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High-Performance Silver Window Electrodes for Top-Illuminated Organic Photovoltaics Using an Organo-molybdenum Oxide Bronze Interlayer

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§Supporting Information

ABSTRACT: We report an organo-molybdenum oxide bronze that enables the fabrication of high-performance silver window electrodes for top-illuminated solution processed organic photovoltaics without complicating the process of device fabrication. This hybrid material combines the function of wide-band-gap interlayer for efficient hole extraction with the role of metal electrode seed layer, enabling the fabrication of highly transparent, low-sheet-resistance silver window electrodes. Additionally it is also processed from ethanol, which ensures orthogonality with a large range of solution processed organic semiconductors. The key organic component is the low cost small molecule 3-mercaptopropionic acid, which (i) promotes metal film formation and imparts robustness at low metal thickness, (ii) reduces the contact resistance at the Ag/molybdenum oxide bronze interface, (iii) and greatly improves the film forming properties. Silver electrodes with a thickness of 8 nm deposited by simple vacuum evaporation onto this hybrid interlayer have a sheet resistance as low as 9.7 Ohms per square and mean transparency ~80% over the wavelength range 400–900 nm without the aid of an antireflecting layer, which makes them well-matched to the needs of organic photovoltaics and applicable to perovskite photovoltaics. The application of this hybrid material is demonstrated in two types of top-illuminated organic photovoltaic devices.

KEYWORDS: electrode, photovoltaic, top-illuminated, molybdenum oxide, charge transport layer

INTRODUCTION

It is widely recognized that the full-cost advantage of solution processed organic and perovskite photovoltaics (OPV and PPV) over conventional crystalline silicon PV will only be achieved if an alternative to the conducting oxide coated glass electrodes used in the current generations of OPV and PPV is forthcoming. This is primarily because conducting oxides are poorly compatible with low cost roll-to-roll manufacturing processes. One promising approach to address this challenge is to fabricate devices with a top-illuminated architecture, using an optically thin metal film as the transparent top electrode, which removes the need for conducting oxide coated glass and increases the range of potential applications by giving more flexibility in terms of the materials used as the supporting substrate. For example, for integrating PVs into buildings and vehicles it is desirable to fabricate onto flexible steel or Al substrates rather than glass. Vacuum evaporation is well-established in the packaging industry as a low cost, large area deposition method for the fabrication of thin metal films and is compatible with roll-to-roll deposition onto flexible substrates, as well as offering the necessary high degree of control over metal film thickness. The potential of this approach to achieve comparable device performance to conventional device architectures based on a conducting oxide window electrode has been demonstrated in wholly vacuum deposited small molecule OPVs by the group of Leo, using Ag as the base metal for the transparent electrode. Ag is the metal of choice for this application because it has the highest conductivity and the lowest optical absorbance of the earth abundant metals over the visible spectrum, combined with relatively high stability toward oxidation in air. However, Ag also has a high surface energy and so thin films of this metal have a high percolation thickness of >10 nm, below which they form a discontinuous island like structure which is poorly conductive, and strongly absorbs visible light due to excitation of localized surface plasmons. This limitation is particularly pronounced when evaporating Ag onto polymer and small molecule semiconductors because Ag tends to bind weakly to these classes of materials and the high surface energy of Ag is a powerful driver for the formation of Ag nanoparticles.

In practice, for PV applications the sheet resistance of the window electrode cannot realistically exceed 10 Ω sq⁻¹ without incurring an unacceptable loss in device fill-factor or requiring a relatively dense array of opaque current carrying bus-bars. Additionally, the electrode transparency across the wavelength range 2λ = 400–900 nm must be ≥80% to be competitive with a 10 Ω sq⁻¹ conducting oxide coated glass (e.g., F:SnO₂ and Sn:In₂O₃). In recent years Schubert et al. and Yang et al.

