Improved power conversion efficiency in Perovskite solar cell using silver nanoparticles modified photoanode

D Eli 1,4*, MY Onimisi1, S Garba2, PM Gyuk3, T Jamila3, and HP Boduku3

1Department of Physics, Nigerian Defence Academy, Kaduna, Nigeria
2Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria
3Department of Physics, Kaduna State University, Kaduna, Nigeria
4Department of Physical Sciences, Greenfield University, Kaduna, Nigeria

*Corresponding author: E-mail: danladielibako@gmail.com

Abstract
Metal nanoparticles have demonstrated outstanding properties in photovoltaic devices through introducing localized surface plasmon effects. The performance of Perovskite solar cell (PSC) by incorporating Ag@P$_4$VP NPs was investigated systematically. The plasmonic enhancement effects are explored based on the combination of UV-visible absorption spectroscopy and Scanning Electron Microscope (SEM). The performance, especially the short circuit current density ($J_{sc}$), and open circuit voltage ($V_{oc}$) of the PSC containing Ag@P$_4$VP NPs was significantly affected. The power conversion efficiency ($PCE$), $J_{sc}$ and $V_{oc}$ of the reference device shows a value of 3.80 %, 11.04 mAcm$^{-2}$ and 0.85 V. Upon introducing AgNPs@P$_4$VP, a $PCE$ of 5.69 %, $J_{sc}$ of 12.61 mAcm$^{-2}$ and $V_{oc}$ of 0.88 V were recorded, which improved the $PCE$ ~ 39.4 % over that of the standard device. The improvement is attributed to an increase in photocurrent density due to enhanced light harvesting by silver nanoparticles.

Keywords: Metal nanoparticles, surface plasmon, AgNPs@P$_4$VP

1 Introduction
PSCs have demonstrated remarkable breakthrough almost a decade now since after its invention by Kojima and group [1], due to its advantages of low cost, high efficiency and simple fabrication process. Its efficiency has grown from 3.9 % in 2009 to over 23 % in late 2018 [2, 3].
Despite its remarkable attainment, further improvement of PSCs performance is still necessary for accelerating its commercialization [4]. The use of metal nanoparticles to trap and confine light energy in designated places in PSC can lead to enhanced and superior optoelectronic properties and has been demonstrated by several researchers [4-7].

One of the important issues in plasmonic PSCs is the stability of the plasmonic NPs. When introduced metal nanoparticles (NPs) make direct contact with the perovskite crystal, problems associated to recombination, and corrosion of metal NPs are witnessed. Reports have demonstrated that TiO$_2$ and SiO$_2$ were applied as encapsulants [4, 6-8] to prevent the effects above, which however, do not allow easy transfer of carriers generated by perovskite nanocrystal surrounding porous semiconductor. The use of polymer as an encapsulating agent has seldom been reported. In this work, we developed a new and efficient plasmonic composite structure to effectively enhance the PCE of PSCs by incorporating AgNPs with poly(4-vinyl pyridine) as encapsulating material. The polymer has the ability of adhesion to small perovskite molecules, increasing exciton lifetime, increasing diffusion and delocalization lengths which will make considerable contribution to the enhancement of the device performance.

2 Materials and methods

2.1 Synthesis of Ag nanoparticles

To fabricate the silver NPs, a modified two-step reduction synthesis procedure was implemented, which was developed based on the conventional reduction method [9-11]. We first heat the mixture containing sodium borohydride (NaBH$_4$) and tri-sodium citrate (TSC) at the ratio of 2:7 (1×10$^{-3}$ mol dm$^{-3}$: 3.5×10$^{-3}$ mol dm$^{-3}$) to 60 °C at 300 rpm for 30 min under vigorous stirring to ensure a formation of homogenous solution. 45 min. Later, 4 ml of an aqueous solution of AgNO$_3$ (4×10$^{-3}$ mol dm$^{-3}$) was added drop-wise to the mixture, and the temperature was further raised to 100 °C to make the solution boil quickly. The reaction proceeded for another 45 min. Finally, the solution was cooled to room temperature with stirring, and the NPs were collected by centrifugation at 4000 rpm and redispersed in ethanol via sonication for 15 min.

