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Facile Synthesis of Anatase–Rutile Diphase N-doped TiO₂ Nanoparticles with Excellent Visible Light Photocatalytic Activity

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Abstract: To further boost the charge separation and photocatalytic activity of TiO₂ under visible light, the anatase–rutile mixed-phase nitrogen-doped (N-doped) TiO₂ nanoparticles were successfully synthesized through a facile one-step calcining procedure using TiN as raw materials. The crystal phases, morphologies, chemical compositions, textural structures, and optical properties of as-obtained N-doped TiO₂ were characterized by the corresponding analytical techniques. The photocatalytic activities of as-fabricated samples were evaluated by degrading 4-chlorophenol (4-CP) and methylene blue (MB) aqueous solution under visible light irradiation. The results revealed that the ratio of rutile to anatase increased with the improvement of sintering temperature, and the sample prepared at 500 °C had the best photocatalytic activity. This might be because it possessed the most appropriate rutile/anatase proportion as well as the nitrogen doping. The transient photocurrent responses, photoluminescence spectra (PL) measurements, and active species trapping experiments were implemented to disclose the photocatalytic mechanism. This work will provide a further insight into the synthesis of highly efficient N-doped TiO₂ photocatalysts for organic contaminant removal.

Keywords: N-doped TiO₂; charge separation; photocatalytic activity

1. Introduction

Semiconductor photocatalysis technology has drawn great attentions in view of its promising application in converting solar energy into chemical fuels and decomposing harmful organic contaminants [1–4]. Titanium dioxide (TiO₂) is a well-known and widely investigated photocatalyst owing to its good photoactivity, high chemical stability, nontoxicity, and low cost. However, the large band gap of TiO₂ (ca. 3.2 eV for anatase TiO₂) and low separation efficiency of photogenerated charge carriers impede its practical application [5–10]. Consequently, it is imperative to develop highly efficient TiO₂-based photocatalysts with visible light response and slow recombination rate of photogenerated electron-hole pairs. To realize this goal, surface modification by plasmonic metal nanoparticles (such as Au), constructing composites by coupling TiO₂ with a narrow bandgap semiconductor, and doping TiO₂ with non-metal elements are all considered as the promising approaches. Among them, loading plasmonic Au nanoparticles on the surface of TiO₂ can improve the photocatalytic activity under visible light due to its exceptional localized surface plasmon resonance (LSPR) effect. In addition, Au nanoparticles can act as electrons sink and active sites for photocatalytic reactions [11–13]. Formation of TiO₂-based composites by combining a narrow bandgap semiconductor can boost the photogenerated charge separation efficiency, and then increase the photocatalytic activity [14–22]. Nonmetal doping

TiO₂ with C, N, S, or B element is a feasible and convenient method, which has been widely explored in the past few years [23–25].

Among various dopants, nitrogen doping TiO₂ has received the most attention because of the atomic radius of nitrogen similar to the oxygen, together with the small ionization energy of nitrogen [26–32]. The nitrogen doping TiO₂ for the extended visible light harvest and enhanced photocatalytic activity has been verified in the previous studies. For example, Sun et al. have fabricated the nitrogen-doped TiO₂ by calcining TiN under carbon monoxide atmosphere in a range of 400–600 °C. The enhanced photocatalytic activity toward the degradation of methylene blue over the obtained samples are achieved [26]. Wang et al. have prepared the nitrogen-doped TiO₂ nanosheets by annealing TiO₂ nanosheets in NH₃ atmosphere with different NH₃ flow rates at 400 °C. The as-prepared N-doped TiO₂ photocatalysts show the remarkably boosted activity for degrading rhodamine B [27]. Yu's group have synthesized nitrogen and sulfur co-doped TiO₂ nanosheets using thiourea as a dopant. The degradation performance of 4-chlorophenol (4-CP) aqueous solution under visible light is significantly improved [28].

On the other hand, it has been reported that the mixed phase TiO₂ possesses higher photocatalytic property than single phase TiO₂, which is ascribed to the formation of surface phase junction in the mixed phase TiO₂. Generally speaking, TiO₂ has three crystalline phases: anatase, rutile, and brookite. Among them, the anatase and rutile phases TiO₂ are the main crystalline structures, while the brookite phase TiO₂ is difficult to prepare, and it is less studied. The anatase–rutile phase junction is supposed to increase charge separation efficiency and then enhance photocatalytic activity. Theory calculation indicates that the conduction band minimum of anatase is about 0.2 eV higher than that of rutile and the valence band maxima of anatase is close to the rutile, which demonstrates that the electrons can transfer from anatase to rutile. Recently, some research groups have constructed the anatase–rutile phase junction photocatalysts by different synthetic approach, and they all present the enhanced photocatalytic performance in contrast with the single phase TiO₂ [33–38]. For instance, Yu's group have designed and prepared the anatase–rutile TiO₂ nanofiber photocatalysts by electrospinning process, which are endowed the excellent photocatalytic H₂ evolution activities [33]. Qiu et al. have constructed the anatase–rutile heterojunction composites by a multiple synthetic route. The resultant photocatalysts present the enhanced photocatalytic H₂ evolution performance and pollutant degradation [34]. The superfine crystallinity TiO₂ particles with tunable anatase–rutile ratios have been synthesized via a solvothermal treatment method by Gao et al., which exhibits the remarkably improved photocatalytic activities toward organic pollutant degradation [35].

