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ARTICLE

Light-Soaking Effects on ZnO-Nanorods/Polymer Hybrid Photovoltaics

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Solar cell properties of polymer/ZnO-nanorods hybrid photovoltaics were improved by UV irradiation. However, the properties of the effects of UV irradiation were different from those reported for polymer photovoltaics made of a bulk heterojunction and a metal-oxide interlayer. In the case of the hybrid photovoltaics, in contrast to the devices with a bulk heterojunction, no inflection points were observed in the photocurrent-voltage curves of fresh devices, and an additional component of the photocurrent was induced by UV irradiation, leading to an increase in the photocurrent. The appearance of the second component of photocurrent was attributed to removal of oxygen, which impedes splitting of excitons into carriers, from the surface of ZnO nanorods by UV irradiation. Removal of oxygen was accelerated by the presence of a small amount of organic materials because oxygen was consumed while organic materials were photocatalytically decomposed by UV irradiation.

1. Introduction

Organic/inorganic hybrid photovoltaics (HPVs) have been widely studied in the past few decades because of their potential for utilizing the advantages of both inorganic and organic materials. HPV devices consist commonly of a p-type polymer such as poly(3-hexylthiophene-2,5-diyl) (P3HT), which acts as the donor layer, and an inorganic material such as zinc oxide (ZnO), which acts as the n-type material.^{1, 2} In general, excitons formed in the donor layer need to diffuse to the polymer/metal oxide interface to dissociate into free carriers. To circumvent the problem of short diffusion lengths of exciton,³⁻⁵ much interest has been shown in metal oxides in the form of nanostructures such as nanorods (NRs) because they can provide an ideal interdigitated structure that can maximize the surface area for dissociation of excitons and provide a continuous pathway for carrier transportation towards electrodes. However, the highest efficiencies of HPVs are less than 3%,^{6, 7} which are lower than the efficiencies of more than 10% reported for photovoltaics that have an organic bulk heterojunction.⁸ In bulk heterojunction devices, derivatives of C₆₀ such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) are commonly used as electron acceptor.⁹⁻¹¹ To improve the efficiency of HPVs, the development of methods to fabricate ZnO nanorods that have a desirable shape for making a junction with a polymer is needed, and a better understanding of the process of free carrier generation at the interface is also needed.

A composition of the structures of these two types of organic solar cells is shown in Fig. 1.

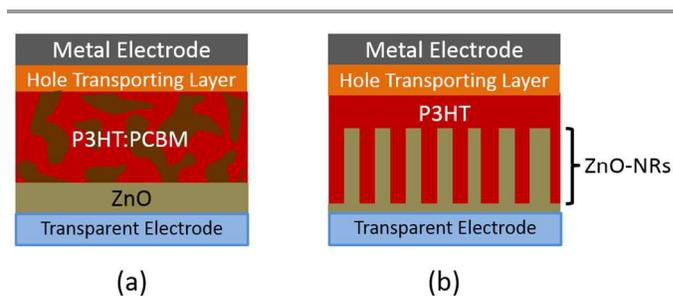


Figure 1: Structures of (a) an OPV device having a P3HT:PCBM bulk heterojunction with a ZnO interlayer, and (b) an HPV device having a ZnO-NRs/P3HT junction.

Concerning organic photovoltaics (OPVs) having a bulk heterojunction, it has been reported that UV irradiation improves solar cell properties. In most cases, series resistance of the devices decreases and efficiency increases. Such changes caused by UV irradiation are commonly referred to as the light-soaking effect, which is thought to be related to photodesorption of oxygen (O₂) from the surface of metal oxides, leading to increased conductivity of the metal-oxide layers.⁹⁻¹¹ Kim et al. reported that UV irradiation of OPVs leads to an increase in the electron density in a TiO_x layer because

photogenerated holes are used for desorption of O_2 , which is chemisorbed as O_2^- on the TiO_x layer. Wilken et al. reported that the removal of O_2^- from the surface of metal oxides by photogenerated holes leads to a decrease in the energy barrier at the interfaces that are included in the metal-oxide layers and at the interface of the metal oxide/transparent electrode.

