

The Synergistic Effect of Nitrogen and Ni₂O₃ over TiO₂ Photocatalyst in the Degradation of 2,4,6-Trichlorophenol Under Visible Light

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The composite photocatalyst, N-TiO₂ loaded with Ni₂O₃, was prepared by N₂ plasma treatment. X-ray diffraction, X-ray fluorescence, N₂ adsorption, UV-vis spectroscopy, photoluminescence, and X-ray photoelectron spectroscopy were used to characterize the prepared TiO₂ samples. The results indicated that the band gap energy was decreased obviously by nitrogen doping, whereas loading of Ni₂O₃ did not influence the band gap and visible light absorption. The photocatalytic activities were tested in the degradation of 2,4,6-trichlorophenol (TCP) under visible light. The photocatalytic activity and stability of composite photocatalyst were much higher than that of catalyst modified with nitrogen or Ni₂O₃ alone. The synergistic effect of doping nitrogen and Ni₂O₃ over TiO₂ was investigated.

Key Words : TiO₂, TCP, Synergistic effect, Ni₂O₃, Stability

Introduction

The use of TiO₂ semiconductor photocatalyst to destroy organic compounds in contaminated air and water has been extensively studied in the last few years. Generally speaking, during irradiation of TiO₂ with ultraviolet (UV) light, a UV photon is absorbed by a TiO₂ particle, an electron (e⁻)-hole (h⁺) pair is generated. The e⁻ and h⁺ may migrate to the surface of the photocatalyst particle and react with adsorbed reactants resulting in the desired process, or they may undergo undesired recombination.¹ However, TiO₂ can be activated only by UV irradiation, the amount of which corresponds to only 3% of total solar energy, for generation of photoexcited e⁻ and positive h⁺.² Moreover, a large proportion of them recombine with each other without being utilized in chemical reactions. Thus, it is highly desirable to shift the absorption edge of TiO₂ to the visible-light region, and prevent recombination in order to make efficient use of the photoexcitation.

In the past decades, many efforts have been made to shift the absorption edge of TiO₂ to the visible-light region. It has been reported that TiO₂ doped with transition metals can absorb visible light.^{3,4} However, the metal cation dopants often serve as recombination centers for the photogenerated electron-hole pairs, leading to a decreased activity.⁵ Recently, the substitution of non-metal atoms, such as nitrogen,⁶ sulfur,⁷ phosphorous,⁸ iodine,⁹ and boron,¹⁰ for oxygen in the lattice of TiO₂ was reported to enhance the catalytic activity of TiO₂ under visible light. But the synthesis of nonmetal-doped TiO₂ materials is much more difficult, because the lattice exchange requires high temperature and complicated procedures. More recently, much interest has been focused on the surface modification of TiO₂ with organic dyes for the construction of dye-sensitized photocatalytic systems under visible light irradiation.¹¹ Since the dye molecules are gene-

rally absorbed on rather than chemically bonded to the surface of TiO₂, a gradual decrease in photocatalytic activity has been observed. To increase the efficiency, the e⁻/h⁺ recombination rate needs to be reduced. Many efforts have been made in this direction. In general, there are three ways to achieve the separation of e⁻ and h⁺. One is to modify TiO₂ by surface deposition of noble metal clusters.¹² The second is to couple TiO₂ with other semiconductors which can trap the photogenerated e⁻ or h⁺.¹³ The third alternative way is to introduce defects into the TiO₂ lattice by doping with transition metal ions, e.g. Fe³⁺ cations.¹⁴

Recently, ternary systems M, M'-TiO₂ (M, M' = metals and non-metals) for use as photocatalyst has been widely investigated. Sakatani *et al.*¹⁵ reported that the N and La co-doped TiO₂ photocatalyst which prepared by means of polymerized method could degrade acetaldehyde under visible light irradiation. Zhao *et al.*¹⁶ reported that the spectral response and photocatalytic efficiency could be improved by co-doping with nonmetal boron and the metal oxide Ni₂O₃. They suggested that incorporation of B into TiO₂ could extend the spectral response to the visible region and that the photocatalytic activity was greatly enhanced when it was further loaded with Ni₂O₃. Wei *et al.*¹⁷ reported the preparation, characterization and photocatalytic activities of boron and cerium co-doped TiO₂ and pointed out that the photocatalytic activity of B-Ce codoped titania was much higher than that of P25.

