



Article Preparation and Characterization of Tubelike g-C₃N₄/ Ag₃PO₄ Heterojunction with Enhanced Visible-Light Photocatalytic Activity

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Abstract: Water pollution caused by dye wastewater is a potential threat to human health. Using photocatalysis technology to deal with dye wastewater has the advantages of strong purification and no secondary pollution, so it is greatly significant to look for new visible-light photocatalysts with high photocatalytic ability for dye wastewater degradation. Semiconductor photocatalyst silver phosphate (Ag₃PO₄) has high quantum efficiency and photocatalytic degradation activity. However, Ag₃PO₄ is prone to photoelectron corrosion and becomes unstable during photocatalysis, which severely limits its application in this field. In this study, a tubelike g-C₃N₄/Ag₃PO₄ heterojunction was constructed by the chemical precipitation method. An Ag₃PO₄ nanoparticle was loaded onto the surface of the tubelike g-C₃N₄, forming close contact. The photocatalytic activity of the photocatalyst was evaluated by the degradation of RhB under visible-light irradiation. The tubelike g-C₃N₄/Ag₃PO₄-5% heterojunction exhibited optimal photocatalytic performance. In an optimal process, the degradation rate of the RhB is 90% under visible-light irradiation for 40 min. The recycling experiment showed that there was no apparent decrease in the activity of tubelike g-C₃N₄/Ag₃PO₄-5% heterojunction after five consecutive runs. A possible Z-type mechanism is proposed to explain the high activity and stability of the heterojunction.

Keywords: photocatalysis; Ag₃PO₄; g-C₃N₄; heterojunction; degradation

1. Introduction

With the rapid development of modern industry, the problem of water pollution is becoming increasingly serious, as it could harm human health [1–4]. Dye wastewater has large discharge, biological toxicity, complex composition, high content of organic matter, and poor biodegradability, which is a difficult problem in wastewater treatment. Semiconductor photocatalysis technology can transform solar into chemical energy and completely decompose organic matter under mild conditions. It shows great potential and good application prospects in solving environmental pollution and energy shortage [5,6]. The development of highly active photocatalysts is key to the application of photocatalysis technology. Various semiconductor photocatalysts, including TiO₂, ZnO, and SnO₂, were studied [7–10]. However, these conventional photocatalytic materials still have many problems, such as photocatalytic activity only under ultraviolet light, electron-hole recombination, and potential toxicity, which are primary obstacles to further application. Thereby, it is greatly significant to explore photocatalysts with high visible-light activity for the application of semiconductor photocatalysis.

In 2010, Ye et al. [11] reported a novel visible light photocatalyst, Ag_3PO_4 , which showed very strong oxidation capacity and high visible-light catalytic activity. In addition, its quantum efficiency reached 90%, far higher than that of other metal oxide semiconductor photocatalysts [12–15]. However, Ag_3PO_4 is prone to photoelectron corrosion and becomes



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). unstable during photocatalytic reaction, which severely limits the application of Ag₃PO₄ in the field of photocatalysis. Therefore, the photocatalytic performance of Ag₃PO₄ was improved by adjusting the morphology [16,17], combining it with carbon materials [18,19], and constructing a heterojunction [20,21]. Among them, the Ag₃PO₄-based heterojunction can effectively separate electrons and holes according to energy band theory, which is regarded as the most effective method to improve the photocatalytic performance of Ag₃PO₄. For example, many semiconductor photocatalysts, including TiO₂, SnO₂, g-C₃N₄, SrTiO₃ were used to couple with Ag₃PO₄ to fabricate heterojunction photocatalysts [22–25]. These heterojunctions showed excellent catalytic performance and stability. g-C₃N₄ is of great interest to researchers due to its matching potentials of the conduction and valence bands with Ag₃PO₄. The interfacial contact of heterojunction catalysts greatly affects electron and hole transport. Most of the reported g-C₃N₄/Ag₃PO₄ heterojunction catalysts, however, are bulk g-C₃N₄. The small specific surface area of bulk g-C₃N₄ is not conducive to the formation of heterojunctions with Ag₃PO₄ [26,27].

