9.05% HTM free perovskite solar cell with negligible hysteresis by introducing silver nanoparticles encapsulated with P₄VP polymer

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Received: 11 June 2020 / Accepted: 28 September 2020

Published online: 06 October 2020

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Abstract

This study is a follow up to our previously published manuscript on “improved power conversion efficiency in Perovskite solar cell using silver nanoparticles modified photoanode”. Three more photoanodes were fabricated which are: Ag@P₄VP NPs mixed with perovskite layer (S2), Ag@P₄VP NPs simultaneously mixed both in TiO₂ and perovskite films (S3) and P25 NP simultaneously mixed both in TiO₂ and perovskite absorber (S4) and their performances were investigated systematically. The performance, especially the photocurrent, and open circuit voltage of PSCs made of Ag@P₄VP NPs were significantly affected. The champion device is S3, which shows enhancement in power conversion efficiency (PCE) from 3.80 to 9.05%, short circuit current density (J_{sc}) from 11.04 to 15.87 mA cm⁻², open circuit voltage (V_{oc}) from 0.85 to 0.88 and fill factor (FF) from 0.41 to 0.65, which demonstrates ~ 2.38 times improvement in PCE over the control device (C). When Ag@P₄VP NPs was mixed with TiO₂, PCE of 5.69%, J_{sc} of 12.61 mA cm⁻², V_{oc} of 0.88 V and FF of 0.51 were achieved, which shows ~ 1.50 times improvement over the performance of the reference cell. Also, when Ag@P₄VP NPs was mixed with the perovskite layer, PCE of 8.08%, J_{sc} of 14.18 mA cm⁻², V_{oc} of 0.89 V and FF of 0.64 were achieved, which shows ~ 2.13 times improvement over the performance of the pristine device. The addition of Ag@P₄VP NPs enhanced exciton generation and dissociation, encouraging charge separation/transfer, as well as reducing quenching losses. For the hysteresis test, it was found that the devices with Ag@P₄VP NPs have almost identical J - V curves with negligible hysteresis, which is attributed to the significant reduction of the trap density of the perovskite film when Ag@P₄VP NPs is incorporated to fill the pores with high trapping rate. We however observed hysteretic behavior in devices C and S4, which makes it difficult to estimate the real PCE.

Keywords Metal nanoparticles · Perovskite · Surface plasmon · AgNPs@P₄VP

1 Introduction

The emergence of perovskite compounds have stimulated many breakthrough developments, showing that they are one of the most important candidates for third-generation solar cells and are the most recent materials. Perovskite solar cells (PSCs) have attracted extensive interest due to the performance in their

power conversion efficiency and lowest manufacturing costs. PSC adopted a structure similar to DSSC in 2009 by employing perovskite instead of dye molecules as sensitizers. In just 9 years, PCE has been reported to exceed 25% [1–4]. Such rapid and extraordinary advances in power conversion efficiency are realized using compact, uniform and high graded perovskite absorption layers achieved using various manufacturing

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techniques. Perovskite material is an important part of PSC, it absorbs light, creates photo stimulated carriers, and plays a crucial role in transferring these carriers into the network. Hybrid perovskite is defined based on the crystal structure of AMX_3 , where A is an organic cation, such as methylammonium or methylamid, M is a metal, and X is a halogen atom. As these perovskite materials are ambipolar, they can allow the conduction of both electrons and holes simultaneously and they also show high electron and hole mobilities [5, 6].

These high mobilities are considered much higher than the mobilities demonstrated by most utilized hole transporting materials in solar cells [7] and the mobilities ($\sim 0.02 \text{ cm}^2/\text{Vs}$) of most utilized electron transporting materials in solar cells [8, 9]. Hypothetically, it is conceivable to let these processes of light absorbing, electron transport and hole transport occur in the perovskite layer, which will simplify solar cell's structure and lower its costs.

Even though perovskite absorbers have demonstrated good absorbing abilities and can efficiently be used in good designed devices, further improvements to the PSC are expected and necessary to surpass other photovoltaic (PV) technologies.

