UTILIZING NITROGEN-DOPED GRAPHENE QUANTUM DOTS TO MODIFY ZnO FOR ENHANCED PHOTOCATALYTIC ACTIVITY IN COMMERCIAL INSECTICIDE DEGRADATION

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Abstract

This study investigates the synthesis and application of nitrogen-doped graphene quantum dots (N-GQDs) for enhancing the photocatalytic activity of ZnO in the degradation of insecticide in water. N-GQDs were synthesized via a hydrothermal method using varying nitrogen percentages in citric acid (ranging from 0% to 0.75%), reveal consistent excitation and emission peaks at 350 nm and 440 nm, respectively. Fluorescence characterization indicates that higher nitrogen doping percentages enhance the fluorescence intensity of N-GQDs, suggesting increased photo-generated electron production. FT-IR spectra confirm successful nitrogen doping, with characteristic peaks at 1345 cm^{-1} attributed to C-N stretching vibrations. Furthermore, UV-V is spectroscopy was employed to analyze the absorbance spectra of a commercial insecticide (beta-cyfluthrin) in water (concentrations: 100-500 ppm), demonstrating a linear increase in integrated absorbance value with concentration. This underscores the potential of UV-Vis spectroscopy for precise insecticide quantification. Photocatalytic degradation experiments using N-GQD-modified ZnO catalysts showed reduced residual insecticide integrated absorbance value compared to pristine ZnO and GQD-modified ZnO, highlighting enhanced photocatalytic activity of N-GQDs. Photocatalytic degradation experiments indicated that ZnO modified with N-GQDs was more effective than ZnO and ZnO modified with GQDs, with the optimal nitrogen doping level found to be 0.65%. This result demonstrates the potential of nitrogen-doped graphene quantum dots as effective photocatalysts for environmental remediation applications.

Keywords: Nitrogen-doped graphene quantum dots, Nitrogen doping effects, Photocatalytic performance, Insecticide degradation, Sustainable water treatment

Introduction

In recent years, the contamination of water bodies with insecticides has become a significant environmental concern due to their persistence, toxicity, and bioaccumulation potential. Traditional methods for insecticide removal are often inefficient or environmentally damaging, necessitating the development of advanced, sustainable solutions. Photocatalysis, a process that leverages the energy from light to accelerate chemical reactions, has emerged as a promising approach for degrading organic pollutants, including insecticides, in water. Among various photocatalysts, zinc oxide (ZnO) has attracted considerable attention due to its high efficiency, chemical stability, and low cost (Pimpang, Thong-on & Choopun, 2018; Pimpang, Sumang & Choopun, 2018; Pimpang & Choopun, 2019; Phophayu et al., 2020; Krobthong et al., 2022). However, the practical application of ZnO is hindered by its wide bandgap and rapid electron-hole recombination, which limit its photocatalytic performance under visible light (Krobthong et al., 2022; Phophayu et al., 2020; Sujinnapram & Wongrerkdee, 2023; Wongrerkdee & Pimpang, 2020). To overcome these limitations, significant research has focused on modifying ZnO with various nanomaterials to enhance its photocatalytic activity (Hameed Hameed, Mohamed & Kadi, 2019; Kaur & Singh, 2020; Krobthong et al., 2022; Ong et al., 2016; Phophayu et al., 2020; Xiang, Yu & Jaroniec, 2012; Zhou et al., 2018). One such promising modifier is carbon base nanomaterial such as activated carbon, graphene, graphene quantum dots (GQDs), due to their low toxicity and high chemical activity.

