Electrosynthesis and Characterization of Semiconducting Molecular Materials in the Electrochemical Module of the Atomic Force Microscope

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The search of new materials for electronics and optoelectronics applications has been the subject of considerable research effort. Early on, inorganic materials received most of the attention in this regard, whereas organic and organometallic derivatives were in a state of relative neglect. Recently, however, these last materials have generated an increasing interest, as some of them may behave as conductors or semiconductors and could potentially be used in diodes, solar cells, transistors and electronic switches, among other devices. A common technique for preparing organic or organometallic materials is electrocrystallization, which is based on the formation of radical ions by electrochemical oxidation or reduction, and simultaneous crystallization of the derived salt with the inorganic counter-ion of the support electrolyte. This process is normally carried out by electrosynthesis in conventional cells. An exciting alternative method uses the electrochemical module of the atomic force microscope (AFM). This use of the AFM is proposed as a more efficient way to generate molecular materials, as it permits thin-film synthesis to be monitored and manipulated before characterization. The proposed method has several advantages when compared with the traditional method. One among these is the fact that cyclical voltammetry studies can be performed while the material is being synthesized to determine the oxidation and reduction potentials of the relevant species. A faster synthesis is another advantage of using the AFM module, as this method requires only about three hours for this process, while the traditional method requires between one week and two months. Another advantage is that the AFM-generated materials are directly deposited in thin-film form, while those materials obtained from the traditional method are deposited in the cell's anode and require an additional evaporation process to produce a thin film. The AFM permits the analysis of samples made from conducting, insulating and semiconducting materials and provides good topographic contrast and lateral resolution when imaging surfaces. In this work, we make a comparative study between the traditional method for synthesizing and characterizing a new molecular material and the method based on the use of the AFM electrochemical module.

Keywords Atomic Force Microscopy; electrosynthesis; molecular materials; thin films

1. Introduction

For a long time, organic compounds were considered prototypical ingredients in the preparation of materials with insulating properties. The synthesis of organic compounds with electric characteristics similar to those of metals began in 1911 [1, 2]. Historically, perylene bromide was the first organic material in which traces of conductivity were observed in 1954; conductivity was reported to be 10^{-1} S·cm^{-1} [3]. Nowadays, there are several organic materials that are capable of conducting electricity. One class of organic conductors is known as molecular materials. Molecular materials are formed by condensation and organization of molecular units that may be organic or organometallic species and are individually characterized in their properties, such as chemical nature, redox potentials, higher orbitals occupied, and lower orbitals unoccupied (HOMO, LUMO), dipolar or multi-polar character, and polarizability, among others. Moreover, due to different molecular tailoring possibilities via chemical synthesis, organic and organometallic materials present an infinite variety in functionality. The design of the molecular structures can be engineered to enhance particular properties (solubility in different solvents, color of light emission, crystal packing).

It has also been well established that some of these solid molecular systems can be conductors or superconductors and some of them even exhibit electronic and magnetic properties with potential technological applications. It is clear that, in some cases, especially for technological applications, the films must exhibit a high degree of molecular anisotropy contained in few thin layers. Therefore, some research work has been directed to the formation and study of thin films of molecular conductors, such as the chemical vapor deposition (CVD) of (TTF)(TCNQ) (TTF = tetrathiofulvalene, TCNQ = tetracyanoquinodimethane) [4, 5], and (organo-) aluminum compounds as thin films for microelectronics [6]. On the other hand, research on molecular electronics involving transition metal complexes have received increasing interest based on the fact that the oxidation states of transition metals can be varied to a great extent and thus that many electron transfer processes can result [7, 8]. A lot of studies of material containing metallic complexes have been reported to date [9-13]. Some important examples are the first superconductor with a paramagnetic metal ion, (BEDT-TTF)$_4$A[Fe(C$_2$O$_4$)$_3$] (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene and A = K, NH$_4$, H$_2$O) [11]; the first molecular metallic ferromagnet (BEDT-TTF)$_3$[Mn^{II}Cr^{III}(C$_2$O$_4$)$_3$], which was formed by infinite sheets of the magnetic coordination polymer interleaved with layers of conducting BEDT-TTF cations, and shown ferromagnetism and metallic conductivity [13].

