Role of Vanadium Pentoxide Hole-Extracting Nanolayer in Rubrene/C\textsubscript{70}-Based Small Molecule Organic Solar Cells

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1. Introduction

Solar cells are presently considered as an important source of renewable and green energy to solve the energy crisis. Due to potential applications of compatibility with flexible substrates, low-manufacturing cost, and large-area fabrication [1–3], organic solar cells (OSCs) have received much attention as one kind of the most promising devices in energy harvesting area. Since the first discovery of donor-acceptor heterojunction cell by Tang [4], the performance of OSCs has greatly improved by the use of new materials [5], nanostructuring [6], and the modification of interfaces [7, 8].

Improvements in the performance of OSCs are commonly achieved by inserting a hole-extracting layer between the indium tin oxide (ITO) transparent conducting electrode and the organic donor materials. The hole-extracting layer improves the efficiency of hole transport from the active layer into the ITO anode as its higher work function lowers the energy barrier at the interface of ITO/organic donor layer [9]. Poly(3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT : PSS) is one of the most commonly used hole-extracting layers in OSCs. However, PEDOT : PSS is burdened with electrical inhomogeneity which limits electron blocking capability as well as acidic nature which limits the stability and the lifetime of the device [10, 11]. This has driven the vigorous development of better hole-extracting layers. Recent literatures have extensively focused on transition metal oxides (TMO) because of their favorable electronic properties, low optical absorption in the visible spectrum, and high level of technological compatibility in organic electronics [12]. For example, molybdenum trioxide (MoO\textsubscript{3}) [13], vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) [14], and tungsten trioxide (WO\textsubscript{3}) [15] have been shown to be promising alternatives to PEDOT : PSS.

In our previous study, we had investigated the rubrene/C\textsubscript{70}-based OSCs, which provided an open-circuit voltage (V\textsubscript{OC}) almost twice as high as that of devices based on CuPc/C\textsubscript{60} [16, 17]. In this paper, we first demonstrate an improvement in rubrene/C\textsubscript{70}-based OSCs efficiency by inserting a transparent metal oxide V\textsubscript{2}O\textsubscript{5} thin film as the hole-extracting layer. The effects of the morphology and the thickness of the V\textsubscript{2}O\textsubscript{5} interlayer on the performance of OSC were investigated. The efficiency is improved in OSC with optimized thickness of V\textsubscript{2}O\textsubscript{5} interlayer, which is higher than that with bare ITO by about 3 times. The mechanism is discussed from perspectives of change in resistance, the film transparency, and the charge transport behavior. Our findings contribute to our understanding of hole-extracting
behavior in OSCs and may be helpful in fabricating an efficient conversion contact layer in tandem OSCs [18, 19].

2. Materials and Methods

Cells were fabricated on commercially available ITO thin film coated glass substrates (180 nm ITO thickness with a sheet resistance less than 10 Ω/□). After successive ultrasonic cleaning processes in acetone, ethanol, and deionized water for 15 minutes each, the ITO glass was then dried by high-purity nitrogen flow before deposition. The organic and metal oxide layers were grown by vacuum deposition in a vacuum thermal evaporation system with a base pressure of 6 × 10⁻⁶ mbar. The organic materials used in cells were rubrene (99%), C70 (99%), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (99%) without further sublimation before deposition. The V2O5 (99%) was used as received. An aluminum thin film with the thickness of 150 nm was deposited in situ as the cathode electrode. The deposition rates of V2O5, rubrene, C70, BCP, and Al were 0.05–0.1/s, 0.06–0.15 nm/s, 0.8–1.5 ˚A/s, 0.01–0.04 nm/s, and 1.0–4.0 nm/s, respectively. The thickness of layers was monitored by an INFICON XTM/2 oscillating quartz thickness monitor. The schematics of cell structure and energy level are shown in Figures 1(a) and 1(b).

The active area of the device irradiated was 0.5 × 0.6 mm². Current density-voltage (J-V) characteristics were measured with a Keithley 2400 sourcemeter under an illumination of 100 mW/cm² with an AM 1.5G solar illumination from ABET Technologies, Sun 2000 Solar simulator. The solar cell was calibrated using a reference Si solar cell. The surface morphology of V2O5 interlayer was analyzed by atomic force microscope (AFM, CSPM 5500), and the transmission spectra of the V2O5 interlayer were measured by UV-Vis spectrophotometer (UV-2550). All measurements were carried out in ambient air without any encapsulation.

