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Facile One-pot Green Synthesis of Zinc Oxide Nanoparticle by Using Lemon Peel and Characterization Studies

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ABSTRACT

This study focuses on the synthesis of zinc oxide (ZnO) nanoparticles using lemon peel as a green and sustainable precursor. ZnO is a metal oxide semiconductor known for its broad direct bandgap and photocatalytic properties. Lemon peel, a waste product rich in natural compounds, is utilized as a reducing and stabilizing agent during the synthesis process. The sol-gel method is employed to extract the active ingredients from lemon peel and combine them with a zinc salt solution. The resulting mixture undergoes controlled thermal treatment to produce ZnO nanoparticles. The synthesized nanoparticles are characterized using techniques such as field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and UV-Vis spectroscopy to analyze their morphology, structure, and optical properties. The results demonstrate the viability of using lemon peel as a sustainable and low-cost precursor to produce ZnO nanoparticles. The environmentally friendly synthesis method offers potential applications in catalysis, optoelectronics, energy conversion, and biomedicine. The findings highlight the benefits of utilizing natural waste products in nanoparticle synthesis, promoting a more eco-friendly and efficient approach to material production.

Keywords: *Zinc Oxide nanoparticles, Lemon peel, Green synthesis*

1. INTRODUCTION

In the field of nanoscience, the creation of metal nanoparticles has been an exciting area of study. Various metal nanoparticles, including iron oxide, silver nitrate, copper oxide, and zinc oxide, have attracted the attention of researchers. Metal oxides such as titanium dioxide (TiO2), zinc oxide (ZnO), magnesium oxide (MgO), and calcium oxide (CaO) are particularly significant due to their stability under harsh conditions and their perceived safety for consumption by humans and animals. Zinc oxide nanoparticles have found diverse applications in areas such as sunscreens, sensors, piezoelectric and photodiode devices, solar cells, anti-reflection coatings, and photocatalysis [1]. Zinc oxide (ZnO) is a well-known member of the metal oxide family. It is a metal oxide semiconductor with a broad direct band gap (3.37 eV) and high excitonic binding energy (60 eV) [2-3].

On a different note, the lemon (scientific name: Citrus limon) is a member of the Rutaceae family within the genus Citrus, which also includes fruits like pomelo, tangerine, grapefruit, and oranges. Lemons are small, spherical fruits that contain numerous nutrients beneficial for health. Lemon trees are evergreen and grow quickly, reaching heights of 10–12 feet in cultivated plantations. They thrive in temperate and tropical habitats but are sensitive to excessively cold and frosty climates, which can cause them to droop, wither, or inhibit their growth [4].

Various techniques are used to create metal nanoparticles, but traditional methods can be time- consuming, expensive, and generate toxic waste. However, the use of plants and plant extracts has emerged as a green and promising approach for the synthesis of metal nanoparticles. Green synthesis offers advantages such as non-toxicity, low cost, and renewability [5-7]. For example, ZnO nanoparticles have been successfully manufactured using green sources such as aqueous Piper betle leaf extract, Lippia adoensis leaf extract, and citrus peel [8]. In this context, lemon peel extracts have been explored as reducing and stabilizing agents to produce ZnO nanoparticles. This study intends to provide a thorough review of the ZnO nanoparticle production process using lemon peel extracts as reducing and stabilizing agents. Citrus Aurantifolia peel was used as a catalyst in the green production of zinc oxide nanoparticles utilizing various solvent extracts to reduce fruit waste and safeguard the environment.

2. MATERIALS AND METHODS

2.1. Materials

In this research, fresh lemons will be procured from a nearby grocery store in Parit Raja. The focus of the study is solely on utilizing the lemon peel, which is typically considered as surplus waste. To prepare the lemon peel for the experiment, it will be necessary to peel the lemons. Before incorporating the lemon peel into the production process of ZnO nanoparticles, it will undergo a rigorous cleaning regimen with deionized or distilled water. Following cleaning, the lemon peel will be finely sliced or cut into small fragments and then subjected to a two-hour drying process in an oven set at 150°C. The dried lemon peel sample will be carefully measured to obtain the required

quantity, processed in a blender to achieve a granular consistency, and finally crushed into a powdered form, ready for the subsequent steps involved in creating lemon peel extract.