However, there have been no reports on the light-soaking effect on HPVs with a metal oxide/polymer junction. We have studied UV irradiation of ZnO nanorods (ZnO-NRs) as a pretreatment of the ZnO-NR layer, which was carried out before depositing a polymer layer.¹² When HPVs were fabricated by depositing a P3HT layer on UV-treated ZnO-NRs, solar cell properties were improved because organic contaminants remaining on the surface of ZnO-NRs were photocatalytically decomposed. During the study on the effect of UV treatment, we noticed that solar cell properties of HPVs consisting of P3HT and UV-treated ZnO-NR layers also show the light-soaking effect, i.e., photocurrent increased by exposing the device to UV light. Interestingly, changes in the photocurrent-voltage curves caused by the light-soaking effect for HPVs having a ZnO-NR layer were different from those reported for OPVs having a metal oxide layer, and these differences provided the motivation for the present study. We also considered that such a study would be helpful to deepen the understanding of the properties of HPVs having metal-oxide nanorods.

2. Experimental Section

ZnO-NRs were prepared by the two-step method that is often used to prepare ZnO-NRs for OPV applications.¹³ First, a ZnO seed layer (ZnO-S) was prepared from a mixed solution of 0.5 M zinc acetate dihydrate (Wako) and 0.5 M monoethanolamine (Wako, 99%) dissolved in 2-methoxyethanol. The solution was cast on an ITO-coated glass (Luminescence Technology Corp., 15 Ω /sq) by spin coating at 2000 rpm for 30 s, followed by drying on a hot plate at 170 °C for 5 min. This process was repeated twice to obtain a ZnO-S layer with a thickness of about 60 nm. ZnO-NRs were deposited on the ZnO-S layer from an aqueous solution containing 0.025 M zinc nitrate hexahydrate (Sigma-Aldrich, 98%) and 0.025 M hexamethylenetetramine (Wako), which had been stirred for 30 minutes at 90 °C and filtered to remove some precipitates. The deposition of ZnO-NRs was carried out by immersing a ZnO-S-coated ITO plate into the solution at 90 °C for 60 min in a capped bottle. After the growth of ZnO-NRs, the samples were ultrasonicated in water, ethanol and water in sequence for 5 s each to remove unreacted chemicals. Organic contaminants still remaining on the surface of ZnO-NRs were decomposed by UV irradiation using a 500 W high-pressure mercury lamp (Wacom BMO-500DY, 1215 $mWcm^{-2}$) at room temperature.¹² In some experiments, the surfaces of the ZnO-NRs were loaded with sorbitol (an organic compound) by spin coating from an aqueous solution of 0.01 M sorbitol at 1000 rpm for 30 s and dried at 90 °C for 5 min. Morphologies of ZnO-NRs formed were analyzed with a scanning electron microscope (Hitachi, S-

5000 FEG) and the dimensions were found to be around 300 nm in length and 25 nm in diameter.

HPV devices with a ZnO-NRs/poly(3-hexylthiophene-2,5-diyl) (P3HT) junction were prepared by spin-coating the ZnO-NR layer with a layer of regioregular P3HT (Sigma-Aldrich, purity of 99.995%) from a chloroform solution with a concentration of 30 mg/ml at 1000 rpm for 30 s in air, followed by annealing at 90 °C for 3 min. MoO_3 (15 nm) and Ag (60 nm), acting as a hole transporting layer and a back electrode, respectively, were then thermally evaporated sequentially on top of the P3HT layer. All thermal evaporation processes were carried out at a pressure lower than 5×10^{-3} Pa. The HPVs were then encapsulated with a cover glass plate under nitrogen flow using a fast curing epoxy resin. For comparison, OPV devices having a P3HT:PCBM bulk heterojunction and ZnO-NRs as an electron accepting layer were fabricated by spin-coating a mixed chloroform solution containing 20 mg/ml P3HT and 18 mg/ml PCBM (Sigma-Aldrich, purity of 99%) on the ZnO-NRs layer in a manner similar to the fabrication of HPVs. To facilitate better separation of P3HT and PCBM domains, OPV devices having a P3HT:PCBM bulk heterojunction were subjected to heat treatment of 60 °C for 30 min before encapsulation.

Current density-voltage (J - V) characteristics of HPVs were measured using a solar cell evaluation system (Bunkoeki, CEP-015) under simulated solar light (AM 1.5, 100 $mWcm^{-2}$) through a UV-cut filter which cuts off wavelengths shorter than 420 nm. The UV-cut filter was used to prevent excitation of ZnO. For light-soaking experiments, the device was repeatedly exposed to the whole AM 1.5 spectrum by removing the UV-cut filter for a few seconds, and the J - V characteristics were measured with the UV-cut AM 1.5 spectrum after each exposure to the whole AM 1.5 spectrum. Responses of the device to chopped light were measured using an electrochemical measurement unit (Solartron, SI1280B).