On the basis of the above mentions, incorporating nitrogen doping with the formation of anatase–rutile phase junction would endow TiO₂ with the excellent visible light photocatalytic activity. Herein, anatase–rutile diphasic N-doped TiO₂ nanoparticles were successfully prepared by a facile direct sintering TiN procedure, which is a facile and eco-friendly approach in contrast to using NH₃ or introducing nitrogenous agents. The as-synthesized N-doped TiO₂ exhibited the significantly enhanced photocatalytic activity comparing with the commercial TiO₂ (P25), as revealed by the degradation of 4-CP and methylene blue (MB) aqueous solution under visible light irradiation. In addition, the stability of the photocatalyst and reaction active species were explored. A possible mechanism for the enhanced photocatalytic activity was proposed based on the experimental results.

2. Results and Discussion

2.1. Photocatalyst Characterization

Figure 1 shows the XRD patterns of N-doped TiO₂, TiN, and P25 powders. For TiN, three characteristic diffraction peaks are observed, which are associated with the (111), (200), and (220) crystal planes of TiN [26]. As for P25, it contains two phases of anatase and rutile, in agreement with previous report [37]. In the case of N-doped TiO₂ samples, they have the similar patterns to the P25,

indicating that the N-doped TiO₂ samples are also constituted with anatase and rutile phase TiO₂. The phase percentage is calculated using the following equation [33]:

$$W_R = \frac{1}{1 + 0.886(I_A/I_R)} \quad (1)$$

where W_R represents the percentage of rutile phase; I_A and I_R are the integrated intensities of the anatase (101) and rutile (110) peaks. The calculation results are listed in the Table 1. Obviously, with the increase in calcination temperature, the contents of rutile phase in the N-doped TiO₂ samples also increase. The crystallite sizes of anatase and rutile phase in these samples are estimated from the peak width according to the Scherrer equation [33]:

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (2)$$

where D is crystallite size, λ is the wavelength of X-ray source, β is the full width at half-maximum of main intensity peak, and θ is the diffraction angle. As presented in Table 1, the sizes of anatase and rutile phases increase with the enhancement of temperature, which may be attributed to the particle agglomeration under the high calcination temperature.

Figure 1. XRD patterns of TiN, P25, and N-doped TiO₂ obtained at different calcination temperatures.

Table 1. Crystallite sizes, rutile ratios, specific surface area of samples obtained at different temperature.

Calcination Temperature/°C	Crystallite Size/nm		Rutile Contents/%	Specific Surface Area m ² /g
	Anatase (101)	Rutile (110)		
400	12.1	12.0	18.3	47.1
500	13.0	12.9	20.2	45.3
600	15.1	13.9	36.9	40.9

The morphology of TiN and N-doped TiO₂ samples are investigated by FE-SEM. As displayed in Figure 2a–d, it can be found that the morphologies of TiN and N-doped TiO₂ samples are all irregularly granular. The particle sizes increase gradually with the improvement of annealing temperatures,

in accordance with the XRD analysis results. The microstructure of N-TiO₂-500 sample is further explored by high resolution transmission electron microscopy (HRTEM) measurement. As shown in Figure 2e, the sample is comprised of a large number of nanoparticles with the sizes about 30–40 nm, consistent with the FE-SEM observation. In Figure 2f, the interplanar spacings of N-TiO₂-500 sample are measured to be 0.352 and 0.324 nm, which are corresponding to the anatase (101) and rutile (110) planes, respectively. The result also confirms that the N-TiO₂-500 sample is constituted with the anatase and rutile phase TiO₂, indicating the anatase–rutile phase junction is formed in the sample.

Figure 2. FE-SEM images of TiN (a), N-TiO₂-400 (b), N-TiO₂-500 (c), and N-TiO₂-600 (d); TEM (e) and HRTEM (f) images of N-TiO₂-500.

The XPS characterization is employed to examine the surface chemical compositions and valence states of N-TiO₂-500 sample. As exhibited in Figure 3a, the XPS survey spectrum demonstrates that the N-TiO₂-500 sample mainly contains the C, Ti, and O elements. The C 1s peak at 284.8 eV is due to the adventitious carbon from the XPS instrument itself. Figure 3b depicts the high resolution Ti 2p XPS spectrum, and the peaks positioned at 458.9 and 464.5 eV could be corresponded to Ti 2p_{1/2} and Ti 2p_{3/2}, which are characteristic of Ti⁴⁺ ions [27]. The O 1s spectrum (Figure 3c) can be fitted into two peaks, and the peaks at 530.1 and 532.2 eV are ascribed to lattice oxygen of TiO₂ and surface hydroxyl groups of adsorbed H₂O, respectively. In the N 1s spectrum (Figure 3d), there exists a weak peak centered at about 400.3 eV. According to previous literatures, the peak can be attributed to the presence of oxidized

N such as Ti-N-O or Ti-O-N bonds, while the anionic N- peak (about 397.0 eV) in the TiN is not found, indicating that the N-doped TiO₂ sample has been successfully prepared by direct calcination at high temperature [26].

