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Conductometric sensor array based on electropolymerized porphyrinoids

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Summary:

Metallocorrole derivatives are a versatile class of coordination complexes successfully exploited in different applications, ranging from medical to environmental fields, due to their peculiar tuneable properties. Herein, a novel class of conductometric sensing films has been deposited directly onto the interdigitated electrodes by the electropolymerization of metallocorroles and metalloporphyrins. Remarkably, not only can the chemical sensing properties be tuned by choice of central-coordination metal, but the electropolymerization protocol can also modulate the conductive nature of polymers (n- or p-type). Finally, the fabricated sensors were tested towards a large family of volatile compounds and gases, finding high sensitivity to nitrogen oxide also in the presence of a high humidity environment.

Keywords: Conductometric sensor, porphyrinoids, polymer, electropolymerization, electrode, gas.

1. Introduction

Corroles and related macrocycles are widely employed in the field of chemical sensors, where they are used as sensing materials for optical, electrochemical, and conductometric transducers [1]. Concerning the employment in conductive sensors, these porphyrinoids are not used by themselves because supramolecular assemblies of these molecules are scarcely conductive, but they are combined with conductive materials such as graphene oxide, carbon nanotubes, or conductive polymers. A novel approach to building conductive sensors with these sensing materials is proposed here, and it consists of producing porphyrin or corrole conductive polymers by an electropolymerization approach. This technique has been mainly utilized in the case of porphyrins that present electron-active substituents, with a typical example represented by the electrochemical oxidation of tetrakis(4-aminophenyl) porphyrins, which leads to the formation of different types of linkers as the phenazine bridge [2]. On the other hand, although corroles present many appealing features in the field of chemical sensing, the polymerization of these macrocycles is scarcely reported. Here, we synthesize and investigate the sensing properties of polycorroles and polyporphyrins as conductive sensors. Thus, we exploit the role of peripheral functional groups, the influence of the coordinated metal and the role of electropolymerization protocol on the final sensing film properties.

2. Materials and methods

The metal complexes of corroles and porphyrins are synthesized according to literature methods [3,4]. The polymers are prepared by electropolymerization of porphyrinoids directly onto interdigitated electrodes (IDE) (see Figures 1A, 1B, and 1C). The polymerization is performed by cyclic voltammetry (CV) or chronoamperometry (CA). The IDEs are immersed in a solution of precursor monomers (1 mM) in CH_2Cl_2 containing 0.1M supporting electrolyte tetrabutylammonium perchlorate, $TBAClO_4$. The influence of the number of scanning cycles on the optical and sensing properties of the film is evaluated.

Finally, conductive organic sensors are allocated in a chamber connected to a mass flow controller system to deliver the desired gas concentrations in synthetic air. Different concentrations of nitric oxide (NO), carbon monoxide (CO), molecular hydrogen (H_2), and carbon dioxide (CO_2) are tested. The resistances of sensors are measured at 1 sample/s with a multichannel multimeter connected to a computer; relative changes in responses have been considered as features, and data analysis is performed in Matlab®.