In this paper, a tubelike g-C₃N₄ was prepared by the molten salt method. A new type of Ag₃PO₄-based heterojunction was formed by chemical precipitation with the tubelike g-C₃N₄. The structure, morphology, and spectral properties of the g-C₃N₄/Ag₃PO₄ heterojunction were characterized by X-ray diffraction patterns, scanning electron microscopy, transmission electron microscopy, UV-vis diffuse reflectance spectra, and photoluminescence spectra. The photocatalytic activity of the photocatalyst was evaluated by the degradation of RhB under visible light irradiation. The effect of g-C₃N₄ content on the photocatalytic performance of the tubelike g-C₃N₄/Ag₃PO₄ heterojunction was investigated. Moreover, the electron transfer mechanism of the tubelike g-C₃N₄/Ag₃PO₄ heterojunction in the degradation of RhB under visible-light irradiation was studied.

2. Materials and Methods

2.1. Synthesis of Tubelike g- C_3N_4

The molten salt method was used to synthesize the tubelike g-C₃N₄ [28,29]. First, 4.5 g of lithium chloride, 5.5 g of potassium chloride, and 1 g of melamine were ground together. The mixture in the crucible was heated in a muffle furnace at 550 °C for 4 h. After the reaction, lithium chloride and potassium chloride were removed by washing with deionized water. Lastly, the tubelike g-C₃N₄ was collected and dried at 80 °C for 24 h. The sample was labeled as TCN.

2.2. Synthesis of Tubelike g-C₃N₄/Ag₃PO₄ Heterojunction

The tubelike g-C₃N₄/ Ag₃PO₄ heterojunction was prepared by chemical precipitation. First, 0.17 g AgNO₃ was dissolved in deionized water, and a certain amount of tubelike g-C₃N₄ was dispersed in the above solution. Then, 0.15 g Na₃PO₄ was dissolved in deionized water and slowly dropped into the AgNO₃ solution. After magnetic stirring for 30 min, the solution was filtered, washed, and dried at 60 °C for 10 h. The tubelike g-C₃N₄/Ag₃PO₄ heterojunctions with different tubelike g-C₃N₄ mass contents of about 1, 3, 5, and 7% were labeled as TCN/Ag₃PO₄-1%, TCN/Ag₃PO₄-3%, TCN/Ag₃PO₄-5%, and TCN/Ag₃PO₄-7%, respectively. For comparison, the pure Ag₃PO₄ nanoparticle was prepared by the chemical precipitation method without tubelike g-C₃N₄.

2.3. Characterization

The crystal structure was determined by Philips X 'pert MPD (Almelo, The Netherlands). Cu target K α was used as the radiation source (wavelength, 0.15418 nm), working voltage was 40 kV, working current was 20 mA, scanning range was 10–70°, and scanning speed was 4° min⁻¹. The surface morphology of the sample was observed by scanning electron microscope (S-4800; working voltage, 5 kV, Kyoto, Japan) and transmission electron microscopy (FEI Tecnai G20; working voltage, 200 kV, Hillsboro, OR, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Kratos Axis Ultra DLD detector (Manchester, UK). The photoluminescence (PL) spectra of the sample

at room temperature were measured with a HORIBA Fluorolog-3(Paris, France). The UV–visible diffuse reflectance spectra of the sample were measured with a Shimadzu UV-3600 spectrophotometer (UV-3600, Shimadzu, Kyoto, Japan).

