



Poly(pyrrole) films efficiently electrodeposited using new monomers derived from 3-bromopropyl-*N*-pyrrol and dihydroxyacetophenone—Electrocatalytic reduction ability towards bromocyclopentane



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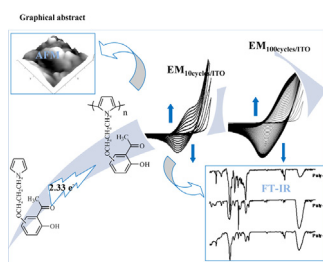
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HIGHLIGHTS

- Elaboration of new modified electrodes electrodeposited on GC and ITO-electrodes.
- Poly(pyrrole) films, analyzed by FT-IR, confirm the presence of functional groups.
- ITO–Poly(pyrrole) films were explored by SEM, EDX and AFM spectroscopy.
- Interesting catalytic properties have been also investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 June 2013

Received in revised form 11 January 2014

Accepted 15 January 2014

Available online 28 January 2014

Key-words:

Anodic oxidation

Poly(pyrrole) films

SEM and AFM

Dispersive energy X-ray spectroscopy

Copper complex

Electrocatalytic reduction

ABSTRACT

Three monomers 6-[3'-*N*-pyrrolpropoxy]-2-hydroxyacetophenone (1), 5-(3'-*N*-pyrrol propoxy)-2-hydroxyacetophenone (2) and 4-(3'-*N*-pyrrolpropoxy)-2-hydroxyacetophenone (3) were synthesized and their poly(pyrrole) films were electrodeposited on glassy carbon (GC) and Indium tin oxide (ITO) conductive electrodes by anodic oxidation in acetonitrile solutions containing $n\text{-Bu}_4\text{N}^+\text{ClO}_4^-$ (TBAP 0.1 M). These films, currently called modified electrodes (noted ME), were obtained by the successive cycling at the appropriate potentials. These films contain chelating sites such as carbonyl group bearing the phenolic function which could play an important role in coordination chemistry. The electrodeposited poly(pyrrole) films on the ITO conductive glass electrodes offer some analytical advantages as the optical and electronic properties. Consequently, these new materials of electrodes were characterized by cyclic voltammetry while the morphology of these films was studied by FT-IR spectroscopy, scanning electron microscopy (SEM), dispersive energy X-ray spectroscopy and atomic force microscopy (AFM). The AFM studies show that the morphology of polypyrrole (PPy) films, electrodeposited on ITO surface, depends on the specific structure of the compound deriving from the monoalkylated dihydroxyacetophenone 1, 2 and 3. The coordination of copper was performed by electroreduction reaction in presence of ligand (3) and copper acetate salt. The resulting electrode material was tested towards the electrocatalytic activity in the reduction of bromocyclopentane.

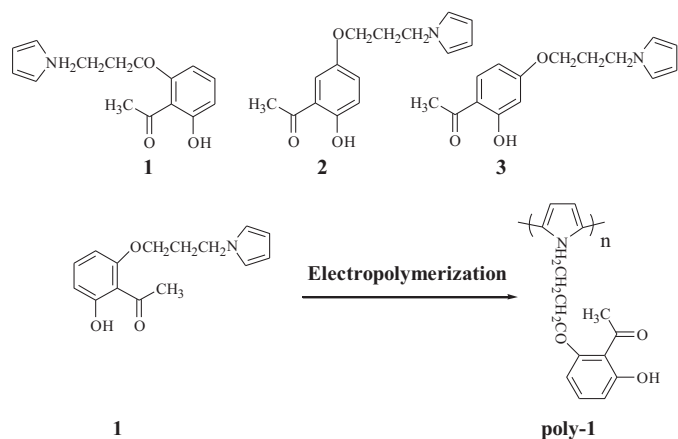
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1. Introduction

Chemically modified electrodes have been the subject of considerable attention since their first conception there is more than thirty years ago [1]. The pioneers of this novel art consisting to

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Scheme 1. Reaction way leading to the formation of the poly(pyrrole) films.

elaborate new materials of electrode was proposed by Lane and Hubbard [1] and then by Miller [2]. In this case, the first observations showed that the main difficulties appear in the loss of the electrochemical signal, caused by the leaching of the modifier agent from the modified electrode surface to the electrolytic solution. Therefore, a new approach consisting to bind the electroactive molecule to the electrode surface by a covalent grafting was proposed. However, since 1979 another class of monomers such as aniline [3], thiophene [4] and pyrrole [5] were described in the literature as the easier electropolymerizable units. These entities can be polymerized either chemically [6,7] or electrochemically [3–5] to give the π -conductors conjugated polymers on which the target molecule could be covalently grafted to avoid its leaching.

For this reason, we have recently undertaken the monoalkylation of dihydroxy-acetophenone derivatives using bromide compounds containing a pyrrole unit. In this respect, it is worthy to note that this topic is of a great interest for the elaboration of modified electrodes [8] by anodic oxidation of pyrrole monomer at moderate potential values about 1 V/(Ag⁺/Ag). Hence, some of these pyrrolic monomers **1**, **2** and **3** are illustrated by Scheme 1.