2.2 Preparation of Ag@P$_4$VP

An aqueous solution of P$_4$VP (purchased from Sigma-Ardrich) was added to the silver formed above, followed by Acetone treatment to modify the silver NPs surface. To facilitate P$_4$VP
coating, the solution was stirred for 24 h at room temperature using a magnetic stirrer plate 78-1 (PEC medicals USA). The P4VP-coating silver NPs are collected by centrifugation and redispersed in deionized water by sonication.

2.3 Preparation of Photoanodes Precursors
A pure perovskite-precursor solution (1.20 mol/l) was prepared following a method earlier used by Luo et al. [7]

2.4 Preparation of Photoanodes
The FTO were cleaned with cotton wool and ethanol. The blocking layer and the mesoporous layer for the control electrode was deposited and sintered following a method earlier demonstrated by Eli et al. [12]. The perovskite was spin coated on the formed mesoporous TiO2, it was annealed at 100°C for 10 min. For the plasmon modified cell (S1), we put into consideration, the melting point of the P4VP polymer (about 170 °C) which is ~2.94 time less than the annealing temperature for TiO2. To disperse the Ag@P4VP NPs into the TiO2 layer homogeneously, spin coating technique was utilized to introduce Ag@P4VP NPs (in ethanol solutions) onto TiO2 layer at 600 rpm for 20 seconds. Thereafter, the ethanol was removed by drying naturally. The formed precursor was deposited onto the blocking layer using spin coating technique followed by the deposition of the perovskite absorber via a successive two-step spin-coating process, at 3000 rpm for 30 seconds.

2.5 Preparation of the Counter Electrode
The counter electrode was prepared by employing screen printing procedure. It involves the use of 120 mesh screen printer to screen print a conductive carbon paste (Elcocarb B/SP, Solaronix) to obtain the carbon back contact with area of 1 cm². It was followed by drying at 160 °C for 5 min, under the monitoring of an IR thermometer and thereafter, sintered at 400 °C for 30 min.

2.6 Solar Cell Assembly
Ethylene-Vinyl Acetate (EVA) was used to thermally laminate the counter electrode to the appropriate photoanode. The EVA consists of 11% vinyl acetate thereby resulting in a non-toxic thermoplastic polymer useful as hot melting adhesives for thin films in electrical application.
2.7 Characterization and Measurement
The surface morphologies were observed by Scanning Electron Microscopy (Phenom Pro X model, Eindhoven de Netherlands) operated at an acceleration voltage of 10 KV. At that point, ISolution Image Analysis was used to measure the size of Ag nanoparticles that was deposited on the TiO$_2$ to be 32 nm. Optical spectra were examined and characterized using ultraviolet-visible light (UV-vis) spectrometer (Axiom Medicals UV752 UV-vis-NIR). The current voltage performance of PSCs are estimated under AM 1.5G irradiation using a setup involving a Xenon lamp, an AM 1.5 light channel, and an Electrochemical Analyzer (Keithley 2400 source meter).

3 Results and Discussion
3.1. Scanning Electron Micrographs
The image of the unmodified TiO$_2$ film in Figure 1(a) demonstrates a dense surface, and there are no shining particles seen. Figure 1(b) demonstrates the SEM picture of Ag@P$_4$VP NPs nanoparticles incorporated into the porous TiO$_2$. From the picture, AgNPs@P$_4$VP were distributed both on the surface of the TiO$_2$ and inside the TiO$_2$. After careful inspection, Ag signals were clearly detected with dense surface and shining particles distributed within. The shining surface is indicative that AgNPs can scatter incident light to increase light absorption surface area.

![Figure 1. SEM image of: (a) bare TiO$_2$ (b) TiO$_2$/AgNPs@P$_4$VP](image)

3.2. UV-visible spectroscopy
Figure 2(a) shows the absorption of the methylammonium lead halide perovskite absorber within the wavelength range of 300-1200 nm. From the Figure, the material absorbed from 350 to 800
nm with absorption peaks observed at ~385 nm, with absorbance height of ~1.81, ~443 nm, with absorbance height of ~1.73, and ~511 nm, with absorbance height of ~1.67. The absorption at the visible region is an indication that this material meets the requirements for its use as light harvester in this research.

