Effect of Thermal Annealing on Device Performance of Organic and Solid-state Dye-sensitized Photovoltaics

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ABSTRACT

In this study, the impacts of thermal treatment on the photovoltaic properties of emerging 3rd generation photovoltaics based on polymer organic and solid-state dye-sensitized solar cells are investigated. We have demonstrated a polymeric organic and solid-state dye-sensitized emerging photovoltaic device with power conversion efficiencies of over 3% under standard AM 1.5 illuminations at 80 mW/cm^2 as well as 100 mW/cm^2 using optimized thermal annealing condition at 80 ^{0}C for 10 minutes. Analysis of experimental results indicates that thermal annealing conditions could reduce the density of defect states, promotes carrier transport, increases photovoltaic characteristic values, and ultimately improve the performance of these photovoltaics. To enhance the maximum photovoltaic performance of these solar cells, soaking in the solvent, followed by spin-coating the P3HT solution and thermal annealing treatment at optimized thermal annealing processing temperature, proved to be a useful technique with power conversion efficiency of 3.6%. Consequently, we found that soaking in the solvent, spin-coating the P3HT solution, and thermal annealing the solid-state dye-sensitized photovoltaic device at 536 nm with a power intensity of 0.1 mW/cm^2 produced an incident photon to collected electron efficiency (IPCE) of 72%.

Keywords: Efficiency. Organic and solid-state dye-sensitized Photovoltaics, Optimization; Thermal annealing mechanisms;

1. INTRODUCTION

Within the next 50 years, the world's energy demand is anticipated to double. However, as fossil fuels become harder to come by, they are blamed for the rise in atmospheric carbon dioxide, which is the primary cause of greenhouse gas emissions and environmental harm. Hence, developing environmentally friendly, renewable energy is one of the challenges to society in the 21st century to mitigate climate change, to reduce greenhouse gas emissions, and increase the security of our global energy supply system. One of the renewable energy technologies is photovoltaics (PV), the technology that directly converts sunlight into electricity through a process called the photovoltaic effect. PV is one of the most well-known and the fastest growing of all the renewable energy technologies at present. The development of affordable solar photovoltaics is one of the most promising long-term solutions to keeping the CO_2 concentration in the atmosphere at safe levels. To date, one of the most significant sources of energy that does not hurt the environment and has the huge potential to replace fossil fuels as a source of energy is solar energy. However, one barrier impeding the expansion of large-scale power source application of solar photovoltaic systems has been the high price of the solar cell module due to high production costs of solar-grade silicon. In order for photovoltaic technology to be made truly competitive with fossil fuels, large-scale manufacturing of these devices will need to be economically and technically viable in order to supply a significant amount of the global energy needs. This will offer a pathway to a sustainable energy source.

Nowadays, the most popular kind of solar cell is a crystalline silicon cell, which can be composed of silicon that is either monocrystalline or polycrystalline. Although they can be expensive to produce, they are effective and long-lasting. Through ongoing research and development, these cells' efficiency has grown dramatically over time and can now reach up to a high power conversion efficiency (PCE) of 26.7% [1], whereas multicrystalline silicon solar cells that are now on the market have power conversion efficiency of between 14 and 19%. On the other hand, recently developed bulk heterojunction organic as well as dye-sensitized photovoltaics “emerging third generation photovoltaics“ could exceed the limits of single junction devices and lead to ultra-high efficiency for the same production costs of first and second generation photovoltaic devices [2]. Several promising technologies for those emerging third-generation low manufacturing cost photovoltaics are currently available and grouped under polymer based organic solar cells [3, 4, 5, 6, 7], small molecule-based organic solar cells [8, 9, 10], dye-sensitized solar cells [11, 12, 13, 14, 15], and solid-state dye-sensitized solar cells [16, 17, 18, 19, 20].

In recent years, researchers have developed organic photovoltaic cells that are more effective, stable, and economical. For solar cell applications, power conversion efficiency (PCE) is a crucial characteristic that can be increased by device engineering, material innovation and tailoring the active layer materials. Emerging third-generation photovoltaic technologies have recently attracted significant interest from industry and academic researchers and demonstrate distinct advantages over their inorganic counterparts due to their lighter weight, potential use in flexible devices, small thickness, inexpensive materials, ability to go through a solution process, and low cost in large-scale industrial production such as doctor-blading [21], spray coating and roll-to-roll processing [22, 2]. While roll-to-roll manufacturing is a potential solution for large-scale production, its practical development and integration into the organic solar cells manufacturing process require further research and discussion. Additionally, emerging third generation photovoltaic technologies are able to produce more power from the same quantity of sunshine than first generation (i.e. silicon-based) solar cells and second generation (i.e. thin films) solar cells due to their higher efficiency levels. They so represent a desirable alternative for both large- and small-scale solar energy applications.

The key property which makes organic photovoltaics so attractive is the potential of roll-to-roll processing on low cost substrate with standard coating and printing processes. However, several challenging scientific and technological problems remain to be solved. Both UV-induced photon exposure and environmental exposures from oxygen and moisture cause organic solar cells to degrade quickly, changing the efficiency of power conversion. It has been shown that the fundamental material properties, such as mobility of holes, defect densities in the absorbing material, and defect densities at the interface change as the device is exposed to air and to environmental exposure. So, the main challenges that today still hamper widespread commercialization are in the areas of cell and module lifetime, reliability, encapsulation barrier and volume manufacturing techniques. It should be noted that bigger area devices currently have a power conversion efficiency of 3.5% to 12% [2, 23], which is significantly lower than other types of devices. Additionally, roll-to-roll manufacturing is being developed and tested for organic photovoltaic devices on a lab scale, including printing or coating methods such screen, inkjet, offset, gravure, slot die, spray, and others [24, 25, 26, 2]. However, for p-i-n type small molecule based organic vacuum deposited tandem solar cells [27], extrapolated lifetimes corresponding to more than 30 years of sun illumination have been achieved. On the other hand, after 72 h of thermal annealing at 150 °C, stable power conversion efficiency of polymeric solar cell as high as 4.7% was maintained [28].

