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Green fabrication of Lanthanum doped Zinc Oxide Nanoparticles (La-ZnONPs) via Pineapple extract: Effects of Calcination Temperature on Photocatalytic Properties

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Abstract. Disposal of pineapple waste is one of the main concern towards sustainability of an environment. In this work, the usage of pineapple waste in the synthesis of Zinc oxide nanoparticles (ZnONPs) could assist to reduce the waste and give us chance to utilize the waste in a useful manner. ZnONPs were produced via green approach employing the extract derived from pineapple waste peels, serving as reducing and stabilizing agent. This article demonstrates the effect of calcination temperatures on the La as a dopant for ZnONPs fabrication. Doping of the materials facilitated the nanoparticles to increase their stability by incorporation of some rare earth metals such as La. The materials (La-ZnONPs) with different calcination temperature were fabricated by co-precipitation method and thoroughly characterized by various spectroscopic techniques like Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy – Energy Dispersive X-ray (SEM-EDX), and UV-Vis. Morphologically evidence given in SEM images that hexagonal shape converted into unique tiny flower images as the dopant added and calcination temperature increased wherein a gradual decrease from 27.83 to 23.02nm in crystallite size was noted with correspondence of rise at calcination temperature in doped La-ZnONPs. The lowest bandgap energy (3.11) with highest surface area along with the lowest crystallite size was obtained for La-ZnONPs calcined at a temperature of 600°C.

1. Introduction

The escalating production of pineapple in the current economy has inadvertently led to a substantial increase in pineapple waste. This surplus waste poses a significant environmental concern and economic challenge due to the lack of efficient disposal methods [1]. The disposal issue not only contributes to environmental degradation but also results in economic losses for pineapple producers. Developing sustainable solutions for the management and utilization of pineapple waste is imperative to mitigate its adverse environmental impact and harness its potential value in various industries. A method to utilize this biodegradable waste or biomass

involves employing it as a raw material for the formation of nanoparticles through environmentally friendly synthesis processes [2]. It serves as a renewable and heterogeneous source that can be chemically integrated, presenting a viable choice for producing desired products due to its ready availability, affordability, sustainability, and common abundance. Pineapple peels, rich in phytochemical constituents, are employed for extracting bioactive substances such as ZnONPs. These phytochemicals played a role as a capping agent to resist the agglomeration of nanoparticles [3].

ZnONPs have gained attention as highly effective semiconductor in different applications such as photodegradation of wastewater due to their affordability, durability, and impressive photocatalytic performance [4]. In order to improve the performance of ZnONPs, researchers have investigated the incorporation of other metals, like lanthanum (La), silver (Ag) and copper (Cu) into ZnO that act as dopant. This technique has been found to enhance efficiency by generating new energy levels within the bandgap of ZnO [5]. Effectiveness of ZnONPs with dopant plays an important role in the photocatalysis application as well as in various applications to resolve the issues of environmental contamination degradation. The concentration of dopant plays a vital role in determining the efficiency, with an optimal value that should not be exceeded. The efficiency can be affected by several factors, such as nanoparticle characteristics and synthesis methods [6].

Driven by the promise of La-doped ZnO nanoparticles, it is desired to seek to make a valuable contribution to the field through this research work by synthesizing these nanoparticles using pineapple waste as an environmentally friendly precursor. Doping with variation in parameters is one of the main research gap to find the optimum value for various parameter with innovation of surface morphology and smallest bandgap. This study exhibit dispersed nanoflower morphology of La-ZnONPs which is a source of high active surface area and shown the decrease in bandgap with the increase of calcination temperature range. This cutting-edge approach is in line with the overall goal of investigating eco-friendly techniques for nanoparticle fabrication [7,8].

2. Experimental

2.1 Materials and reagents:

Pineapple peels used in this study were collected from local market located in Gambang, Pahang. Zinc acetate dihydrate $Zn(CH_3COO)_2$, lanthanum nitrate $(La(NO_3)_2.6H_2O)$ and sodium hydroxide (NaOH) were ordered from Sigma Aldrich, Distilled water and deionized water were taken for UMPSA laboratory.