Using metal nanostructures in solar cells, it is possible to achieve better optical properties by scattering light, or to achieve highly efficient devices through dipole–dipole interaction and resonance energy transfer, thereby completely changing the opportunity for solar energy conversion [10–13].

Metallic nanoparticles have been integrated to minimally enhance the efficiency of DSSCs, [14, 15], also in Si base solar cells [16] and organic photovoltaic (OPV) cells [17–20]. Recently, noble metals have also been utilized to significantly improve the PCE of PSCs.

The question here is “can metal nanoparticles maximize their positive effects while minimizing their negative effects to realize reasonable PCE enhancement, especially when introduced into pure perovskite semiconductors? In this study, we attempt to follow-up our previously published work on “improved power conversion efficiency in Perovskite solar cell using silver nanoparticles modified photoanode” [12], by fabricating three more photoanodes to include $\text{Ag@P}_4\text{VP}$ NPs mixed with perovskite layer, $\text{Ag@P}_4\text{VP}$ NPs simultaneously mixed both in TiO_2 and perovskite films and P25 NP simultaneously mixed both in TiO_2 and perovskite absorber. We extended the study to have a better understanding of hysteretic behavior on our fabricated devices, by scanning the applied voltage from forward bias (FB) to short circuit (SC) and the other way round. It was observed after the scan that the control device is hysteretic.

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 [21, 22]. We first heat the mixture containing sodium borohydride (NaBH_4) and tri-sodium citrate (TSC) at the ratio of 2:7 ($1 \times 10^{-3} \text{ mol dm}^{-3}$: $3.5 \times 10^{-3} \text{ mol dm}^{-3}$) 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 ($4 \times 10^{-3} \text{ mol dm}^{-3}$) 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 $\text{Ag@P}_4\text{VP}$

In order for the P_4VP to encapsulate the AgNPs, the bonding that exist between the chains of the polymer and the surface of the metal must conquer some factors. The interaction that exist between chains of the polymer should be less than the interaction between chains of the polymer and the metal surface and also less than the interactive force for the AgNPs in acetone [23, 24]. This interaction should overcome the limit established between the Ag and the P_4VP , and the increase in surface free energy as a result of the overall strength in polymer active area outside the composite [25].

The synthesis of AgNPs in the presence of P_4VP polymer was reported as follows:

P_4VP was added in silver formed in Sect. 2.1 followed by Acetone treatment to modify the silver NPs surface. To ensure proper coating of P_4VP around the metal, the solution was stirred for 24 h at 25°C (room temperature) using a magnetic stirrer plate 78-1 (PEC medicals USA). The metal nanoparticles coated with P_4VP was collected by centrifugation and distributed in deionized water by sonication.

2.3 Preparation of photoanodes precursors

2.3.1 The perovskite was prepared following a method earlier used by Luo et al. [11] with a slight modification in temperature and timing. It involve having a mixture of MAI (0.198 g) and lead iodide PbI_2 (0.579 g) in γ -butyrolactone (GBL) (650 μL) and dimethylsulfoxide (DMSO) (350 μL) at 70°C for 11 h.

2.3.2 Taking into consideration, the melting point of the P_4VP (about 169 °C) which is ~ 2.94 time less than the annealing temperature for TiO_2 . To disperse the $Ag@P_4VP$ in the TiO_2 layer uniformly, spin coating technique was utilized to introduce $Ag@P_4VP$ NPs (in ethanol solutions) onto TiO_2 layer at 600 rpm for 20 s. Thereafter, the ethanol was removed by drying naturally.

2.3.3 The preparation of the $Ag@P_4VP$ modified perovskite-precursor solution involve having mixture of MAI (0.198 g) and PbI_2 (0.579 g) in γ -butyrolactone (400 μL) and dimethylsulfoxide (100 μL) with γ -butyrolactone/dimethylsulfoxide solution of $Ag@P_4VP$ (450 μL) at 70 °C for 11 h.