2.2 Methods

For the creation of lemon peel extract, 1 g of lemon peel powder was stirred with 50 ml of distilled water for 3 hours on the magnetic stirrer. The solution then transferred to the water bath that was constantly at 60 ^{0}C for 1 hour. The mixture on the magnetic heater was removed after 1 hour of extraction was complete, let the solution cooled, and then finally filtered by using filter paper Whatman No.1 and stored in the refrigerator at 4 °C for later use. There are 6 samples for this research which use different variables in terms of temperature in the end, thus 6 samples for the research are being prepared 42.5 ml for each.

For the study's green production of zinc oxide nanoparticles, Citrus Aurantifolia powder was chosen as a catalyst and zinc nitrate, $Zn(NO_3)_2$ as a precursor. The zinc nitrate method was used in this investigation to create ZnO nanoparticles. For creating nanoparticles, 2 g zinc nitrate precursor was dissolved in 42.5 ml citrus Aurantifolia peel extract and then stirred continuously on a magnetic stirrer for 1 hour. After 1 hour of stirring, the solution is then transferred to the water bath that is constantly at 60 ^{0}C temperature for 1 hour. Next, the solution was dried from the liquid to solid in a form of powder in the oven at 150 ^{0}C for 1.5 hours. Figure 1 shows the schematic diagram presentation of the ZnO NPs synthesis process.

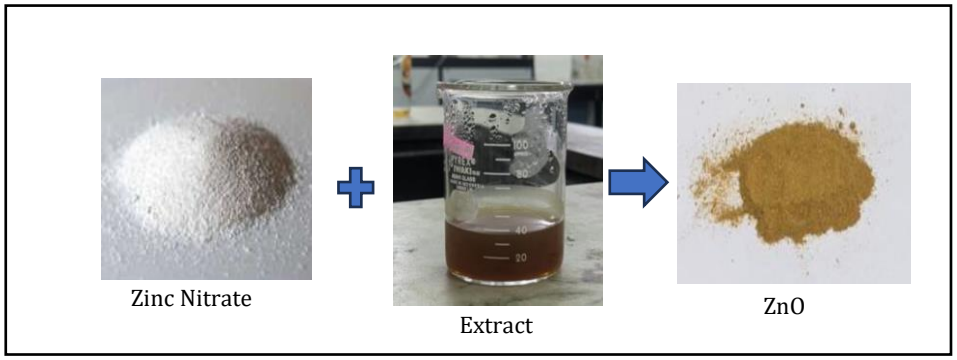

Figure 1. Schematic representation of ZnO NPs synthesis

For the calcination process, all of 6 samples labeled A, B, C, D, E, and F heated at different temperatures which are 300, 400, 500, 600, 700, and 800 ^{0}C, respectively. The variation in physical color will serve as the initial visible distinction, marking the commencement of the nanoparticle characterization tests.

2.3 Characterization of Zinc Oxide

There are many different procedures and techniques that define nanostructure. In general, two processes are used; one to characterize and validate the morphology of the nanostructure, and the other to assess the chemical properties of the nanostructure. The nature of the study and its intended purposes will probably have an impact on the methodologies employed. Numerous techniques and methods revealed several morphological and chemical forms of nanostructure, each with its own unique set of characteristics. The sample pretreatment, instrument class, and experiment condition were all taken into consideration to produce correct results. UV-Vis, XRD, and FESEM methods were used in most of the nanostructure research.

