Preparation of N-TiO$_2$/SiO$_2$ composites by solvothermal method and their photocatalytic properties

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Abstract

In order to improve the visible light catalytic activity of titanium dioxide (TiO$_2$) and ensure its long-term stability on the surface of concrete, an N-TiO$_2$/SiO$_2$ composite was prepared using tetrabutyl titanate, nitric acid, and modified SiO$_2$ nanospheres as the precursors by a solvothermal method. The effect of nitric acid on the phase composition, morphology and photoelectric properties of the synthesized photocatalytic composites was systematically studied by various characterization methods. The results show that the optimum nitric acid/butyl titanate volume ratio is 1/6. The nitrogen-doped TiO$_2$ nanoparticles were uniformly dispersed on the surface of spherical SiO$_2$ with a diameter of 200 nm. The degradation rate of simulated pollutants (RhB) with pH 5 and 7 exceeded 95% within 30 min and the catalytic effect remained excellent after five repetitions without much weakening. The excellent visible photocatalytic performance can be attributed to the doping of N replacing part of the oxygen atoms in TiO$_2$, forming the energy level of N 2p at the O 2p energy level and reducing the TiO$_2$ energy band gap to 2.99 eV. At the same time, the better dispersion of N-TiO$_2$/SiO$_2$ prepared by this new synthesis method also plays an important role in the improvement of visible light photocatalytic activity.

1. Introduction

Nowadays, fossil energy is still the most important source of energy consumed. The inadequate combustion of fossil energy produces a variety of harmful nitrogen oxides, which has carcinogenic effect. Meanwhile, the household furniture and home decoration also hide excessive levels of formaldehyde, benzene and other harmful substances, which are extremely dangerous to human health, and it is necessary to purify them. At present, there are many methods for the purification of air pollutants, including ventilation, biological purification, adsorption, photocatalysis, etc. Among them, photocatalytic method has been a hot spot for research because of its high degradation efficiency and low secondary pollution.

Titanium dioxide (TiO$_2$), as a photocatalytic semiconductor material with stable performance, low price, non-toxic and pollution-free, has attracted extensive attention in scientific research [1–3]. In 1972, the photocatalytic property of TiO$_2$ was first reported by Japanese scientists Fujishima and Honda [4, 5], and it has gradually been widely used in the field of air purification [6–8] and sewage treatment [9–11]. However, the large band gap energy (3.2 eV) and the easy closure of electron-holes of TiO$_2$ lead to poor catalytic effect in visible light. Therefore, the application of TiO$_2$ is also subject to certain restrictions, and its photocatalytic activity need to be improved.

Silicon dioxide (SiO$_2$) is widely used in the modification of TiO$_2$ because of its large specific surface area, high mechanical strength, high stability and aging resistance [12]. It was found that the photocatalytic ability of the TiO$_2$ synthesized with nano-SiO$_2$ as carrier can be enhanced under UV light condition [13]. However, the enhancement of photocatalytic performance is still at physical level, as the improvement of photocatalytic
property only by reducing the agglomeration of TiO$_2$ to increases its specific surface area. Thus, it is still necessary to further improve the catalytic ability of TiO$_2$, and expand the light response band to visible light, which needs to reduce the band gap energy of TiO$_2$ and decrease the closure of electron hole pairs [14]. In addition, due to the high volcanic ash activity of nano-SiO$_2$, it is capable of volcanic ash reaction with Ca(OH)$_2$ produced by cement hydration. Consequently, nano-SiO$_2$ is an ideal carrier when used TiO$_2$ as a decorative material, and it can be stably adhered to the concrete surface in a long-term without other adhesives.

There are two strategies to modify TiO$_2$ through elemental doping, namely metal modification and non-metal modification. The catalytic activity of TiO$_2$ induced by metal doping modification can be attributed to the increase of the electron-hole complexation time [15]. In contrast, the modification of non-metallic elements enables visible response via narrowing the forbidden band width and expanding the corresponding range of visible light [16]. Hence, the non-metallic modified photocatalytic materials have higher visible light activity. The non-metallic element N is the most widely used modified element because it is close to the O element in both atomic radius and elemental position, and some of the O atoms can be replaced by N atoms [17]. Sato et al [18] found the N element doping can endow visible light activity to TiO$_2$ as early as 1986, however, it did not attract widespread attention until 2001 when Asahi [19] reported the results about N doping. And the doping of N can effectively hinder the crystal growth of TiO$_2$, stabilize the structure of the crystal and increase the specific surface area [20]. Most of the N sources used for the visible light modification of TiO$_2$ are mainly from urea and ammonia [21–26]. However, it is necessary to add stabilizers to control the reaction rate to make the reaction process more controllable, so it is easy to cause some pollution. Moreover, the catalytic effect of the obtained N doping semiconductor catalytic materials with visible light is not satisfactory, which needs to be deeply investigated.

