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ARTICLE

Removal of Organic Contaminants from the Surface of ZnO Nanorods for Organic/Inorganic Hybrid Photovoltaics by Using Photocatalytic Reaction

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Hybrid photovoltaics made of ZnO nanorods, which were deposited by solution process, and a polymer layer showed poor properties probably because the surface of ZnO nanorods was contaminated by organic materials used for the deposition. We tried to remove the organic contaminants remaining on the surface of ZnO nanorods by using photocatalytic activity of ZnO under UV light before depositing a polymer layer. We found that the UV-treatment carried out at room temperature is effective to remove the organic contaminants and to improve the solar cell properties. The removal of organic materials was confirmed by X-ray photoelectron spectroscopy. In addition, we found that photoluminescence from poly(3-hexylthiophene-2,5-diyl) (P3HT) was quenched more by a ZnO substrate after the UV-treatment, suggesting that excitons of P3HT were dissociated into carriers more efficiently on the UV-treated ZnO substrate.

1. Introduction

Organic photovoltaics (OPVs) have been studied intensively in these last few decades because of their potential in realizing low cost, large area and flexible solar cells. One typical class of OPVs is the polymer-based devices in which the photoactive layer is made of a mixture of a polymer and a fullerene compound.[1-3] In the photoactive layer, the two materials form separated phases on a nanoscale, each creating its network across the layer. Such a structure is called a bulk-heterojunction (BHJ). When the structure is well constructed, excitons formed in the polymer phase can dissociate into carriers at the interface at high efficiency and be transported to respective electrodes through the networks. In some other types of OPVs, inorganic materials are included in the structure. They work not only as an electrode but also as a material for making a junction for charge separation.[4-7] Zinc oxide (ZnO) has gained much attention as an inorganic material used for OPVs because it has various advantages including high electron mobility, nontoxicity and ease of synthesis. Because of these advantages, ZnO is used as a buffer,[8] as an n-type layer of organic/inorganic hybrid photovoltaics (HPVs),[4-7] or as a porous electrode of dye-sensitized solar cells.[9, 10] In applications to OPVs and HPVs, a ZnO layer made of nanorods structure (ZnO-NRs) have been studied mostly because of their suitability in forming an ideal interdigitated structure with a large surface area, which is

essential for exciton dissociation and in making a continuous pathway for effective charge transportation of electrons toward an electrode.[11-13] However, the highest efficiency reported for ZnO-NRs/polymer type HPVs was about 1.6%[13] whereas that of OPV with a BHJ was about 9%.[14]

Part of the reason for the low efficiency of HPVs is related to properties of the ZnO-NRs/polymer interface. In HPVs having a ZnO-NRs/polymer junction, because excitons formed in a polymer layer need to dissociate at the interface, contaminants that might exist at the interface will be very harmful. This is because it is essential for an electron donor and an electron acceptor to be placed in direct contact for efficient dissociation of excitons. Defect levels existing at the surface of ZnO is another possible reason for the low efficiency of HPVs with a ZnO-NRs/polymer junction.[15, 16] If these problems are solved, HPVs will be attractive because the structure of ZnO/polymer junction can be easily controlled on a nanoscale by adjusting the structure of ZnO-NRs, which can be fabricated by convenient solution methods.

Structure and surface properties of ZnO-NRs are affected by the manufacturing processes. In solution methods such as sol-gel and hydrothermal, various kinds of organic compounds are used as solvents, reactants and complexing agents. These compounds may remain on the surface of ZnO-NRs fabricated.[17, 18] Heat treatment is usually employed to remove these organic contaminants.[17] However, temperatures higher

than 300 °C, which are usually used for decomposing the contaminants, are unfavourable for flexible solar cells fabricated on plastic substrates.[19] Here, in place of heat treatment, we report a method for decomposing contaminants at room temperature using photocatalytic activity of ZnO-NRs under UV light.[20, 21] We demonstrate that the device made of ZnO-NRs which were UV irradiated before deposition of a polymer layer showed improved performance.