These monomers were electropolymerized by anodic oxidation as above mentioned to give their corresponding modified electrodes. This experimental procedure is one of the more successful methods allowing the formation of ultrathin polymeric films owing to the easy colometry control, its simplicity and its good reproducibility [9]. Hence, the conducting polymers such as poly(aniline), poly(thiophene) and poly(pyrrole) constitute a new class of materials opening the way to several applications in the fields of energy storage, analysis, sensors... [10,11]. This study is a continuation of our recent papers [12] focusing to the elaboration of modified electrodes containing the complexes of transition metals, currently applied in heterogeneous electrocatalysis such as the dioxygen activation according the P450 cytochrome model [13,14]. The catalytic properties of the films are most often characterized by changes in resulting voltammograms particularly in the case of the reduction of molecular oxygen [15], carbon dioxide [16] and the alkyl halides [17].

In addition, these conducting polymers are also the promising materials due to their good conductivity, environmental stability and their uncomplicated preparation as films or powder [18]. Their electrodeposition was reported on many substrates such as gold (Au) [19], platinum (Pt) [20], glassy carbon [21], iron (Fe) [22] and semiconducting transparent materials such as indium tin oxide (ITO) and tin dioxide (SnO₂) [23].

In this paper, PPy-organic semiconductor materials (poly-**1-3** films) were electrochemically electrodeposited on two different conductive surfaces, GC and ITO using successive cycling method.

These modified electrodes were characterized by cyclic voltammetry (CV), FT-IR spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). In addition, they were also employed for the catalytic electroreduction of alkyl halides.

2. Experimental

All chemicals were of reagent grade and were used without further purification. The solvents were dried before use with the appropriate drying reagents. FT-IR spectra were recorded on PerkinElmer 1000-FTIR spectrophotometer. Electrochemical experiments were performed with a Voltalab 40, Potentiostat Galvanostat controlled by microcomputer. Thus, the cyclic voltammograms were recorded using a 10 ml-three-electrode cell in CH₃CN solutions containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and 0.001 M of the monomer. The electrodes were polished by diamond paste and rinsed with acetone and acetonitrile. Working electrode was a disc of glassy carbon (diameter 3 mm) or ITO-glass (SOLEMS) with 100 nm of thickness and 50 Ω as resistance while the counter electrode was a platinum wire, and the reference was a saturated calomel electrode (SCE). ITO-electrodes were prepared in the suitable size (electroactive area = 1 cm²). The modified electrodes were characterized by electrochemical methods, spectrometric techniques, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM images, X-ray detector (EDX) analyzer and elemental analysis were carried out at Rennes1- University, France". The surface morphology of these electrodes poly-**1**, **2** and **3** films were explored with a nanoscope IIIa Multimode Atomic Force Microscopy (Laser of 670 nm, Pacific Nanotechnology, Nano-RTM AFM) at room temperature.

The synthesis of these monomers 6-[3'-(*N*-pyrrol)propoxy]-2-hydroxyacetophenone (**1**), 5-[3'-(*N*-pyrrol)propoxy]-2-hydroxyacetophenone (**2**) and 4-[3'-(*N*-pyrrol)propoxy]-2-hydroxyacetophenone (**3**) was carried out by reacting the pyrrolic bromo compound with the suitable dihydroxyacetophenone according the literature [24,25].

Monomers **1**, **2** and **3** were easily electropolymerized by anodic oxidation to yield the corresponding poly-**1**, poly-**2** and poly-**3** films either on glassy carbon or on ITO-electrodes. The poly-**1** films were electrodeposited by successive scanning between –0.3 and +1.3 V/SCE using acetonitrile solutions containing 10^{–1} M TBAP and 10^{–3} M of monomer **1**. This successive scanning shows the growth of polypyrrole films on the surface of GC-electrode. So, Fig. 1, given below, shows obviously the growing of the poly-**1** films as π -conjugated conductor polymer. After 10 scan, the obtained modified electrode was transferred to another cell containing a fresh solution without monomer **1**. Before the transfer, this modified electrode was copiously rinsed with bi-distilled water and then with acetonitrile. For the electrodeposited films of poly-**2** and poly-**3** films, they are polymerized strictly under similar experimental conditions in the potential ranges (+0.100–+1.800) and (+0.000–+1.700) respectively. As well, similar poly(pyrrole) films were electrodeposited on optically transparent electrodes like those of ITO using separately the three monomers **1**, **2**, and **3** by applying the same experimental protocol, described above for the GC-electrodes using different potential range.

3. Results and discussion

The monomers **1**, **2** and **3** were studied by cyclic voltammetry investigating the potentials ranging from –1.500 V to +2.000 V on glassy carbon electrodes. So, the voltammogram obtained for **1** shows two oxidation waves observed at $E_{p_{a1}} = +0.850$ and $E_{p_{a2}} = +1.580$ V/SCE. Concerning **2**, the first wave appears at $E_{p_{a1}} = +0.813$ and $E_{p_{a2}} = +1.118$ V/SCE. As for the monomer **3**,

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