Conjugated Polymers as Organic Electrodes for Photovoltaics

Bakhytzhan Baptayev, Yerbolat Tashenov, and Mannix P. Balanay

Abstract The use of conjugated polymers as organic electrodes for photovoltaics is very attractive due to their ability to form flexible substrates which can be applied either as an anode or a cathode depending on its configuration. Its properties can easily be tuned via synthetic or post-synthetic treatment processes. In this chapter, an overview of the brief history is given to provide a background on solar cell technology. The conjugated polymers are commonly observed in the third generation solar cells specifically in dye-sensitized, perovskite, and organic solar cells, which mostly utilize them as counter electrodes. First, we briefly discuss the components, criteria, and representative conjugated polymers for dye-sensitized solar cells. Then followed by the composition, mechanism, and utilization of conjugated polymers in perovskite solar cells. Lastly, we introduce the basic configuration of organic solar cells that uses conjugated polymers as both cathode and anode.

Keywords Third-generation solar cell · Dye-sensitized solar cell · Perovskite solar cell · Organic solar cell · Counter-electrode

1 Introduction

The advent of technological advancement and industrialization has led to an increase in energy demand. This hastens the depletion of fossil fuels which supplies 84% of the world's energy. Aside from being a non-renewable energy resource, fossil fuels are also a major contributor to large amounts of greenhouse gases in the air that are

---

B. Baptayev
National Laboratory of Astana, 53 Kabanbay Batyr Avenue, Nur-Sultan 010000, Kazakhstan

Y. Tashenov · M. P. Balanay (✉)
Department of Chemistry, School of Sciences and Humanities, Nazarbayev University, 53 Kabanbay Batyr Avenue, Nur-Sultan 010000, Kazakhstan
e-mail: mannix.balanay@nu.edu.kz

Y. Tashenov
Department of Chemistry, L.N. Gumilyov Eurasian National University, 2 Satpayev Street, Nur-Sultan 010008, Kazakhstan

R. K. Gupta (ed.), *Organic Electrodes*, Engineering Materials,
https://doi.org/10.1007/978-3-030-98021-4_8

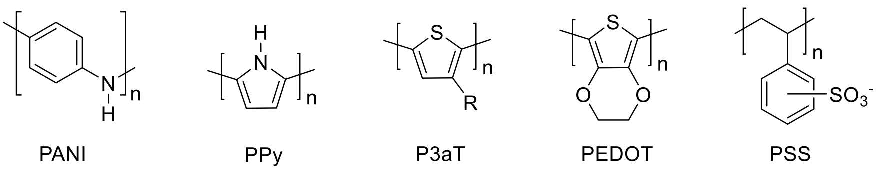

Fig. 1 Structures of the most common conducting polymers used in solar cells

responsible for global warming. A lot of government efforts now focus on investing in the use of renewable energy resources. Among these resources, the energy coming from the sun is the most promising since it can provide the worlds' energy needs that are around 4.5 × 10^4 TWh by the year 2050. The development of the use of solar cells started with the discovery of the photovoltaic effect when the light was irradiated to metal-coated electrodes which were dipped in an electrolyte in 1839 by Becquerel [1]. In 1883, Charles Fritz conceived the first working solar cell that uses selenium wafers with a thin layer of gold having a power conversion efficiency (PCE) of about 1% [2]. The first practical solar cells having a PCE of ~ 6% were developed by the researchers of Bell Laboratories which uses silicon instead of selenium in 1954 [3]. Since then, various types of materials are utilized to generate electricity from sunlight.

The utilization of conjugated polymers (CPs) in solar cells, since its discovery in 1976 by Shirakawa et al. [4], was mostly applied to three types of third-generation solar cells namely (a) dye-sensitized, (b) perovskite, and (c) organic solar cells. The majority of the CPs utilized in solar cells revolve around specific structures such as polyaniline (PANI), polypyrrole (PPy), poly(3-alkylthiophene) (P3aT), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(styrene sulfonate) (PSS) (Fig. 1), wherein the latter two usually are used in mixture with each other.

2 Conjugated Polymers in Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSSCs) originated in 1991 as photoelectrochemical cells mimicking the process of photosynthesis in plants [5]. Since then, DSSCs have been attracting researchers all over the world because of their low cost, ease of fabrication, and remarkable efficiency. Three major components constitute DSSCs: anode, cathode, and electrolyte. The anode is a transparent conducting oxide (TCO) substrate with a thin film of semiconducting nanoparticles such as TiO_2 covered with sensitizing dye molecules. While the cathode is a TCO substrate with a film of an electrocatalyst such as platinum. The third component, a redox electrolyte, is sandwiched between these two electrodes. The schematic representation of the DSSCs is presented in Fig. 2. As electrons of dye become photoexcited upon light absorption, they are injected into the conduction band of the semiconductor and then travel to the cathode via the outer circuit. The redox electrolyte then regenerates

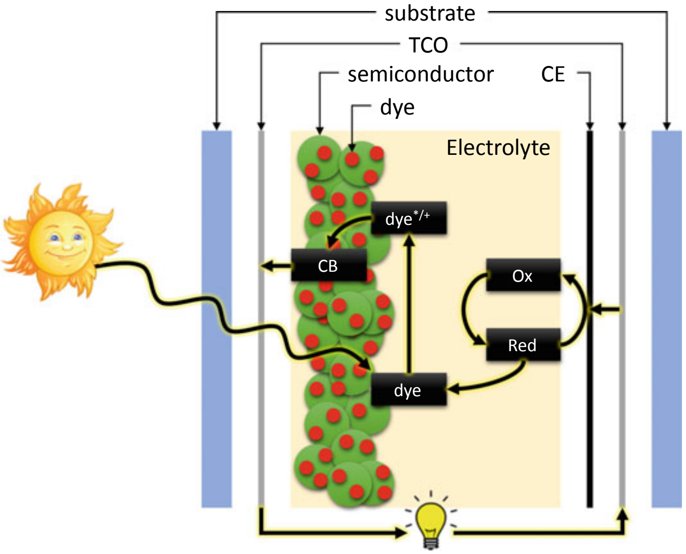

Fig. 2 Schematic representation of the working principle of the dye-sensitized solar cell

oxidized dyes and is subsequently reduced by the electrocatalyst at the cathode. All three components of DSSCs play a significant role in determining device performance; therefore, the design and development of suitable and optimal components is a vital step in constructing a highly efficient DSSCs. The primary criteria in choosing the right component are performance, cost, and processability, in which all of these can be provided by the conductive polymers that make it an attractive material for solar cells. Hence, both anode and cathode can be prepared from transparent and conducting polymers. CPs can replace expensive and scarce platinum electrocatalyst of DSSCs counter electrode (CE) and can also be used as an alternative to the more corrosive liquid redox mediator. In the succeeding sections, we focus on the use of conductive polymers as counter electrodes in DSSCs.