2.4. Photocatalytic Activity Evaluation

We added 0.01 g of the catalyst to a 100 mL RhB solution with an initial concentration of 10 mg/L. In order to achieve adsorption–desorption equilibrium, the RhB solution (with the photocatalyst) was magnetically stirred in the dark for 30 min. Then, the solution was placed under a 300 W xenon lamp (filtering out ultraviolet light) for photocatalytic reaction. The RhB solution was taken every 5 min. After 30 min of centrifugation, the supernatant was removed, and the concentration of RhB solution was measured with a UV-vis spectrophotometer (721 G, Shanghai, China) at 664 nm absorbance value.

3. Results and Discussion

3.1. XRD and XPS Analysis

The XRD patterns of TCN, Ag₃PO₄, and the TCN/Ag₃PO₄ heterojunction are shown in Figure 1. The diffraction peaks of TCN were at 11.7, 20.6, 24.3, 26.6, 29.1, and 32.4°, which reflects different planes from (100), (110), (200), (002), (102), and (210). This is consistent with literature reports [30]. Ag₃PO₄ had obvious diffraction peaks at 20.88, 29.70,33.29, 36.59, 42.49, 47.79, 52.70, 55.02, 57.28, and 61.64°. Compared with the cubic Ag₃PO₄ standard card (PDF 06-0505), the (110), (200), (210), (211), (220), (310), (222), (320), (321), (400) crystal planes corresponded to their crystal phase, respectively. This shows that the pure Ag₃PO₄ phase was successfully prepared by chemical precipitation. The diffraction peak of the TCN/Ag₃PO₄ heterojunction is mainly from Ag₃PO₄, while the characteristic diffraction peak of the tubelike g-C₃N₄ did not appear because of the low content of tubelike g-C₃N₄ in the heterojunction, which is difficult to be detected by X-ray diffraction.



Figure 1. XRD patterns of TCN, Ag₃PO₄, and TCN/Ag₃PO₄ heterojunction.

The chemical composition of the TCN/Ag₃PO₄ heterojunction was characterized by XPS, as shown in Figure 2. Figure 2a is the survey spectrum of the TCN/Ag₃PO₄-5% heterojunction, which shows the presence of Ag, P, O, N, and C. The high-resolution XPS measurements of C 1s, N 1s, Ag 3d, O 1s, and P 2p are shown in Figure 2b–f. There are three peaks in Figure 2b. The peaks with binding energy at 284.6 and 287.5 eV were attributed to the C-C bonds and sp2 carbon in the triazine ring, respectively. The peaks with binding energy at 285.7 eV corresponded to C-O bonds in the hydroxyl state on the sample surface [31]. Results show that there were many hydrophilic hydroxyl groups on the surface of the heterojunction catalyst. These oxygen-containing carbons provided

an active surface to form good contact with the Ag_3PO_4 nanoparticle. Figure 2c shows two peaks in the N 1s spectra. The peak with binding energy at 398.2 eV is attributed to sp2 nitrogen in the triazine ring, and another peak with binding energy at 399.7 eV is ascribed to the terminal amino groups [32]. Results further confirmed the existence of g-C₃N₄ in the TCN/Ag₃PO₄ heterojunction. Figure 2d shows the high-resolution spectra of Ag 3d. Peaks with binding energy at 367.8 and 373.8 eV belonged to the 3d5/2 and

3d3/2 characteristic peaks, respectively, with a valence state of Ag^+ . Ag 3d is a single peak of splitting, indicating that the Ag element existed only in the form of Ag^+ [33]. Figure 2e shows the high-resolution spectrum of O 1s. The peak of O 1s could be fitted into two peaks, which were mainly the lattice oxygen of Ag_3PO_4 with binding energy at 530.6 eV and the surface hydroxyl oxygen at 532.4 eV [34]. Figure 2f is the high-resolution spectrum of P 2p. The electron binding energy at the center of the characteristic single peak was located at 133.2 eV, suggesting that the P element was in a +5 valence state [35]. Results further confirmed the existence of Ag_3PO_4 in the TCN/ Ag_3PO_4 heterojunction.



