Enhanced performance of triple-junction tandem organic solar cells due to the presence of plasmonic nanoparticles

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Abstract
A triple-junction tandem organic solar cell (OSC) having polymer active materials, P3HT:PC70BM, Si-PCPDTBT:PC70BM, and PMDPP3T:PC70BM is presented. These active layer materials cover a 300 nm to 1000 nm broad solar spectrum and have minimally overlapping narrow absorption bands. The performance of the triple-junction tandem OSC was improved by introducing plasmonic nanospheres (NSs) over the top electrode of the OSC. The OSCs were modeled in finite-difference time-domain (FDTD) to optimize the performance of the NSs. Nanospheres of three plasmonic materials—gold (Au), silver (Ag), and aluminum (Al) were individually simulated over the top electrode of the OSCs. The NSs affect absorption in the active layer materials, around their respective plasmonic resonance peaks. The low-cost Al NSs enhance light trapping in the top and middle subcells, leading to a 14% improvement in overall short circuit current density ($J_{SC}$) of the triple-junction tandem OSC in comparison with that of the reference OSC without any NSs. It is also observed that while the enhancement of the overall $J_{SC}$ of the triple-junction tandem OSC due to the Al NSs is greater than that due to the Ag NSs, the presence of Au NSs leads to a decrease in the overall $J_{SC}$ in comparison with that of the reference OSC.

KEYWORDS
broadband absorption, FDTD simulations, light trapping, nanoparticles, organic solar cells, scattering, surface plasmons

1 | INTRODUCTION

Although silicon-based solar cells have traditionally dominated the solar energy industry, they have high material and processing costs. Lately, organic photovoltaic cells have been reported to have higher power conversion efficiencies (PCEs) as compared to the initial research work on organic photovoltaics in the early 2000s.\textsuperscript{1,2} Considering the benefits of organic materials such as lightweight, flexibility, and low processing temperature, several methods are being explored to enhance the PCE of organic polymers-based photovoltaic cells to give the energy industry a strong and viable alternative to silicon solar cell modules.\textsuperscript{3-11}

In organic semiconductors, photo-excitation leads to the generation of bound electron-hole pairs called excitons. The excitons are separated to generate free charge carriers at the electron-acceptor and electron-donor interfaces of the photovoltaic cell.\textsuperscript{12-14} Typical diffusion lengths of excitons in organic polymers are of the order of ~10 nm.\textsuperscript{15} Hence, for effective free carrier generation, the active layer thicknesses...
should be of the same order as the diffusion length of the excitons in the organic material. However, such small thicknesses lead to low absorption of incident photons. For larger active layer thicknesses, fewer excitons reach the interface. The n- and p-type materials are thus mixed into a bulk heterojunction (BHJ) to introduce interfaces within the volume of the active layer, thereby enabling active layer thicknesses of 100s of nanometers.16

Organic semiconductors with a large bandgap translate to a narrow-band absorption of the solar spectrum. Most polymer semiconductors have a bandgap of 2 eV and only absorb about 30% of the solar radiation.17 To improve the PCE of the solar cells, multiple narrow-band semiconducting polymers with minimally overlapping absorption spectra are combined to form tandem organic solar cells (OSCs) in order to absorb a greater range of the solar radiation. Typically, these tandem cells have subcells stacked over each other to yield a higher open-circuit voltage ($V_{OC}$), which is a sum of the individual subcell $V_{OC}$s. Materials are matched over broad bandwidths and adjusted for optimum JSC to obtain a solar cell with a net higher PCE.18-20

In OSCs, photon harvesting can be improved by increasing the optical path length in the active medium.21-23 This has previously been achieved by employing plasmonic nanoparticles within the active region of the OSCs and in the buffer layers.24-28 This enhances the scattering of incident light by the nanoparticles at the plasmon resonance wavelengths of the plasmonic nanoparticles. This in turn leads to a greater light absorption in the active layers of the OSCs. Plasmonic enhancement of absorption in OSCs has been established by the introduction of different geometries of nanoparticles—nanospheres,29-31 nanoshells,32 nanodiscs,33,34 nanorods,35,36 and spiral nanostructures.37 Plasmonic nanoparticles have also been introduced in double-junction tandem cells38-41 and enhancements in properties of the tandem OSCs reported.

