Enhancement of organic solar cells efficiency by altering the zinc oxide photoanode nanostructure morphology

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Abstract

The current paper examines the effects of zinc oxide nanostructure configurations, as photoanode formations of organic solar cells, on the performance of power conversion. To this end, some experiments were conducted during which a near band edge emission red shift of $\sim0.11$ eV from nanoparticles to vertically-oriented nanorods was observed. This bandgap narrowing promotes transferring of photo-excited electrons towards the conduction band of photoanode. A $\sim48\%$ decrease in the deep level emission intensity revealed a smaller nonradiative waves emission due to lower level of crystal disorder. By using vertically-oriented zinc oxide nanorods as photoanodes, the photovoltaic efficiency of the organic solar cell improved considerably. The nanorod-structured photoanodes showed a 0.22 V rise in the open-circuit voltage, from 0.76 V to 0.98 V, and a 2.08 times increment in the overall conversion performance, compared to the zinc oxide nanoparticle-structured photoanodes. This superior performance is attributed to a greater
chance of charge recombination and light-trapping in the cells, more efficient light absorption, and high level of crystallinity that grants easier electron mobility for vertically-oriented zinc oxide nanorods. Moreover, a smaller electron transfer impedance (0.85 Ω) was achieved due to better electrocatalytic action for oxygen reduction for vertical nanorods compared to the other two zinc oxide configurations (1.62 Ω and 5.06 Ω). This boosted the cell performance by increasing the short-circuit current density ($J_{SC}$). The fabricated solar cell may contribute to sustainable and environmentally-friendly electricity generation process through reducing the consumption of non-renewable energy sources.

Keywords: Organic Solar Cells; Zinc Oxide Photoanode; Efficiency; Sustainable Energy

1. Introduction

Sun, as a huge source of energy, can provide immense resources for generating clean, pollution-free, and sustainable electricity without emissions inducing global warming. Infinite solar energy can be an alternative to the limited conventional sources of energy such as natural gas, oil, coal, and/or nuclear power, which can cause different types of pollution [1-5]. Air pollution, acid rain, and emission of greenhouse gasses are some of the most common ones. Employing the organic dyes/metalorganic–complex dyes and oxide semiconductors to fabricate organic solar cells (OSCs) is a reliable approach to the efficient conversion of solar energy [6-9].

Metal oxide semiconductor nanocrystalline materials such as titanium dioxide (TiO$_2$) and zinc oxide (ZnO) have been extensively used for solar cell fabrication due to their excellent physiochemical properties, e.g., surface area, crystalline structure, grain size, grain boundary density, and energy band gap. Moreover, their unique optical and electronic characteristics, versatile functional growth morphologies, low recombination loss, and high electron transport make them promising materials for improving the efficiency of the photovoltaic devices [10-19].

Recently, solar cell has been fabricated based on double-layered photoanode consisting of TiO$_2$ nanoparticles and oriented hierarchical anatase TiO$_2$ nanowire arrays on Ti-foil substrate [20]. In [21], it was reported that, compared to a TiO$_2$ nanoparticle-based cell, the photovoltaic performance of the TiO$_2$ nanowire cell shows superior light scattering, more rapid electron transport, and lower electron recombination rate. Moreover, the solar cell based on a double-layered structure of Ti/TiO$_2$ nanowire + nanoparticle photoelectrode with a total thickness of 31 μm displays the highest power conversion efficiency of 7.92. The enhancement of the efficiency
of this structure is mainly attributed to better light scattering capability, faster electron transport, and lower electron recombination compared to the solar cell based on photoanode with a single layer structure [21].

Common ways to boost the capabilities of OSCs are improving the electron mobility and reducing the recombination rate [22-25]. Several processes exist to synthesize the ZnO nanostructure-based OSCs, e.g., chemical vapor, electrochemical, and hydrothermal/solvothermal deposition. However, their incident photon-to-electron conversion efficiencies (IPCE) are still far from being ideal [26-29].

T. A. Geleta et al. enhanced the efficiency of the power conversion of solar cells by using n-type ZnO and p-type nickel oxide (NiO) photoanodes nanocomposition with adding the carbon quantum dots to the nanocomposites. It was reported that, before carbon doping, the highest efficiency was achieved for ZnO with 8 wt% of NiO additive. The efficiency was further enhanced up to 3.8 times higher when the carbon quantum dots were doped in the mentioned nanocomposites. The highest efficiency value obtained for solar cell with carbon dot-incorporating nanocomposite photoanode was 13.02%, under a 430 nm LED light with 100 W/m² power [30]. M. Peymannia et al. synthesized ZnO quantum dots via co-precipitation in ethanol solutions to improve the performance of dye-sensitized solar cell (DSSC). The results indicated that the efficiency of the modified solar cells with ZnO quantum dots performed 17% better than the unmodified cells [31]. In another research, ZnO nanosheets/rod hierarchical structures was used as photoanodes to fabricate DSSCs. It was reported that the photovoltaic performance with open-circuit voltage was significantly improved from 0.45 V to 0.73 V, and the overall conversion efficiency of ZnO nanosheets was 5.69 times higher than that of ZnO rod. It was found that this superior performance was attributed to the higher surface-area-to-volume ration, greater efficient light absorption, and better electron transfer process, which occurred for nanosheets/rod hierarchical structures [32].

