Symmetric photoelectrochemical behaviour of anion- and cation-doped polybithiophene

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Both anodic and cathodic photocurrents have been observed on a thin-film polybithiophene electrode and are dependent on the type of doping: anion-doped polymer feature cathodic photocurrents, while cation-doped polybithiophene demonstrate anodic photocurrents.

Electronically conducting polymers (ECPs) are promising materials that are attracting considerable attention from researchers. Depending on the doping level these materials can act as metals, semiconductors or insulators and thus can be utilised in a wide range of applications such as electric conductors, batteries and electronic devices. Of particular interest from both fundamental and practical viewpoints are the semiconductor properties of ECPs. Most of the common ECPs like polythiophene, polypyrrole and polyaniline are usually synthesised *via* electrochemical or chemical oxidation of the corresponding monomers and thus come in *p*-doped or anion-doped states. Being partially undoped, these polymers act in many respects as *p*-type semiconductors (for instance, they exhibit cathodic photocurrents).[1–5]

At the same time, it is known[6–11] that some of the polymers under appropriate conditions can exhibit not only anionic or *p*-type doping but also cationic (*n*-type) doping. For polybithiophene this is illustrated in Figure 1 where one can see characteristic doping–undoping peaks in both the cathodic and anodic regions. Therefore, at extreme anodic and cathodic potentials the polymer is doped and behaves as an electronic conductor, whereas in the region between the peaks the polymer is partially undoped and exhibits semiconductor properties. However, while semiconductor properties including the photoelectrochemical behaviour of *p*-doped materials are relatively well examined, those of *n*-doped polymers have been much less well studied, although there have been several attempts to utilise *n*-doped polythiophenes in semiconductor devices.[12] For instance, it is known[13] that undoping of the *p*-type polymer results in formation of a space-charge layer within the polymer film, which is responsible for the observed semiconductor properties and, in particular, photocurrent generation. However, in the case of an *n*-type polymer, there are no data on whether such a space-charge layer exists and whether effective photogeneration processes are possible in such systems. Another important problem that remains obscure is the nature of the photoprocesses involved. In this work we show that, being partially undoped, both *p*-doped and *n*-doped polybithiophene exhibit cathodic and anodic photocurrents, respectively, thus demonstrating the fundamental symmetry in the photoelectrochemical behaviour and semiconductor properties of anion- and cation-doped conducting polymers. Furthermore, we demonstrate that in both cases the photocurrent is related to photoelectrochemical undoping of the polymer itself.

Figure 2 presents the potential dependence of the photocurrent[†] that was observed for *p*-doped polybithiophene electrode. One can see that the polymer exhibits cathodic photocurrents, which is to be expected for the *p*-type material and which agrees well with the literature data for polybithiophene[3] as well as for other polythiophenes.[1,2,4] Figure 3 presents the potential dependence of the photocurrent that was observed on *n*-doped polybithiophene. From Figure 3 it is evident that, being partially undoped, *n*-type polybithiophene featured an anodic photocurrent, which indicates that its semiconductor and photoelectrochemical properties are indeed similar to those of an *n*-type semiconductor. Furthermore, the potential dependences of the cathodic photocurrent for the *p*-type polybithiophene and anodic photocurrent for the *n*-type polybithiophene are rather symmetrical, which suggests a symmetry in the photoelectrochemical behaviour of the two materials.

An important feature that can be seen in the two Figures is that in both cases the photocurrent increases considerably after the polymer is exposed to extreme anodic (cathodic) potentials where its doping occurs. This is indicative of the fact that the photocurrent in both systems originates, at least in part, from photoelectrochemical undoping of the polymer.

Previously[4,13] we demonstrated that the cathodic photocurrents that occur on partially undoped *p*-type poly-3-methylthiophene in the absence of a redox species, *e.g.* oxygen in the solution are related to photoelectrochemical undoping of the polymer itself. In terms of this model, the first step of the photoprocess was the photogeneration and separation of the photoexcited carriers in the polymer bulk. Then, the photogenerated electrons interacted with the oxidised portions of the polymer (polarons or bipolarons) where the doping charge is stored. This process was accompanied by removal of counter ions that pass into the solution. Therefore, the overall photoprocess was the photoelectrochemical undoping of the polymer.

The same model seems to be valid in our case of polybithiophene as well; furthermore, it is applicable to both *p*-

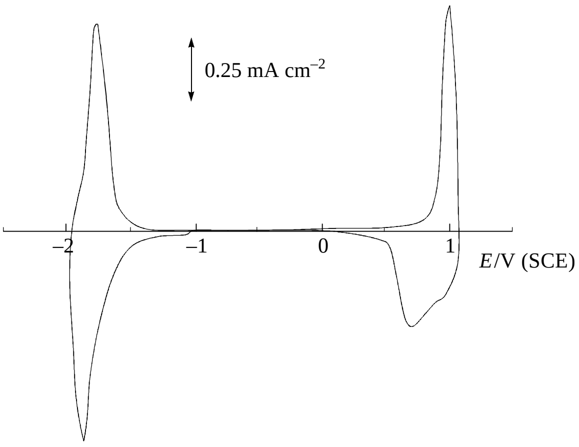

Figure 1 Typical cyclic voltammograms of a thin-film polybithiophene electrode in a 0.1 M acetonitrilic solution of Bu_4NClO_4 taken separately at cathodic and anodic potentials. The scan rate was 50 mV s^{-1}. The potentials were measured and are reported *vs.* aqueous saturated calomel electrode (SCE). The film was prepared by galvanostatic anodic deposition from the same solution but containing 0.01 M of bithiophene at a current density of 0.5 mA cm^{-2}. The film thickness as estimated from the grafting charge was approximately 60 nm.