2.2 Extraction of Pineapple Waste

The pineapple peels rinsed with deionized water, followed by oven-dried at temperature of 60°C for 4h. The resulting dried sample was then processed into a coarse powder using a heavy-duty grinder. Subsequently, 10g of the powder was added to boil in a beaker containing 100mL of deionized water at temperature of 70°C to 80°C for 30 minutes, resulting in the formation of a pineapple extract solution. After attaining a room temperature, the solution filtered via using filter paper provided a clear brown yellowish filtrate, which was subsequently reserved in a chiller at 4°C for future use.

2.3 Fabrication of La doped ZnONPs

ZnONPs were fabricated by a simple Co-precipitation method as described in reference [9]. In a 500mL beaker, a mixture of 50mL of pineapple extract and 10mL of deionized water were mixed. To this solution, 4g of zinc acetate dihydrate was added and pH was adjusted to 11-12 by incorporating 0.1M NaOH into the solution. Subsequently, 0.04g of lanthanum nitrate was introduced. The solution underwent stirring for 1 hour at a temperature range of 40°C to 50°C. After cooling to room temperature, centrifugation of suspension at 4000 rpm for 10 minutes ensued. The resulting solution was dried for 6 hours at 120°C, yielding a white precipitate. The precipitate was ground using mortar and pestle to produce finer powder. Then, the resultant powder was calcined at 300°C. Range of calcination temperature increased within the range of 600°C due to some reported work [10] based on co-precipitation method but the time duration increased to efficient the calcination process. The process was reiterated with calcination temperatures of 400°C and 600°C.

2.4 Characterization of ZnONPs

The La doped ZnONPs produced were characterized by using FTIR, XRD, SEM – EDX and UV-Vis spectroscopy. The FTIR method utilized the absorption of electromagnetic radiation in the mid-infrared range, approximately 4000 –400 cm^{-1}, to characterize the adsorption patterns to identify the functional groups present in both undoped and La-doped ZnONPs. XRD observed to indicate a well-defined crystalline nature of ZnONPs, while broadening at the base of the peaks signified the size of the crystalline structure. SEM-EDX analysis was done by using (JSM-IT200InTouchScope™) to analyse the morphological forms and elemental composition of the by-product. The powders were sputter-coated with gold to prevent charging during analysis process. UV-Vis spectroscopy employed to quantify the extent of each chemical compound to absorb light. This is done by comparing the light transmitted through a sample with reference sample, commonly referred to as a blank. Before the analysis, the wavelength was adjusted to 800nm.

3. Results and discussion

3.1 FTIR analysis of undoped ZnONPs and doped La-ZnONPs

Composition of the functional groups of the synthesized undoped and doped La-ZnONPs that were calcinated at temperatures 300°C, 400°C and 600°C were determined using FTIR spectroscopy captured within the range of 400 to 4000 cm^{-1}. Fig 1 illustrates the FTIR spectra of undoped ZnONPs and doped La-ZnONPs, with different calcination temperatures. The peaks observed in all the FTIR spectra between 400 and 600 cm^{-1} provide information regarding the Zn-O-Zn and La-O-Zn interactions [11]. As depicted at spectrum (c), it was seen an OH bond around 35000 cm^{-1}. This was due to the OH bonding from the pineapple waste extract. The OH bond weakens as the calcination temperature increases. The attributed peaks in pineapple extract shown at 3264 cm^{-1} and 1636 cm^{-1} for O-H stretching and C=O Stretching respectively [4].