2. Experimental Section

ZnO-NRs were prepared by a two-step method that is often used to prepare ZnO-NRs for OPV application.[22] First, a ZnO seed layer (ZnO-S) was prepared on an ITO-coated glass plate (15 Ω/sq) obtained from Luminescence Technology, then ZnO-NRs were deposited on it. The ZnO-S layer was deposited from a mixed solution of 0.5 M zinc acetate dihydrate (Wako Pure Chemical Industries) and 0.5 M monoethanolamine (Wako Pure Chemical Industries) dissolved in 2-methoxyethanol. The solution was cast on an ITO substrate 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 carried out twice to obtain a ZnO-S layer with a thickness of about 60 nm. On top of the ZnO-S layer, ZnO-NRs were deposited by the chemical bath deposition method from an aqueous solution containing 0.025 M zinc nitrate hexahydrate (Sigma-Aldrich, 98%) and 0.025 M hexamethylenetetramine (Wako Pure Chemical Industries). Prior to use, the solution was stirred for 30 minutes at 90 °C and filtered to remove precipitates. ZnO-S-coated ITO was then immersed into the solution at 90 °C for 60 min in a capped bottle for growing ZnO-NRs. Then the samples were sonicated in water, ethanol and water in sequence for 5 s each to remove unreacted chemicals. Morphology of the ZnO structures formed was observed by scanning electron microscope (Hitachi, S-5000 FEG). X-ray diffraction (XRD) pattern was obtained with an X-ray diffractometer (Rigaku, MiniFlex) using Ni-filtered CuKα radiation (λ = 0.15418 nm, 30 kV, 15 mA).

Poly(3-hexylthiophene-2,5-diyl) (P3HT) layers for HPVs were deposited on ZnO-NRs by spin coating at 1000 rpm for 30 s in air from a chloroform solution containing regioregular P3HT (Sigma-Aldrich, purity 99.995%) at a concentration of 30 mg/ml, followed by annealing at 90 °C for 3 min. Layers of MoO_3 (15 nm) and Ag (60 nm), acting as a hole transporting layer and back electrode respectively, were then thermally evaporated sequentially on top of the P3HT layer. All thermal evaporation processes were done at a pressure lower than 5 x 10^{-3} Pa. Current density-voltage (*J-V*) characteristics of solar cells were measured using a solar cell evaluation system (Bunkokeiki, CEP-015) under simulated solar light (AM 1.5, 100 mWcm^{-2}). In some measurements, devices were irradiated through a UV-cut filter that cuts off wavelengths shorter than 420 nm to prevent photoexcitation of ZnO.

UV irradiation of ZnO-NRs was performed using a 500 W high-pressure mercury lamp (Wacom BMO-500DY, 1215 mWcm^{-2}) at room temperature in ambient atmosphere for a period ranging from 15 to 60 minutes. The effect of UV-

treatment on surface properties of ZnO-NRs was studied by X-ray photoelectron spectroscopy (XPS) (Shimadzu AXIS ULTRA). To study the effect on properties of the ZnO/P3HT interface, photoluminescence from P3HT layers deposited on ZnO layers with different UV-treatment periods were measured with a florescence spectrophotometer (JASCO, FP-600). For this purpose, samples that had a flat ZnO-S layer (60-nm-thick) deposited on an alumina plate substrate were used because an alumina substrate was useful for obtaining reproducible results, probably due to its high diffuse reflectivity.

