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ONION PEEL DYE-NANOCOMPOSITE AS LIGHT HARVESTER IN DYE-SENSITIZED SOLAR CELLS

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ABSTRACT
Silver nano-composites (ROPED-AgNPs) were synthesized by bio-reduction of silver ions usingdye extract from red onion peels (ROPED). Both ROPED and ROPED-AgNPs were characterized by UV-Vis, FTIR, XRD, EDS and TEM. While ROPED was amorphous and in micro-scale, ROPED-AgNPs were crystalline, spherically shaped, non-agglomerating and of sizes within the nano range. Both materials were evaluated as sensitizers for dye sensitized solar cells (DSSCs) by assessing their light absorption and photo-electrochemical properties. Results revealed that ROPED and ROPED-AgNPs are potential light harvesters and afford energy conversion efficiency of 0.33 % and 0.78 % respectively.

INTRODUCTION
The conventional inorganic semiconductor photovoltaic devices are expensive to fabricate. In search for alternatives that are more cost effective devices, researchers have given considerable attention to dye sensitized solar cells (DSSCs) as possible replacement (Bhogaita *et al.,* 2016; Taya *et al*., 2015). This is motivated by the fact that dyes have good absorption and light harvesting properties, hence can be deployed for converting solar energy into electrical energy (Sharma *et al*., 2021). Dye molecules in DSSCs sensitize wide band-gap semiconductors to radiation in the visible region of electromagnetic spectrum, hence they are often referred to as 'sensitizers' (Ezike*et al*., 2021). The main composition of a DSSC is a dye-capped nano crystalline porous semiconductor electrode, a metal counter electrode and a redox electrolyte which mediates electron transfer processes that occur in the cell. A schematic representation of DSSC is shown in Fig. 1 (Kushwaha *et al*., 2013). The performance of a DSSC depends mainly on the sensitizer used and the semiconductor electrode material (Taya *et al*., 2015).

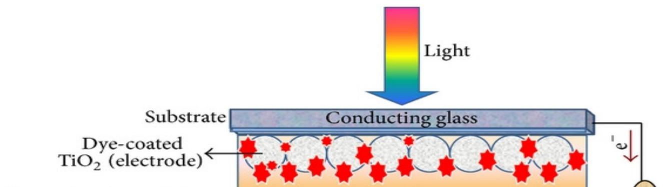

Figure 1. Schematic representation of DSSC

The first reported DSSC deployed ruthenium polypyridyl complexes as a sensitizer due to its intense charge transfer absorption in the visible region as well as longer lifetime of excited electrons (O'regan and Grätzel, 1991). Since then, a wide variety of inorganic and synthetic coloured materials have been investigated as sensitizers for DSSCs (Sharma *et al*., 2021). Concerns such as availability, cost and eco-friendliness of these sensitizers have presented natural dyes as more desirable materials. In addition, natural dyes sensitizers are readily and sustainably available, nontoxic and easy to prepare. Little wonder why several naturally extracted dyes have been tested as sensitizers for DSSCs (Hosseinnezhad *et al.*, 2020; Pathak *et al*., 2019). However, natural dyes are easily degraded by biochemical and microbial agents hence their efficiency could decline after a little while. To overcome this limitation, we sought to modify the natural dye by bio-reduction reaction with silver ions. The resulting silver nano composites were then assessed in comparison with the crude extract. To the best of our knowledge, this is the first time such innovation is being reported.

MATERIALS AND METHOD

Preparation of sensitizer

Red onion peels were washed with distilled water and air-dried under laboratory temperature. Dried peels were grounded to powder using electric blender. Fifty grams of the powder was extracted in 1 L of deionized water after soaking for 24 h at 45^oC. The filtrate was concentrated to paste in rotary evaporator and the paste was oven-dried at 45^oC to powder. Thereafter, 0.1 g of the powder was dissolved in 50 mL of deionized water and labelled as Red onion peels extract dye (ROPED). Then, 25 mL of ROPED was mixed with 25 mL of 0.001 M $AgNO_3$ and stirred at 35- 45^oC until colour change was observed, signalling the completion of bio-reduction reaction and formation of nano particles. This solution was labelled as ROPED-AgNPs.

