Study on Preparation and Photocatalytic Performance of Two-Dimensional Carbon Nitride Nanosheet Materials

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Abstract. The thin g-C3N4 nanosheets were prepared by simple second-time etching approach with melamine as raw material. The microstructure, composition, thickness, specific surface area, and optical properties of the obtained materials were investigated by XRD, XPS, SEM, TEM, AFM, and BET. The results show that the specific surface area of the two-dimensional ultrathin g-C3N4 nanosheets was as high as 139.42 m²/g, and the thickness was around 5nm, which improved the response range to visible light and promoted the separation of photogenerated electron-hole pairs. The photocatalytic degradation performance of g-C3N4 nanosheets for organic pollutants was studied with dye wastewater as model pollutant, the removal efficiency of RhB solution (20 mg/L) reached 91.8% with 20mg catalyst after 30min reaction. The content of total organic carbon in the solution decreased by 58.7%, and the first-order kinetic rate constant was 10 times than that of bulk-C3N4, indicating the high catalytic activity. The stability was excellent since the activity of catalyst was not significantly reduced after used for four times.

1. Introduction
At present, with the rapid development of industrialization, the threat of water pollution to the global environment is becoming increasingly serious, and it is still a huge challenge to develop new and effective methods for remediation of sewage organic pollutants [1, 2]. Solar photocatalysis technology based on semiconductor materials is considered to be a new and effective means to solve the global environmental and energy crisis [3]. As the earliest proposed semiconductor photocatalytic material, TiO2 is used in the treatment of hydrogen production by photolysis of water and environmental pollution, henceforward, semiconductor photocatalysis technology has become a hot research topic in recent years [4-6].

Since 2009, the research group of Professor Wang Xinchen has found a new type of organic semiconductor g-C3N4 and applied it to the photolysis of water to produce hydrogen, opening up its application in the field of environmental and energy catalysis [7]. g-C3N4 is a non-metallic polymer semiconductor material, which has visible light response ability and high thermal and chemical stability. However, its small specific surface area and low utilization rate of visible light severely reduce its photocatalytic activity [8, 9]. To this end, researchers have proposed a variety of strategies to modify g-C3N4, such as controlling its morphology and structure, changing the position of the valence band, doping with metal and non-metal materials, and coupling with other semiconductors [10-12]. Among them, adjusting the morphology and structure is a relatively simple modification method. For
example, Chen et al. [13] used melamine as a raw material, combined hydrothermal and roasting methods to synthesize tubular g-C3N4. The specific surface area and band structure of the g-C3N4 were changed, and the hydrogen production activity of photodegradation of water was much higher than that of g-C3N4 bulk. For this reason, in this paper, two-dimensional (2D) g-C3N4 nanosheets were successfully synthesized by a simple secondary roasting method, and the composition, structure, morphology, optical properties, catalytic activity and stability of the synthetic materials were investigated. In addition, the photocatalytic degradation mechanism of RhB was revealed through the capture experiment of active species.

2. Experiment

2.1. Materials and methods

All reagents (analytical grade) were purchased from Aladdin Reagent Co., Ltd., and deionized water was self-made.

X-ray diffraction spectroscopy (XRD) was measured using the X-ray diffractometer (D8 Advance) of Bruker, Germany, and the Cu target Kα was used as the radiation power source; the nitrogen adsorption isotherm was measured at 77K using the Autosorb-6B adsorption instrument of Quantachrome Instruments, the United States; the scanning electron microscope (SEM) used Hitachi’s SU-8010 to characterize the morphology of the prepared catalyst; the transmission electron microscope (TEM) was carried out using the JEOL-2100F system of Japan’s JEOL company with an acceleration voltage of 200 kV; atomic force microscope (AFM) used the Asylum Research Cypher type atomic force microscope produced by Oxford Company to determine the ultra-thin structure of the prepared sample; the ultraviolet-visible (UV-Vis) diffuse reflectance experiment is to measure the sample using the Agilent Cary 50000 spectrometer produced by Agilent Company in the United States.

2.2. Preparation of catalyst

2.2.1 Synthesis of massive g-C3N4

5g of melamine was put into a crucible and place it in a muffle furnace. Then it was heated to 550°C at a heating rate of 5°C·min and maintained it for 4h to obtain a massive g-C3N4 sample, which was recorded as BCN.

