Natural biomaterial sarcosine as an interfacial layer enables inverted organic solar cells exhibiting over 16.4% efficiency

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1. Experimental section

1.1. Materials

The indium tin oxide (ITO) glass substrates with a sheet resistance of 15 Ω square^{-1} were acquired from South China Science & Technology Company Limited. The sarcosine was purchased from Sinopharm Chemical Reagent Co. Ltd. The used donor and acceptor materials (PM6 and BTP-BO-4Cl) were purchased from Organtec Ltd. The sarcosine was dissolved in blend deionized water and methanol solvents with a weight ratio of 1:9 at a total concentration of 1 mg ml^{-1}, and then the solution was continuously stirred at room temperature for 12 hours. The blend PM6: BTP-BO-4Cl with a weight ratio of 1:1.2 was dissolved in chloroform solvent at a total concentration of 16.17 mg ml^{-1}, and then the solution was continuously stirred at 40 ^{o}C for 12 hours. After that 0.5 vol% CN was doped into the blend PM6: BTP-BO-4Cl solutions.

1.2. Device fabrication

The ITO glass substrates were sequentially pre-cleaned in the ultrasonic baths containing detergent, deionized water, or ethanol, respectively. Then the cleaned ITO substrates were dried with nitrogen gas and then treated by oxygen plasma for 90 s to improve work function and clearance. The Zinc oxide (ZnO) solution (80 μl) was

spin-coated on ITO substrates at 4000 rounds per minute (rpm) for 30 s and then annealed at 150°C for 30 min in atmospheric air. The sarcosine solution (80 μl) was spin-coated on ITO substrates with ZnO film at 2000 rpm for 30 s. Then the ITO substrates with ZnO/sarcosine films were transferred into a high-purity nitrogen-filled glove box. The room-temperature PM6:BTP-BO-4Cl blend solution (20 μl) was spin-coated onto the top of sarcosine layer at 2500 rpm for 40 s. Then, the active layers were annealed by carbon disulfide solvent vapor for 20 s then thermally annealed at 80 °C for 5 min. A thin molybdenum trioxide (MoO_3) layer (10 nm) and a silver (Ag) layer (100 nm) were sequentially deposited by thermal evaporation under 10^{-5} Pa and the thickness was monitored by a quartz crystal microbalance. The active area of each device is approximate 3.8 mm^2, which is defined by the vertical overlap of the ITO cathode and Ag anode.

1.3. Device characterization

The current density-voltage (*J-V*) curves of the PSCs were measured under 1 sun AM 1.5 G illumination (100 mW cm^{-2}) by using a Keithley 2400 source meter in a high-purity nitrogen-filled glove box. The AM 1.5 G illumination was provided by XES-50S2 (SAN-EI Electric Co., Ltd.) solar simulator (AAA class, 40 × 40 mm^2 effective irradiated area). The external quantum efficiency (EQE) spectra of PSCs were measured by using a Zolix Solar Cell Scan 100 in atmospheric air. Absorption spectra and transmission spectra of films were measured by using a PERSEE TU-1900 spectrophotometer. The photoluminescence (PL) spectra of the active layer based on the different ETLs by a fluorescence spectrophotometer (FLS 1000). The contact angles of films were characterized by the Contact Angle meter. The morphology images of films were characterized by an atomic force microscope (AFM, Horiba Bruker Multimode 8). The work functions (WFs) of films were analyzed by Kelvin probe force microscopy (KPFM, Horiba Bruker Multimode 8). The Grazing incidence X-ray diffraction (GIXD) data were obtained using the beamline scientists at Diffuse X-ray Scattering Station (1W1A), Bejing Synchrotron Radiation Facility (BSRF). A grazing incidence angle of 0.2° was chosen to investigate the crystallinity and orientation that prevailed throughout the blend films. A bent-triangle silicon

crystal was used to obtain the X-rays of a wavelength of 1.54 Å. Electrochemical impedance spectroscopy (EIS) was measured by an electrochemical workstation (CHI 760 E) in atmospheric air.

2. Additional experimental results

Table S1. Typical OSCs based on ZnO surface modification in recent years.

