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Functionalized porphyrin conjugate thin films deposited by matrix assisted pulsed laser evaporation

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ABSTRACT

We report on the deposition of nanostructured porphyrin-base, 5(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin thin films by matrix assisted pulsed laser evaporation onto silicon substrates with screen-printed electrodes. AFM investigations have shown that at 400 mJ/cm^2 fluence a topographical transition takes place from the platelet-like stacking porphyrin-based nanostructures in a perpendicular arrangement to a quasi-parallel one both relative to the substrate surface. Raman spectroscopy has shown that the chemical structure of the deposited thin films is preserved for fluences within the range of 200–300 mJ/cm^2. Cyclic voltammograms have demonstrated that the free porphyrin is appropriate as a single mediator for glucose in a specific case of screen-printed electrodes, suggesting potential for designing a new class of biosensors.

1. Introduction

Porphyrins are tetrapyrollic systems whose derivatives are interesting for potential applications in chemistry, biology and medicine. They can be used as photosensitizers for photodynamic therapy [1,2], DNA binding and cleavage [3], and as catalysts for oxydation and reduction chemical reactions [4,5]. However, one of the most prominent applications of porphyrin derivatives is in the sensors field. Porphyrins have been proposed for various types of sensors with signal transduction based on vibration, fluorescence and electrical resistance and/or capacitance. Ref. [6] reviews the use of modified porphyrins with quartz microbalances demonstrating a broad selectivity. Resistive–capacitive sensors based on porphyrin derivatives have been tested and proven functional as temperature, humidity, and illumination sensors [7]. A sensor based on the variation of fluorescent properties of lipophillic porphyrins and metalloporphyrins was efficient in detecting Hg^{2+} in water [8].

When used as the sensing receptor in a sensor, porphyrin is usually deposited as a thin film. The most common techniques used for synthesis of such films are spin coating [9,10], sol–gel [11], Langmuir–Blodget [12] and electropolymerization [13]. Matrix assisted pulsed laser evaporation (MAPLE), a method based on the laser ablation of organic materials from a composite frozen target [14,15] has been used to fabricate metalloporphyrin (Co-, Mn-, and Zn-porphyrin) thin films [16,17]. In this work, we have applied MAPLE method to test availability of free-porphyrin structure, namely 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin, as thin film on screen-printed electrodes (SPE) as a free enzyme glucose amperometric sensors with a large range of detection.

2. Experimental

2.1. Materials

In this work, we used a mixed substituted A_3B porphyrin, namely 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin (CPPOPP) (Fig. 1). It was obtained based on previously reported methods [18,19] by condensing a mixture of pyrrole and two appropriately substituted benzaldehyde, 4-carboxylmethylbenzaldehyde and 4-phenoxybenzaldehyde, in a particular ratio of 1/3. The methyl ester was hydrolyzed in basic condition folowed by neutralization with diluted HCl. [20]

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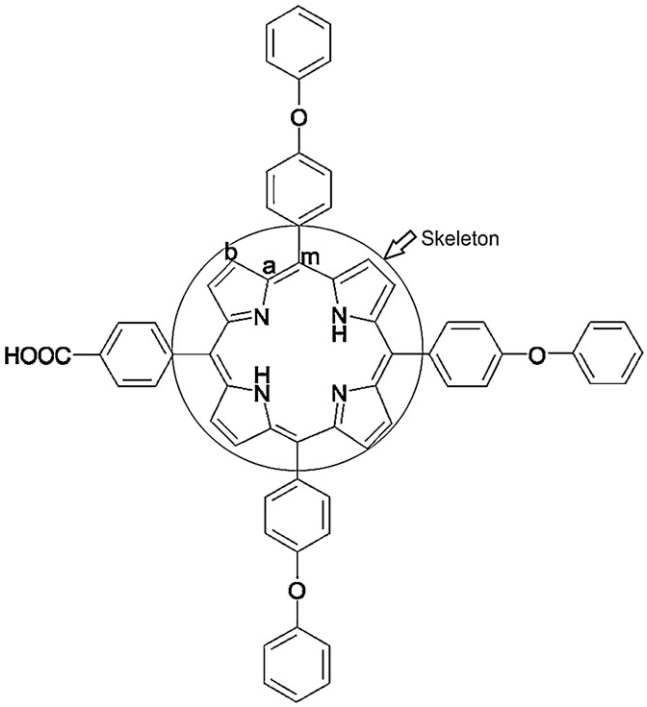

Fig. 1. Chemical structure of 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin (CPPOPP).

Solutions consisting of 1% CPPOPP in chloroform were prepared and tested. All target solutions were poured into a pre-cooled target holder at 173 K and subsequently immersed in liquid nitrogen for 30 min.