Chlorophenols are deadly toxic compounds that present in waste water mainly arise from chemical intermediates or by products in petrochemical, paper making, plastic, pesticidal, and water disinfection. Moreover, chlorophenol is one of the most vulnerable water pollutants, which causes serious damage to the vital organs of human beings.^{18,19} Thus, the removal of the chlorophenols from the waste water is highly imperative. It is widely accepted that N doping was one of

the most effective method to improve the visible light absorption.⁶ Loading of Ni₂O₃ was proved to facilitate the excited electron transfer and hence suppress efficiently the recombination of photogenerated electron-hole.²⁰ Therefore, in this work, the composite photocatalyst, N-TiO₂ loaded with Ni₂O₃, was prepared by N₂ plasma treatment. The photocatalytic performance was evaluated in the degradation of TCP under visible light. The synergistic effect of doping nitrogen and Ni₂O₃ over TiO₂ was investigated.

Experimental

Preparation and Characterization. In a typical experiment, 0.1 mol of titanium isopropoxide was dissolved in 100 mL of anhydrous ethanol to form solution 1. A certain amount of nickelous nitrate (molar ratio Ni/Ti = 0.02) were dissolved in a mixture of 40 mL of deionized water adjusted to pH 2 with nitric acid and 60 mL of ethanol to prepare solution 2. Then, the solution 1 was added dropwise into the solution 2 within 60 min under vigorous stirring at room temperature to form the sol, followed by stirring continuously for 5 h and aging for 3 d at room temperature to prepare the gel. The obtained gel was dried for 10 h at 80 °C, followed by milling and annealing at 500 °C for 2 h to remove the residual organic compounds (at a rate of 5 °C/min). The obtained product was denoted as Ni₂O₃/TiO₂. For comparison, neat TiO₂ was prepared following the same procedure as in the synthesis of Ni₂O₃/TiO₂ but in the absence of nickelous nitrate.

The N doping 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 prepared Ni₂O₃/TiO₂ was charged into the quartz tube. At a constant N₂ flow (50 mL min⁻¹), a high voltage of 10 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 6 min. After discharge, the reactor was cooled down to room temperature. The obtained material was denoted as Ni₂O₃/N-TiO₂. When neat TiO₂ was used to replace Ni₂O₃/TiO₂ following the same procedure as in the synthesis of Ni₂O₃/N-TiO₂, the product is denoted as N-TiO₂. The mechanical mixing sample, Ni₂O₃-N-TiO₂, was obtained for comparison by mixing the prepared N-TiO₂ and commercial Ni₂O₃ with the same Ni/Ti ratio to Ni₂O₃/N-TiO₂.

XRD patterns of the prepared TiO₂ samples were recorded on a Rigaku D/max-2400 instrument using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$). Quantitative X-ray fluorescence analysis (XRF) was performed by using an X-ray fluorescence spectrometer (SXF-1200 analyzer). UV-vis spectroscopy measurement was carried out on a Jasco V-550 spectrophotometer, using BaSO₄ as the reference sample. The Brunauer-Emmett-Teller (BET)-specific surface areas (S_{BET}) of the samples were

determined through nitrogen adsorption at 77 K (Micromeritics ASAP 2010). All the samples were degassed at 393 K before the measurement. Photoluminescence (PL) spectra were measured at room temperature with a fluorospectrophotometer (FP-6300) using an Xe lamp as excitation source. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al K α 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.

Photocatalytic Reaction. Suspensions were prepared in deionised water by mixing TiO₂ catalyst with appropriate solutions of TCP. In a typical procedure, 0.1 g TiO₂ powders were dispersed in 100 mL solution of TCP (initial concentration $C_0 = 60 \times 10^{-6} \text{ g}\cdot\text{mL}^{-1}$) 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 TCP at this point was considered as the adsorption equilibrium concentration C_0' . The adsorption capacity of a catalyst to TCP was defined by the adsorption amount of TCP 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 NaNO₂ solution. All runs were conducted at ambient pressure and 30 °C. The conversion of TCP was determined using an Agilent 1100 series HPLC operated in isocratic mode under the following conditions: methanol-water (80%:20%); flow rate 1 mL·min⁻¹; temperature 25 °C; Column Phenomenex Luna 10 μ Phenyl-Hexyl, 4.6 mm × 250 mm; detector UV at 254 nm; injection volume 5 μ L.

