

Poly(3,4-ethylenedioxythiophene) and Poly(N-methylpyrrole) Clay Exfoliated Nanocomposites

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Abstract—In the present work, The electroactivity, electrochemical stability, electrical conductivity and adherence of films formed by different layers of poly(3,4-ethylenedioxythiophene) and poly(N-methylpyrrole) with various nanoclay concentrations have been characterized and compared with those of pure polymers and copolymers. Results indicate that the electroactivity, electrostability and adherence of the multilayered systems are higher than those of both poly(3,4-ethylenedioxythiophene) and copolymers. On the other hand, the electrical conductivity diminishes by increasing the nanoclay percentage.

Index Terms—5. Nanostructured materials: exfoliated nanocomposite, conducting polymers, poly(3,4-ethylenedioxythiophene), poly(N-methylpyrrole)

I. INTRODUCTION

Poly(3,4-ethylenedioxythiophene), usually denoted PEDOT, is one of the most successful polythiophene derivatives because of its

interesting properties. PEDOT exhibits not only a high conductivity but also an unusual electroactivity and environmental stability. On the basis of these properties, PEDOT derivatives are used in a wide range of electronic, electrochemical and optical applications. In recent years, PEDOT have been combined with other typical conducting polymers with promising applications to produce new copolymers. In particular, copolymers prepared by electrochemical polymerization from mixtures of different monomers have provided interesting materials with, in some cases, promising technological applications. Thus, copolymers of 3,4 ethylenedioxythiophene (EDOT) with pyrrole, N-methylpyrrole (NMPy), bithiophene, 3-methylthiophene, indole, etc, have been prepared by direct electrochemical oxidation. Very recent the copolymer of EDOT and NMPy has been prepared, hereafter denoted poly(EDOT-co-NMPy), via electrochemical oxidation on steel electrodes using monomer mixtures with various concentration ratios. Comparison between poly(EDOT-co-NMPy) and the corresponding homopolymers revealed that, unfortunately, copolymers do not present any practical advantage with respect to PEDOT and poly(N-methylpyrrole) (PNMPy). More specifically, the electroactivity of poly(EDOT-co-NMPy) is lower than that of

both PEDOT and PNMPy, i.e. the formation of electroactive polarons is more difficult in the copolymers. Furthermore, the electrochemical stability of the homopolymers is significantly higher than that of the copolymer. Thus, redox properties of PEDOT and PNMPy are almost unaltered after eight consecutive oxidation-reduction cycles, while the degradation of the poly(EDOT-co-NMPy) properties is observed after only two consecutive oxidation-reduction cycles. In this work we present how all these deficiencies are successfully overcome by fabrication multilayered films of PEDOT and PNMPy (ml-PEDOT/PNMPy) using a layer-by-layer electrodeposition technique. Systems containing different layers that alternate PEDOT and PNMPy have been prepared and their electrochemical and electrical properties determined. In order to provide environmental stability to the multilayered systems, PEDOT has been used for the outside layers. Results indicate that the electroactivity and electrochemical stability of ml-PEDOT/PNMPy are significantly higher than those determined for films of the individual homopolymers generated under identical experimental conditions. On the other hand, the electrical conductivity of the ml-PEDOT/PNMPy prepared in this work were found to be slightly lower than that of PEDOT. The overall of these results indicate that these multilayered systems represent a significant improvement with respect to poly(EDOT-co-NMPy), being considered as very promising materials for different technological applications. Thus, the development of polymer-clay exfoliated nanocomposites is a field of increasing interest due to the important technological applications of these materials. Composite systems formed by organic polymers and clay minerals structured at the nanoscale level, which usually present a unique layered structure, rich intercalation chemistry and availability at low cost, have been used to develop plastic materials which advanced mechanical properties, molecular barrier behavior, fire retardant abilities, enhanced thermal stability compared to the

Individual polymeric materials. The excellent properties of ml-PEDOT/PNMPy systems should be attributed to the interface between the PEDOT and PNMPy layers. Thus, the coupling between the two polymers is, in terms of enhancement of the properties, significantly more positive for the multilayered films than the interaction of EDOT and NMPy monomers in copolymers. However, the dimensions of the interface between consecutive layers are very small with respect to the bulk of the layers, i.e. the dimensional ratio interface :bulk is extremely low.