Carbon dioxide (CO_2) gas evolved from ZnO-NRs by exposure to UV light was measured under vacuum using a thermal desorption spectrometer (TDS) (ESCO, TDS1200). For this experiment, a ZnO-NRs sample was placed in the chamber of the TDS and irradiated through a glass window with simulated light from another solar simulator (Asahi Spectra, HAL-C100) that was equipped with a quartz optical cable. Prior to measurements, the sample was heated at 100°C for 30 minutes in the TDS chamber to remove physisorbed water or other gasses.

3. Results and discussion

The bulk heterojunction of OPVs is usually made of P3HT and PCBM, which form separate phases inside the photoactive layer, as shown in Fig. 1a. It has been reported that OPVs having a ZnO or TiO_2 interlayer, which is usually made of nanoparticles, between the P3HT:PCBM layer and a transparent electrode show a light-soaking effect.⁹⁻¹¹ A typical change in J - V characteristics caused by the light-soaking effect is schematically shown in Fig. 2a. Before exposure to UV light, a

device having this structure show a deformed J - V curve with an S shape having an inflection point. The degree of deformation of the J - V curve depends on the condition for preparation of the interlayer. By exposing the device to UV light, the J - V curve changes to a normal shape of solar cells that has no inflection point. As a result of the effect, J_{sc} , FF, V_{oc} , and efficiency are all improved. These changes suggest that devices having a ZnO or TiO₂ interlayer have inherent faults and that these faults can be removed by exposing the devices to UV light.

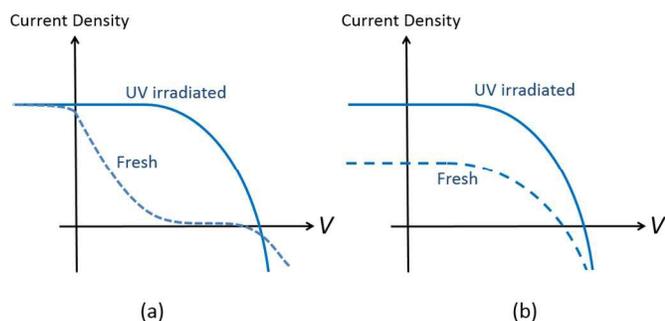


Figure 2: Schematic J - V characteristics before and after the light soaking effect for (a) an OPV device having a ZnO/P3HT:PCBM junction, and (b) an HPV device having a ZnO-NRs/P3HT junction.

We have studied the properties of HPVs in which PCBM or other electron acceptors are not present in the photoabsorber layer, as shown in Fig. 1b. In this type of device, charge carriers are generated at the ZnO-NRs/P3HT interface. A light-soaking effect was also observed with this type of HPV.¹² The effect of light soaking on the J - V curve of HPVs is schematically shown in Fig. 2b; experimentally obtained J - V curves are shown. In contrast to OPVs with a P3HT:PCBM bulk heterojunction, HPVs with a ZnO-NRs/P3HT junction did not show an S-shaped J - V curve. The difference in the light-soaking effect on J - V curves between the devices with a P3HT:PCBM bulk heterojunction and with a ZnO-NRs/P3HT junction is thought to be caused by the difference in the forms of the junctions and the morphologies of the ZnO layers used in them.

In the case of the OPVs with a P3HT:PCBM bulk heterojunction, the carriers are generated at the P3HT:PCBM interface and electrons are captured by ZnO grains forming the interlayer. Then the electrons are transported through the ZnO grains to the transparent electrode. The light soaking effect observed in these devices is thought to be caused by the decrease in the energy barrier for electron transport between the grains.^{9, 10, 14} Before exposure to UV light, oxygen molecules are adsorbed on the grains and charged negatively by accepting an electron from ZnO, leading to band bending inside the grains. By UV irradiation, the oxygen molecules accept a hole photogenerated in ZnO and are desorbed from the surface. This results in a decrease in the energy barrier between the grains and lowers the resistivity for electron transport across the ZnO layer, resulting in a change of the J - V curve, as shown in Fig. 2a.

