Chapter 3

Applications of PEDOT:PSS in Solar Cells

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Abstract

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is increasingly being used in the field of printed and flexible electronics in the form of electrode as well as intermediate layer. PEDOT:PSS belongs to the family of intrinsically conducting polymer materials whose members can conduct electricity in spite of their organic nature without the presence of metals. It is non-toxic, stable in the presence of air and humidity. Above all, it can be easily processed through conventional means. This chapter deals with the applications of PEDOT:PSS in organic solar cells (OSCs), dye sensitized solar cells (DSSCs) and silicon based hybrid solar cells. PEDOT:PSS is being used as electrode, buffer layer and hole conductive layer. It could manipulate the catalytic nature of counter electrode used in DSSCs. Whereas it may help to manipulate the morphological character in Si based hybrid solar cells along with enhancement of cell performance.

Keywords

Dye Sensitized Solar Cells, Hole Transport Layer, Inverted Organic Solar Cells, Organic Solar Cells, PEDOT:PSS, Silicon Based Hybrid Solar Cells

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1. Introduction

The solar or photovoltaic cells (SCs), converting light into electrical energy is grouped into three generations. The traditional first generation solar cells are composed of crystalline silicon. The second generation thin film solar cells are composed of amorphous silicon, cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) cells. The third generation thin-film solar cells are known as emerging photovoltaics because they are under exploration stage and can be based on inorganic or organic materials, organometallic compounds, composites, polymers, etc. Inorganic materials are being replaced with conjugated polymers in solar cells due to several advantages such as cheap processing, eco-friendly technology, etc. Out of these, conducting polymers come under the prime focus of scientific community in order to attain cheap and highly efficient solar cells.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Scheme 1), the intrinsically conducting polymer, is widely used in doped state for preparing solar cells, supercapacitors, sensors, organic light emitting diodes (OLEDs), etc. due to its high electrical conductivity. The PEDOT:PSS film is highly transparent in the visible region, extremely flexible and thermally stable. Therefore, it can be used as organic solar cells (OSCs) anode buffer layer. Low-resistivity PEDOT:PSS layers increase the performance of OSCs by improving the power conversion efficiency (PCE). Platinum (Pt) exhibits efficient catalytic activity for triiodide/iodide redox reaction but it is expensive. PEDOT:PSS is an option to develop cheaper counter electrode (CE) replacement of this expensive metal in dye sensitized solar cells (DSSCs).

(a) PEDOT

(b) PSS

Scheme 1 (a) Structure of PEDOT (b) structure of PSS.

PEDOT:PSS may serve as the catalyst for triiodide/iodide redox reaction. Its excellent catalytic activity and low cost has attracted researchers from around the world. PEDOT:PSS acts as hole transport layer (HTL) and helps in interface improvement along with gap reduction between active layers and indium-tin oxide (ITO) lowest unoccupied molecular orbital (LUMO) levels. The phase separation between PEDOT and PSS causes low conductivity and improper contact between PEDOT:PSS and organic layer [1]. Surface morphology and conductivity of PEDOT:PSS films depends on particle size, PSS

proportion, viscosity of solution, etc. This chapter deals with application of PEDOT:PSS in OSCs, inverted OSCs, DSSCs and Si based hybrid solar cells.

2. Organic solar cells

Organic solar cells (OSCs) also known as plastic solar cell are based on organic electronics and utilize small organic molecules or conductive organic polymers for charge transport and light absorption. They generally contain electron donor and acceptor layers sandwiched between electron/hole layer and electrode. Blocking layer and electrode used depend on the structure of device, whether regular or inverted. Only difference between the regular or inverted devices is that the direction of exit of electric charges is opposite in the two due to the reversal of positive and negative electrodes. Inverted OSCs offer longer lifetimes as compared to the regular OSCs.

2.1 PEDOT:PSS as electrode

Kawano et al. (2006) investigated polymer and fullerene derivative based stacked bulk hetero-junction (BHJ) OSCs obtained by spin-coating method. Poly(2-methoxy-5-3,7-dimethyloctyloxy)-1,4-phenylene vinylene (MDMO-PPV) : [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) blend and 40 nm thick PEDOT:PSS film were used as the active layer and hole conductive layer, respectively [2]. Open-circuit voltage (V_{oc}) is independent of the number of photoactive layers. It is determined by the addition of V_{oc} of the two stacked BHJ OSCs. V_{oc} of 1.34 V was obtained which is about 1.6 times larger than that of single BHJ OSCs. Hoppe and co-workers [3] determined the optical constants for polymer/fullerene based BHJ OSCs having a structure of glass\ITO\PEDOT:PSS\((3,7\text{-dimethyloctyloxy methyloxy poly(paraphenylene vinylene):(1-(3-methoxycarbonyl)propyl-1-phenyl [6,6]C₆₁) blend [MDMO-PPV:PCBM])\Al. Model dielectric functions were fitted to reflection and transmission spectra of the layers present in the OSCs.

Transparent gold (Au), copper (Cu), and silver (Ag) metal-wire electrodes were prepared through nanoimprint lithography on glass substrate coated with PEDOT:PSS [4]. Poly(dimethylsiloxane) (PDMS) was used as a mold. PDMS stamp was prepared through a nano imprinted template and 40 nm-thick layer of Cu was deposited on it. The PEDOT:PSS film was spin-casted on a glass substrate and PDMS stamp was coated over it. Patterned Cu electrodes were obtained on the PEDOT:PSS layer after peeling the PDMS stamp. Anode's work function for Au, Cu, and Ag were found to be 5.22, 4.65 and 4.0 eV respectively. Metal electrodes having work function lower than PEDOT:PSS offered better charge transfer to the electrode from the PEDOT:PSS layer. This resulted into enhanced fill factors (FFs) and power conversion efficiencies (PCEs). The optical

transmittance of Au, Cu, and Ag based electrodes along with indium tin oxide (ITO) based control device measured in visible region with reference to air. ITO, Au, Cu, and Ag electrodes have transmittance of 87, 84, 83 and 78 %, respectively in the visible range. Ag electrode has transmittance lower than Au and Cu electrodes in spite of similar line-width and thickness due to dispersion properties of Ag. ITO, Au, Cu, and Ag electrodes had sheet resistance of 12, 24, 28, 23 $\Omega\cdot\text{sq}^{-1}$ respectively. Decrease in line-width is responsible for higher sheet resistance. Thicker metal layer deposition can compensate this issue. The current-voltage properties of Au, Cu, and Ag electrode based solar cells and were found similar to the ITO electrode, demonstrating the interchangeability of these electrodes.

