Flower shaped ZnO–NPs; phytofabrication, photocatalytic, fluorescence quenching, and photoluminescence activities

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Keywords: biogenic, photocatalytic, fluorescence quenching, photoluminescence, ZnO–NPs

Abstract
Phytofabrication of Zinc Oxide nanoparticles (ZnO–NPs) through Nephelium lappaceum L. and Garcinia mangostana L. plants’ wastes were achieved as an environmentally friendly method of synthesizing nanoparticles. Biogenic ZnO–NPs were characterized by Ultra Violet Visible (UV–vis) spectrophotometry, Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Energy Dispersive Energy (EDX), and Fourier Transform Infrared spectroscopy (FTIR). UV-Visible absorption of ZnO–NPs indicated a characteristic absorption band at 362–368 nm region. The synthesized nanoparticles were flower in shape, as shown by the SEM images, and they were further elucidated by the TEM images. ZnO–NP synthesized via Rambutan Peel Extract (RPE), Rambutan Seed Extract (RSE), Mangosteen Peel Extract (MPE) and Mangosteen Seed Extract (MSE) showed the average particle size of 29 nm–184 nm, 86 nm–260 nm, 92 nm–247 nm, and 233 nm–334 nm respectively. FTIR spectra demonstrated peaks at 3269–3500 cm−1, 2308–2361 cm−1, 2103–2110 cm−1 and 1630–1640 cm−1, 586–632 cm−1 for the plant extracts, whereas an additional peak appeared within the range of 458–499 cm−1 in ZnO–NPs spectra. The photocatalytic activity of the synthesized ZnO–NPs was measured by the degradation of Methylene Blue under sunlight. The highest degradation of Methylene Blue dye was detected in ZnO–NPs using the seed extract of Nephelium lappaceum L., where a Half-life of 78 min and 97% degradation efficiency at 150 min time frame was observed. The ZnO–NPs were identified to possess fluorescence quenching ability of Rhodamine B. The highest quenching ability was recorded in ZnO–NPs synthesized using the seed extract of Garcinia mangostana L. seed. The Photoluminescence study showed that the intensity of spectral lines of biogenic ZnO–NPs were higher compared with the chemically synthesized ZnO–NPs.

1. Introduction
Usage of semiconductor materials for the degradation of organic pollutants, especially in wastewater treatment is gaining attention over the conventional purification methods such as chemical coagulation, chemical oxidation and absorption or adsorption [1]. Other methods, such as degradation through microbes and hydrolysis, have proven to take considerable time [2]. With a variety of applications in fields of sensors, cosmetics, storage, optical and electrical devices, ZnO has exhibited remarkable semiconducting properties due to its large bandgap, bond strength, and large exciton binding energy at room temperature [3–6]. ZnO and TiO2 could be perceived as ideal photocatalysts concerning the inexpensive nature of the materials and high oxidizing power that could attribute to the energy associated with a large bandgap [2].

Nanoparticles and nano metal oxides, including ZnO, have been considered to be a significant breakthrough in nanoscience and interconnected with numerous fields, including biology, chemistry, physics, engineering, and medicine [7, 8]. It is mainly due to their unique properties (shape, size, chemical composition, and dispersity), based on the synthesis process of the nanoparticles and the nanometal oxides [8].

Employing plant extracts as a means of synthesizing metal nanoparticles is an environmentally friendly alternative way to chemical and physical methods [9–11]. In previous studies, the ZnO–NPs have been
synthesized using different approaches such as sol-gel, co-precipitation, microwave assist, thermal decomposition, ultrasonic synthesis, hydrothermal, and electrical method [12–17]. Most of the above methods trigger high temperatures, high pressure, and other harmful toxic substances [18]. The present study is focused on the phytofabrication of ZnO–NPs, which is a single step, cost-effective, and eco-friendly method with minimal use of chemicals [19, 20].

Plant extracts prepared from non-edible parts (peels and seeds) of *Nephelium lappaceum* L. (*Malayan Red variety)* and *Garcinia mangostana* L. were used to phytofabricate the ZnO–NPs to create a value to the agricultural waste generated. Both *N. lappaceum* and *G. mangostana* are two fruit-bearing tree varieties widely cultivated in Sri Lanka, with recorded medicinal and biological properties [21–23].

