ACADEMY JOURNAL
OF
SCIENCE AND ENGINEERING
Available online @
www.academyjsekad.edu.ng
AJSE 18 (1) 2024
Original Research

CAFFEINE DOPED PEROVSKITE SOLAR CELLS WITHOUT HOLE TRANSPORTING MATERIAL

Kure, N.[1, 2,]*, Onimisi, M. Y.[1], Ali, H.[1], Ige, O. O.[1], Owolabi, A.[1] and Ahmed N.[2]

[1]Department of Physics, Nigeria Defence Academy, Kaduna, Kaduna State, Nigeria.
[2]Department of Physics, Kaduna State University, Kaduna, Kaduna State, Nigeria.
[3]Nigerian Upstream Petroleum Regulatory Commission, Utako Abuja, Nigeria.

Abstract

Perovskite photovoltaics is one of the fastest growing research field in materials science. The effect of caffeine in the absorber structure of the Perovskite Solar Cells (PSCs) was studied systematically in this study. Caffeine was added at different concentration ratio of 0.3 ml (S_1), 0.6 ml (S_2), 0.9 ml (S_3) and 1.2 ml (S_4) while the PSCs without caffeine content is denoted as C. The as-prepared PSCs were characterized via Scanning Electron Microscopy (SEM), Ultraviolet-Visible Spectroscopy (UV-vis), Profiler and (Current density - Voltage) J-V analysis techniques. The SEM results shows a nucleated orientation with average diameter of 185.16±0.2 µm. Optical analysis shows a red shift within the visible light spectrum, indicated a more visible lights are being absorbed, thus, a potential photoanode for perovskite solar cells applications. The profiler results shows the as-prepared nanomaterials is within the range of ~40 nm. The electrical performance of PSCs, caffeine nanoparticles (NPs) was observed to have enhanced the PSCs by improving Short circuit current (Jsc), Open circuit voltage (Voc), Field factor (FF) and Power conversion efficiency (PCE) of the fabricated devices. The highest performing PSCs was observed in device S1 with PCE of 9.57%, Jsc of 15.71 mAcm^{-2}, Voc 0.94 and FF 0.65, which shows ~1.57 times improvement in PCE over the control device (C). The addition of caffeine NPs increased the rate of exciton generation and the probability of exciton dissociation, enhancing charge separation, reducing the recombination rate as well as facilitating carrier transport in the device. Thus, in this study, device S_1 showed an improved PCE of 9.57%.

Keywords: Caffeine, Hole Transporting Material, Perovskite, Efficiency and Solar Cells

1.0 INTRODUCTION

The gradual increase in global energy consumption and environmental pollution, has demand for research on sustainable and renewed energy resources since fossil energy resources are limited (Wang, *et al*., 2019a; Zhou *et al*., 2018). The conversion of clean, renewable energy resources into electricity is one of the most promising studies to meet with the increasing demands for future generations without the negative impact of the global climate (Qiu, Ono and Qi, 2018). Among such renewed energy resources are Solar,

Corresponding author's e-mail: kurenicodemus@gmail.com

Geothermal, Tidal and Hydropower energy. Solar cell technology provides an eco-friendly and renewable energy route to convert photon energy into electricity. The most widely commercialized solar cells include crystalline silicon solar cells, multi-crystalline silicon solar cells and Cadmium Telluride (CdTe) solar cells (Im, Jeong-Hyeok *et al*., 2012; Qiu, Ono and Qi, 2018). The certified power conversion efficiencies (PCE) for single crystalline silicon, multi-crystalline silicon and CdTe are 24.4%, 19.9% and 18.6% respectively (Qiu, Ono and Qi, 2018). However, due to high fabrication cost of these solar cell technologies, the total solar energy that they can harvest amounts to only ~1% of the worlds current energy consumption (Qiu, Ono and Qi, 2018). Thus, to make full use of the available solar energy, we must either reduce the cost of existing solar cells technologies or develop new solar cells technologies (Asghar *et al*., 2017).

