Piezoelectric Enhancement of Hybrid Organic/Inorganic Photovoltaic Device

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Abstract. Solar cells are produced using solution processing that combine ZnO nanorods with the conjugated polymer poly(3-hexylthiophene) (P3HT). ZnO nanorods have an average length and diameter of 2.7 µm and 81 nm, and are well coated with P3HT. The solar cells have a power conversion efficiency of 1.24 %, which increases to 1.78 % when 10 kHz acoustic vibrations are applied to the device at 75 dB using a loudspeaker. Transient absorption studies demonstrate that the efficiency increase originates from a decrease in the non-geminate recombination rate in the system. It is proposed that electric fields at the ZnO:P3HT interface arising from the piezoelectric effect in ZnO increase the charge-carrier separation, producing this reduction in recombination and associated efficiency increase.

1. Introduction

Solar cells which combine nanostructured wide band gap inorganic semiconductors with conjugated polymers have the potential to utilize both the strong light absorption of the polymer and the superior charge transport properties and stability of the inorganic material. Metal-oxide semiconductors are generally used in such structures, the most common being TiO₂ and ZnO [1]. ZnO nanorods or wires are attractive for this application because their morphology allows a direct charge transport pathway from the charge separation interface to the cathode [2], and they have good carrier mobility [3].

Poly(3-hexylthiophene) (P3HT) is a well-established conjugated polymer photovoltaic material, which has been studied in combination with ZnO nanostructures [4–9]. The highest reported efficiency for this type of device is 0.76 % [7]. Higher efficiencies are obtained when P3HT is combined with the fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in bulk heterojunction devices, which have achieved efficiencies over 5 % [10]. There is therefore a desire to find strategies to improve the efficiency of inorganic-organic hybrid devices to make use of the improved stability that they may offer. The ZnO:P3HT system is therefore a useful standard system in which to study novel techniques for such improvements.

In addition to photovoltaic applications, ZnO is also a piezoelectric material; when a force (e.g. pressure or vibration) is applied to ZnO it develops an internal polarization and associated electric field due to asymmetric displacement of the anions and cations in the lattice [11]. This has led to ZnO nanorods being used for kinetic energy harvesting where the electric field is used to generate a voltage and/or current [12–15]. Some attempts have also been made to utilize this effect in a photovoltaic...
structure to combine the two energy harvesting methods [16–18]. However, since the voltage and current output of the piezoelectric energy harvester was much smaller than the photovoltaic output, the addition of vibration only led to slight increases in photovoltage [16,17] unless the illumination intensity was reduced significantly to make two outputs commensurate [18]. Therefore alternative approaches may be required to optimally combine piezoelectric and photovoltaic outputs.

2. Experimental Methods

To grow ZnO nanorods indium-tin oxide (ITO)-coated glass substrates seeded with a sputtered ZnO film (100 nm) were suspended in an aqueous solution of 15 mM zinc nitrate and 25 mM hexamethylenetetramine and heated to 90 °C for 4 hours [19] a total of 8 times in fresh solutions followed by annealing in air at 400 °C for 1 hour. ZnO nanorod samples were immersed overnight in a solution of P3HT in chlorobenzene (2 g/l) and then dried by N2 gas. Subsequently a P3HT layer was spin coated from chlorobenzene (45 g/l) at 1100 rpm. Gold contacts were deposited by evaporation.

Photovoltaic performance of the solar cells was measured by recording the current-voltage characteristics of the device with a Keithley 2400 SMU while illuminating with a solar simulator fitted with an AM 1.5 filter at 1 sun (100 mWcm-2) illumination. Transient absorption decays were measured by exciting the sample film under a nitrogen atmosphere using a commercially available optical parametric oscillator (Oppolette) pumped by Nd:YAG laser (Lambda Photometrics) with an excitation wavelength of 500 nm, a pump intensity of 0.4 - 20 μJ.cm-2 and a repetition frequency of 20 Hz. Absorption (980 nm) was probed using a 100 W quartz halogen lamp (Bentham, IL 1) with a stabilised power supply (Bentham, 605). The signal from the photodiode was pre-amplified and sent to the main amplification system with an electronic band-pass filter (Costronics Electronics and was collected with a digital oscilloscope (Tektronics, TDS220), triggered by the signal of the pump laser pulse from a photodiode (Thorlabs Inc., DET210). Two monochromators and appropriate optical cut-off filters were placed before and after the sample to reduce stray light, scattered light and sample emission.

For all tests, the external vibration was applied at a fixed distance through a loud speaker at 75 dB, with frequencies ranging between 1 – 50 kHz.

3. Results

The as-produced ZnO nanorods were on average 81 nm in diameter and 2.7 μm long, giving an aspect ratio of 33:1 (Figure 1a). Using high aspect ratio nanorods maximizes the interface between the ZnO and P3HT, which has been shown previously to lead to increased device photocurrent [7]. This also maximizes the possible response to applied vibration, as longer rods have been shown to produce higher output voltages in energy harvesting devices using similar hybrid structures [14]. The cross-section micrograph of the ZnO structure after coating with P3HT confirms that this interface could be fully utilized, as the P3HT coats the ZnO conformally and penetrates to the base of the rods to the extent that the nanorods are barely visible.

