N 掺杂富含 (001) 晶面 TiO₂ 纳米片的制备及 N 掺杂浓度对可见光催化活性的影响

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摘要: 采用水热法制备了富含 (001) 晶面的锐钛矿型 TiO₂ 纳米片, 并通过改变热处理过程中 NH₃ 流速制备不同 N 掺杂浓度的 TiO₂ 纳米片。运用 X 射线衍射、场发射扫描电镜、高分辨率透射电子显微镜、紫外-可见漫反射光谱、X 射线光电子能谱和荧光光谱对光催化剂进行了结构和性能表征, 并以罗丹明 B 为目标降解物, 考察了 N 掺杂浓度对 TiO₂ 纳米片可见光催化活性的影响。结果表明, NH₃ 流速为 40 ml/min 时制备的 N 掺杂 TiO₂ 纳米片具有最低的光生电子-空穴复合速率, 最高的·OH 产生能力并表现出最高的光催化活性。同时, 讨论了 N 掺杂浓度对 TiO₂ 纳米片可见光催化活性影响的机理。

关键词: 氮掺杂; 二氧化钛纳米片; 氮浓度; 光催化活性; (001) 晶面

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Synthesis, Characterization, and Nitrogen Concentration Dependent Visible-Light Photoactivity of Nitrogen-Doped TiO₂ Nanosheets with Dominant (001) Facets

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Abstract: Anatase TiO₂ nanosheets with dominant (001) facets were prepared by a simple hydrothermal method. Nitrogen-doped TiO₂ nanosheets (TiO₂-N) with different nitrogen concentration were successfully synthesized by annealing TiO₂ nanosheets in NH₃ atmosphere with different NH₃ flow rate at 400 °C for 3 h. The morphology, nanostructures, and properties of TiO₂-N were characterized by X-ray diffraction, field emission scanning electron microscopy, high resolution transmission electron microscopy, ultraviolet-visible diffuse reflection spectroscopy, X-ray photoelectron spectroscopy, and photoluminescence. The effects of NH₃ flow rate on the nanostructures, properties, and visible-light photoactivity in the degradation of rhodamine B (RhB) aqueous solution under visible light ($\lambda > 400$ nm) irradiation of the prepared photocatalysts were investigated. Among all the prepared photocatalysts including nitrogen modified P25 (Degussa), TiO₂-N prepared with a NH₃ flow rate of 40 ml/min gave the highest visible-light photoactivity because of the dominant (001) facets, visible light responsibility, the slowest photogenerated electron (e⁻) and hole (h⁺) pairs recombination rate, and the highest hydroxyl radicle (·OH) generation ability. Based on these experiments and analysis, the mechanisms of how the nitrogen concentration affects the visible-light photoactivity of TiO₂-N were proposed.

Key words: nitrogen doping; titanium dioxide nanosheet; nitrogen concentration; photoactivity; (001) facets

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Titanium dioxide (TiO₂) is one of the most commonly available semiconductors with intrinsic properties, and has been widely studied by a lot of researchers since 1972 [1–3]. However, the large band gap (3.2 eV) causes anatase TiO₂ can only absorb the light with wavelength below 385 nm in the ultraviolet region, which is about 5% of the solar light irradiated on the earth [4]. Therefore, many methods such as metal and nonmetal doping have been used to extend the light absorption edge of anatase TiO₂ to the visible range in order to expand the practical application fields [5–7]. Nonmetal doping seems to be a promising way to improve the photocatalytic activity of TiO₂ under visible light irradiation. Nonmetals such as boron [8], carbon [9], nitrogen [2,8,12], fluorine [10], and sulfur [11] have been investigated and nitrogen is considered as the most effective one to enhance the visible-light photoactivity of TiO₂. Another important factor that affects the photocatalytic activity is the photogenerated h⁺ and e[−] pair separation ability. The photogenerated h⁺ and e[−] are able to form super power radicals on the surface of the photocatalysts to degrade organic contaminants and harmful gases [13]. What is the relationship between N doped concentration and the photo-generated h⁺ and e[−] recombination effect and how it affects the visible-light photoactivity are very promising topics to be discussed.