Figure 3. XPS spectra of N-TiO₂-500: (a) survey spectrum; (b) Ti 2p; (c) O 1s; (d) N 1s.

Raman spectra are utilized to further determine the phase composition. As shown in Figure 4a, these samples all display the prominent featured peaks at 145, 197, 395, 517, and 639 cm⁻¹, which are corresponding to the vibration modes of pure anatase phase TiO₂. Notably, in the P25, N-TiO₂-500, and N-TiO₂-600 samples, two peaks at 446 and 612 cm⁻¹ are observed, which are assigned to the modes of rutile phase TiO₂ [38]. The above two peaks in the N-TiO₂-400 sample are not noticeable, which may be the little amount of rutile phase TiO₂ in this sample. The results further validate that these samples are composed of anatase and rutile phases TiO₂.

UV-vis diffuse reflectance spectra are adopted to investigate the optical properties of samples. As displayed in Figure 4b, the N-TiO₂-600 sample has the similar curve shape to the P25, and only one sharp absorption edge is about at 400 nm. The N-TiO₂-400 and N-TiO₂-500 samples exhibit two absorption edges, which are at around 400 and 500 nm, respectively. According to previous reports, the latter absorption edge is attributed to the nitrogen doping, which improve valence band (VB) edge of TiO₂ and thus induce visible light absorption. The results suggest that the nitrogen-doped TiO₂ samples are only obtained at relatively low calcination temperature under the current conditions. In addition, the color of samples is a related factor of light absorption ability, such as the photos shown in Figure 4b (inset). The color changes gradually from faint yellow of N-TiO₂-400 to white of P25, which is consistent with the capacity of light absorption. The band gap energies of samples are quantitatively calculated by the following equation [31]:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the band gap, and A is a constant. As shown in Figure 4c, through the tangent intercept of these curves to the horizontal axis, the band gap energies of N-TiO₂-400, N-TiO₂-500, N-TiO₂-600, and P25 are estimated to be 2.15, 2.24, 3.00, and

3.02 eV, respectively. Apparently, the N-TiO₂-400 and N-TiO₂-500 samples have the narrow band gap energies and good visible-light-harvest capacities. On the other hand, the higher calcination temperature (>500 °C) will lead to a decline in the light absorption capacity of N-doped TiO₂ sample, which may be that the higher temperatures result in the complete oxidation of TiN and the oxygen atoms have totally replaced nitrogen atoms in the crystalline lattice.

Figure 4. Raman spectra (a); UV-DRS spectra and color photograph (inset) (b); band gap energies curves (c); nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves (d) of different samples.

The BET-specific surface areas and pore size distribution curves of samples are examined by nitrogen adsorption–desorption measurement, as revealed in Figure 4d and Table 1. It can be seen that these adsorption–desorption curves are ascribed to type IV isotherm with type H3 hysteresis loops, demonstrating the existence of porous structures derived from the accumulation of particles. The corresponding pore size distribution curves (inset) uncover that the pore size distributions mainly are in the range of 10–20 nm, verifying the presence of porous structures in these samples [28]. Additionally, the BET-specific surface areas of N-TiO₂-400, N-TiO₂-500, N-TiO₂-600 are calculated to be 47.1, 45.3, and 40.9 m² g⁻¹. It can be found that the specific surface areas slightly decrease with the increase in calcination temperature, suggesting that the sizes of particle gradually enlarge, in good agreement with the FESEM and XRD observation.

2.2. Photocatalytic Activity and Mechanism

The photocatalytic activities are evaluated by degrading 4-CP and MB solution under visible light irradiation. As displayed in Figure 5a, the 4-CP solution exhibits an excellent stability, and there is no appreciable degradation under visible light irradiation for 240 min without photocatalysts. When the TiO₂ photocatalysts are added into 4-CP solution, the degradation efficiencies improve. Among these samples, the photocatalytic degradation activity follows the order: P25 < N-TiO₂-600 < N-TiO₂-400 < N-TiO₂-500. Apparently, the N-TiO₂-500 photocatalyst displays the best activity with the degradation percentage of 87.8% after 240 min visible light illumination. The temporal ultraviolet-visible spectral

variation of 4-CP solution during the photocatalytic degradation process on the N-TiO₂-500 sample is shown in Figure 5b. The characteristic absorption peak (about 224 nm) intensities gradually decrease with the extension of reaction time, implying that the concentration of 4-CP declines along with the photocatalytic reaction. In addition, the MB dye is used as the probe molecule to explore the photocatalytic activity. As shown in Figure 5c, the MB molecules are considerably stable under visible light irradiation, eliminating the self-degradation of MB. Similar to the 4-CP degradation, the order of degradation activity is similar. For the N-TiO₂-500 sample, the degradation percentage of MB is about 90.5% after 120 min visible light illumination. The photostability experiments (Figure 5d) of N-TiO₂-500 sample were also performed by four runs recycling degrading MB solution. In each experiment, the used photocatalysts were collected, washed, and dried. It can be viewed that the photocatalytic degradation efficiency still maintains 85.2% after four successive experiments, implying a good stability.