Nitrogen-doped graphene quantum dots (N-GQDs) are zero-dimensional carbon-based nanomaterials that exhibit unique optical and electronic properties, including strong absorption in the visible range, high quantum yield, and excellent electron transfer capabilities. When integrated with ZnO, N-GQDs can potentially improve light absorption, reduce electron-hole recombination, and facilitate charge transfer processes, thereby enhancing the overall photocatalytic efficiency. Therefore, N-GQDs can significantly enhance the photocatalytic activity of materials such as ZnO through several mechanisms. First, N-GQDs exhibit strong absorption in the visible light region due to their tunable band gap and nitrogen dopants, allowing the composite material to utilize a broader spectrum of sunlight and thereby enhancing overall photocatalytic efficiency (Wu, Wang & Li, 2017; Zhu et al., 2021). Second, N-GQDs act as electron acceptors and donors, facilitating the separation of photogenerated electron-hole pairs in the photocatalyst (Shen et al., 2019; Wu, Wang & Li, 2017). This reduces the recombination rate of electrons and holes, increasing the number of charge carriers available for photocatalytic reactions. Third, the incorporation of N-GQDs increases the surface area of the composite material, providing more active sites for the adsorption and degradation of pollutants and improving the interaction between the photocatalyst and contaminants (Dong, Zhao & Xiong, 2016; Wu, Wang & Li, 2017; Zhang, Li & Wang, 2018). Additionally, N-GQDs promotes the transfer of photo-generated electrons from metal oxide to the N-GQDs. This efficient charge transfer minimizes charge recombination and maximizes the availability of electrons for photocatalytic reactions (Huo et al., 2021).

This study explores the synthesis and application of N-GQDs-modified ZnO nanocomposites for the degradation of insecticides in water. By investigating the optical and photocatalytic properties of these nanocomposites, we aim to elucidate the mechanisms by which N-GQDs enhance ZnO's photocatalytic performance. N-GQDs were synthesized by hydrothermal method using varying mass percentages of nitrogen in citric acid, with urea serving as the nitrogen source. The optical properties of N-GQDs were observed by photoluminescence spectroscopy, the functional groups and chemical bonds were characterized using Fourier Transform Infrared (FT-IR) spectroscopy. The ultraviolet-visible (UV-vis) spectroscopy was carried out to the degradation of insecticides in water. The outcomes of this research could provide valuable insights into designing effective photocatalysts for environmental remediation and contribute to developing sustainable strategies for managing insecticide pollution.

Materials and Methods

1. Preparation of Nitrogen-doped graphene quantum dots

Nitrogen-doped graphene quantum dots (N-GQDs) were synthesized via the hydrothermal method using citric acid and urea as precursors, with varying mass percentages of nitrogen (from urea) ranging from 0% to 0.75%. Urea (CH_4N_2O, Kemaus) and citric acid ($C_6H_{10}O_8$, Loba cheime) served as the nitrogen and carbon sources, respectively. For instance, N-GQDs containing 0.55% nitrogen were prepared using 0.165 g of urea, 7 g of citric acid, and 100 mL of deionized water. The synthesized N-GQDs were stored at room temperature before ethanol was added to maintain an initial volume of 100 mL. The synthesis conditions involved heating the reaction mixture at 200°C in an autoclave for 10 hours.

2. Preparation of photocatalysts

Initially, 5 mL of N-GQDs were combined with 5 g of zinc oxide (ZnO). The mixture of N-GQDs and ZnO was then subjected to grinding. Grinding ensures the uniformity and distribution of N-GQDs on the ZnO particles, which is crucial for the subsequent photocatalytic activity. Finally, the ground mixture was annealed at 300°C for 10 hours to enhance bonding between N-GQDs and ZnO and to remove any residual solvents or impurities.

3. Characterizations of N-GQDs

Excitation-emission contour maps of N-GQDs were performed by utilizing excitation wavelength in the range of 300-400 nm and recording emission wavelengths in the range of 400-700 nm. Fluorescence spectra were assessed in the range of 400-700 nm at excitation wavelength of 350 nm (Shimadzu RF-6000). FT-IR spectra were observed in the range of 400-4000 cm^{-1} (Thermo scientific Nicolet™iS).

