Preparation and Photocatalytic Properties of Ce/g-C₃N₄ Co-doped TiO₂ Nanomaterials

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Abstract. A Ce/TiO₂/g-C₃N₄ composite material was prepared by sol-gel method using g-C₃N₄ as support and Ce(NH₄)₂(NO₃)₆ as dopant. The structural and morphological characterization of the samples was detected by TEM, XRD, FTIR, UV-Vis. RhB was selected as the target pollutant, the photocatalytic and renewable properties of the samples driven by visible light were evaluated. The results showed that Ce/TiO₂/g-C₃N₄ had excellent heterojunction structure. The ternary components cooperate with each other to show excellent photocatalytic performance for RhB solution with molar concentration of 0.5×10⁻⁵ mol·L⁻¹ under the condition of dosage of 20.0 mg, pH 5.0 and visible light-driven 180 min. The degradation rate of RhB was 99.3% better than that of g-C₃N₄, TiO₂ and Ce/TiO₂. Cyclic degradation experiments indicated that the Ce/TiO₂/g-C₃N₄ had high photocatalysis stability and reusability. Active group capture experiments revealed that ·O₂⁻ was the main active species in the photocatalytic degradation of RhB over Ce/TiO₂/g-C₃N₄, and the corresponding contribution rate of ·O₂⁻ was 84.1%.

1. Introduction

As a pollution-free environment-friendly technology with high efficiency and mild reaction conditions, photocatalysis has application values in fields such as pollutants degradation, novel functional materials development and solar energy utilization. Among various photocatalytic materials, TiO₂ displays high research and commercial values due to its high activity, high stability and non-toxicity. It has been widely applied in fields such as photocatalytic degradation of organic pollutants, hydrogen production from water splitting, and bacterial resistance. However, the wide band gap of TiO₂ leads to low sunlight utilization efficiency. In addition, the electron-hole pairs generated by photoexcitation of TiO₂ recombine easily, which inhibits the photocatalytic activity of TiO₂ to some extent. Therefore, the modification of TiO₂ photocatalytic materials has attracted the attention of scholars in the field of photocatalysis.

According to relevant studies on new carbon materials, g-C₃N₄ has a band gap of about 2.7 eV. It is an organic non-metallic semiconductor material with high catalytic activity, superior chemical and thermal stability, and strong visible light absorption capability. Therefore, when a photocatalyst is doped with g-C₃N₄, the photocatalytic performance of the material can be enhanced. Wei et. Al. synthesized ternary heterostructured nanofibers through electrospinning and thermal oxidation/reduction employing noble metal nanoparticles, g-C₃N₄ and TiO₂ as components. The results indicate that the ternary heterostructure possesses superior photocatalytic activity compared with single-component photocatalysts such as g-C₃N₄ or TiO₂. This is caused by the photosensitization effect between plasmon resonance and heterojunction interface sensitization, which results in the
improvement of charge-carrier generation. Ye et al. [4] prepared a g-C3N4/TiO2 composite photocatalytic material by thermal conversion. The material was characterized to display an excellent heterojunction structure, which not only enhanced the light absorption intensity of the material, but also improved the efficiency of charge-carrier separation, thus, leading to significantly enhanced photocatalytic performance of the material under visible light irradiation. Therefore, the g-C3N4/TiO2 composite can form excellent heterojunction nanostructures to effectively expand the photosresponse range of TiO2, suppress the recombination of electron-hole pairs, and improve sunlight utilization and photocatalytic efficiency. In recent years, the doping of rare earth ions such as Ce4+ has also become popular for TiO2 modification to effectively improve the photocatalytic activity of TiO2 [5].

As a basic dye, Rhodamine B (RhB) is largely applied in textile and food industries, and therefore, presents widely in environment. The substance is featured by complex structure, toxicity, and difficult degradation. The wastewater of RhB displays high chromaticity and the solution pH does not affect the absorption spectrum evidently. Therefore, the degradation of RhB is often used as a model reaction in photocatalytic degradation. In the current study, a novel Ce/TiO2/g-C3N4 ternary heterojunction photocatalytic material was prepared by sol-gel method using tetrabutyl titanate (Ti(OC4H9)4) as precursor, g-C3N4 as support and ammonium cerium(IV) nitrate ((NH₄)₂Ce(NO₃)₆) as dopant. The morphologies, crystal forms and chemical structures of the products were characterized by TEM, XRD, FTIR and UV-Vis. The photodegradation experiments of RhB under visible light were carried out to evaluate the catalytic and cyclic properties of the photocatalytic materials, and to investigate the degradation mechanism of RhB.

