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HYBRID ORGANIC-INORGANIC MATERIAL BASED SENSING PLATFORM FOR ENVIRONMENTAL MONITORING OF BIOMARKERS

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Introduction

The monitoring of organic compounds like drugs, pharmaceutical formulations and various chemicals of anthropogenic origin with potential risks of contamination of waters is of increasing interest nowadays. Various analytical methods are currently applied in the detection of these organic pollutants. Amongst them, the spectrometric and chromatographic ones proved high analytical sensitivity and selectivity. Despite this analytical performance, these methodologies require high-cost equipment and sometimes laborious sample treatment procedures. The real-time monitoring of waste waters using portable and cost-effective analytical devices is gaining an increased attention. In this sense, the use of electrochemical sensing platforms based on conventional electrodes or screen-printed electrodes modified judiciously with selective hybrid materials is in progress. In this work, the development, the characterization, and the testing of an electroanalytical sensing platform based on organic polymers and metal nanoparticles containing hybrid material are presented. The sensing platform was characterized by electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy. The incorporation of gold nanoparticles within the sensing material resulted in an increase in the charge transfer capability. The developed sensing platform was successfully tested in the detection of biomarkers like dopamine bearing a catechol moiety as similarly to many organic pollutants of paramount importance in waste waters monitoring. A wide linear working range and a low detection limit for dopamine quantification have been obtained.

Materials and methods

The hybrid material was synthesised in two steps by using a potential scanning approach and a novel method making use of alternate currents (SC). The SC method consists in the application of a selected alternate current over a constant dc current. The hybrid material is composed of polydopamine, PDA, poly(3,4-ethylenedioxythiophene), PEDOT, and gold nanoparticles, AuNPs. The selection of

these pristine materials was aimed to provide an eco-friendly synthesis procedure using water soluble precursors avoiding in this way the use of organic solvents. The novel electrochemical SC method has performed better than the classical ones established on potentiostatic, potentiodynamic, and galvanostatic approaches.
The electrochemical experiments were performed using a potentiostat/galvanostat from Metrohm in the classical 3-electrode system. A glassy carbon disk electrode (d = 3 mm) was used as working electrode, a silver/silver chloride electrode served as reference electrode, and a glassy carbon rod was used as counter electrode. The hybrid material synthesis was accomplished in two steps: firstly, the PDA-PEDOT material was synthesised using the potential scanning approach. In the second step, the gold nanoparticles have been synthesised electrochemically by SC approach using an alternate current applied on a cathodic dc current. The synthesized hybrid organic-inorganic material was characterized by electrochemical techniques.

Results and conclusions
The synthesis of the PDA-PEDOT matrix resulted in the modification of the electrode surface with a high electrical resistance material due to the presence of the formed PDA component. The cyclic voltammograms registered in the solution of the redox probe based on ferro/ferricyanide couple showed the decrease of the anodic and cathodic peak currents due to the presence of the PDA component. However, after the gold nanoparticles electrodeposition, there was a large increase of both the anodic and cathodic peak currents related to the redox probe. This finding underlines the capability of PDA to promote the electrodeposition of metal nanoparticles enhancing in this way the charge transfer capacity of the newly electrodic material. The PDA-PEDOT and PDA-PEDOT-AuNPs based sensing platforms have been investigated in the quantification of dopamine biomarker, which is also used as a drug in different pharmaceutical formulations and could be of interest in the monitoring of waste waters from health care units. The as prepared sensing devices have been tested in buffered aqueous solutions containing various amounts of dopamine biomarker. The analytical parameters of the sensing platforms have been assessed. The PDA-PEDOT sensing platform has displayed a linear response over the range of 4 – 100 μM dopamine, with a detection limit of 3.0 μM dopamine, and a sensitivity of 0.015 μA/μM, respectively. In the case of the PDA-PEDOT-AuNPs sensing platform, the anodic peak current related to the dopamine oxidation has increased linearly with the concentration of the analyte in the range from 1 to 100 μM. A sensitivity value of 0.044 μA/μM was obtained. A low detection limit of 0.34 μM dopamine has been achieved. The PDA-PEDOT-AuNPs sensing platform has achieved a sensitivity that is three times greater than that of the PDA-PEDOT sensing platform, and it also displayed a lower detection limit. These results have demonstrated the advantages provided by gold nanoparticles in the design of novel electrochemical sensing platforms. The PDA-PEDOT-AuNPs based electroanalytical sensing device could be exploited in the detection of other organic compounds bearing a catechol moiety as other many organic pollutants offering in this way a large number of potential environmental applications.