![Figure 1. SEM micrographs of the as-grown ZnO nanorods at 30° tilt (a) and cross-section of the ZnO nanorods coated with P3HT (b).](image-url)
Under illumination the P3HT:ZnO nanorod device produces a power conversion efficiency (PCE) of 1.24% under 1 sun illumination (Figure 2a). When the same test was performed while applying acoustic vibration to the device using a loudspeaker, the device efficiency increased by 44% to 1.78%. This increase in efficiency resulted from an increased open-circuit voltage ($V_{oc}$) of around 0.1 V and short-circuit current density ($J_{sc}$) of around 1 mA/cm$^2$. An increased $V_{oc}$ of 18 mV has been reported previously for ZnO-nanorod-based solar cells, which was attributed to the addition of the piezoelectrically-generated voltage to the photovoltage [16,18]. However, the significant increase in $V_{oc}$ and accompanying increase in $J_{sc}$ reported here has not been observed previously.

To investigate the origin of the increase in efficiency transient absorption spectroscopy (TAS) was performed on the device to monitor the photoinduced absorption of the P3HT cations (Figure 2b). It has been shown previously that such measurements can indicate the yield of dissociated charge carriers and their recombination dynamics in ZnO:P3HT [5]. For ZnO:P3HT the decays show approximately exponential dynamics and the lifetimes in the µs–ms timescale increase significantly with the application of applied vibration. These decays have previously been assigned to non-geminate recombination of dissociated charge carriers [5]. Such an increase in lifetime therefore indicates that the application of external vibration significantly reduces the rate of non-geminate recombination in the ZnO:P3HT system.

![Graph showing current density-voltage measurements of ZnO:P3HT solar cells under 1 sun AM 1.5 illumination without and with applied vibration from a loudspeaker at 10 kHz. Acoustic vibration leads to an increase in both open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$) leading to an overall efficiency increase of 44%. Key device parameters are shown.](image)

![Graph showing transient absorption signals of the ZnO:P3HT system without and with applied vibration. The lifetime of the P3HT$^+$ polaron increases significantly with the application of applied vibration.](image)

**Figure 2.** (a) Current density-voltage measurements of ZnO:P3HT solar cells under 1 sun AM 1.5 illumination without and with applied vibration from a loudspeaker at 10 kHz. Acoustic vibration leads to an increase in both open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$) leading to an overall efficiency increase of 44%. Key device parameters are shown. (b) Transient absorption signals of the ZnO:P3HT system without and with applied vibration. The lifetime of the P3HT$^+$ polaron increases significantly with the application of applied vibration.

**4. Discussion**

Although other effects resulting from vibrations such as local heating, improved interfacial contact and structural reorganisation cannot be fully disregarded, the possibility that the piezoelectricity of the ZnO in this system could influence the recombination dynamics should be considered. It has recently been shown that the application of vibrations to a very similar polymer:ZnO nanorod system can lead to tens of mV being measured in an external circuit [14]. For this to be measured a much higher voltage and therefore electric field must exist in the nanorods, as screening effects by free carriers mean that a large portion of the generated voltage is not measured externally. It is also notable that this effect is much more significant in the ZnO:P3HT system than in the similar ZnO:PCBM:P3HT system reported in the literature [18]. One difference between these two systems is the location of the exciton separation and charge recombination interface. In the ZnO:P3HT system it is at the ZnO surface, whereas in the ZnO:PCBM:P3HT system it is between the P3HT and PCBM, therefore separated from...
the ZnO interface. This gives further support to the hypothesis that the origin of the enhancement lies with the ZnO, or a similar effect would also have been observed with ZnO:PCBM:P3HT.

Considering the evidence from the TAS measurements that the vibration-induced enhancement originates from a reduction in non-geminate recombination (Figure 2a), a model is proposed to explain the origin of this effect. As shown in Figure 3a, in the non-vibration case non-geminate recombination occurs at the ZnO:P3HT interface when an electron from ZnO recombines with a positive polaron from P3HT. When vibrations are applied to the ZnO it will bend and compress, leading to a polarization gradient in each nanorod. This results in an electric field in the nanorod which shifts the bands as shown in Figure 3b. As the electric field oscillates either the electron in ZnO or positive polaron in P3HT drift away from the interface, and the carrier moving towards the interface cannot cross it due to the high energy barrier without an opposite carrier with which to recombine. Therefore the net effect is to reduce the non-geminate recombination in the system, and therefore PCE, as observed. This also explains why the effect is not observed in the ZnO:PCBM:P3HT system, as here the majority of non-geminate recombination occurs at the PCBM:P3HT interface and therefore is not influenced by the polarization in the ZnO.

5. Conclusions
We have shown that the efficiency of a ZnO nanorod:P3HT solar cell increases from 1.24 to 1.78 % with the application of external acoustic vibrations. Transient absorption studies demonstrate that this effect arises largely from a significant decrease in the non-geminate recombination rate. We have proposed a model whereby the vibration-induced piezoelectric polarization creates band bending at the ZnO:P3HT interface which increases the spatial separation of charge carriers and reduces the recombination as observed. It is possible that other effects arising from vibration may also influence the charge carrier dynamics in the solar cell, and more studies are therefore needed to understand the mechanisms in more detail. However, the observation that such significant improvements in solar cell efficiency can be achieved with the application of acoustic vibrations could lead to a new avenue for solar cell optimization where devices are placed in areas of high vibration to utilize this effect.
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