# Research Article In Situ Chemical Oxidation of Ultrasmall MoO<sub>x</sub> Nanoparticles in Suspensions

#### Yun-Ju Lee, Diego Barrera, Kaiyuan Luo, and Julia W. P. Hsu

Department of Materials Science and Engineering, University of Texas at Dallas, 800 W Campbell Road, RL10, Richardson, TX 75080, USA

Correspondence should be addressed to Yun-Ju Lee, yjalee@utdallas.edu

Received 8 June 2012; Accepted 23 July 2012

Academic Editor: Mallikarjuna Nadagouda

Copyright © 2012 Yun-Ju Lee et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Nanoparticle suspensions represent a promising route toward low cost, large area solution deposition of functional thin films for applications in energy conversion, flexible electronics, and sensors. However, parameters such size, stoichiometry, and electronic properties must be controlled to achieve best results for the target application. In this report, we demonstrate that such control can be achieved via *in situ* chemical oxidation of MoO<sub>x</sub> nanoparticles in suspensions. Starting from a microwave-synthesized suspension of ultrasmall ( $d \sim 2 \text{ nm}$ ) MoO<sub>x</sub> nanoparticles in n-butanol, we added H<sub>2</sub>O<sub>2</sub> at room temperature to chemically oxidize the nanoparticles. We systematically varied H<sub>2</sub>O<sub>2</sub> concentration and reaction time and found that they significantly affected oxidation state and work function of MoO<sub>x</sub> nanoparticle films. In particular, we achieved a continuous tuning of MoO<sub>x</sub> work function from 4.4 to 5.0 eV, corresponding to oxidation of as-synthesized MoO<sub>x</sub> nanoparticle (20% Mo<sup>6+</sup>) to essentially pure MoO<sub>3</sub>. This was achieved without significantly modifying nanoparticle size or stability. Such precise control of MoO<sub>x</sub> stoichiometry and work function is critical for the optimization of MoO<sub>x</sub> nanoparticles for applications in organic optoelectronics. Moreover, the simplicity of the chemical oxidation procedure should be applicable for the development of other transition oxide nanomaterials with tunable composition and properties.

# 1. Introduction

Metal oxide nanoparticles represent a large class of materials with applications in areas such as energy conversion and storage, [1, 2] catalysis, [3, 4] sensing, [5] and biomedicine [6]. Major advantages of metal oxide nanoparticle suspensions include compatibility with low-temperature, largearea solution processing, versatile surface functionalization, and formation of complex architectures via self-assembly. Molybdenum oxide  $(MoO_x)$  has attracted much interest as a hole transport layer (HTL) material in organic light-emitting diodes and solar cells because of its high work function ( $\Phi$ ). By matching  $\Phi$  of the HTL to the highest occupied molecular orbital (HOMO) of the organic electron donor material, [7]  $MoO_x$  films inserted between the active layer and the anode have been shown to improve performance of organic photovoltaic (OPV) devices [8-15]. Most work in this area use thermally evaporated  $MoO_x$  films [8–11]. While solution deposition of MoO<sub>x</sub> HTL films has been reported, all approaches thus far have required a postdeposition processing step that must be performed either at high temperature ( $\geq 160^{\circ}$ C) [12–14] and/or in an O<sub>2</sub>-containing ambient [15] to obtain  $MoO_x$  films with high  $\Phi$ . In addition, the solvents currently used for the solution deposition of  $MoO_x$  do not wet the organic layer to form a uniform thin film as required in an inverted OPV architecture, which shows superior stability in air compared to conventional devices [16, 17]. Recently, our group developed a microwaveassisted synthesis of  $MoO_x$  nanoparticles (npMoO<sub>x</sub>) in *n*butanol suspension, demonstrated formation of uniform thin films on poly(3-hexylthiophene): [6,6]-phenyl-C61butyric acid methyl ester (P3HT: PCBM) blends using room temperature solution processing and examined performance of inverted OPV devices using  $npMoO_x$  films as HTLs [18]. Here we focus on *in situ* chemical oxidation to optimize the  $npMoO_x$  properties for HTL application. Specifically, we examined the effect of chemical oxidation conditions on the size and stability of the  $npMoO_x$  suspension to evaluate its suitability for the formation of uniform and pinholefree thin films. We also quantified the impact of chemical oxidation on  $\Phi$  and stoichiometry  $MoO_x$  thin film and demonstrated continuous tuning of  $\Phi$  from 4.4 eV to 5.0 eV through precise control of the chemical oxidation conditions and Mo oxidation state. We show that *in situ* chemical oxidation of  $MoO_x$  nanoparticle is a versatile technique to synthesize stable suspensions of ultrasmall nanoparticles with desired stoichiometry and  $\Phi$  for the formation of thin HTL on top of organic active layer without postprocessing.

