STUDY ON THE PHOTOCATALYTIC ACTIVITY OF ZnO/g-C_3N_4 HETEROJUNCTION FOR PHENOL DEGRADATION UNDER VISIBLE LIGHT IRRADIATION

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ABSTRACT

In this study, the ZnO/g-CN heterostructure material was synthesized via a simple method, in which ZnO was first obtained through a precipitation process and then calcined with urea to form the final product. Characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and diffuse reflectance UV-Vis spectroscopy (DR/UV-Vis) were employed to investigate the crystal structure, surface morphology, particle size, and light absorption properties of the material. The results revealed that the ZnO/g-CN material exhibited nanoparticle sizes in the 25 - 40nm range. The photocatalytic performance was evaluated by the degradation of phenol under visible light, achieving a high degradation efficiency of 87.5% within 120 minutes, with a pseudo-first-order kinetic rate constant (k) of 0.016 min^{-1}. Additionally, the material showed a low electrical energy consumption per order (E_{EO}) of only 92.28WhL^{-1}, indicating its promising potential for wastewater treatment applications. The Z-scheme charge transfer mechanism between ZnO and g-CN enhanced the separation of photogenerated electron-hole pairs (e^-–h^+), thereby promoting the formation of reactive radicals and improving the degradation efficiency of recalcitrant organic compounds.

Keywords: *Phenol, ZnO, g-CN, Photocatalysis.*

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1. INTRODUCTION

Phenol is a toxic organic compound commonly found in industrial wastewater from the petrochemical, pharmaceutical, paper, and paint industries. The manufacturing or recycling processes in these sectors contribute to generating wastewater containing phenol and related compounds, a major environmental concern. Phenol concentrations in industrial wastewater can reach 10g/L, which is ecologically very high. Phenol can have serious effects on human health and aquatic ecosystems, even at low concentrations. Long-term exposure to phenol can cause skin irritation, liver, kidney, and nervous system damage, and endocrine disruption. In addition, even at low concentrations of about 0.05%, phenol exhibits significant toxicity, sufficient to inhibit the growth of many microorganisms [1]. Due to its serious effects on health and ecosystems, phenol is classified as a pollutant requiring strict control. Therefore, effective control and treatment of phenol in wastewater is urgent to help protect the environment and contribute to minimizing risks to public health [2].

g-CN is a two-dimensional nanomaterial with chemical stability, wide light absorption capacity, and high catalytic activity. Notably, g-CN can be flexibly transformed to create hybrid catalyst systems with tunable structures and properties. However, the photocatalytic performance of this material is still limited by some disadvantages, such as a fast electron-hole pair recombination rate, a limited light absorption range, and poor charge mobility. These limitations, while affecting performance, have motivated improvements through material design such as heterojunction construction, elemental doping, or incorporation of co-catalysts. Among them, ZnO is known as an n-type semiconductor with a wide band gap (~3.2eV) with high electron mobility. When combined with g-CN, ZnO acts as an electron transfer agent, contributing to the formation of a heterostructure capable of inhibiting electron-hole pair recombination. The construction of g-CN-based Z-scheme photocatalytic systems has achieved optimal charge separation by ensuring close interfacial contact. Previous studies have shown that Ag-modified ZnO nanorods (ZnO/Ag/Ag_2O) could still decompose up to 99% of phenol after 90 min under white light irradiation after 4 regeneration cycles [3]. The Z-scheme heterogeneous catalyst 10%-$LaFeO_3$/g-C_3N_4/ZnO showed excellent performance in decomposing 97.43% of phenol in 120 min and maintained high stability (92.13%) after 5 cycles [4].

In this study, ZnO/g-CN heterojunction materials were successfully synthesized through two simple steps of precipitation and calcination. The photocatalytic efficiency of the materials was investigated through the ability to decompose phenol under visible light illumination. In addition to evaluating the treatment efficiency, a Z-scheme photocatalytic reaction mechanism was also proposed based on the analysis of material properties. In addition, the study also calculated the power consumption corresponding to each material system to evaluate the practical application in the treatment of phenol-containing water pollution.

