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Photoelectrochemical characterization of Ta/Ta_2O_5/polypyrrole heterojunctions

V. FIGÀ*, F. DI QUARTO
Department of Chemical, Process and Materials Engineering, University of Palermo, Viale delle Scienze- Ed.6, 90128 Palermo, Italy

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A photodeposition of polypyrrole on anodic tantalum oxide thin films was performed in both organic and aqueous media. Pyrrole was photo-oxidised on insulating tantalum oxide by irradiating the electrode with light of suitable energy. Tantalum/ tantalum oxide/ polypyrrole heterojunctions were then characterized by means of photocurrent spectroscopy. The comparison between the photoelectrochemical response of the heterojunctions fabricated in organic and aqueous media, shows that the solvent used for the photodeposition of polypyrrole influences the location of the inversion potential. This result can be attributed to the different structure of polypyrrole films, which strongly depends on the medium used for the electropolymerization.

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1. Introduction

Organic heterojunctions are fundamental components of “plastic” electronics and optoelectronics devices such as organic solar cells [1-3], electrochromic displays, organic field effect transistors [4], organic light emitting diodes [5], electromagnetic interference shielding, etc. The interest in using conducting polymers is due to their properties such as: low cost, low weight, high chemical inertness, possibility to behave like metals, semiconductors or insulators just varying their oxidation state.

In our previous work [6], we showed that it is possible to fabricate a metal-oxide-(organic) semiconductor (MOS_{org}) structure, based on tantalum/ tantalum oxide/ polypyrrole. For the first time, a photoelectrochemical method was used for the deposition of a conducting polymer on an insulating substrate. The tantalum/ tantalum oxide/ polypyrrole heterojunction was synthesized in organic medium and characterized from the morphological point of view by means of scanning electron microscope (SEM).

In this paper, a detailed study of the photoelectrochemical response of tantalum/ tantalum oxide/ polypyrrole heterojunctions fabricated in both organic and aqueous solutions is reported. Through the interpretation of photocurrent spectra (I_{ph} vs λ) and photocharacteristics (I_{ph} vs U_E), the values of the energy gaps and the inversion potentials were estimated.

2. Experimental

Tantalum rods from Goodfellow Metals (Cambridge) were used for the experiments. The rods were sealed into Teflon cylinders with an epoxy resin, leaving a flat circular surface (0.07 cm^2) in contact with the electrolyte. Before each experiment, the metal surface underwent a mechanical treatment with abrasive paper (1200 grit) and alumina powder (1 μm) and an electrochemical treatment of electropolishing in HF and H_2SO_4 (10:120% vol) solution by applying 20 V between the working rotating Ta electrode and a DSA counter electrode for seven minutes. The angular velocity of the working tantalum electrode was of 900 rpm. The electropolished samples were then cleaned in sonicated distilled water. Tantalum was anodized potentiodynamically at 10 mVs^{-1} in 1N H_2SO_4. Pyrrole was distilled before use. The polymerization of pyrrole on tantalum oxide films was performed under N_2 pressure in both 0.1 M $LiClO_4$ acetonitrile (MeCN, 99.8 Sigma-Aldrich) solution and 0.1 M $LiClO_4$ aqueous solution (pH=1.7) with 0.4 M pyrrole concentration under irradiation (λ = 270 nm and photon flux ≈ 10^{15} cm^{-2}). The tantala/ polypyrrole/ electrolyte heterojunctions were investigated by photocurrent spectroscopy in 0.1 M $LiClO_4$ acetonitrile solution. The set up used for the photoelectrochemical investigation is the same used for the photodeposition and it is described below.

Light is generated by a 450W UV-vis xenon lamp (Xenonlampenversorgung Typ SVX 1450, Müller) coupled with a monochromator (Kratos) that allows to select a specific wavelength (λ) or to varying it with different scan rates. A series of lenses is used to address the light ray on the sample. As photocurrent is the difference between the total current and the dark current, a mechanical chopper (Model 650 Light Chopper Controller, EG&G Instruments) was used. It separates the dark current from the total current, with a frequency of 13 Hz. The photocurrent is detected by a two-phases lock in amplifier (Model 7260 DSP, EG&G Instruments) in connection with the mechanical chopper.

A three electrodes cell endowed with quartz windows was used in order to avoid the absorption of high energy photons (hν≥ 4 eV). An Ag/AgCl electrode and a platinum foil were employed as reference and counter electrodes respectively.

