Synthesis of ZnO/NiO/g-C₃N₄ Nanocomposite Materials for Photocatalytic Degradation of Tetracycline Antibiotic

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Abstract

In this study, an approach was utilized to improve the photocatalytic efficacy of g-C₃N₄ by creating a composite photocatalyst through co-precipitation. This process involved incorporating NiO and ZnO into the structure, resulting in enhanced photocatalytic activity. The Scanning Electron Microscopy (SEM) showcases interesting aggregation behavior, revealing extensive arrays of ZnO/NiO/g-C₃N₄ particles. Ultraviolet–Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) confirms the composite’s strong light absorption, especially in the visible spectrum. X-ray diffraction (XRD) analysis provides conclusive evidence of successful material synthesis. The degradation of tetracycline antibiotics under visible light exposure demonstrates an impressive photochemical degradation efficiency of 78.43%. Additionally, the composite exhibits impressive cycles of reuse, retaining its high photocatalytic activity even after four reaction cycles. This performance surpasses that of comparison samples. The synergistic integration of NiO and g-C₃N₄ within ZnO proves to be crucial in enhancing photocatalytic activity by enhancing electron-hole separation and mitigating recombination processes. This composite photocatalyst shows a wide potential for efficiently eliminating tetracycline antibiotics from water systems.

Keywords: ZnO/NiO/g-C₃N₄; nanocomposites; tetracycline; co-precipitation


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1. Introduction

Photocatalysis has emerged as a highly promising and versatile technology with a wide range of applications, including the degradation of toxic organic substances, bacterial inactivation, and wastewater treatment. This field encompasses catalytic reactions that are triggered by the absorption of light by a substrate, offering a sustainable and environmentally friendly approach to address pressing challenges in various industries [1–4].

Among the diverse semiconductor materials investigated as photocatalysts, titanium dioxide (TiO₂) has received significant attention due to its excellent chemical stability, low cost, nontoxicity, and strong oxidative capabilities. These properties have made TiO₂ a benchmark material in photocatalysis research. Under UV light irradiation, it has demonstrated remarkable efficiency in degrading organic pollutants into harmless byproducts, such as carbon dioxide and water. However, TiO₂ has limitations in
terms of its wide band gap, which restricts its absorption of visible light, thus hampering its photocatalytic activity under solar irradiation [5,6].

To overcome the limitations of TiO$_2$ and broaden the range of light absorption, researchers have explored alternative semiconductor photocatalysts [7]. One such material is graphitic carbon nitride (g-C$_3$N$_4$), which has garnered significant interest due to its unique electronic band structure, good light sensitivity, high physicochemical stability, and ability to capture visible light. The structure of g-C$_3$N$_4$ closely resembles graphene, consisting of a two-dimensional layered arrangement of carbon and nitrogen atoms [8]. Despite its advantages, g-C$_3$N$_4$ suffers from low surface area, rapid recombination of electron-hole pairs, poor conductivity, and limited absorption above 460 nm [9]. These drawbacks have prompted researchers to investigate strategies for enhancing the photocatalytic performance of g-C$_3$N$_4$, including modifying its morphological structure, introducing doping with metallic or non-metallic elements, and fabricating heterostructures [10–12].

In recent years, efforts have been focused on developing composite photocatalysts that combine multiple semiconductor materials to harness their synergistic effects and improve overall performance. One such composite is the ZnO/NiO/g-C$_3$N$_4$ system, which offers unique advantages derived from each constituent material. Zinc oxide (ZnO), a low-cost and highly chemically stable semiconductor, has been extensively studied and widely employed in electronics, materials, and energy applications [13,14]. However, its photocatalytic performance is limited by its relatively high band gap energy, resulting in inadequate absorption of visible light and diminished photocatalytic efficiency. Researchers have explored various strategies, such as metal or non-metal ion doping and surface modification, to enhance ZnO light absorption and extend its photocatalytic activity into the visible light region to address this [15,16].

Nickel oxide (NiO), another promising semiconductor, has gained attention as a photocatalyst for environmental remediation, particularly in aquatic environments. NiO can efficiently decompose pollutants, including organic compounds, anions, cations, and toxic substances, under sunlight or UV light irradiation. Moreover, NiO exhibits non-toxic and environmentally friendly properties [17]. However, challenges related to reproducibility and particle size control have prompted further research to enhance NiO's catalytic efficiency and stability. Various strategies, such as combining NiO with carbon nanotubes (CNTs) or doping it with transition metals, have been explored to improve its photocatalytic performance [18].

