Research Article

In Situ Chemical Oxidation of Ultrasmall MoO_x Nanoparticles in Suspensions

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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_x nanoparticles in suspensions. Starting from a microwave-synthesized suspension of ultrasmall ($d \sim 2$ nm) MoO_x nanoparticles in *n*-butanol, we added H₂O₂ at room temperature to chemically oxidize the nanoparticles. We systematically varied H₂O₂ concentration and reaction time and found that they significantly affected oxidation state and work function of MoO_x nanoparticle films. In particular, we achieved a continuous tuning of MoO_x work function from 4.4 to 5.0 eV, corresponding to oxidation of as-synthesized MoO_x nanoparticle (20% Mo⁶⁺) to essentially pure MoO₃. This was achieved without significantly modifying nanoparticle size or stability. Such precise control of MoO_x stoichiometry and work function is critical for the optimization of MoO_x 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, large-area 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 (Φ). By matching Φ 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_x HTL films has been reported,

all approaches thus far have required a postdeposition processing step that must be performed either at high temperature ($\geq 160^\circ\text{C}$) [12–14] and/or in an O₂-containing ambient [15] to obtain MoO_x films with high Φ . 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 microwave-assisted synthesis of MoO_x nanoparticles (npMoO_x) in *n*-butanol suspension, demonstrated formation of uniform thin films on poly(3-hexylthiophene): [6,6]-phenyl-C61-butyric 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 pinhole-free thin films. We also quantified the impact of chemical oxidation on Φ and stoichiometry MoO_x thin film and demonstrated continuous tuning of Φ 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 Φ for the formation of thin HTL on top of organic active layer without postprocessing.

2. Experiments

MoO_x nanoparticle (npMoO_x) suspensions were synthesized using nonhydrolytic sol-gel conversion of molybdenum dioxide bis(acetylacetonate) (MoAcAc) in anhydrous *n*-butanol 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_2 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_2O and O_2 , can be easily removed during subsequent processing. For chemical oxidation, a small amount of 30 wt% H_2O_2 in H_2O (Fisher) was added to the npMoO_x suspension to achieve the desired concentration (e.g., 10.2 μL of 30 wt% H_2O_2 in H_2O per mL of suspension for 0.1 M H_2O_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_x 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 μm PTFE syringe filter. The diluted suspension was analyzed by dynamic light scattering (DLS) under backscattering conditions using a Malvern Zetasizer. Φ 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 μm PTFE syringe filter and spin coated at 1000 rpm on a cleaned ITO coated glass (20 Ω/sq , thin film devices). Φ of the npMoO_x 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_3 on ITO was made by thermal evaporation at a rate of 0.1 Å/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 as-synthesized npMoO_x suspension found a volume weighted mean diameter of $2.1 \pm 0.9 \text{ nm}$ (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 H_2O_2 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_2O_2 at short reaction times ranging from 20 min to 3 hr decreased the npMoO_x diameter to $\sim 1 \text{ nm}$. 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 npMoO_x 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_2O_2 . Nevertheless, the nanoparticles are still small enough to form multilayer films with thickness of $\sim 10 \text{ nm}$. Indeed, we previously showed using atomic force microscopy that a chemically oxidized MoO_x suspension spin coated on top of P3HT:PCBM formed a pinhole-free 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_x nanoparticles significantly altered the electronic properties of npMoO_x films, as measured by their Φ values in air. The as-synthesized npMoO_x exhibited a low Φ of $4.48 \pm 0.02 \text{ eV}$. Addition of 0.05 M H_2O_2 for 20 min caused Φ to increase to $4.82 \pm 0.04 \text{ eV}$, 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_2O_2 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 np MoO_x size to decrease to 1 nm (up to 3 hrs) and then increase back to 2 nm (24 hr). (b) Dependence of nanoparticle film Φ versus chemical oxidation conditions, showing Φ of as-synthesized np MoO_x (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 Φ to 4.9 eV.

increase Φ (Figure 2(b), purple). Increasing H_2O_2 concentration to 0.1 M and above caused Φ to increase to 4.94 ± 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 Φ to decrease to 4.90 ± 0.01 eV. We note that the decrease in Φ corresponded to the change of the nanoparticle suspension color from brown to blue (Figure 1).