The methods generally used to boost the efficiency of the solar cells are precisely designing the electron-transfer-favored nanostructures and exploring the ZnO proper organic dyes. However, the improvement of photo-induced carrier transfer, delaying carrier recombination by morphology control, and alteration of the photoanode configuration are other ways for improving the solar cell performance that have received little attention. Therefore, in this work, OSCs are delicately constructed using ZnO nanostructures as photoanode. Furthermore, the photovoltaic performance
against morphology of the ZnO is investigated. Moreover, the physical and photoelectrical properties of the fabricated OSCs samples are extensively studied to understand the photoanode morphology effects on the solar cell performance.

2. Materials and Methods

2.1. Device Fabrication

The configuration of inverted dye-sensitized solar cell device includes ITO/ZnO/P3HT:PCBM/Ag (10 nm)/PEDOT:PSS/Ag (100 nm), where ITO refers to indium tin oxide, P3HT is an abbreviation for Poly(3-hexylthiophene), PCBM stands for phenyl C61-butyric acid methyl ester, and PEDOT:PSS indicates poly(3,4-ethylenedioxythiophene) polystyrene sulfonate. The configuration is schematically shown in Figure 1. The active area of the cell was 0.4 cm x 0.4 cm. For the fabrication of the device, the following steps were taken. To pattern the ITO on glass, the substrate was tape masked, followed by using concentrated HCl to etch the bare area at 60 °C. Consecutive ultra-sonication in H2O2/NH3/H2O, which had 1:1:5 volume concentration, ultra-pure water, acetone, and 2-propanol, was conducted to clean the substrate, and then it was dried at room temperature. The electroless deposition technique was employed to grow ZnO nanostructure-based photoanode having three different morphologies, i.e., one nanostructure morphology and two different orientations (horizontal and vertical) of nanorods on the ITO layer. Initially, the ITO surface for all three samples was activated as follows. The substrates were sensitized via 30 min immersing in hydrous solutions of SnCl2 (40 g/l) and HCl (20 ml/l, 37% vol.). Then, the samples were activated by 30-min dipping in solutions of PdCl2 (0.1 g/l) and HCl (20 ml/l, 37% vol.) at ambient temperature. These samples were then subjected to the growth of ZnO nanostructures of various shapes, as described below.

ZnO nanoparticles were deposited via immersing the ITO/glass substrate into aqueous deposition solution, as explained below. Immersion took place for 3 hours at 70 °C, then deionized water (DIW) washing was done, followed by open air drying. By mixing a 2.28 g of Zn(NO3)2 and 0.6 g of NaOH, the solution for aqueous deposition was made. Before mixing NaOH and Zn(NO3)2, they were dissolved in 75 ml and 150 ml DIW, respectively.

Horizontally-oriented ZnO nanorods were deposited on ITO/glass substrate. Initially, the ZnO nanorods were produced by 30-min stirring of 0.6 g Zn(NO3)2 in 100 ml DIW, then adding 0.16 g NaOH in 150 ml DIW dropwise by magnetic stirring. This continued to obtain a solution pH of
8.3. Then, the mixture was heated for 10 min using micro-oven. After the sample was cooled down to ambient temperature, it was centrifuged at 4000 rpm for 10 min. The precipitates were then washed by purified water, and the substrate was soaked for 3 hours in a hydrous deposition solution, containing ZnO nanorods, with no stirring at 70 °C.

The preparation of seed and growth solutions, as well as nanorod deposition was used to deposit ZnO vertical nanorods on an ITO/glass substrate. The solution of ZnO seed was produced by dissolving 100 mM zinc acetate dihydrate in 50 ml isopropyl alcohol and stirring for 15 minutes, vigorously, at 70 °C. After that, 700 ml of 5 mmol N(CH₂CH₃)₃ was applied and stirred for 10 minutes at 70 °C. The solution was then cooled down to ambient temperature. To synthesize the ZnO growth solution, 7.71 g of (CH₂)₆N₄ was dissolved in 550 ml of DIW. Separately, at the meantime, 32.8 g/l of Zn(NO₃)₂ was dissolved in 0.5 l DIW. The synthesized formulas were then blended and stirred at ambient temperature for 24 hours. The ITO/glass substrate was first dipped in the seed solution for two hours, and then oven-dried at 70°C. Subsequently, it was dip-coated again and before being suspended in growth solution, it was dried in an oven at 70 °C for 3 hours. Finally, after cooling the sample down to ambient temperature, it was rinsed with DIW and air-dried.