The objective of this study is to evaluate the synthesize molecular materials with electric properties by two methods: electrosynthesis by conventional electrocrystallization cells, and electrosynthesis in the electrochemical module of AFM. Electrosynthesis is the process for synthesizing molecular materials which provides the best results, and is based on the formation of the radical ion by electrochemical oxidation or reduction and the simultaneous crystallization of the derived salt with the inorganic counter-ion of the supporting electrolyte. In this study, the electrochemical reaction in the AFM permits the formation of a thin film over the surface of an electrode with the shape of a plate or disk, which is the reason why the film acquires this morphology and allows the evaluation of the electric properties of the molecular material [14]. To illustrate this work, the proposal is to use the acceptor-donor system of potassium trioxochromate (III), $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and species N-trifluoromethanesulfonyl-1-azahexa-1,3,5-triene compounds (Figure 1) [15], which are highly functionalized pentamethine compounds with interesting physical and chemical properties [16]. These compounds are especially interesting from a structural point of view for several reasons; in a neutral form, they show an extensive electronic delocalization, which confers them a very particular chemical behavior. Furthermore, these pentamethine compounds can behave as monodentate ligands or bidentate ligands, and even interact with metals through π electrons [17].

2. Experimental

The following acceptor compounds were studied: (**1**) 1-trifluoromethanesulfonyl-6-phenylamine-1-azahexa-1,3,5-triene, (**2**) 1-trifluoromethanesulfonyl-3-chloro-6-phenylamine-1-azahexa-1,3,5-triene, (**3**) 1-trifluoromethanesulfonyl-3-[4'-(1'-trifluoromethanesulfonyl)-1',4'-dihydropyridinyl]-6-allylamine)-1-azahexa-1,3,5-triene and (**4**) 1-trifluoromethanesulfonyl–3-[2'(-(S)-(1''-methyl) pyrrolidine)]-6-methylphenylamine-1-azahexa-1,3,5-triene (Figure 1). The counter-ion used was potassium (III) trioxochromate, $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$.
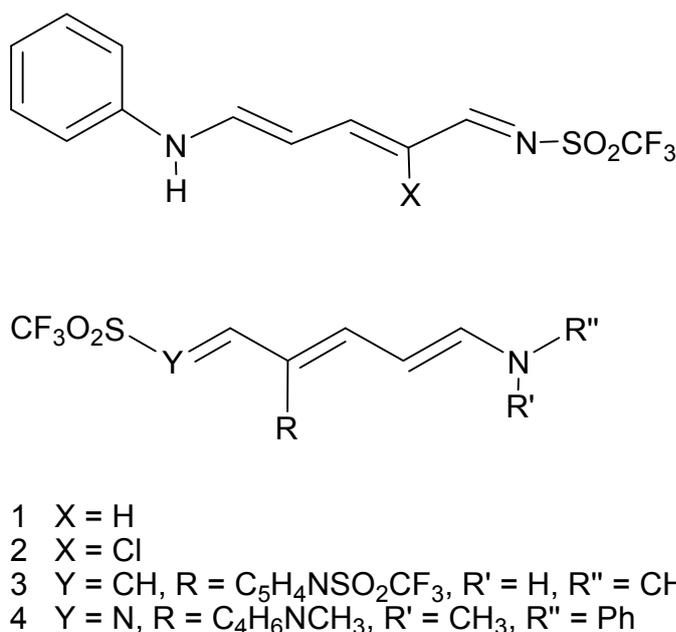

1 X = H
2 X = Cl
3 Y = CH, R = $C_5H_4NSO_2CF_3$, R' = H, R" = CH_2CHCH_2
4 Y = N, R = $C_4H_6NCH_3$, R' = CH_3, R" = Ph

Fig. 1. Chemical structure of pentamethine compounds

The traditional electrosynthesis process of molecular materials took place in electrocrystallization cells, with platinum electrodes and a power source at constant voltage (Figure 2a); a very diluted dissolution of the organic compound was introduced in the anodic compartment, and another, more concentrated dissolution of the inorganic compound was introduced in the cathodic compartment of an electrocrystallization cell with platinum electrodes. A very small electric current (between 0.5 y 2 µA) was applied to ensure that the process be as slow as possible to favor the coexistence of neutral molecules and charged molecules during the whole process, as well as a slow crystal growth [18]. The thin films were prepared by the vacuum vaporization method. On the other hand, the initial stages of electrochemical deposition by cyclic voltammetry and the AFM surface characterization were carried out *in situ* in the electrochemical (EC) fluid cell of the Nanoscope IIIa Digital Instrument atomic force microscope (Figure 2b). Here, highly oriented pyrolytic graphite (HOPG) was used as a working electrode, with platinum wire as a counter electrode and silver wire as a reference electrode. The EC-AFM experiments used cyclic voltammetry between the cathodic (−1.0 V) and anodic (+1.0 V) switching potentials. The potential scan rate was of 75 mV s^{-1} in all cases. The morphological characterization by AFM of the electrodeposited materials was performed *in situ* in the contact mode using low

