

Electronic Supplementary Information

Synergetic plasmonic effect of Al and Au nanoparticles for efficiency enhancement of air processed organic photovoltaic devices

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Experimental Section

Synthesis of Al and Au NPs: The generation of the Al and Au nanoparticles was performed by femtosecond (~100fs@1kHz) laser ablation of Al and Au metallic targets (99.99%) placed into a Pyrex cell and covered by a layer of absolute ethanol. This technique generates a large variety of NPs that are free of both surface-active substances and counter-ions. Additionally, the advanced pulsed laser ablation method used is capable of highly uniform target irradiation, and consequently generation of NPs over a controlled size range with a high degree of reproducibility. More details can be found elsewhere¹.

TiO_x solution preparation: Titanium(iv) isopropoxide (Ti[OCH(CH₃)₂]₄, 5 ml), 2-methoxyethanol (CH₃OCH₂CH₂OH, 20ml) and ethanolamine (H₂NCH₂CH₂OH, 2ml) were added to a three-necked flask in a nitrogen atmosphere. The solution was then stirred for 1 hr at room temperature, followed by heating at 80°C for 1 hr and 120°C for 1 hr. The solution was then cooled to room temperature and 10 ml of isopropanol (IPA) was added.

Device fabrication: PCDTBT and PC₇₁BM was purchased from Solaris Chem. PCDTBT:PC₇₁BM were dissolved in 1,2-dichlorobenzene:Chlorobenzene(3:1) (*o*-DCB:CB) in a 1:4(4mg:16mg) ratio and stirred for at least 72 hours at 80 °C before used. The photovoltaic devices reported were fabricated on 15 mm by 15 mm indium–tin-oxide (ITO) glass substrates with a sheet resistance of 8–12Ω/sq. The impurities are removed from the ITO glass through a 3-step cleaning process. As a buffer layer, poly(ethylene-dioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS), purchased from Heraeus, was spin-cast from an aqueous solution on the ITO substrate at 6000 rpm for 60 seconds and the average thickness of the layer was 30 nm ,

followed by baking for 15 min. at 120 °C inside a nitrogen-filled glove box. Then the metallic NPs were blended into the PCDTBT:PC71BM solution and mixed under sonication for 1h. Composite blends with 9% Al NPs, 5% Au, and 1:1 mixed NPs solution of Al and Au (Dual) were prepared. After sonication, the solutions were left to settle for 24h to allow the heavy NPs (with large diameter) to sediment out. The resultant solution was then centrifuged (10,000 rpm) and the upper 20% of the supernatant was used for spin coating of the active layer. In this way, short circuit effects, which could be caused by the large Al NPs (>60 nm) were avoided. All hybrid photoactive layers were subsequently deposited by spin-coating the blend solutions at 1000 rpm on top of PEDOT:PSS layer until the thickness reaches approximately 80nm determined from cross-sectional SEM images(not shown). The TiO_x interlayer was dissolved in methanol (1:200) and then spin-coated to a thickness of approximately 10 nm (6000 rpm, 40 s) in air². The sample was heated at 80°C for 1 min in air. Lastly, 100 nm of Al was deposited through a shadow mask by thermal evaporation on the devices.

The performances of the devices were measured at room temperature with an Air Mass 1.5 Global (A.M. 1.5 G) solar simulator at an intensity of 100mW/cm². A reference monocrystalline silicon solar cell from Newport was used to calibrate the lamp. The device exhibiting the best initial PCE was that incorporating dual Al and Au NPs. IPCE curves were recorded for the reference and devices with the optimum blend ratio by monitoring the short circuit current of the PV devices with a lock-in amplifier using the chopped, monochromatic light from a Xe lamp as an illumination source. All measurements were carried out in air immediately after device fabrication.

References

1. E. Stratakis, M. Barberoglou, C. Fotakis, G. Viau, C. Garcia, G.A. Shafeev, *Opt. Express*, 2009, **17**, 12650
2. D. H. Wang , S. H. Im , H. K. Lee , J. H. Park , O. O. Park , *J. Phys. Chem. C*, 2009, **113**, 17286 .