In the present work, N-TiO$_2$/SiO$_2$ composites were successfully prepared using tetrabutyl titanate, nitric acid, and modified SiO$_2$ nanospheres as the precursors by a solvothermal method. And the effect of nitric acid on the phase composition, morphology and photoelectric properties of the synthesized composites was systematically investigated. The nitric acid in this process acts as both a stabilizer in the hydrolysis process and a reactant in the solvothermal process, providing a simple and effective idea to improve the visible light activity of TiO$_2$. Meanwhile, the addition of nanoscale active silica not only provides a carrier for TiO$_2$ compounding, but also serves as a good compatible material making it promising for the application of functional photocatalytic treatment of concrete materials.

2. Experimental

2.1. Materials
Ethyl silicate (tetraethyl orthosilicate), butyl titanate (tetrabutyl titanate), concentrated nitric acid and ammonia (ammonia monohydrate) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were of analytical grade and used as received. The water used in this study was purified using a Milli-Q water system.

2.2. Solvothermal synthesis of N-TiO$_2$/SiO$_2$

2.2.1. Synthesis of nano-SiO$_2$
Nano-SiO$_2$ with a diameter of about 200 nm were synthesized using Stöber method [27] by adjusting the amount of ethyl silicate. The detailed processes are as follows: Firstly, 130 ml of anhydrous ethanol, deionized water and ammonia solution with a volume ratio of 10:2:1 was taken as solution A. Then, the solution B was mixed with ethyl silicate and ethanol at a concentration of 12.3%. Finally, the solution B was added dropwise to the solution A at a rate of 20 ml min$^{-1}$ and then stirred magnetically for 12 h. The milky solution obtained after stirring was washed with anhydrous ethanol and centrifuged three times to obtain a white precipitate, which is SiO$_2$ with a diameter of about 200 nm. The samples were dried at 80°C and then ground.

2.2.2. Acidification treatment of nano-SiO$_2$
Take 0.4 g of dried and ground nano-SiO$_2$ and dissolved in 20 ml deionized water, dilute nitric acid was added until the solution pH was 1, and stirred magnetically for 30 min. The treated nano-SiO$_2$ was washed with anhydrous ethanol and centrifuged three times and set aside.

2.2.3. Synthesis of N-TiO$_2$/SiO$_2$
The above treated nano-SiO$_2$ was ultrasonically dispersed into 40 ml anhydrous ethanol, and the solution C was obtained by adding a certain amount of concentrated nitric acid and stirring magnetically for 15 min after dispersion. Add 6 ml tetrabutyl titanate to 20 ml anhydrous ethanol and stirred magnetically for 30 min to obtain solution D. Solution D was added dropwise to solution C at a rate of 10 ml min$^{-1}$ and stirred for 30 min to obtain the N-TiO$_2$/SiO$_2$ precursor. The precursor was transferred to 100 ml teflon-lined autoclave. The
autoclave was sealed and heated in electric oven at 180 °C for 12 h. After the reaction, the autoclave was allowed to cool to room temperature and pour out. The obtained precipitate was washed several times with anhydrous ethanol. Finally, the N-TiO2/SiO2 composite was obtained by oven drying at 80 °C. The following five groups of samples were obtained with different amounts of nitric acid addition TiO2/SiO2, 1/12 N-TiO2/SiO2, 1/6 N-TiO2/SiO2, 1/4 N-TiO2/SiO2, 1/3 N-TiO2/SiO2 (indicates the volume ratio of concentrated nitric acid to tetrabutyl titanate was 0, 1:12, 1:6, 1:4, 1:3, respectively).

The above solvothermal method for N-TiO2/SiO2 composites synthesis possesses the advantages of simple process, easy operation, non-pollution and higher security. And the yield of synthetic products by this method is larger and can be produced in industrial large batches.