Perovskite solar cells (PSCs), the most promising new technology in academia and industry, has promise as a highly competitive alternative to silicon solar cells and other commercial alternatives, although the technology is still in the early stages (Kojima *et al*., 2009; Wali *et al*., 2020). The PSCs are high performance photovoltaic devices which have the potential to enter the market in the near future. Low promising costs and highly abundant raw material may permit a short energy recovery time, hence, reduction in overall CO_2 emissions (Chen *et al*., 2019; Qiu, Ono and Qi, 2018; Salhi *et al*., 2018). Additionally, PSCs exhibit exceptional optoelectronic properties, such as sharp bandgap, high coefficient, low exiton binding energy and tuneable optical bandgaps with applications in light emitting diode, photodetector and solar batteries *(Wang, et al*., 2019).

Herein, this research work intends to look into the stability issue by using an organic substance (Caffeine) as dopant on the absorber and also replacing the conventional organic Spiro-OMeTAD hole transporting material (HTM) with conventional HTM free architecture. The caffeine will not only reduce the rate at which the perovskite absorber is attacked by moisture content, but also thermally enhance the material. The testing will be done at the interval of 5 hours and the results will be compared with the controlled device. Based on the aforementioned, the present study therefore aims to develop PSCs with an architectural design modification involving the replacement of the expensive and less stable HTM (Spiro-OMeTAD) with HTM free architecture. This procedure will thus prevent the tendency of crystallization within the PSCs composition and improve its resistance to degradation due to both moisture and oxygen, thus, enhancing the device PCE.

2.0 MATERIALS AND METHODS

Materials

The various materials and equipment used during the experiment are Dense Titanium (IV) Isopropoxide (Sigma-Aldrich Chemical Company Ltd), Methylammonium Iodide (Solaronix), Amosil 4R (Solaronix), Titanium nanoxide D/sp (Solaronix), Zirconium nanoxide Z/sp (Solaronix), Acetyl-acetone (Guangdong Guanhua Sci-Tech Company Ltd), Caffeine (Sigma-Aldrich Chemical Company Ltd), Lead (II) Iodine (Sigma-Aldrich Chemical Company Ltd), Elcocarb (Solaronix), Frosted glass (Solaronix), N,N-dimethylformamide (DMF) (Solaronix) and Fluorine Doped Tin Oxide (FTO) (Solaronix). All materials were used as procured without further purification.

Preparation and Deposition Methods

The preparation and deposited methods adopted in this study as reported by Kure *et al* (2022).

Characterization

The surface morphologies were observed by Scanning Electron Microscopy (Phenom Pro X model, Eindhoven de Netherlands) operated at an acceleration voltage of 10 KV. Optical spectra were examined and characterized by means of ultraviolet–visible light (UV–vis) spectrometer (Axiom Medicals UV752 UV-vis-NIR). The samples current-voltage performance of PSCs are also analyzed under AM 1.5 irradiation via a setup involving a Xenon lamp, an AM 1.5 light channel, and an Electrochemical Analyzer (Keithley 2400 source meter) to shows the electrical properties within the samples. The intensity of the light was at 100 mW/m^2. And the current-voltage characteristics in the dark was also evaluated to determine the internal parameter of the device.

3.0 RESULTS AND DISCUSSIONS

SEM and UV-vis results was reported earlier in one of our research paper Figure 1, 2, 3 and 4 (Kure *et al*., 2022).

From the histogram below (Figure 1.0) using Image J processing software, its shows the diameter distributions of the photoanode particle sizes with higher average diameter within 185.16 ± 0.2 µm with lowest average diameter 8.98 ± 0.2 µm. The particle size plays a vital role in influencing the recombination rate, the larger the particle size, the lower the recombination rate.

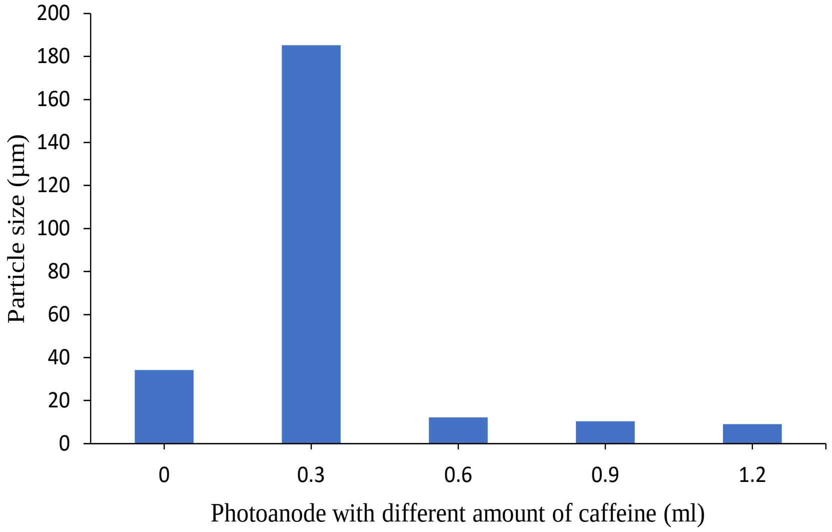

Figure 1: Diameter distributions of photoanodes with different concentration of caffeine