In this paper, triple-junction tandem OSCs with active materials—P3HT:PC70BM, Si-PCPDTBT:PC70BM, and PMDPP3T:PC70BM for the top, middle, and bottom subcells, respectively, have been simulated using FDTD. The resultant tandem OSCs have a broad absorption spectrum bandwidth and a higher $V_{OC}$ than the individual subcell $V_{OC}$s. The effects of adding plasmonic nanospheres (NSs) over the top electrode of the OSC have been investigated for different metals—gold, silver, and aluminum. Although the effect of metallic nanoparticles on the electrical properties such as PCE and fill factor (FF) have been reported,42-45 this paper focuses primarily on the improvement in the optical properties such as absorption in the different active layers due to the presence of the metallic nanoparticles. The effect of varying the NS size and periodicity on the absorption as well as JSC of these tandem OSCs was also investigated. Increasing the size of the NSs introduces higher order plasmonic resonance modes, that enhances the JSC of the subcells.46 The absorption of light is, therefore, effectively enhanced by the Al NSs in the top and middle subcells to give a 14% increase in the overall JSC of the tandem OSC. This is the first report of a triple-junction tandem organic solar cell in which plasmonic nanoparticles are employed to enhance the JSC.

While silver and gold NSs can be chemically synthesized using standard processes,47,48 aluminum NSs can be generated by ultrafast (picosecond or femtosecond) laser ablation of metal targets and collected in a solvent (such as ethanol) that completely surrounds the target while laser ablation is carried out.49,50 The tandem OSC shown in Figure 1 can be fabricated by depositing the silver electrode on a glass substrate. Consequently, the different polymeric layers (ie, the active material layers) can be spin coated inside a glove box, along with the evaporation of the inorganic material layers (TiO2, MoO3, and ITO) using an electron beam evaporation system integrated with a glove box. The solution containing the synthesized or generated NSs can be spin coated over the top surface, followed by encapsulation with suitable material(s) to obtain the plasmonic tandem OSC described in this paper. Hence, the nanospheres are coated on the top surface and would not lead to any rougher surface in the underlying layers. The proposed device has, therefore, been modeled as a planar layer-by-layer device.

2 SOLAR CELL CONFIGURATION AND PARAMETERS SIMULATED

Figure 1A illustrates the schematic diagram for the triple-junction tandem OSC with NSs over the top electrode. An OSC without any NSs—the reference OSC is shown in Figure 1B. The top electrode was a 50 nm layer of indium tin oxide (ITO). For all the subcells, hole transport layer of TiO2 and electron transport layer of MoO3 were defined—each of thickness 10 nm. The back electrode was taken as 100 nm of silver. It can be seen from Figure S1 that there is no change in the absorption spectra of the subcells of the OSC when the glass substrate is present underneath the silver layer as compared to the case when it is not present. As the presence of the glass substrate does not make any difference to the absorption spectra of the subcells of the OSC, we have not taken the glass substrate in our FDTD simulations to reduce the simulation time. Active layer materials were chosen for their high absorption efficiencies in their respective minimally overlapping narrow bands. The wavelength-dependent optical constants of the active layer materials—P3HT:PC70BM, Si-PCPDTBT:PC70BM, and PMDPP3T:PC70BM were taken from reference.51 The complex refractive indices of gold, silver, and aluminum were taken from Palik52 while dielectric constants of MoO3, TiO2, and ITO were obtained from literature.53
Three-dimensional FDTD simulations of the tandem OSCs were performed using the commercially available Lumerical FDTD suite. The light was incident from a plane wave broadband source, having wavelengths from 300 nm to 1000 nm, and placed 500 nm above the top surface of the OSC. The top and bottom boundaries, normal to the direction of incident light, were taken as perfectly matched layers (PML), while the other four domain boundaries were taken to be periodic. A $2 \times 2 \times 2$ nm$^3$ mesh was taken in the NS region to ensure that the Courant stability criteria were satisfied. A nonuniform mesh was taken in the remaining simulation regions. The periodicity, the radius, and the material of the NSs were varied and thus optimized to enhance light absorption in the subcells. Due to the symmetric shape of the NSs, both transverse magnetic (TM) and transverse electric (TE) polarized light yield the same results. Power monitors were positioned at the edges of the active layers to measure the absorption of the subcells. The power monitors of all the subcells are shown in Figure 1B—T$_1$ and T$_2$ for the top subcell, M$_1$ and M$_2$ for the middle subcell and B$_1$ and B$_2$ for the bottom subcell.