2.1 Conjugated Polymers as Counter Electrodes for Dye-Sensitized Solar Cells

In DSSCs, an anode is an electrode where oxidation occurs, thus collecting electrons. Whereas cathode is the electrode where reduction takes place and hence it collects holes. Mostly, the term ‘counter electrode’ (CE) is used to define the cathode. The main functions of the CE in DSSCs are two-fold: (i) it reduces the oxidized species of redox couple and (ii) allows the current to flow out and the electrons to go into the device. Therefore, an ideal CE should have an excellent catalytic activity towards the reduction of the redox mediator and be chemically stable under a corrosive environment of the electrolyte. Other requirements of the CE are large surface area, high conductivity for efficient charge transfer (CT), good optical transparency, and high mechanical flexibility. There are many alternative CEs such as transition metal compounds, carbonaceous materials, metal alloys, and conducting polymers that have outperformed Pt-based CEs. Of the alternatives, CPs are attractive since their properties can be adjusted via synthetic manipulations and post-synthetic treatment methods. Additionally, CPs are abundant, less expensive, have good electrical conductivity, and can be easily synthesized. Common CPs used as DSSC cathode are PANI, P3aT and its derivatives, and PEDOT.

2.1.1 Polyaniline

PANI is one of the conductive polymers which is an extensively studied material as a CE in DSSCs. Among the attractive properties of PANI is that it has three oxidation states with distinct colors. Moreover, it can be fine-tuned via doping with acid or base. A pioneering work of PANI-based cathode for DSSCs was done by Li and colleagues in 2008 [6]. They prepared microporous PANI nanoparticles with a diameter of 100 nm by the aqueous oxidative polymerization reaction with perchloride acid as a dopant in the presence of ammonium persulfate. The porous structure of the polymer benefited its electrocatalytic activity towards reduction of I_3^- which was found higher than the Pt CE. This produced a higher PCE of 7.15% as compared with Pt CE with a PCE of 6.90%. PANI was also used in DSSCs with $Co^{3+/2+}$ electrolytes. Wang et al. reported an oriented PANI nanowire arrays CE which was grown in situ on TCO glass substrate [7]. The 1D structure demonstrated improved electrocatalytic performance compared to random network PANI films and traditional Pt cathode. This resulted in an enhanced short-circuit current density (J_{SC}) and fill factor (FF) in DSSCs with 1D PANI CE which showed a remarkable 8.24% efficiency which is notably higher than in solar cells with random network PANI (5.97%) and Pt CE (6.78%).

The electrocatalytic property, conductivity, and porosity of PANI can be improved through the use of doping. For example, Deng et al. studied the effect of doping PANI with different ions SO_4^{2-}, ClO_4^-, BF_4^-, Cl^-, *p*-toluenesulfonate (TsO^-), and others [8]. Among the ions, it is the sulfate-doped electropolymerized PANI film that demonstrated porous morphology with a higher reduction current compared to Pt CE. It has a low CT resistance (R_{CT}) of 1.3 Ω cm^2, which produces a PCE of 5.6% which is almost comparable to the reference electrode (6.0%).

PANI can also be used to prepare transparent electrodes. Zhao and the company reported on the use of highly uniform transparent PANI counter electrodes prepared by a facile in situ polymerization method [9]. The PANI film exhibited excellent transparency in the visible range 450–750 nm with a maximum of 74% transmittance at 510 nm which made it applicable for bifacial irradiation. Corresponding front and rear side photovoltaic tests of the transparent PANI-based device exhibited 6.54 and

4.26% efficiencies, respectively, which were comparable to Pt-based solar cells with 6.69% PCE.

Methods of preparation of PANI CEs are diverse which include chemical, emulsion-based synthesis, cyclic voltammetric (CV) and potentiostatic polymerization, oxidative polymerization, electropolymerization techniques, etc. Cyclic voltammetric polymerization allows direct deposition of PANI film on the TCO substrate which can be used as a counter electrode. As an example, Zhang et al. reported a CV method-based preparation of PANI CEs with controlled thickness and better adhesion [10]. The electrochemical deposition method can produce PANI with high CT kinetics and good electrical and electrochemical performances [11]. Emulsion polymerization, an economical method of synthesis of CPs, could be useful in preparing hollow structured polymers which is beneficial for increasing surface area and, hence, electrocatalytic activity. Higher photovoltaic performance of emulsion polymerized PANI with hollow spheres compared to a pristine PANI was reported by Ho and colleagues [12]. In addition, the hollow sphered analogs exhibited large surface area and an enhanced electrocatalytic activity towards the reduction of triiodide ions. A novel method based on hexafluoro-isopropanol (HFIP) solution is another cost-efficient method of CPs synthesis. Some reports claim that it may generate a highly concentrated, well dispersed, stable conduction, and more ordered structure of PANI resulting in a remarkable increase of solar cell efficiency [13].

Despite its attractive properties, PANI has several drawbacks as a CE material. Its stability needs to be improved further since it was observed that the self-oxidation of PANI may deteriorate the performance of CEs. Furthermore, PANI's carcinogenic properties may also be a hindrance to its widespread application.

2.1.2 Polypyrrole

Generally, PPy is more of an insulator rather than a conductor but its oxidized form exhibits good conductivity around 2–100 S/cm. The level of conductivity depends on the type of oxidizing agent and oxidation conditions. PPy is thermally stable in the air up to 150 °C. The first application of PPy as DSSC CE was reported by Wu et al. in 2008 [14]. The PPy nanoparticles with a particle size range of 40–60 nm were synthesized following the chemical polymerization method with iodine serving as an initiator. The CE was prepared by soaking the fluorine-doped SnO_2 (FTO) substrate with PPy nanoparticles. The results show that PPy-based CE produced a high electrocatalytic activity with smaller R_{CT} compared to control Pt CE. The PCE of PPy based device outperformed Pt-based DSSC by 11%.

The thickness of PPy film should also be considered for CE fabrication since it was observed that thicker PPy film can negatively affect the performance of the CE due to an increase in R_{CT} [15]. This was observed when ultra-thin PPy nanosheets were synthesized, it exhibited similar morphology as graphene sheets with higher surface area and active sites and a having a 94% transmittance of the CE producing a PCE of 6.8% [16]. As to date, the highest efficiency based on PPy CEs is at 7.73% which is slightly lower than the reference electrode which has a PCE of 8.2% [17].