Devices having a ZnO-NRs/P3HT junction show a different light-soaking effect on J - V curves after UV irradiation, which needs to be elucidated to understand the light soaking of HPVs in general. In our previous study, we found that UV treatment of ZnO-NRs before depositing the P3HT layer is useful to decompose organic contaminants remaining on the surface and to improve the solar cell properties.¹² By UV treatment, organic compounds are decomposed by the photocatalytic activity of ZnO. In the present study, we fabricated devices having the junction of ZnO-NRs/P3HT using a ZnO-NR layer that had been UV-treated for 60 min. This treatment is useful not only to obtain improved properties but also to elucidate the origin of the light-soaking effect by isolating it from the effect of photocatalytic decomposition of contaminants. To prevent the effect of photocatalytic activity during investigation of the characteristics of devices, the J - V characteristics were measured under the AM 1.5 spectrum from which the UV component was removed by inserting a UV-cut filter, which cut wavelengths shorter than 420 nm. Use of the UV-cut filter decreased the number of photons absorbed by P3HT to some extent. As a result, when measured with the UV-cut filter, J_{sc} of a device, which had been exposed to UV light for 40 s, was about 15% lower than that observed without using the filter (see Fig. S1). Figure 3 shows J - V curves of a UV-treated sample measured repeatedly under irradiation with simulated AM 1.5 light, from which the UV component was removed using a UV-cut filter. Between the measurements of the J - V curves, the device was irradiated for 2 s or 10 s with the whole AM 1.5 spectrum containing the UV component, which hereafter is referred to as UV irradiation. With increase in the cumulative time of UV irradiation, the photocurrent increased and the shape of the J - V curve improved until the J - V curve reached the final shape by irradiation for 40 s (red line). Different from this time course, V_{oc} increased and reached the limiting value of about 0.39 V after UV irradiation for only 6 s. The change of the J - V curves shown in Fig. 3 suggests that UV irradiation has two independent effects: increase in photocurrent and increase in V_{oc} .

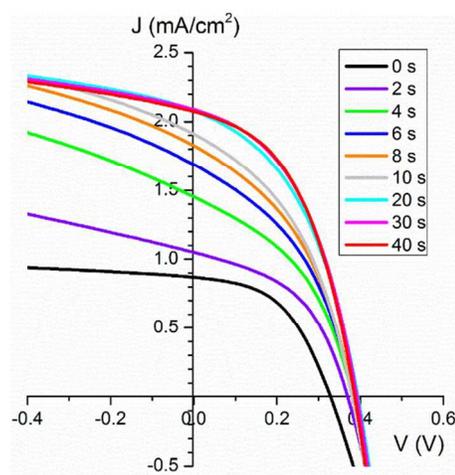


Figure 3: J - V curves of an HPV device with a P3HT/ZnO-NRs junction measured repeatedly after UV irradiation for certain periods. Cumulative UV irradiation times are shown in the legend. Irradiation conditions: AM 1.5, 100 mW/cm² for UV irradiation; the same but the UV component was removed for J - V measurements.

The increase in photocurrent by UV irradiation is thought to be caused by the appearance of an additional component of the photocurrent, which is scarcely included in the photocurrent of the fresh device (black line). Figure 4 shows the J - V curves of Fig. 3 from which the J - V curve of the fresh device was subtracted after making a small modification in the horizontal position so that V_{oc} of the fresh device agreed with V_{oc} of the corresponding J - V curves. This modification was necessary to eliminate the light-soaking effect on V_{oc} . The J - V curves thus obtained show that the FF of J - V curves increased with the time of UV irradiation, but the limiting value of the photocurrent was almost constant: about 1.3 mA/cm². This behavior suggests that the efficiency of electron injection from excitons of P3HT into ZnO-NRs is increased by UV irradiation. More precisely, as UV irradiation time increases, assistance of bias voltage becomes less necessary for electron injection.

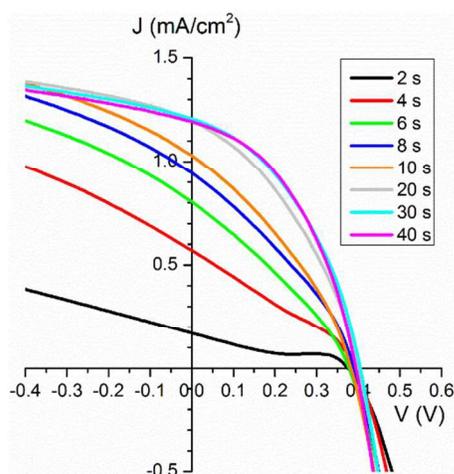


Figure 4: Increased photocurrent components in the J - V characteristics of an HPV device with a ZnO-NRs/P3HT junction by UV irradiation. The curves are drawn using the J - V characteristics shown in Fig. 3 by subtracting the J - V curve of the fresh device which was not UV irradiated. In subtraction, the J - V curve of the fresh device is shifted in the horizontal direction so that V_{oc} of the fresh device agrees with the V_{oc} of the corresponding J - V curves.

