

Low-Temperature Solution-Processed Hydrogen Molybdenum and Vanadium Bronzes for an Efficient Hole-Transport Layer in Organic Electronics

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One of the essential aspects in designing efficient and stable organic electronics such as organic light emitting diodes (OLED) and organic solar cells (OSCs) is the engineering of interfacial carrier transporting layers between the organic layer and metal electrodes.^[1] Among various materials available for interfacial layers, transition metal oxides (TMOs) have great potential owing to their wide range of energy level aligning capabilities.^[2,3] For instance, the formation of low resistance ohmic contact by TMOs has been reported to improve power conversion efficiency (PCE) of OSCs.^[3] Apart from high transparency in visible spectra and desirable band structure, another attractive merit of TMOs compared to other kinds of carrier transport layers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)^[4] is their excellent stability in ambient environment which can extend the lifetime of organic electronics.^[5] Up to now, the most commonly used TMOs for efficient hole-transport layers (HTLs) in organic electronics are molybdenum oxide and vanadium oxide.^[6]

Bearing the compatibility with large-area, low-cost, high-throughout production and all-solution technology, the solution-processed TMOs have attracted great attention from various research groups. The solution-processed MoO₃ layers derived from precursor solution have been reported previously. An annealing temperature as high as 250 °C was required for the conversion of the precursor into MoO₃.^[7] Temperature treatment at as low as 100 °C for MoO₃ films spin-cast from commercially available MoO₃ nanoparticles has also been presented, however, such an approach requires an extra oxygen-plasma treatment to remove the dispersing agents.^[8,9] Moreover, the large roughness (≈15–30 nm) as well as the presence of pin-holes and defects is not ideal.^[8] Recently, important research progress has been made on solution-processed MoO₃ in Prof. Yang's and Prof. Heeger's group.^[10,11] Yang's group reports smooth MoO₃ film as HTL for OSCs by heating a precursor of ammonium

heptamolybdate in distilled water.^[10] Heeger's MoO_x based on low temperature treatment at 70 °C can give photovoltaic efficiency comparable to that utilizing PEDOT:PSS in OSC. However the degradation of device efficiency and S-shape current density–voltage (*J*–*V*) characteristics are found by further increasing the treatment temperature which remain as open issues to be addressed in the future.^[11] As to vanadium oxide, solution-processed V₂O₅ layer prepared from a vanadium-oxitri-isopropoxide/isopropyl alcohol is reported, which requires one hour to hydrolyze at ambient and nanoscopic voids are also observed from spin-cast V₂O₅ film.^[12,13]

Here, we propose a one-step method to synthesize low-temperature solution-processed TMOs such as molybdenum oxide and vanadium oxide for hole-transport layers. Molybdenum and vanadium powders are respectively oxidized by hydrogen peroxide in the presence of ethanol. With the controllable reaction rate by ethanol in the process, the hydrogen metal oxides bronzes (HMOs), including hydrogen molybdenum bronze and hydrogen vanadium bronze, are obtained. In addition, the HMOs are dispersed uniformly and stably into water-free solvents (the solvents can be any alcoholic-based solvents, here we use ethanol for demonstration) which are particularly beneficial to the device stability and processing. With mild temperature treatment no greater than 100 °C, the obtained TMO films with small amount oxygen vacancies exhibit high film quality and desirable electrical properties. Their effectiveness as HTLs for efficient hole extraction in OSCs is demonstrated in detail hereafter. With clear evidences, we have identified the importance of oxygen vacancies in the employment of TMOs as HTL. In our new synthesis method the oxygen vacancies are controllable parameters for TMOs. Our results show that TMOs with excess oxygen are highly undesirable for their application in organic electronics.

In this work, it is noteworthy to emphasize that the functions of ethanol during the synthesis of HMOs solution in below (details are described in experimental section):

- (1) Ethanol alleviates and controls the violent reaction between metal powders and hydrogen peroxide so that the metal powders react with hydrogen peroxide in a manageable rate.
- (2) Ethanol acts as a reducing agent and hydrogen insertion source. During the reaction, ethanol provides e[−] and H⁺ for the reduction of the metal peroxide and meanwhile some amount of H⁺ insert into the TMO lattice to form so-called metal oxide bronzes.^[14]