To complete the solar cell device fabrication, a blend solution of PCBM purchased from the American Dye Source Inc., and P3HT with a regularity of 95% from Reike Metals dissolved in 2-dichlorobenzene (99%, Sigma–Aldrich) was coated on ZnO/ITO substrates in a glove box using the spin coating technique. The spinning rate sequence was 250 rpm for 3 s, 1000 rpm for 15 s, and 1500 rpm for 3 s. It should be mentioned that, prior to mixing, the purification was carried out via a 0.45 mm polytetrafluoroethylene (PTFE) membrane filter (Pall Co.). A thermal evaporator system integrated with the MBraun glovebox was used to deposit a thin film of Ag (~10 nm) through a shadow mask onto P3HT: PCBM at the deposition rate of 0.1 Å/s. A thermally-deposited Ag thin film on organic layer reduces the surface tensions, hence increasing the photoactive layer's wettability in aqueous PEDOT:PSS dispersions. For the deposition of PEDOT:PSS layer, spin coating with a 5000-rpm (30 s) sequential rate was employed. Due to the adhesion improvement, solution was diluted with a similar volume of 2-propanol. The PEDOT:PSS coated substrates were thermally annealed for 10 min at 140 °C in the glove box. Finally, for the completion of the dye-sensitized solar cell device instructed with ZnO nanostructure-based photoanode, a shadow mask at 10-8 Torr vacuum level was used for the thermal deposition of the Ag thin film with the
thickness of ~100 nm. For testing the stability, the fabricated device was annealed at different temperatures of 60° C, 80° C, and 100° C for 10 min.

2.2. Device Characterization

The photovoltaic (J-V) characterization of the OSCs device was carried out using Keithley 4200 under a solar simulator AM 1.5 with 100 mW/cm² Xenon lamp (XES-301S, Nippon Sokki, Osaka, Japan). To measure the IPCE, a machine of QTest Station 1000, with a computer-controlling system under monochromatic light (350-800 nm) source, was used. A monochromatic beam was generated via a tungsten halogen lamp with 150 W power. The standard silicon solar cell was used for calibration. The ZnO photoanode's growth morphology was studied using a field emission scanning electron microscope (FESEM, JEOLJSM 6380LA). The scanning spectrum of 2θ from 20° to 80° was used on a BrukerD8 x-ray diffractometer (XRD) with Cu-K1 radiations (1.540 Å) at 40 kV. The samples' photoluminescence (PL) and absorption were examined using a room-temperature PerkinElmerLs 55 Luminescence Spectrometer with a 335 nm xenon flash lamp and LAMBDA 1050 UV-VIS/NIR spectrophotometers, respectively. The impedance measurements were carried out via a Bio-Logic SP300 potentiostat in which a DC potential bias was used and overlaid by a sinusoidal AC potential perturbation of 15 mV over a frequency range of 7 MHz to 0.1 Hz. The applied DC potential bias was altered from 850 mV to 0 mV by the step of ~50 mV.

3. Results and Discussion

3.1 Device morphology and structure

Top-view FESEM micrograph of the deposited ZnO photoanod on ITO substrate is displayed in Figure 2. The figure illustrates the structure of highly dense nanoparticles and the horizontally- and vertically-oriented nanorods on ITO surface. Strong van der Waals attraction forces between particles leads to occurrence of uncontrolled agglomeration of nanoparticles. It causes elongation of nanorods, which results in a relatively broad-size distribution of these nanostructures. Although this phenomenon inevitably diminishes the expected benefit of the size effect, prime idea of this study focuses on the influence of ZnO photoanode nanostructure configuration on solar cell performance. Thus, the size distribution effect is not studied in the present investigation. The EDX spectroscopy was used to analyze the deposited ZnO nanoparticles and nanorods qualitatively. The
major peaks in the EDX spectra are indications of Zn and O, while there are no detected impurities. The carbon peak is due to the samples being fixed in a holder with a double-sided form. Because of the high thickness of ZnO, the X-rays’ excitation volume produced by the ITO layer was reduced. This caused a weak signal in the EDX spectra due to In and Sn components.