2.3.4 The perovskite-precursor modified with P25 NP was prepared by mixing MAI (0.198 g) and PbI_2 (0.579 g) in γ -butyrolactone (340 μL) and dimethylsulfoxide (200 μL) with 450 μL of a P25 γ -butyrolactone/dimethylsulfoxide solution (40 mmol L^{-1}) at 70 °C for 11 h.

2.4 Preparation of photoanodes

The FTO were cleaned with cotton wool and ethanol. The blocking layer and the mesoporous layer for the reference electrode was deposited and sintered following a method by Eli et al. [18]. The perovskite was spin coated on the formed mesoporous TiO_2 , it was annealed at 100 °C for 10 min. For the second cell with $Ag@P_4VP$ NPs in TiO_2 (S1), the formed precursor in (2.3.2) 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 s. The third cell with $Ag@P_4VP$ NPs in perovskite (S2) was fabricated by depositing the precursor in (2.3.3) onto the mesoporous TiO_2 by spin coating procedure. The fourth cell with $Ag@P_4VP$ NPs in TiO_2 and perovskite (S3) was achieved by depositing the precursor in (2.3.2) via a successive two-step spin coating process, at 3000 rpm for 30 s, thereafter the precursor in (2.3.3) was spin coated on the formed film at 300 rpm for 20 min. The last cell with P25 powder in TiO_2 and perovskite (S4) was prepared by depositing the precursor with powdered P25 in TiO_2 via a successive two-step spin coating process, at 3000 rpm for 30 s, thereafter the precursor in (2.3.4) was spin coated on the formed film at 300 rpm for 20 min.

2.5 Preparation of the counter electrode

The electrode was developed by employing screen printing procedure. It involves the use of 120 mesh screen printer to screen print a conductive carbon paste (Elcocar B/SP, Solaronix) to obtain the carbon back contact with area of 1 cm^2 . 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 utilized thermally to seal 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).

Structural analyses of the fabricated films of the functionalized materials were performed using X-ray diffractometer (XRD, Rigaku D, Max 2500, Japan).

X-ray microanalysis of the elemental composite layer was carried out with INCA EDX analyzer by bombarding with a finely engaged (< 10 nm measurement) electron beam with an acceleration voltage of 10–150 kV under vacuum.

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 microscope (SEM)

Figure 1 shows the SEM images of: (a) the TiO_2 , (b) $AgNPs@P_4VP$ mixed with TiO_2 , (c) $AgNPs@P_4VP$ mixed with perovskite absorber, (d) $AgNPs@P_4VP$ integrated into TiO_2 and perovskite absorber (e) P25 into both TiO_2 and perovskite absorber and (f) $AgNPs$ at an operating voltage of 10 kV.

The TiO_2 film pictured in Fig. 1a describes a dense surface without bright particles. Considering heavy elements such as silver, electron backscattering is easier than light elements such as O and Ti [10, 26, 27].

Figure 1b shows micrographs of $Ag@P_4VP$ introduced within TiO_2 . From the image, $Ag@P_4VP$ are seen distributed on the upper surface of m- TiO_2 and inside TiO_2 . For $Ag@P_4VP$ core mixed in TiO_2 layers, the Ag signal is clearly detected by the dense surface and the bright particles distributed in it. The luminescent surface indicates that $Ag@P_4VP$ can induce scattering effect to improve the active area of light absorption.

Figure 1c, d are $Ag@P_4VP$ on perovskite and $Ag@P_4VP$ on perovskite and TiO_2 . Since the use of $Ag@P_4VP$ in the perovskite precursor solution may hardly change the perovskite particle size, the two perovskite sorbents exhibit very similar top surface morphology. Larger particles

Fig. 1 Shows the SEM images of **a** the TiO_2 , **b** $\text{AgNPs}@P_4VP$ mixed with TiO_2 , **c** $\text{AgNPs}@P_4VP$ mixed with perovskite absorber, **d** $\text{AgNPs}@P_4VP$ integrated into TiO_2 and perovskite absorber, **e** P25 into both TiO_2 & perovskite absorber and **f** AgNPs

(grain size) reduce the overall particle boundary (grain boundary), facilitating transport and charge carrier to meet lesser boundaries. We speculate that the introduction of $\text{Ag}@P_4VP$ improved nucleation compared to the control, which led to an increase in growth rate.

