

Photocatalytic Degradation of Methylene Blue using Zinc Oxide Synthesized by Hydrothermal Method

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Abstract

ZnO nanoparticles (ZnO-NPs) were synthesized by hydrothermal method at low temperatures over a range of different hydrothermal time periods and different calcination temperatures. The synthesized ZnO-NPs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption isotherms (BET). The XRD results showed that all ZnO-NPs were hexagonal wurtzite phase. The photocatalytic activities of the ZnO-NPs were tested through the degradation of methylene blue under UV light. The highest methylene blue (MB) degradation was found to be 99% with zinc oxide synthesized at 48 hours hydrothermal process time and 300 °C calcination temperature conditions during 3 hours degradation time. As a result, the synthesized by hydrothermal method at low temperatures ZnO-NPs have potential applications in the treatment of wastewater.

Key words: Zinc oxide, hydrothermal synthesis, photocatalysis, methylene blue, photodegradation.

1. Introduction

Zinc oxide (ZnO) is the most important material in scientific research and industrial applications with the unique properties such as wide transmission bandwidth, a large bonding energy and a high permeability in the 0.4-2 μ optical wavelength range at room temperature. Therefore, it is used in sensors [1-4], transducers [5-7], generators [8-10], photocatalysts [11-13], laser and diodes [14]. The applications of ZnO are strongly dependent on its own morphology and size of particles. Various methods such as hydrothermal, chemical vapor deposition, sol-gel, electrospinning, spray pyrolysis, vapor transport method, chemical precipitation are used for the synthesis of zinc oxide. Among these methods, hydrothermal method is mostly preferred due to it is low cost, practical, ability to be chemically controlled, obtain a uniform product, avoid the need for processes such as high temperatures and grinding [15-16].

In this study, ZnO nanoparticles were synthesized by hydrothermal method. The effects of hydrothermal synthesis time and calcination temperature were selected as parameters. The characterization of the synthesized samples were performed by SEM (Scanning electron microscope), BET (Brunauer-Emmett-Teller) and XRD (X-ray diffraction) analyzes. Degradation of methylene blue was carried out in home-made UV reactor to investigate photocatalytic activity.

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2. Materials and Method

2.1. Materials

All the chemicals purchased and used without any further purification as follows: Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$): Sigma Aldrich (98%), ammonium hydroxide solution (NH_4OH): Sigma-Aldrich (25-30%), sodium hydroxide (NaOH): Sigma-Aldrich (98%), methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$): Merck, methanol (CH_3OH): Merck (98%). Distilled water was used for all the experimental steps.

2.2. Hydrothermal synthesis of zinc oxide nanoparticles

In order to synthesis ZnO-NPs, 2 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was firstly dissolved in mixture of 0.15 M NH_4OH (45 ml) and distilled water (100 ml). The mixture was stirred for 30 minutes and NaOH was added until the pH of the solution reached 9-10. Then solution was transferred into a 250 mL Schott glass for hydrothermal process. The mixture kept in a furnace at 60 °C with different time periods (24, 48, 72, 96 h). After the hydrothermal process, the white precipitate was centrifuged and washed with distilled water and methanol, respectively. The final precipitate was dried at 60 °C for 12 h, and then calcined in air at different temperatures (180, 300, 400, 500 °C) for 1 h. Figure 1 shows the synthesis flow diagram of the ZnO-NPs.

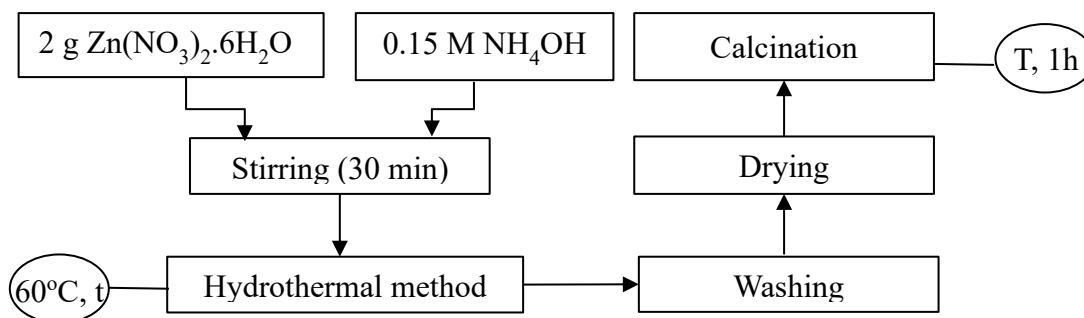


Fig 1. Flow diagram of the preparation steps of ZnO-NPs.