The cytotoxic, UV filtration, antibacterial, antifungal, antioxidant, anti-inflammatory, and wound healing properties of ZnO–NPs with various other biological applications are recognized including in the fields of bio-imaging and drug delivery [24–28]. In addition to the biological properties, ZnO–NPs are widely used as a semiconductor besides their unique electrical, optical, catalytic, and photochemical properties [29]. Though the ZnO–NPs synthesized through green methods have been evaluated in biological and other fields, reports of the effect on fluorescence emission and photocatalytic activities are not extensively reported.

Most textile and paint industrial effluents are contaminated with organic dyes that are not biodegradable and toxic to the ecosystem [2]. Various methodologies for removing dyes from solutions such as oxidation by chemical action, reverse osmosis, coagulation, membrane filtration, and adsorption have been reported [30, 31]. These methods are quite expensive and can form nonbiodegradable side products. In an attempt to overcome this drawback, this study has focused on the synthesis of cheap and nontoxic ZnO–NPs, which can act as a photoinduced catalyst.

Methylene Blue (MB) is one such major contaminant of industrial effluents, which can cause environmental threats as it is not easily degradable. Since it is an aromatic dye, it can contaminate natural water bodies. The photocatalytic degradation of compounds like MB in the presence of ZnO–NPs may provide an efficient method to convert the harmful dyes to non-hazardous products [1, 12]. The lack of publishing work on the pH of the medium in the photocatalytic degradation reaction of the MB using biogenic nanoparticles was brought into attention.

In this study, non-edible parts of the fruits of *Nephelium lappaceum* L. and *Garcinia mangostana* L. were used to obtain biogenic ZnO–NPs, which was characterized by specific techniques. The photocatalytic activity of biogenic ZnO–NPs has been evaluated through the MB degradation. Further, the biogenic ZnO–NPs were estimated for their fluorescence quenching ability on Rhodamine B, and photoluminescence activity.

2. Materials and methods

2.1. Chemicals and instruments
Zinc acetate (purchased from Sigma-Aldrich, Anala R grade), Sodium hydroxide pellet (purchased from Sigma-Aldrich, Anala R grade), Hydrochloric acid (purchased from Sigma-Aldrich, Anala R grade), Methanol (purchased from BDH, Anala R grade), Rhodamine B (purchased from Sigma-Aldrich), Methylene blue (purchased from Sigma-Aldrich), Ultra violet–visible spectrophotometer (U-2910–Hitachi, Japan), Fourier Transform Infrared spectrometer (Horizon ABB-MB 3000 ATR FT-IR), Advance vortex mixture (VELP Scientifica ZX3), Spectrofluorometer (F-2700 FL Hitachi, Japan), Scanning Electron Microscope (Carl Zeiss, Evo), Centrifuge (GEMMYCO, PLC-036h), Transmission Electron Microscope (JEOL JEM-2100 Japan), Analytical balance (RADWAG Wagi Electroniczne, AS-220. R2), Oven (universal oven-UN 55) and pH meter (GENWAY, 3510, benchtop meter)

2.2. Sample collection and preparation of the extract
Prior published methodologies were followed with appropriate modifications to synthesis plant extract mediated ZnO–NPs [32]. The ripened fruits of the common variety of *Nephelium lappaceum* L. and *Garcinia mangostana* L. were gathered from households. Ripened fruits were washed with normal water and then the peel and seed of *N lappaceum*, fruit rind, and seed of *G mangostana* were separated with a sharp knife. The separated parts were washed with water, cut into small portions and air-dried for two days in the shade. The extracts were prepared by placing 3.0 g of the air-dried plant material in a flask containing 300.0 ml of deionized water and heating it for 10 min at 100 °C. The crude extracts were filtered through cotton wool, followed by Whatman No 1 filter paper to separate the plant material from the aqueous extract. Peel extract and seed extract of *N. lappaceum* were labelled as RPE and RSE whereas, fruit rind extract and seed extract of *G. mangostana* were denoted with MPE and MSE, respectively.
2.3. Synthesis of ZnO–NPs
The synthesis of the ZnO–NPs were optimized by varying different volume ratio (plant extract to zinc acetate solution (Zn(CH₃COOH)₂)) to obtain a higher yield. Plant extracts were mixed with Zn(CH₃COOH)₂ solution (0.01 M) in 1: 5 (for plant extract: Zn(CH₃COOH)₂) volume ratios. The pH of the samples was adjusted to 12 by introducing a 2.0 M sodium hydroxide solution to obtain Zn(OH)₂. The resultant mixtures were subjected to stirring for two hours and then centrifuged at 4500 rpm for ten minutes. The residue was washed with deionized water followed by methanol until the supernatant appeared colorless. The residue was oven-dried at 60 °C for twelve hours to obtain ZnO–NPs.

