Supplementary Information for

Application of Solvent Modified PEDOT:PSS to Graphene Electrodes in Organic Solar Cells

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Methods.

Graphene synthesis (LPCVD). Copper foil (25 μm in thickness, ALFA AESAR) was used as a metal catalyst for both conditions. The CVD chamber was evacuated to a base pressure of 30-50 mTorr. The system was then heated to a growth temperature of 1000 °C under hydrogen (H_2, 10 sccm) gas (~320 mTorr) and annealed for 30 minutes. Subsequently, methane (CH_4, 20 sccm) gas was introduced (total pressure: ~810 mTorr) and graphene growth was carried out for 30 minutes. The chamber was then cooled down at ~45 °C/min to room temperature.

Graphene transfer and anode preparation. Transfer was carried out using poly(methyl methacrylate) (PMMA, 950 A9, Microchem). Graphene on one side of the foil was removed via reactive ion etching (RIE) with O_2 gas (Plasma-Therm, 100 Watt at 7×10^{-5} Torr). Cu was etched by a commercial etchant (CE-100, Transene). Graphene films were then thoroughly rinsed with diluted hydrochloric acid (10%) and de-ionized water to remove residual iron ions from the Cu etchant. The PMMA layer was removed by annealing at 500 °C for 2 hr under H_2 (700 sccm) and Ar (400 sccm). Repeated transfers were performed for 3-layer graphene films. The transferred graphene films were patterned into the desired shape through RIE.

OPV device fabrication process. Organic layers (DBP (Luminescence Technology Corp., >99%), C_{60} (Sigma Aldrich, 99.9%), BCP (Luminescence Technology Corp., >99%)), MoO_3 (Alfa Aesar, 99.9995%), and top cathode (Ca (Alfa Aesar, 1 cm shots, 99.5%), Al (Alfa Aesar, 3.175 mm slug, 99.999%)) were thermally evaporated through shadow masks at a chamber pressure of 2×10^{-6} Torr at rates of 1.0 Å/s. C_{60} was purified once via thermal gradient sublimation before use. DBP, BCP, MoO_3, and Al were used as received. Pre-patterned ITO (Thin Film Devices, 20 Ω/sq) substrates were cleaned by solvents followed by 30 sec of O_2 plasma (100W, Plasma Preen, Inc.). Patterned graphene substrates were cleaned by annealing at 500 °C for 30 min under H_2 (700 sccm) and Ar (400 sccm). The device area defined by the opening of the shadow mask was 1.21 mm^2.

Measurements. Scanning electron microscopy was performed with a Helios Nanolab 600 at 5 kV and the transmittance was measured from the UV-Vis_NIR spectrometer (Cary 5000, Varian). Current-voltage measurements were recorded by a Keithley 6487 picoammeter in nitrogen atmosphere. 100 mW cm^{-2} illumination was provided by 150W xenon arc-lamp (Newport 96000) filtered by an AM 1.5G filter.

Scanning Kelvin probe microscope (SKPM). The surface potentials (V_{sur}) of PEDOT:PSS with and without IPA were measured by a dual-pass technique in tapping mode using the scanning Kelvin probe method (SKPM) based on an AFM system Dimension 3000 from Veeco Metrology Group with NanoScope Signal Access Module. The measurement was conducted in air with Olympus (OMCL-AC240TM) Pt-coated cantilevers. The tip curvature radius is ~15 nm, quality factor ~190, spring constant 2 N/m, resonance frequency ~70 kHz, and cantilever length 240 μm. The contact potential difference (CPD) value between tip and sample surface was reordered. The standard deviation of the experiment was ~10 mV.

The surface potential study was performed by a dual-pass technique in tapping mode. Topography information (AFM image) was acquired in the first scan; the second scan was then performed while the tip was maintained at a constant distance (10 nm above the sample surface). Both a DC signal and an AC signal at the resonant frequency of the cantilever are applied to the metal-coated AFM probe while the tip is lifted up. If a potential difference (ΔV_{sur}) exists between the tip and the sample surface, the signal creates a varying electrostatic force, causing an oscillating motion in the cantilever. The ΔV_{sur} is measured by adjusting the DC voltage until there is no DC potential difference. The DC voltage is recorded as the CPD value. Since the CPD value can be affected by the stability of the work function of AFM tip and is also sensitive to the measurement environment, such as humidity and electric grounding, we perform the measurement for various samples in sequence without changing the AFM tip.

