**Research Article** 



# **Evaluation of Avocado Peels Dye as Sensitizer in Dye-Sensitized Solar Cells by Experiment and Computational Intelligence**

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Received: 7 October 2023; Revised: 21 November 2023; Accepted: 21 November 2023

**Abstract:** This work was designed to evaluate the unmodified and modified natural dye obtained from a sensitizer in dye-sensitized solar cells using experimental and computational approaches. Natural dye (APPE) was extracted from Avocado pear (*Persea Americana*) peels and chemically modified into nanocomposite by a one-pot reaction with silver nitrate. The modified dye was characterized by UV-Vis spectroscopy, X-ray diffraction (XRD) spectroscopy, Energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). The APPE and APPE-AgNPs composite show maximum wavelength of light absorption at 542 nm and 493 nm respectively. Both APPE and APPE-AgNPs were evaluated as sensitizers for dye-sensitized solar cells (DSSC). The APPE-AgNPs dye afforded a higher power conversion efficiency of 0.93% compared to 0.44% for APPE. Current-voltage responses and photo-electrochemical properties were determined at one sun illumination. The electronic properties of the major phyto-compounds in the dye, namely perseorangin and cyanidin associated with light harvesting and sensitization were modeled using a quantum chemical computational approach. The power conversion efficiency of APPE-AgNPs obtained from this study compares with other plant-based dye sensitizers and hence could be deployed for practical application.

Keywords: nanoparticles, renewable energy, sensitizer, solar cells

# **1. Introduction**

As global energy consumption continues to increase, demand for renewable and clean energy sources has been at an all-time high. Researchers have also moved to find replacements for fossil fuel which is currently ravaging the environment and posing serious climatic problems. Energy from the sun has been considered to be significantly sustainable, especially in countries with longer periods of dry season or those located in temperate zones. Motivated by this, scientists have fabricated and used several inorganic semiconductor photovoltaic devices for energy generation, conversion and storage [1]. Although many of these cells are efficient in energy storage and conversion, the materials required for their fabrication are very often expensive and the fabrication process is also cumbersome requiring sophisticated and expensive equipment [2]. This does not go well economically with many low-income countries. Therefore, in search of cost-effective alternatives, dye-sensitized solar cells (DSSCs) have attracted research attention

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over the years.

Dyes of different shades (colours) have varying absorption and light harvesting potentials, and when deployed in DSSCs, they absorb solar energy, which can then be converted into electrical energy [3]. The dye, therefore, acts as a sensitizer and sensitizes wide band-gap semiconductors to visible light radiation [4]. The DSSC materials are mainly the dye-capped semiconductor electrode, redox electrolyte and metal counter electrode. These components are mostly low-cost materials and thus desirable because of the price-to-performance ratio [5]. However, the general performance, especially the power conversion efficiency and durability of DSSCs, depends mainly on the sensitizer used and the semiconductor electrode [6]. Therefore, DSSCs with varying performances could be obtained by changing the material used as either the sensitizer (dye) or the semiconductor electrode.

The earliest DSSCs made use of ruthenium polypyridyl complexes as sensitizers [7]. It was opined that the lifetime of excited electrons of these complexes was longer and they also showed intense charge transfer absorption in the visible region of the electromagnetic spectrum. These reasons motivated their selection as sensitizers. From that time till date, a wide variety of inorganic complexes and synthetic materials have been investigated as sensitizers for DSSCs and their performances have been reported [8-10]. Recently, researchers have been paying more attention to low-cost materials and materials that can be easily prepared. Since DSSCs do not last forever and will eventually be discarded into the environment after use, it is very crucial that the sensitizer used should not be toxic or should be an eco-friendly material.

In search for low-cost and eco-friendly DSSC sensitizer materials, researchers have considered natural dyes/ pigments especially those that are obtained from plants. In literature, an avalanche of natural dyes as DSSC sensitizers have been reported [5, 11] and they have shown different power conversion efficiencies. Although natural dyes satisfy conditions of low cost, ease of preparation, biodegradability and eco-friendliness, there are also limitations, which include their low efficiency and ease of degradation by microbial or biochemical agents leading to decline or loss of efficiency. Thus, a DSSC utilizing natural pigments does not last and so does not have good economic value. To overcome this limitation, the natural dye may need to be chemically modified, perhaps to obtain a higher efficiency than the crude dye. In line with this consideration, this study was designed to modify and assess locally sourced natural dye as sensitizer for DSSC. To the best of our knowledge, the findings from the preliminary assessment of modified dye extracted from Avocado pear peels are reported for the first time. Results from a combination of experiment and theoretical modeling have revealed that modification of APPE into APPE-AgNPs improves the sensitizer performance.

