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Effect of the fullerene in the properties of thin PEDOT/C₆₀ films obtained by co-electrodeposition

Dedicated to Prof. Luis Echegoyen.

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Abstract

Organic electronics requires the development of reproducible and highly conductive thin films. The arrangement of poly(3,4-ethylenedioxythiophene) (PEDOT) with fullerene C₆₀ leads to products with the combined properties of both species that are excellent candidates for these applications. However, very little has been studied about the effect of doping PEDOT with C₆₀, and thus there is a lack of information regarding the morphology, electrochemical and electrochromic properties of the resulting films. Herein, simultaneous electrodeposition of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with fullerene C₆₀ was carried out via cyclic voltammetry in the range from 0.0V to +1.5V (*vs* Ag/AgCl) in a three-compartment cell. ITO coated on PET was used as both working and counter electrodes. The fullerene presence within the films was confirmed with MALDI and TGA (36% of fullerene content). The cyclic voltamograms showed that the C₆₀-doped film has a higher oxidation potential, what was attributed to the electron affinity of the fullerene cage. Furthermore, the spectroelectrochemical and electrochromic analyses showed that the PEDOT/C₆₀ films present a dark violet coloration in the reduced state, which differs from the usual dark blue of the PEDOT polymer. Finally, the morphology was analyzed using AFM and SEM, and pillar structure of broccoli-like particles was observed for both films. However, the fullerene doping generated smaller polymer-based particles, thus forming a denser structure with higher surface area, suggesting the use of the cages as nucleation points for the polymerization.

Keywords (max 6)

Fullerene, electropolymerization, co-deposition, poly(3,4-Ethylenedioxythiophene), thin film, electrochromic.

1. Introduction

In the last decade the interest of the scientific community in optoelectronics and energy storage devices has increased abruptly.[1-6] In both cases, the preparation of reproducible and highly conductive thin films is crucial for a successful device performance. Moreover, these devices involve the need of low cost, convenient processibility, and mechanical flexibility. A huge interest grew for the use of fullerenes in organicelectronics, more specifically in light-emitting devices or photovoltaics in particular, due to their high electron affinity and enhancement of the photoelectron charge transfer.[7-9] In addition, fullerenes have good transparency and conductivity, what makes them excellent candidates for electronic applications and the most widely used acceptors for organic photovoltaic devices (OPVd).[10, 11] In 1995 the enhanced power conversion efficiency (PCE) of fullerenes in bulk heterojunctions (BHJ) polymer solar cells was first demonstrated.[12] These films are commonly composed of a photoactive blend film of a conjugated polymer donor and a soluble fullerene derivative acceptor.[13] The main problem in using fullerenes was its low solubility, thus special attention has been focused on derivatives of fullerenes.[14] [6,6]-phenyl-C₆₁-butyric acid methylester or [6,6]-phenyl-C₇₁-butyric acid methylester, commonly known as PCBM, have become the model for photovoltaics research, since PCE up to 7.5% can be reached when blended with polythiophene derivatives.[13]

On the other hand, poly(3,4-ethylenedioxythiophene) (PEDOT) has demonstrated to be one of the most interesting conductive polymers due to its intrinsic properties, such as excellent thermal and electrochemical stability, high electrical conductivity (up to 10³ S/cm), good transparency and electrochromic activity.[15-18] In addition, PEDOT-based films have excellent air stability and reproducibility, as well as being transparent enough to not affect significantly the transmittance of the ITO electrode. PEDOT has been demonstrated to be a very efficient hole extractor from most active layers. Currently, PEDOT:PSS is widely employed in OPV solar cells and other devices by directly coating it onto the electrode surfaces or as TCO layer.[13] PEDOT can function as an electron-donor while the fullerene is a well known electron-acceptor. The combination of both compounds in a same thin film is expected to provide a material with very unique properties.

