Dip and wait: a facile route to nanostructured porphyrin films for QCM functionalization

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Abstract

A facile and straightforward way to deposit nanostructured porphyrin films onto quartz surfaces is presented. The particular peripheral functionalization on the macrocycle is exploited to drive the formation of aggregates in solution, which then spontaneously deposit as ordered solid layers. Film deposition is then achieved by simple dipping the quartz slide into a solution containing porphyrin aggregates and waiting the formation of the related thin films. QCMs covered with different metalloporphyrin derivatives have been exposed to some model VOCs, showing in general good performances especially in all the cases where film morphology is fundamental for sensing interactions.

Keywords: metalloporphyrins; self-assembling deposition; chemical sensors; VOCs detection;

1. Main text

The preparation of thin solid films of porphyrin derivatives is an attractive field of research, owing to their well-known potentialities in many disciplines, ranging from materials science\textsuperscript{1} to sensors applications,\textsuperscript{2} where these organic macrocycles are widely employed as sensing materials. In such a context the development of chemical sensors strictly relies on the film deposition onto the transducer surfaces, which mostly determines sensor performances and reliabilities. The formation of solid layers constitutes a critical step, which necessarily have to preserve the recognition properties of the single molecules and take advantage of the additional interaction pathways that the supramolecular organization can offer.\textsuperscript{3} Several strategies can be followed for the preparation of porphyrin films displaying an ordered morphology. This goal is usually achieved by elaborated deposition techniques, such as Langmuir-Blodgett (LB) or Langmuir-Schaefer (LS) methods, which take advantage of the amphiphilic character of the macrocycles in the step by step formation of the multilayer film.

We recently reported a different approach, where the molecular information inferred by a specific substituent into the porphyrin framework is exploited to drive the self-aggregation of the macrocycle toward the formation of

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specific aggregates in aqueous solution. These ordered supramolecular structures then spontaneously deposit as thin solid layers onto different hydrophobic surfaces, transferring the three-dimensional order from solution to solid state, as clearly indicated by AFM topography studies. Following such a deposition method nanostructured porphyrin films were layered onto silanised glass surfaces, and successfully exploited as a solid-state optical chemosensor for the detection of mercuric ions in water.

In this communication we make use of the same philosophy for the development of QCM (Quartz Crystal Microbalance) chemical sensors for the discrimination of organic vapours, by deposition of different porphyrin derivatives, whose chemical structures are reported in Fig. 1. We surmise for the resulting sensors improved sensing performances toward some model VOCs to respect those of the QCMs normally deposited in our laboratories by conventional methods, which do not allow a neat control of film morphology.

![Molecular structure of the amphiphilic porphyrin derivatives](image)

Fig.1: Molecular structure of the amphiphilic porphyrin derivatives deposited onto QCM surfaces

1.1. Preparation of thin solid films of porphyrin derivatives on QCM surfaces

Preparation of \([5\{-4\text{-}(3\text{-trimethylammonium)propyloxyphenyl}\}-10,15,20\text{-triphenyl} \text{porphyrin}\}] \text{chloride (Fig. 1, M=H)}\) has been accomplished according to procedures previously reported. The insertion of the different metals in such a structure has been carried out following the conventional synthetic methods for the achievement of metalloporphyrins.

Spectroscopic studies on the self-aggregation behaviour of all amphiphilic porphyrin derivatives in hydroalcoholic solutions have been carried out in order to define the optimal solvent composition inducing the aggregation process. UV-visible spectra showed in all the cases the formation of specific, porphyrin J-aggregates by increasing water amount from pure ethanol to a water-ethanol (9:1 v/v) solvent mixture. This is clearly evidenced by the remarkable UV-visible spectral changes for all porphyrin macrocycles, typically ascribable to the formation of supramolecular aggregates in which macrocycles arrange themselves in a J-type, offset conformation.

The Optical Density of the resulting films has been found to follow a linear trend with concentrations of the starting porphyrin solutions. This is an important issue, because it indicates the possibility to easy modulate the amount of the layered material, which could also tune the detection responses of VOCs.

