

Review Article

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## Nanostructured Conducting Polymer Based Counter Electrodes For Dye-sensitized Solar Cells: An Overview

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### Abstract

Dye-sensitized solar cells (DSCs) have gained a significant attention as third generation photovoltaic devices due to their high photo-to-electric conversion efficiencies at low production cost. Platinum has been reported as the most felicitous metal for the fabrication of counter electrodes (CEs) in DSCs for its superior electro catalytic activity towards the redox reaction of  $I_3^-/I^-$ . Nevertheless, the high cost and susceptibility to corrosion of Pt caused the need of new materials to replace Pt in the CE. Among various discovered materials, conducting polymers with extended conjugate electron system have been widely investigated by researchers. Polyaniline (PANI), polypyrrole (PPy) and poly (3,4-ethylenedioxythiophene) (PEDOT) have drawn much more attention from all of the other conducting polymers as alternative CEs in DSCs due to their high conductivity, electro catalytic activity and simplistic synthesis methods at ambient temperature. These three prominent polymers performed with remarkable photovoltaic performances once they were used as CEs for the DSCs. PEDOT-CE based DSCs showed the highest power conversion efficiency but its cost is high compared to the other two polymers. This review paper discusses the development of PANI, PPy and PEDOT polymers as CE materials with the aid of nanotechnology for the improvement of photovoltaic performances in DSCs.

**Key Words:** Dye-sensitized solar cell; Counter electrode; Nanotechnology; Polyaniline; Polypyrrole; Poly (3,4-ethylenedioxythiophene); Platinum;

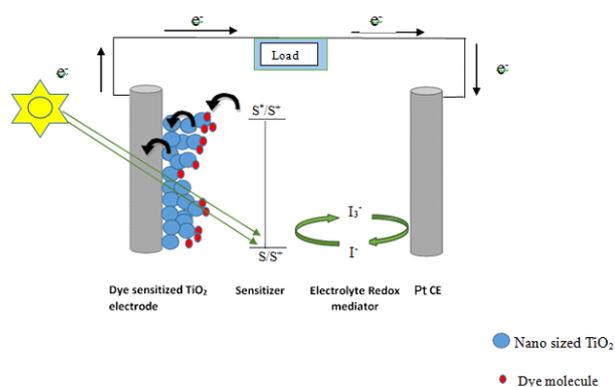
### Introduction

The global energy demand and the depletion of readily available fossil fuels are some of the reasons to the search of alternative energy sources, thus renewable solar energy has become crucial. As the largest source of clean energy, the sun deposits 120,000 TW of radiation on the earth [1]. Solar cells are capable of converting solar energy into electrical energy in an efficient way. Initially silicon photovoltaics were used, but the energy requirement for the production of pure Si was extremely high [2]. Hence, the cost of electricity production from commercial silicon photovoltaics were significantly higher than that produced from the fossil fuels. Subsequently O'Regan and Gratzel discovered dye-sensitized solar cells (DSCs) or "Gratzel Cells" in 1991 as an alternative for the Si solar cells [3]. Since then, DSCs have gained more research attention for the past years due to their low production cost, light weight, flexibility, low toxicity, and high efficiency to convert solar energy into electricity [3-6].

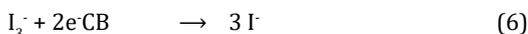
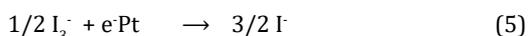
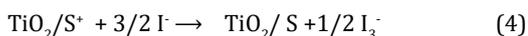
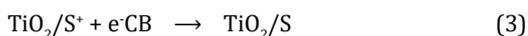
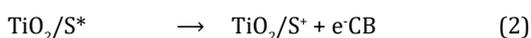
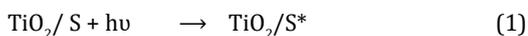
### Dye-sensitized solar cells:

A conventional DSC is typically composed of a photo anode, a dye (sensitizer), electrolyte and a counter electrode (CE) [7,8]. Photo anode is simply a semiconductor with a wide band gap such as  $TiO_2$ , ZnO, NiO etc [9]. The most efficient and widely used photo anode is n-type semiconductor  $TiO_2$ , due to its high charge transport and ability to suppress charge recombination [10]. The photo anodes absorb light in ultra violet region. Dye is an organic compound which is spread over the photo anode which absorbs light in the visible range and produces an electron-hole pair. The excited electron in the conduction band of the dye is then transferred to the conduction band of the  $TiO_2$  semiconductor within picoseconds [11]. Afterwards, the electron is transferred to the counter electrode of the cell via an external circuit. Meanwhile, the redox couple donates its electron to the dye and regenerates the dye. Iodide/tri iodide ( $I^-/I_3^-$ ) is the typical redox couple which is used by the DSC and it is dissolved in a solvent such as acetonitrile.

The oxidized species of electrolyte are reduced at counter electrode. Until the light illumination stops, this operation of the DSC runs as a cyclic process [10]. Following equations from 1 to 6 summarize the above working mechanism of the DSC and figure 1 shows a schematic diagram of a standard DSC [12] (Figure 1).



**Figure 1:** Schematic diagram of a DSC



### Desired properties of a counter electrode

The counter electrode is a vital component in DSCs since it acts as a mediator for collecting electrons from the external circuit, reduces  $\text{I}_3^-$  to  $\text{I}^-$  and regenerates the oxidized dye or the sensitizer [13,14]. Therefore a successful CE should consist with properties such as good conductivity, high catalytic activity and electrochemical stability in the electrolyte system. Additionally it should be mechanically stable [1]. Fabrication of CEs from conventional conductive glasses such as indium-doped tin oxide (ITO) or fluorine-doped tin oxide (FTO) is not sufficient since they provide a low catalytic rate for the reduction process. Thus conducting glass substrate must be coated with a catalytic material to accelerate the reaction.

A CE material in a dye-sensitized solar cell should full fill some unique properties such as a low charge transfer resistance ( $R_{ct}$ ), high surface area, porous nature, optimum thickness, good adhesivity with the transparent conducting oxide (TCO), high reflectance of transmitted light and high exchange current density [15,16]. Platinum has been reported as one of the most appropriate materials to develop CEs in DSCs as it is rich with all the above required properties [17]. However due to the high cost, rarity, susceptibility to corrosion, advance synthetic methods of Pt, a curiosity has been emerged on searching new CE materials such as carbonaceous materials, conducting polymers, transition metal based inorganic materials etc. [18] Among various discovered

materials, conducting polymers with extended conjugate electron system have been widely investigated by researchers due to their superior properties [19].

### Conducting polymer based counter electrodes

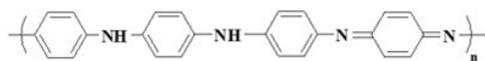
Conducting polymers are organic polymers that possess electrical conductivity ranging from semi-conductors ( $10^{-8}$  S/cm) to metals ( $10^5$  S/cm) [20]. Conducting polymers are rich with attractive properties such as high conductivity, environmental stability, cost effectiveness, easy synthesis, and electrochemical redox properties [21,22]. Conducting polymers provide conductivity through a conjugated bond system along the polymer backbone, thus it contains continuous  $sp^2$  hybridized carbon centers. Two foremost methods to synthesize conducting polymers are chemical oxidative polymerization and electrochemical polymerization [23]. Among them electrochemical polymerization offers unique advantages such as direct deposition of thin film on the substrate, "catalyst free synthetic method", better adhesivity, higher purity, easier fabrication, controllable surface morphology, *in-situ* polymerization and uniform thickness of the resultant film [24-26]. These advantages make electrochemical polymerization method as the most worthy one for DSCs applications. Among huge number of discovered conducting polymers up to now, polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) [24], in their nanostructural forms, have drawn much attention as alternative CEs in DSCs due to high conductivity, electro catalytic activity and simplistic synthesis methods at ambient temperature.

There are three main ways to synthesis conducting polymer nanostructures which are,

1. Templateless synthesis: - The nanostructures are synthesized by selecting the relevant conditions of electrosynthesis at chemically inert electrodes.
2. Template-assisted synthesis: - Nanostructured templates are first created on the surface of the electrode. Afterwards electropolymerization occurs within the nanosized structural units of a template (such as holes, cavities etc.)
3. Molecular template-assisted synthesis: - Molecules which contain nanosized cavities are used as templates. They are arranged on the electrode surface, so the electropolymerization proceeds within these cavities resulting nanostructured polymers.

