Electronic Supplementary Information

ITO-free highly bendable and efficient organic solar cells with Ag nanomesh/ZnO hybrid electrodes

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Experimental section

Fabrication of silver nanomesh, Ag-NW films, and ITO electrodes

A polyurethane acrylate (PUA) mold was replicated from a silicon (Si) master by the replica molding method. A thin Ag layer with a layer thickness of 60–100nm was deposited on the PUA mold using an electron (E) -beam evaporator. To transfer an Ag layer from the PUA mold, a transparent UV-curable adhesive (Norland Optical Adhesive 61) layer with a thickness of ~800 nm was spin-coated on a PES film. To partially cure the UV-curable adhesive, NOA 61-coated substrate was exposed to UV for 20 s. Then, the Ag-deposited PUA mold was set on top of the partially cured substrate and completely UV-cured with 0.2 MPa static pressure for 3 min. Finally, the nanopatterned Ag nanomesh was fabricated on the transparent flexible substrate after peeling the PUA mold.¹

Ag-NW films were prepared through the spin-coating process and were formed on pre-cleaned PES films. An as-received dispersion containing Ag NWs (ClearOhm ink, Cambrios) was spin coated for 60 s at 1500 rpm. The dispersion was sonicated for 60 s and shaken well before spin coating. The ITO/PES films were vacuum sputtered in our laboratory and the ITO/glass film was obtained commercially (Shinhan SNP Co. Ltd.). The ITO/PES films were formed by depositing a layer of ITO on a PES substrate by radio-frequency (RF) superimposed DC magnetron sputtering. The ITO sputtering was carried out at room temperature using an Ar gas flow rate of 30 sccm, an O₂ gas flow rate of 0.3 sccm, and a working pressure of ~ 1.0×10^{-3} Torr. The DC power was controlled by keeping the current constant (~0.5 A), and ~50 W of RF power was imposed simultaneously. The growth rate of the film was ~0.316 nm s⁻¹, and an ITO film with a final thickness of ~100 nm was deposited.

Preparation of the ZnO precursor

The ZnO precursor was prepared by dissolving zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Aldrich, 99.9%, 1.64 g) and ethanolamine (NH₂CH₂CH₂OH, Aldrich, 99.5%, 0.5 g) in 2-methoxyethanol

(CH₃OCH₂CH₂OH, Aldrich, 99.8%, 10 g) under vigorous stirring at 60°C for 30 min to facilitate a hydrolysis reaction in air.

Fabrication of the inverted organic solar cells (IOSCs)

The IOSCs were fabricated using Ag nanomesh film on glass and PES substrates with R_{sheet} values of ~4–15 Ω sq⁻¹. The ZnO precursor solution was spin-cast on top of the Ag-NW film-coated glass and PES substrates. The films were annealed at 150°C for 10 min in air. The ZnO film thickness was approximately 60 nm. The ZnO-coated substrates were transferred into a nitrogen-filled glove box. A solution containing a mixture of PTB7:PC₇₁BM (8 mg:12 mg) was dissolved in chlorobenzene (1 mL). The PTB7 used in this study was purchased from 1-material; the PC₇₁BM was purchased from Solemme BV. The mixed solutions were stirred at 50°C for 12 h. 1,8-Diiodooctane (DIO) (Sigma Aldrich) was then added at a volume ratio of 3% to the solutions containing PTB7:PC₇₁BM before the spin-coating process. The active layer was then deposited onto the ZnO-coated Ag nanomesh electrodes using spin-coating at 1000 rpm for 40 s after passing through a 0.20-µm PTFE syringe filter. The thickness of the active layer was *ca*. 100 nm. The PEDOT-PSS (Clevios P VP AI 4083) diluted using isopropyl alcohol (IPA), with the ratio of PEDOT-PSS:IPA being 1:10, were deposited onto the active layer at 5000 rpm 60 s in a glove box. Finally, the top-electrode Ag metal was deposited through a shadow mask by thermal evaporation in a vacuum of about 3 × 10⁻⁶ Torr. The device area, defined through the shadow mask, was 0.38 cm².

