Supplementary Material

Plasmon-coupled Au-nanochain functionalized PEDOT:PSS for efficient mixed tin-lead iodide perovskite solar cell

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Experimental

Materials

Poly(3,4-ethylenedioxythiophene):poly-(styrene sulfonate) (PEDOT:PSS) (Clevious P VP AI 4083, 1.3~1.7 wt% dispersion in H_2O), PbI_2 (>99.99%), CH_3NH_3I (MAI, ⩾99.5%), $HC(NH_2)_2I$ (FAI, ⩾99.5%), C_{60} (99.9%), and BCP (99.9%) were purchased from Xi'an Polymer Light Technology Co. (PLT). The SnI_2 (beads, -10 mesh, 99.99% trace metals basis), formamidine sulfinic acid (FSA, ⩾98%) and tin powders (99.5%) were purchased from Sigma-Aldrich. SnF_2 (99%) was obtained from Acros. Ultradry solvent of N, N-dimethyl formamide (DMF, >99.9%) and Dimethyl sulfoxide (DMSO, >99.9%) were

obtained from J&K. All the chemicals and solvents were kept in the glove-box before starting our experiment.

Synthesis of AuNCs

Firstly, the Au nanoparticles (AuNPs) were synthesized following Frens' method.[1] In general, under thoroughly stirring, 1.0 mL 12 mg/mL $HAuCl_4$ was added into 79 mL H_2O at 90 °C. The reductant mixtures, composed with 4.0 mL 10 mg/mL tri-sodium citrate, 1.0 mL 25 mM Na_2CO_3, and 15 mL H_2O were also heated to 90 °C. The reductant mixtures were poured into the $HAuCl_4$ solution and the reaction was kept at 90 °C for 10 min. After that, the solution was gradually cooled down to room temperature within 3 h and the stirring was kept. Some deionized water was replenished to get about 100 mL colloid solution in the end. Then, 5 μL HS-C_2H_4-COOH was added into the solution with slightly shaking overnight. The resulting solution was stored at 4 °C. Then the 9.09×10^{-7} M melamine stock solution was individually injected with stirring to get for aggregated AuNPs to form the Au nanochains (AuNCs). The concentration of AuNCs is about 2 mg/ml.

Perovskite precursor solution

The precursor solution (1.8 M) was prepared by mixing solvents of DMF and DMSO with a volume ratio of 3: 1. The molar ratios for FAI/MAI and PbI_2/SnI_2 were 0.7: 0.3 and 0.5: 0.5, respectively. The molar ratio of (FAI+MAI)/(PbI_2+SnI_2) was 1: 1. SnF_2 (10 mol% relative to SnI_2), FSA(0.3 mol%), and tin powders (5 mg ml^{-1}) were added in the precursor solution. The precursor solution was stirred at room temperature for 1 h, and that was filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane before preparing the perovskite films.

Device fabrication

The pre-patterned ITO substrates were cleaned with detergent, deionized water, acetone, and 2-propanol in sequence. The AuNCs aqueous solution with a certain amount (0, 0.5, 1 or 2 wt%) was added into PEDOT:PSS, and the solution was kept stirring for 1h. Then, the blended PEDOT:PSS-AuNCs solution was spin-coated on ITO substrates at 4000 rpm

for 50 s and the films were annealed at 150 °C for 10 min in ambient air. After that, the $FA_{0.7}MA_{0.3}Sn_{0.5}Pb_{0.5}I_3$ precursors were spin-coated onto PEDOT:PSS with a two-step spin-coating procedure: 1000 rpm for 10 s and 4000 rpm for 40 s. Diethyl ether was dropped on the spinning substrate during the second spin-coating step at 20 s before the end. The substrates were then transferred onto a hotplate and heated at 100 °C for 10 min in a glove box. Finally, C_{60}(20 nm)/BCP(5 nm)/Cu (80 nm) were sequentially deposited by thermal evaporation through a shadow mask with an active area of 0.0945 cm^2.