The FTIR spectra depicted in Fig. 1 illustrate that the peaks corresponding to C=O and O-H vibrational modes gradually decrease in intensity in samples subjected to high-temperature annealing. The broad O-H peaks tend to become narrower as the calcination temperature rises, owing to the increased presence of O-H resulting from the reaction of NaOH with $Zn(CH_3COO)_2{\cdot}2H_2O$ at elevated temperatures. The sharpening of the zinc oxide peak and its smoother appearance indicate an augmentation in the crystallinity of nanoparticles as the calcination temperature is raised. Previous investigations [12] have identified the ZnO peak within the 400–600 cm^{-1} range. The slight shift in the peak observed in this current study (ranging

from 400 to 600 cm^{-1}) could be linked to variations in particle size relative to different calcination temperatures. Consequently, fluctuations in particle size lead to shifts in the peaks. These findings find further support in the XRD outcomes.

The pineapple waste extract comprised diverse phytochemicals classes such as polyphenols, phenolic compounds with trace amounts of flavonoids [3]. These bioorganic classes contain hydroxyl groups (OH), carbonyl (C = O), aromatic (C = C), and aliphatic (C-H), which shows the outcome in feasible biosynthesis of ZnONPs. This observation supports the notion that the presence of phenols, polyphenols, and primary amines in the plant extract may be responsible for capping and stabilizing the NPs. The polyphenols derived from pineapple waste generate these functional groups, playing the role in reduction and stabilization of nanoparticles.

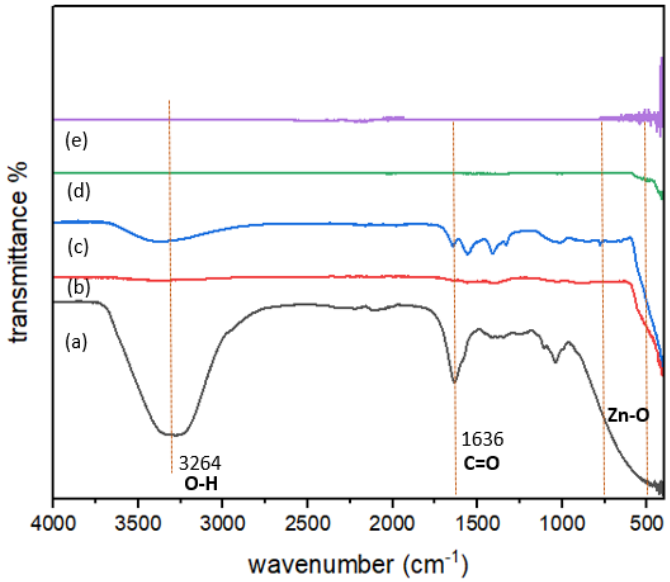

Figure 1 FTIR spectroscopy of (a) Pineapple extract, (b) undoped ZnONPs and doped La- ZnONPs at different calcination temperatures at (c) 300°C and (d) 400°C and (e) 600°C.

3.2 SEM – EDX micrographs of undoped an doped La-ZnONPs

Figure 2 depicts the SEM-EDX examination of both undoped ZnONPs and La-doped ZnONPs that have been exposed to different calcination temperatures of 300°C, 400°C, and 600°C, showcasing a hexagonal structure. The particles exhibited agglomeration, which resulted from the polarity and electrostatic attraction of ZnONPs [12]. From Figure 2, distinct changes in particle morphology were observed. In figures 2b, 2c, and 2d, the La percentages were noted to be 2.84, 2.81, and 2.27, sequentially. This decrease in La % was in contrast with the added La^{3+} concentrations while getting their hydroxide precursors. Loss of La is during heating the precursors during calcination phase[13].

It was proven that calcination temperature poses increment gradually, and particles exhibited more crystallized and less agglomerated structures with dispersed flower shape. These morphologies have significant implications for their photocatalytic performance where higher crystallinity typically correlates with improved photocatalytic activity as it has better morphological properties as a photocatalyst. The composition of pure ZnONPs and doped La-ZnONPs were successfully determined by EDX analysis. The spectrum of ZnONPs (Figure 2a)

indicates the presence of Zn and O, aligning with the formation of ZnO. Figures 2b, 2c and 2d also revealed that La was successfully doped into the ZnONPs.

