Green synthesis of ZnO nanoparticles by pineapple peel extract from various alkali sources

Arrak Klinbumrung\textsuperscript{1,2}, Rattanaphorn Panya\textsuperscript{3}, Apinya Pung-Ngama\textsuperscript{4}, Pitak Nasomjai\textsuperscript{5}, Jumnong Saowalakmeka\textsuperscript{4} and Reungruthai Sirirak\textsuperscript{5,6}

\textsuperscript{1}School of Science, University of Phayao, Phayao, Thailand; \textsuperscript{2}Unit of Excellence on Advanced Nanomaterials, University of Phayao, Phayao, Thailand

\section*{ABSTRACT}
Zinc oxide nanoparticles (ZnO NPs) are concerned as potential materials due to their wide-ranging applications. The green synthesis of ZnO NPs using plant extract as capping agent has been attracted much of interest of researchers. Pineapple peel wastes are abundance in Thailand and its extract contained high levels of phytochemical compounds (flavonoids and their derivatives). In this study, pineapple extract was used as a capping agent in ZnO NP synthesis, and KOH and a lye solution were used as reducing agents for comparison. The XRD patterns exhibit pure-phase ZnO with high crystallinity. The averages of the most petite crystalline sizes obtained from the Scherrer equation calculation of the prepared ZnO powder were 64.61 and 65.41 nm for KOH solution and lye use, respectively. Fourier transform infrared (FTIR) spectroscopy confirmed the presence of ZnO particles and pineapple extract residue in the as-received powder. Scanning electron microscope (SEM) images and transmission electron microscope (TEM) images showed the nano-size of the synthesized particles. The flower-like ZnO-NPs from a 0.06 M zinc precursor and KOH solution exhibited fascinating optical properties. Finally, all the results showed that lye from wood ash could be applied in ZnO nanoparticle synthesis using pineapple peel extract.

\section*{ARTICLE HISTORY}
Received 15 March 2022
Accepted 19 September 2022

\section*{KEYWORDS}
Zinc oxide nanoparticles; green chemistry; alkaline source; pineapple peel extract; phase analysis

\section*{1. Introduction}
Zinc oxide (ZnO) nanoparticles are attracting great interest because they are inexpensive to produce, safe, and easy to prepare [1]. ZnO nanoparticles exhibit enormous semiconducting properties because of their large bandgap (3.37 eV); they also display high catalytic [2], optic [3], anti-inflammatory [4], wound-healing [5], and UV-filtering properties [6].

Physical and chemical processes dominate the synthesis of ZnO nanoparticles. The physical processes concerned require high vacuum and energy consumption, while the chemical processes are environmentally unfriendly. Therefore, the green synthesis approach is gaining increasing attention today as an environment-friendly, cost-effective, and safe alternative. The nanoparticle green synthesis method is an approach to synthesizing nanoparticles using extractions from plants, bacteria, fungi, algae, etc. These plant extracts make excellent phytochemical sources due to the presence of different classes of phytochemicals such as polyphenols, terpenoids, flavonoid alkaloids, and sugar that act as both reducing agents and capping or stabilization agents. Numerous parts of the plants, including the roots, leaves, stems, seeds, fruits, and peels, have also been applied to ZnO nanoparticle synthesis [7–12]. The current Sustainable Development Goals (SDGs) are concerned with economic growth and environmental balance; making the use of fruit peel biowaste is an attractive target. There are a few reports on the use of fruit peel biowaste as a phytochemical source examples include the use of dragon fruit (Hylocereus polyrhizus) peel [13], Garcinia mangostana pericarp [14], Citrus sinensis (orange), Citrus paradisi (grapefruit) and Citrus aurantifolia (lemon) [15].