Solar cell assembly

The current collector used was a 13 Ω/sq fluorine-doped tin oxide (FTO) glass plate. The FTO glass was cleaned with ethanol in an ultrasonic bath for 10 minutes, and the cleaning was repeated using water, then acetone. TiO_2 paste (Ti-nanoxide T/SP, Solaronix) was coated on the FTO plate following previously reported procedures (Tajudeen, 2017)and then air-dried for 5 minutes. The substrates were then annealed at 450^oC in air for 30 minutes. This reduced organic loads which may be present in the film and helps TiO_2 nano particles to interconnect. Film thickness was maintained at about 20 μm. The TiO_2 electrodes used were of 0.18 cm^2 active area. After annealing, the film was cooled to 80^oC, and immersed in ROPED-AgNPs while another film was immersed in ROPED as control. Immersion time was 24 hours to allow for sufficient adsorption/incorporation of the dyes on the film, followed by drying of the film in hot air. A platinum electrode was similarly prepared by coating platinum paste (platisol T/SP, Solaronix) following the above procedures (Singh et *al.*, 2021).

The TiO_2 and Platunium counter electrodes were assembled as a sandwich-type cell. From the hole at the back of the counter electrode, a drop of Iodolyte AN-50 (Solaronix) electrolyte was injected into the cell. Thereafter, the hole was sealed with hot melt ionomer film (SX 1170, Solaronix) and covered with glass. The FTO glass edges were then cleaned and soldered with alloy #143 (Cerasolza) to ensure good electrical contact during measurements.

Materials characterization and tests

Formation of nano-composite and absorption wavelength was determined by UV-Vis spectroscopy (UV-2600 Spectrophotometer). Incorporation of silver into the nano-composite matrix was confirmed by X-ray diffraction (XRD) spectroscopy at 2θ = 20^o – 90^o in comparison with the extract and Energy dispersive X-ray spectroscopy (EDS, EVO MA 15 Zeiss). The morphology and size of the ROPED and ROPED-AgNPs was characterized by transmission electron microscopy (TEM, FEI TECHNAI G2F20). Fourier transform infrared (FTIR) spectroscopy was used to characterize functionalities within 400 - 4500 cm^{-1} using WQF520 spectrophotometer (Beijing Rayleigh). The current-voltage responses and photoelectrochemical properties were determined at one sun illumination (AM 1.5 G, 100 $mWcm^{-2}$) using a Keithley 2400 source measurement unit and by electrochemical impedance spectroscopy (EIS, Gamry REF600 workstation).

RESULTS AND DISCUSSION

Formation and properties of ROPED-AgNPs

From visual observation, the formation of ROPED-AgNPs occurred within 55-60 minutes. This was signalled by change in colour of the solution to reddish brown (Fig. 2 a).XRD results (Fig. 2 b) shows that ROPED-AgNPs is crystalline whereas ROPED is amorphous. Four peaks were obtained at 2θ = 37.98^o, 44.20^o, 64.73^o, and 77.26^o corresponding to (110), (200), (220) and

(311) Braggs crystallographic planes of face centre cubic (FCC) structure (Ituen *et al*., 2020). Analyses of the results using X-PERT High score Plus software package (PANalytical) confirmed the existence of silver in the Ag^0 phase and long range orderly periodic arrangement of Ag atoms in a fcc structure with a = b = c = 4.0968 Å and $\alpha = \beta = \gamma = 90^o$, containing cells of volume 68.76x10^{-6} pm^3 and density (ρ) 10.19 gcm^{-3}. The very high intensity peak at 38.16^o indicates that the (111) plane is the preferred orientation. The calculated crystallite size of nano-composites were about 45 nm.