It should be noted that the device having a P3HT:PCBM bulk heterojunction and ZnO-NRs as an electron accepting layer showed J - V curves similar to those shown in Fig. 3 and did not show the S-shaped curve as shown in Fig. 2(a) before UV irradiation (see Fig. S2). These results suggest that the S-shaped J - V curves are related to the properties of ZnO nanoparticles. It is known that oxygen molecules are adsorbed on the surface of ZnO and charged negatively. In the case of device having a P3HT:PCBM bulk heterojunction and a ZnO layer, which is made of nanoparticles, as the interlayer for

collecting electrons, this leads to an upward shift of bands in a ZnO grain, which impedes the transport of electrons, as shown in Fig. 5a. In contrast, in the case of ZnO-NRs/P3HT, there are no connections of ZnO particles except the interface between ZnO-NRs and thin ZnO-S layers, as shown in Fig. 5b. In this case, there are practically no grain boundaries that impede the transport of electrons. Instead, the dissociation of excitons at ZnO-NRs/P3HT is a crucial process for generating photocurrents. An oxygen molecule at the ZnO-NRs/P3HT interface can be a quencher of the excited state of organic molecules and also a recombination center for carriers generated at the interface because an oxygen molecule is a good electron acceptor.¹⁵

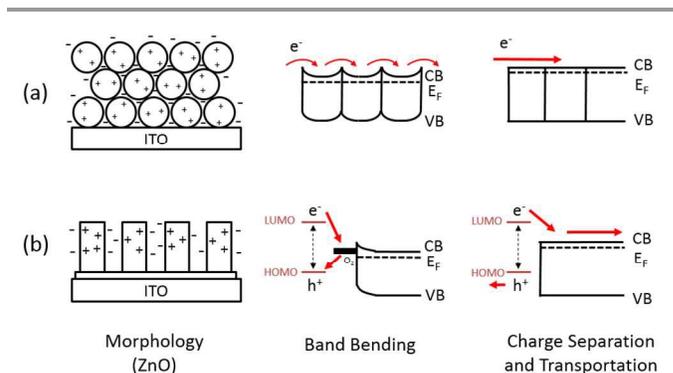


Figure 5: Schematic illustrations of morphologies of and the effects of UV irradiation on (a) an OPV having a P3HT:PCBM bulk heterojunction with a ZnO interlayer and (b) an HPV having a ZnO-NRs/P3HT junction.

We rather arbitrarily consider that the two components of the photocurrent observed with devices having a ZnO-NRs/P3HT junction are due to the photocurrents generated at the {0001} face and {1010} face of ZnO-NRs, which compose the top and sides of each ZnO-NR, respectively. Since oxygen molecules are preferentially adsorbed on the {1010} face,^{16, 17} we assume that a photocurrent is generated only on the {0001} face if a fresh device is used. If this assumption is correct, the black line in Fig. 3 represents the J - V characteristics due to this photocurrent. When UV-irradiated, oxygen molecules adsorbed on the {1010} face of ZnO are desorbed. The increase in photocurrent and FF by UV irradiation is therefore attributed to activation of the {1010} face for exciton dissociation at the interface due to desorption of oxygen molecules by UV irradiation.

The slight increase in V_{oc} by UV irradiation may be due to the disappearance or decrease of the upward shift of the band bending inside ZnO-NRs, as has been proposed for the explanation of improved carrier transportation in the ZnO layer (Fig. 5a). Desorption of negatively charged oxygen molecules lessens the band bending of ZnO and increases the built-in potential of the device, leading to an increase in V_{oc} . On the basis of the assumption that oxygen molecules are adsorbed on the {1010} face, these changes occur on this face. The change in the band structure at the {1010} face should affect the built-

in potential of the whole device because most of the surface of the ZnO-NRs is composed of the {1010} face. The change of V_{oc} was completed by UV irradiation for only 6 s, as shown in Fig. 3, suggesting that most of oxygen molecules are desorbed in a short time. This is in good agreement with the time needed for photodesorption of oxygen, as shown later.

