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Research Paper

Understanding the gas adsorption kinetics of Langmuir-Schaefer porphyrin films using two comparative sensing systems

M. Evyapan[a,c,*], A.K. Hassan[b], A.D.F. Dunbar[c]

[a] Department of Physics, University of Balikesir, Balikesir, 10145, Turkey
[b] Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, S1 2NU, UK
[c] Chemical and Biological Engineering, University of Sheffield, Mappin Building, S1 3JD, UK

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ABSTRACT

This study investigated Langmuir-Schaefer (LS) films of a free base porphyrin 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21H,23H-porphine (EHO) as sensors to detect acetic acid and methylamine. Such films are known to adsorb VOCs, resulting in a color change and a swelling of the film resulting in a thickness increase for the film. The adsorption kinetics of this process were studied using two different techniques, namely UV–vis absorbance spectroscopy and surface plasmon resonance (SPR), to investigate the color change and film thickness change respectively when exposed to acetic acid and methylamine vapors. These two techniques were used to allow a comparative study to be made of the color change and film swelling in order to enhance understanding of the interaction between the thin films and both acidic and basic vapor molecules.

The transfer process of the LS thin films was performed using the constant transfer pressure of 5 mNm^{-1}. EHO films with different numbers of layers were fabricated and exposed to 855 ppm acetic acid and 900 ppm methylamine vapor. Sensor responses were recorded using both UV–vis and surface plasmon resonance techniques. The EHO films exhibited high sensitivity and fast responses using both techniques. Using two different detection systems permitted the investigation of the interaction mechanism with a quantitative, comparative study with the aim of obtaining an enhanced understanding of the nature of the interaction of the organic vapors with the sensor. The interaction between EHO and the analytes can be considered in terms of three processes which are surface adsorption, diffusion and desorption process. Although both the optical techniques have distinct sensing principles, similar vapor interaction characteristics can be distinguished in both sets of experiments. For both techniques the response to the acid was stronger than the response to methylamine. However, apart from this difference in the magnitude of the responses the interaction with the acid and base were remarkably similar. The sensitivity of the sensor is largely independent of the measurement system.

1. Introduction

Gas sensors will play an increasingly important role in life as awareness of the dangers of indoor and outdoor air pollution increases. Therefore research in the field of gas sensing has become an important issue during the last few decades [1,2]. One group of common air pollutants are toxic VOCs (volatile organic compounds) which are extensively used in daily essentials such as paints, cleaning solvents, plastics, cosmetics and wood preservatives. The vapors of VOCs can be highly dangerous when released after using such products and need to be detected before they reach critical levels in the environment. Therefore there is an increasing demand to develop new sensor devices with increased selectivity and sensitivity compared to existing sensors, ideally at lower cost. Organic materials are widely used as sensing materials with a wide range of specific subsections including polymers [3], calixarenes [4], porphyrins [5] and phthalocyanines [6]. The most important part of any adsorption sensor device is the sensing material which directly interacts with the analyte vapor. Accordingly, most of the research reported on gas sensors is related to development of highly sensitive new sensor materials. However an ideal sensor material should simultaneously demonstrate both high sensitivity and selectivity between analyte vapors. Therefore understanding in detail the interaction between the sensor material and analyte

* Corresponding author at: University of Balikesir, Faculty of Art & Science Department of Physics 10145, Cagis, Balikesir, Turkey.
E-mail address: mevyapan@gmail.com (M. Evyapan).

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vapor is required to maximize the advantages of using this type of sensor and therefore improve any new sensor devices.

Porphyrin molecules show a distinctive color change upon exposure to VOCs which can be easily detected using ultra-violet to visible (UV–vis) spectroscopy. Moreover, adsorption of vapor molecules by thin film matrix causes swelling of the thin film and the surface plasmon resonance (SPR) technique is capable of detecting these very small thickness changes. These two techniques were studied and the results analyzed in order to obtain a deeper understanding of the sensing process. It is assumed that the vapor molecules first interact with the surface of the sensor film and then diffuse into thin film layers as reported in the literature [7]. These two steps affect the sensor response depending on their intensity and speed.

The main purpose of this study was to investigate the response mechanism when exposed to acetic acid and methylamine in order to develop a deeper understanding of the response mechanism. This was achieved by investigating the intensity, duration and speed of the sensor response using two the different sensing techniques. These analytes were chosen because they both elicit a response from the porphyrin, the molecules are similar in size but differ in the functional groups present (-COOH and $-NH_2$). Thus the sensor responses can be compared for both techniques. The two sensor measurement techniques have been widely used in literature but previously always in separate studies. This study is unique in applying these two techniques using the same thin film structures with the same organic vapors in order to directly compare the two techniques.

