

Solid-State Polymer/ZnO Hybrid Dye Sensitized Solar Cell: A Review

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ABSTRACT

A highly efficient device concept for solid-state hybrid dye-sensitized solar cells has been recently realized. It has been attracted extensive attention as a promising approach to achieve cost effective solar energy. The key property which makes solid-state hybrid dye-sensitized photovoltaic systems so attractive is the potential of simple fabrication and assembling technology. In this article, firstly, we review the recent developments including device operational mechanism of solid-state hybrid dye-sensitized solar cells incorporating inorganic nanoparticles as electron transporting material, an organic hole transport materials with photoexcited dye molecules as electron injector into the n-type material and the hole-accepting and transporting properties of polymer. In addition, the enhancement of photoresponse through interaction of near-IR dyes and the polymer hole-transport material have also discussed.

Key words: Solid state polymer, Hybrid dye, Sensitized solar cell.

INTRODUCTION

The supply of clean energy for our society is a central challenge to maintain our standard of living. It is important to change from fossil fuels to renewable energy sources for two main reasons: Firstly, the natural resources of gas and oil are limited and will run out. Secondly and more importantly, a continued dependence on fossil fuels would increase an already alarming rate of CO₂ emission. Additionally, other environmental problems caused by the mining of these resources may increase because the remaining resources will be in places which are more difficult to reach. Solar cells are promising candidates for CO₂ emission free energy supply. Hence, developing environmentally friendly, renewable energy is one of the challenges to society in the 21st century. One of the renewable energy technologies is photovoltaics (PV), the technology that directly converts daylight into electricity. PV is one of the

fastest growing of all the renewable energy technologies; in fact, it is one of the fastest growing industries at present ^[1]. Solar cells are designed to convert available light into electrical energy. They do this without the use of either chemical reactions or moving parts. Solar cell manufacturing based on the technology of crystalline, silicon devices is growing by approximately 40% per year and this growth rate is increasing ^[1]. This has been realized mainly by special market implementation programs and other government grants to encourage a substantial use of the current PV technologies based on silicon. The silicon is treated or "doped" in order to create charge carriers, so that when light strikes it electrons are released, leading to generation of electric current. The active materials used for the fabrication of solar cells are mainly inorganic materials, such as silicon (Si), gallium-arsenide (GaAs), cadmium-telluride (CdTe), and cadmium-indium-selenide (CIS). The power conversion efficiency for these solar cells varies

from 8 to 29%. The current status of PV is that it hardly contributes to the energy market, because it is far too expensive. The large production costs for the silicon solar cells are one of the major obstacles. Even when the production costs could be reduced, large-scale production of the current silicon solar cells would be limited by the scarcity of some elements required, e.g. solar-grade silicon. Conventional silicon solar cells usually require high purity Si materials and complicated fabrication processing; therefore they are not cost effective for wide range applications².

The work of the French physicist Antoine – Cesar Becquerel in 1839 laid the founding stone for the development of solar cells. Becquerel discovered the photovoltaic effect while experimenting with a solid electrode in an electrolyte solution. He observed the development of voltage when light fell upon the electrode^[3]. About 50 years later, Charles Fritts constructed the first true solar cells using junctions formed by coating the semiconductor selenium with an ultra thin, nearly transparent layer of gold. Fritts's devices were very inefficient, transforming less than 1% of the absorbed light into electrical energy^{4,5}. By 1927 the transferring capacity of another metal-semiconductor junction solar cell, made of copper and the semiconductor copper oxide, had been demonstrated. Towards 1930 both the selenium cell and the copper oxide cell were being employed in light sensitive devices, such as photometers for the use in photography. These early solar cells, however, still had energy-conversion efficiencies of less than 1%. This impasse was finally overcome with the development of the silicon solar cell by Russell Ohl in 1941. In 1954, American researchers, G.L. Pearson, Daryl Chapin, and Calvin Fuller, demonstrated a silicon solar cell having 6% energy conversion efficiency when used in direct sunlight^{6,7}.

Research has been focused on the development of cheaper thin-film solar cells. Such films may be purely inorganic or contain organic materials as an essential part of the device. Examples of the latter are junctions consisting of thin layers of organic donor and acceptor molecules; bulk heterojunctions in which the donor and acceptor phases exist as an interpenetrating

network^[8]; or dye-sensitized photoelectrochemical solar cells^[9, 10] in which light absorbance occurs in metallo-organic dye molecules, but generated electrons are injected into the conduction band of a wide-bandgap semiconductor, mainly highly porous nanocrystalline TiO₂ (the so-called Grätzel cells).