Various architectures for organic photovoltaic devices have recently been researched. Generally speaking, four crucial processes must be optimized for an organic-based photovoltaic cell [29, 2] to be successful in converting solar energy into electrical energy: (1) light absorption followed by excitons generation; (2) excitons diffusion towards active interface (i.e. charge transfer) and creation of separated charges at the donor - acceptor interface; (3) selective transport of the charges through the bulk of the device; and (4) charge collections by the appropriate dissimilar metallic electrodes (see Figure 1). Figure 1 depicts bulk heterojunction organic photovoltaics that are competitive. The photogenerated charges must migrate to these electrodes without recombining after the charge transfer reaction. Finally, it is important that the photogenerated charges can enter the external circuit at the electrodes without interface problems. The photoactive organic layer's absorption spectrum must match the solar emission spectrum in order for the layer to effectively gather photons, and it must be thick enough to completely absorb input light. It is also possible to improve light harvesting by using narrow band gap polymers; however, it can be difficult to find a polymer that can have a significant amount of overlap with the solar emission spectrum. Additionally, previous studies have demonstrated that optimizing the active layer materials by taking into account band gap, mobility, solubility, morphology, molecular energy level, photon absorption, and other factors is the key to increasing the solar cell efficiency [30].

Scheme of the operation of bulk heterojunction organic photovoltaics is shown in Figure 1. In this kind of device, a blend of a donor and an acceptor organic material is present in the active layer. The lowest unoccupied molecular orbital (LUMO), also known as the conduction band, and the highest occupied molecular orbital (HOMO), also known as the valence band, in one material and the corresponding HOMO and LUMO in the other material, differ energetically in an organic semiconductor. The chemical structure, self-ordering, concentration and mixing ratio of the polymer and fullerene, the impacts of the fullerene on the polymer, thickness, concentration of the solution, and heat and vapor annealing are some of the factors that may affect the nano-morphology of the active layer. The effective operation of solar devices is demonstrated experimentally to need optimal morphology [31]. To increase the performance of the solar cell device, the active layer materials must be tailored taking into account factors like band gap, mobility, solubility, morphology, molecular energy level, photon absorption, and so on.

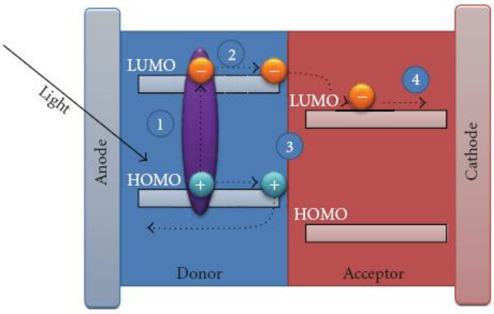


Figure 1. Scheme of operation principle of bulk heterojunction organic photovoltaics

The optimization of bulk heterojunction polymer organic and solid-state dye-sensitized solar cells has a number of unmet research needs. Therefore, it is still difficult to achieve high power conversion efficiencies (PCEs) in solid-state dye-sensitized solar cells as well as polymer-fullerene solar cells. In order to improve PCE, more study is required to optimize device architecture, material properties, manufacturing methods, or device processing conditions. Therefore, in this work in particular, the thermal annealing of emerging 3rd generation photovoltaics based on bulk heterojunction polymer organic and solid-state dye-sensitized solar cells were examined using material properties, manufacturing methods, or device processing conditions. Titanium dioxide (TiO_2) nanoparticles arranged in a porous layer, a dye monolayer covering the particles, and a "hole-transporter" that enters the pores of the TiO_2 layer is the three main components of dye-sensitized solar cells (DSCs). The main research challenges organic-based as well as hybrid solid-state dye-sensitized photovoltaic devices relate to the much needed increase in high power conversion efficiency, stability improvement (through better encapsulation and material degradation prevention) and the development of an adapted low-cost, large area deposition techniques [24, 25, 32] for roll-to-roll manufacturing technologies [26, 33], such as ink-jet printing, doctor-blade coating, screen printing, and spray coating.

The overall energy conversion efficiency, η_e of the photovoltaics cell has been performed using the equation

$$\eta_e = (V_{oc} x I_{sc} x FF) / P_{inc} \qquad (1)$$

under different intensities, where V_{oc}, I_{sc}, FF and P_{inc} are the open circuit potential, short circuit current, fill factor and incident light power, respectively. I_{sc} is the current that is recorded when the externally applied voltage is zero. I_{sc} represents the number of charge carriers that are generated and eventually collected at the electrode at a short circuit condition. Enhanced optical/electrical parameters such as small band gap, high absorption coefficient, smaller phase separation, and high carrier mobility improves I_{sc}. V_{oc} is the open circuit potential when the current density output is zero. V_{oc} has been reported to be mainly dependent on the work function difference of metal contacts. If an ohmic contact is formed at the electrodes, V_{oc} is dependent on the HOMO-LUMO difference between the donor and acceptor molecules. The fill factor defines the shape of the I-V curve and we determine the value of the fill factor of the device, FF, by calculating the area of the maximum power rectangular area under the I-V curve in the 4th quadrant. Therefore, the fill factor is defined as

$$FF = (V_{\max} x I_{\max}) / (V_{oc} x I_{sc}) \qquad (2)$$

where V_{max} and I_{max} are voltage and current at the point of maximum output power of the rectangle with the intersection of the current-voltage curve respectively. FF represents the dependence of current output on the internal field of the device and is quantified by series resistance and shunt resistance. A typical current-voltage curve of photovoltaic device is shown in Figure 2.

