Oxygen and methyl co-modified carbon nitride for enhanced photocatalytic degradation

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Abstract. Carbon nitride (C3N4) is a promising photocatalytic material to degrade various pollutants. However, the degradation activity is restricted by the limited light absorption and fast recombination of photoinduced carriers. Herein, a structure modification strategy by introducing a functional reagent during the polymerization process was adopted. The structure, composition and morphology of prepared materials were investigated by X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy. Benefiting from the implantation of oxygen and methyl groups in triazine unit of C3N4, enhanced light absorption and effective carrier separation are achieved. As a result, the modified C3N4 exhibits a significant enhanced degradation activity and the optimal rate constant of modified C3N4 for Acid Red 9 degradation is 5.83 times that of pristine C3N4. The work demonstrates the effect of structure modification in C3N4 for enhancing degradation activity.

1. Introduction
Semiconductor-based photocatalytic oxidation has attracted extensive interest in recent years because of its potential in the field of environment purification [1]. As an organic polymer semiconductor, carbon nitride (C3N4) is a promising photocatalytic material due to non-toxic, suitable band structure, low-cost and easy availability of source materials [2]. It has been tried to degrade various pollutants [3-4]. However, the degradation activity of C3N4 is restricted by general drawbacks of photocatalysts such as the limited light response region, fast recombination of photoinduced carriers [5]. Therefore, the development of effective strategies to mitigate these drawbacks is highly desirable.

To date, several attempts, such as doping, construction of heterostructure, deposition of cocatalyst and morphological control, have been reported to extend the light response region, reduce the recombination rate of photoinduced carriers and enhance the photocatalytic degradation activity [6-9]. Besides, structure engineering in C3N4 also plays a key role in improving photocatalytic activity by optimizing its intrinsic optical and electronic properties [10]. For instance, fusion of aromatic motifs into conjugated C3N4 was developed by Zhang et al, which results in a red-shift of the absorption edge and an enhanced separation of photoinduced carriers [11]. Xu et al constructed a push-pull system in C3N4 for efficient hydrogen generation by using organic chemistry protocols [12]. Recently, we also fabricated a sulfur doping and structure defect functionalized C3N4 by copolymerization of dicyandiamide and thioacetamide, which exhibits a significant enhanced degradation activity [13].

In this work, light absorption and carrier separation efficiency were ready to be ameliorated by a structure modification strategy. To achieve this, acetylacetone as a functional reagent was introduced during the polymerization process of urea to harvest the modified C3N4. The structure, composition,
morphology and photocatalytic activity of prepared materials were studied. The possible mechanism for the enhancement of degradation activity over the modified C$_3$N$_4$ was also discussed.

2. Methods and Materials

2.1. Materials
Urea (AR, 99%) and acetylacetone (AR, 99%) were purchased from Aladdin and used as received without further purification.

2.2. Preparation of modified C$_3$N$_4$
10 g of urea and a certain amount of acetylacetone were added to a corundum crucible with a cover, heated at 550 °C for 4 h. Then, the modified C$_3$N$_4$ materials were obtained. When the added amount of acetylacetone was 10, 20 and 30 μL, the obtained modified C$_3$N$_4$ were named C$_3$N$_4$-A1, C$_3$N$_4$-A2 and C$_3$N$_4$-A3, respectively. For control experiment, pristine C$_3$N$_4$ was also prepared with the same procedures in the absence of acetylacetone.

2.3. Characterizations
X-ray diffraction (XRD) patterns were measured via a Rigaku MiniFlex 600 X-ray diffractometer. EscaLab Xi+ spectrometer was used to collect X-ray photoelectron spectroscopy (XPS) data. Scanning electron microscopy (SEM) and element mapping images as well as energy dispersive spectroscopy (EDS) data were collected by utilizing a Phenom ProX microscope. PerkinElmer Lambda 750S spectrometer was applied to investigate ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS). Photocurrent density and electrochemical impedance spectroscopy (EIS) data were obtained via a Chenhua CHI 660E electrochemical workstation.