### Polyaniline (PANI)

Polyaniline is one of the most intensively studied versatile CE materials when compared with various other conducting polymers. It has appropriate features like easy synthesis, high-conductivity, good environmental stability and interesting redox properties [9, 27, 28]. PANI can be prepared using chemical polymerization or electro polymerization method [29-31]. Many techniques of electro polymerization are used in the synthesis of PANI CEs such as cyclic voltammetry, constant potential, constant current, pulse current, and pulse potentiostatic methods etc. [32-34]. Figure 2 shows the chemical structure of Emeraldine, one of the oxidation forms of PANI (Figure 2).



**Figure 2:** Structure of Emeraldine

PANI as a CE in DSC has introduced by Li et al. for the first time [35]. Using an aqueous oxidative polymerization reaction with perchloric acid as a dopant in the presence of ammonium persulfate, they synthesized microporous PANI nanoparticles (NPs) with size diameters of 100 nm. The increase of the surface area, lower charge-transfer resistance and higher electro catalytic activity for  $I^-$  to  $I_3^-$  redox reaction in PANI electrode have resulted an overall energy conversion efficiency of the DSC with 7.15%, which is higher than that of the DSC with Pt counter electrode (6.90%) under the same conditions [35].

The conical structured PANI nanotubes were easily synthesized on indium tin oxide (ITO) conducting poly(ethylene terephthalate) (PET) substrates using electrochemical polymerization method [36]. With the increasing potential from 2.0 V to 2.6 V different PANI structures were obtained such as, dendritic PANI, nanosheets, nanotubes, and nanorods. The novel conical nanotube of PANI was obtained at 2.4 V. This PANI electrode showed excellent charge transport property and high electrochemical activity due to the nanotube structure with high surface area and chemical activity with 0.86% increment in efficiency compared to DSC with Pt counter electrode under the same conditions [36].

PANI nanofiber supported Pt nanoparticle film was prepared by a two-step electrochemical deposition method to use as a counter electrode in DSC and obtained a light-electric energy conversion efficiency of 7.69% which is higher than those with pure PANI (6.58%) or Pt counter electrodes (6.52%) [37].

A flexible counter electrode by electrochemical deposition of PANI nanofibers on graphitized polyimide carbon films for the tri-iodide reduction was synthesized. The photovoltaic device which contains this PANI counter electrode showed the charge transfer resistance measured from the impedance data as  $0.5 \Omega \text{ cm}^2$  which is lower than that of  $1.8 \Omega \text{ cm}^2$  for a conventional platinum electrode and an overall energy conversion efficiency of 6.85% under 1 sun illumination [38].

Another flexible CE was fabricated using a composite of PANI and flexible graphite (FG) in DSC had shown a PCE of 7.36%, which is comparable to 7.87% that of Pt CE [39]. In here FG is used as an alternative to rigid FTO glass substrate by facilitating industrial roll-to-roll applications. Low surface granular diameter (20-50 nm) [39], homogeneous and well-adhered nature of PANI on to FG substrate, enhances the catalytic activity of PANI/FG composite CE which prepared by using an *in-situ* chemical polymerization.

A CE was prepared using a nanofibrous thin film by depositing as-prepared PANI nanofiber on FTO glass by Marangoni flow [40,41]. Compared with PANI nano-particulate films, PANI nanofibrous films contain high electro catalytic activity as a counter electrode in DSC, due to the formation of an interconnected network structures

[42]. The DSC with this PANI CE showed a 3.8% light to electricity conversion efficiency compared with 5.1% by Pt [41].

The electrochemical polymerization method is not applicable for large-scale fabrication. Hence, a simple way to large-scale synthesis of PANI nanobelts by mixing aniline and hydrochloric acid without any templates was introduced [43]. The power conversion efficiency of DSC with PANI nanobelt counter electrode was able to attain 90% of the value of the DSC with Pt counter electrode [43].

A novel CE for the DSC was prepared using graphene/PANI nano composite, which was synthesized by *in-situ* polymerization. Due to the electrostatic attraction, when aniline monomers are added into graphene dispersion, they can immediately adsorb onto the graphene surface. When ammonium persulfate solution added into the dispersion at  $0^\circ \text{C}$ , aniline monomers adsorbed are initiated to polymerize from the adsorbed sites on the surface, finally resulting PANI nanoparticles with size of 20 nm, on graphene sheet [44]. When a DSC with PANI CE exhibits a power conversion efficiency (PCE) of 4.78% and a fill factor (FF) of 0.54, a graphene/PANI nanocomposite CE exhibits a PCE of 6.09% and a FF of 0.67. This conversion efficiency is comparable to that of the cell with the Pt counter electrode which exhibits a PCE of 6.88 % [44].

Doping of sulfamic acid (SFA) in to uniform polyaniline nanofibers (PANI NFs) has also been studied since still there is a need to work on PANI NFs to enhance its usefulness. A template free interfacial polymerization process has been used and the obtained SFA-doped PANI NFs-based fabricated DSCs have exhibited a power conversion efficiency of 5.5% while the PANI NFs-based DSC demonstrated a PCE of 4.0%. The study states that the enhancement in the PCE was due to the incorporation of SFA into the PANI nanofibers, which gives a higher electro catalytic activity for the redox reaction of  $I_3^-/I^-$  [45]. It was found, when SAF is doped, the diameter of PANI NFs has increased about to 40 nm from 30 nm. The doping has caused some aggregation of PANI NFs, which might result in the formation of voids into the fibrous network of PANI NFs and ultimately facilitating an efficient redox reaction of the electrolyte [46].

A unique double-layered PANI deposited ITO substrate has been prepared, having a compact layer of PANI nanoparticles and a layer of PANI nanofibers using cyclic voltammetry method [47]. Due to the increment of electrical resistance of the substrate, the growth mechanism of double-layered PANI is proposed to be the reduction of external current. Light-electricity conversion efficiency was exhibits as 6.58% under a simulated solar illumination with an intensity of  $100 \text{ mW cm}^{-2}$ , improving the overall efficiency compared to a DSC with Pt counter electrode [47].

In sight of increasing interface area for redox reaction of the electrolyte, polyaniline-single wall carbon nanotube (SWNT) complex, has been combined with negatively charged graphene oxide (GO) as counter electrodes for DSCs. These PANI/SWCNT complex is combined with negatively charged graphene oxide (GO) by a layer-by-layer self-assembly technique. Covalent bonds between PANI and SWNT accelerate the charge transfer. This multilayer structure of  $(\text{PANI/SWCNT/GO})_n$  ( $n = \text{bilayer numbers}$ ) counter electrode provides a large interface area for high adsorption capacity resulting efficient tri iodide electro catalysis. A successive

light-electricity conversion efficiency of 6.88% was able to obtain from a (PANI/4 wt% SWCNT/GO)<sub>n</sub> multilayer counter electrode [48].

A composite CE for DSCs prepared using PANI, graphene nanoplatelet (GNP) and multi-wall carbon nanotube (MWCNT) deposited on FTO substrate had shown a PCE of 7.45%, which is comparable with that of 7.62% of Pt CE [49]. In here GNPs and MWCNTs have been used as additives to increase conductivity and incorporation of them into PANI lowers the sheet resistance by facilitating high charge transfer [49].

A CE prepared using a nanocomposite of graphene nanosheet (GNS) and PANI which was anchored by NiS had shown a PCE of 5.36% which is comparable to 5.97% of PCE Pt CE [50]. PANI improves the catalytic activity by restricting the aggregation of NiS and GNS on electrodes [50]. This CE was prepared using a paste of NiS/GNS/PANI deposited on FTO glass.

A CE prepared using Nickel nanoparticles, PANI and graphene to replace Pt CE for DSCs had shown a PCE of 5.80%, which is higher than that to Pt CE (5.30%) [51]. In here high PCE is due to the improvement of electro catalytic activity of PANI due to high surface area of Ni-nanoparticles and high electrical conductivity of graphene [51].

Table 1 summarizes the photovoltaic performances of PANI obtained from different methods as CE.

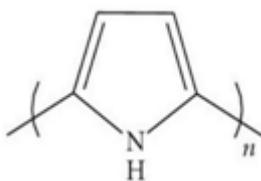
Many research work have been conducted to replace CE from pure PANI nanostructures as well as PANI nano composites [52-56]. While considering the above findings, it emphasizes that still there is a need of enhancing the efficiency of a PANI CE. More research work should be conducted to make PANI composites that not only increase the conductivity but also that can act as a pore former, which can enhance the surface area, thus increase the catalytic activity of the CE (Table 1).