Figures

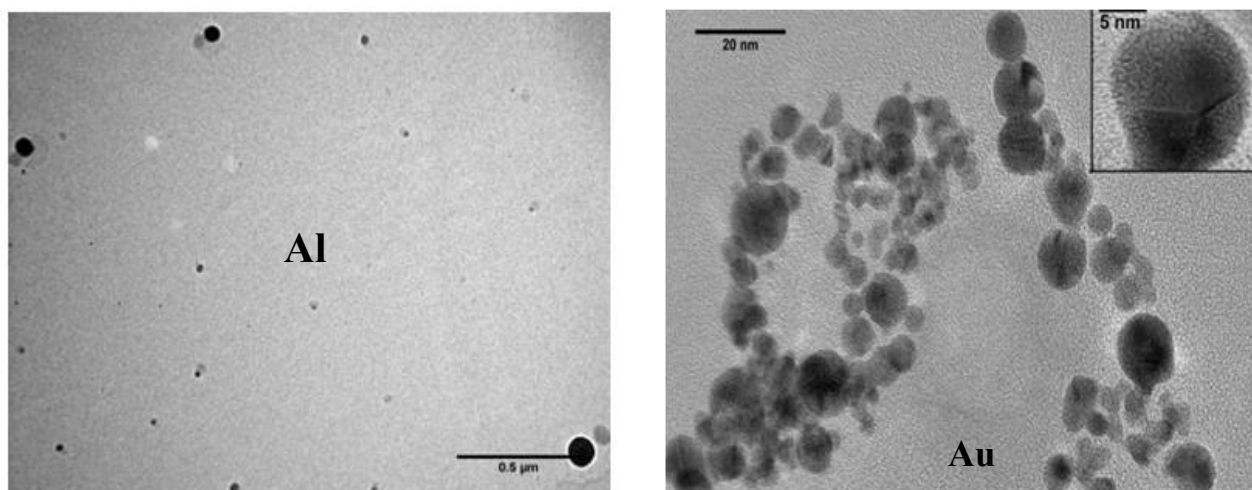


Figure S1. TEM images of the fabricated Al (left) Au NPs (right).

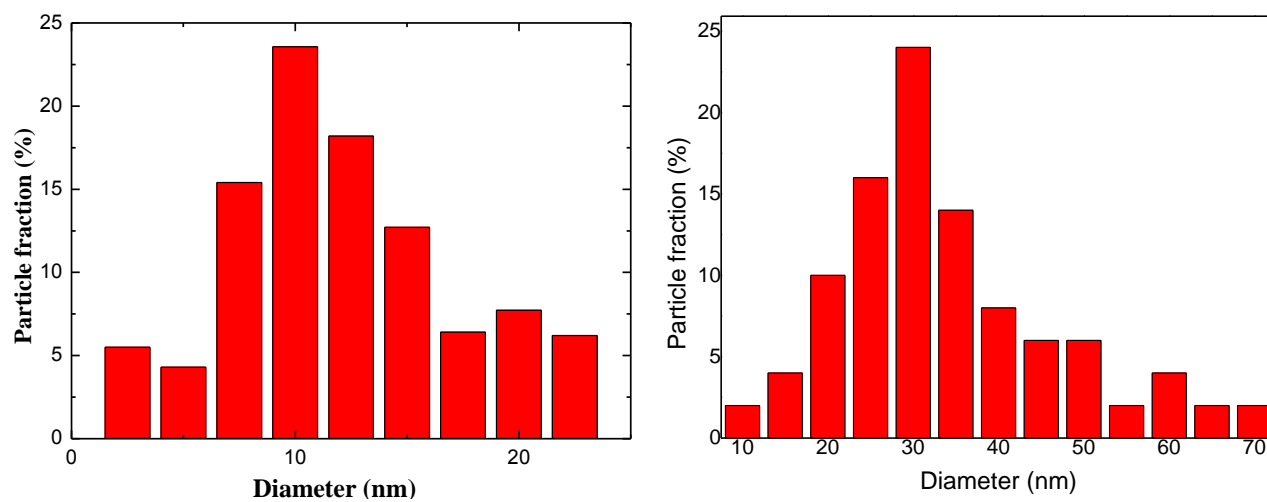


Fig S2 Size distribution of the fabricated Au (left) and Al (right) nanoparticles.