Bending test

To test for mechanical stability, a bending-test system was designed in-house. It was used to measure the critical radii of the Ag nanomesh/PES and ITO/PES electrodes. The system consisted of two contact points: one of the points was fixed and the other could be moved laterally. **Fig. S5** shows the procedure followed in the bending tests for the flexible IOSCs. The bending tests resulted in compressive stresses and were performed on un-encapsulated devices in a nitrogen atmosphere.

Characterization

The performance of the IOSCs was measured under simulated AM 1.5 illumination with an irradiance of 100 mW cm⁻² (Oriels Sol AAATM Class models 94043A.). The irradiance of the sunlight-simulating illumination was calibrated using a standard Si photodiode detector fitted with a KG5 filter. The J-V curves were measured automatically using a Keithley 2400 SourceMeter source measurement unit. The series resistance (R_s) and shunt resistance (R_{sh}) were obtained from the slope of the dark current curves that was fitted with the following Shockley diode equation:²

$$J = J_0 \left\{ \exp\left[\frac{q(V - AJR_s)}{nkT}\right] - 1 \right\} + \frac{V - AJR_s}{AR_{sh}} - J_{ph}$$
(1)

where *J* is the current density, J_{ph} is the voltage-dependent photogenerated current density, J_0 is the reverse saturation current density, *q* is the elementary charge, *n* is the diode ideality factor, *k* is the Boltzmann constant, and *T* is the absolute temperature. The quantum efficiency measurement system used to determine the IPCE spectra (Oriel IQE-200) used a 250 W quartz tungsten halogen (QTH) lamp as a light source and had a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. The film thicknesses, sheet resistances, and optical transmittances were measured using a surface profiler (Alpha Step P-11, Tencor Instruments), a four-point probe system (Mitsubishi Chemical Corporation), and an ultraviolet-visible spectrophotometer (Cary 5000, Varian), respectively. The scanning electron microscope (SEM) micrographs were obtained using a JSM-6700F field-emission scanning electron microscope. Atomic force microscopy (AFM) images were acquired with a Digital Instrument NanoscopeTM 3D ADC5, Multimode (Veeco Instruments Inc., CA) in tapping mode.

Optical analysis of the Ag nanomesh IOSCs

To clarify the optical effect of the Ag nanomesh electrode, finite element method (FEM) simulation was employed to compare the absorption spectra of the OSCs. Based on the cross-section images, we define the simulation region as depicted in Fig. S6 (a) where the reference ITO device has a structure of glass/ITO (150 nm)/ZnO (50 nm)/PTB7:PC71BM (115 nm)/PEDOT:PSS (10 nm)/Ag (200 nm). Periodic boundary conditions were used for the 2D unit simulation region with a period of 1 µm. The refractive index of the adhesive material was assumed to be constant (1.56), and those for others were measured by ellipsometry. The simulation results shown in Fig. S6 (b) are plotted for the active absorption of the PTB7:PC71BM layer, which generates the flow of electron and hole pair. While the value for flat devices such as the ITO reference device is independent of the polarization of the incident light, that of the Ag nanomesh device is different for the TE-polarization mode (where electric field oscillates vertically with respect to the cross-section plane) and for TM-polarization mode (where electric field oscillates in parallel with the cross-section plane). As shown in the figure, the absorption spectra of Ag nanomesh devices are comparable to the reference spectrum, which indicates that Ag nanomesh electrodes can perform as a TCE as well as ITO electrodes, from the optical viewpoint. Some of the previous studies reported a plasmonic light trapping effect of periodic metal structures supplanting TCEs³⁻⁵, but such an effect does not appear in this case since the dispersion relationship indicates that a period of 1 μ m, which is too long to sustain surface plasmon resonance in the visible wavelength range.6-7



Fig. S1. SEM images of Ag nanomesh on glass with line widths of 150 nm and (a) line spacing of 1 μ m, (b) line spacing of 1.6 μ m, (c) line spacing of 3.2 μ m.