3. Results and Discussion

Cells with the architecture ITO/V2O5 (0 or 3 nm)/rubrene (30 nm)/C70 (30 nm)/BCP (6 nm)/Al (150 nm) (Figure 1(a)) were fabricated. Figure 2 shows J-V characteristics of the device with 0 and 3 nm thick V2O5 layer under 100 mW/cm² white light illumination. In the absence of V2O5 interlayer, the simple device presents a power conversion efficiency of 0.42% with a low fill factor of 36.2%. The JSC and VOC are 2.3 mA/cm² and 0.51 V, respectively. However, by inserting a 3 nm V2O5 interlayer between the donor layer and anode, the device exhibits a significant improvement in power conversion efficiency (PCE) to 1.74%, with short-circuit current density (JSC) 4.58 mA/cm², open-circuit voltage (VOC) 0.88 V, and fill factor (FF) 43.3%.

Figure 1(b) shows the diagram of energy level in the rubrene/C70-based OSC [11, 20, 21]. Due to high work function, the thermally evaporated ultrathin film of V2O5 has a more favorable energy level alignment for hole extraction compared to bare ITO [22]. Figure 3 shows the surface morphology of ITO and ITO covered with a 3 nm V2O5 interlayer. The surface of ITO substrate shows a root-mean-square (RMS) roughness of 1.81 nm. After covering with a 3 nm thick V2O5 layer, the RMS roughness decreases to 1.46 nm. ITO
with improved morphology will favor the contact between the anode layer and the donor layer [23]. Some small islands were observed on the surface of ITO covered with 3 nm V$_2$O$_5$, which were made of oxide molecules aggregated together on the surface. Minimization of the surface energy might play a role in the formation of such islands which occupy a very small amount of surface area, and the V$_2$O$_5$ layer below the islands should dominate the performance [24].

By introducing a 3 nm V$_2$O$_5$ hole-extracting layer, the device shows a remarkable increase in $J_{SC}$ from 2.30 mA/cm$^2$ to 4.58 mA/cm$^2$. It is known that the resistance of the active materials and the contact resistance contribute to the series resistance. Theoretically, inserting a V$_2$O$_5$ layer will introduce two additional interfaces (rubrene/V$_2$O$_5$ and V$_2$O$_5$/ITO) which contribute to an increase in the contact resistance, therefore, increasing the series resistance. However, the series resistance ($R_S$, defined by the slope of the $J$-$V$ curve at $J = 0$ mA/cm$^2$) is estimated to be 40 and 95.7 $\Omega$ cm$^2$ for the device with and without V$_2$O$_5$ interlayer, respectively. Consequently, the decrease in series resistance of the device indicates that the insertion of V$_2$O$_5$ interlayer suppresses the contact resistance remarkably. Although most of the carriers are generated in the active layer, their collection is relative to the contact resistance at the organic/electrode interface [25]. Besides, the high work function of V$_2$O$_5$ (7.0 eV) [9] will enhance hole collection at the organic/ITO interface.

It is observable that the cell without a V$_2$O$_5$ hole-extracting layer exhibits a low $V_{OC}$ of 0.51 V, which leads to a lower PCE. However, by incorporating a hole-extracting layer, the $V_{OC}$ has an obvious increase to 0.88 V. Providing a more favorable energy level alignment with the donor HOMO than ITO does, and decreasing the series resistance, the hole-extracting layer allows for an Ohmic contact and decreases the losses in the built-in field, leading to the increase in the $V_{OC}$ since the $V_{OC}$ is the voltage where the applied bias equals the built-in potential in an ideal diode [22, 26]. Similar to $J_{SC}$ and $V_{OC}$, the FF also has an increase from 36.2% to 43.3%. The decrease in series resistance and the better transport property contribute to the increase in FF. As a consequence, the performance of the device with metal oxide is better as compared to the ITO-only device.

For V$_2$O$_5$ placed between ITO and the donor layer, an overall increase in $J_{SC}$, $V_{OC}$, and FF is obtained, which offers a substantial improvement in PCE. However, introducing a thinner layer of V$_2$O$_5$ will generally lead to a low $V_{OC}$ and a high leakage current, while a thicker layer will result in an increased series resistance, consequently reducing the $J_{SC}$ and FF. To find out the optimum thickness, the effect of V$_2$O$_5$ interlayer thickness on device performance is investigated and showed in Figure 4. The detailed result is summarized in Table 1.

There is a pronounced dependency of device performance on the thickness of V$_2$O$_5$ interlayer and the optimum V$_2$O$_5$
Table 1: Characteristics ($\eta_P$, $J_{SC}$, $V_{OC}$, FF, and $R_S$) of OSCs with V$_2$O$_5$ as the hole-extracting layer (varied thickness). The optimum V$_2$O$_5$ thickness is 3 nm (bold values).