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II. SAMPLE PREPARATION

All samples containing PEDOT, PEDOT-MMT ,PNMPy and PNMPy-MMT nanocomposites were prepared by chronoamperometry (CA) under a constant potential of 1.10 V. Electrochemical experiments performed on an galvanostat using a three –electrode two- compartment cell under nitrogen atmosphere (99.995% in purity). The anodic compartment was filled with 40mL of a 10 mL monomer solution in distilled water containing 0.1 LiClO₄ as supporting electrolyte, while the cathodic compartment contained 10 mL of the same electrolyte solution without the monomer. Steel AISI 316 sheets of 4 cm² area were employed as working and counter electrodes. The reference electrode was an Ag/AgCl electrode containing a KCl saturated aqueous solution($E^0 = 0.222 V$ vs. standard hydrogen electrode at 25^oC), which was connected to the working compartment through a salt bridge containing the electrolyte solution. All the potentials (E) give in this work refer to this electrode. The amount of MMT in the monomer solution from 5 % to 50% w/w (dry weight), these concentrations values being referred to that of the EDOT and NMPy monomers. As a typical procedure MMT was exfoliated in de-ionized water at neutral pH, being sonicated for 10 min with an ultrasonic generator. The resulting solution was stirred for 1day using a magnetic stirrer. After this, a 10 mM EDOT solution in distilled water with 0.1 M LiClO₄ was added to the above exfoliated clay solution, and stirred for 20 h in a frozen environment (ice).

A. Materials

3,4-Ethylenedioxythiophene (EDOT) and N-methylpyrrole (NMPy) monomers and MMT (bentonite) were purchased from Aldrich and used as received LiClO₄ analytical reagent grade from Aldrich was stored in an oven at 80^oC before use in the electrochemical trials.

B. Electrochemical characterization

The electroactivity, which indicates the ability to store charge, and electrostability, which reflects the variation of the electroactivity upon successive oxidation and reduction cycle, of both the PEDOT homopolymer and the PEDOT-MMT nanocomposite were determined by cyclic voltammetry (CV). According to this procedure, electroactivity increases with the similarity between the anodic and cathodic areas of the first control voltammogram, while electrostability decreases with the oxidation and reduction areas of successive control voltammograms. A scan rate of 100 mVs⁻¹ was used in all cases. The thickness of the films was estimated according to Schirmeisen and Beck using the mass of polymer deposited in the electrode, m_{pol} which was obtained using the $m_{pol} = Q_{pol} \left(\frac{m}{Q} \right)$, where Q_{pol} is the polymerization charge (in milicoulombs per square centimeter) consumed in the generation of each layer and $\frac{m}{Q}$ the current productivity, the latter being previously determined for PEDOT (0.875mgC⁻¹).

Although the latter value was obtained in acetonitrile, we studied the kinetic for the oxidation –polymerization of EDOT in aqueous solution to check that it can be rightly applied in the current work. The volume of polymer

deposited in the electrode (V_{pol}) Was obtained using the values of m_{pol} and the density previously reported for PEDOT. Accordingly, the thickness of each layer was calculated considering the surface of polymerization (S_{pol}), which is the surface of the electrodes and V_{pol} . The electrical conductivity of oxidized poly (EDOT-co-NMPy) and ml-PEDOT/PNMPy systems were measured using the sheet resistance method.

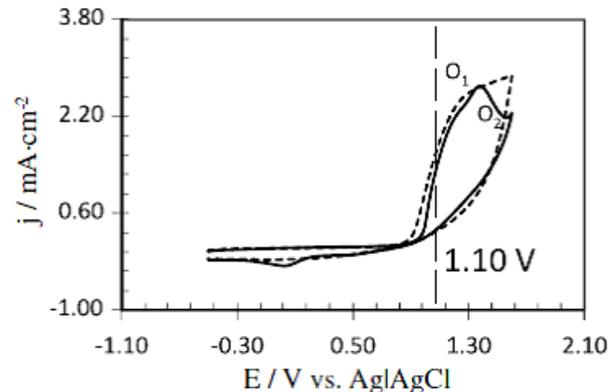


Fig 1. control voltammograms for the oxidation of a 10mM of 3,4 ethylenedioxythiophene (EDOT) solution in distilled water.

