



Optical and electrical behavior of synthetic melanin thin films spray-coated

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Abstract

We investigated the optical and the electrical conductivity properties of synthetic melanin thin films spray-coated on glass. These films showed a broadband monotonic increase of the absorption coefficient, decreasing the wavelength in the Visible-NIR range. Conductivity as a function of the temperature evidenced a semiconductor like character and a hysteretic behaviour after thermal annealing up to 475 K. Thermal activation energies extrapolated by resistance curves have been explained by using the framework of a band-model as for an amorphous semiconductor.

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Organic semiconductor; synthetic melanin; thin film; absorbance; transport properties.

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1. Introduction

Physical and biochemical properties of synthetic melanins have been attracting great interest in the field of condensed matter physics due to the possibility to combine the amorphous semiconductor properties [1, 2], with the broadband monotonic absorption of melanins, from UV to NIR [2], together with the conversion of photons into phonons for the energy dissipation [3]. Synthetic melanin thin films represent the milestone of different device configurations, such as chemi-sensors, next generation solar cells, and a range of other detectors. Melanin thin films also possess a number of physical properties that make them highly attractive for use in organic bioelectronic devices. The potential also exists to use melanin films as an effective radiation sensitizer that could greatly improve the spectral range and efficiency of superconducting transition-edge bolometers [4].

Recently, few researchers have proposed to modify thiol-capped gold nanoparticles with iron-melanin in order to combine magnetic properties and biocompatibility [5]. The preparation of metallic nanoparticles modified with organic, bioorganic or oxide coatings is appealing because of their wide range for potential biological and technological applications in the emerging fields of nanoscience and nanotechnology.

In this context, the development of new strategies capable to functionalize nanoparticles with complex molecular systems by using simple and inexpensive methods is a frontier topic that deserves special attention.

However, despite many theoretical and experimental efforts, the basic structure of the synthetic melanin remains unknown [2], preventing to tailor its structure, and then the improvement of both optical and electrical properties, potentially useful for sensing applications.

The deposition of continuous thin films of synthetic melanin could represent an overcoming of these hurdles, since a wide range of fundamental characterization techniques that are widely used in the field of organic electronics could be employed. Thin films are suitable for detailed electrical characterization, for carrier-type and mobility measurements through time-of-flight and related techniques and for probing by condensed-phase optical spectroscopy.

In this work, we report on optical absorption and electrical conductivity behaviour of synthetic melanin thin films sprayed on heated substrates. By using this technique, we were able to deposit thin films in a controllable and reproducible way. The investigated properties have been correlated to a band-model for an amorphous semiconductor.

2. Experimental details

The solution used in this work was prepared by dissolving melanin powders (M8631 synthetic melanin from Sigma-Aldrich), in a dimethylsulfoxide–methanol mixture (DMSO / CH₃OH; ratio_{v/v} = 1:20) to a final concentration of 0.2 mg/ml.

Thin films of synthetic melanin were deposited by using a spraying evaporator, which allows the fine dosage of the melanin solution sprayed on the glass substrate (Corning Glass 7059) heated at 373 K. The synthetic melanin solution flux were assisted at the evaporator orifice by an out-flowing air breath at a pressure of 6 Pa.

By applying the above mentioned conditions of deposition, we have deposited two samples with thickness of about 100 nm (sample A) and about 800 nm (sample B).

The film thickness, d , of the samples was measured by using a Taly step profilometer (Tencor Alpha step-300), with a vertical resolution of 2.5 nm.

Optical absorption measurements, ranging from 300 nm to 700 nm and normalized to the contribution of the glass substrate, were carried out by a Cary UV-Vis spectrophotometer (mod. 1E), at room temperature. For the electrical characterization, gold contacts were thermally evaporated on glass substrate, prior to melanin film deposition. Gold wires were electrically connected to the grid by silver paint to extract the electrical signals from the samples. Film resistance was investigated in vacuum ($\sim 10^{-3}$ Pa) and in dark conditions as a function of the temperature in the range 310 K – 475 K. The measurement was carried out by a Keithley mod. 617 electrometer, in the V/I mode, applying a constant voltage of 50 V.

3. Results and Discussion

Synthetic melanin thin films present a uniform coverage of the substrate together with a good mechanical adhesion. This result agrees with the experiments carried out by da Silva et al., who demonstrated the strongly improved adherence of synthetic melanin thin films based on DMSO solutions evaporated by casting to Si substrates [6].

However, we point out that samples obtained by casting or spin-coating often present an inhomogeneous distribution of the material on the substrate. This effect does not allow a good control of the film thickness, d , and the reproducibility of the deposition parameters, and it affects both the chemical and the physical properties of the films [7].

Detailed morphological results carried out on samples A and B evidenced a relatively flat (root-mean-square RMS roughness of about 0.41 nm) and homogeneous surface without voids or cracks, which typically appear when synthetic melanin thin films are deposited by simple casting and spin-coating [8].

Figure 1 shows the absorption coefficient, α , of samples A and B. Both films present a monotonic increase of α with the decreasing of the wavelength in the whole range of investigation, with an overlapping of the α values below about 650 nm. A slight difference is observed above 650 nm, suggesting a lower optical density in the thinner film. This fact could be related to a more defected film structure with the presence of small voids due to the solvent drops evaporation. This effect is expected to be more evident reducing the film thickness [8].