EDS results reveals that Ag atoms are absent in the spectrum of ROPED but present in the spectrum of ROPED-AgNPs (Fig. 2 c), confirming that silver nano-composites were actually formed. The nano composites surfaces are richer in N and O than the crude extracts, perhaps due to extensive capping of phyto-compounds on the metal surface in the nano scale. TEM images of ROPED-AgNPs (Fig. 2 d) reveals that they are of 45 nm sizes and are round shaped, distinct and do not aggregate.

In addition, the FTIR spectrum of ROPED (Fig. 3 a) shows prominent peaks at 1100 and 1610 cm^{-1} attributed to C-O stretching (alcohol, carboxylic acid, ester and ether) and N-H stretching (alkaloids, amines, amides and proteins) respectively. However, in the spectrum of ROPED-AgNPs, these peaks shifted to 1120 and1650 cm^{-1} respectively (Fig. 3 b), signifying their involvement in capping to Ag^+ ions. The sharp peak at 3450 cm^{-1}assigned to O-H stretching (alcohol, phenolics, flavonoids, etc) was obtained for ROPED-AgNPs instead of the broad peak at 3400-3500 $cm^{-1}$for ROPED. The peaks at 1400 $cm^{-1}$and 2960 cm^{-1}corresponding to C=C (aromatic) and C-H stretch of methylene groups were more prominent in the spectrum of the nano composites. These may be the active functionalities associated with the formation and stabilization ofROPED-AgNPs.

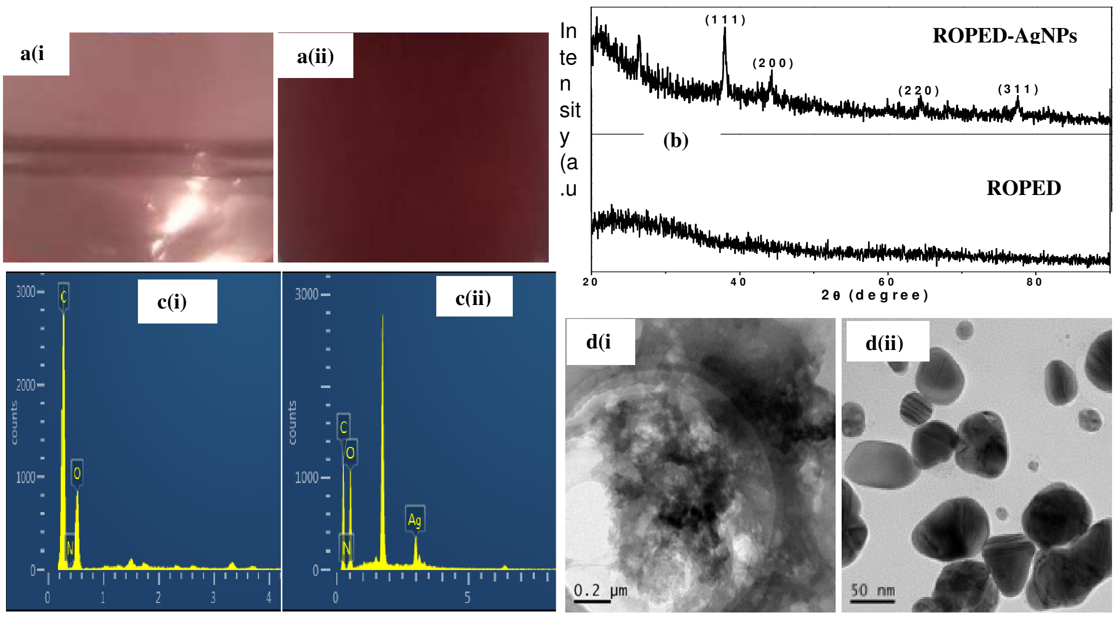

Figure 2: (a) Colour of (i) ROPED and (ii) ROPED-AgNPs (ii) XRD spectra of ROPED and ROPED-AgNPs (c) EDS spectra of (i) ROPED and (ii) ROPED-AgNPs and (d) TEM images of (i) ROPED and (ii) ROPED-AgNPs

Light absorption by ROPED-AgNPs.