Electrolyte support for cyclic voltammetry was phosphate buffer solution (PBS) with pH 7.4. The screen printed electrodes used were based on carbon paste (SPE-110, model DropSense 110) consisting of three electrodes in a planar geometry: (1) a working electrode (WE) that consists of a central carbon paste disc with 0.125 cm^2 area; (2) an auxiliary carbon paste ring electrode (counter) placed at 1 mm distance from WE; and (3) an Ag ring pseudoreference electrode. The solution composition ranged from 0.5 mM to 8 mM glucose in PBS. The glucose concentration used in our experiments has covered the range from hypoglycemia (<4 mM) to hyperglycemia (>7 mM).

2.2. MAPLE experiment

Thin films were fabricated by MAPLE and drop-casting. All MAPLE depositions were conducted using a KrF* (λ = 248 nm, τ_{FWHM} = 25 ns, pulse repetition rate = 10 Hz) laser which was operated at a fluence within the range 200–500 mJ/cm^2, and for 10,000–20,000 pulses. The laser spot area was set at 10 mm^2. The target was rotated at a rate of 0.4 Hz during deposition and the laser beam scanned the entire target surface at an angle of 45°. All MAPLE experiments have been conducted at a base pressure of 30–40 Pa. The substrate-to-target distance was 4 cm. The target was maintained at a temperature of ~173 K by active liquid nitrogen cooling. The thin films were deposited onto one-side polished Si(1 0 0) wafers for Raman and AFM measurements, and carbon paste screen-printed electrodes for cyclic voltammetry. All substrates were ultrasonically cleaned prior to deposition by immersion in ethanol, and then dried in air under UV exposure from a VL-115UV lamp.

2.3. Thin films characterization

CPPOPP-porphyrin thin films were characterized by Raman spectroscopy, AFM and cyclic voltammetry. Raman spectra were recorded by Jasco NRS 3100 apparatus with dual laser beams, 532 and 785 nm, respectively. AFM micrographs were registered by Integrated Platform SPM-NTegra model Prima in semi-contact mode, error mode and phase contrast. Cyclic voltammetry tests were performed with a Voltalb 40 system (Radiometer Analytical) adapted for screen-printed electrodes (SPEs). Both electro-oxidation and reduction potentials have been recorded within the range (−500–500) mV with 100 mV/s scan rate. Normal working conditions of temperature and pressure (25 °C and 1 atm) were kept during all experiments.

3. Results and discussion

3.1. AFM investigations

Typical AFM micrographs of CPPOPP thin films obtained by MAPLE at the laser beam fluence of 200 mJ/cm^2 (a), 300 mJ/cm^2 (b), 400 mJ/cm^2 (c), and 500 mJ/cm^2 (d) are given in Fig. 2. Each inset describes morphological type in detail by edge detection with ImageJ program [21]. At small fluences (200 and 300 mJ/cm^2, insets of Figs. 2a and b), the surface mainly consists of small droplets in platelet-like stacking porphyrin-based nanostructures in perpendicular arrangement onto the substrate surface. At higher fluence

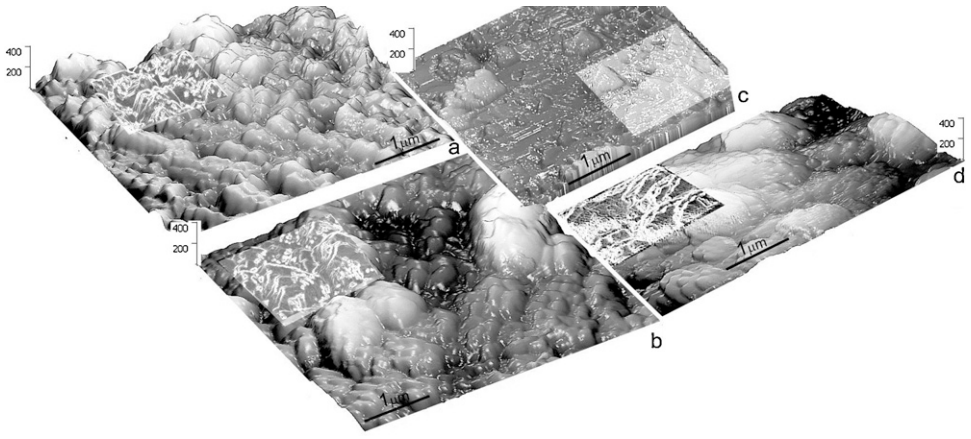

Fig. 2. Typical AFM micrographs of CPPOPP MAPLE-deposited thin films at 200 mJ/cm^2 (a), 300 mJ/cm^2 (b), 400 mJ/cm^2 (c), and 500 mJ/cm^2 (d). The height of AFM profiles is given in nanometers.