2.3 Device characterization

The current density-voltage (*J-V*) characteristics of solar cells were measured in glove-box under 100 mW/cm^2 AM 1.5G solar irradiation (Enlitech SS-F5-3A) with a Keithley 2400 Source Meter, and the irradiation intensity was calibrated by a monocrystalline silicon reference cell (Enlitech SRC-00207). Generally, the devices were directly placed under 100 mW/cm^2 illumination, and then the *J-V* measurement was performed at the scan rate of 120 mV/s without pre-bias. The EQE was measured by Solar Cell Spectral Response Measurement System (Enlitech QE-R3018). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The IQE was calculated by normalizing the EQE spectrum of the device by the absorption spectrum (IQE=EQE/A). For transient photocurrent measurement, the system is similar to that reported previously.[2] The durability of devices were explored by performing the *J-V* characterization periodically under 100 mW/cm^2 AM 1.5G solar irradiation in glove-box, and the unencapsulated devices were stored in glove-box in the rest time. As for SCLC measurements, the mobility values were calculated by fitting the dark *J-V* curves of hole-only devices according to the following equation: $J=9/8\varepsilon_0\varepsilon_r\mu_0(V-V_{bi})^2/L^3\exp(0.89\beta(V-V_{bi})^{0.5}/L^{0.5})$, and the device structure is ITO/HTL/$FA_{0.7}MA_{0.3}Sn_{0.5}Pb_{0.5}I_3$/$MoO_3$/Ag. The dependence of J_{sc} on P_{light} can provide information on the bimolecular recombination occurring in the photoactive layer, which follows a power law dependence, that is, $J_{sc} \propto P_{light}^{\alpha}$. The power-law exponent α will equal to unity when all carriers are swept out prior to recombination, deviation from α=1 is conjectured to arise from a small loss of carriers via bimolecular recombination. The V_{oc} varies logarithmically with P_{light} and follows the relationships of $V_{oc} \propto (nkT/q)\ln(P_{light})$. Under open-circuit conditions, all

photogenerated free carriers recombine, and the slope of V_{oc} versus logarithmical P_{light} will be equal to kT/q if bimolecular recombination dominates, while the deviated slope from kT/q suggests that additional trap-assisted Shockley–Read–Hall (SRH) recombination is involved.

2.4 Thin film characterization

Film thicknesses were measured using a Veeco Dektak XT surface profilometer. UV-Vis-NIR and normal incident reflection spectra were obtained using a Shimadzu 3600 spectrophotometer. A field emission scanning electron microscope (Hitachi SU8010, Hitachi S-4800) was used to acquire SEM images. ASPM-9700 from Shimadzu was used to acquire AFM images. Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. For steady-state PL, a 532 nm cw laser beam at 110 mW cm^{-2} was used as a source of excitation. The PL signal was detected by a Horiba Symphony-IICCD detector. UPS and XPS were performed in an ultrahigh vacuum surface analysis system equipped with a fast entry load-lock, a transfer chamber, and an analysis chamber (base pressure $\approx 10^{-10}$ mbar). UPS employed the HeI (21.22 eV) as the excitation source with an energy resolution of 50 meV. XPS was measured using the monochromatic Al Kα (1486.6 eV).

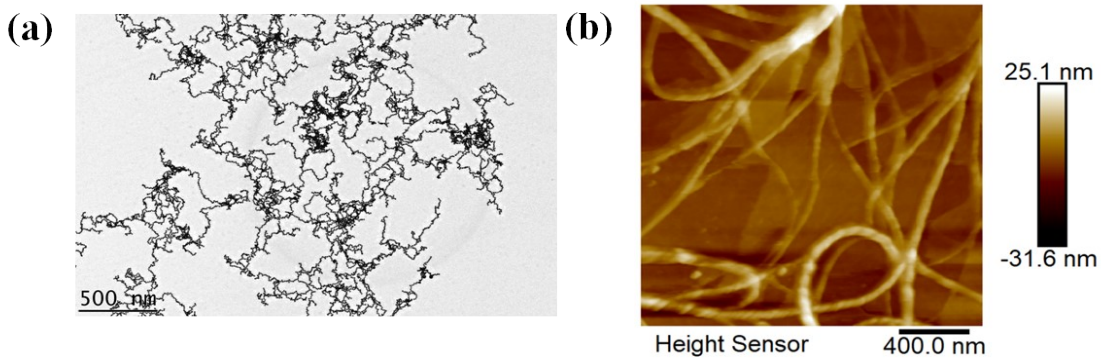

Figure S1. (a) The TEM images of AuNCs with low magnification, the scale bar is 500 nm. (b) The AFM image of AuNCs.

