Synthesis and Photocatalytic Performance of g-C₃N₄ Modified with AgSAPO-5 for Photodegrading Rhodamine B

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Abstract. In this study, AgNO₃ solution was used to modify natural SAPO-5 zeolite and hybrid AgSAPO-5 zeolite was formed. The effect of the concentration of AgNO₃ solution on AgSAPO-5 was discussed. The crystal phase and elements in frameworks of AgSAPO-5 samples were characterized by XRD, FT-IR and EDS. AgSAPO-5 with highest visible-light adsorption verified by DRS was used to prepare AgSAPO-5/g-C₃N₄ composites. The mass ratio of AgSAPO-5 and g-C₃N₄ was changed. AgSAPO-5/g-C₃N₄ composites were also characterized by XRD, DRS and PL. The band structure of g-C₃N₄ was changed successfully so that the light adsorption changed. The much lower intensities of AgSAPO-5/g-C₃N₄ composites declare that the combination rate of g-C₃N₄ was retarded significantly. The composites were tested for photocatalytic activity in rhodamine B (10 mg/L) solution under visible light illumination. The results showed that AgSAPO-5/g-C₃N₄ composite with a mass ratio of 15% exhibited the highest photocatalytic performance with an efficiency of 90.56% within 50 min.

1. Introduction
Since middle of 18th century, human society develops quickly. However, while the economic increases fast, human beings must face many problems, such as environmental deterioration, resource shortage and so on. The emission of “Three wastes” namely waste water, waste gas and waste residue produced by industrial manufacture, is increasing year by year, which does harm to water, gas and soil extremely [1]. The environmental problem caused by “Three wastes” has become an emergent task to be resolved all over the world. Meanwhile, energy crisis also arises because of the fast development of industry. Many non-renewable resources like coal, petroleum and natural gas on the earth are limited. The over-exploitation of these resources will lead to exhausted energy and limit the development of human beings. To settle these puzzles, researchers explore researches on pollution abatement, environmental protection and novel green energy. Nowadays, among the items on “Green Earth” and renewable energy, photocatalytic technology which can utilize sun light and artificial lighting is recognized an efficient solution to resolve the environmental problems, and have become one of the most promising technologies.

Since Fujishima reported that TiO₂ can be used as a UV-respond catalyst in the water splitting, which represent that heterogeneous photocatalysis has stepped into a new stage [2]. Photocatalysis using semiconductors shows great potential in water purification, soil and gas pollution abatements. Because of the advantages such as non-toxic, chemical stability, low-cost and good reutilization, semiconductors attracts wide attention from researchers.
Energy band of semiconductors are made up of discontinuous bands from the top of valence band to the bottom of conductor band. If semiconductors are in the ground state, the electron transition will not happen so that there are no any free carriers inside semiconductors [3]. However, when enough energy is adsorbed, electrons on the valence band of semiconductors will be motivated and transform to conduction band. Then photo-reduced electrons are produced and photo-reduced holes remain in valence band, the lifetime of photo-reduced pairs is within nanosecond. The photo-reduced pairs are sites for redox reactions.

Graphitic carbon nitride (g-C₃N₄), a polymer semiconductor, shows high thermal and chemical stability, and has abundant raw materials. The band gap (2.7 eV) of g-C₃N₄ leads to a strong redox property while the recombination rate of photo-reduced hole-electron pairs are very quick, which indicates that modifications on g-C₃N₄ are imperative [4]. To enhance the separating rate of photo-induced carriers and retard their combination rate, many routes of modifications have been explored for developing novel g-C₃N₄. Among the routes, g-C₃N₄-based heterojunctions are very popular in recent studies for the high efficiency. So far, many kinds of semiconductors have been applied to the construction of g-C₃N₄-based composite catalysts, such as TiO₂ [5, 6], ZnO [7, 8], CdS [9, 10], Bi₂WO₆ [6, 11] and so on.