Kang and co-workers (2010) [5] have reported a transparent electrode of Cu nanowire mesh which was prepared through transfer printing using the flexible PDMS stamp (Figure 1) [5]. The Cu/Ti layer was given a short O_2 plasma treatment followed by transferring the metal to 30 nm thick PEDOT:PSS layer which was spin coated over PET substrate. This electrode exhibits high flexibility, optical transmittance and conductance as compared to the common ITO electrode settled on plastic substrates.

Figure 1 Schematic diagram of PDMS stamp fabrication and the Cu nanowire mesh electrode transfer printing (Reprinted with permission from Elsevier, [5]).

Ultrathin and light weight OSCs with improved flexibility offering 4% PCE were developed by Kaltenbrunner et al. (2012) [6]. These devices were capable of surviving a quasi-linear compression of less than 70%, cyclic stretching and compression of 50% for about 20 full cycles without much decrease in device performance. Qu et al. (2011) [7] studied the role of plasmonic metal nanoparticles in improvement of optical absorption of thin film Poly(3-hexylthiophene) : phenyl-C61-butyric acid methyl ester (P3HT:PCBM) OSCs through finite element method and 3-D model. When Ag nanoparticles were used at active layer and anode layer (PEDOT:PSS) interface, plasmonic enhancement of more than 100% could be gained.

Kymakis et al. (2007) [8] prepared single wall carbon nanotube (SWCNTs) and PEDOT:PSS blends in order to be used as hole collecting electrode in P3HT:PCBM (donor:acceptor) OSCs. This improved the conductivity and optical transparency. Devices having PEDOT:PSS-SWCNTs/P3HT-PCBM/Al, ITO/PEDOT:PSS/P3HT-PCBM/Al and PEDOT:PSS/P3HT-PCBM/Al were studied. PCE of 1.3%, FF of 0.4, Voc of 0.6 V and short-circuit density (Jsc) of 5.6 mA/cm² were obtained for the former device under white light illumination (100 mW/cm²). The results are much similar to that of the ITO glass substrates based reference cells having identical structure and fabrication. However, the fill factor is very low because of the high resistance of the PEDOT:PSS and SWCNT film. But, this work provides a low cost substitute for ITO. The current-voltage (I-V) curves show that introduction of SWCNTs to PEDOT:PSS improves the device performance because the former improve the conductivity of the later. PEDOT:PSS-SWCNTs electrode based devices provide, Jsc slightly lower and Voc similar to the ITO based reference cell. PEDOT/PSS-SWCNTs have a sheet resistance twenty higher and a much lower PCE than that of ITO based devices. Low fill factor is due to the high series resistance of the PEDOT/PSS-SWCNTs.

Li et al. (2015) [9] studied the effect of ethylene glycol additive, sulfuric acid post-treatment and polyethylenimine (PEI) treatment in P3HT: indene-C60 bisadduct (ICBA) based OSCs. PEI treatment reduces the PEDOT:PSS film conductivity. 2-methoxyethanol processing solvent improves the conductivity whereas isopropanol or water renders the conductivity unaltered for pristine PH1000 film. Device with glass/low-WF PEDOT:PSS/P3HT:ICBA/high-WF PEDOT:PSS structure provide a Voc of 0.82V, FF of about 0.62 under white light illumination (100 mW/cm²). Park et al. (2010) [10] used transparent electrodes of graphene sheets developed by chemical vapor deposition in copper phthalocyanine and fullerene (CuPc\C₆₀)based OSCs. PCE similar to ITO electrodes was obtained. But surface wettability between the electrodes and hole-transporting layer remains a major challenge for pristine graphene electrodes due to its hydrophobic nature. Doping of gold (III) chloride (AuCl₃) in graphene changes the

surface wettability leading to formation of uniform hole-transporting layer and improved device success. Doping also enhances the conductivity and PCE of the device.

Noh and co-workers (2014) [11] fabricated ITO-free OSCs based on composite electrode of Ag nanowire (AgNW) and PEDOT:PSS. The electrode was prepared by single step spray coating of AgNW and dimethyl sulfoxide (DMSO)-treated PEDOT:PSS mixture. Spray deposition time was the prime factor for controlling the optical transmittance, thickness and sheet resistance of the electrode film. PCE of about 2.16% was obtained under 100mW.cm^{-2} and AM1.5G illumination. When an extra spray-coated buffer layer of PEDOT:PSS was used, it led to smoothening of the composite electrode surface, decreased shorting and increased cell-efficiency about 2.65%, similar to ITO-based devices. DC conductivity study of sorbitol doped PEDOT:PSS films by Park and co-workers (2011) [12] shows that work function decreases with increase in the concentration of dopant. This was also confirmed by UV photoelectron spectroscopic studies. ITO and PEDOT:PSS have ohmic contact and PEDOT:PSS work function determines the pertinent hole extraction barrier and affects the performance of cells. A preliminary PCE of 3.26% was obtained. Singh and co-workers (2015) [13] have reported the ink-jet printing technique for obtaining transparent and smooth PEDOT:PSS films for using in OSCs. Surface treatment and drop spacing along with substrate temperature throughout the printing and annealing process are the major parameters affecting continuous film formation. Transmittance of 90% was obtained for a 110 nm thick film which was produced by using 30 mm drop spacing and 120°C annealing temperature. The OSCs based on inkjet printed PEDOT:PSS films had a PCE of 2.64% as compared to 3.1%, for OSCs based on common spin coated PEDOT:PSS films.