**Table 1:** Photovoltaic performances of different morphologies of PANI as counter electrodes for DSC

Nature of PANI	Method of Preparation	Jsc (mA cm <sup>-2</sup> )	Voc (V)	FF	PCE (%)	Ref
Microporous PANI	Oxidative Polymerization	14.6	0.714	0.69	7.15	[35]
PANI FG composite	<i>In-Situ</i> Chemical Polymerization	15.41	0.657	0.73	7.36	[39]
Nano fibrous PANI	Maragoni Flow Method	8.9	0.662	0.53	3.8	[41]
PANI nanobelts	Template Free - Chemical Polymerization	13.22	0.714	0.66	6.32	[43]
rGO - PANI nano particles	Chemical Oxidation Polymerization	12.88	0.74	0.65	6.15	[57]
Graphen-PANI nanocomposite	<i>In-Situ</i> Oxidative Polymerization	13.28	0.685	0.67	6.09	[44]
Sulfamic acid doped PANI NFs	Interfacial Polymerization	13.62	0.74	0.53	5.5	[45]
Bilayer PANI	Cyclic Voltammetry Method	13.4	0.728	0.68	6.58	[47]
(PANI/SWCNT/GO) <sub>n</sub>	Chemical Polymerization	-	-	-	6.88	[48]
PANI/GNP/MWCNT	Chemical/Electrochemical Deposition Method	17.51	0.734	-	7.45	[49]
NiS/GNS/PANI	Chemical Oxidation Polymerization	12.13	0.67	0.66	5.36	[50]
Ni PANI G nanocomposite	Chemical Oxidation Polymerization	13.43	0.745	0.85	5.8	[51]

### Polypyrrole(PPy)

Another conducting polymer which was most determinedly studied is polypyrrole (PPy). Basically, it is due to the high polymerization yield, high conductivity, better chemical and mechanical stability, good catalytic activity, successive environmental stability and thermal stability in air up to 150 °C [58-61]. However, when compared with PANI based CEs in DSCs, PPy based CEs yield relatively lower efficiencies due to lower conductivity and high charge transfer resistance in PPy. By using proper dopants, utilizing surface morphologies and synthetic techniques, the efficiency can be improved. Figure 3 shows the chemical structure of PPy (Figure 3).



**Figure 3:** The structure of Polypyrrole

CEs in DSCs have been replaced from PPy nanostructures in various ways [62-66]. As an effort on replacing Pt CE in DSCs from PPy polymer, PPy nanoparticles were synthesized and coated on a FTO glass. When these porous PPy nanoparticles, with diameter of 40-60 nm, covered on the FTO glass and used as a CE, resulted an overall energy conversion efficiency in DSC with 7.66%. This amount is higher (11%) than that of the DSC with Pt CE under the similar conditions [67]. PPy nanoparticles propound good adhesion to substrate, high surface area and small charge transfer resistance and offer a higher electro catalytic activity in PPy electrode.

Furthermore, various efforts have been taken to improve the overall performance of DSCs, such as modifying the morphology of PPy nanoparticles when using PPy polymer as a CE material. Accordingly three kinds of PPy nanoparticles with various morphologies were synthesized by incorporation of a anionic-type surfactant (docusate sodium salt), a cationic type surfactant (acetylmethyl ammonium bromide), and an amphiphilic-type polymer (poly(oxyethylene)<sub>9</sub> methacrylate)) resulting irregular sheet (IS), hierarchical nanosphere (HNS), and nanosphere (NS), respectively [68]. The PPy-HNS film confirmed its largest BET surface area of 61.18 m<sup>2</sup> g<sup>-1</sup> than the PPy-IS films (34.80 m<sup>2</sup> g<sup>-1</sup>) and

PPy-NS (58.42 m<sup>2</sup> g<sup>-1</sup>).

The PPy-HNS based CE showed the highest electro catalytic ability for the reduction of I<sub>3</sub><sup>-</sup> and the lowest charge transfer resistance, as compared to PPy-IS and PPy-NS [68].

The rigidity of FTO glass restricts the development of a flexible CE. Therefore a study has been carried out in order to develop free-standing polypyrrole nanotube films, which can be used as a CE to replace both the Pt and fluorine doped tin oxide (FTO) glass in dye-sensitized solar cells. PPy nanotubes were formed using self-degraded template method [69]. The DSCs produced with these free standing PPy membranes have performed an excellent power conversion efficiency of 5.27%, which is about 84% of the cell with a standard Pt/FTO CE (6.25%) [69].

Monodisperse and spherical PPy nanoparticles (size of 85 nm) have been easily synthesized within micelle template (MTAB) via chemical oxidative polymerization (using FeCl<sub>3</sub> as the oxidizing agent) to employ as a counter electrode to the DSC. This micelle polymerization technique can be used in large scale production of PPy nanoparticles [70]. HCl vapor treatment which was carried out as a post doping to the PPy layer decreased the surface resistivity. Moreover it allowed the electrons to move into the PPy layer efficiently and participate in the electro catalytic reaction of the redox couple. By controlling the thickness and HCl vapor treatment time, the DSCs made of HCl-doped PPy/FTO CEs exhibited power conversion efficiencies of 7.73% which is comparable to the value (8.2%) using conventional Pt CEs [70]. Furthermore ultrathin polypyrrole nanosheets (UPNSs) were synthesized by chemical oxidation via organic single-crystal surface-induced polymerization (OCSP) using sodium decylsulfonate (SDSn) as a template to use as CEs [71]. Dye-sensitized solar cells constructed using HCl-doped UPNS CEs resulted a power conversion efficiency 6.8%, which is comparable to that of Pt CE-based DSCs (7.8%) [71]. These UPNS have showed alike morphology when compared to graphene sheets with higher surface area and active sites.

Nano graphite/polypyrrole (NG/PPy) composite film was prepared via *in-situ* polymerization on FTO glass and performed as CE in DSCs [72]. Doping of nanographite into PPy has resulted in high-efficient catalytic activity due to the fast mass transport at the interface of electrolyte-electrode. Ultimately, a high power conversion efficiency of 7.40% has been recorded under 1 sun illumination compared to a standard Pt electrode based DSC (6.85%) [72].

Furthermore PPy/rGO (polypyrrole/reduced grapheme oxide) composite as a CE material for DSCs has been studied. This composite was fabricated using a two-step electrochemical process. A DSC with PPy/rGO composite based CE has resulted with a power conversion efficiency of 6.45%, which is comparable to a Pt based DSC (7.14%) [73].

*In-situ* reduction was done to obtain reduced graphene oxide (rGO)/PPy composite on FTO glass as CE for DSCs. rGO/ PPy CE had shown a PCE of 8.14%, which is comparable with that to Pt CE (8.34%) [74]. In here rGO sheets act as conductive channels and co-catalyst for the CE of DSCs [74].

Graphene quantum dot (GQD)-doped polypyrrole (PPy) also has been reported as a CE in DSCs. The porous structure of GQDs-doped PPy caused for a high catalytic activity than densely structured normal PPy. Therefore the cell showed an electricity conversion efficiency of 5.27% which is close to the efficiency of platinum CE in DSC [75]. Polypyrrole-cobalt-carbon (PPY-Co-C) nano composites also has been tried out as a CE material for DSCs. Reduction of I<sub>3</sub><sup>-</sup> is supported with large inner surface area and homogeneously distributed Co active sites. The cell performed a power conversion efficiency of 6.01% is comparable to standard Pt CE based DSCs (6.61%) [76].

A complex of PPy-single wall carbon nanotube (SWCNT) synthesized using reflux techniques and subsequent *in-situ* polymerization had yielded an enhanced PCE of 8.30% [77]. Formation of covalent bonds within PPy-SWCNT complexes accelerate the charge transfer and enhance the photovoltaic performances in DSCs due to long-range ordering and good electron dislocation in their structure [77].

A composite film of multiwall carbon nanotubes (MWCNTs) and PPy on FTO substrate had shown PCE of 7.41%, which is higher than that of sputtered Pt (6.85%) on FTO substrate as CE in DSCs [78]. Uniform distribution of MWCNT on the PPy nanoparticles has enhanced the conductivity and the electro catalytic activity by forming a transport network like structure [78].

A nanocomposite of silver-PPy-multiwall carbon nanotube (MWCNT) synthesized via electro deposition method on stainless steel substrate had displayed an acceptable PCE of 7.0% with respect to thermally deposited Pt electrode 7.6% [79]. This enhanced conductivity caused by the increase of average localization length due to composite  $\pi$  conjugated structure of MWCNTs and quinoid rings of polymer chains. Silver nanoparticles allow the formation of well ordered structure as well as larger surface area for reduction of electrolyte [79].

Novel CE made by using a composite film of graphene-coated alumina (GCA) and PPy coated on FTO substrate exhibited an efficiency of 7.33% with respect to 7.57% Pt CE [80]. Al<sub>2</sub>O<sub>3</sub> was added to prevent sheet aggregation of graphene oxide. Therefore, GCA had shown greatly improved catalytic activity of PPy CE and hence improved the photovoltaic performances of DSCs [80]. Table 2 summarizes the photovoltaic performances of PPy obtained from different methods as CE (Table 2).

