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Synthesis and characterization of properties of aluminium coated *Thaumatococcus daniellii* extracts

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ABSTRACT

The focus of this research is to improve upon the bio-semiconductor technology by considering the use of plant extracts and metallic dopant. The plant was *Thaumatococcus daniellii* and it was extracted using three different solutions i.e. methanol, ethanol and butanol to form sample 1, sample 2 and sample 3, respectively. The plant extract was doped with aluminium under room temperature and pressure. The samples were characterized using UV–Vis spectrometry. It was observed that the chemical reaction of the oxide layer growth pattern varied significantly in all samples considered. Hence, the more stable the growth of the oxide layer, the more d-d transitions expected. These results are also unconnected to the inherent chemical components of *Thaumatococcus daniellii* that allows for the quick release of π -electrons to the aluminium atom. The band gap of sample 1, sample 2, and sample 3 was calculated as 1.6 eV, 2 eV and 2 eV respectively. There were 3 d-d transitions in the ethanol extract at wavelength $\lambda = 612 \text{ nm}, \lambda = 485 \text{ nm } \& \lambda = 460 \text{ nm}$ while there 4 d-d transitions in butanol extract. © 2019 Elsevier Ltd. All rights reserved.

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1. Introduction

Current technological revolution is diverting into the green concept. The green concept is the unused or neglected proceeds of nature that is now finding its place in the eco-friendly energy systems [1–4]. For example, Makarov *et al.* [1] proposed that a cost effective and environmentally friendly use of exogenous biomatrices (viral particles, proteins and peptides) from plant extracts in extraction of nanoparticles is better than the chemical and physical approaches used. This research focused on the role of biomolecules of natural plants involved in the bio reduction of metallic salts during synthesis of nanoparticles.

The semiconductor is a vital and an age-long device used in electronics etc. [5–10]. The current challenged is that some components of semiconductor are not eco-friendly when disposed as waste. Electronic wastes are mostly non-biodegradable or contain toxic heavy metals and halogenated compounds. Globally, electronic waste accounts for more than 5% of all solid municipal waste and is growing as electronic product sales in developing countries increase. In other words, there is the need to look at eco-friendly

* Corresponding author. *E-mail address:* moses.emetere@covenantuniversity.edu.ng (E.M. EMETERE). materials for fabricating electronic devices. This paper is tailored to seek-out green semiconductor candidates from synthesized plant extracts. The UV–Vis spectroscopy was used to characterize the plant extract. For example, Traiwatcharanon et al. [11] worked on a flexible and cost-effective room-temperature moisture sensor produced from pure resistive silver nanoparticles (AgNPs) synthesized with Pistia stratiotes extract as a reduction agent for Silver Nitrate (AgNO3) under light illumination. UV–Vis spectroscopy was used to characterize the samples. The results revealed that the composition of silver nanoparticles is strongly affected by different synthesis variables including pH value, AgNO3 concentration level, time of reaction and light irradiation.

Proper study of the UV–Vis spectra on materials provides analysis of optical properties of these materials; such as luminescence, transparency of polymer nano-composites and high or low refractive index UV absorption [12–14]. UV–Vis spectroscopy helps to understand the response of plant extract to optical properties by absorption of UV–Vis electromagnetic spectrum radiation and development of various applications such as color filters and sensors, optoelectronic devices.

The capacity of a medium's radiation absorption depends on various factors such as the wavelength of the radiation, the thickness of the absorbing layer, the electronic and nuclear consti-

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tution of the atoms and molecules of the medium and the variables which determine the state of the medium, with variables such as the temperature and the concentration of the absorbing agent playing a vital role. Precise absorbance measurements at different wavelengths enable a substance to be identified by absorption spectroscopy [15,16]. Illumination of a sample is done from one side and the light intensity leaving the sample is measured in each direction.

2. Methodology

Fresh *Thaumatococcus daniellii* leaves were collected from Ota, Ogun state, Nigeria. The leaves were plucked after rainfall to ensure that most of the particulate deposits have been washed. This process is to enable the clean nature of the leave before grinding. The leaves were divided into three portions. Each portion was grinded in electronic blender using methanol, ethanol and butanol as solution for each portion of the leave. The homogenous liquid was filtered using a sieve. The filtrates were placed in enclosed petri dishes and heated in an oven at 90 °C for 1 h and allowed to cool and settle for 24 h. After cooling, 0.05 mol of aluminum potash sulfate was added and heated for 20 min at 80 °C. The filtrates were stored in airtight bottles. The filtrates were allowed to settle for 24 h. Then the filtrates characterized using the Scientific GENESYS 10S UV–Vis spectrophotometer and water has the diluting medium. The dilution factor is 10.