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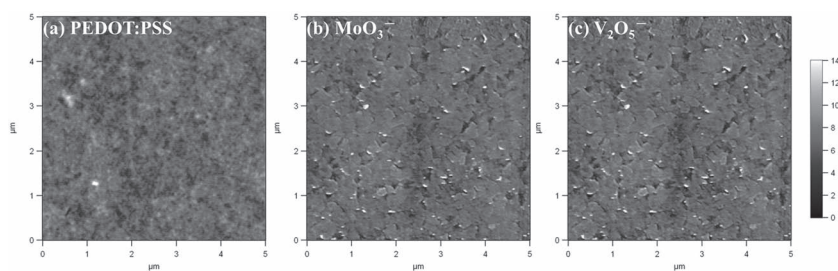


Figure 1. AFM images of thin films: a) PEDOT:PSS; b) molybdenum oxide (MoO_3^-); c) vanadium oxide (V_2O_5^-).

At the end of reaction process, molybdenum oxide solution turned blue and vanadium oxide solution turned bronze as shown in inset of Figure S1 in the Supporting Information attributed to H^+ insertion into the TMO lattice and then the reduction of metal element (Mo^{6+} , V^{5+}) into sub-state (Mo^{5+} , V^{4+}), forming hydrogen molybdenum bronzes (H_xMoO_3) and hydrogen vanadium bronzes ($\text{H}_x\text{V}_2\text{O}_5$).

The HMOs solution were spin-coated on UVO pre-cleaned indium tin oxide (ITO) glasses and then the molybdenum oxide and vanadium oxide films were annealed at 80 °C and 100 °C under ambient environment, respectively. The thickness of the optimized TMO films functioning as an efficient HTL in OSCs is about 8 nm determined by ellipsometry. The light transmission of TMO films is comparable to that of PEDOT:PSS (≈ 30 nm, same as used in OSCs later) and even more transparent in the long wavelength region (see Supporting

Information, Figure S1). Furthermore, the atomic force microscopy (AFM) images in **Figure 1** show very uniform and smooth surface for the three TMO films with root-mean-square (RMS) roughness of 1.33 nm and 1.46 nm for molybdenum oxide and vanadium oxide respectively, which are comparable to that of PEDOT:PSS ($\text{RMS} \approx 1.07$ nm). The flat surface is in contrast to the rough films spin-cast from nanoparticle solutions ($\text{RMS} \approx 15\text{--}30$ nm).^[8,9] Moreover, unlike other reports,^[12] absence of nanoscopic voids or porosity herein indicates the films are very compact. The high film quality of the TMO thin films suggests that they can smoothen the substrate surface (i.e., ITO-coated glass) effectively to avoid local shorts and at the same time be dense enough to prevent the current leakage, which are prerequisites to guarantee their implementation as effective buffer layer for organic electronics.

The stoichiometric composition of TMOs is another crucial consideration for the newly synthesized materials. We will point out later that the oxygen content in TMOs has significant influence on their electrical properties (i.e., band structure). The X-ray photoelectron spectroscopy (XPS) regarding Mo 3d in molybdenum oxide film and V 2p in vanadium oxide film are exhibited in **Figure 2a** and **2b**, respectively. For molybdenum oxide, decomposition of the XPS spectrum reveals that the Mo 3d spectrum can be well fitted by two 3d doublets in the form of a Gaussian function, corresponding to molybdenum in two different oxidation states. The major contributor peaks at 232.8 eV and 236.0 eV which are typical values of 3d doublet of Mo^{6+} . The minor one is centered at 231.7 eV and 234.7 eV which are identified as 3d doublet of Mo^{5+} .^[15] The atomic concentration ratio of Mo^{6+} to Mo^{5+} is obtained to be about 6:1 and the atomic ratio between Mo and O is about 1:2.93, which shows small amount of oxygen vacancies in molybdenum oxide film.

For vanadium oxide, the XPS spectrum of vanadium oxide film consists of two Gaussian-like 2p doublets which, according to their characteristic values, are identified to be V^{5+} and V^{4+} oxidation states, respectively.^[16] Composition analysis reveals that V^{4+} accounts small amount, only about 8% of total vanadium atoms. The atomic ratio between V and O is about 1:2.46 indicating that small amount of oxygen vacancy also exist in the vanadium oxide film. Thus, molybdenum oxide and vanadium oxide herein are very close to exact MoO_3 and V_2O_5 stoichiometry with small amount of oxygen vacancy (denoted as MoO_3^- and V_2O_5^- respectively hereafter for convenience). The oxygen vacancies should be arise from the insertion of the small amount of H^+ into the TMOs (forming H_xMoO_3 and $\text{H}_x\text{V}_2\text{O}_5$, respectively). During annealing treatment, small amount of oxygen vacancies are generated because of the dehydration process.