Recently, anatase TiO₂ nanosheets with a high percentage of (001) facets have attracted much attention due to their higher reactive properties than the traditional TiO₂ nanoparticles dominated by the (101) facets [14]. Experimental and theoretical studies indicate that TiO₂ nanosheets single crystals with fewer defects could reduce the photogenerated h⁺ and e[−] recombination rate, and that will be favorable to the improvement of photoactivity [15]. The density of surface undercoordinated atoms is another factor affecting the photocatalytic activity of the crystal facets [16]. The more of the undercoordinated atoms exist, the higher of the photoactivity. As reported, the unsaturated Ti_{5c} atoms at the (001) facets is 100%, while the unsaturated Ti_{5c} atoms at the (101) facets is 50% [17]. Till now, TiO₂ nanosheets with dominant (001) facets have been used in a lot of fields, such as water slipping for hydrogen, contaminants decomposition, solar cells, and so on [18–20]. However, TiO₂ nanosheets also suffer from the problem of the large band gap. What's more, the condition for the crystal growth of TiO₂ nanosheets is very critical and thus limits the modifi-

cation of TiO₂ nanosheets electronic structure in a certain degree [21]. Some researchers have proposed several methods to improve the visible-light photoactivity of TiO₂ nanosheets. Liu et al. [22] and Xiang et al. [23] synthesized N self-doped intersectional TiO₂ sheets from TiN, which extended the light response edge to about 550 nm. They found that the photocatalytic activity depended much on the size of TiO₂ sheets. Liu and his coworkers [24] synthesized intersectional anatase TiO₂ sheets with oxygen-deficiency from TiB, which also improved the photocatalytic activity. Xiang et al. [25] proposed a simple mixing-calcination method to dope the prepared TiO₂ nanosheets with sulfur and nitrogen. Still, noble metal was also used to improve the visible-light photoactivity of TiO₂ nanosheets [20].

In this study, N-doped TiO₂ nanosheets with a high percentage of (001) facets were obtained by a simple thermal treatment under NH₃ atmosphere. The effect of the N concentration on the structures and properties of as-prepared photocatalysts was analyzed. Modern characterization methods such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS) were applied to detect the crystal form and nanostructures of the prepared samples. Ultraviolet-visible (UV-Vis) diffuse reflection spectra (DRS) technique was used to detect the change of the band gap and light adsorption. Photogenerated h⁺ and e[−] recombination condition of the prepared photocatalysts was studied by the photoluminescence (PL) technique. Further, PL analysis was used to study the •OH generated on the surface of the photocatalysts in the aqueous solution containing terephthalic acid. The photocatalytic activities in the visible range of the prepared photocatalysts were measured by rhodamine B (RhB) degradation under xenon lamp irradiation with UV light filtered. At last, the visible-light photocatalytic mechanism of TiO₂-N was proposed.

1 Experiment

1.1 Preparation of the photocatalysts

1.1.1 Preparation of TiO₂ nanosheets

All the reagents were of analytical grade and were used

without future purification. Distilled water was used in the whole experiment. TiO_2 nanosheets with a large percentage of exposed (001) facets were prepared via the hydrothermal method in the light of the procedure reported by Han and his coworkers [19].

In a typical synthesis, 25 ml of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and 15 ml of hydrofluoric acid solution (with a concentration 24 wt%) were mixed in a dry Teflon-lined autoclave (60 ml) at room temperature, followed by magnetic stirring for 30 min and hydrothermal treatment at 180 °C for 24 h. After the hydrothermal reaction, the white precipitates were collected by centrifuge and were washed with ethanol and distilled water for three times, respectively. At last, they were dried in a vacuum oven at 80 °C for 12 h before further N doping.

1.1.2 Synthesis of N-doped TiO_2 nanosheets and N-doped P25

The as-prepared TiO_2 nanosheets (0.2 g) were annealed under NH_3 atmosphere at 400 °C for 3 h in a tube furnace, and then the samples were cooled down to room temperature naturally. The flow rate of NH_3 was selected to be 20, 40, 70, and 100 ml/min, and the resulting samples were labeled as $\text{TiO}_2\text{-N20}$, $\text{TiO}_2\text{-N40}$, $\text{TiO}_2\text{-N70}$, and $\text{TiO}_2\text{-N100}$, respectively. N-doped P25 with different N concentration were prepared in the same way and were generally named P25-N.