Beyond the selection of good electron complementary compounds, the good interconnection within them as well as a construction of a PEDOT-based thin film with a homogeneous distribution of fullerene is required. Solution-casting from chemically polymerized PEDOT is one of the most studied techniques for film construction. However, not always the required crystallinity and ordered interpenetrating network are granted and the resulting films are usually less reproducible and heterogeneous, forming a phase separation between the fullerene and the polymer.[19] Besides, many efforts have been devoted to avoid the inherent self-aggregation and control the arrangement of fullerene cages along 2D films.[12, 20-23] Taking into account the electroactivity of PEDOT and the fullerene, the electrochemical technique seems to be the best candidate for the controlled synthesis of reproducible and thin PEDOT films with homogeneously distributed fullerene within it. Electrochemistry is a very powerful and promising technique for the thin film preparation, since it allows to control not only the thickness of the deposited layer, but also its morphology.[24] Furthermore, another advantage of the electrodeposition against solution-cast is the strengthening of the electrical contact between the deposited layer and the electrode.[25, 26] There are few examples where this method is employed, most of which based on a previous electrodeposition of the polymer on different substrate electrodes before the introduction of the fullerene dopant.[27-31] For instance,

Benincori reported the first “charm bracelet”...[32] Akiyama *et al.* have reported the electrochemical polymerization of thiophene-derivatized fullerene and EDOT to be used for higher incorporation of the fullerene moiety into the film.[33] Later on, Nasybulin *et al.* developed an electrochemical approach to fabricate a solar cell based on a three-layer codeposition of PEDOT/poly(2,2'-bithiophene)/fullerene.[34]

With all this in mind, in this work we prepared PEDOT-based thin films decorated with C₆₀ fullerene. High quality films have been obtained using fullerene as a co-dopant by co-electrodeposition. Thus, fullerene has been homogeneously distributed along PEDOT chains and with that, the interconnection between both electron donor-acceptor compounds. The electrochemical, spectroelectrochemical and electrochromic characterization of the films, as well as the topography, the morphology and the composition have been carefully investigated.

2. Materials and methods

3,4-Ethylenedioxythiophene (EDOT; >97%) was purchased from Sigma-Aldrich; Buckminster fullerene (C₆₀, 99%) was ordered from BuckyUSA; tetrabutylammonium hexafluorophosphate (TBAPF₆, >98%) was purchased from TCI Europe N.V. Acetonitrile and toluene (synthesis grade) were ordered to Carlo Erba Reagents SAS. All reagents and solvents were used as received with no further purification.

All electrochemical experiments were performed using a one compartment, three-electrode electrochemical cell driven by an Autolab MSTAT204 Potentiostat/Galvanostat. Flexible Indium Tin Oxide (ITO) coated PET slices, purchased from Sigma-Aldrich, were used as both working and counter electrodes with dimensions of 5mm x 20mm. Ag/AgCl was used as the reference electrode

Matrix-free LDI-Tof mass analyses were performed on an Ultraflex extreme III time-of-flight mass spectrometer equipped with a pulsed Nd:YAG laser (355nm) and controlled by FlexControl 3.3 software (Bruker Daltonics, Bremen, Germany). The acquisitions (total of 2000-3000) were carried out in positive reflector ion mode with pulse duration of 70ns, laser fluence of 50% and laser frequency of 1kHz. Laser intensity was set marginally above the threshold of ionization to avoid fragmentation (less than 20% for all the cases). C₆₀ was detected [M]⁺ with high intensity signal (> 5000a.u.). The m/z range was set between 400 and 1200. The acquired data was processed (baseline subtraction and normalized) using the software FlexAnalysis 3.3 (Bruker Daltonics, Bremen, Germany).

Atomic force microscopy (AFM) images were obtained with a Nanoscope IIIa, VEECO Instruments. As a general procedure to perform AFM analyses, tapping mode with an OTESPA-R3 probe (300kHz; 26N/m) (Bruker) were carried out. The obtained AFM-images were analyzed in Gwyddion 2.46 software. Scanning Electron Microscope (SEM) measurements were performed on JEOL JSM-6490LV at 5kV, running in a point by point scanning mode.

