

## Full Length Article

# Plasma functionalized surface of commodity polymers for dopamine detection



Georgina Fabregat<sup>a,b</sup>, Joaquin Osorio<sup>a</sup>, Alejandra Castedo<sup>b,c</sup>, Elaine Armelin<sup>a,b</sup>,  
Jorge J. Buendía<sup>a,b,c</sup>, Jordi Llorca<sup>b,c,\*</sup>, Carlos Alemán<sup>a,b,\*</sup>

<sup>a</sup> Departament d'Enginyeria Química, E.T.S. d'Enginyeria Industrial de Barcelona, Universitat Politècnica de Catalunya, Diagonal 647, 08028, Barcelona, Spain

<sup>b</sup> Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona, E-08028, Spain

<sup>c</sup> Institut de Tècniques Energètiques, E.T.S. d'Enginyeria Industrial de Barcelona, Universitat Politècnica de Catalunya, Diagonal 647, 08028, Barcelona, Spain

## ARTICLE INFO

## Article history:

Received 9 November 2016

Received in revised form

12 December 2016

Accepted 17 December 2016

Available online 19 December 2016

## Keywords:

Conducting polymer

Dopamine

Plasma discharge

Polyethylene

Polythiophene

Surface activation

## ABSTRACT

We have fabricated potentially generalizable sensors based on polymeric-modified electrodes for the electrochemical detection of dopamine. Sensitive and selective sensors have been successfully obtained by applying a cold-plasma treatment during 1–2 min not only to conducting polymers but also to electrochemically inert polymers, such as polyethylene, polypropylene, polyvinylpyrrolidone, polycaprolactone and polystyrene. The effects of the plasma in the electrode surface activation, which is an essential requirement for the dopamine detection when inert polymers are used, have been investigated using X-ray photoelectron spectroscopy. Results indicate that exposure of polymer-modified electrodes to cold-plasma produces the formation of a large variety of reactive species adsorbed on the electrode surface, which catalyse the dopamine oxidation. With this technology, which is based on the application of a very simple physical functionalization, we have defined a paradox-based paradigm for the fabrication of electrochemical sensors by using inert and cheap plastics.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Dopamine (DA), a member of the catecholamine family, acts as an important neurotransmitter in mammalian central nervous system modulating vital functions, such as voluntary movement. It is involved in motor and cognitive functions. In Parkinson's disease patients, DA releasing (dopaminergic) neurons in the central nervous system are dysfunctional or dying, causing a lack of dopamine in the target territories, which leads to impaired motor functions [1–3].

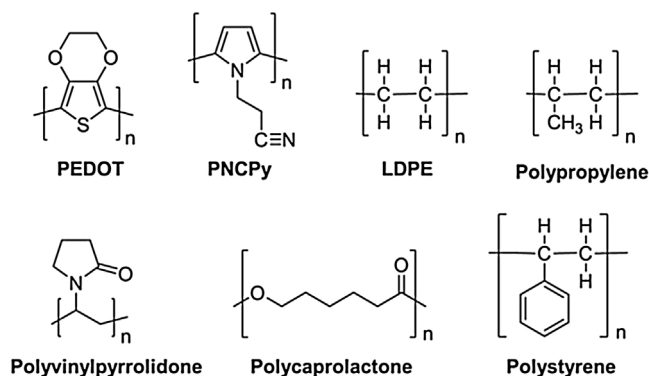
Among the potential methods developed for DA detection in the past decades, electrochemical techniques exhibit their pre-dominance due to important advantages, such as rapid response, low cost and high sensitivity [4]. However, there are some limitations to measure DA under physiological conditions by common electrochemical methods. The main ones are related with the selec-

tivity towards other species that coexist in the organism, such as ascorbic acid (AA) and uric acid (UA), which oxidize at almost the same potential than DA. Also, the detection of very low levels of DA (10 nM–10 μM) represents a sensitivity challenge. Several strategies using, among others, nanocomposites [5,6], graphene [7,8], conducting polymers (CPs) [9–11], magnetic particles [12,13], or carbon nanotubes [14,15], have been reported in recent publications to overcome such problems. Another interesting strategy is the use of anionic ionomer-coated electrodes, which provides a way to increase the selectivity in the detection of DA, due to discrimination towards negatively charged species, such as the anionic forms of AA and UA [16,17]. Nevertheless, the development of these electrochemical sensors require a large number of steps for fabrication since application of the above mentioned compounds usually requires complex chemical functionalization processes, incorporation of catalytic nanoparticles, processing of the nanocomposites, multi-step synthetic processes, etc [9–17].

The present study reports on the application of cold plasma technologies as a very simple and effective functionalization technique for the preparation of DA electrochemical sensors. More specifically, in this work we show that the treatment of polymeric surfaces in a room-temperature air-discharge plasma, which is a simple and powerful means of surface modification, enables the

\* Corresponding authors at: Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona E-08028, Spain.

E-mail addresses: [jordi.llorca@upc.edu](mailto:jordi.llorca@upc.edu) (J. Llorca), [carlos.aleman@upc.edu](mailto:carlos.aleman@upc.edu) (C. Alemán).



**Scheme 1.** Chemical structure of the polymers studied in this work.

fabrication of DA sensors using not only electrochemically active CPs, as for example poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(*N*-cyanoethylpyrrole) (PNCPy), but also conventional insulating and electrochemical inert polymers, as polypropylene, polyvinylpyrrolidone, polycaprolactone and polystyrene. Accordingly, plasma-based functionalization of polymer-coated electrodes have the potential be used and developed into truly selective and sensitive DA sensors, independently of the nature of the polymer, which is very attractive in terms of fabricating efficient but also cost-effective sensors.