The $J_{SC}$ for a subcell was calculated by integrating the absorption in the subcell active layer with solar spectrum AM1.5G, assuming that all electron-hole pairs generated contribute to the current$^{54}$

$$J_{SC} = e \int_{\lambda_1}^{\lambda_2} \frac{\lambda}{h c} I_{AM1.5}(\lambda) A(\lambda) d\lambda$$  \hspace{1cm} (1)$$

where, $e$ is elemental charge, $\lambda_1$ is starting wavelength of simulation, $\lambda_2$ is band edge of the subcell active material, $h$ is the Plank’s constant, $c$ is the speed of light in free space, $A(\lambda)$ is the ratio of the time-averaged power absorbed by the subcell active layer ($P_a(\lambda)$) and the incident optical power ($P_i(\lambda)$), and $I_{AM1.5}$ is the solar spectrum AM1.5G. The starting wavelength, $\lambda_1$, is 300 nm for all the subcells, corresponding to the incident plane source. The wavelength, $\lambda_2$, for the top, middle, and bottom subcells are 650 nm, 800 nm, and 1000 nm, respectively, taken from their respective active layer material band edges. In order to determine the overall $J_{SC}$ of a tandem OSC, firstly, the maximum possible values of $J_{SC}$ are determined for each subcell. The overall $J_{SC}$ of a tandem OSC is the minimum value out of the maximum possible $J_{SC}$s calculated for the different subcells. The $J_{SC}$ enhancement in the tandem OSC is the ratio of the overall $J_{SC}$ of the tandem OSC having NSs to the overall $J_{SC}$ of the tandem OSC without any NSs.

3 | RESULTS AND DISCUSSION

3.1 | Tandem OSCs without nanospheres—reference OSC

Firstly, the optimal values of the active layer thicknesses of the three different subcells in the triple-junction tandem OSC without any NSs were determined. The bottom subcell active layer thickness (with active medium PMDPP3T:PC$_{70}$BM) was varied and optimized to enhance the bottom subcell absorption and to match the $J_{SC}$ of the three subcells. In these calculations, the active layer thickness of both the top subcell (with active medium P3HT:PC$_{70}$BM) and the middle subcell (with active medium Si-PCPDTBT:PC$_{70}$BM) were taken to be 150 nm. From the triple-junction tandem OSC...
simulations, the $J_{SC}$ of the respective subcells were plotted in Figure 2A for a change in the bottom subcell active layer thickness ($t_{bottom}$), keeping thicknesses of the top and middle subcells to be constant at 150 nm. There is almost no change in the $J_{SC}$ of the top subcell, as $t_{bottom}$ increases. This is because the top subcell absorption spectrum does not have a major spectral overlap with the bottom subcell absorption spectrum. We can also observe from Figure 2A that the bottom subcell $J_{SC}$ increases and that of the middle subcell decreases as $t_{bottom}$ is increased. It can be noted from Figure 2B that the middle and the bottom subcells have some overlap in their spectral profiles. For lower values of $t_{bottom}$, the absorption of incident light as well as that reflected back from the silver back electrode is less in the bottom subcell due to its lower thickness. Instead, the light (of wavelengths overlapping between the middle and the bottom subcells) reflected from the silver back electrode and not absorbed in the bottom subcell is absorbed in the middle subcell for these lower $t_{bottom}$. On the other hand, as $t_{bottom}$ increases, the light reflected back by the silver back electrode is primarily absorbed by the bottom subcell (leading to an increased $J_{SC}$ of the bottom subcell) and, therefore, is not available for absorption by the middle subcell, which reduces the $J_{SC}$ of the middle subcell. The bottom subcell $J_{SC}$ increases (up to a certain optimal value) as $t_{bottom}$ increases. The $J_{SC}$ values of the middle and bottom subcells match for a $t_{bottom}$ of about 86 nm, with $J_{SC} = 9.23$ mA cm$^{-2}$.