2.3. Materials characterizations
The phase composition of the samples was tested using a D8 Advance x-ray diffractometer (Bruker, Germany) with a scan range of 2θ = 15° ~ 65° and a scan rate of 8° min⁻¹. The microscopic morphology and lattice dimensions of the samples were obtained using a TEM (FEI Talos F200S, USA) operating at 200 kV of accelerating voltage. The infrared absorption spectroscopy was performed using an infrared spectrophotometer of TENSOR 27 (Bruker, Germany). Elemental valence states and doping positions were observed by x-ray photoelectron spectroscopy (XPS) (Thermo Fisher, ESCALAB 250Xi, USA) with a calibration of C 1s (284.8 eV). The UV–visible NIR spectrophotometer (Shimadzu UV3600 plus, Japan) was used to investigate the UV-visible diffuse reflectance of the samples. Specific surface areas and pore structures were probed by measuring volumetric N2 adsorption-desorption isotherms at liquid nitrogen temperature, using an ASAP 2020 HD88 instrument (Micromeritics, USA).

2.4. Photocatalytic degradation experiments
A multi-channel photocatalytic reaction system (Porphyry PCX-50C Discover, Beijing) with a UV–visible spectrophotometer (Sunyu Hengping 721, Shanghai) was applied for the photocatalytic degradation experiments, and LED visible light was used as the light source with an optical power of 100 mW/cm⁻².

An aqueous solution of rhodamine B (RhB) at a concentration of 10 mg l⁻¹ was used as the contaminant, and weighed 0.05 g sample in 50 ml contaminant. The samples were sonicated in the dark for 1 h to reach adsorption-desorption equilibrium with the contaminants. The equilibrated contaminants were placed in a multi-channel reaction system using 5 W white light irradiation, and in the irradiation stage, samples were taken every 10 min. The absorbance of the samples after centrifugation was measured using a UV-vis spectrophotometer. The catalytic effect of the catalytic material was analyzed by calculating the degradation rate η of RhB according to the concentration changes of RhB. The equation of degradation rate η as following:

\[
\eta = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \tag{1}
\]

where, \(C_0\) is the absorbance of RhB before light after dark reaction, \(C_t\) is the absorbance of RhB after light exposure for \(t\) time.

3. Results and discussion
3.1. XRD analysis
The XRD patterns of TiO2/SiO2 and N-TiO2/SiO2 composites with different nitric acid/butyl titanate volume ratios were shown in figure 1. The positions of the four characteristic peaks (101), (004), (200) and (105) are consistent with the JCPDS card 21-1272 of TiO2. This indicates that the prepared TiO2 is anatase phase and shows a good degree of crystallization. Compared with TiO2/SiO2, the diffraction peaks of N-TiO2/SiO2 were obviously sharper. This could be attributed to N doping in favor of the crystallization of TiO2. As the amount of nitric acid increases, the intensity of each diffraction peak has no significant change. According to Scherrer’s formula, the particle size of TiO2 obtained by this method was about 7 nm, and the diameter of TiO2 in the TiO2/SiO2 sample prepared without nitric acid was about 8 nm. After adding nitric acid, the particle sizes of the samples were 6.4 nm, 6.3 nm, 6.3 nm, and 6.1 nm, and the particle sizes became smaller as the amount of nitric acid increased. The acidification treatment of nano-SiO2 and the addition of nitric acid, which decreased the pH value of the solvent and inhibited the rate of TiO2 production by thermal decomposition of tetrabutyl titanate. This makes the reaction become calm and steady and the particle size of the generated TiO2 is relatively smaller. Since SiO2 is amorphous, the characteristic peaks of SiO2 were not observed in XRD and need to be further verified by FT-IR.
3.2. TEM analysis

Two representative composites of A (TiO$_2$/SiO$_2$) and B (1/6N-TiO$_2$/SiO$_2$) were selected for TEM measurements, the microscopic morphology and load thickness were observed respectively, and the lattice spacing was calculated. From figures 2(A) and (B), it can be seen that SiO$_2$ is in a standard spherical shape with a particle size of about 200 nm, and TiO$_2$ is dispersed around the SiO$_2$. Comparing the two figures, it can be seen that the TiO$_2$ generated from the undoped N sample (figure A) has a serious agglomeration and uneven distribution. There is a part of SiO$_2$ surface without TiO$_2$ attached. In contrast, for the N-doped sample (figure B), TiO$_2$ is more uniformly dispersed on the SiO$_2$ surface, and the agglomeration has been greatly alleviated. It can be seen that the thickness of TiO$_2$ loading is significantly reduced when comparing figures 2(A) and (B), which can increase the light receiving area of TiO$_2$ and improve the catalytic ability. Meanwhile, it can be observed from the figure that the particle size of the prepared TiO$_2$ is approximately 6 nm in general agreement with the XRD calculation. Finally, there was an increase of lattice spacing by calculating the lattice spacing of these two samples, the lattice spacing of the TiO$_2$/SiO$_2$ sample prepared without the addition of nitric acid was found to be about 0.371 nm, while the lattice spacing of TiO$_2$ in the 1/6N-TiO$_2$/SiO$_2$ sample prepared with nitric acid was about 0.374 nm. This might be attributed to the atomic radius of N is larger than O, N atoms replaced O atoms into TiO$_2$, leading to the phenomenon of TiO$_2$ lattice enlargement.

