

ARTICLE

Synthesis and Characterization of Novel N-doped TiO₂ Photocatalyst with Visible Light Active

Feng Peng*, Yi Liu, Hong-juan Wang, Hao Yu, Jian Yang

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

(Dated: Received on December 17, 2009; Accepted on June 1, 2010)

A novel N-doped TiO₂ (N₁-N₂-TiO₂) with substitutional and interstitial N impurities simultaneously was successfully synthesized. The catalyst was characterized by X-ray diffraction, X-ray photoelectron spectroscopy, diffuse reflectance spectroscopy, photoluminescence, and electron paramagnetic resonance. The results demonstrated that the nitrogen was substituted for the lattice oxygen atoms, and was also interstitially doped into the TiO₂ lattice. The photocatalytic tests indicated that the N₁-N₂-TiO₂ showed the highest photocatalytic activities of all the N-doped TiO₂ under visible light, attributing to the synergetic effect of substitutional and interstitial nitrogen of N-doped TiO₂.

Key words: Nitrogen doped titania, Photocatalysis, X-ray photoelectron spectroscopy, Substitutional nitrogen, Interstitial nitrogen

I. INTRODUCTION

Owing to its relatively high photocatalytic activity, biological and chemical stability, low cost and non-toxic nature, TiO₂ has been widely used as a photocatalyst [1, 2]. However, the photocatalytic activity of TiO₂ is limited due to its wide band gap of 3.2 eV (wavelength <380 nm), which accounts for only a small fraction (<5%) of the sun's energy compared to the visible region (45%). Therefore, in the viewpoint of utilizing solar light, visible light responsive TiO₂ photocatalyst has become a hot topic in recent years [3, 4]. Asahi *et al.* reported that the nitrogen-doping improved the photocatalytic reactivity of TiO₂ films for organic molecules degradation under visible light illumination [3], the doping with nitrogen has hitherto been considered one of most effective approaches to improve photocatalytic activity of TiO₂ in visible region [4–10].

Some researchers agreed on that N1s peak of XPS at 396–398 eV is characteristic peak of Ti–N–Ti linkages, indicating nitrogen atom is doped into the TiO₂ lattice as substitutional N [8–10] and responsible for enhanced activity. However, different N1s peaks at 399–401 eV have also been reported and correlated with the photoactivity in visible light. The presence of oxidized nitrogen such as Ti–O–N and/or Ti–N–O linkages should appear at 399–400 eV, which was assigned to interstitial N, namely hosted in an interstitial position and directly bound to lattice oxygen [11]. Diwald *et*

al. suggested that interstitial N-doping on TiO₂ might show higher photocatalytic activity than substitutional N-doping under visible light irradiation [12]. In our previous report, we prepared the substitutional and interstitial N-doped TiO₂, respectively. The effect of types of nitrogen-doping in TiO₂ on photocatalytic activity in visible light was discussed [13].

In this work, we designed two-steps doping to prepare a novel N-doped TiO₂ with substitutional and interstitial N impurities simultaneously. To the best of our knowledge, this is the first example demonstrating the synergetic effect of substitutional and interstitial nitrogen in N-doped TiO₂.

II. EXPERIMENTS

A. Catalyst preparation

In a typical experiment, 0.5 g of P25-TiO₂ (Degussa) powder was annealed under NH₃ flow at 600 °C for 3 h to prepare substitutional N-doped TiO₂ [3], which was denoted as N₁-TiO₂. According to our previous report [13], 0.8 g of P25-TiO₂ powder and 1.2 g of urea were mixed with 40 mL ethylene glycol under microwave irradiation to prepare interstitial N-doped TiO₂, which was denoted as N₂-TiO₂. Using N₁-TiO₂ as raw materials, the same microwave synthesis as N₂-TiO₂ was used to prepare a novel N-doped TiO₂ which was denoted as N₁-N₂-TiO₂.