Organic-inorganic hybrid solar cells become a promising candidate for offering low cost solar energy, since they can be fabricated by solution-based processing, such as dip coating, screen printing, ink jet printing, painting and roll-to-roll processing^{11, 12}. They also have the advantages of being lightweight and mechanically flexible^{13,14}. In recent years, conjugated polymer-inorganic semiconductor hybrid systems have attracted extensive attention and research¹⁵⁻²⁶. These devices combine the advantages from both organic and inorganic materials²⁷. Conjugated polymers (e.g., P3HT), when self organized into crystal structure, can own a high hole mobility²⁸ and can also be easily processed onto the surface of both rigid and flexible substrates. Nanoscale inorganic materials exhibit different optical absorption and photocurrent generation properties from bulk materials due to their quantum size confinement. They have advantages including relatively high electron mobility, high electron affinity and good thermal stability²⁹. Solution-processible nanostructured inorganic semiconductors also provide the possibility to have a large interfacial area for efficient exciton dissociation when blending with soluble polymers²⁹. One-dimensional (1-D) ordered nanostructure inorganic semiconductors aligned on the substrate can provide an ideally straight pathway for carrier transport. Generally when organic and inorganic components are combined into a heterojunction device, the polymers are used as donors to absorb sunlight and transport holes, while the inorganic semiconductors function as acceptors to transport electrons. In such devices, an energy conversion efficiency exceeding 3% has been reached^[30]. More recently, solid state dye sensitized solar cell (DSSC) structure has been adopted to fabricate organic (polymer)-inorganic hybrid solar cell^[31, 32]. In these devices, semiconductors (e.g., porous TiO₂) are sensitized by a traditional dye or a light absorbing inorganic semiconductor (e.g., Sb₂S₃), and the polymers

function as a hole transporter to reduce the dyes and also work as an additional donor to absorb light. A power conversion efficiency of 5.13% has recently been achieved in this type of hybrid solar cells³².

In this paper, the recent developments of solid state polymer/inorganic hybrid dye sensitized solar cells are reviewed. We discuss the photovoltaic properties of three-layered devices, combining the electron transporting properties of metal oxide semiconductor and the hole accepting and transporting properties of organic polymers. The operational principle of the dye-sensitized solar cell (DSSC), mechanism, theory, cell characterization and efficiency prediction of solid state hybrid dye sensitized solar cells are introduced. Finally, the conclusion and outlook to further improve polymer–inorganic hybrid solar cell performance are presented.

Mechanism and theory

Dye Sensitized Solar Cell (DSSC)

DSSCs provide a technically and economically credible alternative concept to the current p–n junction photovoltaic devices. Figures 1(a) and 1(b) schematically depict the working process in conventional solar cells and DSSCs, respectively. For the conventional p–n junction photovoltaic devices (Figure 1(a)), the electrons are excited to the conduction band of the semiconductor upon light absorption. The generation rate of electron–hole pairs as a function of distance from the semiconductor surface alters with the wavelength of light due to the change in the absorbance. The electrons transfer from p to n side in the semiconductor, while holes generated on the absorption move to the p-type region. The expected voltage is the difference between the Fermi levels of p and n regions. Thus, the semiconductor assumes both tasks of light absorption and charge carrier transport.

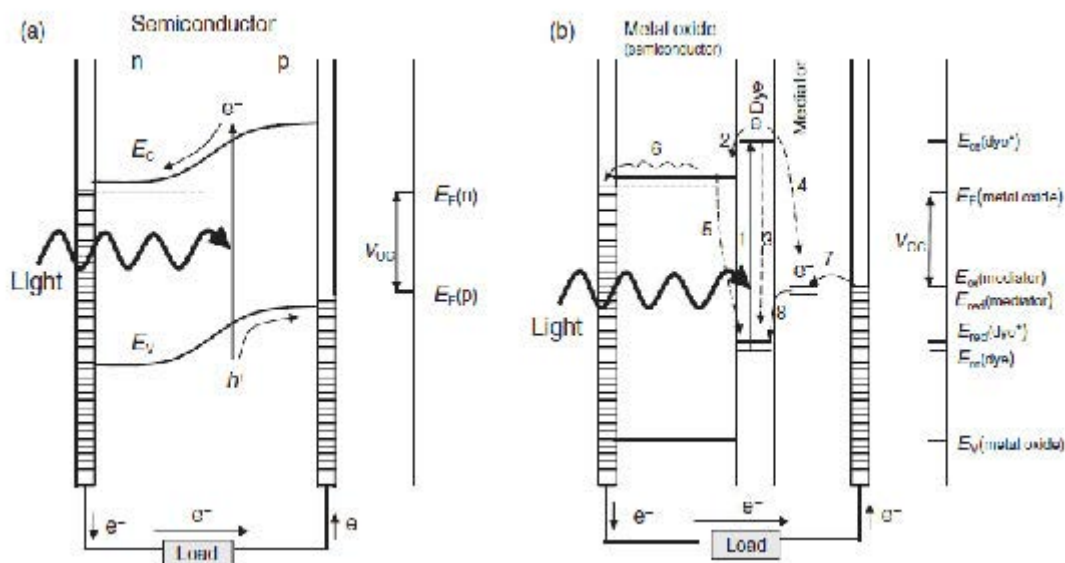


Fig. 1: Functional diagrams of (a) p–n junction solar cell and (b) DSSC. The solid arrows show the steps of operation and dashed arrows show the possible losses in a DSSC

In contrast, the scheme of electron energy transfer for DSSC is different from that of the p–n junction solar cells. The reaction scheme consists of some steps as shown in Figure 1(b):

1. Absorption of photon, which is determined by the absorption spectrum of the dye as

well as the intensity of solar radiation spectrum.