When these TMOs are employed in organic electronics, favorable band alignment is highly desirable. The optical bandgap (E_{opt}) for MoO_3^- and V_2O_5^- , as derived following Tauc's formula (Supporting Information, Figure S6),^[17] are about 3.0 eV and 2.7 eV respectively, which are in good agreement with the commonly reported values.^[9,18] As determined from ultraviolet photoelectron spectroscopy (UPS) (Supporting Information,

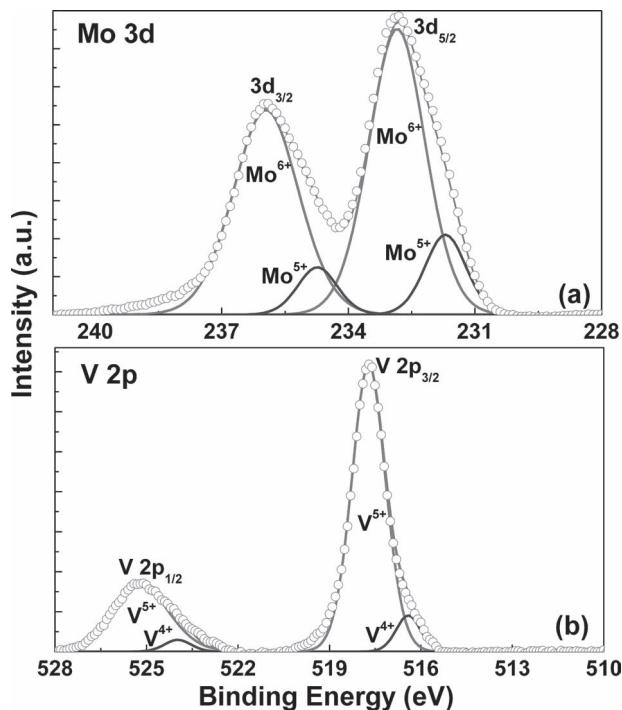


Figure 2. XPS spectra of: a) Mo 3d core level in molybdenum oxide (MoO_3^-); b) V 2p core level in vanadium oxide (V_2O_5^-). The circles represent the experimental XPS spectra; the solid lines are decomposed XPS spectra.

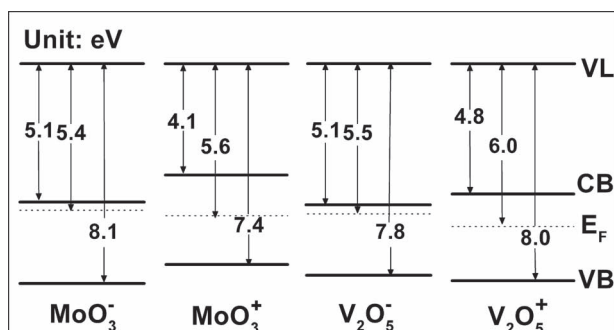


Figure 3. Band diagrams for the molybdenum oxide with oxygen vacancies (MoO_3^-), molybdenum oxide with excess oxygen (MoO_3^+), vanadium oxide with oxygen vacancies (V_2O_5^-), and vanadium oxide with excess oxygen (V_2O_5^+), where VL is vacuum level, E_F is Fermi level, CB is the conduction band, VB is the valence band.

Figure S5), the work function (WF) for ITO, MoO_3^- , and V_2O_5^- are 4.6 eV, 5.4 eV, and 5.5 eV, respectively. The band diagram parameters including electron affinity (EA) and ionization energy (IE) are shown in Figure 3. It can be observed that MoO_3^- and V_2O_5^- film exhibit very low-lying conduction band and n-type characteristics which are very important for their application as HTL in organic electronics. It is because hole transport through the metal oxides with similar features can be realized by extracting electrons through their conduction bands.^[9,19] The n-type band configuration can be explained by the oxygen vacancies. It has been reported that even small amount of oxygen vacancies is capable of causing effective n-type doping.^[9]

