

Supporting Information

Efficient and stable polymer solar cells with electrochemical deposition of CuSCN as an anode interlayer

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Experimental section:

Preparation of CuSCN films:

The ITO-coated glass substrates (AimCore Technology Co., Ltd) were first sonicated in detergent, acetone, ethyl alcohol, and deionized water in sequence. The CuSCN films were then electro-deposited from an aqueous solution containing 12 mM copper sulfate (CuSO_4), 12 mM ethylenediaminetetraacetic acid (EDTA) and 12 mM potassium thiocyanate (KSCN) at a different potential between 0.25 and -0.55 V versus Ag/AgCl (3 M KCl) electrode. After drying with nitrogen flow, the ITO/CuSCN substrates were transferred to N_2 filled glove box for device fabrication.

Fabrication and characterization of the PSCs:

The P3HT:IC₆₀BA active layers (*ca.* 160 nm) were spin-casted on top of ITO/CuSCN in a N_2 filled glove box from the solution of P3HT:IC₆₀BA (1:1 weight ratio in *o*-chlorobenzene) with the overall concentration of 25 mg mL⁻¹. Finally 10 nm of Ca and 100 nm of Al were deposited sequentially under 6×10^{-6} Torr by thermal evaporation through a shadow mask to form an active area of $\sim 0.064 \text{ cm}^2$. In order to ensure the credibility of our results, a batch of device containing 20 cells were fabricated.

The hole mobility test: The structure of hole-only devices is ITO/AILs/MoO₃/Au. In the trap-free region over the trap-filled limit, SCLC can be characterized by the Mott-Gurney square law $J = (9/8)\epsilon_r\epsilon\mu_h(V^2/L^3)$, where ϵ is the vacuum permittivity, ϵ_r is the dielectric permittivity of the active layer, L is the thickness of the AILs, and μ_h is the hole mobility.

Characterization: The electro-deposition of the CuSCN film was performed on a CHI660 electrochemical workstation (CH Instrument, Inc.). A computer-controlled Keithley 2400 source measure unit was used to characterize the J - V performance of devices with an AM 1.5G solar simulator at illumination intensity of 100 mW cm^{-2} . The corresponding incident photon to current conversion efficiency (IPCE) was characterized on the QTest Station 2000ADI system (Crowntech. Inc., USA). The optical transmittance spectra were measured on a Varian Cary 5500 spectrometer. Atomic force microscopy (AFM) height images were obtained using a Bruker Metrology Nanoscope III-D atomic force microscope in tapping mode under atmospheric conditions. The work functions were measured in air by scanning Kelvin probe microscopy (SKPM) with a Bruker Metrology Nanoscope III-D atomic force microscope. Conducting AFM tips (SCM-PIT/PtIr, Bruker, USA) were used for this study with a typical spring constant of 2.8 N m^{-1} and a resonance frequency of 75 kHz . Typical scan line frequency was 0.3 Hz and each image contained 512×512 pixels. The surface potential images were unprocessed original data. Advancing contact angle measurements were performed using a DSA100 system (KRÜSS).

Calculation of Surface Energy:

The surface energy of different films were calculated based on the results of the contact angle measurement and equation (1) from the “three-liquid procedure” developed by van Oss et al. Water and ethylene glycol were selected as the polar pair, whereas the hexadecane was used in terms of the apolar liquid. Surface energy parameters are shown in Table S1.

$$\gamma_{LV1}(1+\cos \theta_1)=2\left(\sqrt{\gamma_s^{LW}\gamma_{LV1}^{LW}}+\sqrt{\gamma_s^+\gamma_{LV1}^-}+\sqrt{\gamma_s^-\gamma_{LV1}^+}\right)$$

$$\gamma_{LV2}(1+\cos \theta_2)=2\left(\sqrt{\gamma_s^{LW}\gamma_{LV2}^{LW}}+\sqrt{\gamma_s^+\gamma_{LV2}^-}+\sqrt{\gamma_s^-\gamma_{LV2}^+}\right)$$

$$\gamma_{LV3}(1+\cos \theta_3)=2\left(\sqrt{\gamma_s^{LW} \gamma_{LV3}^{LW}}+\sqrt{\gamma_s^+ \gamma_{LV3}^-}+\sqrt{\gamma_s^- \gamma_{LV3}^+}\right) \quad (1)$$

$$\gamma=\gamma^{LW}+\gamma^{AB}$$

$$\gamma_i^{AB}=2\sqrt{\gamma_i^+ \gamma_i^-}$$

γ is the surface energy, γ^{LW} refers to the Lifshitz-van der Waals interaction and γ^{AB} refers to the acid-base interaction. γ^+ and γ^- stand for the Lewis acid and base parameters of surface energy.