2. Interfacial electron transfer (electron injection) from the adsorbed dye to the conduction band of a semiconductor.
3. Deactivation of the photoexcited dye, where

- the solar energy is lost as heat (nonradiative deactivation) or light (radiative deactivation).
- Back-transfer to the mediator in the electrolyte.
 - Charge recombination at the dye–semiconductor interface. The electrons transferred to the conduction band will diffuse to the oxidized dye located at the surface.
 - Electron transport through the conduction band of the semiconductor photoelectrode to the conducting electrodes, which may be controlled by the diffusion coefficient of the electron, D_n , in the semiconductor.
 - Reduction of the oxidized form of the redox mediator (I^3) at the counter electrode to the reduced form (I^-). For the next step, the formed I^- should diffuse to the surface of the dye-attached metal oxide electrode.
 - Electron transfer to the oxidized dye from a

redox mediator in the electrolyte (I^-) to generate the oxidized form of the redox mediator (I^3). For step (7), the generated I^3 should diffuse to the surface of the counter electrode. One can see the timescale of each step in Figure 2 ^[33]

To maintain the process of electron generation, a dynamic competition of these processes may take place. In this process, the steps indicated with broken lines (3–5) should be slow as compared to the steps (2, 6–8). As shown in Figure 2, the electron migration across the nanocrystalline film (6) and the redox capture of the electron by the oxidized relay (7) take place within milliseconds. Since the square root of the product of the electron lifetime and the diffusion coefficient corresponds to the diffusion length of the electron, all the photogenerated carriers will be collected if the diffusion length is larger than the film thickness.

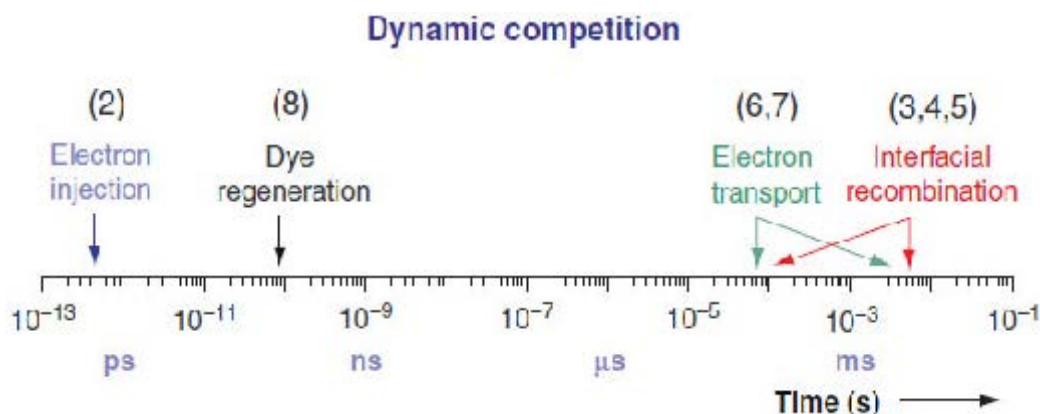


Fig. 2: Dynamics of redox processes involved in the conversion of light to electric power by DSSCs

Dye sensitized photoelectrochemical solar cells have been subject of intensive research in the last years⁹. Such a cell consists of a nanoporous working electrode formed by a sintered film of metal oxide semiconductor nanoparticles with a thickness of several micrometers which serves as electron acceptor and transport layer coated with a monolayer of a dye for light absorption and electron injection into the conduction band of metal oxide. An electrolyte solution, either acetonitrile or a mixture of ethylene/propylene carbonate containing the redox couple iodide/triiodide carbonate containing the redox couple iodide/

triiodide as depicted in Figure 3. Power conversion efficiencies of 10-11 % have been reported³⁴⁻³⁶.

Although these cells show high power conversion efficiencies, their commercial applications are still limited due to stability problems as well as technological aspects of the large module production. The presence of a liquid electrolyte makes the manufacturing process difficult. Therefore, recent efforts in dye sensitized solar cell research are more focusing on replacing the liquid electrolyte with a solid material to eliminate practical problems with sealing. A solid state cell exhibits a

structure similar to the dye sensitized photoelectrochemical cells except for the replacement of electrolyte with a p-type semiconductor or organic hole conductor material³⁷⁻⁴⁰. One of the major differences between dye sensitized solar cells with liquid electrolytes and solid state device lies in the nature of charge transport: in the former case ionic transport is controlled by diffusion whereas in the latter case electronic transport, influenced by conductivity and charge transport mobility, plays an important role^[41]. Polymeric materials are of practical interest as replacement for the electrolyte since they are inexpensive and can be tailored chemically to fit a wide range of technological purposes. Several conducting polymers shown in Figure 4 (a) and (b) such as, poly (bithiophene) (P3BT), poly (3-hexylthiophene) (P3HT) have already been used in solid state dye sensitized solar cells⁴²⁻⁴⁵.