2. Experimental

2.1. Materials and Equipment

Materials: Ti(OC4H9)4 (AR grade) and Ce(NH₄)₂(NO₃)₆ (AR grade) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd; 1,3,5-Triazine-2,4,6-triamine (C₃H₆N₆, CP grade), RhB (AR grade), 1,4-Benzquinone (BQ, AR grade), EDTA·2Na (AR grade), anhydrous ethanol (C₂H₅OH, AR grade), anhydrous methanol (MeOH, AR grade), glacial acetic acid (CH₃COOH, AR grade) and nitric acid (HNO₃, AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd; Deionized water was self-prepared.

Equipment: JEM2100 Transmission Electron Microscope (TEM, JEOL Ltd.); D8 Advance Davinci X-ray diffractometer (XRD, Bruker Corporation) and Vertex 70 Fourier Transform Infrared Spectroscopy (FTIR, Bruker Corporation); Lambda950 Ultraviolet-Visible Spectrum Scanner (UV-vis, Perkin-Elmer, Inc.); UV-6100 Ultraviolet-Visible Spectrophotometer (Shanghai Metash Instruments Co., Ltd.); ULTRA-VITALUX UV Lamp (OSRAM China Lighting Ltd.); DZF-6090 Vacuum Dry Oven (Shanghai Huitai Instrument Manufacturing Co., Ltd.); 5404R centrifuge (Eppendorf Corporate); HJ-3 Magnetic Stirrer (Changzhou Guohua Electric Appliance Co., Ltd).

2.2. Sample Preparation

g-C3N4: A certain amount of C₃H₆N₆ was placed in a muffle furnace after grinding, then heated to 550 °C at a heating rate of 5 °C min⁻¹, and calcined for 3 h. After cooling to room temperature, it was ground again to obtain the pale yellow colored powdery g-C3N4 material.

Ce/TiO2: TiO2 sol (sol A) was prepared from the hydrolysis of the precursor Ti(OC4H9)4. Ce(NH₄)₂(NO₃)₆, glacial acetic acid and 95% ethanol were mixed and stirred using a magnetic stirrer for 30 mins to obtain solution B. Sol A was then added to solution B slowly, and Ce/TiO2 sol was formed with ultrasonic assistance for 1h. After aging at room temperature, the sol was dried in a vacuum oven (80 °C) and ground afterwards. Finally, the product after grinding was subjected to calcination at 550 °C for 3 h in a muffle furnace to obtain Ce/TiO2 powder.

Ce/TiO2/g-C3N4: The prepared Ce/TiO2 powder and C₃H₆N₆ were mixed in a certain ratio followed by grinding. Afterwards, the mixture was calcined at 550 °C for 5 h in a muffle furnace at a heating rate of 5 °C·min⁻¹. Different ternary composites were obtained by controlling the mass ratio of...
Ce/TiO$_2$ to g-C$_3$N$_4$.

2.3. Photocatalytic Experiment

RhB was selected as the target pollutant for photocatalytic experiments. The visible light-driven photocatalytic degradation efficiency of RhB solution by Ce/TiO$_2$/g-C$_3$N$_4$ composite was measured and the photocatalytic activity of Ce/TiO$_2$/g-C$_3$N$_4$ was evaluated. A certain amount of Ce/TiO$_2$/g-C$_3$N$_4$ was dispersed in RhB solution and subjected to simulated visible light degradation for 3h. The intensity of the visible light source was 300W. The solution was sampled and centrifuged every 20 minutes. The supernatant was aspirated and the corresponding absorbance was measured by UV-6100 UV-visible spectrophotometer. Therefore, by measuring the absorbance of every supernatant sample, the absorbance A of RhB solution in every same period of time (20 min) was obtained, based on what the degradation rate was calculated.