To show the systematic effect of caffeine on PSCs performance, devices with the architecture with caffeine modification and standard PSC without caffeine were designed. After the design and preparation, the I-V performance of PSCs was estimated under AM 1.5G irradiation via a setting involving a Xenon light, an AM 1.5 light channel, and an Electrochemical Analyser (Keithley 2400 source meter). The intensity of the light was at 100 mW/m^2. Since the five PSCs function in a way similar to a junction solar cells, their performance parameters were deduced from the I-V and P-V curves following the formulae

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \qquad 1.0$$

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{IRRADIANCE}} \times 100\% \qquad 2.0$$

$$P_{max} = I_{sc} \text{ x } V_{oc} \text{ x } FF \qquad 3.0$$

FF is Fill Factor, η is solar cell efficiency, V_{max} is maximum voltage, J_{max} is maximum current density, J_{sc} is short circuit current density, V_{oc} is open circuit voltage, $P_{IRRADIANCE}$ is light intensity P_{max} is maximum power and I_{sc} short circuit current (Baig *et al*., 2020 ;Kumar *et al*., 2020).

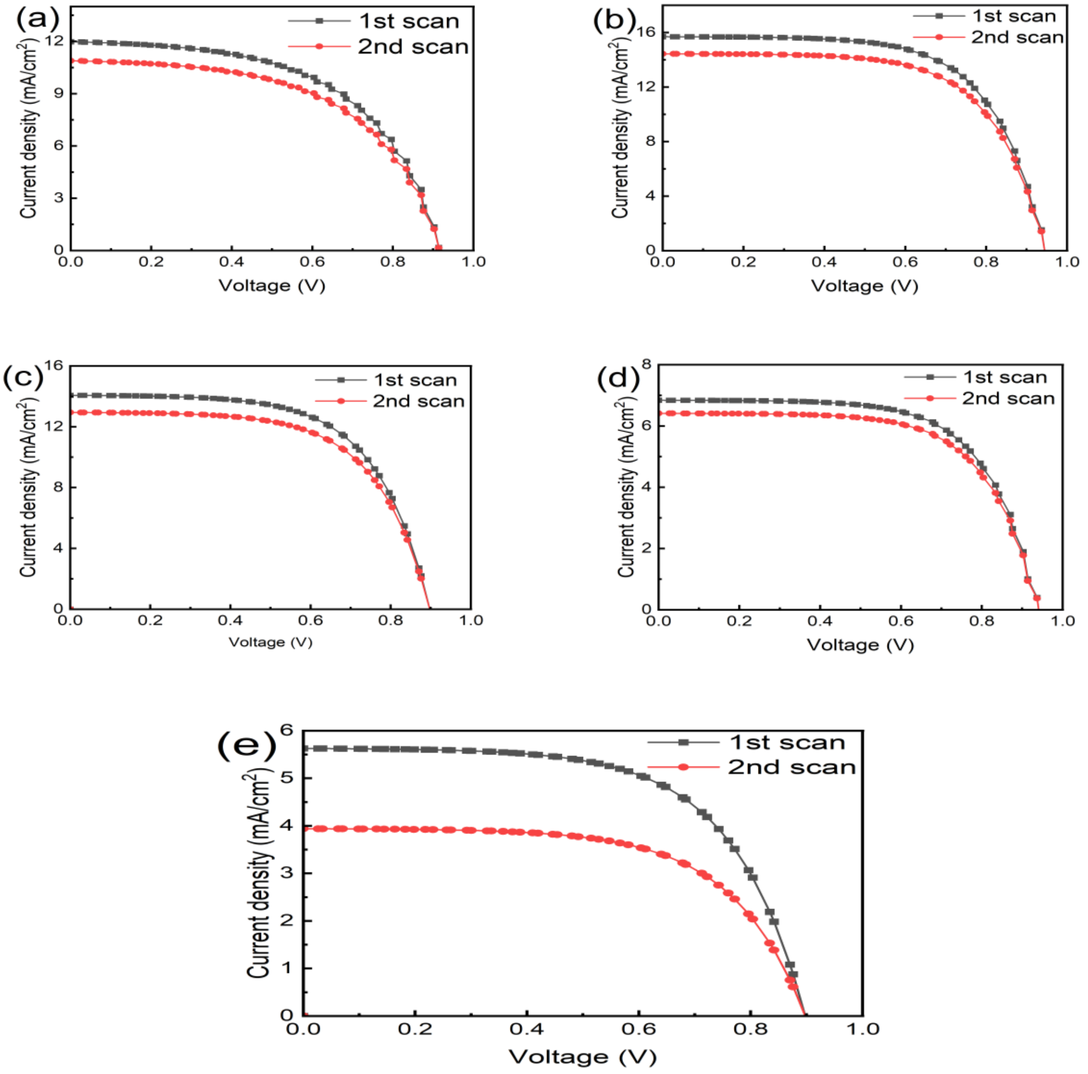

Figure 2: Showing J-V curves for the various PSCs devices

From Figure 2, shows the *J*−*V* images of PSCs devices with different amount of caffeine content. The parameters which include J_{SC}, V_{OC}, PCE, and FF are stated in Table 1.

Table 1: The photovoltaic performance of C, S_1, S_2, S_3 and S_4 PSCs under 100 $mWcm^{-2}$

Device	Scan	PCE (%)	*FF* (%)	J_{sc} (mA/cm^2)	V_{oc} (V)
0 ml	1st	6.087	0.556	11.984	0.913
	2nd	5.533	0.559	10.839	0.913
0.3 ml	1st	9.567	0.645	15.713	0.944
	2nd	8.801	0.649	14.368	0.944
0.6 ml	1st	7.802	0.619	14.041	0.898
	2nd	7.178	0.616	12.982	0.898
0.9 ml	1st	4.181	0.653	6.809	0.940
	2nd	3.919	0.651	6.406	0.940
1.2 ml	1st	3.121	0.619	5.626	0.896
	2nd	2.184	0.619	3.937	0.896

When caffeine NPs was introduced into the absorber layer, an enhanced performance was exhibited after first and second scan, which later reduced with higher concentrations of caffeine. The devices with 0.3 ml, 0.6 ml, 0.9 ml and 1.2 ml of caffeine are denoted as S_1, S_2, S_3 and S_4 respectively. Compared with the device C without caffeine NPs, the devices with caffeine NPs modification S_1 and S_2 exhibited noticeably greater PV performance than devices S_3 and S_4 but device S_1 exhibited a better value of J_{SC} to that of S_2, S_3 and S_4.

