



Photocatalytic degradations of organic pollutants in wastewater using hydrothermally grown ZnO nanoparticles

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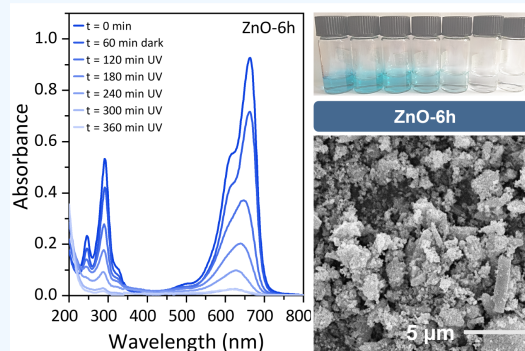
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ABSTRACT

The increasing prevalence of organic pollutants in wastewater poses a significant environmental challenge due to their persistence and harmful effects. Photocatalysis using semiconductor nanoparticles, such as ZnO, has emerged as a promising approach for pollutant degradation, but optimizing the structural and functional properties of these materials remains a critical challenge. In this study, ZnO nanoparticles were synthesized via a hydrothermal method with varying durations (4, 6, and 8 hours) to investigate the impact of synthesis time on their photocatalytic efficiency. The structural and compositional properties were characterized using SEM, XRD, and EDS analyses, revealing that longer synthesis times improve crystallinity and alter the Zn:O atomic ratio, affecting defect density and stoichiometry. Photocatalytic performance was evaluated through the degradation of an organic pollutant under UV illumination. ZnO-6h exhibited the highest rate constant ($k = 0.017 \text{ min}^{-1}$, outperforming ZnO-4h ($k = 0.016 \text{ min}^{-1}$, and ZnO-8h ($k = 0.013 \text{ min}^{-1}$). This superior activity is attributed to an optimal combination of high crystallinity, intermediate morphology, and the presence of oxygen vacancies that enhance charge carrier dynamics. The findings demonstrate that synthesis duration is a critical parameter in tuning the structural and photocatalytic properties of ZnO nanoparticles. This study provides insights into the design of ZnO-based photocatalysts and underscores their potential for environmental remediation. Future research could extend these findings by exploring scalability and pollutant-specific applications, paving the way for more efficient wastewater treatment technologies

Keywords: Photocatalysis, ZnO nanoparticles, Hydrothermal synthesis, Organic pollutant degradation, Wastewater treatment



1. INTRODUCTION

Pollution poses a significant threat to the environment and the survival of living organisms. In 2015, pollution was attributed to 9 million premature deaths, establishing it as the largest environmental risk factor for disease and premature mortality worldwide. A subsequent study in 2019 reported that pollution continued to account for approximately 9 million deaths annually, contributing to 1 in 6 deaths globally. Although pollution-related deaths linked to extreme poverty have declined, those caused by air and water pollution have risen. This increase is driven by rapid industrialization and urbanization, which have grown by 7% since 2015 and more than 66% since 2000 [1]. Among the leading contributors to global water pollution is the textile industry, responsible for over 20% of registered water pollution levels in countries like Indonesia, China, Turkey, Romania, and Bulgaria, and exceeding 44% in Macedonia [2]. A key factor is the extensive use of dyes, such as methylene blue (MB), which are highly toxic and resistant to natural degradation [3, 4].

To address the escalating issue of water pollution, researchers have explored various methods for treating organic

pollutants, which can generally be categorized into chemical, physical, and biological approaches [5, 6]. Chemical methods are particularly effective for removing persistent organic and inorganic pollutants due to their versatility; however, they often produce significant quantities of concentrated sludge and carry the risk of secondary pollution from excessive chemical use [7]. Advanced oxidation processes (AOPs) have emerged as a promising solution to these limitations. Among AOPs, photocatalysis has proven highly effective for degrading persistent water pollutants like dyes [8, 9]. This method typically involves semiconductor photocatalysts suspended in water and exposed to ultraviolet (UV) light. Zinc oxide (ZnO), an inexpensive, non-toxic, and highly effective semiconductor, is widely used for this purpose due to its ability to degrade a broad spectrum of organic compounds [10, 11, 12].