The progress of development of the nano composites was monitored by UV-Vis spectroscopy. On complete development, change in colour of the solution occurred due to bio-reduction of silver (Ag^+) ions to zero-valent silver (Ag^0) by ROPED phyto-compounds. Plasmon resonance absorption caused by combined excitation of electrons results in peak absorbance in the UV-Vis spectrum. While ROPED shows two absorption bands at 508 nm and 585 nm, ROPED-AgNPs shows a broad absorption band at 495 nm, agreeing with previously reported range of 400 – 500 nm for silver nano particles (Ituen *et al.*, 2021). The observed absorption may be attributed to chromophores in phyto-compounds in ROPED, mainly quercetin and kaemferol (Fig. 3 a). These absorption wavelengths are associated with $\pi \rightarrow \pi^*$and $n \rightarrow \pi^*$transitions. While $\pi \rightarrow \pi^*$ transitions are characteristic of the conjugated double bonds in the anthraquininoid moiety of quercetin and kaemferol, $n \rightarrow \pi^*$transitions are also characteristic of the hydroxyl and ether groups which are present in both molecules (Jalali*et al.*, 2020). In general, most previously reported efficient dye sensitizers had absorption their bands within the range of 400 nm to 670 nm, which falls within visible region (Ahmed *et al.*, 2016). This implies that ROPED and ROPED-AgNPs could make an efficient sensitizer or light harvester for DSSCs. Modification of ROPED into nano particles also resulted in increased intensity of absorption, indicating better light harvesting properties.

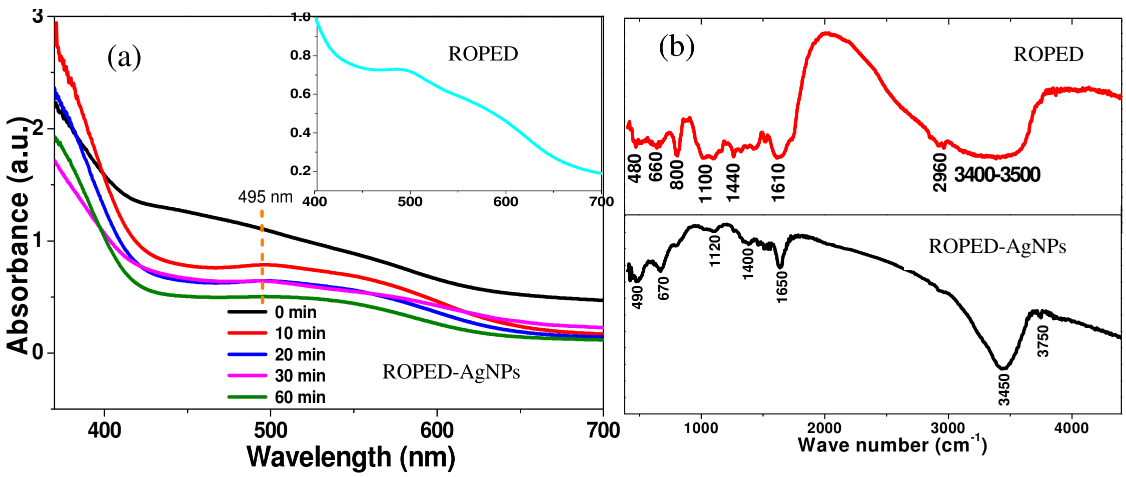

Figure 3: (a) UV-Vis Spectra of ROPED and ROPED-AgNPs at various time during development and (b) FTIR spectra of ROPED and ROPED-AgNPs.

Voltage – Current response and Photo-electrochemical characteristics

The performance and photo-electrochemical properties of both ROPED and ROPED-AgNPs sensitized DSSC were evaluated using some familiar associated parameters. Particularly, the fill factor (FF) and energy conversion efficiency (η) were determined using Eq. 1 and Eq. 2 respectively(Onah*et al.*, 2020).