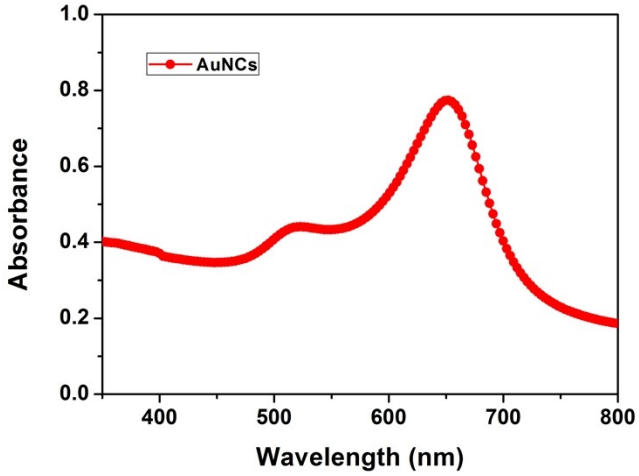

Figure S2. The absorption spectrum of as-prepared AuNCs.

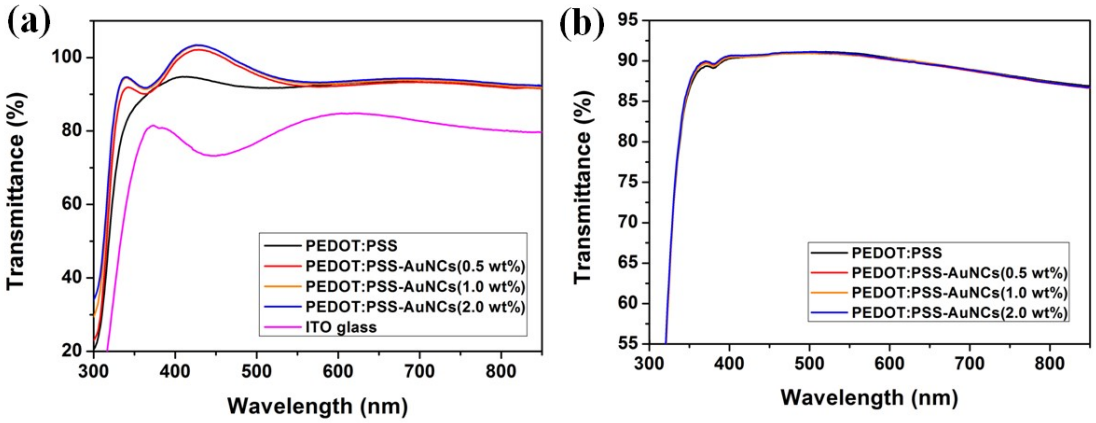

Figure S3. The transmission spectra of PEDOT:PSS HTLs with varied AuNCs on the (a) ITO glass and (b) quartz substrates, respectively. Bare ITO glass is included as the control.