The main drawbacks of polypyrrole-based cathodes are their high R_{CT} and low conductivity. The performance of PPy counter electrodes is dependent on the synthetic method, morphology, and the type of doping. One way to overcome these issues is by adding PPy to other materials forming composites. This is evident when PPy was mixed to carbon nanotubes (CNT) the R_{CT} and exchange current densities (J_0) of the composite CE was comparable with those of Pt CE which resulted in 6.15% PCE ($\approx$ 97% of Pt CE) [18]. Another research incorporates a multiwalled CNT into PPy that produces a transparent CE which can find an application in bifacial DSSCs. Its R_{CT} was found $< 1\ \Omega\ \text{cm}^2$ implying excellent electrocatalytic activity towards reduction of triiodide. Rafique et al. fabricated a CE from copper polypyrrole functionalized multiwall carbon nanotubes (Cu-PPy-FWCNTS) nanocomposite by two-step electrodeposition method on stainless-steel substrate [19]. The hybrid CE exhibited very small R_{CT} ($4.31\ \Omega\ \text{cm}^2$) and the efficiency of DSSC with Cu-PPy-FWCNTS outperformed Pt, with PCEs of 7.1% and 6.4%, respectively. The presence of the third composite can further enhance catalytic activity in composites. A recent study showed that the addition of NiS into graphene oxide/PPy composite boosted its J_0 from 5.01 to 7.94 mA/cm^2 and in turn decreased it's R_{CT} [20]. In general, composite CE-based DSSCs outperform their corresponding components due to the synergetic effect. This opens up a way for highly efficient and low-cost DSSCs.

2.1.3 Polythiophene

Polythiophene-based conjugated polymers that were utilized as electrodes in dye-sensitized solar cells normally use an alkyl group to control the solubility of the polymer in solvents which can help improve its chemical stability and compatibility towards electrolytes in DSSCs. An electrochemical deposition method was used to grow a porous poly-3-methyl-thiophene (P3MT) that was used as a CE [21]. The highest reported efficiency was at 2.76% which is 45% lower than the reference electrode. The low in efficiency was mostly attributed to the low J_{SC} (8.88 mA/cm^2 (P3MT) vs. 15.29 mA/cm^2 (Pt)) that was mainly attributed to the low carrier mobility [21]. A group of researchers utilizes poly(3-hexylthiophene) (P3HT) and C_{61}-butyric acid methyl ester (PCBM) that were deposited through spin-coating on an FTO plate to be applied as CE in DSSCs [22]. The main problems of using the bare polythiophene utilized as CE are due to the low electrical conductivity and dismal catalytic activity. One way to improve this property is by incorporating graphene or transition metals which are known to show good catalytic activities. This was shown when polythiophene/graphene composites were synthesized via the liquid/liquid interfacial polymerization showed a PCE of 4.8% for the composite (5.1% PCE for Pt), while 3.3% for the bare polythiophene [23]. When a transition metal such as MoS_2 was mixed to the bare thiophene, it lowers the R_{CT} by 22% achieving a 38% increase in efficiency compared to the bare polythiophene [24].

2.1.4 Poly(3,4-Ethylenedioxythiophene)

The earliest attempt of using PEDOT as CE for DSSC was reported in 2002 by Saito et al., wherein they applied PEDOT on a conductive glass which demonstrated comparable PCE to the Pt CE in I^-/I_3^- based DSSC [25]. The polymer was synthesized on the TCO substrate while doping it with *p*-toluenesulfonate and poly(styrene sulfonate). TsO-doped PEDOT exhibited almost the same performance as Pt-based cells. The poor performance of PSS-doped PEDOT was due to the reduction of the redox-active site of the conjugated polymer film because of the exposure of PSS preventing the electrolyte to the active site of the PEDOT. The conductivity of PEDOT:PSS can be increased by the means of doping, synthetic conditions, and post-treatment procedures. Ho *et al.* reported that the conductivity of PEDOT:PSS was increased from 2 S/cm to 85, 45, 36, and 20 S/cm after upon treatment with dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl acetamide (DMAc), *N*,*N*-dimethyl formamide (DMF), and dichloromethane (DCM), respectively [26]. To further enhance the conductivity a small amount of carbon black (0.02–2 wt.%) was added to the polymeric solution. The electrochemical characterization revealed that DMSO-PEDOT: PSS-based CE exhibited high R_{CT} with a value of 19.4 Ω. The addition of 0.1 wt.% carbon decreased the R_{CT} to 7.2 Ω bringing it to the value like Pt CE. Thus, DMSO-PEDOT:PSS (C: 0.1 wt%) achieved 5.81% efficiency outperforming the reference electrode (5.66% PCE). In another research, bis(trifluoromethanesulfonyl)imide) (TFSI)-doped PEDOT was electrodeposited using cyclic voltammetry over conducting carbon black coated FTO glass producing a PCE of 9.8% [27]. Recently, a group of researchers synthesized PEDOT CE with a conductivity reaching as high as 1021 S/cm which was prepared via iron oxide vapor-phase polymerization [28]. Remarkably, the CE exhibited six times lower R_{CT} than Pt-based cathode guarantying outstanding catalytic activity towards the reduction of I^-/I_3^- redox couple which produces a PCE of 8.4%.

Apart from I^-/I_3^-, the reduction of other redox mediators in DSSCs can also be catalyzed by PEDOT-based counter electrodes. In this regard, PEDOT CEs can replace traditional Pt and Au metal cathodes. An interesting study of DSSC was implemented at indoor conditions using copper$^{2+/1+}$ complexes as a redox shuttle and PEDOT-covered FTO as the counter electrode [29]. The standard indoor light intensity varies between 200 and 2000 lx, in which the cell demonstrated the highest efficiency of 28.9% PCE at 1000 lx and 11.3% at standard AM1.5 conditions. Later in 2018, the group of Professor Grätzel reported a new record efficiency for indoor used DSSC of novel architecture reaching 32% which exceeds the performance of the best Si and GaAs photovoltaics [30]. In the presented architecture, the dye-coated mesoporous TiO_2 anode and the PEDOT cathode are directly contacted without using any spacer allowing attenuation of the resistance of the redox couple, hence, improving the DSSC performance. Using $Cu^{2+/1+}$ based liquid electrolyte, the solar cell demonstrated 13.1% PCE at standard conditions.