In this work, a free base porphyrin, 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21H,23H-porphine (EHO) was selected as the sensor material because this porphyrin has proven sensitivity to many analytes including alcohols [8], NH_3 [9], acids [10,11], amines [12]. Initially the Langmuir-Schaefer (LS) thin film preparation technique was used to produce EHO films on solid substrates with differing numbers of solid state porphyrin layers. The reproducibility of this process was measured and confirmed by SPR. The sensing properties of these films upon exposure to acetic acid and methylamine were investigated using both UV–vis absorbance spectroscopy and SPR methods. Both methods are highly sensitive and have individually shown remarkable results in previous sensor studies and provide high resolution sensor response results [13,14].

2. Experimental Details

2.1. Materials and LS Film Fabrication

The synthesis and chemical structure of EHO has been described elsewhere [15]. The EHO was dissolved in chloroform at a concentration ~0.5 mg ml^{-1} and the Langmuir-Schaefer (LS) technique was used to transfer different numbers of layers of EHO molecules onto a solid substrate in a precise manner. The chloroform solution of EHO was spread onto an ultrapure water subphase (ElgaPURELab Option >15 MΩcm) using a Hamilton microliter syringe in a NIMA Model 601 BAM Langmuir trough. In order to permit the solvent to evaporate a time period of 15 min was allowed before the area was reduced by closing the trough barriers. Surface pressure – area (Π-A) isotherm graphs were recorded using at a barrier compression speed of 200 cm^2 min^{-1}. All experiments were performed in a cleanroom and at a temperature of ~18 °C.

LS films were transferred onto glass slides for the optical UV–vis measurements and 40 nm gold coated glass substrates for the surface plasmon resonance (SPR) measurements. The gold layers were deposited by thermal evaporation onto pre-cleaned glass slides with a deposition rate of 0.2 nm s^{-1} under a vacuum of 10^{-6} Torr. All substrates were subsequently exposed to 1,1,1,3,3,3-hexamethyldisilazane (HMDS) vapor for min 12 h in order to render the surface of the substrate hydrophobic prior to deposition. Before the deposition process, the monolayer on water surface was compressed to the selected constant surface pressure of 5 mNm^{-1}. The monolayer floating on the water surface was transferred onto the solid substrates by contacting the substrate horizontally onto the floating monolayer and subsequently lifting off a single LS layer. The substrate speed used was 10 mm min^{-1} during the transfer. Each LS layer was allowed to dry for 5 min between subsequent depositions and the surface pressure was allowed to return to the target pressure between each deposition by controlling the trough barrier position. This process was repeated the required number of times in order to produce a multilayer LS film.

2.2. Optical Measurement Systems

In order to investigate the vapor adsorption kinetics of EHO LS films two different optical gas sensing measurements were used to carry out a comparative study. The first one is UV–vis absorbance spectroscopy which was performed using a Mikropack MiniD2 UV–vis–IR light source and an Ocean Optics USB2000 spectrometer. Absorbance spectra of EHO LS films were recorded in the range of 350–800 nm. The second measurement was made using a SPR system which consists of a Kretschmann configuration custom built optical setup [16] incorporating a semi-cylindrical prism (refractive index of 1.515) and optical laser (wavelength of 632.8 nm) the details of which have already been described in another study [17]. A gas cell (PTFE – polytetrafluoroethylene) sealed with a rubber O-ring were integrated to the SPR setup which was placed on the LS films and the reflected light intensity was measured as a function of angle or time depending on the measurement type. The thicknesses of the LS films were evaluated by fitting the SPR curves based on the Fresnell equations. The fitting procedure was achieved using the Winspall 3.01 software which was produced by the Max-Planck Institute [18].

2.3. Vapor sensing measurements

The investigation of the kinetic adsorption of EHO LS films involved recording the dynamic response upon exposure to the analyte vapor. Acetic acid and methylamine vapors were chosen as analytes because they permit a comparison of the sensing response measured using two similar sized molecules with different functional groups. Both analytes have $-CH_3$ functional groups but differ in the one has a –COOH group and the other an $-NH_2$ group. This allows the study to investigate the influence of functional group on the sensor responses and the nature of the adsorption. The analytes were obtained from Sigma-Aldrich and dry nitrogen was used as the carrier and diluent gas in the UV–vis absorbance spectroscopy measurements.

The UV–vis gas sensing measurement setup contains a purpose built gas exposure chamber connected to two Tylan FC-260 mass flow controllers [19]. The analyte in its liquid phase was contained in a small vessel and a mass flow controller was used to deliver a controlled amount of clean dry nitrogen to the vessel. The analyte vessel was maintained at a known temperature in a temperature controlled water bath. When the nitrogen gas passes through the headspace in the vessel it mixes with the analyte vapor present in the headspace and delivers the analyte vapor to the exposure chamber. The concentration of the analyte vapor was subsequently determined in ppm using the known Antoine parameters to determine the partial pressure at the known temperature [20]. The sample was positioned on a Peltier device and the recovery cycle was carried out by gently heating the sample