

## ARTICLE

# Synthesis and Characterization of Novel N-doped TiO<sub>2</sub> Photocatalyst with Visible Light Active

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A novel N-doped TiO<sub>2</sub> (N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub>) 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 TiO<sub>2</sub> lattice. The photocatalytic tests indicated that the N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub> showed the highest photocatalytic activities of all the N-doped TiO<sub>2</sub> under visible light, attributing to the synergetic effect of substitutional and interstitial nitrogen of N-doped TiO<sub>2</sub>.

**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, TiO<sub>2</sub> has been widely used as a photocatalyst [1, 2]. However, the photocatalytic activity of TiO<sub>2</sub> 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 TiO<sub>2</sub> photocatalyst has become a hot topic in recent years [3, 4]. Asahi *et al.* reported that the nitrogen-doping improved the photocatalytic reactivity of TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>, respectively. The effect of types of nitrogen-doping in TiO<sub>2</sub> on photocatalytic activity in visible light was discussed [13].

In this work, we designed two-steps doping to prepare a novel N-doped TiO<sub>2</sub> 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 TiO<sub>2</sub>.

## II. EXPERIMENTS

### A. Catalyst preparation

In a typical experiment, 0.5 g of P25-TiO<sub>2</sub> (Degussa) powder was annealed under NH<sub>3</sub> flow at 600 °C for 3 h to prepare substitutional N-doped TiO<sub>2</sub> [3], which was denoted as N<sub>1</sub>-TiO<sub>2</sub>. According to our previous report [13], 0.8 g of P25-TiO<sub>2</sub> powder and 1.2 g of urea were mixed with 40 mL ethylene glycol under microwave irradiation to prepare interstitial N-doped TiO<sub>2</sub>, which was denoted as N<sub>2</sub>-TiO<sub>2</sub>. Using N<sub>1</sub>-TiO<sub>2</sub> as raw materials, the same microwave synthesis as N<sub>2</sub>-TiO<sub>2</sub> was used to prepare a novel N-doped TiO<sub>2</sub> which was denoted as N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub>.

### B. Catalyst characterization and photocatalytic test

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

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ter (D/max-III A, Japan) using Cu K $\alpha$  radiation and operating at 30 kV/30 mA in the angle range of 5°–80°. The chemical nature of N in TiO<sub>2</sub> was studied using XPS by a Krato Axis Ultra DLD spectrometer with Al K $\alpha$  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 BaSO<sub>4</sub> 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 TiO<sub>2</sub> 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-TiO<sub>2</sub> and N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub>. All samples show mixed phases of anatase and rutile. However, no nitrogen derived peak is detected in N doped-TiO<sub>2</sub>. The reason is that the content of doping nitrogen is low, and possibly nitrogen is well-dispersed at/in the TiO<sub>2</sub> particles. Thus, N doping does not cause the change in crystallite structure of TiO<sub>2</sub>, which is consistent with Refs.[6, 15]. The anatase crystal sizes and Brunauer-Emmett-Teller (BET) specific surface areas for N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub> are 25.8 nm and 44.5 m<sup>2</sup>/g, respectively, which decrease slightly compared with P25-TiO<sub>2</sub> powder (26.2 nm and 50 m<sup>2</sup>/g).

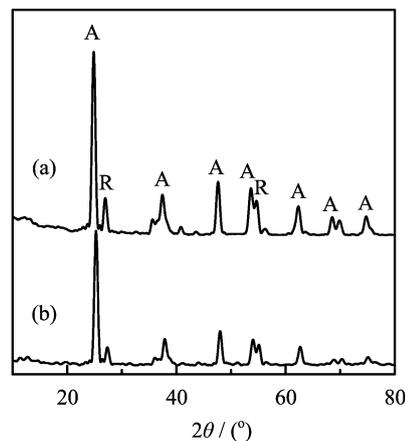


FIG. 1 XRD patterns of (a) N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub> and (b) P25-TiO<sub>2</sub> catalysts. A was anatase and R was rutile.

Compared with N<sub>1</sub>-TiO<sub>2</sub> and N<sub>2</sub>-TiO<sub>2</sub> [13], it is revealed that the microstructures of the TiO<sub>2</sub> could be preserved after different N-doped treatments.