Photocatalytic reaction degrades pollutants through the oxidation of organic substances by reactive groups such as superoxide radicals (•O$_2^-$), holes (h$^+$) and hydroxyl radicals (•OH) generated during the reaction. Therefore, the catalytic mechanism of Ce/TiO$_2$/g-C$_3$N$_4$ composites was analyzed based on active group capture experiment. Specifically, p-benzoquinone (BQ), EDTA-2Na and methanol (MeOH) were introduced in the reaction system as capture agents for •O$_2^-$, h$^+$ and •OH respectively, and the RhB degradation rate was calculated employing the same method as photocatalytic activity evaluation.

3. Results and Discussions

3.1. Characterization of Ce/TiO$_2$/g-C$_3$N$_4$

3.1.1. TEM

The microstructure of the prepared Ce/TiO$_2$/g-C$_3$N$_4$ composite photocatalyst was characterized by TEM. As shown in Fig. 1(A), TiO$_2$ was uniformly dispersed on the surface of g-C$_3$N$_4$, which is mainly attributed to the lamellar structure of g-C$_3$N$_4$. This type of structure provides more active sites for the deposition of TiO$_2$. The lattice spacing of TiO$_2$ was measured to be 0.35 nm based on the diffraction fringes (Fig. 1(B)), indicating the successful synthesis of anatase-type TiO$_2$ with exposed (101) facet. According to the analysis, g-C$_3$N$_4$ suppressed the aggregation of TiO$_2$ nanoparticles, thus, enabling the formation of a superior heterojunction, which then led to improved photocatalytic efficiency.

![Figure 1. TEM image (A, B) of Ce/TiO$_2$/g-C$_3$N$_4$.](image)

3.1.2. XRD

Fig. 2 presents the crystal phase analysis results of g-C$_3$N$_4$, TiO$_2$, Ce/TiO$_2$ and Ce/TiO$_2$/g-C$_3$N$_4$. Characteristic peaks at 2θ = 25.3°, 37.8°, 47.9°, 53.9°, 54.9° and 62.6° were displayed for the XRD pattern of g-C$_3$N$_4$, corresponding to the (100) and (002) planes of g-C$_3$N$_4$ respectively. As for TiO$_2$, significant characteristic peaks of the (101), (004), (200), (105), (211) and (204) planes of anatase TiO$_2$ (JCPDS65-5714) were displayed at 2θ = 25.3°, 37.8°, 47.9°, 53.9°, 54.9° and 62.6° respectively[6]. The positions of XRD diffraction peaks of Ce/TiO$_2$ were basically identical to those of TiO$_2$, implying that
Ce did not form a separate CeO$_2$ phase, instead, the element entered TiO$_2$ lattices as interstitial atoms which were uniformly distributed in TiO$_2$ nanoparticles. Thereby, the growth of anatase nanoparticles and nucleation of the rutile phase were inhibited. Comparing the XRD profiles of Ce/TiO$_2$/g-C$_3$N$_4$ materials, no change in the crystal structure of the ternary composites was observed for the material after calcination, indicating the successful preparation of Ce/TiO$_2$/g-C$_3$N$_4$. Meanwhile, the characteristic diffraction peak of g-C$_3$N$_4$ at 27.3° disappeared in the XRD pattern of the ternary composite, which was caused by the lower crystallinity of g-C$_3$N$_4$ and the strong diffraction peaks of TiO$_2$, implying that Ce/TiO$_2$ had been successfully loaded on g-C$_3$N$_4$ sheets.

![Figure 2. XRD patterns of Ce/TiO$_2$/g-C$_3$N$_4$.](image)

![Figure 3. FTIR spectrum of Ce/TiO$_2$/g-C$_3$N$_4$.](image)