2.3. Photocatalytic degradation

The photocatalytic activity of ZnO-NPs were investigated by photocatalytic degradation of aqueous methylene blue (MB) solution. The photocatalytic degradation tests of MB were performed in a home-made photoreactor which containing four UV-C lamps of 11 W each as shown in Figure 2. In a typical experiment, 0.25 g of the ZnO-NPs was dispersed in 100 mL of MB (20 ppm concentration) under the constant stirring speed. At the beginning of the experiments, suspension stirred in dark conditions in order to reach an adsorption-desorption equilibrium. Periodically, a sample of 5 mL of reaction mixture was withdrawn, centrifuged and the MB concentrations determined by spectrophotometrically.

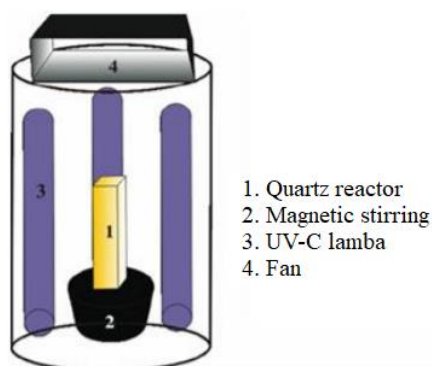


Fig 2. Schematic representation of the home-made photoreactor

The efficiency of photocatalytic degradation can be calculated using Equation (1). Where A_0 is the initial absorbance value of MB solution and A is the absorbance value of MB solution after the irradiation time 't'.

$$n (\%) = ((A_0 - A) / A_0) \times 100 \quad (1)$$

2.4. Characterization

XRD patterns of ZnO-NPs were carried out by using an X-ray diffractometer (XRD, D8 Advance, Bruker Instrument Co., Ltd., Germany) with monochromatic Cu-K α radiation $\lambda = 1.5406$ at a scan speed of $0.5^\circ/\text{min}$ over a 2θ range of 20° - 70° . Microstructural features of the ZnO NPs were investigated by using a field emission gun scanning electron microscopy (FESEM, ZEISS Ultraplus). Nitrogen adsorption and desorption isotherms were measured using a porosimeter (Micromeritics, TriStar II) at 77 K. Prior to adsorption, the ZnO-NPs were outgassed at 150°C for 24 h under vacuum. Measurements of MB concentrations were performed by an UV-Vis spectrophotometer (Agilent - CARY60) with wavelength 200-800 nm.

3. Results

3.1 Effect of hydrothermal process time

The crystal structures of ZnO-NPs synthesized hydrothermal method were characterized by XRD (Fig. 3). The main diffraction peaks are observed at $\sim 32^\circ$, $\sim 35^\circ$, $\sim 36^\circ$, $\sim 47^\circ$, $\sim 56^\circ$, $\sim 64^\circ$, $\sim 66^\circ$, $\sim 68^\circ$ were indexed as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0) and (1 1 2) hkl crystal planes. All the main diffraction peaks in the patterns of the ZnO-NPs fitted the diffraction peaks of hexagonal wurtzite structure of the zinc oxide.

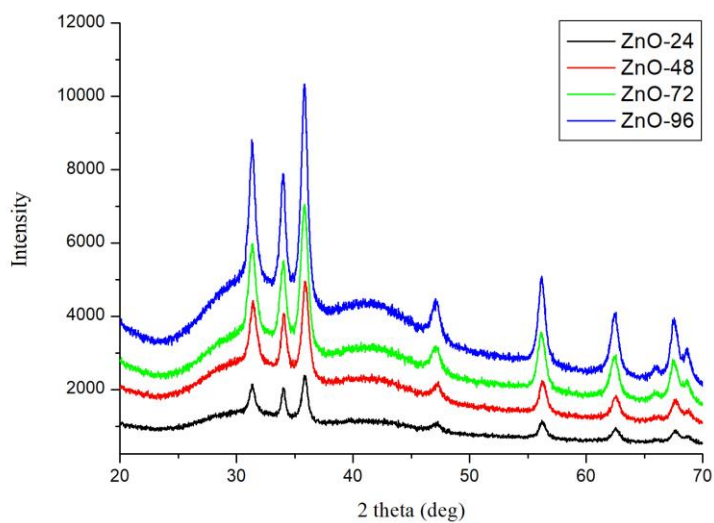


Fig. 3. XRD patterns of ZnO-NPs synthesized at 60 °C with different time periods

SEM analysis was used to investigate the structural morphology of the ZnO-NPs. SEM images of samples show that the particles are uniform in shape and well dispersed (Fig.4.).