The sample with P25 modification shows a significant difference between the pure TiO_2 and $\text{Ag}@P_4VP$ modified samples. While the sample shows a well-densified structure, the morphology of constituted nanoparticles seems to be different. It could be seen that the P25 modified sample shows a granular structure. The presence of agglomerations of nanoparticles was also observed. Figure 1f shows SEM image of the AgNPs. The SEM shows high-density AgNPs synthesized. It was shown that relatively spherical and uniform AgNPs were formed as aggregates with sizes ranging from 12 to 20 nm with average size of 16 nm as obtained from ISolution Image Analyzer. Most of the silver nanoparticles were roughly circular in shape with smooth edges. The nanoparticles were not in direct contact even within the aggregates, indicating stabilization of the nanoparticle (Fig. 2).

Fig. 2 Plot of grain size versus photoanodes

Where:

A: The bare TiO_2

B: $\text{AgNPs@P}_4\text{VP}$ integrated into porous TiO_2 ,

C: $\text{AgNPs@P}_4\text{VP}$ integrated into perovskite semiconductor layer,

D: $\text{AgNPs@P}_4\text{VP}$ integrated into TiO_2 & perovskite semiconductor layer and

E: P25 into both TiO_2 & perovskite semiconductor capping layer.

Grain size of the various photoanode film were obtained with imageJ software. Then, perform statistical analysis of the data using the generated histogram, and determine the particle distribution and average particle size from the particle. The particle analyzer consists of an infinite size range from 0 nm to infinity to help capture including small particles. When $\text{AgNP@P}_4\text{VP}$ is incorporated, the film tends to have a porous enhanced grain growth compared to the unmodified film, which leads to enhanced nucleation of the deposited film. The grain size distribution histogram plots for all photoanodes are shown in Fig. 2. The histogram shows that the particle size and distribution are not uniform at sizes from 30.03–140.04 nm. For photoanodes containing $\text{AgNPs@P}_4\text{VP}$ in TiO_2 and perovskite semiconductor layers, there exist a pattern that is better than that of other films. The photoanodes with grain sizes above 100 nm shows initialization of grain

stability and uniformity. Putting P25 titania in the photoanode decreases the grain size and prevent nucleation and growth of films thereby creating more boundaries that can encourage recombination of generated charge carriers and subsequently reduce device performance.

3.2 Energy dispersive X-ray

By utilizing a method to identify elements in the samples, via energy dispersive x-ray spectroscopy, peaks associated with Ti, O, Ag, Ar, N, Cd, C, Ca, Cl, Al and Si are clearly observed in the five spectra. The Ti and O peaks confirmed the presence of TiO_2 particles, and Ag peak obviously resulted from Ag nanoparticles. C and N in Fig. 3b–e confirmed the presence of P_4VP . Very low peak attributable to the element Al may be related to the manipulation of the specimen during SEM investigation [12]. The signal of Si, Ca, Ar and Cd should be attributed to the building element of the substrate since no other Si, Ca, Ar or Cd-based chemicals were used throughout the synthesis. The presence of C in Fig. 3a originates during the synthesis. Cl was present in Fig. 3a due to TiCl_4 which was applied at a final treatment of the porous TiO_2 while Cl present in Fig. 3b originates from the SnCl_2 . We also observed that the PbI_2 was not detected in the EDX results which shows that lead, and Iodine were discharged from the perovskite and

Fig. 3 Shows the EDX images of **a** the TiO_2 , **b** $\text{AgNPs@P}_4\text{VP}$ mixed with TiO_2 , **c** $\text{AgNPs@P}_4\text{VP}$ mixed with perovskite absorber, **d** $\text{AgNPs@P}_4\text{VP}$ integrated into TiO_2 and perovskite absorber and **e** P25 into both TiO_2 and perovskite absorber

Fig. 4 XRD patterns of **a** TiO_2 , **b** AgNPs, **c** TiO_2 -AgNPs and **d** $\text{CH}_3\text{NH}_3\text{PbI}_3$ films and $\text{CH}_3\text{NH}_3\text{PbI}_3$ with TiO_2

redeposited within the interface which prevented it from being detected. This transport and shifting of the Pb and I indicate the absorber pressure generated during deposition process [28].