The statistics of the absorbance were estimated using correlation coefficient, Principal Coordinates Analysis (PCoA), standard deviation and variance coefficient. The molar attenuation coefficient was calculated using the Beer-Lambert law i.e.,

$$A = \varepsilon l c \tag{1}$$

where A is the absorbance, ϵ is the molar attenuation coefficient of the medium, c is the molar concentration, and l is the path length (cm). For this calculation, the pressure was 1.01×10^{-5} pa, the Boltzmann constant is given as $1.38064852\times10^{-23}~m^2~kg~s^{-2}~K^{-1}$, temperature of 298 K, collision cross-section of $2.83\times10^{-19}~m^2$, where the molar concentration varied between 0.01 and 0.1 M.

3. Results and discussion

The ultraviolet visible spectroscopy characterization of the aluminium coated Thaumatococcus daniellii extracts are presented in Fig. 1. Fig. 1a presents the aluminium coated Thaumatococcus daniellii extract using methanol solution (sample 1). The two d-d transitions were noticed at higher and lower energies $(\lambda = 612 \text{ nm } \& \lambda = 485 \text{ nm})$ as presented in Fig. 1a. The d-d transition depicts the transition between the lower energy d orbital (t2g orbitals: d_{xy} , d_{yz} and d_{zx}) and higher energy d orbital (Eg orbitals: d_{x2-y2} and d_{z2}). The band gap of the sample was calculated as 1.6×10^{-9} eV. Fig. 1b presents the aluminium coated *Thaumatococ*cus daniellii extract using ethanol solution (sample 2). Three d-d transitions were observed at wavelength $\lambda = 612$ nm, $\lambda = 485$ nm & $\lambda = 460$ nm. Certainly, the ethanol solution had created the growth of oxide layers via the diffusion of oxygen and water molecule inside the matrix [17,18]. The band gap of the sample was calculated as 2 eV.

Fig. 1c presents the aluminium coated *Thaumatococcus daniellii* extract using butanol solution (sample 3). Four d-d transitions were observed at wavelength $\lambda = 612$ nm, $\lambda = 532$ nm, $\lambda = 485$ nm & $\lambda = 460$ nm. As already discussed in sample 2, the butanol solution had created more growth of oxide layers via the diffusion of oxygen and water molecule inside its matrix [17,18]. The band gap of sample 3 was evaluated as 2×10^{-9} eV. The results in



Fig. 1. UV–Vis absorption spectrum aluminium coated *Thaumatococcus daniellii* extracts (a) extract in methanol solution (b) extract in ethanol solution (c) extract in butanol solution.





Fig. 1 (continued)



Fig. 2. Linear fit analysis of UV–Vis spec measurement (a) extract in methanol solution (b) extract in ethanol solution (c) extract in butanol solution.





Table 1Statistical analysis of material absorbance.

Parameters	Sample 1	Sample 2	Sample 3
N	234	243	243
Min	2.118	1.191	0.246
Max	4.805	2.937	0.544
Sum	618.524	374.597	72.467
Mean	2.643265	1.541551	0.2982181
Std. error	0.04013688	0.0238137	0.003559832
Variance	0.3769667	0.1378034	0.003079394
Stand. Dev	0.6139762	0.3712188	0.05549229
Median	2.35	1.393	0.276
25 prcntil	2.191	1.243	0.259
75 prcntil	2.93075	1.716	0.32
Skewness	1.502066	1.484937	1.873384
Kurtosis	1.628835	2.010917	4.116856
Geom. Mean	2.583397	1.503842	0.293879
Coeff. Var	23.22795	24.08086	18.60796



Coordinate 1

Fig. 3. PCoA scattered plot of UV–Vis absorption spectrum aluminium coated *Thaumatococcus daniellii* extracts (a) extract in methanol solution (b) extract in ethanol solution (c) extract in butanol solution.



