# Enhanced performance in organic photovoltaic devices with a $KMnO_4$ solution treated indium tin oxide anode modification*

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(Received 19 April 2012; revised manuscript received 6 June 2012)

The properties of poly(3-hexylthiophene):(6,6)-phenyl $C_{61}$ butyric acid methyl ester (P3HT:PCBM) organic photovoltaic devices (OPVs) with an indium tin oxide (ITO) anode treated by a $KMnO_4$ solution are investigated. The optimized $KMnO_4$ solution has a concentration of 50 mg/L, and ITO is treated for 15 min. The modification of ITO anode results in an enhancement of the power conversion efficiency (PCE) of the device, which is responsible for the increase of the photocurrent. The performance enhancement is attributed to the work function modification of the ITO substrate through the strong oxygenation of $KMnO_4$, and then the charge collection efficiency is improved.

**Keywords:** organic photovoltaic devices, indium tin oxide, anode modification, $KMnO_4$

**PACS:** 84.60.Jt, 85.60.Bt, 88.40.hj, 88.40.jr **DOI:** 10.1088/1674-1056/21/12/128402

## 1. Introduction

Organic photovoltaic devices (OPVs) have attracted intensive attention during the past two decades due to their potential applications in solar cells[1−7] and photodetectors.[8] Although encouraging progress has been made in recent years, the power conversion efficiency (PCE) of OPV needs to be increased further to meet the requirements of practical applications. Except for the properties of the photoactive layer, the device performance of the OPV is greatly dependent on the properties of interfaces between the photoactive layer and the two electrodes or an underlying buffer layer. The desired interface should be of Ohmic contact, good interfacial cohesion, and little charge traps for strong charge transportation and collection, and the built-in potential.[9] Therefore, controlling these interfaces is essential to the PCE improvement in an OPV.[10,11]

Much effort has been made to improve device performance of an OPV with surface engineering to the indium tin oxide (ITO), such as plasma treatment,[12] UV-ozone treatment,[13] chloroform solution treatment,[14,15] a self-assembled monolayer,[16] or an oxide buffer layer.[17] Among various methods to modify the ITO anode, oxygen plasma or UV-ozone treatment is most widely used for the performance improvement of the OPV, which can remove the contamination as well as incorporate more oxygen onto the ITO surface for the work function to increase.[18] However, the spin casting of the aqueous solution of poly(3,4-ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) inevitably reduces the efficiency of the oxidative treatment with UV-ozone. To solve this problem, it is necessary to provide a simple way to modify the ITO anode, which is compatible with the aqueous fabrication process of the PEDOT:PSS layer. In this work, ITO anode used in OPV is treated by a $KMnO_4$ solution and then is employed

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10974013 and 60978060), the Research Fund for the Doctoral Program of Higher Education, China (Grant No. 20090009110027), the Beijing Municipal Natural Science Foundation, China (Grant No. 1102028), the New Century Excellent Talents in University , China (Grant No. NCET-10-0220), the Fundamental Research Funds for the Central Universities, China (Grant No. 2012JBZ001), and the Technology Innovation Fund for Outstanding Ph. D. Students of Beijing Jiaotong University, China (Grant No. 48034).

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to study the resulting effect of this treatment on the OPV performance.

## 2. Experiment

The ITO-coated glass substrates with a sheet resistance of 60 Ω/sq were first cleaned with acetone, ethanol, and de-ionized (DI) water ultrasonically. Then, the cleaned ITO glass substrates were immersed into the $KMnO_4$ solution with different concentrations and then treated ultrasonically for different times, and subsequently dried by $N_2$ purging after rinsing with DI water. A highly conducting polymer PEDOT:PSS was spin coated onto treated ITO substrates with a thickness of 50 nm from an aqueous solution, then these ITO coated with PEDOT:PSS were annealed in air at 120 °C for 20 min. The chlorobenzene solution composed of P3HT and PCBM was then spin-coated to form the photoactive layer with a thickness of 100 nm on the top of the PEDOT:PSS layer, and then annealed at 120 °C for 10 min. 100 nm of Al as the cathode was deposited thermally under vacuum ($< 5 \times 10^{-4}$ Pa) on the top of the photoactive layer. The deposited