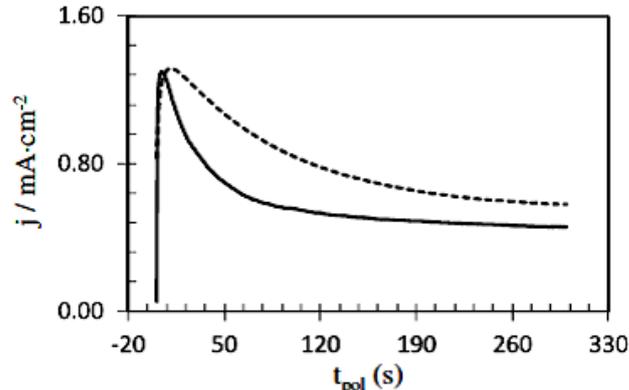


Fig 2. Chronoamperograms recorded for the oxidation of a 10 mM 3,4-ethylenedioxythiophene (EDOT) .oapplyconstanpotential of 1.10 V .

III. RESULTS AND DISCUSSION

A. Preparation of multilayered films

Recently, the oxidation-polymerization processes of EDOT, NMPy and EDOT:NMPY mixtures were studied by cyclic voltammetry (CV) in the potential range of -0.5 V to 1.80 V using a 10mM monomer solution of acetonitrile with 0.1 LiClO₄ and a 4 cm² steel AISI 316 electrode. Multilayered films were generated using a layer by layer electrodeposition procedure. Initially, a layer of PEDOT was generated by immersing the working electrode for a period of time of 100 s in a 10mM EDOT solution of acetonitrile with 0.1 M LiClO₄. Next, the electrode coated with the PEDOT monolayer was immersed in a new cell filled with a 10 mM NMPy solution of acetonitrile with 0.1 M LiClO₄. A layer of PNMPy, which was deposited on top of previously generated PEDOT forming a bilayer, was produced by applying a constant potential of 1.40 V during the same time. After this the electrode coated with the bilayer was immersed in a new cell filled with an EDOT solution identical to that described above.

After applying a potential of 1.40V during 100 s, a 3-layered PEDOT/PNMPy/PEDOT film was obtained.

Multilayered films containing different layers were obtained by using the same procedure to generate layers of PEDOT and PNMPy. The thickness increases with every two additional layers. This is fully consistent with the values determined for single layers of PEDOT and PNMPy generated using identical experimental conditions, which were 1.25 and 1.75 μm and 1.75 μm , respectively. On the other hand, it should be mentioned that the adherence between PEDOT and PNMPy layers was excellent in all cases. Fig 3 shows the three chronoamperograms obtained for the generation of a PEDOT/PNMPy/PEDOT 3 layered system.

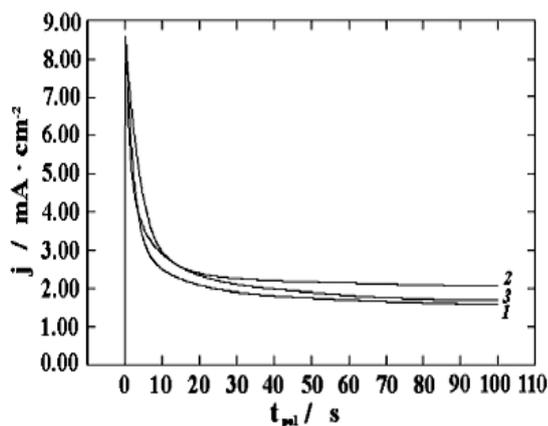


Fig 3. Chronoamperograms recorded at 1.40 V during the generation of a PEDOT/PNMPy/PEDOT 3-layered systems at 25°C.

B. Electrochemical control of multilayered films

Fig. 4 compares typical control voltammograms of pure PEDOT films and ml-PEDOT/PNMPy systems prepared as described above. It is worth noting that single-component PEDOT films were generated by CA at 1.40 V during a polymerization time of $n \cdot 100$ s where n is the number of layers of the corresponding ml-PEDOT/PNMPy systems. Thus polymerization time of 300, 500, 700 and 900 s were used for comparison with the 3, 5, 7 and 9-layered systems, respectively. The cathodic and anodic areas of the ml-PEDOT/PNMPy and pure PEDOT increase considerably with the number of layers and polymerization time, respectively, this rising being specially large and evident for the multilayered systems. Accordingly, it can be stated that the ability to store charge of ml-PEDOT/PNMPy increases significantly with the number of layers. Although this ability is also enhanced when the polymerization time of the single-component PEDOT films grows from 300 to 900 s, the improvement is considerably larger when the number of layers of ml-PEDOT/PNMPy systems increases from 3 to 9. These results reflect a favourable coupling effect between the electroactivity of PEDOT and PNMPy layers. Furthermore, it should be noted that the voltammograms of ml-PEDOT/PNMPy and PEDOT becomes less defined when the number of layers and the polymerization time, respectively increase.