2. MATERIALS AND METHODS

2.1. Materials

Phenol (C_6H_6O, 99.5%) hexamethylenetetramine HMTA ($C_6H_{12}N_4$, 99%), urea ($(NH_2)_2CO$, 99.5%), zinc nitrate hexahydrate (($Zn(NO_3)_2.6H_2O$, 99.5%), trisodium citrate ($Na_3C_6H_5O_7$, 99%) were purchased from Xilong. No further purification of the reagents was necessary before use.

2.2. Synthesis ZnO/g-CN

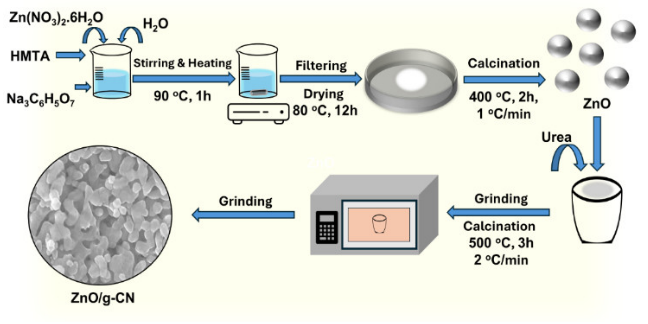


Figure 1. Schemes for the synthesis of ZnO/g-CN

Figure 1 shows the synthesis method for ZnO/g-CN composite. First, ZnO was synthesized by precipitation. A total of 29.7g $Zn(NO_3)_2.6H_2O$, 14g HMTA, and 2.94g sodium citrate were weighed into a 250ml beaker containing 100ml distilled water. Then the mixture was stirred and heated at 90°C for 1 hour. After being filtered and washed many times with distilled water and ethanol, the mixture will be dried at 80°C for 12 hours. After drying, the mixture is crushed and heated at 400°C for 2 hours and then heated at 1°C/min to obtain ZnO nanoparticles. Next, a certain amount of urea was ground with the previously synthesized ZnO. The mixture was calcined at 500°C for 3 hours at a 2°C/min heating rate to form ZnO/g-CN.

2.3. Methods

The diffuse reflectance Ultraviolet-Visible spectra (DR/UV-Vis) were used to determine the light absorption and band gap of the materials. The morphology was observed by scanning electron microscopy (SEM, JEOL-7600F) and transmission electron microscopy (TEM, JEM-JEOL 2100). X-ray powder Diffraction (Bruker D8 Ax, Germany) was used to determine the crystalline phase with a 2θ range of 10 to 80°. The photocatalytic activity of the material was evaluated by the efficiency of phenol degradation in water under visible light irradiation (250W Hg lamp with light intensity of 16000 Lux). Phenol concentration during the reaction was determined by A UV-Vis spectrophotometer (Agilent 8453). The process was as follows: 0.05g of catalyst was added to 100ml of 10mg/L phenol solution and ultrasonicated for 2 min to disperse the material evenly. After 30 min of stirring in the dark to reach adsorption/desorption equilibrium, the solution was illuminated for 120 min, and the phenol concentration was determined every 10 min. The rate constant and degradation efficiency (DE) of phenol were determined through the following equations:

$$\ln\left(\frac{C_0}{C_t}\right) = k \times t \quad (1)$$

$$DE(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Characteristics of materials

Figure 2 shows the XRD patterns of ZnO, g-CN, and ZnO/g-CN samples. The g-CN sample has two diffraction peaks at 13.0 and 27.6°, corresponding to the (100) and (002) lattice planes, confirming the crystal structure of g-CN (JCPDS No. 87-1526) [5]. ZnO material gives sharp diffraction peaks at 2θ = 31.8, 34.4, 36.3, 47.5, 56.6, 63.0, 67.9, and 69.1° corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (112), (201) corresponding to the hexagonal wurtzite structure of ZnO (JCPDS 36-1451) [6]. In particular, ZnO/g-CN composite fully exhibits the characteristic peaks of ZnO, proving that the structure of ZnO is still preserved, however, there is no appearance of g-CN diffraction peaks. This can be explained by the fine dispersion of g-CN, causing its diffraction signal to be weak and obscured by the high-intensity peaks of ZnO. In addition, the samples did not show any characteristic impurities, indicating high purity of the material. The average crystal size of the samples was estimated using the Scherrer equation [7]. The results are 2.5, 17.6, and 25.6nm for g-CN, ZnO, and ZnO/g-CN, respectively. The increased crystallite size in the ZnO/g-CN composite suggests possible crystal growth or improved crystallinity upon composite formation.