Figure 2. The UV-vis spectroscopy of (a) the pure Methylammonium lead triiodide (b) the bare m-TiO\(_2\), (c) m-TiO\(_2\) with Methylammonium lead triiodide, (d) AgNPs (e) AgNPs@P\(_4\)VP, and (f) AgNPs@P\(_4\)VP blended within the p-TiO\(_2\) layer

Figure 2(b) shows the absorbance-wavelength plot for TiO\(_2\) in the absence of methyl ammonium lead halide. As seen, no obvious absorption peak was observed within the Vis-NIR region with TiO\(_2\), but a sharp peak was noticed around 316 nm at absorbance height of ~0.82 within the UV region. This peak is due to electronic transitions between molecules having an intermediate ionic degree, which conform to the synthesized molecular materials. This peak suggests that the modification of TiO\(_2\) is necessary to make it active under visible light. Figure 2(c) shows the UV-vis absorption of TiO\(_2\) after sensitization with the methylammonium lead halide. The optical absorption enhancement was noticed in the CH\(_3\)NH\(_3\)PbI\(_3\) modified TiO\(_2\) film with peaks at 385 nm with absorbance height of ~2.01, 438 nm with absorbance height of ~1.86, and 516 nm with absorbance height of ~1.72 absorbing at the range of 330-750 nm within the visible region.
The properties exhibited above shows that, TiO$_2$ in the presence of CH$_3$NH$_3$PbI$_3$ absorber can absorb more photons, possibly because of the large deformations in the network of lead and iodine atoms caused by light in allowing electric charges to migrate through defects and protecting them from being trapped in the materials. A shift of the extinction spectra was observed when the P$_4$VP shell was coated on AgNPs. Absorption peaks were observed at 453, 496, 679, 855 and 1031 nm with absorbance heights at ~1.14, ~1.11, ~0.80, ~0.66 and ~0.54 for AgNPs (Figure 2(d)). Also resonances were exhibited at 395, 425, 518, 581, 679, 865 and 1031 nm after encapsulating the AgNPs with P$_4$VP shell (Figure 2(e)) which shows a slight blue shift at the resonance. As shown in Figure 2(f), the slightly red shifted extinction spectrum of Ag@P$_4$VP modified samples as compared to that of TiO$_2$ is expected from the change in the LSPR which slightly shifts to longer wavelength upon addition of the AgNPs and P$_4$VP. Also, the absorption intensity increase as AgNPs@P$_4$VP is modified on the reference sample. This behavior was usually ascribed to Ag$^0$ nanoparticles inducing visible light absorption [13, 14]. Moreover, absorption bands at 400-500 nm may be also attributed to Ag clusters.

### 3.3 Photovoltaic performance

Since the five PSCs function in a way similar to a junction solar cells, therefore, their performance parameters was resolved from the $J$-$V$ and $P$-$V$ curves following equations (1) and (2) respectively.

\[
FF = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}} \tag{1}
\]

\[
\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_{IRRADIANCE}} \times 100\% \tag{2}
\]

$FF$ is Fill Factor, $\eta$ 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 and $P_{IRRADIANCE}$ is light intensity.
Figure 3 shows the current density–voltage ($J$–$V$) curves of the performing PSC devices with different modification. The photovoltaic parameters which include $J_{SC}$, $V_{OC}$, PCE and FF are summarized in Table 1.

