Preparation of Phosphorus and Oxygen Co-Doped With Graphite Carbon Nitride and Its Application in Photodegradation of Methylene Blue

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Abstract. In this study, phosphorus and oxygen co-doped graphite carbon nitride has been successfully prepared by simple thermal copolymerization. The as-prepared materials were characterized by SEM, XRD, XPS and UV-vis-DRS. The results showed that phosphorus and oxygen were successfully doped on the structure of graphite carbon nitride. Photocatalytic degradation of MB in solution by the catalyst has been studied, POCN-1 has the best photocatalytic activity among of the as prepared materials, photocatalytic degradation rate of MB is 10.6 times higher than that of g-C_3N_4. The main reason for its enhanced photocatalytic performance is that the co-doped of phosphorus and oxygen elements would change the electronic structure of g-C_3N_4, reduce the forbidden band width of the photocatalyst. At the same time, can extend the absorption boundary of visible light.

1. Introduction

Nowadays, all kinds of water bodies have been polluted to varying degrees, which organic pollutants were common pollutants in waste water. If these pollutants cannot be removed, they will cause serious harm to the ecological environment and human health. Among them, industrial synthetic dyes are common organic pollutants and were widely used, resulting in a large amount of dye wastewater. The commonly used methods for treating those wastewater including coagulation sedimentation, adsorption [1], biological [2] and photocatalytic degradation [3]. Among these methods, photocatalytic degradation has the advantages of high degradation efficiency and without secondary pollution, which was considered to be the best method for degrading organic pollutants [4].

Graphite carbon nitride (g-C_3N_4) is a non-metallic photocatalyst, which has been attracted extensive attention from researchers, because of its visible light response and strong chemical stability. However, it also has the drawback of wide band gap and easy recombination of photogenerated electron pairs [5], which leads to its low photocatalytic efficiency. After further research, researchers have developed a series of modification methods for graphite carbon nitride, mainly including morphology control, element doping, semiconductor recombination and dye sensitization [6]. Among of many modification methods, the shape control was to change the shape of the material itself, in order to promotion the specific surface area of the materials [7, 8]. Elemental doping mainly included non-metal and metal element doping [9], some researchers tried to doping metal and non-metal elements into a material mixed potassium iodide and dicyandiamide thoroughly, and then thermal

polycondensation reaction was carried out at high temperature [10]. Finally, the graphite carbon nitride co-doped with potassium iodide was successfully prepared.

In this study, phosphorus and oxygen were co-doped into the structure of graphite carbon nitride. The concrete steps were to fully mix melamine and melamine polyphosphate (MPP), and then to carry out a simple thermal polymerization reaction at high temperature, the graphite carbon nitride doped with phosphorus (POCN-x) was successfully prepared.

2. Experimental

2.1. Preparation of catalysts

First, a certain amount of melamine and MPP were dissolved in 50ml deionized water and stirred at room temperature on a magnetic stirrer for 12h. Then, the mixed solution was dried at 80 ℃ for 24 h, then added to a crucible, and heat treatment in a muffle furnace at 520 ℃ for 3.0 h with a heating rate of 2.5℃/min. After cooling to room temperature, grinding into powder to obtain phosphorus and oxygen co-doped g-C_3N_4, designated as POCN-x (x=0.1-1.2, representing the mass ratio of MPP to melamine). As a control, melamine was directly heat treatment in a muffle furnace at 520 ℃ for 3.0h, and the obtained solid was milled to powder to obtain pure graphite carbon nitride (g-C_3N_4).

2.2. Characterization of materials

Scanning electron microscopy was used to determine the surface characteristics of the as-prepared catalysts; the specific surface area of the sample was determined by physical adsorption and desorption of N_2 using BET method; X-ray diffractometer was used to characterized the samples structure. The electron binding energy of the catalysts was measured by X-ray photoelectron spectroscopy.

3. Results and discussion

3.1. Study on Photocatalytic Performance

Methylene blue (MB) was used to compared the catalytic performance of the photocatalyst before and after modification. 20 mg of catalysts were added to 50 ml of MB solution and stirred in a dark place for 30 min before the reaction to achieved adsorption-desorption equilibrium. The photocatalytic performances of as-prepared POCN-x are shown in Fig.1 It can be observed that when the feeding ratio increasing from 0.1 to 1, the degradation rate of the catalyst to MB gradually increased, but further increasing the ratio of melamine polyphosphate will lead to decreased. Therefore, the optimal feeding ratio was 1. Compared with pure carbon nitride, the photocatalytic performance of POCN-x is enhanced. The photocatalytic degradation rate of MB by POCN-1 is 10.6 times higher than that of g-C_3N_4.