Thermogravimetric analyses were performed under air (25ml/min flow rate) using a TGA Discovery (TA Instruments). The samples were equilibrated at 100°C for 20 min and then heated at a rate of 10°C/min, in the range from 100°C to 800°C.

3. Experimental

3.1 Electropolymerization

PEDOT/C₆₀ films were electrochemically synthesized via electrochemical polymerization on flexible ITO electrodes (area of deposition of 25mm²). C₆₀ was used as the doping agent. The

deposition was performed running 20 or 100 cycles at 50mV/s from 0.0 to +1.5V vs Ag/AgCl reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1M) was used as electrolyte in a 10mL toluene/acetonitrile solution (4:1, v/v).

The concentration of the EDOT monomer was 50mM, while the concentration of C₆₀ was 0.5mM. As control, also PEDOT films polymerized at the same electrochemical conditions but without C₆₀ were deposited. After the deposition process, the resulting film was rinsed with toluene and acetonitrile to remove the unreacted precursors and the electrolyte.

3.2 Cyclic voltammetry

The cyclic voltammograms of the resulting films were recorded in the range from -1.0V to 1.5V, at a scan rate of 50mV/s in a 10mL solution of TBAPF₆ (0.1M) in toluene/acetonitrile (4:1, v/v). As reference, the electrode of Ag/AgCl was used. All measurements were carried out using fresh ITO slices as counter electrodes and fresh solutions at room temperature.

4. Results and discussion

4.1 Electrochemical deposition on flexible ITO electrode surface

In this work, thin PEDOT/C₆₀ layers were obtained by co-electrodeposition onto the surface of ITO electrodes. This was accomplished by electropolymerization EDOT monomer in the presence of C₆₀ which acted as a co-dopant. Briefly, cyclic voltammetry experiments were carried out by repetitive potential scanning from 0 to +1.5V at 50mV/s leading to bluish films on the working electrode. The electrochemical properties of fullerenes, *i.e.* its ability of both capturing and giving electrons, have been widely studied. Echegoyen first demonstrated its high facility upon reversible reduction of the pristine C₆₀, more specifically up to a hexaanion, without destruction of the fullerene cage.[35, 36] Furthermore, radical polymerization of fullerene is feasible yet at negative reductive values (-0.9V approximately) in the presence of small amounts of oxygen that catalyzes the process.[37-40] In order to avoid reduction of the fullerene species, thus potential polyfullerene deposition, cyclic voltammetries were performed at the positive range up to +1.5V; higher positive potentials may induce over oxidation of the PEDOT compounds.

Figure 1 displays the cyclic voltammetry of the successful electrodeposition of EDOT on an ITO working electrode with and without C₆₀, respectively, running 20 scans. The two voltammetries show a clear increase in the current and displacement of the band to higher potentials is observed after successive scans, indicating the deposition of an electroactive polymeric film on the electrode. The broad oxidation peak corresponds to the transition of the polymer from the neutral to the doped oxidized state.[10, 34] On the other hand, the cathodic counterpart showed also a broad band, resulting from the transition of the oxidized polymer to the neutral state. The final potential was set at 0 V so that the deposited polymer was in its non-oxidized state. Such results are in good agreement with the studies of Nasybulin.[34] They suggested the low polarity of the toluene as the responsible for the shift.