**Table 1.** Photovoltaic performance of Ag@P$_4$VPNPs modified and unmodified PSCs under 100 mWcm$^{-2}$

| Device       | $J_{SC}$ (mAcm$^{-2}$) | $V_{OC}$ (V) | FF   | PCE (%) |
|--------------|------------------------|--------------|------|---------|
| Control Device | 11.04                  | 0.85         | 0.41 | 3.80    |
| S1           | 12.61                  | 0.88         | 0.51 | 5.69    |

From Table 1, the control device which is the reference device exhibits a $V_{OC}$ of 0.85 V, $J_{SC}$ of 11.04 mAcm$^{-2}$ and $FF$ of 0.41, which result in a total PCE of 3.80 %. When Ag@P$_4$VPNPs is introduced into the m-TiO$_2$ layer, a greatly enhanced performance was exhibited. The device S1 exhibits a PCE of 5.69 % with $J_{SC}$=12.61 mAcm$^{-2}$, $V_{OC}$=0.88 V, and $FF$=0.51 which shows an enhancement of ~1.50 times in PCE from the control device. The obvious increase demonstrated in $J_{SC}$ is connected to the enhanced light absorption and broadened light absorption range of the perovskite nanocrystal resulting from the SPR of AgNPs, which stimulates the absorber to generate more charge carriers. Furthermore, the Schottky barrier at the TiO$_2$(Ag@P$_4$VP)/absorber interface will form electron-hole separation centers which would be
beneficial in improving the movement of photogenerated electrons shuttling through the porous TiO$_2$ network, reducing recombination of electrons and holes, thus increasing $J_{sc}$. As well known, silver has long been regarded as being catalytically active [15,16]. However, AgNPs dispersed on metal-oxide supports are active catalysts for a variety of chemical reactions [12, 16-18]. In our work, when AgNPs was added, the catalytic effect of AgNPs sited on TiO$_2$ support could increase the reaction rate between the TiO$_2$ and CH$_3$NH$_3$PbI$_3$, thereby increasing electron mobility. As a consequence, the quenching losses probability between electrons and holes may reduce, thus increasing $J_{sc}$ and $V_{oc}$. The photocurrent enhancement in the perovskite solar cells suggested that localized surface plasmon resonance (LSPR) and electrical effects of Ag NPs enhance the photovoltaic response [12, 15, 19, 20].

4 Conclusion
The effect of plasmonic nanoparticles (NPs) with poly (4-vinylpyridine) as shell nanostructure was investigated systematically. The presence of Ag@P$_4$VP NPs significantly improved the performance of the PSCs by increasing $J_{sc}$, $V_{oc}$, FF and $\eta$. The PSC gave a $J_{sc}$ of 12.61 mAcm$^{-2}$, $V_{oc}$ of 0.88 V and FF of 0.51, yielding a PCE of 5.69 %. The increase of $J_{sc}$ is connected to the enhanced light absorption and spectral enhancement of the composite photoanode due to the Surface Plasmon Resonance (SPR) of the AgNPs, while the improved $V_{oc}$ may be reasonably related to the shift in quasi-Fermi energy towards the negative potential of the composite system as a result of the enhanced electron capture and storage capability resulting from AgNPs addition.

References
[1] Kojima A, Teshima K, Shirai Y, and Miyasaka T 2009 Organometal halide Perovskites as visible-light sensitizers for photovoltaic cells. J. Am. Chem. Soc. 131 (17) pp 6050- 6051.
[2] Li S, Zhu X, Wang B, Qiao Y, Liu W, Yang H, Liu N, Chen M, Lu H and Yang Y 2018 Influence of Ag nanoparticles with different sizes and concentrations embedded in a TiO$_2$ compact layer on the conversion efficiency of Perovskite solar cells. Nanoscale Res. Lett. 13 (1) 210. https://doi.org/10.1186/s11671-018-2626-y.
[3] Green MA, Emery K, Hishikawa Y, Warta W, Dunlop E. D, Levi D H and Ho-Baillie AWY 2017 Solar cell efficiency tables (version 49). Prog. Photovoltaics 25 (1) pp 3-13.
[4] Wu R, Yang B, Zhang C, Huang Y, Cui Y, Liu P, Zhou C, Hao Y, Gao Y and Yang J 2016 Prominent efficiency enhancement in Perovskite solar cells employing silica-coated gold nanorods. *J. Phys. Chem C* **120** (13) pp 6996-7004.

[5] Cheng Y, Chen C, Chen X, Jin J, Li H, Song H and Dai Q. 2016. Considerably enhanced Perovskite solar cells via the introduction of metallic nanostructures. *J. Mater. Chem. A* **5** (14) pp 6515-6521.

