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Improvement of performance and stability of polymer photovoltaic cells by WO_3/CuPc as anode buffer layers

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In this work, bulk-hetrojunction polymer photovoltaic cells based on poly-(3-hexylthiophene) (P3HT): [6, 6]-phenyl C61 butyric acid methyl ester (PCBM) were fabricated with tungsten oxide (WO_3) and copper phthalocyanine (CuPc) as anodic buffer layers. The WO_3 plays an important role in reducing the interfacial resistance, efficiently extracting holes and good band structure matching between the work function of the anode and the highest occupied molecular orbital of the organic material. The insertion of CuPc improves the device performance and expands the absorption spectra range of the photovoltaic devices. The effects of WO_3 and CuPc thickness on the performance of the photovoltaic devices were investigated. The optimum thicknesses of WO_3 and CuPc were 10 nm and 8 nm, respectively. The obtained power conversion efficiency of optimized cell was about 4.21%. Also, the device performance was analyzed based on the surface roughness of bare ITO and ITO that was covered with poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) or WO_3/CuPc. The device stability in an ambient atmosphere without encapsulation under continuous light irradiation was also investigated. For the cell with PEDOT:PSS, the power conversion efficiency reduced down to 50% of the maximum value (half-life) after light irradiation for 12 h, while the half-life of device for WO_3/CuPc was about 120 h. Therefore, the lifetime of unpackaged devices was improved with WO_3/CuPc.

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Keywords: BHJ organic photovoltaic cells, anode buffer layer, Tungsten oxide (WO_3), Copper phthalocyanine (CuPc), stability

1 INTRODUCTION

Bulk-heterojunction (BHJ) polymer photovoltaic cells have attracted much attention as a renewable energy source due to their potential for low cost, easy fabrication, light weight, large area devices and mechanical flexibility [1, 2]. In order to improve the performance of polymer photovoltaic cells, various methods such as annealing treatment [3], enhancement of photon absorption [4], synthesis of multifunction organic materials [5], different structure of device and introduction of buffer layers have been used [6]. In order to improve the charge collection, buffer layers are added to change the interface between electrodes and active layers. The most frequently used anodic buffer layer in BHJ polymer photovoltaic cells is PEDOT:PSS [7, 8]. It has various advantages such as high transparency, smooth morphology, good hole transport and suitable work function. Therefore, the hole collection can be performed via the PEDOT:PSS layer from the highest occupied molecular orbital (HOMO) of a photoactive layer. In spite of the good potential of PEDOT:PSS, it has some disadvantages. The hygroscopic property of the PEDOT:PSS layer is likely to degrade the active layer because of the adsorption of water [9, 10]. The work function of the PEDOT:PSS layer is very sensitive to water [11, 12]. The interface between ITO anode and PEDOT:PSS layer is not stable and the chemical reaction between ITO and PEDOT can degrade cell performance [13]. Also, high series resistance of PEDOT:PSS layer can significantly decrease the fill factor and power conversion efficiency of series connected large area organic photovoltaic module [14]. It was found that some materials such as NiO [15], V_2O_5 [16], MoO_3 [17] and Au nanoparticles [18] are suitable substitutions for PEDOT: PSS in organic solar cells. However, the function and operation mechanism of these buffer layers are still a matter of debate. It has been demonstrated that forming a tunnelling junction to increase built-in electric field, an interfacial dipole layer to change the work function of electrodes or to protect the photoactive layer from damage are the main reasons [19]. In this paper, the enhanced performance of P3HT:PCBM based polymer photovoltaic cells by the insertion of the dual hole transport layer of WO_3/CuPc as the anodic buffer layers was investigated. In order to obtain the best performance, the thicknesses of WO_3 and CuPc layers were optimized. The main role of each layer was discussed from the viewpoints of energy levels alignment, charge carrier transport, light absorption, and surface morphology. Finally, the stability of our cells exposed in air without encapsulation was investigated.