The characterization of green produced zinc oxide nanoparticles was done for many parameters. The characterization with detailed function, which are absorbance peak by UV-Visible spectrophotometer, particle size, shape by Field Emission Scanning Electron Microscope (FESEM), and structure by XRD. The following instruments were used for additional characterization of the optimal treatment concentrations that were achieved during the investigation.

3. RESULT AND DICUSSION

3.1 Influence of Calcination Temperature

The appearances of ZnO NPs powder for as-prepared samples and samples calcined at various temperatures are shown in Figure 2. All the ZnO nanoparticle powders exhibited a fluffy appearance but displayed varying colors. The initially prepared sample had a dark orange hue, primarily because some residues of the lemon peel extract remained. In contrast, the calcined samples presented lighter colors owing to the decomposition of organic substances. Notably, the extent of color lightening was directly correlated with the calcined temperature, with higher temperatures resulting in lighter powder shades.

3.2 X-Ray Diffraction Analysis

The XRD analysis of samples A to F, heated at different temperatures during the calcination process shown in

Figure 3, reveals significant differences in the pattern and spectra. The XRD analysis was performed in the 2θ range of 20° to 80°, commonly used in XRD analysis. The peaks observed in the spectra correspond to the crystallographic planes of ZnO, such as (100), (002), (110), (103), and (112), indicating the presence of ZnO nanoparticles with a hexagonal wurtzite crystal structure [9].

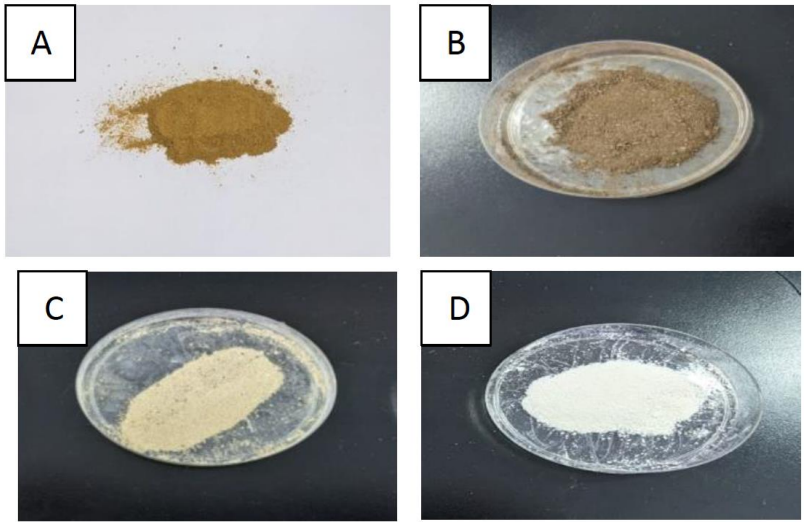

Figure 2. Photographs of ZnO NP powders with different calcine temperatures (a) shows the as-prepared sample and (b), (c), and (d) show samples calcined at 400, 600, and 800 ^{0}C, respectively.

The X-ray diffraction (XRD) analysis of various zinc oxide (ZnO) samples demonstrates the presence of a compound through sharp peaks in their patterns. As shown in Figure 3, samples A and B are confirmed to contain ZnO by the reference number 00-065-0726, while the remaining samples (C, D, E, and F) are identified to have both ZnO and Zincite, indicated by the two-reference numbers 00-065-0726 and 00-036-1451, respectively. The XRD analysis effectively characterizes the crystalline nature and composition of the samples, providing valuable insights into their structure and properties.