Figure 2. XPS spectra of TCN/ Ag₃PO₄-5% heterojunction: (**a**) XPS survey spectrum; (**b**) C 1s; (**c**) N 1s; (**d**) Ag 3d; (**e**) O 1s; (**f**) P 2p.

3.2. SEM Analysis

Figure 3 shows the SEM images of TCN, Ag₃PO₄, and the TCN/Ag₃PO₄-5% heterojunction, respectively. Figure 3A shows that TCN prepared by the molten salt method had a hollow tubelike shape, a square tube mouth with a smooth surface, and length distribution ranging from several microns to more than 10 microns. Figure 3B shows that Ag₃PO₄ prepared by chemical precipitation was composed of many polycrystalline nanoparticles with an average size of 30–50 nm, and particles presented an obvious agglomeration phenomenon. Figure 3C is the SEM image of the TCN/Ag₃PO₄-5% heterojunction. Results show that the Ag₃PO₄ nanoparticle was uniformly loaded onto the surface of tubelike g-C₃N₄. Figure 3D is the TEM image of TCN/Ag₃PO₄-5% heterojunction. The hollow tubelike g-C₃N₄ structure and Ag₃PO₄ nanoparticle were observed more clearly. Results showed that the tubelike g-C₃N₄ both dispersed the Ag₃PO₄ nanoparticle and formed the heterojunction.



Figure 3. SEM images of (**A**) TCN, (**B**) Ag₃PO₄, (**C**) TCN/Ag₃PO₄-5% heterojunction, and (**D**) TEM image of TCN/Ag₃PO₄-5% heterojunction.

3.3. UV–vis Diffuse Reflectance Spectra and Photoluminescence Spectra Analysis

The UV–vis DRS of TCN, Ag_3PO_4 , and the TCN/ Ag_3PO_4 heterojunction are shown in Figure 4a. The Ag_3PO_4 showed obvious absorption from the ultraviolet to the visible region, and its band edge absorption was 532 nm [36]. The band edge absorption of TCN was 460 nm, indicating a certain absorption of visible light. With the addition of TCN, the absorption spectra of TCN/ Ag_3PO_4 heterojunction had a red shift compared to those of TCN and Ag_3PO_4 . The shift is ascribed to the interaction between TCN and Ag_3PO_4 . This result implied that more visible light could be harvested by the TCN/ Ag_3PO_4 heterojunction.

The separation efficiency of a photoelectron-hole pair greatly affects the performance of the photocatalyst [37]. In Ag₃PO₄ systems, the rapid separation of photogenerated electrons is beneficial to reduce the photocurrent corrosion of Ag₃PO₄. Figure 4b shows the photoluminescence spectra of Ag₃PO₄ and the TCN/Ag₃PO₄ heterojunction, with an excitation wavelength of 365 nm. The emission peak of pure Ag₃PO₄ was obvious at 535 nm, indicating that the electron-hole pair in Ag₃PO₄ had a strong recombination rate. With the addition of TCN, the peak intensity of the TCN/Ag₃PO₄ heterojunction was the lowest, indicating a low recombination rate of charges. Therefore, the formation of the TCN/Ag₃PO₄ heterojunction is beneficial to the separation of electrons and holes, thus effectively improving its catalytic performance.



Figure 4. UV–vis diffuse (**a**) reflectance and (**b**) photoluminescence spectra of Ag_3PO_4 and $TCN/Ag_3PO_4-5\%$ heterojunction.

