

Dehydration of Tungsten Oxide Hole Extraction Layers via Microwave Annealing for Efficiency and Lifetime Enhancement in Organic Solar Cells

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Abstract

A significant contribution to the efficiency and lifetime enhancement of organic solar cells is due to the successful engineering of the metal contact/organic interface by introducing appropriate interlayers. In the current work we show that a short microwave post-annealing treatment in air of an under-stoichiometric tungsten oxide (WO_x) hole extraction layer significantly enhanced the performance and lifetime of an organic solar cell based on the poly(3-hexylthiophene):[6,6]-phenylC70butyric acid methyl ester (P3HT:PC₇₀BM) blend. The enhanced performance is mainly driven by the increased work function of the anode, the reduced series and increased shunt resistances and also the higher charge generation efficiency, the reduced recombination losses and the improved hole transport towards the anode contact. In addition, the lifetime of the devices with the microwave annealed WO_x interlayers was also significantly improved compared to those with the as-deposited WO_x and, especially, to those with the PEDOT-PSS interlayer. The above were attributed to the effective dehydration which was also followed by the weak structural transformation and crystallization of the WO_x layer during microwave annealing, as revealed by the x-ray and infrared measurements.

Keywords: microwave exposure, dehydration, tungsten oxide, organic solar cell

1. Introduction

Organic solar cells (OSCs) based on bulk heterojunction (BHJ) structure have attracted considerable attention due to their unique advantages such as light-weight materials, low-cost fabrication, and simple solution-based processing¹, lowering the cost at 10 dollars per square meter. Recently, a significant improvement in the BHJ-OSCs performance has been demonstrated obtained by synthesizing novel photoactive polymers², designing optimal device architecture³, modifying and controlling photoactive film nanomorphology⁴ and inserting interfacial layers⁵. The modification of the photoactive layer/electrode interface is crucial to the improvement of both charge transport and extraction, while reducing the

interfacial charge recombination losses, and thus improving the power conversion efficiency (PCE) of the device. Transition metal oxides (TMOs) such as MoO_3 ⁶, WO_3 ^{7,8} and V_2O_5 ⁹ have been used in various optoelectronic devices. TMOs exhibiting high work functions have been proposed and employed as effective hole extraction interlayers to enhance OSC device performance and also improve the stability of the interfacial photoactive layer/anode contact. The main advantage of TMOs is their deep electronic levels (valence band and work function of WO_3 at 7.7 eV and 6.0 eV, respectively) which largely promote the Fermi level pinning at the polymer/oxide interfaces leading to the reduction of the hole extraction barriers. Recently, great research progress has been made on the use of under-stoichiometric metal oxides to enhance hole extraction through the formation of gap states near the Fermi level of the metal oxides¹⁰. In our previous work, we have explored the benefits of hydrogen ion (H^+) intercalation in the WO_3 lattice to form hydrogenated tungsten oxide ($\text{H}_y\text{WO}_{3-x}$) films, which exhibit gap states near the Fermi level, while maintaining their high work function, thus, allowing energetic alignment at the anode/polymer interface¹¹. Although the hydrogenation of the tungsten oxide enhances the conductivity of the film and facilitate the hole transport, the reduced deposition environment of the oxide containing hydrogen leads to the incorporation of free or coordinated water molecules within the lattice of the tungsten oxide structure, which may results in degradation of the device performance caused by the possible oxidation of electrodes and/or organic semiconductors. Therefore, effective dehydration of metal oxides used as interfacial layers in organic solar cells without altering the material composition poses a great challenge in the enhancement of the device performance. In this work, under-stoichiometric tungsten oxide (WO_x) films are used as hole extraction layers (HELs) in OSC devices after being subjected to a short microwave exposure. It is well known that microwave annealing technology offers great advantages of simple, fast and low-cost materials processing, using a common microwave oven. Herein, we demonstrate the effective dehydration of WO_x obtained by the microwave exposure

of the film. It is also shown that during microwave annealing a short range atomic re-arrangement and crystallization take place in WO_x films as revealed by X-ray diffraction and Fourier-transform infrared measurements. Furthermore, a significant improvement of the PCE and lifetime of the OSCs are observed when microwave-annealed WO_x films are used as hole extraction layers. The reported PCE value of the microwave-annealed WO_x -based device of 4.65 % representing a 50% improvement relative to the device with the as-deposited WO_x interlayer, is attributed to the significant enhancement of J_{sc} and FF arising from increased R_s resistance.