The X-ray diffraction (XRD) analysis of zinc oxide (ZnO) samples with varying calcination temperatures reveals important insights into their crystallographic characteristics and crystallite size. The presence of ZnO is confirmed in samples A and B through sharp peaks that match reference patterns. However, sample A, calcined at 300°C, shows overlapped peaks and broader peaks, indicating contamination and rendering its results inaccurate. Sample B exhibits smaller peak broadening, indicating a larger crystallite size compared to A. Material handling faults are observed in the beginning of the results for B. Samples C and D, calcined at 500°C and 600°C, respectively, show similar XRD patterns with small peak broadening, suggesting large crystallite sizes. Sample E, calcined at 700°C, and sample F, at 800°C, exhibit similar patterns, but F has the smallest peak broadening, indicating the largest crystallite size and increased lattice strain due to higher temperature. The calcination process at higher temperatures encourages the development of larger crystallite sizes and higher crystallinity in the synthesized ZnO.

As the calcination temperature of zinc oxide (ZnO) samples increases from 500 ^{0}C to 800 ^{0}C, the XRD pattern becomes noticeably smoother and more refined. This smooth pattern is a result of the accelerated reaction rate at higher temperatures, driven by the increased energy input into the system. The elevated temperatures facilitate a faster conversion of precursor materials into zinc oxide and aid in the breakdown of precursor substances, ensuring complete transformation into ZnO. This is particularly crucial for compounds containing zinc, which require high temperatures to decompose and release zinc oxide. The higher calcination temperatures also promote the development and crystallization of zinc oxide particles, leading to larger crystallite sizes, well-defined crystallites, and a higher level of crystallinity in the synthesized ZnO. The smooth pattern observed in the XRD results reflects the enhanced crystalline structure and overall quality of the zinc oxide produced under these conditions. The higher temperatures also encourage the development and crystallization of larger, well-defined zinc oxide particles with higher crystallinity [10].

Overall, the XRD analysis provides insights into the presence, crystallite size, and lattice strain of the ZnO nanoparticles in each sample, highlighting the effects of different calcination temperatures on their structural characteristics.

3.3 Microstructural Analysis

The selected samples for observation were B, D, and F due to their significant differences in structure, shape, and size, which are not easily discernible with the naked eye. These samples were chosen to facilitate a clear and distinct discussion regarding the variations among them,

particularly in terms of nanoparticle differences. The focus on these specific samples allows for a more detailed analysis of their unique characteristics and properties, aiding in a comprehensive understanding of the observed differences in their X-ray diffraction patterns.

The ImageJ software was used to measure the particle size of samples B, D, and F, based on Figure 4 (a), (b), and (c), respectively. The particle size was determined by measuring 20 particles in each sample to obtain an accurate average value. The results showed that sample B has an average area of 36.990 nm^2 and an average length of 38.701 nm, while sample D has an average area of 70.749 nm^2 and an average length of 74.732 nm. Sample F exhibited an average area of 86.820 nm^2 and an average length of 91.971 nm. All three samples were found to be in the nanoparticle size range, between 1 and 100 nanometers. Nanoparticles possess unique physical and chemical characteristics that can differ significantly from their larger counterparts and are not visible to the human eye [11].