2.4. Photocatalytic activity measurements
20 mg of photocatalysts were dispersed uniformly in 30 mL of water containing 20 mg/L Acid Red 9. Then, the suspensions were magnetically stirred for 2 h in the dark. Subsequently, a 300 W Xe lamp with a UV cut-off filter was used to irradiate the suspensions under stirring. Every 30 min, about 3 mL of the suspensions were taken out and the photocatalysts in the suspensions were removed. Finally, the concentration was determined by using a UV-Vis spectrophotometer.

3. Results and discussion

3.1. Structure analysis
XRD patterns of the pristine and modified C$_3$N$_4$ are shown in Figure 1a. As can be seen, all materials exhibit two peaks at 12.8° and 27.5°, corresponding to the in-planar repeating triazine peak and typical inter-planar stacking peak of conjugated layer in C$_3$N$_4$. Expressly, the two characteristic peaks in modified C$_3$N$_4$ gradually become broader and weaker compared to that of pristine C$_3$N$_4$ by increasing acetylacetone levels, revealing that the structure and stacking order of modified C$_3$N$_4$ changes to a certain extent when acetylacetone is introduced during the polymerization reaction.

To clarify the composition and structure of modified C$_3$N$_4$, XPS data were collected. The XPS survey spectra in Figure 1b indicate that both pristine and modified C$_3$N$_4$ composed of C, N and O. In order to further point out the chemical structure, high-resolution spectra were fitted. As shown in Figure 1c, O 1s peak located at 532.3 eV is attributed to adsorbed water. Compared to pristine C$_3$N$_4$, two emerging peaks located at 531.8 and 533.4 eV are presented in O 1s spectrum of modified C$_3$N$_4$, which reveals the formation of C-O-C bonds. The C 1s high-resolution spectra (Figure 1d) can be divided into three peaks at 284.8, 286.5 and 288.3 eV for C$_3$N$_4$ and 284.8, 286.2 and 288.1 eV for modified C$_3$N$_4$, corresponding to C-C, C-N at the edge of s-triazine units and sp$^2$ bonded carbon N=C=N in the frame, respectively. Interestingly, the peak intensity of C-C at 284.8 eV in modified C$_3$N$_4$ is much higher than that of pristine C$_3$N$_4$, implying that the methyl is incorporated into the frame of
Moreover, the characteristic peak of C-N in modified C3N4 is obviously intensified compared to pristine C3N4, suggesting that more C-N groups are generated because of the blocking effect of terminal methyl. The result further demonstrates the introduction of methyl during the polymerization process, leading to the generation of structure defects in modified C3N4, which are favorable to enhance the photocatalytic activity. In Figure 1e, N 1s high-resolution spectra can be deconvoluted into three peaks at 398.7, 400.1 and 401.4 eV for C3N4 and 398.6, 400.0 and 401.2 eV for modified C3N4, attributed to sp² bonded N (C=N–C), tertiary N bonded to carbon (N–C₃) and side amino functional groups (N–H), respectively. A small shift of the binding energy of these peaks in both C 1s and N 1s spectra may be caused by the redistribution of electrons in the C3N4 structure with the modification of acetylacetone. According to these results, the diagrams of structure unit in pristine and modified C3N4 are speculated and depicted in Figure 1f.

3.2. Photocatalytic activity

To investigate the photocatalytic degradation activity of modified C3N4, degradation experiments of dye Acid Red 9 was conducted in an aqueous solution under the visible light irradiation. As can be seen from Figure 3a, the self-degradation of Acid Red 9 is negligible in the absence of photocatalyst under the visible light irradiation. When the pristine C3N4 is added, only about 35.3% of Acid Red 9 is degraded after the irradiation of 210 min. Notably, all the modified C3N4 photocatalysts show enhanced activity compared with pristine C3N4. Moreover, the degradation activities of modified C3N4
increase with the increase of moderate acetylacetone content. After being irradiated with visible light for 210 min, approximately 74.6%, 90.0% and 91.9% of Acid Red 9 was purified by C3N4-A1, C3N4-A2 and C3N4-A3, respectively.

Figure 2. SEM images of the (a) pristine C3N4 and (b) C3N4-A2, (c) EDS and (d) elemental mapping images of the C3N4-A2.

