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Solvent-assisted synthesis of porous g-C₃N₄ with efficient visible-light photocatalytic performance for NO removal

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ABSTRACT

Graphitic carbon nitride (g-C₃N₄) with efficient photocatalytic activity was synthesized through thermal polymerization of thiourea with the addition of water (CN-W) or ethanol (CN-E) at 550 °C for 2 h. The physicochemical properties of the g-C₃N₄ were investigated by X-ray diffraction, transmission electron microscopy, ultraviolet-visible spectroscopy, photoluminescence spectroscopy, diffuse-reflection spectroscopy, BET and BJH surface area characterization, and elemental analysis. The carbon content was found to have self-doped into the g-C₃N₄ matrix during the thermal polymerization of thiourea and ethanol. CN-W and CN-E showed considerably enhanced visible-light photocatalytic activity, with NO removal percentages of 37.2% and 48.3%, respectively. Compared with pure g-C₃N₄, both the short and long lifetimes of the charge carriers in CN-W and CN-E were found to be prolonged. The mechanism of improved visible-light photocatalytic activity was deduced. The present work may provide a facile route to optimize the microstructure of g-C₃N₄ photocatalysts for high-performance environmental and energy applications.

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1. Introduction

Photocatalysis is a green technology with significant potential in hydrogen evolution, contaminants degradation, and organic synthesis. Graphitic carbon nitride (g-C₃N₄), a promising candidate organic photocatalyst, has attracted increasing interest because of its favorable physicochemical properties, including earth abundance, metal-free composition, unique electronic structure and suitable band gap, and excellent thermal and chemical stability [1–4]. However, the pristine bulk

g-C₃N₄ exhibits relatively poor photocatalytic activity [5,6]. Therefore, it is highly desirable to develop effective strategies to improve the photocatalytic performance of g-C₃N₄.

By optimizing the electronic structure and engineering the nanostructure of g-C₃N₄, not only can the separation and transport of photo-generated charge carriers be promoted, compared with the pristine bulk, but abundant active sites for the photochemical reaction can also be provided. Effective strategies for such improvements including doping with metal (Fe, K, Li) or nonmetal (I, C, P, B, S) elements [7–14], fine-tuning

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various nanostructural motifs (nanoflowers, nanoparticles, nanotubes, nanofibers, nanorods, ultrathin nanosheets) [15–17], coupling with other semiconductors (TiO_2 , BiOI , MoS_2 , WO_3) [18–21], and constructing plasmonic semiconductors ($\text{g-C}_3\text{N}_4/\text{Au}$, $\text{g-C}_3\text{N}_4/\text{Ag}$, $\text{g-C}_3\text{N}_4/\text{Bi}$) [22–24]. However, these approaches often suffer from complicated processes and high costs. Thus, a facile cost-effective and environmentally-friendly strategy to improve the performance of $\text{g-C}_3\text{N}_4$ is strongly needed. Generally, carbon doping is the most suitable method to fine-tune the electronic structure of $\text{g-C}_3\text{N}_4$ because of the nitrogen triangles having six longed-pair electrons. Dong et al. [25] prepared carbon self-doped $\text{g-C}_3\text{N}_4$ by using porous carbon foam as a soft-template, and the obtained carbon self-doped $\text{g-C}_3\text{N}_4$ samples showed high BET surface areas, extended absorption from visible light to the near-infrared range and accelerated electron-hole separation. Zhang et al. [26] theoretically and experimentally displayed that carbon self-doping could induce changes in the band structure and intrinsic electronic structure of $\text{g-C}_3\text{N}_4$, and apparently enhance both its photoreduction and photo-oxidation abilities. Recently, Dong et al. [27] reported the synthesis of honeycomb-like $\text{g-C}_3\text{N}_4$ samples via the thermal condensation of urea with the addition of water, which exhibited ultralong carrier lifetime and outstanding photocatalytic activity. However, there has been little research into the influence of different solvents on the physicochemical properties of $\text{g-C}_3\text{N}_4$ synthesized by solvent-assisted methods.

In this work, a facile method was developed to prepare porous $\text{g-C}_3\text{N}_4$ with superior photocatalytic activity via thermal polymerization of thiourea with the addition of water or ethanol. Interestingly, it was found that the solvents had a significant influence on the nanostructure and photocatalytic capability of $\text{g-C}_3\text{N}_4$. The water and ethanol molecules played a direct chemical role during the polymerization process of thiourea, resulting in $\text{g-C}_3\text{N}_4$ samples capable of efficient photocatalytic NO removal. The present work demonstrates a novel template-free approach to engineer the nanoarchitecture and optimize the electronic structure of $\text{g-C}_3\text{N}_4$ for improved photocatalysis.