[6] Saliba M, Zhang W, Burlakov VM, Stranks SD, Sun Y, Ball JM, Johnston MB, Goriely A, Wiesner U and Snaith HJ 2015 Plasmonic-induced photon recycling in metal halide Perovskite solar cells. *Adv. Funct. Mater.* **25** (31) pp 5038-5046.

[7] Luo Q, Zhang C, Deng X, Zhu H, Li Z, Wang Z, Chen X and Huang S 2017 Plasmonic effects of metallic nanoparticles on enhancing performance of Perovskite solar cells. *ACS Appl. Mater. Interf.* **9**(40) pp 34821-34832.

[8] Zhang W, Saliba M, Stranks SD, Sun Y, Shi X, Wiesner U and Snaith HJ 2013 Enhancement of Perovskite-based solar cells employing core-shell metal nanoparticles. *Nano Lett.* **13** (9) pp 4505-4510.

[9] Eli D and Gyuk PM 2019 High efficiency dye sensitized solar cells by excitation of localized surface plasmon resonance of AgNPs. *Sci. World J* **14** (2) pp 125-130.

[10] Nourolahi H, Bolorizadeh MA and Behjat A 2016. Light absorption with branched gold cauliflower-like nanostructure arrays. *Vacuum* **123** pp 29-34.

[11] Agnihotri S, Mukherji S and Mukherji S 2014 Size-controlled silver nanoparticles synthesized over the range 5-100 nm using the same protocol and their antibacterial efficacy. *RSC Adv.* **4** (8) pp 3974-3983.

[12] Eli D, Ibeh G J, Ige O O, Owolabi J A, Ugbe R U, Sherifdeen B O, Onimisi M Y and Ali H 2019 Silver nanoparticles as nano antenna for TiO$_2$ activation and its application in DSSC for enhanced performance. *J. Theor. Appl. Phys.* **1** (3) pp 88-98.

[13] Tian Y and Tatsuma T 2004 Plasmon-induced photoelectro-chemistry at metal nanoparticles supported on nanoporous TiO$_2$. *Chem. Comm.* **10** (16) pp 1810-1811.

[14] Castro CA, Jurado A, Sissa D and Giraldo SA 2012. Performance of Ag-TiO$_2$ photocatalysts towards the photocatalytic disinfection of water under interior-lighting and solar-simulated light irradiations. *Int. J. Photoenerg.* ID 261045. 

https://doi.org/10.1155/2012/261045.
[15] Eli D, Onimisi M Y, Abdu S G, Gyuk P M and Ezeoke J 2016 Enhanced performance of a dye sensitized solar cell using silver nanoparticles modified photoanode. *J. Scientif. Res. Rep.* 10 (4) pp 1-8.

[16] Guo K, Li M, Fang X, Liu X, Sebo B, Zhu Y, Hu Z and Zhao X 2013 Preparation and enhanced properties of dye-sensitized solar cells by surface plasmon resonance of Ag nanoparticles in nanocomposite photoanode. *J. Power Sources* 203 pp 155-160.

[17] Eli D, Gyuk PM, Oluwaseyi BS 2018 Size controlled silver nanoparticles for enhanced performance of dye sensitized solar cells. *Nig. J. Phys.* 27 S pp 265-272.

[18] Onimisi M Y, Eli D, Abdu S G, Aboh H O and Ezeoke J 2016 Size effects of silver nanoparticles on the photovoltaic performance of dye sensitized solar cells. *Am. Chem. Sci. J.* 13 (3) pp 1-8.

[19] Wang D H, Kim D Y, Choi K. W, Seo J H, Im S H, Park J H, Park O O and Heeger A J 2011 Enhancement of donor-acceptor polymer bulk heterojunction solar cell power conversion efficiencies by addition of Au nanoparticles. *Angew. Chem.* 50 (24) pp 5519-5523.

[20] Catchpole K R and Polman A 2008 Plasmonic solar cells. *Opt. Express* 16 (26) pp 21793-21800.