From Table 1, C which is the control device exhibits in first and second scan with a V_{OC} of 0.91 V, J_{SC} of 11.98 $mAcm^{-2}$, *FF* of 0.56 and V_{OC} of 0.91 V, J_{SC} of 10.84 $mAcm^{-2}$ and *FF* of 0.56, which results in a total PCE of 6.09 % and 5.53% respectively. We noticed a performance response higher than C when 0.3 ml of caffeine was introduced into the absorber layer. The device S_1 exhibits higher PCE of ~1.57 times (9.57%) and ~1.59 times (8.80%) in the first and second scan respectively with V_{OC} of 0.94 V, J_{SC} of 15.71 $mAcm^{-2}$, *FF* of 0.65 and V_{OC} of 0.94 V, J_{SC} of 14.37 $mAcm^{-2}$, *FF* of 0.65 more than device C, as compared with other researchers with PCE of 7.2% and *FF* of 0.65 (Balis *et al*., 2020; Mei *et al*., 2014; Wang, *et al*., 2019a; Wang *et al*., 2019b). Although, the PCE of the research is about ~1.96 times lower than the relevant literature (Wang *et al*., 2019b). Furthermore, device S_2 also exhibit PCE of 7.80% and 7.18% in the first and second scan respectively with V_{OC} of 0.90 V, J_{SC} of 14.04 $mAcm^{-2}$, *FF* of 0.62 and V_{OC} of 0.90 V, J_{SC} of 12.98 $mAcm^{-2}$, *FF* of 0.62, which are still higher than device C and is about ~1.28 times and ~1.30 times higher PCE than C after first and second scan respectively. Device, S_3 showed a decreased in the PCE with 4.18 % and 3.92 % after first and second scan respectively, with V_{OC} of 0.94 V, J_{SC} of 6.81 $mAcm^{-2}$, *FF* of 0.65 and V_{OC} of 0.94 V, J_{SC} of 6.41 $mAcm^{-2}$, *and FF* of 0.65. Thus, device S_3 PCE is ~1.46 times and ~1.95 times lower than the control device (C) which could arise as a result of agglomeration of the caffeine particles during the annealing process, leading to a resistive electron transport process. Lastly, device S_4 further showed a lower performance compared to device S_3 after first and second scan with 3.13% and 2.18% PCEs respectively, with V_{OC} of 0.90 V, J_{SC} of 5.63 $mAcm^{-2}$, *FF* of 0.62 and V_{OC} of 0.90 V, J_{SC} of 3.94 $mAcm^{-2}$, *FF* of 0.62, thereby, having PCE of ~1.41 times and ~2.54 times lower than C. Adding caffeine NPs above 0.6 ml to the perovskite significantly reduces the cell performance, importantly the Jsc, which is attributed to the fact that the colloidal TiO_2 NPs in TiO_2 paste for forming porous TiO_2 film is less than the average particle size of caffeine NPs. The low performance noticed in the device S_4 and S_5 is attributed to the high electron transport resistance.