2 EXPERIMENTAL DETAILS

Schematic diagram of investigated polymer photovoltaic cells in this research and the energy level diagram of used materials are presented in Figure 1. ITO coated glass substrates with about 15 $\Omega/\square$ sheet resistance (purchased from Sigma-Aldrich) were cleaned ultrasonically with different solutions such as detergent, acetone, ethanol and iso-propanol for 10 min. Then, the substrates were rinsed with de-ionized wa-

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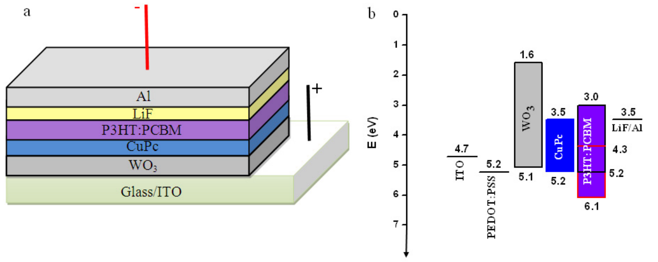

FIG. 1 (a) Schematic structure and (b) energy level diagram of the BHJ photovoltaic cells.

ter and dried with a nitrogen flow. For polymer cells with PEDOT:PSS buffer layer, 40 nm-thick PEDOT:PSS layer was spin-coated on top of the ITO surface at 3000 rpm for 30 s. The produced PEDOT:PSS layer was heated on a hot plate at 120C for 10 min. Tungsten oxide (WO_3) was purchased from Sigma Aldrich and different thicknesses of the WO_3 films as anode buffer layer were thermally evaporated in high vacuum ($3 \cdot 10^{-5}$ mbar) on the ITO substrates. The thickness of evaporated thin films was estimated and monitored in situ with a quartz oscillator crystal. The WO_3 layer was thermally evaporated at a rate of 1 over the anode. A thin copper phthalocyanine (CuPc 99.9%) film as a second anode buffer layer was grown by thermal evaporation technique under pressure of about mbar at room temperature. The CuPc films with different thicknesses at a rate of 0.5 were grown on WO_3 film. Then, samples were transferred to a nitrogen filled glove box, and the solutions of poly-(3-hexylthiophene) (P3HT) and [6, 6]-phenyl C61 butyric acid methyl ester (PCBM) with ratio of 1:1 in dichlorobenzene were coated on CuPc buffer layer using a spin coater as the active layer and then thermally annealed in air at 110C for 20 min. The typical film thickness of P3HT:PCBM is about 205 nm. After transferring the samples to the chamber, 1.5 nm thickness of LiF as cathode buffer layer and 150 nm thickness of Al as top electrode were deposited under a pressure of about $4 \cdot 10^{-5}$ mbar. The active area of the photovoltaic cells was about 0.1 cm^2. UV-visible optical transmission and absorption spectra of samples were done in the wavelength range of 300 to 800 nm with a double-beam spectrophotometer (Shimadzu UV 3100) at room temperature. The current-voltage (I-V) curves were obtained with a Keithley 2400 source meter in dark and under 1 sun global AM 1.5 simulated solar illumination. The electrical measurements were performed in ambient atmosphere without encapsulation at room temperature. The interface morphologies of the as-deposited buffer layer thin films were also investigated using atomic force microscope (AFM) to specify any changes with the growth of film.

3 RESULTS AND DISCUSSION

3.1 Influence of WO_3 and CuPc on cell performance

BHJ photovoltaic cells with a structure of ITO/buffer layer (=x)/ P3HT:PCBM (205 nm)/LiF (1.5 nm)/ Al (150 nm) are investigated in which x is PEDOT:PSS (optimized thickness=40 nm), WO_3/CuPc, or without buffer layer. Device performance can be improved by placing a buffer layer between the anode and active layer. Anodic buffer layer has to include high transparency, good hole transporting capability, and suitable energy level between the active layer and the anode. WO_3 can be an appropriate anode buffer layer because it has high work function, good hole mobility, and high transparency. Moreover, CuPc is introduced in BHJ photovoltaic cells in order to align the energy level and for easy collection of charge carrier, as well as to extend the spectrum absorption range. CuPc as an organic semiconductor material has good chemical, heat, and light stability [20]. It can be used as hole conducting buffer layer in BHJ photovoltaic cells. Here, it is demonstrated that WO_3/CuPc can be employed as effective buffer layers in BHJ photovoltaic cells. In order to obtain the highest efficiency in the device, the thicknesses of WO_3 and CuPc as buffer layers should be optimized. Therefore, in the structure of ITO/WO_3/CuPc/ P3HT:PCBM (205 nm)/LiF (1.5 nm)/ Al (150 nm), the thickness of CuPc layers was fixed at an arbitrary value (10 nm) and the thickness of WO_3 layer was altered from 0 to 12 nm until the best performance of device was obtained. Then, the thickness of the WO_3 layer was fixed and the thickness of the CuPc layer was changed from 4 to 10 nm to obtain the best performance.