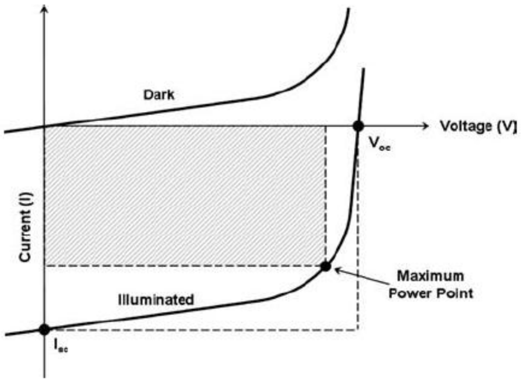
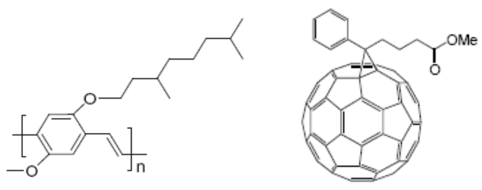


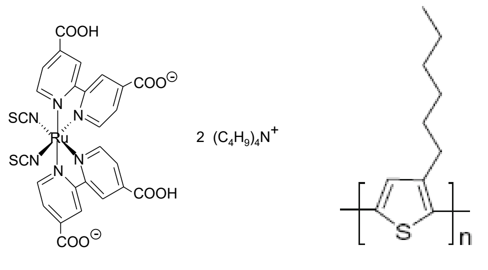
Figure 2. Graph of current versus voltage for photovoltaic devices. The figure shows how the device characteristics change upon illumination [34].

2. MATERIALS AND METHODS

Over the past few decades, research on organic semiconducting materials has become a subject rich in fundamental knowledge of unusual electrical phenomena and photo physics. The creation of organic photovoltaic technology is one application of this fundamental research [2]. In order to improve the efficiency of power conversion, researchers put a lot of work and research into developing potential narrow band gap polymers, dyes, and semiconducting materials [30]. The absorption of the organic photovoltaic (OPV) materials should match the indoor light spectrum and should also have high external quantum efficiency (EQE) in order to produce high-efficiency OPV under the indoor lighting conditions. The chemical compositions of the organic materials employed in this investigation are shown in Figure 3.



MDMO-PPV PCBM



RuL2(NCS)2:2TBA P3HT

Figure 3. The chemical structures of the materials used in this study [5, 20].

All of these organic materials used in this study, such as TiO_2 paste and the solubilized C_{60} derivative [6,6]-Phenyl C61-Butyric Acid Methyl Ester (PCBM), poly (3-hexylthiophene), poly [2-methoxy, 5-(3',7'-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV), were purchased from commercial sources. The use of new materials has enabled significant increases in bulk heterojunction organic solar cells as well as dye-sensitized solar cell efficiencies. Materials and methods [11, 12, 7, 16, 14] are a critical factor for both efficiency and lifetime.

The semi-transparent ITO coated glass substrates with a sheet resistance of ~15Ω/□ used in the fabrication of the polymeric bulk heterojunction organic solar cell devices described here were cleaned in ultrasonic baths of acetone, methanol, and isopropanol before being treated with oxygen plasma. ITO was spin-coated to a thickness of 100 nm with Poly(ethylene dioxythiophene) doped with Polystyrene Sulphonic Acid (PEDOT:PSS, Bayer AG), which enhances and stabilizes the electrical contact between the transparent anode (ITO) and the polymer active layer. Additionally, it reduces the substrate's surface roughness. A mixed composite of donor and acceptor bulk heterojunction organic photovoltaics devices was produced after the PEDOT: PSS film had dried overnight. Thus, the PEDOT: PSS was spin-coated with a photoactive layer made of MDMO-PPV: PCBM (1:4 by weight percent ratio) that had a thickness of 100–120 nm from chlorobenzene solution. MDMO-PPV can be used as a good donor material and PCBM is suitable for accepting charge carriers. LiF and Al were deposited in two layers for the cathode. First, a thin layer of LiF with an average thickness of 0.6 nm was thermally deposited onto the active layer (10^{-6} Torr) from a tungsten boat. Finally, a shadow mask was used to define a device region of 3 mm^2 to 7.5 mm^2 before a 100 nm aluminum cathode layer was thermally placed on top of the LiF. In an argon-filled dry box, device fabrication was carried out. The finished devices were thermally annealed by being placed directly on a hotplate with a digital temperature control in a glove box filled with nitrogen gas. The devices were annealed, then placed in a glove box and cooled to room temperature before the measurements were performed.

On the other hand, hybrid solid-state DSCs were made using ITO or SnO_2:F glass substrates with a sheet resistance of ~15Ω/□ with a 5 mm^2 active area and were constructed using the methods that have been described in the literature [16]. A hybrid solar cell is made up of both organic and inorganic components in this instance. Moreover, inorganic semiconductors can be made as nanoparticles and inorganic semiconductor nanoparticles have the advantage of having high absorption coefficients and size tenability (i.e. functions as an excellent photoanode). However, polymeric hole conducting materials are a viable alternative to liquid electrolyte in DSCs due to their lower cost and ability to be chemically tailored to meet a range of technological requirements. Contrary to the liquid cell, the hole transporting material could pass through the pores of the TiO_2 to make an ohmic contact with the glass substrate coated with transparent conducting oxide (TCO). In general, solid-state dye sensitized solar cells (S-DSSCs) have a number of benefits over those based on a liquid electrolyte, particularly in terms of manufacturing, because printing electronics technologies may easily be adapted for their manufacture.