2.2 PEDOT:PSS as hole transport layer

PEDOT:PSS hole transport layer (HTL) helps in efficient hole transportation, interface improvement and gap reduction between active layers and ITO LUMO levels. Generally PEDOT:PSS layer is spin coated which does not suit large area coating. Low-resistivity PEDOT:PSS layers increase the PCE of OSCs. Therefore, while using PEDOT:PSS, it becomes important to reduce its resistivity in order to stop the movement of generated holes towards the metal electrode. Bulk heterojunction (BHJ) based OSCs offer several advantages including cost effectiveness, eco-friendliness and easy production. They find a lot of applications because poly(3-hexylthiophene) (P3HT) and (6,6) phenyl-C61-butyric acid methyl ester (PCBM) (electron donor and acceptor) based OSCs exhibit PCEs more than 3% (AM 1.5 G illumination). Manipulation of donor and acceptor, electrode and buffer layer as well as annealing temperature can improve the performance of the devices.

BHJ OSC based on 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C_6PcH_2) and PCBM were prepared through spin-coating. PEDOT:PSS served as a hole transport layer and was spin-coated over ITO coated quartz substrate. A PCE of 3.1% and external quantum efficiency higher than 70% in Q-band region of C_6PcH_2 were obtained. [14]. Metal chlorides like lithium chloride (LiCl), sodium chloride (NaCl), cadmium (II) chloride ($CdCl_2$) and copper (II) chloride ($CuCl_2$) were added to PEDOT:PSS hole transport layer in P3HT:PCBM BHJ OSCs and their effect on conductance, transmittance and morphology was studied by Kadem and co-workers(2015) [15]. Transmittance spectra of doped PEDOT:PSS layers increased to 6% and reached 94% in case of LiCl. Doping results into increase of surface roughness and electrical conductivity. The PCE of 6.82%, FF of 61% and J_{sc} of $18 \text{ mA}\cdot\text{cm}^{-2}$ were obtained.

Kim et al. (2010) [16] fabricated OSCs through all spray deposition of PEDOT:PSS and an active layer by substrate heating technique. The conductivity of PEDOT:PSS was enhanced about 10,000 times by addition of dimethylformamide (DMF) or DMSO. PEDOT:PSS transport layer having DMSO had PCE of 3%, V_{oc} of 0.62 V and J_{sc} of $14.02 \text{ mA}/\text{cm}^2$. Transmittance of spin-coated and spray-deposited PH750, and spray-deposited PH750 containing 5% DMSO has been shown in Figure 2 [16]. The transmittance for spray-coated PEDOT:PSS between 300-500nm was 5% lower as compared to the spin-coated layer between 600-800 nm. Spray-deposited layer of PEDOT:PSS having 5% DMSO had transmittance of 90% and less than 85% in short and long wavelength range, respectively. The current density and voltage (J–V) curve show that the current densities of 6, 12 and $14 \text{ mA}/\text{cm}^2$ and PCE of 1.04%, 2.36% and 2.95% were obtained for pure PH750, PH750\5% DMF and PH750\5% DMSO layers, respectively (Figure 3) [16]. Very low fill factor for pure PH750 (0.267) reveals that it had high series resistance due to the presence of stacks of PEDOT:PSS droplets.

Figure 2 Transmittance of spin-coated PH750, spray-deposited PH750, and spray-deposited PH750\5% DMSO films (Reprinted with permission from Elsevier, [16]).

Figure 3 J - V curve for PH750, PH750\5% DMF and PH750\5% DMSO layers (Reprinted with permission from Elsevier, [16]).

Oh and co-workers. (2013) [17] reported hybrid BHJ OSCs based on ZnO nanoparticles blended with P3HT and PCBM and having PEDOT:PSS or DMF modified PEDOT:PSS

buffer layers. Reference device had a configuration of (ITO\PEDOT:PSS)\P3HT:PCBM\(\text{LiF}\backslash\text{Al}\)) with an efficiency of 1.55% (Figure 4) [17]. The device (ITO\PEDOT:PSS(DMF) \ZnO:P3HT:PCBM\(\text{LiF}\backslash\text{Al}\)) having active layer with ZnO nanoparticle-doping and DMF modified PEDOT:PSS buffer layer delivered an efficiency of 3.39% owing to the synergistic effects. The low resistivity of PEDOT:PSS buffer layer and ZnO nanoparticles improved the J_{sc} and V_{oc} value of OSCs, respectively. Energy band diagram of hybrid OSCs based on zinc (II) oxide (ZnO)-nanoparticles has been shown in Figure 5 [17]. DMF-modified PEDOT:PSS had work function similar to that of pristine PEDOT:PSS films. ZnO nanoparticles present in active layer facilitates the transport of electron carriers towards cathode due to high electron mobility as well as low conduction energy level. These electrons cannot be transferred to the anode due to the presence of hole transporting layer of PEDOT:PSS. Therefore, device performance was enhanced. DMF modulated PEDOT:PSS hole-transporting layer improved the electrical properties and had a resistivity of $1.45 \times 10^{-2} \Omega \cdot \text{cm}$ as compared to resistivity of $7.87 \times 10^{-1} \Omega \cdot \text{cm}$ for pristine PEDOT:PSS film. The J–V curves obtained under illuminations of A.M. 1.5 G with $100 \text{ mW}/\text{cm}^2$ intensity has been shown in Figure 6 [17]. The reference cell had an efficiency of 1.55%. ZnO nanoparticle doping improved the V_{oc} and J_{sc} . AFM images show that addition of large sized ZnO nanoparticles to the active layer amplified the films roughness to 5.67 nm as compared to 1.22 nm for pristine P3HT:PCBM layer [Figure 7 (a) and (b)].

Figure 4 Structure of organic and ZnO nanoparticle-doped hybrid solar cell (Reprinted with permission from ACS publications, [17]).

Figure 5 Schematic diagram of the band diagram for ZnO nanoparticles in the active layer (Reprinted with permission from ACS publications, [17]).

Figure 6 Current–voltage characteristics of P3HT:PCBM and ZnO:P3HT:PCBM thin films with PEDOT:PSS and DMF-modulated PEDOT:PSS (Reprinted with permission from ACS publications, [17]).

Figure 7 AFM images of (a) P3HT:PCBM and (b) ZnO:P3HT:PCBM surfaces (Reprinted with permission from ACS publications, [17]).

