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Microwave Synthesis and Photocatalytic Activity of Zinc Oxide Nanoparticles

Environmentally sustainable zinc oxide (ZnO) nanoparticles were synthesized via microwave-assisted method using NaOH as a capping and stabilizing agent. The effects of synthesis time and microwave power on nanoparticle structure and size were analyzed. The synthesized ZnO nanoparticles exhibited uniform morphology and demonstrated effective photocatalytic degradation of methylene blue dye under UV radiation. Results emphasize the critical role of synthesis parameters in determining the structural and functional properties of ZnO nanoparticles.

Keywords: Microwave synthesis; Nanoparticles; Environmental impact, Photocatalyst
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1. Introduction

There has recently been an uptick in interest in metal and metal oxide nanoparticles, which could be useful in a wide range of technological applications. They can be used in a variety of fields, from biotechnology to nanotechnology to biomedical sciences [1,2]. Super capacitors, sensors, photocatalytic degradation, and solar cells are some of the other applications [3,4]. Zinc oxide (ZnO) nanoparticles have attracted great interest among metal oxide nanoparticles because of their distinctive physical, chemical, and biological properties [5]. Many people are interested in the photocatalytic potential of ZnO nanoparticles, which are semiconductor with a high excition binding energy (60 meV) and dielectric constant, typically have a longer lifespan [6]. Greater heat resistance with fewer toxic effects of ZnO nanomaterial have a wide range of properties that make them ideal for applications such as transparent electronics, piezoelectricity, catalytic reactions, and biomedical applications such as biomolecule delivery (drugs, genes, etc.) [7]. Antibacterial and antifungal properties have already been demonstrated in cancer therapy, tissue engineering, bio-imaging, biosensing, and other applications [8,9]. Zinc oxide nanostructures can be made through a variety of methods, including hydrothermal synthesis, precipitation by spray pyrolysis, emulsion precipitation, thermal decomposition, and chemical vapor deposition. According to various reports, ZnO nanoparticles can be synthesized at high temperatures using expensive substrates and complicated procedures that require expensive equipment and high-tech tools. In order to address the issues, a method of producing ZnO nanostructures that is both straightforward and economical is required. This is why we came up with a new simple combustion technique that uses microwave heating to produce uniform ZnO nanoparticles. It is less expensive, safer for the environment, and does not require the use of a template, making it a theoretical and practical step up from the majority of previously reported methods for the application of photo catalysis[10,11].

2. Experimental Work

The formation of these nanostructures required the use of aqueous solutions of zinc nitrate-6-hydrate ($Zn(NO_3)_2.6H_2O$), sodium hydroxide (NaOH), and ZnO nanostructures. Mixing together 50 mL of distilled water, 0.1 M of $Zn(NO_3)_2.6H_2O$ solution, and 0.2 M of NaOH solution results in the production of ZnO nanoparticles. The solution of NaOH was added gradually to $Zn(NO_3)_2.6H_2O$ that was added drop wise (2 min) to the solution described above with magnetic stirring at room temperature to obtain a colloidal system. This system was kept under stirring for 10 minutes, and the pH was kept between 5 and 6. At the end, a white-colored precipitate was obtained as a powder, which was then transmitted to the microwave oven, and the radiation from the microwaves was enabled for a total of 5 minutes and 400 W. After the chemical reaction was completed and allowed to return to room temperature, distilled water was employed to collect the white precipitate, which was then repeatedly washed in deionized water. Finally, the product was dried for 90 min at 70 °C.

The photocatalytic activity of ZnO nanoparticles was tested using a photoreaction setup. Typically, 300 mL of an aqueous solution containing methylene blue (MB) dye at a concentration of 5 ppm is mixed with 0.1 g of ZnO photocatalyst. It should be pointed out that, before irradiation, the mixed solution was left in the

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dark for 20 minutes to allow for equilibrium of dye adsorption and desorption on the ZnO surface. The experiments were conducted under UV light for 140 min and the solution was stirred for the reaction. To ensure reproducibility, samples were collected every 20 min.