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have shown that it is possible to achieve a sheet resistance of ~19 and ~16 Ω sq⁻¹ respectively for sub-10 nm Ag window electrodes in top-illuminated OPV and PPVs, with peak transparencies of ~80%, although with much lower transparency in other useful parts of the spectrum. In both cases the Ag electrodes were fabricated by depositing a 1 nm Au seed layer immediately prior to Ag deposition. The disadvantages of that approach are (i) the cost incurred by adding an extra step to the fabrication process; (ii) and the use of Au which is almost certainly too costly to be used in PV applications, even at such a low thickness.14 It is also unclear as to the extent to which the stability of the Ag window electrode is affected when using a 1 nm Au seed layer. Co-depositing Ag with Ca in conjunction with a 1 nm Al seed layer has also been shown to be a promising approach to enable the fabrication of Ag-based window electrodes for top-illuminated OPV, offering a transparency greater than 90% over a large portion of the visible spectrum. However, the sheet resistance of these Al:Ca:Ag electrodes; 27.3 Ω sq⁻¹, is arguably too high to be implemented in PVs, and the susceptibility of Ca to oxidation is a major drawback.15 What is needed is a means of enabling the formation of highly conductive, sub-10 nm Ag films on the top surface of OPV and PPVs that does not complicate the process of device fabrication and is applicable to solution processed device architectures, since it is widely regarded that solution processing offers the lowest cost path to PV device fabrication.16,17

Herein, we report the development of an organo-molybdenum oxide bronze, MPA:H₂MoO₃ₓ−ₓ, where MPA is 3-mercaptopropionic acid, that combines the function of wide band gap interlayer for the efficient extraction of holes from organic semiconductors, with the role of seed layer for the formation of robust sub-10 nm Ag films for top-illuminated solution processed PV devices. Transition metal charge extraction layers, including transition metal bronzes,18,19 are an essential component of high performance OPVs20,21 and so, unlike the use of an ultrathin Au interlayer, the hybrid reported herein does not complicate the process of device fabrication. Additionally, the composite is processed from ethanol which is environmentally sustainable and ensures orthogonality with a large range of solution processed organic semiconductors.

RESULTS AND DISCUSSION

MoO₃ₓ−ₓ is one of the most widely used hole-extraction materials in organic electronics and is typically deposited by vacuum evaporation, although solution processing methods, which invariably include a postdeposition annealing step, have also begun to emerge.17,21-24 Depositing very thin films (i.e., 5–10 nm) of metal oxides from solution directly onto organic semiconductors is particularly challenging due to the need for solvent orthogonality between layers and the constraint on postdeposition annealing temperature imposed by the underlying organic semiconductor. One transition metal oxide that has been successfully applied from solution directly onto the surface of organic semiconductors is molybdenum oxide bronze, H₂MoO₃ₓ−ₓ.18,25,26 Herein the method used for H₂MoO₃ₓ−ₓ synthesis is an adaptation of this approach, modified to include additional heating steps and an increased reaction time, as detailed in the Experimental Section. In this wide band gap semiconductor oxygen vacancies and hydrogen serve as deep and shallow n-type dopants, respectively.26 MPA was added to alcoholic solutions of H₂MoO₃ₓ−ₓ and all films were briefly annealed at 80 °C under nitrogen to remove residual solvent. Because of the very mild annealing temperature thin films of this material are essentially amorphous as shown by the absence of well-defined peaks in the X-ray diffraction pattern (Figure S1).

X-ray photoelectron spectroscopy (XPS) was used to determine how incorporation of MPA into H₂MoO₃ₓ−ₓ alters its electronic structure. All spectroscopic characterization was performed for samples with loadings of 0.29 or 0.86 MPA molecules per Mo atom, which was found to be the optimal loading for OPV applications, as detailed in subsequent sections of this paper. It is evident from the high resolution XPS (HRXPS) spectrum of the Mo 3d region of H₂MoO₃ₓ−ₓ without MPA, (Figure 1a) that Mo is present in both the 6+ and 5+ oxidation states. The ratio of the Mo 3dₓ₋ₓ₂ peaks at ~232.6 and ~231.4 eV, which are assigned to Mo⁶⁺ and Mo⁵⁺ respectively, is 1:0.6, which yields a mean Mo oxidation state of 5.62. The O 1s region of the spectrum (Figure 1c) can be fitted with two components at ~530.4 and ~531.4 eV which are assigned to Mo−OH and Mo−O−Mo (or Mo=O) chemical environments, respectively,22,23,27 If it is assumed that hydrogenation is the only source of reduction, then the average Mo oxidation state calculated from the O 1s peak intensities is 5.67. The difference between this value and the actual value of 5.62, determined from the Mo⁶⁺:Mo⁵⁺ peak intensities, can be assigned to the presence of oxygen vacancy defects and so the average stoichiometry of the bronze is estimated to be H₂₇₋ₓMo₂₉₊ₓ.