To quantitatively understand the origin of the change in Φ with chemical oxidation, we examined the stoichiometry of np MoO_x films with different H_2O_2 reaction conditions using XPS. As a reference, we measured evaporated MoO_3 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_{5/2} and Mo 3d_{3/2} peaks for Mo^{6+} , plus very weak doublet peaks at 231.0 eV and 233.8 eV corresponding to Mo 3d_{5/2}

and Mo 3d_{3/2} peaks for Mo^{5+} [18, 20]. The Mo^{6+} fraction, defined as the area under the Mo^{6+} peaks divided by the total peak area, was 0.95, indicating that the reference sample was almost pure MoO_3 . The FWHM of the fitted peaks was 1.2 eV, and this value was used for all peaks when fitting XPS spectra of np MoO_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 as-synthesized np MoO_x contain peaks at 232.4 eV and 235.5 eV from Mo^{6+} , 231.4 eV and 234.5 eV from Mo^{5+} , 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 np MoO_x is mostly reduced. Reaction with 0.05 M H_2O_2 for 1 hr caused the Mo^{6+} peaks to increase in intensity at the expense of the Mo^{5+} and Mo^{4+} peaks, (Figure 3(b)), so that the Mo^{6+}

FIGURE 3: Effect of chemical oxidation conditions on MoO_x nanoparticle stoichiometry. (a) Mo 3d XPS spectra of as-synthesized npMoO_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 npMoO_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 npMoO_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 npMoO_x after chemical oxidation with 0.1 M H_2O_2 for 24 hr, showing mixed oxidation states with a majority of Mo^{6+} oxidation state.

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

In our case, H^+ is supplied by the H_2O in the 30 wt% H_2O_2 solution, and e^- may be supplied by oxidation of neighboring Mo^{4+} and Mo^{5+} atoms. This reaction scheme is consistent with the observation that the change in npMoO_x coloration from brown to blue was only observed after 24 hr reaction with 0.1 M and 0.3 M H_2O_2 . The onset of color change, and by reference the proton insertion, also coincides with the increase in nanoparticle size and reduction in Φ . Thus, analysis of XPS spectra reveals that chemical oxidation with H_2O_2 consists of two concurrent processes, a fast oxidation that is complete at 0.1 M and higher H_2O_2 concentrations within ~ 1 hr, and a slow reduction caused

by H^+ insertion that occurs after ~ 24 hr, highlighting the importance of the chemical oxidation conditions on the stoichiometry of the resulting npMoO_x .

Figure 4 depicts Φ and Mo^{6+} fraction that can be achieved using the *in situ* H_2O_2 chemical oxidation approach. For npMoO_x films that were chemically oxidized at different H_2O_2 concentrations for 1 hr (Figure 4, circles) and at 0.1 M H_2O_2 for 24 hr (Figure 4, triangle), the data show a strong correlation between the two parameters, suggesting that a clear relationship exists between MoO_x nanoparticle stoichiometry and electronic properties. A continuous tuning of the Mo^{6+} fraction between 0.2 and 1.0, and Φ from 4.4 eV to 5.0 eV was achieved. Such control should allow us to systematically study the effect of MoO_x 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 ($d \sim 2$ nm) MoO_x nanoparticles in *n*-butanol synthesized by a one-step microwave heating procedure, we found that short time (≤ 3 hr) reactions at room temperature with sufficiently high (≥ 0.1 M) concentration of H_2O_2 result in ≤ 1 nm MoO_x nanoparticles with high work function and almost entirely MoO_3 properties which are desirable for HTL material in OPV devices.

FIGURE 4: Φ versus Mo^{6+} fraction for npMoO_x 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_2O_2 concentrations for 1 hr (circles) and at 0.1 M H_2O_2 for 24 hour (triangle), showing a positive correlation between the two parameters.

However, long chemical oxidation times (≥ 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_x films that have been chemically oxidized under various conditions, we established a clear correlation between the work function and the Mo^{6+} fraction of the npMoO_x and achieved a continuous tuning of work function values from 4.4 to 5.0 eV and Mo^{6+} fraction from 0.2 to 1.0. Such precise control of MoO_x stoichiometry and properties is crucial for the optimization of npMoO_x 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.

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