A facile and controllable electrochemically fabricated nonstoichiometric MoO$_{x}$ film for novel opto-electronic devices

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Abstract
Non-stoichiometric transition metal oxides have received considerable attention because of their excellent optical and electrical properties for novel high performance opto-electronic devices or photocatalysis, among which MoO$_{x}$ was one promising candidate. However, few studies have been focused on its evolution under different controlling parameters and ambient conditions. In this work, we report a facile electrochemical method for smooth and uniform non-stoichiometric MoO$_{x}$ films, with effective control of the morphology, chemical composition and microstructure of molybdenum simply by a few physical/chemical parameters. The modification of roughness, crystallinity, oxygen vacancy concentration can play an important role in their opto-electronic performances, e.g. in the perovskite solar cells. As a result, a conversion efficiency of 9.20% could be obtained by control of oxygen vacancies and crystallinity and could be further improved with the change of transparencies. Furthermore, its wetting properties could be significantly influenced for further applications, especially for fabrication of novel detectors and perovskite solar cells.

Keywords: nonstoichiometric materials, metal oxide, electrochemical fabrication, structural and content evolution, physical and chemical manipulation

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction
In recent years, non-stoichiometric metal oxides such as NiO$_{x}$ [1, 2], CuO$_{x}$ [3, 4], WO$_{x}$ [5], MoO$_{x}$ [5, 6], and TiO$_{x}$ [7–9] have drawn great interest due to their excellent properties (tunable wide band gap, high electron/hole transportability, photo/electrochromic effect and so forth) toward novel optical, electrical and photocatalytic devices with high stability and low cost. In particular, MoO$_{x}$ is one promising candidate for hole transport layer (HTL) in perovskite solar cells (PSCs) owing to its non-toxicity, large band gap and deep electronic state [10, 11]. Xiao et al applied MoO$_{x}$ as HTL in p-i-n type PSC with efficiency of 5.9% [6]. Tseng et al treated MoO$_{x}$ with UV-ozone to improve the surface coverage of the perovskite layer and achieved the efficiency of 13.1% [5]. Moreover, MoO$_{x}$ has also received considerable attention for research and development in a variety of applications, such as photochromic and electrochromic [12–16], gas sensors [17–19], photocatalytic [20], lithium ion batteries [21] and light emitting diodes [22].

According to a previous report [23], amorphous MoO$_{x}$ film is quite a susceptible material, which means the non-uniformity and time evolution of its stoichiometry and
microstructure have been quite significant. This could be an essential issue both in its fabrication and in its performance in devices as a stable element. Up till now, only a few studies have been carried out for the correlation between some properties and the annealing conditions and its consequence, however more systematic investigations concerning such issues under composite conditions are yet to be carried out [24–28]. The aforementioned molybdenum oxide films were all prepared via thermal evaporation in vacuum, which has significant drawbacks in cost and scalability for large area samples. Meanwhile, various chemical synthesis methods in liquid phase have also been developed, such as sol-gel [29], spray pyrolysis [30], and spin coating [11], which are significantly more simple. In those methods, the motion of reactive species only relies on thermal diffusions that could influence the quality of the formation of layers on substrates. To amend that, electrochemical deposition appears to be the more likely promising candidate as a cheap and controllable technique that could provide effective control of morphology, composition as well other properties of the deposit at room temperature under ambient conditions [31–34]. In addition, it also enables large-area film preparation without any mechanical instruments [1, 35].

In this work, we report a facile electrochemical method for non-stoichiometric metal oxide films with studies of evolution of its physical and chemical properties with various parameters. A smooth and uniform MoOx could be easily formed using cyclic voltammetry (CV) method. Its stoichiometry, crystallinity and morphology could be effectively controlled by experimental parameters and ambient conditions (UV illumination, annealing time, temperature and atmosphere) so as to achieve different physical properties for corresponding applications in solar cells and other devices [25]. As a result, the p-i-n type PSCs employing the electrochemically deposited MoOx as HTL can achieve a power conversion efficiency (PCE) up to 9.20% which could be further raised by improvements such as the transparency of light incident side. Furthermore, it has also been found that the wetting property of this MoOx could be significantly influenced by those conditions, which would be important for its further applications, especially for detectors and improvement for the fabrication of stable PSCs.