4. Investigations of photocatalytic activities

UV-vis absorption spectra of a commercial insecticide were recorded in the range of 400-700 nm (Shimadzu UV-2450). UV-Vis spectroscopy was employed to analyze the absorbance spectra of a commercial insecticide (beta-cyfluthrin) in water at concentrations ranging from 100 ppm to 500 ppm. Integrated absorbance values were measured to establish a linear relationship between insecticide concentration and integrated absorbance value, demonstrating the potential of UV-Vis spectroscopy for precise quantification of insecticide levels in water. Photocatalytic degradation of a commercial insecticide (beta-cyfluthrin) was conducted using ZnO, ZnO modified with GQDs (Z/G-0 N), and ZnO modified with N-GQDs (Z/G-0.55 N to Z/G-0.75 N) as photocatalysts. The photodegradation time was controlled to 10 minutes, with an initial insecticide concentration of 500 ppm in all cases. Finally, residual insecticide was retained for analysis.

Results

1. Characteristics of N-GQDs

To determine the characteristics of the N-GQDs, the excitation-emission contour map of the N-GQDs was observed using fluorescence spectroscopy. Emission wavelengths from 350 nm to 700 nm were achieved by varying the excitation wavelength in 1 nm steps from 300 to 500 nm. The bright areas along the excitation wavelength axis (y-axis) correspond to high excitation intensity, which is directly related to light absorption in the N-GQDs. The bright areas along the emission wavelength axis (x-axis) correspond to high emission intensity, which is due to photo-emission by the N-GQDs. Figure 1 shows excitation-emission contour maps of N-GQDs prepared with varying mass percentages of nitrogen in citric acid, with urea serving as the nitrogen source. The mass percentages of nitrogen in citric acid were varied as 0%, 0.55%, 0.60%, 0.65%, 0.70%, and 0.75% nitrogen. It was found that the maximum excitation wavelength was 350 nm and the maximum emission wavelength was 440 nm in all cases. Previous reports showed the effect of GQD size on the peak position of the emission wavelength (Pimpang, Sumang & Choopun, 2018). Hence, the constant emission peak with varying mass percentages of nitrogen in citric acid implies that nitrogen content does not affect N-GQD size.

A thorough understanding the emission spectra of N-GQDs, fluorescence characterization indicated that the N-GQDs can emit strong visible fluorescence under excitation wavelength at 350 nm. Fluorescence spectra of obtained N-GQDs are shown in Figure 2. It was found that the fluorescence intensity increase with increasing mass percentages of nitrogen. The result suggested that nitrogen modification can promote the generation of photo-generated electrons. The fluorescence of GQDs has been previously reported (Wongrerkdee & Pimpang, 2020). Briefly, when the GQDs absorb light (and hence energy), electrons are excited from the ground state to an excited state. As these electrons return to the ground state, a variety of transitions occur, which may involve the emission of light. This effect is termed fluorescence.