The performance of ZnO as a photocatalyst is strongly influenced by its size and morphology, which can be tailored through various synthesis techniques [13, 14]. These include sol-gel, spray pyrolysis, hydrothermal synthesis, electrospinning, vapor transport, chemical vapor deposition (CVD), and chemical precipitation [15, 16]. Among these, the hydrother-

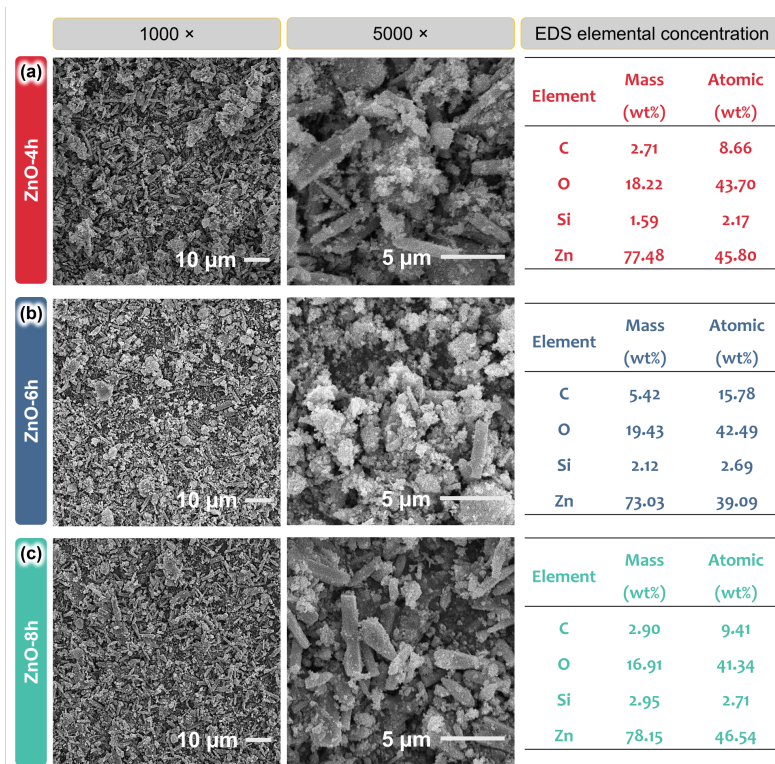


Figure 1. The SEM images and corresponding EDS analysis of the (a) ZnO-4h, (b) ZnO-6h, and (c) ZnO-8h samples.

mal method stands out due to its cost-effectiveness, ease of use, precise chemical control, and ability to produce uniform products without requiring high temperatures or grinding [17]. In this study, ZnO nanoparticles were synthesized using the hydrothermal method and characterized using SEM-EDS and XRD. The photocatalytic activity was evaluated by testing the degradation of methylene blue (MB) in a custom-designed UV reactor. This work investigates how varying hydrothermal reaction times influence the crystal phase, surface morphology, elemental composition, and photocatalytic efficiency of ZnO nanoparticles, providing valuable insights into optimizing their performance for environmental remediation applications.

2. MATERIAL AND METHODS

2.1 Materials

Zinc chloride (ZnCl_2 , EMSURE, Merck, Germany) and hexamethylenetetramine (HMTA , $(\text{CH}_2)_6\text{N}_4$, ACS reagent, $\geq 99.0\%$, Merck, Germany) were used as the main precursors, and deionized water was used as the solvent. Methylene blue (MB) was used as the model dye and was also purchased from Merck (Darmstadt, Germany). All materials were used as received without further purification.