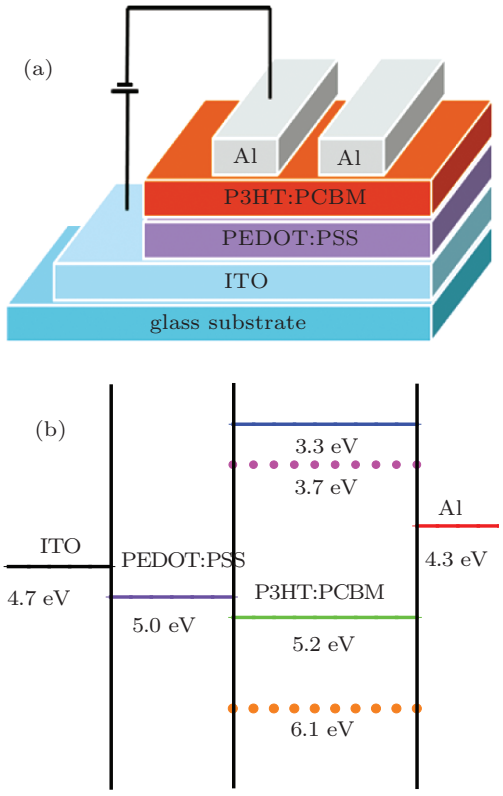



**Fig. 1.** (colour online) Device structure of the OPV (a) and the energy level diagram of the OPV (b).

The Al electrode area, defined as the active area of the device is 0.09 $cm^2$. For comparison, the reference devices with as-cleaned and 8-min UV-ozone treated ITO anodes were also fabricated with identical process parameters during the same batch processing with the $KMnO_4$ solution treated ones. Figure 1 shows the device structure and the energy level diagram of OPVs.

The current density–voltage ($J$–$V$) characteristics were measured with a programmable Keithley 2410 source meter. The power conversion efficiency was calculated from the $J$–$V$ characteristics under a solar simulated light irradiation (AM1.5) of 100 mW/$cm^2$. All the measurements were performed at room temperature in air without any device encapsulation.

## 3. Results and discussion

Figure 2 shows the $J$–$V$ characteristics of the OPVs with an ITO anode treated by $KMnO_4$ solution with different concentrations ranging from 20 mg/L to 500 mg/L and then treated ultrasonically for 15 min. The extracted device parameters are summarized in Table 1. As illustrated in Fig. 2, the $V_{OC}$ remains almost unchanged for devices with different concentrations, while the $J_{SC}$ and fill factor (FF) are different. For the device whose ITO anode has been treated by a $KMnO_4$ solution with a concentration of 50 mg/L, the maximum power conversion efficiency is 2.57%, which is higher than those of the other devices. To research the performance of the devices further, we treat the ITO-coated glass substrates ultrasonically in $KMnO_4$ solution with a concentration of 50 mg/L for various times.

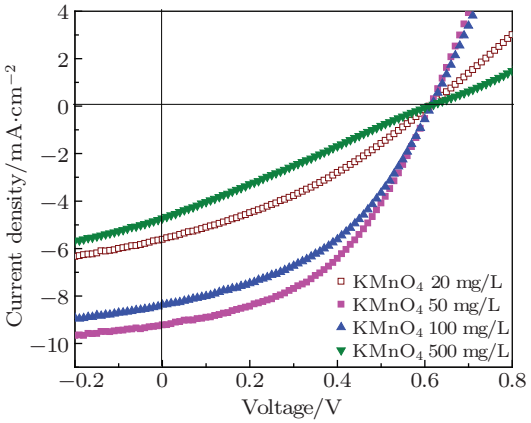



**Fig. 2.** (colour online) The $J$–$V$ characteristics of OPVs with an ITO anode treated by $KMnO_4$ solutions of different concentration, with the ultrasonic time fixed to be 15 min.