### Poly(3,4-ethylenedioxythiophene) (PEDOT)

In 1988, Jonas *et al.* developed poly(3,4-ethylenedioxythiophene) (PEDOT), an electronically conducting polymer, which contains desirable properties such as high room temperature conductivity, transparency and remarkable stabilities [82, 83]. PEDOT yields the highest efficiency and electro catalytic activity towards I<sub>3</sub><sup>-</sup>/I<sup>-</sup> in Pt free DSC, when compared with PANI and PPy. PEDOT exhibits an excellent conductivity (300-500 S cm<sup>-1</sup>) [84], which is higher than those of PANI (0.1-5 S cm<sup>-1</sup>) [85] and PPy (10-50 S cm<sup>-1</sup>) [86]. CE based on PEDOT-nanoparticles [87, 88] PEDOT-carbon nanotubes [89,90], PEDOT-nano fibers [91], PEDOT-nano composites [92,93, 94] etc have been investigated [95,96]. Figure 4 shows the chemical structure of PEDOT (Figure 4).

**Table 2:** Photovoltaic performances of different forms of PPy as counter electrodes for DSC

Nature of PPy	Method of Preparation	Jsc (mA cm <sup>-2</sup> )	Voc (V)	FF	PCE (%)	Ref
PPy film	Electropolymerization	9.66	-	0.66	5.1	[81]
PPy nanoparticles	Synthetic Chemical Method	15.01	0.74	0.66	7.66	[67]
PPy IS (Irregular sheet)	Chemical Oxidative Polymerization	11.52	0.7	0.67	5.46	[68]
PPy HNS ( Hierarchical nanosphere)	Chemical Oxidative Polymerization	16.49	0.7	0.58	6.71	[68]
PPy NS (Nanosphere)	Chemical Oxidative Polymerization	14.1	0.7	0.63	6.31	[68]
PPy nanotube (free ITO)	Self-assembly	13.1	0.716	0.56	5.27	[69]
Spherical PPy	Chemical Oxidative Polymerization	15.5	0.791	0.64	7.73	[70]
PPy UPNSs	Chemical Oxidative polymerization	15.2	0.721	0.62	6.8	[71]
Nano graphite/ PPy	<i>In-Situ</i> Electro deposition	14.83	0.765	0.65	7.4	[72]
PPy/rGO	Electro Chemical Polymerization	15.48	0.695	0.6	6.45	[73]
PPy/rGO	Chemical Oxidative Polymerization	15.81	0.724	0.71	8.14	[74]
PPy SWNT complex	Reflux Process	15.68	0.742	0.71	8.3	[77]
MWCNT/PPy composite	Electrochemical Polymerization	14.83	0.77	0.65	7.42	[78]
Ag Ppy MWCNT nanocomposite	Electro Deposition	13.95	0.798	0.67	7	[79]
PPy/GCA	Electrochemical Polymerization	16.54	0.717	0.62	7.33	[80]

**Figure 4:** Structure of PEDOT

The initial investigation on fabrication of PEDOT CEs by chemical polymerization was published in 2002 [97]. The PEDOT was doped with TsO-(ptoluenesulfonate) and poly(styrenesulfonate) (PSS). Potential current efficiency of PEDOT-TsO was better than PEDOT-PSS due to the exposure of PSS-that resulted in increased over potential [97]. In cyclic voltamogram analysis the oxidation/reduction peaks of I<sub>1</sub>/I<sub>3</sub> observed on the PEDOT-TsO electrode were indistinguishable to the behavior of the Pt electrode. However, in the PEDOT-PSS electrode, the oxidation current was remarkably decreased. The author explains this as the reduction of the redox active site of the PEDOT-PSS film due to the exposure of PSS, which prevent the approach of I<sup>-</sup> or I<sub>3</sub><sup>-</sup> to the active site of the PEDOT chain [97]. Also when the thickness of the PEDOT-TsO increased, the charge transfer resistance has increased.

The performance of PEDOT CEs can also be improved by introducing nanostructures. A study on application of nanotubes (NT) of PEDOT CE has been carried out in order to prove this. It has confirmed that the performance of PEDOT-NT CE efficiency (8.3%) is better than a flat PEDOT CE (7.9%) due to their high effective area and that performance is superior as the conventional platinumized counter electrodes (8.5%). PEDOT has been electropolymerized

onto ZnO Nanowire array templates (working electrode) in a three-electrode electrochemical cell [98].

In addition PEDOT nanofibers were prepared by chemical oxidative polymerization with the aim of obtaining low surface resistance, good adhesion and increased catalytic activity. The PEDOT-NFs with 10-50 nm diameters was prepared from cylindrical micelles formed by sodium dodecyl sulfate (SDS) and FeCl<sub>3</sub>. The conductivity of PEDOT-NF was as high as 83 S cm<sup>-1</sup>, while that of bulk PEDOT was 0.5 S cm<sup>-1</sup> and the PEDOT-NF formed a porous network structure of CEs, which facilitated penetration of the electrolyte for redox reactions. Ultimately, CEs prepared from nanofibers, in DSCs showed an excellent PCE of 9.2% while PEDOT alone showed a PCE of 6.8% [99].

A low-cost nanopatterned highly conductive PEDOT film was synthesized on a flexible plastic substrate using a chemical polymerization method. This was used as Pt, TCO-free CE for DSCs. This exhibited a light-current efficiency of 7.1%, while a reference device with a Pt/FTO paired CE resulted an efficiency of 7.6% [100]. The nanopatterning of the polymer film can increase the number of reactive sites in the CE, hence the catalytic activity also increased [100].

Carbon nanotubes (CNTs) also contain impressive properties, such as high mechanical strength, thermal stability and impressive electronic properties [101]. Therefore CNTs can be used in many electrical devices. Accordingly incorporation of multiwall carbon nanotubes (MWCTNs) as the CE to DSCs have been studied. Composite films of PEDOT and functionalized, multi-walled, carbon nanotubes (PEDOT-MWCNT) were synthesized on a FTO glass substrate by electro polymerization technique. Due to the high porous structure, the power conversion efficiency of the DSC with a PEDOT-MWCNT CE (efficiency 5.47%) was 13.0% higher than when compared with a PEDOT CE (5.43%) using the same

conditions due to the high porous structure [102].

For further improvement of the DSCs Ouyang and coworkers explored the combination between PEDOT:PSS and MWCNT as a composite CE for DSCs for the first time. Film was fabricated from spin coating the aqueous solution of the MWCNT/PEDOT:PSS composite. The device exhibited excellent performance with a power conversion efficiency of 6.5%. This performance is close to the DSCs with Pt CEs [103].

Another interesting study has been carried out on PEDOT films incorporating gold nanoparticles (AuNPs) as CE in DSCs. AuNPs were synthesized according a well-known Turkevich method [104]. With Co(III)/Co(II) based redox couple, the power conversion efficiency has been increased to about 130% compared to the use of PEDOT alone. It was found the efficiency of the solar cell with Pt CE is 1.3%, PEDOT CE is 1.4% and AuNPs/ PEDOT is 3.2% [104].

PEDOT films containing nano-meadows morphology has been prepared by pulse potentiostatic method on FTO plates. It resulted a better electro catalytic activity for the redox reaction than that with Pt CE. It was proved by the cathodic peak current in cyclic voltammogram measurements. The DSC with the nano-meadow PEDOT CE exhibited photo voltaic conversion of 6.40%, which is higher than a DSC with a Pt CE (5.75%) [105].

Moreover a CE has been fabricated from PEDOT/PSS composite deposited on Ag network (Ag NW) substrate. The electrode resulted the electron generation at both sides on illumination. Furthermore PEDOT/PSS layer has been doped with 20% TiO<sub>2</sub> nanoparticles for the enhancement of the cell performance. In order to prevent the Ag NW corrosion by the iodine electrolyte, the Ag NW substrate was covered with a PEDOT/PSS layer. The performance of the DSC was 5.13% in efficiency, which is very similar to those of cells using a platinum counter electrode (5.36%) [106].

In another attempt, PEDOT coated graphene has been used as the CE in DSC to replace both the Pt and TCO. Surface resistance showed a decrement due to the addition of high conductive graphene in PEDOT film. A power conversion efficiency of 6.26% has been resulted [107]. In addition, PSS in PEDOT together with

graphene has been synthesized by spin coating in order to replace Pt on CE. A power conversion efficiency of 4.66% has been reported from the cell in comparison with 5.95% conversion efficiency shown by cells containing platinum CE [108].