3. Results and discussion

ZnO-NRs formed were about 250 nm in length and 25 nm in diameter, as shown in Fig. 1. Preferential orientation in the <001> direction and high crystallinity of ZnO-NRs were proven from the XRD pattern shown in Fig. 2, which shows only a peak due to (002) with FWHM of about 0.2° over the 2θ region of 30 to 40 degrees. The morphology and crystallinity of ZnO-NRs were not affected by UV irradiation for 60 min.
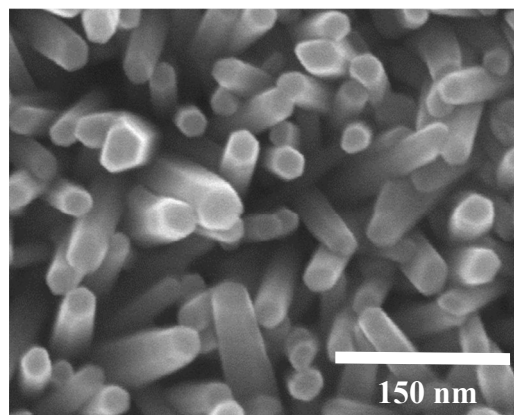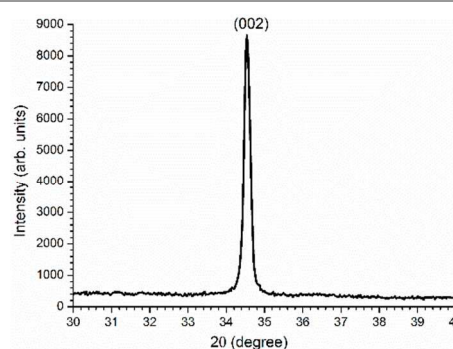

Figure 1: SEM image of as-deposited ZnO-NRs.

Figure 2: XRD pattern of as-deposited ZnO-NRs.

Solar cell properties of HPVs with a ZnO-NRs/P3HT junction changed during photo-irradiation with simulated solar light (AM 1.5G, 100 mW/cm^2) of less than 20 s. This phenomenon is called the light-soaking effect.[23] In the present study, to avoid the change during measurements, we measured

the properties after reaching the stationary state or after photo-irradiation for at least 20 s. The properties of devices having ZnO-NRs with different treatments are shown in Fig. 3. Each curve shown in Fig. 3 is for the device showing the best properties of about 5 devices measured. The device with as-deposited ZnO-NRs (black line) showed a short-circuit current density (J_{sc}) of 2.11 mA/cm^2, open circuit voltage (V_{oc}) of 0.62 V, fill factor (FF) of 0.4 and efficiency of 0.53%, which is comparable to reported values of devices having a similar structure.[11, 22] The device with ZnO-NRs annealed in air at 300 ˚C for 30 min before depositing a P3HT layer (red line) showed J_{sc} of 3.15 mA/cm^2. This improvement in J_{sc} is attributed to the removal of organic contaminants by oxidative decomposition. The decrease in both V_{oc} and FF might be due to remains produced by partial decomposition of the contaminants. For a device with ZnO-NRs UV-treated for 60 min before P3HT deposition (blue line), J_{sc} was almost the same as that of the device with ZnO-NRs annealed at 300 ˚C, and V_{oc} was higher than that of the device with the annealed ZnO-NRs. UV irradiation for 60 min should be enough for activating ZnO-NRs because J_{sc} increased with increasing UV-irradiation time up to 60 min and then reached a limiting value. Table 1 summarizes the solar cell performances of the HPVs obtained with 5 devices.
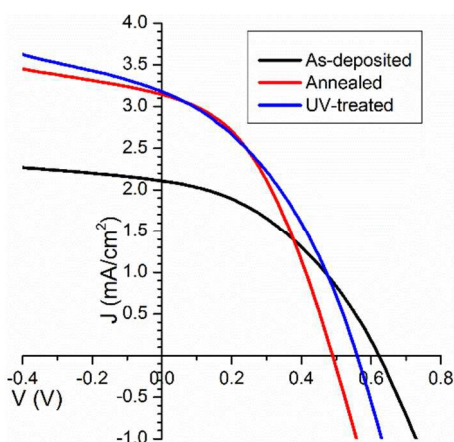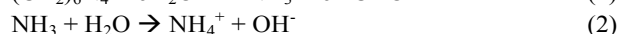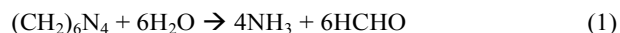