For demonstrating the effectiveness of the TMOs synthesized by our proposal method as HTL, OSCs have been fabricated and characterized. The OSCs have device structures as ITO/TMO or PEDOT:PSS/polymer:PCBM/Ca/Al. The robust material system of poly(3-hexylthiophene) (P3HT):phenyl-C61 butyric acid methyl (PC_{61}BM) is first investigated. And the photovoltaic performance with TMOs treated at different temperature and solution concentrations are summarized in Table S1–S4 and Figure S10–S13 in the Supporting Information. The device performance at the optimized conditions is summarized in Table 1 and Figure 4a. For MoO_3^- and V_2O_5^- based OSCs, temperature treatment as low as 80 °C and 100 °C are applied to achieve the best device performance. The average PCE for P3HT: PC_{61}BM based OSCs using MoO_3^- and V_2O_5^- are 3.94% and 3.86%, respectively. These result shows superior performance compared to that with PEDOT:PSS as HTL (average PCE $\approx$ 3.68%).

When the TMOs are applied to our synthesized small band gap polymeric material of PBDTTT-C-T as shown in Figure 4b and Table 2, the improved PCE of 7.75% and 7.62%, are demonstrated using MoO_3^- and V_2O_5^- as HTL which are also better than that of the control OSCs using PEDOT:PSS as HTL (average PCE $\approx$ 7.24%). The comparable open-circuit voltage (V_{OC}) suggests favorable band alignment for hole extraction when employing MoO_3^- or V_2O_5^- films as HTL. The reduced series resistance (R_s) and enhanced fill factor (FF) indicate good conductivity of the TMO films and low energy barrier for hole

Table 1. Photovoltaic parameters under AM1.5G solar spectrum with light intensity of 100 mW cm^{-2} for organic solar cells. The device structure is ITO/ MoO_3^- , V_2O_5^- , MoO_3^+ , V_2O_5^+ or PEDOT:PSS/P3HT: PC_{61}BM /Ca/Al. R_s is derived from the slope of the dark current density–voltage (J – V) curve at $V = 2 \text{ V}$.

P3HT: PC_{61}BM	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]	R_s [$\Omega \text{ cm}^2$]
MoO_3^-	0.625 ± 0.001	9.38 ± 0.31	67.15 ± 0.97	3.94 ± 0.13	1.55 ± 0.04
V_2O_5^-	0.625 ± 0.000	9.71 ± 0.12	63.61 ± 0.98	3.86 ± 0.02	1.65 ± 0.08
PEDOT:PSS	0.633 ± 0.005	9.28 ± 0.32	62.69 ± 2.17	3.68 ± 0.11	1.85 ± 0.13
MoO_3^+	0.575 ± 0.035	2.45 ± 0.02	51.90 ± 0.46	0.73 ± 0.03	42.85 ± 3.25
V_2O_5^+	0.625 ± 0.001	7.54 ± 0.42	58.57 ± 1.75	2.76 ± 0.15	4.86 ± 0.32

extraction at the TMO/organic interface. Very large rectification ratio (over 10^5 at $\pm 1.5 \text{ V}$, Supporting Information, Figure S14,S15) is a typical indicator of good diode characteristic, suggesting the MoO_3^- or V_2O_5^- layer acts effectively to polarize the internal electric field of OSCs. Consequently, the results of OSCs with either P3HT:PCBM or PBDTTT-C-T: PC_{71}BM as active layer materials all show that the similar improvement in efficiency using MoO_3^- or V_2O_5^- as effective HTL.