2.3 PEDOT:PSS as buffer layer

Yoon et al. (2010) [18] added self-assembled Ag nanoparticle layer between PEDOT:PSS and P3HT:PCBM layer. This resulted in enhancement of short circuit current (I_{sc}) along with decrease in V_{oc} and FF because of the energy barrier due to the self assembled layer of Ag particles. Qiao et al. (2011) [19] used hydrophilic gold nanospheres having a diameter of 15 nm and 5 nm dispersed in the anode buffer layer of PEDOT:PSS. Localized surface plasmon resonance (LSPR) effect depending on the size of Au nanospheres improves the device efficiency. Enhancement of light harvesting by active layer in the region of Au nanospheres along with exciton generation and dissociation was observed. OSCs with 15 nm Au nanosphere doping had an efficiency of 2.36%. UV-ozone treated PEDOT:PSS was used as anode buffer layer in Cu phthalocyanine and fullerene based OSCs by Su et al. (2012) [20]. It had a PCE of about 20% due to improved work function of buffer layer. This leads to better contact between PEDOT:PSS and Cu phthalocyanine. Extraction efficiency of photo generated holes increases whereas electrons and holes recombination probability in active layer gets decreased. Long exposure to UV-ozone treatment declines the device performance due to saturation of work function change, breaking of chemical bonds, and pin hole defect formation in PEDOT:PSS layer leading to decrease in extraction efficiency of charge carriers.

Xi et al. (2010) [21] also studied OSCs based on Cu phthalocyanine and fullerene. PEDOT:PSS/LiF were used as double anode buffer layer which combats with stability

issues of the device as compared to the devices based on single buffer layer. A Metal-Insulator-Semiconductor (MIS) model was put forward to explain the improvement in device performance as well as stability. PEDOT:PSS acts as a conductive organic ink, therefore, it behaves as a metal. CuPc and LiF are semiconductor and insulator, respectively. Therefore, PEDOT:PSS/LiF/CuPc system behaves as MIS model (Figure 8) [21]. Several holes pass from one side of 1 nm thick LiF layer to other by tunneling, when they come across the LiF/CuPc interface. High tunneling efficiency causes most of the holes to pass through the LiF layer. The few holes left get accumulated at LiF/CuPc interface. Due to capacitance like structure of MIS, electrons are induced to accumulate at PEDOT:PSS/LiF interface and build-in electric field acts towards PEDOT:PSS from CuPc. This field has direction parallel to that of the heterojunction, hence, V_{oc} gets enhanced. LiF layer increases the interface quality and decreases the probability of recombination of excitons. J_{sc} can be further improved to a small extent due to pushing of holes across the LiF layer by the build-in field. Hole exporting efficiency is also enhanced due to smoothening of the ITO surface by PEDOT:PSS. The sheet resistance is improved due to hygroscopic nature of PEDOT:PSS [21-23].

Figure 8 The MIS structure formed by PEDOT:PSS/LiF/CuPc system. Since the ITO electrode has been treated by UV-ozone, the work function can be enhanced a lot. It has been reported to increase to increase to over 5.2 eV. In this work, we consider the work function of ITO is enhanced to 5.2 eV after UV-ozone treatment (Reprinted with permission from Elsevier, [21]).

2.4 Inverted organic solar cells

Poor stability and organic semiconductor degradation by oxygen and moisture hampers the use of OSCs. Traditional OSCs lacking encapsulation are unstable due to etching of the ITO by acidic PEDOT:PSS along with easily oxidizable metal electrode having low work function like Al. As already stated, inverted OSCs (IOSCs) offer better stability because PEDOT:PSS is used above the active layer and it does not remain in contact with ITO. Better results can be obtained on using an air-stable metal electrode having high work function like Ag or Au. ITO and metal are generally used as the electron and hole collecting electrode. PEDOT:PSS is generally used as hole transport layer. Kuwabara et al. (2008) [24] prepared ITO/TiO_x electrode through sol-gel method and used it in a device having ITO/TiO_x/PCBM:P3HT/PEDOT:PSS/Au structure and an active area of 1 cm². PCE of 2.47% was attained under simulated sunlight irradiation (AM 1.5G-100mW.cm²). BHJ IOSCs based on fluorine doped TiO_x/electrodeposited amorphous (or anatase) TiO_x electrode delivered PCE of 2.5% under AM 1.5-100 mW.cm² simulated sunlight irradiation [25]. Kang et al. (2012) [26] prepared IOSCs with a configuration of ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag. The electron selective layer, active layer and hole selective layer were deposited through spray-coating. PCE of 3.17 and 1.33% were obtained for device area of 0.36 and 15.25 cm², respectively, when AM. 1.5 simulated illumination was used.

Various properties of solvents like wetting ability, surface tension, boiling point, etc. play important role in uniform coating of organic layers. Peh et al. (2011) [27] reported that Al4083 layer improves the wetting ability of P3HT:PCBM surface. Spray coating dynamics were studied through microscopic videos. Optimization of wetting ability and drying time for the suspension of PEDOT:PSS results into a transparent spray coated anode maintaining the device performance. Application of the vacuum-free method to near IR absorber yields device with 60% transparency. High resolution Ag grid embedded in PEDOT:PSS was used as a transparent hybrid electrode in large-area and high efficiency IOSCs. It has large transparency and small sheet resistance which can be minimized to about 1.2 Ω sq⁻¹ through property tuning of Ag-grid. Device area of 1.21 cm² delivered a PCE of 3.36% and 5.85% for P3HT:PC61BM and PTB7:PC71BM devices, respectively.

Long term stability remains an issue in case of non-encapsulated OSCs. Stability can be improved by removing the ITO/PEDOT:PSS interface use of metal electrode having high work function [28]. In order to combat the wettability issue of hole transport layer of PEDOT:PSS, a fluoro surfactant, Capstone Dupont FS-31 was used as additive in place of Zonyl FS-300 by Lim and co-workers (2012) [29]. An efficiency of 3.1% was obtained along with stability for about 400 hours without encapsulation. Zimmerman and co-

workers (2009) [30] studied the long term stability under sulphur plasma lamp 1000W/m² illumination at 50 °C of inverted P3HT:PCBM solar cells. 2.5% PCE was obtained.

