Bio-synthesis of zinc oxide nanoparticles from bitter leaf (*vernonia amygdalina*) extract for dye-sensitized solar cell fabrication

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**Abstract**

In this paper, we report biosynthesis of Zinc oxide nanoparticles (ZnONPs) from *Vernonia Amygdalina* (bitter leaf) extract. ZnONPs film was deposited on fluorine doped tin oxide (FTO) and characterized using UV visible spectroscopy, Fourier transform infra-red (FTIR) spectroscopy, scanning electron microscopy (SEM) and x-ray diffraction (XRD). Biosynthesized ZnONPs has ~75% absorption at ultraviolet (UV) region. The FTIR spectroscopy shows that ZnONPs was synthesized as peaks at 1650 cm\(^{-1}\) and 725 cm\(^{-1}\) correspond to Zn-O stretching and deformation vibration, respectively which agreed with previous reports. The photovoltaic (PV) performance of the *Vernonia Amygdalina*-synthesized ZnONPs based Dye-sensitized solar cell (DSSC) was determined and compared with synthetic ZnONPs based DSSC. The synthesized ZnONPs based solar cell demonstrated enhanced power conversion efficiency of 0.63 %. This shows that synthesized ZnONPs-based solar cell is found suitable for cost-effective and environmentally friendly energy conversion device.

**Keywords**

- Bio-synthesis
- Zinc oxide
- Nanoparticles
- Dye-sensitized Solar cell
- *Vernonia Amygdalina*

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1. Introduction

The world awareness in green and clean energy is in increase, and solar cells fabricated is expected to be free from environmental pollution [1-4]. The applications of zinc oxide nanoparticles (ZnONPs) in thin-films transistors [5], light emitting devices [6], solar cells [7-9], gas sensors [10,11], biomedical applications [12] and piezoelectric devices [13] are due to its excellent optical and electrical properties [5]. In the family of semiconducting materials, ZnO is known as direct wide band gap at range of 3.2 eV to 3.37 eV and has good transparency [14,15] at room temperature. ZnO could be alternative material for titanium dioxide (TiO\(_2\)) due to its non-degrading nature, environmentally friendly and easiness to be synthesized into various shapes and sizes [16]. RF magnetron sputtering [17], chemical vapour deposition [18], pulsed laser deposition [19] thermal chemical vapor deposition [20], sol-gel spincoating [21,22], spray pyrolysis [23] chemical bath deposition [24] etc are used to prepare ZnO thin films.

The need to use non-toxic and environmentally friendly materials in synthesis of ZnO is highly needed as it will reduce environmental hazard. Different physical, chemical and biological methods have been deployed in synthesis of nanoparticles [25-27]. Using various parts of plants in nanoparticle synthesis is novelty as it involves green chemistry which does not need high pressure, temperature, energy and toxic materials [28]. Recently, use of fruit (tomatoes) [5] bacteria, fungus [29] and leaf extract [30] have been reported for ZnO nanoparticles synthesis. The adoption of the eco-friendly benign materials in ZnO synthesis offers many advantages in the environment, pharmaceutical and biomedical applications.
In this work, we synthesized ZnONPs biologically using bitter leaf extract and some characterizations were carried out. Then, the thin film of biosynthesized ZnONPs was deployed as window layer in fabricated dye-sensitized solar cells using black cherry as active layer.

2. Material and Methods

2.1. Preparation of leaf extract of Vernonia Amygdalina

Vernonia amygdalina leaves were air-dried for one week. The leaves were crushed with ceramic mortar and pestle into fines powder. 100 ml of ethanol added in 5g of the leaf powder in a beaker and heat the mixture using magnetic stirrer at temperature of 60 °C and 700 rpm for 30 minutes. The solution is filtered using Whatman filter paper and the filtrate is collected for further use.

2.2. Synthesis of ZnONPs.

5g of Zinc Sulphate heptahydrate (Merck) was added to the 15 ml of the leaf extract kept on a magnetic stirrer set at 60˚C and 750 rpm and white cloudy appeared. The solution is left for two hours in same condition and overnight incubation at room temperature. Centrifugation at 5000 rpm and 20 minutes, the white pellet is collected and dried in an oven at 150˚C. The white dried powder obtained was collected for further use.

