Improved uniformity in high-performance organic photovoltaics enabled by (3-aminopropyl)triethoxysilane cathode functionalization

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Organic photovoltaics (OPVs) have recently attracted significant interest as potential enablers of large-scale renewable electricity generation. Their feasibility for low-cost production stems from inexpensive materials synthesis, fabrication via solution processable deposition techniques, and the possibility of high throughput, roll-to-roll manufacturing on flexible substrates. Unlike their inorganic counterparts, OPVs function as excitonic solar cells, in which light absorption generates a bound excited state rather than free charge carriers. The first demonstration of a planar heterojunction OPV consisted of electron donor and acceptor films sandwiched between an indium tin oxide (ITO) anode and a low work function metal cathode. Since then, considerable attention has focused on the bulk heterojunction (BHJ) architecture, consisting of an interpenetrating blend of the electron donor and acceptor materials, as this confronts the limitation that excitons have diffusion lengths far lower than the organic semiconductor optical absorption length. Since both active layers contact each electrode, interfacial layers (IFLs) are incorporated into the BHJ device architecture to facilitate carrier-selective charge extraction.

The recent introduction of the electron donor polymer poly[4,8-bis[2-ethylhexyl]oxy]benzo[1,2-b;4,5-b’]dithiophene-2,6-diyl]-[3-fluoro-2-[2-ethylhexyl]carbonyl]thieno[3,4-b]thieno[2,1-b]thiophene-2,6-diyl] (PTB7) in combination with the electron acceptor [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) has enabled power conversion efficiencies (PCEs) of ~7.5% for conventional OPV cells. Thereafter, PCEs were further enhanced up to 8.4% by employing an inverted device geometry with the PTB7:PC$_{71}$BM system, where an n-type zinc oxide (ZnO) IFL on ITO serves as the cathode and a molybdenum trioxide (MoO$_3$) IFL, in conjunction with the high work function metal, silver (Ag), serves as the anode. Moreover, replacing the ZnO electron transport layer (ETL) with a polymeric IFL in an otherwise identical device architecture yields a record PCE of 9.2%.

Interest in inverted OPV stems primarily from increased durability versus conventional devices, since the use of the ubiquitous and corrosive IFL poly-3,4-ethylenedioxy-thiophene:poly(styrenesulfonate) (PEDOT:PSS) is avoided, which has been implicated as a factor limiting device lifetime. Moreover, the donor and acceptor materials typically phase separate preferentially at their appropriate electrodes in inverted OPVs. While inverted OPVs offer a promising route forward, device reproducibility remains a challenge, leading to the common practice of reporting the “champion” PCE as the metric to evaluate new OPVs.

Herein, we demonstrate that (3-aminopropyl)triethoxysilane (APTES) cathode interfacial treatments significantly enhance
performance uniformity in inverted OPV cells. Specifically, we first show that APTES alone functions as an ETL in inverted OPV cells employing PTB7:PC71BM active layers, and then evaluate 100 APTES-treated devices and 100 untreated controls, employing a hybrid ZnO-C70 IFL, to demonstrate its beneficial effects on device reproducibility, where the fullerene layer is deposited on APTES-modified ZnO. APTES has been previously shown to have a marked affinity for carbon nanomaterials, which motivates its exploratory implementation here. In addition, APTES has been used in conventional OPVs to bind gold nanoparticles to ITO for plasmonically enhanced device performance and as a template for active layer phase segregation.

There are, however, few examples of APTES being employed in inverted OPV cells, with one notable exception, where substitution of an ZnO IFL with APTES led to superior PCE for a poly[4,8-bis-alkoxy-benzol[1,2-b:4,5-b’]dithiophene-2,6-diy-alt-4-(alkyl-1-one)-thieno[3,4-b]thiophene-2,6-diy]- (PBDTTT-C):[6,6]-phenyl-C61-butyric acid methyl ester (PC71BM) active layer. In contrast, we present the first application where APTES is employed to boost both device reproducibility and efficiency in a high-performance inverted OPV system, suggesting that advances in IFL engineering will not only enhance PCE, but also improve device uniformity as is required for widespread OPV deployment.

2. Experimental

Substrate cleaning

Patterned ITO (20 Ω sq⁻¹) on glass was purchased from Thin Film Devices Inc. The substrates were sonicated (50 °C) in aqueous detergent for 30 min, and then deionized water, methanol (MeOH), isopropanol (IPA), and acetone (ACE) for 20 min each. The substrates were further sonicated in MeOH, IPA, and ACE for 10 min each (50 °C), just prior to device fabrication. All devices employing a ZnO IFL were subsequently subjected to 5 min of oxygen (O2) plasma (Harrick Plasma, Basic Plasma Cleaner) at 100 mTorr. Otherwise, the as-sonicated ITO was subjected to a 10 min ultraviolet (UV) ozone treatment (Jelight Inc., Model 42) under ambient atmosphere.