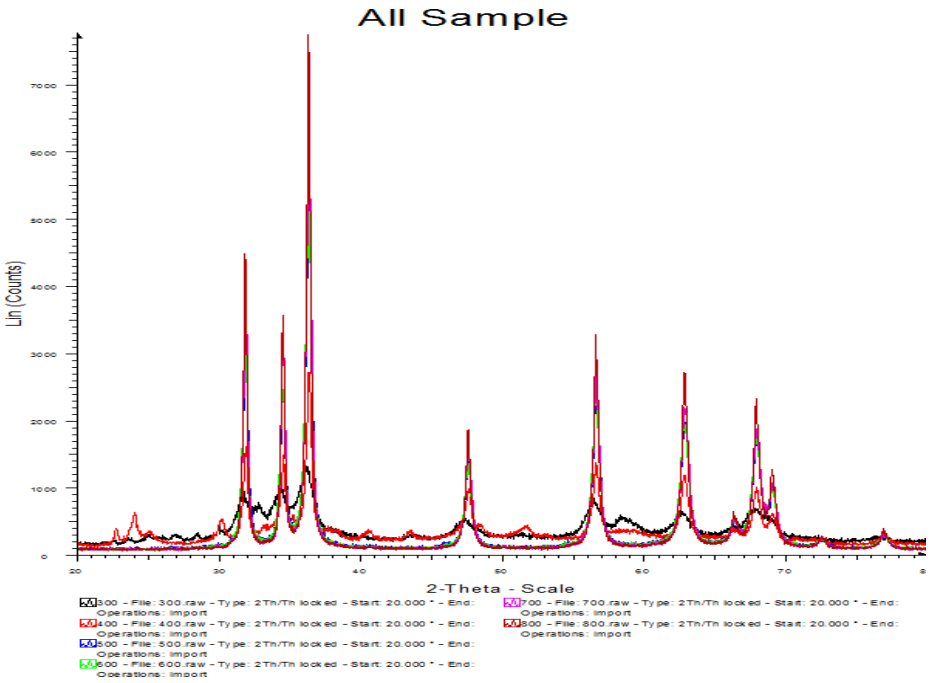

Figure 3. XRD analysis of synthesis ZnO at different calcination temperatures.

This increase in crystallite size can be attributed to the fact that the thermal energy during calcine caused the particles to become reoriented and reduced the number of defects in grain boundaries. This is similar to the finding of previous report by T. U. Doan Thi [12]. Specially, with increasing calcine temperature, the particle size tended to increase and shape larger particles due to crystal growth.

The correlation between XRD and FESEM analysis is evident through the observation of crystallite size. XRD analysis indicated that smaller peak broadening corresponds to a larger crystallite size. On the other hand, FESEM analysis involved measuring the particle size and identifying that agglomeration occurred at higher temperatures, leading to larger crystallite or particle sizes, particularly seen in sample F, which was calcined at 800 ^{0}C. This demonstrates a significant correlation between the two analytical techniques, as both XRD and FESEM findings support the notion that higher calcination temperatures result in larger crystallite sizes, providing complementary evidence for the relationship between the crystallite size and the temperature used during the calcination process.

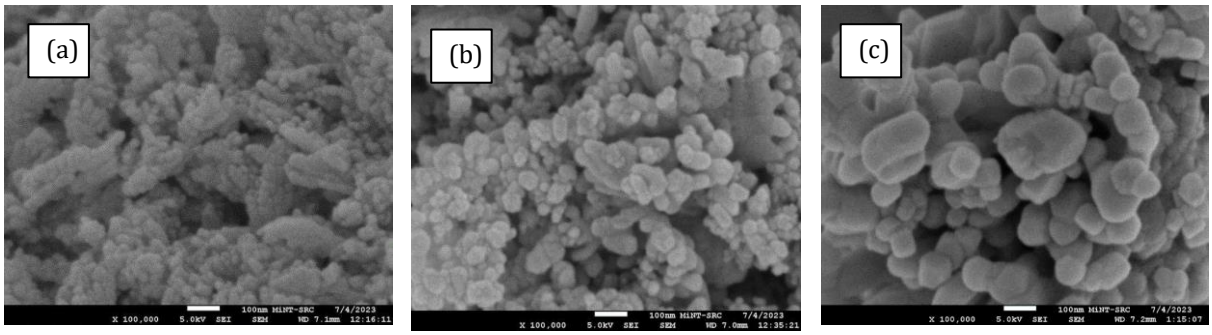

Figure 4. Microstructure analysis image of ZnO powders with different calcine temperatures at. (a) 400, (b) 600, and (c) 800 ^{0}C, respectively.