However, it is worthwhile to note that even the thinner film (sample A) shows a reduced absorption in the NIR region, its light harvesting in the Visible region make synthetic melanin thin films possible candidates for photovoltaic applications.

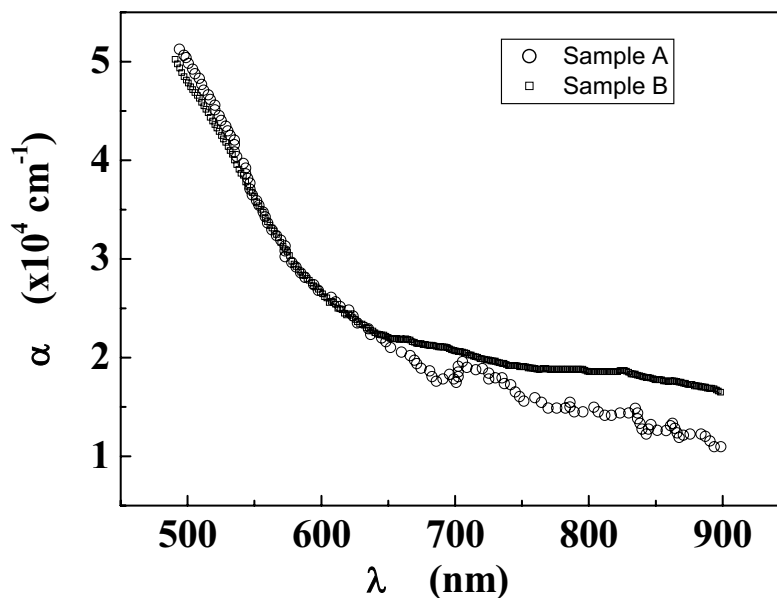


Figure 1: Absorption coefficient as a function of wavelength of the samples A and B.

However, it is worthwhile to note that both samples shows an absorbance tail, up to higher λ values, indicating a possible residual absorption in the NIR optical region, of interest for quantum information applications. Optical absorption features have been reported up to 1600 nm [8]. This last value is well beyond the telecommunication wavelength bands (ranging from 1310 nm to 1550 nm), where optical losses in optical fibers are small.

The strong broadband monotonic light absorption is characteristic of both natural and synthetic melanins in condensed and solution phases, and seems to be more characteristic of an inorganic semiconductor than an organic one [2, 9].

This melanin-typical optical feature can be explained invoking both heteropolymer and stacked oligomer models [2]. In both models, synthetic melanin is formed by the aggregation of monomer units such as 5,6-dihydroxyindolquinone (DHI), hydroquinone (HQ), redox forms of indolequinone (IQ), tautomers quinone-methide (QI1) and quinone-imine (QI2) and 5,6 dihydroxyindole 2-carboxylic acid (DHICA).

Any individual monomer block produces a typical sharp feature when lighted in the UV-visible range. First-principles quantum mechanical calculations inside density functional theory have shown that an average of the absorption spectra obtained by randomly stacked monomers produce a large feature-less spectrum without sharp structures [10]. In other words, typical monomers features are eliminated when the average is taken, and a monotonic smooth absorption spectrum forms, in agreement with the experimental results shown in figure 1.

X-ray photoelectron spectroscopy suggested that the contribution of 5,6-dihydroxyindole-2-carboxylic acid (DHICA) subunit to the oligomeric secondary structure of the molecule is about 35 percent. The latter result is essential for establishing a reliable model for the unknown secondary structure of the macromolecule [8].

Electrical properties of synthetic melanin films have been investigated in vacuum ($<10^{-3}$ Pa), in order to exclude any contribution due to the ambient humidity, which has been reported to deeply affect the electrical response of melanin based samples [11].

The conductivity, σ , increases several orders of magnitude in the range 310 K ÷ 480 K, suggesting a semiconductor-like behaviour (see the figure 2).

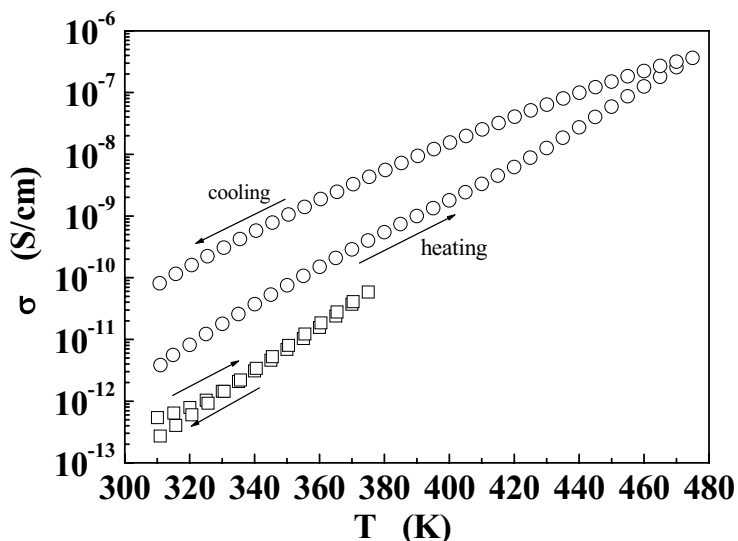


Figure 2: Conductivity as a function of the temperature for the sample A. Different symbols correspond to different heat treatments. Open squares: thermal cycle up to 375 K; Circles: thermal cycle up to 475 K.