3.4. Photocatalytic Activities Analyses

The catalytic activity of different catalysts was investigated by using RhB as a simulated degradation target, as shown in Figure 5a. In the absence of a catalyst, RhB hardly degraded under visible-light irradiation. The TCN and Ag_3PO_4 samples exhibited visible-light photocatalytic activity, and the degradation rate of RhB was 25 and 44%, respectively after 40 min visible light irradiation. Compared with the TCN and Ag_3PO_4 , the TCN/ Ag_3PO_4 heterojunction exhibited enhanced photocatalytic activity. The TCN/ Ag_3PO_4 -5% heterojunction resulted in 90% degradation of RhB within 40 min. It is an important factor for the formation of heterojunction with the appropriate amount of TCN. When the amount of TCN is low, Ag3PO4 particles cannot be fully loaded and thus cannot effectively form the heterojunction. On the other hand, excessive TCN absorbs the visible light and forms a masking effect on the heterojunction, thus decreasing its catalytic efficiency. For low-concentration pollutants, the kinetic behaviors for the degradation reaction can be studied with the following equation:

$$n(c/c_0) = kt \tag{1}$$



1

Figure 5. Degradation curves (**a**) and kinetic plot (**b**) of photocatalytic degradation of RhB by TCN, Ag₃PO₄, and TCN/Ag₃PO₄ heterojunction.

The kinetic constants (k) of different samples were calculated and are shown in Figure 5b. The kinetic constant of RhB degradation with TCN/Ag₃PO₄-5% (0.0077 min^{-1}) was about 5.9 and 3.8 times as high as that of TCN (0.0013 min^{-1}) and Ag₃PO₄ (0.0020 min^{-1}), respectively. This result shows that the formation of the TCN/Ag₃PO₄ heterojunction could efficiently enhance the photocatalytic performances of Ag₃PO₄.

To investigate the stability of Ag_3PO_4 and the TCN/ Ag_3PO_4 heterojunction, the photocatalyst was recovered and dried for the next cycle of degradation. Degradation conditions remained the same as before, and there were 5 cycles. Experimental results are

shown in Figure 6a. In the cyclic experiment, the photocatalytic performance of Ag₃PO₄ obviously decreased, and the degradation rate of RhB for the fifth time was only 15%. The degradation rate of RhB by the TCN/Ag₃PO₄ heterojunction for the fifth time was 85%. Results showed that the TCN/Ag₃PO₄ heterojunction exhibited excellent stability. The samples of Ag₃PO₄ and the TCN/Ag₃PO₄ heterojunction after the cycle experiment were analyzed by X-ray diffraction, and results are shown in Figure 6b. In the XRD of Ag₃PO₄, a new diffraction peak appeared at 38.1°, which is the (111) plane diffraction peak of Ag [38]. Results showed that Ag₃PO₄ was prone to photoelectron corrosion and became unstable during photocatalytic reaction. There was no new diffraction peak in the XRD of the TCN/Ag₃PO₄ heterojunction. Results showed that the TCN/Ag₃PO₄ heterojunction maintained good stability in the cyclic experiment.



Figure 6. (a) RhB degradation rate and (b) XRD patterns over Ag₃PO₄ and TCN/Ag₃PO₄ heterojunction in cyclic experiment.

3.5. Photocatalytic Mechanism of TCN/Ag₃PO₄ Heterojunction

To further investigate the photocatalytic reaction mechanism of the TCN/Ag₃PO₄ heterojunction, the TCN/Ag₃PO₄-5% heterojunction was used as photocatalyst, and different scavengers were selected to carry out the photodegradation experiment. Among them, ethylenediaminetetraacetic acid (EDTA) was the electron hole (h⁺) scavenger [39], benzoquinone (BQ) was the superoxide radical ($^{\circ}O_2^{-}$) scavenger [40], and isopropanol (IPA) was the hydroxyl radical ($^{\circ}OH$) scavenger [41], with a concentration of 1 mmol/L. The effects of various scavengers on the degradation rate of RhB are shown in Figure 7.



Figure 7. Effect of different scavengers on RhB degradation by $TCN/Ag_3PO_4-5\%$ heterojunction under visible–light irradiation.

