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Supporting Information

Spin-coated Ag nanoparticles onto ITO substrates for efficient improvement of polymer solar cell performance

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EXPERIMRNTAL SECTION

Synthesis of Ag NPs

The synthesis method for Ag nanoparticles (NPs) was the typical polyol chemistry. In detail, 3.0 mL of a 94 mM $AgNO_3$ (Sigma-Aldrich) and 3.0 mL of a 147 mM (in terms of a repeating unit) PVP (Alfa Aesar, M_w = 58000) were mixed in a three-necked flask, the solvent of all the solution is 1,4-butanediol (BD). 6 mL of 1,4-butanediol (BD) was added into the three-necked flask, and then heated at 140 ℃ in an oil bath for 1 h under intensely magnetic stirring. The synthesized Ag NPs were collected by a method of centrifugation with the addition of acetone, water and ethanol. Finally, they were re-dispersed in ethanol for the device fabrication.

Device fabrication

Photovoltaic devices based on polymer:$PC_{71}BM$ with a blend of Ag NPs are prepared as shown in Figure 2b. The impurities are removed from the ITO glass (20 Ω/sq.) by means of ultrasonic in detergent, acetone and isopropyl alcohol for 30 min ,respectively. 60 mL of Ag NPs solution was spin-coated at 1300 rpm for 2 min onto cleaned ITO substrates, then the PEDOT:PSS solution (Baytron Al 4083, H.C. Starck) was spin-casted at 2500 rpm on top of Ag NPs (it should mention that we used to filter the PEDOT:PSS solution with a 0.22 μm PES film before use) and dried at 130

℃ for 20 min before transferred into a glove box. The thickness of PEDOT:PSS layer is about 35 nm. It should be mentioned that the thickness of this layer is nearly not change after the Ag NPs incorporated into the PSCs. Under the same condition, we just deposited PEDOT:PSS as the reference device. On top of the PEDOT:PSS layer, we spin-coated the three kinds of active solutions under their optimized conditions respectively[34,35] in a glove box. Finally, LiF (0.6 nm) and Al (100 nm) are sequentially evaporated under high vacuum of 1×10^{-5} Pa onto the active layer as a cathode to create a device of area 0.04 cm^2 defined through a shadow mask. The current density-voltage (*J-V*) performances of the devices were measured on a computer-controlled Keithley 236 Source Measure Unit. The white light source we used is an Air Mass AM 1.5G AAA class solar simulator (model XES-301S, SAN-EI) solar simulator with an irradiation intensity of 100 mW/cm^2 and our light intensity was calibrated with a standard single-crystal Si photovoltaic cell before employment.

Device characterization

UV-vis absorption spectra were measured on a PerkinElmer UV-vis spectrometer model Lambda 750 and reflectance spectra were measured on a UV-vis spectrometer model SPCCORD 200. The SEM and EDS images of the Ag NPs were visually recorded with a field-emission scanning electron microscope (S-4800) operated at an accelerating voltage of 10 kV to 20 kV. The surface morphology and roughness analysis were performed by atomic force microscopy (AFM) with a Digital Instrument Multimode Nanoscope IIIA under ambient conditions operating in the tapping mode. The IPCE of the device was measured as a function of the excitation wavelength with a 150 W xenon lamp (CTTH-150W) and a monochromator (M24-S).The particle size of Ag NPs was observed by High-resolution transmission electron microscopy (TEM, Tecnai F20, FEI) with an accelerating voltage of 200 kV. The thickness of the active layer was obtained by a Dektak 6 M surface profilometer.