### 3.1.3. FTIR

The surface structure analysis of g-C$_3$N$_4$, TiO$_2$, Ce/TiO$_2$ and Ce/TiO$_2$/g-C$_3$N$_4$ was carried out by FTIR. The results are shown in Fig. 3. Characteristic absorption peaks at 808 cm$^{-1}$, 1630 cm$^{-1}$ and 3000–3500 cm$^{-1}$ were observed for g-C$_3$N$_4$, which were attributed to the intra-ring vibration of the triazine rings, C=N stretching vibration and N-H stretching vibration respectively [7], indicating the incomplete condensation of C$_3$H$_6$N$_6$ during the preparation of g-C$_3$N$_4$ and the presence of small amount of -NH$_2$ groups. TiO$_2$ exhibited a broad characteristic absorption peak at 500–600 cm$^{-1}$, which corresponds to the stretching vibration of Ti-O. Meanwhile, the stretching vibration peaks of O-H were observed at 1638 cm$^{-1}$ and 3433 cm$^{-1}$. The presence of O-H in TiO$_2$ is due to the hydroxyl groups generated from the dissociation of moisture adsorbed on the surface of the metal oxide from the atmosphere at ambient temperature. As shown in the FTIR spectrum of Ce/TiO$_2$, which displayed the characteristic peaks of TiO$_2$, indicating the successful preparation of Ce/TiO$_2$. For the Ce/TiO$_2$/g-C$_3$N$_4$ ternary composite, the main stretching bands of g-C$_3$N$_4$ and TiO$_2$ were observed with enhanced C=N peaks at 1000–1600 cm$^{-1}$, implying a certain interaction between g-C$_3$N$_4$ and Ce/TiO$_2$ and the resulted formation of a tight heterojunction structure.

### 3.1.4. UV-Vis

In order to investigate the optical properties of Ce/TiO$_2$/g-C$_3$N$_4$ composite, UV-Vis was applied to determine the light absorption properties, and the corresponding results were subjected to Kubelka-Munk conversion for the analysis of the corresponding band gaps of TiO$_2$, g-C$_3$N$_4$, Ce/TiO$_2$ and Ce/TiO$_2$/g-C$_3$N$_4$ composite. The results are shown in Fig. 4. The band gaps ($E_g$) of g-C$_3$N$_4$ and TiO$_2$ were 2.64 eV and 3.12 eV, respectively, with the $E_g$ being 3.02 eV and 2.28 eV for binary composite Ce/TiO$_2$ and ternary composite Ce/TiO$_2$/g-C$_3$N$_4$. This indicates that the band gap of TiO$_2$ was reduced by doping Ce and compounding with g-C$_3$N$_4$, and an effective synergistic effect among the three components was formed which then enhanced the photocatalytic activity of the material.
3.2. Photocatalytic Property of Ce/TiO$_2$/g-C$_3$N$_4$

The effects of g-C$_3$N$_4$, TiO$_2$, Ce/TiO$_2$ and Ce/TiO$_2$/g-C$_3$N$_4$ as catalysts on photocatalytic degradation of RhB were investigated under visible light. The results are shown in Fig. 5. For the reaction systems with g-C$_3$N$_4$, TiO$_2$ and Ce/TiO$_2$ as the catalyst, after driven by visible light for 180 min, the corresponding degradation rates were 23.4%, 34.0% and 67.0%, respectively. Under identical operating conditions, the Ce/TiO$_2$/g-C$_3$N$_4$ composite displayed better photocatalytic activity than g-C$_3$N$_4$, TiO$_2$ and Ce/TiO$_2$, with a RhB degradation rate of 99% after 180min under visible light. According to the results, with Ce as an electron capture agent and visible light as the light source, the formation of an excellent heterojunction structure between TiO$_2$ and g-C$_3$N$_4$ expanded the photoresponse range effectively, which then inhibited the electron-hole pair recombination and improved the sunlight utilization and photocatalytic efficiency.

3.3. Influencing Factors of The Photocatalytic Property of Ce/TiO$_2$/g-C$_3$N$_4$

3.3.1. Doping Ratio of g-C$_3$N$_4$

As shown in Fig. 6, the photocatalytic properties of Ce/TiO$_2$/g-C$_3$N$_4$ composites with various g-C$_3$N$_4$ doping ratios of 10%, 15%, 20%, 25%, 50% and 60% were evaluated. Under visible light irradiation, the photocatalytic property of Ce/TiO$_2$/g-C$_3$N$_4$ for RhB degradation was improved first and then weakened as the g-C$_3$N$_4$ doping ratio increased. The composite displayed optimal photocatalytic property of complete RhB degradation with the doping ratio being 25%. The reason for this could be that a small amount of g-C$_3$N$_4$ doped into TiO$_2$ lattices affected the active sites on the surface, resulting in low photodegradation efficiency. When the g-C$_3$N$_4$ doping ratio reached a certain level, the carrier transporting ability of the catalyst surface was enhanced, thus, leading to improved photocatalytic performance. However, when the doping ratio of g-C$_3$N$_4$ exceeded 25%, the excess g-C$_3$N$_4$ weakened its synergistic effect with TiO$_2$, hindered carrier transport, prevented the composite from contacting the target pollutants, and therefore, reduced its sunlight utilization and photocatalytic efficiency.

