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Characterization of Faradaic and Capacitive Processes in Organic Photoelectrodes for Artificial Retina Prosthesis

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Abstract (English)

An increasing number of studies about artificial retinal prothesis have been carried out recently demonstrating the possibility to restore sight in partially sighted or blind patients. In all of such devices the fundamental component is an opotobioelectronic layer. When illuminated, this layer produces ionic current pulses of enough intensity to activate the visual cortex’s neurons. The principal objective to achieve is the deep understanding of the processes that occur at the semiconductor-liquid interface, with the purpose to develop materials that present flexibility and biocompatibility and are not subject to deterioration when in contact with an acqueous electrolyte. In this thesis I have analysed organic semiconducting pigments developed by the Linkoping University as active optobioelectronic layer. The purpose of the thesis is to investigate and characterize the faradaic and capacitive processes that occur at the interface when a light stimulated current pulse is generated. The results show that faradaic processes are favoured by a negative potential applied to the optobioelectronic layer, while with a positive potential the photocurrent is almost completely capacitive. The wavelength of the stimulating light pulse has instead no significant effect on the ratio between capacitive to faradaic current generation processes.

Abstract (Italiano)

Recentemente, un numero crescente di studi sulle protesi retiche ha dimostrato la possibilità di ripristinare artificialmente la vista in pazienti ipovedenti o cechi. In tali dispositivi il componente principale è lo stato optobioelettronico che, sottoposto a stimolo luminoso, produce impulsi di corrente ionica di intensità sufficiente per attivare i neuroni della corteccia visiva. Attualmente, il principale risultato da raggiungere è una profonda comprensione dei processi che avvengono all’interfaccia fra liquido e semiconduttore, per poter sviluppare materiali che presentino flessibilità e biocompatibilità e che non siano soggetti a deterioramento a contatto con una soluzione elettrolitica. In questa tesi ho analizzato pigmenti organici semiconduttori realizzati dalla Linkoping University come strato attivo optobioelettronico. Lo scopo della mia tesi è indagare e caratterizzare i processi faradaici e capacitivi che si verificano all’interfaccia quando viene generato un impulso di corrente in seguito a stimolazione luminosa. I risultati mostrano che i processi faradaici sono favoriti quando è applicato un potenziale negativo allo strato optobioelettronico, mentre con un potenziale positivo la fotocorrente è quasi completamente capacitiva. La lunghezza d'onda dell'impulso luminoso stimolante non ha invece alcun effetto significativo sul rapporto tra processi di generazione di corrente capacitivi e faradaici.

Contents

Introduction

The general context in which my thesis is inserted is the one of the artificial retina prothesis.

In the visual process, the retina, through specific cells called photoreceptors, transduces the light stimulus in electric impulse, which in turn stimulates the neurons. The photoreceptors do not regenerate, if they are damaged by a degenerative pathology lead to a progressive blindness. The retinal prosthesis are devices able to generate an artificial visive perception thanks to the electric stimulation of the healthy neuronal cells, bypassing the damaged photoreceptors.

Nowadays, the available devices aimed to this scope are based on the use of silicon photodiodes, which are reasonably efficient and mature technology. Silicon-based devices were extensively studied and some of them are already in commerce. However, this kind of devices presents several limits, such as rigidity in the interface with the soft biological tissues, high thickness caused by the low absorbance coefficient, tendency to corrosion in a physiological setting.

For this reason, the most recent studies have been focusing on the research of novel materials with better proprieties. In particular, the organic semiconductors seem to guarantee the best performances: have shown the ability to photostimulate explant retinas, neurons and there is evidence that they can impart light sensitivity in blind retinas in vivo [6]. Moreover, they are biocompatible, flexible, relatively easy to fabricate and can work in a humid environment avoiding oxidations, corrosions and faradaic processes.

In the analysis of these devices particular attention must be paid to the photovoltaic phenomena of current generation, in particular to the optoelectronics processes that take place at the interface between the organic semiconductor and the electrolytic solution. My thesis is in this framework and its purpose it to characterize and individuate a model for the faradaic and capacitive process that take place at the interface. In fact, with a better understanding of the conditions under which these processes occur, one could fabricate devices that are not subject to the redox reaction associated with the faradaic processes, which can seriously damage the tissues and the device itself.

Chapter 1
Human Visual System

1.1 The Eye

Eyes are the external sense organs of the visual system. The human eye is a hollow sphere with a diameter of about 2.5 cm, it is an exquisitely complicated organ and it acts like a camera. In fact, the optics of the eye create a focused two-dimensional image of the visual world on the retina, the latter serves as a transducer for the conversion of light into neuronal signals, which are sent to the brain through the optic nerve. Every part of the eye has its own physiological role and from outside to inside three layers can be distinguished. The outermost layer is made up of the sclera and the cornea, the latter is the transparent front part through which light enters. The intermediate layer includes the choroid, the iris (a circular pigmented muscle which contracts and relaxes to regulate the amount of light that enter the eye) and the crystalline lens, which refracts light to be focused on the retina. The inner layer is made up of the retina. [1]

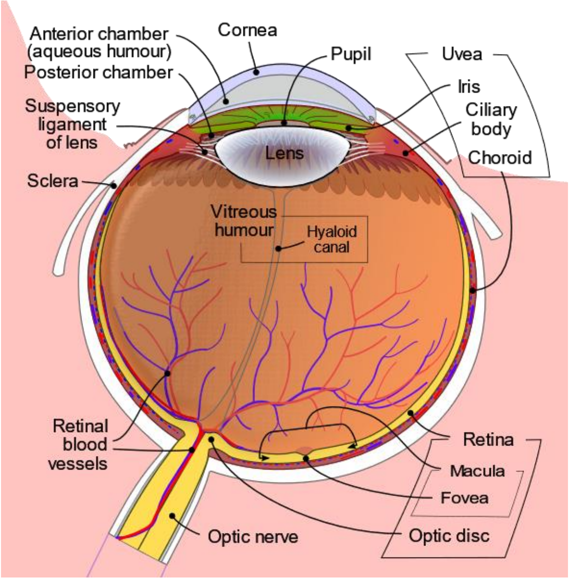


Figure 1.1: *Schematic diagram of the human eye [1].*

1.2 The retina and common retinal diseases

The retina is a thin membrane that convers the inner surface of the eye, it consists of six types of nerve cells, arranged in ten distinct layers. These layers can be grouped into four main processing stages: photoreception, transmission to bipolar cells, transmission to ganglion cells and transmission along the optic nerve. The human retina, as in most of the vertebrates, is inverted, this means that the light sensing cells are in back of the retina, so that light has to pass through layers of neurons and capillaries before it reaches the photoreceptor cells, which efficiently absorb light and transduce it into an electrical/biochemical signal to the bipolar cells. Through a complex path, the signal reaches the optic nerve and the visual cortex in the brain [2]. The photoreceptors are of two types: rods and cones. Cones are responsible for the perception of colour, while rods function mainly in dim light and provide black-and-white vison.