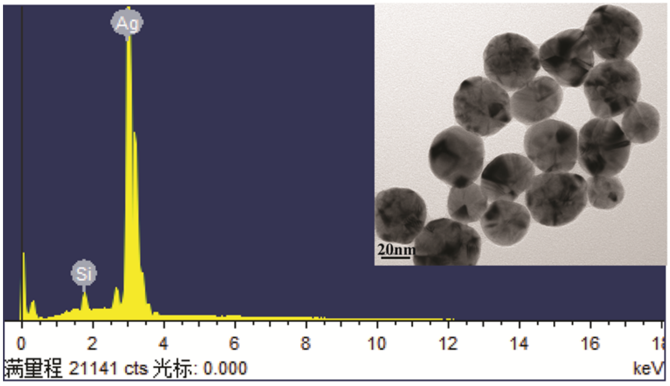
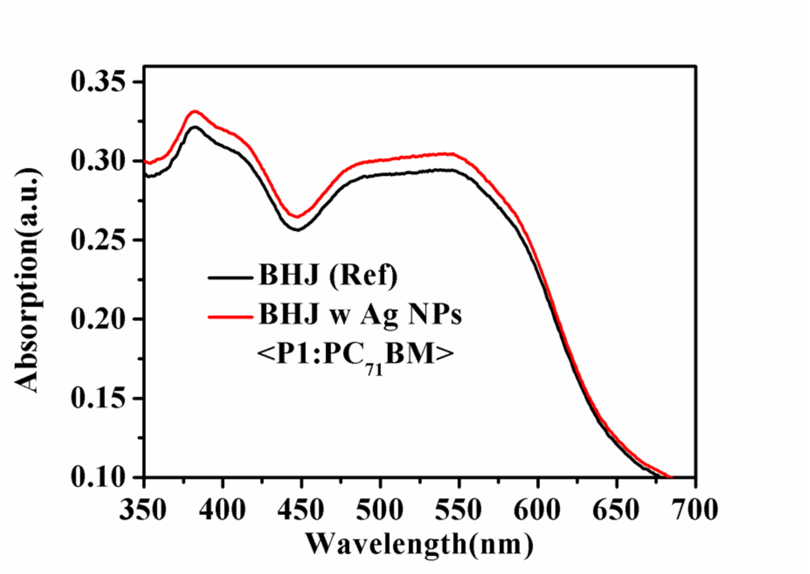


Figure S1. EDS image of Ag NPs with a diameter of 35 nm and the inset figure is the TEM image of the synthesized Ag NPs. The EDS image shows that the synthesized Ag NPs consist of pure silver.

(a)



(b)

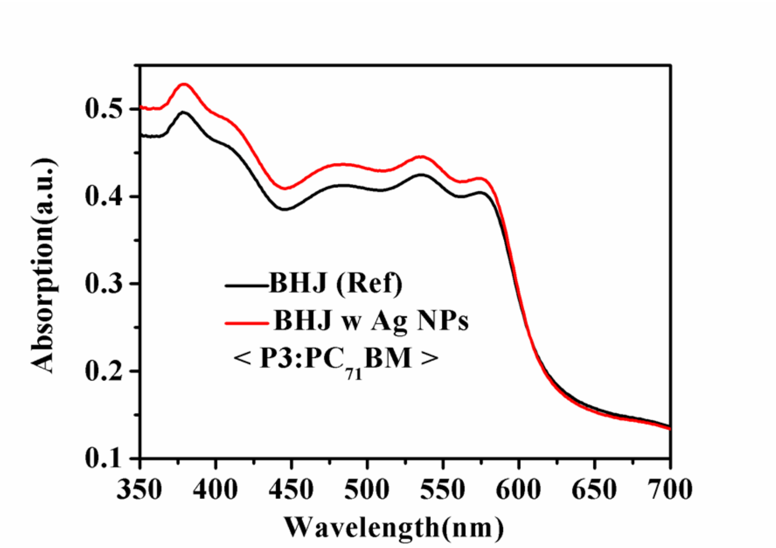


Figure S2. UV-vis images of the plain **P1**/PC$_{71}$BM (a) and **P3**/PC$_{71}$BM (b) BHJ films and their BHJ films with Ag NPs with a diameter of 35 nm.

