Organic Electronics 14 (2013) 1483–1495

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Nanometric ultracapacitors fabricated using multilayer of conducting polymers on self-assembled octanethiol monolayers

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ARTICLE INFO

Article history:
Received 28 December 2012
Received in revised form 1 March 2013
Accepted 3 March 2013
Available online 27 March 2013

Keywords:
Alkanethiols
Conducting polymers
Multilayered films
Self-assembled monolayer
Ultracapacitors

ABSTRACT

Symmetric ultracapacitors have been fabricated considering nanometric 3-layered films made of alternated layers of poly(3,4-ethylenedioxythiophene) (external and internal layers) and polypyrrole (intermediate layer) deposited on steel uncoated and coated with octanethiol self-assembled monolayer. The highest electrochemical and capacitance parameters (i.e. electroactivity, doping level, stored charge, specific capacitance, Coulomb efficiency, energy density and power density) correspond to the ultracapacitor derived from the assembly of 3-layered films deposited on pre-treated steel. Thus, the interface separating the octanethiol monolayer and the most internal layer of the 3-layered film produces a very favorable interaction, which promotes important electrochemical benefits similar to those found for the interfaces in conventional multilayered films. Moreover, the pre-treatment of the steel electrode enhances the roughness and porosity of the film deposited on it, transmitting this effect layer-by-layer. Structural and morphological characteristics, which have been characterized using scanning electron microscopy and atomic force microscopy, have been related with the electrochemical and capacitance properties of the ultracapacitors.

1. Introduction

During the last decades conducting polymers (CPs) have emerged as promising materials in different fields such as electronics, biotechnology and nanotechnology [1–3]. Among CPs, poly(3,4-ethylenedioxythiophene), hereafter, abbreviated PEDOT (Scheme 1), has received special attention due to its excellent electrochemical and thermal properties, high conductivity, good environmental stability in its doped state, mechanical flexibility, relative ease of preparation, and fast doping–undoping process [4–6]. According to these interesting properties, PEDOT has been applied as biomaterial [7–9], solar cell [10,11], electrochromic device [12], hole injection layer in organic light-emitting diodes [13], mechanical actuator [14], electrochemical energy storage [15] and biosensor [16]. The applicability of PEDOT was initially limited by the serious problem of processability that typically affects thiophene-based CPs, its combination with poly(styrenesulfonic acid) (PSS) to form complexes in water emerging as an interesting alternative to overcome this drawback (i.e. PSS keeps PEDOT segments

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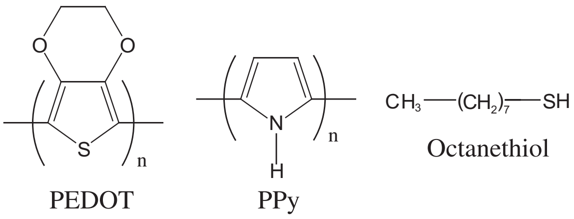
http://dx.doi.org/10.1016/j.orgel.2013.03.010



Scheme 1.

dispersed in the aqueous medium) [4–6]. Thus, although PEDOT–PSS complexes are not truly water soluble, they form stable easy-to-process microdispersions.

The layer-by-layer (LbL) procedure, which was initially reported by Decher and coworkers [17–19], is considered as a very powerful strategy for the fabrication of CPs that can be directly used for applications (i.e. without intermediate steps for their transformation). This methodology permits to build multilayered composites from solutions containing electrolytes of different charge, even though other strategies have been developed to deposit multilayered systems (e.g. spin-coating, Langmuir–Blodgett and vapor techniques). The versatility, inexpensiveness and easiness of the LbL technique have allowed to fabricate biosensors, solar cells, and electrochromic devices [20–23]. In particular, the electrochemical LbL technique has been used to prepare multilayered systems formed by PEDOT and PSS, which have been widely studied and successfully applied in different technological fields [24–27].

In recent studies we developed an alternative approach based on electrochemical techniques to produce multilayered systems formed by two, or even more, CPs [28–31]. This methodology, which is schematically described in Fig. 1a, was used to construct multilayered systems based on PEDOT and different polypyrrole (PPy, Scheme 1) derivatives (e.g. poly(N-methylpyrrole) and poly(N-cyanoethylpyrrole)). In this procedure a substrate is immersed into an initial solution containing the first monomer and the electrolyte (e.g. 3,4-ethylenedioxythiophene, abbreviated EDOT, and lithium perchlorate, respectively). Application of potentiostatic methods leads to the formation of the first

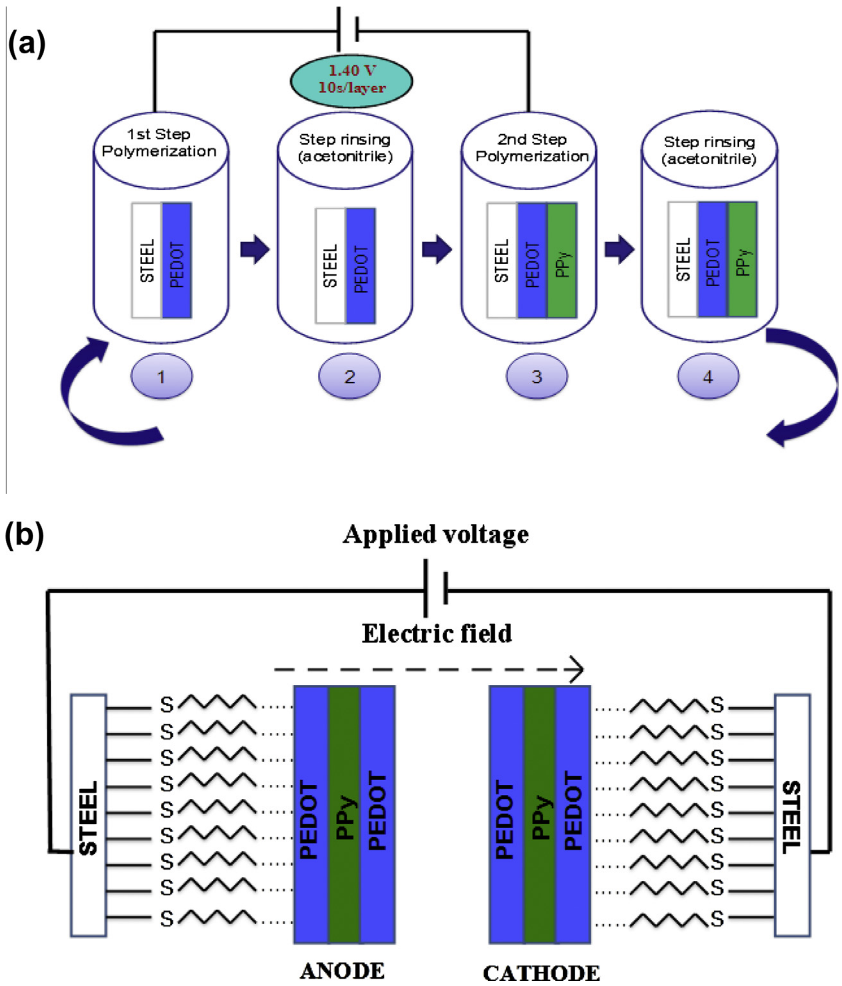


Fig. 1. (a) Scheme of the electrochemical layer-by-layer process used to prepare 3-layered films. (b) Scheme of the ultracapacitor constructed using two identical electrodes of PEDOT/PPy/PEDOT deposited steel treated with octanethiol (3-layered/C_8-SH ultracapacitor).