Figure 5. (a) Comparison of photocatalytic activities for 4-chlorophenol (4-CP) degradation (b) the temporal ultraviolet-visible spectral variation of 4-CP solution during photocatalytic reaction on N-TiO₂-500 sample; (c) comparison of photocatalytic activities for methylene blue (MB) degradation; (d) stability experiments for MB degradation on N-TiO₂-500 sample.

To ascertain the active species in the photoreaction, the trapping experiments were carried out over the N-TiO₂-500 sample during degrading MB solution process. From Figure 6a, the respective introduction of TEOA, IPA, and BQ all results in the decrease in photodegradation efficiency, demonstrating that the h^+ , $\cdot OH$, and $\cdot O_2^-$ are all involved in the degradation reaction. Apparently, the degradation rate decreases most significantly as TEOA is added, indicating that h^+ are the most significant inhibitors to the photodegradation efficiency. Besides, the generation of $\cdot OH$ radicals during the photocatalytic reaction is detected using terephthalic acid (TA) as a probe molecule. Figure 6b depict the variation of PL spectra of TA solution as a function of irradiation time under visible light [28]. The increasing PL intensity at about 425 nm is observed with the reactive time proceeding. Moreover, there is almost no PL signal in the absence of light illumination. As the PL signal comes from the chemical reaction between TA and $\cdot OH$ radicals, this result corroborates that the production amounts of $\cdot OH$ radicals are gradually increasing. Consequently, the generated $\cdot OH$ radicals over the N-doped TiO₂ are proportional to the irradiation time. Additionally, a comparative study of PL intensity for different samples exposed for 240 min to visible light illumination. As presented in Figure 6c, the N-TiO₂-500 has the highest PL intensity among the N-doped TiO₂ and P25 samples.

Considering that the PL intensity is proportional to the total amount of generated $\cdot\text{OH}$ radicals, it is deduced that the N-TiO₂-500 has produced the largest amount of $\cdot\text{OH}$ radicals and suggested that it may possess the best photocatalytic activity. The PL testing result powerfully supports the photocatalytic activity measurements. The effective transfer and separation of photogenerated charge carriers is key for the boosted photocatalytic activity, and the transient photocurrent response measurements of different samples are adopted to evaluate their interfacial charge separation efficiencies. From Figure 6d, it can be found that the photocurrent response of N-TiO₂-500 catalyst is highest among these samples, implying the most efficient transfer of photoexcited electrons at the interface over the N-TiO₂-500 sample. The PL spectra are also utilized to investigate the separation and recombination of electron-hole pairs [28]. As shown in Figure 6e, for the N-doped TiO₂ samples, the PL intensity follows the order: N-TiO₂-600 < N-TiO₂-500 < N-TiO₂-400, which may be related to the ratio of rutile phase TiO₂ in the samples. The higher ratio of rutile phase TiO₂ results in the lower PL intensity. Additionally, the PL intensity of P25 is comparable to that of N-TiO₂-500, since the rutile phase ratio of P25 is similar to the N-TiO₂-500. It can be deduced that the mixed phase TiO₂ (rutile and anatase) is favorable for the separation of photogenerated electron-hole pairs.

Figure 6. Effects of active species on the photocatalytic degradation efficiencies (a), photoluminescence (PL) spectral changes with irradiation time of N-TiO₂-500 sample in the basic solution of terephthalic acid (b), PL spectra of different samples in the basic solution of terephthalic acid after 240 min light irradiation (c), transient photocurrent responses (d), steady PL spectra of different samples with excitation at 320 nm (e), and the possible mechanism for the enhanced photocatalytic activity of N-doped TiO₂ sample (f).

Based on the aforementioned results, a possible mechanism for the enhanced photocatalytic activity of N-doped TiO₂ sample under visible light illumination is tentatively proposed, as depicted in Figure 6f. Among these samples, the N-TiO₂-500 sample presents the best photocatalytic activity, which may be ascribed to the following aspects. On one hand, the suitable annealing temperature enables the samples to possess the proper nitrogen doping concentration, which makes them have good visible-light-absorption abilities. Under visible light illumination, the electrons can be excited from energy level N 2p to the conduction band. On the other hand, the excited electrons can transfer from anatase to rutile on the basis of band gap of rutile (~3.0 eV) comparing with anatase (~3.2 eV), which is an effective way to transfer the electrons in the conduction band of anatase and slows down the recombination of electron-hole pairs. The N-TiO₂-600 sample has the lowest PL intensity at 320 nm excitation, since the rutile phase ratio (~36.9%) is highest among them, evidencing that the electrons can effectively transport between anatase and rutile phase TiO₂. However, it cannot be excited by visible light in consideration of its large band gap (3.0 eV). As a result, its photocatalytic activity is not good. Whereas, the N-TiO₂-500 sample has the maximal photocatalytic activity due to its small band gap (2.24 eV) with visible light response and appropriated anatase–rutile phase ratio in contrast with N-TiO₂-400 and N-TiO₂-600 samples.