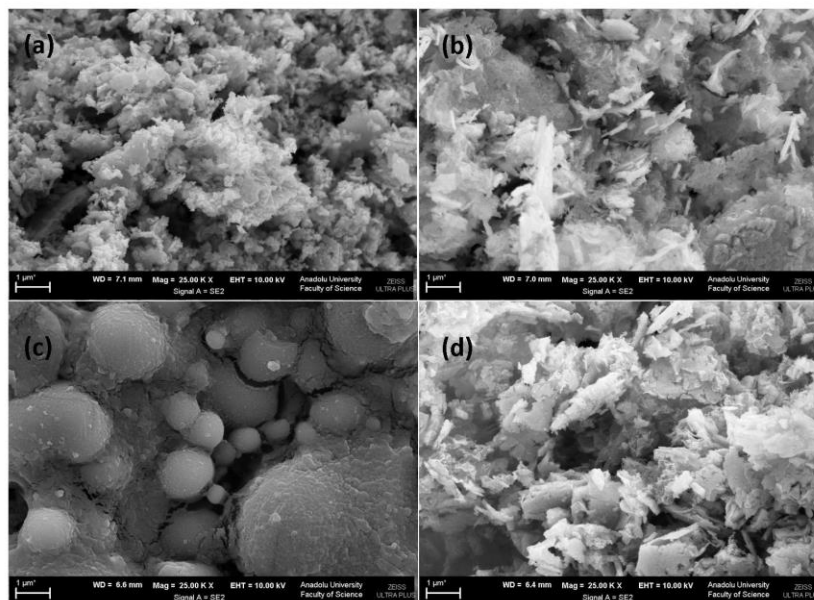


Fig. 4. SEM images of ZnO-NPs a) ZnO-24, b) ZnO-48, c) ZnO-72, d) ZnO-96.

The surface area, pore volume, and pore diameter of the ZnO-NPs are listed in Table 1. As can be seen from Table 1 increasing the hydrothermal process time from 24 hr to 48 hr, the surface area increased almost five-fold. But the increasing the hydrothermal process time from 48 hr to 96 hr, Surface area decreased from 76 m²/g to almost 30 m²/g.

Table 1. The Effect of hydrothermal time on the textural properties of the ZnO-NPs

Samples	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore diameter (Å)
ZnO-24	15.719	0.061	170.018
ZnO-48	76.145	0.324	177.562
ZnO-72	31.874	0.135	194.046
ZnO-96	28.145	0.163	261.660

Figure 5 shows the effect of hydrothermal time on the photocatalytic activity of ZnO-NPs for the MB under the UV light. It's clearly indicated that lowest MB degradation was reached by ZnO-24 synthesized at 60 °C for 24 hours (Fig. 5a) and highest MB degradation was in ZnO-48 synthesized at 60 °C for 48 hours (Fig. 5b).