The XRD patterns in Figure 3 illustrate the different configurations of ZnO deposited on ITO/glass substrate by the electroless deposition method. The XRD signals are matched with JCPDS number of 36-1451 associated to the hexagonal structure of the wurtzite ZnO [33]. Detected diffraction peaks taken place at 2θ = 32.08°, 34.64°, 36.76°, 47.46°, 56.58°, 62.76°, 68.06°, 69.98°, and 77.45° correspond to crystallographic planes of (100), (002), (101), (102), (110), (103), (112), (201), and (202), respectively. The periodicity of atoms per unit area of a specific atomic plane determines peak strength in XRD. Therefore, plane indices cause the peaks to shrink, as seen in all XRD trends. The X-ray diffraction and reflection take place mainly due to Crystallites. Thus, small nanocrystals do not have such strong ordering we can see in bulk crystal. Therefore, nano-sizing broadens the peaks and shrinks the intensity compared to bulk counterpart. From nanorods to nanoparticles, the size of crystallite was reduced consequently, and as illustrated in Figure 3, the peak intensity decreased. The FWHM of the diffraction peak is inversely proportional to the crystallite size (Scherer’s formula) [34]. The relative intensity of (002)/(100) and (002)/(101) for all samples are extracted from the spectra and tabulated as presented in Figure 3. The variation of relative intensity illustrates the sample’s morphological difference. It is noticeable that, compared to the standard reflections, the (0 0 2) reflection planes are extremely stronger for vertically-oriented nanorods. This might be related to the preferential growth along the c-axis direction and confirms its highly crystalline structure grown perpendicular to the substrate surface. This is in consistence with the FESEM images of Figure 2. However, the most intense diffraction spectra for the other two samples is along (101) plane with different relative intensity (see inset Figure 3), which reveals that ZnO nanorods are deposited on the surface with different orientation.

3.2 Optical features of ZnO photoanode

Figure 4 depicts the PL spectra of the ZnO nanostructure samples having different morphologies under 285 nm excitation wavelength. The ZnO nanostructures' PL spectra show a sharp UV emission peak centered at 375 nm to 386 nm, as well as strong visible emission peaks
spanning 552 nm to 560 nm. The rate of UV emission is higher than visible range for vertically-oriented ZnO nanorods. From ZnO nanoparticle to vertically-aligned nanorods, the UV emission shifts towards higher wavelength (~0.11 eV) and simultaneously the intensity of deep level (DL) emission decreases by 48%. The near band edge (NBE) shift towards higher wavelength may be related to quantum confinement induced effects by increasing the nanostructure size from nanoparticles to vertically-oriented nanorods. The quantum confinement modifies the wave function of the electrons and holes; consequently, the energy band structure is modulated and the bandgap energy decreases.

Using the signal intensity, positions and broadening the bandgap; impurity and defect levels can be determined. Moreover, the relative amount of radiative and nonradiative recombination rates emitted from a material directly determines the impurity and disorder level in the nanostructures. The existence of crystalline disorder in ZnO nanoparticle sample leads to the emission of the nonradiative waves and decline of the peak intensity in the UV region compared to vertical nanorods. In contrast, this crystalline disorder increases the intensity of PL emission peak at visible region. This conflict is attributed to the origin of these two emissions. The NBE emission (UV region) peak is typically originated from excitonic recombination, while the DL band (visible region) is usually attributed to optical centers associated with disorders and impurities such as native defects. The energetic NBE and DL emissions can provide two competing routes associated to carrier recombination. Therefore, it is required to minimize the defect centers to increase the UV emission. The electron transferring process and the influence of altering the photoanode bandgap are discussed below.

Figure 5 depicts the band diagram and electron transport mechanism of ZnO photoanode-based OSCs. The energy levels for organic semiconductor, metal, and metal oxides used in solar cell fabrication process were extracted from relevant references [35-38]. In this device, ITO is the anode and Ag acts as cathode. Electrons and holes move in the organic layers mostly by charge hopping in polymer chains [39]. The PEDOT:PSS conjugate thin polymer layer transported holes from anode to the emissive layer of P3HT:PCBM, while the electrons from cathode were transported by ZnO layers. The holes and electrons are combined in emissive layer depending on the charge mobility rates and emissive layer thickness. The electron mobility and recombination delay of vertically-oriented ZnO nanorod OSCs could be assigned to a little shift in the conduction band minimum towards the lower energy state. This phenomenon has a tendency to shift the
conduction band minimum slightly away from the LUMO level of P3HT:PCBM. Therefore, excitations become more probable as the HOMO-LUMO gap converges, and this smaller gap makes an effortless transfer of photo exited electrons towards the conduction band of vertically-oriented nanorods compared to the ZnO photoanode nanoparticles. Consequently, this phenomenon instructively affects the overall performance of the cell. The architecture of vertically-aligned ZnO nanorods compared to the other two configurations offers some benefits. Controlling the ZnO nanorods growth makes the possible systematic and reproducible way for adjusting the morphology of the composite. Furthermore, using the vertically-oriented ZnO nanorods, the electron donor/acceptor interface areas in the solar cell system are expanded. This vertical configuration enables electrons to possess a high mobility to be directly transported towards the electrode. Randomly-dispersed ZnO in all three types of nanostructures of organic semiconductor films enhances the donor/acceptor interface area. This can significantly boost the charge separation for photo-generated charge carriers. For nanoparticles and horizontally-oriented nanorods, the electron transport conducting path is poorly constructed. However, for vertically-aligned ZnO, the electron transport is formed in a direct pathway.