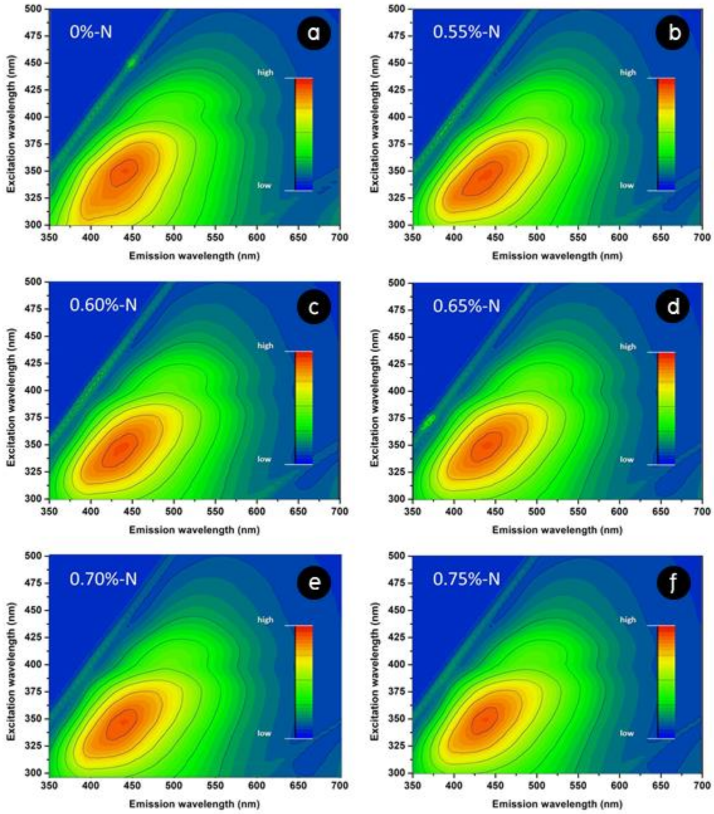

Figure 1 Excitation-emission contour maps of N-GQDs prepared using varying mass percentages of nitrogen in citric acid, with urea serving as the nitrogen source: 0% (a), 0.55% (b), 0.60% (c), 0.65% (d), 0.70% (e), and 0.75% nitrogen (f).

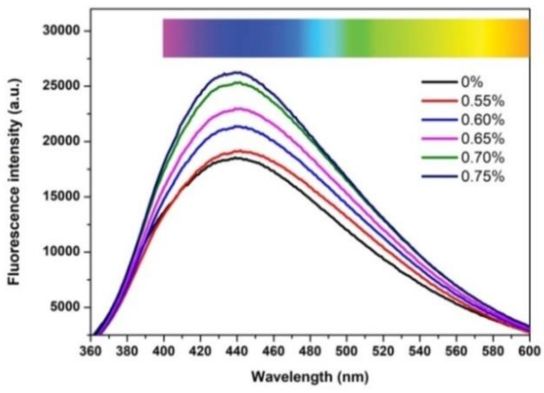

Figure 2 Fluorescence spectra of N-GQDs prepared using varying mass percentages of nitrogen in citric acid, with urea serving as the nitrogen source: 0% (a), 0.55% (b), 0.60% (c), 0.65% (d), 0.70% (e), and 0.75% nitrogen (f). Fluorescence spectra were observed under the excitation wavelength of 365 nm.

Figure 3 presents the typical FT-IR spectra of N-GQDs prepared with 0% and 0.75% nitrogen. The FT-IR spectra of N-GQDs prepared with 0.75% nitrogen represent the molecular composition and structure of nitrogen-doped GQDs prepared with 0.55%, 0.60%, 0.65%, 0.70%, and 0.75% nitrogen, as all vibration modes were quite similar. The FT-IR spectra of N-GQDs prepared with 0% nitrogen showed C-H stretching at 2985 cm^{-1}, C=O stretching at 1706 cm^{-1}, an -OH band at 1374 cm^{-1}, C-OH stretching at 1181 cm^{-1}, and C-O stretching at 1020 cm^{-1}, indicating the vibrations of hydroxyl (OH) and carboxyl (COOH) groups functionalized onto crystalline GQDs (Pimpang, 2018; Wongrerkdee & Pimpang, 2020). It is worth noting that the FT-IR spectra of N-GQDs prepared with 0.75% nitrogen demonstrated C-N stretching at 1345 cm^{-1}. FT-IR spectra of N-GQDs typically show a peak around 1340-1345 cm^{-1} attributed to the C-N stretching vibration, indicating successful nitrogen doping (Li et al., 2015). An FT-IR spectrum of gaseous CO_2 in a porous structure was detected at 2360 cm^{-1}.

