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Photocatalytic Performance of Lemon-Capped ZnO Nanoparticles Synthesized via the Ceramic Method

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Abstract: *Zinc oxide (ZnO) nanoparticles are extensively explored as photocatalysts due to their high chemical stability, non-toxicity, and strong oxidative potential. Nevertheless, their practical application is often limited by rapid electron–hole recombination and particle agglomeration. In this work, lemon extract was employed as a natural capping and surface-modifying agent to enhance the photocatalytic performance of ZnO nanoparticles synthesized through a conventional ceramic method. The use of lemon extract introduces bioactive phytochemicals such as citric acid, flavonoids, and ascorbic acid, which regulate crystal growth and improve surface functionality. Structural, morphological, optical, and photocatalytic properties of lemon-capped ZnO nanoparticles were systematically investigated and compared with uncapped ZnO. X-ray diffraction confirmed the formation of phase-pure hexagonal wurtzite ZnO with a notable reduction in crystallite size due to lemon capping. The findings establish lemon capping as an effective, eco-friendly strategy for improving the photocatalytic efficiency of ZnO nanoparticles synthesized via a scalable ceramic route*

Keywords*:* Zinc oxide

I. INTRODUCTION

The increasing discharge of industrial effluents containing synthetic organic dyes has become a major environmental concern worldwide. These dyes are widely used in textile, leather, printing, pharmaceutical, and cosmetic industries and are characterized by high chemical stability, complex molecular structures, and resistance to natural degradation processes. Even at low concentrations, dye-contaminated wastewater severely affects aquatic ecosystems by reducing light penetration and posing toxic, mutagenic, and carcinogenic risks to living organisms[1]. Conventional wastewater treatment techniques, including adsorption, coagulation, and biological treatment, often prove inadequate for complete mineralization of these pollutants, thereby necessitating advanced remediation technologies.Photocatalysis using semiconductor materials has emerged as a promising and sustainable approach for degrading organic contaminants into environmentally benign products such as carbon dioxide and water[2]. Among various semiconductor photocatalysts, zinc oxide (ZnO) has attracted substantial attention owing to its wide bandgap energy of approximately 3.37 eV, high exciton binding energy, strong redox potential, and excellent chemical stability. ZnO is also cost-effective, abundant, and environmentally friendly, making it a suitable candidate for large-scale environmental applications[3-5].Despite these advantages, the photocatalytic efficiency of ZnO is often limited by rapid recombination of photogenerated electron–hole pairs and the tendency of nanoparticles to agglomerate, which reduces the available active surface area. To overcome these limitations, various strategies such as metal doping, heterojunction formation, and surface modification have been explored[6]. In recent years, green synthesis and bio-capping approaches using plant extracts have gained considerable interest as sustainable alternatives to chemical surfactants and stabilizers. Plant extracts contain a wide range of bioactive molecules that can act as reducing, capping, and stabilizing agents, thereby controlling nanoparticle growth while improving surface properties[7].Lemon (Citrus limon) extract is particularly rich in organic acids, polyphenols, flavonoids, and antioxidants, with citric acid being a dominant component[8]. These phytochemicals can interact with zinc ions and ZnO surfaces, influencing nucleation, crystal growth, and surface chemistry. However, most reported studies employ wet chemical or sol–gel routes for green synthesis, which may involve solvents and complex processing steps[9]. The ceramic method, on the other hand, is a simple, solvent-minimized, and scalable technique that offers high phase purity and thermal stability.In this context, the present study focuses on synthesizing lemon-capped ZnO nanoparticles using the ceramic method and systematically evaluating their structural, optical, and photocatalytic properties[10]. The influence of lemon capping on crystallite size, morphology, bandgap energy, and photocatalytic degradation efficiency of methylene blue dye is discussed in detail, highlighting the potential of this eco-friendly approach for wastewater treatment applications[11].

II. MATERIALS AND METHODS

2.1 Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, analytical grade) was used as the zinc precursor without further purification. Sodium hydroxide was employed for pH adjustment where necessary. Fresh lemons were procured from a local market and used for extract preparation. Methylene blue dye was selected as a model organic pollutant due to its stability and strong absorption in the visible region. Deionized water was used throughout all experimental procedures to avoid contamination.

2.2 Preparation of Lemon Extract

Fresh lemons were thoroughly washed with deionized water to remove surface impurities and contaminants. The fruits were cut and mechanically squeezed to extract the juice, which was subsequently filtered through Whatman No. 1 filter paper to remove pulp and solid residues. The filtered lemon extract was stored at 4 °C and used within 24 hours to preserve the activity of phytochemical constituents.