To prevent direct contact, a blocking layer must be present at the interface between the hole transporting material that transports holes and the SnO_2:F layer. By using the spray pyrolysis process, a compact TiO_2 layer has been used here between the nanocrystalline TiO_2 and SnO_2: F layer [35]. The compact layer's ideal thickness for our solid-state DSCs is roughly 100 nm. Then, a 2 µm thick nanoporous TiO_2 film layer was produced by doctor-blading TiO_2 colloidal paste on SnO_2:F conducting glass [16, 21]. After drying, the nanostructured TiO_2 film was burned at 450 °C for 30 minutes at a rate of 5 °C/min in an oven. The transparent TiO_2 films were submerged for two days in a RuL2 (NCS) 2: 2 TBA solution containing ruthenium dye. After drying under nitrogen flow at room temperature, the dye-coated nanocrystalline TiO_2 films were employed as photoanode electrodes. On top of the dye-coated TiO_2 films, thin films of P3HT spun-coated from chlorobenzene solution were applied to coat the thin hole transport layer. The hole carrying layers were typically between 100 - 150 nm thick. Following a second drying step, the top electrode, 40 nm gold (Au) film was vacuum-deposited on top of the hole-transporting layer. The entire devices were subjected to thermal annealing.

The photo-excited dye molecules sandwiched between the two semiconductors inject electrons into the TiO_2 conduction band and holes into the p-type polymer in the nanoporous TiO_2 semiconductor/Ru-dye/p-type polymeric semiconductor device combination. After the dye has injected electrons into the TiO_2, the hole-transporting polymeric material ought to be able to transfer holes from the dye. The holes are subsequently carried by hopping to the clear counter electrode. The counter electrode needs to be highly conductive, mechanically stable, and chemically and electrochemically stable. Several conditions must be met in order for this to be realized: (i) A method must be available for depositing a p-type polymeric material without dissolving or degrading the ruthenium dye monolayer on TiO_2 nano crystallites; (ii) the p-type polymeric material must be very transparent in the visible spectrum, where the ruthenium dye absorbs light; (iii) The dye's excited level (S*/S+) should be above TiO_2's conduction band (Ec), while the dye's ground state level (S0/S+) must be below the p-type polymeric material's (HOMO) upper edge of the valence band. This is necessary for both hole transfer to the valence band of the p-type polymeric material and electron transport from excited dye molecule to the conduction band of TiO_2; (iv) the upper edge of the valance band of p-type semiconductors (HOMO) must be placed above the ground state level of the dye (S0/S+) in order for the polymer hole conductor to be able to transport holes from the sensitized dye after the dye has injected electrons into the TiO_2, as seen in Figure 4. (v) The transport properties of the p-type polymeric materials must be sufficient or high conductivity. Furthermore, previous studies have shown that the device performance can be enhanced by matching the energy level of each material [17-20]. The potential energy diagram of hybrid solid-state dye-sensitized solar cell components with respect to vacuum level is shown in Figure 4.

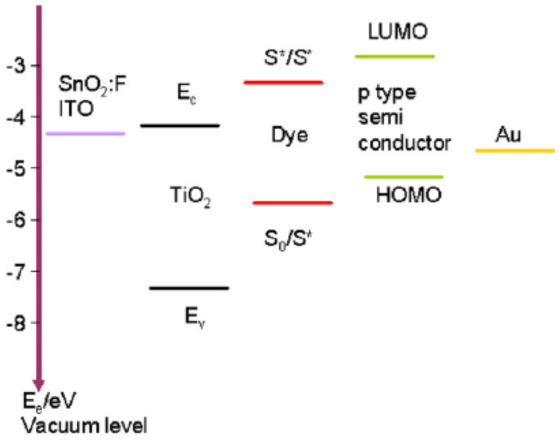
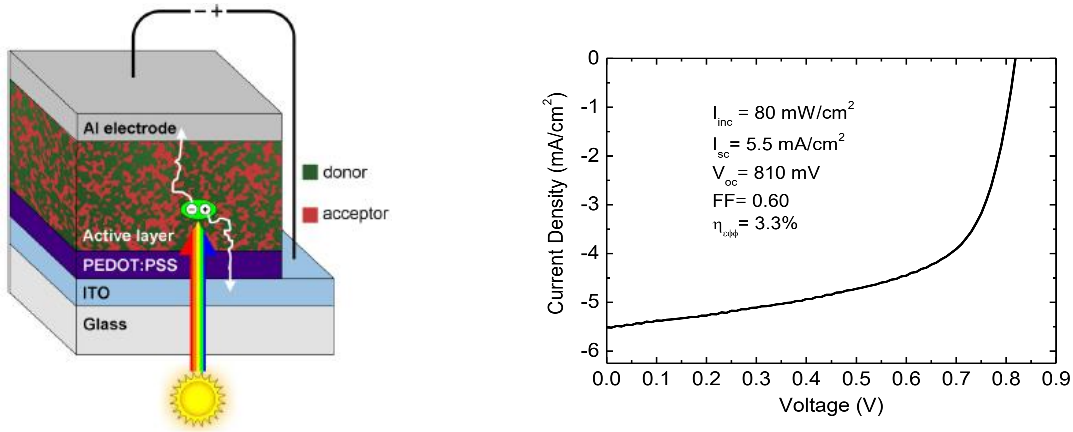


Figure 4. Energy diagram for an efficient charge transfer between hybrid solid-sate dye-sensitized solar cell components [19, 20].