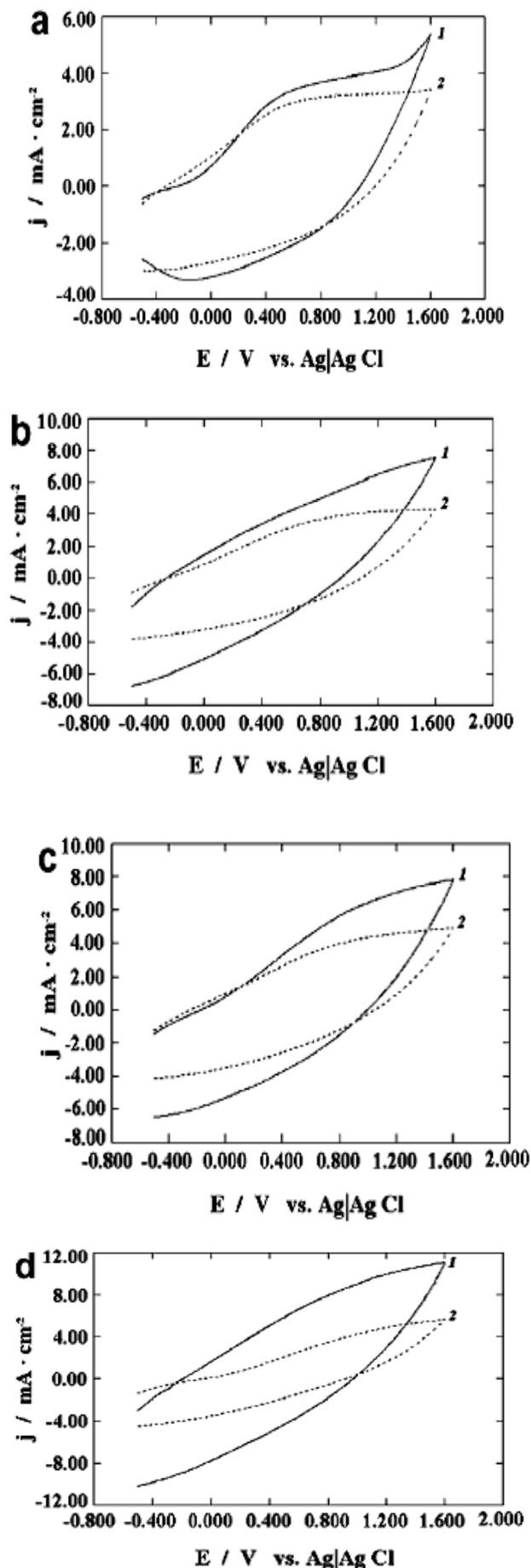


Fig 4. Control voltammograms for the oxidation of multilayered systems with n layers and pure PEDOT generated using a polymerization time of $n \cdot 100$ s: (a) $n=3$; (b) $n=5$; (c) $n=7$; (d) $n=9$.

The electrochemical stability of the ml-PEDOT/PNMPy systems has been investigated by applying consecutive oxidation-reduction cycles. Results have been compared with those obtained for pure PEDOT generated using a polymerization time of $n \cdot 100$ s, where n is the number of layers of the multilayered system used for the comparison. In all cases, the electrochemical stability of the ml-PEDOT/PNMPy was higher than that of pure PEDOT, the difference between such two systems growing with number of layers of the multilayered systems. The stability of single-component PEDOT films is very remarkable at potential lower than 1.80 V. However, when they are oxidized at higher potential, the oxidation and reduction areas of successive control voltammograms decrease gradually. This is reflected in Fig 5, which shows six consecutive oxidation-reduction cycles recorded in the potential range from -0.5 to 2.00 V for single-component PEDOT films generated applying 1.40 V during 300 s. Comparison of the results obtained using different polymerization times reveals that the reduction in the electroactivity of pure PEDOT is less apparent when the polymerization time is higher than 300 s. Indeed, the electrochemical stabilities of the samples generated using 500, 700 and 900 s are almost identical, as was found by determining the cathodic and anodic areas of the corresponding voltammograms. Accordingly, pure PEDOT behaves asymptotically after polymerization time of 500 s, even although the mass of polymer deposited in the electrode, i.e. the thickness of the film, increases with the polymerization time. For comparison, Fig. 6a displays six consecutive oxidation reduction cycle recorded in the same potential range of a PEDOT/PNMPy/PEDOT 3-layered film. As can be seen, in a system with such small number of layers, the oxidation and reduction areas also decrease with the number of cycles. However, a completely different situation was found for the 5-layered systems, which was found to be more stable than pure PEDOT produced using a polymerization time of 500 s. This is illustrated by consecutive oxidation-reduction cycles recorded for the 5-layered system (Fig. 6b).