2.5 Tandem organic solar cells

Single unit OSCs lack practical device efficiency. Tandem OSCs have improved efficiency because the combination of two sub-cells using an interconnection layer allows utilization of wider solar spectrum range. The working of a tandem solar cell is as follows:

1. absorption of photons
2. generation of free carrier;
3. electron and hole collection from front and rear subcells, respectively by interconnecting layer.
4. electron and hole recombination in the interconnecting layer
5. charge collection of holes and electrons in the front and rear subcells, respectively by external circuit.

Step number 3 and 5 get reversed for an inverted tandem solar cell. An ideal serially connected tandem cell has Voc equal to additive sum of Voc of subcells and does not show potential loss in interconnecting layer. The subcells need to be optimizing order to gain best device performance. Liu et al. (2013) [31] PEDOT:PSS as the interconnecting layer in solution-processed homo-tandem device containing conjugated polyelectrolyte. Very high PCE of 10.1% was obtained due to the use of photoactive layer with double thickness. Lee et al. (2011) [32] used solution-processible nanoparticles of ZnO as n-type and MoO₃ or PEDOT:PSS as p-type material. P3HT:PCBM (higher band gap) and ZnPc/C60 (lower band gap) were used in the bottom and top cell, respectively. The ZnO/PEDOT:PSS inter-electrode, has Voc equal to the sum of upper and lower cell Voc, indicating the successful connection of the cells.

Li et al. (2017) [33] reported a solution-processed, tandem OSCs using small compounds ((5Z,5'E)-5,5'-((5'',5''''-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis (3,3'' dioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxo thiazolidin-4-one) (DR3TSBDT) and 5,15-bis(2,5-bis(2-ethylhexyl)-3,6-dithienyl-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione-5'-yl-ethynyl)-10,20-bis(5-(2butyloctyl)thienyl) porphyrin zinc(II) (DPPEZnP-TBO). DR3TSBDT and DPPEZnP-TBO were used as electron donors in the upper and lower cells, respectively. A 40 nm thick hole transport layer of PEDOT:PSS was used. Extremely high PCE of 12.50% was obtained. Figure 9(a) [33] shows the molecular structure of DR3TSBDT and DPPEZnP-

TBO. Their corresponding absorption spectra [Figure 9(b)] shows that DR3TSBDT absorbs in the visible range extending upto 700 nm, whereas DPPEZnP-TBO absorbs the near-IR photons till 907 nm, thus covering the whole solar spectrum. The J-V curves of individual cells has been shown in Figure 9(c). DR3TSBDT:PC₇₁BM and TBO:PC₆₁BM based devices show Voc around 0.9 and 0.73 V, Jsc of about 14 and 18.53 mA.cm⁻², respectively. External quantum efficiency curves (EQE) DR3TSBDT and DPPEZnP-TBO based devices show high response in 300-650 and 300-900 nm range. The later showed appreciable EQE response in 650-900 nm range, whereas the former had weak EQE. This shows the balancing absorption nature of the donor materials used in the top and bottom cells.

Figure 9 (a) Molecular structures of DR3TSBDT and DPPEZnP-TBO. (b) Normalized absorption spectra of DR3TSBDT and DPPEZnP-TBO films. (c) J-V curves (Reprinted with permission from Nature, [33]).

Moet and co-workers (2010) [34] used middle electrode composed of PEDOT:PSS and ZnO in solution-processed tandem OSCs. PEDOT:PSS dispersion was pH modified which results into lowering of PEDOT:PSS work function. The polythiophene: fullerene based device performance remains unaffected but low V_{oc} is obtained for polyfluorene derivative based device due to its larger ionization potential. When perfluorinated ionomer layer is used, anode work function gets recovered and a V_{oc} of 1.92 V is obtained for polyfluorene-based double junction OSCs. Zhou et al. (2012) [35] prepared an inverted tandem polymer solar cells containing PEDOT:PSS. They modified one of the interface using high performance ethoxylated polyethylenimine (PEIE) charge recombination layer having low absorption, high conductivity and front and rear interface work function contrast (1.3 eV). It produces an ideal tandem cell having V_{oc} equal to sum of subcells. But, the fill factor is higher than that of the individual subcells.

3 Dye sensitized solar cells

DSSCs mainly consist of: 1) porous oxide film, 2) dye sensitized photo anode (mesoporous TiO_2 absorbed with molecule of dye), 3) liquid electrolyte of triiodide/iodide, 4) Pt counter electrode (CE).

PEDOT:PSS in its bare or hybrid form is mainly used to enhance the catalytic activity of CE. In this section, we will discuss the effect of using PEDOT:PSS with graphene, CNT, TiS_2 , TiO_2 (nanoparticle), SiO_2 (nanoparticle), CoS (nanoparticles) etc. on the performances of CE.

3.1 PEDOT:PSS as counter electrode

The role of counter electrode (CE) is to collect electron and catalyse redox reaction of triiodide/iodide. Most of the DSSCs consist of Pt on fluorine doped tin oxide glass. Pt exhibits efficient catalytic activity for triiodide/iodide redox reaction but it is expensive too. To develop cheaper CE replacement of this expensive metal is required [36]. In 1998, Yohannes and Inganäs revealed that the PEDOT may serve as the catalyst for triiodide/iodide redox reaction [37]. PEDOT:PSS CE were prepared recently [38] and its excellent catalytic activity and its low cost attracted researchers from around the world.

Ma et al. (2018) [39] prepared composite of reduced graphene oxide (rGO) with PEDOT and applied it as CE for DSSCs. Photoelectric conversion efficiencies of 7.79, 8.33 and 6.88% were observed for rGO/PEDOT, Pt and PEDOT, respectively under the same experimental conditions. Xia et al. (2007) [40] studied electrochemical and catalytic activity of PEDOT CE with different counter ions like ClO_4^- , TsO^- and PSS. PEDOT- ClO_4^- system exhibits better catalytic performances due to higher porosity and smaller

size of ClO_4^- ion. In DSSCs PEDOT:PSS film is a good option for cathodic catalyst. Kitamura and Shiratori (2011) [41] prepared thin film of PEDOT:PSS using layer-by-layer self-assembly method (LbL) for the first time. The as prepared film exhibits highly adhesive nature and its thickness could be manipulated up to the controlled scale. Authors used carbon black as an additive in PEDOT:PSS solution and fabricated extremely mesoporous film. As expected, this film exhibits outstanding catalytic properties as cathode in DSSCs. Authors revealed morphological changes by varying carbon black content and studied the effect of porosity on its performances as a CE. They observed that the film exhibits 8% lower efficiency as compared to the conventional counter electrode.