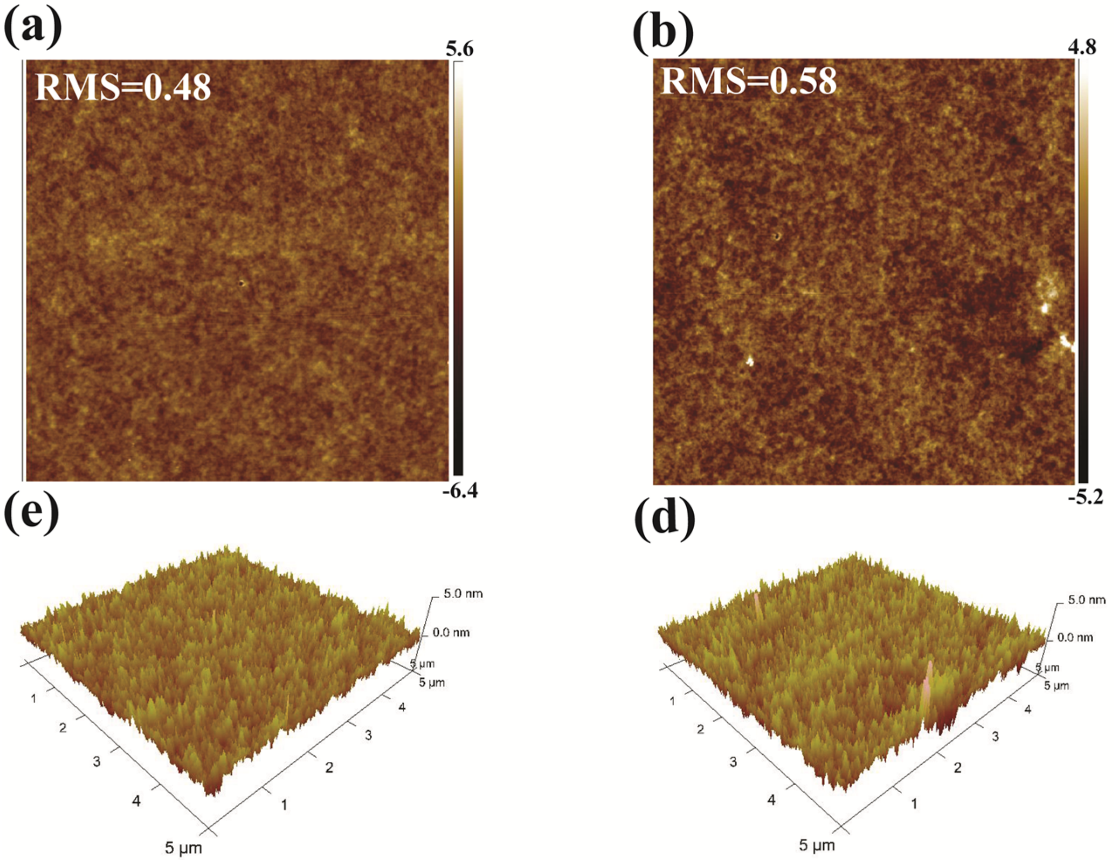
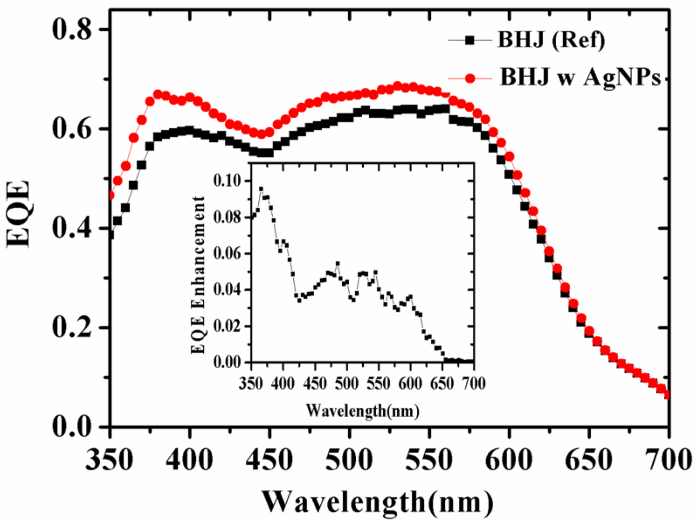


