Showcasing research findings from Shahzada Ahmad and Hans-Jürgen Butt of Max Planck Institute for Polymer Research, Mainz, Germany in a collaborative effort with Laboratory of Photonics and Interfaces, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Title: Dye-sensitized solar cells based on poly (3,4-ethylenedioxythiophene) counter electrode derived from ionic liquids

PEDOT as counter electrode in the fabrication of cost effective dye-sensitized solar cells.

As featured in:

Dye-sensitized solar cells based on poly (3,4-ethylenedioxythiophene) counter electrode derived from ionic liquids

Shahzada Ahmad, a Jun-Ho Yum, b Zhang Xianxi, b Michael Grätzel, b Hans-Jürgen Butt a and Mohammad K. Nazeeruddin b

Received 29th September 2009, Accepted 30th November 2009
First published as an Advance Article on the web 14th January 2010
DOI: 10.1039/b920210b

Poly (3,4-ethylenedioxythiophene) (PEDOT) nanoporous layers were prepared with electro-oxidative polymerization using room temperature hydrophobic ionic liquids as a medium. The synthesized highly porous PEDOT films exhibit room temperature conductivity value of 195 S cm−1 along with reproducible high cycling life. These films were used as counter electrodes in dye-sensitized solar cells yielding ~8% power conversion efficiency, which is close to the classical platinum coated counter electrode (8.7%). The photovoltaic performance increases as we lower the PEDOT film thickness as the thin films has reasonably high catalytic properties.

Introduction

Cost-effective photovoltaic (PV) devices are in urgent need due to the global energy crisis. Several novel PV systems are being developed and are in the process of commercialization. Among them dye-sensitized solar cells (DSSCs) are the undoubtedly, ubiquitous choice due to their low cost and ease of fabrication and are considered as realm of reality for the next generation low cost PV devices.1,2 The advantage of DSSCs is that most of the components are inexpensive and furthermore they do not required high energy treatment during fabrication process. In the fabrication of DSSCs, the counter electrode is one of the vital components, which reduces the I3− ions generated after electron injection from iodide into the oxidized sensitizer. Since transparent conductive oxide (TCO) substrates exhibit slow electron transfer kinetics for tri-iodide (I3−) reduction, a thin layer of platinum (Pt) is coated onto the TCO substrate (platinized counter electrode) and used to catalyze the cathodic reduction of I3− ions and redox couple regeneration in DSSCs.3,4 Given that platinum is an expensive (US $50 g−1) and less abundant metal (37 p.p.b), the development of cost-effective counter electrodes is paramount for I3− reduction.

Several groups have attempted to replace the platinized counter electrode by various carbon based materials and in most of the cases the conversion efficiency of the DSSCs was relatively low compared to the platinized counter electrode.5,12 Stable aqueous dispersions of graphene sheets were also prepared by non-covalent functionalization and by spin casting on ITO substrates to yield graphene films for counter electrodes; the efficiency of 2.2% was, however, not yet satisfactory.13 In another report a composite of graphene and PEDOT:PSS was used to improve the performance of counter electrodes of DSSCs. The authors were able to spin cast the composite film on ITO substrate and reached the efficiency of 4.5%.14 With microporous polyaniline (PANI) as counter electrode a power conversion efficiency of DSSCs 7.1% has been achieved;15 the material is, however, not stable. Due to the high conductivity and electrochemical stability, π-conjugated polymers have the potential to replace platinized counter electrodes in DSSCs. Among them poly(3,4-ethylenedioxythiophene) (PEDOT) is of special interest because of its high conductivity, electrochemical reversibility, transparency, stability, and high catalytic activity compared to other polythiophenes.16,17 Recently an air electrode coated with PEDOT on a porous material has been shown as an oxygen reduction catalyst.18