Zeolite is a kind of semiconductors with unique pores, good chemical and mechanical stability. Many kinds of zeolites have been used as catalysts in a variety of catalytic reactions in industrial production for their huge active sites. Recently, some researchers have found that zeolites also can be used as light-respond photocatalysts, such as HZSM-5 [12] and SAPO-5 [13]. Particularly, SAPO-5 zeolite was found to be an efficient photocatalyst in changing CO₂ to CH₄. For photocatalysis with zeolites, the reaction system is different from system using semiconductors. The introduction of reactants for photocatalysis is related to the microenvironment of zeolites. Ion-exchange is used widely for adjusting the photocatalytic activity of zeolites. Anpo’s group has investigated deeply on the effect of Cu⁺, Ag⁺, and Pr³⁺ exchange on the NOₓ and CO₂ water vapor reduction of modified ZSM-5. It is clearly that ion-exchange can highly disperse the active sites among the cavities of zeolite. Meanwhile, local environment is changed so that more photo-induced hole-electron pairs without separation appear. So far, few studies on applying ion-exchanged SAPO-5 to coupling with semiconductors have been reported.

In this work, Ag hybridized SAPO-5 zeolite is prepared and optimized to be a proper sample to form AgSAPO-5/g-C₃N₄ composite catalyst. Different Ag amounts were mixed with SAPO-5 to form AgSAPO-5, and the samples were characterized by XRD, EDS and optical methods. Then, AgSAPO-5 with the most ideal optical property was used to couple with g-C₃N₄. The effect of the amount of AgSAPO-5 on the optical property of g-C₃N₄ was also discussed. Furthermore, the photocatalytic performances of AgSAPO-5 modified g-C₃N₄ were valued by rhodamine B degradation.

2. Experimental

2.1. Synthesis of AgSAPO-5
Nanometer-sized SAPO-5 has been prepared in our previous work. We prepared AgSAPO-5 by impregnation method. The process was mainly described as follows. Specific amount of SAPO-5 was firstly dispersed in pure water by ultrasonic for 30 min. Then AgNO₃ aqueous solutions with different concentrations were added into glass tubes and mixed with dispersed SAPO-5/water mixtures. The process of Ag substitution in SAPO-5 was proceeding under stirring under the illumination by Xe lamp for 2 h. The specific ratios were list in Table 1.

2.2. Synthesis of g-C₃N₄
Graphitic carbon nitride was simply synthesized by the calcination of urea described in report [14]. Typically, 12 g urea was put into a crucible and covered by silver paper. The calcinations were carried out in a constant-temperature oven. The synthesis temperature and time were 550 °C and 4 h, respectively. The heating and cooling rates were 2.3 °C/min.
Table 1: Ratios of the mixtures for preparing AgSAPO-5.

| Sample name | S-1 | S-2 | S-3 | S-4 | S-5 | S-6 |
|-------------|-----|-----|-----|-----|-----|-----|
| Ag ratio (w.t. %) | 0.50% | 1.00% | 2.00% | 3.00% | 4.00% | 5.00% |
| AgNO₃ amount (mg/ml) | 0.79 | 1.57 | 3.15 | 4.72 | 6.30 | 7.87 |
| SAPO-5(g) | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |

Table 2. Ratios of the mixtures for preparing AgSAPO-5/g-C₃N₄.

| Sample name | S-7 | S-8 | S-9 |
|-------------|-----|-----|-----|
| AgSAPO-5 amount (g) | 0.10 | 0.15 | 0.25 |
| g-C₃N₄ (g) | 1.00 | 1.00 | 1.00 |

2.3. Synthesis of AgSAPO-5/g-C₃N₄
The AgSAPO-5 with the best optical property was chosen to couple with g-C₃N₄. The mass ratio of AgSAPO-5 among g-C₃N₄ was verified from 5% to 25%. Firstly, 1g of as-synthesized g-C₃N₄ was added into 50 mL ethanol. Then different amounts of AgSAPO5 were added into the mixtures in an ultrasonic machine and kept for 30 min. The mixtures were then stirred by 6 h at room temperature. The specific ratios were list in Table 2. The final solids were the expected products and obtained by centrifugation. The solids were dried in a constant-temperature oven at 80 °C over night.

2.4. Characterizations
X-ray diffraction (XRD) was used to analyze the crystal phase of the samples to make sure if there is impurity inside or not. The type is Shimazu XRD-6100 made in Japan. Scanning electrical microscope (SEM) (Zeiss Sigma made in Germany) was used to observe the morphology of the samples. UV-vis diffuse reflection spectrum (DRS) was applied to the analysis on the light adsorption ability of the samples. Photoluminescence (PL) was a sensitive measurement for valuing the photocatalytic activity of photocatalysts. FT-IR was a method for confirming the surface composition of the samples.