3. Results and discussion

3.1. Tantalum oxide growth

Anodic oxide films were grown potentiodynamically on electropolished tantalum electrode at a constant scan rate of 10 mVs^{-1} in 1N H_2SO_4 solution. The formation voltage was 8V. In Fig. 3.1 the anodization plot with the charge circulated during the film formation is shown.

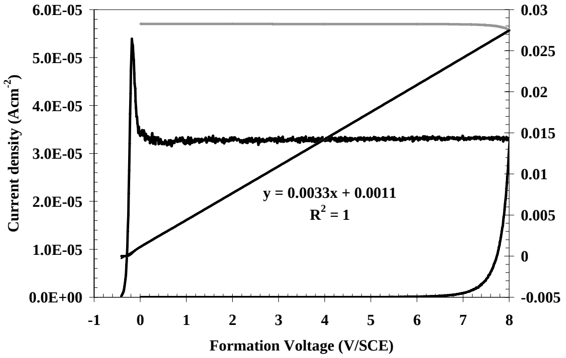

Fig. 1 Anodization plot for a 8 V tantala film grown in 1N H_2SO_4 at a scan rate potential of 10 mVs^{-1}. Black plot: current density vs potential; Grey plot: Charge vs potential with the equation of best fitting.

Current density reaches a maximum value in correspondence of the oxidation peak which is located at around -0.18 V/SCE. For more anodic values of potential, till the formation voltage, current density assumes a constant value of 3.3×10^{-5} Acm^{-2}. By inverting the potential scan direction, current abruptly decreases reaching a quasi-zero value as we expected from anodic films grown on valve metals. According to Faraday's law and by assuming: a molar weight of tantalum oxide PM= 422 gmol^{-1}, F= 96480 Cmol^{-1}, a density ρ= 7.93 gcm^{-3}, z = 10 for the reaction of tantalum pentoxide formation and on considering a circulated charge of 2.5×10^{-2} Ccm^{-2}, a thickness of 13.8 nm was estimated. In addiction an anodizing ratio around 18 ÅV^{-1} was calculated, in good agreement with other values reported in literature [7]. A unitary roughness factor was assumed for electropolished tantalum electrodes.

3.2. Photoelectrochemical Synthesis

Polypyrrole was photodeposited on 8V Ta_2O_5, grown in 1N H_2SO_4, in 0.1 M $LiClO_4$ aqueous solution (pH=1.7) and in 0.1 M $LiClO_4$ MeCN solution with a monomer concentration of 0.4 M. The electrode was irradiated with photons having a wavelength of 270 nm, which corresponds to the maximum of photocurrent of the anodic Ta_2O_5 spectrum. The separation of photogenerated electron-hole pairs was maintained by applying a potential of 3 V/(Ag/AgCl).

Fig. 3.2 shows the photocurrent vs time plot in the case of polypyrrole photodeposited on insulating Ta_2O_5 film, in aqueous solution. Photocurrent decreases with time and reaches a zero value when light is periodically switched off, indicating that the dark current contribution to the polymer deposition is negligible. So, the polymer can be considered entirely photodeposited.

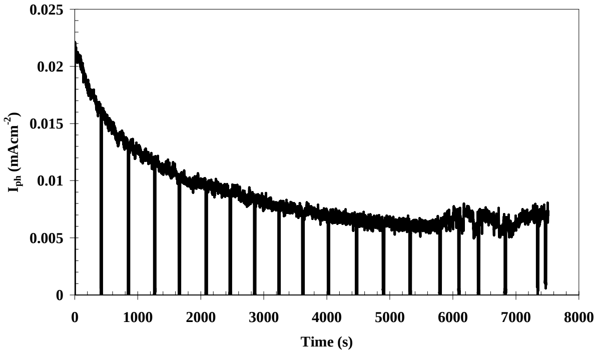

Fig. 2. Photocurrent (λ= 270 nm) vs time curve relating to a-Ta_2O_5 grown to 8V (SCE) in 1N H_2SO_4, recorded by polarizing the electrode at U_E= 3V (SCE) in N_2-saturated 0.1 M $LiClO_4$ (pH=1.7) solution containing 0.4 M of pyrrole. Q_{TOT}= 72 mCcm^{-2}