2.3 Synthesis of Lemon-Capped ZnO Nanoparticles by the Ceramic Method

The ceramic synthesis route involved thoroughly grinding zinc acetate dihydrate in an agate mortar to obtain a fine and homogeneous powder. A predetermined amount of freshly prepared lemon extract was added dropwise during continuous grinding, resulting in the formation of a uniform paste. This paste was dried at 100 °C to remove excess moisture and subsequently calcined at 450 °C for 3 hours in a muffle furnace. During calcination, organic components from the lemon extract decomposed, facilitating crystallization of ZnO nanoparticles while imparting surface modification.For comparison, uncapped ZnO nanoparticles were synthesized following the same procedure but without the addition of lemon extract. This allowed direct evaluation of the influence of lemon capping on material properties.

2.4 Characterization Techniques

The crystalline structure and phase purity of the synthesized nanoparticles were analyzed using X-ray diffraction with Cu-Kα radiation. Crystallite sizes were calculated using the Debye–Scherrer equation. Surface morphology and particle distribution were examined using scanning electron microscopy. Functional group interactions and surface chemistry were investigated through Fourier transform infrared spectroscopy in the range of 400–4000 cm^{-1}. Optical absorption properties were studied using UV–visible spectroscopy, and bandgap energies were estimated using Tauc plots.

2.5 Photocatalytic Activity Evaluation

Photocatalytic activity was assessed by monitoring the degradation of methylene blue under UV irradiation (365 nm). A fixed amount of ZnO catalyst was dispersed in an aqueous dye solution and magnetically stirred in the dark for 30 minutes to establish adsorption–desorption equilibrium. During UV irradiation, aliquots were withdrawn at regular time intervals, centrifuged to remove catalyst particles, and analyzed spectrophotometrically. The degradation efficiency was calculated based on changes in dye concentration over time.

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III. RESULTS AND DISCUSSION

3.1 Structural Analysis

X-ray diffraction patterns of both uncapped and lemon-capped ZnO nanoparticles confirmed the formation of phase-pure hexagonal wurtzite ZnO, with diffraction peaks corresponding to standard JCPDS data[12].The observed diffraction peaks were analyzed using Bragg's law of diffraction ($n\lambda = 2d \sin\theta$, where $n = 1$) to determine the interplanar d-spacings and evaluate the long-range crystallographic order within the nanocrystalline matrix. [13].

$$n\lambda = 2d\sin\theta \quad (1)$$

No additional peaks related to impurities or secondary phases were observed, indicating high purity of the synthesized materials. Notably, diffraction peaks of lemon-capped ZnO were broader than those of uncapped ZnO, suggesting reduced crystallite size.Debye-Scherrer's equation would be applied. This equation indicates that for crystallites smaller than a nanometer, the coherently scattering domains are even smaller than the crystallites themselves [14];

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (5)$$

Where K is the dimensionless form factor, which is 0.9 λ is the wavelength, 1.5406 Å, is the FWHM, and ϴ is the angle.

Table 1. Crystallite size of ZnO nanoparticles

Sample	Crystallite size (nm)
Uncapped ZnO	42.6
Lemon-capped ZnO	27.9

The reduction in crystallite size is attributed to the presence of citric acid and other organic molecules in lemon extract, which adsorb onto particle surfaces and inhibit excessive crystal growth during calcination.

3.2 Morphological Studies

Scanning electron microscopy revealed that uncapped ZnO nanoparticles exhibited irregular shapes with significant agglomeration, which is typical for oxide nanoparticles synthesized without surface modifiers. In contrast, lemon-capped ZnO nanoparticles displayed relatively uniform morphology with improved dispersion and reduced agglomeration. The bioactive molecules in lemon extract act as steric barriers, preventing particle coalescence and leading to a higher effective surface area[15].

