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A REVIEW ON PHOTOVOLTAIC PRODUCTION TECHNOLOGIES

Sule Erten ELA

Ege University Solar Energy Institute 35100, Bornova Izmir, Turkey
sule.erten@ege.edu.tr

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* Corresponding author

Abstract

Tang's introduction of two-layer organic photovoltaic cell, fabricated from copper phthalocyanine and a perylene tetracarboxylic solid thin films, has opened the novel era of organic solar cells. A power conversion efficiency of about 1% has been achieved under simulated 1.5 AM sun illumination. Then Graetzel cell has been developed in 1991. And afterwards solid state dye sensitized solar cells have been developed. And new era has opened for photovoltaic production technologies. This review summarizes working principle of photovoltaic technologies.

Keywords: Photovoltaic production technologies, Plastic solar cells, Tang cell, Graetzel cell

FOTOVOLTAİK ÜRETİM TEKNOLOJİLERİ ÜZERİNE BİR ARAŞTIRMA

Özet

Tang'ın organik fotovoltaik aktif tabakasında bakır ftalosiyanin ve perilen diimid ince filmini kullanması organik güneş pilleri için yeni bir çağı araladı. Standard koşullarda % 1 verim ile başlayan bu serüven 1991 de Gratzel hücrelerin gelişimi ile devam etti ve sonrasında katı hal güneş hücrelerinin gelişimini tetikledi. Böylece fotovoltaik üretim teknolojilerinde yeni bir dönem başladı. Bu yayın geliştirilen farklı çeşit fotovoltaik pillerin çalışma prensiplerini özetlemektedir.

Anahtar Kelimeler: Fotovoltaik üretim teknolojileri, Plastik güneş pilleri, Tang hücresi ve Graetzel hücresi

1 Introduction

Dye sensitized solar cells, Tang cell, Hybrid organic/inorganic materials are promising candidates in photovoltaic (PV) cells production processes. The development of organic–inorganic hybrid solar cells received widespread attention because of its improved performance due to nanoscale fabrication of inorganic components and put a path towards enhanced conversion efficiency. This review summarizes working principle of organic photovoltaic technologies.

2 Dye sensitized solar cells

A novel molecular photovoltaic that simulates the photosynthesis mechanism of a leaf, is introduced by Graetzel, named as dye sensitized solar cell [1-3]. In the dye-sensitized nanocrystalline photovoltaic cell, visible light is absorbed by a organic material adsorbed on the surface of a mesoporous nanocrystalline TiO_2 electrode, and charge separation occurs by rapid electron injection into the TiO_2 while the dye cation is regenerated by a redox active electrolyte. Photoinjected electrons must travel through the porous film to the back contact to complete the circuit. At short circuit this process is apparently very efficient, although slow, and gives rise to a remarkably high internal quantum efficiency [4]. Dye-sensitized TiO_2 solar cells, DSSC, are a promising alternative for the development of a new generation of photovoltaic technology. DSSCs are a successful combination of materials, consisting of a transparent electrode coated with a dye-sensitized film of nanocrystalline particles of TiO_2, an electrolyte containing a suitable redox-couple and a Pt coated counter-electrode (Figure 1). In General, Ru bipyridyl complexes are commonly used as the dye sensitizers. The light-to-energy conversion performance of the cell depends on the relative energy levels of the semiconductor and dye and on the kinetics of the electron-transfer processes at the sensitized semiconductor-electrolyte interface. The rate of these processes depends on the properties of its components [5].

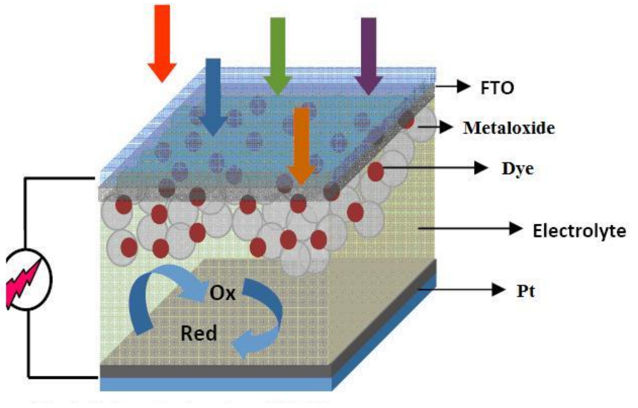

Figure 1. Representation of a dye-sensitized Graetzel type TiO_2 solar cell and the processes involved in energy conversion [6].