2.2 Preparation of ZnO nanoparticles

Zinc oxide nanoparticles (ZnO NPs) were synthesized using a simple hydrothermal process followed by calcination. In a typical synthesis, 1.39 g of ZnCl_2 and 1.42 g of HMTA were dissolved in 70 mL of deionized water under continuous stirring for 30 minutes to ensure complete dissolution. Subsequently, 5 mL of ammonia solution was added to adjust the pH of the solution, and stirring was maintained. The resulting solution was transferred to a Teflon-lined stainless-

steel autoclave with a 100 mL capacity and heated at 100°C for varying durations in an oven. After the reaction, a white precipitate was separated from the solution by vacuum filtration and dried at 60°C for 4 hours to remove residual solvent. The dried precipitate was calcined at 500°C for 2 hours at a heating rate of $5^\circ\text{C}/\text{min}$ to enhance the crystallinity of the ZnO nanoparticles. The resulting nanopowder was used for further characterization and photocatalytic studies. Three different samples were fabricated by varying the hydrothermal reaction time (i.e., 4 h, 6 h, and 8 h), and the corresponding ZnO samples were named ZnO-4h, ZnO-6h, and ZnO-8h, respectively.

2.3 Materials characterizations

The structural, morphological, and optical properties of the ZnO nanoparticles were characterized using various techniques. The crystal structure, crystallinity, and crystallite size were analyzed by X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation (wavelength = 0.154 nm) in the 2θ range of 5° to 80° using XRD, Rigaku, SmartLab SE basic. The morphological structure of the ZnO nanoparticles was examined using a scanning electron microscope (SEM), and their elemental composition was determined by energy-dispersive spectroscopy (EDS) coupled with SEM (SEM-EDS, JEOL JSM-6510). Optical absorption spectra were recorded in the wavelength range of 200–800 nm using a UV-Vis spectrophotometer (Shimadzu UV-1280).

2.4 Photocatalytic investigations

The photocatalytic performance of ZnO was evaluated by monitoring the degradation of methylene blue (MB) under dark and UV light irradiation. The experiments were conducted in a photoreactor chamber equipped with four Phillips UVC lamps (10 W, $\lambda \approx 253.7\text{ nm}$). For each experiment, 100

mL of aqueous MB solution (5 ppm concentration) was prepared, and 0.1 g of ZnO nanopowder was dispersed in the solution. The mixture was stirred at 250 rpm using a magnetic stirrer inside the photoreactor. To study adsorption and degradation, the experiment was conducted both in the dark and under UV light. Initially, the suspension was stirred in the dark for 1 hour to achieve adsorption equilibrium, and a 3 mL sample was withdrawn for measurement. Afterward, the suspension was exposed to UV irradiation for 5 hours, with 3 mL aliquots taken every hour. The absorbance of the MB solution at its maximum wavelength ($\lambda = 663$ nm) was measured using a UV-Vis spectrophotometer (Shimadzu UV-1280). The concentration of MB was determined from the absorbance, and the degradation rate (k) was calculated using the Eq.1.

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (1)$$

where C_0 is the initial pollutant concentration (ppm), C is the pollutant concentration at time t (ppm), k is the rate constant (min^{-1}), and t is the reaction time (min) [18].