<table>
<thead>
<tr>
<th>Hole-extracting layer (nm)</th>
<th>PCE (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>$R_S$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.425</td>
<td>2.304 ± 0.2</td>
<td>0.51 ± 0.05</td>
<td>36.2 ± 0.6</td>
<td>95.7</td>
</tr>
<tr>
<td>2</td>
<td>1.557</td>
<td>4.289 ± 0.2</td>
<td>0.88 ± 0.01</td>
<td>41.2 ± 0.7</td>
<td>43.0</td>
</tr>
<tr>
<td>3</td>
<td>1.745</td>
<td>4.583 ± 0.2</td>
<td>0.88 ± 0.01</td>
<td>43.3 ± 0.1</td>
<td><strong>40.0</strong></td>
</tr>
<tr>
<td>6</td>
<td>1.651</td>
<td>4.606 ± 0.3</td>
<td>0.88 ± 0.01</td>
<td>40.8 ± 0.4</td>
<td>41.2</td>
</tr>
<tr>
<td>10</td>
<td>1.390</td>
<td>3.711 ± 0.1</td>
<td>0.90 ± 0.02</td>
<td>41.6 ± 0.8</td>
<td>68.0</td>
</tr>
<tr>
<td>15</td>
<td>1.320</td>
<td>3.642 ± 0.06</td>
<td>0.88 ± 0.01</td>
<td>41.2 ± 0.3</td>
<td>59.5</td>
</tr>
<tr>
<td>20</td>
<td>1.238</td>
<td>3.563 ± 0.1</td>
<td>0.86 ± 0.02</td>
<td>40.4 ± 1.0</td>
<td>63.2</td>
</tr>
<tr>
<td>25</td>
<td>1.110</td>
<td>3.128 ± 0.2</td>
<td>0.88 ± 0.02</td>
<td>40.3 ± 1.0</td>
<td>71.5</td>
</tr>
<tr>
<td>30</td>
<td>0.731</td>
<td>2.742 ± 0.1</td>
<td>0.88 ± 0.01</td>
<td>30.3 ± 1.0</td>
<td>365</td>
</tr>
</tbody>
</table>

Figure 5: The curve of series resistance-thickness of V$_2$O$_5$ interlayer.

The thickness for our device is 3 nm (bold values in Table 1). When the thickness is 2 nm, the ITO will not be fully covered by V$_2$O$_5$ and two interfaces (V$_2$O$_5$/ITO and organic/ITO) are formed. Therefore, the $J$-$V$ curve of the cell with 2 nm thick V$_2$O$_5$ interlayer can be considered as the overlapping of two independent $J$-$V$ curves of cells with 3 nm of V$_2$O$_5$ interlayer and without V$_2$O$_5$. Due to the bad performance of a cell without V$_2$O$_5$, the overlapping curve will result in a worse performance than that of a cell with 3 nm thick V$_2$O$_5$ layer, as is shown in Figure 4.

With the thickness of V$_2$O$_5$ increasing from 3 nm to 30 nm, the $V_{OC}$ and FF changed slightly. On the contrary, the $J_{SC}$ of a cell with 3 nm thick V$_2$O$_5$ layer is approximately higher than that of a cell with 30 nm V$_2$O$_5$ interlayer by one time. The deterioration of characteristics for devices with V$_2$O$_5$ interlayer thickness larger than 3 nm may be due to the reduction in the quality of both electrical conductivity and optical transmissivity of the V$_2$O$_5$ interlayer [11]. Firstly, we estimated the series resistance of cells with different thickness of V$_2$O$_5$ shown in Table 1. Figure 5 shows the $R_S/R_{30}$-V$_2$O$_5$ interlayer thickness curve ($R_{30}$, defined as the series resistance of a device with 0 nm thick V$_2$O$_5$ layer). As compared to that of the optimum cell, the series resistance of cells with thicker V$_2$O$_5$ film increases, which indicates that the electrical conductivity becomes worse with the increase of the V$_2$O$_5$ thickness from 3 nm to 30 nm. The series resistance of the cell with 30 nm V$_2$O$_5$ interlayer is almost 10 times higher than that with 3 nm thick V$_2$O$_5$ layer.