The most efficient sensitizers in nanocrystalline TiO_2 dye sensitized solar cell are based on bipyridyl complexes of transition metals, particularly ruthenium (II). In General, Ru complexes are suitable as photosensitizers for semiconductors because they show a strong and broad absorption band in the visible range due to metal to ligand charge transfer leading to excited states with long lifetimes. Also, the oxidized Ru(III) complex has long-term chemical stability [6].

Conversion efficiency of more than 10% under AM1.5 sun (100 $mWcm^{-2}$) irradiation conditions was reported by Graetzel when liquid electrolytes consisting of liquid I^-/I^{3-} redox electrolyte were employed [3,6]. The use of liquid electrolyte causes the problems of evaporation or leak of the electrolyte due to difficulty in hermetic sealing. Low temperatures may also induce crystallization of the iodide salts and high temperatures may enhance the leak of the volatile organic solvent and iodine. Replacing the liquid electrolyte with solid-state hole-transport materials is now a challenging research subject for improving the long-time stability of the DSSC cells for technological compatibilities. Attempts have been made to replace the liquid electrolyte with *p*-type semiconductors [7,8] or organic hole transport materials (HTMs). Graetzel group has employed a three dimentional tetraarylmino derivative (2,2′,7,7′-tetrakis(N,N-di-*p*-methoxyphenyl-amine)-9,9′-spirobifluorene), *spiro*-MeOTAD. The charge-transfer events taking place at the junction are depicted in Figure 3. Visible light is absorbed by the sensitizer Ruthenium dye. Electron injection from the excited state of the dye into the conduction band of TiO_2 is followed by subsequent hole transfer from the photooxidized dye to the organic hole conductor, *spiro*-OMeTAD, regenerating the dye's original ground state.

The latter process competes with recapture of the injected electron by the oxidized Ruthenium dye [9-12].

However, the conversion efficiency of these devices was relatively low particularly under high light irradiance ($\eta<4\%$) when compared to the liquid electrolyte systems ($\eta>10\%$). Due to high frequencies of charge recombination to HTMs and/or poor electronic contact between dye molecules and the HTMs caused by incomplete penetration of solid HTMs in the void of the mesoporous TiO_2 electrodes. To avoid these problems, Yanagida proposed all solid DSSCs using in situ photo-electrochemical polymerization of pyrrole as a hole transport phase in the void of the *cis*-$Ru^{II}(L)_2(NCS^-)_2$, (L = 2,2′-bipyridine-4,4′-dicarboxylic acid) adsorbed mesoporous TiO_2 electrodes. All-solid state dye sensitized solar cells, fabricated using in situ polymerized conducting polymers, PPy or PEDOT, as the hole transport phase in place of liquid electrolytes had given conversion efficiencies lower than $\eta>1\%$ [13,14].

Durrant's polymer electrolyte of poly(epichlorohydrin-*co*-ethylene oxide) containing NaI and I_2, have yielded solar to electrical energy conversion efficiencies of up to 2.6%. Durrant has also shown fine discussions on interfacial electron transfer kinetics for the performance of dye sensitized photoelectrochemical solar cells. It is concluded that the primary factor controlling the charge recombination dynamics in dye sensitized, nanocrystalline TiO_2 films is the spatial separation of the dye cation from the electrode surface. In particular, it is show that for the ruthenium dye series, the use of NCS rather than CN results in a 2 Å shift in the dye cation HOMO orbital away from the electrode surface, causing a 7-fold retardation of the recombination dynamics, resulting in the remarkably slow recombination Dynamics [15-18].
Moser has discussed the rationale for kinetic heterogeneity of ultra fast light-induced electron transfer from Ru dye sensitizers to nanocrystalline TiO_2 [19]. The conformal growth of an over layer of Al_2O_3 on a nanocrystalline TiO_2 film is shown to result in a 4-fold retardation of interfacial charge recombination, and a 30% improvement in photovoltaic device efficiency [20, 21].