Suitable characteristics make conjugated polymers a promising cathode material for dye-sensitized solar cells. Common conjugated polymer materials for DSSC counter electrodes are polypyrrole, polyaniline, polythiophenes, etc. Among them,

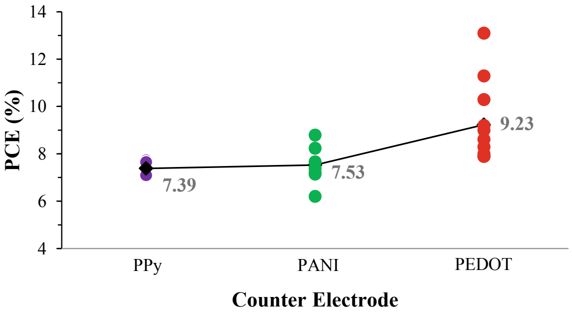

Fig. 3 Reported power conversion efficiencies of conjugated polymer counter electrodes based DSSCs

PEDOT-based polymers are the best in terms of conductivity, electrocatalytic activity, and photovoltaic performance. The comparison of the photovoltaic parameters including power conversion efficiency of the recently reported studies reveals that PEDOT exhibits the highest solar cell efficiency (Fig. 3). PPy, on the contrary, has the lowest average efficiency of the reported studies. The overall trend is PEDOT > PANI > PPy.

3 Conjugated Polymers in Perovskite Solar Cells

Perovskite solar cells (PeSC) are considered the 'rising star' of thin-film photovoltaics for a rapid increase of its power conversion efficiency in a short time. PeSC applies a perovskite structured active layer for light harvesting. Generally, perovskite is any material that has the same structure as perovskite mineral $CaTiO_3$ having a generic form ABX_3, where A and B could be any inorganic or organic cations and X are any combination of halides. In PeSCs, the perovskite structured active layer is sandwiched between the electron-transport layer (ETL) and hole-transport layer (HTL) as shown in Fig. 4.

Currently, the power conversion efficiency of PeSC has exceeded 25% making it the champion among emerging technologies and a potential alternative to silicon-based photovoltaics [31]. PeSC uses common *n*-type semiconductors such as TiO_2, SnO_2, ZnO, PCBM and C_{60} as electron-transport layers (ETL) and the *p*-type semiconductors like 2,2′,7,7′-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (Spiro-OMeTAD), poly(triaryl amine) (PTAA), P3HT, PEDOT:PSS, CuI, CuSCN, NiO, etc. as hole-transport layers (HTL). The electrons from photoexcited perovskite layer are injected into ETL and collected at the cathode, whereas holes are traveled via HTL to the anode.

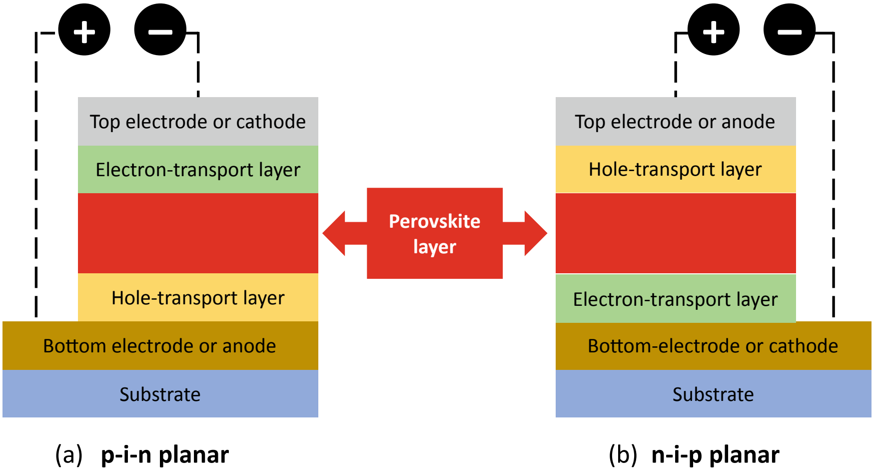

Fig. 4 Schematic diagram of different configurations of perovskite solar cells

3.1 Conjugated Polymer Counter Electrodes for Perovskite Solar Cells

For efficient charge collection and transfer, the CE should have high conductivity and proper work function. Noble metals like Au and Ag are the traditional CEs of the most state-of-the-art PeSCs. The reason is their low sheet resistance (~ 1 Ω/sq) and high light reflectivity. Despite their excellent performance, they have several disadvantages: both Au and Ag can migrate into the device core and react with perovskite halide causing degradation. In addition, their high cost affects the expense of the device. Au CE can take up to 70% of the total device cost [32]. Therefore, there is a need for alternative materials to increase their solar cell lifespan and can be more commercialize.

Conjugated polymers are potential candidates for PeSC counter electrodes. One of the widely used conjugated polymers in PeSC is PEDOT where it can serve both as the bottom and top electrode. In 2014, Jiang et al. first reported the use of PEDOT:PSS as a counter electrode for PeSC [33]. The polymer counter electrode was prepared by transfer lamination technique from its water solution to protect perovskite layer degradation. The final device configuration was glass/FTO/c-TiO_2/m-TiO_2/$CH_3NH_3PbI_3$/Spiro-OMeTAD/PEDOT:PSS and showed a maximum V_{OC} of 1.02 V and PCE of 11.29% under standard AM 1.5 light condition. The fabrication step was done under ambient air conditions.

Stamping transfer is another useful method to fabricate transparent electrodes in perovskite solar cells. Wang et al. fabricated low temperature-based inverted semi-transparent $MAPbI_3$ PeSC where PEDOT served as the top electrode [34]. The device configuration was indium tin oxide (ITO)/PEDOT:PSS/$CH_3NH_3PbI_3$/PCBM/PEDOT:PSS. The work function of

PEDOT electrode was adjusted by treating the polymer solution with PEI (polyethyleneimine) which improved cell efficiency from 0.07 to 4.02%. Park et al. reported improved conductivity and decreased work function of the top electrode after PEI/2-MEA (2-methoxyethanol) modification of PEDOT:PSS [35]. The PEDOT:PSS was dry stamp transferred over PET/ITO/PEDOT:PSS/metal halide perovskite/PCBM to fabricate semi-transparent PeSC. The PCE of the device achieved > 13% at 1 cm^2 area. In 2020, Ma et al. reported on the use of PEDOT:PSS CE in stacking perovskite solar cells with FTO/SnO_2/perovskite/Spiro-OMeTAD/PEDOT:PSS device configuration [36]. The physical and chemical properties of the electrode were modified by treating with hexamethylene diammonium diiodide which improved interface contact between photoanode and counter electrode and energy levels were properly matched. The efficiency of the device with 1 cm^2 area reached 15.21%.