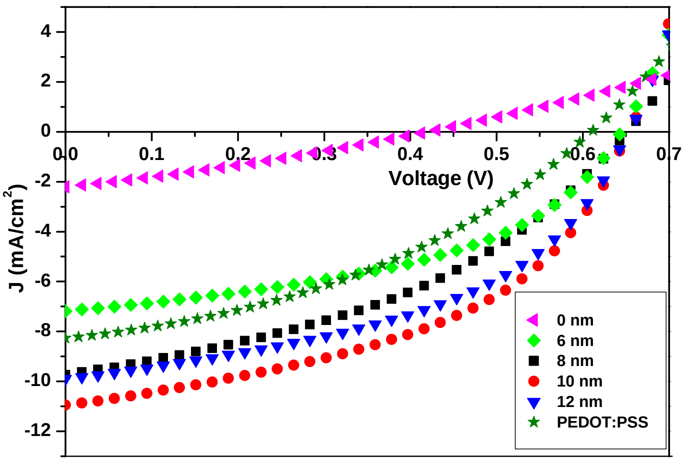

FIG. 2 J-V characteristics under illumination for BHJ photovoltaic devices with different thickness of WO_3 layer.

The dependence of the current density-voltage (J-V) characteristics under illumination for devices with different thickness of WO_3 as anodic buffer layer is shown in Figure 2. Short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η_p) which are obtained from J-V characteristics are presented in Table 1.

The results show that the photovoltaic performance of the devices is substantially improved in comparison to the photovoltaic cells with ITO alone. As seen in Table 1, power conversion efficiency of BHJ photovoltaic cells without anode buffer layer (0.27%) is much lower than that of the other cells with an anode buffer layer. A buffer layer effectively prevents the recombination of charge carriers at the active layer/ITO interface. When an anodic buffer layer is not used in our structure, P3HT:PCBM directly contacts ITO anode. The active layer can transfer the hole to the ITO electrode, thereby causing the recombination rate of charge carriers to increase. As a consequence, based on Table 1, the best η_p of the devices with 10 nm-thick WO_3 is higher than the best $etap$ of the devices with PEDOT: PSS layer. The J_{sc}, FF and η_p increase initially and then reduce abruptly with increasing WO_3 layer thickness. J_{sc} is strongly governed by the quantity of carriers which

Anode buffer layer	Without buffer layer	PEDOT:PSS	WO_3			
Thickness (nm)	0	40	6	8	**10**	12
J_{sc}(mA/cm^2)	2.20±0.28	8.27±0.25	7.19±0.21	9.73±0.20	**10.95**±0.19	9.9±0.20
V_{oc}(V)	0.42±0.01	0.61±0.01	0.65±0.01	0.65±0.012	**0.65**±0.01	0.65±0.01
FF	0.29±0.01	0.387±0.008	0.46±0.01	0.40±0.008	**0.47**±0.01	0.46±0.009
η_p (%)	0.27±0.05	1.95±0.13	2.15±0.14	2.56±0.15	**3.34**±0.17	2.96±0.16

TABLE 1 Parameters of organic photovoltaic devices including PEDOT:PSS and different WO_3 thicknesses as determined from J-V characterization.

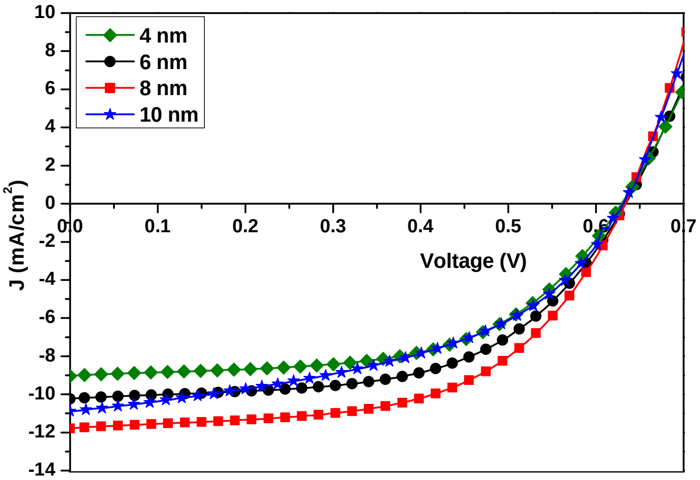

FIG. 3 J-V characteristics under illumination for BHJ photovoltaic devices with different thickness of CuPc layer.