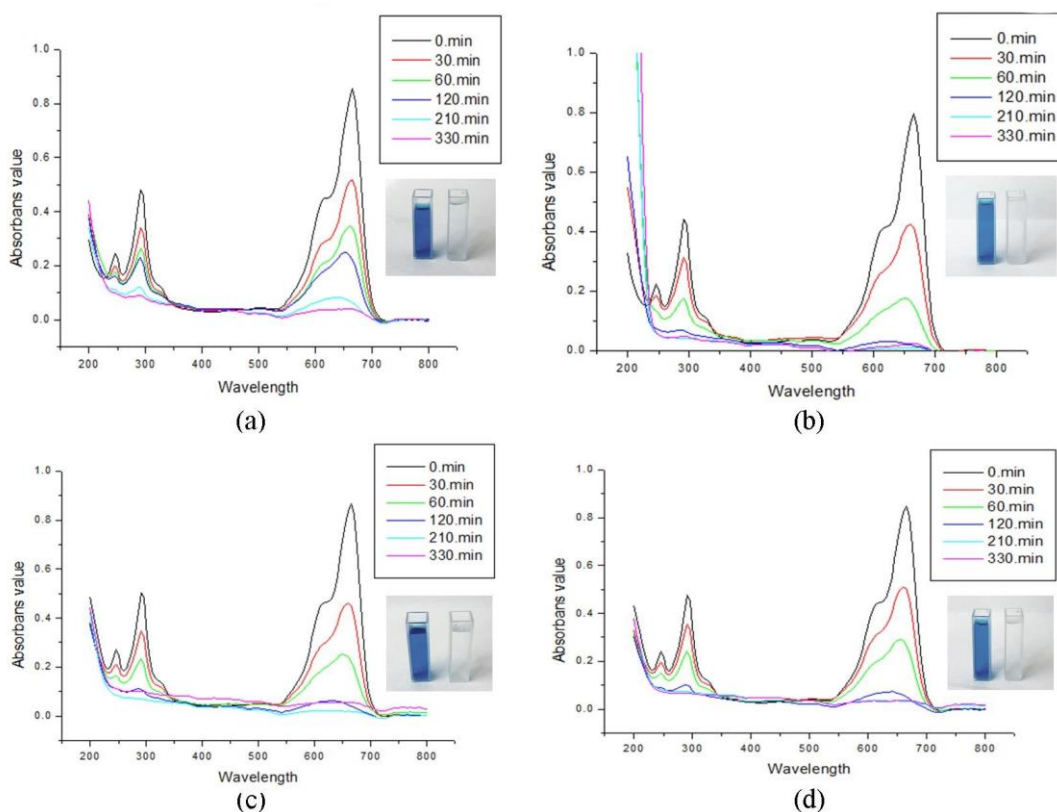


Fig. 5. The effect of hydrothermal treatment time on absorption spectral changes in MB a) ZnO-24, b) ZnO-48, c) ZnO-72, d) ZnO-96

While the degradation time increases, the efficiency of photocatalytic degradation reaches a fixed value after a certain time (Table 2). The ZnO-48 synthesized at 60 °C for 48 hours provides faster photocatalytic degradation and 98.43% decomposition efficiency compared to other samples. So the optimal hydrothermal synthesis time of the ZnO-NPs is seen to be 48 hours.

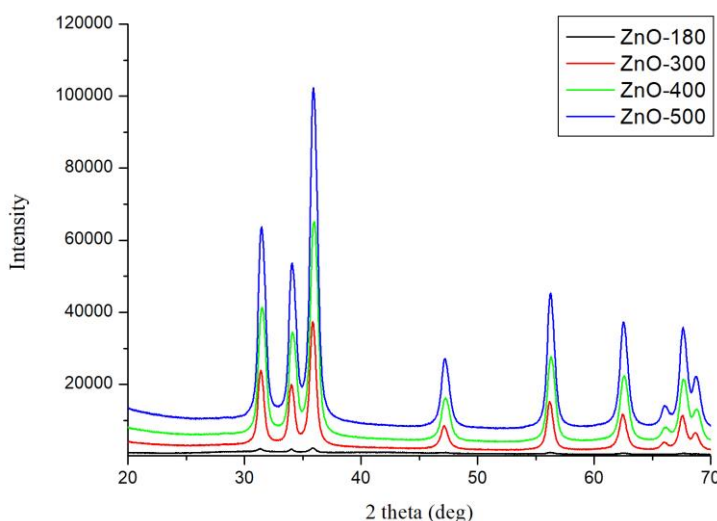
Table 2. The efficiency of photocatalytic degradation of the ZnO-NPs

Time (min)	ZnO-24	ZnO-48	ZnO-72	ZnO-96
30	40.22%	46.98%	47.76%	40.77%
60	59.49%	77.84%	70.92%	65.48%
120	71.34%	96.49%	92.32%	91.44%
210	90.50%	98.42%	98.29%	95.71%
330	90.53%	98.43%	98.30%	95.72%

3.2 Effect of calcination temperature

According to results obtained by the effect of hydrothermal process time, experiments were performed at 60 C and 48 hr hydrothermal process time.

The crystal structures of ZnO-NPs synthesized at different calcination temperature were shown in Fig. 6. The main diffraction peaks are observed at $\sim 32^\circ$, $\sim 35^\circ$, 47° , $\sim 56^\circ$, $\sim 64^\circ$. All the main diffraction peaks in the patterns of the ZnO-NPs synthesized at different calcination temperature also fitted the diffraction peaks of hexagonal wurtzite structure of the zinc oxide.

**Fig. 6.** XRD patterns of ZnO-NPs the calcined in air at different temperatures

The effect of calcination temperature on the surface area, pore volume, and pore diameter of the ZnO-NPs are listed in Table 3. As can be seen from Table 3, increasing the calcination temperature, the surface area and pore volume decreased.

Table 3. Effect of calcination temperature on textural properties of the ZnO-NPs

Samples	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore diameter (Å)
ZnO-180	76.145	0.324	177.562
ZnO-300	16.406	0.074	185.284
ZnO-400	7.694	0.059	321.945
ZnO-500	4.127	0.035	199.526

When the calcination temperature increases, the degradation percentages increase as it is seen in Figure 7. The ZnO-300 calcined at 300 °C for 1 hours provides faster photocatalytic degradation and 98.94% decomposition efficiency compared to other samples (Table 4). So the optimal calcined temperature of the ZnO-NPs is determined to be 300 °C.