The photocatalytic efficiency of RhB decreased significantly after the addition of EDTA and BQ, and the degradation rate of RhB was 39% and 45% after 40 min reaction, respectively. Results showed that $h + and \bullet O_2^-$ were captured by EDTA and BQ, respectively, so the number of h + and $\bullet O_2^-$ in the photocatalytic reaction was greatly reduced, resulting in a lower degradation rate of RhB. When IPA was added, the degradation rate of RhB was 80% after 40 min reaction. The IPA mainly captured •OH, thus slightly decreasing the degradation rate of RhB. It is clear that h^+ and $\bullet O_2^-$ were the main active species for RhB degradation, while •OH only played a minor role. According to previous reports [42,43], the valence band (VB) and conduction band (CB) potentials of Ag₃PO₄ were about 2.69 and 0.24 eV, which are both more positive than those of $g-C_3N_4$ (-1.15 and 1.60 eV), respectively. According to traditional heterojunction theory, the CB of $g-C_3N_4$ is more negative than that of Ag_3PO_4 , and the electrons generated after photoexcitation migrate from the CB of $g-C_3N_4$ to the CB of Ag_3PO_4 . The VB of Ag_3PO_4 is more positive than that of $g-C_3N_4$, and holes generated after photoexcitation migrate from the VB of Ag₃PO₄ to the VB of g-C₃N₄. \bullet O₂⁻/O₂ potential (-0.33 eV) is more negative than that CB of Ag_3PO_4 , so electrons migrating to the CB of Ag_3PO_4 cannot react with oxygen to produce •O₂⁻. This is not consistent with the results of photocapture experiments in which \bullet O₂⁻ is the main active species. A large number of electrons gathering on the crystal surface of Ag_3PO_4 lead to the photocurrent corrosion of Ag_3PO_4 . This is inconsistent with the experimental results of the stability of the TCN/Ag₃PO₄ heterojunction. Second, because the potential of the VB of g-C₃N₄ was more negative than the potential of \bullet OH/H₂O (2.27) eV), the holes that migrated to CB of g-C₃N₄ could not oxidize water to produce •OH. This is not consistent with the results of photocapture experiments in which •OH is also an active species. According to the experimental results of the stability and capture of the TCN/Ag₃PO₄ heterojunction, a possible Z-type photocatalytic mechanism is proposed, as shown in Figure 8. The potential position of the VB of $g-C_3N_4$ was close to the CB of Ag_3PO_4 , so it was easy to combine the holes in the VB and the electrons in the CB. Therefore, the electrons in the VB of g-C₃N₄ and the holes in the VB of Ag₃PO₄ were effectively separated. The electrons in the CB of $g-C_3N_4$ would react with the dissolved O_2 to produce $\bullet O_2^-$, which could directly oxidize RhB. Meanwhile, the holes in the VB of Ag₃PO₄ can also directly oxidize RhB. Its high valence band potential of +2.69 eV could oxidize water to produce •OH, and •OH also had a strong oxidation capacity and can oxidize RhB. The Z-type mechanism is consistent with the experimental results of the photostabilization and photocapture of the heterojunction catalyst.



Figure 8. Photocatalytic degradation RhB and charge transfer mechanism in TCN/Ag₃PO₄ heterojunction.

4. Conclusions

A TCN/Ag₃PO₄ heterojunction was successfully prepared by chemical precipitation. The TCN/Ag₃PO₄ heterojunction catalyst exhibited excellent catalytic activity and stability under visible-light irradiation. A possible Z-type mechanism was proposed in which the Ag₃PO₄-excited electrons were directly recombined with holes generated by the tubelike g-C₃N₄, thus rapidly separating photogenerated electrons from the Ag₃PO₄ crystal surface. The TCN/Ag₃PO₄ heterojunction structure both reduced the photoelectronic corrosion of Ag₃PO₄ and improved the photocatalytic activity of the catalyst. As a photocatalyst with high activity and stability, the TCN/Ag₃PO₄ heterojunction has potential for applications in the field of environmental pollution control.

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