were generated in the active layer and reached the electrodes. The increase in J_{sc} can be attributed to increased charge carrier collection efficiency due to presence of the optimized WO_3 anode buffer layer. Figure 1 shows that the energy band gap of WO_3 is 3.5 eV and the energy levels of WO_3 play an important role as an effective exciton-blocking layer to prevent electrons from reaching the anode. Furthermore, the generated holes can be extracted from the active layer to anode easily because of the energy alignment of WO_3 and the highest occupied molecular orbital (HOMO) energy of CuPC and P3HT. The V_{oc} values showed no significant considerable change in all photovoltaic cells with WO_3 buffer layer. According to the literature, it has been stated that the V_{oc} of polymer BHJ photovoltaic devices depends mainly on the relative energy levels of the donor and acceptor materials. Theoretical maximum V_{oc} is defined as the energy difference between the HOMO of the BHJ donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor material [15]. In our photovoltaic cells, the donor (P3HT) and acceptor (PCBM) are identical for all devices. However, in real devices, the output of V_{oc} is less than the theoretical maximum. The supposed sources of this loss are due to the field-driven nature of the devices, the presence of dark current, and Schottky barriers formed at the interfaces [21]. The numbers and different thicknesses of the thin layers between anode and active layer may result in this loss. Therefore, the V_{oc} of these devices is a little different. On the other hand, the influence of CuPc layer thickness on the performance of BHJ solar cells with a structure of ITO/WO_3 (10 nm)/CuPc/P3HT:PCBM (205 nm)/LiF (1.5 nm)/Al(150 nm) must be investigated. The (JV) characteristics photovoltaic devices are shown in Figure 3 and dependence of photovoltaic parameters of devices on the CuPc thickness is presented in Figure 4.

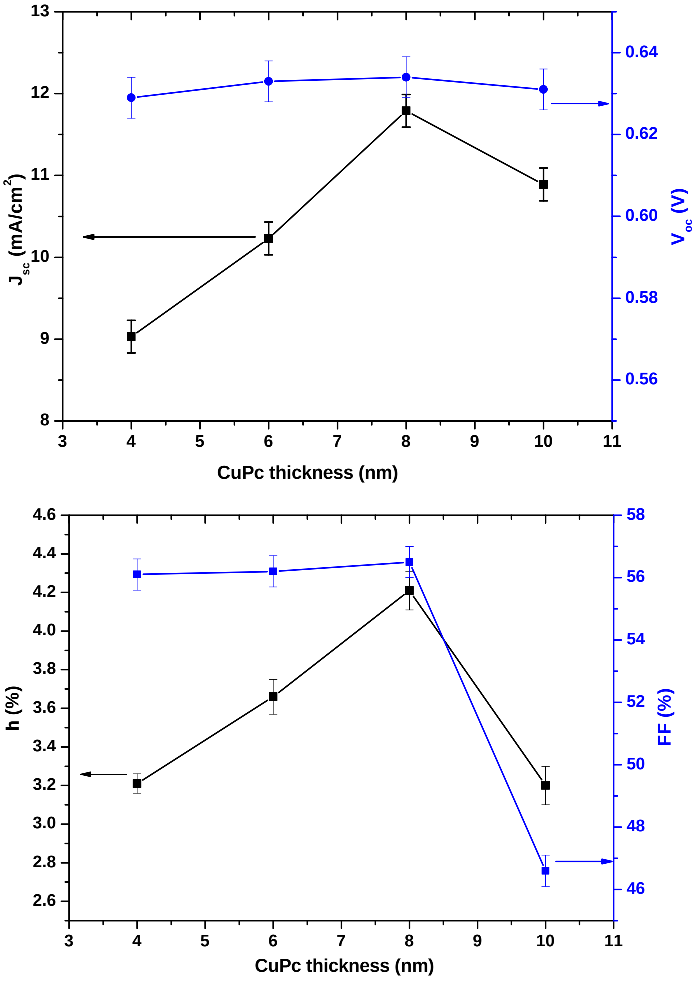

FIG. 4 Dependence of photovoltaic parameters on the CuPc thickness in BHJ photovoltaic cells. (a) J_{sc} and V_{oc}, (b) FF and η_p.