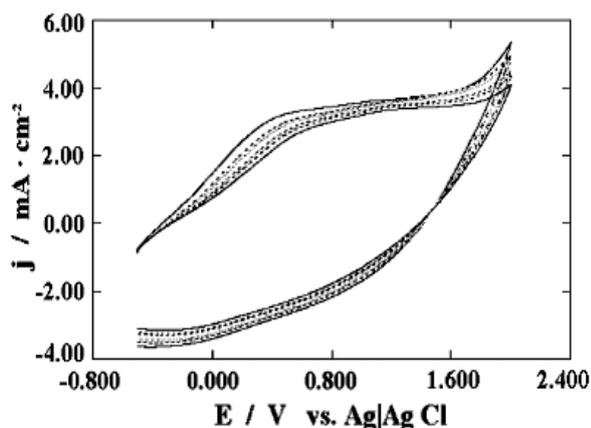


Fig.5. control voltammograms for six consecutive oxidation reduction cycles of pure PEDOT on 4 cm^2 steel electrode in acetonitrile with 0.1 M LiClO_4 , at 100 mVs^{-1} and 25° C . initial and final potential -0.5 V ; reversal potential: 2.00 V . The film was generated by CA at 1.40 V during a polymerization time of 300 s.

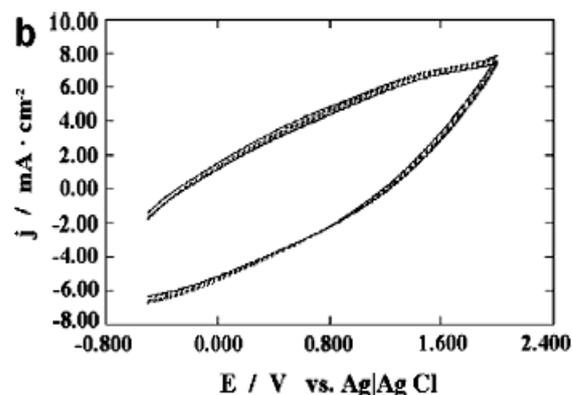
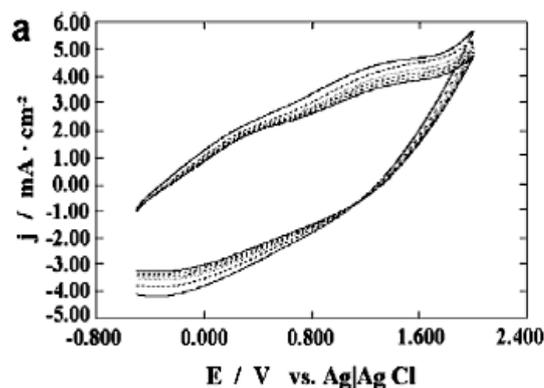


Fig. 6. Control voltammograms for six consecutive oxidation-reduction cycles of ml-PEDOT/PNMPy systems with n layers (a) $n=3$; (b) $n=5$.

Fig 7 and 8 compares the SEM pictures recorded using $\times 350$ and $\times 7500$ enlargement, respectively, of pure PEDOT and 3-layered films yielded using $t=30$ s. As can be seen, the surface of the PEDOT layer in the ml-PEDOT/PNMPy system shows long folds that produce a profile with significant irregularities with respect to pure PEDOT (Fig. 7). On the other hand, high degrees of roughness and porosity are detected in the surface of the two materials, even though SEM images obtained with the largest number of enlargement (Fig 8) suggest that the roughness is higher in the multilayered film than in the single-component one. In order to verify this, AFM was applied to determine from a quantitative point of view the average roughness of pure PEDOT and 3-layered films yielded using $t=30$ s.