3. Experimental

3.1. Material Preparation

Titanium nitride (TiN, about 20 nm, Aladdin Chemical Reagent Co. Ltd., Shanghai, China) and other chemicals (Sinopharm Chemical Reagent Co, Ltd., Beijing, China) were the analytical grade reagents without further purification.

The anatase–rutile diphasic N-doped TiO₂ powders were synthesized by direct calcining TiN sources in a muffle furnace. Typically, 2 g TiN was calcinated at 500 °C for 2 h in an air atmosphere with the heating rate of 2 °C min^{−1}. After the furnace cooling naturally to room temperature, the sample was taken out and labelled as N-TiO₂-500. Another two samples annealed at 400 and 600 °C were named as N-TiO₂-400 and N-TiO₂-600, respectively. As reference, commercial TiO₂ (P25, about 20 nm, 50 m² g^{−1}, 80% anatase, and 20% rutile) was used in the experiment without any treatment.

3.2. Material Characterization

The crystal phases of photocatalysts were determined by a XRD-7000 powder X-ray diffractometer (Shimadzu, Tokyo, Japan) with Cu K α irradiation at a scan rate of 0.05° s^{−1}. The accelerating voltage and applied current were 40 kV and 30 mA, respectively. The morphologies and microstructures were, respectively, examined on a field emission scan electronic microscope (FESEM, Tokyo, Japan) and a 2100F high-resolution transmission electronic microscope (JEOL JEM, Tokyo, Japan). The X-ray photoelectron spectroscopy (XPS) was operated on a VG Multilab 2000 (Thermo Fisher Scientific, Waltham, MA, USA) with Al K α source operating at 300 W. All binding energies were calibrated to the C 1s peak of surface adventitious carbon at 284.8 eV. The ultraviolet-visible diffuse reflectance absorption spectra were recorded by the dry-pressed disk samples on a TU-1901 spectrophotometer (Purkinje General, Beijing, China) using BaSO₄ as the reference sample. The Raman spectra were measured using a RAM HR800 spectrometer (Jobin Yvon Lab, Paris, French) with the excitation wavelength of 514 nm. The Brunauer–Emmett–Teller (BET)-specific surface areas were obtained on a ASAP 2020 nitrogen adsorption apparatus (Micromeritics, Norcross, GA, USA). All of the samples were degassed at 120 °C for 24 h prior to nitrogen adsorption–desorption measurement. The steady PL spectra were recorded at room temperature with the excitation wavelength of 320 nm on a Cary Eclipse fluorescence spectrophotometer (Varian, Palo Alto, CA, USA).

3.3. Photocatalytic Activity Measurement

The photocatalytic activities were evaluated by the degradation of 4-CP and MB solution in a homemade Pyrex glass vessel with a cooling jacket under visible light irradiation. In each procedure of degrading 4-CP, 250 mg photocatalysts were dispersed into 100 mL 4-CP solution with the initial concentration of 10 ppm. For degrading MB solution, 50 mg photocatalysts were introduced into 100 mL 10 ppm MB solution. A 300 W xenon lamp was used as the light source equipped with 420 nm cutoff filters. Before irradiation, the suspensions were stirred in the dark for 30 min to ensure the establishment of an adsorption–desorption equilibrium. At given irradiation time intervals, 4 mL aliquots were sampled and centrifuged to remove the photocatalysts. The residual concentration of 4-CP and MB in the supernatant was determined by a Purkinje General TU-1810 spectrometer at the absorption bands of 224 and 664 nm, respectively.

3.4. Photoelectrochemical Measurement

The transient photocurrent responses were carried out on an electrochemical system (CHI 760D, Shanghai Chenhua Instruments, Shanghai, China) with a standard three electrode system. The Pt sheet and Ag/AgCl electrode were used for the counter electrode and reference electrode, respectively. The working electrodes were prepared as follows: 10 mg photocatalysts were mixed with 1 mL ethanol and 50 μ L Nafion solutions, and the obtained slurry (0.1 mL) was dropped on the indium tin oxide (ITO) glasses with the active work areas about 1 cm². The 0.1 mol L^{−1} Na₂SO₄ aqueous solution was employed as the electrolyte in the whole photoelectrochemical test process.