However, the conductivity exhibited by the sample differs from that of a classical semiconductor in several aspects. In fact, as long as the maximum measurement temperature is kept below 375 K we always observed that the σ curve collected during the heating run overlaps quite well with that of the cooling one (see the figure 2).

On the contrary, increasing the temperature up to 475 K (circles in the figure 2) we observed a conductivity hysteresis, with the σ values, measured during the cooling run, higher than those of the heating one. However, the hysteresis tends to reduce and then to disappear repeating the whole run of measurement [8].

Despite the higher d value of the sample B, this last did not show any appreciable difference in the temperature dependence of σ , when the same thermal treatment is applied to the film. This fact could be related to the conduction mechanism involving charge transport along the melanin molecular chain rather than a thermally activated conduction process typical of inorganic semiconductors.

For the interpretation of the results obtained by the electrical characterization, we report in figure 3 the Arrhenius plot of the σ values for the two samples. We got two activation energies for the heating run and a single energy value for the cooling one. However, the temperature where the conductivity curve changes its slope depends on the thermal treatment history of the sample.

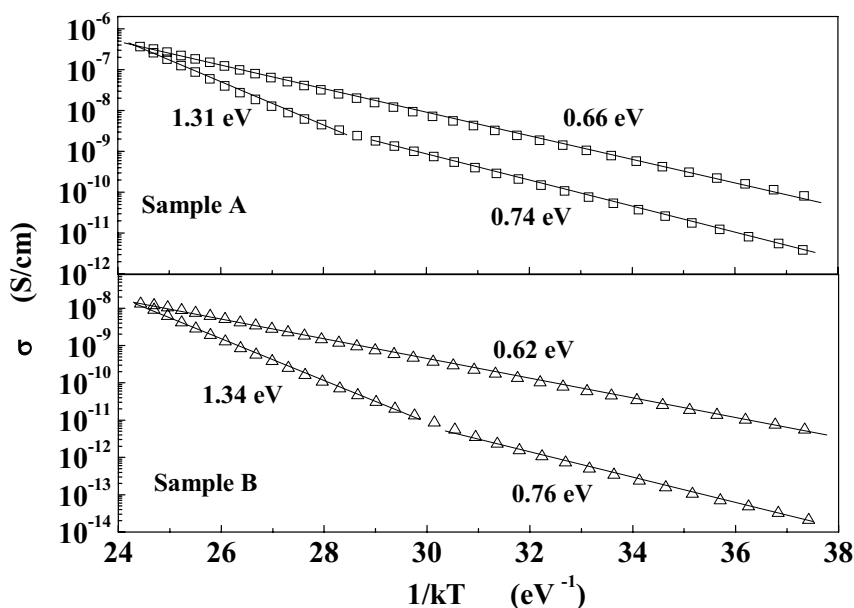


Figure 3: Arrhenius plot of the conductivity as a function of the reciprocal thermal energy for the samples A and B. Numeric values represent the activation energies for the conduction process.

Assuming a conductivity mechanism characteristic of an amorphous semiconductor material [2], we have interpreted the activation energies obtained as due to the presence of a mini-band (MB) at the Fermi level in the mobility gap of the material, linked to the presence of water molecules trapped into the melanin structure. This MB could be responsible of the lower activation energy (about 0.7 eV in both samples) due to transitions from its levels to conduction band (CB) states. Raising T, transitions from valence band (VB) to CB states give rise to the higher activation energies (about 1.3 eV).

As reported in literature, water can be desorbed from the melanin chain by a moderate thermal annealing [12]. This fact is expected to change the electronic density of states of the melanin. In this respect, the observed change of

the activation energy during the cooling can be addressed to the water desorption. In detail, we guess that water molecules desorption could cause the widening of the MB or the Fermi level position change. Both could account for the observation of a single activation energy during the cooling run (about 0.6 eV).

Finally, both samples show a moderate integral photoconductivity response when lighted by halogen tungsten source [8]. This property could suggest a possible use of synthetic melanin in photovoltaic application.

4. Conclusion

We demonstrated, by electrical and optical characterization, that synthetic melanin thin films deposited by spray-coating present features ascribed to an amorphous semiconducting material. However, thermal treatment history affects the electrical behaviour of the films, while a residual optical absorption has been observed in the NIR region. The conduction mechanism has been interpreted in terms of thermal activated transitions either from localized to extended states and/or from valence to conduction band. Water desorption from melanin molecule could be the responsible of the energy values change observed during the thermal cycles.

Due to the properties shown by the samples, further improvement of conductivity together with an increased absorption in the NIR region, by doping the synthetic melanin macromolecule could make this material a good candidate for optical sensing applications.

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