Carbon nanotube (CNT) fiber is well known for its outstanding mechanical and electronic properties at nanoscale as well as microscopic scale. The fiber displays conductivity of 10^3 Scm^{-1} and its tensile strength is of the order of 10^3 MPa .

Guozhen Guan et al. (2013) [42] fabricated CNT–PEDOT:PSS composite from 1:1 concentration of PEDOT:PSS and CNT. In their experiment they observed that the sheet thickness of 2 nm composite exhibits enhanced FF with increasing thickness of CNT and decreasing polymer percentage. However V_{OC} and J_{SC} did not vary much. Aligned CNT sheets help to induce better catalytic activity of bare PEDOT:PSS through p-p interaction. The authors also revealed that the aligned composite of CNT-PEDOT:PSS exhibits the maximum conversion efficiency of 8.3% when it were used as electrodes for DSSCs. Lee et al. (2015) [43] used graphene dots in PEDOT: PSS and observed rough surface morphology, better conductivity and low charge transfer resistance for this CE. Better cell efficiency was also observed and was

found to be 43% higher than the cell containing PEDOT: PSS. PEDOT: PSS performed well with graphene at low light which makes it suitable for indoor use.

Li et al. (2013) [44] compared morphology of different CEs and found high efficiency (7.04%) for TiS_2 /PEDOT:PSS composite due to the larger surface area of PEDOT:PSS. They revealed that TiS_2 particle acts as an electrocatalyst material in redox reaction. Furthermore, the composite serves as catalyst for the conversion of I^- to I_3^- . They demonstrated that this cell could replace the expensive Pt counter electrode based cells. Maiaugree et al. (2012) [45] also incorporated TiO_2 nanoparticles in PEDOT:PSS and observed better catalytic activity as well as energy conversion efficiency for the composite and reduced charge transfer resistance for CE. Its improved catalytic activity has been proved through cyclic voltammogram. Reduction peaks increased by 0.11 mA after incorporation of TiO_2 nanoparticles in PEDOT:PSS. Muto and co-workers (2007) [46] incorporated nano crystals of TiO_2 in PEDPT:PSS. They observed better cathodic activity and energy conversion efficiency of about 4.38%. Cyclic voltammogram studies

revealed that the TiO_2 added PEDOT:PSS has highest reaction rate than PEDOT:PSS. 4 wt% of TiO_2 exhibits maximum cathodic activity due to improved surface area and catalytic/conductive utility of PEDOT:PSS.

Xu et al. (2012) [47] observed better electrocatalytic activity and electrical conductivity when TiN was incorporated in PEDOT:PSS. This composite provides better and efficient interfacial active sites resulting into energy conversion efficiency of 7.06% which is higher than that of the cell having Pt-FTO (6.57%) as CE. Cyclic voltammetric (Figure 10 [47]) analysis shows that the TiN nanorods and nanoparticles based composites with PEDOT:PSS exhibits electron transfer rate comparable to Pt-FTO. Tin mesoporous sphere based composites with PEDOT:PSS exhibits lower electron transfer rate than the Pt-FTO. TiN based composites with PEDOT exhibits better current density (Figure 11 [47]) than the TiN based electrodes. Yeh et al. (2011) [48] observed higher energy conversion efficiency (6.67%) than the counter electrode having s-Pt (6.57%). The counter electrode of TiN nanoparticles with PEDOT:PSS exhibits better catalytic activity, lower charge transfer resistance between CE and electrolyte [49]. TiN-NPs/PEDOT:PSS film provides multifold pathway for electron transfer due to continual connection of TiN-NPs with PEDOT:PSS (Figure 12 [49]). Transmittance at longer wavelengths increased when SiO_2 was added to PEDOT:PSS due to decreased anisotropy and interaction of PEDOT-PSS, as a result of homogeneous mixing of SiO_2 nanoparticles with PEDOT-PSS. Features like mesoporous (Figure 13 [49]) and larger electrochemical surface area results into better catalytic activity of SiO_2 /PEDOT-PSS CE (Figure 14 [49]).

Figure 10 Cyclic voltammograms of Pt, TiN(P)-PEDOT:PSS, TiN(R)-PEDOT:PSS, TiN(S)-PEDOT:PSS counter electrodes in 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄ acetonitrile solution at a scan rate of 20 mV s⁻¹ (Reprinted with permission from ACS publication, [47]).

Figure 11 Characteristic photocurrent density-voltage (J - V) curves of DSSCs with different electrodes, measured under simulated sunlight 100 mW cm^{-2} (AM 1.5). The liquid electrolyte is composed of 0.05 M I_2 , 0.1 M LiI , 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPPI), and 0.5 M 4-*tert*-butyl pyridine in acetonitrile solution (Reprinted with permission from ACS publication, [47]).

Figure 12 (a) Electron transfer pathways in a film of TiN-NPs and (b) electron transfer pathways in a composite film of PEDOT:PSS/TiN-NPs (Reprinted with permission from Royal Society of Chemistry, [48]).

Figure 13 Schematic device structure of bifacial DSCs (Reprinted with permission from ACS publication, [49]).

Figure 14 SEM images from (a) PEDOT-PSS film and (b) SiO₂ (40 mg)/PEDOT-PSS film (Reprinted with permission from ACS publication, [49]).

Sudhagar et al. (2011) [50] incorporated nanoparticle of cobalt sulphide into PEDOT:PSS and the synergistic effect resulted into better catalytic activity. The reduction of triiodide was also observed to be easier than the pristine PEDOT:PSS system. CoS nanoparticles

form two-dimensional sheet like structure and PEDOT:PSS serves as filler agent which results into better contact between triiodide ions and PEDOT:PSS. Cyclic voltammogram (Figure 15 [50]) was also studied for various electrodes.

Figure 15 (a) AFM images of the sheetlike CoS dispersed in PEDOT:PSS and (b) surface profile of the sheetlike CoS on PEDOT:PSS matrix, and (c) CoS/PEDOT:PSS interface (Reprinted with permission from ACS publication, [50]).

