



# Atmospheric pressure plasma polymerisation of metalloporphyrins containing mesoporous membranes for gas sensing applications



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## ABSTRACT

Metalloporphyrins are embedded in an organosilicon matrix by an easily up-scalable atmospheric pressure dielectric barrier discharge method. The integrity of the metalloporphyrins, followed by UV–visible spectroscopy, is successfully preserved and their aggregation prevented. The single molecule properties, rather than the bulk ones, are thus enhanced. Exposure to triethylamine, which reaches the metalloporphyrins through the pores of the organosilicon membrane, led to a shift in the absorption spectrum and confirms the gas sensing potential of such coatings.

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## 1. Introduction

Porphyrin and metalloporphyrin-based colorimetric gas sensors have gained growing interest over the past decade [1,2]. Through changes in their optical absorption spectra, the sensors allow the rapid detection of a wide range of gases including 2,4,6-trinitrotoluene (TNT) [3], NO<sub>2</sub> [4], 4-aminophenol [5], NH<sub>3</sub> and triethylamine [6]. Porphyrin gas sensing layers have been deposited by Langmuir–Blodgett [4], vacuum evaporation [7,8], spin-coating [7,8], and low-pressure plasma techniques [8]. However, to reduce the problems associated with aggregation and to increase the detection sensitivity as well as the thermal and mechanical stability of the films, it is highly desirable to embed the porphyrins into a suitable matrix [9,10]. The composite films formed must be able to keep the sensing porphyrin molecules within the matrix whilst allowing the diffusion of volatile organic compounds to be detected through their pores. Up to date, the synthesis of porphyrin-containing hybrid layers has mainly involved immobilisation in polymers and plasticizers [6,11] or sol–gel deposition [3].

Among the wide range of techniques used to grow smart composite films, atmospheric pressure dielectric barrier discharge (AP-DBD) is a new arising technology. AP-DBD, which generates low-temperature plasmas, offers the opportunity to work with heat-sensitive particles or substrates. In contrast with the limitations in industrial

developments of low-pressure plasmas or sol–gel coatings, AP-DBD can be easily adapted on a coil-to-coil production line and is already used for industrial purposes such as thin film deposition, surface cleaning, wettability or adhesion enhancement [12]. In recent years, the formation of composite layers by AP-DBD has been explored. Hybrid anticorrosion layers have been achieved by dispersing inorganic AlCeO<sub>3</sub> particles in an organosilicon matrix [13]. Whereas luminescent coatings have been obtained by embedding organic lanthanide-containing coordination polymer particles in a SiO<sub>x</sub> matrix polymerised by AP-DBD [14]. However, in both cases the size of the particles (ca. 100 nm) strongly differs from the one of single porphyrin molecules (ca. 1 nm), which are likely to be altered or undergo full disruption of their macrocycle when exposed to inappropriate plasma conditions [15,16]. Moreover, in previous works, aggregation of the particles was not a critical point. However, stacking of the porphyrins within the matrix would possibly hinder the formation of a complex between the coordination site and the analyte [17]. Most importantly, the porosity of the plasma grown layer has to be carefully controlled in order to allow the analyte to reach the coordination site of the metalloporphyrins [18].

In this work, we report, for the first time, the embedment of aqua(chloro)(5,10,15,20-tetraphenylporphyrinato) chromium (III) (Cr<sup>III</sup>Cl(TPP)(H<sub>2</sub>O)) in a mesoporous plasma-polymerised polydimethylsiloxane (PDMS) matrix. The integrity of the metalloporphyrins was assessed by UV–visible (UV–vis) spectroscopy, whilst their dispersion and loading density were determined by secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS), respectively. The morphology of the layer was characterised by scanning electron microscopy (SEM) and the reticulation of the plasma-polymer membrane was evaluated by Fourier-transform infrared spectroscopy (FT-IR). The

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optical sensing capabilities of the layer towards triethylamine were demonstrated.