B. Catalyst characterization and photocatalytic test

The crystal structure of samples was characterized by powder X-ray diffraction (XRD) on X-ray diffractome-

* Author to whom correspondence should be addressed. E-mail: cefpeng@scut.edu.cn, FAX: +86-20-87114916

ter (D/max-III A, Japan) using Cu K α radiation and operating at 30 kV/30 mA in the angle range of 5°–80°. The chemical nature of N in TiO₂ was studied using XPS by a Krato Axis Ultra DLD spectrometer with Al K α X-ray ($h\nu=1486.6$ eV) at 15 kV and 150 W. The binding energy was referenced to C1s line at 284.6 eV for calibration. The UV-Vis light absorption spectra were obtained from a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere assembly, using the diffuse reflection method and BaSO₄ as a reference to measure all the samples. Photoluminescence (PL) spectra were measured with a fluorospectrophotometer (SPEX Fluoromax-2) using a Xe lamp as the excitation source at room temperature. Equally weighed powder samples were used for PL measurements. The entrance and exit slit widths were kept the same. The paramagnetic species of nitrogen in the as-synthesized nitrogen-doped TiO₂ photocatalysts were measured on an electron paramagnetic resonance (EPR) spectroscopy using a Bruker A300 spectrometer instrument.

The photocatalytic reaction was conducted in a 200 mL cylindrical glass vessel fixed in a XPA-II photochemical reactor (Nanjing Xujiang Machine-electronic Plant). The filter system comprises a house-made filter mounted on the lamp to eliminate infrared irradiation and a UV filter which can absorb the light of wavelength less than 400 nm. Photocatalyst powder of 20 mg was dispersed in 200 mL methyl orange dye (MO) solution with the concentration of 20 mg/L. The solution was sonicated for 15 min to obtain an optimally dispersed system and then put in a black box for 60 min to reach complete adsorption/desorption equilibrium. Air was blown into the reaction medium at a flow rate of 50 mL/min during the course of the reaction. Further details of photocatalytic reactor and reaction could be found in Refs.[13, 14]. The concentrations of remaining MO were surveillanced by measuring its absorbance A at 465 nm with a Hitachi UV-3010 spectrophotometer. The degradation ratio X of reactant can be calculated by

$$X\% = \frac{A_0 - A}{A_0} \times 100$$

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of P25-TiO₂ and N₁-N₂-TiO₂. All samples show mixed phases of anatase and rutile. However, no nitrogen derived peak is detected in N doped-TiO₂. The reason is that the content of doping nitrogen is low, and possibly nitrogen is well-dispersed at/in the TiO₂ particles. Thus, N doping does not cause the change in crystallite structure of TiO₂, which is consistent with Refs.[6, 15]. The anatase crystal sizes and Brunauer-Emmett-Teller (BET) specific surface areas for N₁-N₂-TiO₂ are 25.8 nm and 44.5 m²/g, respectively, which decrease slightly compared with P25-TiO₂ powder (26.2 nm and 50 m²/g).

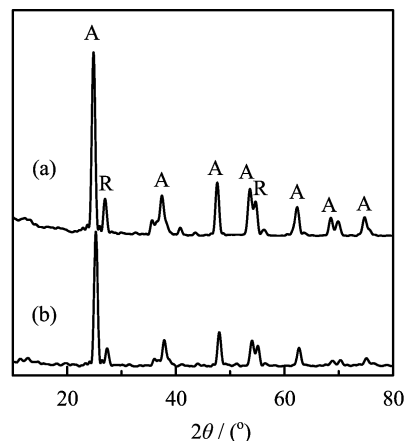


FIG. 1 XRD patterns of (a) N₁-N₂-TiO₂ and (b) P25-TiO₂ catalysts. A was anatase and R was rutile.

Compared with N₁-TiO₂ and N₂-TiO₂ [13], it is revealed that the microstructures of the TiO₂ could be preserved after different N-doped treatments.