### 2. Materials and method

### 2.1 Preparation of sensitizers

Ripe Avocado pears were obtained from the farm at Ikot Ambon Ibesikpo in Ibesikpo Asutan LGA of Akwa Ibom state, Nigeria and conveyed to the laboratory. The edible part of the fruits was consumed while the peels were gathered, washed twice with de-ionized water, cut into smaller pieces and spread to air-dry. Dry peels were blended into powder using an electrical blender and 100 g of the powder was soaked in 1,000 mL of distilled water, warmed at 30-40 °C for 4 h with regular swirling in the water bath, cooled and then filtered using Whatman 1 mm paper. The filtrate was concentrated using a rotary evaporator to obtain a paste, which was dried to powder in the oven at 35 °C. The powder extract was prepared into the concentration of 1,000 ppm, labeled APPE.

The silver nitrate supplied by Sigma Aldrich, USA, was freshly prepared in de-ionized water to 1 mm concentration and stored in amber-coloured bottles inside laboratory cupboards at room temperature. To prepare the modified APPE, the freshly prepared solution of 1 mm of AgNO<sub>3</sub> was reacted with 1,000 ppm APPE in the ratios 1:1 (v/v). The mixture vessel was warmed at 25-50 °C with stirring at regular intervals and observed keenly until a firm colour change was seen [12]. On colour change, the colloidal solution obtained was labeled as APPE-AgNPs and divided into two portions: one portion was concentrated using a rotary evaporator and dried in the oven at 30 °C to powder while the liquid (colloidal) portion was preserved.

On extraction, APPE yielded a pinkish colour whereas APPE-AgNPs yielded a yellowish-brown colour. The colours of APPE and APPE-AgNPs obtained were similar to those reported by Uren [13] and Adebayo [14] respectively. At the beginning of the reaction between APPE and AgNO<sub>3</sub>, the mixture yielded a light pink colour; after 1 h of

reaction, the colour developed to yellowish-brown and remained the same even after 6 hours of observation and when kept overnight. This indicates that the reaction was complete within one hour.

#### **2.2** Characterization of sensitizers

Both APPE and APPE-AgNPs were analysed by UV-Vis spectroscopy at 200-800 nm to determine the wavelength of absorption of radiation. Powder XRD analyses of both sensitizers were conducted by XRD spectroscopy at  $2\theta = 10-90^{\circ}$  [15]. Analyses of the elemental composition of both APPE and APPE-AgNPs were conducted by EDS spectroscopy whereas morphology and particle size were determined by TEM [16].

#### **2.3** Preparation of DSSC materials

The procedures previously reported in the literature [4] was followed without further modification. Briefly, this employs a 13  $\Omega$ /sq fluorine-dopped tin oxide (FTO) glass plate as a current collector. The FTO was subjected to 10 minute ultrasonic bath each in ethanol, followed by de-ionized water, then acetone to ensure thorough cleaning and drying. The FTO plate was then coated with TiO<sub>2</sub> following the procedures reported in the literature [17]. The coated FTO plate was dried for 5 minutes followed by annealing of the substrates at 450 °C in air for 30 minutes. The film was maintained at a thickness of 20  $\mu$ m while the active area of 0.18 cm<sup>2</sup> of TiO<sub>2</sub> electrode was exposed. After annealing, the film was cooled to 80 °C, then immersed in APPE-AgNPs slurry, another film was also immersed in APPE slurry. The concentrations of both APPE-AgNPs and APPE in the slurry were 1,000 ppm. The immersed film was allowed to stand for 24 hours for sufficient adsorption and incorporation of the sensitizers on the film to occur. This was followed by drying the film in hot air. A platinum electrode used as a counter electrode was also prepared similarly by coating with platinum paste [18].