The charge circulated during the electrodeposition was 72 mCcm^{-2}. The optical properties of photodeposited PPy, in terms of absorption coefficient were studied by analizing the best fitting of $\mathrm{Ln}(I_{ph}/I_0)$ vs q_{ph} plots, according to the following equation:

$$I_{ph}(q_{ph}) = I_{ph}(0)\exp\left[\left(-2.5\times10^{-4}\right)\alpha_{PPy}q_{ph}\right] \quad (1)$$

where $I_{ph}(0)$ is the initial photocurrent, α_{PPy} in cm^{-1} is the light absorption coefficient of polypyrrole at the impinging wavelength, q_{ph} is the photocharge density in Ccm^{-2}, and 2.5×10^{-4} is the conversion factor in cm^3 C^{-1} as reported in Ref. [8]. Fig. 3.3 shows the best fitting plots of $\mathrm{Ln}(I_{ph}/I_0)$ vs q_{ph}.

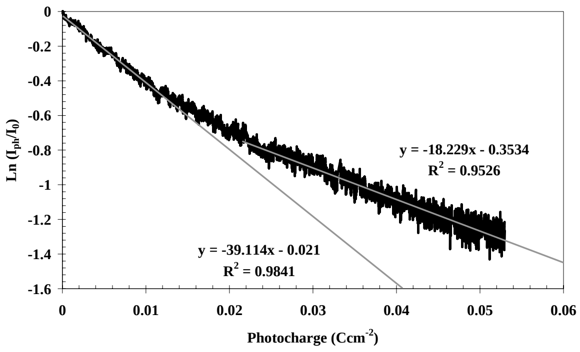

Fig. 3. Fitting of the logarithm of the photocurrent vs photocharge density in the case of polypyrrole photodeposited in 0.1 M LiClO$_4$ (pH=1.7) on 8V Ta$_2$O$_5$.

The differences in the straight lines slope can be attributed to the changing in optical properties of the electrodeposited polymer or to the changes in oxide/PPy reflectivity. The best fitting was obtained for q_{ph}>12 mCcm^{-2} and a α_{PPy}= 0.73×10^5 cm^{-1} was found. The same procedure was used for the photodeposition of polypyrrole on 8V Ta$_2$O$_5$ film in 0.1 M LiClO$_4$ MeCN solution. In this case, from the best fitting of the Ln (I_{ph}/I_0) vs q_{ph}, a value of 1.7×10^5 cm^{-1} was found. The difference between the values of α_{PPy} calculated at the same wavelength for the polymeric film photodeposited in water and in acetonitrile depends on the different morphologies and roughness of the two samples.

Fig. 3.4 shows a tantalum foil anodically oxidised at 8V with a polypyrrole layer on it. It is visible how polypyrrole grows just in that part of the electrode interacting with photons.

Fig. 4. Oxidized tantalum foil with photodeposited PPy. The polymer layer grows just in that part of the electrode interacting with photons.

3.3. Photocurrent Spectroscopy Investigation

The 8V Ta$_2$O$_5$/PPy(ClO$_4$) heterojunction grown in organic solution (8V Ta$_2$O$_5$/PPy(ClO$_4$)$_{ACN}$) (Q_{TOT}= 72 mCcm^{-2}) was characterized by means of photocurrent spectroscopy. Photocurrent spectra were recorded in the same solution of photodeposition. Both anodic and cathodic spectra were recorded. Fig. 3.5 shows the photocurrent spectrum recorded at 3V (Ag/AgCl). It presents a photocurrent peak at around 270 nm, which is the wavelength corresponding to the maximum of photocurrent of the tantalum oxide spectrum. So, under anodic polarization, the 8V Ta$_2$O$_5$/PPy(ClO$_4$) $_{ACN}$ heterojunction gives the same photoelectrochemical response of the substrate (8V Ta$_2$O$_5$) in the same electrolytic solution. This was confirmed by the elaboration of the photocurrent spectrum with the following equation.

$$\alpha(\nu) = \frac{A(h\nu - E_g)^n}{h\nu} \qquad (2)$$

where *α(ν)* is the absorption coefficient, A is a constant, *h* is Planck's constant, *ν* is the frequency of the incident light, E_g is the optical band gap value of the semiconductor and *n* is the power law coefficient. *n* assumes the values 0.5 and 2 for direct and indirect (or non-direct) optical transitions respectively.