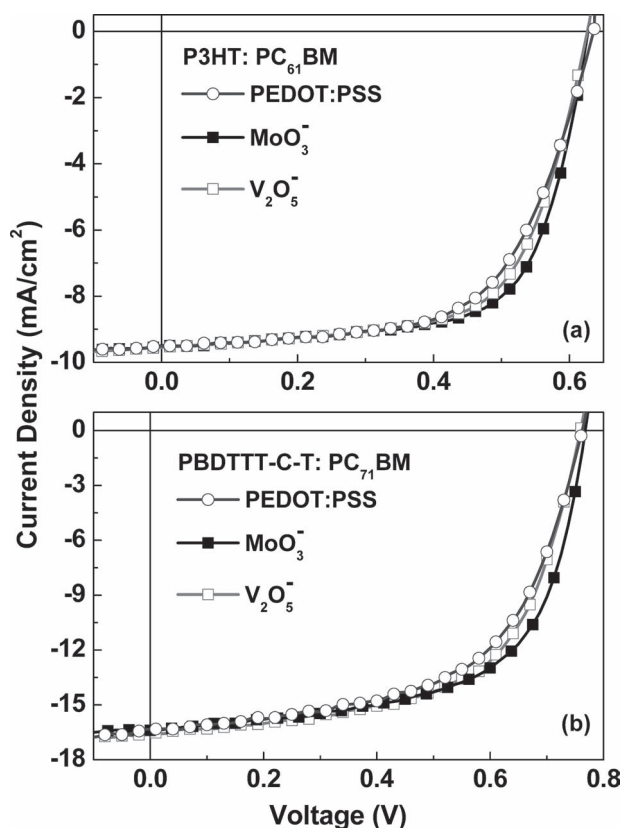


Figure 4. Current density–voltage (J – V) characteristics under AM1.5G solar spectrum with a light intensity of 100 mW cm^{-2} for organic solar cells. The device structures are: a) ITO/ MoO_3^- , V_2O_5^- or PEDOT:PSS/P3HT: PC_{61}BM /Ca/Al; b) ITO/ MoO_3^- , V_2O_5^- or PEDOT:PSS/PBDTTT-C-T: PC_{71}BM /Ca/Al.

Table 2. Photovoltaic parameters under AM1.5G solar spectrum with light intensity of 100 mW cm^{-2} for organic solar cells. The device structure is ITO/ MoO_3^- , V_2O_5^- , or PEDOT:PSS/PBDTTT-C-T:PC₆₁BM/Ca/Al. R_s is derived from the slope of dark current density–voltage (J – V) curve at $V = 2 \text{ V}$.

PBDTTT-C-T:PC ₆₁ BM	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	R_s [Ω cm ²]
MoO_3^-	0.760 ± 0.000	16.38 ± 0.13	62.32 ± 0.81	7.75 ± 0.11	3.42 ± 0.09
V_2O_5^-	0.760 ± 0.000	16.47 ± 0.12	60.91 ± 0.93	7.62 ± 0.12	3.51 ± 0.11
PEDOT:PSS	0.760 ± 0.000	16.32 ± 0.17	58.47 ± 1.17	7.24 ± 0.20	3.80 ± 0.15

From our study, we find that the oxygen vacancy in the film plays an essential role for the employment of TMOs as HTL in organic electronics. As further evidences, we oxidized the molybdenum and vanadium by hydrogen peroxide without the presence of ethanol. The thin films of molybdenum oxide and vanadium oxide were prepared by spin-coating the synthesized solution onto pre-cleaned ITO-coated glass substrate, and then the two TMO films were annealed at 80°C and 100°C under ambient environment, respectively. The XPS analysis (Supporting Information, Figure S3a,S4a) shows that only Mo^{6+} and V^{5+} oxidation state exists for molybdenum oxide and vanadium oxide, respectively, indicating Mo and V are fully oxidized and oxygen vacancies are completely absent. This is further supported by the atomic ratio for Mo:O and V:O as determined to be about 1:3.4 and 1:2.5, respectively. For convenience, the MoO_3 and V_2O_5 with excess oxygen are denoted as MoO_3^+ and V_2O_5^+ , respectively hereafter.

Due to the absence of oxygen vacancies, MoO_3^+ and V_2O_5^+ exhibit quite distinct electrical properties compared with MoO_3^- and V_2O_5^- . The optical bandgap for MoO_3^+ and V_2O_5^+ , as determined following Tauc's formula, are 3.3 eV and 3.2 eV, respectively (Supporting Information, Figure S9). Thus, the absence of oxygen vacancy contributes to an increase of the optical bandgap by about ≈ 0.3 – 0.5 eV for the TMOs. More interestingly, revealed by the band structure as derived from UPS spectra (see Supporting Information, Figure S7,S8), the band diagrams of MoO_3^+ and V_2O_5^+ (Figure 3) exhibit almost near insulating characteristics with Fermi level located near the middle of the bandgap, which is quite different from the case for MoO_3^- and V_2O_5^- with small amount of oxygen vacancies. In the MoO_3^- and V_2O_5^- films, sub-bandgap states could be generated by oxygen vacancies as indicated by the fluctuated features in Figure S6 in the Supporting Information. It could be donor states near the Fermi level, which push the Fermi level close to the conduction band.^[20] Consequently, the findings here also agree well with the previous reports that TMOs are insulators in their stoichiometric forms and tend to be n-type in the presence of oxygen vacancy.^[21]