#### 2.4 Assembly of DSSC

The two electrodes prepared above were assembled as a sandwich-type cell as previously described in the literature [18]. Briefly, a drop of iodolyte AN-50 electrolyte was injected into the cell from a hole created at the back of the counter electrode. The back hole was thereafter sealed with hot-melt ionomer film and covered with a glass plate. The edges of the FTO glass were cleaned, soldered with alloy No. 143 and exposed to sunlight (placed in the sun) for photoelectrical measurements.

### 2.5 Photo-electrochemical tests

Current-voltage responses were determined at open circuit and short circuit conditions at one sun illumination (AM 1.5 G, 100 mWcm<sup>-2</sup>) using a Keithley 2,400 source measurement unit at room temperature in the presence of sunlight [19].

#### 2.6 Computational studies

The structures of perseorangin (PSG) and cyanidin (CND) were each optimized using the forcite function of the Materials Studio Aceryls software to obtain a configuration with the minimum energy. Quantum calculations on electronic properties were carried out using the optimized structure in the Dmol<sup>3</sup> the same software within the framework of density functional theory, using DFT/B3LYP. Frontier molecular orbitals namely, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plots and their energies were obtained. Other quantum chemical parameters such as band gap energy ( $\Delta E$ ), ionization energy (*IE*), electron affinity (*EA*), electronegativity ( $\chi$ ), global hardness ( $\eta$ ) and global softness ( $\sigma$ ), were calculated using the HOMO and LUMO energies according to the following equations:

$$\Delta E = E_{\rm LUMO} - E_{\rm HOMO} \tag{1}$$

$$IE = -E_{\rm HOMO}$$
(2)

$$EA = -E_{\rm LUMO} \tag{3}$$

$$\chi = \frac{1}{2} (IE + EA) \tag{4}$$

$$\eta = \frac{1}{2} (IE - EA) \tag{5}$$

$$\sigma = \frac{1}{\eta} \tag{6}$$

# 3. Results and discussion

### 3.1 Unmodified and modified dyes

On analyses using XRD spectroscopy, the obtained spectrum (Figure 1) reveals that m-APPE is crystalline. Also, from the spectrum, three majors distinctly resolved peaks at 14.3°, 26.6° and 32.2° can be identified. The diffraction angles obtained were in agreement with previously reported silver nanoparticles synthesized from plant extracts [19-20]. Analysis of the spectrum using the X-PERT High Score Plus software package (PANalytical) reveals the presence of zerovalent ( $Ag^0$ ) silver distributed mainly in the (1 1 2) plane in addition to (0 1 1) and (1 1 0) planes. This further supports that the m-APPE is crystalline. EDS spectrum obtained (Figure 2) for m-APPE reveals that silver is incorporated into the APPE-AgNPs matrix whereas APPE contains mostly C, N and O atoms (Table 1). TEM results (Figure 3) also reveal that APPE-AgNPs are in nano-scale with an average particle size of 48.5 nm and spherical in shape.



Figure 1. Powder XRD spectrum of m-APPE

Table 1. Elemental composition of the surfaces of APPE and APPE-AgNPs

Atoms	APPE surface		APPE-AgNPs surface		
Atoms	Wt. (%)	Atom (%)	Wt. (%)	Atom (%)	
С	28.37	30.53	33.28	39.39	
Ν	0.21	0.84	0.18	0.67	
0	71.42	68.63	52.73	36.88	
Ag	-	-	13.81	23.06	

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Figure 2. EDS spectrum of (a) APPE and (b) APPE-AgNPs



Figure 3. TEM images of APPE-AgNPs

# 3.2 UV-Vis spectroscopy

On analysis by UV-Vis spectroscopy, APPE and APPE-AgNPs absorbed radiation at maximum wavelengths of 542 nm and 493 nm, respectively, as shown in Figure 4. Thus, both APPE and APPE-AgNPs dyes absorb within the visible region of the electromagnetic spectrum, hence are capable of producing colours. The obtained wavelengths of maximum absorption of m-APPE fall within the range often reported for most plant extract-mediated silver nanoparticles [20], also supporting that m-APPE could be a silver nanocomposite.



