

Fully understanding the positive roles of plasmonic nanoparticles in ameliorating the efficiency of organic solar cells

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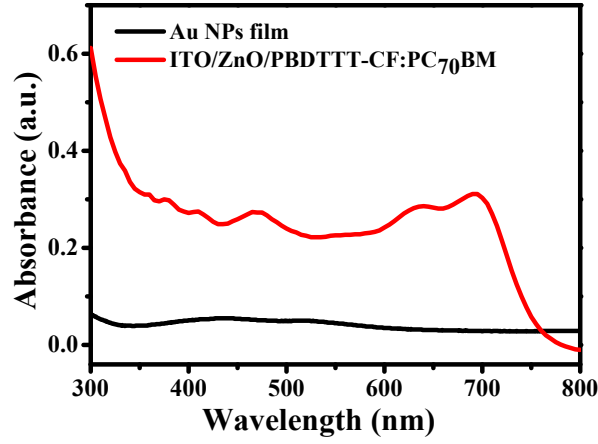


Fig. S1. Absorbance spectra of the Au NP film spin-coated at 2000 rpm and the ITO/ZnO/PBDTTT-CF:PC₇₀BM.

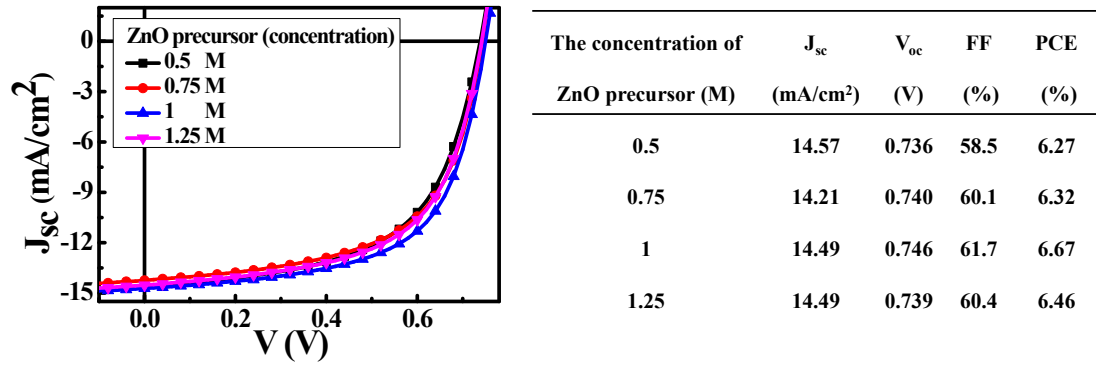


Fig. S2. The optimization of the device performance by the thicknesses of ZnO layer. The ZnO film prepared from the 1 M precursor solution has a thickness of 35 nm and the relevant device presents the best performance. The devices with ZnO film prepared from a lower concentrated precursor solution show a lower performance, probably due to the imperfect coverage of the ZnO thin film on the substrate. In addition, the performance decrease of the device with a thicker layer of ZnO could be attributed to the inefficient charge transport, due to the imperfect crystal quality of the ZnO film.

