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Letter

Hysteresis-type current–voltage characteristics in Au/eumelanin/ITO/glass structure: Towards melanin based memory devices

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ABSTRACT

Hysteresis behaviour of the current–voltage characteristics collected on spin coated synthetic eumelanin layer embedded in the Au/eumelanin/ITO/glass structure is shown. The effect has been observed under dark both in air and vacuum environment and its magnitude has been found related to the eumelanin hydration state. Moreover, in vacuum and under white light illumination, enhancement of the hysteresis loop area respect to those collected under dark has been observed. Space charge storage and charge trapping/detrapping as possible mechanisms responsible of the observed current–voltage behaviour are discussed. Preliminary experimental results have evidenced the possible integration of eumelanin layers in electro-optical charge storage based memory devices.

1. Introduction

Eumelanins are ubiquitous pigments present throughout nature responsible for the color of hair, skin and eyes ranging from red, yellow, brown to black. It is ascertained worldwide that eumelanins exert several functions such as photoprotection, photosensitization, antibiotic activity and thermal regulation. A pioneering work by Mc Ginnes et al. disclosed that eumelanin electrical properties are similar to those of amorphous semiconductors and envisaged its possible implementation as active material in switching devices [1]. Following this original hint, a great deal of work is currently in progress in order to investigate the various optoelectronic properties and possible technological applications of eumelanins. Most research efforts mainly concerned the investigation on synthetic eumelanin powders or pellets: absorption coefficient, dark electrical conductivity, photoconductivity and ac response were explored [2–9] but all of them under the picture of eumelanin as an amorphous semiconductor. However, its broadband absorption that does not strictly follow a Tauc law [5,6,10] pointed out also that the picture of eumelanin as an amorphous structure has to be taken with care [11–13] and the chemical disorder model has been invoked to explain the α vs λ behaviour [3]. The eumelanin conductivity is furthermore strongly related to the hydration state and external environment and can lowers several order of magnitude when water is desorbed [8,9]. The dependence of conductivity on the humidity degree stems in the presence of two forms of water bonded to the macromolecules: one adsorbed on the surface and easily removable under vacuum or by drying, and the other incorporated in the inner polymer

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structure. In the last case the removal can require thermal treatments. The presence of these two kind of water bonding has been assessed by several studies and mainly on pellets [[8,9] and Ref. therein]. Specifically, in air water bridges and/or hydrogen bonds between individual molecules and carboxy, hydroxyl and amino groups are present but, during dynamic vacuum treatment, weakening or partial breaking of hydrogen bonds between planar layer occurs influencing (i.e. lowering) then the conductivity. The residual conductivity is then due to the remaining strong bonded water. Eumelanin is nowadays recognized as primarily formed by various combinations, still unknown at this stage, of 5,6-dihydroxyindole (DHI or HQ) and 5,6-dihydroxyindole-carboxylic acid (DHICA) and their corresponding redox forms.

One of major drawbacks in the application of melanin as active material in electronic devices is represented by its scarce solubility in common solvents, preventing easy deposition of homogeneous layers. As a consequence, in recent years, the focus is on eumelanin layer deposition on various substrates in order to better study electrical properties aiming to foresee a possible integration of this intriguing material in hybrid optoelectronic devices [2,14]. To date, eumelanin layer has been electrochemically deposited on gold, or spin coated and/or spray coated on quartz substrates [2,14,15].

To the best of our knowledge, no paper has been published so far concerning the study of the electrical properties of eumelanin layers on ITO/glass substrates. While, in our opinion this approach is a priority in the view of technological applications. It is well known, in fact, that ITO/glass is a widely used conductive support for organic semiconductors, and the feasibility of building up such a eumelanin/ITO junction, opens the possibility to witness the intriguing electrical properties of eumelanin and to compare its behaviour with that of the widely studied layer of organic molecular or polymeric semiconductors.