3.5. Active Species Trapping and Hydroxyl Radical Measurement

To determine the active species during the photocatalytic reaction, triethanolamine (TEOA), isopropanol (IPA), and p-benzoquinone (BQ) were, respectively, added into photocatalytic system as the scavengers of holes (h⁺), hydroxyl radicals ($\cdot$ OH), and superoxide radicals ($\cdot$ O₂[−]). The measurements were similar to the aforementioned photocatalytic activity tests except for adding scavengers into the MB solution before visible light irradiation. The formation of hydroxyl radicals in the different samples was detected by the photoluminescence (PL) method using terephthalic acid (TA) as a probe molecule. The test procedures were as follows: 50 mg catalyst powders were dispersed into a mixed aqueous solution of 5 $\times$ 10^{−4} mol L^{−1} TA and 2 $\times$ 10^{−3} mol L^{−1} NaOH. After illumination for a period time, the solution was analyzed on a fluorescence spectrophotometer.

4. Conclusions

In summary, N-doped TiO₂ photocatalysts with visible light response were fabricated by directly annealing TiN powder in a muffle furnace. The obtained N-doped TiO₂ was constituted with anatase and rutile phase. Moreover, the rutile phase ratios increased with the improvement of calcination temperature. The XPS and UV-DRS tests powerfully confirmed that nitrogen atoms were incorporated into the lattice of TiO₂. The most active N-doped TiO₂ obtained at 500 °C showed a significantly enhanced photocatalytic activity toward degrading 4-CP and MB solution in comparison to P25, which was mainly due to the synergetic effects of two factors: (i) the absorption in the visible light region of N-doped TiO₂ and (ii) the effective transfer of electrons from anatase to rutile. The active species trapping experiments demonstrated that h⁺, $\cdot$ OH, and $\cdot$ O₂[−] were all involved in photocatalytic reaction process. The as-prepared N-doped TiO₂ would be a promising photocatalyst for the degradation of organic pollutants.

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References

1. Li, H.J.; Zhou, Y.; Tu, W.G.; Ye, J.H.; Zou, Z.G. State-of-the-art progress in diverse heterostructured photocatalysts toward promoting photocatalytic performance. *Adv. Funct. Mater.* **2015**, *25*, 998–1013. [\[CrossRef\]](#)
2. Li, K.; Peng, B.S.; Peng, T.Y. Recent advances in heterogeneous photocatalytic CO₂ conversion to solar fuels. *ACS Catal.* **2016**, *6*, 7485–7527. [\[CrossRef\]](#)
3. Huang, D.L.; Yan, X.L.; Yan, M.; Zeng, G.M.; Zhou, C.Y.; Wan, J.; Cheng, M.; Xue, W.J. Graphitic carbon nitride-based heterojunction photoactive nanocomposites: Applications and mechanism insight. *ACS Appl. Mater. Interfaces* **2018**, *10*, 21035–21055. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Low, J.X.; Yu, J.G.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A.A. Heterojunction photocatalysts. *Adv. Mater.* **2017**, *29*, 1601694. [\[CrossRef\]](#)