Results and Discussion

The XRD patterns of neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂ are shown in Figure 1. All the samples were anatase phase. There was no observable structural difference between neat and modified TiO₂ samples. The lattice parameters of the catalysts were measured using (1 0 1) and (2 0 0) in anatase crystal planes by using equations:²¹

$$d_{(hkl)} = \frac{\lambda}{2\sin\theta} \quad (1)$$

$$d_{(hkl)}^{-2} = h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2} \quad (2)$$

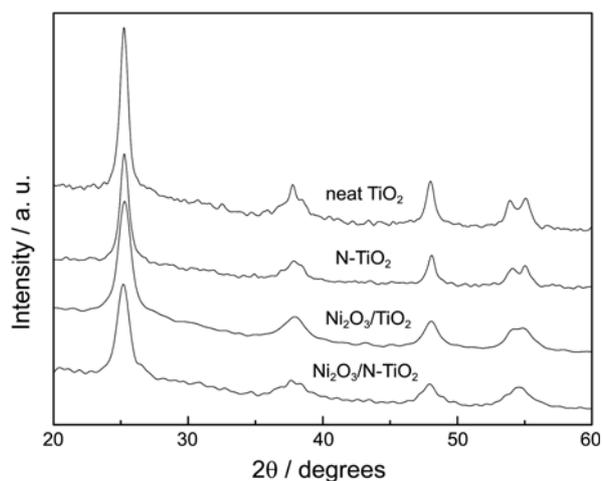
where $d_{(hkl)}$ is the distance between crystal planes of ($h k l$), λ is the X-ray wavelength, θ is the diffraction angle of crystal plane ($h k l$), $h k l$ is the crystal index. The a , b and c are lattice parameters (in anatase form, $a = b \neq c$). The results shown in Table 1 indicated that the lattice parameters of all samples remain almost unchanged along a - and b -axes, whereas the c -axis parameter decreased for N₂-plasma treated samples, N-TiO₂ and Ni₂O₃/N-TiO₂. This indicated that N atoms doped into the TiO₂ lattice, leading to the decrease in the cell volume. Besides, for Ni₂O₃/TiO₂, no obvious change in lattice parameters were observed, indicating Ni is not

Table 1. Summary of physical properties of prepared TiO₂ samples

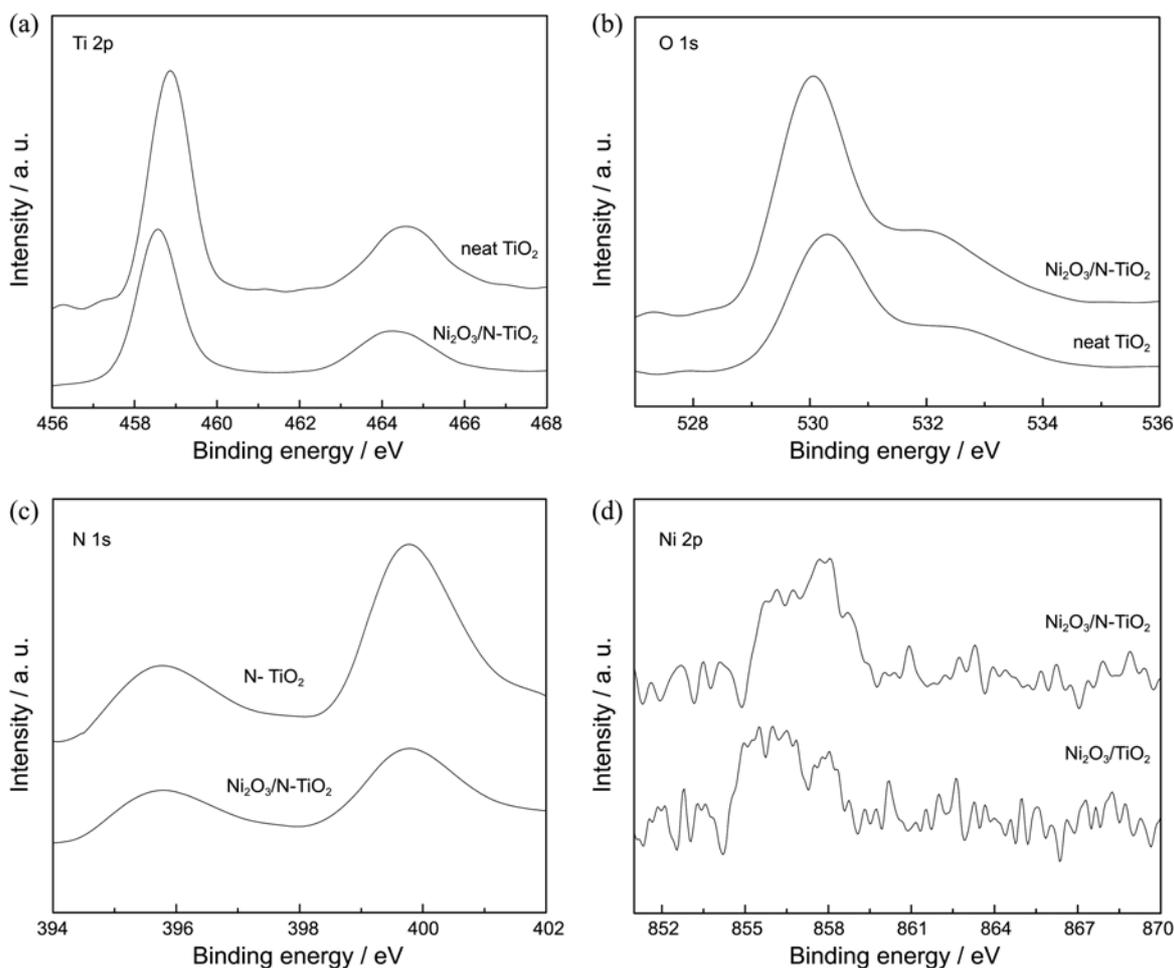
Sample	Size (nm)	S _{BET} (m ² g ⁻¹)	Lattice parameters a = b, c (Å)	E _g (eV)
TiO ₂	15.6	69.8	0.37835, 0.95105	3.07
N-TiO ₂	13.8	82.5	0.37851, 0.94736	2.87
Ni ₂ O ₃ /TiO ₂	9.5	110.3	0.37829, 0.95158	3.04
Ni ₂ O ₃ /N-TiO ₂	8.2	122.7	0.37818, 0.94728	2.82

