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The Comparison of Property and Visible Light Activity between Bulk and Surface Doped N-TiO_2 Prepared by Sol-gel and N_2-plasma Treatment

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A modified sol-gel method and N_2-plasma treatment were used to prepare bulk and surface doped N-TiO_2, respectively. XRD, TEM, UV-vis spectroscopy, N_2 adsorption, Elemental Analyzer, Photoluminescence, and XP spectra were used to characterize the prepared TiO_2 samples. The N doping did not change the phase composition and particle sizes of TiO_2 samples, but increased the visible light absorption. The photocatalytic activities were tested in the degradation of an aqueous solution of a reactive dyestuff, methylene blue, under visible light. The photocatalytic activity of surface doped N-TiO_2 prepared by N_2-plasma was much higher than that of bulk doped N-TiO_2 prepared by sol-gel method. The possible mechanism for the photocatalysis was proposed.

Key Words : TiO_2, Photocatalysis, Bulk doping, Surface doping, N_2-plasma

Introduction

Photocatalysis has been widely used in energy conversion, air purification, and organic contaminant mineralization.[1,2] Titanium dioxide (TiO_2), a kind of typical photocatalyst, has attracted extensive interest because of its high activity, low cost, and long-time stability. However, TiO_2 only becomes active under irradiation with ultraviolet (UV) light. Thus, many efforts have been devoted recently to improve the optical response of TiO_2 in the visible region.

Among the TiO_2 modification methods, N doping is one of the most effective. In 2001, Asahi *et al.*[3] prepared nitrogen doped TiO_2 films by sputtering TiO_2 in a N_2/Ar gas mixture, and concluded that the doped N atoms narrowed the band gap of TiO_2 by mixing N 2p and O 2p states, therefore demonstrating the activity for the decomposition of acetone and methylene blue. Since then, N-doping has become a hot topic and been widely investigated. Heating TiO_2 powders in N_2 and/or NH_3 at elevated temperatures is the conventional method to prepare nitrogen-doped TiO_2.[3] Besides the energy waste, the treatment at such high temperature usually results in the low surface area due to grain growth, which would decrease the number of photoactive sites. Therefore, new strategies for preparing nitrogen-doped TiO_2, such as sputtering,[4] sol-gel,[5] ion implantation,[6] pulsed laser deposition,[7] hydrothermal synthesis,[8] and plasma treatment[9] have been proposed more recently.

Non-thermal plasma is composed of atoms, ions and electrons, which are much more reactive than their molecule precursors. Plasma is able to initiate a lot of reactions, which take place efficiently only at elevated temperatures and high pressures, under mild conditions. So far, some literatures on preparation of N doped TiO_2 by plasma treatment have been reported.[9-12] Yamada *et al.*[10,11] investigated the photocatalytic activity of TiO_2 thin films prepared by plasma treatment using N_2 as nitrogen source. They suggested that the substitutional N-doping contributed to the band-gap narrowing, therefore absorbing visible light and demonstrating the photocatalytic activity. Abe *et al.*[12] prepared N doped TiO_2 by NH_3(10%)/Ar plasma. The influence of the NH_3/Ar gas pressures (50, 300 and 1000 Pa) on the physical and photocatalytic property of the powder was investigated.

It is known that plasma treatment is a kind of surface modification. Thus, it is deduced that the doping N atoms is mainly in the surface layer of TiO_2 samples prepared by plasma treatment. However, for the sol-gel method, the nitrogen source and titanium source mix sufficiently during the preparation process, leading to the N atoms doped mainly in the bulk TiO_2. Therefore, there are two N doping states existed in the N-doped TiO_2, bulk doping and surface doping. Such different doping state maybe influence the property and visible light activity of the prepared samples. Whereas, few literature on the comparison of property and visible light activity between bulk and surface doped N-TiO_2 was reported. In this work, a modified sol-gel method and N_2-plasma treatment method were used to prepare bulk and surface doped N-TiO_2, respectively. The structural and optical properties of prepared N doped TiO_2 were investigated. The photocatalytic performances of prepared samples were evaluated in the degradation of methylene blue under visible light.