Figure 6 displays the UV–visible absorption spectra of OSCs films based on different ZnO nanostructures. All spectra show two absorption bands. One broad visible band centered at 503 nm ascribed to n→π* transition, and the smaller UV absorption peak at 368.5 nm indorsed to π → π* transition attributed to aromatic moieties. The UV–visible spectrum of ZnO nanorods in both regions overlaid the absorption spectra of samples based on the horizontally-oriented ZnO nanorods and ZnO Nanoparticles. This significant rise in the intensity of absorption band is due to their better light harvesting ability in two regions of UV and Visible. This can boost the performance of vertically-aligned ZnO nanorod-based solar cells in comparison with the other nanostructures. The superior absorption feature of the vertically-aligned ZnO nanorods is associated with the greater content of oxygen vacancy attributed to the abundance of specific sites, which strongly depends on the preparation route.

3.3 Photovoltaic performance of the device

Short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), IPCE, and system efficiency (η) can all be used to evaluate the efficiency of a ZnO photoanode-based OSCs with various ZnO nanostructure configurations. The parameters under the AM 1.5 G spectrum
were used to simulate solar irradiation on the surface of the earth with 48.2° of incident angle. The applied irradiation rate was 100 mW/cm², which is comparable to the amount of solar irradiation energy produced per unit area per unit time. The solar cell temperature, once analysis is carried out, was constant at 25 °C. This was because the temperature of solar cell, spectrum, and sunlight incident intensity influence the performance of solar cell.

The photocurrent density-voltage (J–V) features of OSCs having ZnO nanostructures photoanode with various morphologies were assessed, and the results are depicted in Figure 7. The maximum value of $J_{SC}$ and $V_{OC}$ is 30.56 mA/cm² and 0.98 V, respectively, observed for the sample with vertically-oriented ZnO photoanode. The FF of the device can be identified as the ratio of the maximum power ($P_{max}$) to the multiplication of $V_{OC}$ and $J_{SC}$ [40, 41]:

$$FF = \frac{P_{max}}{V_{OC}J_{SC}} \times 100\%$$ (1)

where the $P_{max}$ is the point on the J-V curve where the produced photovoltage and photocurrent is maximum (Figure 7). The most frequently-used parameter for solar cells performance comparison is efficiency. It is determined as the ratio of the device's output energy to the sun's input energy, which can be formulated by Equation (2):

$$\eta = \frac{V_{OC}J_{SC}FF}{I_0}$$ (2)

where $I_0$ is the input power. The greatest efficiency observed for the solar cell containing packed vertically-oriented nanorods shows that configuration and morphology are predominant parameters for altering the efficiency. Compromise between transmission and shape (thickness) is the key role in optimization process. For higher thickness of the ZnO layer (vertically-oriented ZnO), the light transmittance is lower in comparison with other samples, which means that the relatively-lower intensity of light reaches the active area. However, in vertical nanorods, the light-generated carriers travel in longer paths to arrive bottom and top electrodes compared to other two configurations. It consequently delays the probability of charge recombination and increases the light-trapping in the cells.
The current is incredibly low in the dark condition. The contacts begin to inject heavily; therefore, the dark current slightly increases (see Figure 7). The photocurrent per unit of the incident optical power is defined as responsivity ($R_\lambda$) and is calculated using Equation (3):

$$R_\lambda = \frac{\Delta I}{PA}$$

(3)

where $P$ and $A$ are the irradiated power density and irradiated area of the device, respectively. The difference between dark current and photo-excited current is named as $\Delta I$. As presented in Table 1, the vertically-oriented ZnO nanorod-structured OSCs exhibit a higher value of $R_\lambda$. IPCE is another important parameter that can be used to characterize the solar cell device, which is defined by Equation (4) [42]:

$$IPCE(\lambda) = \frac{J_{sc}(\lambda)}{e\phi(\lambda)} = 1240 \frac{J_{sc}(\lambda)[A.cm^{-2}]}{\lambda[nm]I_0(\lambda)[W.cm^{-2}]}$$

(4)

where $e\phi(\lambda)$ is the photon flux that strikes the cell. Furthermore, the IPCE parameter can be used to derive information about the solar cell's monochromatic quantum performances. From another aspect, a series of efficiency processes such as light absorption ($\eta_A$), exciton diffusion ($\eta_D$), charge transfer ($\eta_T$), charge separation ($\eta_S$), and charge collection ($\eta_C$) can practically determine IPCE. Therefore, it can be formulated as follows:

$$IPCE(\lambda) = \eta_A \times \eta_D \times \eta_T \times \eta_S \times \eta_C$$