## 2. Experiments

 $MoO_x$  nanoparticle (npMoO<sub>x</sub>) suspensions were synthesized using nonhydrolytic sol-gel conversion of molybdenum dioxide bis(acetylacetonate) (MoAcAc) in anhydrous nbutanol as shown schematically in Figure 1, following a microwave-assisted synthesis procedure modified from Bilecka and colleagues [19]. We selected this approach because it has been shown to yield various metal oxide nanoparticles with low size polydispersity, good stability, and short reaction times down to 3 min. Furthermore, the procedure does not require additional ligands for nanoparticle stabilization, and thus should allow the deposition of nanoparticle films with good carrier transport properties without the need to remove electrically insulating ligands through a postsynthesis step. We used *n*-butanol as the solvent because of the good solubility for MoAcAc, and because it wets, but does not dissolve or swell hydrophobic organic films such as P3HT: PCBM. For the microwave synthesis, a test tube of MoAcAc solution in n-butanol was mixed in N<sub>2</sub> and placed in a microwave reactor (CEM Discovery) containing a single-mode 2.54 GHz microwave cavity. A MoAcAc concentration of 0.1 M was selected to balance complete dissolution and strong absorption microwave to enable rapid heating to 200°C within three minutes. The MoAcAc solution was maintained at 200°C for 15 min to synthesize the brown  $npMoO_x$  suspension (Figure 1). We chose to chemically oxidize  $npMoO_x$  in suspension using  $H_2O_2$  for three reasons:  $H_2O_2$  is a strong oxidizing agent,  $H_2O_2$  is miscible with *n*-butanol, and byproducts of the reaction, for example, H<sub>2</sub>O and O<sub>2</sub>, can be easily removed during subsequent processing. For chemical oxidation, a small amount of 30 wt% H2O2 in H2O (Fisher) was added to the npMoO<sub>x</sub> suspension to achieve the desired concentration (e.g.,  $10.2 \,\mu\text{L}$  of 30 wt% H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O per mL of suspension for  $0.1 \text{ M H}_2\text{O}_2$ ). The mixture was then stirred at room temperature for times ranging from 20 min to 24 hr for oxidation to occur.

To determine the nanoparticle size and distribution, an aliquot of each npMoO<sub>x</sub> suspension was diluted by a factor of 10 with *n*-butanol, agitated in an ultrasonic bath (Branson) for 5 min and passed through a  $0.2 \,\mu$ m PTFE syringe filter. The diluted suspension was analyzed by dynamic light scattering (DLS) under backscattering conditions using a Malvern Zetasizer.  $\Phi$  was measured using the Kelvin probe technique, and oxidation state of the Mo cation was determined using X-ray photoelectron spectroscopy (XPS).