Overall results of the project presents the over 11% efficiencies dye sensitized solar cells, and over 5% efficiencies for commercial DSSC panels with liquid electrolyte and near to 4% efficiencies for all solid state flexible dye sensitized solar cells employing triarylamine derivatives [22-25]. Arakawa reports employment of diimine(diketonato)ruthenium(II) complexes and 8.4% efficiency of DSSC with ruthenium black dye for a size of 10x10 cm modüle [26]. DSSCs are available in different colours and opacities, so they can replace windows and facades in buildings and other structures. Despite the easy fabrication methods, liquid junction DSSCs currently meet engineering challenges, such as sealing methods and the prevention of electrolyte loss. Miyasaka recently reports a full-plastic DSSC module with 3% efficiency and single DSSC cell at 5.5% efficiency [27]. Meng reports DSSCs with LiI/ethanol/SiO_2 based gel electrolyte at 6.1% [28,29] and Lin reports DSSCs with quasi –solid LiI/I_2/HMImI electrolyte and poly(4-vinylpyridine-co-acrylonitrile) as chemically cross-linking gelator at 5.15% efficieny [30]. An iodine free solid state DSSC is reported by Ikeda at 4.1% efficiency comprising of polyaniline, carbon black and ethyleneoxide-type ionic liquid paste [31]. Hara reports 7.4% efficiencies with novel coumarine dyes in liquid junction DSSCs [32].
Mixed oxide electrodes (MgO-TiO_2) are shown to increase open circuit voltage, V_{oc}, of DSSCs [33]. A similar observation was detected with Nb_2O_5 bay Yanagida et al.[34] and influence of TiO_2 nanoparticle size on electron diffusion and recombination in dye-sensitized TiO_2 solar cells has been investigated throughly [35]. Quasi-solid dye sensitized solar cells (Q-DSSC), fabricated by employing gel electrolytes containing ionic liquids and gelators have shown increased photo-currents, attributed to decreasing resistances in the TiO_2 layers, [36, 37]. Carboxylic acid treatments of TiO_2 films are shown to be enhance the DSSC efficiencies about 4% [38]. Hagfeldt et al. have shown that *p*-type nanostructured semi-conductor NiO in

tandem dye-sensitized solar cells, would enhance the solar cell performance [39]. Parkinson investigated and analyzed squaraine dye surface morphology and sensitization behavior on SnS_2 electrodes and dicarboxylated thiacyanine dyes[40-42]. As an overview to all of the developments on DSSCs, Kang reports a manufacturing method for transparent electric windows using dye-sensitized TiO_2 solar cells [43].

Gregg has experimented carboxyl derivatives perylene as a new sensitizing dye-semiconductor system on SnO_2 electrode [44]. Replacement of TiO_2 electrode with SnO_2 is favorable based on the fact that the LUMO energy levels of perylenes are lower with respect ruthenium dyes. Overall maximum cell efficiency was reported to be 0.9% from perylene-3,4-dicarboxylic acid-9,10-(5-phenanthroline) carboximide only.

Matsui examined 9-substituted 3,4-perylenedicarboxylic anhydride sensitizers in zinc oxide electrode solar. Maximum solar-light-to-electricity conversion efficiency was observed to be only η=0.5% [45]. Perylene dimides experimented by Gregg[46] had given low efficiencies in Graetzel type DSScs, $\eta <$ 0.2%. Solid-state, dye-sensitized nanocrystalline TiO_2 solar cells (DSSC) based on perylene derivative dye, N,N′-bis-2-(1-hydoxy-4-methylpentyl)-3,4,9,10-perylene bis(dicarboximide) (HMPER) with two different polythiophenes as hole conductors; i.e. poly(3-octyl thiophene) (P3OT) and poly (3-hexyl thiophene) (P3HT), respectively constructed by Icli-Sariciftci, had given also low efficiencies, $\eta <$ 0.1% [47]. Monoanhydride perylenes, capable of attaching to nanostructured TiO_2 surface with carboxyl groups, has shown higher solar conversion efficiencies, highest 0.92% efficiency with perylene-3,4-dicarboxylic acid anhydride-*N*-(dodecyl)-9,10-carboximide, under 1.5 AM (100 mW/cm^2) solar emission [48]. Solar conversion efficiency was doubled under 190 mW/cm^2 solar emission of xenon arc lamp. Icli et al. has shown that peryleneimide dyes, that are known to form layered self-assembled in π-π stacks, [49,50] give poor photo-electron injection in dye-sensitized solar cells. Presence of branched long alkyl chains prevents the self-assembled in π-π stacking and as a result solar conversion efficiencies enhances [51]. Introduction of olefinic bond conjugated oligothiophene moieties brings a new era of dyes for DSSCs. Hara et al. has shown enhanced electron lifetimes and J_{sc} = 14.0 mA cm^{-2}, V_{oc} = 0.74 V, and fill factor FF = 0.74, η = 7.7% efficiencies with alkyl chain substituted dyes [52].