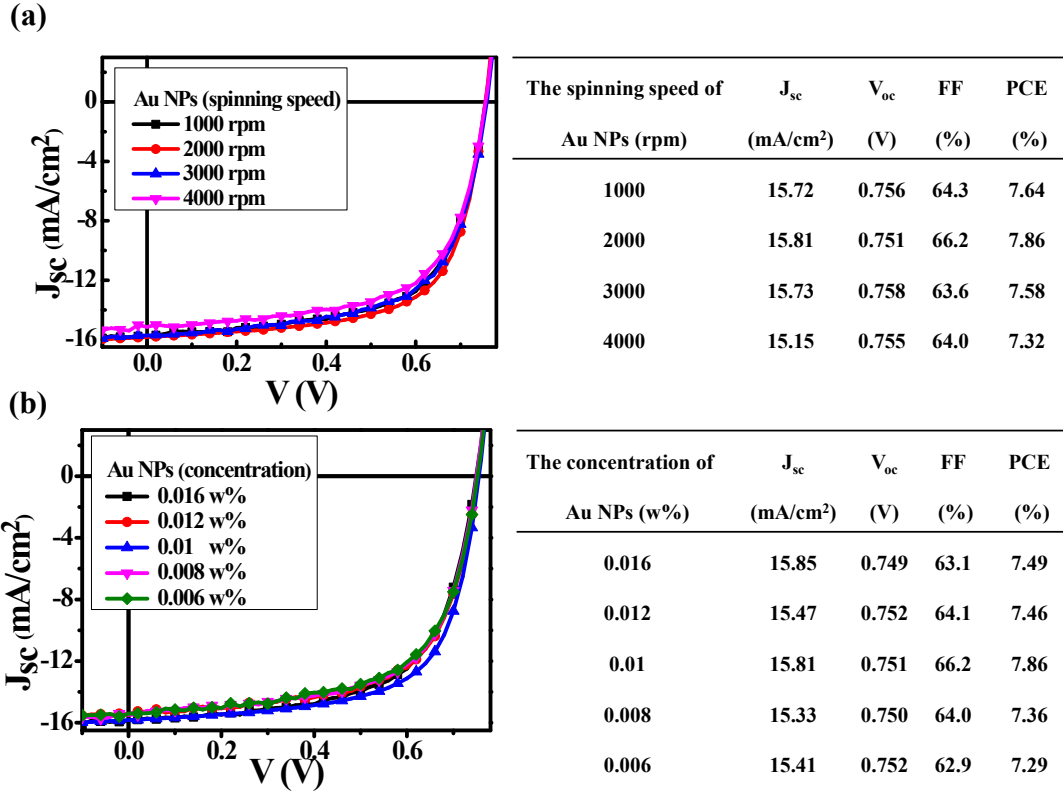
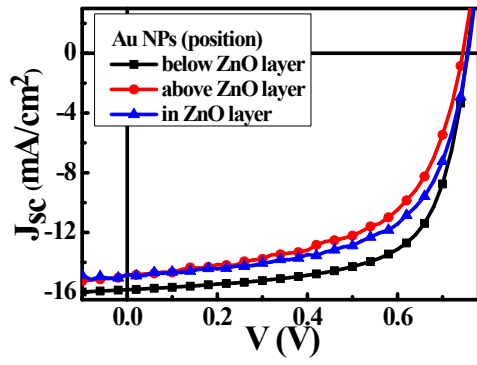


Fig. S3. The optimization of device performance by Au NP (41 nm) density distributions. (a) The influence of spin-coating rate on the device performance. (b) The impact of Au NP concentration in the spin-coating solution on the device performance. These results indicate that the Au NP film prepared from a 0.01 w% solution at the spin-coating rate of 2000 rpm yields the best device performance. The dense distribution of Au particles would deteriorate the performance by blocking the light, and the sparse distribution of Au would not have obvious effects of scattering and SPR.



The position of Au NPs	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
below ZnO layer	15.81	0.751	66.2	7.86
above ZnO layer	14.83	0.745	57.8	6.38
in ZnO layer	14.82	0.756	61.2	6.86

Fig. S4. Impact of Au NPs position on the device performance. The device with Au NPs at the interface of ITO/ZnO presents the best performance. The direct contact of Au NPs with ITO glass is helpful for collecting the charges in the device. When the Au NPs are inserted in the ZnO layer, the efficiency becomes lower. In this case, the charge collecting efficiency of the structure could not be improved. For the device with Au NPs on the top of ZnO layer, the direct exposure of the metallic nanoparticles to the polymer layer could cause the recombination of the photo-generated charge carriers, which deteriorates the device efficiency.