This research aims to synthesize the ZnO/NiO/g-C$_3$N$_4$ composite through a co-precipitation technique and analyze its effectiveness in photocatalytically degrading tetracycline, a prevalent antibiotic pollutant found in wastewater. Tetracycline is known to persist in the environment and can harm ecosystems. The composite will be subjected to LED light sources to evaluate its performance when exposed to visible light. The study will investigate the photocatalytic degradation efficiency and the potential for reuse of the composite as a photocatalyst for removing organic pollutants.

### 2. Materials and Methods

#### 2.1 Materials

In this study, the following chemicals were utilized: Urea ((NH$_2$)$_2$CO, 99%, Xilong Chemical, China), Nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$.6H$_2$O, 96%, Guangdong Chemical, China), Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O, 99.5%, Damao Chemical, China), sodium hydroxide (NaOH, 96%, Xilong Chemical, China), Tetracycline (TCC, 95%, Sigma-Aldrich, European), tert-Butanol (TBA, 99.5%, Sigma-Aldrich, USA), p-Benzoquinone (BQ, 98%, Sigma-Aldrich, USA), Potassium dichromate (K$_2$Cr$_2$O$_7$, 99.8%, Xilong Chemical, China), Sodium oxalate (Na$_2$C$_2$O$_4$, 99.8%, Xilong Chemical, China). All materials are of analytical grade and utilized without further purification before the synthesis process.

#### 2.2 Synthesis of Catalysts

In this study, g-C$_3$N$_4$ was synthesized by thermal decomposition of urea according to the following specific process: First, 10 g of urea was put into a porcelain crucible. Next, the material was placed in a porcelain crucible, which was heated to 550 °C at a heating rate of 10 °C/min in a furnace and for 3 h in air. Finally, the porcelain crucible is cooled down to room temperature after the reaction. The obtained g-C$_3$N$_4$ (CN) material was used for further experiments.

ZnO/NiO/g-C$_3$N$_4$ (ZNG) composites were synthesized by the co-precipitation method. First, 5.94 g of Zn(NO$_3$)$_2$.6H$_2$O and 5.81 g of Ni(NO$_3$)$_2$.6H$_2$O were dissolved in 100 mL of distilled water. Then, g-C$_3$N$_4$ with 200 mg was dispersed in the beaker, and 100 mL of NaOH
solution (2 M) was added to the mixture and stirred for 2 h. The final product was washed with distilled water and ethanol and dried for 12 h. Finally, the material was calcined at 550 °C (2 °C/min) for 2 h. After calcination, the powder was finely ground for further analysis. In addition, ZnO/NiO (ZN), ZnO/g-\(C_3N_4\) (ZG), and NiO/g-\(C_3N_4\) (NG) materials were synthesized using the same method.

2.3 Instruments

The crystalline structures of the prepared samples were examined by X-ray diffraction (XRD, D8 Advance, Bruker, USA). We used a Cary 4000 UV-visible spectrophotometer from Agilent (USA) to obtain the UV-visible diffuse reflectance spectra of the as-prepared sample. The existence of chemical bonds and functional groups was analyzed using a Fourier transform-infrared (FT-IR) spectrometer (EQUINOX 55, Bruker, USA). The microstructures of the as-prepared samples were evaluated using scanning electron microscopy (SEM, JSM 7401F, JEOL, USA). AUTOLAB-PGSTAT204 electrochemical analyzer was used to conduct electrochemical tests.

2.4 Photocatalytic Activity Test

To evaluate the photocatalytic activity of the as-prepared samples in the presence of TCC antibiotics, the following steps were followed under visible light irradiation using a white LED lamp with a power output of 40 W. The catalyzed samples were combined with TC antibiotics at a concentration of 20 ppm, with a catalyst concentration of 0.05 g/L. The reaction solution was stirred in the dark for 30 min, and samples were collected over 15 min. Subsequently, the samples were exposed to the white LED lamp, and at specific time intervals (e.g., 45 min, 90 min, 135 min, etc.), samples were taken out. After extraction, the samples were centrifuged at 7000 rpm for 10 min to ensure complete removal of any solid particles. The results were measured using a UV-Vis instrument. To validate the cycling performance of the catalyst we prepared, following the initial photocatalytic test, the catalyst was subjected to filtration and rinsing employing ethanol and water. Subsequently, the catalyst was dried and employed for a subsequent run. This recycling process was iterated for a total of four cycles.