2. Experimental

2.1. Synthesis and modification of MoOx

Firstly, 0.34 M aqueous solution of hexammonium molybdate (NH4)6Mo7O24·H2O, 99% Energy Chemical) was prepared with deionized water, and then slowly mixed with 20ml ethylene glycol (99% Sinopharm). The solution was stirred via thermal evaporation in vacuum, which has significant drawbacks in cost and scalability for large area samples. Meanwhile, various chemical synthesis methods in liquid phase have also been developed, such as sol-gel [29], spray pyrolysis [30], and spin coating [11], which are significantly more simple. In those methods, the motion of reactive species only relies on thermal diffusions that could influence the quality of the formation of layers on substrates. To amend that, electrochemical deposition appears to be the more likely promising candidate as a cheap and controllable technique that could provide effective control of morphology, composition as well other properties of the deposit at room temperature under ambient conditions [31–34]. In addition, it also enables large-area film preparation without any mechanical instruments [1, 35].

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2.2. Characterization of MoOx

A field emission scanning electron microscope (FE-SEM, Zeiss Ultra Plus) was applied to observe the surface morphology and thickness of the MoOx films on the FTO-coated glass substrates. The chemical state of the samples was analyzed by x-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD). The XPS spectra were fitted with the Gaussian–Lorentzian product using the XPSPEAK41 software package. Their microstructure was detected by grazing incidence x-ray diffraction (GIXRD), at the 7.3.3 beamline (10keV) at advanced light source (ALS) of lawrence berkeley national laboratory (LBNL). The scattering intensity was detected by a PILATUS 2M detector and a two-dimensional (2D) area detector was employed here to obtain more complete crystal information than the diffraction intensity versus 2θ plot. The transmission spectra of the thin film samples were measured by ultraviolet/visible/near-infrared (UV/VIS/NIR) Spectrophotometer (Lamda 950, PerkinElmer). The surface roughness of the films was characterized by an atomic force microscope (AFM, Innova). The contact angles of water droplets were measured on a contact angle measuring system (DSA100, KRUSS) at room temperature.

2.3. Assembling PSCs based on MoOx

The fabrication of the perovskite layer was performed in a N2 protected glove box. 1.45 M PbI2 (99% Sigma-Aldrich) and equimolar MAI (99.5% Materwin) were dissolved in a mixture of γ-butyro lactone (GBL, 99.9% Aladdin) and dimethyl sulfoxide (DMSO, 99.9% Aladdin) by stirring for 12 h. The PbI2/MAI solution was then filtered using a 0.2 μm filter. A solution of PC61BM (20 mg ml−1) as HTL was then deposited on the as-formed samples by spin-coating a chlorobenzene solution of PC61BM (20 mg ml−1) at 2000rpm for 30s and desiccation at 70 °C for 10 min. Afterwards, a bathocuproine (BCP, 99% Xi’an Polymer light Technology Corp.) layer was sequentially deposited on the PC61BM layer by spin-coating
an isopropanol solution of BCP (0.5 mg ml⁻¹) at 500 rpm for 5 s and then at 4000 rpm for 30 s, followed by desiccation at 70 °C for 10 min. Finally, a 120 nm-thick Ag was thermally evaporated on top of the BCP layer of the electrode. The active area of the device is 0.25 cm².

2.4. Characterization of solar cells

The steady-state photoluminescence (PL) was measured by a Raman spectrometer (LABRAM HR800, Horiba Jobin Yvon system (France)) with excitation at 514.5 nm by an argon ion laser. For the PSC devices, the current density–voltage (J–V) characteristics were measured using a standard Solar Simulator (Newport, Oriel Sol-2A) under 1 sun AM 1.5 illumination. The simulator was calibrated by a standard reference Si solar cell (effective area 2 × 2 cm², certified by VLSI Standards Inc.) before the measurement. All J–V curves were scanned from −0.5 V to 1.5 V. The scanning rate and time delay were 0.15 V s⁻¹ and 10 ms, respectively. The external quantum efficiency (EQE) spectra were recorded by a quantum efficiency/IPCE system (PV Measurements Inc., QEX10) in 300–850 nm wavelength range in air.