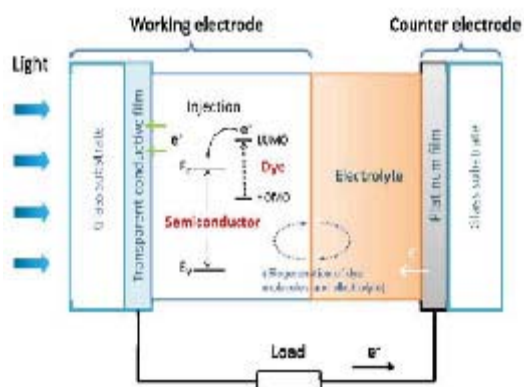


Fig. 3: Outline of a dye-sensitized solar cell constructed with a working electrode consisting of dye-sensitized semiconducting oxide film, a counter electrode made of platinum-coated glass substrate, and electrolyte filled between the working and counter electrodes.

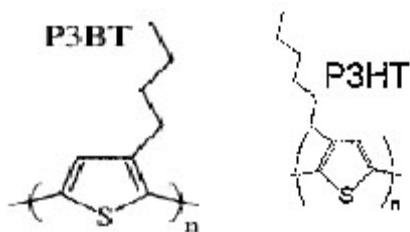


Fig. 4: conducting polymers (a) poly (bithiophene) (P3BT) (b) poly (3-hexylthiophene) (P3HT)

Solid-state polymer/inorganic hybrid dye sensitized solar cell

Compared to dye-sensitized solar cells, the solid nanostructured metal oxide-polymer solar cell has the advantage of utilizing the complete heterostructures for exciton dissociation, potentially leading to thinner devices, since the entire polymer-filled pore volume is available for exciton generation, rather than only a dye monolayer at the metal oxide surface. Further, the rigid structure of metal oxides offers better mechanical stability compared to the organic PVs. The porous structure of nanostructured metal oxide has been investigated as an electron acceptor layer with organic photoactive polymers as the hole conductor extensively. In dye sensitized solar cells organic or complex dyes are generally used to sensitize metal oxide semiconductor (e.g., SiO_2 , ZnO , TiO_2), where the polymers function as a hole transporter to absorb light. The power conversion efficiency of about 5.13% has recently been achieved. ZnO is a direct wide bandgap (3.3 eV at 300 K) II–VI compound semiconductor. ZnO can be grown with simple crystal-growth technologies, resulting in potentially lower costs for ZnO -based devices. High-quality ZnO films can be grown at relatively low temperatures less than 700°C . Further, there are additional properties that make ZnO preferable over other wide bandgap materials. Impurity-created states resulting in enhanced optical absorption at lower energies would be another potential area of interest. A completely different approach on the use of ZnO in organic systems was reported by Gilot et al. They suggested that insertion of an optical spacer into the devices is another approach to increase the total thickness of active layer. The thickness of the device with an optical spacer is not good enough to trap all the incident photons. But, the light intensity inside the device was spatially redistribution due to optical interference effect and it results in enhancing device performance. Over the past few years, research into fabrication techniques for nanocrystals has led to rod-like structures (nanorods) with diameters that range from 2 to 10 nm and lengths ranging from 5 to 100 nm. Due to their intrinsic structural anisotropy, nanorods possess many unique properties that make them potentially better nanocrystals than quantum dots for photovoltaics.

Review of Hybrid solar cell using ZnO

So far, various ZnO nanostructures have been extensively investigated for Solar Cells. In the early reports on ZnO-based DSSCs, ZnO nanoparticles were often used as the photoanode prepared by a conventional doctor blade technique (Keis *et al.*, 2002; Keis *et al.*, 2002). Law *et al.* (2005) presented first the ordered nanowire DSSC. The nanowire DSSC is an exciting variant of the most successful of the excitonic photovoltaic devices. As an ordered topology that increases the rate of electron transport, a nanowire electrode may provide a means to improve the quantum efficiency of DSSCs in the red region of the spectrum, where their performance is currently limited. Law *et al.* (2006) described the construction and performance of DSSCs based on arrays of ZnO nanowires coated with thin shells of amorphous Al_2O_3 or anatase TiO_2 by atomic layer deposition. Wu *et al.* (2007) employed mercurochrome and N3 dyes to be the sensitizers in the ZnO nanowire DSSCs. Hsueh *et al.* (2007) deposited p- Cu_2O onto vertical n-ZnO nanowires prepared on ZnO:Ga/glass templates. With the sputtered Cu_2O , the nanowires became club like (i.e. nanowire with a head). Leschkes *et al.* (2007) combine CdSe semiconductor nanocrystals (or quantum dots) and single-crystal ZnO nanowires to demonstrate a new type of quantum dot-sensitized solar cell. A significant improvement of the efficiency of the ZnO nanowire DSSC has been achieved by the chemical bath deposition of the dense nanoparticles within the interstices of the vertical ZnO-NW anode (Ku *et al.*, 2007). Greene *et al.* (2007) evaluated an ordered organic-inorganic solar cell architecture based on ZnO- TiO_2 core-shell nanorod arrays encased in the hole-conducting polymer P3HT. Chen *et al.* (2009) studied a two-stage growth of a ZnO hierarchical nanostructure consisting of ZnO nanorod at bottom and ZnO nanowire atop in the low pH solutions. Chen *et al.* (2009) reported vertically aligned zinc oxide (ZnO) nanorod arrays coated with gold nanoparticles have been used in Schottky barrier solar cells. Briseno *et al.* (2010) demonstrated the basic operation of an organic/inorganic hybrid single nanowire solar cell. End-functionalized oligo and polythiophenes were grafted onto ZnO nanowires to produce p-n heterojunction nanowires. Gan *et al.* (2010) prepared hybrid ZnO/ TiO_2 photo-anodes for dye-sensitized solar cells