A solar simulator was used to light up photovoltaic devices. Using a calibrated single-crystal Si solar cell, the intensity of the incident light was measured. Keithley Source Meter measuring Unit (SMU) 2400 and Keithley SMU 236 measurements of current-voltage (I-V) characteristics were performed in a nitrogen atmosphere with light shining through the front of the photovoltaic devices. A Steuernagel solar simulator produced light (AM1.5 simulated irradiation at 80 and 100 mW/cm^2). The samples' temperature during measurement was 50 ^{0}C due to heat produced by the solar simulator.

3. RESULTS AND DISCUSSION

First, the device structure and characterization of bulk heterojunction ITO/PEDOT: PSS/MDMO-PPV: PCBM/LiF/Al organic polymer solar cells are presented in Figure 5 below.



(a) **(b)**

Figure 5. Device structure of a bulk-heterojunction polymer-based organic photovoltaics (a) and current-voltage characteristics of annealed at 80 ^{0}C for 10 min, the best bulk-heterojunction polymer-based organic photovoltaics (b). The active layer in this type of device contains a donor and an acceptor organic material.

To investigate how thermal annealing affected the photovoltaics performance of PV devices of the number of devices tested for judging the reliability and accuracy, the bulk heterojunction MDMO-PPV: PCBM organic polymer solar cells at different annealing temperatures (60 ^{0}C, 80 ^{0}C, 100 ^{0}C, 120 ^{0}C) for 10 minutes were studied. This often involves systematically varying one parameter while keeping the other constant. Subsequently, the characteristic values of this annealed device at 80 ^{0}C for 10 minutes, the best device in Figure 5 (b) are V_{oc} = 810 mV, I_{sc} = 5.50 mA/cm^2 and a fill factor FF = 0.60, and the resulting power conversion efficiency is 3.3% under standard AM1.5 illumination with an intensity of 80 mW/cm^2. Whereas the characteristics values of the unannealed bulk heterojunction MDMO-PPV: PCBM organic polymer solar cell are V_{oc} = 800 mV, I_{sc} = 4.75 mA/cm^2 and a fill factor FF = 0.58, and the resulting power conversion efficiency is about 2.8% under standard AM1.5 illumination (80 mW/cm^2).

It is obvious that statistical analysis of a large sample size provides a more reliable and accurate representation of the device's performance. On the basis of several statistical and experimental analyses, the maximum power conversion efficiency of 3.3% for this device was found for a duration of the treatment of 10 minutes using an optimized device annealing temperature of 80 ^{0}C [Fig. 5 (b)]. This results demonstrated that the active layer's morphology is altered by thermal annealing of the device structure, which also alters the material's microstructure, crystallinity, phase separation structure and percolation routes, potentially improving device performance [3, 4, 6, 10, 36].This value is comparable to the previous report of power conversion efficiency of 3.5% obtained for P3HT: PCBM plastic solar cells after annealing for 5 minutes at 75 ^{0}C [36]. Additionally, using the P3HT:PCBM organic photovoltaic device, thermal annealing has shown to be a remarkable performance-enhancing step [37]. The above results demonstrated that the annealing resulted in an improvement photovoltaic properties and solar cell efficiency [14, 4, 3]. These enhancements seen in the short-circuit current density, fill factor and the power conversion efficiency can be explained by an increased charge carrier mobility due to a high degree of intermolecular order for both holes and electrons in the solution-caste photoactive layer and improved nanoscale morphology of the two components (donor/acceptor) in the photoactive layer. On the other hand, device architecture, such as inverted structures and the development of non-fullerene acceptors (NFAs) has led to significant improvements in PCE, with devices surpassing 19% efficiency [38]. Thus, this method helps create high-quality active layers with a more favorable molecular packing orientation, leading to better charge generation, separation, and transport.

Moreover, the photoactive layer morphology of the photovoltaic device is another critical factor for achieving high efficiencies, since the charge - separation and charge-transporting depend on the interface and the interpenetrated networks of a bulk heterojunction organic photovoltaic device [10, 4, 3]. In addition, the improvement of the device performance after annealing can be explained as follows: before annealing MDMO-PPV has an amorphous structure caused by the higher concentration of fullerene. During annealing PCBM diffuses out of the polymer matrix to form a percolated interpenetration of donor-acceptor network with improved electron transport properties. Consequently, the more ordered structure improves the contact between electrodes and photoactive film, which decreases the series resistance of the photovoltaic cells and increases the short circuit current as well as the fill factor. Obviously, there are a number of elements that might affect fill factor [39], but the main ones are charge carrier mobility (hole and electron) and mismatching in carrier mobility, charge collection due to interface state recombination, series and shunt resistances, and so on.

The device structure of an organic photovoltaic system based on bulk heterojunction polymers (a) and the current-voltage characteristics of an annealed bulk heterojunction polymer-based organic photovoltaic system (b) were displayed in Figure 5. Aluminum serves as the positive electrode whereas indium tin oxide (ITO) is a popular transparent positive electrode. The diagram in Figure 5 (a) shows a bulk heterojunction active layer (MDMO-PPV: PCBM), where the blend of the donor and acceptor creates phase-segregated domains [39]. Interestingly several scientific works [5, 36, 41, 42, 43] were already published related to the relationship between the nanoscale morphology of the bulk heterojunction polymeric organic photoactive layer and the performance of the polymeric organic solar cells. Furthermore, previous reports [6, 5, 36, 40, 41, 42] attributed the improved photovoltaic performance to change in the bulk heterojunction organic materials nanoscale morphology induced by the donor-acceptor composition, the solvent and the thermal annealing of the organic photoactive layer. A recent complete study linking the morphology of the MDMO-PPV:PCBM mix made from chlorobenzene to solar cell performance was published [5, 41]. It is advised to compare the effects of reverse thermal annealing (RTA) and conventional/standard thermal annealing (TA) on the performance of organic photovoltaics (OPV). These studies can be shown in Table 1.