## 2. Experimental

### 2.1. Materials and deposition procedure

The  $\text{Cr}^{\text{III}}\text{Cl}(\text{TPP})(\text{H}_2\text{O})$  metalloporphyrins embedded in the plasma polymerised coating described in this paper were synthesised according to reported literature procedure [19]. 7.5 mg of the  $\text{Cr}^{\text{III}}\text{Cl}(\text{TPP})(\text{H}_2\text{O})$  metalloporphyrins were dissolved in a solution composed of 5 mL of dichloromethane (DCM) (99.8%) and 20 mL of hexamethyldisiloxane (HMDSO) (98.5%), both obtained from Sigma-Aldrich and used without further purification. The prepared solution was sprayed by an ultrasonic atomising nozzle (Sono-Tek Corporation) operating at 48 kHz and fed by a syringe driver delivering  $0.2 \text{ mL} \cdot \text{min}^{-1}$  onto  $50 \mu\text{m}$  thick transparent polyethylene terephthalate foils (Goodfellow) placed on the moving stage of an AP-DBD reactor [14]. The moving stage speed, set up to  $6 \text{ m} \cdot \text{min}^{-1}$ , allowed to promptly expose the deposited liquid layer to the plasma discharge in order to polymerise the siloxane precursor. Delay between the liquid layer deposition and plasma treatment was one second. The AP-DBD reactor consists of two flat parallel high voltage electrodes ( $1.5 \times 30 \text{ cm}^2$ ) covered with alumina and the moving stage as grounded electrode [20]. The discharge gap between the high voltage electrode and the substrate placed on the grounded electrode was maintained to 1 mm. The AP-DBD reactor was fed by a  $20 \text{ L} \cdot \text{min}^{-1}$   $\text{N}_2$  flow (Air Liquide, 99.999%) containing 500 ppm of HMDSO. The plasma discharge was ignited by means of a 10 kHz sinusoidal signal, chopped by a 1667 Hz rectangular signal [20]. The operating discharge power density was maintained to  $0.1 \text{ W} \cdot \text{cm}^{-2}$ . 100 passes, corresponding to a 30 s effective deposition times, were performed.

### 2.2. Thin film characterisations

SEM was performed on a Hitachi SU-70 FE-SEM. 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 spectrometer equipped with a Ge-ATR-crystal. XPS analyses were realised with a Kratos Axis-Ultra DLD instrument using a monochromatic  $\text{Al K}\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ ) at pass energy of 20 eV. SIMS measurement was performed with a Cameca NanoSIMS 50.  $\text{Cs}^+$  was used as the primary ion and accelerated at 8 kV towards the sample surface ( $-8 \text{ kV}$ ). The primary ion beam was focalised to a spot size of about 100 nm, which corresponds to a 1.5 pA beam current. The fragments studied simultaneously in multicollection mode were  $^{16}\text{O}$ ,  $^{12}\text{C}^{14}\text{N}$ ,  $^{28}\text{Si}$ ,  $^{35}\text{Cl}$ ,  $^{52}\text{Cr}^{14}\text{N}$  and  $^{52}\text{Cr}^{16}\text{O}$ . Images, with a size of  $20 \times 20 \mu\text{m}^2$ , were recorded as a matrix of  $256 \times 256$  points. Mass resolution ( $M/\Delta M$ ) was 3000. UV-visible absorption spectra were obtained with a PerkinElmer Lambda 950 UV-vis-NIR (InGaAs) spectrophotometer equipped with an integrating sphere. The optical sensing capabilities of the plasma polymerised  $\text{Cr}^{\text{III}}\text{Cl}(\text{TPP})(\text{H}_2\text{O})$ -based coating, followed by UV-vis, were investigated by exposing the sample to triethylamine. Before any triethylamine exposure, an optical absorption spectrum of the film was acquired in air over the visible range (350–700 nm). Then, the sample was exposed to saturated triethylamine vapours in a closed cuvette and a second optical absorption spectrum was acquired. The cuvette was further flushed with air for 1 h to recover the sample. In order to highlight the absorption changes, absorbance difference spectra were calculated as the subtraction of the pre-exposure spectrum to the post-exposure spectrum. For comparison, the absorption spectrum of  $\text{Cr}^{\text{III}}\text{Cl}(\text{TPP})(\text{H}_2\text{O})$  in dichloromethane was normalised prior the calculation to the film spectrum.