Fig. 9 shows the surface of these two materials. As can be deduced from the scales of the two images, the height of the protuberances detected in pure PEDOT is significantly higher than that obtained for the multilayered system. Furthermore, the average roughness determined for pure PEDOT and 3-layered films is 214 and 96 nm, respectively. These results indicate that no quantitative conclusion about the material with a higher degree porosity and roughness can be extracted from SEM pictures, more precise AFM measurement being necessary for this purpose. These results do not allow relate the specific surface, and by extension the incorporation and subsequent diffusion of dopant anions, with the relative electroactivities found for the two materials.

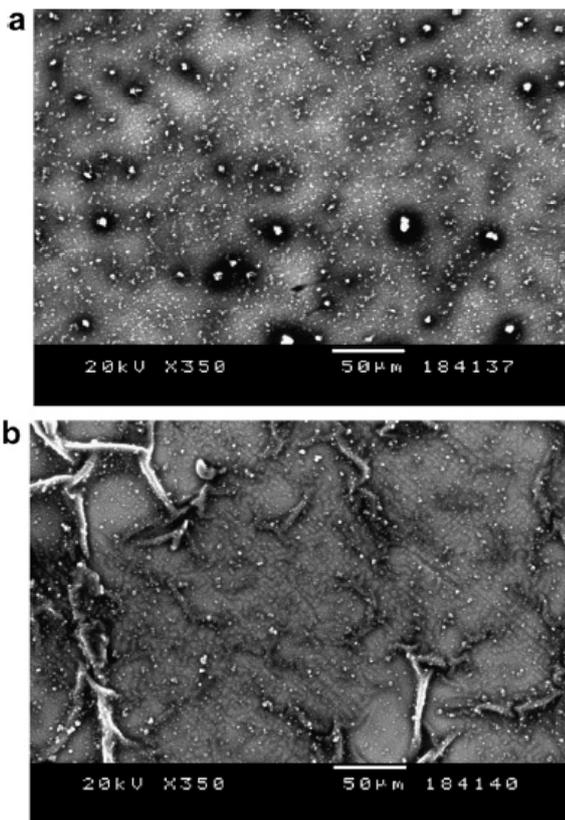


Fig. 7. SEM micrographs (X 350 enlargement) of (a) single-component PEDOT and (b) 3-layered PEDOT/PNMPy films prepared using a total polymerization time of $t=30$ s

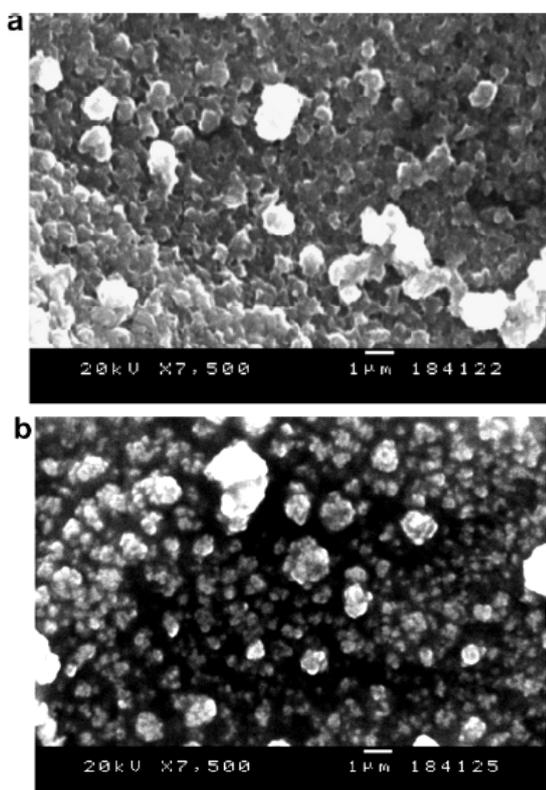


Fig. 8. SEM micrographs (X 7500 enlargement) of (a) single component PEDOT and (b) 3-layered PEDOT/PNMPy films prepared using a total polymerization time of $t=30$ s.