2. Experimental

2.1. Metal oxide preparation

Under-stoichiometric tungsten oxide (WO_x) films were deposited using a homemade deposition system equipped with a W filament, as previously described¹². The samples were positioned in a stainless steel reactor 2 cm below the W filament which was heated at 650 °C by a (AC) current by using two Cu leads. Note that the substrates were maintained at room temperature. The deposition environment contained hydrogen; the base pressure used was 80 mTorr set by the controlled flow of forming gas (FG, a gas mixture of 90 % N_2 and 10 % H_2). After the metal oxide deposition some samples were subjected to microwave irradiation using a microwave oven which generates RF radiation at a nominal frequency of 2.45 GHz and a heating power level of typically 100 – 900 W. The heating power was optimized at 600 W in order to obtain better device performance, while the time of exposure was one minute.

2.2. Device fabrication

OSC devices were fabricated on FTO-coated glass substrates ($2 \times 2 \text{ cm}^2$) with sheet resistance of 20 Ω/sq which served as the anode electrode. The substrates were ultrasonically cleaned with deionized water, acetone and isopropanol. Then a WO_x layer was deposited on top of FTO and subjected or not to microwave irradiation for one minute to serve a hole extraction layer. In some devices a poly (3,4-ethylene-dioxythiophene):polystyrene sulfonate (PEDOT:PSS) film was spin-coated on FTO to serve an HEL for comparison reasons. The photoactive layer consisted of a P3HT:PC₇₀BM (P3HT and PC₇₀BM were purchased from Sigma-Aldrich and Solenne, respectively) blend with a 1:0.8 wt % ratio with a concentration of 10 mg/mL in chloroform solution and it spin-coated on top of the metal oxide layer at 600 rpm. After spin-coating, the photoactive layer was annealed at 135 °C for 10 minutes in air. The devices were completed with a 150 nm thick aluminum cathode electrode deposited in a dedicated chamber.

2.3. Measurements and instrumentation

FTIR transmission spectra of all WO_x films were obtained on a Bruker Tensor 27 spectrometer (at 4 cm^{-1} resolution, 64 scans) with a DTGS detector. X-ray diffraction (XRD) structural analysis was performed using a Siemens D500 diffractometer with Cu-K α radiation. The surface morphology was investigated using a NT-MDT atomic

force microscope (AFM) operated in tapping mode. EQE measurements were carried out using an Autolab PGSTAT-30 potentiostat, with a 300 W Xe lamp in combination with an Oriel 1/8 monochromator for dispersing the light in an area of 0.5 cm^2 . A Thorlabs silicon photodiode was used for the calibration of the spectra. Current density-voltage characteristics of the fabricated solar cells were measured with a Keithley 2400 source-measure unit. Cells were illuminated with a Xe lamp and an AM 1.5G filter to simulate solar light illumination conditions with an intensity of 100 mW/cm^2 (1 sun), as was recorded with a calibrated silicon photodiode