With electrodeposition, thin conducting films can be created in a cost effective way. Electrodeposition is an old synthetic technique that has been recently applied towards the creation of nanostructures. The premise of the technique is quite simple: an applied electric field draws precursor ions towards the substrate’s surface. Once the ion reaches the surface, it binds to the surface. It is well established that the electropolymerization of thiophene in the presence of water (aqueous electrolyte) results in the formation of a non-conducting or passive polymer film.19 Moreover, due to the high vapor pressure of the organic solvent, evaporation is difficult to control during film growth/deposition, which results in the formation of liquid crystalline phases in solution and induce unknown changes in the solution composition. By the use of room temperature ionic liquids (RTILs), which has almost negligible vapor pressure, one of the authors has been able to alter the growth conditions to produce grains with diameters in the nanometre scale.17,20 This is desirable because the catalytic activity of the polymer is almost entirely dictated by its grain size. The combination of these two has successfully yielded many synergistic effects. The realization of long-lived π-conjugated polymer electrochemical devices thus remains a difficult goal because of performance limitations that include poor environmental stability and electrochemically cycling between oxidation states. These problems are derived in part from the electrolytes used in the devices. RTILs are particularly electrochemically stable and thus ideal solvents for

aMax Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany. E-mail: ahmad@mpip-mainz.mpg.de; Fax: +49-6131-379115
bLaboratory of Photonics and Interfaces, Department de Chimie, Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland
a long life of electrochemical processes. Different materials have been electrodeposited from ionic liquids including conducting polymers. Potential applications for these materials range from bulk materials production, energy storage and conversion devices, catalysts and actuators.

In this communication we report on electro-polymerized PEDOT films derived from using RTILs as a medium on conducting transparent conductive oxide (TCO) substrates as a counter electrode for DSSCs applications.

**Experimental**

**Materials**

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (BMITFSI) 99% was obtained from IoLiTec GmbH. 1-Ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide (EMIPFSI) was prepared with a previously reported method and was obtained as a transparent liquid. 3,4-Ethyleneedioxythiophene (EDOT) monomer (Baytron MV-2) was purchased from Bayer and used as received.

**Characterization techniques**

The polymer deposition was carried out using an Eco Chemie AUTOLAB 1260 while cyclic voltammetry of the polymer films were performed in a classical three-electrode set up at ambient conditions. The three-electrode system comprised of FTO as a working electrode, platinum rod as the counter electrode, and Ag/AgCl as the reference electrode. Scanning electron microscope (SEM) images were obtained at 15 kV with the help of a SEM, LEO 440 instrument and the samples were gold (sputter) coated prior to use. Conductivity measurements were made by using standard four-probe method on a Keithley nanovolt meter 181, a constant current source Keithley 224. Thick PEDOT films were grown for conductivity measurements and the conductivity was calculated by taking the geometrical factor in consideration. Films were extracted carefully from conducting substrates in N-methylpyrrolidine and then transferred on to microslide glass.

**Deposition of films**

The working electrode, a SnO₂ : F (FTO) coated glass plate (∼15 Ω cm², Nippon Sheet Glass, Solar 4 mm thickness) having surface roughness of ∼4 nm was placed vertically into the cell, completely through the ionic liquid BMITFSI containing 0.1 M EDOT and the platinum rod as a counter electrode (parallel to the working electrode). The FTO substrates were cleaned ultrasonically before using in deionized water (DIW), acetone and ethyl alcohol and finally dried by blowing dry nitrogen. The polymer films were grown potentiostatically at a DC potential of +1.2 V versus Ag/AgCl (leak free reference electrode procured from Harvard Apparatus GmbH) at 25 °C (Scheme 1). The potential was applied for varying time period i.e. 30, 60 and 120 s to produce different thicknesses of the polymer film. In the text the film with 30, 60 and 120 s deposition are abbreviated as PEDOT30, PEDOT60 and PEDOT120 respectively. The film was removed from the growth solution, washed repeatedly with isopropyl alcohol and dried at room temperature for 5–6 h. The corresponding thickness of these films lies between 300–1000 nm.