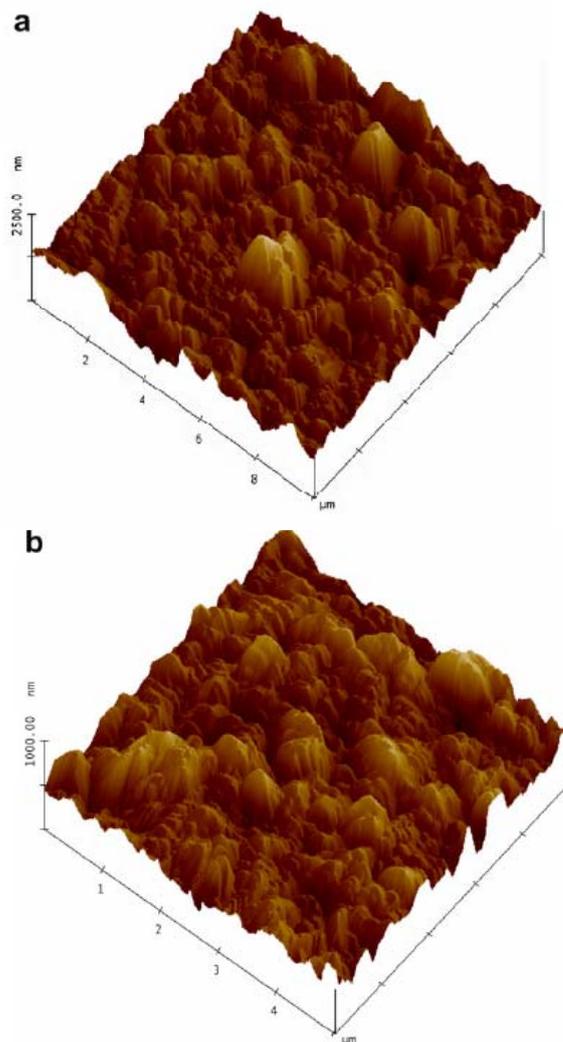


Fig. 9. AFM images of (a) single component PEDOT and (b) 3-layered PEDOT/PNMPy films prepared using a total polymerization time of $t=30$ s.

C. morphology of multilayered films

2D AFM images of films obtained using $t=10, 20, 30, 40$ and 50 s displayed in Fig 10, which also shows the substrate steel surface before deposition for comparison. The surface of the film shows well-defined sharp peaks after the first 10 s of electropolymerization, which is consistent with the initial formation of independent PNMPy molecules that grow perpendicularly to the surface of the steel electrode. Significant changes are detected in the surface of the film yielded using $t=20$ s. The peaks are broad and densely distributed, while the roughness is approximately twice the value determined for the films generated using $t=10$ s. The latter feature is clearly consistent with the linear growing of the molecule chains. Furthermore, the broadness of the peaks is explained by the formation of aggregates, i.e. packing of the molecular chain that grow perpendicular to the steel surface that are probably stabilized by the perchlorate dopant anions.

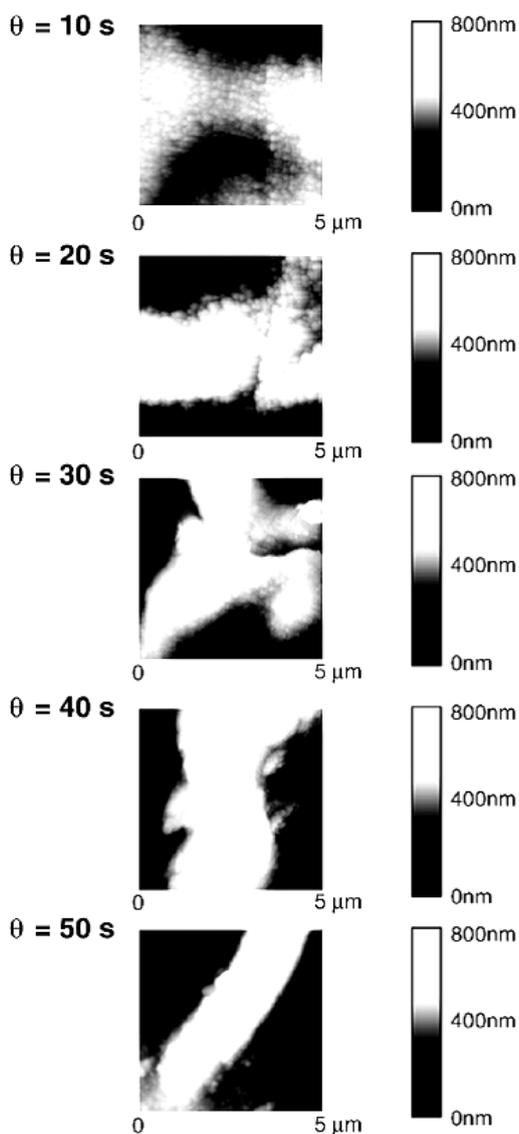


Fig. 10 . 2D AFM images of the substrate steel surface before deposition (top) and the PNMPy films prepared using a total polymerization time of 10, 20, 30, 40 and 50 s.