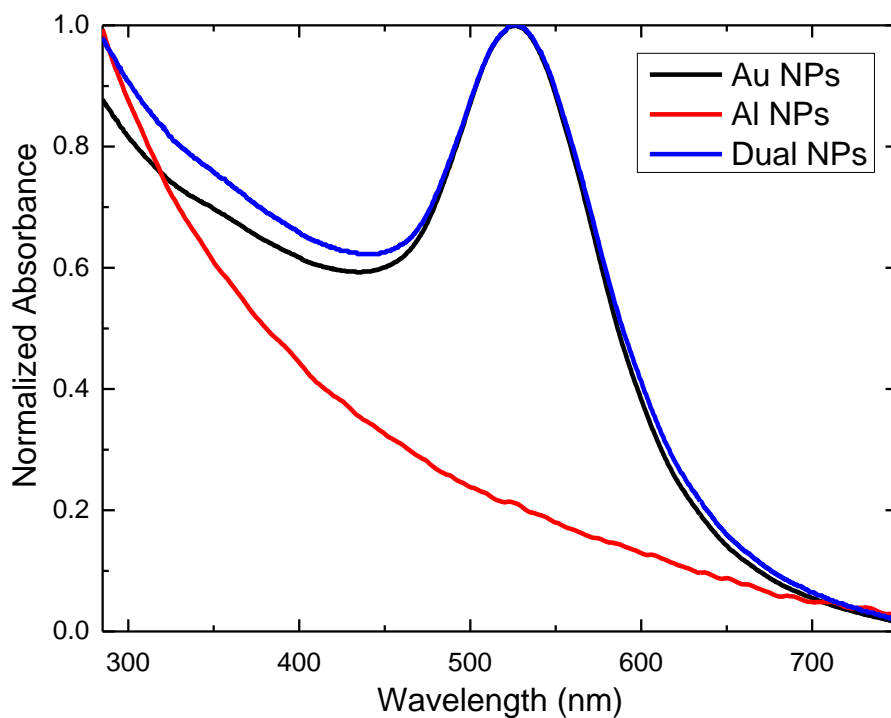


Figure S3. UV-Vis absorption of the fabricated NPs

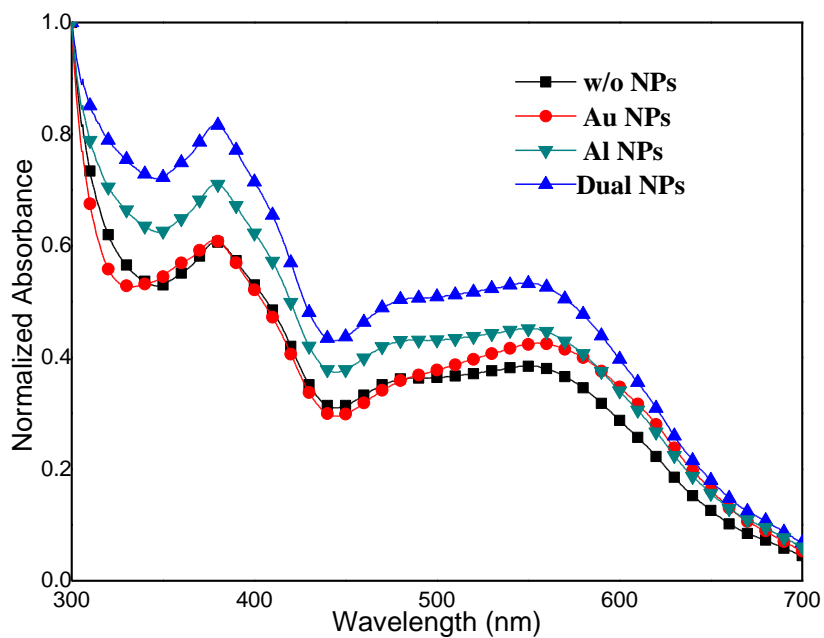


Fig. S4 Absorption spectra of the BJJ devices with Al NPs, Au NPs and dual NPs embedded in the active layer