ZnO surface modification materials	Active layers	PCE (Before)	PCE (After)	Reference
PTCDI-C8	PTB7-Th:PC$_{71}$BM	8.3%	9.3%	*Sol. Energy*, 2017, 158, 278-284
PFS-FTEG	PTB7-Th:PC$_{71}$BM	9.7%	10.7%	*Angew. Chem. Int. Ed.*, 2017, 56, 431-843
MPPA	PTB7-Th:PC$_{71}$BM	9.4%	10.5%	*ACS Nano*, 2018, 12, 5, 4440-4452
C60-4TPB	PTB7:PC$_{71}$BM	7.3%	8.1%	*ACS Appl. Mater. Inter.*, 2018, 10, 2649-2657
PNSO$_3$Na	PBDB-T:ITIC	9.9%	11.2%	*Chem. Commun.*, 2018, 54, 563-566
ITIC	PTB7-Th: PC$_{71}$BM	7.9%	8.7%	*ACS Sustain. Chem. Eng.*, 2019, 7, 12261-12269
PyM	PBDB-T:IT-M	10.4%	11.5%	*Sol. Energy*, 2019, 191, 219-226
SAM1	PBDB-T-SF:ITIC-4F	12.2%	13.3%	*Adv. Energy Mater.*, 2019, 1900887
C60-SAM	PTB7-Th:IEICO-4F	9.5%	10.0%	*Sci. Bull.*, 2020, 65, 208-216

The measured contact angle values θ were input into the Wu model to calculate the polar surface energy (γ^p) and dispersive surface energy (γ^d) of films according to the following equation.

$$\gamma_W(1 + cos\theta_W) = \frac{4\gamma_W^d\gamma^d}{\gamma_W^d + \gamma^d} + \frac{4\gamma_W^p\gamma^p}{\gamma_W^p + \gamma^p}$$

$$\gamma_{EG}(1 + cos\theta_{EG}) = \frac{4\gamma_{EG}^d\gamma^d}{\gamma_{EG}^d + \gamma^d} + \frac{4\gamma_{EG}^p\gamma^p}{\gamma_{EG}^p + \gamma^p}$$

$$\gamma_W = \gamma_W^d + \gamma_W^p$$

$$\gamma_{EG} = \gamma_{EG}^d + \gamma_{EG}^p$$

$$\gamma^{tot} = \gamma^d + \gamma^p$$

Here, W and EG refer to deionized water and ethylene glycol, θ_W and θ_{EG} are contact angle values of deionized water and EG as the probing liquids. γ_W and γ_{EG} are surface energy values of deionized water and EG. The total surface energy γ^{tot} is equal to the sum of γ^d and γ^p.
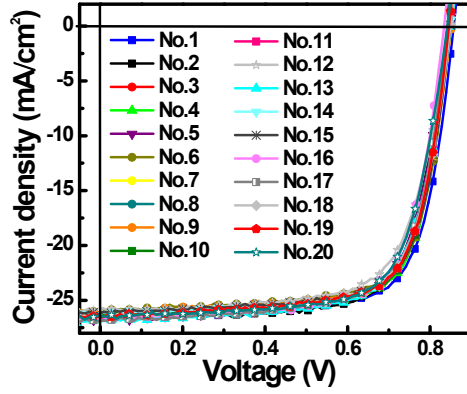
Fig. S1 *J-V* curves of OSCs with ZnO/sarcosine as ETLs.

Table S2 Key photovoltaic parameters of of OSCs with ZnO/sarcosine as ETLs.