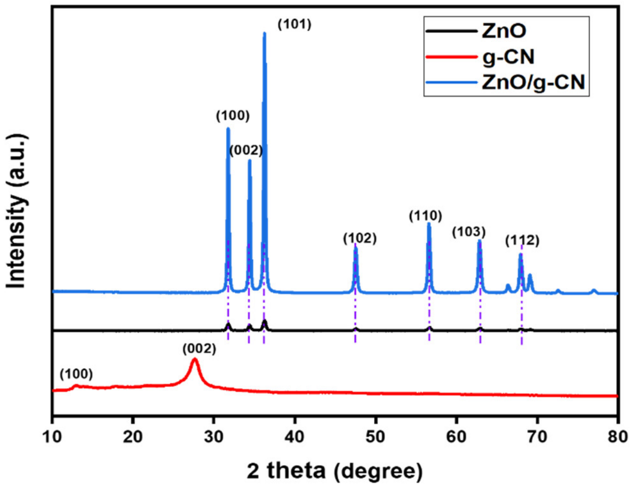


Figure 2. XRD of ZnO, g-CN, and ZnO/g-CN

Figure 3 indicates the morphology of ZnO, g-CN, and ZnO/g-CN, as well as EDS-mapping of ZnO/g-CN. ZnO material has an agglomerated structure with many small particles agglomerated to form large clusters. At higher magnification in Figure 3(b), the observed ZnO particles have a quasi-spherical shape and are distributed quite uniformly. The surface of the material appears porous and uneven, which may be beneficial for photocatalytic applications due to the increased specific surface area. Figure 3(c-d) shows that g-CN has a sheet-like morphology (nanosheets or layered sheets). This is the typical structure of $g-C_3N_4$ materials synthesized by urea pyrolysis. These sheets appear porous, wavy, and unevenly distributed, forming a three-dimensional network with many pores. This thin sheet-like structure can help increase the surface area, facilitate adsorption and catalysis, and create good dispersion conditions when combined with ZnO. Figure 3(e-f) shows the typical surface structure with a relatively uniform distribution of ZnO nanoparticles on the g-CN matrix. The material has a porous, interstitial structure with the presence of densely distributed small particles, suggesting a high potential for a large surface area. The nano-sized ZnO particles (~20 - 50nm) with a nearly spherical shape are distributed on the sheet-like g-CN matrix. Although some small agglomerates appear, the majority of the ZnO particles are well distributed, indicating effective interaction between the two material phases. This contact contributes significantly to the formation of the ZnO/g-CN heterojunction, which can enhance the electron-hole separation efficiency in photocatalytic applications. In addition, the EDS results and elemental maps in Figure 3(g-l) show the uniform dispersion of elements in the ZnO/g-CN material. The EDS spectrum shows that the atomic composition in the ZnO/g-CN composite is 29.5% C, 35.6% O, and 34.8% Zn, respectively.