Zhang et al. (2012) [36] incorporated nanocrystals of CuInS_2 with PEDOT:PSS and applied it as CE for DSSCs. Authors observed better catalytic activity for the composite as compared to PEDOT:PSS or CuInS_2 . Photoelectric conversion efficiencies were reported to be 6.50, 6.51, 5.45, and 3.22 % for the composite, Pt, CuInS_2 and PEDOT:PSS, respectively. Maiaugree et al. (2018) [51] prepared composite of $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.025, 0.05, 0.075$ and 0.1) nanoparticles with PEDOT:PSS and applied it as CE for DSSCs. Outstanding catalytic performances were observed for iodide/triiodide redox reaction. Furthermore, authors observed highest solar conversion efficiency of 8.39% for the composite having composition of $\text{SrTi}_{0.925}\text{Co}_{0.075}\text{O}_3$ NPs/PEDOT-PSS as compared to 8.27% for device having Pt as CE. In Figure 16 [51], indicated plane in brackets are the plane for pervoskite structure. XRD of SrTiO_3 nanoparticles reveals that

the impurities are absent and Ti sites are perfectly substituted by Co. The lowest R_{ct} value for $x = 0.075$ is observed which is associated to the maximum catalytic activity of $SrTi_{0.925}Co_{0.075}O_3$ NPs/PEDOT-PSS film (Figure 17, Figure 18 [51]). It can be concluded that the conductivity and electrocatalytic activity can be affected by doping of Co in $SrTiO_3$ nanoparticles. The enhancement of electrocatalytic activity and conductivity can be achieved by varying Co content.

Figure 16 XRD patterns of $SrTi_{1-x}Co_xO_3$ ($x=0, 0.025, 0.05, 0.075$ and 0.1) NPs (Reprinted with permission from Elsevier,[51]).

Figure 17 Photocurrent density (J) vs. photovoltage (V) curves of DSSCs with based on $STCoO$ NPs/PEDOT films (Reprinted with permission from Elsevier,[51]).

Figure 18 Tafel plots of STCoO NPs/PEDOT-PSS CE (Reprinted with permission from Elsevier,[51]).

Xu et al. (2015) [52] applied PEDOT:PSS film and ten modified films of PEDOT:PSS as CE for the study of bifacial DSSCs. PEDOT:PSS film showed front and rear side efficiencies of 4.71 and 2.38% respectively. They used different additives like iodine, DMSO and PEG (molecular wt. 200) and studied optical properties (Figure 19 [52]) of modified PEDOT:PSS film and J-V curve (Figure 20 [52]) and demonstrated enhanced efficiencies of 5.19, 5.11 and 5.29 % respectively for front side due to poorer sheet resistance. Furthermore, the efficiencies were obtained almost unchanged for rear side illumination. Ahmed et al. (2018) [53] fabricated $\text{Si}_3\text{N}_4/\text{MoS}_2$ -PEDOT:PSS and applied as CE for bifacial DSSCs. They observed better catalytic activity for the CE than that of the pristine $\text{Si}_3\text{N}_4/\text{MoS}_2$ and PEDOT:PSS. The conversion efficiencies (PCE) for $\text{Si}_3\text{N}_4/\text{MoS}_2$ -PEDOT:PSS (5% composition in CE), $\text{Si}_3\text{N}_4/\text{MoS}_2$ or PEDOT:PSS were observed to be 7.16, 3.80 and 4.20%, respectively. Song (2014) [49] added SiO_2 in PEDOT:PSS and used it as CE in bifacial DSSC. Better power conversion efficiency (4.61%) was observed for the rear side irradiation along with enhanced catalytic performance as compared to the bare PEDOT:PSS.

Figure 19 UV-Vis spectra of the different modified PEDOT:PSS films on the FTO substrates in the visible range. (a) the first group including a modified film (PEG400-PEDOT:PSS), showing slightly enhanced transparency; (b) the second group including six modified films, showing almost unchanged transparency (Reprinted with permission from Elsevier,[52]).

Figure 20 J-V curves of bifacial DSSCs using different PEDOT:PSS films as counter electrodes. (a) under photoanode (PA) illumination; (b) under counter electrode (CE) illumination (Reprinted with permission from Elsevier,[52]).

4. Hybrid silicon solar cell

Today, the solar cell market is primarily dominated by silicon wafer solar cells. The main challenges include reduction of production cost, maintaining the efficiency, avoiding high temperature fabrication, avoiding vacuum processes.

To overcome all the above mentioned issues PEDOT:PSS is being used as hetero-emitter. Cost friendliness may be introduced through replacing crystalline Si with wafer Si. PEDOT:PSS forms heterojunction with n type Si. However, flexibility of Si hybrid solar cell is a major issue to be resolved. PEDOT with high work function (5.0 eV) serves as hole transporter. In this section we will go through some details regarding how PEDOT:PSS manipulates the performance of these hybrid solar cells.

Pietsch et al. (2014) [54] studied the variation of substrate doping concentration (N_d) and open circuit voltage (V_{oc}). 645 mV of V_{oc} was observed for $N_d = 2.6 \times 10^{17}$ and 12.6% of PCE for $N_d = 2.5 \times 10^{16}$. Metallic conductivity of PEDOT:PSS were probably responsible for the high PCE and efficient transport of holes for planar hybrid n-Si/PEDOT:PSS solar cells. Thomas et al. (2016) [55] added co-solvent of methanol and ethylene glycol in PEDOT:PSS for better conductivity. When 16 wt% of the co-solvent was added, the so prepared solar cell delivered maximum PCE of 14.6% and open circuit voltage of 620 mV. This is probably due to the ordered grain structure at the macromolecular level. Benzenoid chains were ordered and quinoid chains were found disordered in which segregated PSS chains were present. Microstructural manipulation of PEDOT:PSS attributes better performances for Si hybrid solar cell.

He et al. (2011) [56] fabricated highly efficient hybrid solar cell through silicon nanowires (SiNWs) and PEDOT:PSS. Longer SiNW leads to reduced surface coverage of PEDOT and the PCE for Si/PEDOT:PSS and SiNW/PEDOT:PSS cell were found to be 6.2 and 9%, respectively.