(a) (b) (c)

Fig. (1) Steps of synthesis process (a) the milky white solution after the titration process, (b) the collected powder after washing with ethanol and de-ionized water, and (c) The material was dried at a temperature of 70°C for one and a half hours

In order to determine the structural and optical characteristics of the prepared ZnO nanoparticles, an X-ray diffractometer with Cu-K radiation (λ=1.541840Å) in a 2θ range from 10° to 80°, operated at a voltage of 40 kV and current of 40 mA with a scan speed of 3°/min, was used to identify the crystalline structure and crystallite size. The full-width at half maximum (FWHM) data collected from the XRD analysis was applied in order to calculate the average crystallite size using the following Debye-Scherrer formula

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

where β is the FWHM and k is a constant depending on the crystallite shape, which in this example in the case is equal to 0.94

The field-emission scanning electron microscopy (FE-SEM) was applied in order to investigate the structural properties of ZnO nanoparticles. The UV–visible spectrophotometry using a Shimadzu UV-1601 spectrophotometer was used to explore the optical absorption spectra of ZnO nanoparticles. FTIR spectra were taken using a Shimadzu FTIR 8400S spectrophotometer in the wavenumber range of 4000–400 cm^{-1} (resolution: 2 cm^{-1}; scans: 30). Such spectra were analyzed to find the chemical information of the particles as well as the bonding between the numerous atoms.

3. Results and Discussion

The crystalline structure of the ZnO nanoparticles was validated using the XRD pattern. The structural parameters and average crystallite size were determined and given in table (1). Figure (2) depicts the XRD pattern of ZnO nanoparticles after 5 minutes. The appearance of peaks unrelated to ZnO in XRD may be due to impurities like $Zn(OH)_2$, incomplete crystalline phases, the presence of other mixed oxides, the effect of nanoparticle size, or non-optimal preparation conditions such as temperature and reaction time.

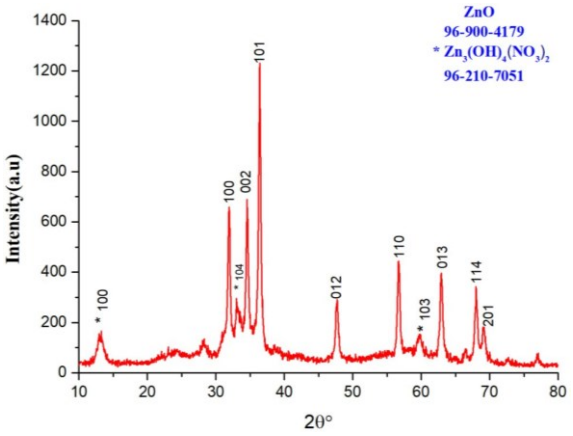

Fig. (2) XRD pattern of ZnO nanoparticles prepared by irradiating them with a microwave for 5 min

Table (1) Structural properties of ZnO nanoparticles for 5 min

2θ (deg.)	(hkl)	FWHM (deg.)	d_{hkl} Exp. (Å)	Crystallite Size (nm)	Average Crystallite Size (nm
31.91	(100)	0.37	2.80	22.33	16.85
34.35	(002)	4.60	2.61	1.81	
36.40	(101)	0.37	2.47	22.60	
47.69	(012)	0.50	1.91	17.37	
56.71	(110)	0.49	1.62	18.42	
62.94	(013)	0.52	1.48	17.91	
68.03	(112)	0.51	1.38	18.79	
69.11	(201)	0.62	1.36	15.56	

The ZnO nanoparticles prepared after 5 min of irradiation with the microwave can be well matched with the miller indices (hkl) at (100), (002), (101), (012), (110), (013), (112), and (201). This result matches the crystallography Open Database (COD) card number [96-230-0451]. Here, ZnO nanoparticles crystallize in a hexagonal structure (Wurtzite-phase) with an average crystallite size of 16.93 nm.

In Fig. (3), the FE-SEM images of the prepared samples confirm the formation of the spherical ZnO particles. These images shed light on the fact that the surface of the ZnO sample contains both voids and pores. The combustion process results in the release of a significant quantity of gases, which itself causes the formation of these pores. Because of the massive amount of heat produced by the combustion reaction, the collection of particles has become somewhat aggregated. This is due to the fact that particles were initially free-floating. It has been established beyond just a possible suspicion that the nanoparticles have a roughly spherical shape but are irregular in both shape and size. This outcome could be the result of the product needing to be filtered and then post-annealed in a conventional furnace at 70 °C for 90 min. The surfaces of ZnO nanoparticles have been observed to be extremely smooth, made even more so

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by the post-annealing treatment.