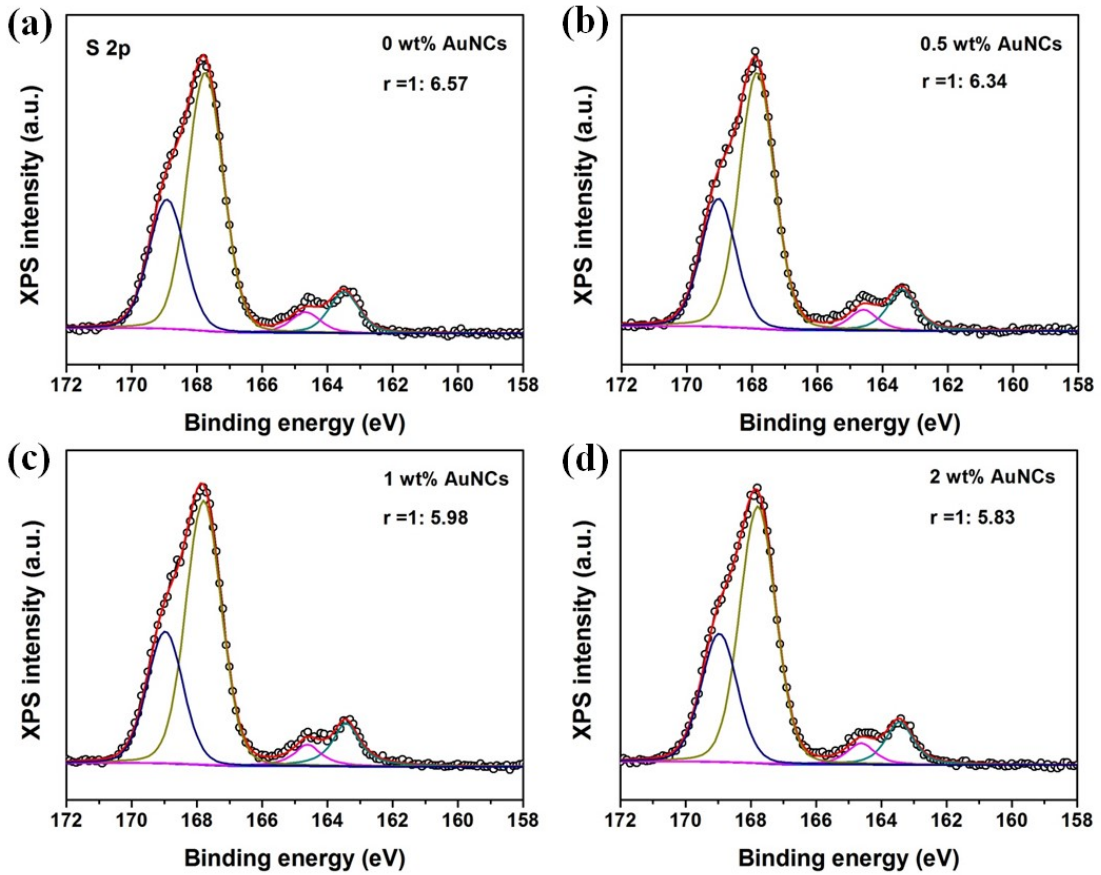

Figure S4. The XPS spectra of S 2p for PEDOT:PSS films with different content of AuNCs.