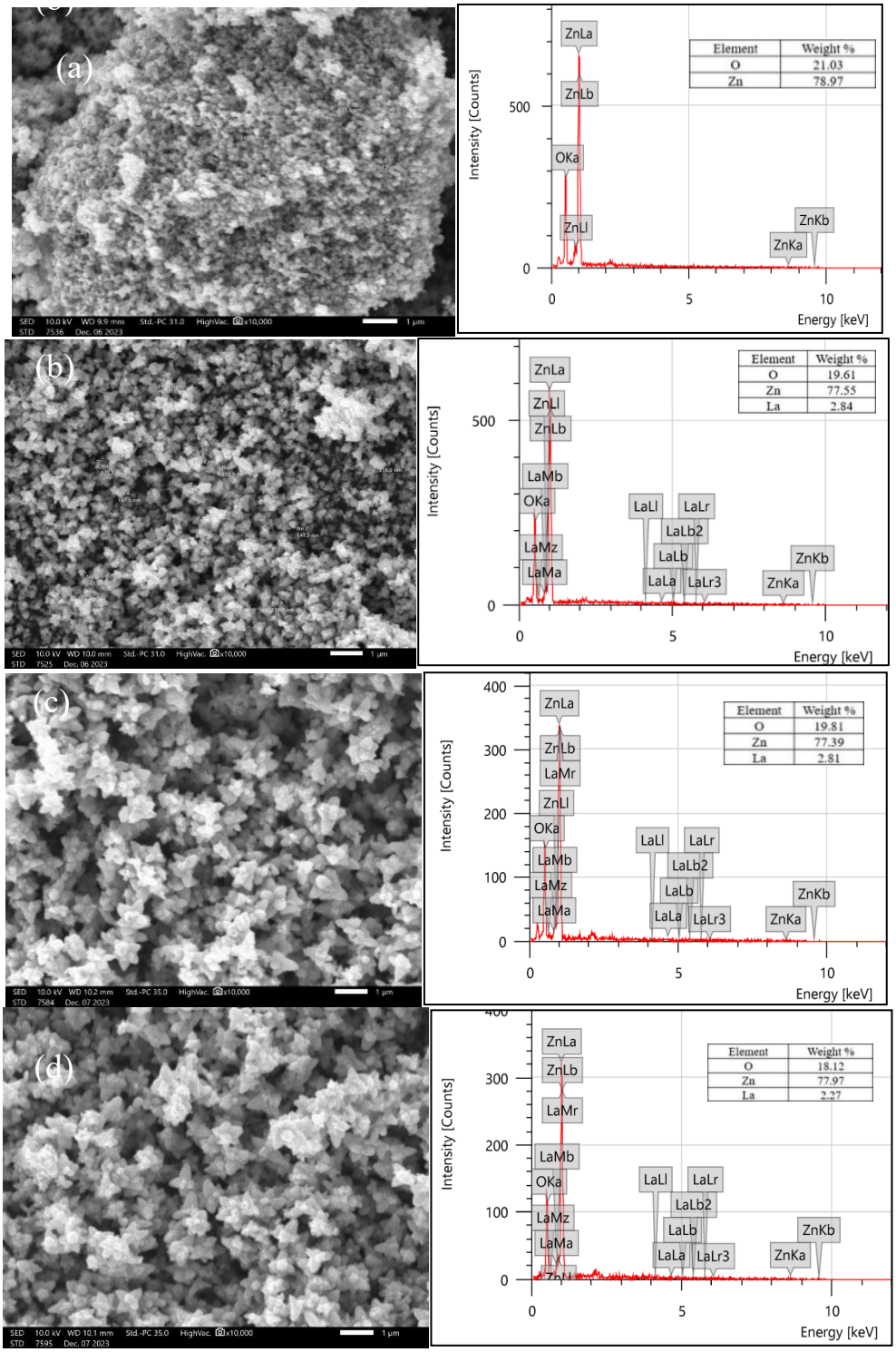

Figure 2 SEM-EDX analysis of undoped ZnONPs and doped La-ZnONPs at calcination temperatures of (a) undoped ZnO NPs, (b) 300°C, (c) 400°C and (d) 600°C.