**DSSCs fabrication**

FTO glass plates (Nippon Sheet Glass, Solar 4 mm thickness) were immersed in 40 mM TiCl₄ aq. at 70 °C for 30 min and washed with water and ethanol. A paste composed of 20 nm anatase TiO₂ particles for the transparent nanocrystalline layer was coated on the FTO glass plates by screen printing. The coating-drying procedure was repeated to increase the thickness to a required one. The TiO₂ electrodes were made of ∼7 μm transparent layer (20 nm) and ∼5 μm scattering layer (400 nm, CCIC, HPW-400). The resulted TiO₂ electrodes were gradually heated under an air flow. The TiO₂ electrodes were immersed into a 0.3 mM solution of bis tetrabutylammonium cis-dithiocyanatobis-2,2'-bipyridine-4,4'-COOH - ruthenium(II) (here after labeled as N719) in 50/50 (v/v) mixture of acetonitrile and tert-butanol and kept at room temperature for 15 h. The applied electrolyte was composed of 0.6 M 1,3-dimethylimidazolium iodide (DMII), 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M tert-butylpyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile. DMII is electron donor, which reduces the oxidized dye after injecting an electron onto the TiO₂ conduction band. The dye-adsorbed TiO₂ electrode and counter electrode were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film, Surlyn (25 μm, DuPont). Four types of counter electrodes were used i.e. platinum, PEDOT30, PEDOT60 and PEDOT120 to fabricate the devices. In order to reduce scattered light from the edge of the glass electrodes of the dyed TiO₂ layer, a light shading mask was used onto the DSSCs, so the active area of DSSCs was fixed to 0.159 cm². The photo current (J)/voltage (V) characteristics and incident photon-to-current conversion efficiency (IPCE) of the DSSCs were measured using previously reported work. The measurement settling time between applying a voltage and measuring a current for the J–V characterization of DSSCs was fixed to 40 ms.

**Result and discussion**

The cyclic voltammogram of a PEDOT film recorded between ±1.5 V in the pristine ionic liquid EMIPFSI at a scan rate of 0.01 V s⁻¹ is shown in Fig. 1. The peak current increases linearly with increasing scan rate. The high anodic and cathodic peaks indicate the high catalytic properties of PEDOT films. The
inset of Fig. 1 shows a linear increase of the anodic peak current density as a function of the scan rate. The result suggests that the redox reaction in the PEDOT films is rate constant dependent as well as diffusion limited due to its high catalytic properties. This illustrates that the electron transfer rate is much faster in the as deposited mono layers of PEDOT. The slope value corresponding to the anodic peak is close to one (0.96), indicating that the doping process is controlled by the RTILs with high mobility of counter ions. Moreover, the ratio of the peak current densities, $i_{pa}/i_{pc}$, is close to unity.

The stable reversibility of the electrochemical doping–dedoping process between the oxidized and neutral states of PEDOT is responsible for the set potential limits. Earlier it has been established that films made at higher polymerization potential (> 1 V) show weak adhesion and tend to peel off the FTO substrates.\(^5\) In the cathodic peak, an ill-defined peak is observed at $\sim 0.5$ V, which shifts upward at higher cycling and finally retains its shape at higher scan rate. The voltammograms shows a reduction peak around $\sim 0.5$ V and an oxidation peak around $0.5$ V. The sign of the arrow denotes an increase in the electrochemical cycling from 1–100th cycles exhibiting an excellent reversibility of these PEDOT films, advocate the use of hydrophobic RTILs, which has not been obtained in the past using classical salt-solvent based electrolytes.

By increasing the cycling number the reduction potential is shifting slightly into the negative direction and the peak current is increasing. Furthermore, with increasing peak current, the peak potential is shifting. This suggests that uncompensated resistance exists within the polymer layers and slowing redox kinetics. The redox activity of the polymer films remains fairly constant and it follows the reversible redox couples as observed during the cycling. No degradation of the PEDOT films was observed when the oxidation potential exceeded beyond the set potential.