J_{sc} increases effectively with increase of the CuPc layer thickness up to 8 nm and decreases with further increase of CuPc thickness. However, a too thick CuPc layer will reduce the performance of device because a very thick CuPc layer will increase the series resistance and hinder carrier transport. In addition, more recombination between holes and electrons occurs by travelling across the thick CuPc layer. Also, a very thick CuPc will decrease the number of photons arriving at the P3HT:PCBM blend layer due to overlap in absorption spectra of CuPc and P3HT:PCBM. Clearly, there is a correlation between the thicknesses of the WO_3 and CuPc layers. These two layers require suitable thickness. High thickness of WO_3 can block parts of incident light into CuPc and P3HT:PCBM layers. Also, a too thick CuPc can reduce the absorption of P3HT:PCBM layer and act as a hindrance for hole-transporting from P3HT:PCBM to WO_3.

The optimized CuPc film thickness was obtained 8 nm.

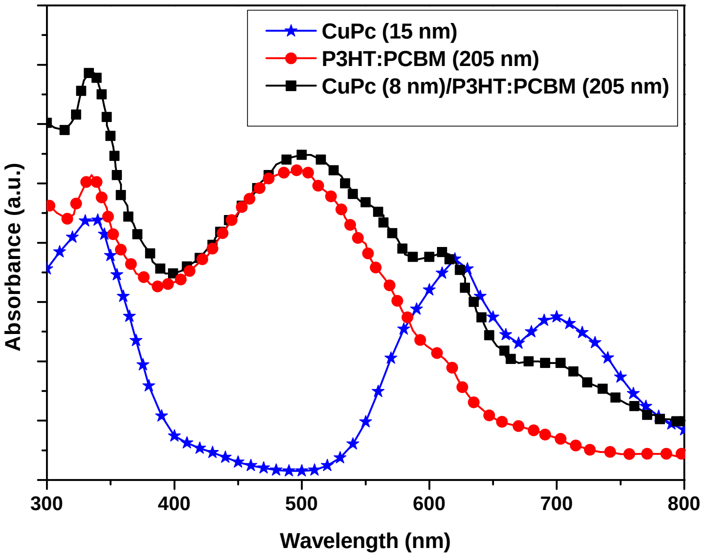

FIG. 5 UV-visible absorption spectra of CuPc (15 nm), P3HT:PCBM (205 nm) and CuPc (8 nm)/P3HT:PCBM (205 nm) films.

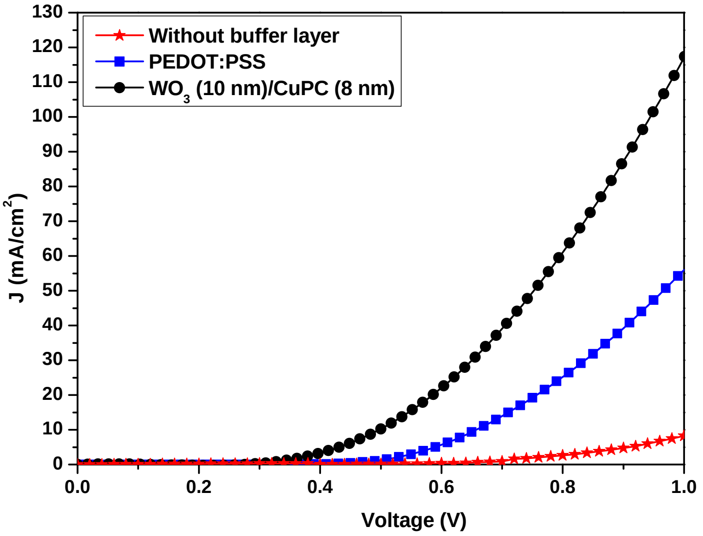

FIG. 7 J-V characteristics of photovoltaic devices without anode buffer layer, PEDOT:PSS and WO$_3$ (10 nm)/CuPc (8 nm) in dark.

By using an 8 nm CuPc layer and 10 nm WO$_3$ layer, the BHJ photovoltaic cell exhibits the highest performance with $J_{sc} = 11.79$ mA/cm^2, $V_{oc} = 0.634$ V, $FF = 56.5\%$ and $\eta_p = 4.21\%$. There are various reasons for this improvement. Firstly, as shown in Figure 5, by adding a CuPc thin film the absorption spectra of the devices are extended and cover almost the entire visible spectrum. The absorption peak of P3HT:PCBM and CuPc layers are situated at 490 nm and 623 nm, respectively. The P3HT:PCBM film absorbs poorly in the wavelength range of 550-750 nm. However, CuPc has a strong band in this range. Thus, the absorption spectra of the CuPc and P3HT:PCBM complement each other and comprise nearly the entire visible region [22]. In other words, this enhanced absorption spectrum is anticipated to produce a larger number of excitons, and thus a larger photocurrent.