weaved into the crystal structure and is separated from the phase. However, no other crystalline phase containing Ni was observed. Therefore, it is deduced that very fine dispersion of Ni₂O₃ loaded in the titania which is below the detection limit of this technique. Besides, the particle sizes of the samples were calculated by their XRD patterns according to the Debye-Scherrer equation,²² and shown in Table 1. Obviously, the particle size decreased for the Ni₂O₃ loaded samples. This is probably due to that the coverage of TiO₂ surface by Ni₂O₃, leading to the restriction of grain growth.

Figure 2 shows the XP spectra of neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂. In the Ti 2p region (Fig. 2(a)), both samples exhibited two peaks which could be assigned to Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2}. The binding energy differences, $\Delta E =$

**Figure 1.** XRD patterns of neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂.

$E(\text{Ti}^{4+} 2p_{1/2}) - E(\text{Ti}^{4+} 2p_{3/2})$, for both samples were around 5.7 eV, which is consistent with previous literature.²³ Besides, compared with neat TiO₂, slight shifts to lower binding energies were observed for Ni₂O₃/N-TiO₂ in the region of Ti 2p and O 1s (Fig. 2(a), (b)). This is probably attributed to change

**Figure 2.** XP spectra of neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂ in the region of Ti 2p (a), O 1s (b), N 1s (c), and Ni 2p (d).

of chemical environment after N doping. The electrons of N atoms may be partially transferred from N to Ti and O, due to the higher electronegativity of oxygen, leading to increased electron density on Ti and O atoms. In the region of O 1s (Fig. 2(b)), the XPS peaks around 529.9 and 531.8 eV are attributed to crystal lattice oxygen (Ti-O) and surface hydroxyl group (O-H) of TiO₂.²⁴ The ratio of these two peak areas (S_{O-H}/S_{Ti-O}) represents the abundance of surface hydroxyl groups. The S_{O-H}/S_{Ti-O} ratios for neat TiO₂ and Ni₂O₃/N-TiO₂ were 0.12 and 0.23, respectively. This indicated that Ni₂O₃/N-TiO₂ sample with smaller particle size could absorb more surface hydroxyl group, which play crucial roles in photocatalytic reactions.