3. Results and discussion

In order to investigate the chemical composition, structure and morphology of the microwave-annealed WO_x films (termed hereafter as mw- WO_x), infrared (IR) spectroscopy, X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) measurements were performed. Note that the microwave-annealed under-stoichiometric tungsten oxide films were prepared by exposing the as-deposited ones to microwave irradiation at 600W for one minute, as mentioned in the experimental section. Figure 1a and b show the IR transmittance spectra of the as-deposited WO_x (termed hereafter as WO_x) and the mw- WO_x , respectively. In the spectrum of the as-deposited WO_x a peak at 1620 cm^{-1} is observed corresponding to the bending of water and O-H groups, and a broad band centered at 3400 cm^{-1} which corresponds to the stretching of water and O-H groups. The appearance of those peaks indicates the incorporation of large amount of water molecules in the structure of the as-deposited tungsten oxide, which is attributed to the hydrogen contained in the deposition environment of the metal oxide. Therefore, the as-deposited WO_x films are considered hydrated. However, the microwave annealing at 600 W of the films nearly quenches the above peaks (Figure 1b) indicating the effective dehydration of under-stoichiometric tungsten oxide films. In the spectrum of the as-deposited WO_x a peak at 629 cm^{-1} and a shoulder near 800 cm^{-1} are also observed corresponding to the vibration of W-O-W chains and another peak near 900 cm^{-1} , which corresponds to the W=O bonds. After the microwave annealing, a red shift of the 629 cm^{-1} peak is observed, while a new peak at 800 cm^{-1} appears. The above results indicate not only the dehydration of the as-deposited samples when exposed to microwave irradiation, but also the atomic re-arrangement in them. In order to investigate the influence of microwave annealing on the morphology of the samples, AFM measurements were performed. Figure 2a and c show the 2D $2 \times 2 \mu\text{m}$ AFM topographies of WO_x and mw- WO_x , respectively, while Figure 2b and d show the histograms representing the grain size dispersion of the same films. It is observed that the distribution of grains is not very different when tungsten oxide films exposed to microwave irradiation. Therefore, we can conclude that microwave annealing has caused no effect on samples morphology. In Figure 3a XRD diffractograms of WO_x and mw- WO_x are shown. As seen in Figure 3a the as-deposited sample is amorphous, while a weak peak at 62° appears in the mw- WO_x diffractogram attributed to various under-stoichiometric tungsten oxide compounds, when the

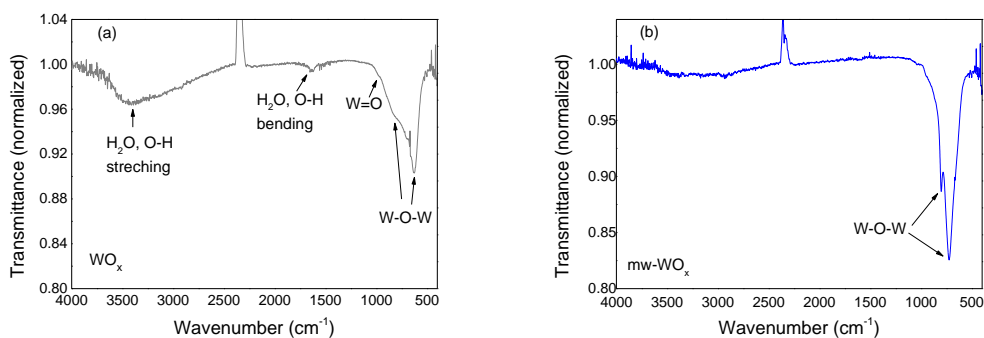


Figure 1. Infrared transmittance spectra of (a) the as-deposited and (b) the microwave-annealed tungsten oxide film.