It is evident from Figure 1b that addition of MPA results in a further reduction in the average Mo oxidation state because the Mo⁶⁺:Mo⁵⁺ ratio is reduced to 5.51 for an MPA:Mo loading of 0.86:1. The O 1s region for H₂MoO₃ₓ−ₓ with MPA (Figure 1d) includes three additional peaks corresponding to two oxygen environments in carboxylic acid; C=O (531.9 eV) and C−OH (533.4 eV),28 and one in deprotonated carboxylic acid; COO− (530.7 eV).26 By constraining the Mo−O and Mo−OH peak positions and widths to those in Figure 1c and assuming a MPA:H₂MoO₃ ratio of 0.86:1 (confirmed from the XPS survey scan), the deconvolution of the O 1s peak is as given in Figure 1d. It is evident from Figure 1(d) that the peak attributed to...
Mo–OH at 531.5 eV has increased in intensity with respect to the Mo=O peak at 530.5 eV, which is further evidence for the reduction of $\text{H}_2\text{MoO}_4$ by MPA. It is also evident that there is a significant amount of deprotonated MPA in the $\text{H}_2\text{MoO}_4$ film and so the additional Mo reduction upon doping with MPA can be attributed to donation of hydrogen by the carboxylic acid group resulting in the formation of Mo–OH. The HRXPS spectrum of the S 2p region (Figure S2) is consistent with this conclusion, since the sulfur is primarily present as untreated thiol.

The ultraviolet photoelectron spectroscopy (UPS) spectra shown in Figure 2 corroborates the conclusion that MPA serves as a source of hydrogen, and therefore as a shallow n-type dopant, since the energy difference between the Fermi level ($E_F$) and the valence band (VB) edge increases from $\sim$3.21 eV with no MPA, to $\sim$3.35 eV and $\sim$3.61 eV with increasing MPA loading. The two small peaks in the bandgap, labeled $d_{1s}$ and $d_{2p}$, can be assigned to occupied defect states due to hydrogen insertion and oxygen vacancies, since both are known to be present in reduced molybdenum oxides. The optical band gap of $\text{H}_2\text{MoO}_4$ was estimated to be $\sim$4.21 eV from the absorption spectrum by plotting $(\alpha h\nu)^2$ versus $h\nu$ in a Tauc plot (Figure S3). Upon addition of MPA the band gap was found to undergo a slight reduction to a value of $\sim$4.14 eV. The absorption coefficient of $\text{H}_2\text{MoO}_4$ films is increased from $\sim$0.2 to $\sim$0.3 m$^{-1}$ in the wavelength range $\lambda = 400–600$ nm and reduced by a commensurate amount for $\lambda = 600–900$ nm and so the mean value across the range $\lambda = 400–900$ nm is not significantly changed.

Addition of MPA to $\text{H}_2\text{MoO}_4$ also resulted in a reduction in its work function, as determined from the secondary-electron cutoff of the UPS spectra (Figure 2b) and measured using the Kelvin probe technique (KP). Figure 2c shows a schematic energy level diagram summarizing these data, along with the band gap estimated from absorption spectra Tauc plots (Figure S3). While UPS and KP show the same trend in work function, the measurements made using UPS are consistently lower than that measured using the KP. This difference can in part be explained by the fact that UPS is known to measure the lowest work function, while the KP technique measures the average work function under the probe. However, for UPS measurements the samples were also briefly exposed to the laboratory environment when loading into the UPS vacuum chamber, and so modification of the surface potential contribution to work function by surface contamination is likely. Conversely the KP measurements were made using a KP located in the same nitrogen filled glovebox as used for film deposition, and so measurements made using the KP technique are considered to be more reliable in this instance, a conclusion corroborated by the device studies described in a subsequent section of this paper. The work function measured using the KP is reduced from 6.33 eV ($\pm0.14$) for the $\text{H}_2\text{MoO}_4$ without MPA, to 5.66 eV ($\pm0.06$) and 5.29 eV ($\pm0.15$) after doping with MPA:Mo loadings of 0.29:1 and 0.86:1, respectively. Since the largest change in work function, $\Delta \approx 1.04$ eV, is much greater than the change in the position of $E_F$ in the bandgap (Figure 2c), the MPA must be acting to lower the surface potential contribution to the work function in addition to changing the chemical potential. A similar decrease in the work function of $\text{H}_2\text{MoO}_4$ upon n-type doping with Cs has been reported by Li et al. and in that case the change in work function was sufficiently large to enable its use as an electron extracting interfacial layer. For transition metal oxide hole-extraction layers efficient hole extraction from an organic semiconductor is only achieved when the oxide work function is higher or comparable to the ionization potential of the adjacent organic semiconductor. In this case, even for the highest MPA doping level tested, the work function of $\text{H}_2\text{MoO}_4$:MPA should still be sufficiently large to ensure optimized interfacial energy level alignment with the HOMO of most donor-type organic semiconductors. This conclusion is supported by the OPV device studies reported in a subsequent section of this paper.

