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Exploratory advancement in the optimal utilization of bio-wastes for ZnO nanoparticle synthesis in antimicrobial applications

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Abstract: The wealth out of Waste (WoW) concept progressively developed for the industrial revolution in recent years. So, bio-waste mediated synthesis of nanoparticles has emerged as a promising approach, leveraging the unique properties of bio-wastes and agricultural wastes. In this study, extracts from Eggshell, Peanut husk, and Orange peels were used to synthesize zinc oxide nanoparticles. The structural, vibration, and morphological properties of the synthesized ZnO nanoparticles were investigated and reported. It reveals that the distinct vibration peaks with strong existence of Zn-O bands from FT-IR spectra. Overall, this study highlights the incomparable structural and morphological properties of bio-waste extracts and their impact on the synthesis and functionality of zinc oxide nanoparticles, paving the way for future research in antimicrobial and targeted drug delivery applications.

Keywords: ZnO, Eggshell, Peanut husk, Orange peel, SEM, web-like structure

1. Introduction

Since a third of the world's food supply, or around 1.3 billion metric tons annually, is wasted, there have been countless, possibly catastrophic incidents worldwide in recent years. Vegetable and fruit peel waste comprise a sizable amount of this biodegradable garbage. Food waste has a significant financial impact, estimated at roughly $940 billion a year, and decomposing bio-waste in landfills releases methane, a strong greenhouse gas contributing to climate change [1]. Agricultural production, food processing, retail, and consumption are some steps by which bio-waste is produced. Markets, restaurants, homes, and the food processing sector are all significant contributors. Despite these challenges, bio-waste utilization for nanoparticle synthesis represents a promising avenue for sustainable material production. By harnessing the abundance and diversity of bio-waste sources, researchers can develop innovative and eco-friendly approaches to nanoparticle synthesis, contributing to the advancement of green nanotechnology and the transition towards a more sustainable future [2].

India produces a significant amount of bio-waste, being one of the top producers of fruits and vegetables. The green synthesis of silver and gold nanoparticles with potential antibacterial applications has been successfully achieved by Indian researchers using fruit peels such as banana, orange, and pomegranate [3-5]. One promising avenue is the utilization of bio-wastes, which are abundant, renewable, and readily available sources of precursors for nanoparticle synthesis. This offers several advantages over conventional methods, including cost-effectiveness, sustainability, and reduced environmental impact [6]. By repurposing waste materials as precursors, these approaches not only mitigate the environmental burden associated with waste disposal but also contribute to the circular economy by promoting resource recovery and reuse.

However, several challenges must be addressed to realize the full potential of bio-waste utilization in nanoparticle synthesis. Firstly, the variability in bio-waste composition and quality poses challenges to reproducibility and standardization of synthesis processes. Furthermore, the extraction and processing of bio-waste precursors may require optimization to enhance efficiency and yield [7]. Additionally, concerns regarding the potential contamination of synthesized nanoparticles with impurities or toxic substances present in bio-waste sources need to be addressed through rigorous characterization and purification techniques.

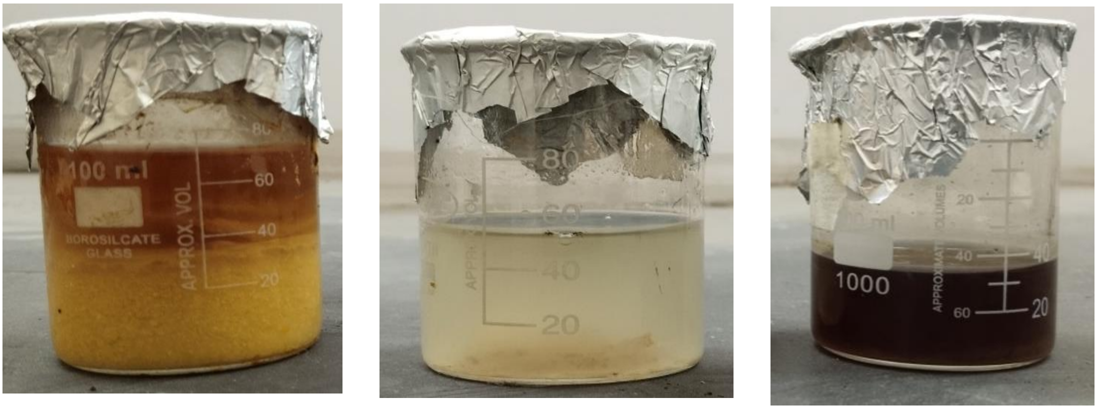
Among different metal oxides nanostructures, ZnO, TiO_2, SnO_2, CeO_2 nanostructures have received a special attention because of intriguing nano size effects on their physio-chemical properties. In particular, ZnO nanostructures are considered to be a good candidate for the fabrication of functional devices. This is because of their good oxidation resistibility, biocompatibility, good thermal stability, low toxicity and high electron mobility [8-10]. The conventional methods employed for the synthesis of ZnO nanoparticles often involve the use of hazardous chemicals and energy-intensive processes, leading to environmental degradation and posing health risks. In response to these challenges, there is a growing interest in developing sustainable and eco-friendly approaches to the synthesis of nanosized materials.