1.2 Characterization of the photocatalysts

The structure characterization of samples was performed on a diffractometer (ARL X'TRA, American Thermo Elemental Company) employing $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406$ nm), with a scanning rate of 5°/min in the 2θ angle ranged from 20° to 80°. The morphology and size of TiO_2 nanosheets were measured by FESEM. TEM and HRTEM analysis were conducted on a JEM-2010 electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. UV-Vis DRS were obtained for the dry-pressed disk samples using an ultraviolet-visible-near infrared (UV-Vis-Nir) 3101 spectrophotometer (Shimadzu) with BaSO_4 as the reflectance sample in the wavelength ranged from 200 to 700 nm. The surface chemical environment and composition were analyzed by XPS on a PHI5000 VersaProbe system (ULVAD-PHI) with monochromatic $\text{Al } K_\alpha$ X-rays. PL emission spectra were conducted on a FL3-221 fluorescence spectrophotometer (Jobinyvon France) equipped with a 450 W xenon lamp as the excitation source at room temperature.

1.3 Visible-light photoactivity and $\bullet\text{OH}$ generation analysis

The visible-light photocatalytic activity measurements of the prepared photocatalysts were performed according to the reported procedure [26]. The photocatalytic reaction was carried out in a 10 cm culture dish with a 500 W xenon lamp (covered with a UV filter) fixed parallel to the reactor. RhB water solution (30 ml, 10 mg/L) and 100 mg of each photocatalyst were injected into the culture dish, followed by magnetic stirring for 1 h in the dark to establish the adsorption-desorption equilibrium. Then the xenon lamp was turned on to start the photocatalytic reaction which was maintained at ambient temperature by the flowing water in the quartz cool trap fixed around the lamp. A 5 ml of the solution was taken at certain time intervals (15 min) during the measurement process and was centrifuged to remove the suspended photocatalysts completely. The absorption spectra of the RhB solutions were analyzed on the UV-Vis-Nir spectrophotometer.

The $\bullet\text{OH}$ radicals formed on the surfaces of the irradiated photocatalysts were analyzed by the PL technique and terephthalic acid was used as the probe molecule. 2-Hydroxyterephthalic acid, a highly fluorescent compound, could be formed when terephthalic acid interacted with the produced $\bullet\text{OH}$ and the PL intensity was in proportion to the total $\bullet\text{OH}$ produced in the water solution [27,28]. The analysis procedures used were almost the same as the photocatalytic activity measurement except RhB solution was replaced by the terephthalic acid water solution (1 mmol/L) with a concentration of NaOH (4 mmol/L). The PL emission spectra of 2-hydroxyterephthalic acid were recorded on the FL3-221 fluorescence spectrophotometer. The excitation and emission wavelength were 315 and 425 nm, respectively.

2 Results and discussion

2.1 Characterization results of the photocatalysts

FESEM, TEM, and HRTEM technologies were used to observe the shape and size of as-prepared photocatalysts. Figure 1(a) and (b) show the typical FESEM and TEM images of TiO_2 nanosheets. The schematic image of TiO_2 nanosheets, which is in consistent with the wulff construction [21], is shown in Fig. 1(a) (inset). As is observed, the structure of the obtained photocatalyst is well defined, and the average side length and thickness are around 50–100 and 5–10 nm, respectively. As calculated, the average percentage of (001) facets is 75%. HRTEM image shown in Fig. 1(c) displays the lattice spacing clearly. One equals to 0.235 nm corresponding to the (001) facets and the other is 0.35 nm which is ascribed to the (101) facets [18,29]. The FESEM image shown in Fig. 1(d) was used to study the effect of thermal treatment on the morphology change of TiO_2 nanosheets. Clearly, although the particles slightly

Fig. 1. FESEM (a), TEM (b), and HRTEM (c) images of TiO_2 nanosheets and FESEM image (d) of $\text{TiO}_2\text{-N40}$.

cohere with each other and the thickness is doubled, the average side length does not change a lot. Most importantly, the (001) facets which are very significant for photoactivity are maintained.