Current–voltage analysis of unipolar diodes with the structure $\text{Au}/\text{H}_2\text{MoO}_4$/Ag (and Au) was used to determine the effect of MPA doping on the electrical conductivity of the bronze and its contact resistance with the Ag electrode (Figure S4a and b). For the $\text{Au}/\text{H}_2\text{MoO}_4$/Ag diode conductivities of $3.94 \times 10^{-3}$ ($\pm 0.53 \times 10^{-3}$), $3.80 \times 10^{-3}$ ($\pm 0.53 \times 10^{-3}$), and $4.33 \times 10^{-3}$ S m$^{-1}$ ($\pm 0.68 \times 10^{-3}$) were measured for films with a Mo:MPA loading of 1:0, 1:0.29 and 1:0.86 respectively. The small increase in the mean conductivity upon MPA doping is consistent with n-type doping and/or a reduction in contact resistance with the Ag electrode. Conversely, for the $\text{Au}/\text{H}_2\text{MoO}_4$/Au diodes conductivities of $1.50 \times 10^{-3}$ ($\pm 0.27 \times 10^{-3}$), $1.41 \times 10^{-3}$ ($\pm 0.35 \times 10^{-3}$), and $1.14 \times 10^{-3}$ S m$^{-1}$ ($\pm 0.13 \times 10^{-3}$) were measured for films with a Mo:MPA loading of 1:0, 1:0.29, and 1:0.86, respectively, and so the mean conductivity is slightly decreased with MPA loading, although again the change in conductivity with MPA loading is barely statistically significant even for the highest MPA loading. Taken together, these data show that there is a small reduction in

![Figure 2. UPS spectra of the valence band edge (a) and secondary-electron cutoff (b) of MPA:MoO$_{4-x}$ films with increasing MPA loading; (c) Energy levels of MoO$_{4-x}$ films with respect to the vacuum level (VL) for loadings of 1:0, 1:0.29, and 1:0.86 Mo:MPA derived from UPS, KP, and absorption spectra Tauc plots.](image-url)
conductivity of the bronze when MPA is added, which is more than offset by the reduction in contact resistance when Ag is used as the electrode.

To investigate the film forming properties when deposited directly onto organic semiconductors two widely used bulk-heterojunctions (BHJs) were used as model substrates; namely, PTB7:PC70BM and PCDTBT:PC70BM (full chemical names given in Experimental Section). The morphology of a ~10 nm H$_2$MoO$_3$-x film spin-cast directly onto a PTB7:PC70BM BHJ film, measured using atomic force microscopy (AFM), is shown in Figure S5, from which it is evident that addition of MPA dramatically reduces the film roughness: The root-mean-square roughness was reduced from 4.3 (±0.5) to 2.0 nm (±0.3). Conversely, H$_2$MoO$_3$-x films spun directly onto glass with and without MPA doping exhibit no significant difference in surface roughness (Figure S6) and so the difference in film roughness when deposited directly onto BHJ films can be attributed to improved wetting due to the presence of MPA, rather than suppression of aggregate formation in the H$_2$MoO$_3$-x solution when MPA is added. This marked improvement in film forming properties is evidence that the H$_2$MoO$_3$-x solution wets the organic semiconductor surface more readily when MPA is added, further evidence for which is provided by measurement of the static contact angle (Figure S7) of droplets of H$_2$MoO$_3$-x solution on PTB7:PC70BM BHJ films; <2° with 1:0.86 MPA doping vs 19.53° (±3.6) without. H$_2$MoO$_3$-x films spin-cast onto PCDTBT:PC70BM showed no significant difference in surface roughness, although static contact angle measurements provided evidence of improved wetting: 13.1° (±2.5) with 1:0.29 MPA doping and 18.6° (±1.8) without (Figure S7).