3.3. BET analysis

Table 1 shows the specific surface area, average pore volume and average pore size of the as-prepared composites. The specific surface area of pristine TiO$_2$ and TiO$_2$/SiO$_2$ composites prepared without N-doping are about 60 m$^2$/g and 93.213 m$^2$/g, respectively, indicating the specific surface area can be increased by using SiO$_2$ as a carrier. The specific surface areas of the 1/12N-TiO$_2$/SiO$_2$, 1/6N-TiO$_2$/SiO$_2$, 1/4N-TiO$_2$/SiO$_2$, and 1/3N-TiO$_2$/SiO$_2$ were further increased with the doping of N elements and the increase of the doping amount. Among them, the specific surface area of 1/6N-TiO$_2$/SiO$_2$ is 178.362 m$^2$/g, which is about three times of the original TiO$_2$, and the specific surface area of 1/12N-TiO$_2$/SiO$_2$, 1/4N-TiO$_2$/SiO$_2$, 1/3N-TiO$_2$/SiO$_2$ are 138.590 m$^2$/g, 103.066 m$^2$/g, and 99.939 m$^2$/g, respectively. It can be seen that the specific surface area of the as-prepared composites tends to increase and then decrease with the increase of N.

| Samples          | Average BET specific surface area (m$^2$/g) | Average pore volume (cm$^3$/g) | Average pore size (nm) |
|------------------|--------------------------------------------|-------------------------------|------------------------|
| TiO$_2$/SiO$_2$  | 93.213                                     | 0.123                         | 6.356                  |
| 1/12N-TiO$_2$/SiO$_2$ | 138.590                                   | 0.231                         | 6.351                  |
| 1/6N-TiO$_2$/SiO$_2$ | 178.362                                   | 0.156                         | 3.674                  |
| 1/4N-TiO$_2$/SiO$_2$ | 103.066                                   | 0.128                         | 4.820                  |
| 1/3N-TiO$_2$/SiO$_2$ | 99.939                                    | 0.119                         | 5.120                  |
element doping compared to TiO$_2$/SiO$_2$. The variation of average pore volume and average pore size are consistent with tendency of specific surface area. The main reason can be attributed to the addition of nitric acid, which can control the reaction rate and makes the generated TiO$_2$ more uniform, better dispersed and smaller.

3.4. FT-IR analysis

Figure 3 shows the FT-IR spectra of N-TiO$_2$/SiO$_2$ composites with different N contents. The broad peak at 3420 cm$^{-1}$ in the spectrum can be attributed to the stretching vibration absorption of the O–H bond in the water and
alcohol molecules. The peaks at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) occurred due to the C–H bond stretching vibration absorption of \(-\text{CH}_3\) and \(-\text{CH}_2\) \(-\text{CH}_2\) respectively. The peak at 1632 cm\(^{-1}\) confirms the flexural vibration absorption of H–O–H in water molecules. From the figure 3, it is observed that the peak gradually strengthens with the increase of nitric acid dosage, indicating the increase of hydrophilicity. The peak at 1105 cm\(^{-1}\) is attributed to the asymmetric stretching vibration of the Si–O–Si bond \[28\]. The 940 cm\(^{-1}\) peak is derived from the vibrational absorption of the Ti–O–Si bond \[29\]. The formation of Ti–O–Si bonds indicates that TiO\(_2\) and SiO\(_2\) are bonded in the form of a chemical bond \[30\], which provides favorable conditions for the long-term stable existence of N–TiO\(_2\)/SiO\(_2\) composite materials. The broad peak below 1000 cm\(^{-1}\) is the stretching vibration absorption peak of Ti–O–Ti \[31\]. The intensity of the peak at 1400 cm\(^{-1}\) gradually increases with the amount of nitric acid, so it is presumed the peak is related to nitrate or N–Ti bonding.