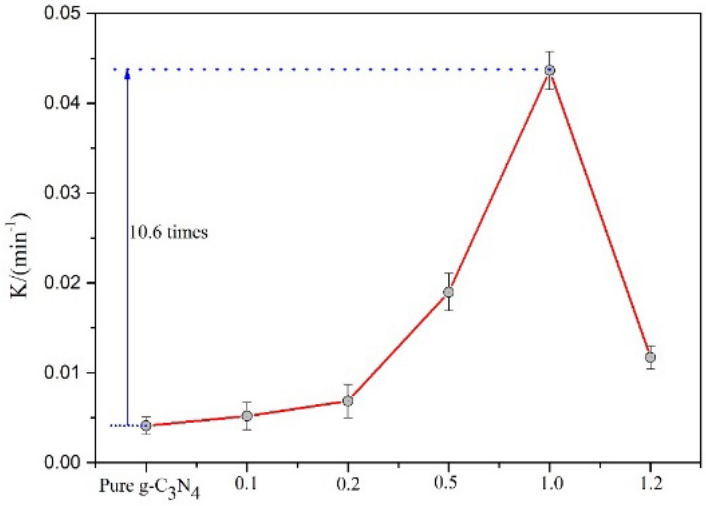

Figure. 1 Comparison of photocatalytic properties of POCN-x

3.2. Characterization of catalyst microstructure and chemical properties

Fig. 2 are SEM images of g-C_3N_4 and POCN-1, sheet structures can be observed from Fig. 2 (a) and (b). Compared with g-C_3N_4, the size of POCN-1 is reduced to form a smaller blocky structure, and a more developed pore structure is produced on the surface, which indicates that the doping of elements can also change the morphology of the material itself to a certain extent [11]. By BET characterization of the materials, observed that the specific surface areas of pure g-C_3N_4 and POCN-1 are 18.6 and 45.7m^2/g, respectively. The specific surface areas are significantly increased, which is confirmed with the results of SEM. A larger specific surface area could provide more active sites for the reaction, and then enhancement of the photocatalytic performance of POCN-1.

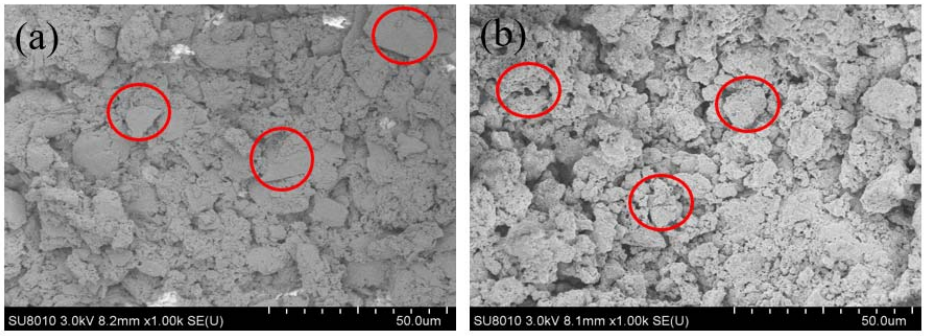

Figure. 2 SEM images of g-C_3N_4 and POCN–1

The XRD patterns of g-C_3N_4 and POCN-1 are shown in Fig. 3 (a). It can be observed that all of the materials have two similar characteristic peaks, the two diffraction peaks appear at 2θ=12.1 and 27.6, corresponding to the (100) and (002) crystal planes, respectively. Where the (100) crystal plane corresponds to the triazine structure in carbon nitride [12]. The crystal face of corresponds to the aromatic ring structure in g-C_3N_4, which indicates that the modified material still retains the crystal structure of g-C_3N_4. After modification, the intensity of (100) crystal plane decreased, indicating that the plane size of the layer decreased, while the diffraction peak at 27.2 decreased slightly, indicating that doping phosphorus and oxygen would lead to a decrease in the crystallinity of g-C_3N_4. In order to study the existing form of doped elements in the sample, the POCN-1 was characterized by XPS. Fig. 3 (b) is the full spectrum scanning of the POCN-1. From the picture, it can be observed that the sample mainly contains four elements C, N, O and P, and their electron binding energies are distributed

around 284.8, 398.9, 531.5 and 133.6 eV. XPS results show that phosphorus and oxygen elements have been successfully doped into the structure.