2.2.2 Synthesis of flake g-C3N4

The obtained BCN was placed in an uncovered crucible and heated to 500°C at a heating rate of 10°C·min and maintained for 2h to obtain a pale yellow ultra-flaky g-C3N4 sample, which was recorded as UCN.

2.3. Photocatalytic performance evaluation

The photocatalytic degradation experiment was carried out in the CEL-HXF300-T3 photochemical reactor (Beijing Zhongjiao Jinyuan Technology Co., Ltd.). The RhB aqueous solution (20mg/L) was used as the target pollutant, and the 300 W xenon lamp (with 420 nm filter) was used as the visible light source to evaluate the activity of the catalyst. The specific experimental process is as follows: 20 mg of catalyst is added to a quartz reactor filled with 50 mL of RhB solution, the reactor is connected to a constant temperature circulating water system, and the reaction temperature is maintained at 25°C. Before illumination, the sample was firstly stirred for 40 min under dark conditions to reach adsorption equilibrium. During illumination, sample was taken every 5 min. The supernatant of each sample was taken after centrifugation, and the absorbance of RhB was detected with an ultraviolet-visible spectrophotometer. The absorption wavelength was 554nm. The degradation efficiency of RhB was represented by C/C0, and C0 and C were the initial concentration of RhB and the concentration after degradation, respectively.
3. Results and discussion

Fig 1. SEM image of BCN (a) and UCN (b), TEM (c~d) and AFM (e~f) images of UCN

The morphological characteristics of the catalyst were analyzed by SEM and TEM, as shown in Figure 1. BCN has a large block structure (Figure 1a). It can be seen from Figures 1b~1d that the UCN obtained after a second firing shows a sheet-like thin layer structure. The analysis by atomic force microscope shows that its average thickness is about 5nm. This ultra-thin structure not only greatly increases the specific surface area, but also facilitates the absorption of visible light and the migration of internal carriers.[14]

Fig 2. XRD patterns (a) and XPS spectra (b~d) of the prepared samples

Although the morphologies of UCN and BCN are different, the crystal structure of the two is the same. From the XRD spectrum (Figure 2a), it can be seen that both UCN and BCN exhibit two characteristic crystal planes, namely the (100) crystal plane at 12.7° and the (002) crystal plane at 27.5°, which correspond to the repetitive arrangement of tris-triazine structures and the stacking of conjugated aromatic structures in the carbon nitride plane [15, 16]. In addition, the surface element composition of the UCN catalyst was analyzed by XPS spectroscopy, and the results are shown in Figures 2b~2d. Among them, Figure 2c shows the XPS spectrum of the C 1s orbital. The peak at 285.8
eV is attributed to the exogenous carbon, and the peaks at 288.1 and 284.8 eV are attributed to the sp2 bond carbon (N-C=N) and sp2 graphitic carbon (C-C) in the triazinyl group \[17\]. In Figure 2d, the binding energy of N 1s is located at the four peaks of 398.5, 399.4, 400.9 and 404.3 eV, corresponding to C=N-C bond, N-(C)_3 bond, C-N-H bond and π excitation, respectively \[18\].

The N2 adsorption-desorption curve and pore size distribution curve of the catalyst are shown in Figure 3. It can be seen from Figure 3a that the adsorption-desorption isotherms of BCN and UCN belong to type IV isotherms with H1 type hysteresis loops, indicating that the materials contain mesoporous structures. The pore sizes of BCN and UCN are distributed between 15-25 nm and 5-10 nm, respectively (Figure 3b). Table 1 lists the average specific surface area, pore volume and pore diameter of the catalyst. After the second calcination, the specific surface area has increased by more than ten times, from 13.21 m²/g to 139.42 m²/g, and the pore volume is also large. It can be seen that UCN has a larger specific surface area and more pore structure distribution, which can not only increase the active sites for pollutant adsorption, but also help reduce the mass transfer resistance to accelerate the reaction kinetics process and improve the photocatalytic activity \[19\].