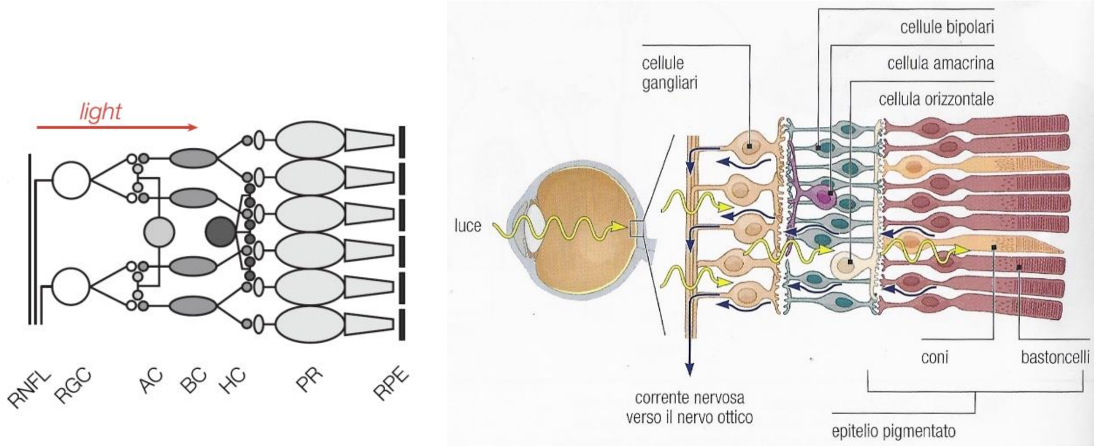


Figure 1.2: *On the left: Schematic diagram of the structure of retina's layers. Light arrives on the Photoreceptor (PR) that are in contact with the Retinal Pigment Epithelium (RPE) and the transduced signal radiates through the Horizontal Cells (HC), Bipolar Cells (BC) and Amacrine Cells (AC), which form the inner nuclear layer. Finally, the signal is processed in the Ganglion Cells (RGC) and is transmitted to the Optic Nerve (RNFL). On the right: Representation of human retina.*

There are many inherited and acquire diseases or disorders that may affect the retina, and the degenerative retinal diseases are one of the main causes of untreatable blindness. Common to all retinal degenerative diseases is the damage to photoreceptor cells of the retina, which malfunctions and cause the image that is received to be blurred, distorted or completely unseen. This is often a progressive disease in which the patient will suffer a continuous decline in vision. The most common diseases are Age-related Macular Degeneration (AMD) and Retinitis Pigmentosa (RP). Currently the only strategy that is applicable to different types of retinal degeneration and to advanced stages of the disease is an artificial retina, which are becoming an interesting field of research in biophysics and nanoparticle physics.

The retinal diseases affect the function of the photoreceptors but in most cases the inner nuclear layer and the ganglion cells survive in high percentages for longer time.

Therefore, retinal artificial devices must stimulate electronically the intact neurons of the retina and consist in a small photovoltaic system that converts directly the light pulses in electric current. The crucial component in such a type of prostheses is the optoelectronic layer that, when is excited by light, must produce a signal in the visual cortex; in this way the optoelectronic material can substitute the compromised photoreceptors. For this type of applications is required an extracellular electric stimulation, which consists in the polarization of the cells using a potential gradient created by electric currents in the inside of an extracellular matrix.

Chapter 2
Organic Semiconductors

2.1 Introduction to the organic semiconductor

Organic semiconductors are solids whose molecular backbone is made up of strong carbon-carbon covalent bonds, but they are soft materials with a high degree of mechanical conformability due to weak supramolecular interactions. Since they are based on carbon as the biological molecules, they are usually considered to be highly biocompatible [2]. The semiconducting proprieties origin from the nature of the carbon double bond: when a carbon atom forms a molecule its p and s atomic orbitals are very close in energy and can combine to create hybrid orbitals (fig 2.1). Each one of the orbitals contains an electron capable to form a covalent bond with an electron from another atom, forming the molecular orbitals. This hybridisation determines the shape of the organic molecule and its chemical-physics proprieties.

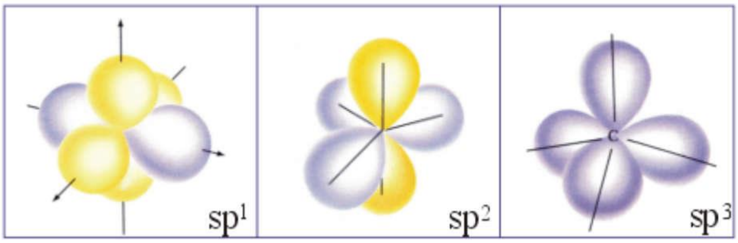


Figure 2.1: *Representation of the hydric orbital of the carbon atom, from left to right:* sp^1 *(combination of one s and one p orbital),* sp^2 *(combination of one s and two p orbitals) and* sp^3 *(one s and three p). [5]*

In a carbon double bond the non-hybrid p_z orbitals combine to form the bonding molecular orbital π and antibonding orbital π^*. Along a carbon-based molecular backbone of alternating double and single bonds, the π-orbitals form a delocalized state along which electrons are free to move. Instead, the sp hybrid orbitals (of any kind of the three types above described) form the bonding and antibonding molecular orbitals σ and σ^*. The delocalized π orbital is the highest occupied molecular orbital (HOMO), and the π^* orbital is the lowest unoccupied molecular orbital (LUMO) in such a molecular system. In organic semiconductor physics, the HOMO takes the role of the valence band while the LUMO serves as the conduction band. [3] The energy difference between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) represent the energy gap, which determinates the radiation able to give the molecular system enough energy for the excitation of an electron from the state HOMO to the state LUMO.

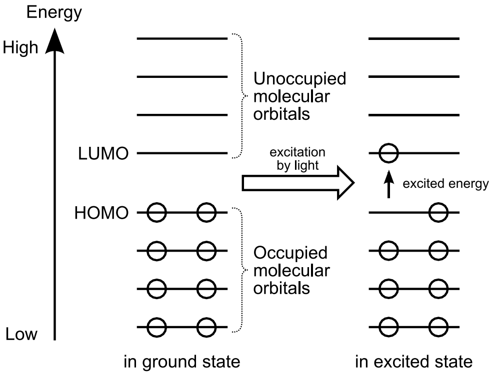


Figure 2.2*: Diagram of the HOMO and LUMO of a molecule. Each circle represents an electron in an orbital; when light of a high enough frequency is absorbed by an electron in the HOMO, it jumps to the LUMO. [4]*

The average lifetime of an excited states is very short in organic semiconductors, between femtoseconds and milliseconds [5] due to the strong coulomb interactions. Moreover, in the semiconductors the relative permittivity is lower than the in the inorganic semiconductors, so there is a greater attraction between the electron and the hole. This instable energetic situation relaxes very fast to a more stable state, called exciton, which is able to move within the molecular system. The excitons formed by absorption of a photon have a bond energy about a few hundred mV. If the exciton migrates to an interface of the semiconductor constituting a heterojunction it can be energetically favoured to dissociated into its constituting charges electron (negative) and hole (positive). The latter can be extracted by diffusion through the material towards two electrodes placed at the ends, so that a current can be generated. [5] This process is exploited in organic semiconductor-based heterojunctions.

2.2 Heterojunctions in organic semiconductors

In organic semiconductors a heterojunction is a p-n junction that forms an interface between two semiconductors with different energy levels. The "p" (positive) side contains a p-type semiconductor that is likely to have an excess of hole charges due to its high HOMO level. Instead the "n" (negative) side contains a n-type semiconductor with a low lying HOMO and LUMO that cause an excess of electrons.

Following classical semiconductor theory, in equilibrium conditions, in the semiconductors the concentrations of free holes in the valence band and of free electrons in the conduction band are respectively:

$$p = N_V e^{-\frac{(E_F - E_V)}{kT}}$$

$$n = N_C e^{-\frac{(E_C - E_F)}{kT}}$$

Where N indicates the number of charges and the subscripts F, V and C specify the Fermi level and the valence and conduction bands.

If the energy difference between the donator's HOMO and the acceptor's LUMO is higher than the bond energy of the exciton, the latter can be separated into a positive hole, placed into the HOMO of the donator, and an electron, placed into the acceptor's LUMO. For this transition to happen the exciton must be in proximity of the interface between donator and acceptor, in order to diffuse through the junction within its time life; otherwise recombination will take place. In figure 2.3 the principal phases of the process are shown; below the figure the process is described more in detail.