Fig. 2. XRD patterns (a) and (101) facets diffraction peaks (b) of $\text{TiO}_2\text{-N}$ with different NH_3 flow rate. (1) 0 ml/min; (2) 20 ml/min; (3) 40 ml/min; (4) 70 ml/min; (5) 100 ml/min.

Fig. 3. UV-Vis DRS spectra (a) and estimated band gap (b) of the prepared photocatalysts.

XRD patterns of the prepared photocatalysts are shown in Fig. 2(a). The diffraction peaks of all samples match well with the diffraction peaks of anatase TiO_2 (JCPDS 21-1272). Further observation indicates an obvious shift of the (101) diffraction peak toward the higher angle region (Fig. 2(b)) after nitrogen incorporates into TiO_2 nanosheets, and the shifted angle increases with the NH_3 flow rate increment. As reported, a high angle (a low lattice spacing value) results from the compressive strain of the TiO_2 lattice, which may origin from the different bonding characteristics of oxygen and nitrogen [30]. This phenomenon proves the influence of N concentration on the modification of the electronic structure of TiO_2 band gap is very important for the visible light response.

To further study the change of light absorbance characteristics of the prepared photocatalysts, UV-Vis DRS analysis was used and the absorption spectra are shown in Fig. 3(a). A new absorption peak around 385–500 nm appears. For N-doped photocatalysts, the absorption ability in the range of 500–700 nm also increases. Meanwhile, the visible light absorption increases with the NH_3 flow rate increment,

and this result accords with the color change (from white to pale yellow) of the N-doped photocatalysts. As reported by other researchers, the visible light absorption peak in the range of 500–700 nm is originated from N doping which introduces some localized states above the valance band [31]. Figure 3(b) shows the estimated band gap spectra of the photocatalysts. The band gap of pure TiO₂ nanosheets is around 3.27 eV and there is no visible light response. After N doping, the band gap of all the doped photocatalysts shifts to 3.19 eV and a new gap 2.21 eV appears. Combined with the XRD analysis, the results have suggested that the method of N doping can alter the electronic and crystal structure of TiO₂ nanosheets. It is noted that the oxygen vacancies introduced by N doping, contaminants, and NO_x on the surface may also improve the light absorb ability [32,33].

PL spectra (shown in Fig. 4) of TiO₂ nanosheets and TiO₂-N were measured at room temperature to characterize the recombination effect of photogenerated electron-hole pairs. Each photocatalyst (0.2 g) was injected into a mold and pressed with a 2 MPa pressure to make dry-pressed disks with a diameter of 5 mm. During the experiment process, each as-pressed disk was irradiated with the light

Fig. 4. PL spectra of the prepared photocatalysts ($\lambda_{\text{ex}} = 300$ nm).

with the same wavelength (300 nm), intensity and spot. As the number of photo fluxing into the photocatalysts was the same in any photocatalysts, the intensity of the PL spectra can be used to directly reflect the recombination degree [13,34]. PL spectra of TiO₂-N have lower intensity than TiO₂ nanosheets, which implies the recombination degree in TiO₂ nanosheets was higher than that in TiO₂-N. Further information about the nature of the photocatalysts can be obtained by comparison of the spectra intensity of TiO₂-N with different NH₃ flow rate. Comparing the four doped samples, the PL intensity order is TiO₂-N100 > TiO₂-N70 > TiO₂-N20 > TiO₂-N40. This means the flow rate of NH₃ is a very important factor affecting the photogenerated h⁺ and e⁻ recombination rate, and this will be revealed in the photocatalytic measurements.

The XPS analysis was conducted to further understand the chemical composition and elemental environment of the photocatalysts. Figure 5(a) shows the XPS survey spectra of TiO₂ nanosheets and TiO₂-N40. For TiO₂ nanosheets, it contains Ti, O, and C, and the C 1s peak appearing at 284.6 eV is always attributed to the contaminants in the preparation process. We also found that a new signal of N 1s, originating from NH₃ thermal treatment, appears in TiO₂-N40.