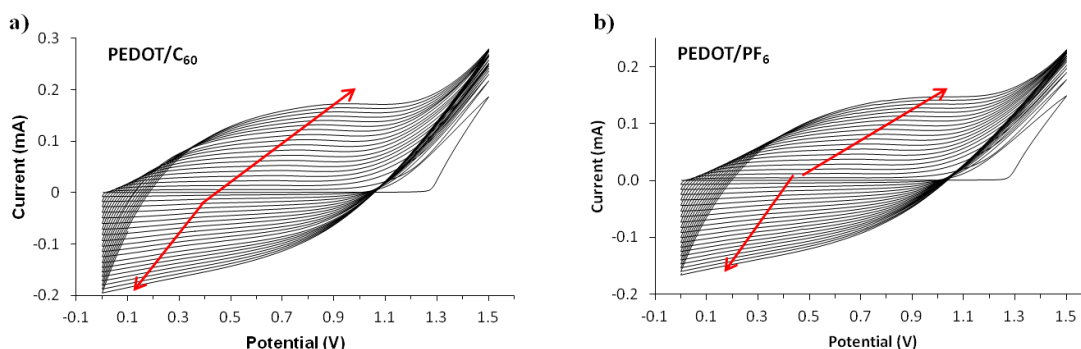


Figure 1. Cyclic voltammetry (20 scans, from 0V to +1.5V) of the electropolymerization of a) PEDOT/C₆₀ and b) PEDOT.

In order to investigate the presence of the C₆₀ molecule within the PEDOT films we carried out MALDI spectroscopy. Thus, the presence of the fullerene dopant was confirmed by MALDI spectroscopy. As plotted in Figure 2, the peak corresponding to the fullerene (720m/z) is the highest peak of the spectrum. Additionally, a peak at 840m/z is present, which corresponds to the C₇₀ impurity (0.6% in the fullerene sample).

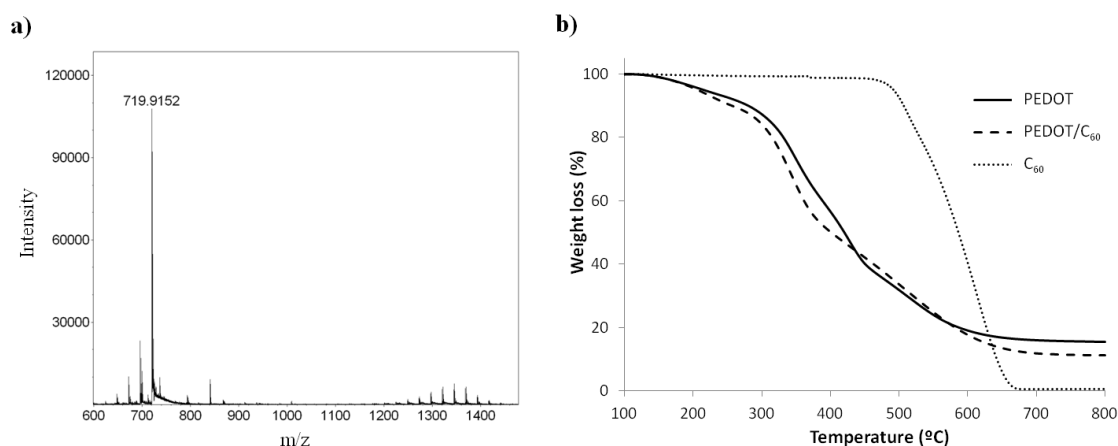


Figure 2. a) MALDI spectrum of the PEDOT/C₆₀ film. b) Thermogravimetric analyses of the PEDOT/C₆₀. Highlighted the temperature range where the fullerene cage is consumed.

Thermogravimetric analyses (TGA) of the film confirmed also the presence of C₆₀ (Figure 2b). The TGA was run under oxygen atmosphere in order to obtain a better separation between the thermal range decomposition temperature of the PEDOT (up to 600°C)[41, 42] and the fullerene (from 400°C to 700°C). The weight loss of PEDOT/C₆₀ at 700°C was 88.7%, while PEDOT and C₆₀ had a weight loss of 84.6% and 99.5%, respectively. Thus, PEDOT/C₆₀ was revealed to contain about 27.5% of C₆₀ and 72.5% of polymer, according to the following equation set (being x and y the weight percentage contribution of PEDOT and C₆₀, respectively):

$$0.846x + 0.995y = 0.887 \quad (1)$$

$$x + y = 1 \quad (2),$$

4.2 Cyclic voltammetry

The electrochemical characterization of the films was performed in a fresh 0.1M TBAPF₆ monomer-free solution. The corresponding cyclic voltammograms were recorded (Figure 3),