3.3.2. Catalyst Dosage

Ce/TiO$_2$/g-C$_3$N$_4$ of various masses (2.5, 5.0, 10.0, 20.0, and 40.0 mg) were introduced to RhB solution with an initial concentration of 1×$10^{-5}$ mol·L$^{-1}$ for photocatalytic degradation experiments. The results are shown in Fig. 7. Under visible light irradiation, the photocatalytic property of Ce/TiO$_2$/g-C$_3$N$_4$ for RhB degradation enhanced first and then stabilized gradually with the increase of catalyst dosage. The initially enhanced performance was due to the increase of active sites with higher catalyst dosage. However, when the dosage reached a certain level, the solution turbidity was worsened, which affected the visible light transmittance through the solution, resulting in a corresponding decrease in the photon energy involved in the catalytic degradation reaction. This then resulted in the stabilized degradation speed of RhB with further increased catalyst dosage.
3.3.3. Initial Concentration of RhB

Keeping the solution pH at 5 and the dosage of Ce/TiO$_2$/g-C$_3$N$_4$ at 10.0 mg, photocatalytic degradation experiments were conducted with the initial RhB concentration being $0.5 \times 10^{-5}$, $1 \times 10^{-5}$, $1.5 \times 10^{-5}$ and $2 \times 10^{-5}$mol·L$^{-1}$, respectively. The results are shown in Fig. 8. The composite displayed the best photodegradation property when the concentration of RhB was $0.5 \times 10^{-5}$mol·L$^{-1}$, achieving a degradation rate of 99.3% after 180 min under visible light. As the initial concentration of RhB solution increased, the photodegradation slowed down. Especially when the concentration was $2 \times 10^{-5}$mol·L$^{-1}$, the corresponding degradation rate was only 48.0% after visible light treatment for 180 min. According to the analysis, the RhB solution of low concentration had weaker absorption of effective photon energy, which enhanced the ability of the composite material to utilize effective photon energy, resulting in an increased reaction rate constant. Therefore, in practical wastewater treatment projects, the optimal dosage of the catalyst can be determined according to the concentration of different pollutants to achieve the best and most economical wastewater treatment effect.

3.3.4. Initial pH

The initial pH of RhB solution was set as 5.0, 6.0, 6.5, 7.0 and 8.0 respectively for photocatalytic degradation experiments with the initial solution concentration being $1 \times 10^{-5}$mol·L$^{-1}$ and the dosage of Ce/TiO$_2$/g-C$_3$N$_4$ being 10.0 mg. The results are shown in Fig. 9. After reacting for 180 min under visible light, the composite displayed the best photocatalytic activity when the initial pH was 5.0, with the degradation rate of RhB being 99.5%. This indicates that acidic condition was beneficial to the hydrolysis of the composite.
3.4. Cyclic Property of Ce/TiO$_2$/g-C$_3$N$_4$

In order to evaluate the reusability and reproducibility of Ce/TiO$_2$/g-C$_3$N$_4$, the catalyst was recycled after reaction and applied for photocatalytic degradation experiment repeatedly for 5 times under the same operating conditions. According to the results, the RhB degradation rate could still reach 98.81% for Ce/TiO$_2$/g-C$_3$N$_4$ after recycling for 5 times. FTIR was carried out for Ce/TiO$_2$/g-C$_3$N$_4$ cycled for 5 times to further investigate the stability of the composite material, as shown in Fig. 10. The cycled material displayed consistent active group positions with the fresh material, which implies that the structure of the cycled material was unchanged. The combination of experimental results indicates that the material possesses excellent reusability and reproducibility, and has broad industrial application prospects.