2. Experimental

2.1. Synthesis of CN, CN-W and CN-E samples

In a typical synthesis, 12 g of thiourea was dissolved in 30 mL of water in an alumina crucible (100 mL). The crucible was semi-closed with a cover and the mixture was heated to 550 °C in a muffle furnace for 2 h at a heating rate of 10 °C/min. After the reaction, the crucible was cooled to room temperature. The resultant sample was collected and ground into powder for further use, and was denoted CN-W. Another material, denoted CN-E, was prepared under the same conditions but with the use of 30 mL of ethanol instead of water. For comparison, thiourea was also treated under the same thermal conditions but without adding either water or ethanol, and the resulting sample was denoted CN.

2.2. Characterization

The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation (Model D/max RA, Japan). The scan rate was 0.02 °/s. The accelerating voltage and the emission current were 40 kV and 40 mA, respectively. The samples' morphology and structure were examined by transmission electron microscopy (TEM: JEM-2010, Japan). Their elemental contents were analyzed using an element analyzer (Elementar Vario EL cube, German). The ultraviolet-visible diffuse reflection spectra were obtained from dry-pressed disks of the samples using a Scan UV-vis spectrophotometer (UV-vis DRS: UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly, using BaSO_4 as the reflectance sample. Their photoluminescence (PL) spectra were measured with a fluorescence spectrophotometer (PL, F-7000, Japan) using a Xe lamp as the excitation source with optical filters. Time-resolved photoluminescence spectroscopy was performed on an FLsp920 Fluorescence spectrometer (Edinburgh Instruments) with excitation at 420 nm. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 150 °C prior to the measurements.

2.3. Visible light photocatalytic performance for NO purification

The photocatalytic activity of the samples was investigated by the removal of NO at ppb levels in a continuous flow reactor at ambient temperature. The reactor was 4.5 L (30 cm × 15 cm × 10 cm), made of stainless steel and covered with Saint-Glass (transmittance: 95%). A 150W commercial tungsten halogen lamp was vertically placed outside the reactor. A UV cutoff filter (420 nm) was used to remove UV light from the light beam. A photocatalyst sample (0.2 g) was coated onto a dish with a diameter of 12.0 cm. The coated dish was then pretreated at 70 °C to remove water from the suspension. The catalyst was adhered firmly enough on the dish to prevent its removal during the air-flowing procedure.

NO gas was acquired from a compressed-gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 500 ppb by the air stream. The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 2.4 L/min by a mass-flow controller. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42i-TL), which monitors NO, NO_2 , and NO_x (NO_x represents $\text{NO} + \text{NO}_2$) with a sampling rate of 1.0 L/min. The removal ratio (η) of NO was calculated as $\eta (\%) = (1 - C/C_0) \times 100\%$, where C and C_0 are the concentrations of NO in the outlet stream and the feeding stream, respectively. Kinetically, photocatalytic NO removal is a pseudo-first-order reaction at low NO concentrations, such that $\ln(C_0/C) = kt$, where k is the

Fig. 1. XRD patterns of CN, CN-W, and CN-E.

Arrhenius rate constant.

3. Results and discussion

3.1. Phase structure

Fig. 1 shows the XRD patterns of the CN, CN-W and CN-E samples. The strong diffraction (002) peaks at 27.6° can be indexed to the interplanar stacking peaks of conjugated aromatic systems, and the small angle (100) peaks at 13.0° correspond to the in-plane tri-s-triazine units. However, no additional peaks can be detected in the spectra of CN-W and CN-E [3,4]. It is interesting to note that the (002) peak intensities decreased in CN-W and CN-E, indicating that the crystal growth of g-C₃N₄ was inhibited by the introduction of water or ethanol [25]. This finding suggests that water and ethanol had a discernible effect on the microstructure of g-C₃N₄ during the thermal polymerization [25].