scanning forces (0.3 N·m^{-2}) at the open circuit mode. For this study, 0.1 M tetrabutylammonium tetrafluoroborate was used as support electrolyte. The AFM characterization of the electrodeposited material was performed in the presence of the aqueous electrolyte (50 μl). In order to compare the electrode surface modifications before and after deposition, the HOPG was imaged before the electrochemical reactions and after different potential scan cycles (PSC).

Elemental analysis of the electrodeposited films was performed with a scanning electron microscope (SEM) Jeol JSM5900 coupled to an energy-dispersive spectrophotometer (EDS) working at 20 keV. The acquisition of the EDS data was stopped when it reached 5000 counts. The infrared spectra were obtained with an IR spectrophotometer Perkin Elmer 282-B. The spectra were recorded by the KBr-pellet technique. Finally, the electric conductivity of the films was studied by means of a four-point probe. For these measurements, the molecular films onto the HOPG substrates were analyzed with four metallic strips that acted as electrodes for the electrical measurements. In order to get an ohmic behavior between the deposited films and the metallic electrodes, four gold or silver strips were deposited by vacuum thermal evaporation onto the glass slices. To prevent the strips from reaching the surface of the substrate, a molybdenum boat with two grids was used as the evaporation source. The boat temperature was 473 °C during evaporation, as measured with a chromel-alumel thermocouple. The electric current as a function of temperature was measured with an applied voltage of 100 V in the ohmic regime by using a programmable voltage source Keithley 230 and a peak-ammeter Keithley 485 coupled to an HP3421 data collector.

(a)

(b)
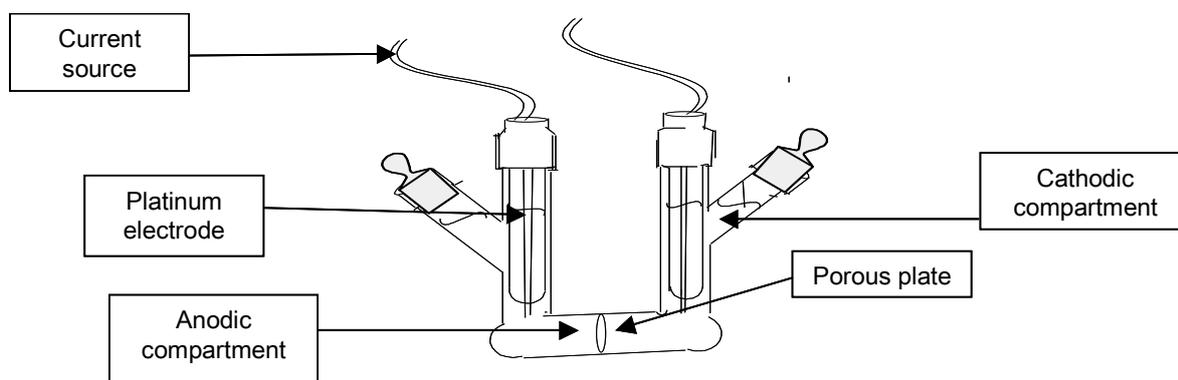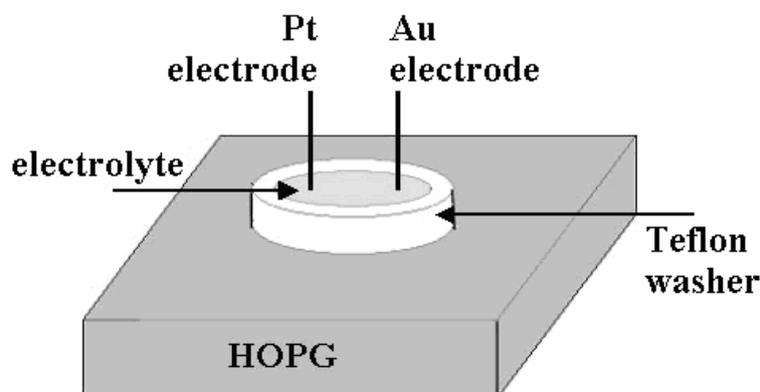
Fig. 2. Electrosynthesis cell for (a) conventional electrosynthesis and (b) AFM electrosynthesis