(5)

Figure 8 represents the experimentally-recorded IPCE of the ZnO-based OSCs. The corresponding spectra for the vertically-oriented ZnO-based solar cell almost reached up to 67% in a wide spectral wavelength band of 470-700 nm, which is greater than that of the other morphologies. As mentioned earlier, the electron collection efficiency, the electron transfer rate from dye into conduction band, and the light harvesting efficiency upon incident wavelength are the factors that affect IPCE. The amount of dye loaded, the dye's absorption wavelength, and the semiconductor structure's construction influence the light harvesting performance. Light harvesting performance is enhanced by increasing the surface area of nanoparticles on vertically-oriented nanorods. The energetic difference between the conduction band edge of ZnO and the excited stage of PCBM determines the electron injection yields. Consequently, the vertically-oriented ZnO nanorods with the lower conduction band edge (lower band gap) provide the greatest
driving force to speed up the charge mobility from excited dye to the conduction band. In photoanodes, electron collection efficiency is attributed to charge carrier transportation and recombination rate. The electron transport can be restricted by arranged disorders, resistance, and boundaries between rods in the case of horizontal nanorods and nanoparticles. Thus, the electron’s straight pathways to be transferred from rods to collectors is blocked. However, electrons within the individual rods are extremely mobile [43, 44]. On the other hand, the high level of crystallinity for vertical nanorods causes easier electron transfer.

An impedance spectroscopy technique, called Nyquist analysis, was adopted to demonstrate the charge transport kinetics and intrinsic interfacial charge transfer at the interface of ZnO/conjugated polymers. For this analysis, -0.6 V forward bias was applied, and the obtained results are presented in Figure 9. The cell’s series resistance (Rs) is defined by the intercept on the real axis in the high-frequency domain. At the interface of electrode/conjugated polymers, Rct is represented by semicircle in the high-frequency domain; it determines the level of oxygen reduction as well as constant phase angle element responding (CPE). The Nernst diffusion impedance of the electron transfer in the solid state device is denoted by the letter ZN. The ZView software was used to fit the Nyquist plots for the ZnO electrodes. The equivalent circuit diagram shown in Figure 9 was used to fit the Nyquist plots. The impedance spectroscopy parameters generated from Nyquist plots of the solid state devices are presented in Table 1. Due to the same absolute Rs obtained for all three ZnO electrodes, the effect of each electrode induced by Rs on photovoltaic activity of cell is negligible. The vertically-oriented ZnO nanorods have an Rct value of 0.85 Ω/cm², which is lower than that of the horizontally-oriented ZnO (4.06 Ω/cm²) and ZnO nanoparticles (1.62 Ω/cm²). The lower Rct shows that the vertical ZnO nanorods have superior electrocatalytic action for oxygen reduction in OSCs in comparison with the other two ZnO configurations. Rct acts as barrier that resists transferring the excited electron from the polymer into the ZnO’s conduction band. Thus, as the electron transfer impedance decreases, more electrons are pumped into the conduction band, resulting in a greater JSC, as can be seen in Table 1.

The performance characteristics of OSC having different thin film materials as a work function were compared with our fabricated solar cell; the results are presented in Table 2. The table shows that the unique characteristics of our proposed device is its higher short-circuit current, open-circuit voltage, fill factor, and efficiency.
The stability test of the proposed solar cell was carried out through considering several categories such as tests under dark, simulated light and humidity. For each degradation test, there were three categories of basic, intermediate, and advanced levels. It should be noted that temperature, light, humidity, and environment were considered the main variables of the experiments. In this study, for indoor testing, the ISOS-L-1 protocols [53] were used to understand the degradation of the vertically-oriented ZnO-based solar cell. The testing protocol for ISOS-L-1 is as follows: (i) the simulator AM 1.5 G is used as light source, (ii) the test is carried out in ambient temperature and humidity, and (iii) the solar simulator is employed as a light source. Figure 10a, b, and c illustrate the stability of $V_{OC}$, $J_{SC}$, and $\eta$, respectively as functions of time. Figure 10a indicates that $V_{OC}$ is very stable for 300 hours. Meanwhile, the solar cell annealed at 60 °C indicates a better durability compared to the other annealing temperatures. However, $J_{SC}$ decreased to ~70% durability. The efficiency ($\eta$) decreased gradually from ~23% to ~15%. The stability of efficiency of the proposed OSC is affected by annealing conditions (Figure 10c). The device structure with 80 °C thermal annealing showed the best efficiency value, which was ~1-2% higher than the other annealing temperatures. In spite of high development potential of fabricating the organic solar cells, their stability and degradation are not extensively investigated in detail. The intrinsic reasons of organic photovoltaic degradation may be attributed to reaction of electrode materials with O$_2$. There are many parameters affecting the stability of OSCs, e.g., glass transition temperature, HOMO-LUMO level, and polymer stability. Therefore, to increase the durability of organic solar cells, it is necessary to carefully select the donor, acceptor, and electrode.