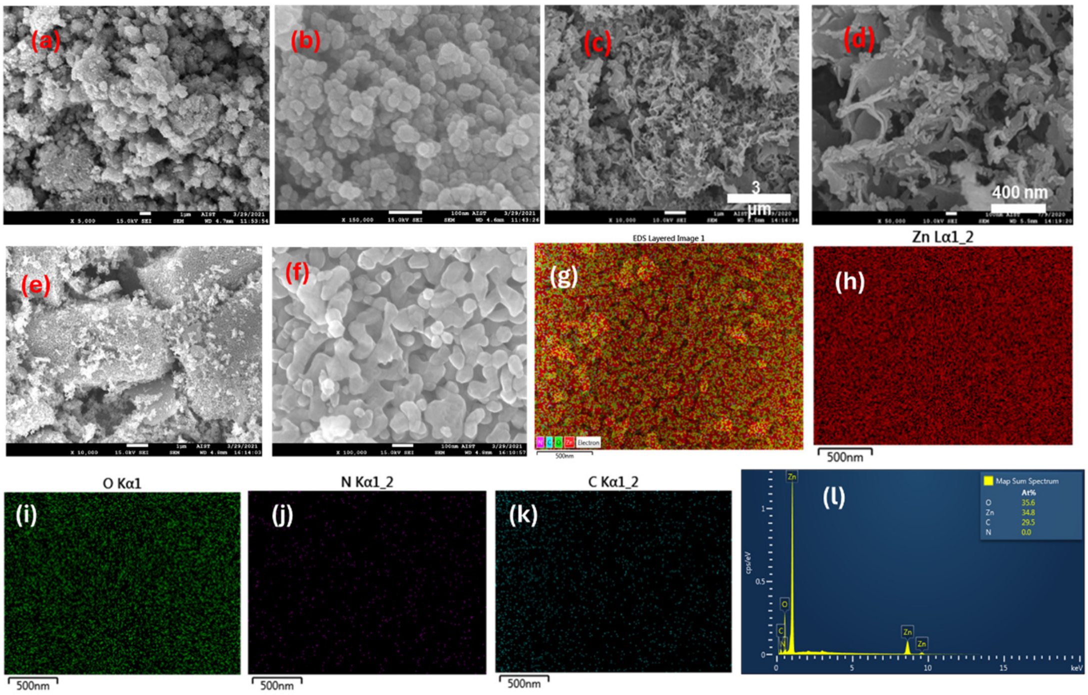


Figure 3. SEM images of (a-b) ZnO, (c-d) g-CN, (e-f) ZnO/g-CN, and (g-l) EDS-mapping images of ZnO/g-CN

The TEM results of the ZnO/g-CN composite in Figure 4(a-d) show that the ZnO particles with sizes in the range of 20 - 40nm are densely distributed and closely bonded with g-CN, indicating the good formation of the composite, which was consistent with the results of the XRD and SEM obtained above. The ZnO particles are nearly spherical, and there is no serious agglomeration. The direct contact between the ZnO particles and g-CN suggests the possibility of forming a heterojunction, which can effectively assist in separating electron-hole pairs, thereby improving the photocatalytic performance of phenol degradation.

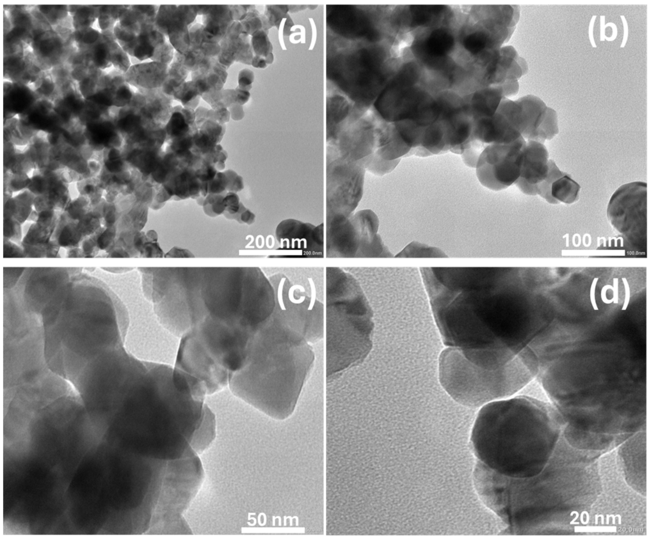
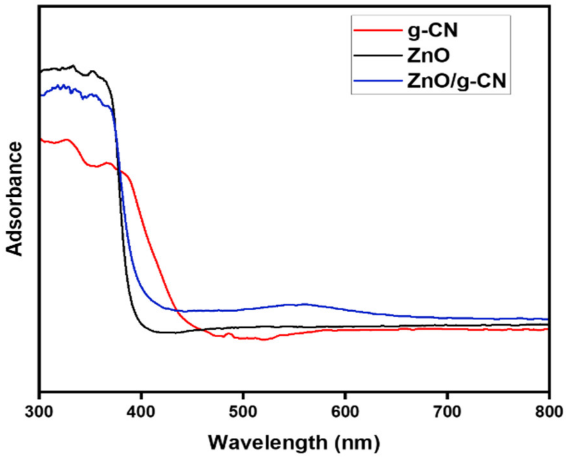
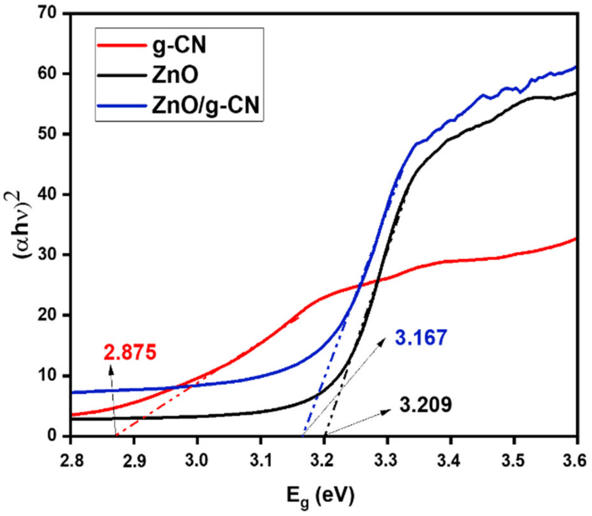