To form thin films for these measurements, the  $npMoO_x$ suspension without dilution was passed through a  $0.2 \,\mu m$ PTFE syringe filter and spin coated at 1000 rpm on a cleaned ITO coated glass (20  $\Omega$ /sq, thin film devices).  $\Phi$  of the npMoO<sub>x</sub> film was measured in air using an isoprobe electrostatic voltmeter (model 244, Monroe Electronics), with Au as the reference material ( $\Phi = 5.1 \text{ eV}$ ). XPS of the  $npMoO_x$  film was carried out using a Perkin-Elmer 5600 ESCA system with monochromated Al KR source (1486.7 eV). All spectra were collected at an angle of 45° to the sample normal, with a pass energy of 58.7 eV and energy step of 0.125 eV. All XPS spectra were fitted using commercial software (MultiPak, PHI) and aligned to the C 1s reference at 284.8 eV. A reference sample of 20 nm MoO<sub>3</sub> on ITO was made by thermal evaporation at a rate of 0.1 A/s. A FWHM of 1.2 eV for each peak was used for peak fitting.

# 3. Results and Discussions

We found that microwave heating of MoAcAc resulted in a brown suspension of  $npMoO_x$  (Figure 1). Even without added ligands, the suspension showed excellent stability and remained dispersed for more than 90 days. DLS of the assynthesized npMoO<sub>x</sub> suspension found a volume weighted mean diameter of  $2.1 \pm 0.9$  nm (Figure 2(a), dashed line), in good agreement with the size determined using small-angle X-ray scattering (SAXS) [18]. Storage of the as-synthesized  $npMoO_x$  in air for up to 120 hrs led to no change in size, as confirmed by DLS (data not shown). In contrast, we found that chemical oxidation with H2O2 modified the size of the resulting nanoparticles in a complex way (Figure 2(a)). For example, 0.1 M (Figure 2(a), blue) and 0.3 M (Figure 2(a), red) H<sub>2</sub>O<sub>2</sub> at short reaction times ranging from 20 min to 3 hr decreased the  $npMoO_x$  diameter to  $\sim$ 1 nm. In comparison, a further increase in reaction time to 24 hr caused the nanoparticle size to increase back to 2 nm. The increase in size with longer reaction time is consistent with our previous observation that the average diameter of chemically oxidized npMoOx from SAXS had increased to 4 nm after ~15 days of chemical oxidation [18] and indicates that Ostwald ripening for these nanoparticles only occurs with the addition of H<sub>2</sub>O<sub>2</sub>. Nevertheless, the nanoparticles are still small enough to form multilayer films with thickness of ~10 nm. Indeed, we previously showed using atomic force microscopy that a chemically oxidized  $MoO_x$  suspension spin coated on top of P3HT:PCBM formed a pinholefree film that planarized the roughness of the underlying P3HT:PCBM layer [18]. Thus, while  $npMoO_x$  size increases after chemical oxidation with  $H_2O_2$ , it remains sufficiently small to form uniform films on top of organic layers at thickness values that are relevant for HTL in OPV devices.

Chemical oxidation of the MoO<sub>x</sub> nanoparticles significantly altered the electronic properties of npMoO<sub>x</sub> films, as measured by their  $\Phi$  values in air. The as-synthesized npMoO<sub>x</sub> exhibited a low  $\Phi$  of 4.48 ± 0.02 eV. Addition of 0.05 M H<sub>2</sub>O<sub>2</sub> for 20 min caused  $\Phi$  to increase to 4.82 ± 0.04 eV, and longer reaction times did not significantly



FIGURE 1: Schematic of microwave synthesis and chemical oxidation of  $MoO_x$  nanoparticles. A mixture of molybdenum oxide bis(acetylacetonate) in *n*-butanol was placed in a microwave reactor (CEM Discover) and heated using 2.45 GHz radiation. When heated at 200°C for 15 minutes, MoAcAc reacted, forming a brown suspension of nanoparticles. Chemical oxidation of the nanoparticle suspension with 0.1 M H<sub>2</sub>O<sub>2</sub> for 24 hours yielded a blue suspension of nanoparticles.