To fabricate Ag window electrodes with properties comparable to that in top-illuminated OPV devices Ag films of thickness 8 nm were thermally evaporated onto H$_2$MoO$_3$-x coated BHJ films supported on glass. Again the widely used BHJs PTB7:PC70BM and PCDTBT:PC70BM were used as model substrates. A Ag thickness of 8 nm was chosen because it was found to be the minimum needed to achieve the target sheet resistance ($R_{\text{sheet}}$) of ~10 Ω sq$^{-1}$, as measured using the Van der Paw method. The results from a representative batch of electrodes on PTB7:PC70BM films are shown in Figure 3a, which show that the mean $R_{\text{sheet}}$ is decreased from 14.8 (±2.2) to 11.1 Ω sq$^{-1}$ (±0.6) when MPA is added to H$_2$MoO$_3$-x (MPA:Mo ratio of 0.86:1). The decrease in $R_{\text{sheet}}$ correlates with a significant decrease in Ag film roughness, which is ~20% lower upon addition of MPA (Figure 4), primarily due to a smoother underlying Mo bronze layer (Figure S5). This reduction in electrode roughness inevitably decreases ohmic losses due to scattering of electrons, which offers a plausible explanation for the improvement in $R_{\text{sheet}}$ upon addition of MPA. In addition to the ~25% reduction in sheet resistance the addition of MPA to the Mo bronze also greatly improves the electrode stability: After 70 h storage in nitrogen (≤1 ppm of O$_2$ and H$_2$O) the $R_{\text{sheet}}$ of films supported on MPA doped H$_2$MoO$_3$-x was essentially unchanged at 11.5 Ω sq$^{-1}$ (±0.7) (Figure 3a). In contrast $R_{\text{sheet}}$ of Ag electrodes supported on H$_2$MoO$_3$-x without MPA was either in the range 18.3 Ω sq$^{-1}$ (±1.8) or too high to measure ($R_{\text{sheet}}$ ≥ 200 000 Ω sq$^{-1}$). The AFM images in Figure 4 (and Figure S8) show that the surface roughness of Ag films supported on H$_2$MoO$_3$-x without MPA greatly increases upon storage in nitrogen due to the formation of large aggregates which do not form when MPA is incorporated into the H$_2$MoO$_3$-x underlayer. This data supports the conclusion that the MPA serves as a molecular adhesive, helping to bind Ag atoms onto the H$_2$MoO$_3$-x and so counteract the thermodynamic instability in thin Ag films that stems from the high surface energy of this metal.

The stability of these films was further tested as a function of storage time in ambient air (20 °C and relative humidity 30–40%) (Figure 3a). After 70 h in air the sheet resistance of Ag films supported on MPA doped H$_2$MoO$_3$-x had increased from 10.2 (±0.8) to 20.4 Ω sq$^{-1}$ (±1.9). Without MPA the change was much more pronounced, since the $R_{\text{sheet}}$ increased from 13.7 (±2.1) to 51.1 Ω sq$^{-1}$ (±5.8). In both cases, the increase in $R_{\text{sheet}}$ did not correlate with an increase in surface roughness, presumably due to the formation of a constraining silver oxide capping layer.

To test the generality of these results the same experiment was performed using PCDTBT:PC70BM in place of...
PTB7:PC70BM. Again, the sheet resistance of the electrode is reduced when MPA is incorporated into the H$_2$MoO$_{3-x}$ layer, from 10.9 $\Omega$ sq$^{-1}$ (±0.4) without MPA to 9.7 $\Omega$ sq$^{-1}$ (±0.5) (MPA: Mo loading of 0.29:1), and for the latter there is no significant increase in the $R_{\text{sheet}}$ when stored under N$_2$, even after 384 h. However, in this case the electrode without MPA in the H$_2$MoO$_{3-x}$ layer also exhibits good stability when stored under N$_2$. This result is attributed to the lower surface roughness of the underlying BHJ film; ~1.6 nm PCDTBT:PC70BM vs ~2.8 nm for PTB7:PC70BM, which results in a smoother H$_2$MoO$_{3-x}$ layer, which in turn results in a smoother more compact Ag electrode with higher intrinsic stability due to a reduced surface area (Figure S9). Conversely, as shown in Figure 3b, the difference in the rate of electrode degradation in ambient air is very pronounced. After 400 h the $R_{\text{sheet}}$ of electrodes without MPA in the H$_2$MoO$_{3-x}$ layer increases by a factor of 20 times from 10.9 ($\pm$0.4) to 222.6 $\Omega$ sq$^{-1}$ (±18.8), whereas those with MPA increased by less than a factor of 3 from 9.7 $\Omega$ sq$^{-1}$ (±0.5) to 27.6 $\Omega$ sq$^{-1}$ (±1.5).