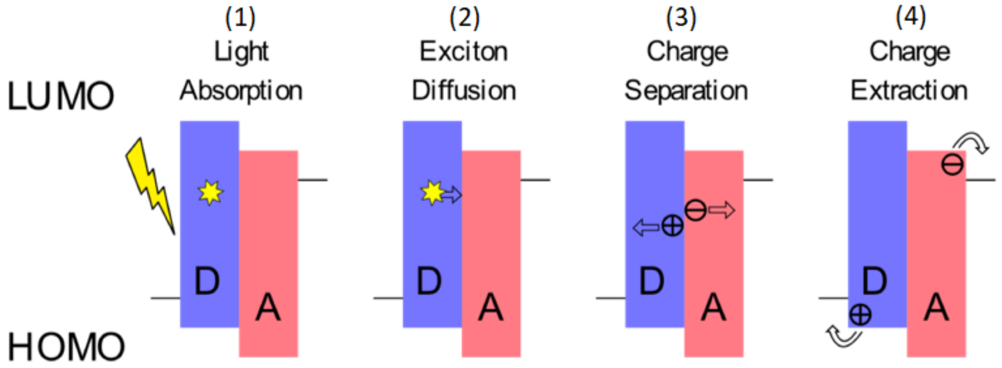


Figure 2.3: *Diagram that describes the fundamental passages to generate and extract mobile charges in an organic semiconductor heterojunction. The exciton created in the donor (1) diffuses through the interface (2), here there is a charge separation into electron and hole (3) and then the charges are extracted under the action of an external potential.*

Consider an incident light radiation: when a photon of energy $E = h\nu$ higher than the *bandgap* between donator and acceptor is absorbed, an electron jumps to an excited state. Quickly, the electron loses part of its energy because of the thermic and Colombian interactions with the hole, so an exciton is formed. The exciton consists of a couple electron-hole with a Columbian bond and is able to diffuse, so it may reach the interface between donator and acceptor. If this happens, the electron can reduce its energy arriving in the acceptor's LUMO, in such way a so-called *C-T State* (Charge Transfer State) is created and the exciton is separated into two mobile charges: free electron in Acceptor's LUMO and free hole in Donor's HOMO. With the application of an external potential the electron moves toward the cathode and the hole moves toward the anode so that a photocurrent is produced.

Therefore, at the previous analytical discussion we need to add a contribution due to the light stimulus at the initial concentration of electrons and holes. In fact, the Fermi level is shifted by an amount of Δ_{photo}, depending on the amount of hole and electronic charges

Δn, Δp created due to the stimulation. As a consequence, so-called quasi Fermi levels $E_{F,n}$ and $E_{F,p}$ are introduced.

$$n = n_0 + \Delta n = N_C e^{-(E_C - E_{F,n})/kT}$$

$$p = p_0 + \Delta p = N_V e^{-(E_{F,p} - E_V)/kT}$$

When the heterojunction is placed in contact with an electrolyte solution, a electrical double layer forms at the semiconductor-electrolyte interface. If the heterojunction is in contact with the electrolyte by the n-type conductor side, the double layer is composed by the photogenerated electrons of the n-type semiconductor and positive ions of the solution attracted by the photogenerated field. These two layers are separated by a layer of solvent molecules (in the case of an aqueous electrolyte they are polar water molecules) that act like a dielectric. Therefore, physically the region of the interface acts like a capacitor, because there are two layers of opposite charge separated by a dielectric with a thickness in the order of Ångström (corresponding to size of the molecules). The amount of electric charge stored in double-layer capacitor depends on the voltage difference between the heterojunction and the electrolyte. [10].

2.3 Organic heterojunctions for neurostimulation

The first kind of devices studied for artificial retinal devices is an array of photodiode as a substitute of the damaged photoreceptor [5]. At present, the range of available devices suitable to facilitate neuronal response under illumination is limited; silicon photodiodes, which interconvert optical and electrical pulses, are reasonable efficient and mature technology. These devices were extensively studied and some silicon-based devices for artificial retinal are in clinical trials or already in commerce. However, despite the advantages, the silicon-based devices present several limits. They necessitate passivation and encapsulation because are subject to corrosion in a physiological setting. These devices are hard and rigid and so not ideally suited to interface with soft and sensitive biological tissues. Moreover, the low silicon's absorbance coefficient requires a thickness to tens to hundreds of micrometres for efficient light absorption. [6]

Therefore, finding novel materials with better proprieties for optobioelectronics application was the focus of several recent studies. In such direction, organic semiconducting polymers are very promising and have shown the ability to photostimulate neurons [7] and explanted retinas [8,9].

The capacitive coupling is general considered the most safe and effective photostimulation mechanism. In fact, an electric stimulation of truly capacitive nature allows to avoid the unwanted redox effects that may causes degradation of the dispositive as well as irreversible damage to cells. So, the photosensitive systems for neuronal stimulation is a high conversion efficiency of a light into a capacitive displacement current sufficient for cell depolarization. To this requirement are added other important structural characteristics: biocompatibility, small dimensions, lightness, simple fabrication and wide scale reproduction.

The devices whose photocurrent spectrum has been studied in this thesis is the organic electrolyte photocapacitor. The device comprises a thin (80 nm) tri-layer of metal on which are deposed p-n semiconducting organic nanocrystals. A surrounding physiological electrolyte is in contact with both the bottom metal and the top of the p-n junction. When illuminated in such solution, the metal-semiconductor device acts like a photodiode and produces electrical double layers (Figure 2.4).

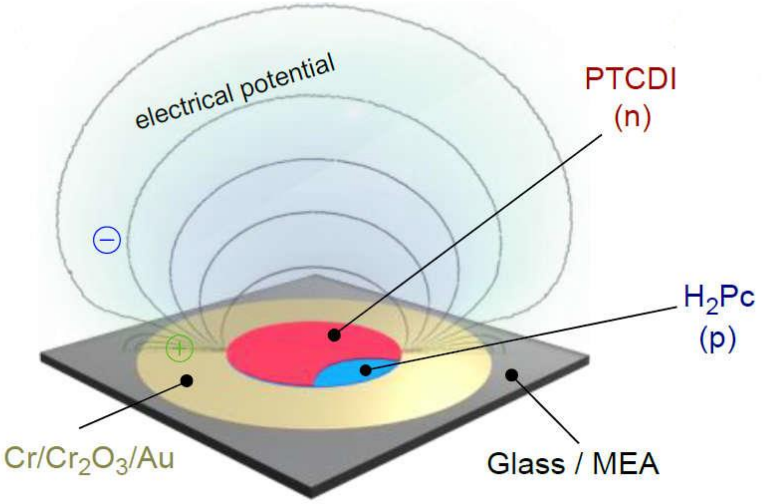


Figure 2.4: *Representation of the electrical potential generated by an organic photo capacitor device.*

The process at base of the functioning of the device is the one discussed in the previous section. Photogenerated excitons separate into free carries at the p-n interfaces, the holes are injected into the metal and form an electrical double-layer with the adjacent solution, the electrons accumulates in the n-type semiconducting layer and attract positive charges, so that a opposite charged double layer is formed at the semiconductor-liquid interface. The photovoltage so induced is the one that a cell in close contact with the photocapacitor will "feel", and in principle can be large enough to induce action potential generation via the capacitive coupling mechanism [5].

The photocapacitor should be integrated in Microelectrodes Arrays (MEAs) that allow both the photoexcitation and the registration of the neuronal and muscular cells.

Chapter 3
Experimental Apparatus

The experimental apparatus used for the photoelectrochemical measurements is composed of a lamp, a monochromator, the Photoelectrochemical cell (PEC), a data acquisition board, a computer and a potentiostat. The individual components are described in detail below.

3.1 Examined samples

The device examined in this thesis is the organic electrolytic capacitor, which is an efficient nanoscale semiconducting optoelectronic system optimized for neuronal stimulation. The device comprises a thin (80 nm) tri-layer of metal (Au or ITO, indium tin oxide) and p-n semiconducting organic nanocrystals. The most indicated photosensitive semiconductor p-n materials are hydrogen-bonded crystalline pigments, due to their favourable semiconducting proprieties combined with outstanding stability. In particular, after a research [5], the materials combination which emerged as most promising comprises a 30 nm layer of metal-free phthalocyanine (H_2Pc) and a 30 nm layer of N,N'-dimethyl perylene-3,4:9,10-tetracarboxylic diimide, PTCDI for short.