Figure S3. AFM 2D height images（left）and 3D height images (right) for **P3**/PC$_{71}$BM active layer on ITO/(Ag NPs)/PEDOT:PSS. The corresponding mean roughnesses (RMS) of these films are 0.48 nm, 0.58nm, respectively. Imaging area: 5

µm × 5 µm.

(a)



(b)

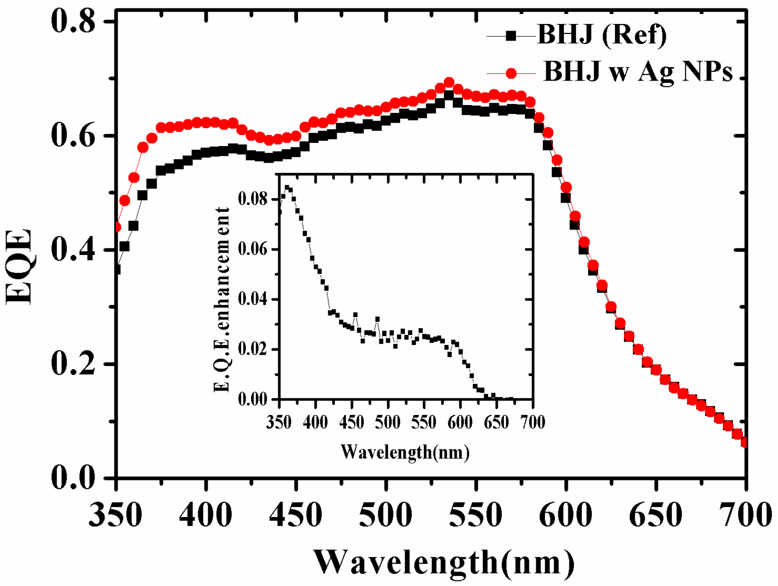
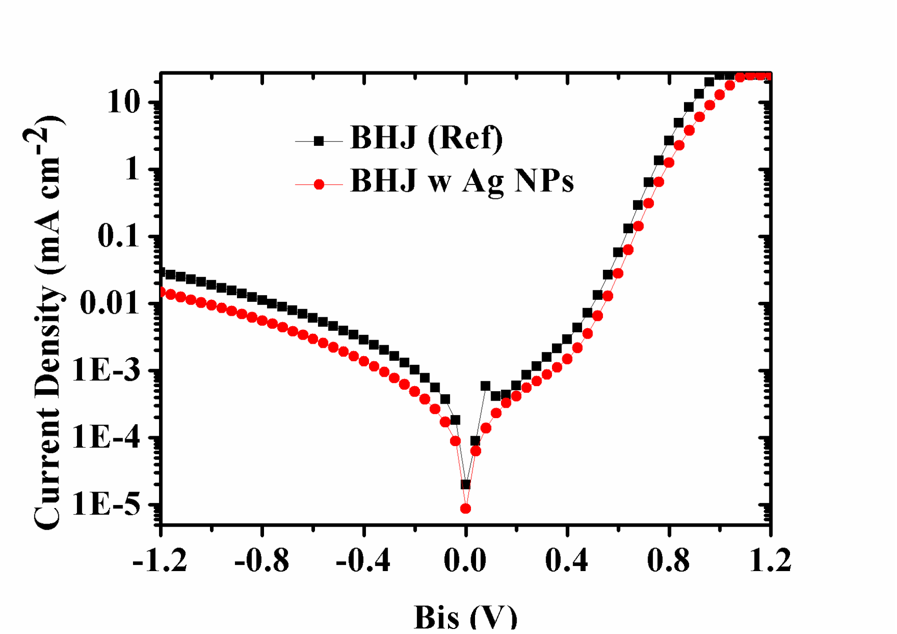


Figure S4. EQE spectra of the plain **P1**/$PC_{71}BM$ (a) and **P3**/$PC_{71}BM$ (b) BHJ and the BHJ with Ag NPs. The inset figures show EQE enhancement after incorporating 35 nm-sized Ag NPs into the PSCs .