3.2. Morphology

The morphologies and microstructures of CN, CN-W and CN-E were observed by TEM. As shown in Fig. 2, all the samples consisted of numerous layered nanosheets with wrinkles and irregular shapes. Fig. 2(a) and 2(b) show that the layered structure of CN was composed of thick, dense nanosheets. Compared with CN, both CN-W and CN-E contained thinner, less dense layered nanosheets with a much looser morphology and a more porous structure. These results clearly indicate that water and ethanol had significant effects on the morphologies and microstructures of CN-W and CN-E, respectively [25,28]. The formation of porous nanosheets can most likely be ascribed to the soft-template effect of gas bubbles during thermal treatment [25].

Table 1

Elemental contents of the samples.

Sample	N (%)	C (%)	H (%)	C/N ratio	C/H ratio	H Factor	C Factor	N Factor
CN	60.75	34.85	2.188	0.5736	15.9284	1.1595	1.1107	1.1017
CN-E	60.65	34.9	2.15	0.5755	16.2368	1.1595	1.1107	1.1017
CN-W	60.35	34.81	2.321	0.5768	15.0016	1.1595	1.1107	1.1017

Fig. 2. TEM images of CN (a, b), CN-W (c, d), and CN-E (e, f).

3.3. Element analysis

The elemental composition of CN, CN-W and CN-E were analyzed by an Elementar Vario EL cube element analyzer. As detailed in Table 1, all the samples were composed mostly of C and N, with relatively low concentrations of H, in agreement with previous reports. Moreover, it is interesting to observe that the concentration of C was significantly higher in CN-E than in CN and CN-W, indicating that the C content had self-doped into the g-C₃N₄ matrix during the thermal polymerization of thiourea and ethanol [26].

3.4. Optical properties

The CN, CN-W and CN-E samples absorbed visible light with high efficiency, as shown in Fig. 3(a). However, the absorption spectra of CN-W and CN-E exhibited blue-shift and red-shift, respectively, compared with CN. Furthermore, CN-W displayed

Fig. 3. UV-vis DRS (a) and PL spectra (b) of CN, CN-W, and CN-E.

a lower absorption intensity for visible light than did CN and CN-E [25,27]. Fig. 3(b) displays the PL spectra for CN, CN-W, and CN-E under excitation by visible light with a wavelength of 464 nm. It is worth noting that CN exhibited higher PL intensity than CN-E and CN-W, indicating that the recombination of photogenerated charge carriers was rapid in the pristine g-C₃N₄. Meanwhile, structural imperfections in CN-W may have promoted the nonradiative recombination of charge carriers at defect sites, thus causing this sample to exhibit the least intense PL emission. In contrast, the low PL intensity of CN-E may be attributable to the effective transportation of charge carriers, rather than their loss via nonradiative recombination [29,30].

To investigate the transfer dynamics of the charge carriers in these samples under irradiation, time-resolved fluorescence decay spectra at the nanosecond (ns) level were recorded, as shown in Fig. 4. Each sample exhibited two distinct radiative lifetimes, the relative percentages of which were calculated by fitting the decay spectra, as indicated in Table 2. For CN, the short lifetime (τ_1) and long lifetime (τ_2) of CN is 0.805 and 3.269 ns, respectively. For CN-W and CN-E, in which thiourea was treated by the addition of water or ethanol during the thermal polymerization, the short lifetime decreased to 0.756 and 0.743 ns, respectively. Furthermore, τ_2 of the charge carriers also decreased in both samples, to 3.125 ns for CN-W and 2.749 ns for CN-E. These results indicate that the reduced thickness of nanosheets of CN-W and CN-E promote the storing and shuttling of the electrons from photoexcited g-C₃N₄, thus

Table 2

Kinetic parameters of emission decay of CN, CN-W, and CN-E.

Sample	Component	Life time (ns)	Relative percentage (%)	χ^2
CN	τ_1	0.805	30.1	1.054
	τ_2	3.269	68.4	
CN-W	τ_1	0.756	39.89	1.189
	τ_2	3.125	62.22	
CN-E	τ_1	0.743	37.78	0.942
	τ_2	2.749	60.11	

enhancing electron transfer in both materials. In addition, the apparent electron transfer (ET) rate (K_{ET}) in CN-W and CN-E can be obtained according to the following equation [31]:

$$K_{ET} = 1/\tau_1(\text{CN-E}) - 1/\tau_1(\text{CN}) \quad (1)$$

$$K_{ET'} = 1/\tau_1(\text{CN-W}) - 1/\tau_1(\text{CN}) \quad (2)$$

The calculate values for CN-E and CN-W are $1.04 \times 10^8 \text{ s}^{-1}$ and $0.81 \times 10^8 \text{ s}^{-1}$, respectively, revealing that both materials promoted the effective ET quenching of the photoexcited state of g-C₃N₄ [24].