We also investigated the optical properties of V$_2$O$_5$ films shown in Figure 6. With a thickness of 30 nm interlayer, the V$_2$O$_5$ film shows significant optical absorption in the visible band and wavelengths below 400 nm. Based on the transmittance data, we propose that a V$_2$O$_5$ layer with the thickness of 3 nm almost transmits 100% of light intensity at wavelength higher than 390 nm whilst a 30 nm V$_2$O$_5$ interlayer absorbs 23% of light intensity at 390 nm (the maximum of the spectral absorption of C$_{60}$). At 350 nm wavelength, a 3 nm thick layer transmits 96% of the photons while a 30 nm thick layer only transmits 58% of light intensity, which is similar to the result reported by Zilberberg et al. [11]. Thus, it appears reasonable that the deterioration of cell performance with thicker V$_2$O$_5$ (>3 nm) interlayer is related...
to the lower electrical conductivity and optical transmissivity of the \( \text{V}_2\text{O}_5 \).

The typical FF of OSCs based on small molecules is typically between 0.5 and 0.65 [5]. But as-prepared rubrene/\( \text{C}_{70} \)-based OSCs have the highest FF of 43.3%, which is much lower than the typical value. The reverse bias photocurrent \( J_{ph} \) (\( J_{ph} = J_L - J_D \), \( J_L \) and \( J_D \) are defined as the current density of the device under illumination with 100 mW/cm\(^2\) white light and in the dark) of a device with FF > 50% saturates at the high reverse bias, indicating the fact that almost all the photogenerated free charge carriers are extracted [27]. However, in Figure 7(a), the \( J_{ph} \) in the reserve bias shows strong field dependence. In other words, the exciton dissociation rate of a device with 3 nm interlayer is moderately dependent on voltage.

Besides the field-dependent exciton dissociation rate, unbalanced transports of charge carriers also play a role in reducing the FF. Figure 7(b) shows the \( J_{ph} \)\( (V_0 - V) \) curve of optimum device (\( V_0 \) is the compensation voltage, defined as the voltage at \( J_{ph} = 0 \), here \( V_0 \) is equal to 0.96 V). At low effective field (\( V_0 - V \) \( \leq \) 0.1), \( J_{ph} \) shows linear dependence on the voltage, due to the competition between drift and diffusion of photogenerated free charges to the electrodes [28]. However, at high effective field (\( V_0 - V \) \( \geq \) 0.1), \( J_{ph} \) clearly illustrates a square-root dependence on the voltage, especially, at the field range from 0.2 V to 1 V, which can be clearly seen from the inset of Figure 7(b). During this field region, in case of mobility-lifetime limit, the \( J_{ph} \) is given by

\[
J_{ph} = qG[(\mu\tau)_{\text{slow carrier}}]^{0.5}V^{0.5}.
\]  

While in case of space charge limit, the \( J_{ph} \) can be described by

\[
J_{ph} = q\left(\frac{q\varepsilon_0\varepsilon_rH_{\text{slow carrier}}}{8q}\right)^{0.25}G^{0.75}V^{0.5}.
\]  

where \( \varepsilon_0\varepsilon_r \) is the dielectric permittivity. Therefore, the \( J_{ph} \) is influenced by the unbalanced transport in the case of space charge limit or mobility-lifetime limit. For a photocurrent varying with a square-root dependence on the applied voltage, the FF amounts to 42% [27, 28]. It appears from Figure 7(b) that \( J_{ph} \) does not saturate with effective voltages exceeding 1 V but gradually increases for larger effective voltage. This is mainly because not all the photogenerated bound e-h pairs dissociate into free charge at the field lower than 1 V and the dissociation of a fraction of bound e-h pairs is dependent on field [29]. Hence, to some extent, the lower FF in rubrene/\( \text{C}_{70} \)-based OSC is due to the field-dependent \( J_{ph} \) as well as unbalanced transport.

4. Conclusions

We have explored the role of \( \text{V}_2\text{O}_5 \) hole-extracting layer in rubrene/\( \text{C}_{70} \)-based OSCs. Due to the favorable electronic properties, \( \text{V}_2\text{O}_5 \) interlayer effectively extracts holes and suppresses the contact resistance. Because of the thickness-dependent electrical conductivity and the optical transmissivity of the \( \text{V}_2\text{O}_5 \) layers, the performance of OSCs changes differently with the thickness of \( \text{V}_2\text{O}_5 \) layer. The highest PCE of 1.745% is achieved for the device with a 3 nm thick \( \text{V}_2\text{O}_5 \) interlayer and a high \( V_{\text{OC}} \) of 0.88 V is also obtained. As \( \text{V}_2\text{O}_5 \) interlayer can be used as the conversion contact layer in the tandem device, this work may contribute to further development of tandem solar cells.
Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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