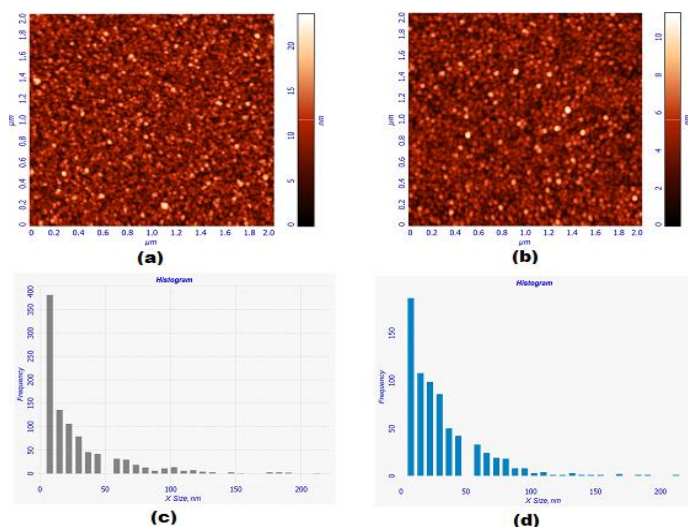


Figure 2. 2D 2x2 μm AFM topographies of (a) WO_x and (b) mw-WO_x film.

sample exposed to microwave irradiation. It is observed that although a short microwave exposure caused atomic re-arrangement of the under-stoichiometric oxides, it didn't affect its crystallinity. Although the weak influence of microwave annealing on the crystallinity and morphology of the samples, changes in the hydrophilicity of them are observed, as revealed from the contact angle measurements. Figure 3b shows the measured contact angle between a droplet of deionized water and the as-deposited and/or microwave annealed WO_x film. The contact angle for the WO_x substrate is 16.5° , while the film

subjected to microwave exposure (mw-WO_x) shows a reduced contact angle of 3° , which may be attributed to the formation of oxygen bonds on the mw-WO_x surface caused by the dehydration of the film. This improved hydrophilicity could lead to the formation of a good-quality P3HT:PC₇₀BM film coated on top of them. Therefore, we have fabricated organic solar cells using WO_x films as hole extraction layers. In particular, the device structure was FTO/ WO_x or mw-WO_x /P3HT:PC₇₀BM/Al, as shown in Figure 4a. A PEDOT:PSS based device is used for comparison reasons.

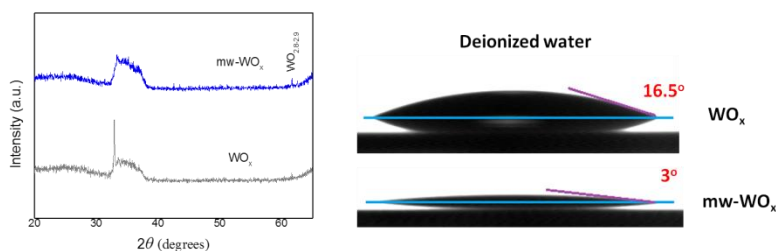


Figure 3. (a) XRD diffractograms of WO_x and mw-WO_x film. (b) Contact angle measurements between a droplet of deionized water and tungsten oxide films.

The current density-voltage characteristics of the OSC devices under 1.5AM illumination using WO_x or mw- WO_x as HELs are presented in Figure 4b, while the dark J-V are shown in Figure 4c. Also, the corresponding electrical output parameters of those devices are summarized in Table 1. For the mw- WO_x based device, a high PCE of 4.65 % is obtained representing a nearly 50 % improvement in comparison to the PCE value of 3.08 % obtained in the device using the WO_x HEL. In addition, the reference device based on PEDOT:PSS exhibits a PCE value of 2.9 %. From the results presented in Table 1 becomes evident that mw- WO_x HEL leads to a significant improvement in the short-circuit current density (J_{sc}) and fill factor (FF). Also, a substantial increase of the shunt resistance and a short decrease of the series resistance of the mw- WO_x based device are observed indicating an improved anode contact compared to the devices with PEDOT:PSS and WO_x HELs. Furthermore, the dark J-V characteristics (Figure 4c) are improved greatly in the case of mw- WO_x devices compared to PEDOT:PSS and WO_x ones. In particular, the distinctly different regions in the J-V curves for diode operation are observed in the case of tungsten oxide, suggesting that mw- WO_x reduces shunt

current, which leads to enhanced hole extraction and thus improving J_{sc} . In addition to the significant efficiency improvement, the environmental stability of the above devices is also improved when using mw- WO_x HEL as shown in Figure 4d. It is observed that the mw- WO_x based device maintains the 92 % of the initial PCE value after being stored in ambient conditions for 200 hours. In contrast, the PCE of WO_x based devices degrades to 87 % of its original value when stored at the same conditions, while the device using the PEDOT:PSS layer exhibits a fast reduction of its PCE value.