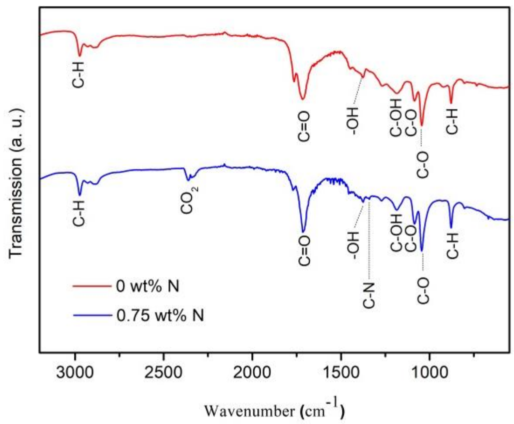

Figure 3 Typical FT-IR spectra of GQDs and N-GQDs prepared using 0.75% nitrogen.

2. Photocatalytic activity of ZnO modified with N-GQDs

To determine the relationship between insecticide concentration in water and light absorption, this research analyzed the absorbance spectra of insecticide in water at concentrations ranging from 100 to 500 ppm. For example, water containing 100 ppm of insecticide was prepared using 10 μL of commercial insecticide (beta-cyfluthrin) in 100 mL of deionized water. The study used a commercial insecticide with beta-cyfluthrin as the active ingredient. Figure 4 shows UV-vis absorbance spectra of commercial insecticide in distilled water at concentrations ranging from 100 to 500 ppm. Because we used a commercial insecticide that contains a mixture of various chemicals, the peak of beta-cyfluthrin was not detected. It is possible that the peaks of different chemicals overlapped, making the beta-cyfluthrin peak unclear. Hence, an integrated absorbance value was defined, which can be the sum of absorbance values over a spectrum of wavelengths. This provides an overall measure of how much light a sample absorbs across the entire range. It was found that the integrated absorbance value increased with the concentration of the commercial insecticide. This result implies the potential of UV-Vis spectroscopy to quantify the amount of insecticide. Therefore, we used this technique to investigate the degradation of insecticides through photocatalysis.

Figure 5 shows UV-Vis absorbance spectra of a commercial insecticide after photocatalysis using different photocatalytic materials, including ZnO, ZnO modified with GQDs (referred to as Z/G-0 N), and ZnO modified with N-GQDs. The N-GQDs were prepared using varying mass percentages of nitrogen: 0.55%, 0.60%, 0.65%, 0.70%, and 0.75%, labeled as Z/G-0.55 N, Z/G-0.60 N, Z/G-0.65 N, Z/G-0.70 N, and Z/G-0.75 N, respectively. The integrated absorbance value of a commercial insecticide after photocatalysis with ZnO modified with N-GQDs was lower than those with ZnO and ZnO modified with GQDs, suggesting a lower remaining insecticide concentration in the water and demonstrating the potential of ZnO modified with N-GQDs. Interestingly, the integrated absorbance value of a commercial insecticide decreased with increasing N doping from 0.55% to 0.65%, but then increased with further N doping from 0.70% to 0.75%. This result implies that the optimal condition was Z/G-0.65 N.

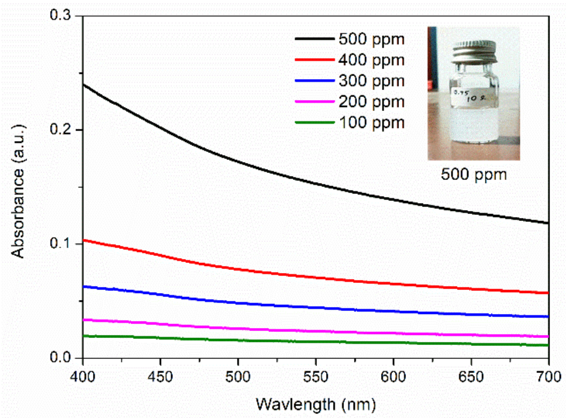

Figure 4 UV-vis absorbance spectra of a commercial insecticide (beta-cyfluthrin) at concentrations ranging from 100 to 500 ppm.