This may be due to strong intermolecular interaction between C=O in caffeine and Pb^{2+} ions in the absorber layer serves as a ‘‘molecular lock’’ that increases the activation energy during film crystallization, delivering a perovskite film with preferred orientation, improved electronic properties, reduced ion migration, and greatly enhanced thermal stability by prohibiting the thermal-induced decomposition, which indicates that more energy is required to break the interaction between caffeine and the perovskite precursors (Wang *et al.*, 2019b). The relative increased in the J_{SC} of device S_1, is as a result of the improved absorber layer response and the expansion of the light absorption range by the caffeine NPs, thereby stimulating the absorber layer to dissociate the electron-hole pair. Also, the enhanced J_{SC} and FF may be associated with decreased non-radiative recombination and crystal defects owing to the passivation effect induced by the incorporation of caffeine (Wang *et al.*, 2019b). In addition, the Schottky barrier at the TiO_2/absorber (caffeine) interface forms an electron-hole separation centre and the movement of photoelectrons back and forth through the m-TiO_2 network, help in improving the device Jsc by reducing the recombination of electrons and holes. Caffeine is catalytically active, which can enhance the bonding formation that exist in m-TiO_2 and absorber layer, thus, increasing the electron mobility of the device. Hence, a reduction in the quenching losses between electron-hole pair, thereby making the J_{SC} and V_{oc} values to increase, which is due to the incorporation of caffeine NPs (Balis *et al.*, 2020). Figure 3 shows the plots of V_{oc}, J_{sc}, FF, and PCE with respect to the fabricated PSCs.