Experimental

Preparation and Characterization. A modified sol-gel method was used to synthesize bulk doped N-TiO_2 (mole ratio of 1:20:1:1:1 for TTIP:EtOH:HNO_3:H_2O:urea). First, TTIP was dissolved in EtOH under stirring for 30 min to form solution A. EtOH was mixed with H_2O which contained HNO_3 to form solution B. After mixing both solutions, precipitation readily occurred. Then the urea was added dropwised. The obtained homogeneous transparent solution was stirred at 5 ºC for 30 min and dried at 100 ºC for 3 h. The powder was collected and calcined at 400 ºC for 3 h. The obtained N-doped TiO_2 was denoted as N1-TiO_2. For comparison, U-TiO_2 was prepared by the same procedure above but in the absence of urea.

The surface doped N-TiO_2 was conducted in a dielectric barrier discharge (DBD) reactor, consisting of a quartz tube and two electrodes. The high-voltage electrode was a stainless-steel rod (2.5 mm), which was installed in the axis of the quartz tube and connected to a high voltage supply. The grounding electrode was an aluminum foil which was wrapped around the quartz tube. For each run, 0.4 g U-TiO_2 was charged into the quartz tube. At a constant N_2 flow (20 mL min^{-1}), a high voltage of 9-11 kV was supplied by a plasma generator at an overall power input of 50 V × 0.4 A. The discharge frequency was fixed at 10 kHz, and the discharge was kept for 10 min. After discharge, the reactor was cooled down to room temperature. The obtained TiO_2 sample was denoted as N2-TiO_2.

XRD patterns of the prepared TiO_2 samples were recorded on a Rigaku D/max-2400 instrument using Cu-Kα radiation (λ = 1.54 Å). TEM images were measured using a Philips Tecnai G220 model microscope. UV-vis spectroscopy measurement was carried out on a JASCO V-550 model UV-vis spectrophotometer, using $BaSO_4$ as the reflectance sample. Doping N content in the bulk was analyzed by using Elemental Analyzer (vario MACRO cube). XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al Kα radiation as the exciting source. The binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. Nitrogen adsorption was measured at −196 ºC on a Micromeritics 2010 analyzer. All the samples were degassed at 393 K before the measurement. BET Surface area (S_{BET}) was calculated according to the adsorption isotherm. Photoluminescence (PL) spectra were measured at room temperature with a fluorospectrophotometer (FP-6300) using an Xe lamp as excitation source.

Photocatalytic Reaction. Methylene blue (MB) was selected as model compound to evaluate the photocatalytic performance of the prepared TiO_2 particles in an aqueous solution under visible light irradiation. 0.1 g TiO_2 powders were dispersed in 100 mL aqueous solution of MB (initial concentration C_0 = 50 ppm) in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor, and stirred for 30 min in darkness to achieve the adsorption equilibrium. The concentration of MB at this point was considered as the absorption equilibrium concentration $C_{0'}$. The adsorption capacity of a catalyst to MB was defined by the adsorption amount of MB on the photocatalyst (C_0-$C_{0'}$). In the photoreaction under visible light irradiation, the suspension was exposed to a 110-W high-pressure sodium lamp with main emission in the range of 400-800 nm, and air was bubbled at 130 mL/min through the solution. The UV light portion of sodium lamp was filtered by 0.5 M $NaNO_2$ solution.[13] All runs were conducted at ambient pressure and 30 ºC. At given time intervals, 4 mL suspension was taken and immediately centrifuged to separate the liquid samples from the solid catalyst. The concentrations of MB before and after reaction were measured by means of a UV-vis spectrophotometer at a wavelength of 665 nm. The percentage of degradation $D\%$ was determined as follows:

$$D\% = \frac{A_0 - A}{A_0} \times 100\% \qquad (1)$$

Where A_0 and A are the absorbances of the liquid sample before and after degradation, respectively.

Results and Discussion

It is reported that the phase composition and particle size of TiO_2 have significant influence on its photocatalytic activity.[2] The XRD patterns of the U-TiO_2, N1-TiO_2 and N2-TiO_2 (Fig. 1) indicated that all TiO_2 samples are pure anatase phase. The particle sizes which calculated by their XRD patterns according to the Debye-Scherrer equation are 24.5, 25.1, and 24.3 nm for U-TiO_2, N1-TiO_2, and N2-TiO_2. This result indicates that no remarkable changes is observed in particle sizes.