Figure 2 shows the XPS spectra of N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub> samples. Figure 2(a) clearly shows the binding energies of N1s at 398.8 and 400.2 eV for the novel N doped TiO<sub>2</sub>. 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 TiO<sub>2</sub> 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 (N<sub>2</sub>O<sub>2</sub>)<sup>2-</sup> to nitrite (NO<sup>2-</sup>) and nitrate species. As expected, the N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub> 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 N<sub>1</sub>-TiO<sub>2</sub> [13]. It was demonstrated that we designed two-steps doping to prepare the N-doped TiO<sub>2</sub> catalyst with substitutional and interstitial N impurities simultaneously.

In general, the Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks at 458.9 and 464.7 eV which are attributed to the Ti2p peaks of O–Ti–O in TiO<sub>2</sub> [6, 8, 9]. Most of the reports agreed on the lower binding energy of Ti2p in N-TiO<sub>2</sub> [6, 8]. It was interesting that two couples of different Ti peaks are observed for N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub>, as shown in Fig.2(b). Main one pair of Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> 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-TiO<sub>2</sub>. The BE of the Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks shift to the lower energies by 1.5 and 1.7 eV compared with pure TiO<sub>2</sub>. 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-TiO<sub>2</sub> [13]. The BE of the Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks shift to the lowest energies by 2.5 and 2.9 eV compared with TiO<sub>2</sub>, when Ti<sup>4+</sup> is reduced to Ti<sup>3+</sup> (Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> core levels appear at 455.1 and 461.0 eV for TiN) [8–10, 16]. This suggests that the TiO<sub>2</sub> lattice is considerably modified due to nitrogen-doping in our experiment.

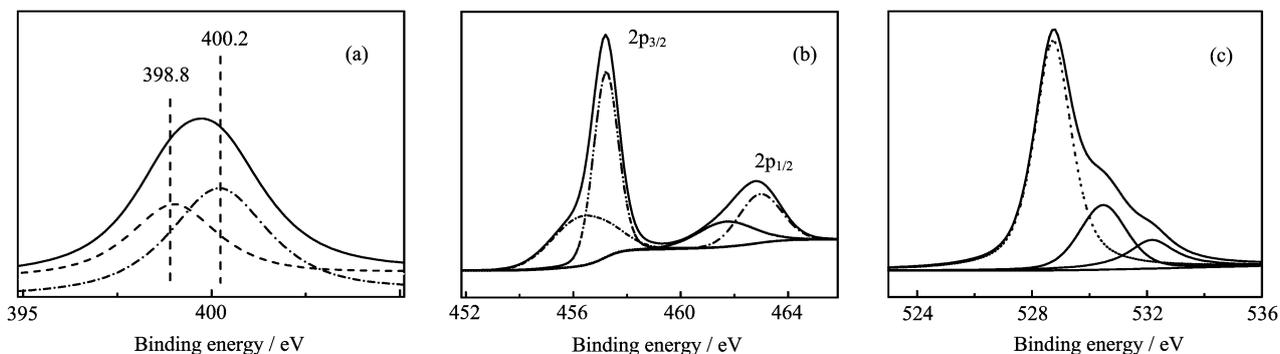


FIG. 2 XPS spectra of (a) N1s, (b) Ti2p, and (c) O1s for the N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub>.

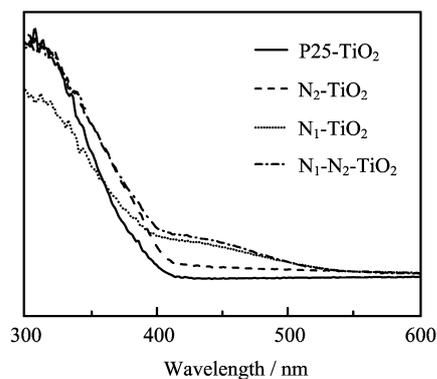


FIG. 3 UV-Vis DRS of TiO<sub>2</sub> and N-TiO<sub>2</sub> catalysts.

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 TiO<sub>2</sub>, 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-TiO<sub>2</sub>. It is found that O1s peak of nitrogen-doped TiO<sub>2</sub> shifts toward the lower binding energy, which is consistent with that of most reported [8, 9]. In view of O1s peak of –NO and –NO<sub>2</sub> 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<sub>x</sub>, due to the N interstitially doping into the TiO<sub>2</sub> lattice. It is further supported by N1s XPS.