FIGURE 2: Effect of chemical oxidation with  $H_2O_2$  on  $MoO_x$  nanoparticle properties. (a) Dependence of nanoparticle size on chemical oxidation time (up to 24 hrs), showing that compared to as-synthesized nanoparticles (dashed line), both 0.1 M  $H_2O_2$  (blue) and 0.3 M caused npMoO<sub>x</sub> size to decrease to 1 nm (up to 3 hrs) and then increase back to 2 nm (24 hr). (b) Dependence of nanoparticle film  $\Phi$  versus chemical oxidation conditions, showing  $\Phi$  of as-synthesized npMoO<sub>x</sub> (black) was increased from 4.48 eV to 4.85 eV with 0.05 M  $H_2O_2$  (purple) and that the increase was independent of the reaction time between 20 min and 24 hr. In contrast, 0.1 M (blue), 0.2 M (green), and 0.3 M (red)  $H_2O_2$ , all caused work function to increase to 5.0 eV with a reaction time of up to 3 hr. However, a further increase in reaction time to 24 hrs decreased  $\Phi$  to 4.9 eV.

increase  $\Phi$  (Figure 2(b), purple). Increasing H<sub>2</sub>O<sub>2</sub> concentration to 0.1 M and above caused  $\Phi$  to increase to 4.94  $\pm$  0.01 eV after 1 hr, and the value remained unchanged when increasing the reaction time to 3 hr (Figure 2(b)). However, a further increase in reaction time to 24 hr caused  $\Phi$  to decrease to 4.90  $\pm$  0.01 eV. We note that the decrease in  $\Phi$  corresponded to the change of the nanoparticle suspension color from brown to blue (Figure 1).

To quantitatively understand the origin of the change in  $\Phi$  with chemical oxidation, we examined the stoichiometry of npMoO<sub>x</sub> films with different H<sub>2</sub>O<sub>2</sub> reaction conditions using XPS. As a reference, we measured evaporated MoO<sub>3</sub> and found that the Mo 3d XPS spectra can be fitted to doublet peaks at 232.3 eV and 235.4 eV, corresponding to Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> peaks for Mo<sup>6+</sup>, plus very weak doublet peaks at 231.0 eV and 233.8 eV corresponding to Mo 3d<sub>5/2</sub>

and Mo 3d<sub>3/2</sub> peaks for Mo<sup>5+</sup> [18, 20]. The Mo<sup>6+</sup> fraction, defined as the area under the Mo<sup>6+</sup> peaks divided by the total peak area, was 0.95, indicating that the reference sample was almost pure MoO<sub>3</sub>. The FWHM of the fitted peaks was 1.2 eV, and this value was used for all peaks when fitting XPS spectra of  $npMoO_x$  films where there are significant contributions to the overall signal from multiple oxidation states, in order to quantify the atomic fraction from each oxidation state. For example, the Mo 3d XPS spectra of assynthesized npMoO<sub>x</sub> contain peaks at 232.4 eV and 235.5 eV from Mo<sup>6+</sup>, 231.4 eV and 234.5 eV from Mo<sup>5+</sup>, and 229.8 eV and 232.9 eV from  $Mo^{4+}$  (Figure 3(a)). The  $Mo^{6+}$  fraction was 0.21, showing that as-synthesized  $npMoO_x$  is mostly reduced. Reaction with 0.05 M H<sub>2</sub>O<sub>2</sub> for 1 hr caused the Mo<sup>6+</sup> peaks to increase in intensity at the expense of the Mo<sup>5+</sup> and Mo<sup>4+</sup> peaks, (Figure 3(b)), so that the Mo<sup>6+</sup>



FIGURE 3: Effect of chemical oxidation conditions on  $MoO_x$  nanoparticle stoichiometry. (a) Mo 3d XPS spectra of as-synthesized np $MoO_x$  on ITO (crosses) and curve fit (solid), showing mixed oxidation states with contributions from  $Mo^{5+}$ ,  $Mo^{4+}$ , and a small amount of  $Mo^{6+}$ . (b) Mo 3d XPS spectra of np $MoO_x$  after chemical oxidation with 0.05 M  $H_2O_2$  for 1 hr, showing mixed oxidation states with a majority of  $Mo^{6+}$  oxidation state. (c) Mo 3d XPS spectra of np $MoO_x$  after chemical oxidation with 0.1 M  $H_2O_2$  for 1 hr, showing almost complete oxidation to  $Mo^{6+}$  oxidation state. (d) Mo 3d XPS spectra of np $MoO_x$  after chemical oxidation with 0.1 M  $H_2O_2$  for 24 hr, showing mixed oxidation states with a majority of Mo<sup>6+</sup> oxidation state.