From the initial simulation trends, it was observed that adding the NSs over the top electrode affects absorption of the top and middle subcells. Hence, the absorption and $J_{SC}$ of the top and middle subcells were optimized by varying the parameters of plasmonic NSs. On the other hand, it was observed that adding the NSs over the top electrode reduces the absorption of the bottom subcell. Hence, optimization of absorption and $J_{SC}$ of the bottom subcell was carried out by varying the bottom subcell active layer thickness—for both the reference OSC (containing no NSs) as well as for the tandem OSCs containing the plasmonic NSs. As the addition of plasmonic NSs (for Ag and Al NSs) on top of the tandem OSCs leads to a higher $J_{SC}$ of the top and middle subcells above 9.5 mA cm$^{-2}$ for certain optimized geometries of the NSs (as discussed later in Sections 3.2, 3.3, and 3.4), $t_{bottom}$ was chosen such that the $J_{SC}$ of the bottom subcell is also greater than 9.5 mA cm$^{-2}$ so that the overall $J_{SC}$ of the triple-junction tandem OSC is above 9.5 mA cm$^{-2}$. We can observe from Figure 2A that for a reference OSC, the $J_{SC}$ of the bottom subcell is greater than 9.5 mA cm$^{-2}$ for values of the $t_{bottom}$ between 100 nm and 130 nm. Hence, the optimal value of $t_{bottom}$ was determined to be 100 nm—for both the reference OSC (containing no NSs) as well as for the tandem OSCs containing the plasmonic NSs—as this enabled the desired performance to be achieved for the least amount of the active layer material. Hence, the value of $t_{bottom}$ equal to 100 nm was taken in all the subsequent simulations carried out for optimizing the NS parameters so as to achieve a high overall $J_{SC}$ of the tandem OSCs containing plasmonic NSs.

The absorption spectra of the OSCs without NSs (ie, of the reference OSC) are plotted in Figure 2B—with the active layer thickness of the top subcell (P3HT:PC$_{70}$BM), $t_{top} = 150$ nm; the middle subcell (Si-PCPDTBT:PC$_{70}$BM), $t_{middle} = 150$ nm; and the bottom subcell (PMDPP3T:PC$_{70}$BM), $t_{bottom} = 100$ nm. We observe in Figure 2B that the absorption spectra for the three different active layer materials have minimal spectral overlap and have different spectral regions.

**FIGURE 2** (A) $J_{SC}$ for variation in bottom subcell active layer thickness ($t_{bottom}$), having constant top and middle subcell active layer thicknesses of 150 nm. (B) Absorption in the OSC without NSs—that is, in the reference OSC. The thicknesses of the OSC layers were ITO—50 nm, TiO$_2$—10 nm, MoO$_3$—10 nm, P3HT:PC$_{70}$BM—150 nm, Si-PCPDTBT:PC$_{70}$BM—150 nm, PMDPP3T:PC$_{70}$BM—100 nm, and silver back electrode—100 nm.
where absorption is high. The top subcell has a higher absorption in the 300-600 nm wavelength range; the middle subcell in the 600-800 nm wavelength range; and the bottom subcell beyond 800 nm. This reference OSC has top subcell $J_{SC} = 8.43$ mA cm$^{-2}$, middle subcell $J_{SC} = 8.68$ mA cm$^{-2}$, and bottom subcell $J_{SC} = 10.33$ mA cm$^{-2}$. The overall $J_{SC}$ of the reference OSC without any NSs is determined from the top subcell $J_{SC}$, which is equal to 8.43 mA cm$^{-2}$. The overall $J_{SC}$ (8.43 mA cm$^{-2}$) and the absorption spectra of this reference OSC provide the baseline for further comparisons with tandem OSCs containing plasmonic NSs.