The diffuse reflectance spectra of samples are shown in Fig.3. As expected, pure TiO<sub>2</sub> exhibits absorption only in the UV region, whereas the optical response of N-TiO<sub>2</sub> is extended into the visible light region, which is the typical absorption feature of the N-TiO<sub>2</sub>. Compared to TiO<sub>2</sub>, the N<sub>1</sub>-TiO<sub>2</sub> enhances the absorption of visible range but lower the UV absorption. The N<sub>2</sub>-TiO<sub>2</sub> not only keeps the absorption of UV, but also enhances the absorption of visible range. The N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub> has the strongest absorption of all samples, maybe it is the synergetic effects of substitutional and interstitial nitrogen-doped TiO<sub>2</sub>. The light absorption of N-doped

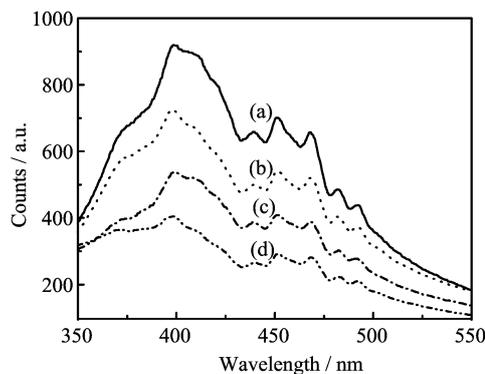


FIG. 4 PL spectra of (a) TiO<sub>2</sub>, (b) N<sub>1</sub>-TiO<sub>2</sub>, (c) N<sub>2</sub>-TiO<sub>2</sub>, and (d) N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub>.

TiO<sub>2</sub> 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 TiO<sub>2</sub>. 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 TiO<sub>2</sub> catalysts show a significant decrease. A trend in the peak intensity has been observed in the following order: TiO<sub>2</sub> > N<sub>1</sub>-TiO<sub>2</sub> > N<sub>2</sub>-TiO<sub>2</sub> > N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub>. 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 TiO<sub>2</sub>. So the N-TiO<sub>2</sub> has the enhanced photocatalytic activity, it is confirmed by photocatalysis experiments.

Figure 5 shows the electron paramagnetic resonance of the N<sub>1</sub>-N<sub>2</sub>-TiO<sub>2</sub> samples. The paramagnetic N species is observed in N doped TiO<sub>2</sub>. The value of  $g_1$ ,

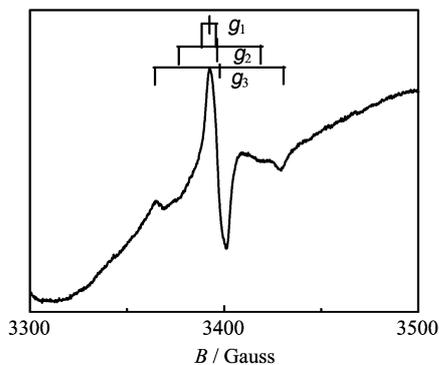


FIG. 5 EPR spectrum of N species in  $N_1$ - $N_2$ - $TiO_2$ .

$g_2$ , 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

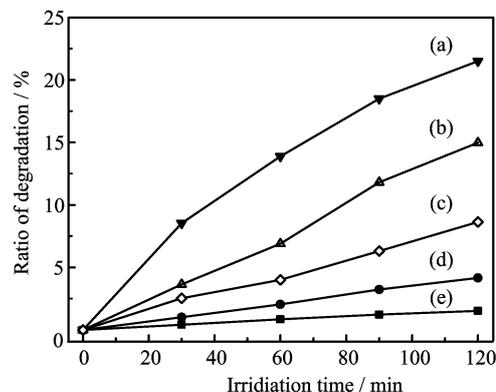


FIG. 6 The photocatalytic decomposition of methyl orange under visible-light irradiation. (a)  $N_1$ - $N_2$ - $TiO_2$ , (b)  $N_2$ - $TiO_2$ , (c)  $N_1$ - $TiO_2$  and  $N_2$ - $TiO_2$  (mixed), (d)  $N_1$ - $TiO_2$ , (e) P25- $TiO_2$ .

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

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