| Cells	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)	Cells	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
No.1	26.65	0.85	72.64	16.45	No.11	26.53	0.85	71.63	16.15
No.2	26.59	0.85	72.50	16.38	No.12	26.88	0.85	70.13	16.02
No.3	26.12	0.85	73.82	16.39	No.13	26.87	0.85	70.27	16.04
No.4	26.55	0.85	72.49	16.36	No.14	26.19	0.85	72.70	16.18
No.5	26.72	0.85	71.51	16.24	No.15	26.09	0.85	72.65	16.11
No.6	26.14	0.85	72.12	16.02	No.16	26.67	0.85	71.47	16.20
No.7	26.62	0.85	71.60	16.20	No.17	26.84	0.85	70.71	16.13
No.8	26.64	0.85	71.71	16.23	No.18	26.50	0.85	71.18	16.03
No.9	26.10	0.85	72.53	16.09	No.19	26.61	0.85	71.53	16.17
No.10	26.41	0.85	72.64	16.31	No.20	26.73	0.85	71.10	16.15
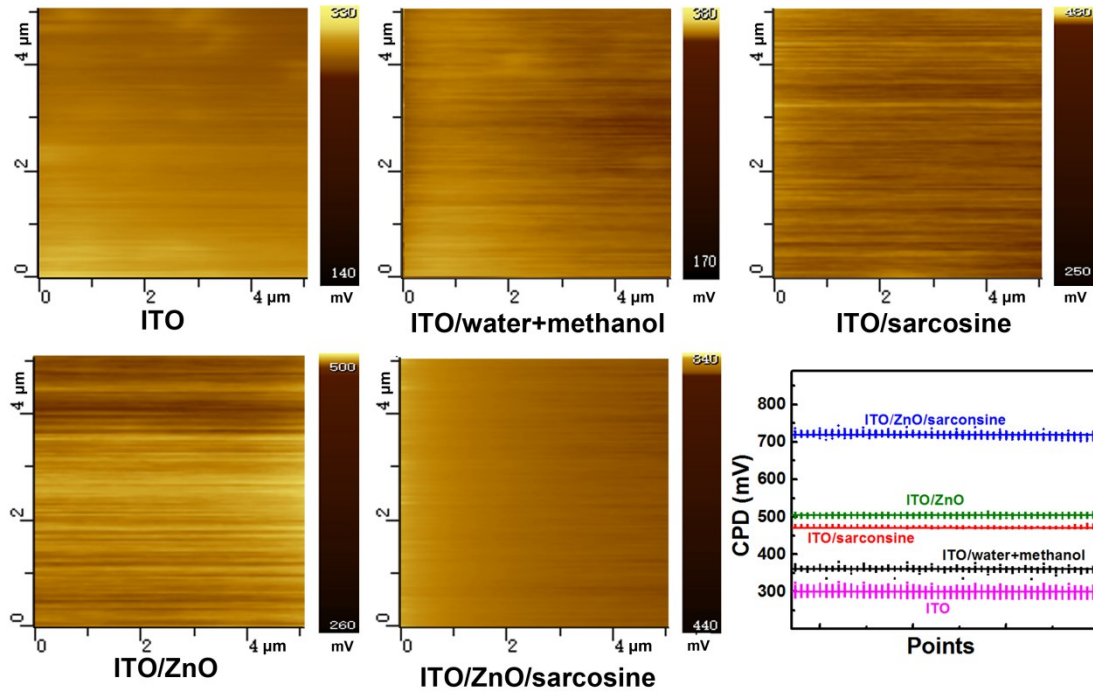
Fig. S2. CPD images and CPD data of ITO modified by different ETLs captured in

KPFM.

Table S3. WFs and CPD of ITO modified by different ETLs.

ETLs	CPD (mV)	WF (eV)
without	300	4.70
Water+methanol	361	4.64
Sarcosine	472	4.53
ZnO	505	4.49
ZnO/sarcosine	720	4.28

The electron transport properties of sarcosine films at different temperatures were evaluated with the electron-only device structure of ITO/Al (100 nm)/sarcosine (400 nm)/PDIN/Al (100 nm). The structure of electron-only devices is ITO/ETL/active layer/PDIN/Al (100 nm). The structure of hole-only devices is ITO/PEDOT:PSS/active layer (120 nm)/MoO$_3$/Ag (100 nm). The fabrication conditions of the active layer films are the same with those for the OSCs. The charge mobilities are generally described by the Mott-Gurney equation:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

where J is the current density, ε_0 is the permittivity of free space, ε_r is the dielectric constant of used materials, μ is the charge mobility, V is the applied voltage and L is the active layer thickness. In organic materials, charge mobility is usually field dependent and can be described by the disorder formalism, typically varying with the electric field, E=V/L, according to the equation:

$$\mu = \mu_0 \exp[0.89\gamma \sqrt{\frac{V}{L}}]$$

where μ_0 is the charge mobility at zero electric field and γ is a constant. Then, the Mott-Gurney equation can be described by:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp[0.89\gamma \sqrt{\frac{V}{L}}]$$