2.4. Characterization of synthesized ZnO–NPs
Ultra Violet-Visible spectroscopy (UV–vis spectroscopy) was used to confirm the formation of ZnO–NPs, and the wavelength was compared with the chemically synthesized ZnO–NPs. The physical characteristics of the NPs (shape and particle diameter of NPs) were analyzed by Scanning Electron Microscopy (SEM) and Transmission Electron Microscope (TEM) with Energy Dispersive X-ray (EDX) system. The Gold-coated ZnO–NPs were used for SEM analysis and ZnO–NPs suspension on a copper grid at room temperature was used for the TEM analysis. Fourier transform spectroscopy was used to analyze the functional groups present in the plant extracts as well as the synthesized ZnO–NPs using a diamond sampling disk.

2.5. Photocatalytic activity of synthesized ZnO–NPs
Degradation of MB was studied in the presence of the synthesized ZnO–NPs under the Sunlight [31, 33]. The ZnO–NPs (5 mg) were dispersed in 25.00 ml of MB (0.5 mg/100 ml), prepared in distilled water and was adjusted to pH 4. The beaker was placed directly under the sunlight with continuous stirring. Degradation of the MB was monitored by withdrawing 4.00 ml aliquots from the reaction mixture at every 30 min interval. The aliquots were centrifuged, then the supernatants were used to assess the UV–vis absorbance at 661 nm.

2.6. Fluorescence quenching activity of the synthesized ZnO–NPs
The fluorescence enhancing or quenching ability of Rhodamine B compound by the ZnO–NPs were evaluated by fluorescence spectrometry. Previously published methods were used with appropriate modifications [34]. A Rhodamine B solution (0.05 mM) was prepared in methanol. From the prepared Rhodamine B solution, 1000 μl was treated with 50 μl, 100 μl, 250 μl, 500 μl, 1000 μl and 2000 μl volumes of ZnO–NPs (0.4 mg ml⁻¹) in methanol, synthesized from RPE, RSE, MPE and MSE. The treated solutions were topped up to 3000 μl by adding an appropriate amount of methanol followed by vortexing, and then the fluorescence intensities were recorded.

2.7. Photoluminescence of the synthesized ZnO–NPs
Photoluminescence (PL) measurements of the synthesized ZnO–NPs were carried out at room temperature using a solid sample by spectrophotometer. The photoluminescence of the biogenic ZnO–NPs and a sample of chemically synthesized ZnO–NPs was prepared according to published work and they were compared [35].

3. Results and discussion

3.1. UV–vis spectra
The synthesis of nanomaterials is with great interest as they have the ability to demonstrate properties in contrast to the bulk material that was used to synthesize them [9]. Many techniques are used in synthesizing ZnO–NPs such as co-precipitation, hydrothermal, sol-gel and electrodeposition [36]. Liquid phase synthesis of ZnO–NPs is considered as a technique with high adaptability [36]. Different colours of the NPs are one such property that arise due to the Surface Plasmon Resonance of the NPs [9].

Isolated ZnO–NPs appeared to be in off-white, indicating absorbance of visible range light. UV–vis absorbance spectroscopy was used as the preliminary step to monitor the formation of ZnO–NPs. Earlier published literatures were used to detect and compare the λ_max values of the synthesized ZnO–NPs. The peak absorbance wavelengths were recorded within the range of 300–400 nm [2, 5, 37].

The UV–vis absorbance spectra of synthesized ZnO–NPs via RPE, RSE, MPE, and MSE dispersed in methanol (enhanced to give the peaks) are shown in figure 1.

The recorded wavelength of biogenic synthesized ZnO–NPs were compared with the chemically synthesized nanoparticles, which was fallen with the range of 350–380 nm. In figures 1 (a) and (b), the optimum λ_max values were observed at 362 nm for ZnO–NPs/RPE and 368 nm for ZnO–NPs/RSE. Both ZnO–NPs/MPE and ZnO–NPs/MSE’s maximum absorbance were at 366 nm, and absorbance spectra obtained for the synthesized samples are given in figures 1 (c) and (d).
3.2. SEM analysis

The morphology of NPs is an important aspect that contributes to the physicochemical properties of the substances \[38\]. The SEM analysis was performed to observe the physical appearance and aggregation state of the synthesized ZnO–NPs. Synthesized NPs were imaged at different magnitudes from 15 000 to 75 000. The images obtained from the SEM analysis are given in figure 2.