Figure 3: *J-V* curves of HPVs, each having a ZnO-NRs layer as-deposited (black line), annealed at 300 °C for 30 min (red line) and UV-treated for 60 min (blue line). Irradiation: AM 1.5, 100 mWcm^{-2}. The devices were photo-irradiated for more than 20 s before the measurements so that the light-soaking effect took place. Each of the curve is for the device showing the best properties of about 5 devices measured.

Table 1: Solar cell performances of HPVs having a ZnO-NRs layer as-deposited, annealed at 300 °C for 30 min or UV-treated for 60 min. Irradiation: AM 1.5, 100 mWcm^{-2}.

Sample	η (%)	Fill Factor FF	J_{sc} (mA/cm^2)	V_{oc} (V)
As-deposited	0.51 ± 0.02	0.39 ± 0.01	2.06 ± 0.05	0.61 ± 0.02
Annealed	0.60 ± 0.03	0.40 ± 0.01	3.07 ± 0.08	0.48 ± 0.01
UV-treated	0.65 ± 0.03	0.37 ± 0.01	3.10 ± 0.08	0.55 ± 0.01

We were not able to identify the organic contaminants on ZnO-NRs because the amount was very small. The amount and species should be closely related to the conditions for depositing ZnO-S and ZnO-NRs. As described in the experimental section, the ZnO-S layer was deposited by the sol-gel method from a precursor solution containing zinc acetate and monoethanolamine. Li et al. proposed that a Zn^{2+}-monoethanolamine complex is formed in the sol-gel solution and a ZnO layer made of fine ZnO grains is deposited on a substrate from the complex.[24] This complex may be the origin of the contaminants. An amine compound used for deposition of ZnO-NRs on the ZnO-S film may also be the source of contaminations. ZnO-NRs were grown through different reaction steps represented by Eqs. 1-3:[25]

$$(CH_2)_6N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \quad (1)$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$
$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad (3)$$

It has been reported that unreacted materials included in the precursor solution remain as contaminants on the surface of ZnO-NRs.[26, 27] These contaminants are expected to prevent dissociation of excitons of P3HT at the ZnO/P3HT interface. In the case of normal OPVs with a BHJ, the contaminants at the interface will increase the internal resistivity of the devices. However in the case of HPVs, the problem is more serious because excitons generated in the P3HT layer need to dissociate into carriers at the ZnO/P3HT interface.

For devices fabricated on glass plates, ZnO-NRs are usually annealed at about 300 ˚C before depositing P3HT or other polymers. This process is useful to remove organic contaminants. However, it cannot be applied to devices fabricated on plastics because of their vulnerability to heat. In contrast, a photocatalytic process may be applicable to those devices. In photocatalytic processes, when a photon with energy larger than the band gap of ZnO (3.2 eV) is absorbed by ZnO, an electron in the valence band is promoted into the conduction band, leaving behind a hole (Eq. 4). The electron and hole will interact with other chemical species on the surface of ZnO such as surface OH, molecular oxygen and water. Although the mechanism of photocatalytic reactions have not been completely elucidated, the processes shown by Eqs. 4-8 are often used for explaining photocatalytic decomposition of organic materials.[28, 29]

$$ZnO + h\nu \rightarrow e^- + h^+ \quad (4)$$
$$H_2O + h^+ \rightarrow H^+ + \cdot OH \quad (5)$$
$$h^+ + OH^- \rightarrow \cdot OH \quad (6)$$
$$e^- + O_2 \rightarrow \cdot O_2^- \quad (7)$$
$$\cdot OH + \text{organic species} \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \quad (8)$$