Figure 4. UV-Vis spectrum of APPE and m-APPE (APPE-AgNPs)

From the obtained values of wavelengths of maximum absorption ( $\lambda_{max}$ ), molar extinction coefficients ( $\xi_{max}$ ) were determined by applying Eq. 7. The magnitude of  $\xi_{max}$  connotes how strongly the dyes absorb light at the given wavelengths and depends on the structure of the active compounds in the dye responsible for the colour.

$$\xi_{\max} = \frac{\alpha \lambda_{\max}}{4\pi} \tag{7}$$

where  $\alpha$  is the absorption coefficient and can be determined from spectral value of absorbance (A) at  $\lambda_{max}$  and the path length (l) based on Beer-Lambert's law as shown in Eq. 8.

$$\alpha = \frac{2.303A}{l} \tag{8}$$

The obtained values of  $\xi_{max}$  (Lgcm<sup>-1</sup>) for APPE and m-APPE were  $3.12 \times 10^4$  and  $6.57 \times 10^4$  respectively. For DSSCs, the higher the extinction coefficient, the better the sensitizer. Therefore, it can be implied from the above results that APPE-AgNPs would be a better sensitizer for DSSC than APPE. Attempts were made to correlate the  $\xi_{max}$  to the type of electronic transitions taking place in the active colour-producing compound(s) in APPE and APPE-AgNPs. Usually, electronic transitions could emanate from sigma ( $\sigma$ )-bonding, pie ( $\pi$ )-bonding or non-bonding (n) electrons. However,  $\sigma$ -transitions are associated with saturated bonds which do not produce colour, and hence do not occur in the visible region. Transitions that occur in the visible spectrum have  $\xi_{max}$  values in the range up to 10<sup>4</sup>. From the results obtained, the possible transitions could be occurring within either the bonding  $\pi$ -electrons or n-electrons or both to the corresponding bonding or anti-bonding orbitals. Further study would be required to elucidate details on these transitions.

#### 3.3 Photo-electrochemical properties

Current and voltage measurements using the constructed DSSC sensitized by each of APPE and APPE-AgNPs were conducted under open circuit (oc) and short circuit (sc) conditions and the obtained results are displayed in Table 2. The obtained experimental data were used to evaluate the performance of the cells by elucidating the fill factor ( $\Gamma$ ) and the power conversion efficiency (*PCE*) according to Eq. 9 and 10 respectively [21].

$$\Gamma = \frac{I_{\max}V_{\max}}{I_{SC}V_{OC}} = \frac{P_{\max}}{I_{SC}V_{SC}}$$
(9)

$$PCE = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{P_{\text{max}}}{P_{\text{in}}} = \Gamma\left(\frac{I_{\text{SC}}V_{\text{OC}}}{EA}\right)$$
(10)

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where  $I_{\text{max}}$  and  $I_{\text{SC}}$  represent the maximum current and the short circuit current,  $V_{\text{max}}$  and  $V_{\text{OC}}$  represents the maximum voltage and the open circuit voltage,  $P_{\text{max}}$  represents the maximum power or output power ( $P_{\text{out}}$ ), E represents the incident light irradiance and A is area of deposited film. Results (Table 2) reveal that both APPE and APPE-AgNPs act as sensitizers in DSSC with efficiencies of 0.44% and 0.93%, respectively. Despite the low efficiency obtained, the values of *PCE* for APPE and m-APPE are significantly high and compete effectively with other natural dyes from plants reported in the literature [22-23] but not as high as those dyes reported recently by Yadav and co-workers [24]. Thus, modification of APPE to APPE-AgNPs results in an increase in power conversion efficiency by over 111%.

Sensitizer	$V_{\rm oc}~({ m mV})$	$I_{\rm sc}$ (mA)	$I_{\rm max}$ (mA)	$V_{\rm max}~({ m mV})$	Г	PCE (%)
APPE	247.60	3.22	2.44	214.72	0.66	0.44
APPE-AgNPs	382.50	6.01	4.81	229.24	0.48	0.93

Table 2. Photo-electrochemical properties of APPE and APPE-AgNPs

### 3.4 Computational study

From the first principle, for DSSCs, when light incidents on the TiO<sub>2</sub> film, the dye molecules prepared on the film will absorb photons and become excited from HOMO to LUMO state. This is called photo-excitation and leads to the injection of electrons from the photo-excited dye species to the conduction band of the TiO<sub>2</sub> electrode. Having lost electrons through the injection process, the dye species becomes oxidized, and can subsequently accept electrons from the electrolyte to restore it to the ground state dye, and the process continues. The electron so injected travels through the TiO<sub>2</sub> film to the FTO layer where it is driven through an external circuit to a load to deliver electrical energy. From the external load, the electron diffuses to the cathode and gets transferred to the electrolyte. This causes the electrolyte to also be regenerated.