Additionally, to identify and scavenge the free radicals responsible for the degradation of TCC, electron capture experiments were conducted under the same experimental conditions as the photodegradation study. These additional experiments aimed to pinpoint and neutralize the specific free radicals by introducing electron-capturing agents, also known as scavengers, into the solution before exposure to light. The substances used for this purpose included TBA (\(\cdot\)OH), BQ (\(\cdot\)O\(_2^−\)), \(K_2Cr_2O_7\) (\(e^−\)), and \(Na_2C_2O_4\) (\(h^+\)).

Figure 1. (A) XRD pattern of the as-prepared sample, (B) FT-IR spectra of the synthesized samples.
3. Results and Discussion

3.1 Crystal Structure and Morphological Characteristics

Figure 1(A) presents the XRD results for several samples, including CN, ZnO, NiO, ZG, NG, ZN, and ZNG. The diffraction patterns obtained for all synthesized samples aligned with the standard positions corresponding with wurtzite ZnO (JCPDS file 72-1100) and NiO (JCPDS 04-0835). Importantly, slight changes in the lower angle (2θ) values and broader main peaks at 31.75°, 34.38°, and 36.14° are observed in the XRD patterns of the ZN and ZNG samples. These observations confirm the successful incorporation of NiO into ZnO and the integration of NiO/ZnO with g-C₃N₄. Notably, the doping of NiO into ZnO does not alter the overall structure or introduce any new diffraction peaks in the XRD patterns of the ZN and ZNG samples. The XRD pattern of pure CN exhibits a prominent peak at 27.4°, indicating the presence of nanolayers in g-C₃N₄, consistent with previous research findings [19–21]. However, in the XRD pattern of the ZNG composite, the diffraction peaks of the g-C₃N₄ sample are not observed due to the higher content of NiO and ZnO [22,23].

The FTIR spectra in Figure 1(B) showed the samples CN, ZnO, NiO, ZG, NG, ZN, and ZNG. The appearance of an additional peak at 550 cm⁻¹ is attributed to the presence of NiO as an impurity incorporated into the structure of NiO/ZnO nanoparticles, resulting in a sharper peak. The peaks at 420 cm⁻¹ and 430 cm⁻¹ are assigned to the combined absorption of ZnO and NiO bonds. Furthermore, the substitution of NiO for ZnO positions has been detected in the spectra peaks at 670 cm⁻¹ [24]. Spectral peaks related to water absorption on NiO/ZnO catalysts appear around 1700 cm⁻¹. The peak at 1645 cm⁻¹ is explained by the stretching vibration mode of the C−N group, and the peaks at 1570 cm⁻¹, 1408 cm⁻¹, 1319 cm⁻¹, and 1238 cm⁻¹ may be attributed to the stretching vibrations of aromatic C−N bonds. The peak at 812 cm⁻¹ is associated with the C−H stretching vibration of aromatic C−H bonds in the g-C₃N₄ structure.

Figure 2. SEM images of samples: (A) CN, (B) NiO, (C) ZnO, and (D) ZNG.
cm\(^{-1}\) corresponds to the stretching vibration mode of the triazine structure. The peak at 3161 cm\(^{-1}\) indicates the stretching vibration mode of the N-H group [25].

The SEM images of the prepared samples (Figure 2) show that pure NiO has a nanoparticle morphology. ZnO also exhibits a similar nanoparticle morphology, while CN has a stacked plate structure. After doping NiO and ZnO, the ZNG mixture tends to aggregate into large arrays, regardless of the shape of CN. This aggregation, as shown in Figure 2, enhances the specific surface area and improves the material’s ability to degrade antibiotics effectively.