Pineapple (Ananas cosmosus) is the popular fruit that is most widely planted in Thailand. Countless tons of pineapple waste are generated each year, creating disposal problems due to the fruits wide range of applications in the food industry, such as in beverages, jams, purees, and pastes. The present phytochemicals such as total phenolic and alkaloid content in dried pineapple peel [16], wet pineapple peel [17], and pineapple slice [18] extracts were reported. Subsequently, the pineapple peel extract was used and studied with respect to ZnO NPs synthesis [19,20]. Nevertheless, the resulting green synthesis of ZnO nanoparticles was not exactly a green method, because sodium hydroxide (NaOH) or potassium hydroxide (KOH) pellets or solution were still employed as the alkali source and reducing agent in the reaction. Traditionally, lye is an alkaline liquid obtained by leaching wood ash with water. Lye most commonly refers to...
metal hydroxides such as sodium hydroxide or potassium hydroxide, which are highly soluble in water to produce basic caustic solutions. The major elements of wood ash are calcium (7–33%), potassium (3–4%), magnesium (1–2%), manganese (0.3–1.3%), phosphorus (0.3–1.4%), and sodium (0.2–0.5%) [21]. Moreover, the synthesis of ZnO nanoparticles from pineapple peel waste using lye from wood ash has not been reported previously. Therefore, in this work, the lye from wood ash and KOH solution was used as a reducing agent in the green synthesis of ZnO nanoparticles with pineapple peel extract acting as the capping agent. The ZnO NPs prepared from the two alkaline sources were investigated by X-ray diffraction analysis, scanning electron microscopy, and transmission electron microscopy for physical properties. Fourier transform infrared spectroscopy was employed to confirm the presence of pineapple peel extract and the existence of ZnO in the synthesized NPs.

2. Materials and methods

2.1. Materials

Analytical grade chemicals were used in the green synthesis of ZnO nanoparticles. Zinc nitrate hexahydrate (Zn(NO₃)₂ · 6H₂O, 98% purity) was purchased from Millipore Sigma (USA) and used as a precursor to synthesize ZnO nanoparticles. The “Phulae” pineapple cultivars (Ananas comosus L. Merr) were planted, harvested, and sold by the Agri Coffee Pavilion shop, The School of Agriculture and Natural Resources, at the University of Phayao. The pineapple peels were collected from October to November 2020. Potassium hydroxide (KOH) pellets were purchased from Millipore Sigma (USA) and a reducing agent for comparison. Wood ash was collected from a dried longan factory in Lamphun province, Thailand. De-ionized (DI) water and 95% ethanol were used in the synthesis or solution preparation.

2.2. Methods

In this study, the procedures were divided into three parts, as follows:

2.2.1. Preparation of pineapple extract solution

The fresh pineapple peels were washed with water three times to remove dirt, then cut into pieces with a knife and crushed and mixed with a blender. The resulting 600 g crushed pineapple peel was soaked and boiled in 3 L of the DI water for 60 minutes, and the DI water was then drained three times. The received crushed pineapple peel was soaked in 95% ethanol in a 1:3 ratio for 24 hours at ambient temperature. The extracts were filtered using Whatman No. 1 filter paper and the filtrates were then concentrated by evaporation using a rotary evaporator. The filtered solution was collected and stored in a clean, dry beaker at 4 °C for further use.

2.2.2. Preparation of the ZnO NPs

The ZnO nanoparticles were synthesized using 2 different alkali sources, 5 M KOH solution and lye. For KOH use, the zinc precursor was prepared by combining 0.02, 0.04, 0.06, 0.08, and 0.1 M in 10 ml of the prepared-pineapple peel extract to achieve optimized conditions. The 0.06 M zinc nitrate solution was prepared in 10 ml of the prepared-pineapple peel extract for lye employment. The pH of the solution was maintained at around pH 12. The solution was refluxed at boiling temperature continuously for 1 hour until a white precipitate was observed. The precipitate was centrifuged at 15,000 rpm for 2 minutes and washed several times with distilled water and then with 95% ethanol. The precipitate was further dried in an oven at 80 °C overnight.

2.2.3. Characterization

2.2.3.1. Total phenolic content analysis

The total phenolic content of the crude pineapple peel extract (PPE) was determined using the method described by Singleton [22] with some modifications. Gallic acid was used as a standard calibration curve. Briefly, into 0.20 mL of extract (1 mg/mL) was added 1.00 mL Folin–Ciocalteu reagent (10-fold dilution in deionized water), mixed thoroughly, and kept in the dark for 5 min. Then, 0.40 mL of 7.5% (w/v) sodium carbonate solution was added, mixed well, and incubated in the dark for 60 min. The absorbance was measured at 765 nm (Thermo Fisher Scientific UV-Vis Spectrophotometer) using deionized water as a blank. The above procedure was conducted in triplicate. TPC was calculated from the linear equation of a gallic acid standard curve and expressed as milligrams of gallic acid equivalent (GAE) per 1 g of dry weight (mg GAE/g).