Si nanoholes (SiNH) were studied by Hong et al. (2013) [57]. Planar Si shows high reflectance due to the huge variation of refractive indices between Si and air. On the contrary, SiNH exhibits lower reflectance. Moiz et al. (2012) [58] prepared PEDOT:PSS–silicon nanowire based hybrid solar cell. Sound linking and linear alignment of PEDOT:PSS on n-Si are the reason for enhanced efficiency, better short-circuit current and open-circuit voltage of the cell. Polymer thickness more than 70 nm leads to increased resistance as well as decreased electric field between the electrodes. Authors successfully prepared stamped channel of PEDOT:PSS of lesser thickness and overcame these two factors. Low mobility of free carriers in bulk polymer also increases the carrier recombination and lower the cell efficiency. Whereas stamped polymer provides lower surface area to interact with SiNW which consequently decreases the recombination losses and current leakage. Thin (about 10 nm) stamped channel of PEDOT:PSS also improves the extinction decay losses hence improves PCE. Park et al. (2015) [59] also prepared SiNW/PEDOT:PSS hybrid solar cell and observed 13.2% PCE. Using SiNW/PEDOT:PSS interface for hybrid solar cell leads to better stability. When ITO is used with PEDOT:PSS, degradation is a major issue. Authors used Au (200- μ m pitch)

mesh for the front electrode and observed excellent PCE (13.2%), FF (67.8%), short-circuit current density, J_{sc} (36.03 mA/cm^2) and open-circuit voltage, V_{oc} (539.2 mV) as compared to the ITO. Syu and co-workers (2012) [60] prepared SiNW/PEDOT:PSS hybrid solar cell. They observed better light trapping and poor light reflectance for the cell as compared to the planar Si/PEDOT:PSS solar cell. PCE for less than 0.5 micrometer SiNWs was observed to be 8.40% for the cell. Sharma et al. (2014) prepared hybrid solar cell of SiNW arrangement and PEDOT:PSS and obtained a PCE of 6.62% [61]. Junghanns et al. (2015) [62] fabricated hybrid solar cells using multicrystalline Si and PEDOT:PSS. They studied the effect of SiO_x and aluminium (III) oxide (Al_2O_3) on surface of Si. PCE were reported to be 10.3 and 7.3% for mc-Si/ Al_2O_3 /PEDOT:PSS and mc-Si/ SiO_x /PEDOT:PSS, respectively (Figure 21 [62]).

Figure 21 I-V characteristics of the hybrid solar cells with 1 nm SiO_x (blue) and 0.75 nm Al_2O_3 (red) as a passivation layer (Reprinted with permission from AIP publishing, [62]).

Si/PEDOT:PSS core/shell nanowire arrays were prepared by Lu et al. (2011) [63]. PCE was obtained to be 6.35% for the Si/PEDOT:PSS core/shell nanowire solar cell (Figure 22, Figure 23 [63]). Nagamatsu et al. (2014) [64] prepared silicon/PEDOT:PSS heterojunction through spin coating technique below 100°C for blocking electron. PCE was observed to be 11.7% at AM1.5 illumination. PEDOT with PSS forms

macromolecular salt in which oxidation takes place on PEDOT and reduction takes place on PSS forming cation and anion, respectively. PEDOT:PSS gets easily dispersed in aqueous medium, which can be further spin casted. Furthermore, as-obtained film of PEDOT:PSS is highly transparent as well as conductive. PEDOT thin film serves as the doped p-type semiconductor.

Figure 22 (a) Schematic illustration of the fabrication process of Si/ PEDOT:PSS core/shell nanowire array solar cells; photographs of (b) as-purchased and (c) ethanol diluted PEDOT:PSS solution on Si nanowire arrays, indicating different wettability (Reprinted with permission from Royal Society of Chemistry,[63]).

Figure 23 Structural characterization of the Si/PEDOT:PSS core/shell nanowire arrays. (a) Cross-sectional SEM image of Si/PEDOT:PSS core/ shell nanowire arrays; (b) and (c) TEM images of a Si/PEDOT:PSS core shell nanowire (Reprinted with permission from Royal Society of Chemistry,[63]).

Sheng et al. (2014) [65] improved wettability of Si surface through oxidizing agents nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Treatment with these oxidizing agents enhanced surface coating of Si with PEDOT:PSS. The better heterojunction of inorganic-organic hybrid solar cell was prepared. Dry etching technique on Si was used to prepare Si nanocones/PEDOT SC. Monolayer polystyrene (PS) nanospheres were masked on Si/PEDOT SC. Outstanding light trapping and 7.1% of PCE were observed [66]. Zielke et al. (2014) [67] prepared ‘back PEDOT’ cell by using PEDOT:PSS at the rear side of the cell. Li et al. (2015) [68] prepared flexible Si/PEDOT:PSS hybrid solar cells. They demonstrated schematic preparation of solar cell with micro pyramidal Si and reported

the PCE for planar flexible cell and micro pyramidal Si/PEDOT:PSS solar cell to be 4 and 6.3%, respectively.

Conclusion

PEDOT:PSS has been widely used in OSCs, inverted OSCs, DSSCs for improving performances of these solar cells. Vital application of combination of PEDOT:PSS with different materials is continuously attracting researchers from all over the world. Fullerene and fullerene based derivatives, single walled carbon nanotube, nanomaterials, metallic nanowires, etc. have been used to improve the performance of PEDOT:PSS in solar cells. The effect of additives like ethylene glycol, DMSO and various post-treatment has also been observed. It has been observed that inverted OSCs have better stability as compared to OSCs. Tandem OSCs use a combination of two sub-cells offer better efficiency and wider solar spectrum can be utilized. Combination of PEDOT:PSS with various counter ions, nanocrystals of CuInS_2 , composite of $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$, nanoparticle of CoS , nanoparticle of SiO_2 , nanorods of TiN , nanocrystals of TiO_2 , nanoparticles of TiO_2 , CNT fibre etc. improved the performance of CE for DSSCs. Similarly, combination of PEDOT:PSS with SiNW, SiNH etc. enhances the performance of Si based hybrid solar cells. There is a vast scope to imply PEDOT:PSS in above discussed solar cells.

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