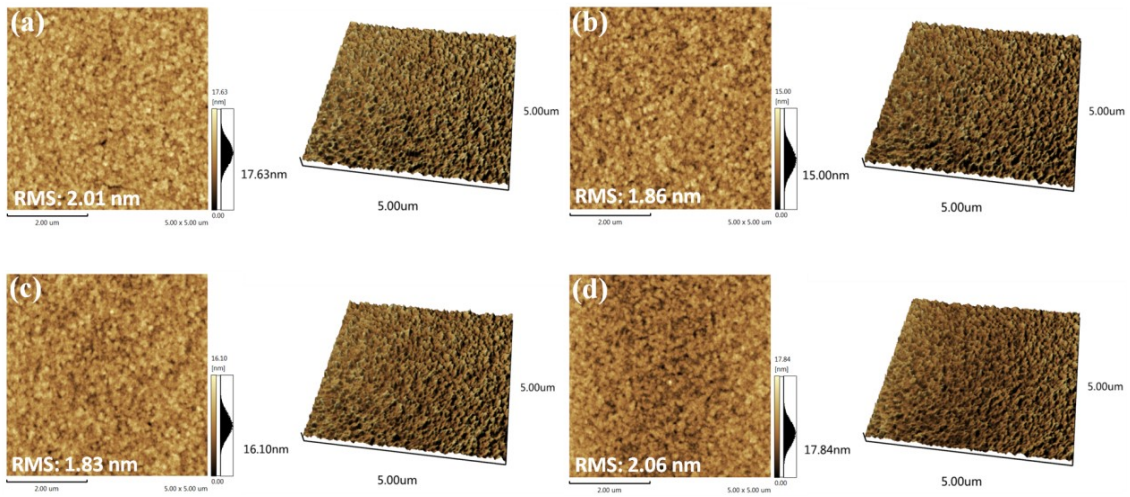

Figure S5. AFM topography images of (a) pristine PEDOT:PSS, and (b-d) PEDOT:PSS films with 0.5 wt%, 1.0 wt%, and 2.0 wt% AuNCs, repectively. The area is 5.0×5.0 μm^2.

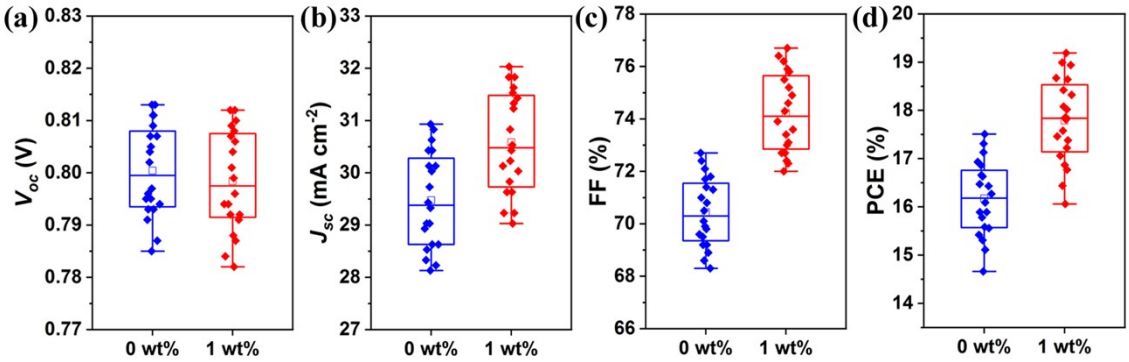

Figure S6. Statistical photovoltaic parameters obtained from 20 PSCs based on the HTLs without and with optimal 1 wt% AuNCs, (a) V_{oc}, (b) J_{sc}, (c) FF, (d) PCE.

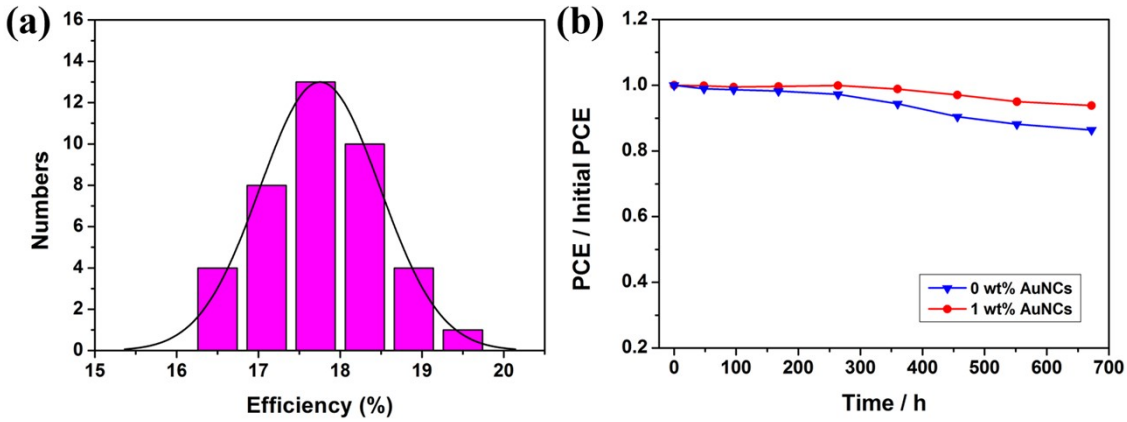

Figure S7. (a) Histograms of PCEs measured for 40 PSCs with optimal 1 wt% AuNCs. (b) Durability of the unencapsulated devices without and with AuNCs stored in a glove-box.