2.2.3.2. Total carbohydrate content

A total sugar assay was performed according to the method of Nielsen [23] with minor modifications. Glucose was used to produce a calibration curve. A series of test tubes containing 0, 10, 20, 40, 60, 80 µg/mL of standard solution in a total volume of 2 mL were filled with glucose stock solution (100 mg/L). To each test tube, 0.05 mL of 80%w/v phenol solution was added and shaken well. A direct stream of 5 mL concentrated sulfuric acid was then added and shaken well. The tubes were set aside for 10 min and kept in a water bath at 25°C for 20 min. Absorbance was read at 490 nm using DI as a blank. The same procedure was repeated with PPE before and after ZnO NP synthesis at a concentration of 5 mg/mL each time.
2.2.3.3. Total flavonoid content. Total flavonoid content (TFC) was determined by the aluminum chloride colorimetric method as reported by Woisky and Salatino [24] with minor modifications. Quercetin was used to produce a standard calibration curve. A series of 0, 20, 40, 60, 80 and 100 mg/mL samples of quercetin standard solution were prepared from 100 mg/L quercetin stock solution. Into 0.5 mL of each standard solution was entered 1.5 mL of 95% ethanol, 0.1 mL of 10% aluminum chloride, 0.1 mL of 1 M potassium acetate, and 2.8 mL of distilled water. After incubation at room temperature for 30 min, the absorbance was read at 415 nm using ethanol as a blank. The actions were conducted in triplicate. The above procedure was repeated with PPE before and after production of the ZnO NP synthesis solutions (5 mg/mL). TFC was calculated from the linear equation of the quercetin standard curve and expressed as milligrams of quercetin equivalents (QUE) per 1 g of dry-weight crude extract (mg QUE/g).

2.2.3.4. Material characterization. The functional groups of the synthesized-ZnO particles and the residue of the extract were characterized by Fourier transform infrared (FTIR) spectroscopy in the frequency range from 400 to 4000 cm\(^{-1}\) using a Thermo Nicolet Nexus FTIR spectrophotometer (iD5-ATR, USA). X-ray diffraction (XRD) patterns were collected by Rigaku X-ray diffractometer (MiniFlex500, Japan). Data were recorded in the 2θ range from 20° to 80° (diffraction angle 2θ) using Cu-Kα radiation (\(\lambda = 1.5418\) Å) generated at 30 kV and 30 mA. The as-received ZnO particles were investigated by scanning electron microscope (SEM) to obtain morphological information. The entire sample was coated with gold before SEM analysis. A TEM micrograph was obtained using a JEM 2010 (JEOL) by dropping a droplet of sonicated dispersion of the sample directly onto a carbon-coated copper grid that was subsequently dried. Finally, the optical properties of the as-received ZnO NPs were examined by diffused reflectance spectroscopy (DRS).

3. Results and discussion

Bioorganic molecules in the crude pineapple peel extract (PPE) before and after ZnO NPs synthesis were assessed. Total phenolic content (TPC) was determined based on the method described by Singleton [22]. The gallic acid standard curve is shown in Figure 1. The TPC values for the PPE before and after ZnO NP synthesis were determined to be 3.71 and 0.3 mgGAE/g of the crude extract. Total carbohydrate content (TCC) was determined based on a phenol-sulfuric colorimetric assay [23] using glucose as a standard and the calibration curve is shown in Figure 2. The TCC values for the PPE before and after ZnO NPs synthesis were 1.12% and 0.33% glucose equivalent. Total flavonoid content (TFC) was determined by aluminum trichloride colorimetric assay using quercetin as standard [24] and the calibration curve is shown in Figure 3. The TFC values for PPE before and after ZnO NPs synthesis were 0.09 and 0.01 mgQUE/g of the crude extract.

The IR spectrum of PPE (Figure 4) showed a broad peak from at 3369 cm\(^{-1}\) corresponding to the hydroxyl group (OH). The peaks at 2927, 2853, and 1462 cm\(^{-1}\) correspond to aliphatic CH (CH\(_2\); CH\(_3\)), the peaks at 1604 cm\(^{-1}\) and 1514 cm\(^{-1}\) belong to the aromatic ring (C = C) and the peaks at 1030 cm\(^{-1}\) belong to the C-O group of alcohol, ether, or ester [25].
Figure 2. Quercetin standard curve for total flavonoid content assay.

Figure 3. Glucose standard curve for total carbohydrate content assay.