2.3. Substrate cleaning

Fluorine doped tin oxide (FTO) glasses were used as transparent substrate. Before usage, they were immersed in distilled water with detergent in an ultrasonic bath for 15minutes at 30 °C with the help of a VWR ultrasonic cleaner (model 07043-986 Symphony). They were then rinsed with distilled water in ultrasonic cleaner at the same condition, later with ethanol at the same condition and lastly, with Isopropyl alcohol at the same condition and dried.

2.4. Preparation of the zinc oxide (ZnO) electrodes.

2.5 g of biosynthesized ZnO was hydrolyzed at 90 °C in 10ml of Isopropyl alcohol and distilled water of same ratio for 40 minutes, respectively. The mixture was mixed using an ultrasonic heat-stir (Stuart heat-stir UC152). Smooth and milky solutions were obtained. The result paste were deposited on fluorine doped tin oxide (FTO) coated glass using a spin-coating machine (WS-650MZ-23NPP Laurell). The deposited ZnONPs thin film was dried on a hot plate at 100 °C for 10 minutes. Later, the film was annealed at 500 °C for 30 minutes in a furnace to increase the adherence between particles and with the FTO layer. Thereafter it was left in the furnace to cool till the next day to avoid cracking of the film.

2.5. Solar cells fabrication

Black cherry fruit (Figure 1) was used as source of natural dye. The cooked black cherry fruits were crushed using mortar and pestle. The dye was filtered out using Whatman filter paper. The absorbance of dyes solutions was characterized using UV-Vis spectrophotometer (JENWAY 6705).

![Figure 1: Images of black cherry fruits](image)

Then, the ZnO electrodes were immersed into the dye solutions for 18 hours. The dye solution immersed ZnO electrode was kept in dark room. After, 18 hours, the ZnO substrates adsorbed dye were rinsed in ethanol so as to remove excess dye.
Counter electrode was prepared by scratching 2B pencil (graphite) on the cleaned FTO glass substrate. The electrolyte solution (Iodide/triiodide) was placed at the edges of the plates. The liquid electrolyte was drawn into the space between the electrodes by capillary action. Binder clips were used to hold the electrodes together. I-V measurement was carried using I-V source meter (Keithley 2400).

3. Results and discussion
3.1. Optical properties of ZnONPs Film
Absorption spectrum (Figure 2) shows film characterized at ultraviolet (UV) to visible regions (200 – 800 nm). In the figure, there are strong absorption (λ<347 nm) and strong transmittance (λ >347 nm) regions which corresponds to the reported by Khan et al. (2017) [22]. The 347 nm marks the transition wavelength from high absorption to low absorption. The average absorption at 200 to 320 nm is ~ 75 %. It is expected that at low absorption, high transmission value of visible light results. At visible range, it was observed that ZnONPs has very low absorption at visible range. The activity of the film shows that it can be used to protect UV radiation in optoelectronic devices since its absorption at the UV region is high [31, 32].

![Absorption spectrum of biosynthesized ZnONPs](image2.png)

**Figure 2:** Absorption spectrum of biosynthesized ZnONPs

3.2. Surface morphology characterization
The morphology of the ZnONPs thin film (Figure 3) deposited by solution method was carried out using scanning electron microscope (SEM). It shows that the glass substrate is entirely covered with spherically nanograined ZnO film.

![SEM image of ZnONPs thin film](image3.png)

**Figure 3:** SEM image of ZnONPs thin film.
The SEM micrograph contains uniform size of particles which could be due to low viscosity of the solution [33]. In the film, ZnONPs were dispersed into the ZnONPs thin film. The SEM reveals that the particles are spherical and have granular nature. The morphology of the film shows that the film are uniformly distributed on substrate. The uniform distributed films in the sample could reduce short circuiting in solar cells.

### 3.3 X-ray diffractometry (XRD) analysis

The XRD of ZnONPs synthesized with bitter leaf is as shown in Figure 4. According to the spectrogram of the crystal structure, the well defined peaks typical of ZnONPs in the crystal structure are clearly noticed. The peaks are in well defined shape and form. This indicates the crystallinity of the biosynthesized ZnONPs. The peaks are indexed as 31.67°(100), 34.28°(002), 36.43°(101), 47.48°(102) and 56.46° (211), respectively[34, 35]. All diffraction peaks of the sample correspond to the characteristic hexagonal wurtzite structure of ZnONPs \((a = 0.315 \text{ nm} \text{ and } c = 0.529 \text{ nm})\) [36].

Average particle size of ZnONPs is found to be 9.5 nm according to Scherrer equation [37].