This research work aims to explore the feasibility and efficacy of utilizing various bio-wastes as precursors for the green synthesis of ZnO nanoparticles. By leveraging the inherent properties of bio-wastes, such as their high organic content and diverse chemical composition, this study seeks to establish a sustainable and cost-effective approach to the synthesis. Through a combination of experimental techniques and comprehensive characterization analyses, the synthesized ZnO nanoparticles are evaluated for their physical, chemical, and structural properties.

2. Materials and Methodology

2.1 Preparation of Bio-waste extract

Bio-waste and fruit peels like Eggshell, Peanut husk, and Orange peels were collected from our locality. After being repeatedly cleaned with tap water to eradicate any dust found in the air, the fresh shells and peels were allowed to dry in an enclosed space. A mortar and pestle were used to crush the 5g of dried and cleaned peels and shells, which were then dissolved in 100 ml of distilled water. After ten minutes of boiling at 80 degrees Celsius, the produced extracts were allowed to cool to ambient temperature before being filtered using Whatmann filter paper. The resulting yellow, pale white and dark brown filtrates (Figure 1) were utilized as capping and stabilising agents after the filtrate was centrifuged for 30 minutes at 8000 rpm.



Orange peels extract Eggshell extract Peanut husk extract

Figure 1. Illustration of various bio-waste and fruit peel extracts

2.2 Synthesis of ZnO nanoparticles

Zinc acetate is chosen as the precursor material. The salt is dissolved in a water, to form a clear solution. The concentration of the precursor solution is adjusted to 0.5M. A stabilizing agent that is the extracts prepared from Eggshell is slowly added to the precursor solution under constant stirring. This gradual addition is crucial for controlling the rate of nucleation and growth of the zinc hydroxide particles, which we will later convert to zinc oxide. The addition of the stabilizing agent leads to the formation of zinc hydroxide ($Zn(OH)_2$) precipitates due to the reaction between the zinc ions from the precursor solution and hydroxide ions from the base. The zinc hydroxide precipitate is then subjected to thermal treatment or calcination at elevated temperatures (typically in the range of 300-600°C). This step leads to the decomposition of zinc hydroxide into zinc oxide. The calcination process also facilitates the removal of any residual organic compounds and enhances the crystalline nature of the zinc oxide nanoparticles.

The same method was applied to the other two extracts namely Peanut husk, and Orange peels. The resulting slurry exhibited a pale and dark brown colour. The synthesized ZnO nanoparticles were labelled as Egg shell as (E), Peanut husk as (G), and Orange peel as (O). These powders are thoroughly described using a range of methods to assess their characteristics, with an emphasis on their antimicrobial activity.

3. Result and Discussion

3.1 Structural analysis

The XRD pattern of the pure ZnO nanoparticles (designated as Z) is displayed in the Figure 2. It distinctly shows the appearance of intense peaks observed at 2 theta values 31.85, 34.55, 36.35, 47.69, 56.75, 63.09, 68.16, 69.29, which corresponds to the lattice planes (100), (002), (101), (102), (110), (103), (112), (201) respectively [11]. The highest and lowest intensity peaks are observed as (101) and (200) respectively. The obtained peaks are matched with JCPDS card no. 01-079-0205, and portrays the existence of the popular hexagonal wurtzite crystal structure with space group P63mc, and lattice parameters a=b=3.24, c=5.18.

This observation reveals that the pure ZnO nanoparticles have a pronounced hexagonal lattice with a preferential orientation along the (101) direction. The ZnO nanoparticles with orange peel extract exhibits a similar hexagonal wurtzite crystal structure. The highest peak exhibited remains unchanged along (101), but there exhibits a significantly reduction at (002), (100), (201) orientations.