Figure 2 shows the representative TEM images of N1-TiO_2 (left) and N2-TiO_2 (right). The prepared N doped TiO_2 samples exhibited the small particle sizes around 20-30 nm, which is consistent with the XRD result. Besides, it is shown that N1-TiO_2 exhibited a much narrower particle size distribution compared with that of N2-TiO_2. This indicated that bulk doping of TiO_2 is favorable for the formation narrow particle size distribution.

Up to date, the mechanism of the enhancement by N-doping is still controversial. Asahi *et al.*[3] concluded that the doped N atoms narrowed the band gap of TiO_2 by mixing N 2p and O 2p states, therefore demonstrating the activity. Irie *et al.*[14] argued that the isolated narrow band located above the valence band is responsible for the visible light response. Lee *et al.*[15] suggested that substitutional N-doping would

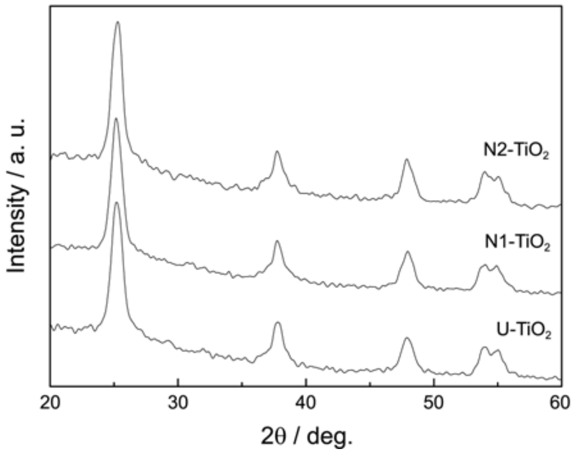

Figure 1. XRD patterns of U-TiO_2 and prepared N-doped TiO_2 samples.

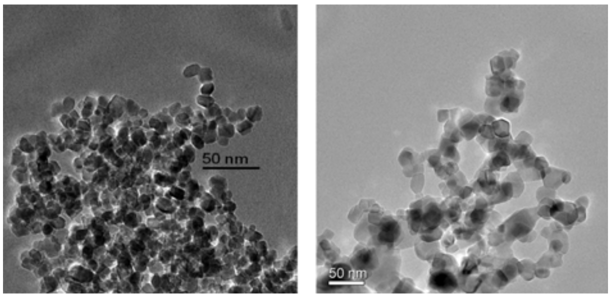

Figure 2. TEM images of N1-TiO_2 (left) and N2-TiO_2 (right).

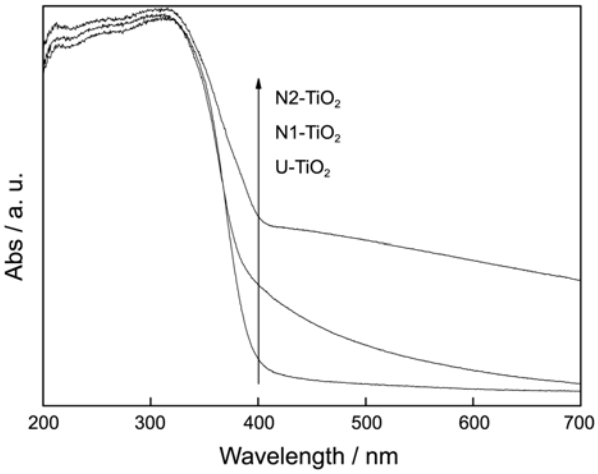

Figure 3. UV-vis spectra of U-TiO_2 and prepared N-doped TiO_2 samples.