**Table 1.** Device performance parameters of OPVs with an ITO anode treated by $KMnO_4$ solution with different concentrations.

| ITO/mg·L$^{-1}$ | $V_{OC}$/V | $J_{SC}$/(mA/cm$^2$) | FF/% | $\eta$/% |
|---|---|---|---|---|
| 20 | 0.61 | 5.62 | 33.9 | 1.16 |
| 50 | 0.61 | 9.22 | 45.5 | 2.57 |
| 100 | 0.61 | 8.37 | 43.6 | 2.25 |
| 500 | 0.61 | 4.72 | 26.2 | 0.75 |

As shown in Fig. 3, the performance of the device depends on the treatment time. The $V_{OC}$ does not change with ITO treatment time, while the $J_{SC}$ and FF increase as treatment time increases. The best performance is achieved when the treatment time is 15 min. In the case of treatment time longer than 15 min, the $J_{SC}$ and FF decrease. We believe that the $V_{OC}$ is determined by the difference in energy between the highest occupied molecular orbital of the donor of P3HT and the lowest unoccupied molecular orbital of the acceptor of PCBM. These two materials are not changed, so the $V_{OC}$ remains almost unchanged. On the other hand, the trends in $J_{SC}$ and FF with respect to the treatment using different $KMnO_4$ solutions can be related to the contact resistance of the treated anode ITO by a $KMnO_4$ solution. It was proposed that the number changes of In, Sn, O, surface carbon, and the generation of a type of oxygen species of ITO treated by UV-ozone account for the increase of the work function, which could be attributed to the reduction of carbon atoms and the formation of the Sn-deficient and O-rich surface by the treatment.[13] The treatment by $KMnO_4$ solution is very similar to the treatment by UV-ozone. So this treatment by $KMnO_4$ solution results in the increasing of the work function of ITO and the lowering of the potential barrier between the ITO and PEDOT:PSS. Therefore, $J_{SC}$ of the OPV is enhanced. From the comparison of all the fabricated devices, it is found that the best optimized concentration of $KMnO_4$ solution is 50 mg/L, and the ultrasonic treatment time is 15 min.

It can be observed that both $J_{SC}$ and $\eta$ of OPVs decrease when the $KMnO_4$ solution and the treated time are higher than their corresponding suitable values. It was reported that the carrier concentration of the ITO thin film could arise from both the oxygen vacancy $V_O^{2+}$ and the activated $Sn^{4+}$ ions on $In^{3+}$ sites. The excess oxygen introduced could fill the oxygen vacancies and can deactivate the substituted $Sn^{4+}$ ions by forming Sn–O complexes,[19] which results in the decreased carrier concentration and conductivity. Therefore, the resistivity of the ITO and $R_S$ of the prepared OPV increase. As a result, $J_{SC}$ and $\eta$ of OPVs decrease when ITO is treated with a higher concentration of $KMnO_4$ solution and for a longer treatment time.

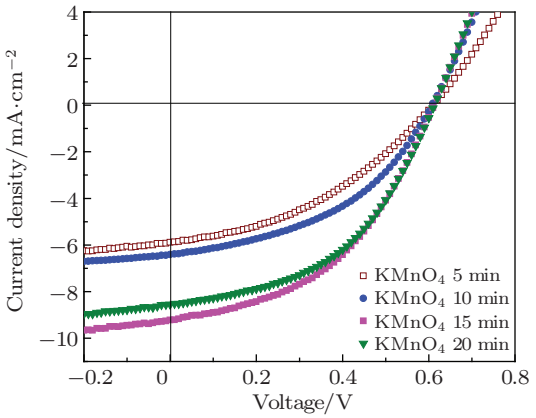



**Fig. 3.** (colour online) The $J$–$V$ characteristics of OPVs with an ITO anode treated by $KMnO_4$ solution for different ultrasonic times, with the $KMnO_4$ solution concentration fixed to be 50 mg/L.