The Peanut shell extracted ZnO nanoparticles has a similar pronounced hexagonal lattice, but the extract seems to completely change the preferential orientation towards (100) lattice plane. There also exists various changes such as the decrease along (002) plane, a slight increase along (101).

For the egg shell extract mixture of ZnO nanoparticles, the XRD pattern also exhibits a pronounced hexagonal lattice with preferential orientation along the (101), similar to pure ZnO. New distinct peaks can also be observed alongside the ZnO peaks. It has been reported that the peaks at 12.3, 16, 19, 20, 21, 22, 23, 25 are distinct peaks of (ovoalbumin, ovotransferin) proteins present in egg shells. This observation successfully elucidates the integration of the extract into the ZnO lattice [12, 13].

ZnO nanostructures prepared from orange peel extract strongly uplift the intensity of the triplet peaks (100), (002), and (101) whereas those prepared from eggshell and peanut husk diminish the intensity of the triplet peaks because of the development of a new phase [14]. The overall XRD results demonstrated that the orange peel extracted ZnO nanoparticles marvellously sharpen the crystalline properties of the material due to the presence of cellulose, lignin, and hemicellulose in the surface. The peanut husk extracted ZnO nanoparticles slightly fortify the quality of their crystalline nature owing to the existence of primary chemical compounds like pectin, tannins, and anthocyanins. The crystalline quality is significantly impacted by ZnO nanoparticles made from eggshell extract, which also trigger the development of a new phase due to the existence of peaks connected to ovalbumin and ovotransferrin.