The quite distinct band structures for TMOs due to different level of oxygen content can significantly influence the electrical properties for TMOs and determine their applications on organic electronics accordingly. It is a universal trend that energy level alignment can be achieved between TMOs with a wide range of work function variations and organic molecules through Fermi level pinning transition.^[21] This principle is expected to be well applied to the investigated MoO_3^- or V_2O_5^- /organic interface, while may not apply to the MoO_3^+ or V_2O_5^+ /

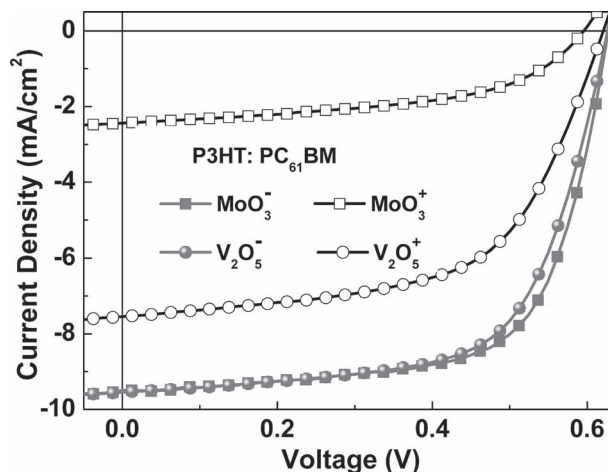


Figure 5. Current density–voltage (J – V) characteristics under AM1.5G solar spectrum with light intensity of 100 mW cm^{-2} for organic solar cell. The device structure is ITO/ MoO_3^+ , MoO_3^- , V_2O_5^+ or V_2O_5^- /P3HT:PC₆₁BM/Ca/Al. MoO_3^+ and MoO_3^- thin films were annealed at 80°C for 10 min, and V_2O_5^+ and V_2O_5^- were annealed at 100°C for 10 min.

organic interface given that the insulating characteristics of MoO_3^+ and V_2O_5^+ will inhibit the charger transfer remarkably so that Fermi level pinning cannot be achieved. Moreover, the nearly insulating property of MoO_3^+ and V_2O_5^+ is expected to result in high resistance for thin films, which will further limit their effectiveness as HTL in organic electronics. This can be strongly evidenced by employing MoO_3^+ and V_2O_5^+ as HTL in OSCs. When MoO_3^+ and V_2O_5^+ are used as HTL in P3HT:PC₆₁BM based OSCs, their PCEs are only about 0.73% and 2.76% respectively (see Table 1 and Figure 5), which show that TMOs with excess oxygen (i.e., MoO_3^+ and V_2O_5^+) cannot offer good HTL for high performance OSCs.

In summary, we reported a simple one-step method to synthesize low-temperature solution-processed TMOs of molybdenum oxide and vanadium oxide with oxygen vacancies as n-dopants for good HTL. Importantly, the oxygen level of the TMOs can be controlled in our approach for achieving high performance OSCs. In addition, the synthesized HMOs can be dispersed uniformly and stably into water-free solvents. The investigated low-temperature solution-processed TMOs thus are very compatible with organic materials, and can be applicable for cost-effective organic electronics such as all solution-processed OSCs and tandem OSCs towards high efficiency. We also demonstrated that oxygen vacancy plays an essential role for TMOs when they are employed as HTL, and TMOs with excess oxygen are highly undesirable for their application on organic electronics. This can provide useful guideline for the synthesis and application of TMOs in the future.

Experimental Section

Material Oxides Synthesis: Metal powders (molybdenum, vanadium and tungsten) were purchased from Aladdin Reagent. 0.1 g metal powder (molybdenum and vanadium) was dispersed in 10 ml ethanol with stirring for several minutes. Then 0.35 ml and 0.5 ml H_2O_2 (30%)

solution were added into the two metal power (molybdenum, vanadium) suspension solution, respectively. After 18 hours' reaction, the molybdenum oxide solution turned from grey to yellow and finally turned to blue. After 3 hours' reaction, the vanadium oxide solution turned to orange and then turned to brown. The two solutions were dried under vacuum chamber, and then the dried molybdenum oxide and vanadium oxide were dispersed uniformly into 10 ml ethanol, respectively.