Although PEDOT-based top electrodes have shown notable results in perovskite solar cells there are some drawbacks of the polymer which need further investigation. The polymer is usually produced as a water solution and possesses some level of acidity which can cause damage to the cell via degradation. Another issue is the low conductivity of PEDOT-based films compared to metal CEs and ITO that causes sheet resistance to be high. To increase the conductivity certain additives are added to the polymer. Other methods of improving the conductivity need to be studied. The short lifespan of the PEDOT films is another problem that requires attention.

4 Conjugated Polymers in Organic Solar Cells

Organic solar cells (OSCs) have received great attention as a source of green energy because of their considerable advantages associated with low-cost manufacturing, easy fabrication technique, and possibilities to construct lightweight, flexible, and ultrathin devices. Moreover, the implementation of a solution-processing technique for deposition of active layers in OSCs, like roll-to-roll and ink-jet printing technologies, can be transmitted in large area sizes, thereby facilitating the production of OSCs on an industrial scale. Owing to the substantial progress in the synthesis of new materials and device engineering, the PCE of recently developed OSCs has improved significantly and has reached 18.22% in 2020 [37]. However, this PCE indicator is far behind solar cells based on inorganic materials or from perovskite solar cells, which restricts the practical application of OSCs. To overcome this limitation in photon-to-electron conversion efficiency, tremendous research efforts are needed in terms of the introduction of new organic materials, the development of a more effective device structure, and the optimization of solar cell fabrication techniques in OSCs.

To date, among existing devices of OSCs where photoactive layers are represented by single, double (p–n junction bilayer), or bulk-heterojunction (BHJ) structures, the most efficient is based on the latter. The possibility of achieving a relatively high PCE by BHJ configuration is associated with the resolving of two important internal limitations which are the charge separation from the excited state of the organic semiconductor and the charge transport inside active layers to electrodes surfaces. As illustrated in Fig. 5, the OSC devices with a “normal” and “inverted” structure usually consist of the following layers stacked in parallel: substrate (glass, polymer materials)/bottom or hole-collecting electrode/anode interfacial or hole-transport layer/BHJ active layer/cathode interfacial or electron-transport layer/top or electron-collecting electrode which is an almost similar configuration to PeSCs (Fig. 4). Electrical power generation in OSCs can be summarized as four main steps: (1) incident photons are absorbed by organic polymer active layer resulting in excision generation at the donor–acceptor interface inside BHJ system; (2) separation of generated excision into free charge carriers (electrons and holes); (3) transportation of charge carriers; electrons are transferred through *n*-type organic semiconductor toward cathode surface and holes through *p*-type domains to anode surface; and (4) extraction and collection of charge carriers by electrodes to produce photocurrent.

Maintaining the mobility of charge carriers in one direction and reducing recombination are imperative and depend on the work functions of both electrodes. Mostly, ITO on a glass substrate is generally operated as a transparent hole collecting layer (anode), and metal layer (Al, Ag, Au, etc.) is commonly employed as electron collecting layer (cathode). A high conductivity, transparency, and excellent mechanical stability are the main advantageous properties of ITO, while its rigid structure and high cost are the main highlighted drawbacks. In most cases, the top electrode is a metal layer, the preparation of which requires expensive vacuum deposition facilities, which limits the size and cost of the devices. Therefore, the development

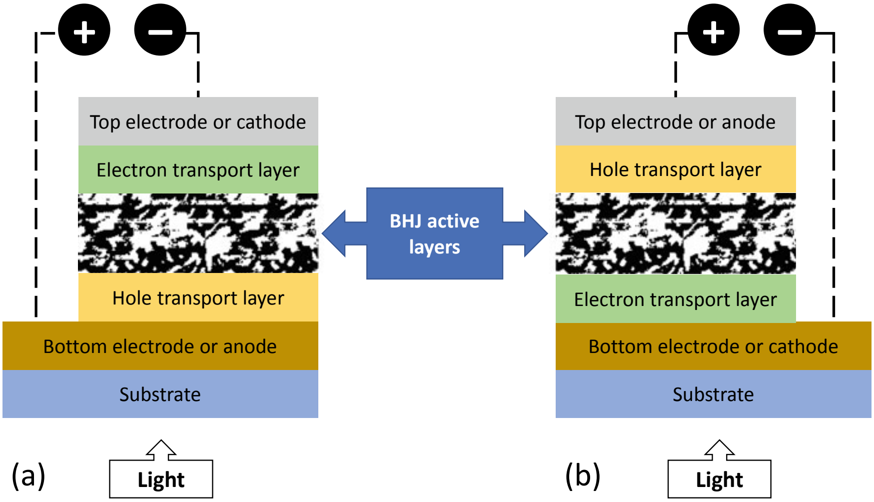

Fig. 5 Device architecture OSCs with **a** conventional and **b** inverted structures

of alternative materials for electrodes has crucial importance. In this aspect, conjugated polymers have become as main alternative materials for both top and bottom electrodes manufacturing.

The most popular CPs used as OSC cathode and anode is PEDOT:PSS. It exhibits a low sheet resistance, a tunable work function (5.0–5.2 eV), a wide range of conductivity (10^{-3}–4 x 10^{3} S/cm), remarkably high optical transparency (>90%) in the visible light region, flexibility, and thermal stability. In addition, the application of PEDOT:PSS as electrode materials can be achieved using inexpensive, solution-processed technologies and implemented on a large surface area [38]. Despite the fact, that primary PEDOT:PSS films possess poor conductivity there are several methods to increase it; this can be attained via doping with strong acids, polar organic solvents, various nanomaterials, and pre-and post-treatment methods. For the manufacture of OSC electrodes, PEDOT:PSS aqueous solutions are commercially available under the trade names Clevios PH500, PH510 and PH1000, in which the ratio of PEDOT to PSS is 1:2.5. In addition, aqueous solutions of PEDOT:PSS with a ratio of 1:6 are well known as a commercial product with the market name Clevios PVP AI 4083, which is commonly used as a hole transfer layer in the OSC devices [39].