![Figure 10. FTIR spectrum of Ce/TiO$_2$/g-C$_3$N$_4$ and samples after 5 cycles.](image1)

3.5. Photocatalytic Mechanism of Ce/TiO$_2$/g-C$_3$N$_4$

The active species for the photocatalytic reaction were investigated through active group capture experiment. The results are shown in Fig. 11. EDTA-2Na and MeOH were introduced to the reaction system respectively. After 180 min under visible light irradiation, both chemicals were found to impose obvious inhibitory effect on the photocatalytic activity of the catalyst for RhB degradation, with the degradation rate being 75.3% and 54.5% respectively. This indicates that both h$^+$ and ·OH participated in the photocatalytic reaction. Meanwhile, comparing the degree of inhibition introduced by EDTA-2Na, MeOH and BQ on the reaction system, it can be concluded that the catalytic reaction process was dominated by ·O$_2^-$ in the Ce/TiO$_2$/g-C$_3$N$_4$ catalytic system. As shown in Table 1 is the fitting of the degradation speed according to the first order kinetic equation. By introducing BQ in the reaction system, the photocatalytic degradation speed of RhB decreased from the original 0.0183min$^{-1}$ to 0.0024min$^{-1}$, and the corresponding contribution rate of ·O$_2^-$ was 84.1%. It was higher than that of h$^+$ (55.0%) and ·OH (77.5%), indicating ·O$_2^-$ was the main active species in the Ce/TiO$_2$/g-C$_3$N$_4$ catalytic system, followed by ·OH, while h$^+$ was not as significant.

![Figure 11. Effect of capture agents on photocatalytic activity.](image2)

| Capture agents | First order kinetic equation | Rate constant (min$^{-1}$) | Contribution rate (%) |
|----------------|------------------------------|----------------------------|----------------------|
| Blank          | ln(C$_0$/C$_t$)=0.0183t-0.1275 | 0.0183                    | —                    |
| MeOH           | ln(C$_0$/C$_t$)=0.0034t+0.2411 | 0.0034                    | 77.5                 |
| EDTA-2Na       | ln(C$_0$/C$_t$)=0.0068t+0.2199 | 0.0068                    | 55.0                 |
| BQ             | ln(C$_0$/C$_t$)=0.0024t+0.2089 | 0.0024                    | 84.1                 |

According to the above analysis, the photocatalytic mechanism of the composite material is as follows: at the heterojunction interface of g-C$_3$N$_4$ and TiO$_2$, holes with weak oxidizing ability in the valence band of g-C$_3$N$_4$ and the photogenerated electrons transferred in the conduction band of TiO$_2$ recombine, which retains electrons with strong reducing ability in the valence band of g-C$_3$N$_4$ and...
holes with strong oxidizing ability in the valence band of TiO₂, while increasing the efficiency of photo-generated carriers. During the photocatalytic degradation process of RhB, the electrons with strong reducing ability in the valence band of g-C₃N₄ form ·O₂⁻ with O₂, and the holes with strong oxidizing ability in the valence band of TiO₂ oxidize OH⁻ to produce ·OH. The highly active oxygen-containing radicals (·O₂⁻ and ·OH) produced during this process continue to participate in the subsequent reactions of photocatalytic degradation of RhB, thereby realizing efficient degradation of RhB by Ce/TiO₂/g-C₃N₄ composites.

4. Conclusions
A Ce/TiO₂/g-C₃N₄ composite material was prepared by sol-gel method using tetrabutyl titanate (Ti(OC₄H₉)₄) as precursor, g-C₃N₄ as support and ammonium cerium(IV) nitrate ((NH₄)₂Ce(NO₃)₆) as dopant. The microstructure, active groups and light absorption range of the composite catalyst were analyzed by various characterization techniques. The results indicate that Ce-TiO₂ was successfully loaded on g-C₃N₄ sheets, both excellent heterojunction nanostructure and effective synergistic effect were formed among the three components, which then expanded the light absorption range of the composite material. RhB was selected as the target pollutant for the current study. The visible light-driven photocatalytic degradation experiments were carried out to evaluate the catalytic and cyclic properties of the photocatalytic materials. The Ce/TiO₂/g-C₃N₄ composite catalyst displayed optimal photocatalytic performance for acidic solution with low RhB concentration. The positions of active groups were retained for the cycled material (5 times) compared with the fresh material, which means that the structure of the material was unchanged during cycling. Furthermore, based on the analysis of active group capture experiment, ·O₂⁻ was identified as the main active species in the catalytic system of Ce/TiO₂/g-C₃N₄, with a contribution rate of 84.1%.

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