Studies on Morphological Effects and Surface Modification of Nanostructured Zinc Oxide for Hybrid Organic/Inorganic Photovoltaics

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All renewable energy sources are generated from solar radiation, which can be converted directly or indirectly into various kinds of energy.[1] The annual solar energy that strikes the earth is at a rate of 175,000 TW y^{-1}.[2] This energy is around four orders of magnitude higher than the total global energy consumption by human (18 TW y^{-1}).[3,4] The solar spectrum spans over a wide range from short-wave infrared to ultraviolet with the power of 342 W m^{-2} at the upper atmosphere and 168 W m^{-2} at surface of the earth.[5]

The solar energy striking the earth is mostly converted into chemical energy, in the form of carbohydrates, by plants and microorganisms during their photosynthetic process. Humans, on the other hands, have developed photovoltaic (PV) devices or solar cells that are able to convert solar energy directly to electricity since the early 1950s.[6] Nowadays, the efficiency of commercial photovoltaic modules is achieved 16 -18 %.[7] However, the price of electricity produced using PV systems is still more expensive than that generated by traditional power generation like coal and gas centrals, as well as hydroelectric and nuclear power plants.[8,9] Therefore, science and technologies needed to enable scalable production, effective conversion efficiency and storage of solar radiation are required.[10]

One of the key points to obtain significant enhancement in the photovoltaic performance is the efficient charge generation over entire distances of the photovoltaic devices. This approach requires the development of new semiconductor materials for efficient light absorption over the full range of solar radiation, and new efforts based on nanostructured architectures.[11] Hybrid organic/inorganic photovoltaics (HPVs) have potential to achieve these goals since they are able to combine the unique properties of organic and inorganic materials.[12] Conjugated polymers (e.g. poly(3-hexylthiophene) or P3HT), serving as electron donor, own advantages of easily processible, flexible, and high optical absorption coefficients with thickness of several hundred nanometers.[13] On the other hands, inorganic semiconductors have several attributes as electron acceptors, including relatively high electron mobility, high electron affinities, and good physical and chemical stability.[14,15] Especially, nanoscale inorganic materials show different optical and electrical properties from bulk materials owing to their quantum size confinement.[16]

Inorganic semiconductors like CdSe,[17] TiO_2,[18] and ZnO[19] with different kinds of nanostructures were broadly investigated. ZnO is one of great candidates since it is less toxic and relatively easy to be synthesized in large-scale production with low cost technologies.[19] Moreover, ZnO has a great variety of different morphologies which can be synthesized using a wide range of methodologies at low temperature.[20] Among various nanostructured morphologies of ZnO, vertically-aligned ZnO nanorod arrays have great potential for HPVs since they can easily be processed at low temperatures[21] and they provide a direct electron-transport pathway to the electrode without charge recombination at the grain boundary.[22-24]

However, when ZnO nanorods are matched with the most widely p-type organic semiconductors in HPVs or organic-based photovoltaics (OPVs), P3HT, measured power conversion efficiencies (*PCEs*) are quite low (less than 0.6%).[25-29] To improve the *PCE* of HPV devices, many different methods have been investigated such as nanostructuring the inorganic semiconductors to enhance photogenerated charge carriers *via* an increased donor-acceptor interface area,[23,30] and modifying the interface to promote charge transfer.[31-33]

In this work, vertically-aligned ZnO nanorod arrays are used as electron acceptor in combination with P3HT, serving as electron donor. In particular, this research is mainly focused on: (a) the preparation and optimization of ZnO-based nanorods, (b) modification of nanostructured ZnO for electron acceptor substrates of the devices, and (c) study on charge generation and charge transport mechanisms.

The study on the preparation and modification of nanostructured ZnO and their application as electron acceptor materials of HPVs may help provide significant information for the better understanding of the properties and functional mechanisms of electron acceptor materials and device configurations. Such mechanisms may support studies in the development of highly operative materials and the production of highly efficient photovoltaic modules.

Vertically-aligned ZnO nanorods coated on ITO substrates were prepared using two-step methods; sol-gel and hydrothermal methods.[34] Sol-gel technique was performed to prepare dense ZnO seed layer and hydrothermal method was done to grow ZnO nanorods perpendicularly to the substrates. The HPV devices with structure of ITO/dense ZnO (30 nm)/ZnO nanorods/P3HT/VO_x (5 nm)/Ag (100 nm) were fabricated. The pristine P3HT/ZnO nanorod device showed low *PCE* of 0.26%. In order to enhances such low *PCE*, modification methods via Li incorporation into ZnO, surface modification with organic dyes and self-assembled monolayers (SAMs), and tuning dimension of ZnO and surface, were studied and carried out. Moreover, morphological effects of nanostructured ZnO were investigated in order to understand charge transport mechanisms in such systems.