Figure 2 shows the XPS spectra of N₁-N₂-TiO₂ samples. Figure 2(a) clearly shows the binding energies of N1s at 398.8 and 400.2 eV for the novel N doped TiO₂. According to our previous report [13], we attributed the N1s peak at 396.5–398.0 eV to the presence of a Ti–N bond resulting from substitution for oxygen sites by nitrogen atoms in the TiO₂ lattice; and the N1s peak at 400.2 eV to a characteristic peak of interstitial N which is in a positive oxidation state ranging from that of typical hyponitrite species (N₂O₂)²⁻ to nitrite (NO²⁻) and nitrate species. As expected, the N₁-N₂-TiO₂ has two peaks of N1s at 398.8 and 400.2 eV, but the peak of N1s at 398.8 eV shifts to higher binding energy compared with N₁-TiO₂ [13]. It was demonstrated that we designed two-steps doping to prepare the N-doped TiO₂ catalyst with substitutional and interstitial N impurities simultaneously.

In general, the Ti 2p_{3/2} and 2p_{1/2} peaks at 458.9 and 464.7 eV which are attributed to the Ti2p peaks of O–Ti–O in TiO₂ [6, 8, 9]. Most of the reports agreed on the lower binding energy of Ti2p in N-TiO₂ [6, 8]. It was interesting that two couples of different Ti peaks are observed for N₁-N₂-TiO₂, as shown in Fig.2(b). Main one pair of Ti 2p_{3/2} and 2p_{1/2} core level peaks appear at 457.4 and 463.0 eV, which can be assigned to Ti2p peaks of Ti–O–N–O in N-TiO₂. The BE of the Ti 2p_{3/2} and 2p_{1/2} peaks shift to the lower energies by 1.5 and 1.7 eV compared with pure TiO₂. Another pair of peaks appear at 456.5 and 461.8 eV, which can be assigned to Ti2p peaks of N–Ti–N or O–Ti–N in N-TiO₂ [13]. The BE of the Ti 2p_{3/2} and 2p_{1/2} peaks shift to the lowest energies by 2.5 and 2.9 eV compared with TiO₂, when Ti⁴⁺ is reduced to Ti³⁺ (Ti 2p_{3/2} and 2p_{1/2} core levels appear at 455.1 and 461.0 eV for TiN) [8–10, 16]. This suggests that the TiO₂ lattice is considerably modified due to nitrogen-doping in our experiment.

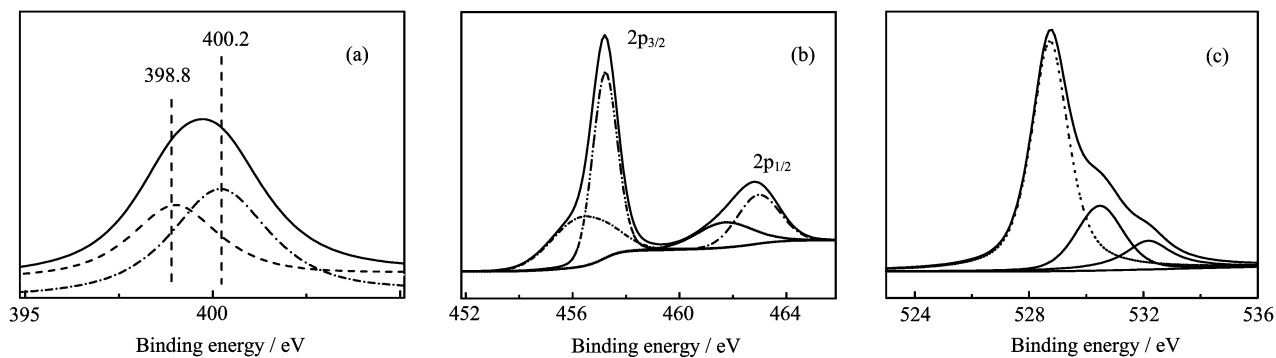


FIG. 2 XPS spectra of (a) N1s, (b) Ti2p, and (c) O1s for the N₁-N₂-TiO₂.

