

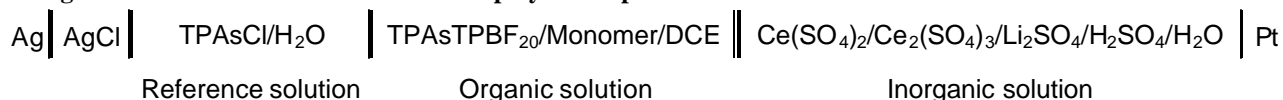
Polythiophene-nanotubes PV cells made by electropolymerisation.

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The most efficient polymeric solar cells use the bulk-heterojunction structure. So far, these structures have been produced by evaporating a solution of conductive polymer to produce thin films. The polymer is the electron-donor phase: the electron acceptor, which can be a fullerene derivative or inorganic particles, is mixed in with the solution to produce the connected 2-phase structure. Recently there has been a trend towards the use of polythiophene-based polymers, which generally resist photooxidation better than other conductive polymers, as well as being cheaper than PPV. However, this method of production requires a conductive polymer which is soluble. To make a conducting polymer soluble, organic tails (usually alkyl side-groups) are attached to the main conjugated chain. This reduces conductivity by disrupting the electron delocalisation and impeding chain-to-chain conduction by separating the chains and reducing crystallinity. More importantly, side-groups also greatly degrade resistance to photo-oxidation. Although the presence of the electron acceptor in a bulk heterojunction can improve photo-oxidation resistance by quenching excitons, existing cells still need airtight encapsulation and gettering to attain an acceptable lifetime. Encapsulation of silicon solar cells is less demanding, but already accounts for more than half the module cost. Therefore, we think that polymer cells will only become much cheaper than silicon ones if they can be made stable in air and light without the need for expensive encapsulation.

Our approach to improve the stability and efficiency of polymer PV cells is to use electropolymerisation, which can produce plain polymer without tails. Early results seem to confirm the validity of the choice of the electropolymerisation as method of production and of the 2,2':5,2'' terthiophene as the starting monomer. In fact, a layer of polyterthiophene (P3T) still conducts, even after one year in light and laboratory air, in the range of 0.005 to 0.1 $\Omega^{-1} \text{cm}^{-1}$ (minimum and maximum value measured at different thickness). These layers were produced by electropolymerisation at the interface between two immiscible electrolyte solutions (ITIES); the polymer was then extracted on glass. Fig. 1 specifies the cell used: electropolymerisation takes place at the organic/inorganic interface, shown by the symbol \downarrow .

Fig. 1: Electrochemical cell used for the polymer deposition with the ITIES method.



It is difficult to extract the film made by ITIES without mechanical damage. To electropolymerize directly onto ITO-coated glass slides, a new 3-electrode cell was made in PTFE (Fig. 2).

Dichloroethane (DCE) is used as solvent and tetraphenylarsonium-tetraphenylborate pentafluoride (TPAsTPBF₂₀) as supporting electrolyte. The reference electrode was immersed in an aqueous side-cell containing tetraphenylarsoniumchloride hydrate (TPAsCl) in water (18.2 M Ω -cm). The side-cell connected via a Luggin capillary (a drill-hole in the PTFE) to just above the slide in the main cell.

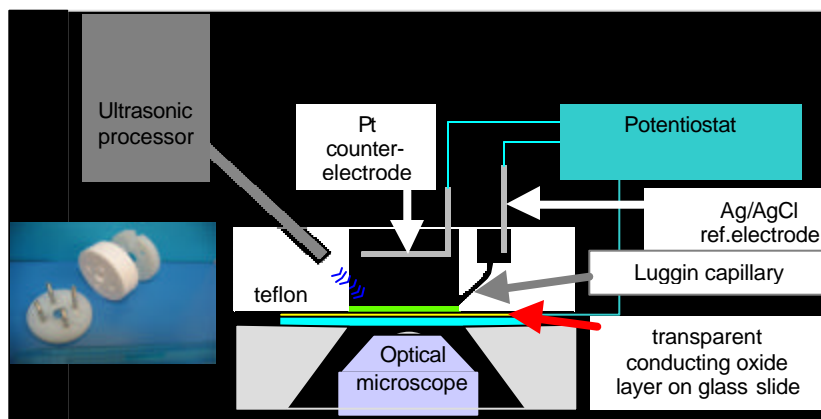


Fig. 2: new 3-electrode cell

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Early experiments with this cell were conducted on gold to test the method of polymerisation and the reference system. The produced layer was very uniform showing a Schottky diode I-V behaviour. Later experiments were conducted on ITO-coated glass. Concentrations were 1,2,4,8,10 mM for the 3T and 1,2 and 5 mM for the TPAsTPBF₂₀. The film starts to be deposited at 8mM 3T/2mM TPAsTPBF₂₀ but is less uniform than with the 10 mM 3T/5mM TPAsTPBF₂₀. Our system is characterised by 3T polymerisation at about 1.05 V vs Ag/AgCl, where no reactions are observed for the solvent and supporting electrolyte (Fig.3). This voltage was chosen for subsequent potentiostatic depositions with thicknesses of the order of 1 μm calculated from the anodic charge. The polymerisation reaction required the solution to be aerated.