Figure 4. IR spectrum of the crude pineapple peel extract.
prepared ZnO powders were examined for residue of the pineapple extract by Fourier-transform infrared (FTIR) spectroscopy. The FTIR spectra of the synthesized ZnO nanoparticles with different zinc precursor concentrations and alkaline sources are displayed in Figure 5. The prominent broadband corresponding to stretching vibrations of the hydrogen bond (O-H) of phenol appears in the range of 3600–3400 cm⁻¹ in all infrared spectra. The small peaks at 2977.50 cm⁻¹ correspond to alkane C-H stretch vibrations. The bands at 1645.68 cm⁻¹ were attributed to the C = C stretching vibration of the carbon bond in the aromatic ring. The strong band located at about 897.70 cm⁻¹ is a signal of C-H bending in the aromatic ring [26]. The peaks below 400–600 cm⁻¹ are in the region known as the characteristic region of the intrinsic adsorption bands of metal oxides [27]. The strong bands located at about 559.26 cm⁻¹ and 420.41 cm⁻¹ are signals of the intrinsic adsorption bands of metal oxides corresponding to the Zn-O bond of the zinc oxide phase [28,29]. The FTIR results show the phytochemical residues from pineapple peel extract and the formation of ZnO nanoparticles.

The mechanism of ZnO-NP formation from aqueous zinc nitrate has been shown to occur via layered zinc salts through zinc nanoparticles [30], while biogenic synthesis of ZnO-NPs is not well elucidated. Two plausible mechanisms of ZnO-NP formation using zinc ion precursors via biogenic synthesis have been proposed. In both mechanisms, bioorganic molecules such as carbohydrates, phenolic compounds, and flavonoids play a crucial role in ZnO NP formation [31]. In the first mechanism, bioorganic molecules form complexes with Zn²⁺ ions, which are then under high pH conditions; these complexes then collapse to generate zinc hydrate. This pathway requires a further calcination process to obtain ZnO NPs. Another mechanism occurs via bioreduction of Zn²⁺ ions to Zn metal by bioorganic substances, followed by oxidation of metallic zinc, probably with dissolved oxygen molecules in the media to form ZnO nuclei. Bioorganic molecules act as stabilizers to prevent the ZnO NPs from agglomerating [31,32]. The PPE comprised diverse chemical entities, mainly carbohydrates and phenolic compounds with trace amounts of flavonoids. These bioorganic substances contain hydroxyl groups (OH), carbonyl (C = O), aromatic (C = C), and aliphatic (C-H) (Figure 6), which are required to facilitate the biogenic synthesis of ZnO-NPs [31–33]. These molecules donate electrons from hydroxyl groups to the Zn²⁺ ions to form metallic zinc. The metallic zinc reacts with an oxidizing substance, presumably oxygen, in the solution to form ZnO NPs, and bioorganic molecules then act as a capping agent to stabilize the resulting ZnO-NPs. The investigation of PPE before and after ZnO NP synthesis showed that the carbohydrate and phenolic contents were reduced by 70% and 91%, respectively. This could imply the involvement of these bioorganic molecules in the biogenic synthesis of the ZnO NPs by PPE.

X-ray diffraction spectroscopy was employed for phase characterization of the as-synthesized ZnO nanoparticles using pineapple peel extract as a capping agent with a reducing agent of KOH solution or lye. All the results indicate that pure ZnO nanoparticles were successfully synthesized. The peak patterns of the as-prepared ZnO nanoparticles are shown in Figure 7. Crystallographic planes of (100), (002), (101), (102), (110), (103), and (112) are observed, corresponding to the data in JCPDS Card No. 36–1451, a result reflecting wurtzite zinc oxide formation [19]. The crystallite sizes of ZnO were estimated according to the

![Figure 5](image-url)
The well-known Scherrer equation: $D = \frac{0.9 \lambda}{\beta \cos \theta}$, where $D$ represents crystallite size (Å), $\lambda$ is the wavelength of CuKa radiation (Å), and $\beta$ is the corrected full width at half maximum (FWHM) of the diffraction peak. Basically, the defect and residual strain in crystal are directly related to the crystalline size because they obstruct crystal growth. The reduction in crystalline size reflects the higher degree of internal defect and strain. The strain ($\varepsilon$) and dislocation density ($\delta$) can be further studied by applying XRD data using the following equations: $\varepsilon = \frac{\beta \cos \theta}{4}$ and $\delta = \frac{1}{(L)^2}$. As shown in Table 1, the crystal planes of (100) were considered for the crystallite size, strain, and dislocation density calculations. When synthesizing KOH solution conditions, the crystallite sizes are found to be 83.98, 64.61, 64.62, 76.37, and 83.99 nm as the KOH concentration increases. With respect to the crystallite sizes, the results of strain and dislocation density give contrary values, exhibiting a strain analysis of 0.00041, 0.00054, 0.00054, 0.00045 and 0.00041, and