The lower $R_{\text{sheet}}$ reduced contact resistance and improved stability of the electrodes on both model BHJs upon incorporation of MPA into the H$_2$MoO$_{3-x}$ layer is consistent with improved adhesion at the bronze-Ag interface. XPS studies were conducted to probe the nature of this interaction by acquiring spectra before and after depositing an ultrathin Ag layer, which in turn results in a smoother more compact Ag electrode with higher intrinsic stability due to a reduced surface area (Figure S9). Conversely, as shown in Figure 3b, the difference in the rate of electrode degradation in ambient air is very pronounced. After 400 h the $R_{\text{sheet}}$ of electrodes without MPA in the H$_2$MoO$_{3-x}$ layer increases by a factor of 20 times from 10.9 ($\pm$0.4) to 222.6 $\Omega$ sq$^{-1}$ (±18.8), whereas those with MPA increased by less than a factor of 3 from 9.7 $\Omega$ sq$^{-1}$ (±0.5) to 27.6 $\Omega$ sq$^{-1}$ (±1.5).

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PCDTBT:PC70BM BHJ there is an also improvement in spectrum. Similarly, for OPV devices based on a that the improvement in PCE is due to an increased external quantum efficiency (EQE) upon MPA doping.38 It is evident from the efficiency (EQE) data for top-illuminated OPVs with the structure: AlCuAl|PTB7:PC70BM|MoO3|Ag (8 nm) (a and b) and AlCuAl|PCDTBT:PC70BM|MoO3|Ag (8 nm) (c and d), with and without MPA in the H2MoO4−x layer.

loadings of MPA (from 0.15 to 0.86 molecules per Mo) yielding an optimized ratio of 0.86:1 at which point the improvement saturates (Figure S10a). This improvement cannot be attributed to the increased conductivity of the H2MoO4−x with MPA doping since the contribution to device series resistance from a ~10 nm H2MoO4−x layer is calculated to be 0.030 and 0.024 Ω cm2 for undoped and doped H2MoO4−x layers respectively, which is small compared to the total series resistance in the OPV (Table 1). This does however explain why there is no significant improvement in device fill factor (FF) upon MPA doping.38 It is evident from the external quantum efficiency (EQE) data shown in Figure 7b that the improvement in PCE is due to an increased photoconversion in the longer wavelength region of the spectrum. Similarly, for OPV devices based on a PCDTBT:PC70BM BHJ there is an also an improvement in Jsc (Figure 7c) upon incorporation of MPA into the H2MoO4−x layer, which is optimized for a lower MPA loading, 0.29:1 MPA:Mo (Figure S10b). It is evident from Figure 7d that this improvement is also due to increased photoconversion in the longer wavelength region of the spectrum. Scanning electron microscopy and AFM imaging (Figure S11) of the Ag electrode surface reveals a large difference in surface roughness for Ag films supported on H2MoO4−x films with and without MPA: 2.8 nm (with MPA) versus 10.1 nm (without). This difference must in large part result from a difference in wetting of the BHJs on the AlCuAl electrode as compared to glass, and is further compelling evidence that adding MPA to H2MoO4−x greatly improves the film forming properties. The differences in Jsc are therefore tentatively ascribed to losses due to plasmon-excitation on the rougher Ag film when the H2MoO4−x layer is used without MPA. Preliminary stability tests under 1 sun illumination of the PCDTBT:PC70BM OPVs (Figure S12) also show greatly enhanced stability for devices using an MPA doped H2MoO4−x layer, which is further evidence for improved adhesion at the Ag electrode/H2MoO4−x interface.

### CONCLUSIONS

In summary, we have developed a new solution processed layer for top-illuminated organic photovoltaics that combines the function of wide band gap hole-extraction layer with the role of seed layer for the formation of robust 8 nm Ag window electrodes. The advantages of this hybrid electronic material are (i) that it does not add to the complexity of device fabrication, since oxide charge extractions layers are an essential component of high performance OPVs, (ii) it does not use costly materials, such as Au, (iii) and it is compatible with a large range of organic semiconductors, since it is processed from ethanol. We have shown that the key organic component, 3-mercaptopropionic acid, (i) binds to the oxide matrix and silver electrode, promoting silver film formation and robustness at low silver thickness, (ii) reduces the contact resistance at the Ag/molybdenum oxide bronze interface without significantly adversely affecting the optical properties, and (iii) improves the film forming properties on the surface or organic semiconductor films. Ag film electrodes with a thickness of 8 nm deposited onto this hybrid interlayer have a sheet resistance as low as 9.7 Ohms per square and mean transparency ~80% over the wavelength range λ = 400–900 nm, even without the aid of an antireflecting layer. This performance is superior to that previously reported using a Au seed layer and compares well to that of 8.5 Ω sq−1 indium tin oxide coated glass across the wavelength range λ = 400–900 nm. These properties, combined with greatly improved stability toward nitrogen and air exposure makes these electrodes an excellent match to the needs of high performance top-illuminated OPVs. Since solution processed PPVs also employ organic semiconductor charge extraction layers the results are expected to be equally applicable to the advancement of PPVs.

