

## Surface Modification of Nano-Structured ZnO as Electron-Transporting Layer for Polymer Based Organic Photovoltaics

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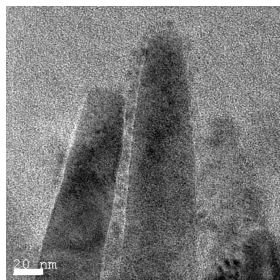
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Organic thin-film solar cells (*viz.* organic photovoltaics; OPVs) have multi-interfaces because of the multilayered structure. The contact between the active layer and the electrode is one of the most critical interfaces in the devices. Metal oxides like TiO<sub>2</sub> or ZnO have been found to be a good carrier transporter for these interfaces [1, 2]. In this context, the high performance of OPVs is a result of the fine control that has been achieved over the flow of the charge carriers, charge injection and extraction through an electrical contact. Interdigitated structure by the use of one-dimensional (1D) nanomaterials is one of the strategies for the achievement. ZnO nanorod arrays had been used and demonstrated as hybrid solar cell devices [3, 4]. In these devices, open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), and fill factor ( $FF$ ) were quite low, because of the insufficient contact between the metaloxide and the polymer. Interface modification between ZnO nanorods and poly(3-hexylthiophene) (P3HT) with dye molecules was examined and realized effective enhancement both of  $V_{oc}$  and  $J_{sc}$ , resulting the improvement of power conversion efficiency ( $PCE$ ) as follows. The use of indoline dye D205, which has dipole moments directing away from the ZnO surface, was found to suppress the reverse saturation dark current density and charge recombination, and to consequently lead to  $V_{oc}$  and improved  $PCE$  from 0.22% to 0.71%. Squaraine derivative (Sq) was synthesized and found to improve device performance by extending the light-harvesting range to the near infrared region, leading to increased  $J_{sc}$  and the highest  $PCE$  of 1.02% [5, 6]. The introduction of PCBM into these hybrid systems also improved the  $PCE$ , which was over 2% [7-9].

In this study, it was found that the efficiency of ZnO/P3HT based OPVs can be further enhanced to 1.37% from 1.02%. This is obtained with a combination of Sq modified ZnO nanorod arrays and nanoparticles as an electron-transporting layer of the inverted device without fullerene. The device photophysics is investigated through optoelectrical measurements in addition to spectroscopic and electron microscopic observations in terms of light harvesting, photocurrent generation, charge carrier transport, work function, interface dipole, crystallinity, and morphology.

ZnO nanorods with diameter of ~25 nm and length of ~400 nm growing from a dense ZnO layer were prepared. For the ZnO nanoparticles, the diameter of ~4 nm was obtained. It was also found that the ZnO nanoparticles do not distribute homogeneously onto the ZnO nanorods but the nanoparticle cluster was observed at the end of the ZnO nanorods (**Figure 1**).

**Figure 1.** Energy-Filtering (EF)-TEM (zero-loss) image of the cross-section of ZnO nanoparticle-coated ZnO nanorods/P3HT based OPV (scale bar: 20 nm).



Insertion of ZnO nanoparticles onto the ZnO nanorods increases the ZnO/P3HT interface area, confirmed by the improvement in  $J_{sc}$  of the nanoparticle-coated ZnO nanorods/P3HT device (2.07 mA/cm<sup>2</sup>) in comparison to that of the pristine ZnO nanorods/P3HT device (1.42 mA/cm<sup>2</sup>).

Incident photon to current efficiency (IPCE) spectra of the nanoparticle-coated ZnO nanorods/P3HT device and the pristine ZnO nanorods/P3HT one across the spectral range of 300 – 650 nm with the strong peak in the visible region and the shoulder in the UV region. The peak in the visible region is the result of the light adsorption of the P3HT and the exciton separation at the ZnO/P3HT interface. A shoulder in the UV region is attributed to the UV light absorption of the ZnO and subsequent hole transfer to the P3HT. The IPCE profile of the nanoparticle-coated ZnO nanorods/P3HT device shows the enhancement of the peak in the visible region (20.7%) in comparison to that of the pristine ZnO nanorods/P3HT device (11.5%). This indicates that the photogenerated charge carriers at the ZnO nanoparticles/P3HT interface can transport through the ZnO nanoparticles to the ZnO nanorods. This results in the enhanced  $PCE$  of 0.49% for the nanoparticle-coated ZnO nanorods/P3HT device, which is higher than that of the pristine ZnO nanorods/P3HT one (0.26%).

Further improvement in  $J_{sc}$  of the nanoparticle-coated ZnO nanorods/P3HT device was achieved by adsorption of Sq onto the ZnO surface. Significant increase of  $J_{sc}$  from 2.07 mA/cm<sup>2</sup> for the unmodified device to 6.04 mA/cm<sup>2</sup> for the Sq-modified one was observed.

Increase in  $J_{sc}$  is mainly on the expansion of the light-absorption property of the device as previously reported [5]. The device modified with Sq demonstrates the enhancement of the main IPCE peak in the visible region and expansion of the photoconversion range into the orange-red region with an additional peak at ~680 nm. This indicates that exciton separation occurs at the Sq/P3HT interface and the dye molecule can transport the electrons and the electrons are collected into the ZnO. Therefore, photocurrent of the device is contributed by the light absorption of P3HT, ZnO and Sq, leading to the  $J_{sc}$  improvement and the highest  $PCE$  of 1.37%.

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