ZnO film deposition

A 0.50 M ZnO sol gel solution was prepared by mixing 440 mg of zinc acetate dihydrate (Zn(CH3COO)2·2H2O), 99.999%, Sigma-Aldrich) with 4.0 mL of 2-methoxyethanol (CH3O–CH2CH2OH, anhydrous, 99.8%, Sigma-Aldrich). To this, 124 mg of ethanolamine (NH2CH2CH2OH, ≥ 99%, Sigma-Aldrich) was added as a stabilizer. The solution was sonicated for a few minutes at ambient temperature and then allowed to age for at least overnight prior to use. Next, 1.0 mL of this solution was added to 50 mL of 2-methoxyethanol to afford a ~0.10 M ZnO precursor solution. This solution was then filtered through a 0.45 μm polyvinylidene difluoride (PVDF) filter and spun at 4000 rpm for 40 s onto the O2 plasma treated ITO in a dry box, with ≤ 5% relative humidity. The spun cast substrates were then placed onto a hot plate (180 °C) for at least 10 min. Non-APTES-modified substrates were immediately transferred to a nitrogen-filled glove box.

APTES treatment

Approximately 40 mL of IPA (ACS grade) was added to a 50 mL polypropylene beaker (Fisherbrand). A micropipette was used to add 50 μL of APTES (H2N(CH2)3Si(OC2H5)3, 99%, Sigma-Aldrich) and the mixture was stirred with tweezers (0.125 vol% APTES). The prepared substrates were then submerged in this solution (no more than four substrates were placed into one beaker). The beakers were covered with aluminium foil during the APTES treatment. Once complete, the substrates were removed, rinsed with IPA, and immediately blown dry with nitrogen. Once removed from the APTES-IPA solution, the substrates were promptly transferred to the glovebox. Both control and APTES-modified substrates were stored in the glovebox until solar cell fabrication was finished. Samples were also prepared on silicon dioxide (SiO2) for thickness characterization on a J.A. Woollam M2000U spectroscopic ellipsometer.

X-Ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific ESCALAB 250Xi system using a monochromated Al Kα X-ray source at hν = 1486 eV with a base pressure of 8 × 10⁻¹⁰ mbar (UHV).

C70 deposition

A 3 nm C70 layer (Alfa Aesar, 99+%) was deposited at ~0.4 Å s⁻¹ in a glovebox-enclosed thermal evaporator with a chamber pressure of ~2 × 10⁻⁶ Torr.

Active layer

The active layer was prepared by dissolving PTB7 (1-material) and PC71BM (American Dye Source) at a concentration of 10 mg mL⁻¹ (1.0:1.5 ratio by weight) in a 0.97/0.03 (mL mL⁻¹) solution of chlorobenzene:1,8-diodooctane (Sigma-Aldrich). This solution was stirred under nitrogen at ~65 °C for two days to ensure complete dissolution. This solution was then spun cast (unfiltered) onto the as-prepared substrates at 1500 rpm for 30 s in a glovebox.

MoO3 and Ag deposition

A dry cotton swab was used to etch the active layer, defining a contact area for the thermally evaporated electrodes. The substrates were loaded into a glovebox-enclosed thermal evaporator, which was subsequently pumped down to ~3 × 10⁻⁶ Torr. MoO3 (10 nm, 99.999%) and Ag (100 nm, 99.99%) were deposited sequentially without breaking vacuum at rates of ~0.2 Å s⁻¹ and 1.5–2 Å s⁻¹, respectively. Both materials were deposited through a shadow mask to define a cathode bus bar and four 0.06 cm² devices per substrate (the device area was 0.12 cm² for the devices in this study not having a ZnO IFL). Before removal from the glovebox, the devices were encapsulated using a glass slide and UV-curable ELC-2500 epoxy, which was cured for 10 min in a UV chamber (Electro-Lite).

Device evaluation

A Class A Spectra-Nova Technologies solar cell analyzer, employing a Xe lamp simulating AM 1.5G light from 400–1100 nm, was used.
to test the devices at ambient temperature. Spectral mismatch was brought close to unity via calibration with a monocrystalline Si diode fitted with a KG3 filter that was calibrated by the National Renewable Energy Laboratory. External quantum efficiency (EQE) measurements were performed using a Newport Oriel Quantum Efficiency Measurement Kit. All short-circuit current density values measured by the solar cell analyzer were EQE corrected, using the Open Photovoltaics Analysis Platform program. The solar cell analyzer was also used to obtain dark current–voltage data, which were analyzed using a web-enabled tool “PV Analyzer”.