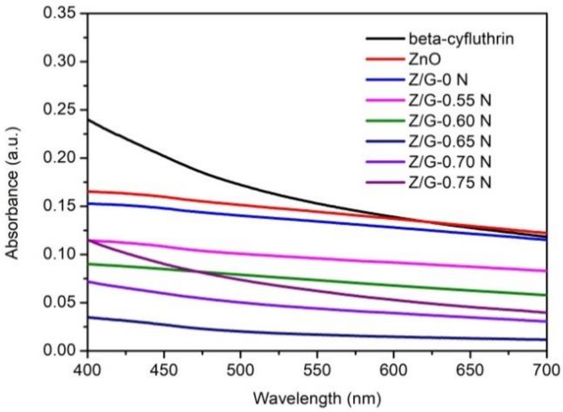

Figure 5 UV-Vis absorbance spectra of a commercial insecticide (beta-cyfluthrin) after photocatalysis using different photocatalytic materials: ZnO, ZnO modified with GQDs (Z/G-0 N), and ZnO modified with N-doped GQDs (Z/G-0.55 N, Z/G-0.60 N, Z/G-0.65 N, Z/G-0.70 N, and Z/G-0.75 N). The photodegradation time was controlled to 10 minutes, with an initial insecticide concentration of 500 ppm in all cases.

Discussion

N-GQDs were synthesized via the hydrothermal method using citric acid and urea as precursors, with varying mass percentages of nitrogen (from urea) ranging from 0% to 0.75%. The fluorescence intensity of N-GQDs increased with higher nitrogen doping percentages, indicating enhanced photo-generated electron production due to nitrogen modification. This finding underscores the potential of nitrogen doping to improve the optical and electronic properties of GQDs. To assess the practical application of N-GQDs, UV-Vis spectroscopy was employed to analyze the absorbance spectra of a commercial insecticide (beta-cyfluthrin) in water at concentrations ranging from 100 to 500 ppm. The results demonstrated that the integrated absorbance value increased linearly with insecticide concentration, highlighting the effectiveness of UV-Vis spectroscopy for quantifying insecticide levels in water. Photocatalytic degradation experiments using ZnO and N-GQD-modified ZnO catalysts showed promising results. ZnO modified with N-GQDs exhibited lower integrated absorbance value of residual insecticide compared to ZnO and GQD-modified ZnO, indicating enhanced photocatalytic activity. Interestingly, the integrated absorbance value of a commercial insecticide decreased with increasing N doping from 0.55% to 0.65%, but then increased with further N doping from 0.70% to 0.75%. This result implies that the optimal condition was N-GQD-modified ZnO with 0.65% N doping. For

0.70% to 0.75% N doping, the integrated absorbance value was higher than that of 0.65% N doping because the N-GQDs may compete with ZnO for light absorption (Batvandi et al., 2022). Accordingly, this study demonstrates the potential of nitrogen-doped graphene quantum dots as effective photocatalysts for environmental remediation applications.

Conclusion

This study successfully characterized N-GQDs using fluorescence spectroscopy and FT-IR, revealing important insights into their properties and interactions. The excitation-emission contour map showed that the maximum excitation and emission wavelengths were consistent at 350 nm and 440 nm, respectively, across different nitrogen doping levels. This consistency indicates that the size of N-GQDs is unaffected by varying nitrogen content. Fluorescence intensity increased with higher nitrogen doping, suggesting enhanced photo-generated electron production due to nitrogen modification. FT-IR spectra confirmed the presence of characteristic functional groups and successful nitrogen doping, as evidenced by the C-N stretching vibration at 1345 cm^{-1}. The UV-Vis absorbance spectra of the commercial insecticide, analyzed at concentrations ranging from 100 to 500 ppm, demonstrated the method's potential for quantifying insecticide concentration. Photocatalytic degradation experiments indicated that ZnO modified with N-GQDs was more effective than ZnO and ZnO modified with GQDs, with the optimal nitrogen doping level found to be 0.65%. Higher doping levels resulted in decreased efficiency due to competition between N-GQDs and ZnO for light absorption. This study highlights the importance of precise control over nitrogen content in optimizing the photocatalytic properties of N-GQDs.

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