The high resolution XPS spectra for the Ti 2p region of TiO₂ nanosheets and TiO₂-N40 in Fig. 5(b) show significantly change upon nitrogen doping. Compared to the Ti 2p binding energy of TiO₂ nanosheets, the Ti 2p binding energy of TiO₂-N40 decreases 0.2 eV. This is because the electronegativity of nitrogen, lower than oxygen, can induce partial electron transition from N to Ti. Indeed, such phenomenon suggests that the nitrogen species were incorporated into TiO₂ nanosheets successfully.

Figure 5(c) shows the high resolution N 1s XPS spectrum taken on the surface of TiO₂-N40 and its fitting curves. As can be seen, there is a broad peak ranged from 396 to 404 eV, which is a typical character of N-doped TiO₂. After fitting the peak, two peaks at 399.0 and 399.9 eV are obtained.

Fig. 5. XPS survey spectra (a) and high resolution Ti 2p XPS spectra (b) of TiO₂ nanosheets and TiO₂-N40, and high resolution N 1s XPS spectrum of TiO₂-N40 (c). (1) TiO₂ nanosheets; (2) TiO₂-N40.

Considering the experiment process, the N 1s signal obtained at 399 eV can be mainly attributed to the presence of substitutional N [32] and some adsorbed NH_3 may also has a little effect [2,35]. In some cases, the peak at 396 eV which is attributed to the signal of substitution N also appears [36,37]. However, in the present study, this signal does not exist which may result from the different experimental process [37–39]. The N 1s signal fitted at 399.9 eV can be ascribed to the intersectional N in the form of O–Ti–N [40–42]. As is known, the substitutional and intersectional N can form π^* N–O and N 1s when the impurity level is above the VB, respectively. Still, the substitutional N may introduce some oxygen vacancies existing below the conduction band [32] which is another positive factor narrowing the band gap.

2.2 Photocatalytic analysis and mechanisms

The visible light photoactivities of the prepared photocatalysts were measured by the photodegradation of RhB water solution under xenon lamp irradiation ($\lambda > 400$ nm). The photocatalytic degradation percentage is recorded as C/C_0 (C refers to the intensity of RhB absorption spectra at 553 nm, and C_0 is the intensity of the absorption spectra at 553 nm when adsorption-desorption equilibrium is established).

Figure 6(a) presents the PL emission spectrum of the light source used in the photocatalytic measurement. Figure 6(b) and (c) show a comparison of photocatalytic activity of the prepared photocatalysts. As can be observed from the presented results, the NH_3 flow rate plays a significant effect on the photocatalytic activity of the photocatalysts, which is also discussed in the PL analysis. TiO_2 nanosheets and P25 don't show the visible light photocatalytic activity since they don't have visible light responsibility. However, a slight decrease of the RhB concentration during TiO_2 nanosheets and P25 photoactivity measurement process is observed, which may result from the adsorption effect of the nanoparticles. In the N-doped samples, $\text{TiO}_2\text{-N40}$ holds the highest photocatalytic activity, although $\text{TiO}_2\text{-N70}$ and $\text{TiO}_2\text{-N100}$ have much higher visible light absorption ability. Further, the photoactivity of $\text{TiO}_2\text{-N40}$ is higher than P25-N40. This is probably, on one hand, due to the excessive concentration of N in the doped TiO_2 nanosheets and the higher concentration defects [25]. On the other hand, combined with the FESEM analysis, these results further confirm the importance of (001) facets in the visible-light photoactivity.