In Figure 3(a) and Table 1, the bandgap energies of the synthesized samples were estimated. The UV-visible spectra of the prepared sample were determined using the Tauc plot equation (Equation (1)).

\[
(ahv) = A(hv - E_g)^n
\]

Here, \(\alpha\) is the absorption coefficient, \(A\) is a constant, and \(n = 1/2\) for a direct band gap material. The majority of the synthesized samples exhibit a narrow absorbance in the ultraviolet (UV) light region. However, ZNG demonstrates enhanced light absorption and a shift in the absorption edge towards the visible light range compared to the other samples. This increased light absorption and shift towards visible light in ZNG were consistent with previous studies on synthesized materials that had been specifically designed to possess visible light absorption properties.

Furthermore, the enhancement of electron-hole separation by ZNG was demonstrated through electrochemical impedance spectroscopy (EIS) analysis. Figure 3(b) illustrates the EIS spectra of the prepared samples. Compared to the other samples, ZNG exhibits a smaller arc radius in the EIS Nyquist plot, indicating more efficient transfer and separation of photogenerated charge carriers on the perovskite structure. This observation highlights the effective separation of photoinduced electron-hole pairs in ZNG.

Figure 3. (a) UV-Vis DRS and (b) EIS spectra of the synthesized samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_g) (eV)</th>
<th>(k) (min(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>2.64</td>
<td>0.0013</td>
<td>0.97482</td>
</tr>
<tr>
<td>NiO</td>
<td>3.20</td>
<td>0.0004</td>
<td>0.95326</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.05</td>
<td>0.0025</td>
<td>0.94112</td>
</tr>
<tr>
<td>NG</td>
<td>2.90</td>
<td>0.0004</td>
<td>0.80211</td>
</tr>
<tr>
<td>ZG</td>
<td>2.96</td>
<td>0.0021</td>
<td>0.9609</td>
</tr>
<tr>
<td>ZN</td>
<td>2.97</td>
<td>0.0016</td>
<td>0.8905</td>
</tr>
<tr>
<td>ZNG</td>
<td>2.62</td>
<td>0.0065</td>
<td>0.9747</td>
</tr>
</tbody>
</table>

Table 1. Band gap energy and kinetic parameters of photocatalytic reactions by different samples.
3.2 Photocatalytic Performance

In Figure 4, the photocatalytic activity of the synthesized samples against 20 ppm TCC antibiotic was shown. The results reveal that the ZNG sample exhibited the highest decomposition activity of 78.43% after 300 min of light exposure, surpassing the activity of the other samples. Furthermore, the UV-Vis analysis of the sample shows no significant shift in the absorption peak of TCC (357 nm), and the photodegradation of TCC in the absence of the material is negligible. This result confirms that the ZNG sample has good photocatalytic activity, as the combination of CN, ZnO, and NiO assisted in decomposing antibiotics under visible light.

Figure 5 indicated that the presence of Na$_2$C$_2$O$_4$, K$_2$Cr$_2$O$_7$, TBA, BQ, and the initial sample had a varied impact on the degradation yield and overall efficiency of the optimal photocatalyst. Na$_2$C$_2$O$_4$ shows a significant reduction in degradation yield (9.18%), suggesting its inhibitory effect on the photocatalytic process. Similarly, K$_2$Cr$_2$O$_7$, TBA, and BQ also contribute to reduced degradation yields of 68.32%, 73.29%, and 15.77%, respectively, indicating their interference with the photocatalytic efficiency. Furthermore, the initial sample has the highest degradation efficiency of up to 78.43%. These results suggest that the electron capturers partially hinder the photocatalytic performance, while Na$_2$C$_2$O$_4$ specifically impedes the TCC antibiotic degradation, high-

![Figure 4](image1.png)

Figure 4. (A) Photocatalytic degradation of as-prepared samples under visible light. (B) The UV-vis absorption spectra were obtained for the photodegradation reaction of the ZNG sample.

![Figure 5](image2.png)

Figure 5. Effect of electron captures on the degradation of TCC.

![Figure 6](image3.png)

Figure 6. Photocatalytic mechanism diagram of ZNG sample.
Figure 7. (A) Experiment to evaluate the durability of the material, (B) XRD spectrum of the material before and after the reaction.

Figure 8. The main by-products of TCC degradation were detected by LC-MS.