Analyzing the FESEM images of sample F (Figure 3(c)), it is evident that the crystallite particle size is larger compared to sample B and sample D. The XRD analysis confirms that smaller peak broadening corresponds to larger crystallite sizes. The shape of sample F is clearly observed to be hexagonal, which distinguishes it from the spherical shape of sample B and the rod-like shape of sample D. Sample F also exhibits agglomerated particles, indicating the tendency of particles to cluster together on the surface. In contrast, sample B and sample D show well-dispersed particles with good separation. The calcination process with different temperatures influences the structure and shape of the particles. Higher calcination temperatures can lead to particle development, agglomeration, and changes in surface texture, resulting in larger crystallite sizes and smoother surfaces. Lower calcination temperatures, on the other hand, may result in smaller and more scattered particles with porous structures or surface characteristics [13].

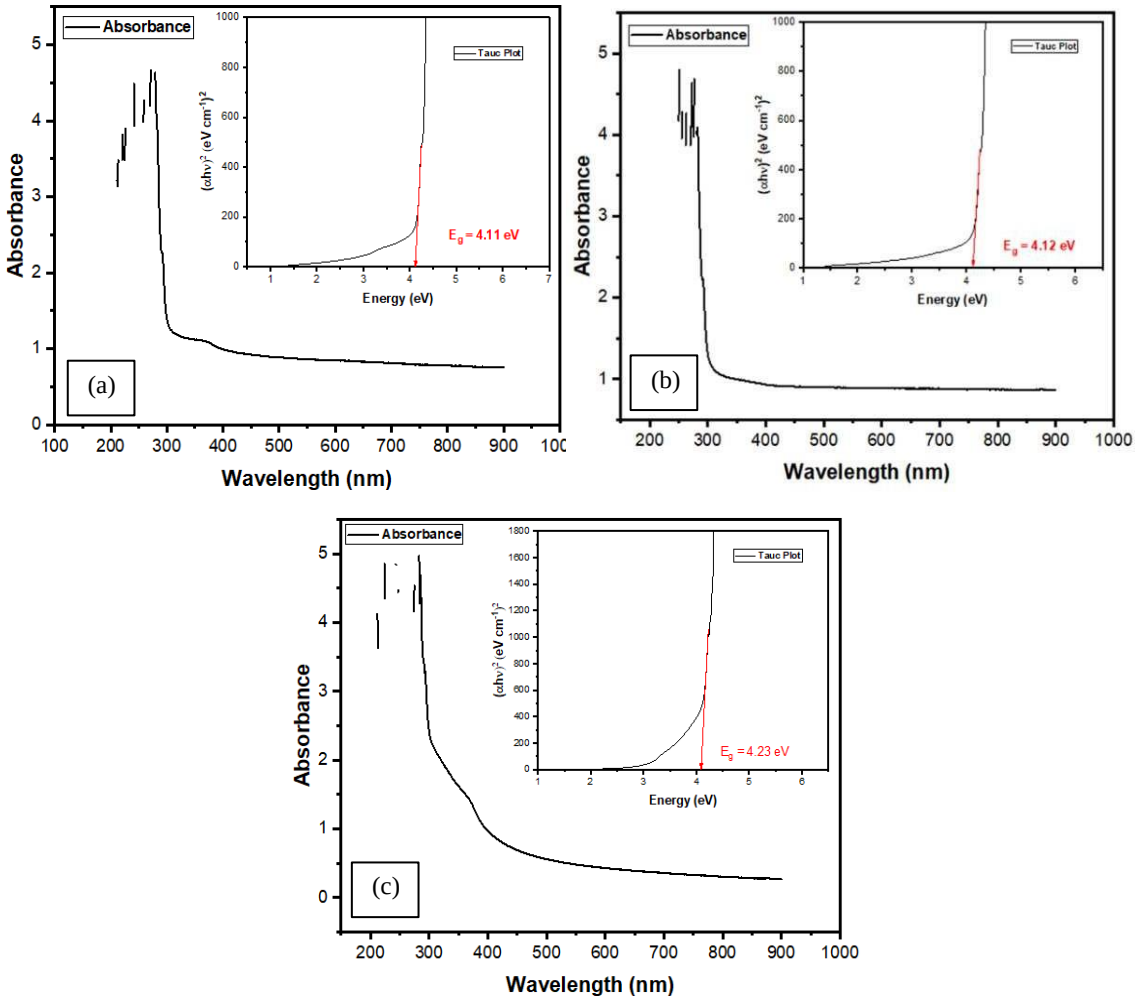

Figure 5. UV-Vis analysis of ZnO powders with different calcine temperatures at 400, (b) 600, and(c) 800 ^{0}C, respectively.