The proposed method consisted of arranging the electrochemical module of the AFM as an electrosynthesis cell, composed of a conducting, highly oriented pyrolytic graphite (HOPG) substrate, permitting the observation of changes at the surface of the substrate. The graphite is mounted over a metallic disc by conducting glues that assure conductivity between graphite and disc. At the center of the graphite substrate, a teflon sheave (washer) was placed containing the electrolytic solution constituted by the donor and acceptor species (figure 2b). This electrochemical cell, unlike conventional electrochemical cells (figure 2a), consists of three electrodes: the reference electrode and the counter-electrode, consisting of thin wires, and the working, or task, electrode, where the deposition of synthesized material occurs and which has a flat surface area larger than those of the other two electrodes. The AFM works by scanning a high resolution tip over the surface under study -which in this case refers to the surface of the material formed *in situ*. In this way, one can observe the growth of material as it settles on the surface layer. The pyramid-shaped tip is placed at the end of a hoop or strip of a hundred microns length. The tip deflects as it closely traces the surface of the contour

underneath, and the magnitude of the deflection is detected by an optic system coupled to an electronic mechanism that provides the topographic information from the sample. The use of AFM for the synthesis of molecular materials permits the study of the reduction-oxidation electrochemical processes occurring in the cell, with the aid of an electrochemical module (potentiostat/galvanostat). The electrochemical modification of molecular materials as they synthesize and settle over the task (graphite) electrode can thus be studied in real time.

3. Results and discussion

It is normally required to investigate the redox behavior of the starting compounds and to discard an independent reaction of the solutions [19], a cyclic-voltammetry study on each of them was performed. Figure 3 shows the cyclic voltammetry response of donor species 3 alone. The first positive scan shows an oxidation peak at +420 mV and a very small reduction peak at +50 mV Vs Ag. After the first cycle, the voltammetric profile was considerably different, with an important reduction in current density. The first advantage of using the AMF electro-synthesis module is found at this point, as the redox study initially required in the molecular materials' electro-synthesis can be performed in the AFM as soon as the material is formed, while the conventional method requires two isolated steps (the redox study followed by the electro-synthesis step.
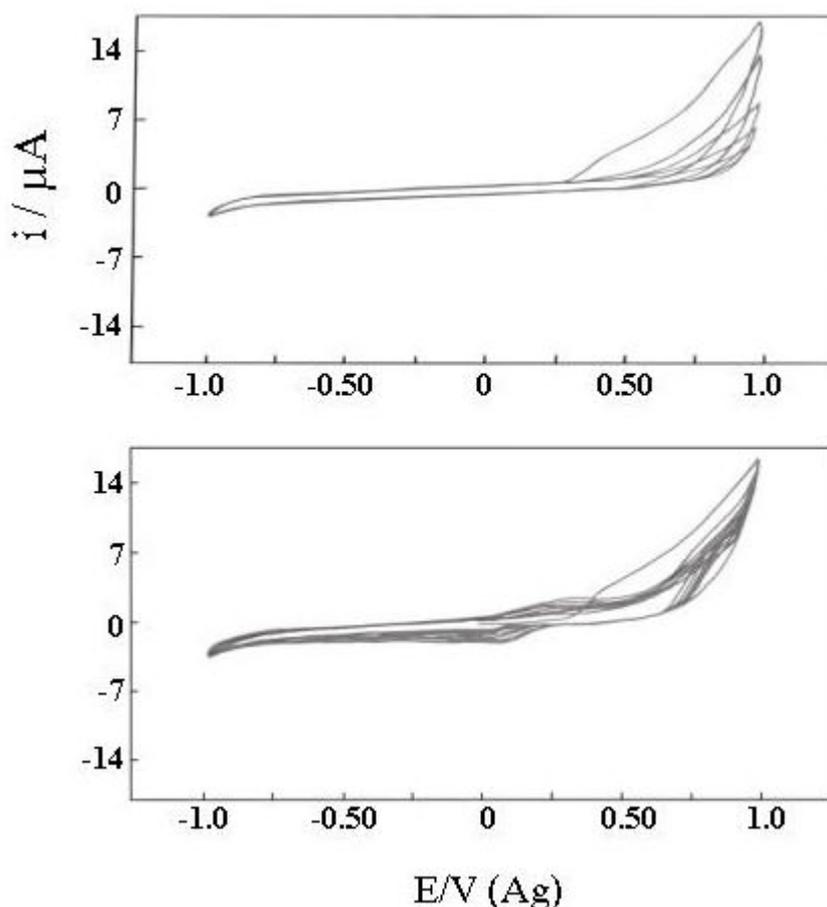