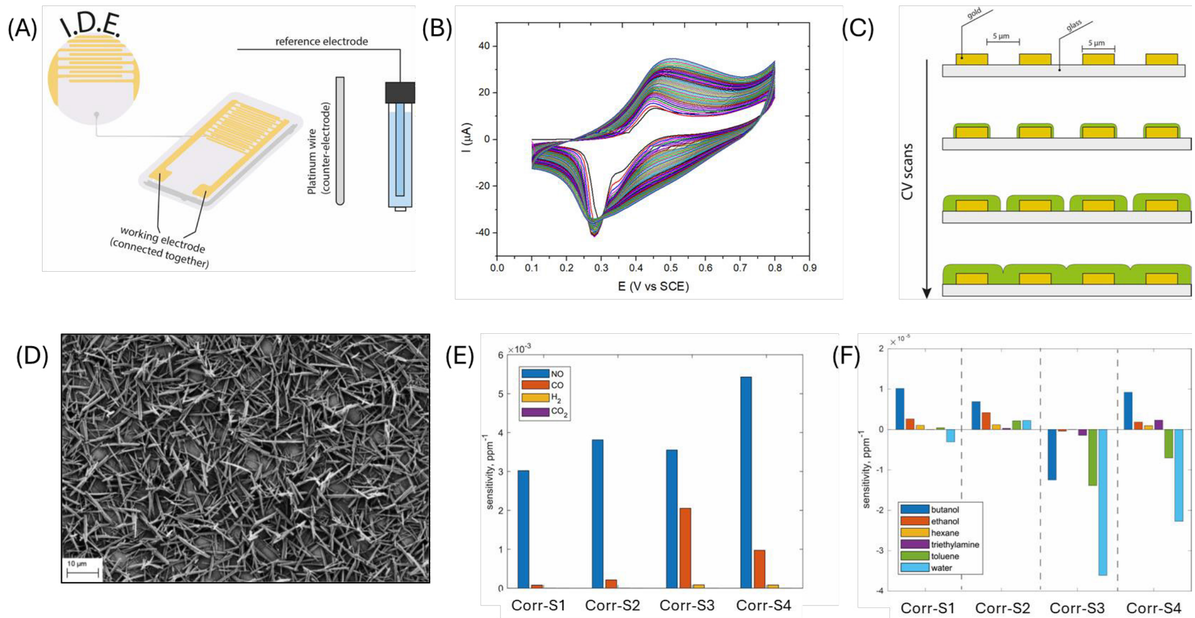

Fig. 1. A) Set-up for sensor fabrication via cyclic voltammetry. B) Typical cyclic voltammogram upon polymer formation. C) Mechanism of polymeric film growth and electrode connection. D) SEM image of polycorrole film. E) Selectivity of polycorrole films; tuning the sensing properties to obtain a high selective sensor to NO is possible. F) As well it is possible to tune the selectivity toward VOCs to produce a conductometric e-nose

3. Result and discussion:

The conductive polymers are formed via the oxidation of peripheral anilino groups of the monomeric precursors and consecutive coupling to the second monomer molecule. The continuous increase of the anodic current amplitudes with repeated potential scans evidences the growth of a conductive polymeric film onto the substrate (Figure 1B). The films have been characterized by spectroscopic techniques (UV-Vis), Scanning Electron Microscopy (SEM, Figure 1D), and Electrochemical Impedance Spectroscopy (EIS). The sensing performances of the most promising materials have been investigated by testing gases (NO, CO, H_2, CO_2) and volatile compounds (such as humidity, alcohols, and hydrocarbons). Remarkably, we found out that the electropolymerization protocol can influence the nature of the resulting polymers and, the selection of p- or n-type semiconductor film formation. This outcome has been evidenced by the behavior of sensors toward oxidizing and reducing gas. The conductive polymer based on [5,10,15-(4-aminophenyl) corrolato] copper showed very high sensitivity to NO (with a detection limit in the order of tens of ppb, see Figure 1E) and negligible sensitivity variations to this compound under environmental relative humidity changes. This first outcome suggests this kind of sensor's potential role for detecting NO in human breath for medical applications.

Second, we produce a sensor array to investigate the possibility of realizing a conductometric electronic nose based on porphyrinoids polymers. The results showed the capability of a minimal set of sensors to correctly group and recognize both tested VOCs and gases (selectivity pattern modulation is reported in Figure 1F). This may be a great breakthrough for applying porphyrins and corroles since they are scarcely applied in conductometric sensors, which can be considered the cheapest and easiest way to miniaturize a class of sensors. Finally, the possibility of modulating the semiconducting nature of this material may open the way to the fabrication of more sophisticated sensors based on non-linear organic electronic elements.

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