The decisive requirement is that for a dye to be suitable for DSSC application, the LUMO energy should not be below the conduction band edge of the  $TiO_2$  semiconductor to enhance the effective injection of electrons [25]. On the other hand, the HOMO energy should not be above the redox potential of the electrolyte for efficient regeneration of the oxidized dye molecule [26]. In addition, the HOMO-LUMO energy gap of the dye should be narrow to shift light absorption into the visible region. A distinct orbital localization that is capable of ensuring charge separation is also very desirable. These parameters are not easy to determine by experiments, therefore, we sought to investigate them by quantum mechanical calculations.

It has already been established that perseorangin (PSG) and cyanidin (CND) are the key compounds in APPE responsible for colour [24, 27]. While PSG typically should convey a yellow-orange colour, CND should convey a reddish-purple colour [27]. The structures of both PSG and CND were optimized and results are shown in Figure 5.



Figure 5. Optimized chemical structures of (a) cyanidin and (b) perseorangin using DFT/B3LYP

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plots were also obtained (Figure 6) and the respective energies of the orbitals are also obtained (Table 3).



Figure 6. HOMO of (a) cyanidin and (b) perseorangin and LUMO of (c) cyanidin and (d) perseorangin using DFT/B3LYP

Parameters (ev)	PSG	CND	
$E_{HOMO}$	-5.42778	-2.81198	
$E_{LUMO}$	-2.62042	-0.32871	
$\Delta E$	2.807359	2.483276	
IE	5.427778	2.811985	
EA	2.620419	0.328709	
χ	4.024099	1.570347	
η	1.403679	1.241638	
σ	0.712414	0.805387	
Binding energy	-3997.24	-1907.87	

Table 3. Energy parameters determined by quantum chemical calculations using DFT/B3LYP

The energies of the frontier molecular orbitals ( $E_{HOMO}$  and  $E_{LUMO}$ ) were determined by computational intelligence approach using Materials Studio software. Results reveal that the  $E_{LUMO}$  for PSG and CND are -2.62 eV and -0.33 eV respectively. The conduction band of TiO<sub>2</sub> has been experimentally determined to be -4.0 eV [27]. In other words, both PSG and CND have  $E_{LUMO}$  values that are higher than the conduction band of TiO<sub>2</sub> as required for easy and effective injection of electrons from APPE and m-APPE into the TiO<sub>2</sub> conduction band. On the other hand, the  $E_{HOMO}$  of PSG and CND are -5.43 eV and -2.82 eV respectively. Except for CND, the values are sufficient to effect efficient regeneration of the dye molecules after oxidation since they are not above the redox potential of the electrolyte. The HOMO-LUMO energy gap is 2.81 eV and 2.48 eV for PSG and CND respectively. According to Gahnn and co-workers [26, 28], this gap is narrow enough to shift light absorption to the visible region. Analyses of molecular orbitals reveal that the HOMO orbitals are concentrated in different regions from that of the LUMO. Other parameters such as ionization energy (*IE*), electron affinity (*EA*) and global hardness ( $\eta$ ) that can be used as reactivity descriptors were also calculated and results are presented in Table 3 and may be related to the light-harvesting potential of PSG and CND in other ways.

## 4. Conclusion

The dye obtained from Avocado peels was assessed as a light harvester or sensitizer in DSSCs in its unmodified and chemically modified form. APPE-AgNPs were crystalline and of an average size of around 48 nm. Both APPE and m-APPE absorbed radiation from the visible region of the electromagnetic spectrum and converted the light radiation to electrical energy with power conversion efficiencies of 0.44% and 0.93%, respectively. Quantum computational studies reveal that the active compounds in APPE, namely, PSG and CND exhibit HOMO and LUMO energies within the range that supports efficient sensitizer performance.

### Acknowledgements

The authors appreciate the support of Tertiary Education Trust Fund (TETFund) of Federal Republic of Nigeria, through the TETFund Centre of Excellence in Computational Intelligence Research as well as the Management of the University of Uyo, Uyo, Nigeria.

# **Conflict of interest**

The authors declare no competing financial interest.

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