3. Results and discussion

In conventional electrochemical deposition of metal oxides, experiments are normally carried out in acidic or alkaline electrolytes, for which a good control of the pH value becomes necessary and needs to be successively controlled by titration method throughout the process. In this work, we carried out the fabrication in hexaammonium molybdate solution and no titration was needed. For higher quality of film growth, the CV method has been applied and investigated [1, 33, 36, 37]. Figure 1(a) shows corresponding I–V curves recorded at the sweep rate of 3 mV s⁻¹, 5 mV s⁻¹, and 10 mV s⁻¹, respectively. The curves are almost coincident at the rate of 3 mV s⁻¹ but the peak of the negative cycle becomes stronger at 5 mV s⁻¹. As shown in figures 1(b)–(d), the film thickness gradually decreases as the cycle rate increases. However, at 10 mV s⁻¹, the as-deposited film could not completely cover the FTO-coated glass substrate in figure 1(d). Therefore, the sweep rate of 5 mV s⁻¹ appeared to be a more suitable condition for deposition. Moreover, we have investigated the influence of the lower limit of the potential on the morphology of the electrodeposited film. The CV experiments were then carried out using a series of lower potential limits of −1.2, −1.0 and −0.8 V. As shown in figure 1(f), when the lower limit potential was −0.8 V, the reduction current was very low and the film could not completely cover the substrate. The film became uniform for the lower limit at −1.0 and −1.2 V and increased with the value of lower limit potential. At −1.2 V in figure 1(h), the film was too thick, which could eventually lead to high series resistance and lower transparencies [38]. Therefore, the moderate condition (−1.0 to 0.5 V at 5 mV s⁻¹ for 1 cycle) appears more suitable for p-i-n PSCs in which MoO₃ acts as both HTL and light incident side.

lower limit in CV method could be used in other fields such as the photocatalysis, where a longer light path would be more important and serial resistance becomes less important.

To qualitatively determine the formation of MoO₃, XPS measurements have been carried out to confirm the stoichiometric composition of the virgin film, in which 284.8 eV of C1s orbit has been chosen as the reference binding energy. First of all, the full spectrum in figure 1(g) shows the peaks of Mo3s, Mo3d, Mo3p, Mo4s, C1s and O1s. Secondly, the high resolution XPS spectrum of Mo3d core level peaks is exhibited in figure 1(j). The Mo3d spectrum can be divided into one 3d doublet in the form of Gaussian function, corresponding to the oxidation state of Mo. The fitting peaks located at 235.2 eV and 231.9 eV are assigned to the Mo⁵⁺ valence state [32, 39], then the O1s spectrum is shown in figure 1(k). According to previous studies, it is known that the peak at ~530 eV is due to the oxide, the one at ~532 eV is attributed to oxygen species dissolved in the metal or adsorbed oxygen (such as O²⁻, OH⁻, or H₂O) [40]. This result represents the significant existence of molybdenum Mo⁵⁺ valence state in the as-fabricated sample. Taking into account the previous characterization, it can be confirmed that the as-deposited sample was non-stoichiometric MoO₃ (x = 2.5).