leading to a quasi-reversible oxidation process at +0.80V for PEDOT/C₆₀ and +0.55V for the PEDOT. As expected, the redox process of the PEDOT in both cases appears at lower oxidation values than the EDOT monomer, as a consequence of the increase in the conjugation along the polymeric chain. [43, 44] Interestingly, there is a shift to higher potentials on the Eox of PEDOT/C₆₀ compared to PEDOT, as well as a broadening of the curve, indicating the effect of C₆₀ in the film. The same behaviour was observed with the reduction bands. We hypothesize that such effect comes from the presence of the C₆₀ within the PEDOT layer, where the fullerene can easily absorb the electrons released by the PEDOT chains and give them back to the oxidized PEDOT before arriving at the ITO electrode. Thus, higher oxidation potentials are monitored. It is worthy to mention that the opposite effect is observed when PEDOT is deposited on top of a drop casted layer of fullerene,[45] suggesting that the electrochemical properties of the PEDOT layers can easily be modulated with the design of the electrode, *i. e.* the proximity of the fullerene to the PEDOT layers.

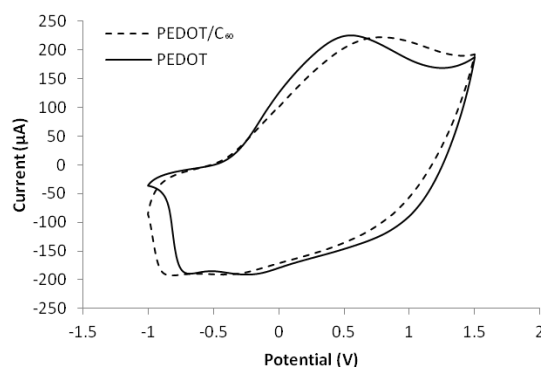


Figure 3. Cyclic voltammograms (2nd scan) of a) PEDOT doped with (dotted line) and without (dark line) C₆₀.

Furthermore, the reduction potentials of C₆₀ are significantly decreased when multi-layers of polymer are deposited. This effect was already observed by Damlin *et al.*[45]

4.3 Spectroelectrochemical and electrochromic properties

The electrochromic behavior of the PEDOT films is well understood when doped with conventional anions, such as polystyrene sulfonate (PSS), perchlorate (ClO₄⁻) or hexafluorophosphate (PF₆⁻). The polymer suffers a color change depending on its oxidation state: the dark blue of the neutral reduced state (-1.0V) becomes light blue when the film is fully oxidized (+1.0V).[46] Intermediate shades of blue are observed in the stepwise oxidation corresponding to an optical absorption in the same Visible wavelength range, although with a lower intensity.

To the best of our knowledge, the electrochromic response of PEDOT films doped with fullerenes has never been studied before. In order to fulfill this gap, the film layer PEDOT/C₆₀ was deposited on transparent ITO electrode so that the UV-Vis could be recorded. As well, PEDOT was analyzed as a control. At first glance, a color difference is observed with the naked eye in the reduced state of the polymers (-2.0V, -1.0V, 0.0V): as shown in Figure 5, the PEDOT/C₆₀ films are dark violet while, in agreement to the literature, an intense dark blue coloration is observed for PEDOT. Interestingly, light blue coloration appeared when both films were fully oxidized at +1.0V and +1.5V, with no evident color difference between the C₆₀ and the doped films.