Further study in this case was conducted by $\cdot\text{OH}$ PL spectra. Figure 7(a) shows a comparative study of the PL intensity for the prepared photocatalysts after being irradiated under the visible light for 15 min. As mentioned before,

Fig. 6. PL emission spectrum of the light source used (a) and photocatalytic activity of $\text{TiO}_2\text{-N}$ (b) and P25-N (c) with different NH_3 flow rate. (1) 0 ml/min; (2) 20 ml/min; (3) 40 ml/min; (4) 70 ml/min; (5) 100 ml/min.

the PL intensity is proportional to the total amount of $\cdot\text{OH}$ generated. It is clear that $\text{TiO}_2\text{-N40}$ has the highest PL intensity under the same time of visible light irradiation which means there are more $\cdot\text{OH}$ produced on the $\text{TiO}_2\text{-N40}$ surface among the measured photocatalysts. This result is in good agreement with the photocatalysis measurements. However, no PL signal at 425 nm is observed for TiO_2 , which means there is almost no $\cdot\text{OH}$ produced. This phenomenon can also be proved by the UV-Vis DRS analysis.

The PL spectra of $\text{TiO}_2\text{-N40}$ under visible light irradiation are shown in Fig. 7(b). It is shown that the PL intensity increases with the irradiation time. On one hand, this result indicates the produced $\cdot\text{OH}$ was proportional to the irradiation

Fig. 7. PL spectra of TiO₂-N with different NH₃ flow rate in a 1 mmol/L aqueous solution of terephthalic acid irradiated for 15 min (a) and PL spectral changes with time of TiO₂-N40 in a 1 mmol/L aqueous solution of terephthalic acid (b).

tion time. On the other hand, $\cdot\text{OH}$ had sufficient oxidation power and could be transferred to the surface-adsorbed water molecules [25].

Based on the aforementioned experiments and analysis, the mechanisms for the photocatalysis reactivity are proposed. The high visible-light photoactivity of as-prepared

TiO₂-N may result from the following factors: (1) the existence of high reactive (001) facets, (2) enhanced light adsorption in the visible range, and (3) the reduction of photogenerated h^+ and e^- recombination rate.

Firstly, calculation and experiment studies in many literatures indicated that (001) facets had a lower band gap and a high reactivity. Also, these facets could absorb the organic molecules easily, which was positive for photocatalysis [13,14]. Secondly, N doping can narrow the band gap by the formation of $\pi^* \text{N-O}$, N 1s and oxygen vacancy impurity levels. For this, TiO₂-N can be activated by visible light. Photogenerated h^+ and e^- on the particles can interact with the absorbed O₂, H₂O, and OH to form O₂⁻, $\cdot\text{OH}$, H₂O₂, and OH⁻ for RhB degradation. Thirdly, h^+ and e^- recombination rate is reduced by N doping, and this allows the production of more reactive centers. As we can see, the visible-light photoactivities of TiO₂-N do not always increase with the N doping concentration increment. However, a proper concentration of N will enhance the photoactivity significantly. The schematic diagram of the visible light response and radicals production is shown in Fig. 8. The reaction steps can be explained as follows:

Fig. 8. Schematic diagram of the photocatalysis mechanism of TiO₂-N under visible light irradiation.

3 Conclusions

Pure TiO₂ nanosheets with dominant exposed (001) facets were successfully prepared by hydrothermal method and they were post thermal treated under NH₃ atmosphere for N doping. The NH₃ flow rate, resulting in different N concentration, seriously influences the properties of TiO₂-N. Among all the photocatalysts, TiO₂-N40 has the highest visible-light photoactivity. The UV-Vis DRS analysis displays N doping narrows the band gap of TiO₂ nanosheets,

and the visible light absorption increases with the increment of NH₃ flow rate. The XRD and XPS measurements further confirm that N doping change the lattice and electronic structures of TiO₂ nanosheets. The N species located are the combination of NH₃, substitutional and intersection N. After N doping, photogenerated e^- and h^+ recombination rate is reduced, and the total amount of $\cdot\text{OH}$, generated at the surface of the photocatalysts and aqueous solution, is improved. Totally, a proper N doping concentration is the main factor for improving the visible light photocatalytic activity

of N-doped TiO₂. A large percentage of (001) facets, the improvement of visible light adsorption and •OH generation on the nanosheets surface, as well as the reduction of e⁻ and h⁺ recombination are responsible for the visible light photo-activity enhancement of TiO₂-N. This study gives a new insight on the mechanisms of TiO₂-N with different N concentration. The as-prepared TiO₂-N is one of the very promising photocatalysts to extend their application fields and to improve solar light efficiency.

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