5. Luo, B.Y.; Chen, W.W.; Ma, J.; Tian, W.; He, C.; Shui, A.Z.; Du, B. Fabrication of tunable 1D rod-like and 3D yolk-like TiO₂ hierarchical architectures for efficient photocatalysis. *J. Mater. Sci.* **2020**, *55*, 3760–3773. [\[CrossRef\]](#)
6. Wang, Z.N.; Liu, S.M.; Cao, X.; Wu, S.M.; Liu, C.Q.; Li, G.; Jiang, W.W.; Wang, H.L.; Wang, N.; Ding, W.Y. Preparation and characterization of TiO₂ nanoparticles by two different precipitation methods. *Ceram. Int.* **2020**, *46*, 15333–15341. [\[CrossRef\]](#)
7. Wang, H.H.; Zhang, N.; Cheng, G.; Guo, H.; Shen, Z.W.; Yang, L.; Zhao, Y.S.; Alsaedi, A.; Hayat, T.; Wang, X.K. Preparing a photocatalytic Fe doped TiO₂/rGO for enhanced bisphenol A and its analogues degradation in water sample. *Appl. Surf. Sci.* **2020**, *505*, 144640. [\[CrossRef\]](#)
8. Qiu, H.; Ma, X.J.; Sun, C.Y.; Zhao, B.; Chen, F. Surface oxygen vacancies enriched Pt/TiO₂ synthesized with a defect migration strategy for superior photocatalytic activity. *Appl. Surf. Sci.* **2020**, *5056*, 145021. [\[CrossRef\]](#)
9. Bharati, B.; Mishra, N.C.; Sinha, A.S.K.; Rath, C. Unusual structural transformation and photocatalytic activity of Mn doped TiO₂ nanoparticles under sunlight. *Mater. Res. Bull.* **2020**, *123*, 110710. [\[CrossRef\]](#)
10. Zhao, Z.H.; Omer, A.A.; Qin, Z.R.; Osman, S.; Xia, L.L.; Singh, R.P. Cu/N-codoped TiO₂ prepared by the sol-gel method for phenanthrene removal under visible light irradiation. *Environ. Sci. Pollut. Res.* **2020**, *27*, 17530–17540. [\[CrossRef\]](#)
11. Khalil, M.; Anggraeni, E.S.; Ivandini, T.A.; Budianto, E. Exposing TiO₂ (001) crystal facet in nano Au-TiO₂ heterostructures for enhanced photodegradation of methylene blue. *Appl. Surf. Sci.* **2019**, *487*, 1376–1384. [\[CrossRef\]](#)
12. Liu, B.; Wang, Y.; Shang, S.X.; Ni, Y.M.; Zhang, N.; Cao, M.H.; Hu, C.W. One-step synthesis of mulberry-shaped TiO₂-Au nanocomposite and its H₂ evolution property under visible light. *Colloid Surf. A* **2018**, *553*, 203–209. [\[CrossRef\]](#)
13. Yang, X.J.; Wu, X.L.; Li, J.; Liu, Y. TiO₂-Au composite nanofibers for photocatalytic hydrogen evolution. *RSC Adv.* **2019**, *9*, 29097. [\[CrossRef\]](#)
14. Zeng, T.Y.; Shi, D.J.; Cheng, Q.R.; Liao, G.Y.; Zhou, H.; Pan, Z.Q. Construction of novel phosphonate-based MOF/P-TiO₂ heterojunction photocatalysts: Enhanced photocatalytic performance and mechanistic insight. *Environ. Sci. Nano* **2020**, *7*, 861–879. [\[CrossRef\]](#)
15. Tang, Y.; Yin, X.H.; Mu, M.M.; Jiang, Y.; Li, X.L.; Zhang, H.; Ouyang, T.W. Anatase TiO₂@MIL-101(Cr) nanocomposite for photocatalytic degradation of bisphenol A. *Colloid Surf. A* **2020**, *596*, 124745. [\[CrossRef\]](#)
16. Guo, X.L.; Duan, J.H.; Li, C.J.; Zhang, Z.S.; Wang, W.W. Fabrication of g-C₃N₄/TiO₂ photocatalysts with a special bilayer structure for visible light photocatalytic application. *Colloid Surf. A* **2020**, *599*, 124931. [\[CrossRef\]](#)
17. Zhao, C.; Wang, Z.H.; Chen, X.; Chu, H.Y.; Fu, H.F.; Wang, C.C. Robust photocatalytic benzene degradation using mesoporous disk-like N-TiO₂ derived from MIL-125(Ti). *Chin. J. Catal.* **2020**, *41*, 1186–1197. [\[CrossRef\]](#)