4.1 PEDOT:PSS as a Bottom Electrode for Organic Solar Cells

The pioneers who utilized PEDOT:PSS deposited on a glass substrate as an anode were Zhang et al. in 2002 [40]. Their result showed for the first time the possibility of using lower-cost and mechanically flexible PEDOT:PSS instead of traditional ITO for the manufacture of rigid OSC electrodes. They achieved an increased conductivity of PEDOT:PSS (10 S/cm) by doping it with glycerol or D-sorbitol. As a result, the OSC device consisting of D-sorbitol-doped PEDOT:PSS anode showed a PCE of 0.36%, while the OSCs with an ITO bottom electrode demonstrated efficiency of 0.46%. This created many research efforts on improving the conductivity of PEDOT:PSS electrodes by doping PEDOT:PSS with various polar solvents such as ethylene glycol, methanol, 2-chloroethanol, and DMSO producing a much higher PCE value than the D-sorbitol-doped PEDOT:PSS. To cite an example, Na et al. firstly reported a high conductive PEDOT:PSS electrodes deposited on rigid (glass) and flexible (PET) substrates [41]. A high conductivity value (550 S/cm) was achieved by doping the CP with 5% DMSO, which led to 3.27% and 2.8% efficiency of the ITO-free OSCs fabricated on glass and plastic substrates, respectively. The exhibited PCE results for PEDOT: PSS-based cells were similar to those of ITO-based devices. Recently, Kim and co-workers compared the performance of the 2-chloroethanol-treated PEDOT:PSS and standard 5% DMSO-doped PEDOT:PSS. According to their study, the 2-chloroethanol-treated CP electrodes showed superior PCE value rather than the DMSO-added films (9.04 vs. 7.63%) due to the electrical conductivity (762 vs. 439 S/cm) [42].

Another effective technique for improving PCE value of OSCs by increasing conductivity is the post-treatment of PEDOT:PSS films with either inorganic or organic acids. For example, Ge and his research group fabricated flexible transparent OSCs with CH_3SO_3H-treated PEDOT:PSS electrode on PET substrate at room temperature (20 °C). Modified PEDOT:PSS film was characterized with excellent electrical and optical parameters: high conductivity (2860 S cm^{-1}), superior optical transparency (90% at 450–900 nm), and smooth surface (RMS = 2.14 nm). Ultimately, the constructed solar cell containing a mixture of poly[(2,6-(4,8-bis(5-(2-ethyl-hexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene)-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c′]-dithiophene-4,8-dione)] and methyl-substituted 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2′,3′-d′]-s-indaceno [1,2-b:5,6-b′]-dithiophene active layer exhibited a high PCE of 10.12% [43]. Regarding the fact that relatively strong acids could be corrosive and harmful to the flexible plastic substrate, Ge's group has recently resolved this issue. They have discovered a high efficiency of 14.17% by folding-flexible OSCs composing of D-sorbitol micro-doped PEDOT:PSS/PET electrode treated with natural acids (citric acid, malic acid, or tartaric acid) [44].

A prominent improvement in the conductivity of PEDOT:PSS films for OSCs can be accomplished by a composite generation with a variety of conductive inorganic materials, including nanocarbon and metallic nanowires (NW). A highly conductive PEDOT:PSS: sulfonated carbon nanotubes (SCNT) composite electrode was prepared by Chen's group. The PEDOT:PSS:SCNT films as a cathode in "inverted" OSCs revealed a high PCE of 9.91% due to great optoelectronic effects (conductivity > 3500 S/cm, transmittance ~83%) [45]. Recently, Shim et al. have fabricated PEDOT:PSS:CuNW-based transparent composite electrodes for ITO-free OSCs. Based on the PH1000/CuNWs, the optimized flexible OSC with P3HT: indene-C_{60} bisadduct (ICBA) as active layer exhibits the highest PCE of 17.6% under 1000-lx light-emitting diode illumination, with an open-circuit voltage of 713 mV, a short-circuit current of 103 $\mu A/cm^2$ and a fill factor of 67.2% [46].

4.2 PEDOT:PSS as a Top Electrode for Organic Solar Cells

Commonly used top electrode materials for OSCs are MoO_3/Ag or LiF/Al. The manufacture of metal electrodes requires expensive and energy-consuming high vacuum equipment. Hence, the replacement of inorganic electrode materials with more profitable ones is a priority task. In this respect, the top electrode based on PEDOT:PSS is an alternative material, which provides tunable conductivity and high transmittance.

One of the effective methods for improving the characteristics of OSC is to minimize the resistance of the PEDOT:PSS electrode, which directly depends on its morphology. Various technologies have been used to make PEDOT:PSS films, including solution-processed, spin coating, screen printing, spray coating, bonding, doctor-blade coating, etc. Lee's group has recently constructed a sequentially printed

PEDOT:PSS/ionic liquid (IL) composite successfully applied as top electrode for OSCs, exhibiting a PCE of 6.32% at an average visible transmittance (AVT) of 35.4% [47]. In 2020, Kim et al. fabricated window-film-type OSCs with PEDOT:PSS as top electrode treated with sulfuric acid. Their OSC device with the following structure PEN/PA/ZnO-NP/PTB7-Th:$PC_{70}BM/Mo_x$/H-PEDOT showed excellent performance with PCE of 4.9% along with high transparency (AVT = 42%) [48]. Recently, Ma and co-workers reported a novel composite of phosphomolybdic acid (PMA) and PEDOT:PSS that revealed high affinity with the active layer and printed top Ag nanowires. A spin-coating or doctor-blade coating method were implemented for deposition of constructed buffer layer on a substrate surface (polymer). The use of this composite as top electrodes demonstrated the PCE of 5.01% with an excellent AVT of 50.3% [49]. These research outputs have proved PEDOT:PSS to be an excellent alternative material for both top and bottom electrodes because of their superior optical, electrical, and mechanical properties. Furthermore, the performance of PEDOT:PSS electrodes can be enhanced by the incorporation of miscellaneous doping agents, including carbonaceous nanocompounds, metal grids, and metal nanowires. For future perspective, there are some issues relating to improvement of conductivity, transmittance, and persistence to inner and outer stimuli.