(a)



(b)

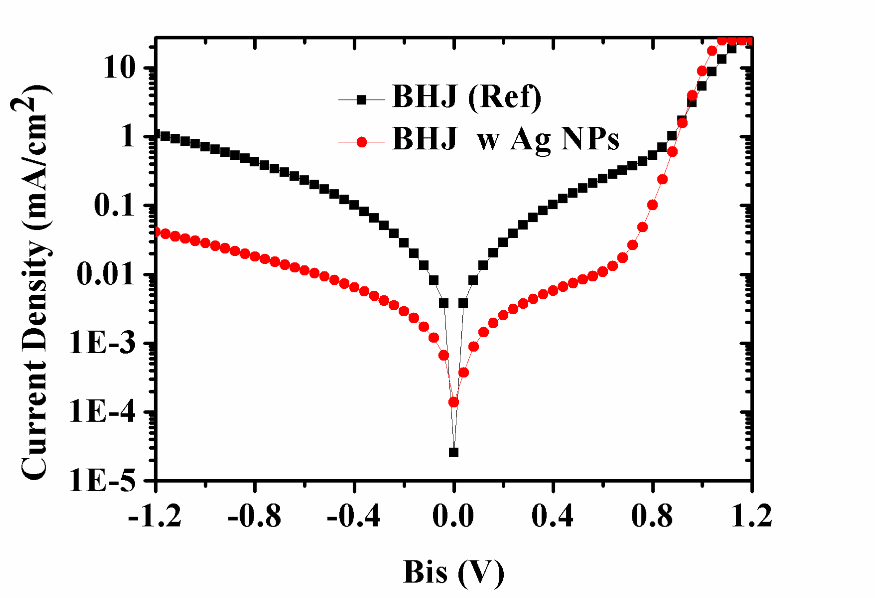
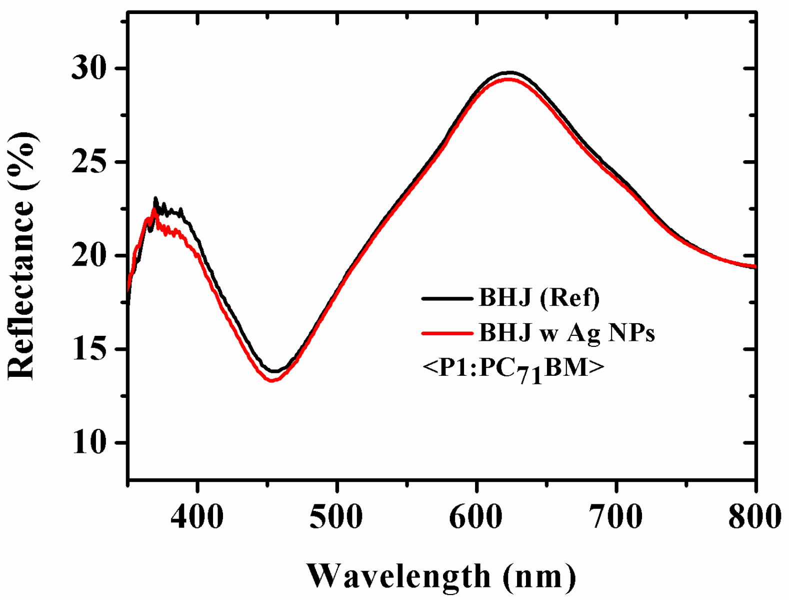