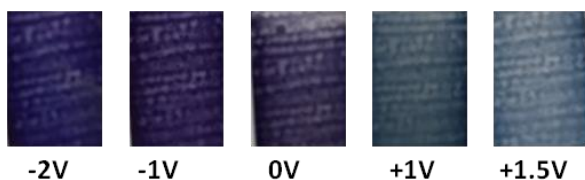


Figure 4. Electrochromic behavior of PEDOT/C₆₀ at different potentials

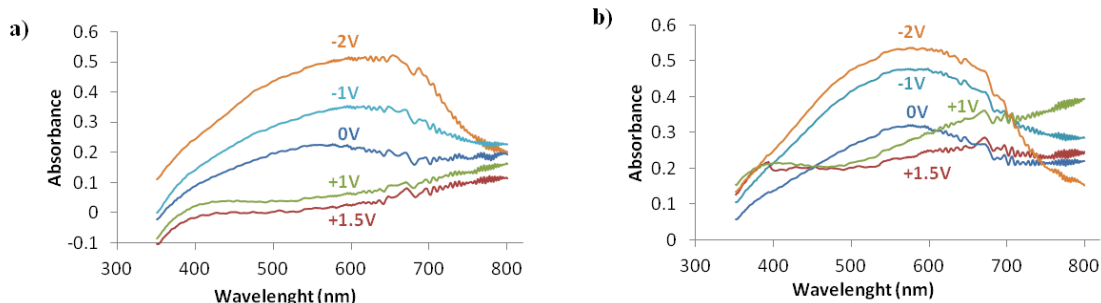


Figure 5. UV-Vis spectroelectrochemistry for a) PEDOT/C₆₀ and b) PEDOT.

The absorbance spectra, plotted in Figure 5, were recorded in the range between 350nm and 800nm; no further wavelengths were possible to record due to the limitations of the equipment. In good agreement with the literature, the reduced states of PEDOT (up to 0V) present a maximum wavelength at 575nm. Interestingly, a completely new and different behavior is observed for the PEDOT/C₆₀ films: not only there is a shift in the maximum wavelength for the reduced states, confirming the abovementioned change in the color, but also that maximum is displaced towards the typical 575nm band of the PEDOT during the stepwise oxidation. Thus, for -2V the maximum appeared at 615nm, for -1V appeared at 600nm and for 0V at 575nm, suggesting that the fullerene effect in the coloration is more intense as the negative potential increases. This observation might be related to the own reduction of the fullerene cages present in the film. Furthermore, the bands are broader for the films doped with C₆₀ than those doped with PF₆. This broadening was also observed in the cyclic voltammograms of PEDOT/C₆₀. In both spectra, the intensity of the bands decreased until they are undetectable in the oxidized states (+1V and +1.5V), where no distinguishable bands can be observed within this wavelength range.

4.4 Topography of the films (AFM and SEM)

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were conducted to characterize the morphological differences between the two types of film. For the AFM analysis, PEDOT/C₆₀ and PEDOT films were deposited onto the ITO electrode running 20 scans, while for the SEM 100 scans were necessary to reduce the transparency of the film and obtain high-quality images. The AFM images are displayed in Figure 6 a-c. The deposition of both PEDOT/C₆₀ and PEDOT onto the ITO surface (Figure 6 a and b) showed unique pillar morphology with diameters ranging from 150 to 300nm. The nanoparticles have a tendency to grow bottom-up leading to a brush-like architecture with high surface area. Such pillars are much smaller in the PEDOT/C₆₀ structure; in addition, the density of this film is higher when compared to the PEDOT one and, consequently, so is the surface area. Since the deposition of the ITO on PET is not homogeneous, pristine ITO was also imaged and showed a surface roughness as low as 15nm (Figure 6c), thus we estimate it does not interfere significantly with the film morphology during the polymerization process.