Conductivity

Fig. 2 exhibits an Arrhenius plot of conductivity of PEDOT in the temperature range 50–300 Kelvin. The obtained plot shows non-Arrhenius behavior and a value of 195 S cm$^{-1}$ at room temperature. The activation energy was calculated using best fit and is found to be 0.0068 eV. The low activation energy is due to the high conductivity value of the synthesized PEDOT films, which states that a small amount of energy is required for hopping the electrons. The conductivity values change only by a factor with temperature even at a lowest measured temperature of 50 Kelvin. These obtained films can be useful for many applications where high conductivity > S cm$^{-1}$ is a prerequisite for device operation even at very low temperatures. The conductivity of FTO lies around $\sim 0.002–0.004$ S cm$^{-1}$, while the synthesized PEDOT is almost four orders of magnitude higher than FTO.

Morphology

Electropolymerized PEDOT films exhibits homogeneous morphologies and are highly porous with uniform grains size and this dictates its catalytic activity (Fig. 3). The porous structure has a high specific surface area and can be regarded as a potential

![Fig. 1](image1.png)

**Fig. 1** Cyclic voltammograms of the PEDOT films cycled in EMIPFSI at a scan rate of 10 mV s$^{-1}$ in the range $\pm 1.5$ V.

![Fig. 2](image2.png)

**Fig. 2** Conductivity ($\sigma$) as a function of the inverse of temperature of PEDOT film.

![Fig. 3](image3.png)

**Fig. 3** SEM micrographs of PEDOT films at (a) $200 \times 10^3$ (b) $500 \times 10^3$ (c) $500 \times 10^3$ and (d) $1000 \times 10^3$, times magnification and on different scale bar.
candidate for a counter electrode with high catalytic efficiency. The inset of Fig. 3(d) illustrates an artistic image of the PEDOT chain, which we suppose has growth and results in a stacking like structure with porous morphology. The use of porous polymers will in principal allow the post functionalization of the pore walls with the suitable dopant when used in combination with electrolytes. These microporous polymers are envisioned as potential energy materials or some times also referred to as energy polymers, due to their catalysis and catalyst supporting behavior. The porous structure will be of advantages for the improvement of electrocatalytic activity of $I_3^-/I^-\text{ redox reaction}$. The obtained highly porous microstructure was possible due the use of RTILs, which not only work as a supporting electrolyte in the synthesis of polymers but can also totally alter reaction pathways and product microstructure. Earlier we have shown that the unique morphology obtained from RTILs is due to both cation and anion incorporation in the film.17

Photovoltaic performance

Fig. 4 illustrates the schematic of the operating principles and energy level diagram of dye-sensitized solar cell using PEDOT as a counter electrode. The photo-excitation of the adsorbed sensitizer on nanocrystalline semiconductor (eqn (I)) leads to injection of electrons into the conduction band of the semiconductor (eqn (II)). The oxidized dye is subsequently reduced by electron donation from an electrolyte containing the redox system (eqn (III)). The injected electron flows through the semiconductor network to arrive at the back contact and then through the external load to the counter electrode. At the counter electrode, reduction of the oxidized redox system regenerates reduced redox species (eqn (IV)), which completes the circuit. With a closed external circuit and under illumination, the device then constitutes a photovoltaic energy conversion system, which is regenerative and stable. However, there are undesirable reactions, such as injected electrons that may recombine either with oxidized sensitizer (eqn (V)) or with the oxidized redox couple at the TiO$_2$ surface (eqn (VI)), resulting in efficiency losses. In these cells, ruthenium polypyridyl complexes as sensitizer showed over 11% solar-to-electric power conversion efficiencies in standard global air mass 1.5 (AM 1.5 sun light). Here we have investigated the photovoltaic properties of the bis tetraethylammonium cis-dithiocyanatobis-2,2'-bipyridine-4-COOH,4'-COO' – ruthenium(II) (N719) dye with PEDOT and standard Pt counter electrodes (Fig. 5, Table 1).