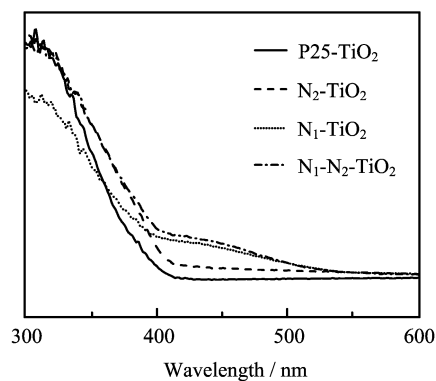


FIG. 3 UV-Vis DRS of TiO₂ and N-TiO₂ catalysts.

In Fig.2(c), O1s core level peaks appear around 528, 530, and 532 eV, indicating the nature of oxygen to be different. O1s peak at 530.3 eV comes from Ti–O–Ti linkages in TiO₂, which is consistent with that of most reported ones [6, 8, 9]. We attribute the O1s peak at 528.7 eV to Ti–O–N–O linkages in N-TiO₂. It is found that O1s peak of nitrogen-doped TiO₂ shifts toward the lower binding energy, which is consistent with that of most reported [8, 9]. In view of O1s peak of –NO and –NO₂ at 533.5 eV [17], we suggest that the appearance of this peak at 532.2 eV is attributed to the presence of the oxygen of NO_x, due to the N interstitially doping into the TiO₂ lattice. It is further supported by N1s XPS.

The diffuse reflectance spectra of samples are shown in Fig.3. As expected, pure TiO₂ exhibits absorption only in the UV region, whereas the optical response of N-TiO₂ is extended into the visible light region, which is the typical absorption feature of the N-TiO₂. Compared to TiO₂, the N₁-TiO₂ enhances the absorption of visible range but lower the UV absorption. The N₂-TiO₂ not only keeps the absorption of UV, but also enhances the absorption of visible range. The N₁-N₂-TiO₂ has the strongest absorption of all samples, maybe it is the synergetic effects of substitutional and interstitial nitrogen-doped TiO₂. The light absorption of N-doped

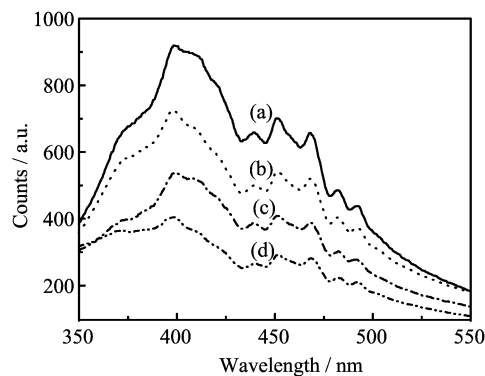


FIG. 4 PL spectra of (a) TiO₂, (b) N₁-TiO₂, (c) N₂-TiO₂, and (d) N₁-N₂-TiO₂.

TiO₂ in the visible light region is of great importance to its practical application since it can be activated even by solar light.

Figure 4 shows the PL spectra of undoped and nitrogen doped TiO₂. The sample quantity used for the measurement was the same (50 mg), and the samples were excited at a wavelength of 300 nm. The spectra show distinct peaks at about 399 and 480 nm. The first emission at 399 nm is attributed to the direct transition from the conduction band to the valence band, whereas the latter at 480 nm is emission signal originating from the charge transfer transition from an oxygen vacancy trapped electron [11]. Interestingly, the intensities of PL spectra for N-doped TiO₂ catalysts show a significant decrease. A trend in the peak intensity has been observed in the following order: TiO₂ > N₁-TiO₂ > N₂-TiO₂ > N₁-N₂-TiO₂. Because the PL emission is the result of radiative recombination of excited electrons and holes, the lower PL intensity of the N-doped sample clearly implies decreased recombination of excited electrons and holes in the N-doped TiO₂. So the N-TiO₂ has the enhanced photocatalytic activity, it is confirmed by photocatalysis experiments.