In this study, the ZnO–NPs mostly appeared as flower-shaped, and in one case, rod-shaped NPs were also observed. The flower/star shape was highly visible in ZnO–NPs/RPE, ZnO–NPs/RSE, and ZnO–NPs/MSE, where rod-like NPs were prominent in ZnO–NPs/MPE. Agglomeration could be considered as low in all the samples according to the SEM images as particle shapes are distinctly visible. With a close inspection it could be seen that flower-like arrangement is a cluster formed by linking the bases of the crystals with roughly obelisk/rod shape crystals where the cross-sectional diameter of these obelisk/rod-shaped crystals were in the range of 109.4–164.1 nm (in ZnO–NPs/RPE), 218.8–273.4 nm (in ZnO–NPs/RSE), 109.4–136.7 nm (in ZnO–NPs/MPE) and 154.9–182.3 nm (in ZnO–NPs/MSE) as shown in the SEM images.

In a previous study, ZnO–NPs with hexagonal, rod-shaped, spherical, nanobelt, nanoplate, and hallow spheres have obtained \[38\]. Flower-shaped ZnO–NPs have attained through zinc nitrate and Zn(CH₃COOH)₂ solutions \[36, 38\]. A study suggests that the annealing temperature would exert an effect on the shape of the NPs, wherein some cases, the morphology of the NPs seemed to change after calcination at elevated temperatures \[38\]. Though the temperature range is used here is quite low (60 °C), which is a contrast to high-temperature ranges. Calcination at high temperatures (250 °C–500 °C) would give further information about the stability and shape of the obtained NPs.

**Figure 1.** UV-Vis absorbance spectra obtained for the NPs, (a) ZnO–NPs/RPE (b) ZnO–NPs/RSE and (c) ZnO–NPs/MPE (d) ZnO–NPs/MSE.
3.3. EDX analysis
The EDX profile of the synthesized NPs illustrates the elemental composition of the samples. The EDX distribution demonstrated in figures 3–6, confirmed the existence of Zn and O elements synthesized via RPE, RSE, MPE, and MSE. In ZnO–NPs (/RPE/RSE/MPE) the atomic percentage of Zn were recorded as 0.6%, 0.41%, 0.33% and 0.34%, while the atomic percentage of O were recorded as 81.50%, 78.06%, 77.48% and 78.29% respectively.

3.4. TEM analysis
The average particle size further confirmed from the TEM images for ZnO–NPs, which differed based on the plant material that was used to synthesis the NPs. Figure 7 shows representatives of the TEM images of the synthesized ZnO–NPs via RPE (figures 7(a) and (b)), RSE (figures 7(c) and (d)), MPE (figures 7(e) and (f)), and MSE (figures 7(g) and (h)). The diameter sizes of ZnO–NPs synthesized via RPE and RSE varied from 29 nm to 184 nm and 86 nm to 260 nm, respectively, whereas ZnO–NPs/MPE and ZnO–NPs/MSE fluctuated from 92 nm to 247 nm and 233 nm to 334 nm. According to the TEM images, particle shapes are flowered shape, and agglomerations are noticeable. Rod/obelisks shapes have come together and interconnected at the base to form the cluster shape, which was further confirmed from the SEM images as well.

Atomic resolution cross-section TEM image of ZnO–NPs synthesized via MPE is given in figure 8(a), which depicted the well-arranged equidistant fringes. The atomic interlayer distance of ZnO–NPs was calculated to be 0.2721 nm (figure 8(b)), which can be closer to the lattice spacing of 0.2821 nm of the (100) lattice plane of Bulk ZnO [39].
3.5. FTIR analysis of the plant extracts and synthesized NPs

Phytochemicals present in the plant extracts usually behave as the reducing and capping agents in plant-mediated NPs synthesis [32]. However, a reasonable mechanism for the formation of ZnO–NPs in the presence of secondary plant metabolites has not been presented yet, as the oxidation state of the Zn ion does not change in the NPs formation. Though an accepted mechanism is not yet derived for plant extract mediated synthesis of ZnO–NPs, various phytochemicals and proteins in these extracts are considered to provide the action of capping agents and stabilize the NPs formation through electrostatic and steric stabilization [6].