Reduced grapheme oxide (rGO)/PPy/PEDOT thin film was synthesized to deposit on FTO glass and performed as a CE in DSC. Power conversion efficiency was 7.1% due to the effect of conducting polymer and graphene. The efficiency is comparable to that of Pt-based cells made under similar Conditions [109].

PEDOT was electrochemically deposited on porous hard template film of TiC nanoparticles (50 nm) to fabricate TiC-PEDOT CE for DSCs, which had shown the efficiency of 8.09% to Co(bpy)<sub>2</sub><sup>+/3+</sup> redox couple [110]. On the other hand, a TiN-PEDOT CE had shown even better efficiency of 8.26% for the same redox couple. An interconnected conductive network between TiN or TiC nanoparticles with PEDOT facilitate better electron transport properties. Another article reported a PCE of 7.06% for CE fabricated with TiN-PEDOT:PSS for I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple [111].

An inorganic/organic nanocomposite film composed of Si nanoparticles (Si-NPs) and PEDOT:PSS obtained from a mechanical way used as the CE of DSCs had a PCE of 5.7% and a FF of 0.51 [111], both in which are higher than that of PEDOT:PSS CE. Due to the increased electrochemical surface with the addition of Si-NPs led to enhance those photovoltaic parameters for Si-NPs/PEDOT:PSS CE. This novel CE had shown a comparable PCE with Pt CE (6.6%) [112] for DSCs.

Both PEDOT and PPy are promising candidates to make Pt free CEs for DSCs. A composite film of PEDOT:PSS and PPy fabricated using an electrochemical polymerization method had reached a PCE of 7.60% which is comparable with Pt sputtered CE (7.73%) for DSCs [113]. A uniform porous film structure had resulted from PEDOT:PSS and PPy particles are expected to facilitate an effective electro catalytic surface to ensure higher PCEs for DSCs.

Table 3 summarizes the photovoltaic performances of different forms of PEDOT obtained from different methods as CE for DSC (Table 3).

**Table 3:** Photovoltaic performances of different forms of PEDOT obtained from different methods as counter electrodes for DSC

Nature of PEDOT	Method of Preparation	JSC(mA cm <sup>-2</sup> )	VOC(V)	FF	PCE (%)	Ref
PEDOT:PSS	Chemical Polymerization	11.2	0.67	0.61	4.6	[95]
PEDOT nanotube	Template Assisted Electro Polymerization	16.24	0.72	0.7	8.3	[56]
PEDOT flat film	Electro Polymerization	15.38	0.73	0.69	7.9	[56]
PEDOT nanofiber	Template Assisted Chemical Oxidative Polymerization	17.5	0.72	0.73	9.2	[96]
PEDOT/MWCNT	Electro Polymerization	11.5	0.74	0.64	5.47	[99]
PEDOT-Au nanoparticles	Electro Polymerization	7.6	0.71	0.6	3.2	[84]
PEDOT:PSS/MWCNT	Spin Coating	15.5	0.66	0.63	6.26	[103]
PEDOT:PSS-Graphene	Spin Coating	12.96	0.72	0.48	4.66	[104]
RGO-PEDOT:PSS	Spin Coating	17	0.75	0.55	7.1	[105]
TiN-PEDOT for Co <sup>2+</sup> /3 <sup>+</sup> redox couple	Electro Polymerization	13.21	0.84	0.75	8.26	[107]
TiC-PEDOT for Co <sup>2+</sup> /3 <sup>+</sup> redox couple	Electro Polymerization	12.68	0.84	0.76	8.09	[107]
TiN-PEDOT: PSS for I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> redox couple	Mechanical Mixture	14.45	0.73	0.67	7.06	[108]
PEDOT: PSS/PPy	Electro Polymerization	14.27	0.75	0.71	7.6	[109]

## Summary

DSCs, as a power generation device, have gained more research attention for the past years due to their low production cost and high efficiency to convert solar energy into electricity. Counter electrode plays a major role in this device and Pt has been reported as the most appropriate material to develop CEs in DSCs. However, due to the high cost, susceptibility to corrosion, advance synthetic methods of Pt, the need of alternative materials to replace Pt is crucial. Among various discovered materials, conducting polymers with extended conjugate electron system have been widely investigated by researchers due to their superior properties. PANI, PPy and PEDOT polymer nanostructures and hybrid composites have been found as cost effective CE materials in Pt free DSCs. PANI has appropriate features like easy synthesis, high-conductivity, good environmental stability and interesting redox properties to replace Pt. PPy based CEs in DSCs perform with lower efficiencies compared to PANI, due to low conductivity and high charge transfer resistance. PEDOT-CE based DSCs performed the highest efficiency compared to PANI and PPy with the highest conductivity and electro catalytic activity towards  $I_3^-/I^-$  among the three polymers considered in this review. When the morphologies of these polymers are developed with various nanostructures and when the polymers make hybrid nano composites they earn high surface area:volume ratio which leads to a high level of reactivity. Thus CEs in DSCs exhibit enhanced efficiencies. All the above discussed methods are cost effective and therefore more research work should be carried out in order to investigate nanostructure polymer based novel CEs for DSCs in future.

## References

1. Saranya K, Subramania A and Rameez Md. Developments in conducting polymer based counter electrodes for dye-sensitized solar cells - An overview. *European Polymer Journal*. 2015;66:207-227. doi: 10.1016/j.eurpolymj.2015.01.049
2. Almosni S, Delamarre A, Jehl Z, Suchet D, Cojocar L, Giteau M, et al. Material challenges for solar cells in the twenty-first century: directions in emerging technologies. *Science and Technology of Advanced Material*. 2018;19(1):336-369. doi: 10.1080/14686996.2018.1433439
3. Brian O Regan and Michael Gratzel. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal  $TiO_2$  films. *Nature*. 1991;353(6346):737-740. doi: 10.1038/353737a0
4. Wei D. Dye Sensitized Solar Cells. *Int J Mol Sci*. 2010;11(3):1103-1113. doi: 10.3390/ijms11031103
5. Gong J, Sumathy K, Qiao Q and Zhou Z. Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. *Renewable and Sustainable Energy Reviews*. 2017;68:234-246. doi: 10.1016/j.rser.2016.09.097
6. Ye M, Wen X, Wang M, Iocozzia J, Zhang N, Lin C, et al. Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes. *Materials Today*. 2015;18(3):155-162. doi: 10.1016/j.mattod.2014.09.001
7. Sharma K, Sharma V and Sharma SS. Dye-Sensitized Solar Cells: Fundamentals and Current Status. *Nanoscale Research Letters*. 2018;13(1). doi: 10.1186/s11671-018-2760-6
8. Gratzel M. Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2003;4(2):145-153. doi: 10.1016/S1389-5567(03)00026-1
9. Odobel F, Le Pleux L, Pellegrin Y and Blart E. New photovoltaic devices based on the sensitization of p-type semiconductors: challenges and opportunities. *ACC Chem Res*. 2010;43(8):1063-1071. doi: 10.1021/ar900275b
10. Hagfeldt A, Boschloo G, Sun L, Kloo L and Pettersson H. Dye-Sensitized Solar Cells. *Chem Rev*. 2010;110:6595-6663. doi: 10.1021/cr900356p
11. Thomas S, Deepak TG, Anjusree GS, Arun TA, Nair SV and Nair AS. A Review on counter electrode materials in dye-sensitized solar cells. *J Mater Chem A*. 2014;2(13):4474-4490. doi:10.1039/C3TA13374E
12. Zhang B, Wang D, Hou Y, Yang S, Yang XH, Zhong JH, et al. Facet-dependent catalytic activity of platinum nanocrystals for triiodide reduction in dye-sensitized solar cells. *Sci Rep*. 2013;3:1836. doi: 10.1038/srep01836
13. Wu J, Lan Z, Lin J, Huang M, Huang Y, Fan L, et al. Counter electrodes in dye-sensitized solar cells. *Chem Soc Rev*. 2017;46(19):5975-6023. doi: 10.1039/C6CS00752J
14. Wu M and Ma T. Platinum-Free Catalysts as Counter Electrodes in Dye-Sensitized Solar Cells. *Chem Sus Chem*. 2012;5(2):1343-1357. doi: 10.1002/cssc.201100676
15. Theerthagiri T, Senthil AR, Madhavan J and Maiyalagan T. Recent Progress in Non-Platinum Counter Electrode Materials for Dye-Sensitized Solar Cells. *Chem Electro Chem*. 2015;2(7):928-945. doi: 10.1002/celec.201402406
16. Yun S, Freitas JN, Nogueira AF, Wang Y, Ahmad S and Wang ZS. Dye-sensitized solar cells employing polymers. *Prog Polym Sci*. 2015;59:1-40. doi: 10.1016/j.progpolymsci.2015.10.004
17. Mathew S, Yella A, Gao P, Humphry-Baker R, Curchod BFE, Ashari-Astani N, et al. Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nature Chemistry*. 2014;6(3):242-247. doi: 10.1038/nchem.1861
18. Wu M and Ma T. Platinum-Free Catalysts as Counter Electrodes in Dye-Sensitized Solar Cells. *Chem Sus Chem*. 2012;5(8):1343-1357. doi: 10.1002/cssc.201100676
19. Saranya K, Rameez M and Subramania A. Developments in conducting polymer based counter electrodes for dye-sensitized solar cells-An overview. *Eur Polym J*. 2015;66:207-227. doi: 10.1016/j.eurpolymj.2015.01.049
20. Rahman MS, Hamed WA, Yahya RB and Mahmud HNME. Prospects of conducting polymer and graphene as counter electrodes in dye-sensitized solar cells. *Journal of Polymer Research*. 2016;23(9):192. doi: 10.1007/s10965-016-1090-6