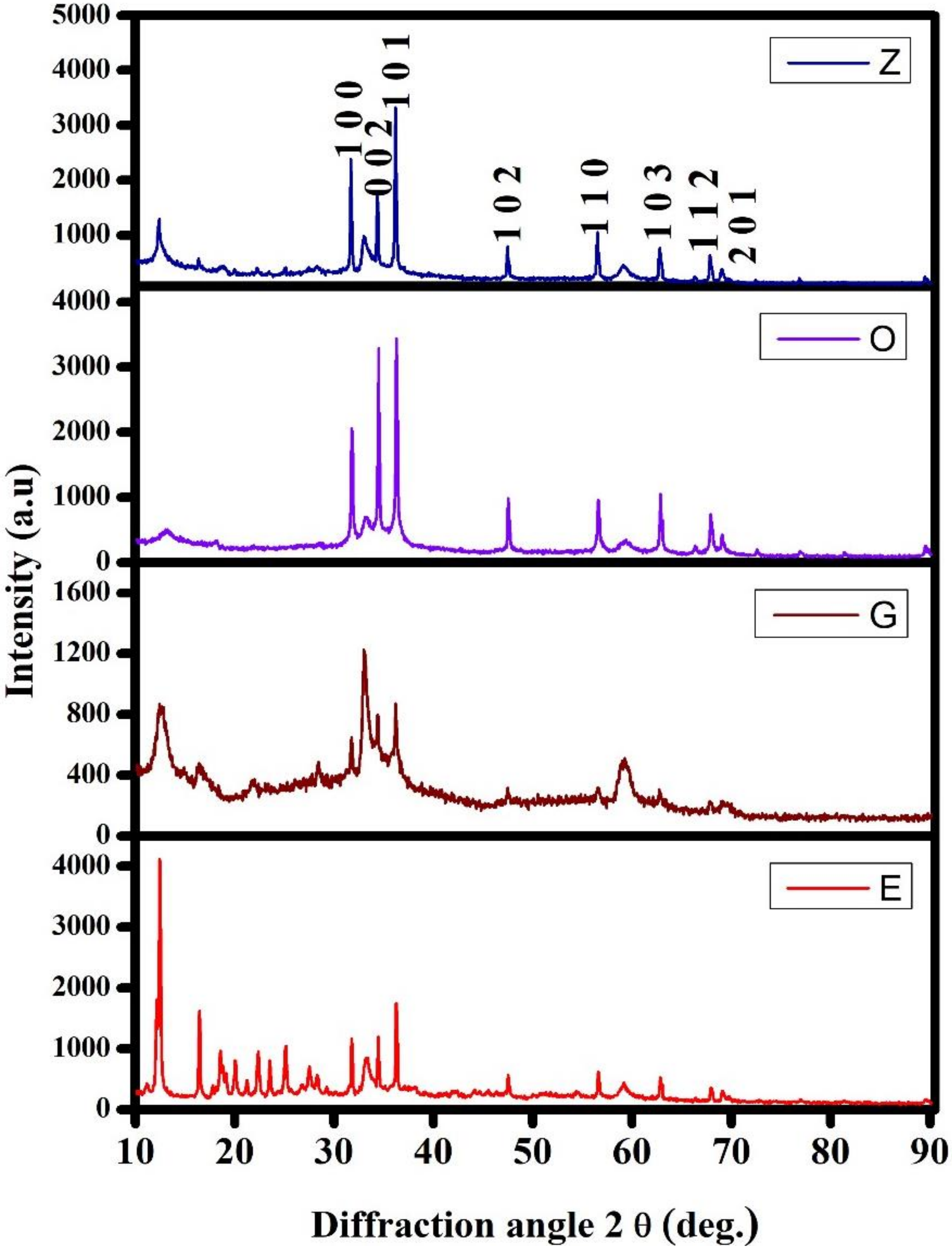


Figure 2 XRD pattern of various extracts capped ZnO nanoparticles.

3.2 Functional analysis

The vibrational spectra of bio-waste extracted ZnO nanoparticles are represented in Fig. 3. The strong and broad vibration peak observed at 3200–3460 cm^{-1} is attributed to symmetric stretching vibrations of hydroxyl (o-H) groups in the samples because of chemisorbed water molecules on the surface [15]. FT-IR representation exhibits the intense stretching vibration band at 1532 and 1478 cm^{-1} indicates the bending vibration of O-H (H_2O) and C-O (CO_2) group of environment moisture present in the KBr pellet. The intense peak at 615 cm^{-1} corresponds to the surface's anti-symmetric Zn-O stretching mode of bridging oxide [16]. The FT-IR spectra of ZnO nanoparticles treated with various extracts shifted the stretching frequency toward the lower wave number and appeared at 458 cm^{-1} which is slightly lower than the pure ZnO (615 cm^{-1}). ZnO nanomaterials treated with eggshell extract enhance the vibrational intensity of hydroxyl groups while the same treated with peanut husk and orange peel extracts reduce the hydroxyl group peak. The presence of ovalbumin and ovotransferrin in the eggshell extracted ZnO nanoparticles robustly proliferate the intensity of carbonyl groups on the surface while the other two extracts diminish the carbonyl group intensity. The existence of phytochemicals inside the bio-wastes like eggshell, peanut husk, and orange peel strongly distress the vibration bands of the Zn-O network.

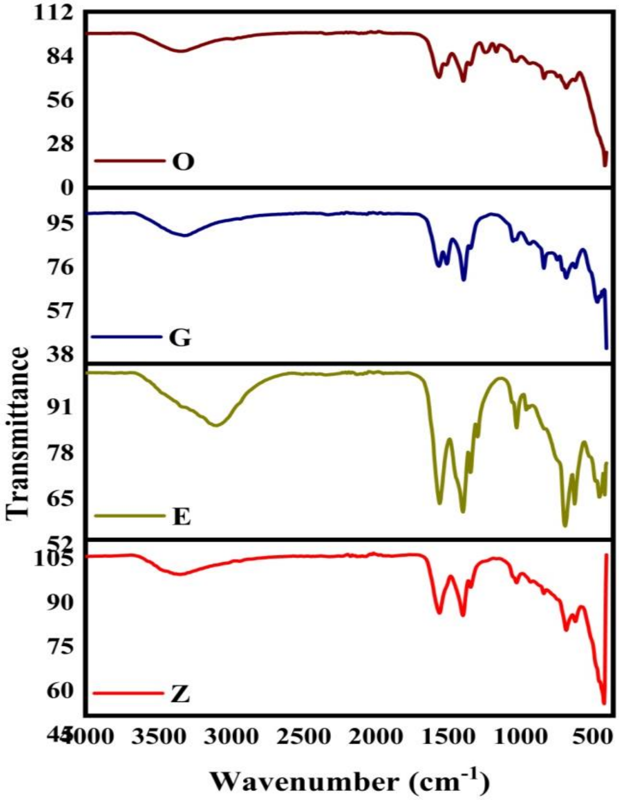


Figure 3. FT-IR spectra of extract mediated ZnO nanoparticles

3.3 Morphological analysis

Scanning Electron Microscopy (SEM) analysis of the pure ZnO nanoparticles revealed the presence of irregular shaped agglomerates with a broad size distribution ranging from 20 nm to several hundred nanometers (Figure 4). Notably, some agglomerates reached micrometer dimensions, with smaller nanoparticles adhering to their surface. This observed agglomeration likely originates from the specific parameters employed during the synthesis process, which can be further optimized to achieve desired nanoparticle morphologies [17]. The smallest individual nanoparticles exhibited a near-spherical morphology and were randomly distributed throughout the sample. This spherical shape is attributed to the high surface energy inherent to small particle sizes, which favours a minimum surface area configuration. The larger agglomerates are most likely composed of arrangements of these smaller, near-spherical nanoparticles. Furthermore, the high surface area to volume ratio associated with the small spherical particles suggests a potential for enhanced antimicrobial properties.