The challenges of future energy are tied to consuming eco-friendlier and environmental-friendlier resources and cutting down on the amount of nonrenewable energy usage. Conceptual understanding of energy conversion for future perspectives would be possible by the estimation of output energy of photovoltaic systems and the equivalent fossil fuel consumption. The energy output of photovoltaic systems is estimated using Equation (7):

$$E = A\eta IP_R$$

where $A$ is the total solar panel area, $\eta$ and $I$ are the panel efficiency and daily irradiation average on inclined panels, respectively, and $P_R$ is the loss coefficient or the performance ratio. Data on losses are dependent on the location, technology, and device size. The losses occurred in solar cell panel because of inverter, temperature losses, DC and AC cable, shading, weak irradiation, and
dust. Suppose that 1 m$^2$ solar panel using our proposed structure is irradiated in Malaysia with an annual average irradiation on tilted panels (shadings not included) of approximately 1750 kWh/m$^2$. The output energy obtained from this system is calculated to be $\sim$ 328 kWh. According to independent statistics and analyses carried out by the U.S. Energy Information Administration Unit, the amount of fuel such as coal, petroleum liquids, and natural gas used to generate electricity depends on the efficiency and the heat content of the fuel. The data show that for producing 328 kWh electrical energy, approximately 361 pound of coal, 26 gallons of petroleum liquids, and 2453 cubic feet of natural gas must be consumed [54]. Introducing renewable electrical energy generated by OSCs constructed by vertically-oriented ZnO nanostructures instead of fossil fuels can lead to an economically-effective reduction of greenhouse gas emissions.

4. Conclusions

The electronic contact layers' configuration and morphology are crucial factors in deciding the photovoltaic efficiency of organic supply chains (OSC), as an optoelectronic device. In this study, ZnO nanostructures having different morphologies were deposited using the electroless deposition technique on ITO/glass substrate and was applied as a photoanode to OSCs. The light conversion efficiency for vertically-aligned nanorods was improved 2.08 times compared to that of ZnO nanoparticles. Physical characteristics such as PL, UV-Vis absorption, and XRD showed that the vertically-aligned ZnO nanorods had $\sim$0.11 eV red change in the band gap, a significant increase (60%) in the strength of the absorption band, and a higher degree of crystallinity. With the use of our proposed green energy alternation OSCs system with vertically-aligned ZnO nanorods as photoanode, significant reduction on fossil fuel consumption is highly expected.

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Table caption

Table 1  Photovoltaic characteristics data for ZnO-based OSCs with various photoanode nanostructure morphologies

Table 2  Comparison of the proposed solar cells with the available literature OSCs having different thin film materials as a work function.

Figure caption

Figure 1  Solar cell device structure.
Figure 2  Top-view FESEM image of photoanodes made from ZnO nanoparticle (a), horizontally-aligned nanorods (b), and vertically-aligned nanorods (c). Inset shows the corresponding cross section FESEM images. The EDX spectra of ZnO nanoparticle (d), horizontally-aligned nanorods (e), and vertically-aligned nanorods (f).
Figure 3  XRD pattern of ZnO nanostructure having different morphologies deposited on ITO/glass substrate.
Figure 4  P-L spectra of ZnO nanostructures having different morphologies.
Figure 5  Approximate band diagram and electron transport in the ZnO photoanode-based OSCs.
Figure 6  UV-Vis optical absorption spectra of the ZnO nanostructure with different morphologies.
Figure 7  J-V properties of the ZnO-based OSCs at sun (a) and dark (b) conditions with different ZnO photoanode configurations.
Figure 8  IRCEs with different ZnO photoanode configurations.
Figure 9  Nyquist plots of ZnO-based OSCs having various configurations with applied bias voltage of -0.6 V.
Figure 10  ISOS-L-1 study of vertically-oriented ZnO-based solar cell under standard solar irradiation of 100 mW/cm² (AM 1.5G); V<sub>OC</sub> (a), J<sub>SC</sub> (b), and η (c).
References


Table caption
Table 1 Photovoltaic characteristics data for ZnO-based OSCs with various photoanode nanostructure morphologies

Table 2 Comparison of the proposed solar cells with the available literature OSCs having different thin film materials as a work function.