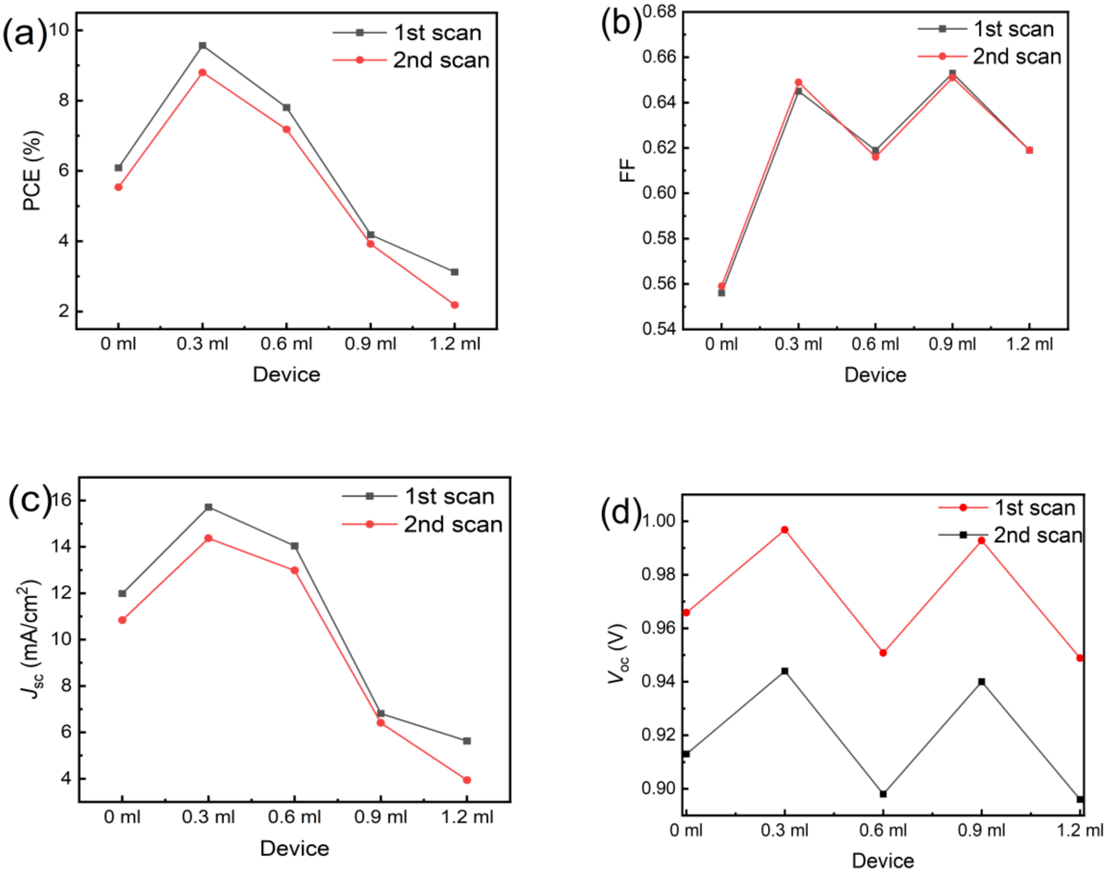

Figure 3: The variation in performance parameters of the fabricated PSCs

Figure 3 shows the plots of V_{oc}, J_{sc}, *FF*, and PCE with respect to the device. Observation shows that PCE, *FF* maximum values are at 9.57 % after first scan with FF of 0.65 which was displayed by device S_1 while the control device (C) has PCE of 6.09% and FF of 0.56. Device S_1 demonstrates the highest V_{oc} with value 0.94 V both after first and second scan. Highest value of *Jsc* was 15.71 $mAcm^{-2}$ which was observed in device S_1 after first scan. The highest PCE recorded in this research can be compared with result of Kim *et al*., 2012 which has PCE of 9.7 % (Elumalai *et al*., 2016; Im, Jeong-Hyeok *et al*., 2012; Roy *et al*., 2020). The usage of caffeine with HTL free architecture improved the stability and PCE of the PSCs devices. Figure 4, illustrates the plots of the PSCs in the dark.