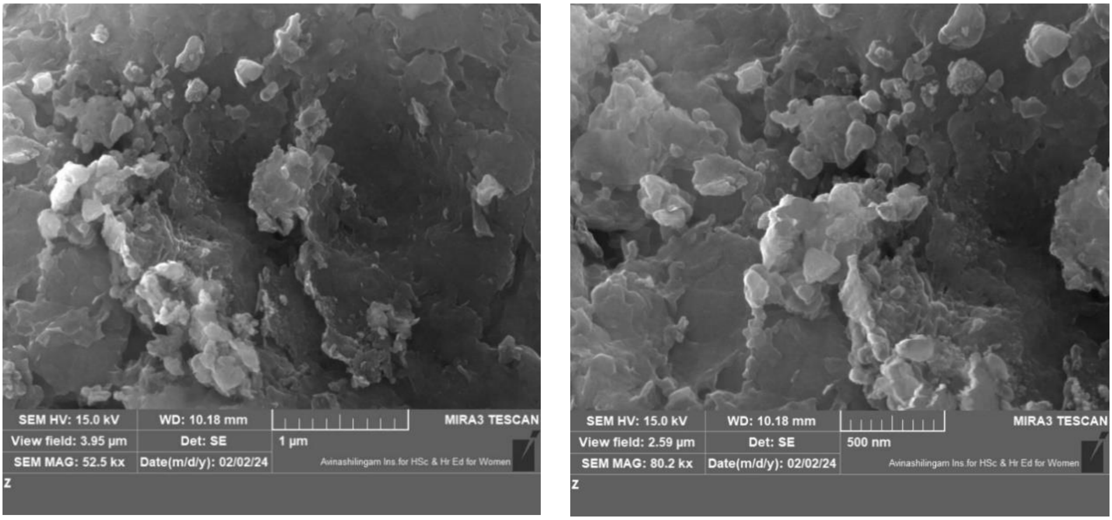


Figure 4. SEM images of pure ZnO nanoparticles

SEM images of ZnO nanoparticles treated with egg shell residue extract reveals the presence of highly agglomerated, rough platelet structures at low magnification alongside large aggregates of various shapes as indicated in Figure 5. Furthermore, the image depicts layered plate-like structures interspersed amongst the rough surfaces and embedded within the larger aggregates.

The higher magnified image express the presence of uniformly distributed smooth surfaced pineapple fruit-like structured particles (size 68 nm) without voids due to the development of new phase exerted by ovoalbumin and ovotransferin. These plate-like layered structures could be indicative of the characteristic hexagonal wurtzite structure of ZnO nanoparticles, as confirmed by the XRD analysis. The observed high degree of agglomeration could be attributed to bridging or interactions between these organic molecules and the ZnO surfaces [18]. The egg shell residue extract might have interacted with the ZnO surface, potentially involving specific proteins like albumen. This interaction might have influenced the growth process, which could have led to the formation of composite structures where organic components are integrated with the ZnO nanoparticle surface, further contributing to the observed agglomeration.