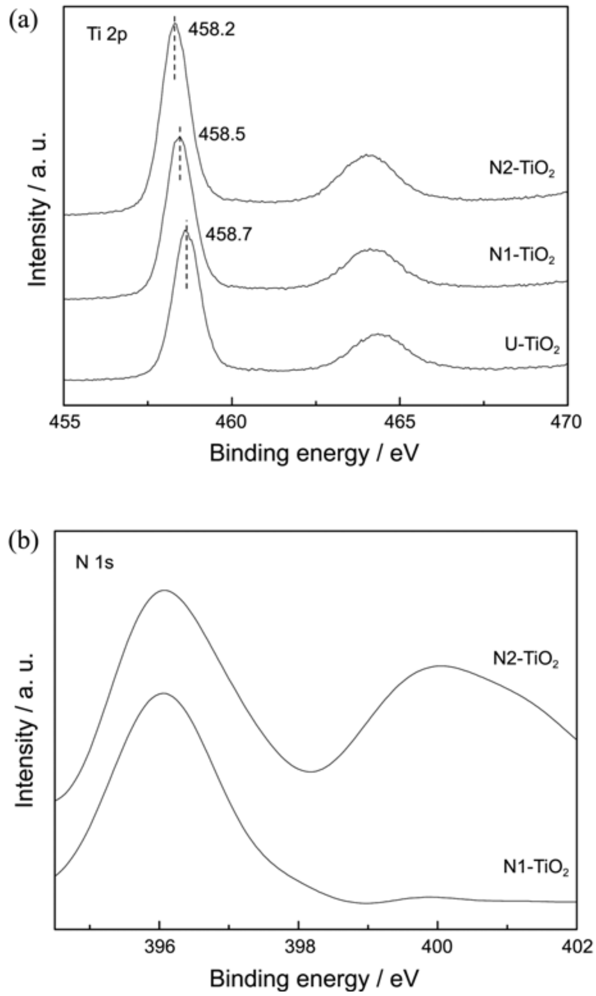

Figure 4. XP spectra of U-TiO_2 and N-doped TiO_2 samples in the region of Ti 2p (a) and N 1s (b).

narrow the band gap by the coupling of the O 2p and N 2p orbitals, while interstitial N-doping would create an additional defect state between the conduction band and valence band. The UV-vis diffuse reflectance spectra of prepared samples are shown in Figure 3. Compared with U-TiO_2, obvious shifts of the absorption band into the visible light region were observed for N1-TiO_2 and N2-TiO_2. However, the spectra in the visible region of prepared N-doped TiO_2 samples are obvious different, which is probably due to the different doping N state. In the spectrum of N1-TiO_2, the obvious absorption in 400-550 nm is observed, which is a typical absorption region for N doped TiO_2 materials. This typical absorption is due to the electronic transition from the isolated N 2p level, which is formed by incorporation of nitrogen atoms into the TiO_2 lattice, to the conduction band.[16] This is consistent with the result of Irie.[14] However, in the spectrum of N2-TiO_2, distinct shift of the absorption band into the visible light region were observed. The band-gap energies of TiO_2 samples which calculated according to the method of Oregan and Gratzel[17] indicate that the band-gap energies of U-TiO_2, N1-TiO_2, and N2-TiO_2 are 3.1, 3.1, and 2.7 eV. This indicated that the band gap of N2-TiO_2 was narrowed by N doping which is agreement with the result of Asahi.[3] Therefore, it is concluded that the doping N state can be influenced by the preparation method. According to the result of Lee,[15] the substitutional N-doping existed in the surface doped N2-TiO_2, whereas interstitial N-doping existed in the bulk doped N1-TiO_2. Besides, the distinct absorption in the whole visible light region is observed in the spectra of N2-TiO_2. Huang *et al.*[18] prepared the visible light responsive TiO_2 by nitrogen-plasma surface treatment, and found the similar broad absorption in visible light region. They suggested that such broad absorption is attributed to the presence of Ti^{3+}, which might be formed by plasma treatment.

XPS is an effective surface analysis technique for characterizing elemental composition and chemical states. Figure 4 shows the XP spectra of prepared samples in the region of Ti 2p (A) and N 1s (B). Compared with the spectra of U-TiO_2, slight shifts to lower binding energies were observed for N-doped TiO_2 in the Ti 2p region (Fig. 4(a)). It is known that the binding energy of the element is influenced by its electron density. A decrease in binding energy implies an increase of the electron density. Therefore, This shift is probably attributed to the change of chemical environment after N doping.[19] The electrons of N atoms may be partially transferred from N to Ti, due to the higher electronegativity of oxygen, leading to increased electron densities on Ti atoms. Besides, compared with N1-TiO_2, more shift to lower

Table 1. Summary of physical properties of U-TiO_2 and prepared N-doped TiO_2 samples

Sample	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Central pore size (nm)	$^aN_{bulk}$ (at. %)	$^bN_{surface}$ (at. %)	$N_{surface}/N_{bulk}$	(O+N)/Ti
U-TiO_2	71	0.12	3.5	0	0	-	1.99
N1-TiO_2	67	0.11	3.6	0.69	0.77	1.1	1.95
N2-TiO_2	70	0.12	3.4	0.66	1.90	2.8	1.85

$^{a,b}N_{bulk}$ and $N_{surface}$ which present the atom percentage of doping N in bulk and surface layer are obtained by the results of Elemental Analyzer and XPS measurement, respectively.

binding energy was observed for N2-TiO_2 (Fig. 4(a)). This is probably due to the presence of Ti ion with low valence (Ti^{3+}), which exhibit the higher electron density.