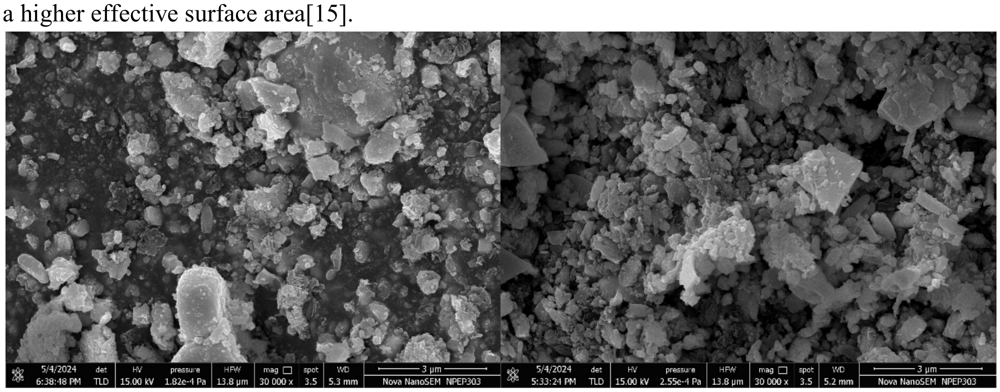

Figure 1. SEM images of (a) uncapped ZnO and (b) lemon-capped ZnO nanoparticles

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3.3 FTIR Analysis

FTIR spectra confirmed the presence of characteristic Zn–O stretching vibrations below 600 cm^{-1} for both samples. Lemon-capped ZnO exhibited additional weak absorption bands in the region of 1400–1650 cm^{-1}, corresponding to carboxylate and hydroxyl functional groups. These features indicate successful surface interaction between ZnO nanoparticles and lemon-derived phytochemicals, which enhance surface reactivity and hydrophilicity[16].

3.4 Optical Properties

UV–visible absorption spectra showed strong absorption in the ultraviolet region for both samples. Lemon-capped ZnO exhibited a slight red shift in the absorption edge compared to uncapped ZnO, indicating modification of the electronic structure. Tauc plot analysis revealed a reduction in bandgap energy.

Table 2. Optical bandgap values

Sample	Bandgap energy (eV)
Uncapped ZnO	3.21
Lemon-capped ZnO	3.02

This bandgap narrowing enhances photon absorption and promotes more efficient generation of charge carriers during photocatalysis.

3.5 Photocatalytic Performance

The photocatalytic degradation of methylene blue under UV irradiation demonstrated that lemon-capped ZnO nanoparticles exhibited significantly higher degradation efficiency compared to uncapped ZnO. After 120 minutes of irradiation, lemon-capped ZnO achieved approximately 95% degradation, whereas uncapped ZnO showed about 82%.

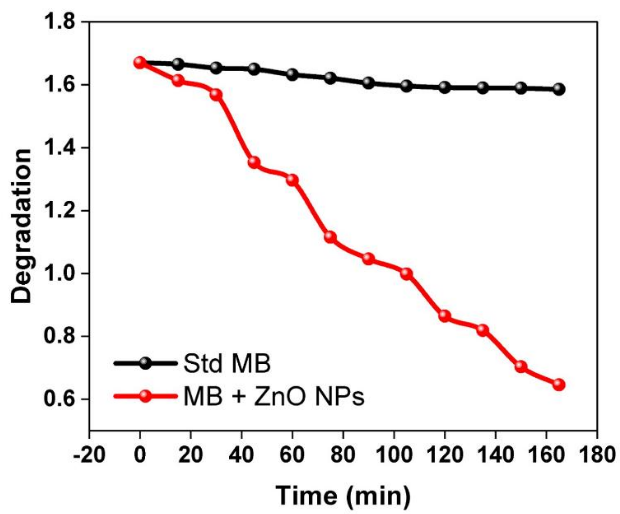

Figure 2. Photocatalytic degradation of methylene blue under UV light

The enhanced performance is attributed to reduced crystallite size, improved surface area, enhanced adsorption of dye molecules, and suppressed electron–hole recombination[17, 18].

3.6 Kinetic Analysis

The degradation kinetics followed pseudo-first-order behavior, consistent with the Langmuir–Hinshelwood model for heterogeneous photocatalysis.

Table 3. Photocatalytic rate constants

Sample	Rate constant k (min^{-1})
Uncapped ZnO	0.013
Lemon-capped ZnO	0.026

The higher rate constant for lemon-capped ZnO confirms faster reaction kinetics and improved photocatalytic efficiency.

3.7 Photocatalytic Mechanism

Upon UV irradiation, ZnO nanoparticles generate electron–hole pairs. Lemon capping improves charge separation by providing surface states that trap charge carriers and suppress recombination[19, 20]. The photogenerated electrons reduce dissolved oxygen to form superoxide radicals, while holes oxidize surface hydroxyl groups to generate hydroxyl radicals. These reactive oxygen species attack methylene blue molecules, leading to stepwise degradation and eventual mineralization[21, 22].

IV. CONCLUSIONS

Lemon-capped ZnO nanoparticles were successfully synthesized using a simple and scalable ceramic method. Lemon extract played a crucial role in controlling crystallite growth, improving surface morphology, and modifying optical properties. The lemon-capped ZnO exhibited superior photocatalytic degradation efficiency and faster kinetics compared to uncapped ZnO. This study demonstrates that lemon capping is an effective, eco-friendly approach for enhancing the photocatalytic performance of ZnO nanoparticles, offering promising potential for wastewater treatment and environmental remediation applications.

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