Figure 6. Plausible biogenic synthesis mechanism of ZnO-NPs formation using PPE. The zinc ions are reduced by a hydroxyl group of phenolic and carbohydrate compounds resulting in metallic zinc particles. The metallic zinc particles are oxidized to form ZnO NPs and stabilized by organic molecules [27–29].

Figure 7. XRD patterns of ZnO nanoparticles synthesized from various zinc nitrate concentrations: (a) 0.02 M Zn(NO$_3$)$_2$ + KOH, (b) 0.04 M Zn(NO$_3$)$_2$ + KOH, (c) 0.06 M Zn(NO$_3$)$_2$ + KOH, (d) 0.08 M Zn(NO$_3$)$_2$ + KOH, (e) 0.1 M Zn(NO$_3$)$_2$ + KOH, (f) 0.06 M Zn(NO$_3$)$_2$ + lye.
Table 1. The calculated crystallite size, strain and dislocation density of ZnO nanoparticles synthesized using a KOH solution with lye as a reducing agent.

| Alkaline source / Concentration (M) | 2θ (°) | FWHM (2θ) | Crystallite size (nm) | Strain (ε) | Dislocation density (S) (line/m²) |
|-------------------------------------|--------|------------|----------------------|------------|----------------------------------|
| KOH/0.02                           | 31.69  | 0.12       | 83.98                | 0.00041    | 0.00014                          |
| KOH/0.04                           | 31.65  | 0.25       | 64.61                | 0.00054    | 0.00024                          |
| KOH/0.06                           | 31.71  | 0.25       | 64.62                | 0.00054    | 0.00024                          |
| KOH/0.08                           | 31.82  | 0.21       | 76.37                | 0.00045    | 0.00017                          |
| KOH/0.10                           | 31.74  | 0.19       | 83.99                | 0.00041    | 0.00014                          |
| Lye/0.06                           | 31.75  | 0.26       | 65.41                | 0.00053    | 0.00023                          |

A dislocation density of 0.00014, 0.00024, 0.00024, 0.00017, and 0.00014 line/m². Due to the correlation between crystal formation and residual strain and defect, 0.04 and 0.06 M prepared ZnO exhibits the smallest crystal size of about 64.4 nm, corresponding with the highest strain and dislocation density amounts that are approximated as 0.00054 and 0.00024 line/m². This finding confirms the assumption that residual stress causes low crystal growth. Similarly, lye-prepared ZnO exhibits a crystallite size of 65.41 nm with values of 0.00053 and 0.00023 line/m² for strain and dislocation density, respectively. This result clearly shows that lye is a good reducing agent. Green synthesis with lye solution has potential for ZnO nanoparticle production. Interestingly, lye-prepared nanostructured metal oxide production extends our understanding of the synthesizing process.

SEM images (Figure 8) show aggregated nanoparticles with different morphologies of ZnO obtained under various desired conditions. These nano-sizes correspond with the above Debye–Scherrer calculation results. Especially notable are the flower-like clusters of prepared ZnO nanoparticles acquired from 0.06 M zinc precursor using KOH solution and lye. For further confirmation, the EDS spectras of the elemental analysis of ZnO NPs are shown in the inserted image. Only zinc...
and oxygen signals are detected in the spectrum, confirming that the synthesized nanoparticles are pure ZnO. For transmission electron microscope analysis, the ZnO nanoparticles from 0.06 M zinc precursor were selected. The TEM image in Figure 9(a) shows clusters of irregular and hexagonal ZnO-NPs shapes whose diameter was under 100 nm. The selected area electron diffraction (SAED) pattern in Figure 9(b) exhibits the combined spotty ring pattern of the (100), (101), (102), and (103) planes of the hexagonal ZnO structure (P63m), which is consistent with JCPDS card No. 36–1451, and the above XRD results. The HRTEM image (Figure 9(c)) of single nanoparticles reveals a reticular distance of 0.24 nm. This value is consistent with the (101) crystal space distance of the ZnO hexagonal wurtzite structure (JCPDS No. 36–1451).