Table 1 BET surface areas, pore volume, and pore size of prepared samples

| Catalyst | S_{BET} (m²/g) | Pore volume (cm³/g) | d_p (nm) |
|----------|----------------|---------------------|----------|
| BCN      | 13.21          | 0.083               | 19.4     |
| UCN      | 139.42         | 0.459               | 8.1      |

Fig 3. N₂ adsorption-desorption isotherms (a) and pore size distributions of prepared samples

Fig 4. UV-Vis diffuse reflectance spectra (a), band gap energy (b), XPS valence band, and energy position diagram (d) of the prepared samples
The optical properties and band gap structure of the catalyst have been studied in depth. As shown in Figure 4a, from the UV-Vis diffuse reflectance absorption spectra of BCN and UCN, it can be seen that the light absorption band edge of UCN has a slight red shift, indicating that the visible light absorption range of flaky carbon nitride is enhanced to a certain extent compared with that of bulk carbon nitride [20]. At the same time, the Kubelka-Munk equation was used to calculate the band gap energy of the prepared samples. The band gap energies of BCN and UCN are 2.82 and 2.73 eV, respectively (Figure 4b). In addition, through XPS analysis, the valence band edge potentials of the two are 1.73 and 1.85 eV, respectively, the conduction band edge potentials of the two are calculated to be -1.09 and -0.88 eV, respectively, and the band gap structure diagram of the sample is finally determined. As shown in Figure 4d, compared with bulk carbon nitride, flaky carbon nitride has a narrower band gap width and a corrected valence band position, which is beneficial to the enhancement of the visible light absorption range and the enhancement of the oxidation capacity of pollutants.

![Fig 5. (a) Photocatalytic degradation efficiency for RhB, (b) kinetics curves, (c) TOC removal efficiency, and (d) the stability of prepared samples.](image)

The activity of the prepared catalyst was evaluated by the degradation efficiency of RhB under visible light irradiation. As shown in Figure 5a, the catalytic activity of the block carbon nitride obtained after a single calcination is low. After 30 minutes of light, only 23.4% of the RhB is decomposed; The prepared flaky carbon nitride shows excellent degradation performance, and the degradation efficiency of RhB can reach 91.8% in the same illumination time. It can be seen from Figure 5b that the degradation rate of UCN is 0.076 min\(^{-1}\), which is ten times higher than the degradation efficiency of BCN. At the same time, the changes in the total organic carbon content during the degradation process were measured (Figure 5c). The total organic carbon removal efficiencies of BCN and UCN were 4.32 and 58.74, respectively, indicating that UCN has higher pollutant mineralization ability. Finally, the repeated use performance of the catalyst was investigated, and the catalyst after each reaction was separated, washed, dried and then recycled. It can be seen from Figure 5d that the catalytic activity of UCN was not significantly decreased during the four-consecutive use of UCN, indicating that its stability is good.
Fig 6. Effect of different scavengers on degradation efficiency of RhB

The free radical capture experiment was adopted to further determine the active oxide species produced during the degradation reaction. By adding different capture reagents such as nitrogen ($N_2$), isopropanol (IPA) and ammonium oxalate (AO), the role of free radicals such as superoxide ($\cdot O_2^-$), hydroxyl ($\cdot OH$) and holes ($h^+$) in the degradation process was investigated, and the results are shown in Figure 6. It can be seen that after IPA is added, the degradation efficiency has a certain increase. This may be because the $H^+$ generated after IPA captures $\cdot OH$ consumes electrons, which accelerates the electron-hole separation, thereby promoting the degradation of RhB. The introduction of $N_2$ and AO has an inhibitory effect on the degradation of RhB, indicating that both $O_2^-$ and $h^+$ appear in the degradation process and play an oxidative effect. From the perspective of the degree of inhibition, the addition of AO has a more obvious impact on the degradation efficiency, which shows that $h^+$ is the main active oxide species in the degradation process.

4. Conclusion

(1) The g-C$_3$N$_4$ nanosheets were successfully synthesized by a simple secondary roasting method, which not only effectively increased the specific surface area, but also improved its optical properties, promoted the separation of photo-generated electron-hole pairs, and significantly improved the photocatalytic degradation of pollutants.

(2) The activity and reusability of the catalyst were investigated through photocatalytic degradation experiments. After 30 minutes of visible light irradiation, the degradation efficiency of RhB reached 91.8%, the first-order kinetic rate constant was as high as 0.076 min$^{-1}$, and the total organic carbon content in the solution had a decrease of 58.7%, showing high photocatalytic reaction activity; the catalyst has no significant decrease in activity after 4 cycles of usage, indicating that it has good stability.

(3) Through free radical capture experiments, it is found that the active oxide species produced in the degradation process are $\cdot O_2^-$, $\cdot OH$ and $h^+$, and $h^+$ plays a key role in oxidation.

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