**Table 2.** Device performance parameters of OPVs with an ITO anode treated by a $KMnO_4$ solution for different ultrasonic times.

| ITO/min | $V_{OC}$/V | $J_{SC}$/(mA/cm$^2$) | FF/% | $\eta$/% |
|---|---|---|---|---|
| 5 | 0.61 | 5.89 | 39.6 | 1.42 |
| 10 | 0.61 | 6.41 | 44.5 | 1.74 |
| 15 | 0.61 | 9.22 | 45.5 | 2.57 |
| 20 | 0.61 | 8.55 | 47.3 | 2.48 |

Figure 4 shows the $J$–$V$ properties of different P3HT:PCBM-based OPVs in which ITO anodes are non-treated and treated by $KMnO_4$ solution and the traditional UV-ozone respectively. It is obvious that the devices with the ITO anode are treated, respectively, by $KMnO_4$ solution and the traditional UV-ozone treatment each show a better property than that of the untreated device. In particular, the devices with ITO treated by $KMnO_4$ solution shows a more enhanced performance with a PCE of 2.57%, an FF of 45.5%, a $V_{OC}$ of 0.61 V, and a $J_{SC}$ of 9.22 mA/cm$^2$.

In order to further explain the influence of $KMnO_4$ solution treatment on the performance of the device, $R_S$ and $R_{Sh}$ of the devices are analysed (shown in Table 3). It is shown that $R_S$ of the device treated by $KMnO_4$ solution decreases and $R_{Sh}$ increases significantly, which results in the FF of the solar cell increasing from 33.8% to 45.5%.

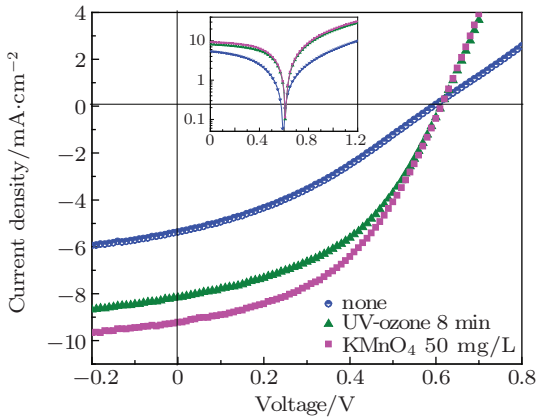



**Fig. 4.** (colour online) The $J$–$V$ characteristics of OPVs with an ITO anode treated by as-cleaned, UV-ozone, and $KMnO_4$ solution.

Figure 5 shows the external quantum efficiency (EQE) of the corresponding OPVs. For the entire wavelength range, the device with a $KMnO_4$ solution treated ITO anode exhibits a higher EQE than those of the other two devices. In addition, there is no noticeable difference in the shape of the EQE spectra among these devices. This gives the proof that the morphology and crystallinity of the P3HT:PCBM bulk-heterojunction (BHJ) in each OPV are similar and have no significant influence on the charge generation and transport. Therefore, the performance enhancement with $KMnO_4$ solution treatment cannot be attributed to the photoactive layer.

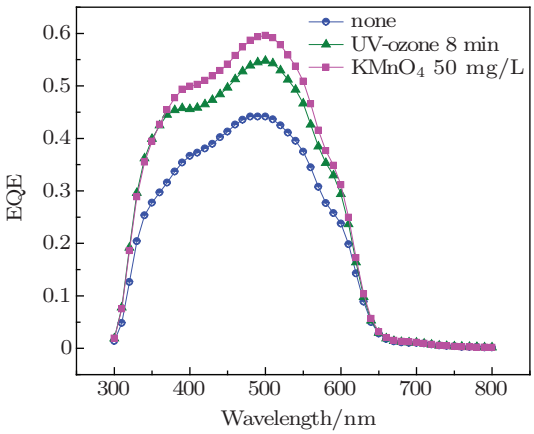



**Fig. 5.** (colour online) Curves of EQE versus wavelength for devices with an ITO anode treated by as-cleaning, UV-ozone, and $KMnO_4$ solution.