For further confirmation of the ZnO-NP purity, thermogravimetric analysis (TGA) was employed on the ZnO NPs green-synthesized via 0.06 M precursors of KOH and lye solution. For KOH use, Figure 10a shows a slight 0.6% weight loss initiated at 114°C, followed by a 1% weight loss at 200°C owing to water evaporation. The slight weight loss occurred between 350°C and 600°C, which was about 3.8% of the actual weight due to the

![Figure 9](image_url)

**Figure 9.** TEM results for 0.06 M Zn(NO$_3$)$_2$ + KOH conditions: (a) TEM image of ZnO, (b) electron diffraction pattern, (c) HRTEM image.

![Figure 10](image_url)

**Figure 10.** Thermogravimetric analysis (TGA) of green synthesis ZnO NPs. 0.06 M Zn(NO$_3$)$_2$ + KOH conditions, (b) from 0.06 M Zn(NO$_3$)$_2$ + lye conditions.
elimination and breakdown of organic groups resent in the specimen throughout the green-synthesis process. Similarly, for lye use, water evaporation caused a 1.1% weight loss at 200°C. The disappearance of organic substances contributed to the 3.7% weight-loss at 350–600°C. Additionally, DSC results from Barzinjy’s work [34] were reported to confirm that organic matter decomposes at temperatures above 365°C. These results are consistent with Barzinjy’s research, but the ZnO-NPs obtained from this experiment contain fewer organic impurities since they show lower weight loss than hat obtained in Barzinjy’s research.

The plots of optical absorbance (A) and reflectance (R) responding to the photon wavelength are shown in Figure 11. The absorbance of all ZnO nanostructures increases abruptly at about 350 nm as the excitation wavelength shows. At the proper energy excitation, a multiplied free electron concentration was observed. The reflectance spectra are contrary to the absorbance spectra showing a decrease of the reflectance intensity at 350 nm. The absorbance intensity of the 0.06 M KOH concentration is the highest. This finding can be attributed to the appearance of higher levels of free carriers or defects.

Diffused reflectance spectroscopy (DRS) is a nondestructive analytical technique that can be used to approximate the bandgaps of solid...
nanostructured semiconductors. The obtained diffuse reflectance spectra are analyzed according to the Kubelka-Munk theory, which describes the relationship of the diffuse reflectance (R) to the absorption coefficient (α), as shown by [35]: F(R) = k/s = (1−R)^2/2 R = α, where F(R) is the Kubelka-Munk function, k is the absorption coefficient, and s is the scattering coefficient.

The F(R) value is considered to replace the α amount for evaluating the optical bandgap [36]. Therefore, the tauc equation can be rewritten as follows: F(R)hv = A(hv-Eg)^2, where hγ is photonic energy, Eγ is the bandgap of materials, and n is an integer that indicates the transition process: n = 1/2 for direct allowed, n = 2 for indirect allowed, n = 3/2 for direct forbidden, and n = 3 for indirect forbidden transitions.

The plot of (F(R)hv)^2 as a function of hv is shown in Figure 12. The energy bandgap (Eγ) is estimated from the slope and the linear plot to zero F(R) value. The Eγ values of the samples were found to be 2.81, 3.03, 3.33, 2.85, and 2.86 eV for KOH concentrations of 0.02, 0.04, 0.06, 0.08 0.10 M, respectively. The obtained value of 3.33 eV is based on the smallest particle size synthesizing condition (63.46 nm). This result is close to that obtained in the report of Ajala [37] which presented an Eγ of 3.20 eV for ZnO with a 52 nm particle size. An increase in Eγ as a decreasing particle size can be described as due to the quantum size effect. The distance of the coulomb interaction between electron and hole plays an important role because the charge carrier leads to the valence and conduction bands of semiconductor modification [38].