3. Results

Shown in Fig. 1a are the chemical structure of APTES and a representation of an APTES-modified electrode. Once APTES is mixed with the ACS grade IPA, it undergoes hydrolysis of the Si–O–Et groups. Following hydrolysis, the organosilane first chemisorbs to the substrate via hydrogen-bonding between the organosilane SiOH groups and substrate surface OH groups. This step is followed by condensation reactions to form covalent bonds between the organosilane and the substrate surface.12 Fig. 1b and c show nitrogen (N) 1s XPS spectra of ITO/glass and APTES (1 h treatment time)/ITO/glass, respectively, with the latter N 1s peak indicative of surface-bound APTES.

The APTES-modified ITO was employed as a substrate for OPV device fabrication using PTB7:PC71BM as the active layer. The structure of PTB7 and a representation of PC71BM are shown in Fig. 2a, and the inverted OPV device architecture is detailed in Fig. 2b, where APTES/ITO functions as the cathode and MoO3/Ag as the anode. Shown in Fig. 2c are the champion current–voltage (J–V) curves for different APTES treatment times. The champion cell efficiency parameters are summarized in Table 1, including the short-circuit current density (JSC), open-circuit voltage (VOC), fill factor (FF), and PCE (η). Note that under AM 1.5G illumination, the PCE is given by the product of VOC, JSC, and FF. The APTES treatment leads to an increase in device PCE, with the best device yielding a PCE of 6% for the three-hour treatment time.

Since ZnO and MoO3 have been previously employed as IFLs in high efficiency inverted OPVs employing the PTB7:PC71BM active layer,14,33 we proceeded to self-assemble APTES on ZnO/ITO. The XPS spectra in Fig. 3a and b show the N 1s signal for ZnO/ITO/glass and APTES (1 h treatment time)/ZnO/ITO/glass, respectively. Similar to the APTES-treated ITO, there is a clear N 1s signal for the APTES-treated ZnO.

In addition to introducing ZnO, a thin fullerene layer (3 nm of C70), as detailed in Fig. 4a, was also incorporated in these
inverted cells. Next, 100 devices with the three-hour APTES IFL treatment (carried out after ZnO spin casting) were fabricated, as were 100 devices without the interfacial treatment. Shown in Fig. 4b are the champion current density–voltage ($J$–$V$) curves with and without the APTES IFL. Spectral ellipsometry measurements (previously used to characterize APTES films\textsuperscript{34}) indicate that the APTES thickness is approximately 10 nm on both bare SiO$_2$ and ZnO-modified SiO$_2$. The APTES treatment leads to a slight PCE increase, with the best APTES device now exhibiting an 8.30% PCE and the best non-APTES device exhibiting an 8.13% PCE. Frequency histograms for the 100 devices are shown in Fig. 4c (non-APTES) and Fig. 4d (with APTES). Qualitative examination of both histograms reveals that the APTES interfacial treatment consistently suppresses the underperforming tail of the distribution. This observation is quantitatively confirmed by the reduced skewness for the APTES distribution (−0.291) in comparison to the non-APTES distribution (−1.86). Moreover, the average PCE of the 100 APTES devices (8.08%) surpasses the average PCE of the 100 non-APTES devices (7.80%). Table 2 details the average PCE parameters for both APTES and non-APTES distributions and includes the standard deviation and skewness for each PCE parameter. The contrast in the average PCE for the APTES and non-APTES distributions can be attributed to reproducible differences in the $J_{SC}$ and FF values.

Dark $J$–$V$ data were also collected for both device distributions. Shown in Fig. 5a are representative $J$–$V$ curves, qualitatively demonstrating a case where an APTES device has lower current in the shunting (leakage) current region than a non-APTES device.\textsuperscript{13} The dark current data were analyzed using the Space-Charge Limited (SCL) current conduction model (dark current data for thin film solar cells is typically described as a parallel combination of a parasitic shunt current and an exponential diode current, \textit{i.e.} $I_{Dark} = I_{Shunt} + I_{Diode}$).\textsuperscript{23} In particular, the pre-factor from the SCL formula $I_{SHO}$ (eqn (1)) was extracted for all 200 devices (where $V$ is the applied bias, and $\gamma$ is determined by the shallow trap distribution in the absorber\textsuperscript{35}) using the PV Analyzer.\textsuperscript{31} Shown in Fig. 5b and c are frequency histograms of $\ln(I_{SHO})$ for the non-APTES distribution and the APTES distribution, respectively. The positive skewness for the devices (where $V$ is the applied bias, and $\gamma$ is determined by the shallow trap distribution in the absorber\textsuperscript{35}) using the PV Analyzer.\textsuperscript{31} Shown in Fig. 5b and c are frequency histograms of $\ln(I_{SHO})$ for the non-APTES distribution and the APTES distribution, respectively. The positive skewness for the...
non-APTES devices indicates that the distribution has a tail towards higher shunt currents, whereas the negative skewness for the APTES devices indicates that the distribution has a tail towards lower shunt currents.