In the N 1s region (Fig. 2(c)), the peaks around 396 and 400 eV are observed in both samples, which are attributed to the formation of lattice-nitrogen and other surface N species such as N-N and N-O bond, respectively. This is consistent with our previous results.²⁵ Yamada *et al.*²⁶ prepared N doped TiO₂ by N₂ plasma method. They suggested that the scission of Ti-O bond on TiO₂ surface took place under the nitrogen plasma state, which had a high electron temperature (5-6 eV). Thus, nitrogen atoms will replace lattice oxygen easily. No obvious difference in binding energy between N-TiO₂ and Ni₂O₃/N-TiO₂ was observed, indicating loading of Ni₂O₃ did not influence the doping of N. In the region of Ni 2p (Fig. 2(d)), the binding energy for the broad peak was around 856.0 eV, which assigned to Ni 2p_{3/2} in Ni₂O₃ according to the literature.²⁷ This proved that Ni existed as Ni₂O₃ in the catalyst, which is consistent with XRD result. The molar ratio of Ni/Ti on the TiO₂ surface was 0.044, calculated according to the XPS data. However, the XRF result indicated that the molar ratio of Ni/Ti in the bulk was 0.018, which is coincident with the experimental method. This confirmed that Ni₂O₃ existed mostly on the TiO₂ surface. Besides, it should be noted that the binding energy for Ni₂O₃/TiO₂ shifted slightly after N₂ plasma treatment. This is probably due to the formation of interaction between Ni₂O₃ and TiO₂ caused by the plasma treatment, leading to the change of chemical environment of Ni. The surface hydroxyl group of TiO₂ was probably activated by the plasma treatment, and bond with Ni, leading to the lower electron density. Thus, the binding energy of Ni 2p increased slightly after plasma treatment.

UV-Vis spectra for neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂ are shown in Figure 3. It could be seen that there were strong absorptions in the visible light region and that the absorption edges were shifted to the lower energy region for the sample of N-TiO₂ and Ni₂O₃/N-TiO₂, whereas no absorption in visible light region for the sample of neat TiO₂ and Ni₂O₃/TiO₂ was observed. The red shift of the absorption edge implied a decrease in the band gap energy. In order to calculate the onsets of absorption edges, a tangent was drawn on absorption spectra and was extrapolated, and the intercept on the wavelength axis was obtained. The results were 402.5, 408, 432.4, and 439 nm for the sample of neat TiO₂, Ni₂O₃/TiO₂, N-TiO₂, and Ni₂O₃/N-TiO₂, respectively. Therefore, the band gap energies could be calculated accord-

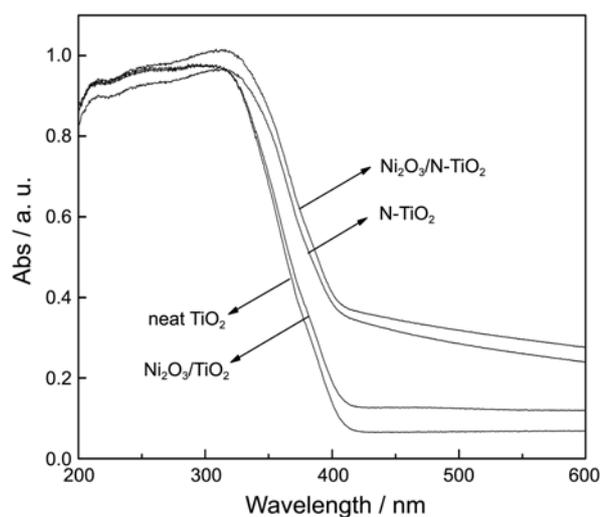


Figure 3. UV-vis spectra of neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂.

Table 2. Comparison of lattice-nitrogen stability in N-TiO₂ and Ni₂O₃/N-TiO₂

Sample	Fresh catalyst (at %)	1st reuse (at %)	2nd reuse (at %)	3rd reuse (at %)
N-TiO ₂	0.28	0.22	0.19	0.16
N-TiO ₂ + KI (0.1 M)	0.27	0.26	0.25	0.25
Ni ₂ O ₃ /N-TiO ₂	0.25	0.24	0.23	0.23

ing to the method of Oregan and Gratzel,²⁸ and the values were 3.07, 3.04, 2.87, and 2.82 eV for neat TiO₂, Ni₂O₃/TiO₂, N-TiO₂, and Ni₂O₃/N-TiO₂ (Table 1). These results clearly indicated that the band gap energy was decreased obviously by nitrogen doping, whereas loading of Ni₂O₃ did not influence the band gap and visible light absorption.