### EXPERIMENTAL SECTION

Glass substrates were thoroughly cleaned using a four stage process with ultrasonic agitation in (i) deionized water/surfactant (Decon, EXPERIMENTAL SECTION). Glass substrates were thoroughly cleaned using a four stage process with ultrasonic agitation in (i) deionized water/surfactant (Decon, EXPERIMENTAL SECTION). Glass substrates were thoroughly cleaned using a four stage process with ultrasonic agitation in (i) deionized water/surfactant (Decon, EXPERIMENTAL SECTION). Glass substrates were thoroughly cleaned using a four stage process with ultrasonic agitation in (i) deionized water/surfactant (Decon, EXPERIMENTAL SECTION). Glass substrates were thoroughly cleaned using a four stage process with ultrasonic agitation in (i) deionized water/surfactant (Decon, EXPERIMENTAL SECTION). Glass substrates were thoroughly cleaned using a four stage process with ultrasonic agitation in (i) deionized water/surfactant (Decon, EXPERIMENTAL SECTION).

**Table 1. Key Device Parameters of AlCuAl|PTB7:PC70BM|MoO3|Ag (8 nm) and AlCuAl|PCDTBT:PC70BM|MoO3|Ag (8 nm) OPVs**

<table>
<thead>
<tr>
<th>BHJ</th>
<th>Jsc (mA cm−2)</th>
<th>VOC (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Rseries (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7:PC70BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>no MPA</td>
<td>8.27 (±0.71)</td>
<td>0.64 (±0.02)</td>
<td>0.51 (±0.04)</td>
<td>2.69 (±0.40)</td>
<td>13.46 (±1.32)</td>
</tr>
<tr>
<td>with MPA</td>
<td>10.92 (±0.28)</td>
<td>0.65 (±0.03)</td>
<td>0.51 (±0.07)</td>
<td>3.65 (±0.62)</td>
<td>13.24 (±1.82)</td>
</tr>
<tr>
<td>PCDTBT:PC70BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no MPA</td>
<td>6.06 (±0.28)</td>
<td>0.81 (±0.03)</td>
<td>0.58 (±0.15)</td>
<td>2.88 (±0.15)</td>
<td>13.19 (±0.74)</td>
</tr>
<tr>
<td>with MPA</td>
<td>6.56 (±0.40)</td>
<td>0.86 (±0.01)</td>
<td>0.59 (±0.02)</td>
<td>3.33 (±0.17)</td>
<td>11.72 (±0.83)</td>
</tr>
</tbody>
</table>

*Series resistance estimated from the gradient of the JV curve under open circuit.
Neutracon) solution, (ii) deionized water, (iii) isopropanol, (iv) and finally acetone vapor, followed by blow drying with nitrogen. Substrates were then UV/O₃ treated to remove surface organic contaminants.

All fabrication and testing was carried out in a N₂ filled glovebox with a base O₂ level of <1 ppm unless otherwise stated. Evaporation of metals was carried out using a Creaply Organic molecular evaporator collocated in the same glovebox. The thickness of all vacuum deposited layers was measured using a calibrated quartz-crystal microbalance (QCM) mounted adjacent to the substrates. All metals were thermally evaporated using tungsten boats at a system pressure of <1 × 10⁻³ mbar.

H₂MoO₃ₓSynthesis. H₂MoO₃₋ₓ was synthesized by dispersing molybdenum powder (0.1 g) in ethanol (10 mL) by ultrasonication for 10 min. This solution was heated to 40 °C followed by addition of H₂O (30%, 0.35 mL) under vigorous stirring. The solution turned yellow after 10 h then blue after 48 h. After 72 h reaction the solution was removed from the heat, filtered through 0.2 μm PTFE filter and dried using a rotary evaporator. Solutions with a concentration of 20 mg mL⁻¹ in ethanol were prepared by ultrasonic agitation to fully dissolve the powder followed by centrifuging at 10000 rpm for 10 min to remove large particulates.