Up to now the electrical characterization of eumelanin layers have been interpreted under the picture of melanin as an amorphous semiconductor [14]. However, it was stated that in order to perform conductivity measurements on melanin under stationary conditions, the current should be collected after a certain time interval thus evidencing the presence of transient phenomena which cannot be overcome in any way [14]. However, such effects can be useful to shed light on the nature of a carrier (electron or hole) dominating the transport which is still an open issue. As a matter of fact, current relaxation phenomena have been well known and studied in several organic Au/polymers/ITO/glass interfaces and ascribed to space charge storage or to trapping/detrapping mechanisms under voltage application. Based on these phenomena, a possible integration of these materials in memory devices has been foreseen [16–18]. The experimental evidence of space charge storage or charge trapping effect is the hysteresis-type behaviour of current–voltage (I vs V) characteristics [16,17]. This communication shows for the first time similar hysteresis behaviour in I vs V characteristics observed in Au/eumelanin/ITO/glass interfaces and a first insight on the mechanisms responsible of this behaviour will be discussed.

2. Materials and methods

Eumelanin layers have been spin coated on ITO/glass substrates starting from synthetic melanin powder (140 mg, Sigma–Aldrich) dissolved in water (1 mL) and 28% aq. ammonia solution (2 mL). The solution was stirred and sonicated for 1 h, and subsequently centrifuged at 3500 rpm for 15 min. Before layer deposition, ITO/glass substrates were submitted to an oxygen plasma treatment (30 min, room temperature), in order to improve the adhesion of organic layers onto ITO/glass substrates [19].

AFM measurements were performed in air, in the weak repulsive regime of contact mode. Gold coated Si_3N_4 cantilevers with a force constant of 0.05 N/m and a statistical apical radius of 5–20 nm were used. Constant force images were acquired with a scan rate of 3.0–4.0 s/row.

The optical absorption spectrum has been calculated following the Ritter–Weiser expression on reflectance (R) and transmittance spectra (T) collected in air in the wavelength range $\lambda = 400$–800 nm by using a Perkin–Elmer Lambda 9 spectrophotometer [20]. The chosen wavelength range was dictated by the glass absorption at $\lambda < 330$ nm and high ITO reflectance at $\lambda = 800$ nm. Moreover, T and R spectra were collected from both the film and substrate side to estimate the film roughness and scattering effects on the absorption [21]. The film thickness was estimated from reflectance interference fringes.

Current–voltage (I vs V) characteristics have been performed on Au/eumelanin/ITO/glass structure at room temperature by using an electrometer and a power supply. For these measurements an Au slab ($0.25 * 0.25$ cm^2) has been gently placed on top of the melanin layer in order to avoid possible macromolecule modification induced by metal evaporation contacting procedure. The I vs V loops have been collected in air and in vacuum ($p = 10^{-5}$ mbar), and waiting several minutes between consecutive sweeps, under dark and white light irradiation at different voltage sweep speed starting from zero bias to a maximum positive value $+V_L$, and then alternating back and forth between $+V_L$ and $-V_L$. A halogen lamp simulating the solar spectrum at a power of AM 1.5 (100 mW/cm^2) was used for white light irradiation.

3. Results and discussion

The optical absorption spectra (Fig. 1(a)) display the characteristic broadband absorption observed in spin coated 400 nm thick eumelanin layer on quartz [2,3,7]. The α values have been found varying between 5×10^5 m^{-1} and 3×10^6 m^{-1} in the wavelength range $\lambda = 400$–800 nm, thus confirming the good film density. Also the calculated surface roughness (10 nm) agrees with values observed by AFM measurements. The estimate of the scattering coefficient was around 2–3% in the range 400–700 nm, i.e. <6% in the overall λ range, so that scattering has practically no influence in determining the layer broadband absorption [22]. AFM acquisitions (see Fig. 1(b and c) and inset herein) show that the surface of eumelanin layer is homogeneous, with a RMS roughness [23] of about 7 nm estimated over the entire area imaged in