Figure 5 shows the electron paramagnetic resonance of the N₁-N₂-TiO₂ samples. The paramagnetic N species is observed in N doped TiO₂. The value of g_1 ,

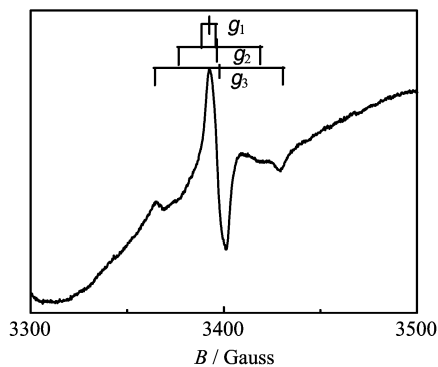


FIG. 5 EPR spectrum of N species in N_1 - N_2 - TiO_2 .

g_2 , and g_3 are 2.006, 2.004, and 2.003, respectively. According to EPR results and theoretical modeling, they are assigned to a species containing a nitrogen atom trapped in TiO_2 lattice or in the bulk of TiO_2 , it is labeled Nb^{\cdot} (NO_2^-) [18]. However, the features of Nb^{\cdot} are unambiguously present in all the spectra reported. A conclusive choice between the two possible sites in TiO_2 structure ("substitutional" with N occupying an O site or "interstitial" with an extra N atom in a lattice cavity stuck to a O^{2-}) was not also totally achieved [18]. But, the paramagnetic species cannot be removed from the solid by thermal treatment (250 °C) and by washing in water. It indicates that it is stable species located in the bulk of the solid.

According to diffuse reflectance UV-Vis spectra, the optical response of TiO_2 was shifted slightly from UV to the visible light region due to the introduction of nitrogen. This implied that N doped TiO_2 might be active under visible light irradiation. The direct decomposition of methyl orange without the presence of photocatalysts was not detected under visible light irradiation in a control experiment.

Figure 6 depicts the degradation of MO in the presence of P25- TiO_2 and N-doped TiO_2 under visible light irradiation. Low photocatalytic activity is observed for P25- TiO_2 under visible light due to their wide band gap. N-doped TiO_2 catalysts have higher photocatalytic activities under visible light, indicating that visible light can generate photon-induced electrons and holes in N-doped TiO_2 . However, the N_2 - TiO_2 prepared by microwave method has a significantly higher photocatalytic activity for MO degradation under visible light than N_1 - TiO_2 . The visible light activity of interstitial N-doped TiO_2 is higher than that of substitutional N-doped TiO_2 , which is in agreement with the reported results [12, 13]. The mixed catalyst of N_1 - TiO_2 and N_2 - TiO_2 (1:1 mass ratio, mechanical compound) has a mean photocatalytic activity of N_1 - TiO_2 and N_2 - TiO_2 , not showing the synergetic effect. But the N_1 - N_2 - TiO_2 with substitutional and interstitial N impurities simultaneously shows the highest photocatalytic activities of all the N-doped TiO_2 under visible light, indicating that

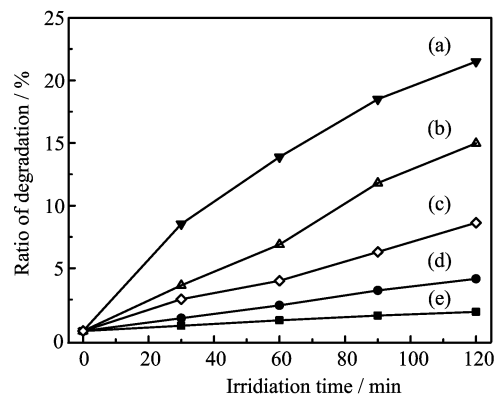


FIG. 6 The photocatalytic decomposition of methyl orange under visible-light irradiation. (a) N_1 - N_2 - TiO_2 , (b) N_2 - TiO_2 , (c) N_1 - TiO_2 and N_2 - TiO_2 (mixed), (d) N_1 - TiO_2 , (e) P25- TiO_2 .

the as-prepared N-doped TiO_2 is not a simple combination of N_1 - TiO_2 and N_2 - TiO_2 . The novel N-doped TiO_2 exhibits the synergetic effect of interstitial N and substitutional N. Further research of photocatalytic mechanism will be progressed later.