In contrast, longer UV irradiation was needed for increasing the photocurrent. We assume that generation of the photocurrent is impeded by a small amount of oxygen present at the interface of ZnO-NRs/P3HT because an oxygen molecule acts as an efficient electron-hole recombination center, as shown in Fig. 5b. In addition, the fact that final photocurrent density obtained by UV irradiation was about 3-times higher than that of the fresh device, as shown in Fig. 3, suggests that not all of the side walls but a limited region near the top of the ZnO-NRs contributes to the photocurrent generation. This is probably due to the fact that a strong electric field, which is necessary for dissociation of excitons at the ZnO/P3HT interface, cannot be formed at places far from the top of ZnO-NRs because ZnO has a lower resistivity than that of P3HT. This understanding suggests that the interdigitated structure of HPVs made of long ZnO-NRs does not necessarily lead to a large photocurrent. To further increase the photocurrent, the length as well as spacing between NRs needs to be optimized by taking into account the distribution of the electric field developed along the ZnO-NRs/P3HT interface.

Change in the built-in-potential of the device by UV irradiation, which is suggested in the above discussion, was confirmed from analysis of the photocurrent response, as shown in Fig. 6. Under forward bias, the device showed a small photocurrent in the forward direction, which is opposite to the normal photocurrent. The voltage at which the polarity of the photocurrent changes (V_{pc}) should be closely related to the built-in potential formed inside the device. The V_{pc} values for devices having a ZnO-NRs/P3HT junction before and after being UV-irradiated for 10 and 20 s are shown in Table 1. The change in V_{pc} by UV irradiation was completed in almost 10 s and the magnitude of the shift in V_{pc} was very close to the shift of V_{oc} by UV irradiation, as shown in Fig. 3. These results support our understanding that V_{oc} is increased by UV irradiation because molecular oxygen molecules adsorbed on ZnO, which decrease the built-in potential, are removed by UV irradiation.

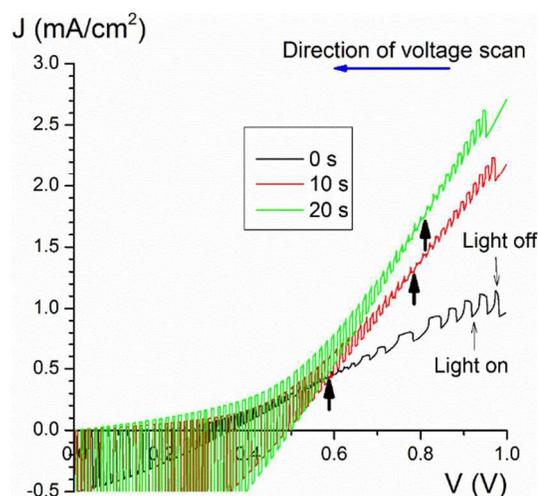


Figure 6: Photoresponse of an HPV having a ZnO-NRs/P3HT junction measured before and after UV-irradiated for 10 and 20 s. Irradiation conditions: AM 1.5, 100 mW/cm² for UV irradiation; the same but the UV component was removed for photoresponse measurements. Voltage was scanned from positive to negative. Thick arrows show the points at which the polarity of photoresponse changes.

Table 1: V_{pc} values determined from the results shown in Fig. 6 for devices having a ZnO-NRs/P3HT junction before and after UV irradiation for 10 and 20 s.

Light soaking time / s	V_{pc} / V
0	0.59
10	0.79
20	0.80

Figure 7 shows the performance of the devices containing a ZnO-NR layer that had not been UV-treated to remove organic contaminants. The performance was poorer than that of the devices having a UV-treated ZnO-NR layer, as shown in Fig. 3. This is due to the fact that a larger amount of organic contaminants remained on the surface of ZnO-NRs for the device used in Fig. 7. Interestingly, however, with the device having a ZnO-NR layer without UV treatment, the light-soaking effect was completed in a shorter time period: about 10 s. This result suggests that organic contaminants contribute to the removal of oxygen molecules from the surface of ZnO-NRs, as will be discussed later.