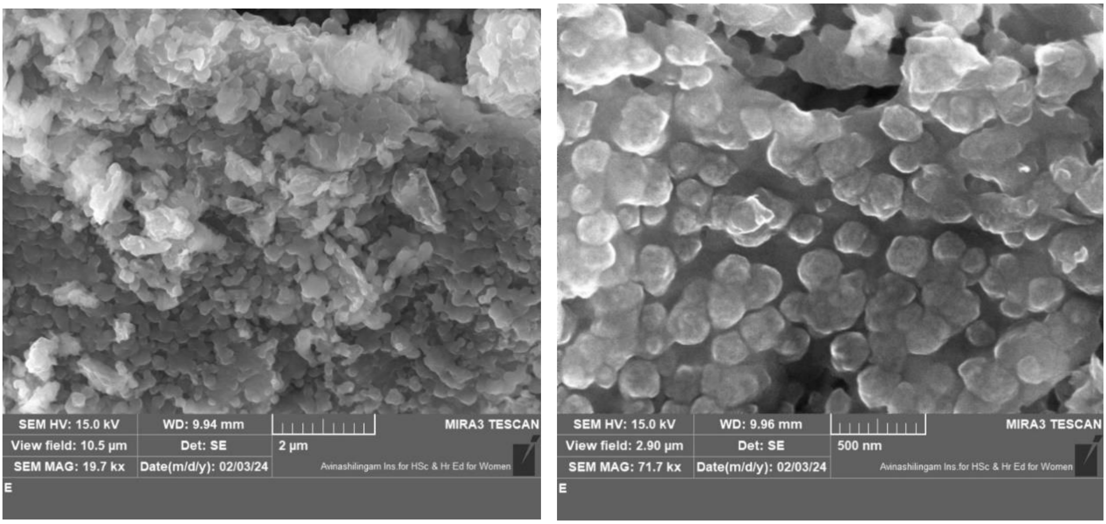


Figure 5 SEM images of eggshell capped ZnO nanoparticles

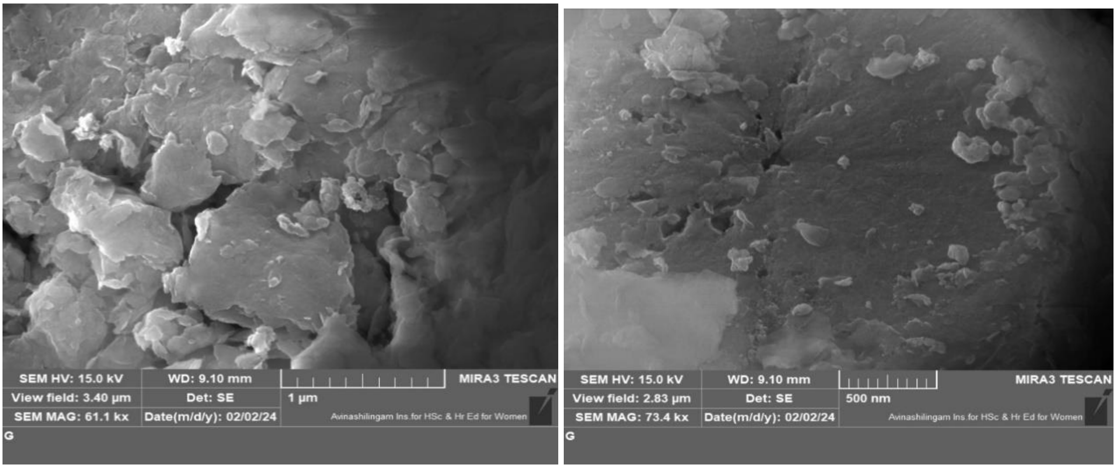


Figure 6. SEM images of ZnO nanoparticles treated with peanut husk

The SEM image (Figure 6) illustrates the ZnO nanoparticles treated with Peanut husk extract. There exists an observed heterogeneity, which is manifested as the coexistence of large, plate-like structures with rounded edges and smaller spherical structures. The observed morphology of the ZnO nanoparticles suggests an influence of the Peanut husk extract on the growth process. The presence of large, plate-like structures with rounded edges could be attributed to the higher degree interaction of ZnO particles with biomolecules in the extract [19].

However, the relatively small particle size (~21 nm) obtained from XRD analysis might be attributed to the spherical structures, which might be ZnO particles formed by lower degree of interaction with the extract. This coexistence of plate-like and spherical structures highlights the heterogeneity in the ZnO nanoparticle population. This heterogeneity underscores the potential for variations in the interaction between the extract components and the ZnO precursor during synthesis.

Notably, the image depicts a colossal, aggregated sphere-like structure encompassing both sphere and plate-like morphologies. The existence of this super-large aggregated structure suggests a very strong tendency for the ZnO nanoparticles to clump together in the presence of the Peanut husk extract.

The SEM analysis (Figure 7) reveals a unique morphology for the ZnO nanoparticles treated with orange peel extract. The treated sample exhibits a collection of large, irregular agglomerates, suggesting a strong tendency for the nanoparticles to clump together in the presence of the extract. Interestingly, a small number of isolated, irregularly shaped particles with a size of approximately 17-25 nm are also observed. The most striking feature in the SEM image is the presence of an intricate, interconnected web-like structure with a mesh size of approximately 72 nm, with branches ranging as low as 11 nm in size. Clusters of ZnO nanoparticles, varying in size, appear grafted onto this web-like structure. These grafted nanoparticles can be observed either in smaller groups, or agglomerated into larger particles with hundreds of nanometers in diameter.

