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On polythiophene film as a photocathode

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Abstract. The photoelectron emission from thin films of lightly doped polythiophene was investigated in the ultraviolet and vacuum ultraviolet spectral region. Absolute quantum yields rising from 4×10^{-6} at 5 eV to 3×10^{-3} at 10.5 eV were measured. The photoemission threshold was determined to be $E_{th} = 5.06 \pm 0.05$ eV. The films were produced electrochemically with perchlorate ions as the dopant.

Conducting polymers have received a lot of attention from a scientific point of view. The possibility of increasing the electrical conductivity by doping up to values of metallic conductivity is one of the main areas of interest in this field. Detailed theoretical pictures of the electronic band structure have been developed for various types of polymers (Skotheim 1986). The application of highly conductive polymers as electrodes in batteries has been described. Other possible applications depend on the investigation of the pertinent physical properties of specific conducting polymers.

In recent years, some research effort has been devoted to the development of organic photocathodes. For the detection of scintillation and Cerenkov light produced in high energy physics experiments, liquid and solid solutions of aromatic compounds in hydrocarbons were investigated (Peskov *et al* 1988). For accelerators, the need exists for rugged electron sources that can stand exposure to air or operation in a poor vacuum without loss of emission yield (*CERN Courier* 1989). Thin layers of organic dyes excited by pulsed laser light have been investigated for this purpose. (Massey *et al* 1987). Highly monoenergetic and highly directed electrons can be produced using photoemission from layers of hexatriacontane ($n\text{-C}_{36}\text{H}_{74}$) deposited on metallic substrates (Cartier *et al* 1987, Rei Vilar *et al* 1988). Conductive polymers have not been studied within this context although ultraviolet photoelectron spectroscopy (UPS) has been used as a powerful tool for the investigation of the electronic band structure of such materials. From a fundamental and practical point of view the quantum yield of photoelectrons as a function of photon energy is a most important quantity.

We wish to report here on the photoelectric properties of polythiophene films that were lightly doped with ClO_4^- . The measurements were carried out in the photon energy range from 5 eV to 10.5 eV. In addition, some ESCA measurements were included.

Polythiophene films were produced by electrochemical polymerisation on platinum substrates. Perchlorate ions were added to the electrolyte as the dopant. Films of

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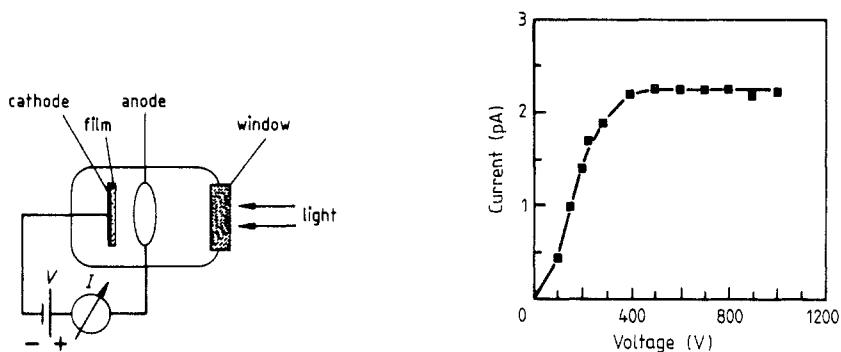


Figure 1. A schematic diagram of the experimental set-up and typical current–voltage characteristic at constant wavelength and light intensity.

approximately $0.1 \mu\text{m}$ thickness were selected for the investigation. The doping level was verified by ESCA measurements of the atomic ratio of Cl and S (x-ray photoelectron spectroscopic measurements were carried out with an ESCA machine made by Vacuum Generators, model Mk II). Typically, values of one ClO_4^- ion for 10 to 15 thiophene rings were obtained.