3. RESULTS AND DISCUSSION

3.1 ZnO characteristics

The hydrothermally synthesized ZnO nanoparticles were systematically characterized and evaluated for their photocatalytic potential in degrading organic pollutants in wastewater. Figure 1 shows the SEM-EDS analysis of the ZnO prepared using various hydrothermal temperatures. SEM imaging revealed insignificant changes in morphology with increasing synthesis duration. ZnO-4h Fig. (1a) consisted of small, irregularly shaped particles, indicative of incomplete crystal growth. With extended synthesis times, ZnO-6h Fig. (1b) and ZnO-8h Fig. (1c) displayed progressively refined morphologies, culminating in the rod-like structures observed in ZnO-8h. The EDS analysis (shown in right side of each sample) confirmed the predominance of Zn and O across all samples, consistent with ZnO formation. It also shows that distinct variations in the Zn:O atomic ratios across the samples synthesized at different durations. ZnO-4h exhibited a Zn:O ratio of 1.05, indicating near-stoichiometric ZnO with minimal deviation from the ideal 1:1 ratio. This suggests that even with a shorter synthesis time, the hydrothermal process was effective in forming ZnO with relatively balanced stoichiometry. ZnO-6h displayed a Zn:O ratio of 0.92, reflecting a slightly oxygen-rich composition. This may be indicative of a higher concentration of oxygen-related surface defects, which are characteristic of intermediate synthesis times, where the material undergoes further crystal growth and atomic re-ordering [19, 20]. Meanwhile, ZnO-8h demonstrated a Zn:O ratio of 1.13, signifying a zinc-rich composition likely due to enhanced atomic ordering and reduced oxygen-related defects as a result of prolonged synthesis. The increasing Zn:O ratio with synthesis duration reflects the gradual refinement in material stoichiometry and the diminishing presence of defects associated with oxygen excess.

The XRD patterns of ZnO nanoparticles (see 2) synthesized under hydrothermal conditions for 4, 6, and 8 hours exhibit characteristic peaks at 2θ values corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), and (201), planes of the hexagonal wurtzite structure of ZnO. The observed 2θ values for these planes are approximately 31.8° (100), 34.4° (002), 36.3° (101), 47.5° (102), 56.6° (110), 62.8° (103), 66.4° (200), 68.0° (112), and 69.1° (201). These

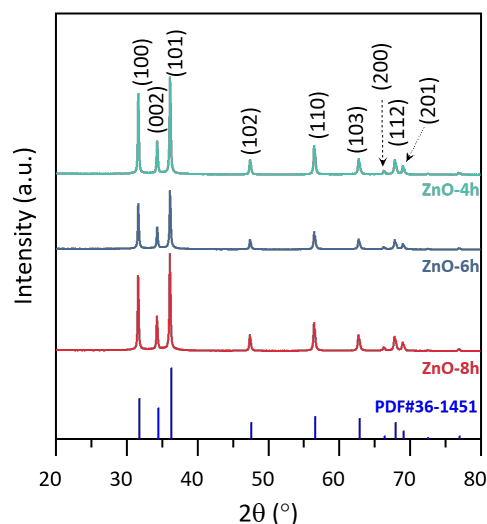


Figure 2. X-ray diffraction (XRD) patterns of ZnO nanoparticles synthesized hydrothermally for 4 hours (ZnO-4h), 6 hours (ZnO-6h), and 8 hours (ZnO-8h)

peaks match well with the standard JCPDS card (PDF#36-1451), confirming the phase purity and successful formation of ZnO in all samples [21, 22]. As the synthesis duration increases, the intensity of the diffraction peaks becomes sharper and more pronounced, particularly for the ZnO-8h sample. This trend is corroborated by the crystallinity analysis, which shows a slight increase in the crystallinity percentage with extended synthesis times. The refined crystallinity values indicate 64.13%, 62.92%, and 64.51% for ZnO-4h, ZnO-6h, and ZnO-8h, respectively. The ZnO-8h sample exhibits the highest crystallinity, reflecting its superior atomic ordering and reduced defect density due to prolonged hydrothermal treatment.

The XRD results were further analyzed by calculating the crystallite sizes of ZnO nanoparticles using the Scherrer equation, which is based on the broadening of the diffraction peaks. The calculated crystallite sizes for ZnO-4h, ZnO-6h, and ZnO-8h are 79.6 nm, 92.8 nm, and 79.6 nm, respectively [23]. The larger crystallite size observed for ZnO-6h suggests a temporary growth in particle dimensions during intermediate synthesis durations, while the comparable sizes of ZnO-4h and ZnO-8h indicate a stabilization in crystallite size with prolonged hydrothermal treatment. This observation aligns with the changes in peak sharpness and intensity, further highlighting the influence of hydrothermal reaction time on the structural properties of the ZnO nanoparticles.