In the many applications of non-stoichiometric metal oxides, their crystallinity and stoichiometry have always been important factors that determine its performance in gas sensors, photocatalysis, and photochromic/electrochromic devices and so forth [12–14, 18]. As commonly known, amorphous MoO₃ film is quite susceptible to ambient conditions [23]. Therefore, we have systematically studied the effects of these conditions (UV-ozone, temperature, time and atmosphere) on the MoO₃ film. To investigate the crystallinity of the sample fabricated, we have applied 2D GIXRD (incident x-ray angle at 0.3°) for the FTO substrate (figure 2(a)), the thin MoO₃ film obtained (figure 2(b)) and the MoO₃ films after different post-treatments (figures 2(c)–(f)). Figures 2(a) and (b) indicate that the as-deposited film was amorphous because no significant diffraction peak of MoO₃ was detected during q = 0.5–4.0 A⁻¹. The results with UV-ozone (figure 2(c)) show no other significant diffraction peak compared to figure 2(a), indicating that the corresponding films were still amorphous. However, more diffraction peaks can be observed in figures 2(d) and (e), for samples annealed in air and oxygen, respectively. In figure 2(d), there were broad diffraction peaks related to the (002), (040) and (060) crystal planes, while the one related to (020) plane was quite sharp and intense. Since the (020) plane is located close to the q, axis, it indicates that the grains in the MoO₃ film annealed in air had their face-on orientation parallel to the surface of the film. As for the case of O₂, there was observed four diffraction peaks along the Debye rings, with their intensity stronger than that in figure 2(d), especially the ones at the (020) and (060) directions. Surprisingly, for the sample annealed in nitrogen (figure 2(f)), there was no significant additional diffraction peak discovered, which means quite weak crystallization in the MoO₃ annealed in N₂. The average grain size of MoO₃ can be obtained from the
The Debye-Scherrer equation of $D = 0.89 \lambda / (\beta \cos \theta)$, where $\beta$ is the half-width of the diffraction peak, $\lambda$ is the wavelength of the x-ray and $\theta$ is the diffraction angle [41]. The $\beta$ for the samples annealed in air and oxygen atmospheres are 0.0037 and 0.0025 rad, respectively. Therefore the average crystalline sizes for MoO$_x$ annealed in air and oxygen are around 37 and 55 nm, respectively. According to the experimental observations of Andreas et al, peaks at 12.76°, 25.70°, and 38.98° indicate formation of $\alpha$-MoO$_3$, consistent with the positions shown in figure S4 in the supplementary information (stacks.iop.org/JMM/29/065012/mmedia) [42].

The stoichiometry of the post-treated samples was characterized by high resolution XPS, as shown in figure 3. The Mo3d spectra contained only one 3d doublet located at 236.3 eV, 233.2 eV (figure 3(a)), 236.0 eV, 232.8 eV (figure 3(b)), and 236.3 eV, 233.2 eV (figure 3(c)) that are all related to Mo$^{6+}$ [39, 43]. The MoO$_x$ has seemingly completely turned into MoO$_3$ by UV-ozone and annealing processes in air or O$_2$, with the Mo$^{5+}$ all being oxidized to Mo$^{6+}$. For the MoO$_x$ film annealed in nitrogen atmosphere, there are two 3d doublets in the form of a Gaussian function as shown in figure 3(d). The ones centered at 236 eV and 232.8 eV are the typical doublet of Mo$^{6+}$, while the other ones centered at 234.6 eV and 231.9 eV are the typical doublet of Mo$^{5+}$ [31, 43]. Assuming the ratio of the quantity of Mo$^{5+}$/Mo$^{6+}$ (calculated from the ratio of integrated peak area) is $k$, it can be easily calculated that $x = 2.5 + (2k + 2)^{-1}$. In this situation, the ratio of Mo$^{5+}$/Mo$^{6+}$ is 0.77, which means $x = 2.78$.