Fig. 3. Cyclic voltammogram for the ethanol-water dissolution containing (a) only compound 3 after 5 PSC and (b) compound 3 and $K_3[Cr(C_2O_4)_3]\cdot3H_2O$ species (combined) after 10 PSC. The potential sweep rate was 75 mV s^{-1}.

The electro-synthesis was carried out repeatedly, modifying operation parameters such as working temperature, reagents' concentration, electric current intensity, solvent used and type of electrodes. It is noteworthy that the time to perform an electro-synthesis can go from one or two weeks to almost two months, considerably more than the corresponding AFM crystallization and synthesis processes. Figure 4 shows AFM images of the electrode surface after a) 0 (bare HOPG surface) and b) 30 potential scan cycles (PSC) when using DS1 and the $[Cr(C_2O_4)_3]^{3-}$ anion. The electrodeposited material in this case is almost uniformly distributed on the electrode surface and the final film texture is thin and grainy. From the vertical scale bar, it is clear that the size of the grains is very small. A root mean square (RMS) roughness analysis of the surface, which is a quantitative measurement of the film texture, shows that the film

did not change after 40 PSC and its final RMS value was 21 nm. The surface morphology of the materials on the electrode surface as seen by AFM by using the $[Cr(C_2O_4)_3]^{3-}$ anion and the DS2 and DS4 compounds was very similar.
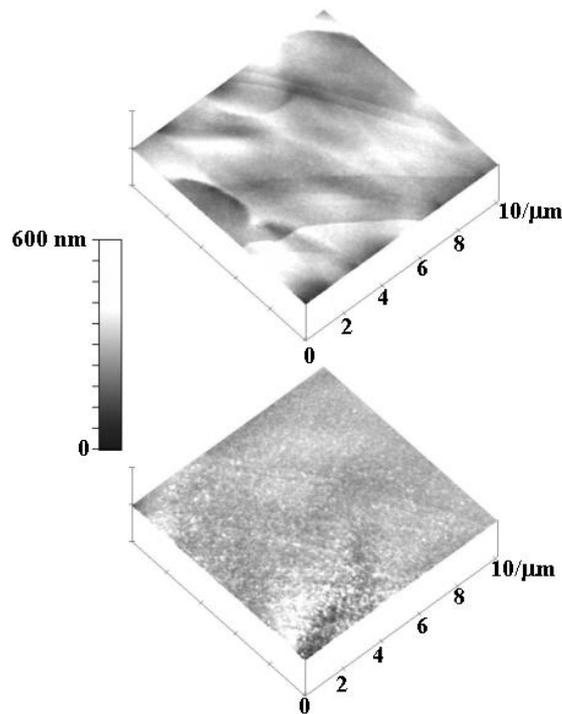

Fig. 4. *In situ* AFM images of the electrode surface after a) 0 PSC (bare HOPG) and b) 30 PSC for the electrodeposited material from the combined species DS1 and $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$. Images sizes 10 x 10 μm.

Figure 5 shows the AFM images corresponding to the DS3 compound. Figure 5a shows the electrode surface after 15 PSC using DS3 only. The surface is barely modified, although two small spots appeared on the electrode surface. In the presence of the $[Cr(C_2O_4)_3]^{3-}$ anion, the film exhibits an important amount of electrodeposited material after 15 PSC as shown in Figure 5b. Here, the growth of randomly distributed nodules is observed. A section analysis of the surface (not shown here) determined features of different heights (up to two microns) irregularly distributed on the electrode surface. In this case, the surface coverage was not uniform and the RMS roughness value after 15 PSC was 79 nm.