3.2 ZnO photocatalytic degradations performance

The photocatalytic performance of ZnO nanoparticles synthesized for 4, 6, and 8 hours was assessed by monitoring the degradation of an organic pollutant under UV illumination. The UV-Vis absorbance spectra (Figures 3a–c) show a progressive decrease in the intensity of the characteristic pollutant absorption peaks, indicating effective degradation over time. All three ZnO samples demonstrated significant photocatalytic activity, with noticeable differences in their degradation efficiencies. The C/C_0 versus time plots (Figure 3d) highlight the temporal changes in pollutant concentration under UV light and dark conditions. Initially, a slight reduction in pollutant concentration was observed during

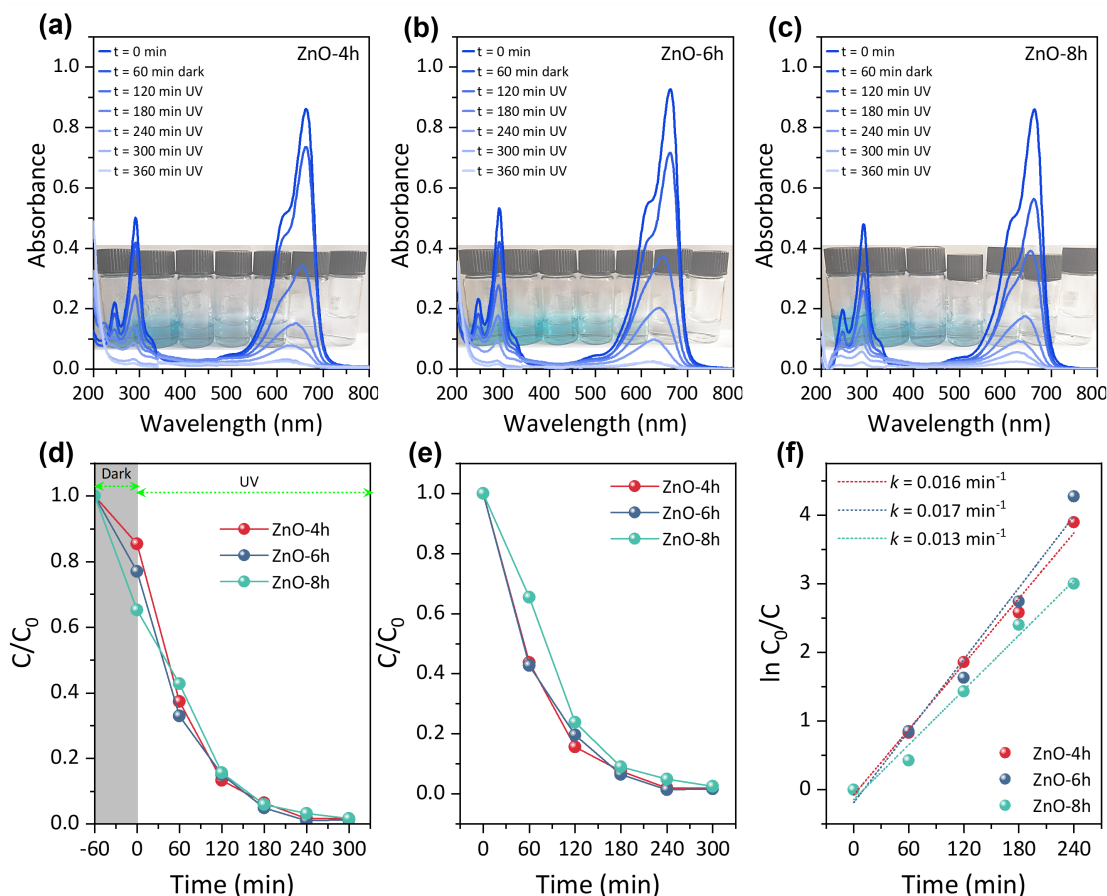


Figure 3. Photocatalytic degradation analysis of an organic pollutant using ZnO nanoparticles synthesized for different durations (ZnO-4h, ZnO-6h, and ZnO-8h). (a-c) UV-Vis absorbance spectra showing the degradation of the pollutant over time under UV light exposure for ZnO-4h, ZnO-6h, and ZnO-8h, respectively. Insets display corresponding color changes of the pollutant solution over time. (d) The C/C_0 versus time plots. (e) Comparison of photocatalytic degradation efficiencies for all ZnO samples. (f) Pseudo-first-order reaction kinetics.

the dark experiment, indicating minimal degradation likely due to adsorption onto the ZnO surface. This suggests that while adsorption equilibrium was largely established before UV exposure, some interactions between the pollutant and the catalyst surface contributed to the minor degradation under dark conditions. Upon UV illumination (Figure 3e), all ZnO samples achieved substantial degradation, with ZnO-6h exhibiting the most rapid and complete removal of the pollutant, followed by ZnO-4h and ZnO-8h. This ranking reflects the interplay of surface area, crystallinity, and defect density in influencing photocatalytic performance.

The pseudo-first-order kinetic analysis (Figure 3f) revealed linear relationships in the $\ln(C/C_0)$ versus time plots, confirming that the degradation process follows first-order kinetics. The calculated rate constants (k) were 0.016 min^{-1} for ZnO-4h, 0.017 min^{-1} for ZnO-6h, and 0.013 min^{-1} for ZnO-8h. The highest rate constant observed for ZnO-6h underscores its superior photocatalytic efficiency, attributed to an optimal balance of crystallinity, surface properties, and defect chemistry that enhance charge carrier dynamics and active site availability. The variation in photocatalytic activity across the ZnO samples is closely linked to their structural, morphological, and compositional characteristics. ZnO-6h, with its intermediate morphology and high crystallinity, provides an ideal configuration for photocatalytic reactions. Additionally, the

