



Optical sensing responses of Cr^{III}Cl(TPP)(H₂O)-based coatings obtained by an atmospheric pressure plasma method – Application to the detection of volatile amines

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ABSTRACT

Food spoilage processes are a considerable concern for both the food industry and the consumer, due to financial, food quality and food safety aspects. A primary issue is the prevention/monitoring of the formation of biogenic and volatile amines, such as occurring in fish and in other microbiologically unstable food items rich in proteins, produced by e.g. oxidative decarboxylation of amino acids. One strategy for their monitoring is the development of films with colorimetric sensing properties that are able to indicate food spoilage. The aim of this investigation was the development of a novel metalloporphyrin-based coating allowing the sensitive detection of typical volatile amines, such as trimethylamine (TMA), triethylamine (TEA) and dimethylamine (DMA), which were tested under static and dynamic flow conditions. Aqua(chloro)(5,10,15,20-tetraphenylporphyrinato)chromium(III) in solution at 0.75 mg mL⁻¹ was deposited by means of an atmospheric pressure dielectric barrier discharge deposition method onto 50 μm thick transparent polyethylene terephthalate foils. Produced foils were able to detect volatile amines, as indicated via a hypsochromic shift of the Soret band of 5 nm and differential absorption at 442 nm, at 10 ppm, while detectable static concentrations were higher (ca. 150 ppm). Sensitivity was significantly higher for TMA, TEA and DMA than for NH₃ ($P < 0.001$), and sufficient humidity was a prerequisite for sensitive detection. Results were confirmed by experiments with spoiled fish (mackerel, trout). Further investigations of metalloporphyrins that could act as selective food spoilage indicators amenable to naked-eye detection are warranted.

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1. Introduction

Food freshness indicators incorporated within food packages have become a topic of great interest for the food industry in the past years, including several applications such as detection of CO₂ by chitosan-based detectors [1], pH sensing detectors [2], or oxygen detection by fluorescent dyes [3]. One important area is the development of gas sensing surfaces that result in colorimetric changes which can be easily monitored, even by the consumer without expensive equipment, and such simple yet powerful devices for the inspection and control of food freshness are especially needed. One area where intelligent foils have been employed includes the detection of volatile amines, which are e.g. formed during fish

spoilage, albeit also other protein rich foods such as chicken meat are potential applications [4]. Fish is especially prone to spoilage due to the protein rich matrix, soft tissue, and the microbiota associated with fish skin such as *Pseudomonas* or *Acinetobacter* [5], resulting in the production of a variety of biogenic amines such as cadaverine or histamine, which may cause toxic effects upon consumption such as headache, nausea, and dizziness [6]. Along with the formation of these biogenic amines, volatile amines such as trimethylamine (TMA), dimethylamine (DMA) and others are produced from trimethylamine-oxide (TMAO, e.g. via TMAO-ase or TMAO demethylase), that are, as they appear to correlate with the formation of biogenic amines, also used as spoilage indicators, termed total volatile bases (TVB). One existing example on the market is the Fresh-Tag developed by the food packaging company COX technologies (Belmont, NC) [3], employing a proprietary dye changing colour with increased concentrations of volatile amines.

A potential candidate for the colorimetric detection of amines are metalloporphyrin-based coatings, as these have been reported

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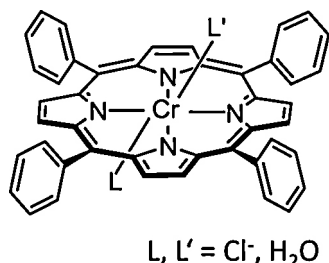


Fig. 1. Molecular structure of aqua(chloro)(5,10,15,20-tetraphenylporphyrinato)chromium(III) employed as the sensing molecule in the plasma deposited thin films.

to possess a high affinity towards these functional groups [7,8]. In addition to the choice of indicator, appropriate coating techniques are crucial in order to assure optimal functionality, such as optimal access of the sensed molecules. The preparation of metalloporphyrin-based gas sensing layers has notably been achieved by spin coating [9,10], vacuum evaporation [10] and glow-discharge induced sublimation [11]. However, such methods are hardly compatible with typical industrial requirements. Moreover, to reduce the problems associated with aggregation, to improve the detection sensitivity and to increase the thermal and mechanical stability of the films, it is more desirable to trap the porphyrins into a suitable matrix [12,13]. The formed composite films are able to keep the sensing metalloporphyrin molecules in the matrix while allowing the diffusion of small volatile organic compounds (VOCs) to be detected through their pores. The synthesis of metalloporphyrin-containing hybrid layers has notably involved the sol-gel deposition of silica films [14] or other wet methods [13,15]. A promising arising technology for the preparation of colorimetric gas sensing surfaces is the atmospheric pressure dielectric barrier discharge (AP-DBD) deposition of metalloporphyrin-based coatings [16]. AP-DBD, which can be readily adapted on a roll-to-roll production line, has been successfully used to immobilise aqua(chloro)(5,10,15,20-tetraphenylporphyrinato)chromium(III) ($Cr^{III}Cl(TPP)(H_2O)$) [16] and (5,10,15,20-tetraphenylporphyrinato)zinc(II) ($Zn^{II}(TPP)$) in porous plasma-polymerised polydimethylsiloxane (pp-PDMS) layers [17]. The pp-PDMS scaffold, which ensured the mechanical and water stability of the layer, allowed the analyte permeation to the sensing molecule. Upon exposure to a saturated triethylamine atmosphere, the Soret and Q bands of the embedded $Cr^{III}Cl(TPP)(H_2O)$ metalloporphyrin did undergo a characteristic hypochromic shift, confirming the interaction of the amine and the dye [16].