In the case of molecular materials' electro-synthesis in conventional electrocrystallization cells, the material is obtained in the dust (or powder) form, and not in film form, as was the case with AFM. For ulterior measurements of electric properties, it was necessary to prepare a thin film by the vacuum vaporization method, after a thermogravimetric assessment indicating the maximum temperature at which the powder could be obtained without decomposition. IR spectra were recorded for powder samples and the thin films. This in order to determine the presence of the most important and representative functional groups and whether there were significant chemical changes in the materials during the thermal evaporation process. Table 1 shows the characteristic bands for powder and thin films. The signals from the material in the thin-film form show slight location changes, as thin films settled by any method undergo inner stress that affects the angles and energy of intramolecular bonds. Nevertheless, the material did not suffer any alteration during the evaporation and preparation of the film.
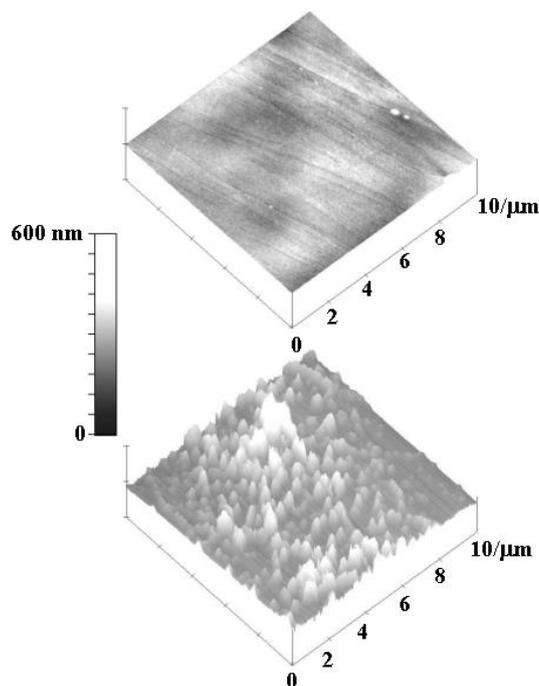
Fig. 5. *In situ* AFM images of the HOPG electrode surface for a) DS3 alone after 15 PSC and b) the combined species DS3 and $K_3[Cr(C_2O_4)_3]\cdot 3H_2 0$ after 15 PSC. Images sizes 10 x 10 μm.

Table 1 IR data for the thin films obtained in the electro-synthesis module of the AFM (module) and by conventional cell (cell), cm^{-1}.

DS1 module	DS1 cell	DS2 module	DS cell	DS3 module	DS3 cell	DS4 module	DS4 cell	vibration Mode
2920	2918	2920	2925	2920	2918	2920	2923	arom CH str
1598	1592	1645	1641	1608	1610	1627	1625	COO str (asym)
1529	1533	1568	1569	1560	1564	1531	1533	C=N str
1390	1394	1390	1388	1449	1446	1495	1499	SO_2 str (asym) + CC str.
1265	1261	1325	1321	1390	1389	1390	1389	COO str (sym)
1190	1194	1200	1210	1233	1230	1267	1270	SO_2 str (sym)
1181	1186	1166	1170	1180	1177	1184	1186	CF_3 str (asym)
1099	1101	1105	1108	1074	1079	1030	1030	CF_3 str (sym)

   After each molecular material was synthesized and prepared in thin-film form, it was analyzed by EDS to determine the corresponding qualitative chemical composition. Table 2 shows the results for molecular materials synthesized in a conventional cell and in the electro-synthesis module of the AFM. The presence of elements related to organic species, as well as the inorganic species, is found in both cases, indicating the reaction between the two chemical species. On the other hand, the EDS studies show that, because of the characteristics of the film settled over the HOPG layer, it is not possible to perform a quantitative analysis that allows the exact characterization of the film, which is a disadvantage of using the electrochemical module of the AFM for the preparation of molecular materials. The large concentration of carbon in the substrate, as compared to the amount from the deposited materials, makes it hard to detect the film compounds.

Table 2 EDS analysis of the electrodeposited films in a conventional cell and in the electro-synthesis module of the AFM

Molecular Material (Synthetic method)	%C	%O	%S	%K	%Cr	%Cl	%F
DS1 (electro-synthesis module)	74.39	21.80	0.13	1.67	2.01	-	-
DS1	74.43	21.14	0.18	1.71	2.11	-	-

