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The influence of the surface morphologies of Langmuir Blodgett (LB) thin films of porphyrins on their gas sensing properties

D. Çaycı[a], S.G. Stanciu[b], İ. Çapan[a,*], M. Erdoğan[a], B. Güner[a], R. Hristu[b], G.A. Stanciu[b]

[a] Balikesir University, Science and Arts Faculty, Physics Department, 10100 Balikesir, Turkey
[b] Center of Microscopy-Microanalysis and Information Processing, University 'Politehnica' of Bucharest, 313 Splaiul Independenteti, 060032 Bucharest, Romania

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ABSTRACT

In this work, 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine (OEP) in its free base form and metalated with iron (III) chloride (FeOEP), magnesium(II) (MgOEP) and cobalt(II) (CoOEP) have been used to fabricate Langmuir–Blodgett (LB) thin films. Using the surface pressure–surface area (Π–A) isotherm graphs optimum conditions for thin film deposition have been determined and by changing the deposition parameters various thin films have been deposited. Quartz Crystal Microbalance (QCM) system was used to investigate their gas sensing performances during exposure to Volatile Organic Compounds (VOCs) including chloroform, benzene and toluene. The surface properties have been investigated using Atomic Force Microscopy (AFM) and analyzed together with the QCM results to understand the effect of the surface properties on gas sensing mechanism. It is observed that larger surface area leads to higher response in gas sensing applications in terms of resonance frequency change.

1. Introduction

The porphyrin compounds which are known to be highly sensitive in gas sensing applications are of great interest in recent years in developing gas sensing technology. Their performance in detecting inorganic compounds has already been proven [1–4]. The detection of organic toxic compounds is of commercial interest because of their toxicity and frequent use in the industry [5,6]. The investigations have been performed by using different techniques including electrical [7–9], gravimetric [10] or optical [11,12] measurement of the gas sensing response.

The Langmuir Blodgett (LB) thin film fabrication technique which is an excellent method in fabricating well-ordered monolayer or multilayered thin films is used to investigate gas sensing performances of thin films. LB thin film deposition technique allows the fabrication of various thin films by changing the thin film fabrication conditions such as deposition dipper speed, surface pressure, dipper movement direction [13].

In gas sensing research the investigation of the gas sensing mechanism is still a phenomenon to clarify. As to the gas sensing mechanism for porphyrin and its derivatives' thin films, a number of mechanisms have been proposed including π–π^* interactions between the porphyrin macrocycles [7,14], affinity between porphyrin layers and the interacting vapour species [10,15], photoassisted ligand exchange route [12], the changes in van der Waals force between the film and the adsorbed gas molecules [8]. As the analyzed toxic gas firstly interacts with the surface of the thin film, the morphology of the thin film surface may play an important role in the gas sensing mechanism. However, only a limited number of researches have been conducted to understand the influence of the surface properties of these thin films [16–19].

This work is a study of four different porphyrins: (OEP) in its free base form, when metalated with iron (III) chloride (FeOEP), with magnesium (MgOEP) and with cobalt (CoOEP). The selected porphyrins were used to fabricate solid state Langmuir–Blodgett (LB) thin films which were subsequently exposed to saturated organic vapors. To better understand the sensing mechanism and to obtain different architectures, the thin films' fabrication has been performed with different surface pressure values. Atomic Force Microscopy (AFM) and Quartz Crystal Microbalance (QCM) technique have been employed to explore the surface properties and gas sensing properties towards saturated vapors of selected volatile organic analytes respectively. The selected analytes are commonly produced in industrial processes. Benzene is formed from both natural processes and human activities. It is produced from volcanoes and forest fires, and is a natural part of crude oil, gasoline, and cigarette smoke. Toluene is a toxic ingredient in solvents, paints, and other household products. Chloroform can contribute to the formation of harmful ground-level ozone and major release of chloroform happens as a result of its production and use in the chemicals industry. Smaller releases result from the chlori-

* Corresponding author. Tel.: +90 266 612 1000/1301; fax: +90 266 612 1215.
E-mail addresses: inci.capan@gmail.com, ibasaran@balikesir.edu.tr (İ. Çapan).

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nation of water and from agricultural products where it is used as a solvent. The gas sensing responses of LB thin films of porphyrins were investigated and the effect of surface morphology on gas sensing which is one of the dominating effects like central metal atom effect and molecular size of the gas molecules were discussed.

2. Experiments

2.1. Chemicals

Four different porphyrin chemicals namely 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine (OEP), 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine iron(III) chloride (FeOEP), 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine magnesium(II) (MgOEP) and 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine cobalt(II) (CoOEP) were purchased from Sigma Aldrich, used without further purification and coded as porp1, porp2, porp3 and porp4 respectively. The chemical structures of these porphyrins were given in a previous publication [20]. Other chemicals, used in gas sensing experiments, chloroform, toluene and benzene were also purchased from Sigma Aldrich and used without further purification.