Fig. 3.6 shows the best fitting of the spectrum recorded at 3V (Ag/AgCl) corrected for the efficiency of the system lamp-monochromator. Under the hypothesis of non-direct optical transitions (n=2), the best fitting of Eq. 3.2 gave an indirect bandgap of 3.96 eV, which is the bandgap of tantalum oxide in acetonitrile and lithium perchlorate.

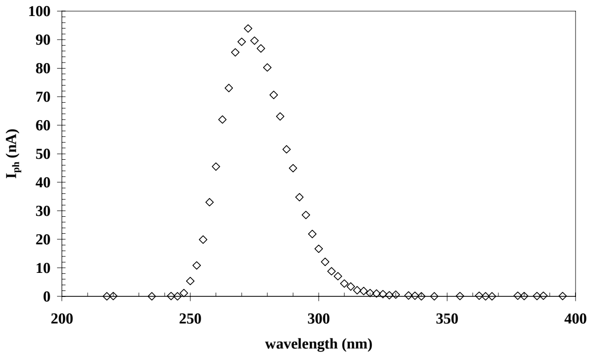

Fig. 5. 8V Ta$_2$O$_5$/PPy(ClO$_4$)$_{ACN}$ photocurrent spectrum recorded in acetonitrile and 0.1 M LiClO$_4$, by applying 3V (Ag/AgCl).

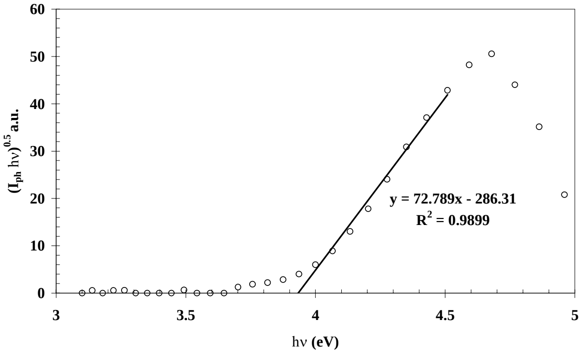

Fig. 6. 8V Ta$_2$O$_5$/PPy(ClO$_4$)$_{ACN}$ photocurrent spectrum recorded in acetonitrile and 0.1 M LiClO$_4$, by applying 3V (Ag/AgCl) fitted with Eq. 3.2 under the hypothesis of non-direct optical transitions.

The photoelectrochemical response of the insulating tantalum oxide suggests that the polymeric layer behaves like a metal or a strongly degenerate p-type semiconductor. In addiction to the photoelectrochemical process, i.e. the photogeneration of electron-hole pairs, also the doping of the polymer takes place; in fact, under anodic polarization, ClO_4^- anions migrate from the electrolytic solution towards the polymeric matrix increasing its electrical conductivity.

Fig. 7 shows a photocharacteristic (both photocurrent and phase angle vs potential) recorded at 270 nm starting from 3 V (Ag/AgCl) towards the cathodic direction, with a constant scan rate potential of 10 mVs^{-1}.

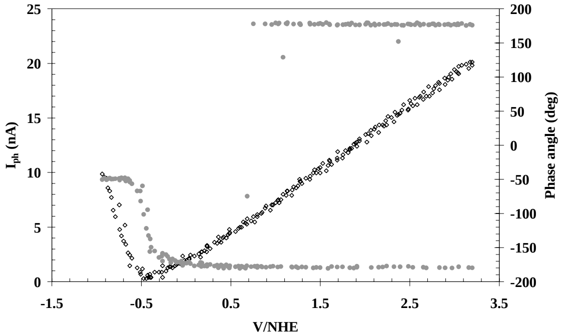

Fig. 7. 8V Ta_2O_5/PPy(ClO_4) $_{ACN}$ photocharacteristic recorded in acetonitrile and 0.1 M $LiClO_4$, at 270 nm with a scan rate potential of 10 mVs^{-1}. Black plot: Photocurrent vs potential; Grey plot: Phase angle vs potential.

Photocurrent decreases linearly with the applied electric field, reaching a zero value at -0.5 V/NHE. For more cathodic potentials, current increases again. The presence of a cathodic photocurrent is confirmed by the changing in photocurrent phase angle from -170° to -50°. The cathodic photocurrent comes from the photoelectrochemical response of the polymer. In fact, the flat band potential of Ta_2O_5 calculated in the same electrolytic solution is at around -1.1 V/NHE, while the flat band potential of polypyrrole is at around 0 V/NHE [9]. Fig. 3.8 shows a cathodic photocurrent spectrum recorded by polarizing the heterojunction at U_E=-1.8 V (Ag/AgCl).