The PL technique has been useful in the field of photocatalysis over semiconductors for understanding the surface processes. PL spectrum is an effective way to study the electronic structure, optical and photochemical properties of semiconductor materials, by which information such as surface oxygen vacancies and defects, as well as the efficiency of charge carrier trapping, immigration and transfer can be obtained.²⁹ It is well known that the PL signals of semiconductor materials result from the recombination of photo-induced charge carriers. In general, the lower the PL intensity, the lower the recombination rate of photo-induced electron-hole pairs, thus the higher the photocatalytic activity. Figure 4 shows the PL spectra of prepared TiO₂ samples, using excitation at 320 nm. Compared with neat TiO₂, the PL intensities decreased slightly after N doping (N-TiO₂). However, for Ni₂O₃ loaded samples, the PL intensities decreased markedly. 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 are present to trap the electrons or holes, the electron-hole recombination can be suppressed. Ganesh *et al.*^{30,31} prepared the nickel ions modified Fe/TiO₂ catalyst, and found the presence of Ni²⁺

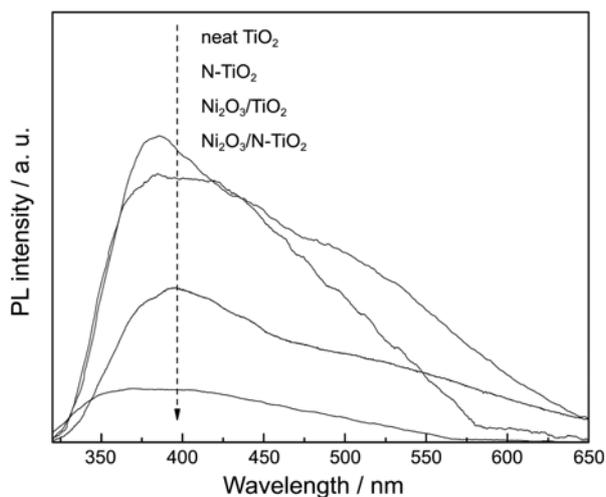


Figure 4. PL spectra of neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂.

and Ni³⁺ by EPR. They considered that Ni³⁺ will trap the photogenerated electron to form Ni²⁺ during the irradiation process. Therefore, in this investigation, Ni₂O₃ will trap the photogenerated electron, hence suppress efficiently the recombination of photogenerated electron-hole.²⁰ Besides, it is shown that PL intensity of Ni₂O₃/N-TiO₂ was much lower than that of Ni₂O₃/TiO₂ sample. This indicated that the recombination of photogenerated electron-hole for Ni₂O₃/TiO₂ sample decreased after plasma treatment. It has been proved that N doping slightly decreased the PL intensity, indicating inapparent influence on recombination. Therefore, such difference in recombination rate should be attributed to the interaction between Ni₂O₃ and TiO₂ after plasma treatment (Fig. 2(d)), leading to the electron transfer more effectively in Ni₂O₃/N-TiO₂.

The adsorption of TCP on TiO₂-based catalysts was measured by the equilibrium adsorption capacity. Compared with neat TiO₂, slight decrease in the adsorption capacity was shown for N-TiO₂, whereas the adsorption capacity of Ni₂O₃ loaded TiO₂ samples increased markedly (Fig. 5). It is reported that such decreased adsorption capacity is attributed

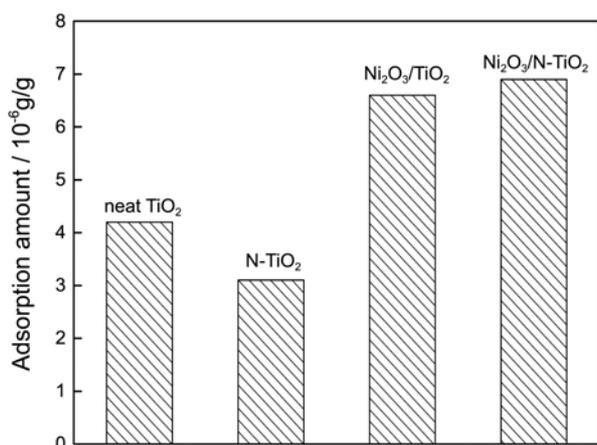


Figure 5. Adsorption capacity of TCP on neat TiO₂, N-TiO₂, Ni₂O₃/TiO₂, and Ni₂O₃/N-TiO₂.

to the coverage of TiO₂ surface by excess surface N species (Fig. 2(c)), leading to the reduced surface sites for adsorbing.³² The BET specific surface areas (S_{BET}) of prepared samples are listed in Table 1. It is obvious that the S_{BET} increased with the decreased particle size. The S_{BET} of Ni₂O₃/TiO₂ and Ni₂O₃/N-TiO₂ were much higher than that of samples without Ni₂O₃ loading. Such increased S_{BET} for Ni₂O₃/TiO₂ and Ni₂O₃/N-TiO₂ lead to the increased equilibrium adsorption capacity.