To confirm photocatalytic decomposition of organic contaminants that had been adsorbed on the ZnO layers during deposition processes, XPS of ZnO-NRs on which P3HT layers were not deposited was measured. Figure 4a shows the C1s spectra of ZnO-NRs with and without UV irradiation. The peaks at 284.6 eV and 288.5 are attributed to C-C and O-C=O, due mostly to adventitious contaminants from the XPS

system.[17, 30] After UV irradiation, the signal intensity of the 284.6 eV peak was decreased to some extent. In contrast, as shown in Fig. 4b, both the $Zn2p_{1/2}$ and $Zn2p_{3/2}$ peaks increased after the UV-treatment. These results suggest that contaminants remaining on the top surface of ZnO-NRs were removed by UV-treatment.
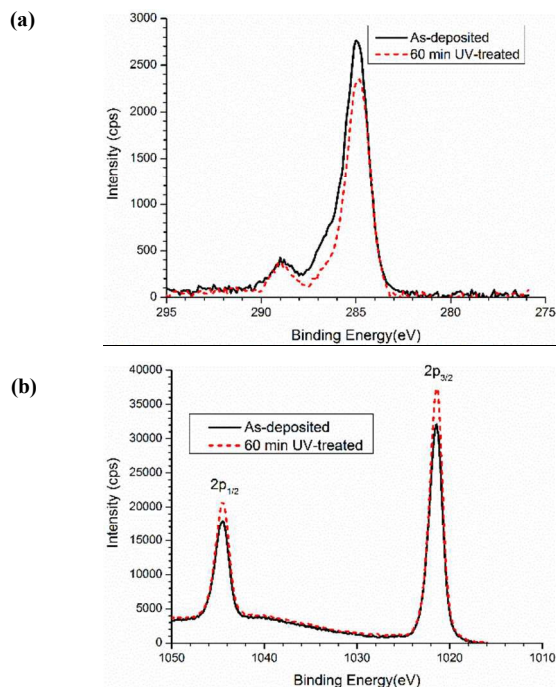

Figure 4: XPS of ZnO-NRs with and without UV treatment for the peaks of (a) C1s and (b) Zn2p. Spectra shown in panels (a) and (b) were obtained with the same samples. The binding energy was calibrated against the 284.6 eV peak C1s.

To further investigate the effect of contaminants on the dissociation of excitons into carriers at the P3HT/ZnO interface, photoluminescence (PL) quenching of P3HT by ZnO was measured. For this purpose, a flat ZnO layers made by the sol-gel method, which had been deposited on alumina plates, was used to obtain better reproducibility of the PL intensity. After ZnO had been UV-treated for different periods, a 75-nm-thick P3HT layer was deposited on the top by spin coating from a chloroform solution containing P3HT at a concentration of 5 mg/ml. The P3HT layer was made thinner than that used in HPVs so that quenching of its PL by ZnO could be easily detected. PL from the P3HT layer was measured by photoexcitation of P3HT at the wavelength of 500 nm. The PL intensity from the P3HT layer deposited on the ZnO film which had not been UV-treated was about 5% lower than the intensity from the P3HT deposited on an alumina plate without inserting a ZnO film, as shown in Fig. 5. This small decrease in PL intensity cannot be attributed to the quenching of excitons of P3HT by the ZnO film because the surface morphology of the ZnO film was not exactly the same as that of a bare alumina plate. However, the morphology of the ZnO layer was not affected by UV-treatment. Therefore, the decrease in PL intensity of P3HT deposited on ZnO layers with the increase in the UV-treatment time, as shown in Fig. 5, is attributed to the quenching of the PL intensity by the ZnO layers. PL of the P3HT layer is quenched more by the ZnO layer UV-treated for longer time. This indicates that UV-treatment of ZnO is useful to decompose organic contaminants remaining on the ZnO surface and to improve the quality of the ZnO-NRs/P3HT interface for excitons dissociation. Compared with the time needed for increasing J_{sc}, which will be discussed later, it took longer UV-irradiation time for bringing the degree of PL quenching to the limiting value. The difference is attributed to the fact that in the PL quenching measurements, a ZnO-S layer, which had poorer crystallinity than ZnO-NRs, was used. It is known that high-crystallinity semiconductor materials shows higher photocatalytic activity.[31]
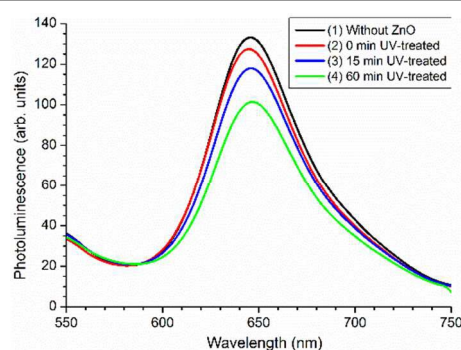