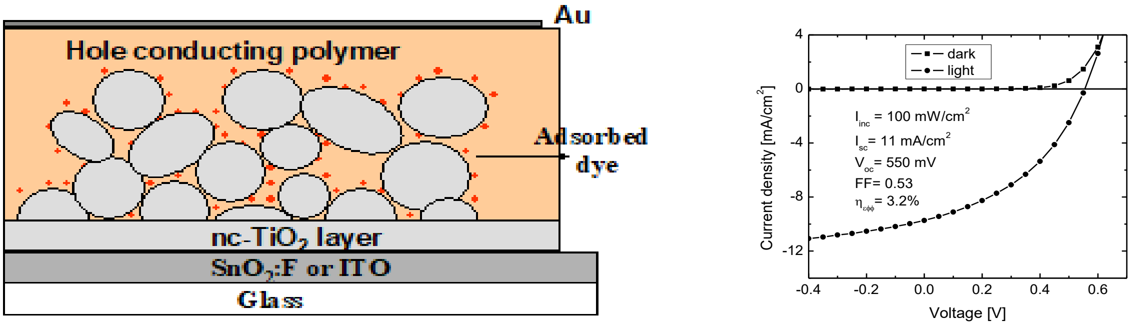
Table 1. Overview of comparative studies between conventional or standard thermal annealing (TA) and reverse TA (RTA) methods

Feature	Conventional Thermal Annealing (TA)	Reverse Thermal Annealing (RTA)
Primary goal	Improves phase segregation and molecular ordering for charge transport.	Enhances dielectric constant, forming a smaller Coulomb capture radius and optimal nano-scale aggregation and stacking orientation
Impact on film properties	Can improve vertical morphology, decrease defect density, and cause a de-doping process.	Affects the dielectric constant, which improves active layer quality and ordered molecular packing.
Typical outcome	Generally increases open-circuit voltage (Voc), short-circuit current density (Jsc) and fill factor (FF), leading to higher power conversion efficiency (PCE).	May lead to higher PCE by improving the active layer's charge carrier extraction and transport properties through enhanced film characteristics.

According to scholarly literatures in this study [3, 4, 6, 10, 36, 37, 43], the AFM/SEM images of the bulk heterojunction MDMO-PPV: PCBM organic polymer solar cells influenced by the donor-acceptor composition of materials, the solvent, device processing conditions and the thermal annealing of the organic photoactive layer demonstrated an enhancement to nano-scale morphology and phase separation. Hoppe *et al.* [44] also stated that, in accordance with theoretical predictions, experimental evidence indicates that the size of the phase-separated domain and the percolation of both hole- and electron-conducting phases are critical for enhancing the power conversion efficiency of organic solar cell devices. However, the morphological analyses (AFM/SEM/TEM images) of our PV devices were not investigated in this study due to a lack of necessary experimental equipment. A thorough investigation into the variation in energy level alignment brought on by thermal annealing and its associated impact on the Voc of organic solar cells has not yet been conducted, despite considerable efforts to explain the effect of thermal annealing on morphological alterations of solution-processed organic solar cells. Nonetheless, Ali et al. [37] showed that thermal annealing is thought to help improve the Voc, Jsc, and FF in the polymer blend with improved charge transport characteristics for the devices that are annealed.

Second, the device structure and characterization of hybrid solid–state dye-sensitized photovoltaic device: SnO_2:F/compact TiO_2/ nc-TiO_2/Ru-dye/P3HT/Au is presented and shown in Figure 6. To investigate how thermal annealing affected the photovoltaics performance of PV devices, the hybrid solid–state dye-sensitized photovoltaic device: SnO_2:F/compact TiO_2/ nc-TiO_2/Ru-dye/P3HT/Au at different annealing temperatures (60 ^{0}C, 80 ^{0}C, 100 ^{0}C, 120 ^{0}C) for 5 minutes were studied. Consequently, the characteristic values of this annealed device at 100 ^{0}C for 5 minutes, the best device in Fig. 6 (b) are V_{oc} ~ 550 mV, I_{sc} ~ 11 mA/cm^2 and a fill factor FF ~ 0.53 under white light illumination with 100 mW/cm^2. The overall energy conversion efficiency, η_e for this annealed hybrid solid-state dye-sensitized solar cell was calculated to be over 3.2 % under standard AM1.5 illumination with intensity of 100 mW/cm^2. This maximum efficiency of the device was found for a duration of the treatment of 5 minutes for optimal annealing temperature at 100 ^{0}C.