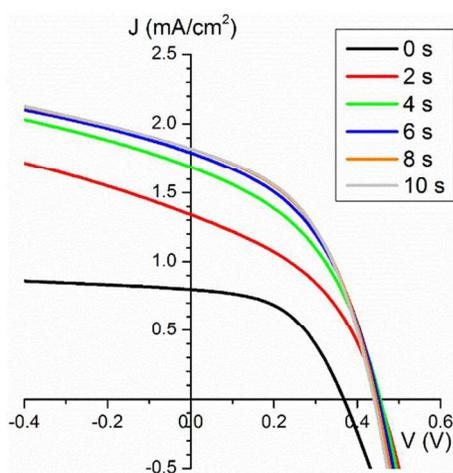


Figure 7: J - V curves measured repeatedly after UV irradiation for certain periods for an HPV device having ZnO-NRs without UV treatment. Cumulative UV irradiation times are shown in the legend. Irradiation conditions: AM 1.5, 100 mW/cm^2 for UV irradiation; the same but the UV component was removed for J - V measurements.

We tried to detect molecules released from the surface of ZnO-NRs caused by UV irradiation using high-sensitivity thermal desorption spectroscopy (TDS). A ZnO-NR sample placed in a TDS chamber (base pressure: 3×10^{-7} Pa) was irradiated with UV light from a solar simulator. However, a noticeable increase in the level of the oxygen signal was not detected by UV irradiation. This may be due to the fact that a small amount of oxygen molecules is included in the system, which made the detection of desorbed oxygen difficult. Another possible reason is that the oxygen molecules are consumed by the photocatalytic reaction of organic molecules. This explanation is supported by the fact that emission of CO_2 molecules was detected in response to UV irradiation, as shown in Fig. 8a. When a UV-cut filter that cuts off light having a wavelength of more than 580 nm was used during the TDS measurement, CO_2 gas evolution was negligibly small. These results indicate that organic contaminants, which came from the organic materials used for the growth of ZnO-NRs, are oxidatively decomposed by the photocatalytic activity of ZnO under UV light.¹²

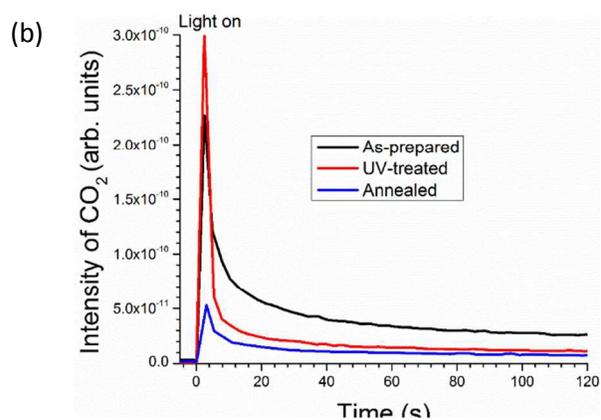
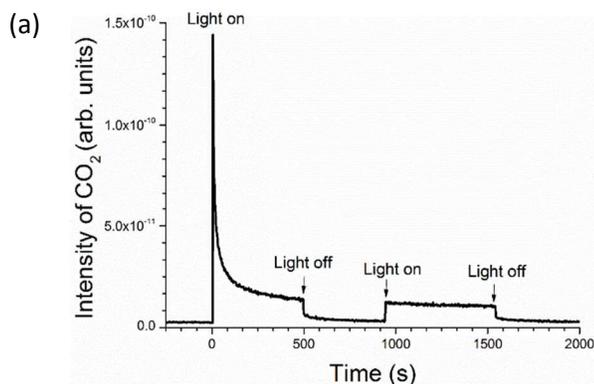


Figure 8: CO_2 gas emission during UV irradiation from (a) ZnO-NRs without UV treatment, and (b) ZnO-NRs without UV treatment, UV-treated for 16 hours and annealed at 400°C for 30 min. Irradiation conditions: AM 1.5, 100 mW/cm^2 .