$$FF = \frac{I_{max}V_{max}}{I_{sc}V_{oc}} = \frac{P_{max}}{I_{sc}V_{oc}} \quad (1)$$

$$\eta = \frac{P_{out}}{P_{in}} = \frac{P_{max}}{P_{in}} = FF\left(\frac{I_{sc}V_{oc}}{EA}\right) \quad (2)$$

whereI_{max} and V_{max} represent the maximum current output value and the maximum voltage output value corresponding to the output power or maximum power (P_{max}), I_{sc} and V_{oc} represents the short circuit current and the open circuit voltage respectively and $E$and A represent the incident light irradiance and area of deposited film (Ossai*et al.*, 2021). The results obtained are displayed in Table 1. Results reveal that ROPED-AgNPs yields higher energy conversion efficiency than ROPED, hence is a better photo sensitizer. This observation was also supported by EIS measurement- the radius of the depressed semicircle obtained from Nyquist plot for ROPED-AgNPs sensitized DSSC (Fig. 4) is larger than that of ROPED sensitized DSSC. Usually, the larger the radius of the semicircle, the higher the charge transfer, the lower the rate of recombination and the better the photoelectrical performance of the DSSC (Onah*et al.*, 2020).

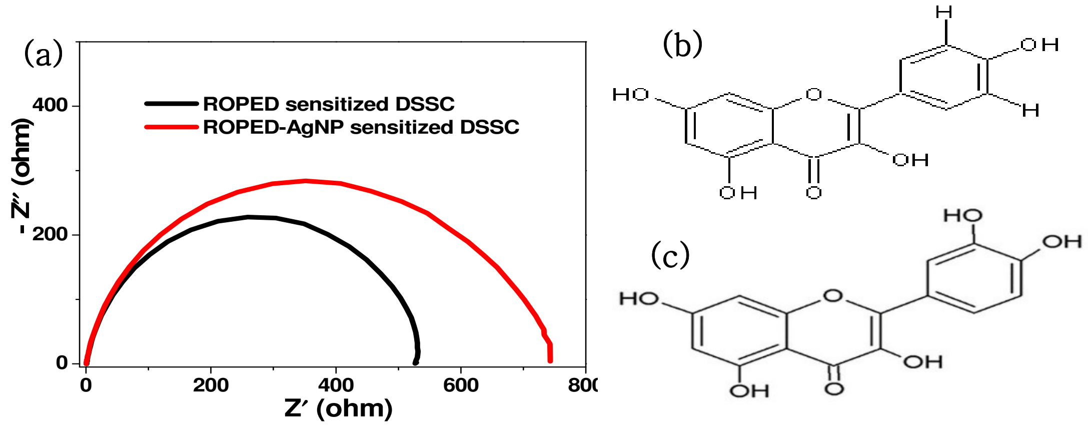

Figure 4:(a) Nyquist plots obtained from EIS study of ROPED sensitized and ROPED-AgNPs sensitized DSSC (b) molecular structure of kaemferol and (c) molecular structure of quercetin.

Table 1. Photo-electrochemical properties of ROPED and ROPED-AgNPs

Sensitizer	V_{oc}(mV)	I_{sc} (mA)	I_{max}(mA)	V_{max} (mV)	FF	η(%)
ROPED	338.21	4.383	2.679	221.73	0.401	0.33
ROPED-AgNPs	412.47	7.062	4.922	286.46	0.484	0.78

CONCLUSION

Dye extracted from red onion peels (ROPED) and the dye-silver nano-composite (ROPED-AgNPs) act as sensitizers in dye sensitized solar cell. Both ROPED and ROPED-AgNPs showed intense absorption in the visible region of electromagnetic spectrum resulting in $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$transitions. ROPED-AgNPs showed to be better sensitizer than ROPE judged from the magnitude of energy conversion efficiency of 0.78 % and 0.33 % obtained for ROPED-AgNPs and ROPED respectively. Based on the obtained results, modification of dye extracts into nano particles can improve its performance as sensitizer in dye sensitized solar cells.

REFERENCES

AhAhmed, S., Ahmad, M., Swami, B. L. and Ikram, S. (2016). A review on plants extract mediated synthesis of silver nano particles for antimicrobial applications: a green expertise. *Journal of Advanced Research*, 7(1): 17-28.