3.3 X-ray diffraction

Figure 4 shows the XRD patterns of the perovskite film, perovskite with TiO_2 , TiO_2 , AgNPs and Ag: TiO_2 .

The crystal peaks at the 2θ angles were noticed at 14.021° , 22.612° , 28.462° , 32.010° and 49.062° for both perovskite film and perovskite with TiO_2 and assigned to 110, 211, 220, 310 and 440 planes, respectively. The crystallinity of the films shows a good pattern with similar peak of diffraction and intensity. The pattern agrees with the orthorhombic crystalline structure of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ [29, 30]. From the XRD pattern for TiO_2 , AgNPs and Ag: TiO_2 ,

the diffraction peaks at 16.126° , 25.365° , 37.868° , 57.974° , 54.932° , 25.264° , 48.080° were indexed to (100), (110), (110), (111), (111), (100), (200) crystalline planes respectively. This agrees with anatase phase of TiO_2 in accordance to JCPDS Card No. 21-1272. The anatase phase of TiO_2 is preferred over rutile and brookite for photocatalytic degradation of organic compounds [31]. The Ag peaks could not be observed in the modified TiO_2 XRD patterns, which indicated that silver was only homogenously distributed on the surface of the TiO_2 [32, 33]. These results were consistent with the UV-vis results of our previous studies and that of other authors, where there was also no peak characteristic of silver around 450 nm detected [12, 34]. The XRD patterns showed no peak which was not indexed or corresponding to silver oxide phase observed. This suggested that the nanocomposites prepared were of high purity.

Fig. 5 Schematics of the fabrication process

3.4 Solar cells photovoltaic performance

To show the systematic effect of Localized Surface Plasmons on PSCs performance, devices with architecture of Ag@P₄VP NPs, P25, Ag@P₄VP NPs and P25 modification and standard PSC with just TiO₂ NPs as photoanodes are designed and fabricated as shown schematically in Fig. 5.

After the design and preparation, the *I*–*V* performance of PSCs were estimated under AM 1.5 G irradiation utilizing a setting involving a Xenon lamp, an AM 1.5 light channel, and an Electrochemical Analyzer (Keithley 2400 source meter). The intensity of the light was at 100 mW/m². Since the five PSCs function in a way similar to a junction solar cells, their performance parameters was resolved from the *J*–*V* and *P*–*V* curves following Eqs. (1) and (2) respectively.

$$FF = \frac{J_{\max} \times V_{\max}}{J_{sc} \times V_{oc}} \quad (1)$$

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{\text{IRRADIANCE}}} \times 100\% \quad (2)$$

Figure 6a depicts the *J*–*V* images of PSC devices with different configuration. The parameters which include *J*_{sc}, *V*_{oc}, *PCE* and *FF* are stated in Table 1.

From Table 1, the control device which is the reference device exhibits a *V*_{oc} of 0.85 V, *J*_{sc} of 11.04 mA cm^{−2} and *FF* of 0.41, which result in a total *PCE* of 3.80%. We noticed a performance response lower than the control when P25 NPs was introduced into the TiO₂ and the absorber. We denote the device as (S4) and exhibits *PCE* of 3.21% and *V*_{oc}=0.84 V, *J*_{sc}=10.67 mA cm^{−2} and *FF*=0.36%. Adding P25 NPs to the perovskite significantly reduces the cell performance, importantly the *J*_{sc}, which is attributed to the fact that the Colloidal TiO₂ NP in TiO₂ paste for forming porous TiO₂ film is less than the average particle size of P25 TiO₂ NPs [11]. The low performance noticed in the device is attributed to the high electron transport resistance.