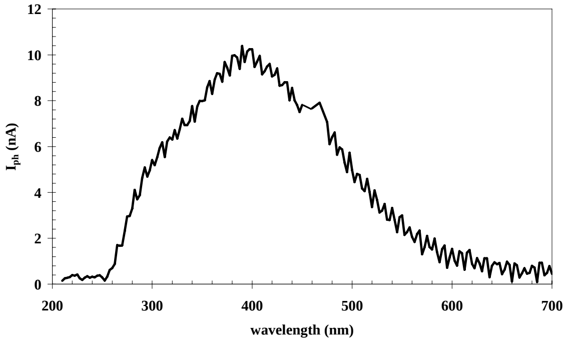

Fig. 3.8 8V Ta_2O_5/PPy(ClO_4)$_{ACN}$ photocurrent spectrum recorded in acetonitrile and 0.1 M $LiClO_4$, applying – 1.8V (Ag/AgCl).

Under cathodic polarization, the 8V Ta_2O_5/PPy(ClO_4)$_{ACN}$ heterojunction shows photoactivity also in the region of low energies (long wavelengths). The cathodic spectrum presents the photocurrent peak at around 380 nm. By fitting the low energies region of the corrected spectrum with Eq. 3.2, both direct and non-direct optical band gaps were estimated. Figures 3.9 and 3.10 display the best fitting of the spectrum at U_E=-1.8V (Ag/AgCl) in the case of direct and non-direct optical transitions.

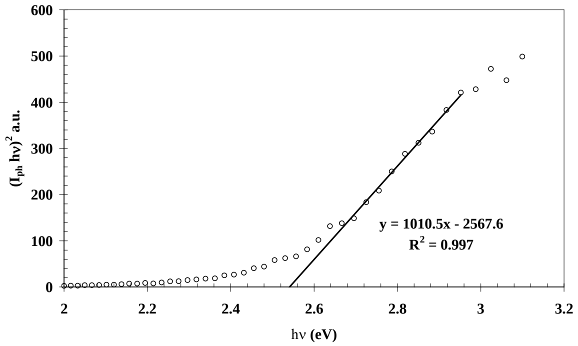

Fig. 9. 8V Ta_2O_5/PPy(ClO_4)$_{ACN}$ photocurrent spectrum recorded in acetonitrile and 0.1 M $LiClO_4$, applying - 1.8V (Ag/AgCl) fitted with Eq. 3.2 considering direct optical transitions.

A direct optical band gap of 2.54 eV was found by fitting Eq. 3.2 for n=0.5. This value is in good agreement with the direct optical band gap of polypyrrole reported in literature [9,10]. This value represents the distance in eV between the HOMO and LUMO; so the direct optical transitions are the transitions from the bonding, π, to the antibonding, π*, orbitals.

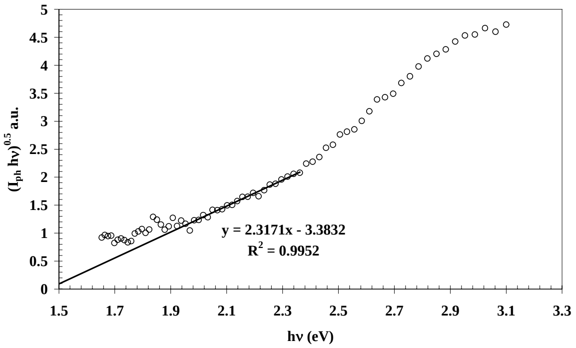

Fig. 10. 8V Ta_2O_5/PPy(ClO_4)$_{ACN}$ photocurrent spectrum recorded in acetonitrile and 0.1 M $LiClO_4$, applying - 1.8V (Ag/AgCl) fitted with Eq. 3.2 considering non-direct optical transitions.

A lower value of about 1.46 eV was found by fitting the experimental data with Eq. 3.2 for n=2. This value of non-direct band gap is due to the presence of an energetic level located in the energy gap which is 1.46 eV above the HOMO or below the LUMO. So this energy level can be polaronic or bipolaronic. Under cathodic polarization, the photoelectrochemical response is that of the polypyrrole layer which behaves like a p-type semiconductor. After recording the cathodic spectrum, photocharacteristics at different wavelengths were recorded from the cathodic to the anodic direction, with a scan rate potential of 10 mVs^{-1}.