3.5. BET-BJH analysis

Fig. 5 shows the N₂ adsorption-desorption isotherms and the corresponding pore-size distribution curves of the as-obtained samples. It shows that all the samples were of type IV (BDDT classification), implying that the presence of mesopores. These isotherms display hysteresis loops of type H3,

Fig. 4. Time-resolved PL spectra at the ns-level monitored at 466 nm under excitation by 420nm light for CN (a), CN-W (b), and CN-E (c).

Fig. 5. N₂ adsorption-desorption isotherms (a) and the corresponding pore-size distribution curves (b) of CN, CN-W, and CN-E.

indicating the formation of slit-like pores arising from the aggregation of sheet-like particles [32,33]. In Fig. 5(b), the presence of mesopores can be directly inferred from the BJH pore-size distribution curves. The BET specific surface areas (A_{BET}) and total pore volumes (V_{p}) of the samples are shown in Table 3. Both parameters were higher in CN-W and CN-E than in CN, i.e., they were increased by the water/ethanol-assisted synthesis of g-C₃N₄. The increase of A_{BET} and V_{p} in CN-W and CN-E can be ascribed to the release of H₂S, CO₂ and NH₃ gases and the generation of additional H₂O and C₂H₅OH vapor during the thermal polymerization of thiourea, which promote the expansion of the packing layers and the formation of abundant porous structures, respectively. The existence of those features is also evident in the TEM images.

3.6. Photocatalytic activity

To determine the intrinsic photoactivity of the as-synthesized samples under visible-light irradiation, their photocatalytic properties were evaluated via the removal of gas-phase NO. Previous studies of this process have found that the photocatalytic oxidation of NO to NO₃⁻ is the major pathway, with NO₂ as an intermediate oxidation product, and that most of the NO is oxidized to the final product HNO₃. The

Table 3

BET surface areas (A_{BET}) and total pore volumes (V_{p}) of CN, CN-W, and CN-E.

Sample	A_{BET} (m ² /g)	V_{p} (cm ³ /g)
CN	13.81	0.12
CN-W	32.73	0.22
CN-E	25.59	0.18

process involves the following four main reactions (Eqs. (3)–(6)) [34].

After 30 min irradiation, the NO removal percentages achieved by CN, CN-W, and CN-E were 19.5%, 37.2% and 48.3%, respectively. The CN-W and CN-E samples not only outperformed CN, but also achieved greater NO removal than several other visible-light photocatalytic materials reported in the literature, including BiOBr, C-doped TiO₂, and BiOBr/C₃N₄ heterojunctions, indicating their high efficiency as photocatalysts [34–36]. They were also kinetically superior to CN, with rate constants of 0.101 min⁻¹ for CN-W and 0.126 min⁻¹ for

Fig. 6. Photocatalytic activity (a) and Arrhenius rate constants (b) of CN, CN-W and CN-E for the removal of NO in air under visible-light irradiation ($\lambda > 420$ nm).

CN-E, compared with 0.049 min^{-1} for CN [34]. The enhancement of photocatalytic activities of CN-W and CN-E can be ascribed to the following factors. First, the enlarged surface areas and pore volumes of CN-W and CN-E provide more active sites for the absorption and subsequent photocatalytic oxidation of NO. Second, this photocatalytic removal was further facilitated by the enhanced electron transfer rates in CN-W and CN-E. Our work demonstrates that the solvent-assisted procedure is a simple and effective strategy for synthesizing g-C₃N₄ with improved photocatalytic performance.

4. Conclusions

Water and ethanol as solvents played a direct chemical role in increasing the specific surface areas and total pore volumes of g-C₃N₄. Furthermore, the use of ethanol resulted in the production of carbon-self-doped g-C₃N₄, which could be used to engineer the electronic structure and band structure. Electron transfer quenching was also found to be effective in both CN-W and CN-E because of enhanced electron transfer, favoring the photocatalytic removal of NO_x. Moreover, in CN-E, the enhanced electron transfer played a more important role than the enlarged surface areas and pore volumes in promoting the photocatalytic removal of NO. This work could provide a facile and low-cost route to engineer the structure of g-C₃N₄ for enhanced visible light photocatalytic performance.

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Graphical Abstract

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The porous g-C₃N₄ and C-doped g-C₃N₄ thin nanosheets with efficient visible-light photocatalytic performance were synthesized via thermal polymerization of thiourea with the addition of water and ethanol, respectively.