IV. CONCLUSION

A novel nitrogen doped TiO_2 (N_1 - N_2 - TiO_2) with substitutional and interstitial N impurities simultaneously was successfully synthesized by a simple method, which were used to decompose MO dye under visible light radiation. The surface states of N-doped TiO_2 were investigated based on XPS spectra of N1s, O1s, and Ti2p. The N_1 - N_2 - TiO_2 showed the highest photocatalytic activities of all the N-doped TiO_2 under visible light, indicating the synergetic effect of interstitial N and substitutional N in N-doped TiO_2 . This study has developed two-steps doping pathway to prepare a novel N-doped TiO_2 with substitutional and interstitial N impurities simultaneously.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.20873044) and the Fundamental Research Funds for the Central Universities (No.2009ZZ0032).

- [1] A. L. Linsebigler, G. Lu, and J. T. Yates, *Chem. Rev.* **95**, 735 (1999).
- [2] A. Fujishima and X. T. Zhang, *C. R. Chim.* **9**, 750 (2006).
- [3] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science* **293**, 269 (2001).

- [4] C. Hu, Y. Lan, J. Qu, X. Hu, and A. Wang, *J. Phys. Chem. B* **110**, 4066 (2006).
- [5] C. Burda, Y. B. Luo, X. B. Chen, A. C. S. Samia, J. Stout, and J. L. Gole, *Nano Lett.* **3**, 1049 (2003).
- [6] M. Sathish, B. Viswanathan, R. P. Viswanath, and C. S. Gopinath, *Chem. Mater.* **17**, 6349 (2005).
- [7] Y. Liu, X. Chen, J. Li, and C. Burda, *Chemosphere* **61**, 11 (2005).
- [8] X. B. Chen and C. Burda, *J. Phys. Chem. B* **108**, 15446 (2004).
- [9] M. S. Wong, H. P. Chou, and T. S. Yang, *Thin Solid Films* **494**, 244 (2006).
- [10] S. Sakthivel, M. Janczarek, and H. Kisch, *J. Phys. Chem. B* **108**, 19384 (2004).
- [11] Y. Cong, J. L. Zhang, F. Chen, and M. Anpo, *J. Phys. Chem. C* **111**, 6976 (2007).
- [12] O. Diwald, T. L. Thompson, T. Zubkov, E. G. Goralski, S. D. Walck, and J. T. Yates, *J. Phys. Chem. B* **108**, 6004 (2004).
- [13] F. Peng, L. F. Cai, H. Yu, H. J. Wang, and J. Yang, *J. Solid State Chem.* **181**, 130 (2008).
- [14] F. Peng, H. J. Wang, H. Yu, and S. H. Chen, *Mater. Res. Bull.* **41**, 2123 (2006).
- [15] H. X. Li, J. X. Li, and Y. I. Huo, *J. Phys. Chem. B* **110**, 1559 (2006).
- [16] T. C. Jagadale, S. P. Takale, and R. S. Sonawane, *J. Phys. Chem. C* **112**, 14595 (2008).
- [17] J. A. Rodriguez, T. Jirsak, J. Dvorak, S. Sambasivan, and D. Fischer, *J. Phys. Chem. B* **104**, 319 (2000).
- [18] S. Livraghi, M. R. Chierotti, and E. Giamello, *J. Phys. Chem. C* **112**, 17244 (2008).