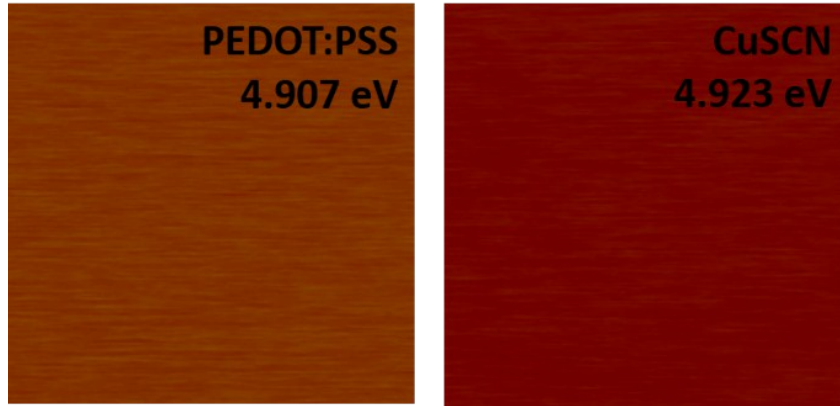
Table S1. Surface Energy Parameters (in mNm^{-1}) of Testing Liquids.

	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Water	72.8	21.8	51	25.5	25.5
Ethylene Glycol	48	29	19	1.92	47.0
Hexadecane	27.5	27.5	0	0	0

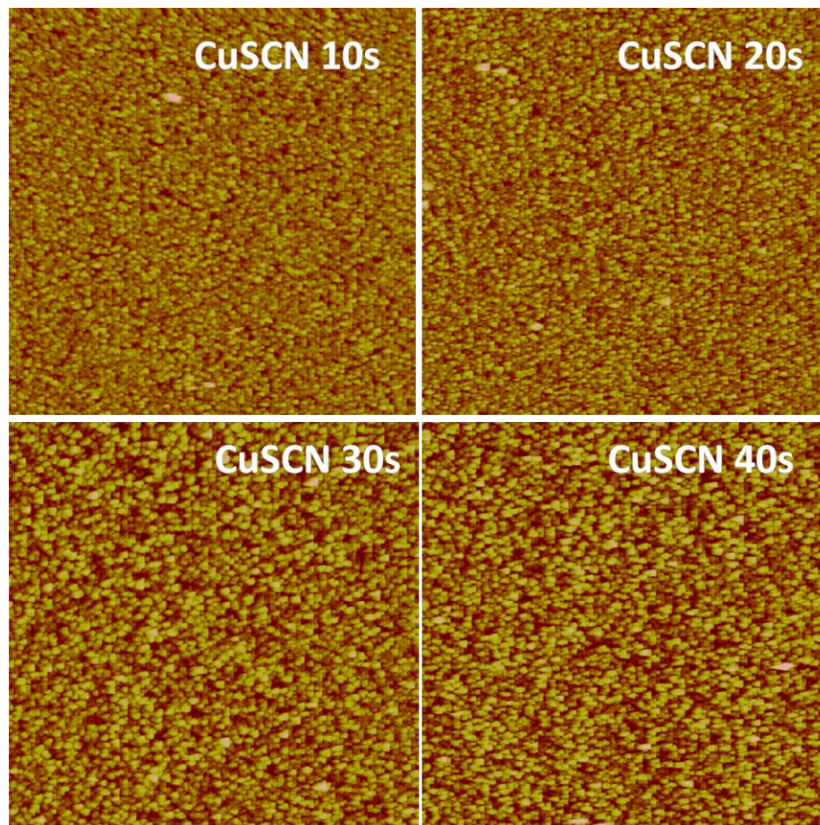
The specific calculation results are shown in the TableS2 below.

Table S2. The advancing contact angles of three probing liquids on various surfaces at stable state and the corresponding calculated surface energies (mNm^{-1}).