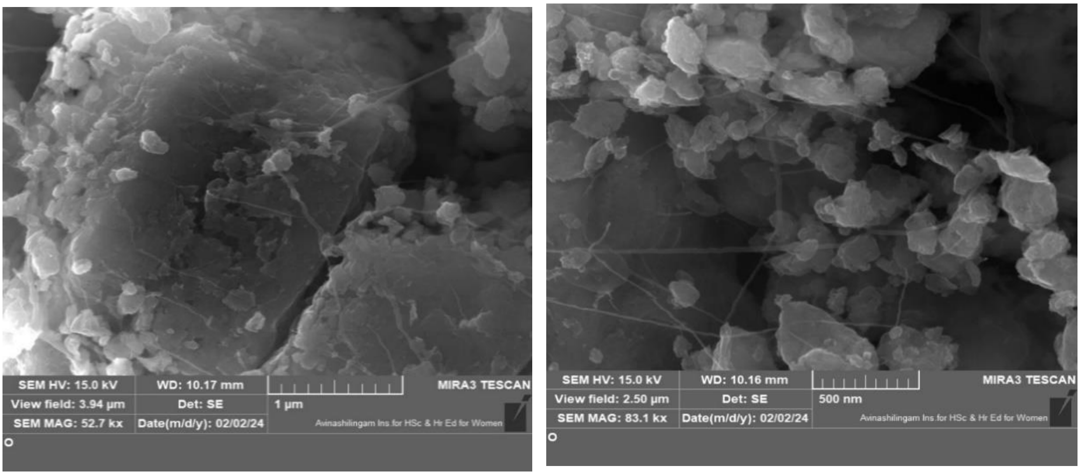


Figure 7 SEM images of ZnO nanoparticles treated with orange peel

The absence of the web-like structure in control samples, coupled with the known presence of cellulose fibers in orange peels, suggests a potential link to the extract. It's hypothesized that this intricate network might originate from fragmented cellulose fibers present in the extract. During the extraction process, these fibers could have broken down into smaller components that subsequently self-assembled into the observed web structure.

3.4 Elemental analysis

Elemental analysis of ZnO nanoparticles was performed using energy-dispersive X-ray spectroscopy (EDAX). Figure 8 presents the EDAX spectra of ZnO nanoparticles prepared from various extracts. The spectra exhibits distinct peaks at approximately 0.85 keV, 0.98 keV, 8.63 keV, and 9.7 keV, corresponding to the K and L shell emission lines of zinc (Zn), respectively. A prominent peak at 0.50 keV confirms the presence of oxygen (O) atoms. These observations strongly substantiate Zn and O as the primary elemental constituents of the ZnO nanoparticles. A minor peak observed around 0.28 keV can be attributed to the presence of carbon (C) atoms.