3.3 X-ray Diffraction analysis of undoped ZnONPs and doped La-ZnONPs

The X-ray diffraction patterns depicted in Figure 3a for undoped ZnONPs reveal peaks at 2θ angles of 31.7736, 34.4219, 36.2578, 47.5442, 56.6064, 62.8623, 66.3941, 67.3941, 69.0985, 72.5741 and 76.9761 corresponding to the (100), (002), (101), (102), (110), (103), (002), (112), (201),(004) and (202) cross-lattice planes of ZnO, respectively. Hexagonal geometry was verified and the peaks seem to be consistent with the reference data [9]. The peak patterns of the as fabricated ZnONPs are observed, corresponding to the data in JCPDS Card No. 36–1451 [11], reflecting crystalline ZnONPs formation. Figure 3 shows the XRD spectra of both doped and undoped ZnONPs with the angle of 2θ ranging from 10˚ to 80˚.

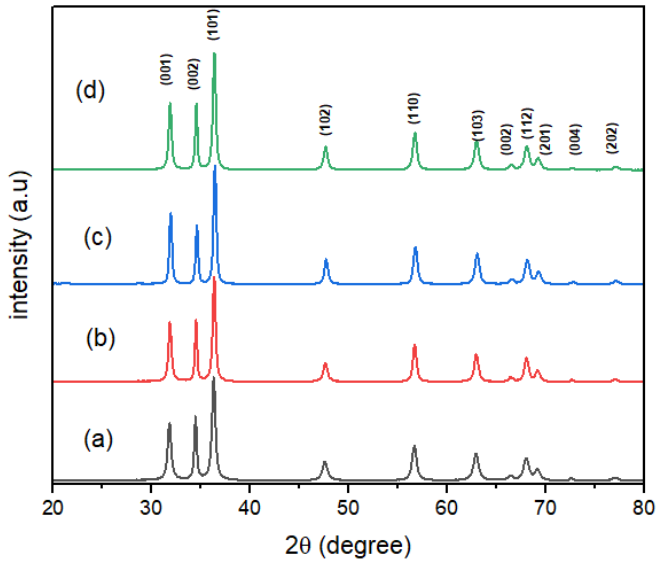

Figure 3 XRD patterns of undoped ZnO and La doped ZnO NPs at calcination temperatures of (a) undoped ZnO NPs, (b) 300°C, (c) 400°C and (d) 600°C

Evidently, the introduction of La as a dopant has no impact on crystal structure of ZnO, as the distinctive diffraction peaks of La-doped ZnO are observed at 2θ, angles 31.82˚, 34.47˚, 36.31˚, 47.59˚, 56.65˚, 62.90˚, 66.42˚, 67.99˚, 69.13˚, 72.60˚ and 77.00˚ [5]. It also displays the narrowing of peaks as the calcination temperatures increase. The alterations observed in particle dimensions and lattice parameters within La-doped ZnONPs can be ascribed to the impeded diffusion and subsequent growth of ZnO crystalline grains. This obstruction arises from the distinct ionic radii of 0.74 Å for Zn^{2+} and 1.26 Å for La^{3+}. The distinctive dimensional characteristics of La-doped ZnO materials confer notable advantages concerning their photocatalytic efficiency. The mean crystallite size D was determined utilizing Scherrer's Equation 1, as delineated below.

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad \text{-------- Equation 1}$$

Here, D,λ, β and θ are the average crystal size in nm, wavelength, Full width at half maximum (FWHM) of the XRD peak in radians and the maximum of Bragg diffraction peak (in radians) respectively.

