Supporting Information

Flexible graphene electrode-based organic photovoltaics with record-high efficiency

Hyesung Park^{1,2†}, Schoon Chang^{2†}, Xiang Zhou², Jing Kong^{1*}, Tomás Palacios^{1*}, Silviya Gradečak^{2*}

¹ Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

² Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

* Corresponding author email address: jingkong@mit.edu; tpalacios@mit.edu;
gradecak@mit.edu

† These authors contributed equally to this work.

1. MoO₃ annealing with varying temperature

Annealing temperature (°C)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
100	15.0	0.68	45.7	4.7
150	14.4	0.69	64.6	6.4
200	13.6	0.65	64.5	5.7

Figure S1. MoO₃ morphology and device performance of ITO/MoO₃/PTB7:PC₇₁BM/Ca/Al at various MoO₃ annealing temperatures. J - V characteristics recorded under 100 mW cm⁻² AM1.5G illumination.

Various annealing temperatures of MoO₃ electron blocking layer (EBL) were investigated by considering the solvent resistance of the MoO₃ film and T_g of PEN substrate for flexible devices. Uniform morphology of the MoO₃ film was maintained after annealing (above 150°C) even upon the spin-coating of chlorobenzene (CB) with 1,8-diiodooctane (DIO). Therefore, our devices were annealed at 150°C, which results in robust MoO₃ EBL resistant to the solvent erosion. We note that annealing at higher temperatures above 200°C was not considered for our device fabrication since annealing above T_g of PEN (155°C) causes the deformation of the flexible devices and degradation of PEDOT:PSS layer (~235°C for PEDOT)¹.

2. ZnO ETL deposition with various solvents

Conventional way to deposit ZnO layer is by spin-coating zinc acetate dihydrate dissolved in 2-methoxy ethanol with ethanolamine followed by annealing above 175 °C to convert zinc acetate into ZnO form². However, zinc acetate in 2-methoxy ethanol does not form uniform coating on graphene surface due to the stable and hydrophobic nature of graphene³ (Supplementary Figure S2.). To overcome this issue, various other solvents were investigated such as ethanol, or nitromethane to achieve uniform coverage of ZnO electron transporting layer on graphene, which is necessary for the efficient charge transfer at the interface. Zinc acetate dissolved well in ethanol, methanol, and 2-methoxyethanol, but not in nitromethane, so zinc acetate in nitromethane was excluded for further study. After spin-coating zinc acetate in various solvents, we discovered only zinc acetate in methanol without the aid of stabilizer results highly uniform ZnO film (20 nm) on graphene surface (Supplementary Figure S2d,g), which consequently produced the promising device performances in our study.

Figure S2. (a) Zinc acetate dissolved in various solvents. (b-d) Scanning electron micrographs and (e-g) optical micrograph of ZnO spin-coated on graphene with various solvents utilized.

3. Inverted cathode-based devices fabricated on graphene electrodes without the ZnO layer

Figure S3. Device performance of graphene/PTB7:PC₇₁BM/MoO₃/Ag. J – V characteristics recorded under 100 mW cm⁻² AM1.5G illumination.

Table S1. Summary of photovoltaic performance parameters of graphene- and ITO-based devices, indicating values from champion devices and the average results shown in Fig. 1 and Fig. 4.

Anode	Hole transport layer	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
ITO (quartz)	PEDOT:PSS	17.3 (17.2±0.5)	0.74 (0.74±0.00)	62.9 (62.6±1.3)	8.0 (7.9±0.1)
ITO (quartz)	PEDOT:PSS/ MoO ₃	2.6 (2.5±0.1)	0.57 (0.57±0.00)	31.3 (30.3±1.7)	0.5 (0.4±0.1)
ITO (quartz)	PEDOT:PSS/ MoO ₃ (anneal)	16.1 (16.3±0.2)	0.68 (0.68±0.00)	60.7 (60.1±0.5)	6.7 (6.6±0.1)
Graphene (quartz)	PEDOT:PSS-IPA/ MoO ₃ (anneal)	15.7 (15.7±0.3)	0.67 (0.67±0.01)	58.6 (55.0±2.2)	6.1 (5.8±0.2)
Graphene (PEN)	PEDOT:PSS-IPA/ MoO ₃ (anneal)	14.4 (14.3±0.2)	0.72 (0.69±0.05)	58.7 (57.0±2.9)	6.1 (5.6±0.3)

Table S2. Summary of photovoltaic performance parameters of graphene- and ITO-based devices, indicating values from champion devices and the average results shown in Fig. 3 and Fig. 4.

Cathode	Electron transport layer	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
ITO (quartz)	ZnO	14.3 (13.7±0.5)	0.73 (0.73±0.00)	72.8 (73.0±0.8)	7.6 (7.3±0.2)
Graphene (quartz)	ZnO	14.0 (13.9±0.1)	0.72 (0.71±0.00)	68.6 (66.8±2.6)	6.9 (6.6±0.3)
Graphene (PEN)	ZnO	14.1 (13.9±0.7)	0.72 (0.72±0.01)	69.5 (68.2±1.8)	7.1 (6.8±0.3)

Table S3. Summary of photovoltaic performance parameters of graphene-based devices, indicating values from champion devices and the average results shown in Fig. 4.

Anode	Flexing cycles	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
Graphene (PEN)	0	13.7 (13.9±0.3)	0.67 (0.66±0.02)	65.3 (61.5±3.3)	6.0 (5.7±0.3)
Graphene (PEN)	20	14.9 (14.3±0.6)	0.71 (0.69±0.02)	56.8 (58.0±2.7)	6.0 (5.7±0.3)
Graphene (PEN)	50	14.9 (14.3±0.5)	0.71 (0.67±0.04)	58.1 (57.8±3.1)	6.2 (5.6±0.6)
Graphene (PEN)	100	14.8 (14.2±0.8)	0.71 (0.67±0.04)	57.6 (58.4±1.4)	6.1 (5.6±0.5)

References

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