3 Tang Cell

Tang's introduction of two-layer organic photovoltaic cell, fabricated from copper phthalocyanine and a perylene tetracarboxylic solid thin films, has opened the novel era of organic solar cells. A power conversion efficiency of about 1% has been achieved under simulated 1.5 AM sun illumination. The charge-generation efficiency is found to be relatively independent of the bias voltage, resulting in cells with fill factor values as high as 0.65. The interface between the two organic materials, rather than the electrode/organic contacts, is as expected crucial in determining the photovoltaic properties [53]. Friend-Bradley has applied poly(**p**-phenylene vinylene)-PPV conducting polymer in light-emitting diodes-LED, proving the possibility of using these materials in photo-electronic devices. Mechanism is based on the injection of an electron and a hole on the conjugated chain can lead to a self-localized excited state which can then decay radiatively[54]. Following Heeger announced that light-emitting diodes can be fabricated by casting the polymer film from solution. The mechanism for light emission was outlined by tunneling of electrons from the rectifying metal contact into the gap states of the positive polaron majority carriers which dominates the current flow [55].

4 Plastic Solar Cell

Independently, Yoshino[56] and Sariciftci-Heeger-Wudl[57] have reported investigations on the photophysics of mixtures of conjugated polymers and fullerenes. These studies paved the way to opening of a novel polymeric photovoltaic devices, named as Plastic Solar Cells, and Sariciftci et al. has introduced pioneering applications. In order to be able to enhance the power efficiencies of solar cell devices fullerene-C_{60} addition to the conjugated polymers led to the development of polymer–fullerene bulk heterojunction, where fullerene-C_{60} was dispersed in semiconductor polymer. Photoinduced electron transfer occurs when it is energetically favorable for the electron in the S_1-excited state of the *p*-type polymer to be transferred to the much more electronegative *n*-C_{60}, thus resulting in an effective quenching of the excitonic photoluminescence of the polymer [58]. These developments created two types of organic solar cells; i) Tang type bilayer-OSC and ii) *p*-polymer/*n*-fullerene bulk heterojunction-BHJSC. Figures 2 and 3 illustrates both of these organic solar cell types [59]. Figure 2 represents the schematic energy diagram of a bilayer solar cell: the excitons photogenerated in the donor or in the acceptor can diffuse to the interface where they are dissociated; the released electrons are transferred to the *n*-fullerene (acceptors); holes and electrons then diffuse or drift in their respective environment to their respective electrode. The main drawback of this concept resides in the rather short diffusion length of excitons (5–15 nm). Thus, only those that are created within a distance from the sharp donor–acceptor interface shorter than their diffusion length may contribute to the photocurrent. This limits drastically the photocurrent and hence the overall efficiency of the bilayer solar cells[60, 61].

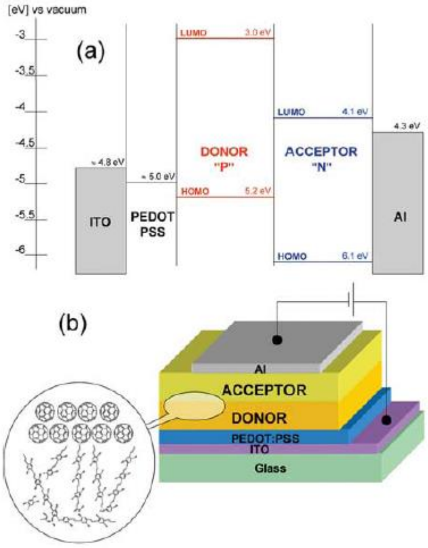

Figure 2. (a) Energetic diagram and (b) cross section of a bilayer Tang type polymer organic solar cell. The energetic

levels given in (a) for the donor and the acceptor correspond to MDMO-PPV and PCBM, respectively [59].