Figure caption
Figure 1 Solar cell device structure.
Figure 2 Top-view FESEM image of photoanodes made from ZnO nanoparticle (a), horizontally aligned nanorods (b), and vertically aligned nanorods (c). Inset shows the corresponding cross section FESEM images. The EDX spectra of ZnO nanoparticle (d), horizontally aligned nanorods (e), and vertically aligned nanorods (f).
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Table 1

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>$J_{SC}$ [mA cm$^{-2}$] ±0.02</th>
<th>$V_{OC}$ [V] ±0.02</th>
<th>FF [%]</th>
<th>η [%]</th>
<th>$J_{SC}$ (dark) [mA cm$^{-2}$] ±0.02</th>
<th>$R_s$ [Ω cm$^2$]</th>
<th>$R_s$ [Ω cm$^2$]</th>
<th>$R_{ct}$ [Ω cm$^2$]</th>
<th>IPCE [%]</th>
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<tr>
<td>ZnO vert.</td>
<td>30.56</td>
<td>0.98</td>
<td>0.79</td>
<td>23.65</td>
<td>0.24</td>
<td>1.89</td>
<td>0.24</td>
<td>2.46</td>
<td>0.85</td>
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<td>ZnO horiz.</td>
<td>27.82</td>
<td>0.84</td>
<td>0.77</td>
<td>17.98</td>
<td>0.20</td>
<td>1.72</td>
<td>0.20</td>
<td>2.49</td>
<td>1.62</td>
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<tr>
<td>ZnO NPs</td>
<td>22.12</td>
<td>0.76</td>
<td>0.71</td>
<td>11.93</td>
<td>0.18</td>
<td>1.37</td>
<td>0.18</td>
<td>2.52</td>
<td>4.06</td>
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Table 2

<table>
<thead>
<tr>
<th>Device structure</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>η [%]</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>ITO/α-In$_2$Se$_3$/PBDB-T:ITIC/Ca/Al</td>
<td>16.69</td>
<td>0.88</td>
<td>0.65</td>
<td>9.58</td>
<td>[45]</td>
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<tr>
<td>ITO/PEDOT:PSS-GO/PM$_6$:Y$_6$/PDINO-G/Al</td>
<td>25.65</td>
<td>0.85</td>
<td>0.76</td>
<td>16.52</td>
<td>[46]</td>
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<tr>
<td>ITO/WS$_6$/PM$_6$:Y$<em>6$/PC$</em>{71}$BM/PFN-Br/Al</td>
<td>26.00</td>
<td>0.84</td>
<td>0.76</td>
<td>17.00</td>
<td>[47]</td>
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<tr>
<td>ITO/ZnO/BP/PTB$<em>{7}:$:PC$</em>{71}$BM/MoO$_3$/Ag</td>
<td>18.78</td>
<td>0.72</td>
<td>0.61</td>
<td>8.25</td>
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<td>ITO/ZnO/PBD/PBDB-T:IT-M/MoO$_3$/Ag</td>
<td>16.7</td>
<td>0.93</td>
<td>0.74</td>
<td>11.6</td>
<td>[49]</td>
</tr>
<tr>
<td>ITO/ZnO/ P$_6$:HT:PCBM/MoO$_3$/Ag</td>
<td>10.71</td>
<td>0.50</td>
<td>0.44</td>
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<tr>
<td>FTO/NiO/MA$_3$Pb$_6$Bi$_5$/ZnO/BCP/Ag</td>
<td>15.2</td>
<td>0.87</td>
<td>0.33</td>
<td>4.39</td>
<td>[51]</td>
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<tr>
<td>ITO/G-MoS$_2$/PEDOT:PSS/P$<em>6$:HT:PC$</em>{71}$BM/Ca/Ag</td>
<td>17.20</td>
<td>0.77</td>
<td>0.72</td>
<td>9.50</td>
<td>[52]</td>
</tr>
<tr>
<td>ITO/ZnO/P$_6$:HT:PCBM/Ag/PEDOT:PSS/Ag</td>
<td>30.56</td>
<td>0.98</td>
<td>0.82</td>
<td>23.65</td>
<td>Current study</td>
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</table>

Fig. 1
Fig. 2

<table>
<thead>
<tr>
<th>Relative intensity</th>
<th>Vert.</th>
<th>Horiz.</th>
<th>NPs</th>
<th>St.</th>
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</thead>
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<tr>
<td>(002)/(100)</td>
<td>4.42</td>
<td>0.82</td>
<td>0.69</td>
<td>0.76</td>
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<tr>
<td>(002)/(101)</td>
<td>2.34</td>
<td>0.54</td>
<td>0.46</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Fig. 3
Fig. 4

Fig. 5
Fig. 6

Fig. 7
Fig. 8

Fig. 9

\[
\begin{align*}
Z' & (\text{Ohm cm}^2) \\
Z'' & (\text{Ohm cm}^2) \\
2R_s & \\
2R_d & \\
Z_N & \\
\text{1/2 CPE} & \\
\end{align*}
\]
Fig. 10