Figure 5: PL spectra of P3HT layer (1) deposited on an alumina plate without ZnO layer, deposited on ZnO layers UV treated for (2) 0 min, (3) 15 min, and (4) 60 min. All samples were prepared on an alumina plate. Excitation wavelength: 500 nm.

To study the effect of removal of organic contaminants by the UV-treatment on solar cell properties of HPVs, light-soaking effect need to be taken into account. As mentioned above, the *J-V* properties of fresh HPVs changed under irradiation of the AM 1.5 spectrum because of the light-soaking effect induced by photoexcitation of ZnO. It should be useful for the readers to have some information about the light-soaking effect on HPVs, although detailed discussion about it is beyond the scope of the present study. Figure 6 shows the results relating to the light-soaking effect on an HPV with ZnO-NRs. A fresh HPV with as-deposited ZnO-NRs showed J_{sc} of about 0.55 mA/cm² under the AM 1.5 spectrum from which the UV component was removed (black line). However, when the properties were measured with the normal AM 1.5 spectrum after exposing the device to this light for 20 s, J_{sc} increased to 2.11 mA/cm², due to the light-soaking effect (red line). No further increase in J_{sc} was observed by exposing the device to the light for longer time. When the properties of the device experienced the light-soaking effect were measured again with the AM 1.5 spectrum from which the UV component was removed, J_{sc} was decreased by 16% (blue line). This decrease is due to the decreased photoabosorption of the P3HT layer at wavelengths shorter than 420 nm, indicating that the light-

soaking effect maintained for a certain time period. The period was longer than 10 min, which seemed dependent on device preparation conditions.
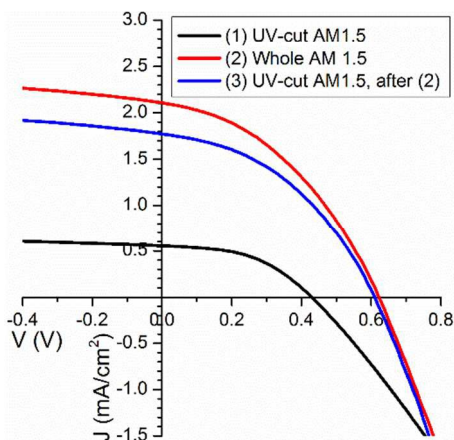

Figure 6: *J-V* curves of an HPV with ZnO-NRs measured successively, (1) using a UV-cut filter (black line), (2) under the whole AM1.5 spectrum after light soaking for 20 s (red line), and (3) again using a UV-cut filter (blue line). Light source for the *J-V* measurements and light soaking: AM 1.5, 100 mWcm^{-2}, if a UV-cut filter was not used.