by combining ZnO nanowire arrays and TiO_2 nanoparticles with the assistance of the ultrasonic irradiation assisted dip-coating method. Myung *et al.* (2010) synthesized high-density ZnO-CdS core-shell nano-cable arrays by depositing CdS outer-layers on pre-grown vertically aligned ZnO (wurtzite) nanowire arrays using the chemical vapor deposition method. Seol *et al.* (2010) a novel CdSe/CdS/ZnO nanowire array fabricated by a 3-step solution-based method was used as a photoanode of a quantum dot sensitized solar cell, which generated a maximum power conversion efficiency of 4.15%. Wu *et al.* (2010) reported a 74% enrichment of the efficiency of ZnO nanowire DSSCs is achieved by the addition of a novel light scattering nanocrystalline film.

State-of-the-art in solid-state polymer/inorganic hybrid dye sensitized solar cell

Dye cells have three major parts, a porous layer of metal-oxide [titanium dioxide (TiO_2)] nanoparticles, a monolayer of dye that covers the particles, and a hole-transporter that infiltrates the pores within the transparent conducting oxide (TCO) layer. TCO (e.g., TiO_2 , ZnO) have been used for several decades as a white powder pigment worldwide. A porous layer, or more specifically amesoporous layer, because the particle's sizes range from 10 to 50 nm, is needed within the structure to provide a large surface area onto which the dye will adsorb. The dyes in the highest efficiency cells are based on ruthenium, another rare earth metal, though considerable effort is being made to transition to organic dyes such as porphyrin dyes, the class chlorophyll dyes are in, or "donor- λ -acceptor" dyes, named for the electronic functionality of the molecule's components. The hole-transporting material (HTM) is made of an iodide/triiodide liquid electrolyte in the highest performing cells, though steps are being made to incorporate solid HTMs instead, due to the thermal instability of liquids and the problems posed for sealing by thermal expansion. Both polymers and small molecules are being examined for their use in solid state dye-sensitized solar cells. 2,2',7,7'-tetrakis-(N,N-di-pmethoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) and conducting polymers like poly (3-hexylthiophene) (P3HT) are the most widely used solid-state hole conductors. The dye-sensitized cell begins to perform when a

dye molecule attached to the metal oxide (e.g., titania) surface absorbs a photon. The molecule becomes excited and an electron makes an energetic transition from the ground-state highest occupied molecular orbital (HOMO) to an excited state, the lowest unoccupied molecular orbital (LUMO). Energetically, the LUMO of the dye needs to be higher than the conduction band of the metal oxide such that injection from the dye to metal oxide is favored. Though TiO_2 is an insulator and not typically thought of as a material well-suited to

conducting charge, the large band gap allows electrons to flow relatively freely within its conduction band. Meanwhile, the dye cation is regenerated by electrons from the hole-transport material, P3HT, and the hole diffuses through this layer to the cathode, completing the circuit. Recombination processes occur when electrons and holes meet and release energy, reducing the cell's efficiency. A diagram of a complete dye-sensitized cell and a scheme of electronic processes occurring in the cell are presented in Fig. 5.