Figure 9. Proposed degradation pathways of TCC.
Table 2. Compare the degradation efficiency of various photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Reaction parameters</th>
<th>Band gap energy (eV)</th>
<th>Light source</th>
<th>Organic compound</th>
<th>Degradation efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/NiO/g-C_3N_4</td>
<td>co-precipitation</td>
<td>2.62</td>
<td>40 W white LED</td>
<td>Tetracycline</td>
<td>78.43% Tetracycline after 300 min</td>
<td>This word</td>
</tr>
<tr>
<td>g-C_3N_4/Ni-ZnO</td>
<td>co-precipitation</td>
<td>2.25</td>
<td>Under sunlight</td>
<td>Methylene blue</td>
<td>89.45% Methylene blue after 90 min</td>
<td>[33]</td>
</tr>
<tr>
<td>g-C_3N_4/Mn-doped ZnO</td>
<td>co-precipitation</td>
<td>-</td>
<td>Under sunlight</td>
<td>Methylene blue</td>
<td>89.45% Methylene blue (100%) after 60 min</td>
<td>[34]</td>
</tr>
<tr>
<td>Cu doped ZnO/g-C_3N_4</td>
<td>one-pot pyrolysis</td>
<td>3.0</td>
<td>500 W Xe light</td>
<td>Eriochrome Black T</td>
<td>99% after 90 min</td>
<td>[35]</td>
</tr>
<tr>
<td>g-C_3N_4/NiO/ZnO/Fe_3O_4</td>
<td>hydrothermal</td>
<td>2.8</td>
<td>Philips 23 W white LED</td>
<td>Esomeprazole</td>
<td>95.05% within 70 min</td>
<td>[36]</td>
</tr>
<tr>
<td>CuO/ZnO/g-C_3N_4</td>
<td>solution combustion</td>
<td>-</td>
<td>400 W hallow lamp</td>
<td>Methylene blue</td>
<td>98% within 45 min</td>
<td>[37]</td>
</tr>
<tr>
<td>ZnO/Au/g-C_3N_4</td>
<td>liquid phase pulsed laser</td>
<td>3.09</td>
<td>300 W Xe lamp</td>
<td>Methylene blue</td>
<td>99% within 120 min</td>
<td>[38]</td>
</tr>
<tr>
<td>g-C_3N_4/Ce-ZnO/Ti</td>
<td>electrophoretic deposition</td>
<td>-</td>
<td>36-72 W LED</td>
<td>Cefixime</td>
<td>80% within 180 min</td>
<td>[39]</td>
</tr>
<tr>
<td>ZnO/g-C_3N_4</td>
<td>Physic mixing calcination</td>
<td>3.195</td>
<td>Hg lamp 250 W</td>
<td>Methylene blue</td>
<td>93.2% within 90 min</td>
<td>[40]</td>
</tr>
</tbody>
</table>
stability was relatively good. The LC-MS spectrum accommodated valuable insights into the potential pathway of intermediate compound formation during the degradation of TCC observed in Figures 8 and 9. This analytical technique provides valuable insights into the transformations occurring during the degradation process of TCC, elucidating its mechanistic pathway and associated degradation products. The peak corresponding to TCC (m/z = 455) has notably decreased due to the photo-induced degradation of TCC during the photocatalytic process. Additionally, several new peaks have emerged after 300 minutes of degradation, corresponding to the degradation intermediates (m/z = 109, 148, 271, 278) [29–32].

4. Conclusions

ZNG nanocomposites were successfully synthesized using the co-precipitation method. The resulting nanocomposites exhibit large arrays as the ZnO, NiO, and CN components clumped together. Notably, the nanocomposites display an absorption edge that extends toward the visible light range, indicating their potential for visible light photocatalysis. Regarding photocatalytic activity, the nanocomposites achieve a TCC photodegradation efficiency of 78.43%. Furthermore, the stability of the nanocomposites is assessed after four reaction cycles, and they exhibit good performance, indicating their durability and potential for repeated use. In conclusion, the synthesized ZNG nanocomposites demonstrate promising photocatalytic properties, with high TCC photodegradation efficiency, absorption in the visible light range, and good stability over multiple reaction cycles.

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CRediT Author Statement

Author Contributions: Linh X. Nong: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing; Oanh T. K. Nguyen: Review and Editing, Supervision.

References