21. Nguyen D and Yoon H. Recent Advances in Nanostructured Conducting Polymers: from Synthesis to Practical Applications. *Polymers*. 2016;8(4):118. doi: 10.3390/polym8040118
22. Malinauskas A, Malinauskiene J and Ramanavicius A. Conducting polymer-based nanostructured materials: electrochemical aspects. *Nanotechnology*. 2005;16(10):51-62. doi: 10.1088/0957-4484/16/10/R01
23. Cai Y and Zhang BM Newby. Marangoni flow-induced self-assembly of hexagonal and stripelike Nanoparticle patterns. *J Am Chem Soc*. 2008;130(19):6076-6077. doi: 10.1021/ja801438u
24. Hou W, Xiao Y, Han G and Lin JY. The Applications of Polymers in Solar Cells: A Review. *Polymers*. 2019;11(1):143. doi: 10.3390/polym11010143
25. Perera IP, Thennakoon SKS and Gunathilake SS. Screen printed Sri Lankan vein graphite/polyaniline composite counter electrode for dye sensitized solar cells. *Ceylon J Sci*. 2019;48(3):209-215. doi: 10.4038/cjs.v48i3.7644
26. Nawarathna HMCP, Abeysingha DUSN, Wickramasinghe WMTN and Gunathilake WSS. Conducting polymer blends (polyaniline/polypyrrole) as counter electrode materials in dye sensitized solar cells. *Ceylon J Sci*. 2018;47(3):263-268. doi: 10.4038/cjs.v47i3.7532
27. Kang ET, Neoh KG, Tan KL. Polyaniline: a polymer with many interesting intrinsic redox states. *Prog Polym Sci*. 1998;23(2):277-324. doi: 10.1016/S0079-6700(97)00030-0
28. N Parvatikar, S Jain, S Khasim, M Revansiddappa and SV Bhoraskar. Electrical and humidity sensing properties of polyaniline/WO<sub>3</sub> composites. *SENSOR ACTUAT B-CHEM*. 2006;114(2):599-603. doi: 10.1016/j.snb.2005.06.057
29. Milica M Gvozdenovic, Branimir Z Jugovic, Jasmina S Stevanovic and Branimir N Grgur. Electrochemical synthesis of electro conducting polymers. *Polymers*. 2014;68(6):673-684. doi: 10.2298/HEMIND131122008G
30. Ourari, R Zerdoumi, RR Rosas and E Morallon. Synthesis and Catalytic Properties of Modified Electrodes by Pulsed Electrodeposition of Pt/PANI Nanocomposite. *Materials*. 2019;12(5):723. doi: 10.3390/ma12050723
31. Z Tang, S Liu, Z Wang, S Dong and Wang. Electrochemical synthesis of polyaniline nanoparticles. *Electrochem commun*. 2000;2(1):32-35.
32. A Malinauskas, J Malinauskiene and A Ramanavicius. Conducting Polymer-based nanostructured materials: electrochemical aspects. *Nanotechnology*. 2005;16(10):51. doi: 10.1088/0957-4484/16/10/R01
33. S Peng, J Liang, SG Mhaisalka and S Ramakrishna. In situ synthesis of platinum/polyaniline composite counter electrodes for flexible dye-sensitized solar cells. *J Mater Chem*. 2012;12:5308. doi: 10.1039/C2JM16534A
34. K Wu, L Chen, X Sun, M Wu. Transition metal-modified polyaniline nanofiber counter electrode for dye-sensitized solar cells. *Chem Electro Chem*. 2016;3(11):1002. doi.org/10.1002/celc.201600326
35. Q Li, J Wu, Q Tang, Z Lan, P Li and J Lin. Application of microporous polyaniline counter electrode for dye-sensitized solar cells. *Electrochem commun*. 2008;10(9):1299-1302. doi: 10.1016/j.elecom.2008.06.029
36. QQin, FHeandWZhang. One-step electro chemical polymerization of polyaniline flexible counter electrode doped by graphene. *Journal of Nanomaterials*. 2016. doi:10.1155/2016/1076158
37. Z Tang, J Wu, M Zheng, Q Tang, Q Liu, JLin and JWang. High efficient PANI/Pt nanofiber counter electrode used in dye-sensitized solar cell. *RSC Advances*. 2012; 2(10):4062-4064. doi:10.1039/C2RA20180A
38. J Chen, B Li, J Zheng, J Zhao, H Jing, Z Zhu. Polyaniline nanofiber/carbon film as flexible counter electrodes in platinum-free dye-sensitized solar cells. *Electrochimica Acta*. 2011;56(12):4624-4630. doi: 10.1016/j.electacta.2011.02.097
39. H Sun, Y Luo, Y Zhang, D Li, Z Yu, K Li, Q Meng. In Situ Preparation of a Flexible Polyaniline/Carbon Composite Counter Electrode and Its Application in Dye-Sensitized Solar Cells. *J. Phys. Chem. C*. 2010;114(26):11673-11679. doi: 10.1021/jp1030015
40. Y Cai, B M Zhang Newby. Marangoni flow-induced self-assembly of hexagonal and stripelike nanoparticle patterns. *J. Am. Chem. Soc*. 2008;130(19):6076-6077.
41. F Guo, H Hu, Q D Tai, B L Chen, B Sebo, C H Bu, X Z Zhao. Facile preparation of nanofibrous polyaniline thin film as counter electrodes for dye sensitized solar cells. *J RENEW SUSTAIN ENER*. 2012;4(2). doi: 10.1063/1.3699618
42. V Gupta, N Miura. Electrochemically deposited polyaniline nanowire's network a high-performance electrode material for redox supercapacitor. *ELECTROCHEM SOLID ST*. 8(12) (2005) 630-632. http://doi: 10.1149/1.2087207.
43. Z Lan, J Wu, S Gao, J Lin, M Huang, X Chen. Template-free synthesis of polyaniline nanobelt as a catalytic counter electrode in dye-sensitized Solar cells-POLYM ADVAN TECHNOL. 25(3) (2004), 343-346. http://doi: 10.1002/pat.324
44. G Wang, S Zhuo, W Xing. Graphene/polyaniline nanocomposite-counter electrode of dye-sensitized solar cells. *Materials Letters*. 2012;69:27-29.
45. S Ameen, M Akhtar, YS Kim, OBYang, HS Shin. Sulfamic acid-doped polyaniline nanofibers thin film-based counter electrode: application in dye-sensitized solar cells. *Phys, Chem. C*. 2010;114(10) :4760-4764.
46. G Li, C Martinez, J Janata, J A Smith, M Josowicz, S Semancik. Effect of morphology on the response of polyaniline-based conductometric gas sensors: Nanofibers vs. thin films. *ELECTROCHEM SOLID ST*. 2004;7(10):44-47.
47. Q Tang, H Cai, S Yuan, X Wang. Counter electrodes from double-layered polyaniline nanostructures for dye-sensitized solar cell applications. *J. Mater. Chem. A*. 2013;1[2]:317- 323.
48. M Wang, Q Tang, H Chen, B He. Counter electrodes from polyaniline-carbon nanotube complex/graphene oxide multilayers for dye-sensitized solar cell application. *Electrochimica Acta*. 2014;125:510-515.