Coordinate 1





Coordinate 2

Fig. 3 (continued)

Fig. 1 shows that the inherent chemical components of *Thaumato-coccus daniellii* (i.e. tetracontane (28.76%) and L-ascorbic acid (15.07%); hexadecanoic acid (21.62%) and γ -sitosterol (11.06%) [19]) allows for the quick release of π -electrons to the aluminium atom.

The second step is to perform the statistical analysis of the absorbance to ascertain other qualities in the samples. In regression analysis, the difference between the observed value of the dependent variable and the predicted value is called the residual. The residuals of the absorption are essential to understand the oxide layer growth patterns as presented in Fig. 2. It was observed that the oxide layer growth was more prominent at energies within wavelengths 380–600 nm for all the samples. It was also observed that the growth mode differs according to the samples. This affirms the increasing d-d transition points described in Fig. 1. It was observed that the oxide layer growth of the oxide layer growth pattern was more vigorous in sample 2 and more stable in sample 3. Hence, the more stable the growth of the oxide later, the more d-d transitions expected.



Fig. 4. Molar attenuation coefficient (a) sample 1 (b) sample 2 (c) sample 3.



Fig. 4 (continued)



The statistical analysis of the absorbance of samples 1–3 is presented in Table 1. The data points in sample 1 are lower because of the uniform dilution factor used for all the samples. Sample 1 and 3 had the highest and lowest absorbance respectively. Due to the high and low values of the mean, same results are expected to reflect in other parameters such as minimum, maximum, standard error, variance, median, standard deviation, geometric mean, kurtosis, 25% and 75% percentile. The skewness shows that sample 3 and 2 are the highest and lowest respectively. The skewness was able to validate the results presented in Fig. 2. The coefficient variances also affirm the magnitude of the reaction rates of the samples.

The principal coordinate analysis is presented in Fig. 3. Principal Coordinates Analysis (PCoA) is a method to explore and to visualize similarities or dissimilarities of data. The principal coordinate for sample 1 (coordinate 1) and sample 2 (coordinate 2) are presented in Fig. 3a below. It shows that sample 1 and 2 had more similarities (positive y-axis) than dissimilarity. The dissimilarity in both samples is in the oxide layer growth pattern. The PCoA had a negative parabolic pattern.

The principal coordinate for sample 1 (coordinate 1) and sample 3 (coordinate 3) are presented in Fig. 3b below. Like in Fig. 3a, there are more similarities (positive y-axis) than dissimilarity (negative y-axis) in sample 1 & 3. The dissimilarity in both samples is in the oxide layer growth pattern. The principal coordinate for sample 2 (coordinate 2) and sample 3 (coordinate 3) are presented in Fig. 3c below. There are more dissimilarities than similarities between sample 2 and sample 3. Aside, the creation of an extra d-d transition (as seen in Fig. 1), the vigorous reaction that led to the formation of oxide layers in the sample differs.

The third step is to analyse the dynamics of the chemical reaction using molar attenuation coefficient analysis. Also Beer-Lambert law was used to estimate the molar attenuation coefficient for each sample, as displayed in Fig. 4. At lower molar concentration i.e., 0.01 M, the molar attenuation coefficient was very significant. In other words, the molar concentration is inversely proportional to the molar attenuation coefficient. Since molar attenuation coefficient is a measurement of how strongly a chemical species attenuates light at a given wavelength, it means that at low molar concentration the higher chemical component of the samples attenuate light. Hence, the chemical dynamics can be monitored more efficiently as presented in Fig. 4.

4. Conclusion

The Thaumatococcus daniellii leaf has proven to be a good bio-semiconductor based on its susceptibility to dopants and the bandgap energy that classifies it as a good solid-state device. The ethanol and butanol plant extractions were better solid-state based on the values of the bandgap, and principal coordinate analysis. The 3 d-d transitions in sample 2 (i.e., ethanol plant extraction) and 4 d-d transitions in sample3 are evidence that the lattice have been significantly affected by the aluminium doping.

Thaumatococcus daniellii leaf extracts allows the extra methyl bond to significantly create growth of oxide layers via the diffusion of oxygen and water molecule inside the matrix. Also, it was clearly proven that the molar concentration is inversely proportional to the molar attenuation coefficient.

CRediT authorship contribution statement

E. Moses EMETERE: Conceptualization, Validation. M. Ikechukwu AHIARAI: Methodology, Data curationa

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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