For Li-incorporation into ZnO, Li-doped ZnO nanorod substrates were prepared, characterized and employed as electron acceptor in the HPV systems. Li was selected as dopant because the acceptor level of Li in ZnO crystal has a small binding energy (Li_{Zn})[35]

and Li is highly soluble in ZnO.[36] The presence of Li in ZnO nanorods has been detected using energy-loss spectrum in a scanning transmission electron microscope (STEM-EELS). The STEM images indicate a Li-rich phase on the top of ZnO nanorods. The difference in photovoltaic properties brought about by Li doping was determined from concentrations of the precursor solution. It is found that appropriate Li doping improves both short circuit current density (J_{sc}) and open circuit voltage (V_{oc}).

The photoluminescence quenching of P3HT/Li-doped ZnO nanorod films indicates effective charge transfer at the P3HT/Li-doped ZnO nanorod interface at 15 atom% doping, corresponding to the enhancement of J_{sc}. The effective charge transfer at the interface can be explained by oxygen-enrichment of the ZnO surface, observed by stronger photoluminescence in red emission after Li incorporation.

The improvement in V_{oc} observed at 5 atom% doping is attributed to the upward shift of the conduction band to vacuum level. The presence of substitution of Li to Zn (Li_{Zn}) has been determined to be at 5 atom% and its saturation is at 15 atom%. The interstitial Li (Li_i) concentration started increasing at 10 atom% and additional Li atom would tend to be Li_i rather than Li_{Zn} after 15 atom%. These excess Li_{Zn} and Li_i in the crystal act as recombination centers, which result to the increased reverse saturation current density (J_0) and decreased open-circuit voltage (V_{oc}) when the doping concentration is higher than 5 atom%. Therefore, the maximum doping concentration is at 5 atom% and the obtained *PCE* is 0.37% higher than that of the pristine device (0.26%).

The modification of the ZnO nanorod surfaces with organic molecules was carried out to change the surface properties of the ZnO nanorods without the effects of impurity in the ZnO crystal and to investigate appropriate properties of interface modifiers for HPV systems. Four different type of dyes, N719 (Ru-based complex), NKX2677 (coumarin dye), D205 (indoline dye), and derivertized squaraine (Sq), were selected as interface modifiers. These dyes have different functional groups, absorption ranges, and dipole moments (μ). It was found from fourier transform infrared (FT-IR) spectroscopy analysis that the dye molecules attach onto the ZnO surface using their carboxylic or carboxylate group, and face their bulky terminal groups to P3HT.

In the charge generation process, the absorption range of the dye molecules is one of the important parameters in determining the change of J_{sc} for the dye-modified HPV devices. By analyzing incident photon to current efficiency (IPCE) spectra, for the devices modified with the N719, D205, and Sq dyes, the charge carriers are photogenerated from the light absorption of P3HT, dye molecules and ZnO components. Especially, for the modification with Sq dye, since the light absorption of Sq dye is in the near IR range, which does not overlap that of ZnO (UV region) and P3HT (visible region), the J_{sc} of the Sq-modified device (~5 mA cm^{-2}) increased significantly in comparison to that of the unmodified one (~1 mA cm^{-2}). This improvement results to the maximum *PCE* of ~1%, higher than that of ~0.26 % obtained from the unmodified one.

The direction of μ of the molecules plays an important role on the change of built-in potential (V_{bi}) and V_{oc} of the HPV devices. The modification with dye molecules having dipole pointing away from the ZnO surface (D205 and NKX2677) improves V_{bi} and V_{oc} of the subsequence devices, and shows an opposite effects for the ones have dipole pointing toward the ZnO surface (N719 and Sq). The highest enhancement in V_{oc} (0.65 eV from 0.40 eV for the unmodified one) is achieved from the HPV device modified with D205 dye.