2.5. Photocatalytic experiments
Photodegradation of rhodamine B was chosen as a model to value the photocatalytic activity of the synthesized AgSAPO-5/g-C₃N₄ composites. 50 mL rhodamine B solutions with a concentration of 10 mg/L were added to quartz test tubes, and 50mg photocatalysts were added into the solutions under stirring. The mixtures were stirred under dark until an adsorption-desorption balance occurred. At the end of the adsorption, one sample was taken and the concentration of the solution was marked as C₀. After that, visible light was turned on and samples were taken every 10 min. The concentrations of the degraded dye were marked as C. The adsorption intensity of the degraded dye was measured by a spectrophotometer at the wavelength of 554 nm. The initial adsorption intensity and adsorption after being degraded were marked as I₀ and I, respectively. The change of adsorption intensity is regarded as same as the change of dye concentration, which is convenient for calculating dye degradation efficiency.

3. Results and discussion
Figure 1 showed the XRD patterns of SAPO-5 and Ag substituted SAPO-5 samples. Compared to the pattern of pure SAPO-5, Ag substituted SAPO-5 samples have strong and pure typical peaks of SAPO-5. It indicated that the crystal structure is not destroyed at all. However, XRD patterns were not able to identify the existence of Ag element in the structure of SAPO-5. Energy dispersive spectrometer (EDS) was used to solve this problem. Data from all the AgSAPO5 samples were collected for two times. The results were list in Table 3 shown as follow. Obviously, Ag was introduced into SAPO-5 structure successfully.

FT-IR patterns recorded within 400–4000 cm⁻¹ were shown in Figure 2. AgSAPO-5 samples showed typical valleys at similar wavenumbers compared with that of pure SAPO-5. The bands were
mainly located at 540 cm\(^{-1}\), 1100 cm\(^{-1}\), 1620 cm\(^{-1}\) and 3500 cm\(^{-1}\), which were due to the Al-O-Si tetrahedrons, Si-O-Si stretching vibrations, vibration of hydroxyl groups adsorbed in samples and vibration of Si-OH, respectively [15].

Diffuse reflection spectrum was used to analyzing the light adsorption ability of AgSAPO-5 samples. As presented in Figure 3, all the samples showed UV light response at wavelength less than 300 nm. However, when the wavelength was longer, pure SAPO-5 showed almost no adsorption, while Ag substituted SAPO-5 samples exhibited obvious adsorption ability, especially when the wavelength was larger than 350 nm. As shown in Table 3, as AgNO\(_3\) concentration increased, the amount of the substituted Ag in SAPO-5 increased gradually. When the Ag concentration was 3.00%,
the visible light adsorption ability of AgSAPO-5 was the most strong as shown in Figure 3. Thus, we chose S-4 to couple with g-C\textsubscript{3}N\textsubscript{4} to synthesize AgSAPO-5/ g-C\textsubscript{3}N\textsubscript{4} composites.

Pure g-C\textsubscript{3}N\textsubscript{4} and the composites of AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} with different AgSAPO-5 ratios were measured by XRD to verify the crystal phase. The patterns were collected and showed in Figure 4. For pure g-C\textsubscript{3}N\textsubscript{4}, the typical peak was located at $2\theta = 27.2^\circ$ [16]. After forming heterojunctions, all the composites only showed peaks of SAPO-5 and g-C\textsubscript{3}N\textsubscript{4} without any impurities. It confirmed that the synthesis process did hardly harms to the crystal structure of the two samples during the combination.