Figure 4. TEM images of ZnO/g-CN with different scale bars (a) 200nm, (b) 100nm, (c) 50nm, and (d) 20nm

Figure 5(a) shows that all samples have strong light absorption in the UV region of 300 - 400nm and a steep absorption edge at about 385nm due to the band-to-band excitation of ZnO nanoparticles. In particular, the ZnO/g-CN sample shows better light absorption efficiency in the visible light region of 400-800 nm compared to ZnO and g-CN. In addition, the band gap energies of the composites were also calculated based on the Tauc equation, as shown in Figure 5(b) [8]. The results are 2.875, 3.209, and 3.167eV for g-CN, ZnO, and ZnO/g-CN, respectively. The decrease in the band gap energy of ZnO/g-CN compared to ZnO may be due to the formation of a heterojunction between the two semiconductor phases. When ZnO is combined with g-CN, electronic interactions between the two materials occur at the interface, leading to the redistribution of the electron state density and adjustment of the energy levels of the conduction and valence bands. This heterostructure contributes to the formation of intermediate energy levels or shortens the distance between the energy levels, thereby reducing the energy required to excite electrons from the valence band to the conduction band. In addition, the nanoscale combination effect can also change the band structure and affect the E_g value. As a result, the ZnO/g-CN composite material can absorb light more effectively and support the e^-/h^+ separation process during the photocatalytic decomposition of phenol.



(a) The DR-UV/VIS spectra

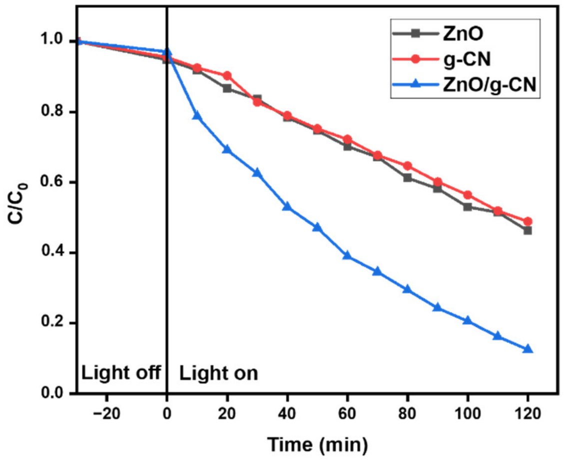


(b) the Tauc plots

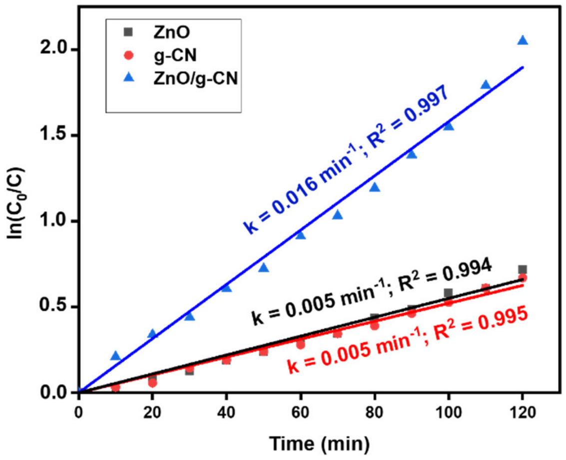
Figure 5. UV-Vis analysis and band gap estimation