In this case, the charge mobilities were estimated using the following equation:

$$\ln(\frac{JL^3}{V^2}) = 0.89\gamma\sqrt{\frac{V}{L}} + \ln(\frac{9}{8}\varepsilon_r\varepsilon_0\mu_0)$$
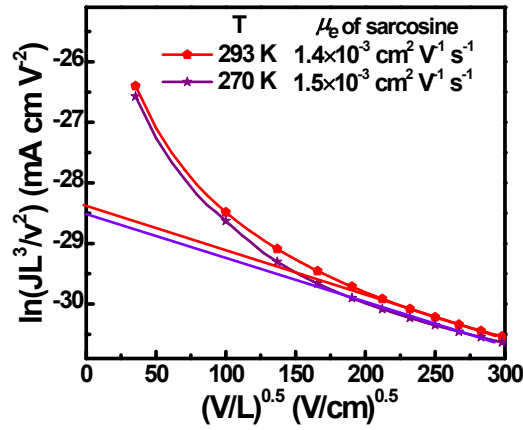

Fig. S3 $\ln(Jd^3/V^2)$–$(V/d)^{0.5}$ curves of electron-only devices with the electron-only device structure of ITO/Al/sarcosine/PDIN/Al at different temperatures.
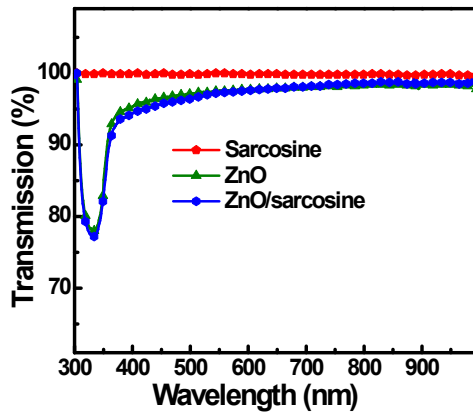

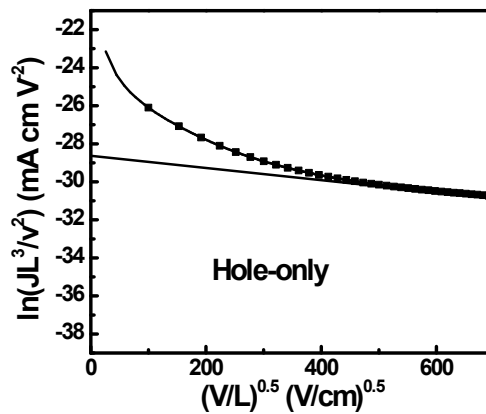**Fig. S4** Transmission spectra (e) of different ETLs films.

Fig. S5 $\ln(JL^3/V^2)$-$(V/L)^{0.5}$ curves for SCLC fitting of hole-only devices with the structure of ITO/PEDOT:PSS/active layer/MoO$_3$/Al.
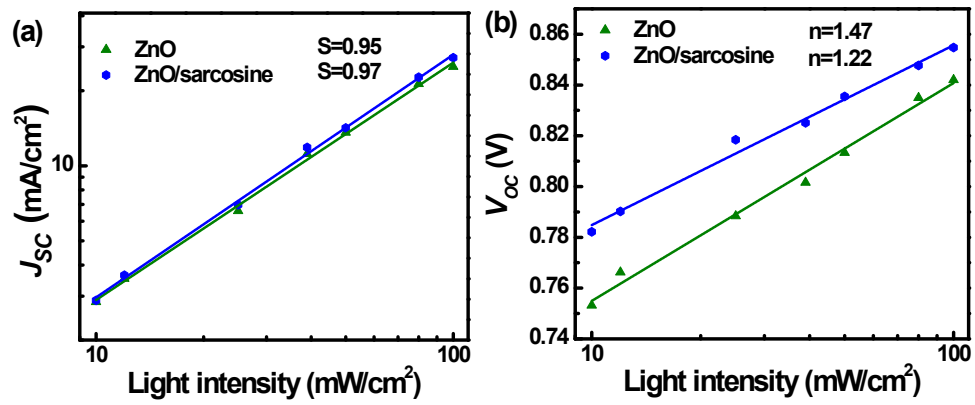
Fig. S6 J_{SC} and V_{OC} dependence on light intensity of OSCs with ZnO or ZnO/sarcosine as ETLs.