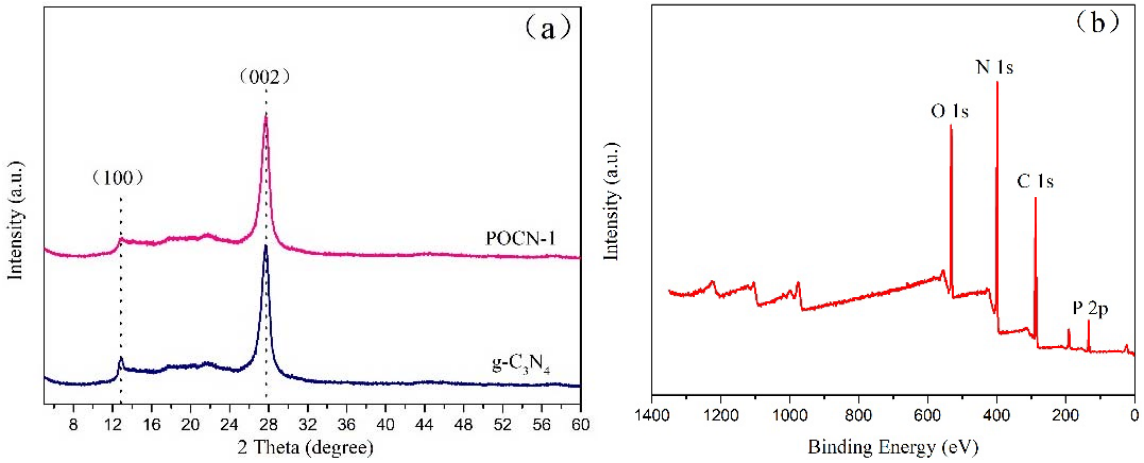

Figure. 3 (a) XRD pattern of photocatalyst and (b) XPS pattern of POCN–1

3.3. Mechanism of Photocatalytic Degradation of MB

The UV-vis-DRS diagram of the photocatalysts are shown in Fig. 4 (a), it can be observed that g-C_3N_4 mainly absorbed light with a wavelength below 440 nm. The photocatalyst of POCN-1 has a red-shift, which extend the visible light absorption range from 440 nm to 460 nm. In order to study the mechanism of degradation MB by POCN-1, sodium oxalate, isopropanol (IPA) and p-benzoquinone (BQ) were used to reveal the main active species. The photocatalytic reaction was carried out in MB solution with POCN-1 as photocatalyst, with sodium oxalate and BQ concentrations of 10 mM and IPA concentrations of 0.5M, respectively. The experimental results are shown in Fig. 4 (b), it can be observed from the graph that the degradation rate of POCN-1 to MB in solution at 30 min is 92.5 % without added any scavengers. The degradation rate was decreased to 59.1 % when sodium oxalate was added. When IPA was added, the degradation rate was basically not affected. When BQ was added, the degradation rate is only 20.9 %. The results showed that the active factors that played a major role in the photocatalytic reaction are holes (h^+) and superoxide radicals ($\bullet O_2^-$).

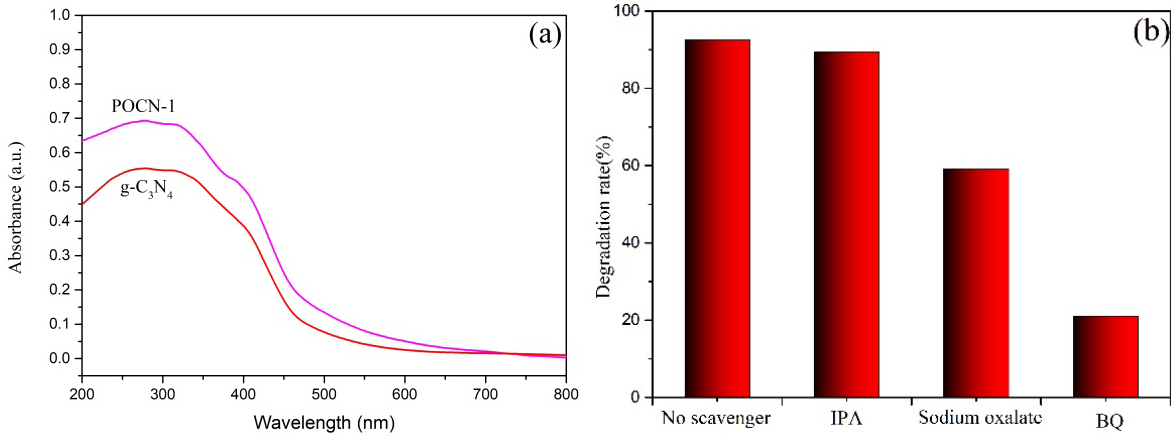

Figure. 4 (a) UV-visible diffuse reflectance absorption spectrum of the catalyst, (b) influence of scavengers on photocatalytic degradation of methylene blue

4. Conclusion

In this study, phosphorus and oxygen co-doped graphite carbon nitride has been prepared, it can

broaden the light absorption range to 460 nm from 440 nm. The photocatalytic performance of the modified material is significantly improved contrast with g-C_3N_4. Under the irradiation of visible light, the degradation rate of MB by POCN-1 is 10.6 times higher than that of g-C_3N_4. The active groups that played a major role in the photocatalytic process are holes and superoxide radicals.

Acknowledgments
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