18. Zhang, Y.F.; Fu, F.; Zhou, F.; Yang, X.; Zhang, D.S.; Chen, Y.Y. Synergistic effect of RGO/TiO₂ nanosheets with exposed (001) for boosting visible light photocatalytic activity. *Appl. Surf. Sci.* **2020**, *510*, 145451. [\[CrossRef\]](#)
19. Mohamed, R.M.; Kadi, M.W.; Ismail, A.A. A facile synthesis of mesoporous α -Fe₂O₃/TiO₂ nanocomposites for hydrogen evolution under visible light. *Ceram. Int.* **2020**, *46*, 15604–15612. [\[CrossRef\]](#)
20. Sun, L.M.; Yuan, Y.S.; Wang, F.; Zhao, Y.L.; Zhan, W.W.; Han, X.G. Selective wet-chemical etching to create TiO₂@MOF frame heterostructure for efficient photocatalytic hydrogen evolution. *Nano Energy* **2020**, *74*, 104909. [\[CrossRef\]](#)
21. Yao, X.X.; Hu, X.L.; Zhang, W.J.; Gong, X.Y.; Wang, X.H.; Pillai, S.C.; Dionysiou, D.D.; Wang, D.W. Mie resonance in hollow nanoshells of ternary TiO₂-Au-CdS and enhanced photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2020**, *276*, 119153. [\[CrossRef\]](#)
22. Wang, Q.; Zhang, L.X.; Guo, Y.K.; Shen, M.; Wang, M.; Li, B.; Shi, J.L. Multifunctional 2D porous g-C₃N₄ nanosheets hybridized with 3D hierarchical TiO₂ microflowers for selective dye adsorption, antibiotic degradation and CO₂ reduction. *Chem. Eng. J.* **2020**, *396*, 125347. [\[CrossRef\]](#)
23. Yin, Z.G.; Wang, Z.H.; Wang, J.N.; Wang, X.Y.; Song, T.T.; Wang, Z.L.; Ma, Y. HF promoted increased nitrogen doping in TiO₂ (B) photocatalyst. *Chem. Commun.* **2020**, *56*, 5609–5612. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Zhou, L.; Cai, M.; Zhang, X.; Cui, N.X.; Chen, G.F.; Zou, G.Y. In-situ nitrogen-doped black TiO₂ with enhanced visible-light-driven photocatalytic inactivation of *Microcystis aeruginosa* cells: Synthesis performance and mechanism. *Appl. Catal. B Environ.* **2020**, *272*, 119019. [\[CrossRef\]](#)
25. Zhang, E.M.; Pan, Y.; Lu, T.; Zhu, Y.A.; Dai, W.J. Novel synthesis of S-doped anatase TiO₂ via hydrothermal reaction of Cu-Ti amorphous alloy. *Appl. Phys. A* **2020**, *126*, 606. [\[CrossRef\]](#)
26. Sun, M.X.; Song, P.; Li, J.; Cui, X.L. Preparation, characterization and applications of novel carbon and nitrogen co-doped TiO₂ nanoparticles from annealing TiN under CO atmosphere. *Mater. Res. Bull.* **2013**, *48*, 4271–4276. [\[CrossRef\]](#)
27. Wang, W.; Lu, C.H.; Su, X.X.; Ni, Y.R.; Xu, Z.Z. Synthesis, characterization, and nitrogen concentration depended visible-light photoactivity of nitrogen-doped TiO₂ nanosheets with dominant (001) facets. *Chin. J. Catal.* **2012**, *33*, 629–636. [\[CrossRef\]](#)
28. Xiang, Q.J.; Yu, J.G.; Jaroniec, M. Nitrogen and sulfur co-doped TiO₂ nanosheets with exposed {001} facets: Synthesis, characterization and visible-light photocatalytic activity. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4853–4861. [\[CrossRef\]](#)
29. Jin, X.D.; Zhou, X.Q.; Sun, P.; Lin, S.Y.; Cao, W.B.; Li, Z.F.; Liu, W.X. Photocatalytic degradation of norfloxacin using N-doped TiO₂: Optimization, mechanism, identification of intermediates and toxicity evaluation. *Chemosphere* **2019**, *237*, 124433. [\[CrossRef\]](#)
30. Li, X.J.; Zhang, G.Q.; Wang, X.F.; Liu, W.P.; Yu, K.F.; Liang, C. Facile synthesis of nitrogen-doped titanium dioxide with enhanced photocatalytic properties. *Mater. Res. Express* **2019**, *6*, 115019. [\[CrossRef\]](#)
31. Erdogan, N.; Bouziani, A.; Park, J.; Micusik, M.; Kim, S.Y.; Majkova, E.; Omastova, M.; Ozturk, A. Synthesis and enhanced photocatalytic activity of nitrogen-doped triphasic TiO₂ nanoparticles. *J. Photochem. Photobiol. A Chem.* **2019**, *377*, 92–100. [\[CrossRef\]](#)
32. Jiang, J.X.; Zhang, Q.Q.; Li, Y.H.; Li, L. Three-dimensional network graphene aerogel for enhancing adsorption and visible light photocatalysis of nitrogen-doped TiO₂. *Mater. Lett.* **2019**, *234*, 298–301. [\[CrossRef\]](#)
33. Xu, F.Y.; Xiao, W.; Cheng, B.; Yu, J.G. Direct Z-scheme anatase/rutile bi-phase nanocomposite TiO₂ nanofiber photocatalyst with enhanced photocatalytic H₂-production activity. *Int. J. Hydrog. Energy* **2014**, *39*, 15394–15402. [\[CrossRef\]](#)
34. Qiu, C.W.; Lin, J.J.; Shen, J.N.; Liu, D.; Zhang, Z.Z.; Lin, H.X.; Wang, X.X. Regulation of the rutile/anatase TiO₂ heterophase interface by Ni₁₂P₅ to improve photocatalytic hydrogen evolution. *Catal. Sci. Technol.* **2020**, *10*, 3709–3719. [\[CrossRef\]](#)
35. Gao, Y.N.; Wang, H.; Wu, J.; Zhao, R.H.; Lu, Y.F.; Xin, B.F. Controlled facile synthesis and photocatalytic activity of ultrafine high crystallinity TiO₂ nanocrystals with tunable anatase/rutile ratios. *Appl. Surf. Sci.* **2014**, *294*, 36–41. [\[CrossRef\]](#)
36. Ramezanisani, S.; Rajabi, M.; Mohseni, F. Influence of nitrogen doping on visible light photocatalytic activity of TiO₂ nanowires with anatase-rutile junction. *Chem. Phys. Lett.* **2020**, *744*, 137217. [\[CrossRef\]](#)

37. Fang, Y.X.; Huang, W.X.; Yang, S.Y.; Zhou, X.F.; Ce, C.Y.; Gao, Q.Z.; Fang, Y.P.; Zhang, S.S. Facile synthesis of anatase/rutile TiO₂/g-C₃N₄ multi-heterostructure for efficient photocatalytic overall water splitting. *Int. J. Hydrog. Energy* **2020**, *45*, 17378–17387. [[CrossRef](#)]
38. Assayehegn, E.; Solaiappan, A.; Chebude, Y.; Alemayehu, E. Fabrication of tunable anatase/rutile heterojunction N/TiO₂ nanophotocatalyst for enhanced visible light degradation activity. *Appl. Surf. Sci.* **2020**, *515*, 145966. [[CrossRef](#)]

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