Following deposition, the doping of the film could be controlled by holding at different electrode potentials. This was shown by a colour change from the original dark-brown anodically-doped polymer to orange as the potential is reduced. This is the colour change expected when the inter-band transitions of polarons are removed. Higher cathodic currents caused film dissolution.

The polyterthiophene layer on ITO shows strong photoconductive and photovoltaic effects even with a simple Cu-Be point contact. Fig.4 shows a typical I-V

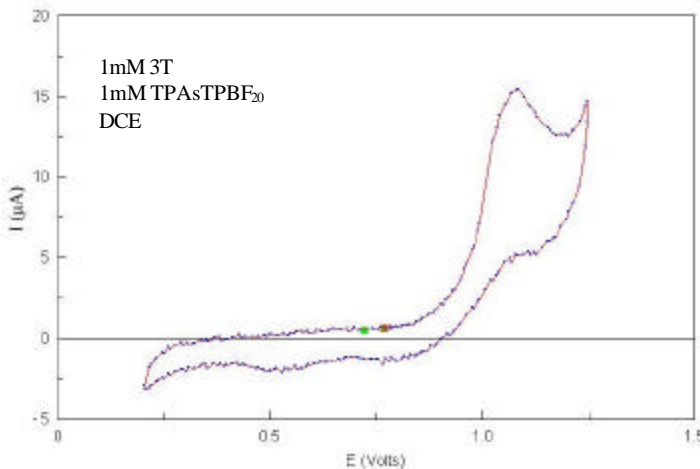


Fig. 3: cyclic voltammery, scan rate=10 mV/sec.

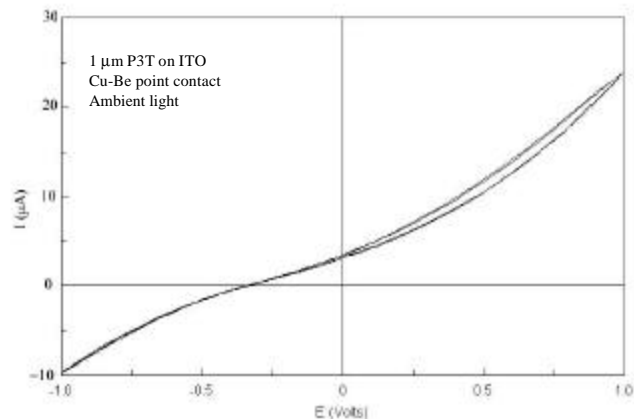


Fig. 4: Schottky diode I-V behavior on ITO coated glass in ambient light.

response in ambient light and Fig. 5 shows the effect of switching on and off more intense illumination during the test (1V to -1V).

Now we are investigating a PV cell using a simple P3T film on ITO with graphite contacts. The next step will be to make a thin continuous P3T layer followed by a thicker layer incorporating SWNTs which are suspended in a fresh Monomer/Salt/DCE solution by ultrasonic agitation.

Electropolymerisation of plain polyterthiophene promises to produce a PV cell which can survive in air and light. We are on the way to make a cell which will incorporate carbon nanotubes as electron acceptor, ohmically connecting to a graphite back contact (Fig.6).

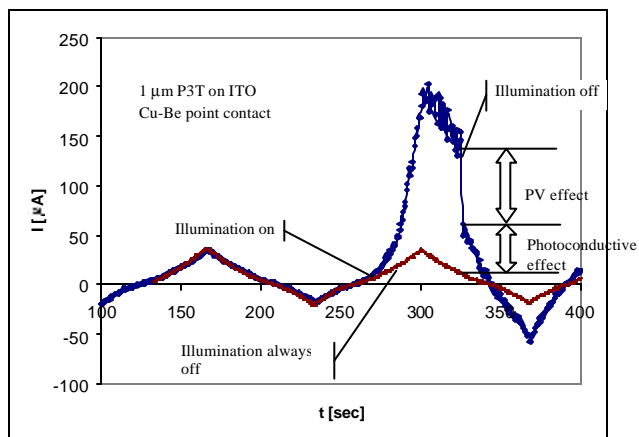


Fig. 5: response to an imposed Voltage (-1V to 1V, n=30mV/sec) in ambient light with and without extra illumination.

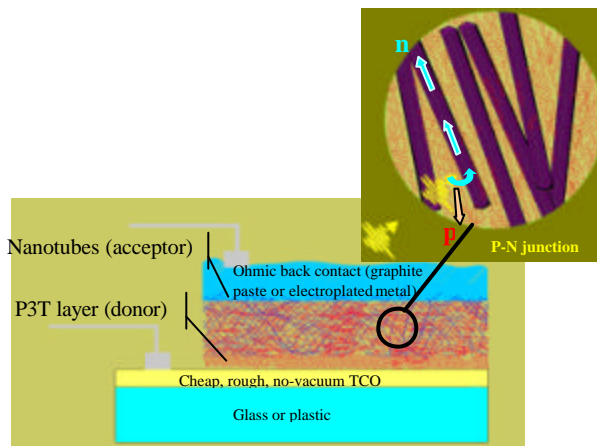


Fig. 6: a new concept of P3T-nanotubes PV cell made by electropolymerisation.