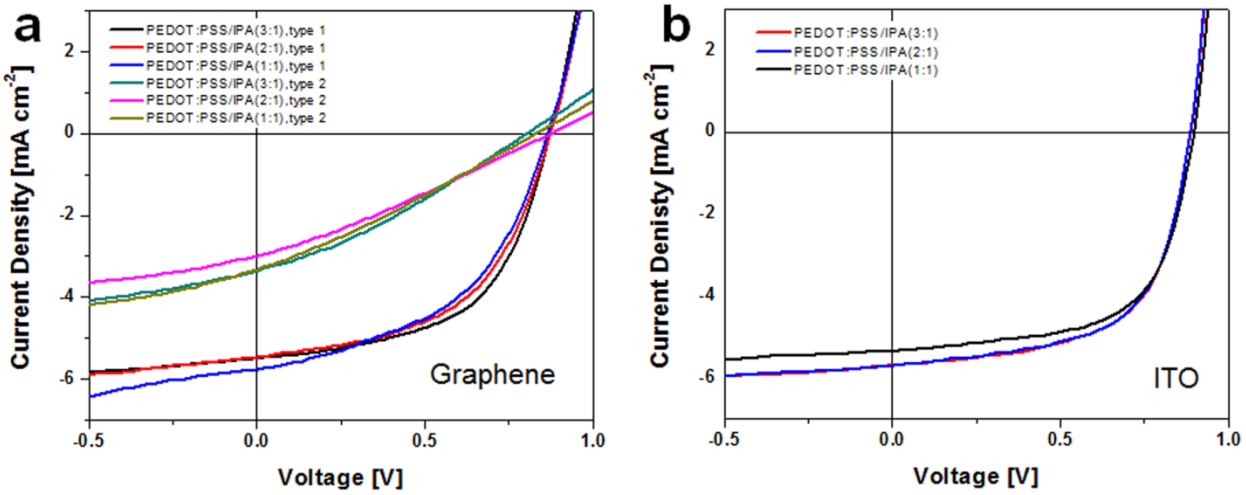

Figure S1 *J-V* characteristics of representative graphene/ITO OPV devices (Graphene, ITO/PEDOT (40nm)/DBP, 25nm/C_{60}, 40nm/BCP, 8.5nm/Al, 100nm) with different mixing ratios of PEDOT:PSS/IPA under AM 1.5G illumination at 100 mW/cm^2. (a) Graphene devices with different mixing ratios of PEDOT:PSS/IPA (3:1/2:1/1:1, v/v) HILs (type 1 and 2) showing similar improvements in the photo-response. (b) ITO reference devices with various mixing ratios of PEDOT:PSS/IPA (3:1/2:1/1:1, v/v) HILs.

Table S1 Summary of photovoltaic parameters of graphene and ITO devices shown in Figure S1, indicating champion and average values.

Anode	HTL	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
ITO	PEDOT:PSS/IPA (3:1)	5.70 (5.62±0.09)	0.89 (0.88±0.01)	0.61 (0.60±0.01)	3.08 (2.96±0.10)
ITO	PEDOT:PSS/IPA (2:1)	5.72 (5.60±0.11)	0.89 (0.88±0.01)	0.61 (0.60±0.01)	3.08 (2.94±0.09)
ITO	PEDOT:PSS/IPA (1:1)	5.35 (5.21±0.12)	0.90 (0.90±0.01)	0.62 (0.62±0.00)	2.97 (2.91±0.08)
Graphene	PEDOT:PSS/IPA (3:1), type 1	5.49 (5.36±0.13)	0.87 (0.87±0.01)	0.56 (0.53±0.02)	2.65 (2.47±0.13)
Graphene	PEDOT:PSS/IPA (3:1), type 2	3.35 (3.17±0.18)	0.80 (0.72±0.06)	0.31 (0.30±0.01)	0.83 (0.69±0.11)
Graphene	PEDOT:PSS/IPA (2:1), type 1	5.47 (5.38±0.12)	0.87 (0.87±0.02)	0.52 (0.51±0.01)	2.49 (2.39±0.07)
Graphene	PEDOT:PSS/IPA (2:1), type 2	2.98 (2.87±0.14)	0.87 (0.85±0.03)	0.28 (0.28±0.00)	0.74 (0.68±0.06)
Graphene	PEDOT:PSS/IPA (1:1), type 1	5.76 (5.62±0.09)	0.87 (0.87±0.01)	0.48 (0.47±0.02)	2.39 (2.30±0.11)
Graphene	PEDOT:PSS/IPA (1:1), type 2	3.32 (3.20±0.13)	0.83 (0.78±0.05)	0.28 (0.28±0.00)	0.78 (0.71±0.08)