3.2. Degradation of phenol

The photocatalytic activity of the materials was evaluated by the phenol degradation ability as shown in Figure 6(a-b). The DE values of phenol in 120 min of ZnO, g-CN, and ZnO/g-CN were 53.7, 51.1, and 87.5%, respectively. The phenol degradation process followed the first-order kinetic model. The rate constants of phenol degradation were 0.005, 0.005, and 0.016 min^{-1} for ZnO, g-CN, and ZnO/g-CN, respectively. ZnO/g-CN showed both better rate constant and phenol degradation efficiency than ZnO and g-CN, which was consistent with the above material characterization analyses. The significant improvement in phenol degradation efficiency when using ZnO/g-CN materials can be explained by the individual advantages of each component as well as the synergistic effect when combining them. ZnO can effectively generate electron–hole pairs, while g-CN can absorb light in the visible region, exhibiting high stability. When combined, the ZnO/g-CN composite material not only takes advantage of the broad absorption spectrum of both components but also creates a heterojunction that enhances charge separation and transfer. This mechanism contributes to minimizing e^-–h^+ recombination and enhancing the ability to generate active free radicals, thereby promoting the photocatalytic efficiency in phenol degradation.



(a) The phenol degradation efficiency



(b) kinematic curves

Figure 6. Phenol degradation efficiency of ZnO, g-CN, and ZnO/g-CN. Conditions: [phenol] = 10mg/L, [catalyst] = 0.5g/L, and a 250W Hg lamp

3.3. Photocatalyst mechanism for degradation of phenol

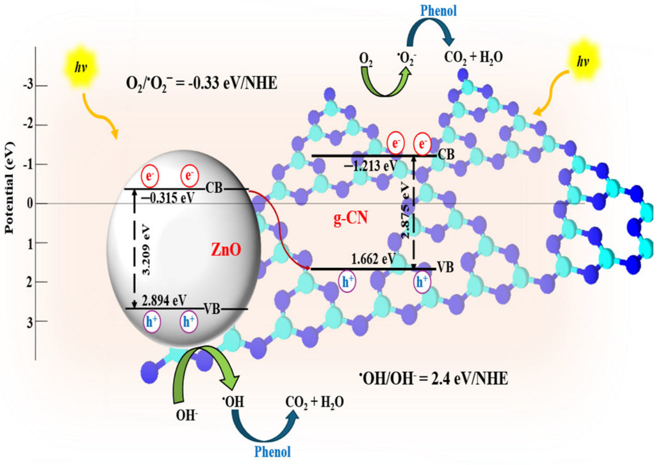


Figure 7. Photocatalytic mechanism of the ZnO/g-CN composite

In this study, a Z-scheme mechanism is proposed, as illustrated in Figure 7. First, under visible light irradiation, both ZnO and g-CN absorb photons, causing electrons in their respective valence bands (VB) to be excited to the conduction bands (CB), thereby generating e^-–h^+ pairs. At the sites where electrons are generated, equivalent h^+ are also formed. Next, due to the energy level difference between the two semiconductors, electrons from the CB of ZnO are directly transferred to the VB of g-CN, which induces an internal electric field resulting from the charge flow between the components. Since the CB of g-CN (-1.213eV) is more negative than the redox potential of $O_2/{}^{\cdot}O_2^-$ (-0.33eV), the electrons accumulated at the CB of g-CN react with dissolved oxygen to form superoxide radicals (${}^{\cdot}O_2^-$).

$$ZnO/g\,CN + h\nu \rightarrow ZnO/g\,CN\,(h^+ + e^-) \quad (3)$$

$$e^- + O_2 \rightarrow {}^{\cdot}O_2^- \quad (4)$$

$$2{}^{\cdot}O_2^- + 2H_2O \rightarrow H_2O_2 + 2OH^- + O_2 \quad (5)$$

$$e^- + H_2O_2 \rightarrow {}^{\cdot}OH + OH^- \quad (6)$$

Similarly, the holes at the VB of ZnO can oxidize H_2O or OH^- to produce hydroxyl radicals (•OH), since the VB of ZnO (2.894eV) is more positive than the standard redox potential of •OH/H_2O (2.4eV).

$$h^+ + H_2O \rightarrow {}^{\cdot}OH + H^+ \quad (7)$$

$$h^+ + OH^- \rightarrow {}^{\cdot}OH \quad (8)$$

These reactive oxygen species play a major role in the oxidation of phenol molecules, decomposing them into intermediate compounds and eventually into CO_2 and H_2O.

$$({}^{\cdot}O_2^-;\ {}^{\cdot}OH) + MB \rightarrow Intermediates \rightarrow CO_2 + H_2O \quad (9)$$

The Z-scheme charge transfer pathway between ZnO and g-CN effectively separates photogenerated charge carriers, significantly reducing their recombination. This built-in electric field enhances the mobility of photogenerated electrons and holes, suppresses recombination, and ultimately facilitates the complete mineralization of phenol, resulting in high photocatalytic efficiency.