Fig. 6 **a** Combined *J*–*V* characteristic curves of PSCs under illumination and in the dark. **b** *P*–*V* characteristic curves of Ag@P₄VP and P25 modified and unmodified PSCs

When Ag@P₄VP NPs is introduced into either the TiO₂ or the absorber layer, a better performance was exhibited. The devices with Ag@P₄VP in TiO₂, CH₃NH₃PbI₃ and TiO₂

Table 1 Photovoltaic performance of AgNPs@P₄VP and P25 modified and unmodified PSCs under 100 mW cm⁻²

Device	<i>J</i> _{sc} (mA cm ⁻²)	<i>V</i> _{oc} (V)	<i>FF</i>	<i>η</i> (%)
Control device	11.04	0.85	0.41	3.80
S1	12.61	0.88	0.51	5.69
S2	14.18	0.89	0.64	8.08
S3	15.87	0.88	0.65	9.05
S4	10.67	0.84	0.36	3.21

and CH₃NH₃PbI₃ are denoted as S₁, S₂ and S₃. Compared with the device without Ag@P₄VP NP, the devices with Ag@P₄VP NP modification S₁, S₂ and S₃ exhibited noticeably greater PV performance and device S₃ exhibits a better value *J*_{sc} to that of S₁ and S₂.

When Ag@P₄VP NPs is mixed with porous TiO₂ layer, S₁ exhibits a PCE of 5.69% with *J*_{sc} = 12.61 mA cm⁻², *V*_{oc} of 0.88 V, and *FF* of 0.51 which shows an enhancement of ~ 1.50 times in PCE from the control device. Amazingly, when Ag@P₄VP NPs is added within the absorber layer, the device S₂ attained a PCE of 8.08% with *V*_{oc} of 0.89 V, *J*_{sc} of 14.18 mA cm⁻² and *FF* of 0.64% which demonstrates an improvement of ~ 2.13 times in PCE, ~ 1.28 times in *J*_{sc}, ~ 1.05 times in *V*_{oc} and ~ 1.58 times in *FF* over the reference device. Moreover, by simultaneously introducing Ag@P₄VP NPs into both the TiO₂ and the absorber, the device demonstrated further enhanced performance. As shown from Table 1, the device S3 achieved a PCE of 9.05%, *V*_{oc} of 0.88 V, *J*_{sc} of 15.87 mA cm⁻² and *FF* of 0.65 which shows an enhancement that is ~ 2.38 times that of the pristine device in PCE. When compared with the pristine device, the champion device (S3) shows a significant increase in *J*_{sc} from 11.04 to 15.87 mA cm⁻², the *FF* recorded an enhancement from 0.41 to 0.65, and the value of the *V*_{oc} improves from 0.85 to 0.88 V. The apparent increase in *J*_{sc} is as a result of the improve absorber response and the expansion of the light absorption range by the SPR of AgNP, which stimulates the absorber to dissociate/separate e⁻/h⁺. In addition, the Schottky barrier at the TiO₂(Ag@P₄VP)/absorber or TiO₂/absorber(Ag@P₄VP) interface forms an electron-hole separation center and the movement of photoelectrons back and forth through a porous TiO₂ network help improve *J*_{sc} by reducing the recombination of electrons and holes. As is well known, silver has long been considered catalytically active [14, 35]. When Ag@P₄VP is dispersed on metal oxide substrates catalytic action with chemical reactions are observed [9, 18, 35, 36]. In our work, when Ag@P₄VP was added, photoactive behavior of Ag@P₄VP on the TiO₂ support enhanced the bonding formation that exist between TiO₂ and CH₃NH₃PbI₃, thereby increasing electron mobility. Due to the reason, the quenching losses between e⁻/h⁺ was reduced, thereby making the *J*_{sc} and *V*_{oc} values to increase. Improvement of photocurrent

in Ag@P₄VP modified cells indicate that the electrical effects of LSPR and Ag@P₄VP enhance the photoelectric response [37, 38]. In addition, the *V*_{oc} of Ag@P₄VP device may also be related to plasmon coupling between Ag@P₄VP, which helps in transferring electron to the CB of TiO₂ as a result, the built-up potential of the device increases [11, 39]. The high *FF* in S₃ may be due to low series resistance [11]. Current does not flow under dark condition thereby behaving as a diode as depicted in Fig. 6a. This rectifying behaviour is a feature of photovoltaic devices and is a consequence of the asymmetric junction needed to separate charges.