Fig. 11 displays the superimposition of 8V $Ta_2O_5/PPy(ClO_4)_{ACN}$ photocharacteristics recorded in acetonitrile and 0.1 M lithium perchlorate at different wavelengths.

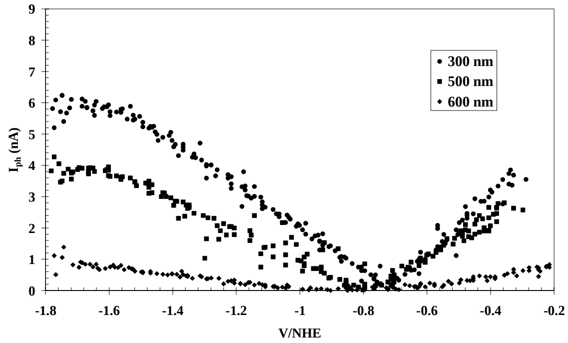

Fig. 11. Superimposition of 8V $Ta_2O_5/PPy(ClO_4)_{ACN}$ photocharacteristics recorded in acetonitrile and 0.1 M lithium perchlorate at different wavelengths, with a scan rate potential of 10 mVs^{-1}.

By moving from the cathodic to the anodic direction, photocurrent decreases reaching a zero value at around -0.72 V/NHE. For more anodic values, photocurrent increases. The presence of an anodic photocurrent is confirmed by the change in photocurrent phase angle. At the fixed wavelengths, the anodic photocurrent is due to the photoelectrochemical response of the polypyrrole layer.

The same photoelectrochemical measurements were carried out also for polypyrrole film photodeposited (Q_{TOT}= 72 mCcm^{-2}) on insulating 8V Ta_2O_5 in aqueous solution of lithium perchlorate (8V $Ta_2O_5/PPy(ClO_4)_{aq}$). The PCS characterization was performed in acetonitrile and lithium perchlorate. By applying the anodic potential of 3V (Ag/AgCl), the typical spectrum of tantalum oxide was recorded. By fitting the corrected spectrum with Eq. 3.2, under the hypothesis of non-direct optical transitions, an energy gap of 4.0 eV was estimated. It means that under anodic polarization, polypyrrole behaves as a metal or a strongly degenerate p-type semiconductor.

Fig. 12 shows the photocharacteristic (both photocurrent and phase angle vs potential) recorded at 270 nm starting from 3 V (Ag/AgCl) towards the cathodic direction, with a constant scan rate potential of 10 mVs^{-1}. Photocurrent decreases linearly with the applied electric field, reaching a zero value around -0.9 V/NHE. For more cathodic potentials, current increases again. The presence of a cathodic photocurrent is confirmed by the changing in photocurrent phase angle from 150° to -50°. Under a cathodic polarization of U_E=-2.0V (Ag/AgCl), the 8V $Ta_2O_5/PPy(ClO_4)_{aq}$ heterojunction shows photoactivity also in the region of low energies (long wavelengths).

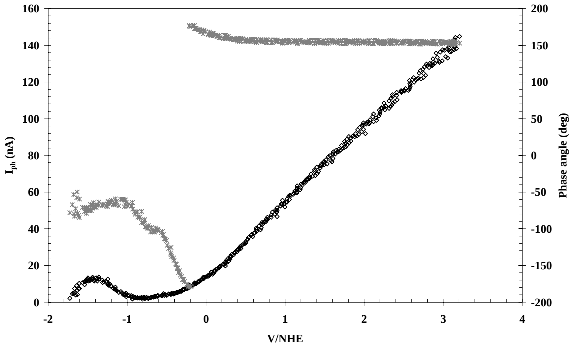

Fig. 3.12 8V $Ta_2O_5/PPy(ClO_4)_{aq}$ photocharacteristic recorded in acetonitrile and 0.1 M $LiClO_4$, at 270 nm with a scan rate potential of 10 mVs^{-1}. Black plot: Photocurrent vs potential; Grey plot: Phase angle vs potential.