The FTIR spectra of the non-edible part of the *N. lappaceum* and *G. mangostana* plant extracts were analyzed to identify the functional groups present in the phytochemicals of each extract and are given in figures 9–12, along with the FTIR spectra of the NPs synthesized using the relevant extract. Prominent peaks were observed in the region related to –OH, –C=O, C=C, and C≡C in all the spectra.

Prominent peaks from plant extracts were observed at 3269–3300 cm\(^{-1}\), 2308–2361 cm\(^{-1}\), 2100–2134 cm\(^{-1}\), 1630–1640 cm\(^{-1}\) and 586–632 cm\(^{-1}\) in all the spectra. These high amplitude peaks can be attributed to –OH vibration, –CN stretching, carbon-carbon triple bond stretching, C=O stretching and C≡N vibration stretching, respectively. Peaks at 2918–2919 cm\(^{-1}\) and 2849–2851 cm\(^{-1}\) occurred in both seed extracts corresponding to the vibration of C–H in the –CH\(_2\) group. In addition to the absorption bands of all four-plant
extracts, the characteristic new peak of ZnO molecules appeared within the range of 458–499 cm\(^{-1}\) in the FTIR spectrum of ZnO–NPs which is in accordance with the published literature \([7]\). The FTIR spectra were observed as an evaluation between the plant extracts and the synthesized ZnO–NPs, which could reveal information about the surface adherence of molecules. A low intensity peaks correlated with the –OH was observed in ZnO–NPs \([37, 38, 40]\).

3.6. Photocatalytic activity of ZnO–NPs

ZnO as a semiconductor material is known to possess photocatalytic activity, and the published literature states that ZnO–NPs exhibit superior catalytic activity compared with TiO\(_2\) and could be used in the purification of contaminated water with mixtures of organic compounds \([2]\). The particle size and surface area are two factors that could affect the efficiency of a catalyst \([2, 8, 12]\). The photocatalytic mechanism is based on the interaction between ZnO–NPs (catalyst) and the reactive hydroxyl radicals or superoxide species, which are induced by the Sunlight to degrade the dye molecules through interactions \([31, 41, 42]\).

It has observed that the MB dye undergoes degradation under Sunlight without any catalyst present. This degradation was high in basic medium and lowered in acidic medium. In this study, the photocatalytic activity of

![Figure 4. EDX (a) mapping and (b) spectrum of ZnO–NPs synthesized via RSE.](image-url)
the synthesized ZnO–NPs using the non-edible parts of the extracts was investigated by the degradation of the MB.

The attention was drawn to the lack of published work that addresses the acidic/basic nature of the reaction medium when conducting photocatalytic assays of ZnO–NPs. It was observed that ZnO–NPs tend to dissolve at lower pH values (such as pH 2 and pH 3), and visible stability was only achieved closer to pH 4. Hence, pH 4 was selected as the pH of the medium to conduct the degradation assay of MB dye. To monitor the self-degradation of the MB dye at pH 4, a separate sample was analyzed without the ZnO–NPs. The spectra obtained are shown in figure 13. To the best of our knowledge, this is the first attempt to evaluate the degradation of MB dye by ZnO–NPs synthesized through biological means.

All the synthesized NPs were able to increase the degradation of MB dye compared with the test control (which was kept under Sunlight at pH 4 without the involvement of ZnO–NPs). The UV–vis absorbance plots gathered to monitor the degradation of MB dye are shown in figure 14.

Out of the synthesized NPs, ZnO–NPs/RSE enhanced the degradation of MB with 97% efficiency within the time period of 150 min. Scientific literature suggests that the efficiency of a semiconductor catalyst is affected by the morphology of the catalyst and is a critical factor in the lifetime and regeneration of the material. Semiconductor particles below the radius of 50 nm is considered to be most effective [2].

The degradation efficiency of the MB dye was calculated according to the previously published work [11, 42, 43]. The following equation was used to calculate the degradation efficiency of the MB.