3.4 UV- Visible Spectroscopy Analysis

Analysis of the UV-Vis spectra of sample B, sample D, and sample F is shown in Figure 5 (a), (b), and 4(c), respectively, reveals the absorption edge for each sample. The spectrum was scaled on a wavelength from 300 to 800 nm of the UV-Vis absorption spectra, The absorption edge for ZnO nanoparticles is typically observed between 350 and 380 nm. Sample B exhibits a less sharp absorption edge compared to the other samples. Sample F shows a higher bandgap energy, indicated by a sharp and steep absorption edge in the UV region of the spectrum. This suggests a larger energy difference between the valence band and conduction band, requiring shorter wavelengths (higher energy) for electronic transitions to occur. The high energy cutoff wavelength, marking the beginning of significant absorption, occurs at a shorter wavelength (higher energy) for materials with a high bandgap. This implies that sample F has the highest bandgap energy among the samples. Sample B exhibits the highest absorbance intensity, indicating the highest light absorption. However, absorbance breaking may occur in all graphs, possibly due to the limited dynamic range of the measurement or inappropriate sample preparation with a high concentration that exceeds the detection range.

The energy band gap was determined by plotting (αhν)2 versus hν on the x-axis; where α, h, and ν are the absorption coefficient, Planck constant, and frequency, respectively [9]. The band gap energy was found in the range of 4,11 to 4.23 eV, and did show a noticeable change with growth of the ZnO NPs on increasing calcination temperature. In summary, UV-Vis spectroscopy allows researchers to analyze the optical properties of ZnO, including its absorption edge, bandgap energy, and absorbance intensity. The calcination temperature can influence the steepness of the absorbance pattern, with higher temperatures resulting in steeper patterns and higher bandgap energies [14].

4. CONCLUSION

The synthesis of zinc oxide nanoparticles using lemon peel via the sol-gel process at different calcination temperatures was successful, as evidenced by the presence of zinc oxide in all samples. XRD analysis confirmed the presence of ZnO in each sample, with sample A showing an overlapped peak indicating faulty preparation. The peak broadening in XRD spectra revealed the crystallite size, with decreasing broadening corresponding to larger crystallite sizes. FESEM analysis identified different shapes for each sample - spherical, rod-like, and hexagonal. The crystallite size measured through ImageJ software showed an increase in size due to agglomeration at higher calcination temperatures, corroborating the correlation between XRD and FESEM results. UV-Vis analysis showed higher bandgap energy with steeper absorbance patterns at higher calcination temperatures.

Using lemon peel as a precursor for zinc oxide synthesis offers several advantages, including its affordability, easy accessibility, and environmentally friendly nature. The active components in lemon peel contribute to the stabilization and reduction of zinc oxide nanoparticles. This method avoids the need for hazardous chemicals and complex synthetic processes, reducing the environmental impact. The synthesized zinc oxide nanoparticles display promising properties, such as stability, biocompatibility, and photocatalytic activity, making them suitable for various applications in catalysis, optoelectronics, energy conversion, and biomedicine.

In summary, the environmentally friendly synthesis of zinc oxide nanoparticles from lemon peel provides functional and customizable materials. The combination of FESEM, UV-Vis spectroscopy, and XRD allows for comprehensive material analysis and characterization. This approach demonstrates the potential for sustainable and eco-friendly nanoparticle synthesis, highlighting the advantages of utilizing natural reducing and stabilizing agents from lemon peel to produce valuable nanomaterials.

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