Surface modification with SAMs was performed in order to investigate a relationship between μ and V_{oc} and to support the change in V_{oc} when the devices were modified with organic dyes. Benzoic acid based molecules with different *para* groups are selected because their molecular sizes are comparable and they provide a range of different magnitudes and directions of the μ (-3.69 D to 4.68 D). It was found that the relationship between μ and V_{oc} is linear. The V_{oc} are enhanced by the use of the molecules with their dipole moment pointing away from the ZnO surface and vice versa. The enhancement in V_{oc} is attributed to the shift of surface potential of ZnO and P3HT after surface modification. Moreover, the relationship between μ and J_0 indicates that the modification with the molecules have dipole pointing away from the ZnO surface are able to block leakage current across the P3HT/ZnO interface, leading to less recombination activity in the devices. These results support the results observed in the case of surface modification with organic dyes.

Not only in the P3HT/ZnO nanorod HPV system, the surface modification with organic dyes was done, but the method was also performed in the P3HT/ZnO nanoparticle HPV system, in order to study the morphological effects of ZnO morphology on the P3HT infiltration and charge transport mechanisms. D205 and Sq dyes were selected as the interface modifiers. It was found from cross-sectional FE-SEM images and contact angle analysis that the P3HT is able to infiltrate into the accessible inter-rod space of the ZnO nanorod substrates properly. This leads to homogenous P3HT/ZnO junction interface, which results to efficient charge generation and charge transport. However, these analyses cannot be used to determine the P3HT infiltration into the voided space between the ZnO nanoparticles since the pore sizes are relatively small. Energy dispersive X-ray spectrometry (EDS) analysis was performed instead. The results indicates that the P3HT infiltration into the ZnO nanoparticles layer is poor. Especially, after the surface modification with dyes, the P3HT infiltration is blocked by the dye molecules that partially fill the voided space between the ZnO nanoparticles even though the surface wettability is enhanced. This leads to the non-workable ZnO/dye/air interface, where exciton separation process cannot occurs. Although the surface area of ZnO nanoparticles was relatively larger in comparison to that of ZnO nanorods, because of the non-workable interface, the J_{sc} of the ZnO nanoparticle device are lower.

For the difference in V_{oc} of between two device architectures, the ZnO nanoparticle devices show higher V_{oc} than the ZnO nanorod ones. This is because the conduction band edge of ZnO nanoparticles locates above that of the ZnO nanorods, showing larger interface energy gap. These results indicate that the ZnO nanoparticles/P3HT interface is more appropriate than that of the P3HT/ZnO nanorods in terms of larger interface energy gap and obtaining higher V_{oc} but the ZnO nanorods are more efficient in terms of homogeneous junction interface and charge transport.

Therefore, the additional improvement in photovoltaic performances of nanostructured P3HT/ZnO nanorod systems was carried out by the insertion of ZnO nanoparticles in the combination with surface modification with Sq dye. The ZnO nanoparticles were spin-coated on top of the ZnO nanorods. The morphologies of nanostructured ZnO was confirmed using cross-sectional transmission electron microscopy (TEM). The TEM images show that the distribution of ZnO nanoparticles is not homogeneous on the ZnO nanorod surface. The ZnO nanoparticle cluster is found on the end of ZnO nanorods. This cluster blocks the P3HT infiltration into the voided space, especially after the modification with Sq dye. However, the maximum *PCE* of 1.37% with high J_{sc} of ~6 mA cm^{-2} is achieved. The enhanced *PCE* is mainly attributed to the increase in P3HT/ZnO interface area and expansion of light-harvesting properties.

In summary, vertically-aligned ZnO nanorod arrays are able to act as electron acceptor substrates for HPV devices in combination with P3HT materials. The incorporation of Li atoms into the ZnO crystal is not an efficient method to improve the PCE due to the increase in the number of recombination centers, while the surface modification with organic dye molecules having dipole moment pointing away from the ZnO surface and non-overlap absorption range provides more efficient enhancement in the interface properties and light-harvesting properties. The interface properties at the P3HT/ZnO junction plays an importance role on the charge generation, charge transfer, and leakage-blocking behavior. Moreover, the morphology of ZnO nanorods is found to be more appropriate than the ZnO nanoparticles in terms of the polymer infiltration, homogeneous junction interface, and charge transport. The highest *PCE* is 1.37% obtained from the combination of ZnO nanorods, ZnO nanoparticles and surface modification with derivertized squaraine dye. Although this value cannot completely answer the requirement for practical photovoltaic usage, these investigated results may provide significant information in the design of materials and device structure for efficient optoelectronic devices.

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