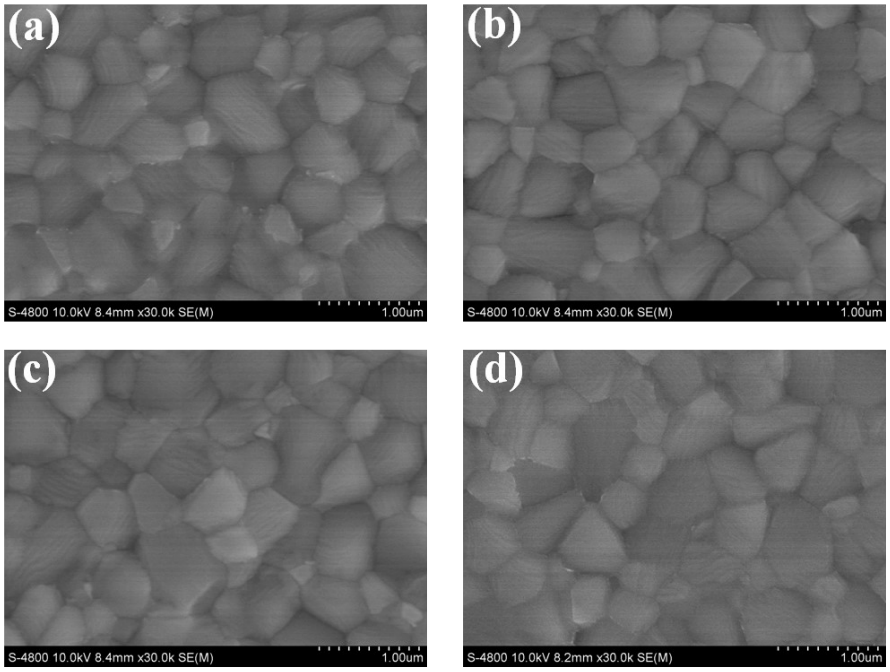

Figure S8. Top-view SEM images of perovskite film on different HTLs: (a) PEDOT:PSS, (b) PEDOT:PSS-AuNCs (0.5 wt%), (c) PEDOT:PSS-AuNCs (1.0 wt%) and (d) PEDOT:PSS-AuNCs (2.0 wt%). The scale bar is 1 μm.

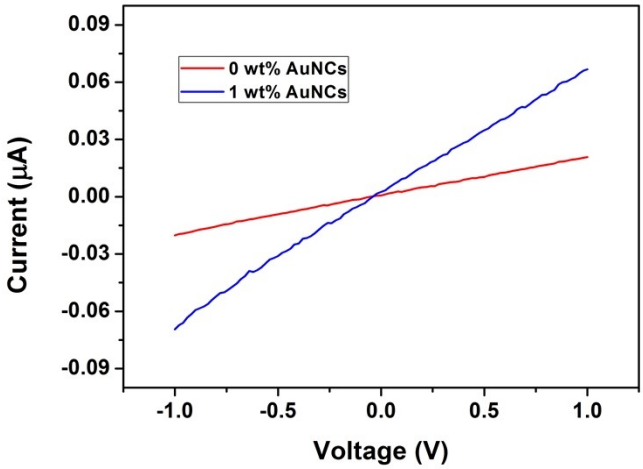

Figure S9. The current-voltage (I-V) characteristics of the PEDOT:PSS films. The conductivity (σ) is proportional to the current and determined by σ=L/(R·A)=I·L/(U·A). L

is the distance between the two electrodes, R is the resistance and A is the cross-sectional area of films.