**Table 3.** Device performance parameters of OPVs with an ITO anode treated by as-cleaned, UV-ozone, and $KMnO_4$ solution.

| | $V_{OC}$/V | $J_{SC}$/(mA/cm$^2$) | FF/% | $\eta$/% | $R_S$/Ω·cm$^2$ | $R_{Sh}$/Ω·cm$^2$ |
|---|---|---|---|---|---|---|
| None | 0.60 | 5.37 | 33.8 | 1.08 | 33.9 | 260.1 |
| UV-ozone 8 min | 0.61 | 8.17 | 44.9 | 2.25 | 16.6 | 305.5 |
| $KMnO_4$ 50 mg/L | 0.61 | 9.22 | 45.5 | 2.57 | 15.3 | 349.6 |

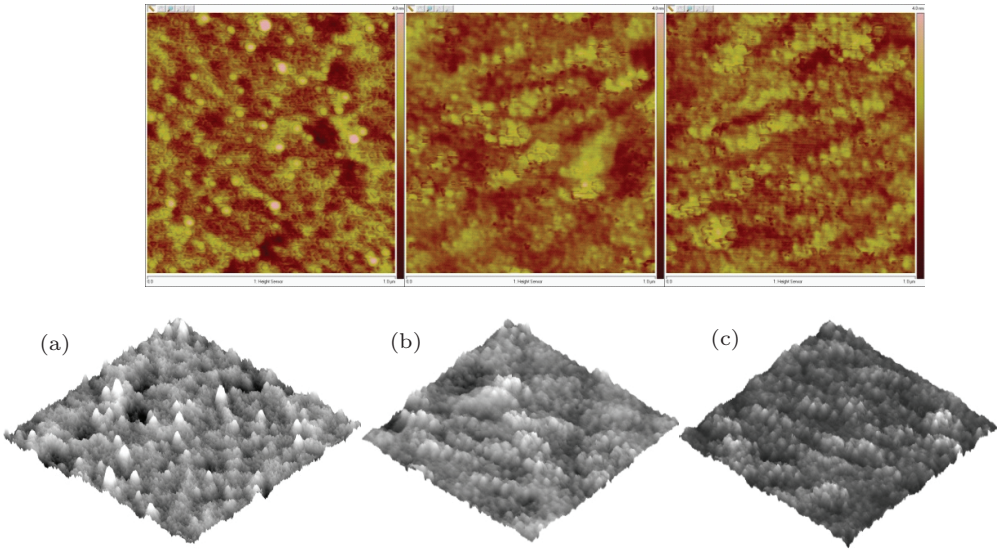



**Fig. 6.** (colour online) AFM images of the ITO interface treated by as-cleaned (a), UV-ozone (b), and $KMnO_4$ solution (c).

In order to deeply understand the origin of the observed $J_{SC}$ and PCE enhancements with respect to the surface treatment, we analyzed the ITO-coated glass substrate surface. Figure 6 shows the atomic force microscopy (AFM) images of the ITO surfaces treated by as-cleaned, UV-ozone, and $KMnO_4$ solution. According to the images, the ITO surface is smoothed by the treatment, which indicates that adhesion between ITO and PEDOT:PSS is improved by the treatment. And also the surface activation of ITO is enhanced due to the strong oxygenation of $KMnO_4$.[20] The performance enhancement is attributed to the improved work function of ITO substrate through the strong oxygenation of $KMnO_4$, thus improving the charge collection efficiency and energy level alignment between the ITO anode and the PEDOT:PSS buffer layer.

## 4. Conclusion

In this paper, we investigated the effects of a $KMnO_4$ solution-treated ITO anode on the performance of an OPV based on P3HT and PCBM blend. Instead of the traditional UV-ozone treatment, the optimized 50 mg/L $KMnO_4$ solution treatment with a treatment time of 15 min results in an enhancement in the power conversion efficiency of the device. This enhanced performance originates from the increase of $J_{SC}$ and FF. The increase of $J_{SC}$ and FF is attributed to the improved work function of the ITO substrate through the strong oxygenation of $KMnO_4$, and thus the charge collection efficiency is improved. This method to increase $J_{SC}$ and FF provides a simple way to improve the performance of an OPV.

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