Beside direct characterizations, it is important to study opto-electronic properties of the MoO$_x$ samples before being integrated with different materials in devices. Firstly, the UV–vis transmission spectra of various MoO$_x$ films have been studied and illustrated in figure 3(e). It is clearly observed that the untreated film has shown quite high transparency in the region from 350 to 800 nm, which is important to avoid the parasitic absorption loss of perovskite. When the molybdenum oxide films were subjected to different post-treatments, the transmittance shows no substantial change. However, the transmittance of the film annealed in a nitrogen atmosphere was lower (figure S3). Such a change might be attributed to the content of oxygen vacancies in the films, according to some previous report [13]. Furthermore, we can deduce the bandgap information from the transmittance measurement. According to Lee et al, MoO$_3$ is a wide, indirect bandgap semiconductor [26]. The optical band-gap ($E_g$) of the samples can be calculated from the equation $\alpha h \nu = A (h \nu - E_g)^{1/2}$ [43], where $A$ is the proportionality constant, $\alpha$ is the absorption coefficient and $h \nu$ is the photon energy. As shown in figure 3(f), taking $h \nu$ as the horizontal axis and $\alpha h \nu$ as the vertical axis, $E_g$ can be estimated by extrapolating the linear portion of the curve to zero absorption. The $E_g$ of the MoO$_x$ films was estimated to be 3.31 eV, 3.90 eV, 3.89 eV, 3.88 eV and 3.85 eV for the samples unprocessed, treated with UV-ozone, annealed in air, O$_2$ and N$_2$, respectively. In general, the $E_g$ of the post-treated films were all significantly larger than the original one. Such increase of $E_g$ may be due
attributed to the crystallization in the MoO薄膜 annealed in air, oxygen, and nitrogen, respectively. There was a corresponding to samples untreated, treated by UV-ozone, UV-ozone, UV-ozone, and comparing to the samples treated with UV-ozone. The PL intensity was the most intense peak intensity, while the ones treated in air exhibited significantly weaker peaks. The lowest PL intensity was obtained for MoO薄膜 annealed in nitrogen atmosphere. The samples treated in oxygen atmosphere show the lowest PL intensity, which could be due to the great enhancement of structural defects in the band gap and transporting carriers, and compared to the stoichiometric MoO3, the devices using non-stoichiometric MoO3 display a good performance [26, 44]. In the meantime, too high oxygen vacancy concentration might also be a problem due to possible semiconductor-metal transition, and eventually lead to device failure [26]. According to this, the main origin for the distinctive performance of PSCs by annealing with N2 and O2 atmosphere is the amount of oxygen vacancies and complete absence of oxygen vacancies (according to previous calculation for figure 3) under these two conditions, respectively. The annealing under air atmosphere can generated a smaller quantity of oxygen vacancies than that under O2 atmosphere (though it may not be significantly detected in XPS due to its sensitivity limitation), which has induced higher performance of PSCs. More interestingly, combining both the PL and GIXRD results, it can be seen that the highest performance in PSCs was with the lowest level of crystallization by annealing with N2. Work from other researchers have reported good performance of cells with amorphous substrate as well [11]. Nevertheless, the mechanism of this phenomenon—why less crystallinity and better performance manifests under N2—still needs further investigation, for example theoretical calculations.

The influence of temperature and time on the PSCs was studied further with nitrogen atmosphere annealing toward better optimization for the device performance, as shown in figure 4(d) (detailed performance data can be found in table S2). For the temperature, VOC, JSC, FF and PCE were all significantly increased with the increasing of the annealing temperature from 250 °C to 300 °C. However, when the temperature was higher than 300 °C, the efficiency began to significantly decrease with a considerable decrease of the Rsh, which could be due to the great enhancement of inhomogeneity of the film under such a high temperature (can be referred from the SEM image in figure S5(a)). The PCE gradually increased with the annealing time increasing from 60min to 210min, and then began to decrease after 210min,
which could also be due to the inhomogeneity of the film as shown in figure S5(b). Therefore, as shown in figure 4(d), conditions around 300 °C and 210 min would be more suitable for a better performance of the MoO$_x$ in the PSCs.