fraction increased to 0.60. Nevertheless, the XPS spectra clearly show that 0.05 M H<sub>2</sub>O<sub>2</sub> only partially oxidized the as-synthesized  $MoO_x$  nanoparticles to  $MoO_3$ . Increasing the H<sub>2</sub>O<sub>2</sub> concentration to 0.1 M resulted in Mo 3d XPS spectra consisting almost entirely of peaks at 232.6 eV and 235.7 eV from Mo<sup>6+</sup>, with a miniscule contribution from Mo<sup>5+</sup>peaks at 230.9 eV and 234.1 eV (Figure 3(c)). The corresponding Mo<sup>6+</sup> fraction of 0.97 indicates that 0.1 M H<sub>2</sub>O<sub>2</sub> for 1 hr oxidized  $npMoO_x$  to the extent similar to the evaporated MoO<sub>3</sub> film. Increasing the reaction time to 24 hr at 0.1 M  $H_2O_2$  caused the Mo<sup>5+</sup> and Mo<sup>4+</sup> peaks to reappear in the Mo 3d XPS spectra (Figure 3(d)), decreasing the Mo<sup>6+</sup> fraction to 0.55. We believe the partial reduction of  $npMoO_r$ with increased  $H_2O_2$  reaction time can be explained by the electrochromism of MoO<sub>3</sub>. MoO<sub>3</sub> is known to change to a blue coloration upon the insertion of small cations such as  $H^+$ , following the reaction [21]

$$MoO_3 + xH^+ + xe^- \longrightarrow MoO_{3-x}(OH)_x$$
 (1)

In our case, H<sup>+</sup> is supplied by the H<sub>2</sub>O in the 30 wt% H<sub>2</sub>O<sub>2</sub> solution, and e<sup>-</sup> may be supplied by oxidation of neighboring Mo<sup>4+</sup> and Mo<sup>5+</sup> atoms. This reaction scheme is consistent with the observation that the change in npMoO<sub>x</sub> coloration from brown to blue was only observed after 24 hr reaction with 0.1 M and 0.3 M H<sub>2</sub>O<sub>2</sub>. The onset of color change, and by reference the proton insertion, also coincides with the increase in nanoparticle size and reduction in  $\Phi$ . Thus, analysis of XPS spectra reveals that chemical oxidation with H<sub>2</sub>O<sub>2</sub> consists of two concurrent processes, a fast oxidation that is complete at 0.1 M and higher H<sub>2</sub>O<sub>2</sub> concentrations within ~1 hr, and a slow reduction caused

by H<sup>+</sup> insertion that occurs after ~24 hr, highlighting the importance of the chemical oxidation conditions on the stoichiometry of the resulting npMoO<sub>x</sub>.

Figure 4 depicts  $\Phi$  and Mo<sup>6+</sup> fraction that can be achieved using the *in situ* H<sub>2</sub>O<sub>2</sub> chemical oxidation approach. For npMoO<sub>x</sub> films that were chemically oxidized at different H<sub>2</sub>O<sub>2</sub> concentrations for 1 hr (Figure 4, circles) and at 0.1 M H<sub>2</sub>O<sub>2</sub> for 24 hr (Figure 4, triangle), the data show a strong correlation between the two parameters, suggesting that a clear relationship exists between MoO<sub>x</sub> nanoparticle stoichiometry and electronic properties. A continuous tuning of the Mo<sup>6+</sup> fraction between 0.2 and 1.0, and  $\Phi$  from 4.4 eV to 5.0 eV was achieved. Such control should allow us to systematically study the effect of MoO<sub>x</sub> composition on device performance in various applications.