Figure 6b illustrates *P*-*V* plot of the control, S1, S2, S3, S4 devices. Their maximum powers are observed at 3.80, 5.69, 8.08, 9.04 and 3.21 mW cm⁻².

Figure 7 shows the curves *V*_{oc}, *J*_{sc}, *FF* and PCE with respect to the device.

Since at the standard fabrication condition we developed five PSCs using the same fabrication process for all the devices, the statistics based on the devices was compared as shown in Fig. 7. As shown, devices with silver nanoparticles inclusive demonstrated better photovoltaic performance in average short circuit current density, open circuit voltage, fill factor and power conversion efficiency. The average PCEs of device C, S1, S2, S3 and S4 are 2.74 ± 1.04%, 4.56 ± 1.14%, 8.21 ± 1.20%, 9.4 ± 1.25 and 2.60 ± 1.02%, respectively. The champion device (S3) shows an average PCE enhancement of ~ 3.43 times as compared to the pure device without impurity. When compared with the device with silver nanoparticles in the perovskite absorber, the average PCE shows improvement of ~ 3.00 times. Also the device with AgNPs@P4VP in TiO₂ shows average enhancement of ~ 1.66 times over the reference cell.

For the hysteresis test, Fig. 8 describe the *J*-*V* characteristics curves measured under both reverse and forward-scan directions. It is observed from the plots that the devices with Ag@P₄VP NP have almost same *J*-*V* plots with negligible hysteresis, even when it is measured using forward and reverse scan.

In general, the hysteresis of PSCs is due to the interfacial capacitance caused by the accumulation of interfacial charges caused by ion transport, high trap density and imbalance of charge transport within the perovskite device [40–42]. We can speculate that, the size of the grains in the absorber layer is significantly increased with Ag@P₄VP NPs introduction, which reduces the grain boundaries with high trapping rate, and enhances the optical and electrical properties thereby making the devices almost hysteresis free [40, 43], it is one of the main causes of minimal hysteresis.

We observed hysteretic behaviour from the *J*-*V* characteristic of the reference PSC which becomes difficult to

Fig. 7 Statistics of device performance parameters with PCE, J_{sc} , V_{oc} and FF of PSC devices with different configurations

estimate the actual PCE. To have a better understanding of the hysteresis on our device performances, the J - V curves of PSCs was obtained by scanning the applied voltage from forward bias (FB) to short circuit (SC) and the other way round. It was observed after the scan that the control device is hysteretic.

From Table 2, the forward and reverse scan of pristine based device showed a 3.80 and 3.03% of PCE, thereby yielding a mean PCE of 3.41%. Just 0.77% in PCE was noticed as can be seen in that of FB scan. The mean values in SC and FB scans exhibits a J_{sc} of 9.93 mA cm^{-2} , V_{oc} of 0.85 V (no changes observed), and FF of 0.40. The partial increase of the grain size that reduces the trapping nature in the boundary during reverse condition is suggested to form a region of depletion at TiO_2 /perovskite interface, which would cause a shift in the Fermi level and gradually prevent dissociation of e^-/h^+ , thereby resulting to bad PCE during reverse scan [44, 45]. On the other hand, negligible hysteresis effect is observed with the $\text{Ag@P}_4\text{VP}$ NPs based devices. The grain boundaries that act as trapping sites under large FB is applied during