2.2. Thin film fabrication

For the fabrication of the LB thin films Alternate Layer Nima 622 model LB film trough provided with a filter paper Wilhemly balance has been employed. The surface pressure–area (Π–A) isotherm graphs were recorded to determine the surface pressure value which will be held constant during the transfer of the monolayers on the water surface onto the solid substrates. Porphyrin solutions that have been prepared by dissolving the porphyrins in chloroform with a concentration of 0.2 mg ml^{-1} have been spread onto the pre-cleaned water subphase using a Hamilton syringe allowing 10 min for the solvent to evaporate. The isotherms were recorded with the compression speed of 30 cm^2 min^{-1} at room temperature. Y-type LB films have been fabricated at constant surface pressure values changing between 12.5 and 17.5 mN m^{-1}. Transfer speeds for both downstroke and upstroke deposition were 25 mm min^{-1} with a transfer ratio value of approximately 0.90. 11 layers of thin films have been deposited onto quartz crystal substrates for gas sensing experiments and onto glass substrates for AFM measurements for all four kinds of porphyrins.

2.3. Gas sensing experiments

QCM system measures the resonance frequency of a quartz crystal which is sandwiched between two metal electrodes and inserted into an electronic unit that enables to record the resonance frequency value at a mass change. In QCM system a mass change range of nanograms can be detected which leads to a gravimetric sensitivity. The piezoelectric behaviour of the quartz crystal was first described by Sauerbrey [21] and the resonance frequency shift (Δf) on a quartz crystal against a mass change per unit area (Δm) is given by:

$$\Delta f = \frac{-2f_0^2}{\rho_q^{1/2}\mu_q^{1/2}A}\Delta m \quad (1)$$

where f_0 is the resonant frequency of the fundamental mode of the crystal, A (1.13 cm^2) is the piezoelectrically active area, ρ_q is the density of quartz (2.648 g/cm^3) and μ_q is the shear modulus of quartz (2.947 $\times$ 10^{11} dyn cm^2).

An in-house made QCM has been employed to investigate the gas sensing properties of the porphyrin thin films and its schematic

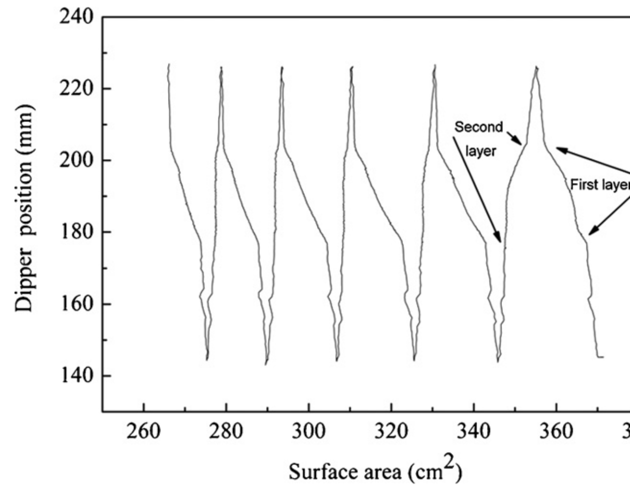

Fig. 1. The number of LB deposition cycles of porp2 thin film at a constant surface pressure value of 15 mN m^{-1}.

illustration can be found elsewhere [20]. The AT-cut quartz crystal with a nominal frequency of 3 MHz coated with the porphyrin thin film was inserted into the electronic unit and the resonance frequency was monitored during exposure to toxic gas and its recovery. Diluted amounts of saturated toxic gas ranging between 20% and 100% were introduced into the gas cell for 2 min followed by flushing with dry air for another 2 min. All measurements were performed at room temperature.

2.4. Atomic Force Microscopy (AFM) measurements and SPIP programme

The surface investigations were made by using an atomic force microscope, Quesant-350. The microscope worked in the contact mode, the tip had a height of 20 μm, radius less than 20 nm, and cone angle less than 30° at the apex. A typical force constant of the cantilever is 0.15 Nm^{-1} and typical resonance frequency is 12 kHz. The scan rate was 1 Hz.

The image analysis was performed with the use of Scanning Probe Image Processor (SPIP^{TM}). SPIP is a comprehensive software platform containing many analytical and visualization tools which can be used in order to extract and highlight typical useful information from images collected by various scanning probe microscopy techniques. SPIP is a commonly used tool for AFM based high precision surface characterization.

3. Results and discussion

3.1. Fabrication of the thin films

To fabricate the thin films of porphyrins, LB thin film fabrication parameters including the dipper speed and the surface pressure value that will be held constant during the fabrication need to be determined. The isotherm graphs of the porphyrin thin films showed that the surface pressure values which form regular monolayers on the water subphase namely solid phase were 12.5–17.5 mN m^{-1} that have been already found in previous studies [22,23]. By varying that value LB thin films with different textures can be obtained. In this study LB thin films were fabricated at constant surface pressure values of 12.5, 15.0 and 17.5 mN m^{-1}. In Fig. 1 the deposition graph which gives information on the reduction of the surface area of the monolayer versus dipper position during the deposition of the LB layers onto the substrates are plotted for porp2 thin film at 15 mN m^{-1} constant surface pressure. The average reduction of the surface area was similar in all cycles indicating