AFM images and electrochemical results obtained for pedot films are displayed in Fig 11.

As can be seen, films electrogenerated using $t=10$ and 20 s show similar surface topology.

This consists on relatively dense distributions of sharp peaks that are grouped forming small and well-defined clusters that resemble mountain ranges.

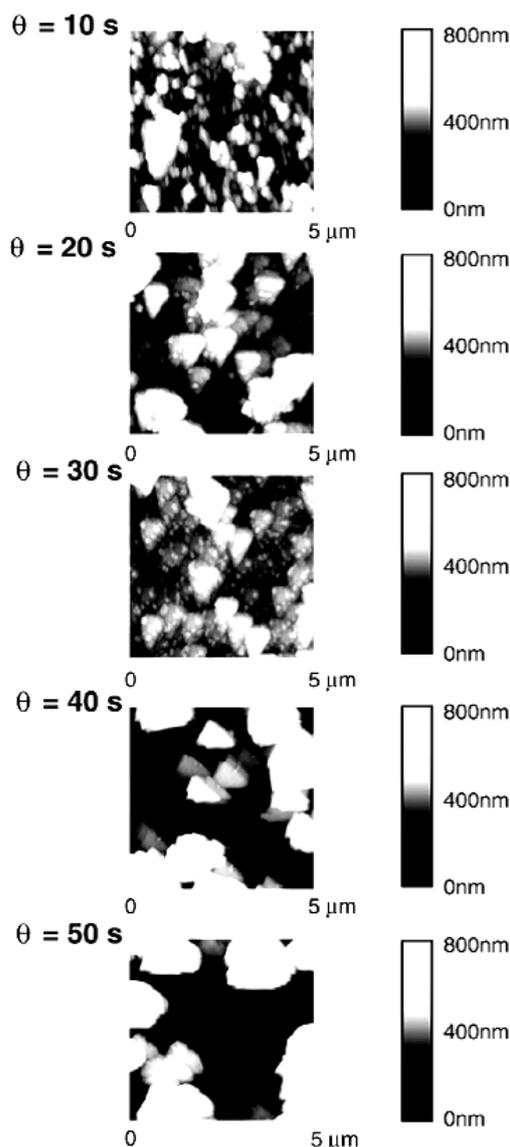


Fig. 11. 2D AFM images of PEDOT films prepared using a total polymerization time of 10, 20, 30, 40 and 50 s.

D. Electrical conductivity of multilayered films

The influence of the number of layers in the electric properties of ml-PEDOT/PNMPy system has been also subject of study. Unfortunately, the films generated using polymerization time of 100 s per layer were very fragile and, in all cases, they broke when separated from the electrode. In order to determine the electric conductivity of ml-PEDOT/PNMPy, new films with better mechanical properties of the 3, 5 and 7- layered systems were generated layer-by-layer using the procedure described above but with larger polymerization times. In this way the thickness of the layers, especially of that directly attached to the electrode, was large enough to separate the films without breaking them.

IV. CONCLUSION

Films of ml-PEDOT/PNMPy containing different layers have been prepared using a layer by layer electrodeposition technique. Electrochemical studies indicate that the ability to store charge of multilayer films is higher than that of single-component PEDOT films. Furthermore, this ability increases significantly with the number of layers in

multi-PEDOT/PNMPy . The electrochemical stability of ml-PEDOT/PNMPy is considerably higher than the of poly(EDOT-co-NMPy) evidencing that films constituted by alternated layers of PEDOT and PNMPy present significant advantages with respect to copolymers of EDOT and NMPy . Indeed, the electrochemical stability of multilayered systems, which increases with the number of layers, is higher than that of pure PEDOT, which does not depend on the thickness of the film after a threshold value. Finally, the conductivity of multilayered systems has been found to be slightly lower than that of PEDOT, which is the most conductive system investigated in this work. However, the copolymers present low conductivity , which are closer to that PNMPycloser to that of PNMPy than to that of PEDOT. The overall of the results evidence that ml-PEDOT/PNMPy systems present significant advantages, especially in terms of electrochemical properties , not only with respect poly(EDOT-co-NMPy) but also with respect PEDOT.

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