Supporting Information

Critical Role of Polystyrene Layer on Plasmonic Silver Nanoplates in Organic Photovoltaics

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**Figure S1.** Synthesis of polystyrene (PS) using reversible addition-fragmentation chain transfer (RAFT) polymerization. The chain transfer agent used here is 2-phenyl-2-propyl benzodithioate (CDB) and the final polymer is denoted as PS-CDB.

**Figure S2.** Reduction of PS-CDB to thiol terminated polystyrene (PS-SH) by NaBH₄.
Figure S3. $^1$H NMR spectra of PS-CDB (black) and PS-SH (red). Peaks (a) correspond to the aromatic hydrogens in polystyrene. The thiol peak (~1.7 ppm) is indistinguishable due to overlap with the proton peaks (b) in the polystyrene backbone. Peaks around 5.25 and 5.76 ppm correspond to the residual styrene monomers.
Figure S4. Graphical representation of OPV devices. Each sample contains eight devices (one for each Al strip) that can be individually tested. The exposed ITO anode and the non-overlapping Al cathode are used as electrodes in J-V and EQE measurements.
Figure S5. The current density – voltage (J-V) characteristics of OPV devices with active layer thicknesses of 75, 90, 100, 115, and 130 nm.

Table S1. The J-V characteristics of the OPV devices with active layer thicknesses of 75, 90, 100, 115, and 130 nm.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$R_s$ ($\Omega$·cm$^2$)</th>
<th>$R_{sh}$ ($\Omega$·cm$^2$)</th>
<th>PCE (%)</th>
<th>Largest PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 nm</td>
<td>-5.51 ± 0.08</td>
<td>0.61 ± 0.01</td>
<td>0.57 ± 0.03</td>
<td>11.6 ± 0.8</td>
<td>1432 ± 200</td>
<td>1.89 ± 0.06</td>
<td>1.96</td>
</tr>
<tr>
<td>90 nm</td>
<td>-7.05 ± 0.02</td>
<td>0.60 ± 0.01</td>
<td>0.52 ± 0.03</td>
<td>13.2 ± 0.9</td>
<td>890 ± 153</td>
<td>2.18 ± 0.27</td>
<td>2.40</td>
</tr>
<tr>
<td>100 nm</td>
<td>-7.88 ± 0.16</td>
<td>0.62 ± 0.01</td>
<td>0.51 ± 0.02</td>
<td>12.1 ± 2.2</td>
<td>502 ± 159</td>
<td>2.45 ± 0.05</td>
<td>2.61</td>
</tr>
<tr>
<td>115 nm</td>
<td>-6.47 ± 0.72</td>
<td>0.59 ± 0.01</td>
<td>0.46 ± 0.02</td>
<td>11.7 ± 1.0</td>
<td>447 ± 160</td>
<td>1.70 ± 0.11</td>
<td>1.89</td>
</tr>
<tr>
<td>130 nm</td>
<td>-4.91 ± 0.44</td>
<td>0.57 ± 0.01</td>
<td>0.45 ± 0.03</td>
<td>13.5 ± 0.9</td>
<td>376 ± 60</td>
<td>1.28 ± 0.19</td>
<td>1.61</td>
</tr>
</tbody>
</table>
The thickness of the P3HT:PCBM (1:0.8) active layer was varied from 75 to 130 nm to optimize the performance. Although optical absorption scales linearly with thickness, it is well-known that the thickness induces oscillatory characteristics of the average light intensity within the active layer, the overall exciton generation, the short-circuit current density ($J_{sc}$), and the power conversion efficiency (PCE). The oscillatory characteristics arise from optical interference of the standing waves within the different layers of the device. Often, an active layer provides the highest performance when the thicknesses corresponds to the first interference maxima (typically in the vicinity of 100 nm). As the thickness further increases, the device performance degrades due to increasing recombination. In our system, the increasing recombination levels are evidenced by a deteriorated $R_{sh}$. After this analysis, we have discovered the first interference maxima and the optimal performance of our reference devices at a thickness of 100 nm for the P3HT:PCBM active layer.

Figure S6. Absorption coefficient ($\alpha$) of P3HT:PCBM (1:0.8) as a function of wavelength.
Figure S7. Statistical size distributions of (a) unfunctionalized nanoparticles and (b) functionalized nanoparticles.

Figure S8. TEM image of the PS-functionalized AgNPs (PS-AgNPs).
Figure S9. Absorption spectrum of P3HT:PCBM before and after spin-coating a blank solution of 500 µl of MeOH at 800 rpm, showing that the P3HT:PCBM is not dissolved.

Figure S10. AFM height images of thermally annealed P3HT:PCBM films with PS-AgNPs of (a) 0, (b) 0.29, (c) 0.57, (d) 1.14, and (e) 2.90 nM concentrations.
Table S2. Arithmetic mean roughness (R\textsubscript{a}) and RMS roughness (R\textsubscript{q}) of the thermally annealed P3HT:PCBM films with PS-AgNPs of various concentrations (0 ~ 2.90 nM). The roughness values were averaged over at least five AFM images.

<table>
<thead>
<tr>
<th>PS-AgNPs</th>
<th>R\textsubscript{a} (nm)</th>
<th>R\textsubscript{q} (nm)</th>
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<tbody>
<tr>
<td>0 nM</td>
<td>1.5 ± 0.3</td>
<td>2.0 ± 0.4</td>
</tr>
<tr>
<td>0.29 nM</td>
<td>1.8 ± 0.6</td>
<td>2.4 ± 0.8</td>
</tr>
<tr>
<td>0.57 nM</td>
<td>2.2 ± 0.2</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>1.14 nM</td>
<td>3.2 ± 0.2</td>
<td>4.2 ± 0.2</td>
</tr>
<tr>
<td>2.90 nM</td>
<td>3.8 ± 0.5</td>
<td>5.0 ± 0.7</td>
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Figure S11. Absorption spectra of pristine P3HT films (no PCBM) with a layer of (a) PS-AgNPs and (b) AgNPs of various concentrations.
Figure S12. Reflectance of PS-AgNPs of various concentrations deposited on P3HT:PCBM. The films were thermally annealed and covered with the Al cathode.

Figure S13. Absorption spectra of (red curve) AgNPs in water and (black curve) aggregated AgNPs after transferring to a solution of MeOH. (inset) A photograph of an aggregated AgNP solution in MeOH.
**Figure S14.** TEM image of unfunctionalized and aggregated AgNPs in MeOH.

**Figure S15.** Absorption spectra of the unfunctionalized AgNPs on P3HT:PCBM.
**Figure S16.** SEM image of the unfunctionalized and aggregated AgNPs on P3HT:PCBM.

**Figure S17.** (a) The current density – voltage (J-V) characteristics of OPV devices with unfunctionalized AgNPs and (b) the corresponding external quantum efficiency (EQE).
**Figure S18.** EQE enhancement spectra of the OPV devices and normalized extinction of the colloidal suspension of PS-AgNPs.

**References:**