**Thick Film Fabrication.** For XPS/UPS and Kelvin probe measurements a 5 mg mL⁻¹ solution of H₂MoO₃₋ₓ, doped with either 0, 10, or 30 mM MPA, was spin coated onto Au (50 nm) electrodes at 800 rpm for 60 s followed by annealing at 80 °C for 10 min under N₂. This was repeated 6 times to achieve thick films. To measure conductivity unipolar diodes were fabricated on Au (50 nm) electrodes by spin-casting H₂MoO₃₋ₓ (20 mg mL⁻¹) solution with 0, 40, or 120 mM MPA, which correlate to 0:1, 0.29:1, and 0.86:1, respectively, MPA:Mo ratios respectively, at 1000 rpm for 60 s, followed by annealing at 80 °C for 10 min under N₂. Onto these was then evaporated Au (50 nm, 0.1 nm s⁻¹).

**Thin Film Fabrication.** 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:3,4-b’]-dithiophenediyl]];[6,6]-phenyl-C₆ₓ-butyric acid methyl ester (PTB7:PC₇₀BM) and poly[N-(9′-heptadecanoyl)-2,7- carbazole-alt-5,5-(4′,7′-dithiophene-2,1′,3′-benzothiadiazole)];[6,6]-phenyl-C₆ₓ-butyric acid methyl ester (PCDTBT:PC₇₀BM). For %T and Rₘ.measurements a BHJ of PTB7:PC₇₀BM (4 mg: 6 mg in 0.4 mL dichlorobenzene:diodoocetane, 97:3 vol %, stirred at 80 °C for 16 h prior to use) was deposited on cleaned 18 × 18 mm² glass slides by spin coating at 1000 rpm for 60 s followed by 6000 rpm for 4 s then dried under N₂ for 30 min. H₂MoO₃₋ₓ solution (5 mg mL⁻¹) was then spin coated at 3000 rpm for 60 s followed by annealing at 80 °C for 10 min under N₂ to achieve 10 nm thick films. Au (8 nm, 0.2 nm s⁻¹) was then deposited. This was repeated with a BHJ of PCDTBT:PC₇₀BM (2 mg: 6 mg in 0.5 mL chloroform stirred at 70 °C for 1 h) which was spin-cast dynamically onto a slide spinning at 6000 rpm for 60 s.

**OPV Fabrication.** Devices were fabricated as above except with an initial electrode deposition by thermally evaporating Al (50 nm, 0.5 nm s⁻¹)/Cu (8 nm, 0.1 nm s⁻¹)/Al (0.8 nm, 0.02 nm s⁻¹) electrodes without breaking the vacuum between Al and Cu layer deposition. J–V curves were measured using a Keithley 2400 source-meter under AM1.5G solar illumination at 100 mA cm⁻² (1 sun).

EQE measurements were carried out using a Scientech SF150 xenon arc lamp and a PTI monochromator, with the monochromatic light intensity calibrated using a Si photodiode (Newport 818-LV). The incoming monochromatic light was chopped at 500 Hz. For signal measurement a Stanford Research Systems SR 830 lock-in amplifier was used.

Tapping mode atomic force microscopy (AFM) imaging was performed in air using an Asylum Research MFP3D. Unless otherwise stated, all surface roughness values are root-mean-square roughness.

Work function measurements were performed using a Kelvin probe referenced to freshly cleaved highly oriented pyrolytic graphite in a nitrogen-filled glovebox coated with the thermal evaporator.

The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra DLD spectrometer. The samples were illuminated using X-rays from a monochromated Al Kα source (hv = 1486.6 eV) and detected at a takeoff angle of 90 deg. The resolution, binding energy referencing and transmission function of the analyzer were determined using a clean polycrystalline Ag foil. Analysis of the data was undertaken with the CasaXPS package, incorporating Voigt (mixed Gaussian–Lorentzian) lineshapes and a Shirley background. UPS spectra were recorded using UV photons with energy 21.21 eV from a He I plasma source.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b02647.

Grazing incidence X-ray diffraction, XPS, absorption, Tauc plots, AFM, and SEM of H₂MoO₃₋ₓ films, current–voltage field plot of unipolar diodes for conductivity of H₂MoO₃₋ₓ films, and J–V plots of varied loadings of MPA in H₂MoO₃₋ₓ films (PDF).

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


(8) Lynch, D. W.; Hunter, W. R. Comments on the Optical Constants of Metals and an Introduction to the Data for Several


(13) Yang, Y.; Chen, Q.; Hsieh, Y.-T.; Song, T.-B.; De Marco, N.; Zhou, H.; Yang, Y. MultiLayer Transparent Top Electrode for Solution Processed perovskite/Cu(In,Ga) (Se,S)2 Four Termainal Tandem Solar Cells. ACS Nano 2015, 9, 7714.