In order overcome the limitations in bilayer-polymer organic solar cell, the surface area of the donor–acceptor interface can to be increased by creating a mixture of donor and acceptor materials with a nanoscale phase separation resulting in a three-dimensional interpenetrating network, the “bulk heterojunction”, as seen in Figure 2. Contrary to the situation in bilayer-OSC, excitons experience dissociation wherever they are created within the bulk. As a result, the next interface between donor and acceptor phases is present within the exciton diffusion length everywhere in the device. Another problem for polymer organic solar cells is the stability; the lifetime of polymer solar cells like the PPV-based ones is rather poor in the ambient environment, since photodegradation induced by oxygen and moisture occurs. Moreover, top electrode materials are usually chosen among the low work function metals like Al in order to optimize the V_{oc}. These metals undergo severe oxidation when exposed to air, leading to the formation of insulating thin oxide barriers that hinder electrical conduction [59-63]. Isolation of the solar cells with sealants, to prevent oxygen and moisture contacts, are experimented by the authors in order to increase the lifetimes of polymer based organic solar cells [59]. Fullerenes have only very weak absorption in the visible spectral range; therefore the main component of the photoactive blend is actually almost optically inactive. To overcome this limitation, alternative electron acceptors that are capable of absorbing visible light preferably at the lower energy part of the spectra, $CuInS_2$ is being experimented as inorganic *n*-type semiconductors. Overall efficiencies have improved in bulk-heterojuction polymer solar cell-BHJSC with respect to bilayer devices, but did not exceed 3% under AM 1.5. Hummelen-Sariciftci have shown that power conversion efficiency of organic photovoltaic devices based on a conjugated polymer/methanofullerene blend is dramatically affected by molecular morphology [64,65]. It is apparent that power efficiencies are still well below 5% a value which is at the lower limit of interest in practical ‘‘niche’’ applications, and falling well short of 24% and 17% achieved for crystalline and thin film Si, respectively [66].

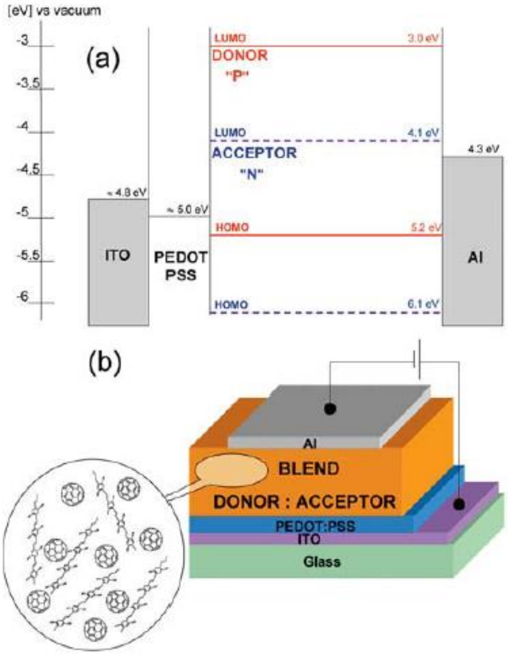

Figure 3. (a) Energetic diagram and (b) cross section of a bulk-hererojuction polymer solar cell-BHJSC. The energetic levels given in (a) for the donor and the acceptor correspond to MDMO-PPV and PCBM, respectively [59].

A fine review of Forrest[66] discusses the physics underlying the operation of single and multiple heterojunction, vacuum-deposited organic solar cells based on small molecular weight thin films. Organic solar cells are divided as single heterojunction and multiple heterojunction solar cells. Single heterojunction devices are discussed under bilayer and double heterostructure devices. Mechanisms of solar cell devices are examined in line with theoretical evaluations and experimental results. It is reported that in single heterojunction cells, the need for direct contact between the deposited electrode and the active organics leads to quenching of excitons. The double heterojunction, is shown to confine excitons within the active layers, allowing substantially higher internal efficiencies to be achieved. Energy level offsets at heterojunctions are essential to the operation of organic detectors because of the fundamental nature of the photogeneration process in organic materials.