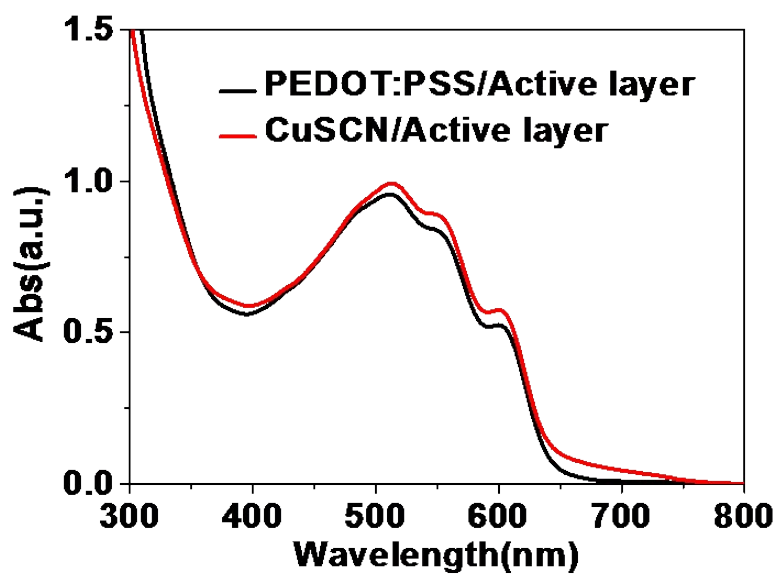
		ITO	PEDOT:PSS	CuSCN	P3HT:PC ₆₁ BM
Contact Angle(deg)	water	40.29	19.5	95.5	107.23
	Ethylene glycol	35.31	18.2	45.34	80.67
	hexadecane	0	0	0	30.69
Calculated Surface Energy Component (mN/m)	γ	38.67	58.78	8.72	24.00
	γ^{LM}	27.5	6.875	6.875	23.88
	γ^{AB}	11.17	51.9	1.84	0.12
	γ^+	0.62	72.97	14.83	0.02
	γ^-	49.98	9.23	0.06	0.19



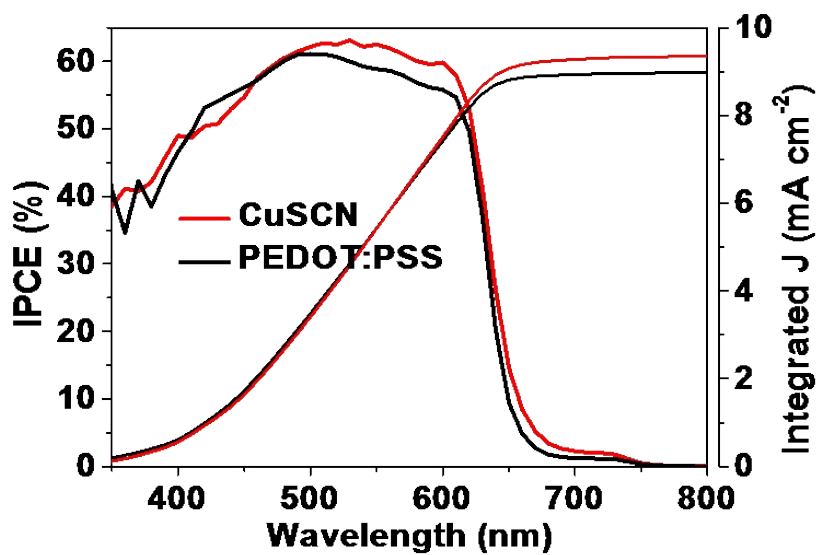
FigureS1. Work functions of the PEDOT:PSS and CuSCN films



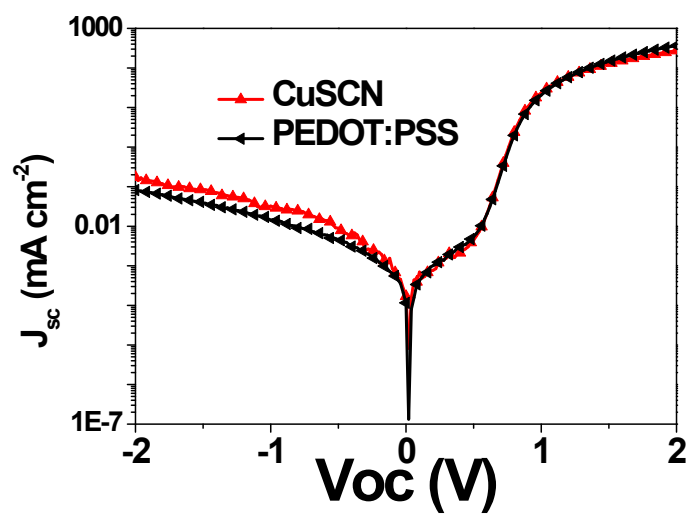
FigureS2. AFM images of CuSCN films with different electro-deposition times.



FigureS3. Absorption spectra of the ITO/CuSCN/active layer and ITO/PEDOT:PSS/active layer films.



FigureS4. IPCE spectra of P3HT:IC₆₀BA devices with CuSCN and PEDOT:PSS as AIL.



FigureS5. Dark J-V curves of P3HT:IC₆₀BA devices with CuSCN and PEDOT:PSS as AILs.