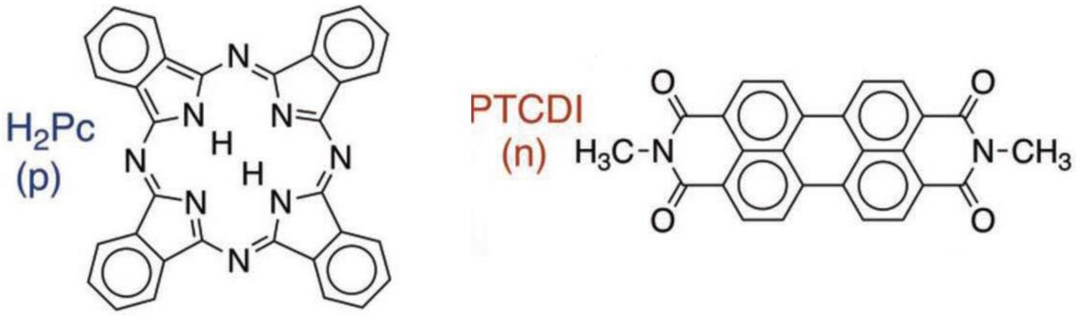


Figure 3.1: *Molecular structures of pigment semiconductors, on the left PTCDI and on the right* H_2Pc

The PTCDI functions as the n-type electron-acceptor, which attains a negatively charged surface upon illumination and is in contact with the saline solution, while the H_2Pc acts as the primary light-absorbing layer and p-type electron donor and is in contact with the metal back-contact. The choice was to fabricate a p-n junction, instead of n-p, as p-n gives a negative surface potential on the extremity in contact with the solution, thereby leading to a depolarization of the attached cell membrane.

From preliminary researches on the energetic levels it has emerged that the H_2Pc at the interfaces with ITO has a Fermi level almost corresponding to the HOMO, as typical for the p-type semiconductors. At the interface with the ITO the PTCDI has a Fermi level near the LUMO, this is due to the formation of intergap states and/or the doping in proximity of the ITO layer. In the double layer structure (ITO-H2PC-PTCDI), the Fermi level is placed nearly at the band-gap's centre, as expected for an intrinsic semiconductor material.

3.2 Photoelectric Cell (PEC)

The PEC is a 10x6x2 cm hollow parallelepiped made of plastic material. On one of the two major faces there is a quartz window, through which the light pulses reach the sample; the window is made of quartz instead of glass (or other materials) because the quartz provides a full transparency in all the spectrum from UV to almost IR (the transmission is more than 90% between 200 nm – 2.2 µm).
On the other major face the sample holder takes place, it is composed of two disks of the same plastic material which can be fixed to the cell, the sample under test is placed between the disks. On the external disk there is a small hole through which a contact linked to the sample may exit and then be connected to external appliances. On both disks there is an additional hole of diameter of 0.5 cm, which allows the light to reach the sample, so the light pulses can hit the sample both frontally and posteriorly. Inside the PEC there is an electrolytic solution of KCl 0.1 molar, the sample is in contact with this solution by the surface of the 0.5 diameter hole. The remain part of the sample's surface, and in particular the metal back-contact, are isolated from the solution by an o-ring made of PDMS (Polydimethylsiloxane, a silicon-based organic polymer, transparent and high hydrophobic). The Cell is closed by a lid that has three holes so the three electrodes used in the measurements (WE, RE, CE) can be inserted in the solution, the water tightness of the cell is ensured by several rubber seals between the plastic components.

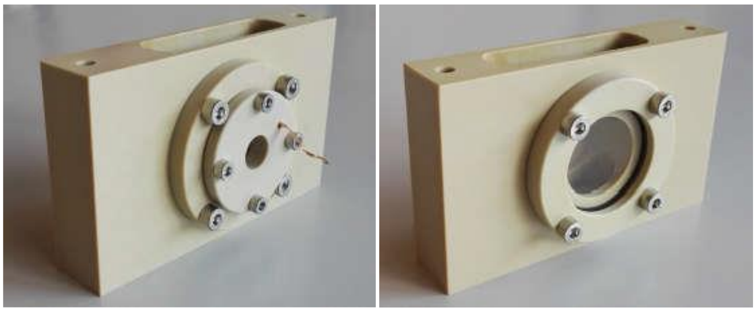


Figure 3.2: *PEC, on the left the face with the sample holder and the metal back-contact, on the right the face with the quartz window.*

3.3 Electrodes

The working electrode (WE) represents the photoanode which is under test, i.e. the sample of the ITO/p/n layer stack on which the measures are made, slide covered. The potential E applied to the WE is a relevant parameter for the study of the photoelectrode's properties; this potential should be measured in relation to a fixed reference potential, so that every variation of the potential will reflect an effective variation of the potential applied to the WE. The counter electrode (CE) cannot be taken as reference because the potential that forms at the interface between the CE and the electrolytic solution is unknown and it changes with the current circulating through the cell. In order to avoid this complication, the so-called reference electrode (RE) is used, in this way the WE potential can be measured in relation to a fixed potential (the one of the RE, through which the nominal current circulating is zero). The kind of RE used in the scope of this thesis is the electrode Ag/AgCl. The counter electrode is of platinum, which presents good catalytic properties and a high reaction rate, so that it doesn't compromise the cell's performances.

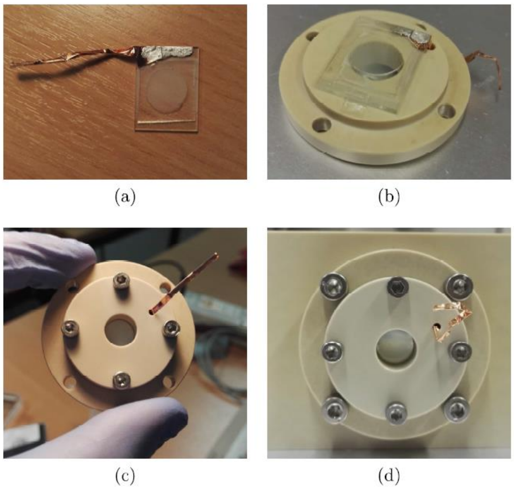

(a) (b)
(c) (d)

Figure 3.3: *Assembly sequence of the photoanode.*

3.4 Potentiostat

The potentiostat is one of the fundamental apparatus for the photoelectrochemical measurements, the one used in this work is the PGSTAT204 by Metrohm Autolab (fig 2.3 shows a simplified inner diagram). The potentiostat has always been used in the three-electrodes configuration, with the fourth optional electrode (S) connected directly to the WE. The final function of the potentiostat is quite simple: it measures the potential difference between the RE and the WE and maintain it equal to the desired value modifying the potential of the CE in relation to the one of the RE. In the three electrodes configuration the CE's potential is unknown, but this is not a problem since the only function of the CE is to provide voltage and current to keep the potential between WE and RE at a chosen value. During the measurements, therefore, this value is constantly controlled and eventually corrected by means of a feedback mechanism.

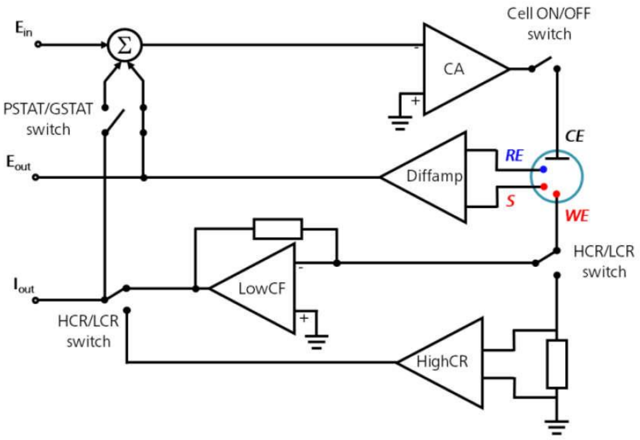


Figure 3.4: *Simplified scheme of the inner structure of a potentiostat..*

3.5 Lamp

The lamp used is XBO R 300W/60 C OFR by OSRAM. It is a Xe-lamp, during operation is connected to a recirculating cooling water system. The lamp's spectrum is shown in fig 2.4 and in the data analysis it has been used to normalize the produced photocurrent. The set up for this measure is the same as for the photocurrent measurements, but instead of the PEC I placed a Si photodiode (Hamamatsu - S2281 series) with a photosensitive area of 1 cm^2.