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the X-ray wavelength, equals to 0.154 nm, \(\theta\) is the Bragg diffraction angle, and \(\beta\) is the full width half maximum (FWHM) of the XRD peak appearing at the diffraction angle \(\theta\). Also, the analysis of ZnO nanoparticle showed that weight percent of 80.34 and 19.66 correspond to zinc and oxygen, respectively. This corresponds to the result gotten from EDX and confirms that ZnONPs was synthesized.

![Figure 4: XRD pattern of synthesized ZnONPs](image)

### 3.4 Energy dispersive x-ray (EDX)

The analysis of the elemental composition of biosynthesized ZONPs (Figure 5) (CBD) using Energy-Dispersive X-ray (EDX). The EDX analysis shows that the compound composed of zinc and oxygen. Zinc has 82.32 weight %, 53.27 atomic % and oxygen has 17.68 weight %, 46.74 atomic %. The revelation of elemental composition of the sample shows that zinc and oxygen are present which confirm that ZnO was actually deposited.

![Figure 5: Elemental composition of biosynthesized ZONPs](image)
3.5 Fourier transform infrared spectroscopy (FTIR)
The FTIR spectrogram of biologically synthesized ZNONPs with bitter leaf is shown in Figure 6. The FTIR spectrum of was carried spectrometer using KBr pellet technique in the range of 400 – 4000 cm⁻¹ to determine the level of purity and ascertain the metal nanoparticle synthesized.

![Figure 6: FTIR spectrum of biosynthesized ZnONPs](image)

The absorption/transmission bands of metal oxides generally occur in fingerprint region i.e. between 400 cm⁻¹ and 1500 cm⁻¹ arising from inter-atomic vibrations [36]. The peaks observed at 3400 cm⁻¹ and 1050 cm⁻¹ could be due to O-H stretching and deformation, respectively. The peaks at 1650 cm⁻¹ and 725 cm⁻¹ correspond to Zn-O stretching and deformation vibration, respectively. The metal-oxygen frequencies observed for the respective metal oxides are in accordance with literature [38,39]. Kumar and Rani [36] reported similar FTIR spectra observed of zinc oxide nanoparticles in their investigation.

3.6 Performance of Solar cell based on biosynthesized and synthetic ZnONPs
Dye-sensitized solar cell based on green-synthesized and synthetic ZnONPs were fabricated using black cherry as active material. Both cells have the same Isc of 18.05 mA but different Voc, as shown in Figure 7, of 0.4147 V and 0.3900 V for bio-synthesized (CBd) and synthetic (CSd) ZnONPs, respectively. The data obtained from I-V measurement for both biosynthesized and synthetic based solar cells are shown in Table 1. Decrease in Voc as seen in the CSd based cell could be attributed to very high series resistance of the cell [38]. In addition, imperfection on the film surface could lead to lower Voc in the cell. The η of CBd and CSd based cells are 0.703 and 0.627 %.

![Figure 7: I-V curves of DSSC based on biosynthesized (CBd) and synthetic (CSd) ZnONPs](image)
Table 1: I-V values from the fabricated cells based on biosynthesized (CBd) and synthetic (CSd) ZnONPs

<table>
<thead>
<tr>
<th>Dye</th>
<th>V_{oc} (V)</th>
<th>I_{sc} (mA)</th>
<th>P_{max}</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBd</td>
<td>0.39</td>
<td>18.05</td>
<td>2.53</td>
<td>0.36</td>
<td>0.63</td>
</tr>
<tr>
<td>CSd</td>
<td>0.41</td>
<td>18.05</td>
<td>2.81</td>
<td>0.38</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Conclusion

The experimental results reported in this paper revealed that biosynthesized ZONPs from *Vernonia Amygdalina* leaf could be potential of anti-UV in solar cell. The dye extract absorbs UV radiation and allows visible light to pass through in significant amount. Both biosynthesized and synthetic ZnONPs were deployed in solar cells as window layer and it was observed that cell based on biosynthesized ZnONPs has power conversion efficiency of 0.63% comparable with synthetic ZnONPs based solar cell of 0.70%.

The deployment of the both ZnONPs in solar cell allowed us to establish that there could be grain boundaries in biosynthesized ZnONP which lowered performance of the cell. Therefore, it is found the eco-friendly-biosynthesized ZnONPs could be synthesized from *Vernonia Amygdalina* leaf and perform comparable with synthetic ZnONPS when deployed in solar cell as window layer.

References

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