### 3.2 Tandem OSCs with Au nanospheres

In the triple-junction tandem OSCs, plasmonic metal NSs of varying periodicity and radii were added over the top electrode, as shown in Figure 1A. The periodicity and radius of the NSs were changed to implement a changing surface coverage. Surface coverage is the ratio of the shadow area of the NSs to the period area of the solar cell. Gold (Au) NSs taken had periodicity varying from “P” = 250 nm to 450 nm, in increments of 50 nm, and radii varying from “r” = 30 nm to 100 nm, in increments of 10 nm. The $J_{SC}$ maps for the three subcells, as a function of “P” and “r” of the Au NSs, are shown in Figure 3A–C. In all the plots, the highest $J_{SC}$ (marked by the star) is obtained for the smallest 30 nm radius Au NS, placed 450 nm apart. The respective $J_{SC}$ values from the top, middle, and bottom subcells are 8.41, 8.97, and 9.95 mA cm$^{-2}$. This tandem OSC with Au NSs (“P” = 450 nm and “r” = 30 nm) over the top electrode has an overall $J_{SC} = 8.41$ mA cm$^{-2}$.

Figure 3D illustrates the absorption spectra of the three subcells—with and without plasmonic NSs over the tandem OSC. The top subcell, in the presence of gold NSs, does not have any improvement in absorption over the reference OSC. The middle subcell has a marginal improvement in the absorption beyond 800 nm. This reference OSC provide the baseline for further comparisons with tandem OSCs containing plasmonic NSs.

The introduction of Au NSs over the tandem OSC generates a lower overall $J_{SC}$ (8.41 mA cm$^{-2}$) in comparison with the reference OSC (8.43 mA cm$^{-2}$) and hence leads us to conclude that gold is not a suitable NS material for performance enhancement in this triple-junction tandem OSCs.

### 3.3 Tandem OSCs with Ag nanospheres

The triple-junction tandem OSCs were then simulated with silver (Ag) NSs over the top electrode. The Ag NS periodicity here was varied from “P” = 250 nm to 450 nm, with radius changing from “r” = 50 nm to 100 nm. $J_{SC}$ maps of the three subcells, as a function of “P” and “r” of the Ag NSs are shown in Figure 4A–C, with the maximum $J_{SC}$ of each subcell marked with a star.

The maximum possible values of $J_{SC}$ (ie, the optimal values of $J_{SC}$ for each subcell) of the top, middle, and bottom subcells were determined to be 8.93, 9.49, and 10.01 mA cm$^{-2}$, respectively. The maximum $J_{SC}$ was obtained in the top subcell of the OSC in which Ag NSs have periodicity “P” = 400 nm and radius “r” = 70 nm. The $J_{SC}$ values for the top, middle, and bottom subcells of a tandem OSC with Ag NSs having a periodicity “P” of 400 nm and radius “r” of 70 nm were calculated to be 8.93, 9.38, and 10.01 mA cm$^{-2}$, respectively. The overall $J_{SC}$ of the tandem OSC is taken as the minimum value from the highest possible $J_{SC}$s calculated for the three subcells, that is, the overall $J_{SC}$ of the tandem OSC is 8.93 mA cm$^{-2}$. Thus, there is a 6% improvement in the overall $J_{SC}$ of the tandem OSC having Ag NSs, in comparison with that of the reference OSC.

Nanoparticles placed close to each other (ie, for low values of periodicity) block the incident radiation from reaching the active layers. On the other hand, particles spread out too far apart are ineffective in scattering sufficient light into the active layer. We optimized the NS periodicity and the NS size so as to maximize the absorption in the OSCs. Moreover in Figure 4D, the absorption in the top subcell of the OSC having the Ag NSs is less than that of the reference OSC for wavelengths less than 450 nm. This can be attributed to Fano resonance, wherein the presence of NSs causes the incident light and the scattered light to interfere destructively.
for wavelengths less than the characteristic resonance wavelength of the NSs.\textsuperscript{55,56} For wavelengths longer than 450 nm, absorption in the top and middle subcells of the OSC having Ag NSs is greater than that of the reference OSC due to the plasmonic-enhanced scattering of the incident light into the top and middle subcell active layers.