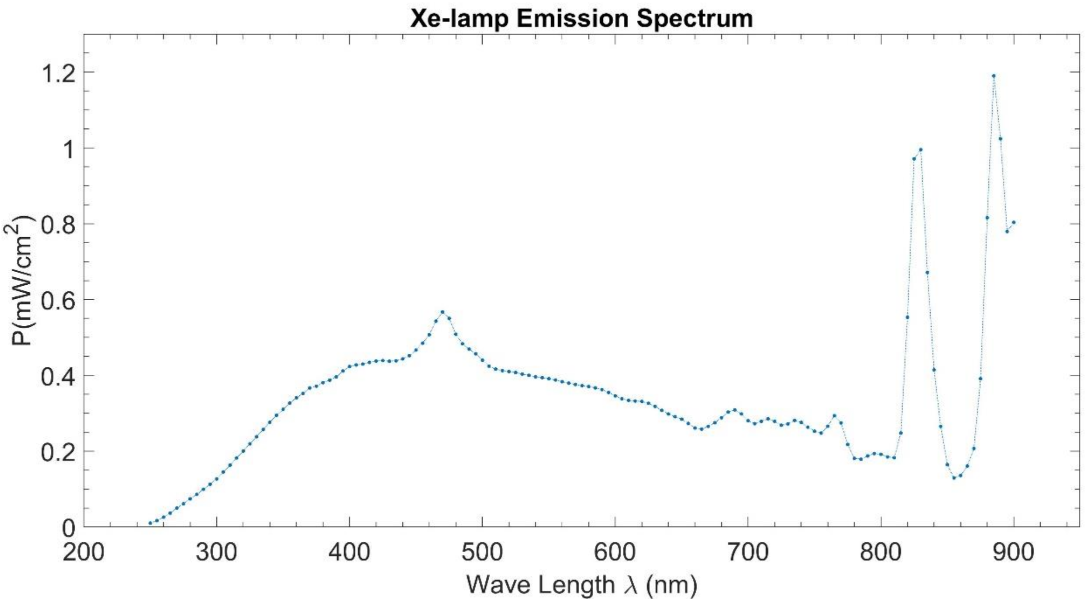


Figure 3.5 *Emission Spectrum of the Xe-lamp, which has been used to simulate the sunlight.*

3.6 Monochromator

The used monochromator is a Cornerstone 260 by Oriel Instruments, software controlled through the development environment LabView.

The monochromator separates the beam of white light coming from the lamp into components of various wavelengths, so that it is possible to analyse the behaviour of the photoanode in function of the incident wavelength. The monochromator uses a diffraction grating to spatially separate the colours of light and has a mechanism of mirrors for directing the selected colour to an exit slit. An inevitable consequence of the physics of the diffraction grating is the presence of second order harmonics (with half wavelength respect the fundamental harmonic), that overlap with the fundamental harmonic. The only way to resolve this problem is to use a long pass filter, which transmit light only above a certain wavelength (in this case the cut-off is 400 nm).

3.7 Photocurrent Measurements

A diagram of the experimental apparatus set up for the measure of photocurrent is shown in fig. 2.5. The semiconductor sample is back-lit: the radiation passes through the sample-holder's hole, glass, ITO and strikes the p-side of the junction (anyway several measurements has shown that this doesn't affect the results [4]). The working electrode is connected to the ITO back-contact of the sample by means of silver paste, while the counter and reference electrodes are inserted into the electrolytic solution. All the photocurrent measures are carried out with variation of the parameter *E*, which is the potential between WE and RE (set with potentiostat). The values of the potential *E* between the WE and the RE used in this thesis are (-0.15, -0.05, 0.00, 0.05, 0.15, 0.25, 0.35, 0.45) V.

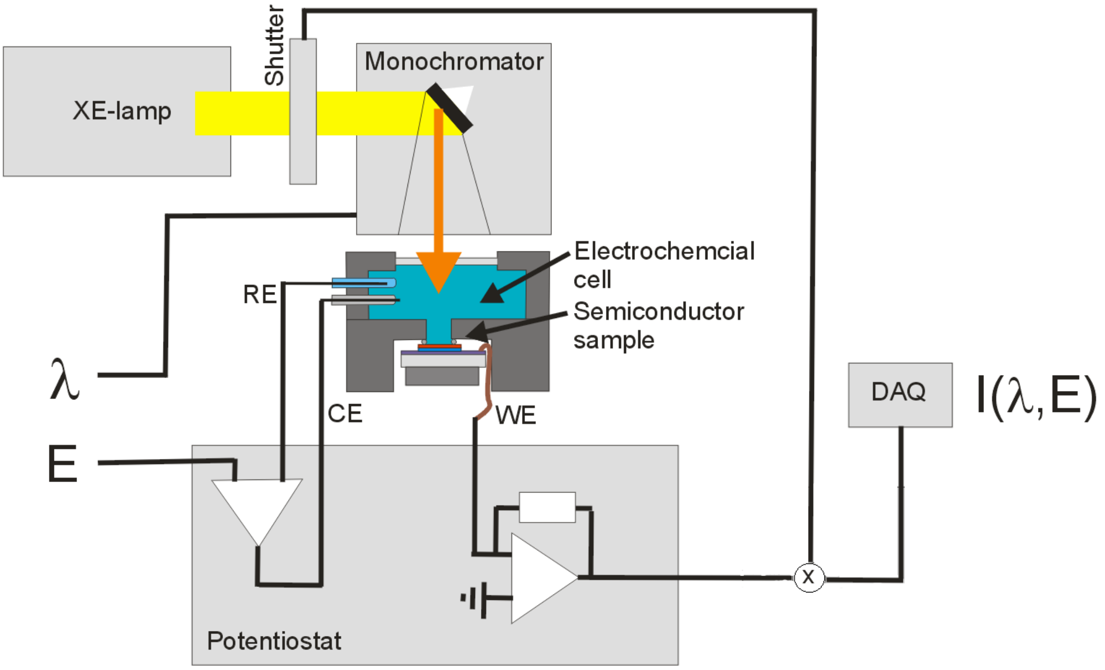


Figure 3.6: *Schematic diagram of the set-up of the experimental apparatus for the photocurrent measurements.*

Chapter 4
Data Analysis and Results

4.1 Experimental Transients of Photocurrent

The principal measurements made within this thesis are the one of photocurrent as a function of wavelength λ and potential applied to the sample E. The light pulse which strikes the photocapacitor surface is composed by several light-dark cycles, regulated by the shutter. In the light phase the charge density in the semiconductor varies and this causes a transient of electric field and an ionic current in the electrolyte until the charge neutrality is restored. Therefore, the photocurrent signal is a transient. Figure 4.1 shows the experimental photocurrent transients for a potential E between the photoanode and the reference electrode of 0.25V.

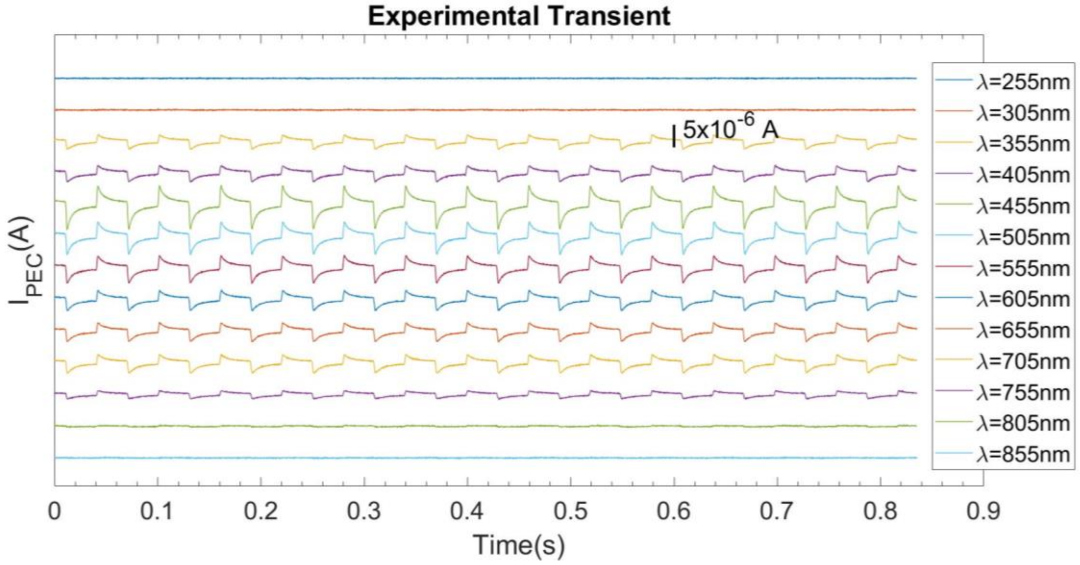


Figure 4.1: *Experimental transients for E=0.25 V. The transient of each wavelength has been shifted for more clarity, the scale bar represents a value of photocurrent of* $5x10^{-6}$ *A.*

The photocurrent spectrums have been normalized with the powerdensity of the lamp (whose spectrum is shown in fig 3.5) to eliminate eventual peaks due to the light incident spectrum. The normalized transient for a potential between WE and RE of 0.25V is shown in figure 4.2. The photocurrent is a function of the potential E and also of the incident wavelength.