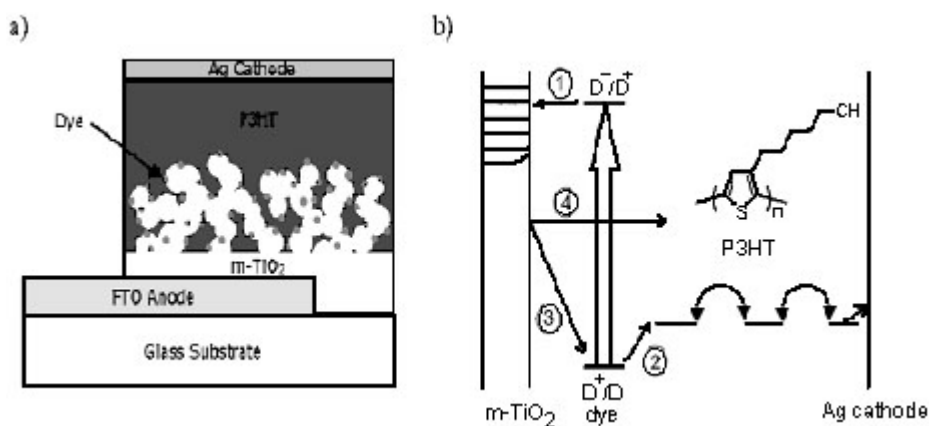


Fig. 5(a): A complete dye-sensitized solar cell showing the mesoporous TiO_2 , the dye, and the hole-transporter, P3HT (b) A schematic of basic electronic processes taking place in a dye-sensitized cell

In fig 5 b, the x-axis corresponding roughly to vertical displacement in the cell shown in a) and the y-axis corresponding relatively to energy levels with respect to vacuum; 1) after absorbing a photon, the dye injects an electron in the conduction band of the TiO_2 ; 2) the hole from the oxidized dye transfers into the hole-transporter, a step equivalent to the regeneration of the dye with electrons from the hole-transporter; 3) and 4) are unfavorable processes in which electrons from the conduction band of TiO_2 recombine with either the oxidized dye or holes in the polymer, respectively. Adapted from Snaith, Schmidt-Mende, 2010 [46].

Enhancement of photoresponse through interaction of near-IR dyes and the polymer hole-transport material

The photoresponse of solid-state dye-sensitized cells can be extended by the incorporation of polymers like P3HT because P3HT can plausibly act as both a hole-transporter and a

light absorber—P3HT is red. The goal is to take advantage of a resonant energy transfer (FRET) process that would be expected to occur if the absorbance spectrum of the dye correctly overlaps with the photoluminescent spectrum of the P3HT and the molecules are within several nanometers of one another. It is known that P3HT photoluminescence at around 725 nm, though the number of dyes with such a small band gap is very low, which presents a challenge to experimentation. If both the P3HT and the dye absorb light and the P3HT serves as an antenna, relaying the energy absorbed to the dye, with the dye injected the electrons into the metal oxide mesostructure, clear panchromatic response could be reasonably attained and efficiencies for solid-state devices markedly improved.

Characterization of polymer/metal oxide hybrid dye sensitized solar cell performance

Solar cell is a device that produces

electricity from sunlight. Upon illumination, photons are absorbed by an active layer in a solar cell, and then electron-hole pairs are generated as excitons. The excitons need to diffuse to a donor-acceptor (DA) interface to dissociate into free charges. After that, electrons and holes need to transport to electrodes through their corresponding percolation pathway^[57]. During these processes, six main steps affect device performance : i) photon absorption (s_a); ii) exciton generation (s_{ex}); iii) exciton diffusion (s_{diff}); iv) exciton dissociation (s_{ed}); v) charge transport (s_{tr}); vi) charge collection (s_{cc}). The h is the yield of each process. These six processes determining a solar cell performance can be better understood in a connection with external quantum efficiency (EQE) of a device. EQE is defined as a percentage of the number of charge carriers collected at the electrode under short-circuit condition to the number of photons incident on the device^[58] EQE can be expressed as the product of the above steps.

$$EQE = \eta_a \times \eta_{ex} \times \eta_{diff} \times \eta_{ed} \times \eta_{tr} \times \eta_{cc} \quad \dots(1)$$

Solar cell efficiency can be calculated from its current density voltage (J-V) characteristic curves. From such curves, open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF) can be obtained. Then energy conversion efficiency can be determined by:

$$\eta = \frac{J_{sc} V_{oc} FF}{P_s} \quad \dots(2)$$

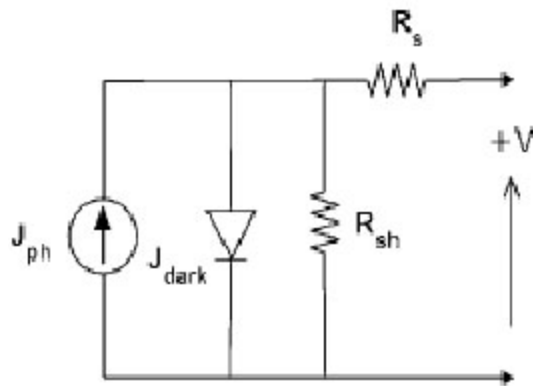


Fig. 6: Equivalent circuit of a solar cell

Where P_s is the incident light power density

Equivalent circuit of a solar cell is shown as Figure 6. A series resistance R_s originates from contact and bulk semiconductor, and a shunt resistance R_{sh} comes from poor diode contact⁴⁷. The J-V characteristics can be described as⁴⁸.