The cathodic spectrum presents the photocurrent peak at around 380 nm. By fitting the low energies region of the corrected spectrum with Eq. 3.2, both direct and non-direct optical band gaps were estimated. A direct optical band gap of 2.47 eV was found by fitting Eq. 3.2 for n=0.5. This value is in good agreement with the direct optical band gap of polypyrrole reported in literature [9,10]. This value represents the distance in eV between the HOMO and LUMO; so the direct optical transitions are the transitions from the bonding, π, to the antibonding, π*, orbitals. This value is lower than the direct band gap of polypyrrole photodeposited on tantalum oxide in organic medium. This can depend on the different electronic properties of the polymeric films grown in different experimental conditions. A lower value of about 1.35 eV was found by fitting the experimental data with Eq. 3.2 for n=2. This value of non-direct band gap is due to the presence of an energetic level located in the energy gap which is 1.35 eV above the HOMO or below LUMO. Under cathodic polarization, the photoelectrochemical response is that of the polypyrrole layer which behaves like a p-type semiconductor. Photocurrent is due to the formation of an accumulation of electrons in the polymer/electrolyte interface that reduce a redox couple in solution. In the same time the de-doping of the polymer takes place.

After recording the cathodic spectrum, photocharacteristics at different wavelengths were recorded from the cathodic to the anodic direction, with a scan rate potential of 10 mVs^{-1}. Even in this case an inversion of photocurrent sign was observed. So, starting from the cathodic to the anodic direction, current decreases, reaches a zero value after which, it increases again. The photocharacteristics recorded at long wavelengths display an inversion potential at around -1.06 V/NHE.

4. Conclusions

A study of the photoelectrochemical response of Ta/Ta_2O_5/Polypyrrole heterojunctions fabricated in acetonitrile and water was performed. Both anodic and cathodic photocurrent spectra were recorded in organic solution of acetonitrile and lithium perchlorate, for the two heterojunctions. Independently from the solvent used for the photodeposition of polypyrrole on insulating tantalum oxide, under anodic polarization, polypyrrole behaves like a metal or a strongly degenerate p-type semiconductor. In fact, by applying a potential of 3 V(Ag/AgCl), the photoelectrochemical response gives the typical photocurrent spectrum of tantalum oxide ($E_g^{ind} \approx 4$ eV). So, under anodic polarization, the two heterojunctions work like Metal-Insulator-Metal (MIM) structures. By applying a potential of -1.8 V(Ag/AgCl), the photoelectrochemical response gives the typical photocurrent spectrum of the polymer, with a HOMO-LUMO gap of 2.5±0.3 eV. It indicates that under cathodic polarization, the polymeric layers behave like p-type semiconductors. So, the two heterojunctions work like Metal-Insulator-Semiconductor (MIS) structures.

From photocharacteristics recorded at long wavelengths from the cathodic to the anodic directions, an inversion of photocurrent sign was observed. As at long wavelengths Ta_2O_5 is not photoactive, the anodic photocurrent can only come from the photogenerated holes inside the polymer, which oxidise a redox couple in solution. The presence of both cathodic and anodic photocurrents, at these wavelengths, suggests that the polymer is sufficiently reduced to behave like an insulator. These results are in agreement with literature about the behaviour of oxidised and reduced polypyrrole.

The difference in the photoelectrochemical response of the two hetrojunctions, fabricated in different solvents, regards the inversion potential at 270 nm, value of wavelength in correspondence of which, both the tantalum oxide and polypyrrole are photoactive. In the case of polypyrrole photodeposited in acetonitrile, the inversion potential is located at -0.5 V/NHE. This value is more anodic than the flat band potential (≈-1.1 V/NHE) of tantalum oxide in the same electrolytic solution. It means that the cathodic photocurrent comes from the photoelectrochemical response of the polymer, whose flat band potential is located at 0 V/NHE [9].

In the case of polypyrrole photodeposited in water, the inversion potential is located at around -0.9 V/NHE. This value is close to the flat band of the tantalum oxide. This result suggests that, in this case, the cathodic photocurrent is due to the photogenerated electrons in the anodic tantalum oxide.

An explanation to the different values of the inversion potential of the heterojunctions fabricated in acetonitrile and water, can be found in the different morphologies of the polymeric layer. Polypyrrole electrodeposited in organic solvents displays a very compact structure compared to the morphology of polypyrrole electrodeposited in aqueous solution [11]. So, the porous structure of polypyrrole electrodeposited in aqueous solution allows photons to interact with the insulating Ta_2O_5 substrate which, under cathodic polarization, displays cathodic photocurrent.

Other investigations are in press in order to model the band structure of these heterojunctions.

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[*] Corresponding author: viviana_fg@yahoo.it