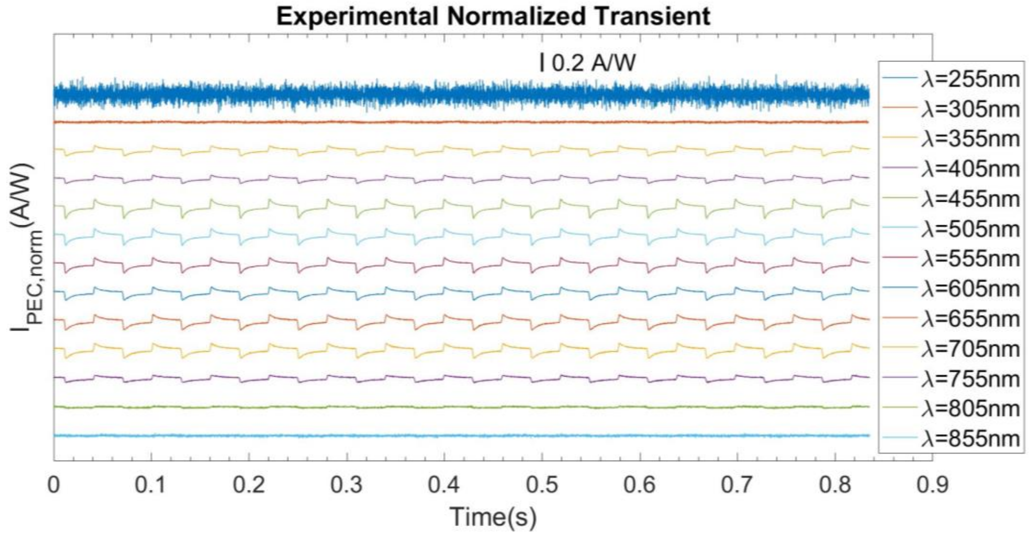


Figure 4.2: *Transients of Normalized Photocurrent, the transients have been shifted for more clarity, the scale bar represent a normalized photocurrent of 0.2 A/W. The potential value is 0.25 V.*

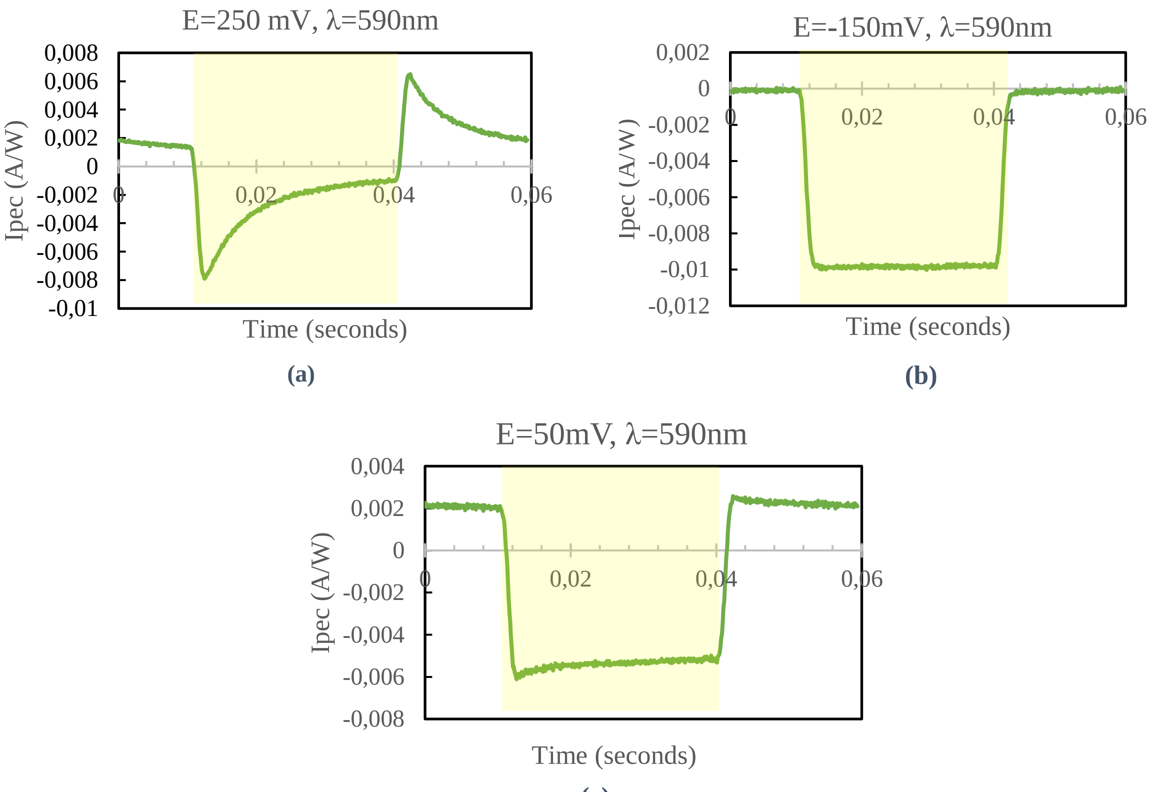
Confronting normalized and experimental transients for the same value of E, we can see that for wavelength in the UV (under 350 nm) the normalized photocurrent is almost completely composed by noise, that because the powerdensity of the lamp at these wavelengths is very low. The sample produces low photocurrents also for wavelength in the IR (infrared) part of the light spectrum (above 750 nm), that is caused by the fact that the phocapacitor has a low level of absorption for these wavelengths.

4.2 Photocurrent Spectra: Capacitive and Faradaic Current

The proprieties of the experimental photocurrent spectrums are analysed in the averaged and normalized transients, as shown for $E = 0.25\text{ V}, -0.15\text{ V}$ and 0.05 V in figure 4.3.

In the light phase the charge density in the semiconductor varies and this causes a transient of electric field and an ionic current in the electrolyte until the charge neutrality is restored. Therefore, the interface between the n part of the junction and the electrolytic solution has a capacitive behaviour and the photocurrent has generally a capacitive transient shape, as fig 4.3.a shows for a value of the parameter E of 0.25 mV.

However, for the negatives or near zero values of the potential the photocurrent is DC and the capacitive behaviour disappears, in some cases completely (figure 4.3.b). This fact is caused by an electrochemical current generated at the interface between the n layer and the electrolytic solution, the impact of this current increases with decreasing (more negative) values of the parameter *E*. This faradaic current is a consequence of the reactions that takes places between the chemical species of the electrolyte and the electrode (in this case the n layer of the semiconductor).



(a) **(b)**

(c)

Figure 4.3: *Averaged and Normalised Transient for a fixed wavelength 590nm, the yellow coloured area indicated the period of lighting conditions, for different values of the Potential applied to the photoelectrode (WE) respect to the RE: a) E=0.25V. b) E=-0.15V c) E=0.05V*

For negative values of the potential *E* there is an evident asymmetry between light conditions and darks conditions (figure 4.3.b), this fact indicates that the electrochemical current is present only in light conditions and the capacitive current is almost disappeared. Instead for positive values of the potential applied to the photoelectrode there is completely symmetry because the electrochemical current is negligible at these potential values and the spectrum is simply the transient of a capacitor (fig 4.3.a). For positive but near zero potential the current has a consistent amount of electrochemical nature, so the capacitive shape of the transient is almost loss, even if the spectrum is not totally DC (fig 4.3.c).