49. Y C Shih, H L Lin, K F Lin. Polyaniline/Graphene/Multi-Walled Carbon Nanotube Composites as Counter Electrode for Dye-Sensitized Solar Cells. *MRS Proceedings* (2014) 1667. <https://doi.org/10.1557/opl.2014.900>.
50. B C Nath, K J Mohan, B J Saikia, G A Ahmed, S K Dolui. Designing of platinum free NiSanchoredgraphene /polyanilinenanocompositesbasedcounterelectrodefordyesensitized solarcell. *J. Mater. Sci.:Mater. Electron.* 2017;28(1):10421050.
51. X Chen, J Liu, K Qian, J Wang. Ternary composites of Ni polyaniline graphene as counter electrodes for dye sensitized solar cells. *RSC Advances*. 2018;8(20): 10948 -10953.
52. QH Niu, S Zhang, Q Ma, S Qin, L Wan, J Xu, S Miao. Dye-sensitizedSolarCellsbased on Flower- -Fe<sub>2</sub>O<sub>3</sub> as a Photoanode andReduced Graphene Oxide/Polyaniline Composite as a Counter Electrode. *RSC Advances* (2013). <https://doi.org/10.1039/C3RA42214>
53. K CHuang, J HHuang, C H Wu, C U Liu, H W Chen, C W Chu, et al. Nanographite/ polyaniline compositefilmsasthecounterelectrodesfordyesensitizedsolar cells. *J. Mater. Chem.* 2011;21:10384-10389.
54. J Zhang, T Hreid, X Li, W Guo, L Wang, X Shi, H Su, Z Yuan. Nanostructured polyaniline counter electrode for dye-sensitized solar cells: Fabrication and investigation of its electrochemical formation mechanism. *Electrochimica Acta.* 2010;55(11):3664-3668.
55. M Wu, G Snook, V Gupta, M Shaffer, D J Fray, G Z Chen. Electrochemical fabrication and capacitance of composite films of carbon nanotubes and polyaniline. *J. Mater. Chem.* 2005;15(23):2297-2303.
56. S Guo, S Dong, E Wang. Polyaniline/Pt Hybrid Nanofibers: High-Efficiency Nanoelectrocatalysts for Electrochemical Devices. *Small.* 2009;5(16):1869-1876.
57. W Sun, T Peng, Y Liu, S Xu, J Yuan, S Guo, X Z Zhao. Hierarchical-lyporoushybrids of polyaniline nanoparticles anchored on reduced graphene oxide sheets as counter electrodes for dye-sensitized solar cells, *J. Mater. Chem. A.* 2013;1(8):2762-2768.
58. X Ma, G Yue, J Wu, Z Lan, Efficient Dye-Sensitized Solar Cells Made from High Catalytic Ability of Polypyrrole @Platinum Counter Electrode. *Nanoscale Res. Lett.* 2015;10(1) :327. doi: 10.1186/s11671-015-1015-z
59. P Jha, P Veerender, S P Koiry, C Sridevi, P Chabbi, S Samanta et al. Freestanding polypyrrole films as counter electrode for low cost dye sensitized solar cells, *AIP Conf. Proc.* 1832 (2017). <https://doi.org/10.1063/1.4980500>
60. J Xia, L Chen, S Yanagida. Application of polypyrrole as a counter electrode for dye-sensitized solar cell, *J. Mater. Chem.* 2012;1(12):4644-4649.
61. J Y. Lee, K T Song, S Y Kim, Y C Kim, D Y Kim, C Y Kim. Synthesis and characterization of soluble polypyrrole, *Synth. Met.* 1997;84(1-3):137-140.
62. S Bose, T Kuila, E ddin, N H Kim, A K T Lau, J H Lee. In-situ synthesis and characterization of electrically conductive polypyrrole/graphenenanocomposites. *Polymer.* 2010;51(25):5921-5928.
63. Makris, M Dracopoulos, V Stergiopoulos, T Lianos, P. A quasi solid-state dye-sensitized solar cell made of polypyrrole counter electrodes, *Electrochimica Acta.* 2011;56(5):2004-2008.
64. S P Lim, A Pandikumar, Y S Lim, N M Huang, H N Lim. In-situ electrochemically deposited polypyrrole nanoparticles incorporated reduced graphene oxide as an efficient counter electrode for platinum-free dye-sensitized solar cells. *Sci Rep.* 2015;5:305.
65. J Xu, J Hu, B Quan, Z Wei. Decorating Polypyrrole Nanotubes with Au Nanoparticles by an In Situ Reduction Process. *Macromol. Rapid Commun.* 2009;30(11):936-940.
66. Y Liu, N Lu, S Poyraz, X Wang, Y Yu, J Scott, J Smith, M J Kim, X Zhang. One-pot formation of multifunctional Pt-conducting polymer intercalated nanostructures. *Nanoscale.* 2013;5:3872-3879.
67. J Wu, Q Li, L Fan, Z Lan, P Li, J Lin, S Hao. High-performance polypyrrole nanoparticles counter electrode for dye-sensitized solar cells. *J. Power Sources.* 2008;181(1):172-176.
68. L Y Chang, C T Li, Y Y Li, C P Lee, M H Yeh, K C Ho et al. Morphological Influence of polypyrrole nanoparticles on the performance of dye sensitized solar cells. *Electrochimica Acta.* 2015;155:263-271.
69. T Peng, W Sun, C Huang, W Yu, B Sebo, Z Dai et al. Self-assembled free-standing polypyrrole nanotube membrane as an efficient FTO-and Pt-free counter electrode for dye-sensitized solar cells. *ACS Appl. Mater. Interfaces.* 2013;6(1):14-17.
70. S S Jeon, C Kim, J Ko, S S Im. Spherical polypyrrole nanoparticle-sasahighlyefficient counter electrode for dye-sensitized solar cells. *J. Mater. Chem.* 2011;21(22):8146-8151.
71. D K Hwang, D Song, S S Jeon, T H Han, Y S Kang, S S. Im. Ultrathin polypyrrole nanosheets doped with HCl as counter electrodes in dye-sensitized solar cells. *J. Mater. Chem. A.* 2014;2(3):859-865.
72. G Yue, X A Zhang, L Wang, F Tan, J Wu, Q Jiang. Highly efficient and stable dye-sensitized solar cells based on nanographite/polypyrrole counter electrode. *Electrochimica Acta.* 2014;129:229-236.
73. W Liu, Y Fang, P Xu, Y Lin, X Yin, G Tang, M He. Two-step electrochemical synthesis of polypyrrole/reduced graphene oxide composites as efficient Pt-free counter electrode for plastic dye-sensitized solar cells. *ACS Appl. Mater. Interfaces.* 2014;6(18):16249-16256.
74. F Gong, X Xu, G Zhou, Z S Wang. Enhanced charge transportation in a polypyrrole counter electrode via incorporation of reduced graphene oxide sheets for dye-sensitized solar cells. *Phys. Chem. Chem. Phys.* 2013;15(2):546-552. doi: 10.1039/C2CP42790G
75. L Chen, C X Guo, Q Zhang, Y Lei, J Xie, S Ee et al. Graphene quantum-dot-doped polypyrrole counter electrode for high-performance dye-sensitized solar cells, *ACS Appl. Mater. Interfaces.* 2013;5(6):2047-2052. doi: 10.1021/am302938a.
76. Wang L, Zhang K, Cheng F, Chen J, Polypyrrole-cobalt-carbon nanocomposites as efficient counter electrode materials for dye-sensitized solar cells. *Sci. China Chem.* 2014; 57;(11):1559-1563.
77. He B, Tang Q, Luo J, Li Q, Chen X, Cai H. Rapid charge-transfer in polypyrrole single wall carbon nanotube complex counter electrodes: Improved photovoltaic performances of dye-sensitized solar cells. *J. Power Sources.* 2015;256:170-177.