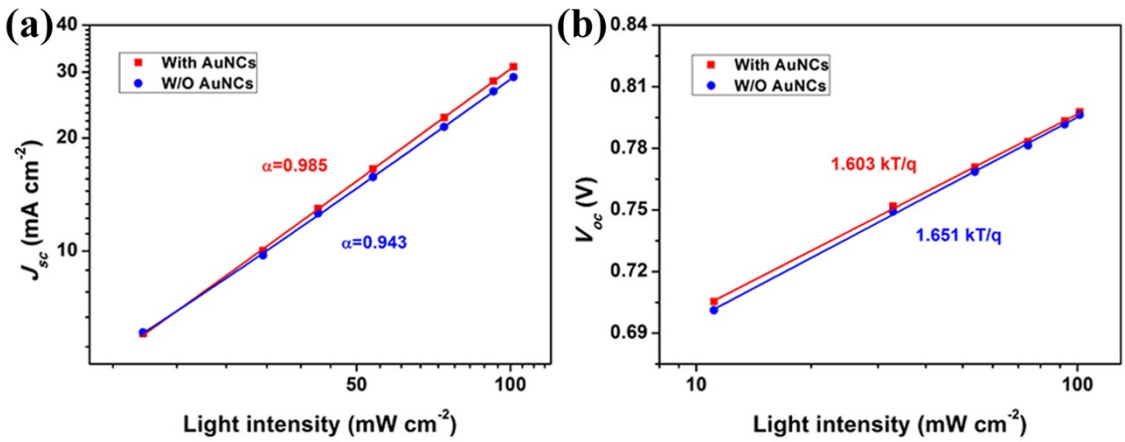

Figure S10. (a) J_{sc} and (b) V_{oc} as function of light intensity for PSCs with and without AuNCs.

The effect of AuNCs on the band structure of HTLs

The ultraviolet photoelectron spectroscopy (UPS) of these PEDOT:PSS films was also characterized. As shown in **Fig. S9**, the work function (W_F) of HTLs is slightly elevated from -4.97 eV to -4.86 eV as the content of AuNCs increases, determined by the difference between the photon energy (21.22 eV) and the value of E_{cutoff}. It is reported that the V_{oc} is proportional to the quasi-Fermi level difference between ETL and HTL.[3] In this case, the W_F result is consistent with the decreasing trend of V_{oc} listed in **Table 1**. Nevertheless, the addition of AuNCs affected the variation of V_{oc} values of PSC devices minimally, especially when the content of AuNCs is no more than the optimal 1 wt%. The reduced recombination energy loss derived from improved interfacial trap-state might somewhat mitigate the effect of band structure on V_{oc}.

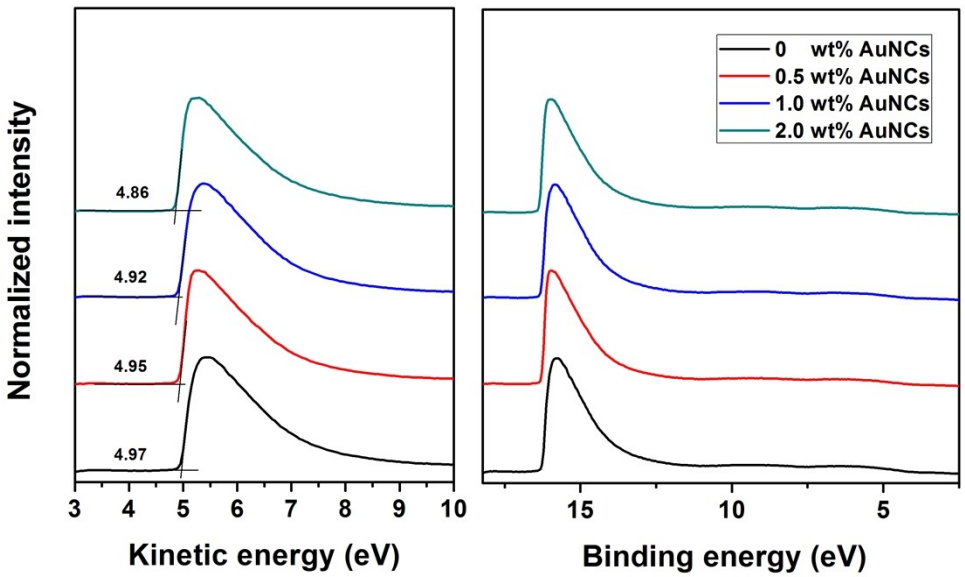

Figure S11. UPS spectra of PEDOT:PSS HTLs with various content of AuNCs: work function (left) and cutoff region (right).