### 3.4 Tandem OSCs with Al nanospheres

Finally, aluminum (Al) NSs were added over the top electrode of the tandem OSCs. The Al NS variation parameters were same as that of Ag NSs, that is periodicity, “P” = 250 nm to 450 nm and radius, “r” = 50 nm to 100 nm. The effect of these Al NSs, as a function of “P”, and “r” as seen in Figure 5A–C, is more pronounced than the effect of the Au and Ag NSs. The maximum $J_{SC}$ values of all the individual subcells are close to each other. This leads to a good matching condition across the subcells, generating a high overall $J_{SC}$ of the tandem OSC. The lowest $J_{SC}$ value selected out of the maximum $J_{SC}$ values for each of the three subcells was obtained for the top subcell with the Al NSs, having periodicity “P” = 350 nm and radius “r” = 70 nm. These dimensions were taken as the optimized parameters because they result in the maximum overall $J_{SC}$.
values of the top, middle, and bottom subcells are 9.61, 9.62, and 9.96 mA cm\(^{-2}\). The \(J_{SC}\) increases in the top and middle subcells and decreases in the bottom subcell due to the introduction of Al NSs over the top electrode. The \(J_{SC}\) can be enhanced in the bottom subcell by increasing the bottom subcell active layer thickness, and in the top and middle layers by adding NSs over the top electrode. The overall \(J_{SC}\) of the tandem OSC was evaluated to be 9.61 mA cm\(^{-2}\). Thus, there is a 14\% improvement of the overall \(J_{SC}\) of the tandem OSC having Al NSs over that of the reference OSC (8.43 mA cm\(^{-2}\)).

From the absorption spectra for the different subcells shown in Figure 5D, we can observe an enhancement in the absorption of the top and middle subcells for most of the spectrum. Similar to the case of the tandem OSCs containing Au and Ag NSs, the bottom subcells of the tandem OSCs containing Al NSs over the top electrode also have a lower \(J_{SC}\) than that of the bottom subcell of the reference OSC. This could be ascribed to the slightly higher absorption of light within the NSs between wavelengths 800 nm and 900 nm—as indicated by a slight peak in the absorption cross-section spectrum for Al NSs in the spectral range from 800 nm to 900 nm, illustrated in Figure 6B. Moreover, the longer wavelengths of light scattered by the Al NSs are partly absorbed by the middle subcell layer due to some overlap in the absorption spectral profiles of the middle and the bottom subcell layers.
Comparison of different tandem OSCs containing nanospheres

The introduction of the Al NSs of optimized periodicity and size over the tandem OSC leads to an improvement in the performance of the top and middle subcells, and closely matched values of $J_{SC}$ for the three subcells. The performance of the optimized Al NSs—periodicity, “P” = 350 nm and radius, “r” = 70 nm was compared with that of identically sized Au and Ag NSs, to better understand the effects of the NSs. In Figure 6A, the scattering cross-sections of the 70 nm radius Au, Ag, and Al NSs have been plotted. The absorption cross-section of the 70 nm radius Au, Ag, and Al NSs is shown in Figure 6B. These results were obtained from simulations carried out with the NSs placed on an ITO substrate, under PML boundary conditions. The absorption spectra of the three subcells of the three different tandem OSCs with Au, Ag, and Al NSs over the top electrode are plotted in Figure 6C along with the absorption spectra of the reference OSC.

It can be observed from the absorption spectra in Figure 6C that the absorption in the top subcell of the tandem OSC with the Al NSs is less than the absorption in the reference OSC for wavelengths shorter than ~350 nm. This can be attributed to Fano resonance—a destructive interference between the scattered light and the incident light, leading to a reduced absorption of light.\textsuperscript{55-57}