Up till now, the performance of the MoO$_x$ in PSCs appeared to be low compared to previous methods. According to the principle of the reaction, bubbles of hydrogen can be generated during the electrochemical reactions, so mechanical stirring is another favorable factor for further optimization [45]. Hence, we have carried out the fabrication with different mechanical stirring rates using the optimized annealing condition. As indicated in figure 5, the performance of the PSCs was significantly improved by the application of stirring. The PCE reached 7.70% (with $V_{OC} = 0.89$ V, $J_{SC} = 12.04$ mA cm$^{-2}$ and FF = 0.72) at 50 rpm and became gradually higher at 100 rpm ($\eta = 9.20\%$, $V_{OC} = 0.91$ V, $J_{SC} = 14.27$ mA cm$^{-2}$, and FF = 0.71). As the stirring speed was further increased to 150rpm, the device performance improved.
began to slightly decrease, which indicated that too high a stirring rate might influence the ionic current so that the stability of deposition deteriorates. The corresponding EQE spectra are shown in figure 5(b), including the integrated current densities as a function of wavelength. All the devices have exhibited a strong response in a broad range from 400 to 750 nm, and the EQE of the sample at 100 rpm exceeded other devices within the entire region. In addition, the $J_{SC}$ values calculated from the EQE curves were 18.47, 22.11 and 17.07 mA cm$^{-2}$ at stirring rates of 50, 100 and 150 rpm, respectively, which is consistent with the variation of the $J$–$V$ curve. As can be observed, the FF was significantly improved, which means the quite good conductivity of the as-fabricated MoO$_x$ film, which is also important for its application in devices other than solar cells. The main reason why the efficiency of those cells was still lower than the commonly known PSCs is most likely due to the low transparency of the electrochemically fabricated MoO$_x$ film, which is also important for its application in devices other than solar cells. According to above results and previous reports, MoO$_x$ has been quite susceptible to ambient conditions, and as widely recognized in practice, the combination of the layer with other materials has always been important for real devices. Therefore, it will also be important to study any macroscopic changes of the surface situation that could be induced by previous experiments. We have therefore carried out measurement of the contact angles of the samples under different conditions. As shown in figure 6, significant changes have taken place after the treatments. In general, all the contact angles have been reduced after annealing. Among those results, the final contact angle was the lowest in air, a mixture of N$_2$ and O$_2$, and highest in pure N$_2$. Such variation could be due to the composite effect of oxygen vacancies and morphology change due to nucleation [46, 47]. On the one hand, the formation of oxygen vacancies can result in lattice relaxation and a decrease of surface tension, which explains the relatively higher contact angle under N$_2$ compared to O$_2$ and air cases. On the other hand, more heterogeneous nucleation (as shown in figure S3) can occur because of the formation of fewer oxygen vacancies in air than under pure O$_2$, which induces a rougher surface compared with oxygen conditions and therefore the lowest contact angle. The variation of the contact angle was seemingly consistent with the performance of MoO$_x$ in the PSCs, as indicated in figure 4. This could be understood by the correlation of the wettability of MoO$_x$ and the grain morphology of perovskite. According to the literature, the wettability of DMF droplets is similar with water on the MoO$_x$ surface [48]. A larger contact angle enables faster diffusion of the droplets and less drag force to the precursors so that less heterogeneous nucleation is induced. Moreover, as shown in figure 5(e), the UV-ozone treatment induces a very small contact angle, which could be a deteriorating factor for the formation of the perovskite layer in PSCs. Nevertheless, such a low contact angle could be beneficial for other devices such as gas sensors or photocatalytic devices based on MoO$_x$.

4. Conclusion

To summarize, we have fabricated the MoO$_x$ material using a controllable electrochemical method and have systematically investigated its evolution of stoichiometry, morphology and
microstructure under different conditions (electrochemical parameters, annealing, chemical atmosphere, UV radiation, etc) for the first time. It can be seen that the oxygen vacancies can be effectively controlled by these conditions, to achieve the highest efficiency so far of 9.20%, and to influence the performance of MoO₃ after integration into devices such as PSCs. Interestingly, the highest performance was obtained with the fewest oxygen vacancies by annealing under N₂ where the crystallization of MoO₃ was not seen. The crystallography and oxygen vacancy control in the application of MoO₃ material. Furthermore, this suggests the dominant importance of the oxygen vacancy according to its characterization as well as its transparency. The variation of conditions has significantly influenced the wettability of the MoO₃ film with the variation of the contact angle quite consistent with the results in corresponding solar cell performance, which have been attributed to the cooperation of the oxygen vacancies and nucleation under different conditions. This work will hopefully provide ideas for performing different post-treatments to achieve higher conversion efficiency of cells.

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