



## Macromolecular Nanotechnology

## Clay incorporation at the dielectric layer of multilayer polymer films for electrochemical activation



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## ABSTRACT

The electrochemical properties (i.e. electroactivity, electrostability and specific capacitance) of 3-layered films made of poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(N-methylpyrrole) (PNMPy) arranged alternatively have been activated by incorporating exfoliated montmorillonite (MMT) at the intermediate layer. 3-Layered films were prepared using the layer-by-layer electropolymerization technique, whereas the previously exfoliated clay was incorporated into PNMPy layer using an *in situ* polymerization procedure. The influence of the clay on the properties has been investigated as function of the thickness of the internal and external PEDOT layers, which has been controlled through the polymerization time. Micrometric PEDOT layers have been found to exert a template effect on the topography and morphology of the intermediate PNMPy or PNMPy-MMT layer, this effect being practically inexistent for films with nanometric PEDOT layers. The ability to exchange charge reversibly (electroactivity) and the electrochemical stability (electroactivity) of films with MMT at the intermediate layer are higher than those of films without clay, these effects being more pronounced for films with micrometric PEDOT layers. The influence of the thickness is even more remarkable in the specific capacitance, which decreases rapidly with increasing thickness. The clay at the intermediate layer improves the specific capacitance of micrometric films and, most importantly, protects the capacitive behavior against electrochemical degradation in all cases. In summary, the presence of MMT in the intermediate PNMPy layer makes 3-layered films sensitive to the dielectric breakage, activating their electrochemical and capacitive properties. Such clay-induced effects are more pronounced for films made of micrometric PEDOT layers.

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## 1. Introduction

Conducting polymers (CPs) have recently attracted considerable scientific and technological interest because of their interesting electrical, electrochemical, optical and magnetic properties [1–4]. Within this context, the high ability of CPs

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to store charge (i.e. electrical energy) deserves special consideration since such electrochemical activity (electroactivity) plays an important role in electronic devices, such as capacitors and supercapacitors. The latter are electrochemical capacitors that can be used as charge storage devices to provide higher power density, energy density, and longer life cycle than batteries and conventional capacitors [5–9]. Therefore, improvement of electrode materials to achieve supercapacitors with better electrochemical properties is a challenge.

Poly(3,4-ethylenedioxythiophene), hereafter abbreviated PEDOT, is one of the most important CPs due to its high conductivity (up to 500 S/cm for as prepared films and up to 2000–4000 S/cm after treatment with acids), good thermal and chemical stability, fast doping–dedoping processes, and excellent biocompatibility [10–16]. Moreover, PEDOT presents excellent electrochemical behavior in terms of electroactivity and electrostability [17,18]. In recent years, significant efforts have been devoted to improve the intrinsic capacitive properties of PEDOT [11,19]. Within this context, composites based on transition-metal oxides (e.g.  $\text{MnO}_2$ , NiO,  $\text{Fe}_3\text{O}_4$  and  $\text{V}_2\text{O}_5$ ) embedded into the PEDOT matrix showed better capacitive properties than pure PEDOT [20–23]. Other approaches were based on the preparation of nanocomposites of PEDOT and nanotubes [24–26].

A few years ago we used the layer-by-layer (LbL) electrodeposition technique to prepare multilayered conducting systems based on PEDOT and poly(N-methylpyrrole) (PNMPy) layers arranged alternatively [27,28], hereafter abbreviated ml-PEDOT/PNMPy. These multilayered materials showed better electrochemical properties and a higher ability to store charge than each of the two individual CPs. Moreover, such improvement increased with the number of layers, which was attributed to a synergistic effect produced by the favorable interaction between the PEDOT and PNMPy layers at the corresponding interfaces. Thus, the coupling between PEDOT and PNMPy was found to be, in terms of enhancement of the electrochemical properties, significantly more positive in multilayered films than the interaction between the two monomers in the corresponding copolymers [29]. In addition, the specific capacitance, SC, of ml-PEDOT/PNMPy (SC = 90 F/g) was found to be significantly higher than that of pure PEDOT (SC = 41 F/g), even though both were lower than those reported for PEDOT-inorganic hybrid nanocomposites [8,30].

The development of CP-clay nanocomposites is a field of increasing interest due to the important technological applications of these materials [9,31–35]. Some hybrid PEDOT-clay nanocomposites based on montmorillonite (MMT), which is a smectite group mineral clay that belongs to the general family of 2:1 layered silicates, have been reported in the last few years [9,33,36–38]. Since exfoliated CP-MMT nanocomposites usually have better properties (e.g. stiffness, strength and barrier property) than the intercalative ones, it is rationalized that the higher the degree of exfoliation, the greater the enhancement of these properties [39]. Unfortunately, PEDOT-MMT nanocomposites prepared by Letaïef et al. [33] and Rajapakse et al. [36] showed an intercalative structure rather than the more desirable exfoliated organization. Han and Lu [37] reported exfoliated PEDOT-MMT nanocomposites that were obtained by *in situ* polymerization in aqueous media using modified clays. Although the thermal stability of such nanocomposites was better than that of pristine PEDOT, their electrical conductivity was very low (i.e. from  $10^{-7}$  to  $10^{-2}$  S/cm) [37]. More recently, some of us reported an *in situ* electropolymerization procedure to prepare exfoliated PEDOT-MMT nanocomposites using non-modified clays, the electrical conductivity of the produced materials ranging from 1 to 4 S  $\text{cm}^{-1}$  [37]. Differences in the electrical conductivity of such two classes of PEDOT-MMT nanocomposites were attributed to both the efficiency of the dopant agent (i.e. the oxidant power of  $\text{LiClO}_4$  is higher than that of the organic dopant agents used in Ref. [37]) and the length of PEDOT chains, which is larger when prepared by anodic polymerization. Also, we extended our *in situ* polymerization procedure to the preparation of PEDOT-MMT nanocomposites with relatively high clay concentrations (i.e. of even 50% w/w – dry weight – in the monomer solution) [9]. The specific capacitance of supercapacitors prepared using an asymmetric PEDOT/PEDOT-MMT configuration (SC = 116 F/g) was found to be 40% higher than that obtained for the symmetric PEDOT/PEDOT configuration (SC = 82 F/g) [9].

In this work, we explore the structural, electrochemical and capacitive properties of 3-layered films made of two layers of PEDOT and an intermediate layer of PNMPy-MMT. The properties of this clay-containing multilayered system, hereafter denoted PEDOT/PNMPy-MMT/PEDOT have been compared with those of the corresponding free-clay system, denoted PEDOT/PNMPy/PEDOT. The influence of the thickness, which has been controlled through the polymerization time ( $\theta$ ), on the clay-containing and clay-free 3-layered systems has been also investigated. Structure–property relationships have been established using morphological and topographical analyses based on scanning electron microscopy (SEM) and tapping-mode atomic force microscopy (AFM).

## 2. Methods

### 2.1. Materials

3,4-Ethylenedioxythiophene (EDOT), N-methylpyrrole (NMPy) and acetonitrile were purchased from Sigma-Aldrich (Spain) and used as received. Montmorillonite (MMT) was purchased from Sigma-Aldrich (Spain) and used after sonication as described later. Anhydrous lithium perchlorate ( $\text{LiClO}_4$ ) was purchased from Sigma-Aldrich (Spain) and was stored in an oven at 80 °C before use in the electrochemical trials. All chemicals were analytical reagent grade.

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