4. Conclusions

The ZnO NPs under the six desired conditions show clusters of ZnO nanoparticles. The XRD and the SAED patterns of all the synthesized ZnO NPs show single-phase patterns consistent with JCPDS card No. 36–1451. FTIR and TGA confirm the purity of all the as-received ZnO NPs. For pH control by lye, the obtained NPs are on a nano-scale in the same phase as the KOH solution. Impressively, the ZnO NPs from the real green synthesis (using lye) exhibit a flower-like shape similar to that obtained using KOH in 0.06 M of sodium nitrate precursor. Moreover, the ZnO NPs obtained using 0.06 M zinc precursor in KOH solution show highly interesting results for physical and optical properties results.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Ministry of Science and Technology of Thailand [FF65-RIM056]; University of Phayao [SC18/2563].

References

[1] Jayaseelan C, Rahuman AA, Kirthi AV, et al. Novel microbial route to synthesize ZnO nanoparticles using aeromonas hydrophila and their activity against pathogenic bacteria and fungi. Spectrochim Acta A Mol Biomol Spectrosc. 2013;90:78–84.
[2] Rawal TB, Ozcan A, Liu SH, et al. Interaction of zinc oxide nanoparticles with water: implications for catalytic activity. ACS Appl Nano Mater. 2019;2(7):4257–4266.
[3] Kumar SS, Venkateswarlu P, Rao VR, et al. Synthesis, characterization and optical properties of zinc oxide nanoparticles. Int Nano Lett. 2013;3(1):1–6.
[4] Nagajyothi PC, Cha SJ, Yang I, et al. Antioxidant and anti-inflammatory activities of zinc oxide nanoparticles synthesized using polygala tenuifolia root extract. J Photochem Photobiol B. 2015;146:10–17.
[5] Kaushik M, Niranjan R, Thangam R, et al. Investigations on the antimicrobial activity and wound healing potential of ZnO nanoparticles. Appl Surf Sci. 2019;479:1169–1177.
[6] Belay A, Mekuria M, Adam G. Incorporation of zinc oxide nanoparticles in cotton textiles for ultraviolet light protection and antibacterial activities. Nanomater Nanotechnol. 2020;10:184780420970052.
[7] Sangeetha G, Rajeshwari S, Vencentesh R. Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract: structure and optical properties. Mater Res Bull. 2011;46(12):2560–2566.
[8] Bala N, Saha S, Chakraborty M, et al. Green synthesis of zinc oxide nanoparticles using Hibiscus subdariffa leaf extract: effect of temperature on synthesis, anti-bacterial activity and anti-diabetic activity. RSC Adv. 2015;5(7):4993–5003.
[9] Jamdagni P, Khatri P, Rana JS. Green synthesis of zinc oxide nanoparticles using flower extract of Nyctanthes arbor-tristis and their antifungal activity. J King Saud Univ Sci. 2018;30(2):168–175.
[10] Alrajhi AH, Ahmed NM, Shafouri AM, et al. Green synthesis of zinc oxide nanoparticles using salvia officinalis leaves: antimicrobial activity. Mater Sci Semicond Process. 2021;125:105641.
[11] Rambabu K, Bharath G, Banat F, et al. Green synthesis of zinc oxide nanoparticles using Phoenix dactylifera waste as bioreducing agent for effective dye degradation and antibacterial performance in wastewater treatment. J Hazard Mater. 2021;402:123560.
[12] Alyamani AA, Albukhaty S, Aloufi S, et al. Green fabrication of zinc oxide nanoparticles using phlomis leaf extract: characterization and in vitro evaluation of cytotoxicity and antibacterial properties. Molecules. 2021;26(20):6140.
[13] Aminuzzaman M, Ng PS, Goh W, et al. Value-adding to dragon fruit (Hylocereus polyrhizus) peel biowaste: green synthesis of ZnO nanoparticles and their characterization. Inorg Nano-Met Chem. 2019;49(11):401–411.
[14] Aminuzzaman M, Ying LP, Goh WS, et al. Green synthesis of zinc oxide nanoparticles using aqueous extract
of Garcinia mangostana fruit pericarp and their photocatalytic activity. Bull Mater Sci. 2018;41(2):1–10.

[15] Nava OJ, Soto-Robles CA, Gómez-Gutiérrez CM, et al. Fruit peel extract mediated green synthesis of zinc oxide nanoparticles. J Mol Struct. 2017;1147:1–6.

[16] Romelle FD, Rani A, Manohar RS. Chemical composition of some selected fruit peels. J Food Sci. 2016;4 (4):12–21.

[17] Saraswaty V, Risdian C, Primadona I, et al. Pineapple peel wastes as a potential source of antioxidant compounds. IOP Conf Ser Earth Environ Sci. 2017;60(1):012013.