In Figure 4(b), the peaks around 396 and 400 eV are observed in N2-TiO_2 whereas only the peak around 396 eV is observed in N1-TiO_2. According to the previous literatures,[10,11] they are attributed to the formation of lattice-nitrogen and other surface N species such as N-N and N-O bond. The surface elemental compositions of U-TiO_2 and prepared N-doped TiO_2 samples obtained from XP spectra and Elemental Analyzer were summarized in Table 1. No obvious difference in N_{bulk} is shown between N1-TiO_2 and N2-TiO_2 samples, indicating the total doping N content of two samples is almost same. The $N_{surface}/N_{bulk}$ ratio of N1-TiO_2 is 1.1, indicating the distribution of doping N is almost uniform in the whole sample. However, for N2-TiO_2, the $N_{surface}/N_{bulk}$ ratio is 2.8. This indicates the doping N atoms in N2-TiO_2 sample existed mainly in the surface layer. Besides, the (O+N)/Ti ratio of U-TiO_2 is 1.99. This value decreased after N doping indicating the presence of oxygen vacancies in prepared N doped TiO_2. The (O+N)/Ti ratio of N2-TiO_2 is much lower than that of N1-TiO_2, which indicate more oxygen vacancies were formed by N_2-plasma treatment.

The adsorption of MB on TiO_2-based catalysts was measured by the equilibrium adsorption capacity. No obvious difference in the adsorption capacity was shown between N1-TiO_2 and U-TiO_2, whereas the adsorption capacity of N2-TiO_2 decreased markedly (Fig. 5). The BET specific surface area (S_{BET}), pore volume, and central pore size are listed in Table 1. Compared with U-TiO_2, no obvious decrease in S_{BET}, pore volume, and central pore size are shown for the N-doped TiO_2 samples, excluding its influence on the adsorption capacity. Therefore, it is possibly that such decreased adsorption capacity is attributed to the coverage of TiO_2 surface by excess surface N species, leading to the reduced surface sites for adsorbing MB.

PL emission spectra are used to determine the efficiency of trapping, migration, and transfer of a charge carrier, and to understand the fate of electron-hole pairs in semiconductors.[20] Figure 6 shows the PL spectra of U-TiO_2 and N-doped TiO_2 samples, using excitation at 300 nm. It is shown that the PL intensities increased in the order: N1-TiO_2 < N2-TiO_2 < U-TiO_2. This phenomena may result from the photoluminescence quenching after N doping. It is known that most of the electrons and holes recombine within a few nanoseconds in the absence of scavengers. If scavengers or surface defects (doping N and oxygen vacancy) are present to trap the electrons or holes, the electron-hole recombination can be suppressed, leading to an enhancement of the subsequent photocatalytic reactions.[21] Therefore, it is concluded that the electron-hole recombination is restrained by N doping.

The photocatalytic activities of U-TiO_2 and prepared N-doped TiO_2 samples under visible light are shown in Figure 7. It is shown that U-TiO_2 exhibited no activity. After N doping, obvious improvement in photocatalytic activities were observed for N1-TiO_2 and N2-TiO_2. Since no obvious changes were observed in phase compositions and particle sizes between U-TiO_2 and prepared N-doped TiO_2 samples, the enhanced photocatalytic activity must result from the

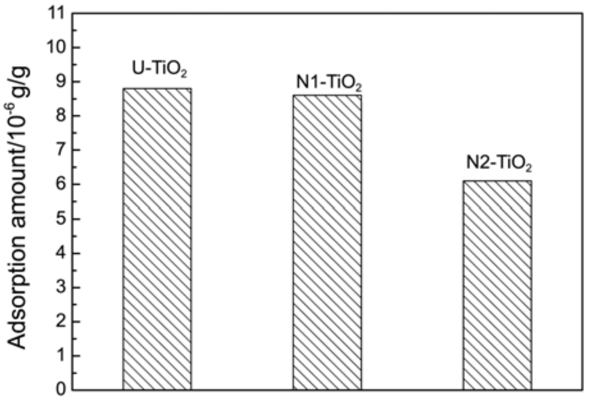

Figure 5. Adsorption capacity of MB on U-TiO_2 and N-doped TiO_2 samples.