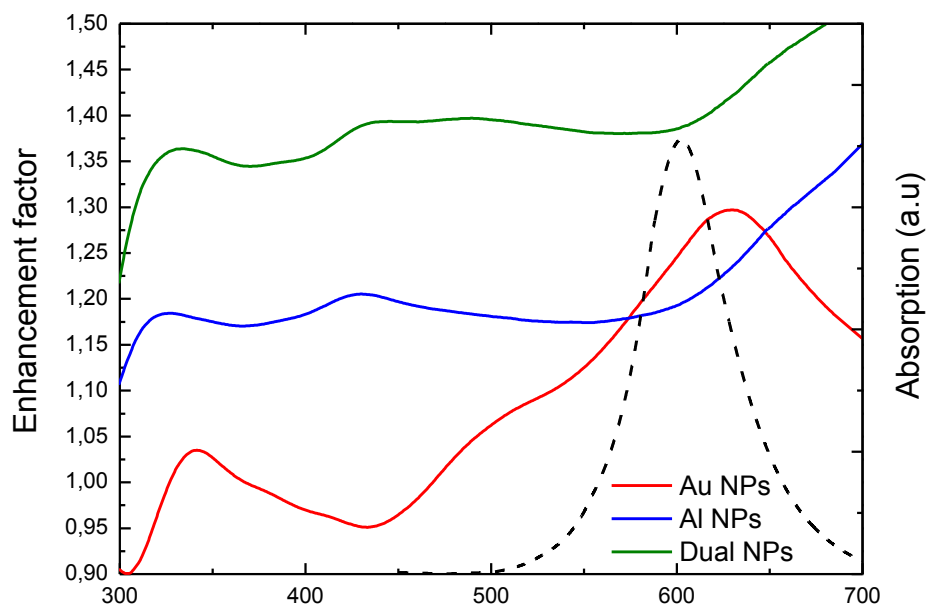


Fig. S5 Absorption enhancement factor of the devices (Relative ratios of the absorption spectra of NPs-embedded devices to that of the pristine one). The calculated extinction spectrum of the Au NPs embedded in the PCDTBT:PC₇₁BM medium is plotted for comparison. The dielectric constants of PCDTBT:PC₇₁BM were obtained from the Ref. Organic Electronics 14 (2013) 74–79).

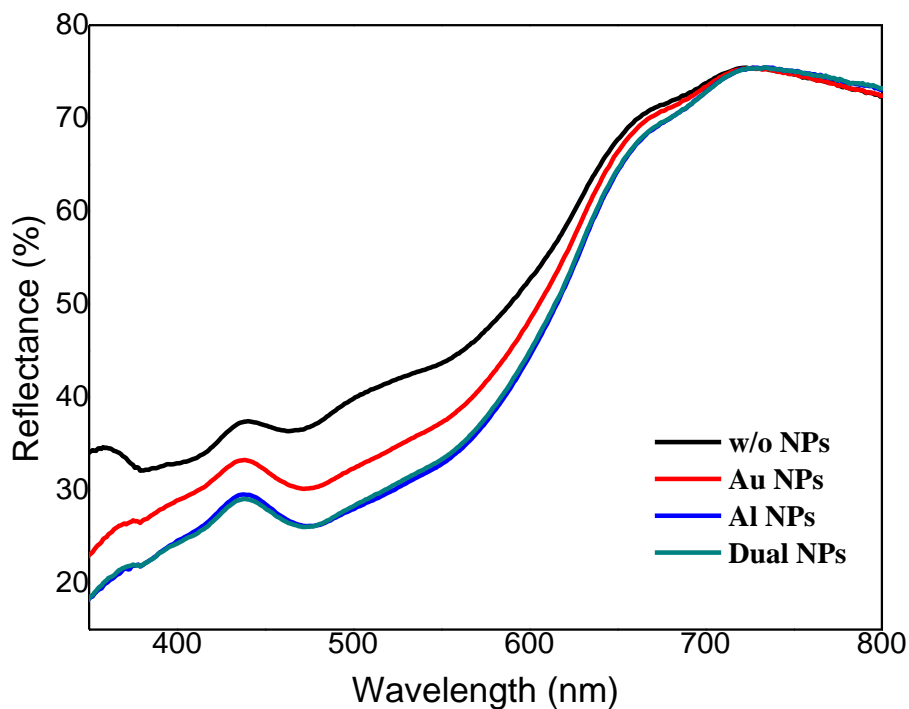


Fig.S5 Reflectance spectra of the devices fabricated