The authors would like to point out that the enhancement of the absorption in the active layers is due to the forward scattering of the incident light by the nanospheres—that is, due to the enhanced far-field scattering by the plasmonic
nanoparticles at the resonant wavelengths. Hence, the incident light undergoes far-field scattering from the plasmonic nanoparticles present on top of the ITO layer and effectively reaches the BHJ layers. This results in enhancement of both the EM fields as well as absorption in the BHJ active layers. Hence, light scattered by the nanoparticles into the far-field gets suitably concentrated within the BHJ active layers where it is effectively absorbed. It can be seen from Figure S2 that the active layers of the OSC containing the aluminum nanoparticles have higher electric fields as compared to the reference OSC (when no plasmonic nanoparticles are present on top of the OSC) due to the enhanced far-field scattering by the plasmonic nanoparticles at the plasmon resonance wavelengths. It has to be noted that while enhanced far-field scattering of light due to the addition of the NSs leads to an improvement in the absorption of light in the subcell active layers of the tandem OSC, absorption of light by the plasmonic NSs themselves diminishes the total radiation available for absorption in the active layers. From the absorption cross-sections of the plasmonic NSs shown in Figure 6B, it can be observed that Au NSs have a strong absorption in the spectral region from 450 nm to 600 nm. Absorption by the Ag NSs is also significant between 400 nm and 550 nm. In comparison, absorption by the Al NSs is considerably lower in the spectral region between 400 and 600 nm. Figure 7 shows the electric-field spatial distribution profiles of the Au, Ag, and Al NSs of radius, “r” = 70 nm highlighting their modes of plasmonic resonance. The electric-field enhancement profiles corresponding to the quadrupole peaks in the scattering cross-sections of Au, Ag, and Al NSs (occurring at wavelengths of 520, 460, and 370 nm, respectively) are shown in Figure 7A,C,E. On the other hand, the dipole peaks in the scattering cross-sections of Au, Ag, and Al NSs (occurring at wavelengths of 690, 660, and 610 nm, respectively) are shown in Figure 7B,D,F. From the E-field enhancement profiles shown in Figure 7A,C,E, it can be observed that Al NSs have a significantly lower penetration of the electric field into the NSs (for the quadrupole resonance wavelength) as compared to the electric-field penetration in Ag and Au NSs, indicating a lower optical absorption in the Al NSs. On the other hand, absorption in Al NSs is slightly larger than that in Au and Ag NSs at longer wavelengths (λ > 600 nm), which can be attributed to a weak interband transition in Al NSs at around 800 nm. Yet, the overall total absorption losses due to the introduction of the plasmonic NSs are significantly lower in Al NSs as compared to the Ag and Au NSs. Therefore, there is greater enhancement of absorption in the top and middle subcell layers of the tandem OSC when Al NSs are added on top of the tandem OSC as compared to when Ag or Au NSs are present (see Figure 6C).

Table 1 shows the comparison of the \( J_{sc} \) enhancement, when the NSs of different metals are present over the top electrode of the OSCs. We observe from Table 1 that there is a 14% improvement in overall short circuit current density (\( J_{sc} \)) of the triple-junction tandem OSC in comparison with that of the reference OSC without any NSs. The OSCs
containing Al NSs over the top electrode show a higher $J_{SC}$ enhancement as compared to the OSCs having Al NSs in the different subcell active layers, as shown in Table S1. It has been observed in single-junction OSCs that plasmonic nanoparticles placed in the active layers of the OSC have led to improved performance of the cells. In the case of the triple-junction OSC proposed in our paper, addition of nanoparticles to selectively target and improve the performance of each subcell is greatly limited by the $J_{SC}$ matching requirements of the different subcells—because of the

**Figure 7** Electric-field spatial distribution profiles showing the different plasmonic modes associated with plasmonic NSs present on top of an ITO layer. Quadrupole resonance modes in NSs of (A) Au, $\lambda = 520$ nm (C) Ag, $\lambda = 460$ nm, and (E) Al, $\lambda = 370$ nm. Dipole resonance modes in NSs of (B) Au, $\lambda = 690$ nm (D) Ag, $\lambda = 660$ nm, and (F) Al, $\lambda = 610$ nm. The NS radius, “$r$” was taken to be 70 nm and simulated over an ITO substrate under PML boundary conditions.