$$S(\text{adsorbed on TiO}_2) + h\nu \rightarrow S^+(\text{adsorbed on TiO}_2) \quad (I)$$

$$S^+(\text{adsorbed on TiO}_2) \rightarrow S^*(\text{adsorbed on TiO}_2) + e^- \quad (\text{injected}) \quad (II)$$

$$S^*(\text{adsorbed on TiO}_2) + R^- \rightarrow S(\text{adsorbed on TiO}_2) + R \quad (III)$$

$$R + e^-(\text{cathode}) \rightarrow R^- \quad (\text{cathode}) \quad (IV)$$

$$e^- (\text{TiO}_2) + S^*(\text{adsorbed on TiO}_2) \rightarrow S(\text{adsorbed on TiO}_2) \quad (V)$$

$$e^- (\text{TiO}_2) + R \rightarrow R^- \quad (\text{anode}) \quad (VI)$$

The N719 dye-sensitized solar cell using a thin PEDOT counter electrode gave a short circuit photocurrent density $J_{sc}$ of 15.0 mA cm$^{-2}$, 693 mV open-circuit potential and 0.76 fill factor resulting in 7.93% power conversion efficiency (at standard global AM 1.5 solar condition). Under similar conditions the efficiency using a Pt counter electrode was 8.71%. Upon increasing the PEDOT film thickness by increasing the polymerization time from 30 s to 120 s, the photocurrent increased from 15.0 mA cm$^{-2}$ to 15.5 mA cm$^{-2}$, which is similar to the photocurrent obtained using with Pt counter electrode. By contrast, the open-circuit voltage $V_{oc}$ decreased 20 mV of 693 mV decreased to 673 mV as the thickness of PEDOT films increased.

**Table 1 J-V characteristics of N719 sensitized solar cells with various counter electrodes**

<table>
<thead>
<tr>
<th>Counter</th>
<th>$J$ (mA/cm$^2$)</th>
<th>$V$ (mV)</th>
<th>FF</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Pt</td>
<td>15.9</td>
<td>747</td>
<td>0.73</td>
<td>8.71</td>
</tr>
<tr>
<td>PEDOT30</td>
<td>15.0</td>
<td>693</td>
<td>0.76</td>
<td>7.93</td>
</tr>
<tr>
<td>PEDOT60</td>
<td>15.2</td>
<td>683</td>
<td>0.75</td>
<td>7.86</td>
</tr>
<tr>
<td>PEDOT120</td>
<td>15.5</td>
<td>673</td>
<td>0.75</td>
<td>7.87</td>
</tr>
</tbody>
</table>
The incident photon-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength reaches more than 60% in most of visible light region and a slightly higher IPCE with Pt counter electrode is consistent with photovoltaic performance (Fig. 6). Integration of the IPCE curve obtained using PEDOT counter electrodes resulted in a well-matched photocurrent with Pt counter electrode is consistent with photovoltaic performance (Fig. 6). Integration of the IPCE curve obtained using PEDOT counter electrodes resulted in a well-matched photocurrent with Pt counter electrode. The obtained efficiency is the highest till now of 7.93%, which is almost equivalent to classical platinum based counter electrode. The comparable efficiency of N719 sensitized solar cells with various counter electrodes.

Conclusions
PEDOT films were synthesized on TCO substrate by electro-oxidative polymerization using hydrophobic, room temperature ionic liquids as a medium. These films were used as a counter electrode in the fabrication of DSSCs resulting power conversion efficiency of 7.93%, which is almost equivalent to classical platinum based counter electrode. The obtained efficiency is the highest till date using any polymer as a counter electrode. We believe that with further fine tuning of the polymer in the polymer matrix, the performance of PEDOT based counter electrode can be improved, which are cost effective for DSSCs.

Acknowledgements
One of us (SA) gratefully acknowledges the Alexander von Humboldt-Foundation for financial assistance.

References