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Histamine detection using functionalized porphyrin as electrochemical mediator

Détection de l'histamine par l'utilisation d'une porphyrine fonctionnalisée comme médiateur chimique

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ABSTRACT

This study reports on deposition of asymmetrical substituted *meso*-phenyl porphyrin, 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (CPTPP) thin films by matrix-assisted pulsed laser evaporation (MAPLE) on screen-printed electrodes, aiming for histamine detection. Raman spectrometry confirmed that CPTPP chemical structure was preserved in MAPLE-deposited thin films at 200 mJ/cm^2 laser fluence. Atomic force microscopy topography revealed that MAPLE-deposited thin films have a better coverage on the working electrode made of carbon compared to the ones obtained by dropcasting. Cyclic voltammetry demonstrated that CPTPP is an appropriate mediator for histamine detection in trichloroacetic acid solution. We proved that MAPLE serves as a soft technique in fabrication of porphyrin thin films and patterns.

Mots-clés:
Porphyrine
Couches minces
Évaporation laser assistée par matrice
Médiateur électrochimique
Électrochimie de l'histamine

SOMMAIRE

Cet article traite du dépôt de couches minces, par évaporation laser assistée par matrice (MAPLE), de 5-(4-carboxyphényl)-10,15,20-triphénylporphyrine (CPTPP) substituée asymétriquement. Les couches minces ont été déposées sur des électrodes imprimées, avec comme objectif la détection de l'histamine. La spectroscopie Raman a confirmé que la structure chimique de la CPTPP a été préservée dans les couches minces déposées par MAPLE avec une fluence laser de 200 mJ/cm^2. La topographie AFM a révélé une meilleure couverture de l'électrode de carbone par MAPLE par rapport au *dropcast*. La voltamétrie cyclique a démontré que la CPTPP est un médiateur approprié pour la détection de

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l'histamine dans une solution d'acide trichloracétique. On montre que MAPLE est une technique douce pour la fabrication de couches minces et de motifs de porphyrine.

1. Introduction

Histamine is an important biogenic amine present in many foods, vegetables, and fruits. It acts as a chemical messenger in biological systems [1–3]. When food is not processed and packed in hygienic conditions, the amounts of histamine and all biogenic amines can increase to toxic levels. The meat freshness is related to the level of biogenic amines (histamine, cadaverine, and putrescine to name few [4]). For histamine, the caution level is 50 ppm, whereas the maximum accepted levels range from 200 ppm (in EU) to 500 ppm (USA), respectively [5]. Such a low level of detection requires advanced functional materials with high sensibility/selectivity in chemosensor science. Traditionally, high performance liquid *chromatography* (HPLC) mass spectrometry is used to analyze the biogenic amines with precolumn or postcolumn derivatization [1,6,7]. The electrochemical methods, inexpensive and less time-consuming in analysis, still have to overcome the high oxidation potential and all polyamines that are considered electroinactive in aqueous solutions [8]. For instance, the histamine has the oxidation potential ∽1.2 V versus standard calomel electrode in 0.1 M phosphate-buffered solution (pH = 7) at a glassy carbon or boron-doped diamond electrode [9]. These values are close to the water oxidation, with respect to the carbon electrode oxidation that induces a high background current. There are three approaches in designing electrochemical sensors for biogenic amine detection: (1) mediator-less electrode with large window potential such as boron-doped diamond films or oxides with transfer of oxygen atoms from H_2O to the analyte oxidation [6,10]; (2) enzyme-modified electrode (amino-oxidases or horseradish peroxidase) [11,12] where the oxidation potential reduces down to +700 mV versus Ag/AgCl; and (3) chemically modified electrode with different sensitive layers, nanoparticles, and so forth [13,14]. The chemically modified electrodes with porphyrins and metalloporphyrins have opened a new approach in sensing of biogenic amines taking into account their ability in molecular recognition for different analytes [15–18]: (1) Porphyrins have a large window potential on average 2.2 V between oxidation and reduction potentials [19,20]. (2) The oxidation potential is close to the oxidation potentials of the biogenic amines, favorable to design a porphyrin-based screen-printed electrode (SPE). (3) They could be bonded to the electrode (carbon paste, glassy carbon, carbon nanopowders, etc.) via carboxyl or hydroxyl groups during surface treatment [21,22]. (4) Porphyrins are known as building blocks for a large class of biomolecules, biocatalysts with extensive applications in life processes, and in sensing. For example, chlorophyll fluorescence is used for monitoring CO_2 uptake by earth vegetation [23] or new optoelectronic devices in hybrid combinations with other biomolecules [24,25]. (5) Low solubility in water to allow for the use of acidic or basic water solutions as electrolyte with different biomolecules. (6) The dications of free base porphyrins (generated in acidic electrolyte solutions) have a high affinity for the electron-donating molecules reducing their oxidation potentials or amplifying the electron transfer to the electrode surface [15].

There are few porphyrin-related reports for biogenic amine sensing [26]; to date, there has been no optimized couple, chemically modified electrode–appropriate electrolyte, that could initiate the electrochemical oxidation of biogenic amines in a potential window less than 1 V. In this respect, we propose to explore the histamine sensing using a novel asymmetrical substituted *meso*-phenyl porphyrin, namely, 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (CPTPP) thin films deposited on an SPE by matrix-assisted pulsed laser evaporation (MAPLE) [27,28]. MAPLE technique has been enabled to transfer complex molecules onto a substrate at a specific laser fluence, preserving the conformational and molecular structure, thus maintaining the intrinsic properties [29] including, in this case, the sensing capability [30–32]. The electrolyte consists of aqueous trichloroacetic acid (TCA) solution. TCA is used in standard HPLC methods for derivatization of biogenic amines, acting as an electron acceptor. The molecular complex TCA–histamine has a high electronegativity, favorable for both the improved electron transfer and CPTPP oxidation. This work shows that the histamine is not directly electro-oxidized, rather the CPTPP oxidation is improved by TCA–histamine complex.

2. Experimental section

2.1. Materials and methods

Sensitive layer consists of asymmetrical substituted *meso*-phenyl porphyrin, CPTPP, synthesized and characterized similar to previously reported [33–35]. In text, H_2TPP–*p*-COOH (Fig. 2) will be used also for discussions in Section 3.3. H_2TPP– refers to the free base tetraphenylporphyrin macrocycle, whereas –*p*-COOH represents the *p*-carboxyphenyl as the only functional substituted group on *meso* position of the porphyrin periphery.

The SPE (SPE-110, DropSense) contains three electrodes: (1) a working electrode (WE), which is a carbon disc with 4 mm diameter; (2) a counter electrode ring at 1 mm distance from WE; and (3) a Ag ring pseudoreference electrode. SPE-110 is convenient for working with maximum 50 μL volume (Fig. 3 inset).

For comparison, two SPEs are fabricated: (1) SPE with CPTPP dropcasted over WE from a solution of 1% CPTPP in

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