In addition, the kinetic curves were gained based on a linear plot of ln(C0/C) against degradation time to quantitatively compare the degradation activities of pristine and modified C3N4. As can be seen from Figure 3b, the degradation of Acid Red 9 by pristine and modified C3N4 is follows as the quasi-first-order reaction kinetic model, and the degradation rate constants for pristine C3N4, C3N4-A1, C3N4-A2 and C3N4-A3 are 0.206% min\(^{-1}\), 0.630% min\(^{-1}\), 1.065% min\(^{-1}\), and 1.200% min\(^{-1}\), respectively. The rate constant of C3N4-A1, C3N4-A2 and C3N4-A3 for Acid Red 9 degradation is 3.06, 5.17 and 5.83 times that of pristine C3N4, respectively.

Figure 3. (a) Photocatalytic degradation efficiency of Acid Red 9 and (b) kinetic curves for Acid Red 9 degradation over the pristine C3N4, C3N4-A1, C3N4-A2 and C3N4-A3.

3.3. Mechanism of improved photocatalytic activity

The optical properties of pristine and modified C3N4 were studied by UV-Vis DRS and the results are shown in Figure 4a. It can be seen that all the modified C3N4 exhibit enhanced absorption in the visible light region with the introduction of the acetylacetone. The significant red-shift of absorption edge from about 450 nm for pristine C3N4 to 470 nm for C3N4-A1, 505 nm for C3N4-A2 and 560 nm for
C₃N₄-A3 is obtained, well consistent with the change trend of the material color. The result suggests the C₃N₄ can absorb more visible light by modifying it with acetylacetone, thereby generating more electrons and holes.

Figure 4b shows the photocurrent density of pristine and modified C₃N₄ electrodes under visible light irradiation. As can be seen, pristine C₃N₄ electrode only exhibits a low photocurrent density. After modification with acetylacetone, an obvious enhanced photocurrent density is obtained. The result shows that structure modification by introducing an appropriate amount of acetylacetone is beneficial to enhance the separation and transfer efficiency of photoinduced carriers in C₃N₄. To further demonstrate the point, EIS measurements of pristine and modified C₃N₄ electrodes were performed. As illustrated in Figure 4c, the C₃N₄-A2 electrode shows a smaller arc radius in comparison with pristine C₃N₄ electrode, indicating that C₃N₄-A2 electrode has a lower resistance, resulting from the enhanced carrier separation and transfer.

According to above results, the improved photocatalytic activity of modified C₃N₄ for the degradation of Acid Red 9 could be mainly attributed to two factors (Figure 4d). The first is that light absorption of modified C₃N₄ is enhanced in comparison to pristine C₃N₄ due to O doping. The second is that the implantation of O and methyl on the triazine unit can enhance the separation and transfer efficiency of photoinduced carriers. As a result, more carriers are expected to participate in reactions, realizing the improvement of Acid Red 9 removal efficiency.

![Figure 4](image_url)

Figure 4. (a) UV-Vis DRS of the pristine C₃N₄, C₃N₄-A1, C₃N₄-A2 and C₃N₄-A3, (b) photocurrent density and (c) EIS plots of the pristine C₃N₄ and C₃N₄-A2 electrodes, (d) schematic illustration of the improved photocatalytic degradation activity of modified C₃N₄.

### 4. Conclusions

In summary, structure modification in C₃N₄ has been successfully achieved by introducing the acetylacetone during the polymerization process of urea. On one hand, the lattice N is replaced by O to form C-O-C bond. On the other hand, the methyl is incorporated on the edge of triazine unit to induce structure defect. Compared with C₃N₄, the modified C₃N₄ exhibits significant enhanced photocatalytic activity for the degradation of Acid Red 9.
activity towards the degradation of Acid Red 9. The enhanced activity can be attributed to the enhanced light absorption and separation and transfer efficiency of photoinduced carriers, thereby more carriers are expected to participate in photocatalytic reactions. The work offers a route to modify the structure of C$_3$N$_4$ for constructing efficient photocatalysts.

**Acknowledgments**

The work was supported by the Science and Technology Research Project of Jiangxi Provincial Department of Education (Grant No. GJJ190865, GJJ180835).

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