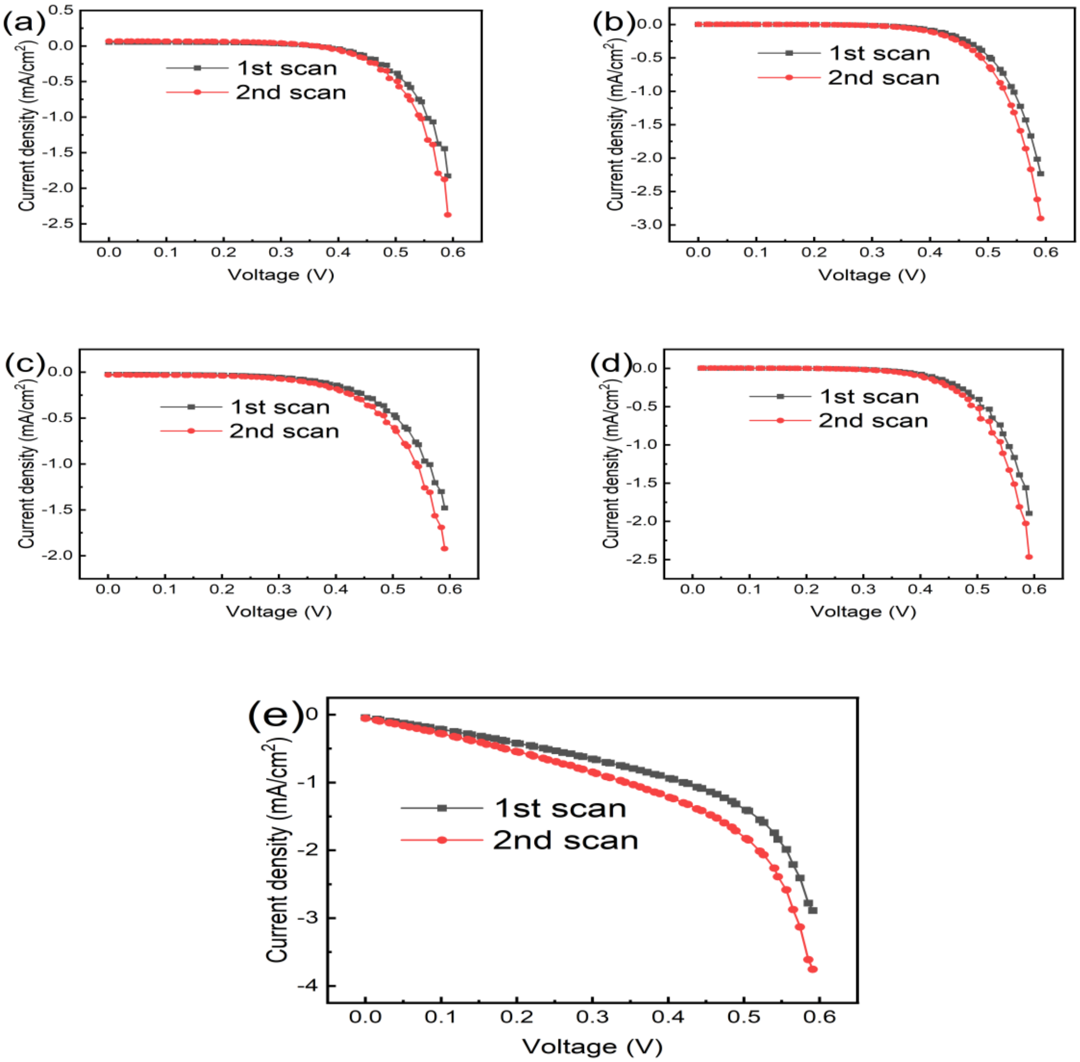

Figure 4: Showing Performance of the (a) C, (b) S_1, (c) S_2, (d) S_3 and (e) S_4 PSCs in the Dark

Figure 4 illustrates the plots of the PSCs in the dark. Current does not flow under this condition thereby behaving as a diode (Eli *et al*., 2021). This rectifying behaviour is a feature of photovoltaic devices and is a consequence of the asymmetric junction needed to charges.

4.0 CONCLUSION

In this research report, the effect of caffeine NPs on the as-prepared PSCs was studied systematically. Morphological and Optical properties of the as-prepared samples were investigated via SEM, UV-vis and Profiler by caffeine NPs into porous TiO_2 and/or perovskite semiconductor capping layers. The SEM results shows a nucleated orientation of the NPs with average diameter of 185.16±0.2 µm. The Optical results shows a red shift indicating more absorption of visible light as the caffeine NPs are incorporated, thus, a good light absorber organic nanostructures. The Profiler results the nanosize of the deposited nanomaterials used in the PSCs, which is ~40 nm. Thus, these results offer a possible method to enhance the optical absorption of solar cells materials by employing organic nanostructures.

The electrical studies of this research shows that, the presence of caffeine NPs actually enhanced the PCE of the PSCs by improving J_{sc}, V_{oc}, FF, and PCE. The best performing PSC contained 0.3 ml of caffeine incorporated in the perovskite layer (S_1). The PSC gave a J_{sc} of 15.71 $mAcm^{-2}$, V_{oc} of 0.94 V, and FF of 0.65, resulting in the best PCE of 9.57%. The device (S_1) demonstrated an improvement of ~1.57 times over the PCE (6.09%) of the device without caffeine NPs (C). The increase in J_{sc} is explained by the improvement of spectrum absorption of electromagnetic radiation and the expansion towards the higher spectrum of light in the composite photoanode as a result of caffeine NPs, while the increase in V_{oc} can be attributed to a shift from a positive potential as a result of improved electron dissociation. Thus, device S_1 showed an improved PCE of 9.57%.