### 3.5. XPS analysis

XPS measurements were carried out to investigate the valence and doping positions of N atomic. Figures 4(A)–(C) show the XPS high-resolution spectra of Ti 2p, O 1s and N 1s on the surface of the composites, respectively. As seen from figure 4(A) that the Ti 2p of each sample is composed of two symmetrical peaks with a comparative standard peak shape, which corresponds to the electronic binding energy of Ti 2p\(^{3/2}\) and Ti 2p\(^{1/2}\), respectively. The electron binding energy difference between the two Ti 2p peaks of TiO\(_2\)/SiO\(_2\) without N doping is 5.85 eV. With the doping of N element, the difference of electron binding energy between the two peaks of N-TiO\(_2\)/SiO\(_2\) is basically 5.8 eV. Compared with the 5.85 eV of TiO\(_2\)/SiO\(_2\), the peak position of Ti 2p\(^{3/2}\) also gradually shifted to the direction of low binding energy with the increase of N content. From figure 4(B), it is observed that there...
have O 1s peaks near 530 eV and 533 eV, which belongs to the O 1s peak in TiO2 and SiO2 respectively. It can be seen that the O 1s peak of TiO2 at 530 eV that the doping of N element reduces its electron binding energy and the greater the shift toward lower energy as the doping of N element increases. As N atomic has smaller electronegativity compared with O atomic, electrons in N can be transferred into Ti atomic, which makes the electron cloud density around Ti increase, and similarly the electron cloud density around Si also undergoes similar changes. Therefore, the electron binding energy between the two peaks of Ti 2p3/2, O 1s, and Ti 2p in N-doped TiO2/SiO2 is reduced, which indicates N has entered into the lattice of TiO2 [32, 33]. Meanwhile, the XPS high resolution spectrum of N 1s displays that with the increase of N doping, the peak of N 1s at 399.8 eV appears and gradually enhances, indicating the gradual formation of O—Ti—N [34]. Thus, it can be confirmed by XPS measurement that N atoms replaced some O atoms and successfully entered the TiO2 lattice, and the characterization results are consistent with TEM. From the XPS element analysis in table 2, the N element content in the TiO2/SiO2 samples originated from the ammonia added during the preparation of SiO2.

Table 2. Element analysis of N-TiO2/SiO2 composite photocatalyst materials with different N content.

| Sample         | χTi (%) | χN (%) | N 1s peak position (eV) | Ti 2p3/2 peak position (eV) | O 1s peak position (eV) |
|----------------|---------|--------|-------------------------|----------------------------|------------------------|
| TiO2/SiO2      | 29.15   | 0.45   | —                       | 458.75                     | 530                    |
| 1/12N-TiO2/SiO2| 31.49   | 0.63   | 399.8                   | 458.75                     | 529.95                 |
| 1/6N-TiO2/SiO2 | 40.97   | 0.68   | 399.8                   | 458.7                      | 529.9                  |
| 1/4N-TiO2/SiO2 | 36.71   | 0.72   | 399.8                   | 458.65                     | 529.9                  |
| 1/3N-TiO2/SiO2 | 40.80   | 0.79   | 399.8                   | 458.7                      | 529.8                  |

3.6. UV–vis DRS (diffuse reflectance spectra) analysis

To further verify the effect of N element on the electronic structure of TiO2, the light absorption range of the prepared composites were probed through ultraviolet-visible diffuse reflectance (UV–vis) spectroscopy. It can be obtained from figure 5 that the doping of N elements in the UV region makes the activity relatively weaker compared with that of TiO2/SiO2 composites. However, in the visible light region, the light absorption of the composite doped with N element is obviously enhanced, and there is a tendency to increase and then decrease with the overall doping amount, which can be attributed to the formation of a localized intermediate band gap N 2p energy level in the O 2p valence band of TiO2 with the doping of N elements. As a result, the electrons in this energy level can be excited to the conduction band of TiO2, so that photons with longer wavelength can be absorbed as well, making the optical response of TiO2 red-shifted and improving the absorption ability in visible light.

The energy band gap of each sample was calculated based on the UV–vis data using the Tauc plot method as shown in figure 6. Figure 6 also demonstrated that the energy band gap of TiO2 in the TiO2/SiO2 composite...
without N element doping is about 3.213 eV. The forbidden band widths of the prepared N—TiO₂/SiO₂ photocatalytic composite materials were all reduced when N was doped. Among them, the minimum band gap of TiO₂ in the 1/6 N-TiO₂/SiO₂ sample is about 2.987 eV, which again shows that the doping of N element broadens the light response range of the sample.