In conclusion, it is possible to separate two distinct contributions to the photocurrent: the one capacitive due to the n-electrolyte interface, and the faradaic one due to the electrochemical current. Both currents have been determined as a ratio between the amount of accumulated charge and the time interval.

The faradaic current has been calculated as the ratio between the amount of faradaic charge and half period:

$$I_{far} = \frac{Q_{far}}{T/2} \qquad (4.2.1)$$

$$Q_{far} = \frac{1}{2}\int_{t_1}^{t_2} I_{PEC}\, dt \qquad (4.2.2)$$

where t_1 indicates the time instant when start the light phase and t_2 indicates the last time instant of the dark phase, just before the next light phase begins.

The capacitive current has been calculated as the ratio between the capacitive charge accumulated in a single light-dark cycle and the characteristic time τ of the transient. Using a time-interval that is small with respect to τ, we approximate the current transient by the first term of a Taylor expansion. As the transient in capacitive current follows an exponential function:

$$I = I_{max}\, e^{-\frac{t-t_{max}}{\tau}} \qquad (4.2.3)$$

we obtain:

$$I = I_{max} + \frac{\partial I}{\partial t}\,(t - t_{max}) + \cdots \ \sim I_{max} - \frac{I_{max}}{\tau} \cdot (t - t_{max}) \qquad (4.2.4)$$

Performing a linear fit

$$I_{norm,avg}(t) = a \cdot (t - t_{max}) + b \qquad (4.2.5)$$

we calculate

$$\tau = -\frac{b}{a} \qquad (4.2.6)$$

No significant evidence for a dependency of τ on the wavelength was found, so I calculated τ as a mean value of different transients. Based on the standard deviation a statistical error has been assigned to τ. The capacitive charge has been determined as half of the integral of the absolute value of photocurrent about an individual light-dark cycles minus the faradaic contribution.

$$I_{cap} = \frac{Q_{cap}}{\tau} \qquad (4.2.7)$$

$$Q_{cap} = \frac{1}{2}\left(\int_{t_1}^{t_2} |I_{PEC}(t)| dt - Q_{far}\right) \qquad (4.2.8)$$

The capacitive and total photocurrent spectra are shown in figure 4.4 for some significant values of the applied potential E. The photocurrent spectra show that the capacitive behaviour of the photocapacitor disappears for potential values under 0.05 V, in this situation the photocurrent spectra is entirely faradaic. While for positive potentials, such as 0.25 V, the spectrum is entirely capacitive and there is not a faradaic current.

It is interesting to compare the photoelectric current spectra with the absorption spectra of the organic photocapacitor (fig 4.5). The photocurrent spectra correlate closely with optical absorbance of the p-n stack, of which reproduces most of the peaks. However, for the wavelengths in the ultraviolet region, the absorption spectrum is no longer related with the PEC spectra, this is due to the fact that the sample is back-lit and the light radiation passes through the glass slide before striking the sample. The glass is opaque to the UV radiation and filtrated it, so that the wavelengths under 400 nm does not strike the sample and the photocurrent produced is obviously zero, this reflects on the absorption spectrum of the photocapacitor.

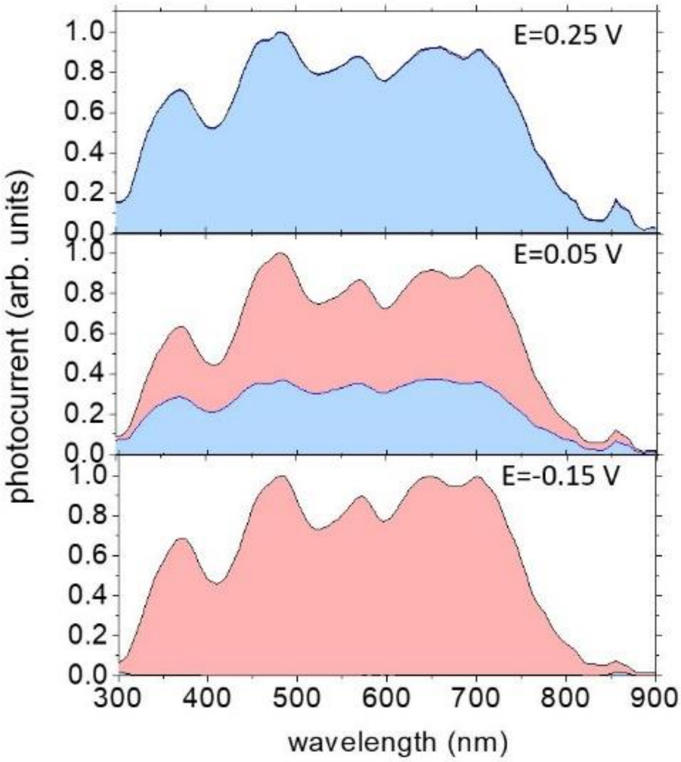


Figure 4.4: *Photocurrent spectra for different values of the potential between WE and RE, from up to down: 0.25V, 0.05V, -0.25V. The area coloured in red represents the faradaic contribution, while the blue area represents the capacitive contribution.*

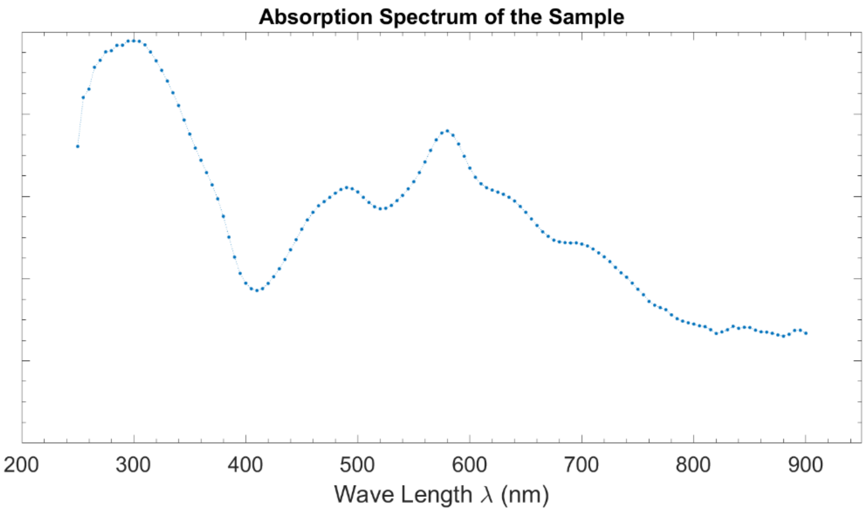


Figure 4.6: *Absorption Spectrum of the p-n stack. The region under 400 nm loses of meaning because of the presence of the glass lite.*

4.3 Quantification of the Capacitive vs Faradaic Current Ratio

The aim of this thesis is to provide a model of the quantification of faradaic versus capacitive current ratio and investigate eventual dependencies of this ratio from the potential E and the wavelength of the incident light. In order to numerically quantify this ratio, it has been defined a parameter, called α, that gives an indication of the amount of capacitive current respect with the total photocurrent for a certain value of the potential E and as a function of the wavelength. The parameter has been therefore defined as the ratio between the capacitive current and the total amount of photocurrent produced by the organic electrode:

$$\alpha\ (\lambda, E) = \frac{I_{cap}}{I_{cap}+I_{far}} \tag{4.3.1}$$

where I_{far} and I_{cap} are defined by the expressions (4.2.1) and (4.2.7) respectively.

From the above expression it is evident that the parameter α is dimensionless and can assume values from zero to the unity. A value of α about the unity means that the photocurrent transient has a completely capacitive shape and the electrochemical processes are negligible, while a value of α about zero means that the photocurrent transient is almost totally DC and many electrochemical processes occur. For the retinal prothesis applications it is required that the photocurrent has a capacitive behaviour, because in the extracellular matrix the electrochemical reactions may damage the biological tissues or corrode the device itself.

In fig 4.6 the parameter α is graphed versus the wavelength λ for different values of the potential applied to the organic photoelectrode respect to the reference electrode. The values of the parameter α for the potential E=0.45 V and E=0.35 V have not been graphed for clarity as they almost completely overlap to the graphic trend for the potential of 0.25V.