In this pursuit, we report the optical sensing capabilities of plasma deposited $Cr^{III}Cl(TPP)(H_2O)$ -based coatings. UV-visible (UV-vis) spectroscopy was used to investigate the integrity of the embedded metalloporphyrins and the optical gas sensing properties of the films. The response magnitude of the samples exposed to triethylamine fluxes at different concentration was related to the layer composition determined by Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). Finally, the developed coated films were tested during fish (Atlantic mackerel and trout) spoilage experiments.

2. Experimental

2.1. Materials and deposition procedure

Unless stated otherwise, all chemicals were obtained from Sigma-Aldrich (St. Louis, MO) and were of HPLC reagent quality or higher, and only 18 M Ω water (Millipore, Billerica, MA) was used. The $Cr^{III}Cl(TPP)(H_2O)$ metalloporphyrin (Fig. 1) embedded

in the plasma polymerised coatings described in this paper were synthesised according to a reported literature procedure [18]. Around 7.5 mg of the $Cr^{III}Cl(TPP)(H_2O)$ metalloporphyrin with a purity of ca. 98% were dissolved in a solution composed of 8 mL of vinyltrimethoxysilane (VTMOS) (98%) and 2 mL of dichloromethane (DCM) (99.8%). The prepared solution was sprayed by an ultrasonic atomising nozzle (Sono-Tek Corporation, Milton, NY) operating at 48 kHz and fed by a syringe driver delivering 0.25 mL min⁻¹ onto 50 μ m thick transparent biaxially oriented polyethylene terephthalate foils (DuPont, Wilmington, DE) or 200 μ m thick 8011 series cold-rolled aluminium foils (Eurofoil, Belvaux, Luxembourg) placed on the moving stage of an AP-DBD reactor [19]. The moving stage speed, set to 6 m min⁻¹, allowed to promptly expose the deposited liquid layer to the plasma discharge in order to polymerise the siloxane precursor. Delay time between the liquid layer deposition and plasma treatment was one second. The AP-DBD reactor consisted of two flat parallel high voltage electrodes (0.7 cm \times 13 cm) covered with alumina and the moving stage as grounded electrode. The discharge gap between the high voltage electrode and the substrate placed on the grounded electrode was maintained at 1 mm. The AP-DBD reactor was fed by a 20 L min⁻¹ nitrogen flow (Air Liquide, Pétange, Luxembourg, 99.999%) containing up to 500 ppm of hexamethyldisiloxane (HMDSO) vapours. The additional siloxane precursor, HMDSO, was injected into the reactor using a bubbler system made of a cylinder and a frit. Three flow rates of nitrogen through the HMDSO bubbler were investigated, 0.0 (for **1**), 0.2 (for **2**) and 0.5 L min⁻¹ (for **3**). The plasma discharge was ignited by means of a 10 kHz sinusoidal signal, chopped by a 1667 Hz rectangular signal. The operating discharge power density was maintained at 0.5 W cm⁻². One hundred passes, corresponding to 14 s effective deposition times, were performed. The deposited film was stored in dry plastic containers at room temperature under light exclusion.

2.2. Thin film characterisation

Scanning electron microscopy (SEM) was performed on a Hitachi SU-70 FE-SEM (Hitachi, Tokyo, Japan). Prior to SEM observations, the non-conductive sample was sputter-coated with 5 nm of platinum to prevent charging and distortion. FT-IR analysis was performed on a Bruker Hyperion 2000 (Bruker, Ettlingen, Germany) spectrometer equipped with a Ge-ATR-crystal. XPS analyses were realised with a Kratos Axis-Ultra DLD instrument (Kratos, Manchester, UK) using a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) at a pass energy of 20 eV. UV/vis absorption spectra of the film exposed to volatile amines were obtained with a DU800 Beckman Coulter UV/vis spectrophotometer (Beckman Coulter, Krefeld, Germany), employing 10 mm quartz type cuvettes (Starna Scientific, Hainault, UK).

2.3. Optical gas sensing experiments

The gas sensing properties of the $Cr^{III}Cl(TPP)(H_2O)$ -based coatings towards triethylamine (TEA) vapours were investigated by a homebuilt gas flow setup and a DU800 Beckman Coulter UV/vis spectrophotometer (Fig. 2). All gas-flow sensing measurements were performed at 20 $^{\circ}$ C in a temperature controlled room. Nitrogen (99.999%), used as a reference and carrier gas, was continuously fed into the measurement chamber at a total flow of 100 mL min⁻¹. Three mass flow controllers (MKS instruments, Andover, MA) were used to control the triethylamine vapor concentration and the relative humidity (RH) of the overall nitrogen gas stream. The triethylamine gas concentration was ensured by passing a clean dry nitrogen flow into a bubbler containing the analyte to be detected. Control of the bubbler temperature, immersed into an isothermal

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