(conventional cell)							
DS2 electro-synthesis module	77.88	18.70	0.15	1.76	0.71	0.10	0.70
DS2 (conventional cell)	77.08	18.29	0.20	1.92	0.78	0.13	0.76
DS3 (electro-synthesis module)	76.42	17.38	0.23	3.99	1.40	-	0.58
DS3 (conventional cell)	76.44	17.41	0.19	4.03	1.44	-	0.61
DS4 (electro-synthesis module)	42.05	38.92	0.97	9.29	6.18	-	2.59
DS4 (conventional cell)	42.15	38.89	0.91	9.32	6.27	-	2.70

The electrical conductivity of each material was evaluated at 25°C. The results are presented in Table 3, which shows that the thin film synthesized in the AFM is the one with the largest conductivity, possibly due to graphite's conducting nature and to better ordering in the synthesized material. The conductivity values at room temperature for both materials are in the range of electric conductivities for semiconducting molecular materials (10^2 to 10^{-6} S/m) [20]. This is important because a molecular semiconductor is generally defined in terms of its conductivity at room temperature, besides its structure, stacking form and orbital overlap. The presence of adhesive conductors between the substrate and the metallic discs that hold the sample to the microscope may be a disadvantage of the AFM electrosynthesis process, as they may interfere with the measurement of conductivity in the transversal direction with respect to the electrode.

Table 3 Electrical conductivity results for electrodeposited films in a conventional cell and in the electro-synthesis module of the AFM (T = 25°C).

Molecular Material (Synthetic method)	Electrical conductivity σ (Scm^{-1});
DS1 (electro-synthesis module)	4.5×10^4
DS1 (conventional cell)	2.3×10^{-6}
DS2 (electro-synthesis module)	5.7×10^4
DS2 (conventional cell)	2.5×10^{-6}
DS3 (electro-synthesis module)	6.3×10^4
DS3 (conventional cell)	6.2×10^{-6}
DS4 (electro-synthesis module)	6.9×10^4
DS4 (conventional cell)	$6.3 \, E10^{-6}$

4. Conclusions

Electrosynthesis produces molecular materials with amorphous appearance in electrochemical cells, as well as in the electro-crystallization module of the AFM. The traditional method is extremely slow compared to the alternative procedure using the AFM, which could be the most recommendable method for thin-film manufacturing. The traditional method, which generates molecular material in the powder form, requires an additional step of vacuum vaporization for thin-film production.

On the other hand, a greater amount of molecular material is produced in the electrochemical cells, due to the cell size, which is larger than the one used in the AFM electro-synthesis module. Nevertheless, from the structural and chemical standpoints, both techniques lead to molecular materials formed by the electrochemical oxidation of neutral molecules that give rise to compounds of mixed valence. In both cases, in order to get a salt derived from an electronic donor, a much diluted dissolution of donor is introduced in the anodic compartment, as the solution of the basic salt is in the cathodic compartment. The role of the basic salts in both electrocrystallizations is twofold: first, to ensure the conductivity by acting as the supporting electrolyte, and then to provide the counter-ion for the ionic radical salt to form.

The method here proposed has considerable advantages when compared with the traditional method: in first place, the fact that the synthesis of material can be carried out at the same time as the cyclic voltammetry study permits the determination of the reduction and oxidation potentials of the involved species, while the traditional method required two different stages (namely, cyclic voltammetry followed by the electro-synthesis of the material). A second advantage is the faster synthesis of materials, which requires about three hours in the AFM, while the traditional method takes from one week to two months. Furthermore, the materials settle in film form when using the AFM, whereas those

obtained by the traditional method settle as powder in the anode of the cell and must be vaporized before a thin film is available. Some objections can be set at the AFM method proposed in this work, concerning some techniques that may provide a better characterization of the synthesized materials: using conventional electro-synthesis, the material is produced in powder form that is suitable for analysis with techniques such as IR spectroscopy, elemental analysis, and X-ray diffraction, among others. The films obtained at the electro-synthesis module of the microscope, can only be analyzed by techniques such as EDS, which does not provide enough information about the structural and chemical composition of the materials. Moreover, from the information provided by the EDS, the material that is going to be used as task electrode must be very carefully chosen in order to clearly discern between the chemical elements belonging to the electrodeposited material and those that belong to the conductor substrate. The amount of material that is deposited on the working electrode surface is limited by the small volume of electrolyte ($50\mu l$) that is introduced in the electrochemical cell. The measurement of electric properties of materials synthesized in the electrochemical module of the microscope is affected by the conducting graphite substrate over which they are deposited, so it was not possible to evaluate the dependence of electric current on temperature, which was possible when working with films of molecular materials prepared by the conventional method.

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