## 2. Experimental

### 2.1. Materials

3,4-Ethylenedioxythiophene (EDOT), *N*-(2-cyanoethyl)pyrrole (NCPy), acetonitrile, anhydrous lithium perchlorate ( $\text{LiClO}_4$ ), DA hydrochloride (3-hydroxytyramine hydrochloride), AA (L-configuration, crystalline), UA (crystalline) of analytical reagent grade were purchased from Sigma-Aldrich (Spain). All chemicals were used without further purification. Phosphate buffer solution (PBS) 0.1 M with pH = 7.4 was prepared as electrolyte solution by mixing four stock solutions of NaCl, KCl,  $\text{NaH}_2\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$ . High-purity nitrogen was used for de-aeration of the prepared aqueous solutions.

### 2.2. Synthesis of conducting polymers

PEDOT and PNCPy (Scheme 1) films were prepared by chronoamperometry (CA) under a constant potential of 1.40 V [18] using a three-electrode two-compartment cell under nitrogen atmosphere (99.995% in purity) at 25 °C. A bare glassy carbon electrode (GCE) with a diameter of 2 mm was used as working electrode while a steel AISI 316 sheet with an area of 1 cm<sup>2</sup> was employed as counter electrode. The surface of the GCE was polished with alumina powder and cleaned by ultrasonication prior to the deposition of the polymer. The reference electrode was an Ag|AgCl electrode containing a 3 M KCl aqueous solution.

All electrochemical experiments were conducted on a PGSTAT302N AUTOLAB potentiostat-galvanostat (Ecochimie, The Netherlands) equipped with the ECD module to measure very low current densities (100  $\mu\text{A}$ –100 pA), which was connected to a PC computer controlled through the NOVA 1.6 software. PEDOT and PNCPy films were obtained using a 10 mM monomer solution in acetonitrile with 0.1 M  $\text{LiClO}_4$  and a polymerization time of 6 and 10 s, respectively.

### 2.3. Preparation of inert polymer-modified GCE

The following inert polymers were considered for this study (Scheme 1): low density polyethylene (LDPE), polypropylene, polyvinylpyrrolidone, polycaprolactone and polystyrene. Inert plastic-modified electrodes were prepared by depositing each plastic dissolved into an appropriate volatile solvent (i.e. chloroform, dichlorobenzene or methanol) onto GCE (i.e. solvent casting). Chloroform (10 mL) was used to dissolve 43 mg of polyvinylpyrrolidone, 46.5 mg of polycaprolactone and 33.5 mg of polystyrene, while dichlorobenzene (10 mL) was used to dissolve 34.4 mg of low density polyethylene (LDPE) and 52.4 mg of polypropylene. Polymer-modified GCEs were prepared by 6  $\mu\text{L}$  of the corresponding polymer solution onto the GCE for solvent evaporation.

### 2.4. Cold plasma treatment

PEDOT-, PNCPy- and inert polymer-modified GCEs were prepared with a corona discharge in ambient atmosphere using a BD-20AC from Electro-Technic Products. The treatment of the polymers was performed using a Spring Tip wire electrode and a voltage of 45000 V at a frequency of 4.5 MHz. After plasma-treatment, modified GCE electrodes were used for DA detection experiments within 24 h. Treatment with the nitrogen-plasma was performed using the same equipment and conditions with the obvious exception that the corona discharge was conducted in a nitrogen atmosphere. This inert atmosphere was created through a continuous nitrogen flow. After finishing the treatment with nitrogen plasma, material were exposed to air for characterization and electrochemical measurements.

### 2.5. Electrochemical measurements for DA detection

Electrochemical detection was carried out by cyclic voltammetry (CV) using the Autolab PGSTAT302N equipment described above. All electrochemical experiments were performed in a glass cell containing 10 mL of PBS 0.1 M (pH = 7.4) at room temperature and equipped with saturated Ag|AgCl as reference electrode and platinum (Pt) wire as counter electrode. Voltammograms were recorded in the potential range from –0.40 to 0.80 V at a scan rate of 50  $\text{mV s}^{-1}$  unless other scan rate is explicitly specified. All the modified electrodes were in contact with the electrolyte solution for 5 min prior to CV measurements.

### 2.6. FTIR and scanning electron microscopy (SEM)

IR absorption spectra were recorded on a FTIR Jasco 4100 spectrophotometer. Samples were placed in an attenuated total reflection accessory (Top-plate) with a diamond crystal (Specac model MKII Golden Gate Heated Single Reflection Diamond ATR). For each sample 32 scans were performed between 4000 and 600  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

The surface morphology of untreated and plasma treated samples was examined by SEM. Samples were mounted on a double-side adhesive carbon disc and sputter-coated with a thin layer of carbon to prevent sample charging problems. Microscopy studies were carried out using a Focused Ion Beam Zeiss Neon40 scanning electron microscope equipped with an energy dispersive X-Ray (EDX) spectroscopy system and operating at 5 kV.

### 2.7. X-ray photoelectron spectroscopy (XPS)

XPS assays were performed on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos MCD-9 detector. The pressure in the analysis chamber was always below 10<sup>–7</sup> Pa. The pass energy of the hemispherical analyzer was set at

Download English Version:

<https://daneshyari.com/en/article/5351097>

Download Persian Version:

<https://daneshyari.com/article/5351097>

[Daneshyari.com](https://daneshyari.com)