The quantum yield measurements were carried out with two separate experimental set-ups. For wavelengths greater than 200 nm, a high pressure xenon lamp and a Bausch and Lomb monochromator with a grating for 200 to 400 nm were used. The reciprocal dispersion was less than 3 nm. For the vacuum UV spectral range, a deuterium lamp equipped with a MgF_2 window was used as the light source, followed by an Acton Research monochromator, model VW 502. This installation allowed measurements between 400 and 115 nm. Here the reciprocal dispersion was 1 nm. The sample, of approximately 1 cm^2 area, was placed into a measurement chamber made from UHV stainless steel components. The cathode feedthrough was connected to the platinum substrate while the anode feedthrough was connected to a wire loop placed 1 cm above the polythiophene film. The sample chamber was evacuated to a pressure of the order of 10^{-6} mbar. The photoelectric current was measured with a Keithley picoammeter applying voltages up to 600 V. Above 400 V a plateau of the photocurrent was observed (figure 1). The photocurrents were stable in time and insensitive to exposure of the film to air.

The calibration for the absolute quantum yield was carried out separately for the two installations. For the longer wavelength region a calibrated photomultiplier was used for the determination of the photon flux. The vacuum UV quantum flux had been determined previously by using a special ionisation chamber filled with NO for which the photoionisation quantum yield is known (Samson 1967, Buschick 1987). The two calibrations agreed at 200 nm within a factor of 2.

The absolute quantum yield of photoelectrons as a function of photon energy is given in figure 2. In the energy range investigated, the yield increases with photon energy over more than four orders of magnitude reaching 0.3% at 10.5 eV. An emission threshold can be obtained by plotting the quantum yield Y as a function of the photon energy $h\nu$ according to a power law

$$Y = B(h\nu - E_{\text{vac}})^n \quad (1)$$

where n was taken as $n = 2$ or $n = 3$. The plots of the data near the threshold are shown

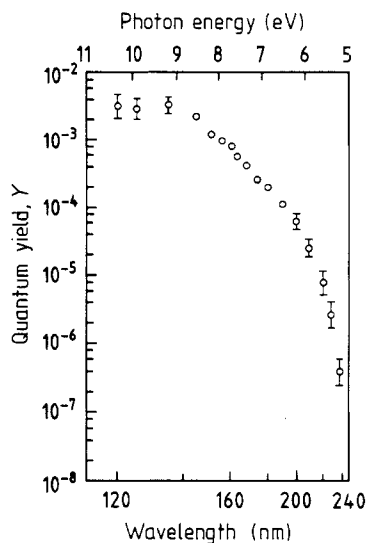


Figure 2. The absolute quantum yield of photoelectrons from a lightly doped polythiophene film as a function of photon energy.

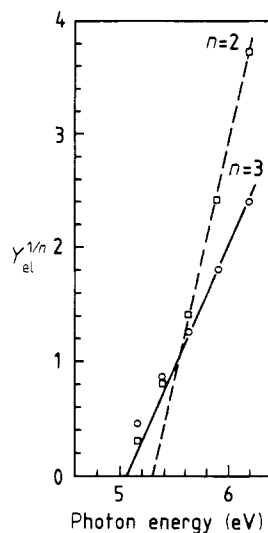


Figure 3. A plot of the data of figure 2 according to equation (1).

in figure 3. Both representations give straight lines over a limited energy range with threshold values of $E_{\text{vac}}(n=3) = 5.06$ eV and $E_{\text{vac}}(n=2) = 5.3$ eV, respectively. While $n=2$ is the usual Fowler plot (Fowler 1932) found for metals, $n=3$ seems to give a better fit to our data. The latter dependence has also been reported for photoemission from molecular crystals (Pope and Swendberg 1982). This dependence is derived under the assumption of a nearly linear energy dependence of the density of states in the highest valence band. Near the threshold a deviation from the linear dependence occurs with the data lying above the dependence according to equation (1). It is well documented that in the band gap of polythiophene, polaron states can be created from which electron emission is possible.

Optical absorption measurements reported in the literature (see Skotheim 1986) yielded a band gap of 2.1 to 2.2 eV for neutral or lightly doped polythiophene. With our data on $E_{\text{vac}}(n=3)$ a work function of $\Phi = 4.0 + 0.1$ eV is obtained for lightly doped polythiophene.

Doped polythiophene can serve as a photocathode although the quantum yield for photoelectrons is rather low. The material has the advantage of being very stable and insensitive to exposure to air.

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