REFERENCES

Asghar, M. I., Zhang, J., Wang, H., & Lund, P. D. (2017). Device stability of perovskite solar cells – A review. *Renewable and Sustainable Energy Reviews*, *77*(July 2016), 131–146.

Balis, N., Zaky, A. A., Athanasekou, C., Silva, A. M., Sakellis, E., Vasilopoulou, M., Stergiopoulos, T., Kontos, A. G., & Falaras, P. (2020). Investigating the role of reduced graphene oxide as a universal additive in planar perovskite solar cells. *Journal of Photochemistry and Photobiology A: Chemistry*, *386*(October 2019), 112141.

Chen, M., Ju, M. G., Garces, H. F., Carl, A. D., Ono, L. K., Hawash, Z., Zhang, Y., Shen, T., Qi, Y., Grimm, R. L., Pacifici, D., Zeng, X. C., Zhou, Y., & Padture, N. P. (2019). Highly stable and efficient all-inorganic lead-free perovskite solar cells with native-oxide passivation. *Nature Communications*, *10*(1), 1–8.

Elumalai, N. K., Mahmud, M. A., Wang, D., & Uddin, A. (2016). Perovskite solar cells: Progress and advancements. *Energies*, *9*(11).

Im, Jeong-Hyeok, Kim, H.-S., Lee, C.-R., Lee, K.-B., Moehl, T., Marchioro, A., Moon, S.-J., Humphry-Baker, R., Yum, J.-H., Moser, J. E., Gratzel, M., & Park, N.-G. (2012). Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Scientific Reports*, *591*(2), 1–10.

Kojima, A., Teshima, K., Shirai, Y., & Miyasaka, T. (2009). *Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic*. 6050–6051.

Kumar, N., Rani, J., & Kurchania, R. (2020). A review on power conversion efficiency of lead iodide perovskite-based solar cells. *Materials Today: Proceedings*, *xxxx*.

Kure, N., Onimisi, M. Y., Ali, H., Ige, O. O., Eli, D. (2022). Optical Behaviour of Caffeine Mixed Perovskite Photoanode for Photovoltaic Application. Physicsaccess, S (1), PP 30-36.

Mei, A., Li, X., Liu, L., Ku, Z., Liu, T., Rong, Y., Xu, M., Hu, M., Chen, J., Yang, Y., Grätzel, M., & Han, H. (2014). A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science*, *345*(6194), 295–298.

Qiu, L., Ono, L. K., & Qi, Y. (2018). Advances and challenges to the commercialization of organic–inorganic halide perovskite solar cell technology. *Materials Today Energy*, *7*, 169–189.

Roy, P., Numeshwar, K. S., Sanjay, T., & Ayush, K. (2020). A review of aspects of additive engineering in perovskite solar cells. *Solar Energy*, *198*, 665–688.

Salhi, B., Wudil, Y. S., Hossain, M. K., Al-Ahmed, A., & Al-Sulaiman, F. A. (2018). Review of recent developments and persistent challenges in stability of perovskite solar cells. *Renewable and Sustainable Energy Reviews*, *90*(March), 210–222.

Wali, Q., Iftikhar, F. J., Khan, M. E., Ullah, A., Iqbal, Y., & Jose, R. (2020). Advances in stability of perovskite solar cells. *Organic Electronics*, *78*(December 2019), 105590.

Wang, Q., Phung, N., Di Girolamo, D., Vivo, P., Abate, A., Girolamo, D., & Vivo, P. (2019). Enhancement in lifespan of halide perovskite solar cells. *Energy and Environmental Science*, *12*(3), 865–886.

Wang, R., Mujahid, M., Duan, Y., Wang, Z. K., Xue, J., & Yang, Y. (2019a). A Review of Perovskites Solar Cell Stability. *Advanced Functional Materials*, *February*.

Wang, R., Xue, J., Meng, L., Lee, J. W., Zhao, Z., Sun, P., Cai, L., Huang, T., Wang, Z., Wang, Z. K., Duan, Y., Yang, J. L., Tan, S., Yuan, Y., Huang, Y., & Yang, Y. (2019b). Caffeine Improves the Performance and Thermal Stability of Perovskite Solar Cells. *Joule*, *3*(6), 1464–

1477.

Zhou, D., Zhou, T., Tian, Y., Zhu, X., & Tu, Y. (2018). Perovskite-Based Solar Cells: Materials, Methods, and Future Perspectives. *Journal of Nanomaterials*, *2018*.