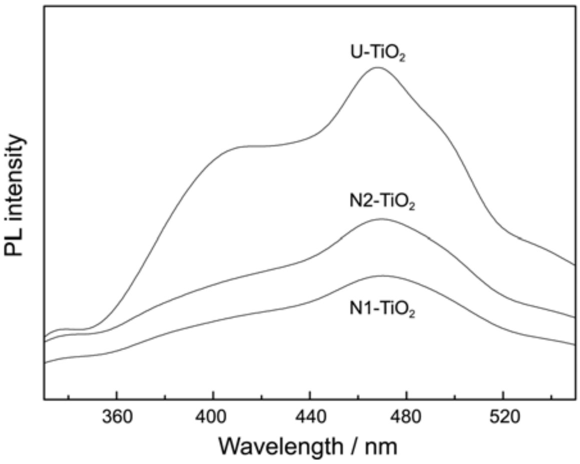

Figure 6. PL spectra of U-TiO_2 and N-doped TiO_2 samples.

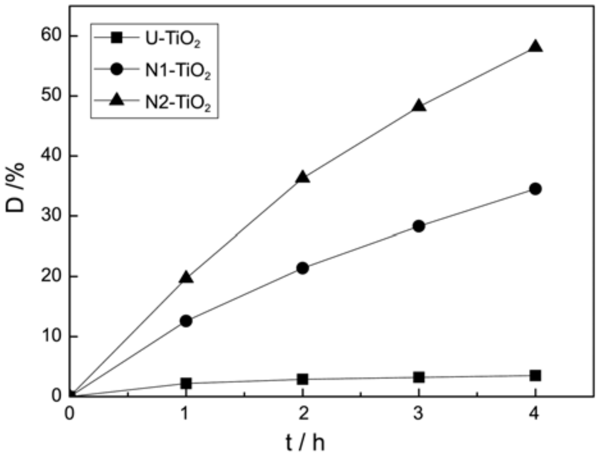

Figure 7. Photocatalytic performances of U-TiO$_2$ and prepared N-doped TiO$_2$ samples in the degradation MB under visible light irradiation.

doping of nitrogen in TiO$_2$, which gave rise to the enhanced absorption in the visible region. Besides, N2-TiO$_2$ showed much higher activity than that of N1-TiO$_2$. This may be due to the following reasons. Firstly, the stronger absorption in visible light region of N2-TiO$_2$ caused the visible light utilization more effectively, thus leading to the much higher activity than that of N1-TiO$_2$. Secondly, compared with N1-TiO$_2$, much more doping N in N2-TiO$_2$ existed on the surface layer (Table 1). Feng *et al.*[22] prepared N-doped TiO$_2$ by heating TiO$_2$ powders in NH$_3$ at elevated temperatures, and concluded that the oxygen vacancy ($V_o^{\bullet}$) accompanied with doping N in the surface layer was the surface active site for the visible light photoactivity. In this investigation, the doping N content in the surface layer and oxygen vacancy content of N2-TiO$_2$ were much higher than that of N1-TiO$_2$. This probably caused that more surface active sites were formed in N2-TiO$_2$, leading to its higher photocatalytic activity.

Conclusion

The bulk and surface doped N-TiO$_2$ were prepared by a modified sol-gel method and N$_2$-plasma treatment. The N doping did not change the phase composition and particle sizes of TiO$_2$ samples, but increased the visible light absorption. The doping N states were influenced by the preparation method. The substitutional N-doping existed in the surface doped N2-TiO$_2$, whereas interstitial N-doping existed in the bulk doped N1-TiO$_2$. The photocatalytic activity of surface doped N2-TiO$_2$ prepared by N$_2$-plasma was much higher than that of bulk doped N1-TiO$_2$ prepared by sol-gel method. This is probably due to that the doping N content in the surface layer and oxygen vacancies content of N2-TiO$_2$ were much higher than that of N1-TiO$_2$, which caused more surface active sites formed in N2-TiO$_2$, leading to its higher photocatalytic activity.

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