**Table 1** $J_{SC}$ of the OSCs containing plasmonic NSs over the top electrode

|                | Top subcell $J_{SC}$ (mA cm$^{-2}$) | Middle subcell $J_{SC}$ (mA cm$^{-2}$) | Bottom subcell $J_{SC}$ (mA cm$^{-2}$) | NS period (nm) | NS radius (nm) |
|----------------|-------------------------------------|----------------------------------------|----------------------------------------|----------------|----------------|
| Without NSs    | 8.43                                | 8.68                                   | 10.33                                  | -              | -              |
| With Au NSs over the top electrode | 8.41                                | 8.97                                   | 9.95                                   | 450            | 30             |
| With Ag NSs over the top electrode  | 8.93                                | 9.38                                   | 10.00                                  | 400            | 70             |
| With Al NSs over the top electrode  | 9.61                                | 9.62                                   | 9.96                                   | 350            | 70             |
requirement of synergy between the improvements of the individual subcells and how they perform as a whole in a triple-junction solar cell. Moreover, the freedom in variation of the active layer thicknesses is also limited by the $J_{sc}$ matching requirements of the different subcells. Hence, for the case of a triple-junction solar cell simulated in this paper, the top and middle subcell $J_{sc}$s are substantially higher for the case when the Al or Ag nanospheres are on the top surface of the solar cell as compared to the cases when the nanospheres are present in the active layers of the different subcells (see Table S1). We would like to mention that in our solar cell, placing the nanoparticles on top of the solar cell not only leads to enhanced far-field scattering (from the nanospheres placed on the top of the solar cells) into the top and middle subcells, but also leads to satisfaction of the $J_{sc}$ matching requirement for the multiple junction OSC for higher values of $J_{sc}$s. We would also like to highlight that the introduction of nanoparticles within the active layer is not without its disadvantages. Due to the highly conductive nature of plasmonic nanoparticles, they are also prone to act as trap cites for the excitons created in the active layers from the absorption of light.64-66 Placing the nanoparticles over the top surface of the OSCs eliminates this possibility and, therefore, reduces losses in the OSCs. Additionally, the sizes of the nanoparticles placed in the active layers are limited by the active layer thickness which again needs to be fixed as per the $J_{sc}$ matching criteria of the subcells in the multiple junction OSCs. Moreover, larger nanoparticles would require thicker active layer thicknesses, which would lead to greater re-absorption and trap site losses for the subcells.

We also observed that as the thickness of the ITO electrode increases, the $J_{sc}$ of the top subcell and of the bottom subcell decrease slightly, and that of the middle subcell increases. There is only a slight decrease in the overall $J_{sc}$ of the OSC (having Al nanospheres over the top surface) as the thickness of the ITO electrode increases. Hence, even for higher thicknesses of the ITO layer (~100 nm thickness), the triple-junction solar cell with the presence of Al nanospheres on its top surface has a considerable enhancement (~6% enhancement) in $J_{sc}$ when compared to an OSC with no nanospheres. The proposed OSCs with NSs over the top electrode also have higher $J_{sc}$ enhancements as compared to OSCs having plasmonic hemispheres or plasmonic ellipsoids over the top electrode, as tabulated in Tables S2 and S3.

4 | CONCLUSIONS

The plasmonic enhancement of metal NSs added over the top electrode of triple-junction tandem organic solar cells were studied in this paper. Gold, silver, and aluminum NSs were individually optimized for periodicity and size with the objective of enhancing the absorption and $J_{sc}$s in the different subcells of the tandem OSCs. It was observed that while aluminum and silver NSs enhance the values of the overall $J_{sc}$s of the tandem OSCs, gold NSs lead to a reduced overall $J_{sc}$s of the tandem OSCs as compared to the reference OSCs without any NSs. Aluminum NSs of periodicity, “$P$” = 350 nm and radius, “r” = 70 nm were most effective in enhancing the $J_{sc}$ values of the top and middle subcells so as to match the $J_{sc}$ of the bottom subcell. The resultant tandem OSC with the optimized Al NSs has a $J_{sc}$ of 9.61 mA cm$^{-2}$. This is an improvement of 14% over the tandem OSC without any NSs.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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