References

1. Becquerel, M.: Mémoire sur les effets électriques produits sous l'influence des rayons solaires. C. R. Hebd Seances Acad. Sci. **9**, 561–567 (1839)
2. Fritts, C.E.: On a new form of selenium cell, and some electrical discoveries made by its use. Am. J. Sci. **s3–26** (156), 465–472 (1883)
3. Chapin, D.M., Fuller, C.S., Pearson, G.L.: A new silicon p-n junction photocell for converting solar radiation into electrical power. J. Appl. Phys. **25**(5), 676–677 (1954)
4. Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K., Heeger, A.J.: Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH). J. Chem. Soc. Chem. Commun. **16**, 578–580 (1977)
5. O'Regan, B., Grätzel, M.: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. Nature **353**(6346), 737–740 (1991)
6. Li, Q., Wu, J., Tang, Q., Lan, Z., Li, P., Lin, J., Fan, L.: Application of microporous polyaniline counter electrode for dye-sensitized solar cells. Electrochem. Commun. **10**(9), 1299–1302 (2008)
7. Wang, H., Feng, Q., Gong, F., Li, Y., Zhou, G., Wang, Z.-S.: In situ growth of oriented polyaniline nanowires array for efficient cathode of Co(iii)/Co(ii) mediated dye-sensitized solar cell. J. Mater. Chem. A **1**(1), 97–104 (2013)
8. Li, Z., Ye, B., Hu, X., Ma, X., Zhang, X., Deng, Y.: Facile electropolymerized-PANI as counter electrode for low cost dye-sensitized solar cell. Electrochem. Commun. **11**(9), 1768–1771 (2009)
9. Tai, Q., Chen, B., Guo, F., Xu, S., Hu, H., Sebo, B., Zhao, X.-Z.: In situ prepared transparent polyaniline electrode and its application in bifacial dye-sensitized solar cells. ACS Nano **5**(5), 3795–3799 (2011)
10. Zhang, J., Hreid, T., Li, X., Guo, W., Wang, L., Shi, X., Su, H., Yuan, Z.: Nanostructured polyaniline counter electrode for dye-sensitised solar cells: fabrication and investigation of its electrochemical formation mechanism. Electrochim. Acta **55**(11), 3664–3668 (2010)

11. Tang, Q., Cai, H., Yuan, S., Wang, X.: Counter electrodes from double-layered polyaniline nanostructures for dye-sensitized solar cell applications. J. Mater. Chem. A **1**(2), 317–323 (2013)
12. Huang, K.-C., Hu, C.-W., Tseng, C.-Y., Liu, C.-Y., Yeh, M.-H., Wei, H.-Y., Wang, C.-C., Vittal, R., Chu, C.-W., Ho, K.-C.: A counter electrode based on hollow spherical particles of polyaniline for a dye-sensitized solar cell. J. Mater. Chem. **22**(29), 14727–14733 (2012)
13. Chiang, C.-H., Chen, S.-C., Wu, C.-G.: Preparation of highly concentrated and stable conducting polymer solutions and their application in high-efficiency dye-sensitized solar cell. Org. Electron. **14**(9), 2369–2378 (2013)
14. Wu, J., Li, Q., Fan, L., Lan, Z., Li, P., Lin, J., Hao, S.: High-performance polypyrrole nanoparticles counter electrode for dye-sensitized solar cells. J. Power Sources **181**(1), 172–176 (2008)
15. Makris, T., Dracopoulos, V., Stergiopoulos, T., Lianos, P.: A quasi solid-state dye-sensitized solar cell made of polypyrrole counter electrodes. Electrochim. Acta **56**(5), 2004–2008 (2011)
16. Hwang, D.K., Song, D., Jeon, S.S., Han, T.H., Kang, Y.S., Im, S.S.: Ultrathin polypyrrole nanosheets doped with HCl as counter electrodes in dye-sensitized solar cells. J. Mater. Chem. A **2**(3), 859–865 (2014)
17. Jeon, S.S., Kim, C., Ko, J., Im, S.S.: Spherical polypyrrole nanoparticles as a highly efficient counter electrode for dye-sensitized solar cells. J. Mater. Chem. **21**(22), 8146–8151 (2011)
18. Lee, J.H., Jang, Y.J., Kim, D.W., Cheruku, R., Thogiti, S., Ahn, K.-S., Kim, J.H.: Application of polypyrrole/sodium dodecyl sulfate/carbon nanotube counter electrode for solid-state dye-sensitized solar cells and dye-sensitized solar cells. Chem. Pap. **73**(11), 2749–2755 (2019)
19. Rafique, S., Rashid, I., Sharif, R.: Cost effective dye sensitized solar cell based on novel Cu polypyrrole multiwall carbon nanotubes nanocomposites counter electrode. Sci. Rep. **11**(1), 14830 (2021)
20. Noorani, B., Ghasemi, S., Hosseini, S.R.: Nanostructured nickel sulfide/graphene oxide-polypyrrole as platinum-free counter electrode for dye-sensitized solar cell. J. Photochem. Photobiol. A **405**, 112966 (2021)
21. Torabi, N., Behjat, A., Jafari, F.: Dye-sensitized solar cells based on porous conjugated polymer counter electrodes. Thin Solid Films **573**, 112–116 (2014)
22. Yahia, I.S., Mansour, S.A., Hafez, H.S., Ocakoglu, K., Yakuphanoglu, F.: Photovoltaic properties and negative capacitance spectroscopy of PCBM:P3HT/FTO nanostructured counter electrode for TiO_2-based DSSC. J. Inorg. Organomet. Polym. Mater. **22**(6), 1240–1247 (2012)
23. Bora, C., Sarkar, C., Mohan, K.J., Dolui, S.: Polythiophene/graphene composite as a highly efficient platinum-free counter electrode in dye-sensitized solar cells. Electrochim. Acta **157**, 225–231 (2015)
24. Asok, A., Naik, A.A., Arunachalam, S., Govindaraj, R., Haribabu, K.: Microwave assisted synthesis of polythiophene–molybdenum sulfide counter electrode in dye sensitized solar cell. J. Mater. Sci.: Mater. Electron. **30**(14), 13655–13663 (2019)
25. Yasuteru, S., Takayuki, K., Yuji, W., Shozo, Y.: Application of poly(3,4-ethylenedioxythiophene) to counter electrode in dye-sensitized solar cells. Chem. Lett. **31**(10), 1060–1061 (2002)
26. Chen, J.-G., Wei, H.-Y., Ho, K.-C.: Using modified poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) film as a counter electrode in dye-sensitized solar cells. Sol. Energy Mater. Sol. Cells **91**(15), 1472–1477 (2007)
27. Zhang, J., Long, H., Miralles, S.G., Bisquert, J., Fabregat-Santiago, F., Zhang, M.: The combination of a polymer–carbon composite electrode with a high-absorptivity ruthenium dye achieves an efficient dye-sensitized solar cell based on a thiolate–disulfide redox couple. Phys. Chem. Chem. Phys. **14**(19), 7131–7136 (2012)
28. Kouhnavard, M., Yifan, D., D'Arcy, J.M., Mishra, R., Biswas, P.: Highly conductive PEDOT films with enhanced catalytic activity for dye-sensitized solar cells. Sol. Energy **211**, 258–264 (2020)
29. Freitag, M., Teuscher, J., Saygili, Y., Zhang, X., Giordano, F., Liska, P., Hua, J., Zakeeruddin, S.M., Moser, J.-E., Grätzel, M., Hagfeldt, A.: Dye-sensitized solar cells for efficient power generation under ambient lighting. Nat. Photonics **11**(6), 372–378 (2017)