J - V investigation to reduce depletion regions and minimize band bending effects [44]. The S1 device exhibited 0.88 V of V_{oc} , 12.52 mA cm^{-2} of J_{sc} , 0.51 of FF, and 5.57% of PCE, for the reverse scan and under forward scan, a 0.88 V of V_{oc} , 12.62 mA cm^{-2} of J_{sc} , 0.51 of FF, and 5.69% of PCE, with average PCE of 5.63%. The S2 device exhibited 0.89 V of V_{oc} , 14.06 mA cm^{-2} of J_{sc} , 0.64 of FF, and 8.00% of PCE, for the reverse scan and under forward scan, a 0.89 V of V_{oc} , 14.18 mA cm^{-2} of J_{sc} , 0.64 of FF, and 8.08% of PCE, with average PCE of 8.04%. The S3 device exhibited 0.88 V of V_{oc} , 15.70 mA cm^{-2} of J_{sc} , 0.65 of FF, and 8.95% of PCE, for the reverse scan and under forward scan, a 0.88 V of V_{oc} , 15.87 mA cm^{-2} of J_{sc} , 0.65 of FF, and 9.05% of PCE, with average power conversion efficiency of 9.00%. Also, we observed hysteretic behavior in the J - V curve of device S4, 3.21 and 2.57% for the FB can RB scans. These results further justify how efficient our devices and prove the role of integrating $\text{Ag@P}_4\text{VP}$ NPs in PSCs.

From the results, the observed characteristics are attributed to the change in the nature of electronic

Fig. 8 Hysteresis test for the prepared PSCs

Table 2 Photovoltaic performance of the forward and reverse scan of AgNPs@P₄VP and P25 modified and unmodified PSCs under 100 mW cm⁻²

Device scan	<i>J</i> _{sc} (mA cm ⁻²)	<i>V</i> _{oc} (V)	<i>FF</i>	<i>η</i> (%)
Control F	11.04	0.85	0.41	3.80
R	8.82	0.85	0.40	3.03
S1 F	12.61	0.88	0.51	5.69
R	12.52	0.88	0.51	5.57
S2 F	14.18	0.89	0.64	8.08
R	14.06	0.89	0.64	8.00
S3 F	15.87	0.88	0.65	9.05
R	15.70	0.88	0.65	9.00
S4 F	10.67	0.84	0.36	3.21
R	8.55	0.84	0.36	2.57

contact between perovskites and p- and n-type contact materials, but emphasizes that this explanation requires additional reasons. There are three possible origins that contribute to that. (1) The perovskite absorber deformation in structure which can generate boundaries that can act as trap sites [43, 46]. (2) Organometallic trihalide perovskites have shown ferroelectric properties, which may result in slow polarization, depending on the voltage applied [43, 47]. (3) Excess ions due to the presence of gap defects (iodide or methylammonium) and predominant instability all through the material. During operational process interstitial ions can move to either side of the material, creating a shield space charge accumulation and assisting in collection of charges while on working standard [43].

4 Conclusion

In this research report, we follow up to our previously published manuscript on “improved power conversion efficiency in Perovskite solar cell using silver nanoparticles modified photoanode” by developing three more photoanodes to include Ag@P₄VP NPs mixed with perovskite layer, Ag@P₄VP NPs simultaneously mixed both in TiO₂ and perovskite films and P25 NP simultaneously mixed both in TiO₂ and perovskite absorber and compared their performances systematically. The results show that the presence of Ag@P₄VP greatly enhanced the PCE of the PSCs by improving *J*_{sc}, *V*_{oc}, *FF* and *η*. The best performing PSC contained Ag@P₄VP-NPs simultaneously incorporated in both TiO₂ and perovskite layer. The PSC gave a *J*_{sc} of 15.87 mA cm⁻², *V*_{oc} of 0.88 V and *FF* of 0.65, resulting to the best performance of 9.05%. The device demonstrated an improvement of ~ 2.38 times over the performance (3.80%) of the device without Ag@P₄VP NPs. 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 localized surface plasmon resonance from AgNP, while increase in *V*_{oc} can be attributed to a shift from a positive potential as a result of improved electron dissociation due to AgNPs@P₄VP incorporation.

Acknowledgements Authors wish to acknowledge the Sheda Science and Technology Complex, Abuja for providing characterization facilities.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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