The time courses of CO_2 emission from ZnO-NRs depended on the surface treatments, as shown in Fig. 8b. From ZnO-NRs annealed at 400°C for 30 min, CO_2 emission was small because most of organic contaminants were removed by the treatment. From the ZnO-NRs UV-treated for 16 h, a sharp large peak of CO_2 emission was observed. This peak may be due to photodesorption of carbonate or CO_2 produced as a result of photocatalytic reaction. From the non-treated ZnO-NRs, after a sharp peak of CO_2 emission, CO_2 emission continued with a relatively high intensity. This CO_2 emission is thought to be due to photocatalytic oxidation of organic contaminants using oxygen atoms existing on the surface of metal oxides as OH groups or lattice O atoms.^{18,19} The width of the sharp peak of CO_2 emission after the first UV irradiation was less than 10 s, irrespective of the surface treatments of ZnO-NRs, as shown in Fig. 8b, which suggests that most of the oxygen molecules adsorbed on the surface of ZnO-NRs are desorbed in this time range. This time range agrees with the time needed for increasing V_{oc} , as shown in Fig. 3, which therefore suggests that the shift of V_{oc} is due to the desorption of oxygen molecules from the surface of ZnO-NRs, as discussed above. The annealing process is most effective for removal of organic contaminants from the surface of ZnO-NRs. However, this high temperature cannot be applied to HPVs or OPVs fabricated on plastic substrates.²⁰ Hence, we consider that the UV treatment has advantages for improving the properties of flexible solar cells.

When the photocatalytic reaction of organic compounds proceeds, oxygen molecules are converted to CO_2 and H_2O .^{21,22} This suggests that organic compounds remaining on the surface of ZnO-NRs play a role in removal of oxygen molecules by UV irradiation, although their presence in a large amount is harmful to solar cell properties. This may be the reason for the faster increase of J_{sc} by the light-soaking effect with the device having as-prepared ZnO-NRs (Fig. 7) than with the device having ZnO-NRs UV-treated for 60 min (Fig. 3).

On the basis of the above arguments, it is expected that oxygen molecules adsorbed on the surface of ZnO-NRs are

removed efficiently if organic compounds, which are easily oxidized, are placed on the surface of ZnO-NRs. To confirm the effectiveness of organic compounds for removal of oxygen from the surface, sorbitol, which is a good reducing agent, was placed on the surface of a ZnO-NR layer by spin coating from an aqueous solution of 0.01 M sorbitol at 1000 rpm for 30 s. The increase in photocurrent of the HPV made of this ZnO-NR layer by the light-soaking effect was completed in only about 2 s, as shown in Fig. 9. This is in contrast to the fact that it took more than 30 s for the device having a UV-treated ZnO-NR layer to complete the light-soaking effect, as shown in Fig. 3. These results suggest that because the photocatalytic reaction of sorbitol is very efficient, oxygen molecules are effectively removed from the ZnO-NRs/P3HT interface and also from the surrounding region. We consider that by placing sorbitol or another reducing agent at the ZnO-NRs/P3HT interface in an optimized amount, oxygen can be removed from the device without serious harmful effects. Such compounds may also be effective for preventing oxidative decomposition of the photoactive layer used in OPVs and HPVs.

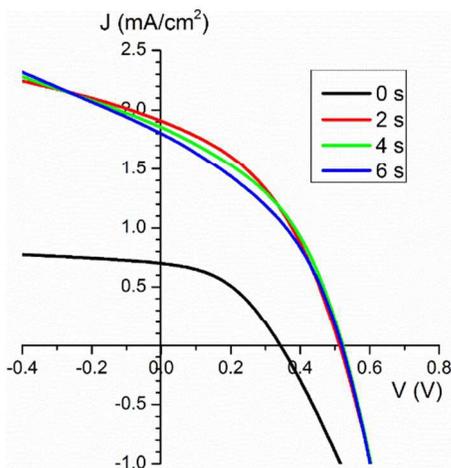


Figure 9: *J-V* curves measured repeatedly after UV irradiation for certain periods for an HPV device having ZnO-NRs on which sorbitol was deposited. Cumulative UV irradiation times are shown in the legend. Irradiation conditions: AM 1.5, 100 mW/cm² for UV irradiation; the same but the UV component was removed for *J-V* measurements.

4. Conclusions

HPVs having a polymer/ZnO-NRs junction have an advantage of easy control of the junction morphology by controlling the structure of ZnO-NRs over OPVs having a bulk heterojunction consisting of two organic phases. In the case of HPVs, oxygen adsorbed on ZnO nanorods is very harmful for dissociation of excitons into carriers at the polymer/ZnO-NRs interface, leading to poor performance of the devices. However, by UV irradiation of HPVs, solar cell properties are improved by the light-soaking effect, because oxygen adsorbed on ZnO is removed. Loading of a small amount of sacrificial organic compounds will be useful to remove oxygen effectively

because their photocatalytic reactions on the ZnO surface consume oxygen molecules adsorbed on it.

Notes and references

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