

Graphitic Carbon Nitride Catalyzes the Reduction of the Azo Bond by Hydrazine under Visible Light

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Abstract

Graphitic carbon nitride is a semiconducting material of a graphite-like 2D layered structure. It is well known for its photocatalytic properties, which can be exploited for solar-light-driven water splitting and degradation of organic pollutants. Here, we report its capabilities of catalyzing the reduction of the azo bond by hydrazine to two amines under visible light. This photocatalytic reaction provides a novel, appealing way to reduce azo dye wastes as pollutants other than degradation. With this method, the azo dye wastes can be photochemically converted to amines, which can be used as precursors for new azo dyes.

Introduction

- Azo dyes are widely used in industries like textiles, producing vibrant colors, but they are a significant source of environmental pollution due to their toxic and non-biodegradable nature.
- Traditional methods for treating azo dye pollution, such as chemical oxidation and biological degradation, are often costly, energy-intensive, and produce harmful byproducts.
- This study explores a novel photocatalytic process using **graphitic carbon nitride (g-C₃N₄)** and **hydrazine** to safely reduce azo dyes under visible light, breaking them down into harmless amines.
- The process is environmentally friendly, cost-effective, and scalable, offering a green alternative to current dye treatment technologies by converting toxic waste into reusable materials.

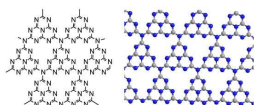


Figure 1. The structure and composition of g-C₃N₄.

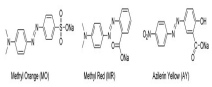


Figure 2. Structure of azo dyes.

Methodology

- Graphitic carbon nitride (g-C₃N₄) was synthesized via pyrolysis of melamine at varying temperatures (500°C–700°C) to create a porous, efficient photocatalyst.
- Azo dyes (methyl orange, methyl red, alizarin yellow) were mixed with hydrazine in aqueous solutions, and the reaction was carried out under visible light in the presence of g-C₃N₄.
- The reduction of azo bonds was monitored through the decoloration of dye solutions, with periodic measurement of absorbance to track the reaction's progress.
- The relative photocatalytic efficiency of g-C₃N₄ was evaluated by comparing the reaction rates under different conditions (light and catalyst presence) using colorimetric analysis and spectroscopic methods.

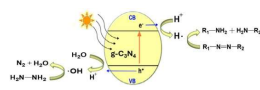


Figure 10. The proposed mechanism for the photocatalytic reduction of azo compound to amine by hydrazine under visible light.

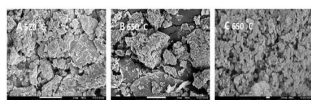


Figure 4. SEM images of catalysts: (A) made at 500 °C × 2700, (B) made at 650 °C × 2300, and (C) made at 650 °C × 43,000.

Table 1. The yield of the g-C₃N₄ catalysts and reaction conditions.

Temperature (°C)	Pyrolytic Time (hour)	Melamine Used (mg)	g-C ₃ N ₄ Produced (mg)
500	4	5055.9	2624.9
525	4	5055.3	2353.3
550	4	5055.1	2385.5
575	2	5055.9	1955.5
600	2	5055.4	1611.9
625	2	5033.5	1782.4
650	2	5055	1955.2
675	1	5055.2	1125.3
700	1	5055.5	887.2

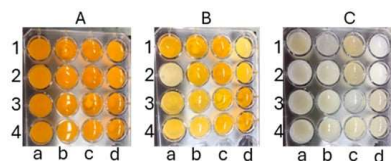


Figure 3. Appearance and color of reaction mixtures in the wells of a plastic plate during exposure to visible light: (A) at the beginning of the exposure, (B) 5 min after the light exposure, and (C) at the end of light exposure.

Results

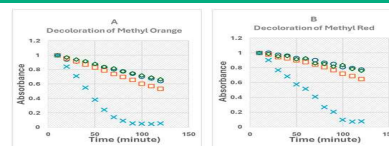


Figure 5. Decoloration rates of azo compounds (A) MO and (B) MR in hydrazine aqueous solution under different reaction conditions: ○ with no light and no catalyst; □ with light but no catalyst; △ with catalyst but no light; and × with light and catalyst.



Scheme 1. Photocatalytic and dark (when light not applied) reduction of MO and MR by hydrazine and products.

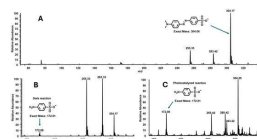


Figure 6. (A) MS spectrum of MO 20 min after addition of 3000 equivalent of hydrazine. (B) A part of MS spectrum of reaction mixture of MO and 6000 equivalent of hydrazine after 60 min reaction in the dark. (C) A part of MS spectrum of reaction mixture of MO with 3000 equivalent of hydrazine 20 min after the photocatalytic reaction under visible light.

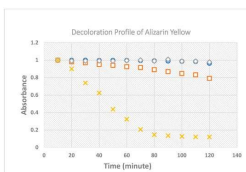
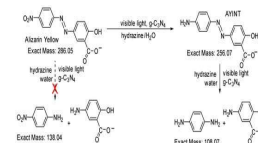


Figure 8. Decoloration rate of AY in hydrazine aqueous solution under different reaction conditions: ○ with no light and no catalyst; □ with light but no catalyst; △ with catalyst but no light; and × with light and catalyst.



Scheme 2. Photocatalytic and dark (when light not applied) reduction of AY by hydrazine and products.

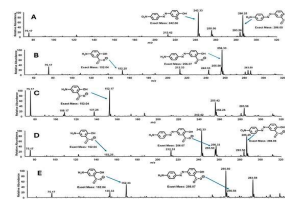


Figure 9. (A) MS spectrum of the starting reaction mixture of AY with hydrazine photocatalyzed by g-C₃N₄. (B) MS spectrum of the photocatalytic reaction mixture of AY with 1000 equivalent hydrazine, 20 min after the initial point. (C) MS spectrum of the photocatalytic reaction mixture of AY with 1000 equivalent hydrazine, 40 min after the initial point with a colorless solution formed. (D) MS spectrum of the reaction mixture of AY with 5000 equivalent hydrazine for 3 h in the dark. (E) MS spectrum of the reaction mixture of AY with 5000 equivalent hydrazine for 27 h in the dark.

Conclusion

- The photocatalyst, graphitic carbon nitride (g-C₃N₄), effectively catalyzed the reduction of azo dyes (e.g., methyl orange, methyl red) to harmless amines using hydrazine under visible light.
- The process offers an environmentally friendly alternative to traditional methods, as it produces no harmful byproducts, and the amines generated can be reused in producing new dyes.
- The g-C₃N₄ catalyst synthesized at higher temperatures (above 600°C) showed the highest photocatalytic activity, significantly speeding up the dye degradation process.
- Hydrazine played a critical role as a reducing agent, breaking the azo bonds in the dyes and preventing the oxidation of the resulting amines.
- This method could be a scalable and cost-effective solution for reducing azo dye pollution from industrial wastewater, providing a cleaner and greener approach.
- In addition to the reduction of azo bonds to amines, a nitro group in the organic compound was also reduced to an amino group in this process, at an even faster rate than for the azo group.
- Therefore, this photocatalytic process may also provide a new method for the reduction of a nitro group into an amine.

References

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