Hence, by optimizing the morphology and reducing the density of defects, annealing enhances charge carrier mobility, leading to better short-circuit current density (Isc), open-circuit voltage (Voc) and fill factor (FF), which in turn boosts PCE. Whereas the characteristics values of the unannealed solid–state hybrid photovoltaic device: SnO_2: F/compact TiO_2/ nc-TiO_2/Ru-dye/P3HT/Au are V_{oc} ~ 530 mV, I_{sc} ~ 9.54 mA/cm^2 and a fill factor FF ~ 0.48, and the resulting power conversion efficiency is 2.4% under standard AM1.5 illumination (100 mW/cm^2). The rise in device performance following thermal annealing can be attributed to the burning of the shunts. The increase in short-circuit current density suggests an enhancement in the mobility of the charge carriers inside the photoactive layer as well as the filling of transparent hole conductors into the pores between the TiO_2 nanoparticles. Previous studies [16, 17, 18, 19] demonstrated that annealing helps achieve a stable, well-ordered morphology in the active layer, including appropriate phase separation and crystallinity, which are vital for efficient charge separation and transport. Novel p-type semiconductor materials and various techniques for depositing p-type material onto dye-coated nanoporous films are also likely to increase the efficiency of this cell. Figure 6 below demonstrated the (a) Device structure [20] and (b) I-V characteristics of annealed hybrid solid-state dye-sensitized photovoltaic devices.



(a) (b)

Figure 6. (a) Device structure and (b) I-V characteristics of annealed at 100 ^{0}C for 5 min, the best hybrid solid-state dye-sensitized photovoltaic devices: SnO_2:F/compact TiO_2/nc-TiO_2/Ru-dye/P3HT/Au (solid squares: dark, solid circles: illuminated with 100 mW/cm^2).

According to the scholarly literatures in this study [16, 17, 18, 19, 20, 21], the AFM/SEM images of the hybrid solid–state dye-sensitized photovoltaic devices influenced by thermal annealing of the hybrid solid-state dye-sensitized photovoltaic devices demonstrated an enhancement to nano-scale morphology and infiltration of the organic / polymer hole-conductor into nanoporous TiO_2. However, the morphological analyses (AFM/SEM/TEM images) of our PV devices were not investigated in this study due to a lack of necessary experimental equipment.

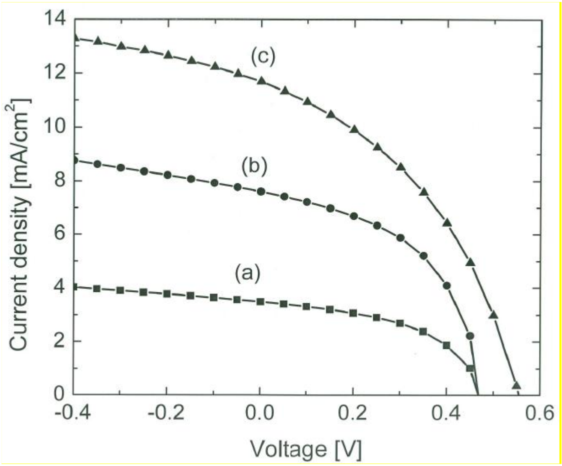


Figure 7 Current-voltage characteristics of solid-state DSCs upon three different ways of infiltration of the polymer hole-conductor P3HT into nanoporous TiO_2 under white light illumination with 100 mW/cm^2: (a) 10 times repeated spin-coating of the P3HT solution, (b) soaking in the solvent with subsequent spin-coating of the P3HT solution, and (c) soaking in the solvent with subsequent spin-coating of the P3HT solution and annealing treatment at 100 ^{0}C for 5 minutes

Third, Figure 7 shows the measured I-V curves and photovoltaic performance metrics of solid-state hybrid DSCs: SnO_2:F/nc-TiO_2/Ru-dye/P3HT/Au under white light illumination with 100 mW/cm^2.

It was discovered that the effectiveness of solid-state dye-sensitized solar cells depends on how well Titania nanostructures are filled with a solid hole-conducting material. Since a transparent hole conductor was not completely filled into the pores between the nanoparticles of TiO_2 and because fewer charges were removed, solution casting, or one-time spin coating, of the polymer, performed poorly. The polymer hole-conductor P3HT, however, infiltrated into Titania nanostructures in three different ways, each of which resulted in an effective photovoltaic performance. Filling by ten times repeated spin coating granted reasonable efficiencies up to 0.91% [Fig. 7 (a)]. However, soaking nanoparticles of TiO_2 film in toluene solvent with subsequent spin coating of the P3HT solution showed higher efficiencies up to 2% [Fig.7 (b)], and soaking in toluene solvent with subsequent spin coating of the P3HT solution as well as annealing treatment at 100 ^{0}C for 5 minutes resulted in the best efficiencies up to 3.6% % [Fig.7 (c)] under white light illumination with 100 mW/cm^2. Hence, efficient solid-state hybrid DSCs performances demonstrated that an increasing filling of the pores in the Titania nanostructures with P3HT is observed from filling by repeated spin coating via filling, by solution casting to filling by soaking in the solvent with subsequent spin coating and annealing treatment at 100 ^{0}C for 5 minutes. The results show the usefulness of conducting polymers as hole-transport materials for the possible replacement of the liquid electrolyte in nanoporous TiO_2 type solar cells and optimization of these devices is a promising approach from both academic and industrial sides.

Table 2 shows the measurements of summarized photovoltaic parameters of solid-state DSCs for the different kinds of P3HT infiltration into dye-coated TiO_2 nanostructures. These results indicate that the performance of solid-state DSCs can be strongly affected by the device processing conditions. The improved short-circuit current density (I_{sc}) as high as 12 mA/cm^2 in Table 2 is mainly due to the improved charge carrier mobilities and ascribed to the enhanced charge transport rate associated with the improved charge collection efficiency. Additionally, we observe that open circuit voltage (V_{oc}) has slightly higher value upon annealing which can be surmised due to reduced charge recombination pathways because of a different local morphology in the polymer for the annealed device.