![Figure 3. DRS patterns of pristine SAPO-5 and AgSAPO-5 with different Ag substitution ratios.](image)

![Figure 4. XRD patterns of pristine g-C\textsubscript{3}N\textsubscript{4}(CN) and AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} with different AgSAPO-5 ratios.](image)

Diffuse reflection spectrum was an efficient way to estimate the light adsorption ability of modified g-C\textsubscript{3}N\textsubscript{4}. Figure 5 exhibited the DRS results of pure g-C\textsubscript{3}N\textsubscript{4} and AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} composites. It was clearly that all the samples have visible-light adsorption. For AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} composites, the adsorption intensities at wavelength within 400 nm were all lower than that of pure g-C\textsubscript{3}N\textsubscript{4}, which should be ascribed to the low adsorption of AgSAPO-5 shown in Figure 3. From the
insets in Figure 4, we can find that AgSAPO-5/g-C₃N₄ composites have adsorption at higher wavelength near 700 nm, which was due to the substitution of Ag into SAPO-5 structure. Photoluminescence was applied to value the combination rate of photo-reduced electron-hole pairs of photocatalysts. In Figure 6, the PL patterns of g-C₃N₄ and AgSAPO-5/g-C₃N₄ composites were shown. The higher the combination rate was, the higher intensity of the pattern will be. It was evident that after the combination of AgSAPO-5 and g-C₃N₄, the energy band structure of g-C₃N₄ was changed and the combination of photo-reduced electron-hole pairs was retarded successfully. When the mass ratio of AgSAPO-5 was 15%, the AgSAPO-5/g-C₃N₄ composite (S-8) has the lowest PL intensity, which should lead to a higher photocatalytic performance of the sample.

Figure 5. DRS patterns of pristine g-C₃N₄(CN) and AgSAPO-5/g-C₃N₄ with different AgSAPO-5 ratios.

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Photocatalysis for degrading rhodamine B was carried out using pure g-C$_3$N$_4$ and AgSAPO-5/g-C$_3$N$_4$ composites. Comparing to the degradation line of pristine dye, when catalysts were used, rhodamine B solutions can be degraded significantly. When pure g-C$_3$N$_4$ was used, the degradation efficiency was 70.45% within 50 min under visible light illumination. After introducing AgSAPO-5, the photocatalytic performances of the composites increased a lot. Particularly, for S-8, the degradation efficiency was increased to 90.56% within 50 min, which was 28.55% higher than that of pure g-C$_3$N$_4$. The data of Figure 7 (left) were fit to pseudo first order kinetic model. The kinetic rate constant can be obtained from the slopes of the lines Figure 7 (right). The kinetic rate constants of the photocatalytic reaction with pure g-C$_3$N$_4$, S-7, S-8 and S-9 are 0.024 min$^{-1}$, 0.03 min$^{-1}$, 0.049 min$^{-1}$ and 0.028 min$^{-1}$, respectively.

![Figure 7. Photocatalytic performance (left) and ln(C/C_0) versus visible-light irradiation time for rhodamine B degradation of pristine g-C$_3$N$_4$(CN) and AgSAPO-5/g-C$_3$N$_4$ with different AgSAPO-5 ratios.](image)

4. Summary
In this paper, we reported the processing and characterizations of AgSAPO-5/g-C$_3$N$_4$ composites, including the evaluation for photocatalytic performance. For this, we firstly prepared Ag hybridized SAPO-5 by impregnation method. AgNO$_3$ solutions with different concentrations were used for substituting Ag into SAPO-5 frameworks. EDS results indicated the existence of Ag in SAPO-5 structure while XRD patterns can’t reflect it. Based on the DRS results, AgSAPO-5 forming with a Ag
concentration of 3% showing stronger visible-light adsorption was chosen to prepare AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} composites. The effect of AgSAPO-5 ratio in the composites was discussed and all the AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} composites have more excellent visible light adsorption near 700 nm. Pure g-C\textsubscript{3}N\textsubscript{4} and AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} composites were applied to degrading rhodamine B (10 mg/L) under visible-light illumination. After degrading for 50 min, all the rhodamine B solutions were degraded to a large extent. Comparing to the performance of pure g-C\textsubscript{3}N\textsubscript{4}, AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} composite with 15% AgSAPO-5 showed the highest degradation efficiency of 90.56%, which was 28.55% higher than that of pure g-C\textsubscript{3}N\textsubscript{4}. The photocatalytic results also followed a first order kinetic, the rate constant of the most ideal AgSAPO-5/g-C\textsubscript{3}N\textsubscript{4} composite was 0.049 min\textsuperscript{-1} which was twice of that of pure g-C\textsubscript{3}N\textsubscript{4}. The reported results in this paper indicate a promising potential for zeolites to be used as a good material to couple with other photocatalysts to form heterojunctions which are active in photodegrading dye aqueous solutions, such as rhodamine B.

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