slightly oxygen-rich composition of ZnO-6h, as indicated by the Zn:O atomic ratio of 0.92 from EDS analysis, suggests the presence of oxygen vacancies. These vacancies act as active sites for pollutant degradation and improve charge separation by trapping photogenerated electrons, thereby reducing recombination rates. The superior performance of ZnO-6h relative to ZnO-8h, despite the latter's higher crystallinity, highlights the critical role of a balanced defect density in providing reactive sites without compromising structural stability. In contrast, ZnO-4h, with a higher surface area but lower crystallinity, demonstrates slightly reduced activity due to limited charge separation efficiency. Overall, the exceptional photocatalytic performance of ZnO-6h is a result of its synergistic combination of structural integrity, sufficient surface area, and the beneficial role of oxygen vacancies in enhancing reactivity.

4. CONCLUSION

This study demonstrates that hydrothermal synthesis duration significantly impacts the structural, compositional, and photocatalytic properties of ZnO nanoparticles. XRD analysis showed improved crystallinity with synthesis time, with refined crystallinity percentages of 64.13%, 62.92%, and 64.51% for ZnO-4h, ZnO-6h, and ZnO-8h, respectively. EDS analysis revealed Zn:O atomic ratios of 1.05, 0.92, and 1.13, indicating

stoichiometric variations and defect density changes. ZnO-6h exhibited the highest photocatalytic activity due to its optimal balance of intermediate morphology, high crystallinity, and oxygen vacancies, enhancing charge carrier separation and pollutant degradation. While ZnO-4h and ZnO-8h showed notable performance, their efficiencies were constrained by lower crystallinity and reduced surface area, respectively. These results underscore the importance of optimizing synthesis parameters to enhance ZnO's photocatalytic efficiency, with further research recommended to explore environmental and pollutant-specific factors for real-world applications.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest.

DATA AVAILABILITY

The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

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