4. Conclusion

To conclude, under-stoichiometric tungsten oxide films were subjected to microwave irradiation for one minute and then used as hole extraction layers in organic solar cells. It is demonstrated that microwave annealing caused dehydration of the tungsten oxide films; however, almost no changes in crystallinity and morphology of them were observed. In addition, a significant enhancement in the performance and stability of the organic solar cells was obtained when using microwave annealed tungsten oxide as anode interfacial layer.

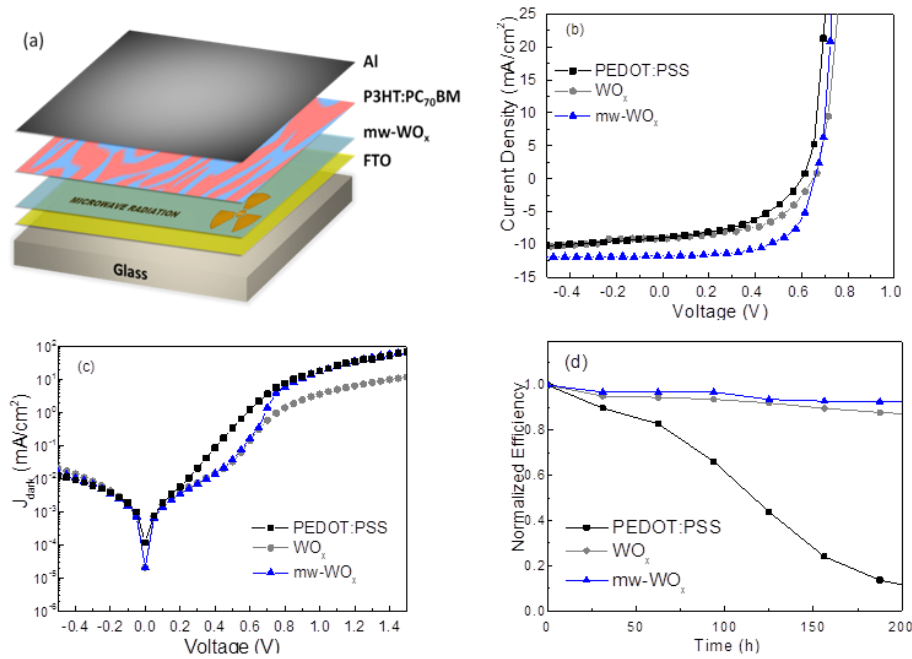


Figure 4. (a) Device architecture of organic solar cells based on as-deposited and microwave annealed tungsten oxide anode interfacial layers. Current density-voltage characteristics (b) under 1.5AM solar illumination and (c) in dark of the devices with PEDOT:PSS, as-deposited WO_x and microwave annealed WO_x anode interfacial layers. (d) Stability measurements: Variation of PCE values over a period of 200 hours of the same devices.

Table 1. Photovoltaic parameters of OSCs with structure FTO/ WO_x , mw- WO_x or PEDOT:PSS/P3HT:PC₇₀BM/Al.

HEL	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	R_s (Ωcm^2)	R_{sh} (Ωcm^2)
PEDOT:PSS	8.72	0.62	0.53	2.9	15	225
WO_x	9.1	0.65	0.53	3.08	7	678
mw- WO_x	11.74	0.65	0.61	4.65	5	1250

The enhanced power conversion efficiency values were attributed to the improved short-circuit current density and fill factor due to reduced series and increased shunt resistance

Disordered Molybdenum Oxide Films, *Journal of Physical Chemistry C*, 117, 18013.

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