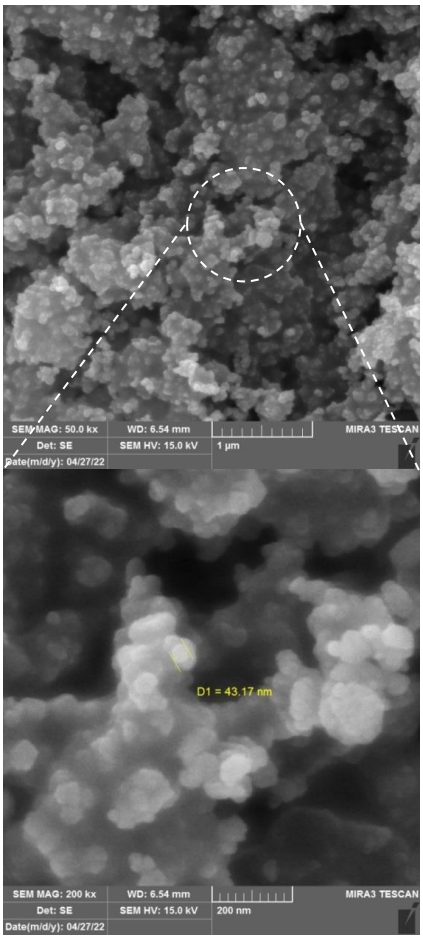
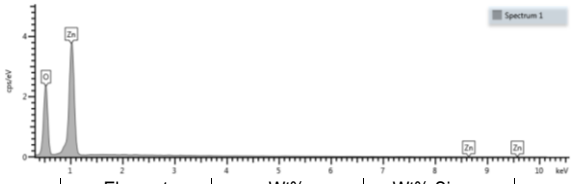


Fig. (3) FE-SEM images of ZnO nanoparticles prepared after 5 min irradiation with microwaves at 400W

Figure (4) displays the EDX spectra of a ZnO nanoparticles. The labeling explains the weight percentages of elements making up the ZnO sample. There is no doubt that Zn and O are the primary components of the sample, the presence of Si and Ca in the EDX analysis is due to the effect of the glass substrate, as the glass contains SiO_2 and CaO as main components. During the analysis, the x-rays penetrate the thin ZnO layer, leading to the detection of elements from the glass [13].



Element	Wt%	Wt% Sigma
O	26.83	0.55
Zn	73.17	0.55
Total:	100.00	

Fig. (4) EDX spectrum of ZnO nanoparticles

Figure (5) displays the UV-visible absorption spectrum, and gives the absorption peaks of ZnO nanoparticles in the wavelength range of 190–800 nm. ZnO nanoparticles sample microwaved for 5 min showed a single absorption peak ranging from 288 to 350 nm, keeping the absorption in the UV range only. Tauc's equation is used to calculate the direct allowed energy bandgap (E_g) of ZnO (5 min.) by extrapolating a straight line on the energy axis, as shown in Fig. (6). Therefore, the E_g value is obtained by plotting $(\alpha h\upsilon)^2$ vs. photon energy ($h\upsilon$). This result agrees with literature. Based on the above findings, the E_g value of ZnO (5 min.) may be due to the particle size and quantum confinement effect.

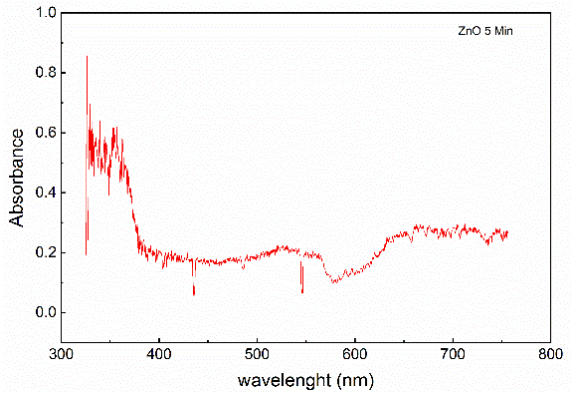


Fig . (5) UV-visible absorption spectrum of ZnO nanoparticles prepared after 5 min irradiation with microwaves

The difference between the peak position in the absorption spectrum in Fig. (6) and the band gap energy position in Fig. (5) is due to the physical nature of the optical absorption process. The band gap energy (E_g) represents the minimum energy required to excite electrons from the valence band to the conduction band, thereby defining the absorption edge, which marks the onset of strong absorption.

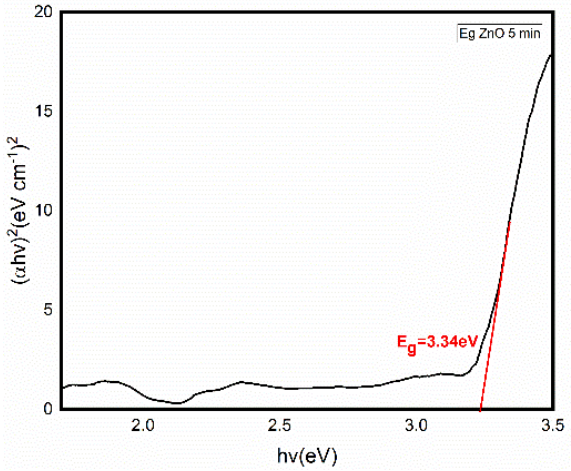


Fig. (6) Determination of energy bandgap (E_g) of ZnO nanoparticles prepared after 5 min irradiation with microwaves

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However, the main peak in the absorption spectrum does not necessarily coincide with this edge, as it is influenced by other factors such as additional energy states arising from crystal defects, surface interactions, and quantum confinement effects in nanomaterial's. These factors can alter the distribution and density of electronic states, leading to stronger absorption at wavelengths shorter than the one corresponding to E_g.