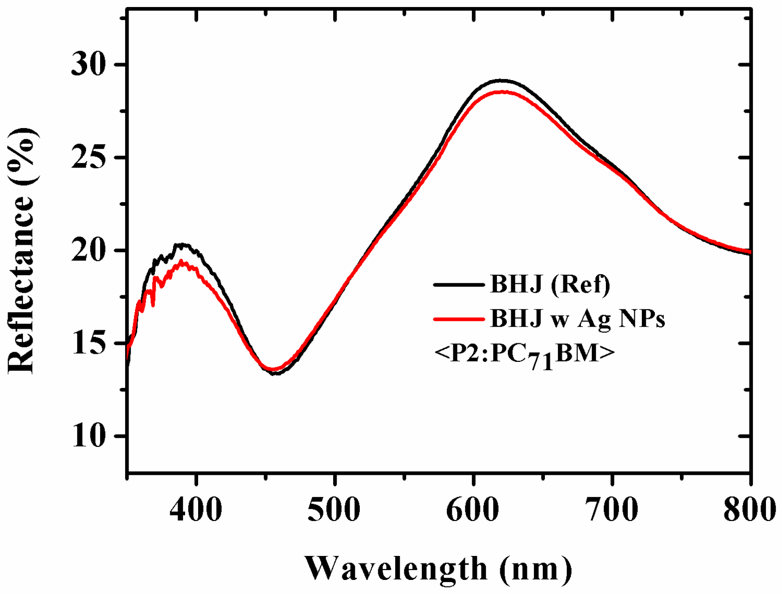
Figure S5. *J–V* curves of the devices with the plain based on **P1**/PC$_{71}$BM (a) and **P3** /PC$_{71}$BM (b) BHJ and the BHJ with the Ag NPs in the dark current.

(a)



Reflectance (%)
30
25
20
15
10
400
500
600
700
800
Wavelength (nm)
BHJ (Ref)
BHJ w Ag NPs
<P1:PC$_{71}$BM>

(b)



Reflectance (%)
30
25
20
15
10
400
500
600
700
800
Wavelength (nm)
BHJ (Ref)
BHJ w Ag NPs
<P2:PC$_{71}$BM>

(c)

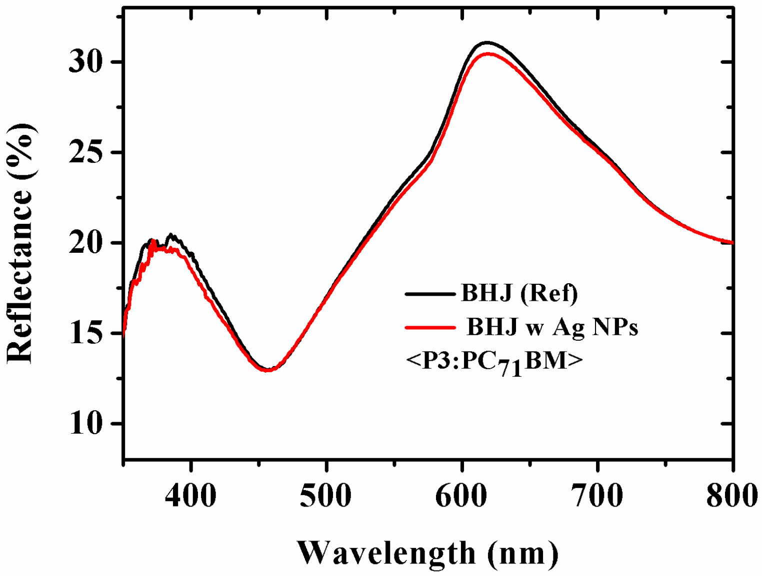


Figure S6. Diffuse reflectance spectra of the plain **P1**/PC$_{71}$BM(a), **P2**/PC$_{71}$BM (b) and **P3**/PC$_{71}$BM (c) BHJ films and the BHJ films with Ag NPs.