4. Discussion

APTES is typically used to assist in binding carbon nanomaterials to various substrates, due to its affinity for carbon nanotubes, and has been used to create uniform nanotube networks. With this in mind, we chose to incorporate a 3 nm C70 layer in the high efficiency device architecture explored here, shown in Fig. 4a. The APTES-modified ZnO could potentially yield a more uniform C70 deposition, as the fullerene is the zero-dimensional analogue to a carbon nanotube. Moreover, incorporating fullerene layers between the device active layer and cathode has been shown to enhance performance and reproducibility via enhanced electron collection. In addition, interfacial modifications to metal oxides have been previously used to enhance inverted cell OPV performance, when incorporated at the metal oxide-active layer interface, and even at the metal oxide–electrode interface. The XPS spectrum shown in Fig. 1c indicates the presence of APTES on ITO. We note that XPS has been used previously to assess the presence of APTES, and that organosilane coupling to tin oxide substrates has been previously reported, including APTES on ITO.

The J–V curves shown in Fig. 2c clearly indicate that differing APTES treatment times lead to variations in device PCE. It is likely that the APTES layer thickness is different for the five cases tested here. We do not assert that layer thickness should increase concomitantly with treatment time, since the organosilane layer can be detached due to amine catalyzed hydrolysis of siloxane bonds. Nevertheless, a respectable PCE of 6% is achieved for the three-hour treatment time. This observation can be attributed in part to APTES decreasing the magnitude of the ITO work function, which is the likely reason for the enhanced VOC and FF relative to the untreated device.

Note here that PCEs of ~7.5% can be achieved in conventional PTB7:PC71BM OPV cells. Furthermore, PCEs exceeding 8% are possible using the PTB7:PC71BM system in an inverted device geometry, where ZnO acts as the ETL and MoO3 acts as the hole transport layer. Thus, APTES was deposited on ZnO/ITO, with the goal of realizing higher PCEs. In the case of APTES deposition on ITO, a brief 10 min UV ozone treatment preceded the APTES treatment, as this enhances the substrate surface hydrophilicity. The J–V curves shown in Fig. 2c clearly indicate that differing APTES treatment times lead to variations in device PCE. It is likely that the APTES layer thickness is different for the five cases tested here. We do not assert that layer thickness should increase concomitantly with treatment time, since the organosilane layer can be detached due to amine catalyzed hydrolysis of siloxane bonds. Nevertheless, a respectable PCE of 6% is achieved for the three-hour treatment time. This observation can be attributed in part to APTES decreasing the magnitude of the ITO work function, which is the likely reason for the enhanced VOC and FF relative to the untreated device.

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The non-APTES distribution exhibits log normal characteristics, with the tail of the distribution extending out toward lower PCE values. The inclusion of APTES essentially eliminates the under-performing tail of this distribution and reduces the standard deviation by a factor of two. Moreover, this study includes the effect of batch-to-batch variability since all 200 devices were fabricated over five experimental runs. It should be noted that there are few studies in the open literature that fabricate hundreds of OPV cells to explore reproducibility. In the more recent example, a respectable PCE and variability of 8.1 ± 0.4% was achieved for 102 inverted OPV cells, employing a composite ZnO ETL. The results here demonstrate that additional reductions in variability can be realized via hybrid IFL engineering.

To further explore the effect of including APTES, the OPV dark J–V data were analyzed. In particular, the shunt current coefficients were extracted for all devices in each distribution. We note the enhanced $J_{SC}$ and reduced standard deviation and skewness of the fill factor in Table 2 for the APTES distribution. This observation correlates with the positive skewness of the $I_{S(c)}$ histogram for the APTES distribution (Fig. 5b). On the other hand, the negative skewness for the non-APTES distribution (Fig. 5c) indicates that these devices tend to exhibit relatively higher shunt currents. A potential explanation for the modulation of the shunt current distribution is that APTES inclusion may reduce the electrical non-uniformity of the ZnO surface and planarize the contact work function. Another possibility is that APTES modifies the log-normal active layer grain size distribution. The reduction of the tail of higher shunt currents is promising, as this would reduce parasitic power consumption in OPV devices manufactured at the module scale.

5. Conclusions

In this work, we have demonstrated that APTES alone can function as an ETL in inverted OPV cells employing a PTB7:PC$_{71}$BM active layer. We have also shown that APTES can self-assemble on ZnO films, enabling the fabrication of 100 APTES-treated devices and 100 untreated controls in OPV cells employing a hybrid ZnO–C$_{70}$ ETL. The results quantitatively reveal that APTES improves OPV uniformity and reproducibility, thus establishing that proper IFL engineering can advance OPV feasibility for large-scale manufacturing.

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