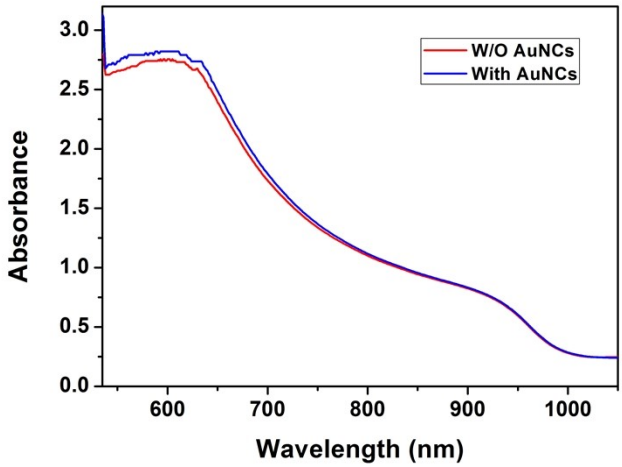

Figure S12. UV-vis absorption spectrum of perovskite films based on PEDOT:PSS HTL without and with AuNCs (1 wt%).

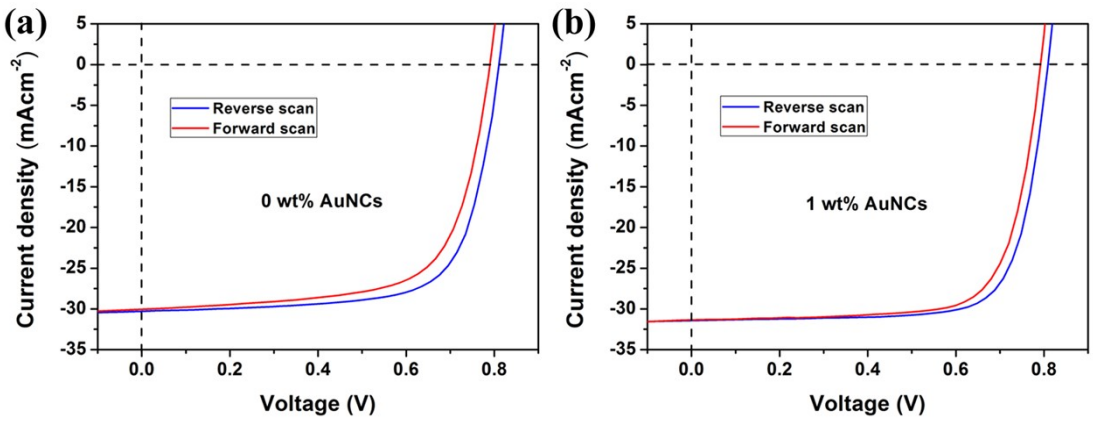

Figure S13. The *J-V* characteristics of devices a) without and b) with 1 wt% AuNCs measured at 100 mWcm^{-2} AM 1.5G illumination under different scanning directions.

Table S1. The corresponding photovoltaic performance parameters for PSC devices under different scanning directions in Figure S13.

AuNCs concentration	Direction	V_{oc} / V	J_{sc} / mA cm^{-2}	FF / %	PCE / %
0 wt%	forward	0.790	30.05	67.8	16.10
	reverse	0.811	30.28	71.3	17.51
1 wt%	forward	0.792	31.35	73.5	18.25
	reverse	0.809	31.43	75.5	19.20

References

[1] G. Frens, Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nature Phys. Sci.*, 1973, **241**(105), 20-22.

[2] Y. Li, Y. Zhao, Q. Chen, Y. (Michael) Yang, Y. Liu, Z. Hong, Z. Liu, Y.-T. Hsieh, L. Meng, Y. Li, Y. Yang, Multifunctional fullerene derivative for interface engineering in perovskite solar cells, *J. Am. Chem. Soc.* 2015, **137**, 15540-15547.

[3] H. Kim, K.-G. Lim, T.-W. Lee, Planar heterojunction organometal halide perovskite solar cells: roles of interfacial layers, *Energy Environ. Sci.* 2016, **9**, 12-30.