The photocatalytic activities of prepared TiO₂ samples under visible light are shown in Figure 6. It is shown that neat TiO₂ and Ni₂O₃/TiO₂ exhibited no activity, agreeing well with the result from the UV-vis analysis that the two samples had no response to visible light. After N doping, obvious improvement in photocatalytic activities were observed. Those enhanced photocatalytic activities must result from the doping of nitrogen in TiO₂, which gave rise to the enhanced absorption in the visible region. Compare the N doped samples, it is observed that Ni₂O₃/N-TiO₂ exhibited the highest activity, whereas N-TiO₂ and Ni₂O₃-N-TiO₂ showed almost the same activity. This must result from the interaction between Ni₂O₃ and TiO₂ caused by plasma treatment, which accelerate the excited electron transfer and hence suppress efficiently the recombination of photoproducted electron-hole, increase photo quantum efficiency. Therefore, the activity of Ni₂O₃/N-TiO₂ was much higher than that of N-TiO₂. For Ni₂O₃-N-TiO₂, mechanical mixing sample, the large intermolecular distance between Ni₂O₃ and TiO₂ cause no interaction between them, leading to the same activity with N-TiO₂.

In our previous report, it is concluded that the optimal discharge time was 6 min for N doping. When the discharge time beyond 6 min, the excess surface N species cover the TiO₂ surface, cause a dramatic decrease of equilibrium adsorption capacity, thus leading to the activity decrease.³² Therefore, in this investigation, the discharge time was 6 min. Besides the nitridation condition, the Ni₂O₃ content plays an important role in the photocatalytic activity. In

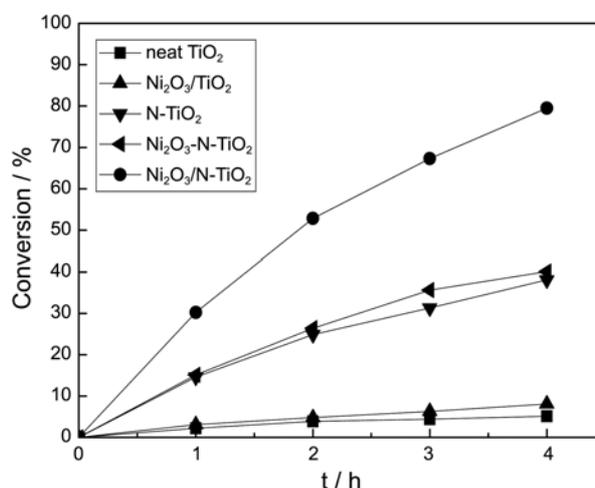


Figure 6. Photocatalytic performances of prepared samples in the degradation TCP under visible light irradiation.

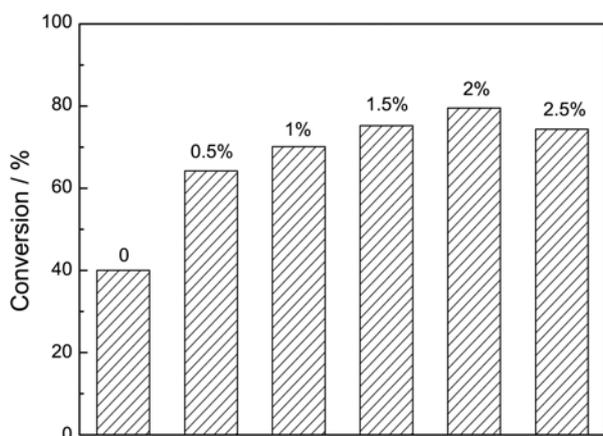


Figure 7. The effect of Ni₂O₃ content on the photocatalytic performance.

Figure 7, the effect of Ni₂O₃ content on the photocatalytic performance, it is shown that the photocatalytic activity of the catalyst without Ni₂O₃ loading was lower than 40%. After loading with Ni₂O₃, the activities increased obviously. However, when the atomic ratio of Ni to Ti beyond 0.02, the photoactivity decreased. Therefore, the optimum atomic ratio of Ni to Ti was 0.02. In fact, the appropriate amount of Ni₂O₃ could suppress the recombination of e⁻/h⁺ whereas the excess amounts of Ni₂O₃ might cover the surface of TiO₂, increased the number of recombination centers, decreased the photo quantum efficiency and led to low photoactivity.