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溶剂辅助合成介孔 $g-C_3N_4$ 及其增强的可见光催化去除NO性能研究

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摘要: 类石墨相氮化碳($g-C_3N_4$)具有特殊的层状二维结构、独特的电子结构、合适的能带结构、良好的热稳定性和化学稳定性等理化性能, 因而在可见光催化净化环境污染领域广受关注. 但原始块状 $g-C_3N_4$ 的可见光催化活性较弱, 还不能满足实际应用需求. 因此, 亟需开发一种高效的改性方法来提高 $g-C_3N_4$ 的光催化性能. 本课题组发展了一种有效的改进 $g-C_3N_4$ 方法, 以硫脲为前驱体, 去离子水(制备样品标记为CN-W)或无水乙醇(制备样品标记为CN-E)为溶剂, 通过一步高温缩聚制得具有高可见光催化性能的介孔 $g-C_3N_4$. 然而, 对于不同溶剂效应原位改性 $g-C_3N_4$ 及其增强可见光催化性能的机理还不清楚. 因此, 本文采用X射线衍射(XRD)、透射电镜(TEM)、紫外-可见漫反射光谱(UV-Vis DRS)、荧光光谱(PL)、 N_2 吸附和元素分析等手段研究了去离子水和无水乙醇作为溶剂原位改性 $g-C_3N_4$ 的理化性能差异及增强可见光催化性能的原因.

XRD结果表明, 去离子水和无水乙醇不会改变 $g-C_3N_4$ 的晶体结构, 但会抑制其晶体结构的生长. 由TEM图像可见, 因去离子水和无水乙醇在热聚合过程中产生的气泡可以作为软模板, 导致CN-W和CN-E纳米片均为酥松多孔层状结构, 其中CN-W更薄更小. 元素分析测试结果表明, 无水乙醇和硫脲在热聚合过程中导致碳自掺杂 $g-C_3N_4$. UV-Vis DRS结果显示, CN-W和CN-E分别发生了相对的蓝移和红移现象. 荧光寿命测试结果显示, CN的短荧光寿命和长荧光寿命(0.805 ns, 3.269 ns)明显高于CN-W(0.756 ns, 3.125 ns)和CN-E(0.743 ns, 2.749 ns), 表明CN-W和CN-E纳米薄片可以促进光生电子的储存和往复运动, 有利于光生电子的迁移. 此外, 通过理论计算得CN-E的电子迁移速率($1.04 \times 10^8 \text{ s}^{-1}$)明显快于CN-W($0.81 \times 10^8 \text{ s}^{-1}$), 表明CN-E和CN-W都有利于光生电子的迁移猝灭. 另外, BET-BJH测试结果显示, CN-W($32.73 \text{ m}^2/\text{g}$, $0.22 \text{ cm}^3/\text{g}$)和CN-E($25.59 \text{ m}^2/\text{g}$, $0.18 \text{ cm}^3/\text{g}$)的比表面积和孔容均显著高于未改性的 $g-C_3N_4$ ($13.81 \text{ m}^2/\text{g}$, $0.12 \text{ cm}^3/\text{g}$), 表明溶剂和前驱体在热聚合过程中产生的 H_2O , C_2H_5OH , H_2S , CO_2 和 NH_3 气体有利于层状结构和丰富孔结构的形成, 因而CN-W和CN-E的比表面积和孔容显著增加. 由此可见, 无水乙醇和去离子水在辅助制备介孔 $g-C_3N_4$ 过程中表现出不同的作用.

可见光催化去除NO的测试结果表明, CN-E(48.3%)和CN-W(37.2%)的光催化活性明显高于 $g-C_3N_4$ (19.5%), CN-E和CN-W的可见光催化活性也明显优于我们以前报道的 $BiOBr$ 、C掺杂 TiO_2 和 $BiOBr/C_3N_4$ 异质结. 结合表征结果, CN-E和CN-W可见光催化性能增强的原因主要有两个: (1) CN-E和CN-W增大的比表面积和孔容有利于NO的吸附、反应中间产物的转移和提供更多的活性位点参与光催化氧化反应; (2) 更薄的纳米片结构和C掺杂 $g-C_3N_4$ 有利于促进光生电子的迁移, 从而显著提高其光催化活性.

关键词: 溶剂辅助; 类石墨相氮化碳; 可见光; 光催化性能; 一氧化氮去除

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