Device Fabrication: ITO-coated glass substrates with sheet resistance of $15 \Omega/\square$ were cleaned and then ultraviolet-ozone treated for 15 minutes. Either PEDOT:PSS (Baytron Al 4083) or TMOs (molybdenum oxide, vanadium oxide) was spin-coated with thickness of ≈ 30 nm and ≈ 8 nm, respectively. The PEDOT:PSS, molybdenum oxide and vanadium oxide films were then annealed at 140°C , 80°C , and 100°C , respectively for 10 minutes on a hotplate in air. All the samples were transferred into a glove box to spin-coat active layer. For P3HT:PC₆₁BM (1:1, 40 mg/ml in 1,2-dichlorobenzene (DCB)) as active layer, it has a thickness of ≈ 220 nm. Solvent annealing was conducted and then the samples were annealed at 130°C for 10 minutes. For PBDDTT-C-T:P₇₁CBM (1:1.5, 25 mg/ml in DCB, with addition of 3% 1,8-diodooctane (DIO) in volume concentration) as active layer, it has a thickness of ≈ 100 nm. Ca(20 nm)/Al (80 nm) were finally thermally evaporated as the cathode with a device area of 4.5 mm^2 defined by a shadow mask.

Characterizations: UPS spectra were obtained using a He discharged lamp (He I 21.22 eV, Kratos Analytical) with an experimental resolution of 0.15 eV. The samples were biased at -10 V to favor the observation of secondary-electron cut-off from the UPS spectra. XPS measurement was carried out using a Physical Electronic 5600 multi-technique system (monochromatic Al K α X-ray source). All the spectra were adjusted according to the standard value of C 1s peak at (284.6 ± 0.1) eV. AFM was measured by using NanoScope III (Digital Instrument) in the tapping mode. Transmittance measurement was performed under a dark ambient environment by using spectroscopic ellipsometry (Woollam). Current density–voltage (J – V) characteristics were obtained by using a Keithley 2635 source meter and Newport AM 1.5G solar simulator with $100 \text{ mW}/\text{cm}^2$ illumination.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] a) C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S. W. Tsang, T. H. Lai, J. R. Reynolds, F. So, *Nat. Photonics* **2012**, 6, 115; b) Z. A. Tan, W. Zhang, Z. Zhang, D. Qian, Y. Huang, J. Hou, Y. Li, *Adv. Mater.* **2012**, 24, 1476; c) J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, A. J. Heeger, *Science* **2007**, 317, 222; d) T. Yang, M. Wang, C. Duan, X. Hu, L. Huang, J. Peng, F. Huang, X. Gong, *Energy Environ. Sci.* **2012**, 5, 8208; e) H. L. Yip, A. K. Y. Jen, *Energy Environ. Sci.* **2012**, 5, 5994; f) L. S. Sista, M. H. Park, Z. Hong, Y. Wu, J. Hou, W. L. Kwan, G. Li, Y. Yang, *Adv. Mater.* **2010**, 22, 380; g) J. You, C. C. Chen, L. Dou, S. Murase, H. S. Duan, S. A. Hawks, T. Xu, H. J. Son, L. Yu, G. Li, Y. Yang, *Adv. Mater.* **2012**, 24, 5267; h) H. Ma, H. L. Yip, F. Huang, A. K. Y. Jen, *Adv. Funct. Mater.* **2010**, 20, 1371; i) F. Huang, H. Wu, Y. Cao, *Chem. Soc. Rev.* **2010**, 39, 2500.
- [2] a) M. T. Greiner, M. G. Helander, W. M. Tang, Z. B. Wang, J. Qiu, Z. H. Lu, *Nat. Mater.* **2012**, 11, 76; b) J. Meyer, S. Hamwi, M. Kröger, W. Kowalsky, T. Riedl, A. Kahn, *Adv. Mater.* **2012**, 24, 5408; c) R. Steim, F. R. Kogler, C. J. Brabec, *J. Mater. Chem.* **2010**, 20, 2499.