[†] The sign of the photocurrent magnitude corresponds to the sign of the real component of the photocurrent.

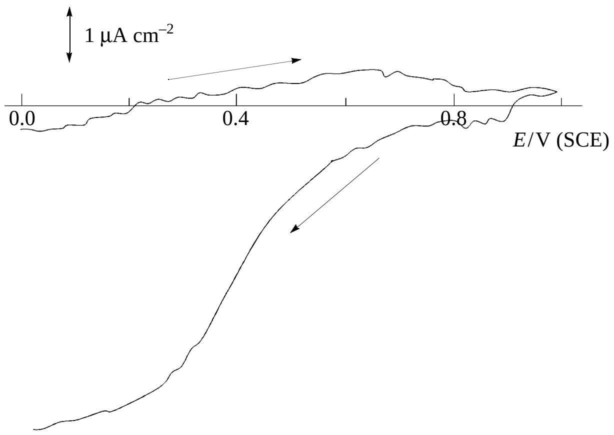

Figure 2 Potential dependence of the photocurrent taken on a p-doped polybithiophene electrode in 0.1 M acetonitrilic solution of Bu_4NClO_4. The scan rate was 50 mV s^{-1}. The film was prepared as described above. Prior to measurements, the electrode was held at a potential of –1.0 V in light for 10 min. The electrode was illuminated with 487 nm light from a 2 mW He–Cd laser. The light intensity was modulated with an electrooptical modulator at a frequency of 28 Hz and the resulting ac photocurrent was measured using the lock-in technique.

doped and n-doped polymers. Indeed, after the polymer (either p- or n-doped) was held in light at the potentials where the photocurrent occurs, the photocurrent values gradually decrease reaching almost zero due to a corresponding decrease in the concentration of positively (negatively for n-doping) charged polarons in the polymer bulk. This is illustrated in the direct scans of Figures 2 and 3 that were taken after the polymer was undoped in light at appropriate electrode potentials. The dominant photoprocess in these conditions seems to be the bulk recombination.

After the polymer was doped (again, either at extreme anodic or extreme cathodic potentials), the photocurrent significantly increase (reverse scans in Figures 2 and 3). In terms of this model, this can be attributed to an increase in the polaron (bipolaron) concentration within the polymer due to their generation in the process of polymer doping. As a result, the concentration of the photoelectrochemically active species increases, which gives rise to a corresponding increase in the photocurrent. After an initial increase the photocurrent reaches some plateau (Figure 2) or even starts to decrease (Figure 3), which indicates a decrease in the polaron concentration in the process of photoelectrochemical undoping of the polymer.

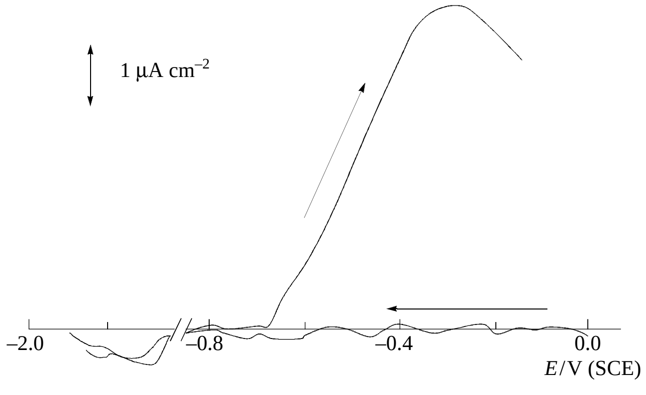

Figure 3 Potential dependence of the photocurrent taken on an n-doped polybithiophene electrode in a 0.1 M acetonitrilic solution of Bu_4NClO_4. The scan rate was 50 mV s^{-1}. The film was prepared as described above and then was cathodically doped in the background solution at a potential of –1.9 V for 10 min in dark. Prior to photocurrent measurements, the electrode was held at a potential of +0.5 V in the light for 10 min. The electrode was illuminated with 487 nm light from a 2 mW He–Cd laser. The light intensity was modulated with an electrooptical modulator at a frequency of 28 Hz and the resulting ac photocurrent was measured using the lock-in technique.

Therefore, we conclude that, being partially undoped, both anodically and cathodically doped polybithiophene feature photocurrents that are consistent with the type of polymer doping. Furthermore, in both cases the main photoprocess seems to be photoelectrochemical undoping of the polymer itself. These regularities present important evidence for the fundamental symmetry in the photoelectrochemical and semiconductor behaviour of p-doped and n-doped polybithiophene.

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