3.4. The electrical energy consumption

Power consumption is an important factor to be considered in addition to photocatalytic efficiency. The amount of power consumed not only directly affects the operating cost but also determines the economic feasibility of the material in practical applications. Therefore, the evaluation of the electrical energy consumption is necessary to clarify the overall efficiency of the material system. For a reaction following the first-order kinetic model, the E_{EO} can be calculated according to the following formula:

$$E_{EO} = \frac{P_{el} \times t \times 1000}{V \times 60 \times \log\left(\frac{C_0}{C}\right)} \quad (WhL^{-1}) \tag{10}$$

Table 1 shows that the ZnO/g-CN sample had the highest phenol degradation efficiency and the lowest E_{EO} value of ZnO/g-CN, only $92.28 WhL^{-1}$, while those of ZnO and g-CN were 248.97 and $268.01 WhL^{-1}$, respectively. These results demonstrate that the combination of ZnO and g-CN to form the ZnO/g-CN heterojunction material significantly enhances the photocatalytic efficiency while reducing the energy consumption during phenol treatment. The performance improvement may come from the Z-scheme mechanism, which enhances the e^-–h^+ separation and prolongs the charge lifetime, thereby enhancing the free radical generation ($^\bullet OH$, $^\bullet O_2^-$) for more efficient phenol degradation.

Table 1. The phenol degradation efficiency and electrical energy consumption values ($W.h.L^{-1}$) of the different samples

Samples	DE (%)	E_{EO} ($W.h.L^{-1}$)
ZnO	53.7	248.97
g-CN	51.1	268.01
ZnO/g-CN	87.5	92.28

Remarkably, the photocatalytic efficiency of phenol degradation was also compared with previous studies, as shown in Table 2. From that, it can be seen that the ZnO/g-CN material has a degradation efficiency equivalent to or higher than previous reports, while the reaction time is shorter. This shows that ZnO/g-CN is a potential photocatalytic material, meeting both treatment efficiency and economics. The results achieved contribute to opening up the direction of applying this material in wastewater treatment containing organic compounds that are difficult to decompose.

Table 2. Comparison of the degradation of phenol by various materials

Catalyst	Reaction conditions	Observation	References
TiO_2/SiO_2 (TS05)	[Cat.] = 0.10g/L, [phenol] = 10mg/L, under 26W compact fluorescent lamp	53.5% of phenol was removed in 4 hours	[9]
TiO_2	[Cat.] = 0.71g/L, [phenol] = 10mg/L, pH = 4.8, H_2O_2/phenol molar ratio: 100, applied current: 25mA, under UV-LED	87% of phenol was removed in 4 hours	[10]
g-C_3N_4/CNT/ $BiVO_4$	[phenol] = 10mg/L, under solar light irradiation	80.6% of phenol was removed in 120 min	[11]
$Bi_2WO_6/C_3N_4/TiO_2$	[Cat.] = 1.5g/L, [phenol] = 10mg/L, pH = 7, under simulated sunlight illumination	84.7% of phenol was removed in 180 min	[12]
ZnO/g-CN	[Cat.] = 0.5g/L, [phenol] = 10mg/L, under visible light irradiation	87.5% of phenol was removed in 120 min	This work

4. CONCLUSION

The results of this study demonstrate that the ZnO/g-CN material synthesized via a simple method exhibits excellent photocatalytic performance under visible light irradiation. With a phenol degradation efficiency of nearly 90% and a higher reaction rate constant compared to the individual components, ZnO/g-CN outperforms in the treatment of organic pollutants. Notably, its low energy consumption indicates not only high technical performance but also economic feasibility for practical applications. Furthermore, the Z-scheme charge transfer mechanism plays a crucial role in enhancing the separation and utilization of photogenerated charge carriers, contributing to the generation of strong oxidative radicals essential for degradation processes. These findings highlight the promising potential of ZnO/g-CN for sustainable and efficient wastewater treatment applications

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