For single heterojunction cells, the need for direct contact between the deposited electrode and the active organics leads to quenching of excitons. Low efficiencies of single layer solar cells are evident in Table 1. An improved device architecture in the double heterojunction arises from the confinement of excitons within the active layers, allowing substantially higher internal efficiencies. Combining the double heterostructure with novel light trapping schemes, devices with external efficiencies approaching their internal efficiency are obtained; η=1.0% under 1 sun AM1.5 illumination, devices with external power conversion efficiencies of η=2.4% . Forrest has shown that using materials with extended exciton diffusion lengths L_D, such as C_{60}, can create a highly efficient double heterojunction photovoltaic cell at 3.6% solar power efficiency under 1 sun AM1.5 illumination [66, 67].

Zhang-Hummelen reports a bulk heterojunction solar cells based on blends of photoactive layers of polyfluorene copolymer Poly((2,7-(9-(29-ethylhexyl)-9-hexyl-fluorene)-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole))-*co*-(2,7-(9-(2′-ethylhexyl)-9-hexyl-fluorene)-*alt*-2,5-*thiophene*))-(LBPF3) acting as electron donor, and (6,6)-phenyl-C_{61}-butyric acid methylester (PCBM), acting as electron acceptor, at 1.7% efficiency [68]. Chen-Cao has constructed an organic solar cell of ITO/PEDOT/PVC/emitter/CsF/Al at 0.91% efficiency, emitter: 9,9′-dioctylfluorene and 4,7-di-2-thienyl-2,1,3-benzoselenadiazole, PVC: poly(vinylcarbazole) [69]. First report of conformal deposition of parylene on bulk heterojunction solar cells, and the effects of protection on performance characteristics is demonstrated by Zakhidov [70]. The intramolecular photoinduced energy and electron transfer in a fullerene–oligothiophene–fullerene triad with nine thiophene units (C_{60}–9T–C_{60}) has been thoughly clarified by Janssen, photoexcitation of the oligothiophene and intramolecular electron transfer from the oligothiophene to the fullerene were found at time constants of 95 fs and 10 ps, respectively, charge-separated state with a lifetime of 80 ps [71, 72]. Kroon has shown the photochemical degradation of the polymers upon prolonged irradiation on bulk heterojunction solar cells causing detrimental effects, by a thorough systematic stability studies on encapsulated laboratory cells [73].
Morikawa has shown a %2 efficiency for the Tang's cell under 10 mW/cm^2 irradiation % 1 under 1.5 AM solar irradiation [74]. Meissner experimented also monolayer and bilayer solar cells constructed from perylene tetra carboxylic acid, zinc phthalocyanine, zinc phthalocyanine-C_{60} and titanyl phthalocyanine (TiOPc)-C_{60} at <%2 efficiencies under simulated 1.5 AM solar radiation[75-82]. Yamagida reports a monolayer TiO_2/PPY-C/Au cell at only %0.2 of 1.5 AM, PPY: 3-(trimethoxysilyl) propyl methacrylate [83].

A *p*-i-*n*-type heterojunction for organic solar cells was described where the active region is sandwiched between two doped wide-gap layers in the form *p*-doped layer and *n*-doped layer, such as ITO/*p*-MeO-TPD/ZnPc:C_{60}/C_{60}/*n*-C_{60}/Al structure. These tandem cells have shown ~2.4% efficiency [84, 85]. Power conversion efficiencies of 3.9% have been achieved by blending polymers with electron-accepting materials such as C_{60} derivatives, cadmium selenide, and titanium dioxide [86]. McGehee predicts that efficiencies higher than 10% can be achieved by optimizing the cell's architecture to promote efficient exciton splitting and charge transport and by reducing the band gap of the polymer so that a larger fraction of the solar spectrum can be absorbed[87-89].

4 Conclusion

This review summarizes the working principle of dye sensitized solar cells, Tang Cell and Plastic solar cells. Today organic photovoltaic production Technologies have been developed all over the World. And now all scientists in the worlds are working to to develop these Technologies to reduce the cost of solar cells. New generation photovoltaics are future low cost Technologies for solar cell senergy conversion.

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