3.7. Photocatalytic activity

Figure 7 shows the results of visible light catalytic activity measurement of the photocatalytic composites. The degradation rate of SiO₂/TiO₂ photocatalytic composite was less than 10% for 10 mg/L RhB under 50 min visible light irradiation. The degradation efficiency was extremely weak, and there was almost no visible light catalytic effect. For the N-SiO₂/TiO₂ series photocatalytic composites, the catalytic efficiency under visible light was obviously improved, and the order of photocatalytic efficiency is: 1/6N-TiO₂/SiO₂ > 1/12N-TiO₂/SiO₂ > 1/4N-TiO₂/SiO₂ > 1/3N-TiO₂/SiO₂. The catalytic efficiency exhibits a trend of increasing and then decreasing with the increase of N element doping. The degradation rate of 1/6N-TiO₂/SiO₂ was over 99% at 30 min to the dying agent, which had high visible light catalytic activity. The catalytic activity measurement indicates that N doping promotes the catalytic effect of the material, but too much N doping will inhibit the catalytic effect. This could be attributed to the appropriate amount of N incorporation promotes the effective
separation of photo-generated charges, but excessive N elements leads to compounding of photogenerated electrons during the transport process, and final resulting in a decrease in photocatalytic activity [34].

The charge on the catalyst surface reflects the pH of the solution, which in turn directly and qualitatively responds to the charge properties of the catalyst surface, the charge properties of the dye molecules, and the adsorption capacity of the catalyst. The presence of different amounts of H$^+$ or OH$^-$ has a corresponding effect on the redox reaction of the pollutants. Therefore, the degradation experiments were carried out using 1/6N-TiO$\_2$/SiO$\_2$ for pollutants at 10 mg l$^{-1}$ and different pH to investigate the effect of pH on the catalytic activity. As can be seen from figure 8, the photocatalytic composite performed well in five groups of pollutants with different PH values of 3, 5, 7, 9 and 11, respectively, in which the catalytic activity showed a trend of increasing and then decreasing with the PH varies from low to high. The catalytic composites performed the best with the highest catalytic activity in pollutants with pH 5 and 7, followed by the performance in pH 3.

Reproducibility of catalytic materials, that is, the reusable nature of catalytic materials, reflects the stability. In order to verify the recyclable nature of the photocatalytic material, the 1/6N-TiO$\_2$/SiO$\_2$ batch was selected for reproducible experiments, the results are shown in figure 9. It can be seen that the reduction of photocatalytic effect after five times of repeated use is not much, and the degradation is basically finished in 30 min, so the reproducibility effect is acceptable.

Figure 8. Activity of photocatalytic materials at different pH values.

Figure 9. Photocatalytic activity of materials with different repetition times.
4. Mechanism analysis

According to the analysis of the characterization results, we speculate the reaction mechanism of N-doped n-TiO₂/SiO₂, as shown in figure 10. With the addition of N element, a local intermediate band gap N 2p level is formed on the O 2p valence band of TiO₂, so that the electrons at this level can be excited to the conduction band of TiO₂, and the photons with longer wavelength can also be absorbed, the optical response range of TiO₂ is red shifted and the band gap width is reduced. At the same time, SiO₂ as a carrier weakens the agglomeration of TiO₂ and increases the specific surface area of TiO₂. At the same time, SiO₂ can inhibit the closure of photogenerated electron hole and greatly improve the conversion efficiency. Therefore, the prepared composite photocatalytic materials have high visible light photocatalytic activity.

5. Conclusion

In this study, the N–TiO₂/SiO₂ composites exhibit visible light catalytic activity were successful synthesized, and their phase composition, morphologies and photoelectric properties were investigated. The results show that the TiO₂ with a diameter of about 7 nm is uniformly distributed on the surface of the 200 nm diameter SiO₂ nanospheres, and the TiO₂ is bonded to SiO₂ by Ti–O–Si bonds. The N atom replaces part of the O atom into the TiO₂ lattice, resulting in a redshift of the TiO₂ photoresponse range and a narrowing of the band gap from 3.213 eV to 2.987 eV. The catalytic effect was optimal when the ratio of nitric acid to butyl titanate was 1:6 and the ambient pH value was neutral or weakly acidic, and the degradation rate of RhB solution with a mass concentration of 10 mg/l for 30 min reached more than 99%, and the composites show acceptable stability in use.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
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