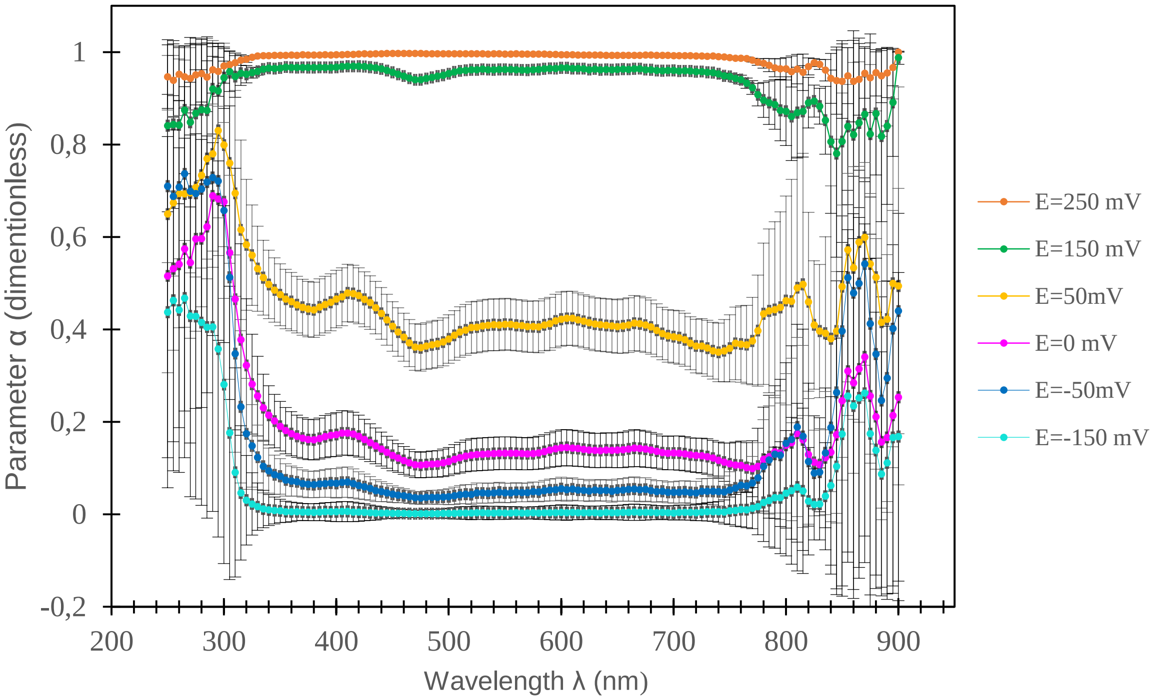


Figure 4.6 *Parameter that indicates the ratio between the capacitive current and the faradaic current versus the wavelength for various values of the potential applied to the photoelectrode, which are reported by the legend.*

The values of the parameter are consistent with the shape of the photocurrent transient, in fact, for positive values of the potential E applied to the photoelectrode the values are about the unity, which mean that the total current is nearly 100% capacitive and the electrochemical reactions between the electrons donator side of the organic photoelectrode and the electrolyte are very unlikely to occur. Instead, the value of the parameter is about zero for negative potential, in accordance with the fact that in this case the capacitive current produced by the photoelectrode almost disappears and the amount of faradaic current is significant, this indicates that a large number of oxidoreductions between the n side of the sample and the chemical species of the solution occur. For null or nearly null potential the parameter has an intermediate value, this means that the faradaic current is present but there is still a capacitive current that contributes to the total amount of current. For example, if the parameter is 0.2 the capacitive current represents the 20% of the total current.

From the above considerations is clear that the capacitive versus faradaic current ratio is highly dependent on the value of the potential E, so this parameter must necessarily be taken into account for the implementation of systems that involves this kind of organic photoelectrode. Instead, the graph of the parameter α versus the wavelength points out that the ratio between the capacitive and the electrochemical current hasn't a significant dependence on the wavelength.

Another relevant consideration to make is that error associated to the parameter α becomes enormous for wavelength in the ultraviolet region (under 350 nm) and in the infrared region (above 750 nm) of the light spectrum because the photocurrent produced is nearly null. Therefore, the parameter α looses its meaning in this regions, this can be caused by the fact that in these regions the intensity of the light is not sufficient high for the photocapacitor to produce a current, or by the fact that the sample does not absorb light radiation.

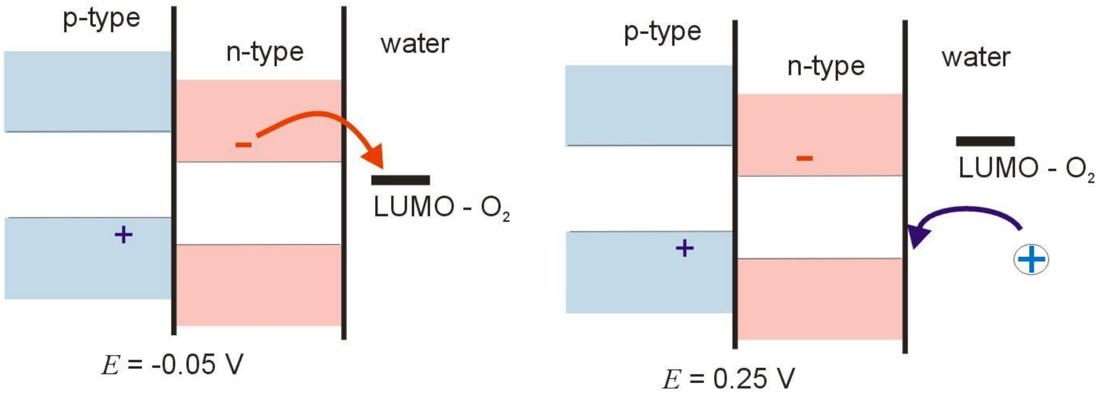
The error associated to the parameter α has been calculated by propagation. The error on the period T and on Q_{FAR} are negligible when compared to the error on Q_{CAP}. In fact, by integrating on the photocurrent's absolute value the electrical noise is not cancelled and, even though itself is small, when it is summed become larger and represent the error on such integral.

Conclusions

The purpose of the thesis was to understand the nature of the transients generated by an organic photocapacitor when illuminated in electrolytic solution and to provide a model for the characterization of the two kinds of processes that can occur at the semiconductor-electrolyte interface: a capacitive accumulation of charge on the junction and unidirectional faradaic processes which determinates the electrochemical transfer of negative charge from the donator layer of the heterojunction to the physiological solution.

From the analysis of the acquired photocurrent transient it emerged that the incident wavelength has not an impact of the nature of the processes at the interface, while the potential difference between the electrolyte and the pn junction is a fundamental parameter to consider during the realization of these devices. In fact, for potentials higher than 0.15 V the faradaic contribution is negligible and the photocurrent can be considered almost 100% capacitive. On the contrary, for negative potentials, the faradaic processes are favoured and constitutes the major contribution to the photoelectrical current. Therefore, for the use as artificial retinal prothesis the organic photocapacitor must have a potential difference between the electrolyte and the pn junction above than 0.15 V, because the products of oxidoreductions from faradaic processes can seriously damage the close biological tissues and cause the corrosion of the device.

The physical explanation of why positive or negative potential favourer one kind of process in preference of another is complex and is not in the framework of this thesis. However, it can be briefly discussed in qualitative mode, with the help of an energy level diagram.



The faradaic current is due to the transfer of an excited electron from the LUMO-level of the n-type semiconductor into the LUMO of an oxygen molecule, which is present in the aqueous electrolyte. As this transition can take place only if it is energetically favoured, it happens when the electron in the n-type is in a level of higher energy than the LUMO of the O_2. The application of a negative potential causes a raising of the energy levels in the p-n junction, so that the electron is favoured to jump to the LUMO of the O_2, whose energy level is unchanged. Instead, a positive potential lowers the pn-junction energy levels. In this situation the photogenerated field attracts further positive ions that accumulate in the double layer on photoelectrode interface until the photogenerated field is screened. The change in charge density of the double layer under illumination and its reconstitution in darkness give rise to the capacitive current.

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