#### 4. Conclusions

In conclusion, through a systematic study of the effect of  $H_2O_2$  concentration and reaction time on nanoparticle size, work function, and stoichiometry, we demonstrate that *in situ* chemical oxidation of  $MoO_x$  nanoparticle suspensions with  $H_2O_2$  is a simple but versatile method to control their stoichiometry and electronic properties. Starting from suspensions of ultrasmall ( $d \sim 2 \text{ nm}$ ) MoO<sub>x</sub> nanoparticles in *n*-butanol synthesized by a one-step microwave heating procedure, we found that short time ( $\leq 3 \text{ hr}$ ) reactions at room temperature with sufficiently high ( $\geq 0.1 \text{ M}$ ) concentration of  $H_2O_2$  result in  $\leq 1 \text{ nm MoO}_x$  nanoparticles with high work function and almost entirely MoO<sub>3</sub> properties which are desirable for HTL material in OPV devices.



FIGURE 4:  $\Phi$  versus Mo<sup>6+</sup> fraction for npMoO<sub>x</sub> as-synthesized and chemically oxidized at 0.025 M, 0.035 M, 0.042 M, 0.05 M, 0.1 M, and 0.3 M H<sub>2</sub>O<sub>2</sub> concentrations for 1 hr (circles) and at 0.1 M H<sub>2</sub>O<sub>2</sub> for 24 hour (triangle), showing a positive correlation between the two parameters.

However, long chemical oxidation times ( $\geq$ 24 hr) increase nanoparticle size and reduce Mo oxidation state and film's work function. By comparing Kelvin probe results and XPS spectra of npMoO<sub>x</sub> films that have been chemically oxidized under various conditions, we established a clear correlation between the work function and the Mo<sup>6+</sup> fraction of the npMoO<sub>x</sub> and achieved a continuous tuning of work function values from 4.4 to 5.0 eV and Mo<sup>6+</sup> fraction from 0.2 to 1.0. Such precise control of MoO<sub>x</sub> stoichiometry and properties is crucial for the optimization of npMoO<sub>x</sub> as a solution processible material for various applications. Moreover, the simplicity of the chemical oxidation procedure should be generally applicable in synthesizing other transition oxide nanomaterials with tunable stoichiometry and properties.

### Acknowledgments

This project is supported by the University of Texas at Dallas. D. Barrera acknowledges financial support from Consejo nacional de Ciencia y Tecnología and Centro de Investigación en Materiales Avanzados, Unidad Monterrey. J. W. P. Hsu acknowledges the support of Texas Instrument Distinguished Chair in nanoelectronics.

#### References

- A. S. Aricò, P. Bruce, B. Scrosati, J. M. Tarascon, and W. Van Schalkwijk, "Nanostructured materials for advanced energy conversion and storage devices," *Nature Materials*, vol. 4, no. 5, pp. 366–377, 2005.
- [2] P. V. Kamat, "Meeting the clean energy demand: nanostructure architectures for solar energy conversion," *Journal of Physical Chemistry C*, vol. 111, no. 7, pp. 2834–2860, 2007.
- [3] D. R. Rolison, "Catalytic nanoarchitectures—the importance of nothing and the unimportance of periodicity," *Science*, vol. 299, no. 5613, pp. 1698–1701, 2003.