Fig. S2. (a) Characteristic J-V curves of IOSCs fabricated on Ag nanomesh electrodes (with ZnO buffer layer) on glass with PTB7:PC₇₁BM photoactive materials under AM 1.5G illumination (100 mW cm⁻²) and (b) their IPCE spectra. Characteristics dark J-V curve of these IOSCs fabricated on (c) Ag nanomesh/PES electrode and (d) Ag nanomesh/glass electrode.



Fig S3. Characteristics J-V curve of IOSCs without ZnO buffer layer fabricated on Ag nanomesh electrodes under AM 1.5G illumination (100 mW cm⁻²).



Fig S4. SEM images of (a) Ag NWs (top) and Ag nanomesh (bottom) and (b) measured changes in their sheet resistance during the oxidation-resistance test. (c) SEM images of Ag NWs and (d) changes in sheet resistance as function of sonication time.



Fig. S5. Photographs of the bending test for flexible IOSCs.



Fig. S6. Optical simulation of (a) an IOSC with a Ag nanomesh electrode consisting of glass/Ag nanomesh/ZnO/PTB7:PC₇₁BM/PEDOT:PSS/Ag. (b) The photoactive layer absorption for TE-polarization and TM-polarization modes.

Table S1. Photovoltaic characteristics of IOSCs without a ZnO interlayer under AM 1.5G illumination (100 mW cm⁻²). The listed values represent an average of 5 samples. Shunt resistance (R_{sh}) and series resistance (R_s) of the IOSCs were estimated by fitting the dark *J*–*V* curves.

Device	J _{sc} (mA/cm ²)	$V_{oc}\left(\mathbf{V}\right)$	FF (%)	PCE (%)	$R_s(\Omega \cdot \mathrm{cm}^2)$	$R_{sh}(\Omega \cdot \mathrm{cm}^2)$
Ag nanomesh/PES	10.72 ± 0.71	0.40 ± 0.06	27.65 ± 2.14	1.21 ± 0.38	96 ± 2.6	4.6×10 ²
Ag nanomesh/glass	12.45 ± 0.52	0.43 ± 0.04	31.99 ± 1.17	1.69 ± 0.10	70 ± 1.5	8.2×10 ²

Table S2. Comparison of our work with previously reported flexible OSCs with metal mesh/grid electrodes.

Materials	Active layer	J_{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)	Reference
Ag mesh/PEDOT:PSS	P3HT:PC ₆₁ BM	6.25	0.54	57	1.93	S8
Ag nanomesh/ZnO NPs	P3HT:PC ₆₁ BM	9.39	0.60	57	3.21	S9
Embedded Ag mesh/ITO	PBDTTT-C:PC61BM	9.7	0.73	57	4.01	S10
Embedded Ag mesh	P3HT:PC ₆₁ BM	6.46	0.62	63	2.54	S11
Ag NP grid/PEDOT:PSS	Si-PCPDTBT:PC71BM	13.77	0.61	58	4.91	S12
Cr/Al/Cr grid	P3HT:PC ₆₁ BM	7.7	0.61	56	2.64	S13
Ag mesh/PEDOT:PSS	P3HT:PC ₆₁ BM	8.8	0.56	49	2.64	S14
Cu mesh/PEDOT:PSS	P3HT:PC ₆₁ BM	8.8	0.56	49	2.46	S15
Ag nanomesh/ZnO	PTB7:PC71BM	16.03	0.73	60.9	7.15	Our work

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Graphical Table of Contents

ITO-free highly bendable and efficient organic solar cells with Ag nanomesh/ZnO hybrid electrodes

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High efficiency and bendable organic solar cells were fabricated using Ag nanomesh/ZnO hybrid transparent electrodes