Secondly, according to the energy levels in Figure 1, CuPc and PCBM form a bilayer heterojunction cell. This is because PCBM and P3HT are mixed and CuPc as donor can be connected to the PCMB as acceptor and excitons can be dissociated at CuPc/PCBM interface. The HOMO levels of CuPc, P3HT and WO$_3$ are nearly the same and produced holes can be transported through to WO$_3$ buffer layer and collected by the anode. Thirdly, the series resistance (RSA) of organic photovoltaic cells is related to the intrinsic resistance, morphology, and thickness of the layer [23]. The smaller value of RSA is useful for the performance of the devices and the J_{sc} would be improved due to low series resistance. In our samples, the calculated RSA for 4, 6, 8 and 10 nm thickness of CuPc layer was 13.7, 12.2, 9.2 and 12.5 (Ωcm^2), respectively. The minimum RSA was obtained for device with 8 nm thickness of CuPc. Also, for evaluating the influence of thin buffer layer on the interface between donor/anode, AFM images of the bare ITO surface, ITO/WO$_3$ (10 nm), and ITO/WO$_3$ (10 nm)/CuPc (8 nm) were prepared and shown in Figure 6(a)–(c). The surface root-mean-square (RMS) roughness of mentioned films was found to be 2.04, 0.314 and 0.253 nm, respectively. It can be found that the surface roughness of ITO films was polished by WO$_3$ and CuPc layers. It is known that a flat surface in a photovoltaic device is very useful to decrease leakage current and contact resistance [24]. As a consequence, it is concluded that the smoothed anode surface may effectively reduce series resistance and increase charge carrier transfer. Dark current densityvoltage plots of various devices are presented in Figure 7. It can be observed that the WO$_3$/CuPc anode buffer layers are useful to charge carrier injection, and dark current density at 1 V is increased by a factor of 14.28 and 6.8 for WO$_3$/CuPc and PEDOT:PSS, respectively. This shows a good interface contact between P3HT:PCBM and anode.

3.2 Stability of optimized polymer photovoltaic cells

The durability test for the devices with PEDOT:PSS and WO$_3$ (10nm)/CuPc (8 nm) as anode buffer layers was accurately carried out in an ambient atmosphere. The light intensity is adjusted to the 1 sun light intensity of 100 mW/cm^2 and continuous light was used to measure photovoltaic parameters of the devices. The stability test was measured just after light irradiation. The power conversion efficiency versus irradiation time in the ambient atmosphere for WO$_3$/CuPc is shown in Figure 8. For the photovoltaic cell with PEDOT:PSS, the η_p reduced down to 50% of the maximum value (half-life) after light irradiation for 12 h. In contrast, the η_p for the solar cell with the WO$_3$/CuPc anode buffer layers was maintained under continuous light irradiation for 40 h, and its high durability in the ambient atmosphere was demonstrated. The half-life of device with WO$_3$/CuPc was about 120 h. It is well-known that the photo-degradation of polymers and polymer/oxide composites and the degradation at the ITO anode and the metal electrodes in organic thin film photovoltaic cells occur by reactions with oxygen and water [13, 25]. More progress in the durability of the polymer photovoltaic cells is accessible by encapsulating the devices from water and oxygen. Since the environmental conditions are the same for both devices, significant difference in the results can be attributed to the nature of anode buffer layer. Deterioration of the PEDOT:PSS is a key factor for degradation of organic photovoltaic cells [26]. Water diffusing in PEDOT:PSS layer increases its resistance, and the interface between PEDOT:PSS and active layer can be damaged. In addition, high water content in the PEDOT:PSS layer would decrease its work function significantly [12], and increases the barrier of energy for the hole extraction from the HOMO of P3HT. Also,