- [4] M. Fernández-García, A. Martínez-Arias, J. C. Hanson, and J. A. Rodriguez, "Nanostructured oxides in chemistry: characterization and properties," *Chemical Reviews*, vol. 104, no. 9, pp. 4063–4104, 2004.
- [5] M. Franke, T. Koplin, and U. Simon, "Metal and metal oxide nanoparticles in chemiresistors: does the nanoscale matter?" *Small*, vol. 2, pp. 36–50, 2006.
- [6] A. K. Gupta and M. Gupta, "Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications," *Biomaterials*, vol. 26, no. 18, pp. 3995–4021, 2005.
- [7] R. Steim, F. R. Kogler, and C. J. Brabec, "Interface materials for organic solar cells," *Journal of Materials Chemistry*, vol. 20, no. 13, pp. 2499–2512, 2010.
- [8] V. Shrotriya, G. Li, Y. Yao, C. W. Chu, and Y. Yang, "Transition metal oxides as the buffer layer for polymer photovoltaic cells," *Applied Physics Letters*, vol. 88, no. 7, Article ID 073508, 2006.
- [9] A. K. K. Kyaw, X. W. Sun, C. Y. Jiang, G. Q. Lo, D. W. Zhao, and D. L. Kwong, "An inverted organic solar cell employing a sol-gel derived ZnO electron selective layer and thermal evaporated MoO<sub>3</sub> hole selective layer," *Applied Physics Letters*, vol. 93, no. 22, Article ID 221107, 2008.
- [10] D. Y. Kim, J. Subbiah, G. Sarasqueta et al., "The effect of molybdenum oxide interlayer on organic photovoltaic cells," *Applied Physics Letters*, vol. 95, no. 9, Article ID 093304, 3 pages, 2009.
- [11] M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, and A. Kahn, "Role of the deep-lying electronic states of MoO<sub>3</sub> in the enhancement of hole-injection in organic thin films," *Applied Physics Letters*, vol. 95, no. 12, Article ID 123301, 2009.
- [12] F. Liu, S. Shao, X. Guo, Y. Zhao, and Z. Xie, "Efficient polymer photovoltaic cells using solution-processed MoO<sub>3</sub> as anode buffer layer," *Solar Energy Materials and Solar Cells*, vol. 94, no. 5, pp. 842–845, 2010.
- [13] J. Meyer, R. Khalandovsky, P. Görrn, and A. Kahn, "MoO<sub>3</sub> films spin-coated from a nanoparticle suspension for efficient hole-injection in organic electronics," *Advanced Materials*, vol. 23, no. 1, pp. 70–73, 2011.
- [14] C. Girotto, E. Voroshazi, D. Cheyns, P. Heremans, and B. P. Rand, "Solution-processed MoO<sub>3</sub> thin films as a holeinjection layer for organic solar cells," ACS Applied Materials & Interfaces, vol. 3, pp. 3244–3247, 2011.
- [15] S. R. Hammond, J. Meyer, N. E. Widjonarko et al., "Lowtemperature, solution-processed molybdenum oxide holecollection layer for organic photovoltaics," *Journal of Materials Chemistry*, vol. 22, pp. 3249–3254, 2012.
- [16] M. Jørgensen, K. Norrman, and F. C. Krebs, "Stability/degradation of polymer solar cells," *Solar Energy Materials and Solar Cells*, vol. 92, no. 7, pp. 686–714, 2008.
- [17] M. T. Lloyd, D. C. Olson, P. Lu et al., "Impact of contact evolution on the shelf life of organic solar cells," *Journal of Materials Chemistry*, vol. 19, no. 41, pp. 7638–7642, 2009.
- [18] Y.-J. Lee, J. Yi, G. F. Gao et al., "Low-temperature solution processed molybdenum oxide nanoparticle hole transport layers for organic photovoltaic devices," *Advanced Energy Materials.* In press.
- [19] I. Bilecka, I. Djerdj, and M. Niederberger, "One-minute synthesis of crystalline binary and ternary metal oxide nanoparticles," *Chemical Communications*, no. 7, pp. 886–888, 2008.
- [20] J. G. Choi and L. T. Thompson, "XPS study of as-prepared and reduced molybdenum oxides," *Applied Surface Science*, vol. 93, no. 2, pp. 143–149, 1996.
- [21] T. C. Arnoldussen, "Electrochromism and photochromism in MoO<sub>3</sub> films," *Journal of the Electrochemical Society*, vol. 123, no. 4, pp. 527–531, 1976.