

Photocurrent and photovoltage generation dynamics at the organic semiconductor/water interface in p-type conjugated polymers

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Summary. — Photoactive organic semiconductors are envisioned as a novel class of materials able to transduce light into stimulating signals inside biological cells or tissue. The direct interface between the semiconductor and the electrolyte gives rise to different, competing electrochemical phenomena. A detailed understanding of such chemical and photo-induced interactions is necessary to develop and optimize future devices. We addressed the problem in organic polymeric photoelectrodes by gaining insights into the energetics of the involved processes, identifying the kinetics of light stimulated charge transfer processes, and then determining the role of interfacial energy levels in the photoactivated processes. We highlight how energy diagrams enable a comprehensive understanding of the photoelectrochemical reaction pathways.

1. – Introduction

P-type photoactive semiconducting polymers are recently gaining interest as photo-transducer material for optically-controlled bioelectronics able to transduce light into stimulating signals inside biological cells or tissue [1]. After comprehensive investigations as solar cell active materials, they are now studied and developed for medical purposes [2-4], such as cancer phototherapies, photo-triggered drug release, bioimaging, and phototriggers of reactive oxygen species (ROS) due to their intrinsic conductivity and optical properties. When used as bioactive photoelectrodes, the direct interface between the semiconductor and the electrolyte gives rise to different, competing electrochemical phenomena such as photofaradaic or photocapacitive processes, depending on whether the photogenerated charges get involved in redox processes or accumulate at the interface [5,6]. Understanding the different competing optoelectronic phenomena arising from the direct interface between the OSC and the aqueous electrolyte is of central importance for the development of future devices. This research is of particular relevance to understand wireless, optically triggered bioelectronic transduction as achieved with

p-type OSC in the form of transducer patches or micro- and nanoparticles in contact with biological cells [7, 8].

2. – Experimental

Photoelectrodes are made of a thin polymeric organic semiconductor deposited by spin-coating on a fully oxidized indium-tin-oxide (ITO) coated glass slide. For the study we employed the well-established prototypical polymeric OSC P3HT and two medium/low bandgap thiophene-based conjugated polymers commonly used in high performance organic solar cells, namely PTB7 and PBDB-T. The photoelectrode's active surface was exposed to the PBS electrolyte via a photoelectrochemical cell developed for the purpose as in fig. 1(a). In a three-electrode setup, the photoelectrode was operated as the working electrode. A silver chloride reference electrode was used in combination with a platinum counter electrode. In spectroscopic measurements, the monochromatic illumination of the photoelectrode was achieved with a xenon lamp combined with a monochromator. The signal was collected and amplified by the monitoring output of a potentiostat for photocurrent measurement or by a voltage amplifier for photovoltage measurements. The potentiostat was also used for impedance spectroscopy measurements. For transient measurements, the monochromated xenon lamp light was replaced with monochromatic LEDs.

3. – Results and discussion

The objective of the work is to identify the role of the electrolyte and the impact of electrochemical reactions. To do this we compare transient measurements of intrinsic photovoltage generation as observed both in the presence and in absence of the electrolyte. These measures show that the presence of the electrolyte causes an almost two orders of magnitude larger photovoltage signal. The build-up of the large photovoltage signal takes seconds, showing a much larger time scale in the presence of electrolyte with respect to the milliseconds build-up observed without the electrolyte. By comparing photocurrent and photovoltage transients in the presence and absence of oxygen we show that such a large photovoltage in the electrolyte only builds up when oxygen is present. This finding points to the important role of redox—reactions with oxygen as electron acceptor in photovoltage build-up. To further inquire on the energetic states involved in photovoltage generation, we performed spectroscopic measurements, which

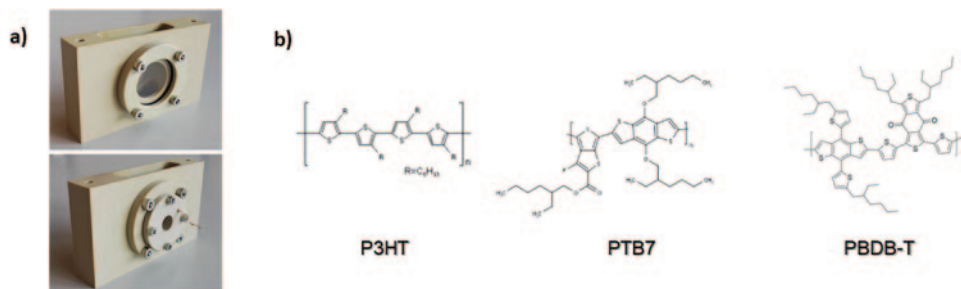


Fig. 1. – Here are depicted the Photoelectrochemical Cell (PEC cell) used for the experiments (a) and the repeating units of the three investigated polymers (b).

demonstrate that excitation exceeding the optical bandgap leads to photovoltage generation in open circuit conditions and photocurrent generation in short circuit conditions at suitable applied potentials.