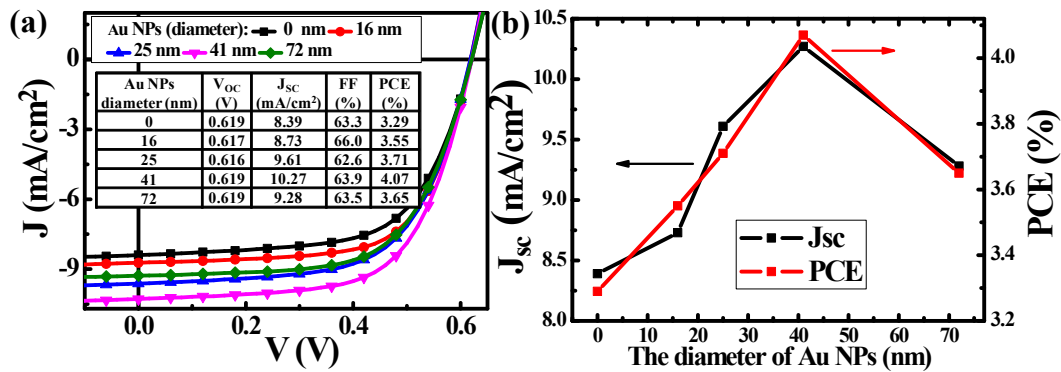


Fig. S5. (a) J-V curves of the devices (P3HT:PC₆₀BM) with different diameters of Au NPs. (b) J_{sc} and PCE vs the diameter of Au NPs. To be exciting, these results show the same trend in OSC performance vs Au NP sizes with that in the OSC based on PBDTTT-CF:PC₇₀BM, indicative of the feasibility of using plasmonic particles to enhance the energy conversion efficiency of the solar cells.

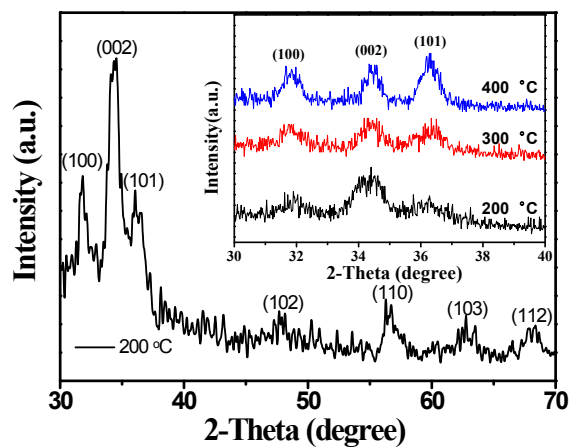


Fig. S6. X-ray diffraction pattern of the ZnO film annealed at different temperatures. The ZnO film annealed at 200 °C shows a series of diffraction peaks, which are corresponding to the wurtzite structure of ZnO (Zincite, JCPDS 5-0664). When the annealing temperatures are increased from 200 °C to 400 °C, the crystalline quality of the ZnO films can only be improved slightly, which should not render an obvious difference in the photovoltaic performance for the devices with 35 nm ZnO layer.

Table S1. The parameters of bi-exponential model for fitting the photoluminescence decay curves.

The diameter of Au NPs (nm)	B₁	T₁ (ns)	B₂	T₂ (ns)	<τ> (ns)
0	0.001479	4.731	0.323	0.1417	0.75027±0.0928
16	0.4004	0.135	0.0033	3.039	0.58947±0.132
25	0.6818	0.083	0.0073	1.528	0.32093±0.0254
41	0.7263	0.081	0.0046	1.740	0.27968±0.118
72	0.001684	3.266	0.3649	0.1241	0.46437±0.0207

The fitting was performed with the bi-exponential model:

$$A + B_1 * \exp\left(-\frac{t}{T_1}\right) + B_2 * \exp\left(-\frac{t}{T_2}\right) \quad (\text{S1})$$

The lifetime was calculated by:

$$\langle \tau \rangle = \frac{B_1 \times T_1^2 + B_2 \times T_2^2}{B_1 \times T_1 + B_2 \times T_2} \quad (\text{S2})$$