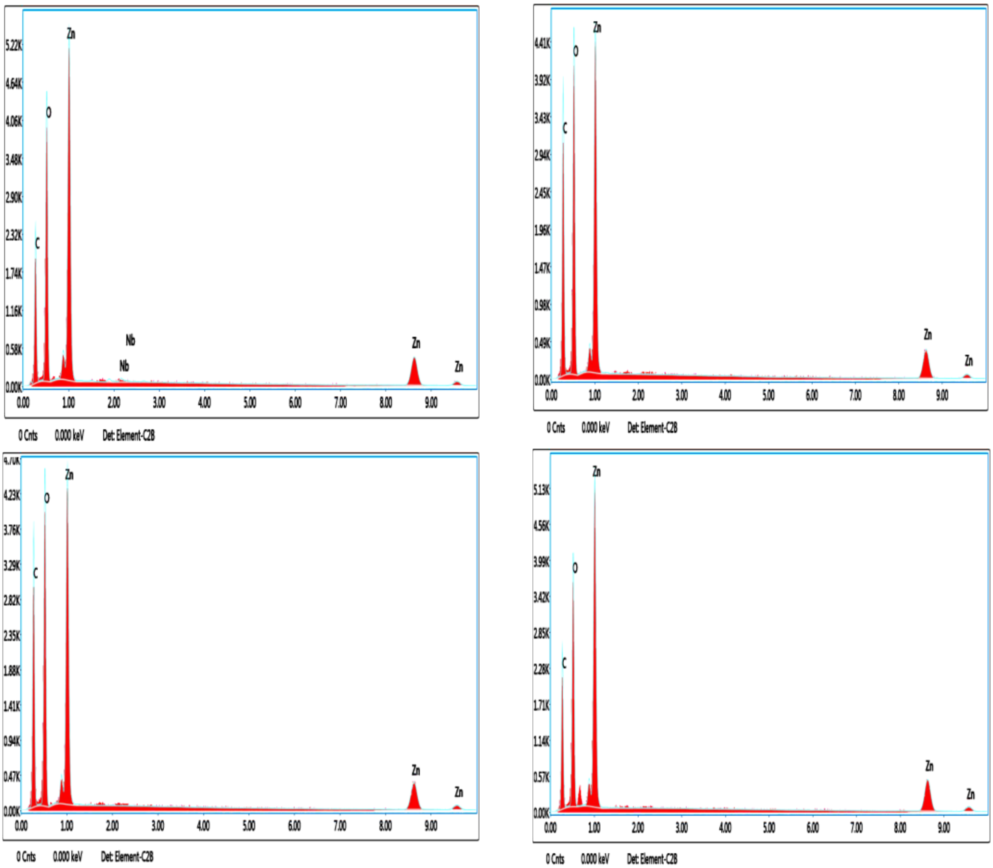


Figure 8. EDX analysis of ZnO nanoparticles prepared with various extracts

This is likely due to the residual acetate groups originating from the zinc acetate precursor employed in the synthesis [20]. However, compared to the pure ZnO, a slight increase in the weight percentage (Wt%) of carbon (C) and zinc (Zn) was observed, accompanied by a slight decrease in oxygen (O). The obtained atomic and weight percentage values of expected elements are indexed in table 1.

Table 1. Atomic and weight percentage of zinc oxide nanoparticles

SAMPLE	ELEMENT	WEIGHT %	ATOMIC %
Pure ZnO	C K	25.33	46.74
	O K	26.70	36.99
	Zn K	47.97	16.27
ZnO with Egg shell extract	C K	32.99	54.03
	O K	27.78	34.16
	Zn K	39.23	11.81
ZnO with Orange Peel extract	C K	25.97	49.31
	O K	23.09	32.92
	Zn K	50.94	17.77
ZnO with Peanut husk extract	C K	32.87	53.72
	O K	28.19	34.59
	Zn K	38.94	11.69

4. Conclusion

This work reports the successful synthesis of zinc oxide nanoparticles utilizing bio-waste extracts from eggshells, peanut husks, and orange peels via co-precipitation technique. The influence of these bio-waste extracts on the properties of the synthesized ZnO nanoparticles was systematically investigated using various characterization techniques, including XRD, FT-IR, and FESEM & EDAX.

- X-ray diffraction (XRD) analysis confirmed the presence of the hexagonal wurtzite crystalline phase of ZnO in all the bio-waste extracted samples. Interestingly, the sample treated with eggshells additionally showed the presence of ovoalbumin in the lattice sites of ZnO.
- ZnO nanostructures prepared from orange peel extract strongly uplift the intensity of the triplet peaks (100), (002), and (101) whereas those prepared from eggshell and peanut husk diminish the intensity of the triplet peaks because of the development of a new phase.
- The presence of ovalbumin and ovotransferrin in the eggshell extracted ZnO nanoparticles robustly proliferate the intensity of vibration bands on the surface while the other two extracts diminish the vibration intensity.

- SEM analysis revealed the characteristic hexagonal wurtzite structure of ZnO nanoparticles. However, the images also displayed evidence of irregular agglomeration. Notably, the SEM image of ZnO nanoparticles prepared with orange peel extract exhibited a unique interconnected web-like structure with branches and pineapple fruit-like structure.
- It further demonstrated significant morphological changes in the ZnO nanoparticles induced by the bio-waste extract incorporation during synthesis.
- EDAX analysis suggested a potential interaction between the bio-waste extracts and the ZnO nanoparticles. The presence of a significant amount of carbon-containing organic material on the surface of the nanoparticles implies close attachment or adsorption of the bio-molecules during the synthesis process.

These observations highlight the influence of bio-waste extract incorporation on the morphology of ZnO nanoparticles. Such morphological variations can be significantly utilizable for the applications of the resulting ZnO nanomaterials, especially for antimicrobials.

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Conflict of interest: The Authors have no conflicts of interest to declare that they are relevant to the content of this article.