Bhogaita, M., Shukla, A. D. and Nalini, R. P. (2016). Recent advances in hybrid solar cells based on natural dye extracts from Indian plant pigment as sensitizers. *Solar Energy*, 137: 212-224.

Ezike, S. C., Hyelnasinyi, C. N., Salawu, M. A., Wansah, J. F., Ossai, A. N. and Agu, N. N. (2021). Synergestic effect of chlorophyll and anthocyanin Co-sensitizers in TiO2-based dye-sensitized solar cells. *Surfaces and Interfaces*, 22: 100882.

Hosseinnezhad, M., Gharanjig, K., Yazdi, M. K., Zarrintaj, P., Moradian, S., Saeb, M. R. and Stadler, F. J. (2020). Dye-sensitized solar cells based on natural photosensitizers: A green view from Iran. *Journal of Alloys and Compounds*, 828: 154329.

Ituen, E., Singh, A., Yuanhua, L. and Li, R. (2020). Synthesis and evaluation of anticorrosion properties of onion mesocarp-nickel nano composites on X80 steel in acidic cleaning solution. *Journal of Materials Research and Technology*, 9(3): 2832-2845.

Ituen, E., Yuanhua, L., Verma, C., Alfantazi, A., Akaranta, O. and Ebenso, E. E. (2021). Synthesis and Characterization of Walnut Husk Extract-Silver Nano composites for Removal of Heavy Metals from Petroleum Wastewater and Its Consequences on Pipe work Steel Corrosion. *Journal of Molecular Liquids*. https://doi.org/10.1016/j.molliq.2021. 116132

Jalali, T., Arkian, P., Golshan, M., Jalali, M. and Osfouri, S. (2020). Performance evaluation of natural native dyes as photosensitizer in dye-sensitized solar cells. *Optical Materials*, 110: 110441.

Kushwaha, R., Srivastava, P. and Bahadur, L. (2013). Natural pigments from plants used as sensitizers for TiO2 based dye-sensitized solar cells. *Journal of Energy*, 2013.http://dx.doi.org/10.1155/2013/654953.

Onah, E. O., Offiah, S. U., Chime, U. K., Whyte, G. M., Obodo, R. M., Ekechukwu, O. V., Ahmad, I., Ugwuoke, P. E. and Ezema, F. I. (2020). Comparative photo-response performances of dye sensitized solar cells using dyes from selected plants. *Surfaces and Interfaces*, 20: 100619.

O'regan, B. and Grätzel, M. (1991). A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature*, 353(6346): 737-740.

Ossai, A. N., Ezike, S. C., Timtere, P. and Ahmed, A. D. (2021). Enhanced Photovoltaic Performance of Dye-Sensitized Solar Cells-Based Carica Papaya Leaf and Black Cherry Fruit Co-Sensitizers. *Chemical Physics Impact.* https://doi.org/10.1016/j.chphi.2021. 100024

Pathak, C., Surana, K., Shukla, V. K. and Singh, P. K. (2019). Fabrication and characterization of dye sensitized solar cell using natural dyes. *Materials Today: Proceedings*, 12: 665-670.

Sharma, S. S., Sharma, K., Singh, R., Srivastava, S., Rana, K. B. and Singhal, R. (2021). Natural pigments: Origin and applications in dye sensitized solar cells. *Materials Today: Proceedings*, 42: 1744-1748.

Singh, S., Singh, P. K., Kakroo, S., Hachim, D. M., Dhapola, P. S. and Khan, Z. H. (2021). Eco-friendly dye sensitized solar cell using natural dye with solid polymer electrolyte as hole transport material. *Materials Today: Proceedings,* 34: 760-766.

Tajudeen, H. (2017). Synthesis of dye-sensitized solar cells using chromophores from West African plants. *International Journal of Science and Engineering Research*, 8: 631-635.

Taya, S. A., El-Agez, T. M., Elrefi, K. S. and Abdel-Latif, M. S. (2015). Dye-sensitized solar cells based on dyes extracted from dried plant leaves. *Turkish Journal of Physics*, 39(1): 24-30.