The photocatalytic performances of N-TiO₂ and Ni₂O₃/N-TiO₂ were investigated in three cycles to check the photocatalytic stability (Fig. 8). It is shown that the activity of Ni₂O₃/N-TiO₂ decreased slightly after three reuse (79.5% to 78.8%), whereas the continuous decrease was shown in N-TiO₂, from 38% for fresh catalyst to 27.5% for 3rd reused catalyst. Chen *et al.*³³ reported that the lattice-nitrogen was oxidated by photogenerated holes during the degradation reaction, cause the decrease of lattice-nitrogen content, thus leading to the poor stability. Therefore, the lattice-nitrogen contents of fresh and reused N-TiO₂ and Ni₂O₃/N-TiO₂ are calculated according to the relevant XPS data and shown in Table 2. For N-TiO₂, continuous decrease in lattice-nitrogen content was observed, which is consistent with the result of Chen.³³ However, the lattice-nitrogen content of Ni₂O₃/N-TiO₂ kept stable in the three cycles. Rabani *et al.*³⁴ used iodide ion as scavenger to investigate the effect of h⁺ on the photocatalytic process. Therefore, in this investigation, 0.1 M KI was added to check whether lattice-nitrogen was oxidated by photogenerated h⁺. The result shown in Figure 8 indicated that the activity of N-TiO₂ decreased whereas the photocatalytic stability improved obviously when KI was added. Besides, the lattice-nitrogen stability of N-TiO₂ shown in Table 2 also improved after KI addition. This confirmed the loss of lattice-nitrogen was due to the oxidation by photogenerated h⁺. It is reported that the Ni³⁺ will trap the photogenerated electron to form Ni²⁺ during the irradiation process, thus decrease the recombination rate.^{30,31} Then, the formed Ni²⁺ will react with photogenerated h⁺ and back to

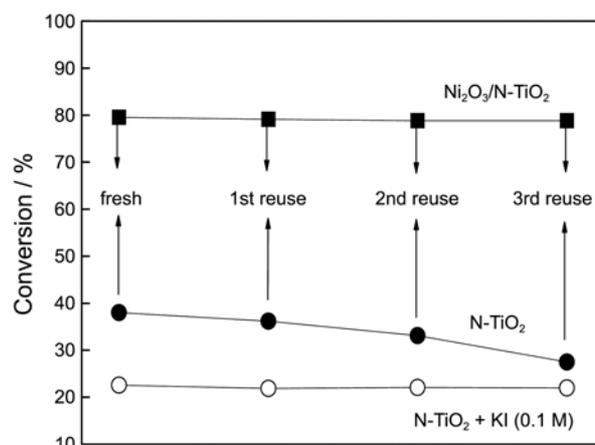
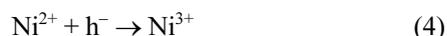


Figure 8. Photocatalytic stability of N-TiO₂ and Ni₂O₃/N-TiO₂ in the degradation of TCP.

Ni³⁺ (Eq. 3, 4).^{35,36} Therefore, it is deduced that loading of Ni₂O₃ not only facilitate the excited electron transfer and increase the photo quantum efficiency, but also played the role of nitrogen stabilizer, restrained the oxidation of lattice-nitrogen by trapping the photogenerated h⁺, thus improve the photocatalytic activity and stability.



Conclusion

The composite photocatalyst, N-TiO₂ loaded with Ni₂O₃, was prepared by N₂ plasma treatment. The coverage of TiO₂ surface by Ni₂O₃ caused the restriction of grain growth, thus leading to the decreased particle size. The band gap energy was decreased obviously by nitrogen doping, whereas loading of Ni₂O₃ did not influence the band gap and visible light absorption. Some interaction between Ni₂O₃ and TiO₂ was formed by N₂ plasma treatment, leading to the accelerated electron transfer from TiO₂ to Ni₂O₃, hence suppress efficiently the recombination of photoproduced electron-hole. Besides, the photocatalytic stability of N doped TiO₂ catalyst was obviously improved by Ni₂O₃ loading. This indicated that loading of Ni₂O₃ not only facilitate the excited electron transfer and increase the photo quantum efficiency, but also played the role of nitrogen stabilizer, thus improve the photocatalytic activity and stability.

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