1.2. Experimental set up and procedure

Aggregates deposition from solution on quartz substrate was achieved by dipping QCM (AT-cut, 83 µm thickness, 20 MHz fundamental vibration frequency), into the appropriate volume of a freshly prepared porphyrin derivative solution \((2.0\times10^6 \text{ M to } 2.0 \times 10^5 \text{ M; H}_2\text{O-EtOH 9:1 v/v})\) and waiting for 12-24 h the formation of the related solid film, depending on the concentration of the starting aqueous solution. Detailed studies on the deposition of amphiphilic derivatives on silanised glasses showed that the thickness of the deposited film depend on the bulk concentration of the porphyrin.
Each sensor was located on a Teflon® board in the measurement cell and the signal generated was revealed by a frequency counter. The gases and vapours were flowed at different concentrations by using a computer-assisted 4-channel mass-flow controller (MKS). Pure NO and CO were diluted with nitrogen, used as gas carrier. Saturated organic vapours (Benzene, Ethanol, Triethylamine, Cyclohexene and Toluene) were obtained by N₂ bubbling into liquid phase of the stock solution and then diluted with N₂ gas carrier at the desired concentration. All the measurements were performed at constant temperature (298 K) and flow rate (200 mL/min).

Saturated vapour concentrations were calculated by Antoine’s law using parameters available on the database of NIST. The sampling data have been carried out every 10 measurements.

1.3 Results and discussion

The porphyrin based QCMs were exposed to different gases and vapours to compare their performances with those of standard QCMs functionalized by spray coating technique. Because the amount of porphyrin deposited depended on the solution starting concentration, all analytical data have been processed normalizing the Δf values to the mass spontaneously deposited onto quartz surface. Furthermore some sensors have been evaluated in duplicate with various amount of coated masses (Table 1) to verify the influence of the deposited mass onto the sensing properties of the resulting QCM.

Table 1. QCM vibration frequency decrease after porphyrin film formation and related porphyrin mass deposited

| Sensor       | CoP(+) | ZnP(I) | ZnP(II) | MnP(+) | FeP(I) | FeP(II) | H₂P(I) | H₂P(II) |
|--------------|--------|--------|---------|--------|--------|---------|--------|---------|
| Δf (MHz)     | 0.0078 | 0.0153 | 0.0094  | 0.0784 | 0.0364 | 0.0598  | 0.0061 | 0.0152  |
| Mass (µg)    | 3.12   | 61.24  | 37.60   | 313.84 | 145.93 | 239.30  | 24.48  | 60.80   |

The developed QCMs have been exposed to model gases and VOCs usually exploited in our laboratories to study sensor properties, because they can test the different sensing mechanisms of porphyrin layers, ranging from coordination to dispersion interactions. Some results obtained are illustrated in Fig. 2; it is interesting to note that the developed QCMs show performances similar to those of spray-coated analogues when the main interaction mechanism is related to coordination to the central metal ion of the porphyrin core, while they are superior when the sensing mechanism can capitalize the supramolecular self-organization. This is for example the cases of aromatic hydrocarbons, such as benzene or toluene, when π-π intercalation of the aromatic rings is the dominant interaction for sensing purposes.

This result is particularly promising if we consider that a chiral appended functionality on the porphyrin macrocycle leads similarly to the formation in solution of supramolecular aggregates featuring elements of chirality. The deposition of these aggregates still occurs by following the same “dip and wait” approach affording chiral layers, which can be exploited for chiral discrimination, a hot and difficult topic in chemical sensing.

1.4 Conclusion

The deposition by self-assembling is a facile way to obtain ordered films without laborious procedures or expensive instrumentations. The performances of these sensors show comparable and in some cases better (Fig. 2) efficiency than those obtained by spray coated deposition method.

The possible deposition of chiral porphyrins on hydrophobic surfaces following this dip-wait approach could lead to their exploitation for stereoselective sensors, which is obviously the natural goal. Some preliminary results obtained in this direction underline the potentialities of such an approach.
Fig 2. Sensitivities of the amphiphilic porphyrin films towards model VOCs, compared with those of conventional spray-deposited porphyrin films

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