30. Cao, Y., Liu, Y., Zakeeruddin, S.M., Hagfeldt, A., Grätzel, M.: Direct contact of selective charge extraction layers enables high-efficiency molecular photovoltaics. Joule **2**(6), 1108–1117 (2018)
31. Jeong, J., Kim, M., Seo, J., Lu, H., Ahlawat, P., Mishra, A., Yang, Y., Hope, M.A., Eickemeyer, F.T., Kim, M., Yoon, Y.J., Choi, I.W., Darwich, B.P., Choi, S.J., Jo, Y., Lee, J.H., Walker, B., Zakeeruddin, S.M., Emsley, L., Rothlisberger, U., Hagfeldt, A., Kim, D.S., Grätzel, M., Kim, J.Y.: Pseudo-halide anion engineering for α-FAPbI3 perovskite solar cells. Nature **592**(7854), 381–385 (2021)
32. Chang, N.L., Yi Ho-Baillie, A.W., Basore, P.A., Young, T.L., Evans, R., Egan, R.J.: A manufacturing cost estimation method with uncertainty analysis and its application to perovskite on glass photovoltaic modules. Prog. Photovoltaics Res. Appl. **25**(5), 390–405 (2017)
33. Jiang, F., Liu, T., Zeng, S., Zhao, Q., Min, X., Li, Z., Tong, J., Meng, W., Xiong, S., Zhou, Y.: Metal electrode-free perovskite solar cells with transfer-laminated conducting polymer electrode. Opt. Express **23**(3), A83–A91 (2015)
34. Kim, K.M., Ahn, S., Jang, W., Park, S., Park, O.O., Wang, D.H.: Work function optimization of vacuum free top-electrode by PEDOT:PSS/PEI interaction for efficient semi-transparent perovskite solar cells. Sol. Energy Mater. Sol. Cells **176**, 435–440 (2018)
35. Lee, J.H., Heo, J.H., Im, S.H., Park, O.O.: Reproducible dry stamping transfer of PEDOT:PSS transparent top electrode for flexible semitransparent metal halide perovskite solar cells. ACS Appl. Mater. Interfaces **12**(9), 10527–10534 (2020)
36. Ma, H., Shao, Y., Zhang, C., Lv, Y., Feng, Y., Dong, Q., Shi, Y.: Enhancing the interface contact of stacking perovskite solar cells with hexamethylenediammonium diiodide-modified PEDOT:PSS as an electrode. ACS Appl. Mater. Interfaces **12**(37), 42321–42327 (2020)
37. Liu, Q., Jiang, Y., Jin, K., Qin, J., Xu, J., Li, W., Xiong, J., Liu, J., Xiao, Z., Sun, K., Yang, S., Zhang, X., Ding, L.: 18% Efficiency organic solar cells. Sci. Bull. **65**(4), 272–275 (2020)
38. Fan, X., Nie, W., Tsai, H., Wang, N., Huang, H., Cheng, Y., Wen, R., Ma, L., Yan, F., Xia, Y.: PEDOT:PSS for flexible and stretchable electronics: modifications, strategies, and applications. Adv. Sci. **6**(19), 1900813 (2019)
39. Lövenich, W.: PEDOT-properties and applications. Polym. Sci. Ser. C **56**(1), 135–143 (2014)
40. Zhang, F., Johansson, M., Andersson, M.R., Hummelen, J.C., Inganäs, O.: Polymer photovoltaic cells with conducting polymer anodes. Adv. Mater. **14**(9), 662–665 (2002)
41. Na, S.-I., Kim, S.-S., Jo, J., Kim, D.-Y.: Efficient and flexible ITO-free organic solar cells using highly conductive polymer anodes. Adv. Mater. **20**(21), 4061–4067 (2008)
42. Jang, H., Kim, M.S., Jang, W., Son, H., Wang, D.H., Kim, F.S.: Highly conductive PEDOT:PSS electrode obtained via post-treatment with alcoholic solvent for ITO-free organic solar cells. J. Ind. Eng. Chem. **86**, 205–210 (2020)
43. Song, W., Fan, X., Xu, B., Yan, F., Cui, H., Wei, Q., Peng, R., Hong, L., Huang, J., Ge, Z.: All-solution-processed metal-oxide-free flexible organic solar cells with over 10% efficiency. Adv. Mater. **30**(26), 1800075 (2018)
44. Song, W., Peng, R., Huang, L., Liu, C., Fanady, B., Lei, T., Hong, L., Ge, J., Facchetti, A., Ge, Z.: Over 14% efficiency folding-flexible ITO-free organic solar cells enabled by eco-friendly acid-processed electrodes. iScience **23**(4) (2020)
45. Hu, X., Chen, L., Tan, L., Ji, T., Zhang, Y., Zhang, L., Zhang, D., Chen, Y.: In situ polymerization of ethylenedioxythiophene from sulfonated carbon nanotube templates: toward high efficiency ITO-free solar cells. J. Mater. Chem. A **4**(17), 6645–6652 (2016)
46. Ahsan Saeed, M., Hyeon Kim, S., Baek, K., Hyun, J.K., Youn Lee, S., Won Shim, J.: PEDOT:PSS:CuNW-based transparent composite electrodes for high-performance and flexible organic photovoltaics under indoor lighting. Appl. Surf. Sci. **567**, 150852 (2021)
47. Park, H., Lee, J.-H., Lee, S., Jeong, S.Y., Choi, J.W., Lee, C.-L., Kim, J.-H., Lee, K.: Retarding ion exchange between conducting polymers and ionic liquids for printable top electrodes in semitransparent organic solar cells. ACS Appl. Mater. Interfaces **12**(2), 2276–2284 (2020)
48. Kim, S., Lee, E., Lee, Y., Kim, J., Park, B., Jang, S.-Y., Jeong, S., Oh, J., Lee, M.S., Kang, H., Lee, K.: Interface engineering for fabricating semitransparent and flexible window-film-type organic solar cells. ACS Appl. Mater. Interfaces **12**(23), 26232–26238 (2020)

49. Ji, G., Wang, Y., Luo, Q., Han, K., Xie, M., Zhang, L., Wu, N., Lin, J., Xiao, S., Li, Y.-Q., Luo, L.-Q., Ma, C.-Q.: Fully coated semitransparent organic solar cells with a doctor-blade-coated composite anode buffer layer of phosphomolybdic acid and PEDOT:PSS and a spray-coated silver nanowire top electrode. ACS Appl. Mater. Interfaces **10**(1), 943–954 (2018)