$$J = J_0 \left\{ \exp \left[\frac{q(V - JR_s A)}{n k_B T} \right] - 1 \right\} - \frac{V - JR_s A}{R_{sh} A} - J_{ph}$$

Where k_B is Boltzmann's constant, T is temperature, q is elementary charge, A is device area, n is ideality factor of the diode, J_0 is reverse saturation current density, J_{ph} is photocurrent, R_s is series resistance and R_{sh} is shunt resistance. The J-V curves and photovoltaic parameters including V_{oc} and FF strongly depend on the n , J_0 , R_s , and R_{sh} . Figure 7 shows typical dark and illuminated current density-voltage (J-V) curves, in which three distinctive regions can be seen⁴⁹. The first (I) is the linear region in negative potentials and low positive potentials, in which the current density is dominated by the shunt resistance (R_{sh}). The second (II) is the region at mediate positive regions where the curve shows an exponential behavior and the current density is related to the diode. The third (III) is another linear region in high positive potentials where the current density is related to the series resistance (R_s)^[49]. The ideality factor (n) is a figure 7 which shows how closely a diode behaves like an ideal diode and it is typically deviated from the ideal by recombination in the junction^[50].

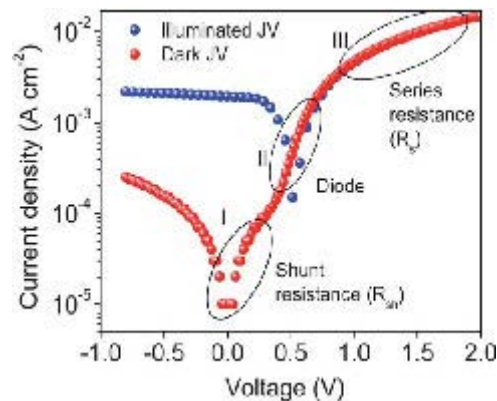


Fig. 7: Dependence of open circuit voltage (V_{oc}) on ideality factor (n) and reverse saturation current density (J_0)

The reverse saturation current density (J_0) is also an important parameter affecting the J-V curves in the exponential regimes and thus cell performance. The J_0 is an indicator of how many charges can overcome the energetic barrier in the reverse direction. These charges are regarded as minority charges at the donor/acceptor interface. In a typical p-n junction, J_0 can be described as^{49, 51, 52}

$$J_0 = J_i \exp\left(\frac{-q\phi}{nkT}\right) \quad \dots(4)$$

Where J_i depends on material purity and x is energetic barrier voltage. x was found to be in good agreement with energy difference of the acceptor's LUMO and the donor's HOMO. The J_0 value increases with increasing temperature (T), but decreases as the material quality (purity) and energetic barrier improve. The series resistance (R_s) is another parameter that affects the J-V characteristics and solar cell performance. The R_s results from limited conductivity of organic layer, contact resistance between organic layer and its corresponding electrodes, and connecting resistance between the electrodes and external circuit. The R_s can reduce the FF and it can also reduce the J_{sc} if it is too high. Generally the R_s has no impact on open circuit voltage (V_{oc}) since the entire current flows through the diode at the V_{oc} condition, but no current flows through the R_s . However, at the points close to the V_{oc} , the R_s greatly affect the J-V curves, providing a simplified method to estimate the R_s by measuring the slope of the J-V curves in the regime close to the V_{oc} [50]. The R_s should be minimized to reduce the energy loss, especially in large area solar cells [49,52]. The shunt resistance (R_{sh}) is also a parameter affecting the J-V characteristics and solar cell performance. The R_{sh} may be related to the device structure and film morphology. For example, R_{sh} can be lowered by the leakage current through the pinholes and recombination of charge carriers in the devices [53]. The morphology and thickness can be processed with care to reduce the pinholes and recombination in the devices so that the R_{sh} can be increased. The R_{sh} needs to be maximized to reduce the power loss caused by the current that bypasses the solar cell junction and load through an alternate current path from the low R_{sh} . A small R_{sh} lowers the current

flowing through the diode (junction) and thus reduces the V_{oc} . A simplified way to approximately calculate the R_{sh} is to measure the slope of the J-V curves in the regime close to the J_{sc} [50]. The above discussed n , J_0 , R_s and R_{sh} can strongly affect the photovoltaic parameters including V_{oc} , FF, J_{sc} and cell efficiency (η). V_{oc} is defined as the voltage across the cell under illumination with a zero current at which the dark current and short circuit photocurrent was exactly cancelled out [54]. By solving the current density verse voltage equation (eq 3), V_{oc} can be derived as:

$$V_{oc} = \frac{nk_B T}{q} \ln\left(\frac{J_{ph}}{J_0} + 1 - \frac{V_{oc}}{J_0 R_{sh}}\right) \quad \dots(5)$$