78. Yue G, Wang L, Zhang X, Wu J, Jiang Q, Zhang W, Lin J. Fabrication of high performance multi-walled carbon nanotubes/polypyrrole counter electrode for dye-sensitized solar cell, *Energy*. 2014;67:460-467.
79. Rafique S, Sharif R, Rashid I, Ghani S. Facile fabrication of novel silver-polypyrrole-multiwalled carbon nanotubes nanocomposite for replacement of platinum in dye-sensitized solar cell, *AIP Advances*. 2016;6(8):085018.
80. Thuy CTT, Jung JH, Thogiti S, Jung WS, Ahn KS, Kim JH. Graphene coated alumina-modified polypyrrole composite films as an efficient Pt-free counter electrode for dye-sensitized solar cells, *Electrochimica Acta*. 2016;205:170-177.
81. Lu S, Wang S, Han R, Feng T, Guo L, Zhang X. The working mechanism and performance of polypyrrole as a counter electrode for dye-sensitized solar cells, *J Mater Chem A*, 2004;2(32):12805.
82. Yohannes TO, Ingana's. Photoelectrochemical studies of the junction between poly [3-(4-octylphenyl) thiophene] and a redox polymer electrolyte. *SOL ENERG MAT SOL C*. 51 (1998) 193.
83. Wang Y. Research progress on a novel conductive polymer - poly(3,4-ethylenedioxythiophene) (PEDOT). *J Phys* 2019;152:12023.
84. Jonas F, Schrader L. Conductive modification of polymers with polypyrrole and polythiophene. *Synthetic Metals*. 1991;49:831-836.
85. Ryu KS, Kim KM, Park YJ, Park NG, Kang MG, Chang SH. Redox supercapacitor using polyaniline doped with Li salt as electrode. *Solid State Ion*. 2002;152:861-866.
86. Faverolle F, Attias AJ, Bloch B, Audebert P, Andrieux CP. Highly conducting and strongly adhering polypyrrole coating layers deposited on glass substrates by a chemical process. *Chemistry of Materials*. 1998;10:740-752.
87. Tsai TH, Yang CY, Chen SM. Indirect Determination of Water and Hydrogen Peroxide Oxidation by Oxygen Evolution Studies using Multiwalled Carbon Nanotube-Nickel Oxide film as Electrocatalyst, *Int. J. Electrochem*. 2012;7:12764-12773.
88. Dai C, Chang CJ, Chi HY, Chien HT, Su WF, Chiu WY. Emulsion Synthesis of Nanoparticles Containing PEDOT Using Conducting Polymeric Surfactant: Synergy for Colloid Stability and Intercalation Doping. *J POLYM SCI POL CHEM*. 2008;46:2536-2548.
89. Xiao Y, Lin JY, Tai SY, Chou SW, Yue G, Wu J. Pulse electropolymerization of high performance PEDOT/MWCNT counter electrodes for Pt-free dye-sensitized solar cells. *J. Mater. Chem*. 2012;22(37):19919-19925.
90. Zhang J, Li X, Guo W, Hreid T, Hou J, Su H, Yuan Z. Electropolymerization of a poly (3, 4-ethylenedioxythiophene) and functionalized, multi-walled, carbon nanotubes counter electrode for dye-sensitized solar cells and characterization of its performance. *Electrochimica Acta*. 2011;56(9):3147-3152.
91. Lee TH, Do K, Lee YW, Jeon SS, Kim C, Ko J, Im SS. High-performance dye-sensitized solar cells based on PEDOT nanofibers as an efficient catalytic counter electrode. *Energy Mater*. 2012;22:21624.
92. Chen PY, Li CT, Lee CP, Vittal R, Ho KC. PEDOT-decorated nitrogen-doped graphene as the transparent composite film for the counter electrode of a dye-sensitized solar cell. *Nano Energy*. 2015;12:374-385.
93. Peng Y, Zhong J, Wang K, Xue B, Cheng YB. A printable graphene enhanced composite counter electrode for flexible dye-sensitized solar cells. *Nanoenergy*. 2013;2:235-240.
94. Gangopadhyay R, De A. Conducting Polymer Nanocomposites: A Brief Overview. *Chem Mater*. 2000;12:608.
95. Wei W, Wang H, Hu YH. A review on PEDOT-based counter electrodes for dye-sensitized solar cells. *J. Energy Res*. 2014;38:1099-1111.
96. Sukchol K, Thongyai S, Praserttham P, Sotzing GA. Effects of the addition of anionic surfactant during template polymerization of conducting polymers containing PEDOT with sulfonated poly(imide) and poly(styrene sulfonate) as templates for nano-thin film applications. *Synth. Met*. 2013;179:10-17.
97. Saito Y, Kitamura T, Wada Y, Yanagida S. Application of poly (3, 4-ethylenedioxythiophene) to counter electrode in dye-sensitized solar cells. *Chem. Lett*. 2002;31(10):1060-1061.
98. Trevisan R, Döbbelin M, Boix PP, Barea EM, Tena R, et al. PEDOT nanotube arrays as high performing counter electrodes for dye sensitized solar cells. Study of the interactions among electrolytes and counter electrodes. *Adv. Energy Mater*. 2012;1(5):781-784.
99. T.H. Lee, K. Do, Y.W. Lee, S.S. Jeon, C. Kim, J. Ko, S.S. Im, High-performance dye-sensitized solar cells based on PEDOT nanofibers as an efficient catalytic counter electrode. *J. Mater. Chem*. 22(40) (2012) 21624-21629. <https://doi.org/10.1039/C2JM34807A>
100. J. Kwon, V. Ganapathy, Y.H. Kim, K.D. Song, H.G. Park, Y. Jun, J.H. Park, Nanopatterned conductive polymer films as a Pt, TCO-free counter electrode for low-cost dye-sensitized solar cells. *Nanoscale*. 2013;5(17):7838-7843. DOI: 10.1039/c3nr01294h
101. S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tomblor, A.M. Cassell, H. Dai, Self-Oriented Regular Arrays of Carbon Nanotubes and their Field Emission Properties. *Science*. 199;283(5401) 512.
102. J. Zhang, X. Li, W. Guo, T. Hreid, J. Hou, H. Su, Z. Yuan, Electropolymerization of a poly (3, 4-ethylenedioxythiophene) and functionalized, multi-walled, carbon nanotubes counter electrode for dye-sensitized solar cells and characterization of its performance. *Electrochim. Acta*. 2011;56(9):3147-3152.
103. B. Fan, X. Mei, K. Sun, J. Ouyang, Conducting polymer/carbon nanotube composite as counter electrode of dye-sensitized solar cells. *Appl. Phys. Lett*. 2008; 94(14):143103.
104. Y.M. Xiao, J.Y. Lin, J.H. Wu, Pulse potentiostatic electropolymerization of high performance PEDOT counter electrodes for Pt-free dye sensitized solar cells. *Electrochim. Acta*. 2012; 83:221-226.

105. Okada, S. Shiratori, Rare-metal-free flexible counter electrodes for dye-sensitized solar-cells produced using wet processes only. *ACS Appl. Mater. Interfaces*. 2013;5(10):4144-4149.
106. K S Lee, Y Lee, J Y Lee, J H Ahn, Park JH. Flexible and Platinum-Free Dye-Sensitized Solar Cells with Conducting-Polymer-Coated graphene Counter Electrodes *chem sus chem*. 2012;5(2):379-382. doi: 10.1002/cssc.201100430
107. V Sharma, D Hynek, L Trnkova, D Hemzal, M Marik, R Kizek et al. Electrochemical determination of adenine using a glassy carbon electrode modified with graphene oxide and polyaniline. *Microchim Acta*. 2016;183:1299-1306 doi: 10.1007/s00604-015-1740-0
108. W Hong, Y Xu, G Lu, C Li, G Shi. Transparent graphene/PEDOT PSS composite films as counter electrodes of dye-sensitized solar cells. *Electrochem. Commun.* 2008;10(10):1555-1558. doi: 10.1016/j.elecom.2008.08.007
109. M S Ramasamy, A Nikolakapoulou, D Raptis, V Dracopoulos, G Paterakis, P Lianos. Reduced graphene oxide/Polypyrrole/PEDOT composite films as efficient Pt-free counter electrode for dye-sensitized solar cells. *Electrochim. Acta*. 2015;173:276-281. doi: 10.1016/j.electacta.20
110. J He, J M Pringle, Y B Cheng, Titanium Carbide and Titanium Nitride-Based Nanocomposites as Efficient Catalysts for the Co<sup>2+</sup>/Co<sup>3+</sup> Redox Couple in Dye-Sensitized Solar Cells. *J PHYS CHEM C*. 2014;118(30):16818-16824. doi: 10.1021/jp4127418
111. H Xu, X Zhang, C Zhang, Z Liu, X Zhou, S Pang, et al. Nanostructured Titanium Nitride/PEDOT:PSS Composite Films As Counter Electrodes of Dye-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces*. 2012;4(2):1087-1092. doi: 10.1021/am201720p
112. D Song, M Li, F Bai, Y Li, Y Jiang, B Jiang, et al. Silicon nanoparticles/PEDOT PSS Nanocomposite as an efficient counter electrode for Dye-sensitized solar cells. *Funct. Mater. Lett.* 2013;06(04). doi: 10.1142/S1793604713500483
113. G Yue, J Wu, Y Xiao, J Lin, M Huang, Z Lan, Application of Poly(3,4-ethylenedioxythiophene): Polystyrenesulfonate/Polypyrrole Counter Electrode for Dye-Sensitized Solar Cells. *J PHYS CHEM C*. (2012); 116(34):18057-18063. <https://doi.org/10.1021/jp303958r>