The average crystallite size of undoped ZnONPs and doped La-ZnONPs at different calcination temperatures were found to be 27.83nm, 25.67nm, 23.59nm and 23.02 nm respectively shown in Table 1. As the undoped ZnONPs has higher crystallite size as compared to doped La-ZnONPs due

to ionic radius difference between La^{3+} and Zn^{2+}. The fluctuation in ionic radius is an important factor in determining the probability of the dopant atom residing in the interstitial site of the crystal lattice or displacing the host atom.

The decreasing of crystallite size observed herein was instigated by varied ionic radius between La^{3+} (1.16 Å) and Zn^{2+} (0.74 Å) [14]. La^{3+} effectively substitutes Zn^{2+} within the crystal lattice, leading to lattice distortion. Doping accelerates the aggregation as reported in previous research [15]. Specific amount of energy accumulated to support the substitution process and the chemical bonds between La-ZnONPs could easily happen due to increasing calcination temperature because calcination already suppressed the growth of crystal nucleus and give sites to La^{3+} to fit into the active surface lattice of ZnONPs [16]. The crystallite size depicted in Table 1 shows that the decrease of crystallite size with the increase of calcination temperature on the doped La-ZnONPs. This is due to the electrostatic repulsion force between ZnONPs and pineapple extract constituents such a polyphenols[17].

3.4 Ultraviolet-visible spectroscopy (UV-Vis) of undoped and doped La-ZnONPs

UV–visible absorption spectroscopy was employed to investigate an optical characteristics of undoped and doped ZnONPs with La at various calcination temperatures. As depicted in Figure 4, both pure ZnONPs and La-ZnONPs exhibited elevated absorbance in the ultraviolet range (300–400 nm). Notably, in the visible range (400–800 nm), the absorbance of La-doped ZnO samples demonstrated enhancement compared to undoped ZnO.

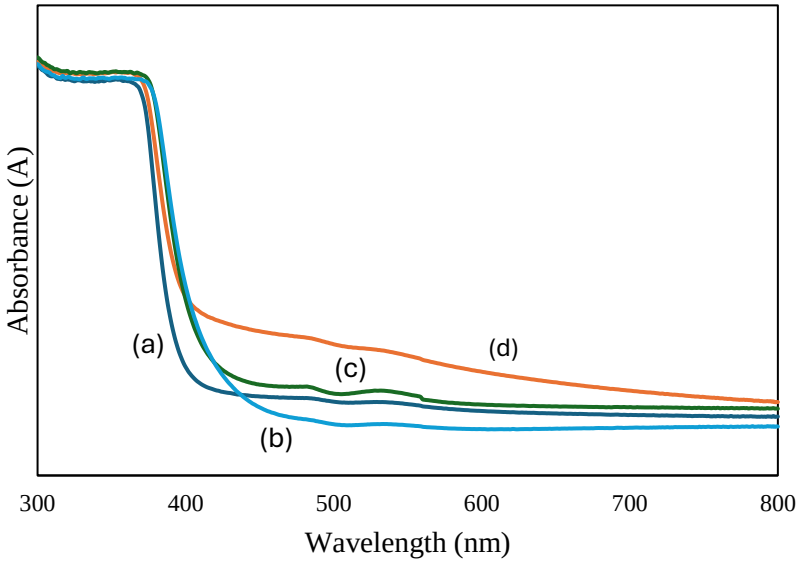

Figure 4 UV-Vis spectra of undoped ZnONPs and La-ZnONPs at calcination temperatures of (a) undoped ZnO NPs, (b) 600°C, (c) 400°C and (d) 300°C.

ZnONPs bandgap calculated by plotting the tauc plot between αhv^2 and energy (hv) curve as depicted in Figure 5. The fabricated undoped ZnONPs has bandgap of 3.23eV that shows decrease in bandgap as compared to other plants such as *Garcinia Cambogia* [12]. Shorter range of band gap permits the doped La-ZnONPs as increase in calcination temperature to yield more photons with more radicals that required for photocatalysis mechanism. The Eg values for undoped ZnONPs, and doped La-ZnONPs at 300°C, 400°C and 600°C were found to be 3.23, 3.18, 3.15 and 3.11 eV respectively. Hence, elevated calcination temperature within the material composition led to a reduction in the band gap energy, thereby promoting potential photocatalytic performance

under sunlight. The alteration in the band gap values between produced undoped and doped La-ZnONPs is attributed to discrepancies in the crystal structure of the nanoparticles.