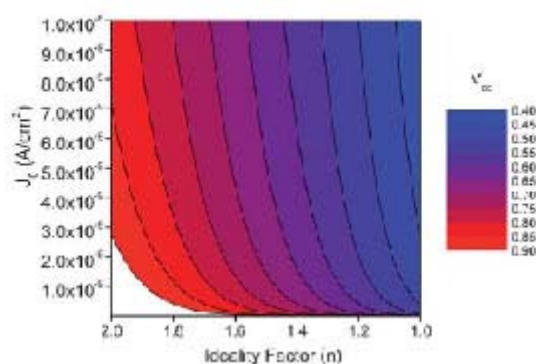


Fig. 8: Dependence of open circuit voltage (V_{oc}) on ideality factor (n) and reverse saturation current density (J_0)

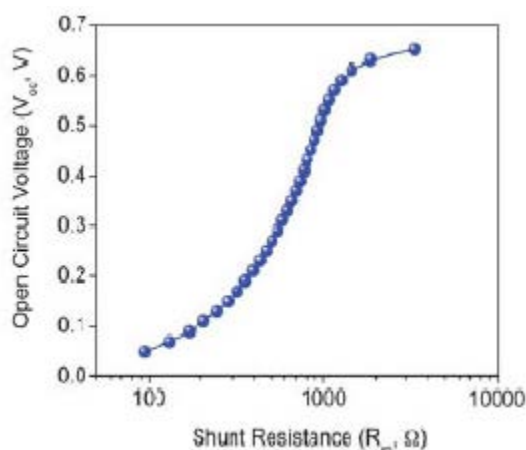


Fig. 9: Dependence of open circuit voltage (V_{oc}) on shunt resistance (R_{sh})

Figure 8 shows the dependence of V_{oc} on n and J_0 , calculated using eq. 6 that is derived from eq. 5 by assuming an infinitely large R_{sh} . It can be seen that the decrease of J_0 and increase of n can significantly increase the V_{oc} .

$$V_{oc} = \frac{nk_B T}{q} \ln \left(\frac{J_{ph}}{J_0} + 1 \right) \quad \dots(6)$$

$$FF(R_s, R_{sh}) \approx FF(0, \infty) \left[\left(1 - \frac{J_{sc} R_s}{V_{oc}} \right) - \left(\frac{V_{oc}}{J_{sc} R_{sh}} \right) \right] \dots(7)$$

When the R_{sh} is not large enough, it can also affect the V_{oc} of Polymer–inorganic hybrid solar cells. Figure 9 shows the dependence of V_{oc} on the R_{sh} plotted using eq 5. The FF is greatly affected by the R_s and R_{sh} . The relationship has been reported previously [55]. High FF can be achieved with low R_s and high R_{sh} . Therefore, the R_s needs to be minimized and the R_{sh} should be maximized to ensure a high FF.

Summary and outcome

Polymer–inorganic hybrid solar cells have gained extensive attention and recent research progress. While power conversion efficiencies exceeding 3% have recently been achieved for polymer–inorganic hybrid solar cells, these efficiencies are still lower than those of polymer–fullerene solar cells, which have recently reached as high as 8.13%. In physically blended polymer–inorganic hybrid solar cells, although charge separation has improved. To resolve poor electron transport, pre-synthesized inorganic nanostructures have been used to either infiltrate the polymers or in situ polymerize donor materials within the nanopores. Among these approaches, ordered nanostructures are considered an ideal configuration for achieving high efficiency utilizing one dimensional (1-D) inorganic semiconductors to realize continuous charge transport pathways [56]. To further improve device performance of polymer–inorganic hybrid solar cells, several challenges need to be considered including

morphology control, polymer and inorganic material engineering, and donor–acceptor interface modification. A more efficient morphology control of polymer–inorganic active layer is needed to achieve not only an effective charge separation, but also an efficient charge transport and collection. Numerous experiments have been designed and carried out to test the effects of additives and the effects of atmospheric oxygen on the conducting polymer hole-transporter, P3HT. Tests of additives in devices have confirmed and in some cases optimal concentrations have been determined. A fairly highly efficient device concept for solid-state hybrid dye-sensitized solar cells has been realized. The device is fabricated from inorganic nanoparticles as electron transporting material, an organic hole transport materials with photoexcited dye molecules as electron injector into the n-type material and the hole accepting and transporting properties of polymer like P3HT. Since the dye is regenerated by the hole injection in the p-type material, the operating principle of DSC based on liquid electrolyte is similar to that of solid-state hybrid DSC. It has been investigated through I-V characterization that the device shows open-circuit voltages of up to 550 mV and short circuit currents up to 11 mA/cm². The results show the usefulness of conducting polymers as hole transport materials for the possible replacement of the liquid electrolyte in nanoporous metal oxide semiconductor type solar cells and optimization of these devices is a promising approach from both academic and industrial sides. These advances are a testimony to the rapid progress being made in the field of DSCs and to the promise they hold for growing into a viable technology as a low-cost renewable energy source. Several challenging scientific and technological problems, however, remain to be solved. The major problems associated with solid-state cells seem to be the imperfect filling of a transparent hole conductor into the pores between the nanoparticles and the nature of the contact between the p-type semiconductor and the dye monolayer.

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