Figure 5. EDX (a) mapping and (b) spectrum of ZnO–NPs synthesized via MPE.
The absorbance is directly proportional to the concentration of the MB dye at a selected time, where initial absorbance and absorbance at a time were denoted by \( C_0 \) and \( C \), respectively. Figure 15 presents the plots generated for the change of \( C / C_0 \) and \( [1 - C / C_0] \times 100\% \) with time from 0 min to 150 min [1]. The degradation efficiency was obtained at 150 min by \( [1 - C / C_0] \times 100\% \) and Half-life of the MB degradation was taken at the crossover point of the plots. The highest percent degradation was obtained for ZnO–NPs/RSE (97%) and ZnO–NPs/MSE (92%), and the lowest was given by ZnO–NPs/RPE (84%). The lowest Half-life of MB was recorded for ZnO–NPs/RSE at 78 min, and the highest was in ZnO–NPs/RPE at 112 min. All other information gathered is given in table 1.

3.7. Fluorescence quenching activity of the synthesized NPs
ZnO has many applications in the fields of optical and electrical due to its fluorescence quenching ability [3]. To the best of our experience, this remains the first endeavor that used biogenic ZnO–NPs to quench the fluorescence ability of Rhodamine B, which was prepared in methanol solution. The prepared Rhodamine B dye was treated with synthesized ZnO–NPs, and the fluorescence emission was recorded and compared with the non-treated Rhodamine B sample, which kept as the control. A decreased in the fluorescence emission was observed in every sample with increasing NP concentration. This drop of fluorescence was highest in Rhodamine B treated with ZnO–NPs/MSE. Below figure 16 presents the fluorescence emission spectra of

\[
\text{Degradation Efficiency} = \left(1 - \frac{C}{C_0}\right) \times 100\%
\]
Figure 7. TEM images of ZnO–NPs Synthesized via RPE (a), (b), RSE (c), (d), MPE (e), (f), MSE (g), (h).

Figure 8. (a) TEM images of ZnO–NPs Synthesized via MPE and (b) line profile of the HRTEM image of ZnO–NPs Synthesized via MPE.
Figure 9. FTIR spectra of RPE (A) and ZnO–NPs (B).

Figure 10. FTIR spectra of RSE (A) and ZnO–NPs (B).

Figure 11. FTIR spectra of MPE (A) and ZnO–NPs (B).
Rhodamine B (light blue) and ZnO–NPs treated Rhodamine B in red (50 μl), grey (100 μl), yellow (250 μl), dark blue (500 μl), green (1000 μl) and purple (2000 μl).

ZnO–NPs/MPE and ZnO–NPs/RSE were appeared to be linear with $R^2 > 0.9596$, which can be identified with the dynamic quenching mechanism. At low concentration, ZnO–NPs synthesized via MSE and RPE behaved in a linear fashion, and at higher ZnO–NPs concentrations, they have deviated from initial linearity. This deviation could be due to the presence of simultaneous dynamic and static quenching mechanisms and also because of the formation of excited-state collisions or chemical complex [43]. However, to confirm whether this arises as a combination of static and dynamic quenching mechanisms, further experiments should be carried out in a higher concentration range. Stern Volmer plots obtained for the fluorescence quenching activities of the ZnO–NPs are given in figure 17.

3.8. Photoluminescence activity of the synthesized NPs
Photoluminescence spectroscopy is a non-destructive technique, which helps to distinguish the point defects, including intrinsic and extrinsic defects in a material [44]. It can also use as a measurement to identify the quality and to examine the physical parameters of nano-semiconductor materials [44]. Photoluminescence activity was

**Figure 12.** FTIR spectra of MSE (A) and ZnO–NPs (B).

**Figure 13.** UV-Vis absorbance spectra for the degradation of MB dye at pH 4 under Sunlight.
monitored according to the previously published literature \[42, 45\]. The main focus was to obtain more details about excitation intensity (EI) effects on ZnO nanomaterials with corresponding morphologies and the comparison of ZnO–NPs in chemical method and the green method.

Figure 18 gives the photoluminescence emission spectra of all four ZnO–NPs synthesized in this study. The spectra consist of two significant emission peaks: a sharp peak located at UV region, and a broad peak with weak intensity in the visible region. As stated by the previous studies, the presence of two peaks correspond to the native defects in ZnO material \[44\]. The height of the UV peak reduces with the decreasing EI (Excitation Wavelength 335 nm to 285 nm). However, there is no significant variation in the height of the visible region peak. Moreover, with the lowering of EI, the UV and visible emission peaks, direction shifted towards the lower wavelength side. The weak broad (500–600 nm) emission peak detected due to the recombination of holes (photogenerated) with a single ionized charge state of unique defects. Moreover, the sharp UV emission peak (approximately at 390 nm–400 nm) attributed of the ZnO near band edge emission and due to free exciton recombination \[31, 46–48\].