In Fig. (7), the FTIR spectrum of ZnO nanoparticles in the range of 400–4000 cm^{-1} is presented. Consistent with literature, there is a strong peak at 1508 cm^{-1} that may be attributed to the Zn-O stretching vibration mode. The peaks next to 832 and 3000 cm^{-1} are caused by the -OH bending, which is probably triggered by moisture in the atmosphere. C-H bend is directly to blame for the other bands viewed around 800 and 900 cm^{-1}, while the C=O and O-C-O bonds are accountable for the bands seen between 1600 and 1300 cm^{-1} [14]. C-O bond bending modes were observed at 1525–1580 cm^{-1} [15], respectively, for symmetric and asymmetric materials. The absorption of CO_2 molecules in the air causes the bending at a frequency of about 2300 cm^{-1}. Based on the results, we conclude that ZnO nanoparticles synthesis was successful. Using a straightforward, minimal, and quick technique encompassing microwaves for supporting combustion. One of the most researched materials, ZnO has potential applications in a wide variety of technological fields, making it crucial to develop a simple and efficient method for replicating this oxide. When compared to ZnO prepared via classical pyrolysis methods, the purification of samples prepared using our method is incomparable.

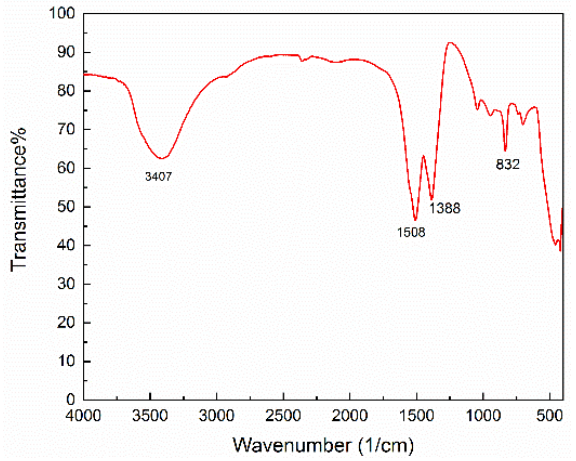

Fig. (7) FTIR spectrum of ZnO nanoparticles prepared after 5 min irradiation with microwaves

Activation of the prepared ZnO photocatalyst under UV light is depicted in Fig. (8). Results indicate that the prepared material exhibited promising photocatalytic activity, with 90% degradation of MB dye after exposure to UV light for approximately 140 minutes. These findings represent a significant step toward developing more efficient photocatalytic materials, with potential applications in water treatment and the removal of organic pollutants, matches with [16].

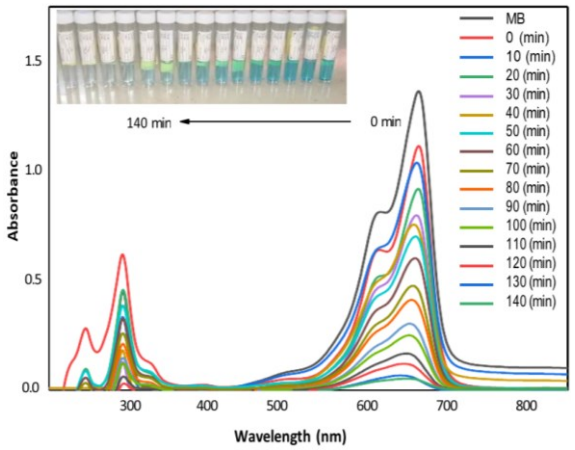

Fig. (8) UV-visible spectra of desorbed MB dye solution using ZnO nanoparticles prepared after 5 min irradiation with microwaves

4. Conclusion

ZnO nanoparticles were synthesized using a microwave-assisted combustion method, with sodium hydroxide facilitating the formation of uniform and highly crystalline structures. The study revealed that reaction time and microwave power significantly influence morphological properties, while this method proved to be more cost-effective and efficient compared to conventional techniques. The synthesized nanoparticles demonstrated excellent photocatalytic performance, achieving 90% degradation of methylene blue under UV light, highlighting their potential for environmental and industrial applications.

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