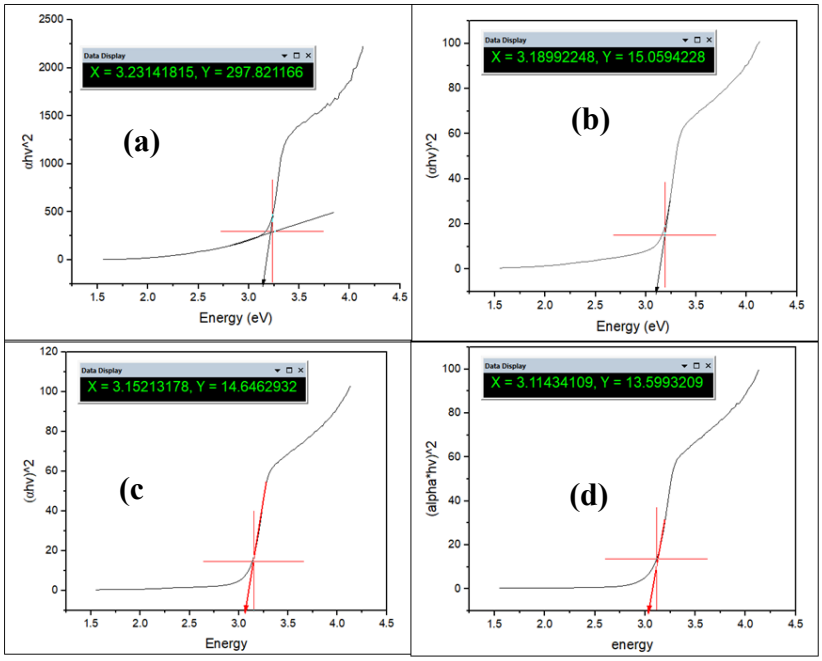

Figure 5 Tauc plot of fabricated (a) undoped ZnONPs and doped La-ZnONPs (b) 300°C, (c) 400°C and (d) 600°C.

Table 1 Average crystallite size of undoped ZnONPs and doped La-ZnONPs.

Sample	Average Crystallite Size (nm)	Bandgap
Undoped ZnONPs	27.83 nm	3.23
La doped ZnONPs (300°C)	25.67 nm	3.18
La doped ZnONPs (400°C)	23.59 nm	3.15
La doped ZnONPs (600°C)	nm	3.11

4.Conclusion

Undoped and La-doped ZnONPs were successfully produced through a green synthesis technique utilizing pineapple waste extract as a phytochemical reducing agent as indicated by XRD, SEM-EDX, FTIR and UV-Vis results. Based on all characterization results, as the calcination temperature elevated the crystallite size and band gap of the synthesized ZnONPs are decreasing. SEM morphology of the La-ZnONPs calcinated at 600°C revealed less agglomerations compared to those synthesized at different calcination temperatures. Even, the morphology become clearer as the calcination temperature increased to 600°C. Larger crystals, with a more developed crystal lattice, tend to have fewer surface defects and electron-hole recombination, potentially leading to more efficient photocatalytic activity. Supporting these observations, the XRD spectrum indicates the narrowest peaks for La-doped ZnO nanoparticles calcinated at 600°C. No doubt, the undoped shows exceptional result but the doping and increasing in calcination temperature played an

important role to fabricate efficient nanoparticles. In summary, the increased calcination temperatures in synthesizing La-doped ZnO nanoparticles indeed bring about significant alterations in their photocatalytic properties and efficiency. Therefore, there is further need of analyze the parameters with various values to achieve alternative values of optimum calcination temperature for better testing the photocatalytic performance of the synthesized nanoparticles in real-world applications.

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