Table 2. Overview of solid-state DSCs parameters for the different kinds of P3HT infiltration into dye-coated TiO_2 nanostructures

Way of Filling	Voc [mV]	Isc [mA/cm^2]	FF	η[%]
10 times spin-coating of the P3HT solution	450	3.5	0.58	0.91
Soaking in the solvent with subsequent spin coating of the P3HT solution	450	7.6	0.6	2
Soaking in toluene solvent with subsequent spin coating of the P3HT solution as well as annealing treatment at 100 ^{0}C for 5 minutes	550	12	0.54	3.6

This maximum power conversion efficiency η_e of the solid-state hybrid DSC device was found due to an enhancement of the mobility of the charge carriers inside the photoactive layer and upon filling of nanoporous TiO_2 film by soaking in the solvent with subsequent spin-coating of hole conducting polymer material, P3HT as well as for a duration of the treatment of 5 minutes in nitrogen atmosphere for annealing the solid-state DSC using a temperature of 100 ^{0}C. Additionally, the photo-physical study conducted by Sai Santosh Kumar et al. [45] revealed that the increased crystallinity of the P3HT thin-film after thermal annealing results in increased hole-transfer from the organic dye to polymer, along with increased hole-mobility and decreased charge recombination. These factors directly influence the observed improvement in the device performances.

Finally, the photovoltaic external quantum efficiency (η_c) or the spectrally resolved incident photon-to-converted electron efficiency (IPCE) is defined as the number of electrons flowing through an external circuit under short circuit conditions per incident photon should be mentioned and is calculated from the spectrally resolved short-circuit current,

$$\eta_c(\%) = 1240/\lambda[nm] x I_{sc}[\mu A/cm^2]/I_{inc}[W/m^2] \quad (3)$$

Where I_{inc} is the intensity of the incident light. Figure 8 displayed a comparison between the spectrum resolved photon-to-electron conversion efficiency (IPCE) of a solid-state hybrid dye-sensitized nanocrystalline TiO_2 solar cell under xenon arc lamp illumination from the TiO_2 side plotted on the right axis and the optical density on the left axis of a solid–state hybrid dye-sensitized nc-TiO_2 solar cell. One can see very clearly, that the two curves have the same onset and spectrally resolved maxima at 536 nm. The maximum value of the photon-to-electron conversion efficiency of a solid–state hybrid dye-sensitized nc-TiO_2 solar cell was calculated to be about 72% under monochromic illumination at 536 nm with power intensity of 0.1mW/cm^2.

Furthermore, the decline of the IPCE above 600 nm towards the red is caused by the decrease in the extinction coefficient of RuL2(NCS)2. This enhancement of the IPCE originates from an enhanced absorption, electron transfer and transport due to an enhancement of the charge carrier mobility of the bulk.

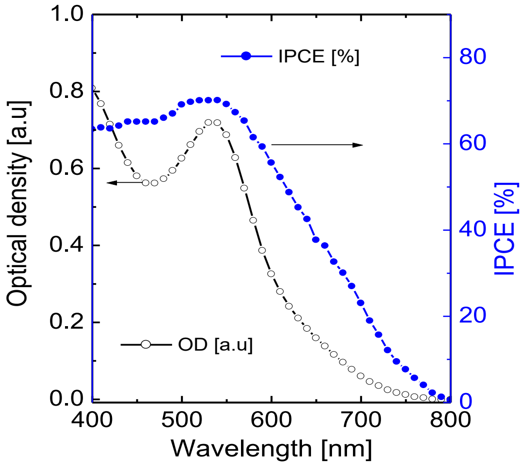


Figure 8. Spectral resolved photon-to-electron conversion efficiency, IPCE (solid circles) of a solid-state hybrid dye-sensitized nanocrystalline TiO_2 solar cell (plotted on the right axis) through illumination from TiO_2 side by xenon arc lamp and optical absorption (open circles) for nanocrystalline TiO_2 film coated with ruthenium-dye (plotted on the left axis).

4. CONCLUSIONS

In conclusion, organic and hybrid solid–state dye-sensitized solar cells are considered as emerging third generation technologies to replace conventional silicon solar cells as well as thin film solar cells. Experimentally, in optimized annealed devices, we achieved above 3% power conversion efficiencies performances under AM 1.5 global illuminations at 80 mW/cm^2 as well as 100 mW/cm^2. In addition, we observed an incident photon to collected electron efficiency (IPCE) of 72%. These advances are a testimony to the rapid progress being made in the field of organic and dye-sensitized emerging 3rd generation photovoltaic technologies. The impact of thermal annealing on the performance of organic and solid-state dye-sensitized photovoltaics devices, as well as a more comprehensive contextual discussion regarding morphological optimization, device performance enhancements, and a more efficient and economical production process in comparison to the current body of knowledge, would therefore be crucial. The conversion of sunlight to electricity by organic and hybrid solid-state dye-sensitized solar cells is very interesting and promising since organic and dye-sensitized solar cells offer the possibility of fabricating large area, low-temperature processing, flexible, lightweight, cost-effective devices using simple and environmentally friendly techniques. Obviously, roll-to-roll processing is at the heart of organic photovoltaics as well as solid-state dye-sensitized solar cells in the future and that the successful realization of lowcost emerging 3rd generation photovoltaics will be closely linked to this. These advantages have so far drawn a lot of research attention and commercialization effort. Furthermore, overcoming limitations in device stability, particularly "burn-in" degradation and long-term operational stability, remains a key challenge and area of future research.

CONFLICT OF INTEREST

The author affirms that there were no financial or commercial ties that might be interpreted as a potential conflict of interest during the research.

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