercury lamp, the MB degradation rate by the film after EF&H treatment was as high as 95%. Under the irradiation by 40 W fluorescent lamp, the degradation rate was as high as 83%, in comparison to only 39% without treatment. This result showed that the composite film prepared under EF&H treatment possessed excellent visible light catalytic reactivity.

TABLE 1: Degradation rate of the coextruded film annealed at 500°C for 3 h: (a) 0 V and (b) 6000 V/cm.

Sample	Degradation rate (%)	
	Fluorescent lamp (40 W)	High-voltage mercury lamp (365 nm)
(a) 0 V	39	91
(b) 6000 V/cm	83	95

4. Discussion

The improved performance of photocatalytic degradation of MB by the film under visible light condition could be attributed to the following effects. Doping of the film in N_2 atmosphere generated $TiO_{2-x}N_x$ in the presence of EF&H treatment, which increased the impurity levels and decreased the band gap of TiO_2 [8]. Doping of N can narrow band gap as the increase in impurity level could result in band gap reduction of TiO_2 after mixing the 2p state of N atom and 2p state O atom. Theoretical calculation shows that the red shift of absorption edge could be achieved via N-doping. This is mainly due to the potential transition of N atoms to d_{xy} state of Ti by replacing the electrons of $2p\pi$ state in TiO_2 [8, 13]. Additionally, doping of N could generate Ti^{3+} on the surface of TiO_2 film. As the Ti^{3+} on the surface increases, the Fermi level of TiO_2 increases, resulting in an increase in light absorbing potential for catalyst.

5. Conclusion

The EF promoted the phase transformation. When the external EF is 6000 V/cm and the heat treatment is 500°C for 1 h, $TiO_{2-x}N_x$ was generated in the ZrO_2 - TiO_2 composite film. The XPS and XRD analyses indicated that partial N atoms appear in TiO_2 resulting from the replacement of O by N atoms. The composite film containing $TiO_{2-x}N_x$ could absorb visible light around 550 nm, as reviewed by the UV-Vis DRS analyses. The N-doped ZrO_2 - TiO_2 composite had a higher UV and visible light catalytic reactivity. The doped N partially replaced O, which plays a very significant role in narrowing the band gap and improving the photocatalytic reactivity of the film under visible light conditions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [2] M. R. Saleem, P. Silfsten, S. Honkanen, and J. Turunen, "Thermal properties of TiO_2 films grown by atomic layer deposition," *Thin Solid Films*, vol. 520, no. 16, pp. 5442–5446, 2012.
- [3] B. Barrocas, O. C. Monteiro, M. E. M. Jorge, and S. Sérgio, "Photocatalytic activity and reusability study of nanocrystalline TiO_2 films prepared by sputtering technique," *Applied Surface Science*, vol. 264, pp. 111–116, 2013.
- [4] R. Su, R. Bechstein, J. Kibsgaard, R. T. Vang, and F. Besenbacher, "High-quality Fe-doped TiO_2 films with superior visible-light performance," *Journal of Materials Chemistry*, vol. 22, no. 45, pp. 23755–23758, 2012.
- [5] M. Khan, J. N. Xu, W. B. Cao, and Z. K. Liu, "Mo-doped TiO_2 with enhanced visible light photocatalytic activity: a combined experimental and theoretical study," *Journal of Nanoscience and Nanotechnology*, vol. 14, p. 6865, 2014.
- [6] M. Khan, Y. Song, N. Chen, and W. Cao, "Effect of v doping concentration on the electronic structure, optical and photocatalytic properties of nano-sized V-doped anatase TiO_2 ," *Materials Chemistry and Physics*, vol. 142, no. 1, pp. 148–153, 2013.
- [7] Y. X. Wang, H. Liu, Z. Q. Li, X. X. Zhang, R. K. Zheng, and S. P. Ringer, "Role of structural defects on ferromagnetism in amorphous Cr-doped TiO_2 films," *Applied Physics Letters*, vol. 89, no. 4, 2006.
- [8] S. Sato, R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Photocatalysts sensitive to visible light," *Science*, vol. 295, no. 5555, pp. 626–627, 2002.
- [9] S. Sato, "Photocatalytic activity of NO_x -doped TiO_2 in the visible light region," *Chemical Physics Letters*, vol. 123, no. 1-2, pp. 126–128, 1986.
- [10] J. L. Gole, J. D. Stout, C. Burda, Y. Lou, and X. Chen, "Highly efficient formation of visible light tunable $TiO_{2-x}N_x$ photocatalysts and their transformation at the nanoscale," *Journal of Physical Chemistry B*, vol. 108, no. 4, pp. 1230–1240, 2004.
- [11] M. Maeda and T. Watanabe, "Visible light photocatalysis of nitrogen-doped titanium oxide films prepared by plasma-enhanced chemical vapor deposition," *Journal of the Electrochemical Society*, vol. 153, no. 3, pp. C186–C189, 2006.
- [12] K. Tanaka, K. Kashima, K. Hirao, N. Soga, A. Mito, and H. Nasu, "Second harmonic generation in electrically poled $Li_2ONb_2O_5TeO_2$ glasses," *Journal of Non-Crystalline Solids*, vol. 185, no. 1-2, pp. 123–126, 1995.
- [13] R. Asahi, Y. Taga, W. Mannstadt, and A. J. Freeman, "Electronic and optical properties of anatase TiO_2 ," *Physical Review B*, vol. 61, no. 11, pp. 7459–7465, 2000.