Finally, we discuss the properties of HPVs with ZnO-NRs unaffected by the light soaking effect. Figure 7 shows the *J-V* characteristics of HPVs with ZnO-NRs which had been UV-treated for different periods before deposition of the P3HT layer, and the *J-V* characteristics of a HPV with ZnO-NRs annealed at 300 ˚C for 30 min. All of them were not light-soaked and the *J-V* characteristics were measured under irradiation with the AM 1.5 spectrum from which the UV component was removed. Note that the properties of these devices are much worse than those shown in Fig. 3 because they did not experience the light-soaking effect. For devices with UV-treated ZnO-NRs, J_{sc} increased with UV-treatment time. J_{sc} reached the limiting value of 0.87 mA/cm^2 after UV-treatment for 60 min and about 80% of the improvement was obtained after treatment for 15 min. As for V_{oc}, it decreased when UV-treatment was 5 min, then recovered with increasing UV-treatment time, although it did not reach the original value. The increase in J_{sc} suggests that the ZnO-NRs/P3HT interface was improved after organic contaminants remaining on ZnO-NRs were decomposed by the photocatalytic reaction. However, when the treatment time was not long enough, intermediates of the decomposition are formed as partially oxidized products, which may act as carrier traps or impede dissociation of excitons. This may be the reason for the decrease in V_{oc} after UV treatment for about 5 min. However, even after UV-treatment for 60 min, at which we suppose contaminants were all decomposed, the V_{oc} was much smaller than the value observed for the device which experienced the light-soaking effect, as shown in Fig. 3. This suggests that the light-soaking effect changes favorably the structure of the electric double layer (or dipole moments) formed at the ZnO-NRs/P3HT interface. In addition, it suggests that the UV-treatment and the

light-soaking effect have different mechanisms. Increase in J_{sc} was also observed with the device having ZnO-NRs annealed at 300 ˚C for 30 min. However, both of the J_{sc} and V_{oc} values were smaller than the values of the devices having ZnO-NRs that were UV-treated for longer than 15 min, as shown in Fig. 7. We consider that annealing temperature of 300 ˚C is not high enough to decompose the organic contaminants completely. This is related to the low V_{oc} and FF observed with the annealed device even after experiencing the light-soaking effect, as shown in Fig. 3. The solar cell properties are expected to improve by increasing the annealing temperature. However, its application to devices fabrication on plastics will become very difficult.
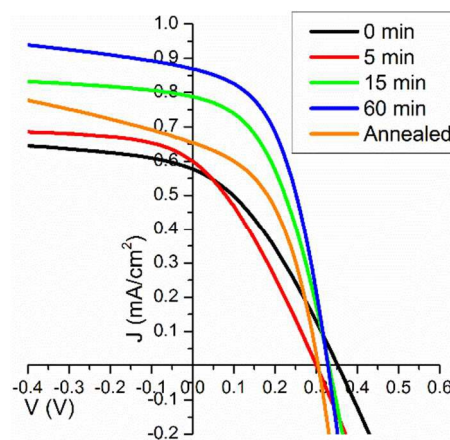

Figure 7: *J-V* curves of devices with ZnO-NRs UV-treated for different periods and of a device with ZnO-NRs annealed at 300 ˚C for 30 min. Light source for *J-V* measurement: AM 1.5 spectrum from which the UV component was removed with a UV-cut filter. Light source for UV-treatment: a 500 W Hg lamp.

4. Conclusions

We found that utilization of the photocatalytic activity of ZnO is useful for removing organic contaminants remaining on the surface of the ZnO-NRs layer used in organic/inorganic HPVs. By the UV-treatment of ZnO-NRs before depositing a polymer layer, solar cell properties were much improved because efficiency of excitons dissociation at the ZnO-NRs/P3HT was improved. Although we have done the measurement with devices fabricated on glass plates, we believe that the advantage of the UV-treatment is applicable to devices fabricated on plastic sheets. However, the treatment time need to be shortened to apply the method to the practical fabrication process of solar cells, as it takes more than 15 min for improving the solar cell properties by the method reported.

Notes and references

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