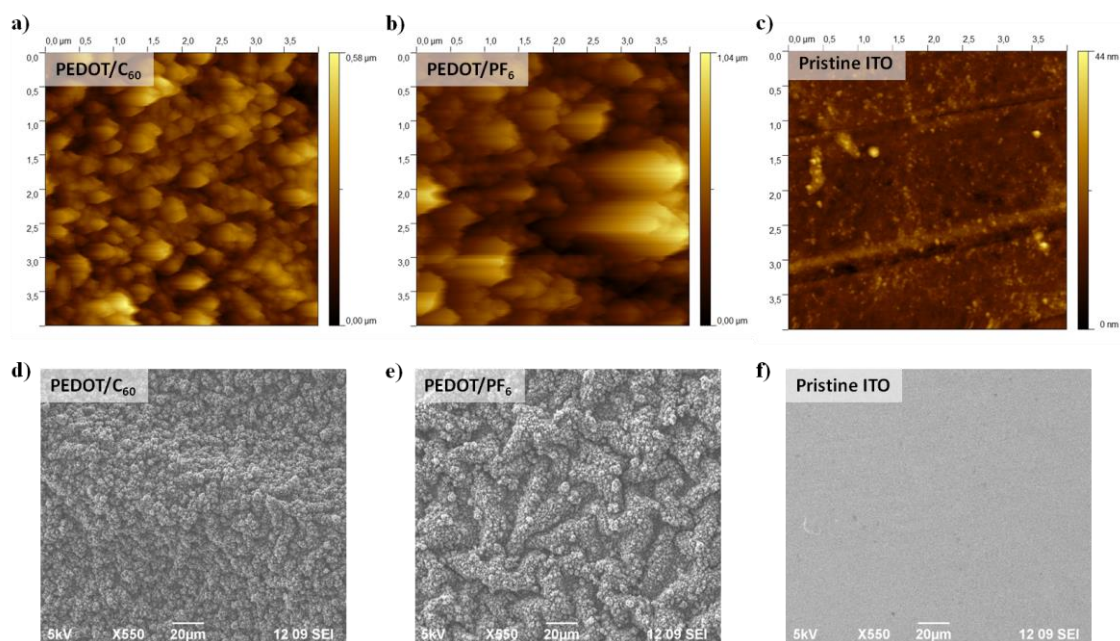


Figure 6. AFM images (a-c, 20 scans) and SEM micrographs (d-f, 100 scans) of the electrodepositing films onto PEDOT/C₆₀ (a,d) and PEDOT (b,e). As well, pristine ITO surface was imaged as control (c,f).

SEM micrographs are showed in Figure 6d-f. In general, a clear difference in the morphology of the two electrodeposited films is evident: in good agreement with the AFM images, the PEDOT/C₆₀ film presents smaller nanoparticles and higher density than the PEDOT film. In the case of PEDOT/C₆₀, the nanoparticles have a characteristic broccoli-like shape, which is the predominant geometry in the whole structure, randomly pillared along the surface. On the other hand, the PEDOT nanoparticles present a rougher broccoli-like morphology and tend to aggregate forming grooves. Our results are in good agreement with previous studies of the electrochemical, morphological and structural properties dependence of PEDOT.[47] All this results presented suggest that C₆₀ acts not only as the dopant but also as a nucleation point for the polymerization process, what explains the higher density and lower dimension of the structures observed in the PEDOT/C₆₀ films.

5. Conclusions

We have performed an extensive and detailed study of electrodeposited PEDOT/C₆₀ films, including morphology, electrochromic and electrochemical properties, to determine the effect of the fullerene in the film. The fullerene C₆₀ was used as the doping agent to counterbalance the positive charge of the oxidized PEDOT polymer, thus it was deposited on the film simultaneously with the electrodepositing the monomer. The successful deposition of C₆₀ has been corroborated via MALDI and TGA analyses, the last one giving a composition of 36% of fullerene in the film. All the polymerization reactions were performed via cyclic voltammetry and, intriguingly, significant differences have been observed in the properties of the resulting films. The oxidation of the PEDOT/C₆₀ happens at higher potentials, what we suggest to be due to the close proximity and blending between the fullerene and the polymer: electrons released from the PEDOT may be absorbed by the fullerene cages to then travel back to the electron-deficient PEDOT, thus being necessary stronger conditions, *i. e.* higher potentials, to oxidize the polymer. Furthermore, this effect seems to be easily modulated with the design of the disposition of the fullerene in the film. The presence of the fullerene is also reflected in the

electrochromic properties, supported by UV-Vis recordings. Reduced states of the film gave a deep violet coloration and larger wavelengths compared to the dark blue observed for the control PEDOT; on the other hand, no difference in the coloration is observed for the oxidized states of both films. Finally, AFM and SEM imaging revealed pillar morphology of broccoli-like structures for both PEDOT/C₆₀ and PEDOT films. Interestingly, those pillars were smaller and denser in presence of the fullerene, thus giving higher surface area, what may be attributed to the use of the cages as nucleation points for the polymerization.

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