From these findings, we can derive a first interpretation of the strong photovoltage generation observed in p-type organic semiconductor photoelectrodes. Figure 2 shows a basic scheme with the relevant energy levels for the materials present at the photoelectrode/electrolyte interface. During illumination, photogenerated excitons are formed and diffuse in the thin film. In absence of the electrolyte, exciton separation happens throughout the organic semiconductor generating charge transfer states or free electrons and holes. However, as there is almost no preferential direction in the thin film, a minimal dipole is generated and the photovoltage is very small. Also, the presence of the ITO substrate does not impart a directed charge separation as its Fermi level acts as acceptor for electrons as well as for hole charges [9]. In the presence of an electrolyte containing oxygen, the situation changes. Now free electrons are transferred onto the acceptor in the electrolyte. The energy-level for the one-electron transfer to oxygen depends on the hydration of the molecule and the local concentration of the reduced form, but yet electrons in the conduction band have a strong driving force for the electron transfer process. With the transfer of electrons across the interface, holes accumulate in the OS layer and negative ionic charges in the electrolyte. The shift in vacuum level caused by the charge accumulation progressively reduces the driving force for the aforementioned electron transfer and increases the driving force for redox reactions in the opposite direction. At a certain photovoltage, forward and backward electron transfer counterbalance and the photoelectrode reaches a stable photovoltage as indicated in fig. 2(b). By combining the obtained findings with electrochemical impedance spectroscopy (fig. 3(a)), we develop a simple equivalent circuit model to explain the large observed photovoltage and its build-up dynamics in OSC floating photocathodes in contact with the electrolyte. Based on Butler-Volmer kinetics describing the photoreduction process, we obtain a quantitative description of the photovoltage transients and charging behaviour (fig. 3(b)) of p-type photoelectrodes following a simple equation. The obtained findings are further combined with nanoscale morphological investigations and Kelvin-Probe Force Microscopy leading to a quantitative interfacial energy diagram. Of all the possible chemical and electrochemical pathways that can be taken by the reduced oxygen molecule, the most

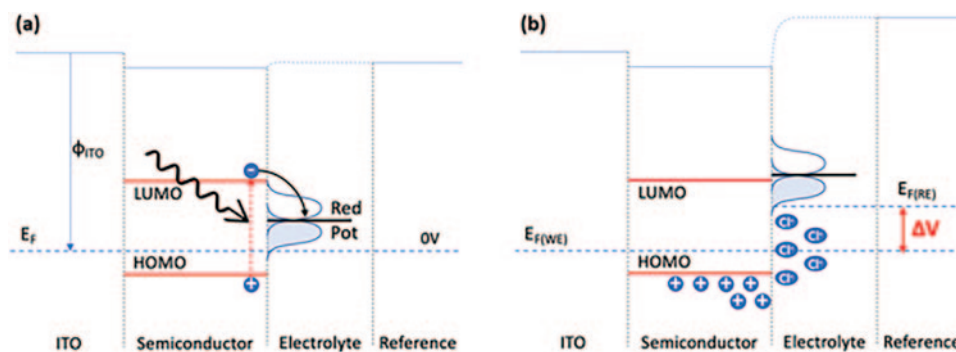


Fig. 2. – Energy diagrams explaining initial photovoltage generation and saturation: (a) Upon illumination electrons are transferred from the HOMO level onto oxygen acceptor state in the electrolyte. Therefore, an interfacial double layer builds up. (b) The acceptor level rises in energy, further transfer of excited electrons becomes unlikely.

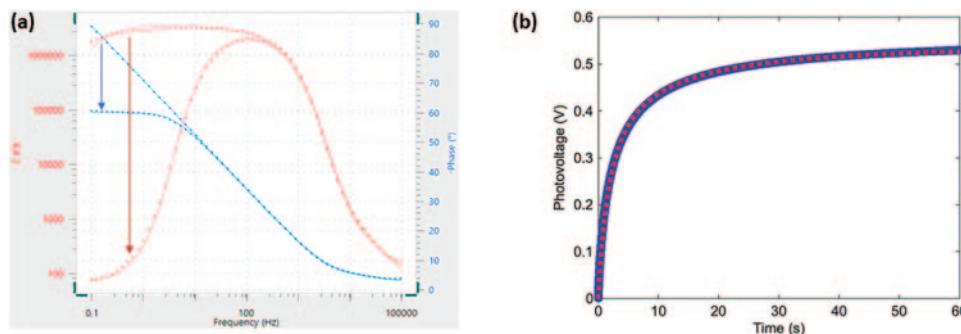


Fig. 3. – (a) Electrochemical impedentiometry showing how phase (red dots, data, red line, fit) and impedance (blue dots, data, blue line, fit) change from dark to illuminated. (b) Example of photocurrent transient. (c) Photovoltage transient fit using the Butler-Volmer derived equation.

interesting one for indirect chemical cell stimulation purposes is the one that brings to hydrogen peroxide.

For this reason, we performed a quantitative determination of hydrogen peroxide generation with the HRP-TPM assay to further determine the electrochemical conversion efficiencies for the three different materials. We found that the electron-to-peroxyde efficiency is similar in all three materials, leading to the conclusion that the best performing in photocurrent generation would be also the best one for hydrogen peroxide generation.

4. – Conclusions

By combining transient and spectroscopic measurements of both photocurrent and photovoltage, electrochemical impedance spectroscopy, and Kelvin-Probe Force Microscopy, we developed a simple equivalent circuit model based on Butler-Volmer kinetics describing the photoreduction process, obtaining a quantitative description of the photovoltage transients and charging behaviour of p-type photoelectrodes. The findings are further combined with nanoscale morphological investigations and Kelvin-Probe Force Microscopy leading to a quantitative interfacial energy diagram. We highlight how the energy diagram enables a comprehensive understanding of the photoelectrochemical reaction pathways and how findings can be translated to predict the response of novel materials and devices. This research is of particular relevance to understand wireless, optically triggered bioelectronic transduction as achieved with p-type OSC in the form of transducer patches or micro- and nanoparticles in contact with biological cells.

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