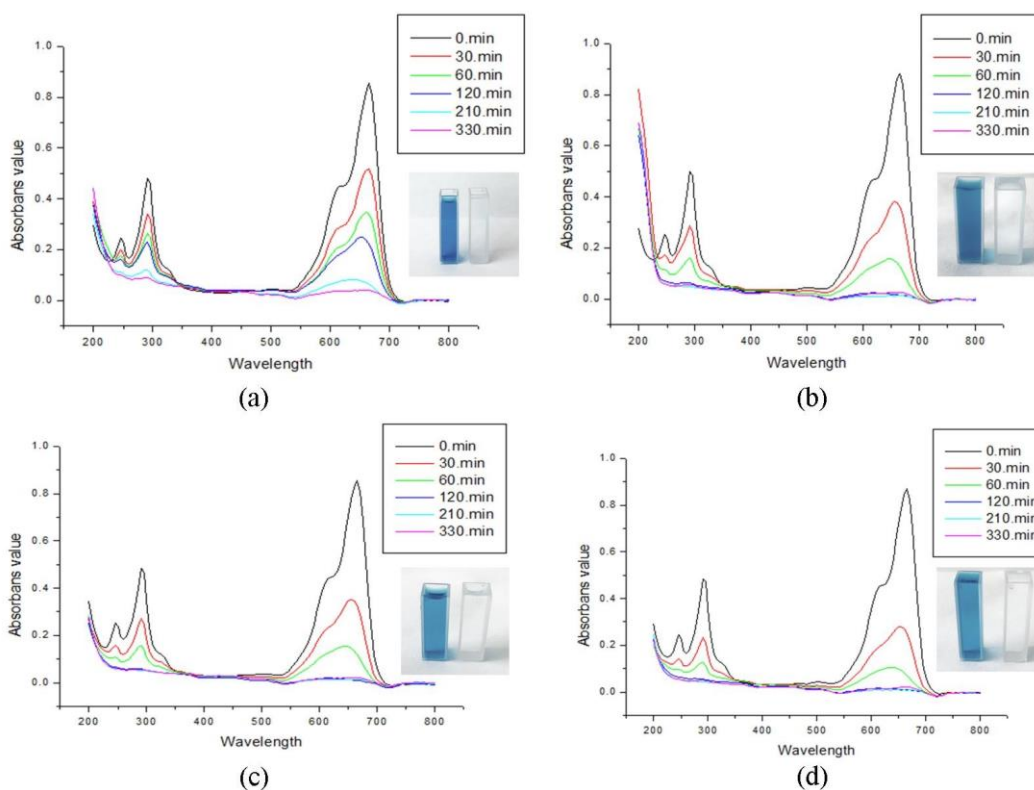


Fig. 7. The effect of calcined temperature on absorption spectral changes in MB a) ZnO-180, b) ZnO-300, c) ZnO-400, d) ZnO-500

Table 4. The efficiency of photocatalytic degradation of the ZnO-NPs

Time (min)	ZnO-180	ZnO-300	ZnO-400	ZnO-500
30	40.22%	58.92%	56.78%	13.77%
60	59.49%	83.04%	82.08%	29.72%
120	71.34%	98.08%	97.68%	54.32%
210	90.50%	98.94%	98.36%	76.34%
330	90.53%	98.95%	98.36%	90.45%

4. Discussion

For the hydrothermal synthesis of zinc nanoparticles, two parameters were determined in this study: hydrothermal time and calcination temperature. The changes in surface and crystal properties were investigated when the hydrothermal time was increased from 24 hours to 96 hours. The surface area increased almost 5 times when the hydrothermal process time was increased from 24 hours to 48 hours. Then increasing the hydrothermal process time up to 96 hours reduced the surface area. This is consistent with photocatalytic activity. The highest MB degradation was obtained with the materials synthesized in hydrothermal process time of 48 hours. On the other hand, the surface area was decreased by increasing the calcination temperature. However, there is no correlation between MB degradation and surface area. The highest MB degradation was obtained with the samples calcined at 300 and 400 °C. This can be explained by the improvement of the crystal structure in this temperature range.

5. Conclusions

The hydrothermal method described in this study has proved to be a successful and green method for the synthesis of ZnO-NPs at low temperature. The experimental results indicated that the morphology of ZnO-NPs was influenced by hydrothermal treatment time and calcined temperature. The highest MB degradation (99%) was achieved with zinc nanoparticles synthesized at 48 hours hydrothermal time and 300 °C calcination temperature conditions. The study provides a rapid, low-cost and efficient approach for the degradation of organic dye and could be envisioned further for waste water purification.

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