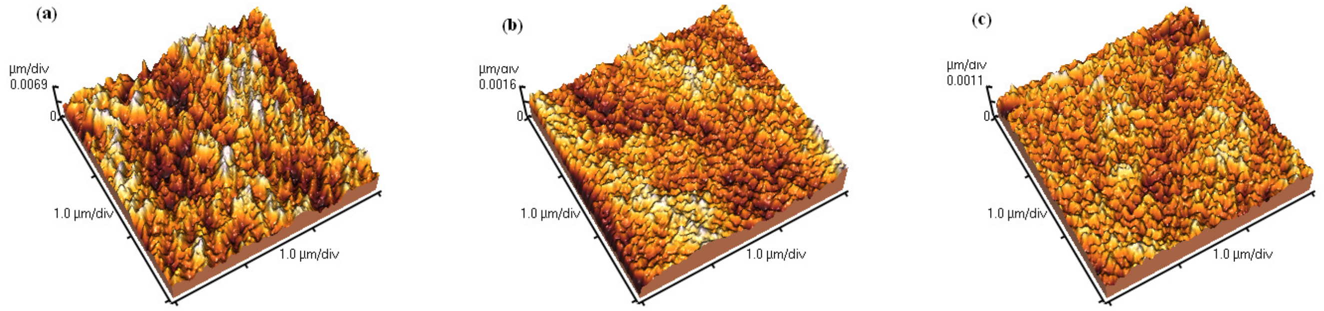

FIG. 6 Atomic force microscope (AFM) images of the surface of (a) ITO, (b) ITO/WO_3 (10 nm) and (c) ITO/WO_3 (10 nm)/CuPc (8 nm).

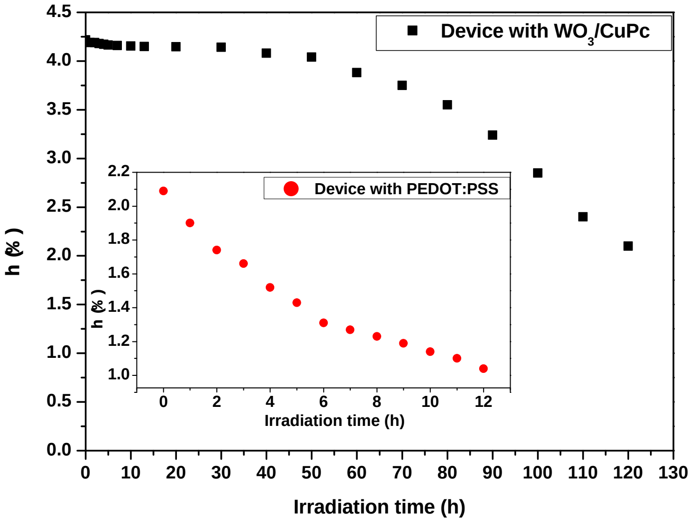

FIG. 8 Irradiation time dependence of the η_p for the BHJ photovoltaic devices with WO_3/CuPc. Inset: Irradiation time dependence of the η_p with PEDOT:PSS buffer layer.

appearance of insulating patches and the increase of the energy barrier at the interface of PEDOT:PSS/donor materials decreases the current density, which reduces charge collection efficiency [26, 27]. Thus, dual buffer layers of WO_3/CuPc instead of PEDOT:PSS layer increase the performance and the lifetime of our photovoltaic cells. This increase is mainly attributed to stability of WO_3/CuPc buffer layers and the better extraction of the holes due to the well modified interface of anode and active layer.

4 CONCLUSIONS

In summary, it was demonstrated that dual buffer layers of WO_3/CuPc can improve the performance of P3HT:PCBM BHJ photovoltaic cells by inserting between the anode and active layer. It was shown that the WO_3 buffer layer efficiently extracts holes and block electrons, and CuPc buffer layer can broaden the absorption spectra of the devices. Higher charge injection and lower series resistance were observed by choosing optimum thickness of WO_3 (10 nm) and CuPc (8 nm) layers. The results show that the obtained power conversion efficiency of optimized cell was about 4.21% which is 2.15 times greater than the cells with PEDOT:PSS buffer layer. Also, the AFM results show that the surface roughness of ITO film is decreased by WO_3/CuPc layers, which is desirable to enhance the device performance. In addition, this device without encapsulation showed a high durability under continuous irradiation compared with the traditional devices using PEDOT:PSS layer. The half-life of our device was tenfold greater than a device with conventional PEDOT:PSS. Finally, we believe that the dual WO_3/CuPc buffer layers play an important role in hole extraction and stability of BHJ polymer photovoltaic devices.

5 ACKNOWLEDGMENT

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