The figure 19 depicted the comparison of PL UV emission spectra of phytofabricated ZnO–NPs using RPE, RSE, MPE and MSE as capping material and chemically synthesized ZnO–NPs. Powdered NPs samples were excited at 285 nm, which is indicating the effect of particle size on PL intensity \[43\]. It can derive that; the PL intensity of all biogenic ZnO–NPs are higher than the PL of chemically synthesized ZnO–NPs. This may be due to the formation of smaller sized ZnO–NPs in the green method compared with the chemically synthesized ZnO–NPs \[46\]. The asymmetric spectral band of UV feature implies the native defects state of ZnO–NPs, which enhances the characteristics of the luminescence \[47\].
4. Conclusion

The peel and seed of *N. lappaceum*, fruit rind, and seed of *G. mangostana* can be used to achieve the phytofabrication of ZnO–NPs. UV–vis spectrophotometry confirmed the formation of ZnO–NPs by exhibiting characteristic UV–vis absorbance bands within the range of 362–368 nm. FTIR analysis indicates the low surface adherence of phytochemical molecules on NPs. The SEM images produced flower and rod-like arrangement of nanocrystals and it was further confirmed by TEM analysis. As per the TEM analysis, the average diameter of RPE, RSE, MPE, and MSE were recorded as 29 nm–184 nm, 86 nm–260 nm, 92 nm–247 nm, and 233 nm–334 nm respectively.

Photocatalytic activity was measured through the degradation of MB dye at pH 4. Consequently, it was demonstrated that the ZnO–NPs synthesized using the seed extract of *N. lappaceum*, showed the highest activity with a Half-life of 78 min and 97% degradation efficiency at 150 min time frame. The fluorescence quenching ability of Rhodamine B compound by the plant–mediated ZnO–NPs were evaluated for the first time. All four biogenic ZnO–NPs synthesized in this experiment were able to quench the fluorescence activity of Rhodamine B. The PL intensities of spectral were higher and asymmetric in biogenic ZnO–NPs compared with chemically synthesized ZnO–NPs, which enhances the characteristics of the luminescence.

Table 1. Photocatalytic efficiency of the synthesized ZnO–NPs on degradation of MB at pH 4.

| ZnO-NPs synthesized | Half-life (min) | Degradation efficiency % |
|---------------------|----------------|--------------------------|
| RPE                 | 124            | 84                       |
| RSE                 | 78             | 97                       |
| MPE                 | 108            | 85                       |
| MSE                 | 102            | 92                       |

Figure 15. Percentage degradation plots obtained for MB dye, showing C/Co in blue and [1−C/Co]×100% in red for (a) ZnO–NPs/RPE, (b) ZnO–NPs/RSE and (c) ZnO–NPs/MPE (d) ZnO–NPs/MSE.
Figure 16. Fluorescence emission spectra of Rhodamine B dye treated with NPs synthesized using (a) ZnO–NPs/RPE, (b) ZnO–NPs/RSE and (c) ZnO–NPs/MPE (d) ZnO–NPs/MSE.

Figure 17. Stern Volmer Plots generated for the fluorescence emission of Rhodamine B dye treated with NPs synthesized. ZnO–NPs/RPE (blue), ZnO–NPs/RSE (orange) ZnO–NPs/MPE (grey) and ZnO–NPs/MSE (yellow).
Figure 18. PL emission peak intensity variation with EI intensity. Photoluminescence emission spectra of (a) ZnO–NPs/RPE, (b) ZnO–NPs/RSE and (c) ZnO–NPs/MPE (d) ZnO–NPs/MSE.

Figure 19. Photoluminescence spectra of ZnO–NPs at UV region’s emission (with RPE, RSE, MPE and MSE as four capping materials) and chemically synthesized ZnO–NPs at 285 nm.
Acknowledgments

College of Chemical Sciences, Institute of Chemistry Ceylon, Sri Lanka, is acknowledged for the continued support.

Conflict of interests

Authors of this research article declare no conflict of interest.

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