## 3. Results and discussion

The composite coating described in this paper exhibits a uniform pale green colour and was adherent to the substrate. Neither visually noticeable cracks nor particles were observed at the surface of the sample. Furthermore, the sample is shown to be stable in water. Scanning electron microscopy (SEM) revealed spherical features assembled in a porous structure (Fig. 1a). Both grains and pores were shown to have a mean grain size lower than 50 nm (Fig. 1b). At highest magnification, the pattern observed at the surface of the particles is attributed to the sputtered platinum grains. In contrast to previous hybrid coatings obtained by AP-DBD [14,15], no second phase was observed by SEM. This is consistent with the initial size of the metalloporphyrins and suggests that they do not form large aggregates. The thickness, measured by cross-section SEM, was  $1 \mu\text{m}$ .

Fourier-transform infrared spectroscopy (FT-IR), shown in Fig. 2, confirms the formation of a PDMS-like coating. The strong and broad band observed at  $1051 \text{ cm}^{-1}$  is assigned to a Si–O–Si network vibration, whilst the peaks at  $2960$  and  $2904 \text{ cm}^{-1}$  ( $\nu(\text{CH}_3)$ ),  $1410 \text{ cm}^{-1}$  ( $\nu^{\text{a}}(\text{CH}_3)$ ),  $1255 \text{ cm}^{-1}$  ( $\delta^{\text{s}}(\text{Si}-\text{CH}_3)$ ),  $847 \text{ cm}^{-1}$  ( $\rho(\text{CH}_3)$  and  $\nu(\text{Si}-\text{C})$ ),  $806 \text{ cm}^{-1}$  and  $758 \text{ cm}^{-1}$  ( $\nu(\text{Si}-\text{CH}_3)$ ) indicate the high retention of methyl groups from the siloxane monomer [20]. Due to a possible overlapping of the strong bands related to the siloxane network with the metalloporphyrin bands, expected around  $700\text{--}800 \text{ cm}^{-1}$  ( $\nu(\text{C}-\text{H})$ ),  $1000 \text{ cm}^{-1}$  ( $\nu(\text{C}-\text{C})$  and  $\nu(\text{C}-\text{N})$ ) and  $1070 \text{ cm}^{-1}$  ( $\delta(\text{C}-\text{H})$ ) [21], no evidence of  $\text{Cr}^{\text{III}}\text{Cl}(\text{TPP})(\text{H}_2\text{O})$  in the plasma polymerised coating could be detected by FT-IR.

Nevertheless, the presence of chromium in the plasma polymerised coating was both detected by X-ray photoelectron spectroscopy (XPS) and nano secondary ion mass spectrometry (SIMS). The chromium content in the embedded metalloporphyrin,  $\text{C}_{44}\text{H}_{28}\text{N}_4\text{Cr}$ , being rather low (ca. 1.4%), only traces of the Cr element (ca. 0.3%) were detected in the plasma polymerised  $\text{Cr}^{\text{III}}\text{Cl}(\text{TPP})(\text{H}_2\text{O})$ -based coating, which

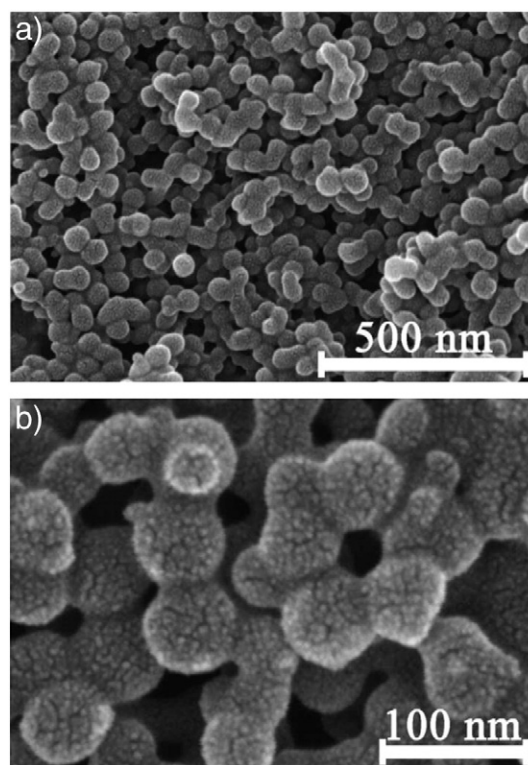


Fig. 1. Scanning electron micrographs of the plasma polymerised  $\text{Cr}^{\text{III}}\text{Cl}(\text{TPP})(\text{H}_2\text{O})$ -based coating at (a) intermediate magnification ( $\times 100,000$ ) and (b) high magnification ( $\times 350,000$ ).

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