- [3] Z. B. Wang, M. G. Helander, M. T. Greiner, J. Qiu, Z. H. Lu, *Phys. Rev. B* **2009**, 80, 235325.
- [4] M. P. de Jong, L. J. van Ijzendoorn, M. J. A. de Voigt, *Appl. Phys. Lett.* **2000**, 77, 2255.
- [5] a) Y. Kanai, T. Matsushima, H. Murata, *Thin Sol. Films* **2009**, 518, 537; b) Y. Sun, C. J. Takacs, S. R. Cowan, J. H. Seo, X. Gong, A. Roy, A. J. Heeger, *Adv. Mater.* **2011**, 23, 2226.
- [6] a) T. Matsushima, G.-H. Jin, H. Murata, *J. Appl. Phys.* **2008**, 104, 054501; b) X. Fan, C. Cui, G. Fang, J. Wang, S. Li, F. Cheng, H. Long, Y. Li, *Adv. Funct. Mater.* **2012**, 22, 585; c) I. Hancox, K. V. Chauhan, P. Sullivan, R. A. Hatton, A. Moshar, C. P. A. Mulcahy, T. S. Jones, *Energy Environ. Sci.* **2010**, 3, 107; d) J. Meyer, K. Zilberberg, T. Riedl, A. Kahn, *J. Appl. Phys.* **2011**, 110, 033710; e) M. Vasilopoulou, A. M. Douvas, D. G. Georgiadou, L. C. Palilis, S. Kennou, L. Sygellou, A. Soultati, I. Kostis, G. Papadimitropoulos, D. Davazoglou, P. Argitis, *J. Am. Chem. Soc.* **2012**, 134, 16178.
- [7] a) C. Girotto, E. Voroshazi, D. Cheyns, P. Heremans, B. P. Rand, *ACS Appl. Mater. Interfaces* **2011**, 3, 3244; b) T. Yang, M. Wang, Y. Cao, F. Huang, L. Huang, J. Peng, X. Gong, S. Z. D. Cheng, Y. Cao, *Adv. Energy Mater.* **2012**, 2, 523.
- [8] T. Stubhan, T. Ameri, M. Salinas, J. Krantz, F. Machui, M. Halik, C. J. Brabec, *Appl. Phys. Lett.* **2011**, 98, 253308.
- [9] J. Meyer, R. Khalandovsky, P. Görrn, A. Kahn, *Adv. Mater.* **2011**, 23, 70.
- [10] S. Murase, Y. Yang, *Adv. Mater.* **2012**, 24, 2459.
- [11] J. J. Jasieniak, J. Seifter, J. Jo, T. Mates, A. J. Heeger, *Adv. Funct. Mater.* **2012**, 22, 2594.
- [12] K. Zilberberg, S. Trost, H. Schmidt, T. Riedl, *Adv. Energy Mater.* **2011**, 1, 377.
- [13] K. Zilberberg, S. Trost, J. Meyer, A. Kahn, A. Behrendt, D. Lützenkirchen-Hecht, R. Frahm, T. Riedl, *Adv. Funct. Mater.* **2011**, 21, 4776.
- [14] S. Ayyappan, C. N. R. Rao, *Mater. Res. Bull.* **1995**, 30, 947.
- [15] M. A. Bica de Moraes, B. C. Trasferetti, F. P. Rouxinol, R. Landers, S. F. Durrant, J. Scarmínio, A. Urbano, *Chem. Mater.* **2003**, 16, 513.
- [16] a) G. A. Sawatzky, D. Post, *Phys. Rev. B* **1979**, 20, 1546; b) J. Mendiola, R. Casanova, Y. Barbaux, *J. Electron Spectrosc. Relat. Phenom.* **1995**, 71, 249.
- [17] a) A. Abdellaoui, G. Lévêque, A. Donnadiou, A. Bath, B. Bouchikhi, *Thin Solid Films* **1997**, 304, 39; b) A. Szekeres, T. Ivanova, K. Gesheva, *J. Solid State Electrochem.* **2002**, 7, 17.
- [18] a) M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, A. Kahn, *Org. Electron.* **2009**, 10, 932; b) J. Meyer, K. Zilberberg, T. Riedl, A. Kahn, *J. Appl. Phys.* **2011**, 110, 033710; c) S. Han, W. S. Shin, M. Seo, D. Gupta, S. J. Moon, S. Yoo, *Org. Electron.* **2009**, 10, 791.
- [19] M. Kroger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, A. Kahn, *Appl. Phys. Lett.* **2009**, 95, 123301.
- [20] M. T. Greiner, L. Chai, M. G. Helander, W. M. Tang, Z. H. Lu, *Adv. Funct. Mater.* **2012**, 22, 4557.
- [21] M. T. Greiner, M. G. Helander, W. M. Tang, Z. B. Wang, J. Qiu, Z. H. Lu, *Nat. Mater.* **2012**, 11, 76.