[18] Izli N, Izli G, Taskin O. Impact of different drying methods on the drying kinetics, color, total phenolic content and antioxidant capacity of pineapple. CYTA J Food. 2018;16(1):213–221.

[19] Hassan BH, Talib RA, Sukor R, et al. Effect of synthesis temperature on the size of ZnO nanoparticles derived from pineapple peel extract and antibacterial activity of ZnO–starch nanocomposite films. Nanomater. 2020;10 (6):1061.

[20] Mirgane NA, Shivankar VS, Kotwal SB, et al. Waste pericarp of ananas comosus in green synthesis zinc oxide nanoparticles and their application in waste water treatment. Mater Today: Proc. 2021;37:886–889.

[21] Wood Ash SR. Waste materials and by-products in concrete. Berlin: Springer; 2008.

[22] Vernon LS, Rudolf O, Rosa M, et al. Analysis of total phenols and other oxidation substrates and antioxidants by means of folin-ciocalteau reagent, meth. Enzymol. 1999;299:152–178.

[23] Nielson SS. Phenol-Sulfuric Acid Method for Total Carbohydrates. Food Analysis Laboratory Manual 2th ed. Food Science Text Series. (New York (NY): Springer. 2010;47–53.

[24] Woisky R, Salatino A. Analysis of propolis: some parameters and procedures for chemical quality control. J Apic Res. 1998;37:99–105.

[25] Larkin PJ. Infrared and raman spectroscopy: principles and spectral interpretation. United States (US): Elsevier; 2011.

[26] Soto-Robles CA, Luque PA, Gómez-Gutiérrez CM, et al. Study on the effect of the concentration of Hibiscus sabdariffa extract on the green synthesis of ZnO nanoparticles. Results Phys. 2019;15:102807.

[27] Pholnak C, Sirisathitkul C, Harding DJ. Characterizations of octahedral zinc oxide synthesized by sonochemical method. J Phys Chem Solids. 2011;72(6):817–823.

[28] Matinise N, Fujiig XG, Kaviyarsku K, et al. ZnO nanoparticles via moringa oleifera green synthesis: physical properties & mechanism of formation. Appl Surf Sci. 2017;406:339–347.

[29] Rini AS, Rahayu SD, Hamzah Y, et al. Effect of pH on the morphology and microstructure of ZnO synthesized using ananas comosus peel extract. J Phys Conf Ser. 2021;2019(1):012100.

[30] Liang MK, Limo MJ, Sola-Rabada A, et al. New insights into the mechanism of ZnO formation from aqueous solutions of zinc acetate and zinc nitrate. Chem Mater. 2014;26(14):4119–4129.

[31] Bandeira M, Giovanela M, Roesch-Elly DM, et al. Green synthesis of zinc oxide nanoparticles: a review of the synthesis methodology and mechanism of formation. Sustainable Chem Pharm. 2020;15:100233.

[32] Makarov VV, Love AJ, Sinitsyna OV, et al. “Green” nanotechnologies: synthesis of metal nanoparticles using plants. Acta Naturae. 2014;6(1):35–44.

[33] Khalafi T, Buazar F, Ghanemi K. Phycosynthesis and enhanced photocatalytic activity of zinc oxide nanoparticles toward organosulfur pollutants. Sci Rep. 2019;9:6868.

[34] Barzinjy AA, Azeez HH. Green synthesis and characterization of zinc oxide nanoparticles using eucalyptus globulus labill. leaf extract and zinc nitrate hexahydrate salt. SN Appl Sci. 2020;2(5):1–14.

[35] Kubelka P. Ein beitrag zur optik der farbanstriche (Contribution to the optic of paint). Z Tech Physik. 1931;12:593–601.

[36] Zanatta AR. Revisiting the optical bandgap of semiconductors and the proposal of a unified methodology to its determination. Sci Rep. 2019;9(1):1–12.

[37] Ajala F, Hamrouni A, Houas A, et al. The influence of Al doping on the photocatalytic activity of nanostructured ZnO: the role of adsorbed water. Appl Surf Sci. 2018;445:376–382.

[38] Geetha MS, Nagabhushana H, Shivananjahia HN. Green mediated synthesis and characterization of ZnO nanoparticles using Euphorbia Jatropha latex as reducing agent. J Sci Adv Mater Dev. 2016;1(3):301–310.