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Controlling surface adsorption to enhance the selectivity of porphyrin based gas sensors

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ABSTRACT

This study reports an enhancement in the selectivity of the vapor sensing properties of free base porphyrin 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21H,23H-porphine (EHO) Langmuir–Schaefer (LS) films. These sensors respond by changing color upon adsorption of the analyte gas to the sensor surface. The enhanced selectivity is achieved by adding selective barrier layers of 4-tert-Butylcalix[4]arene, 4-tert-Butylcalix[6]arene and 4-tert-Butylcalix[8]arene embedded in PMMA (Poly(methyl methacrylate)) on top of the porphyrin sensor films to control the gaseous adsorption onto the sensor surface. The Langmuir properties of EHO, PMMA and calix[*n*]arene monolayers were investigated by surface pressure–area (Π–A) isotherms in order to determine the most efficient transfer pressure. Six layer EHO films were transferred onto glass and silicon substrates to investigate their optical and structural characteristics. The three different calix[*n*]arenes were embedded within PMMA layers to act as the selective barrier layers which were deposited on top of the six layer EHO films. The different calix[*n*]arene molecules vary in size and each was mixed with PMMA in specific ratios in order to control the selectivity of the resulting barrier layers. Spectroscopic Ellipsometry (SE) and Atomic Force Microscopy (AFM) measurements were carried out to analyze the structure of the porous barrier layers. It was found that the orientation of the calix[8]arene molecules was well controlled within the Langmuir layers such that molecular ring lies flat on the EHO layers when deposited. However, the calix[6]arene and calix[4]arene molecules were quite not so reliably oriented. The sensor films (with and without the addition of the different selective barrier layers) were exposed to various carboxylic acid vapors. More specifically, acetic acid, butyric acid and hexanoic acid were chosen due to their different molecular sizes. The uncovered EHO films were highly sensitive to all the carboxylic acids. The porosity of the barrier layers which influences their selectivity was investigated by changing the size of the acid molecules. Upon deposition of a barrier layer on top of EHO film the sensing response rate and magnitude were changed depending on both the barrier layer structure and molecular size of the analyte vapor. The optical sensing results show that by controlling the size of the pores in the barrier layer it can be used as a size selective layer which limits the diffusion of analyte molecules into the sensor and in extreme cases stopping the diffusion completely. Therefore the selectivity of this sensor system has been enhanced by adding a controllable barrier layer. The enhanced sensors have been used to differentiate between acetic, butyric and hexanoic acids.

1. Introduction

Increased awareness of the dangers of indoor and outdoor air pollution has meant that availability of suitable gas sensors has become an increasingly important issue [1,2]. Toxic volatile organic compounds (VOCs) are extensively used in paints, cleaning solvents, wood preservatives, plastics and cosmetics. The VOC vapors released when using such products can be highly dangerous so it is desirable to be able to detect their presence before they reach critical levels in the environment. There is an increasing motivation to develop new gas sensors with high sensitivity and selectivity for such VOCs. Porphyrins are attractive materials to use in such sensors because of their high sensitivity and reversibility.

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Several studies have already been performed to develop a porphyrin based sensor system using thin film preparation techniques such as Langmuir–Blodgett [3,4], Langmuir–Schaefer [5], spin coating [6] and self-assembly [7]. Porphyrins have a strongly conjugated π-electron system [8] which results in their bright color and interesting optical properties [9,10] which are highly beneficial for gas sensing applications [11–13].

An ideal sensor device should possess both high sensitivity and selectivity. Much of the research reported on new sensors is related to improvements in the sensitivity of the sensor materials. Often the chemical composition of the sensor material can be improved to increase the sensitivity of the sensor device. Porphyrin based sensor devices have shown significant sensitivity to lots of analytes such as alcohols [14], NH_3 [6], acids [3,15], amines [16] and antibacterial (*Escherichia coli*) activity [17]. However, an ideal gas sensor also has to show selectivity in order to distinguish between different kinds of VOC vapors. In some applications, the selectivity of the sensor devices may in fact be more important than its sensitivity. It is well know that for porphyrins the interaction between the sensor material and the analyte being detected depends on the functional groups present in the analyte. Therefore the sensor response typically does not show significant selectivity between analytes containing the same functional group. In order to distinguish these similar analytes it is essential to improve the selectivity of the porphyrin based sensor systems.

This work describes the use of a selection mechanism which differentiates between carboxylic acid vapors based on their molecular size by using a diffusive size selective barrier layer deposited on top of the vapor sensitive porphyrin surface. Initially Langmuir–Schaefer (LS) thin films of EHO were prepared and the sensitivities of the resulting solid-state porphyrin films were tested in their uncoated form. It is well known that the selected porphyrin shows a dramatic optical response upon exposure of the sensor surface to carboxylic acid which manifests itself as a color change. In order to investigate the molecular size selectivity of the porphyrin sensor device, three different sized carboxylic acids, acetic acid, butyric acid and hexanoic acid were selected as analytes. All three analytes could be easily detected by the EHO sensor films. The main focus of this work was to use the different selective barriers to differentiate between the sensor responses to each of the different sized analytes, thereby improving the selectivity of the sensors. In order to control the access of the vapor molecules to the underlying porphyrin film, a barrier layer was added on top. The effect of a barrier layer on the sensor response has been studied before [5]. This work clarifies the function of the barrier layer by diversifying the barrier structure and enhances the selectivity of a sensor system using advanced barrier layers. The selective barrier layers consisted of calix[4]arene, calix[6]arene and calix[8]arene molecules and PMMA. The calix[*n*]arene molecules increase the porosity of the barrier layer. They have a cylindrical molecular structure and the diameter of the open cylinder depends upon the number of calix units within the molecule. Therefore, a calix[4]arene film should have smaller pores than a calix[6]arene film and so on. In contrast a compressed PMMA film has closely packed polymer chains and therefore is expected to be almost impermeable to the VOC vapors. The structural characteristics of the porphyrin film and the barrier layers were investigated using Spectroscopic Ellipsometry (SE) and Atomic Force Microscopy (AFM). Absorbance spectroscopy measurements were performed to determine the color changes associated with the porphyrin upon exposure to the carboxylic acids. Sensor films covered with the various barrier layers were tested against the three acid vapors. The optical sensor responses are discussed and compared considering with the relative porosity of the barrier layers employed and the analyte vapor size.

2. Experimental details

2.1. Materials and film fabrication

Free base porphyrin of 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21H,23H-porphine (EHO) was selected as a sensing material and the synthesis has been described elsewhere [18], the chemical structure is shown in Fig. 1. In order to investigate the selectivity properties of EHO, Langmuir-Schaefer (LS) film was prepared and coated with a size selective barrier layer which consisted of poly(methyl methacrylate) (PMMA) and 4-tert-Butylcalix[*n*]arenes. Three different calix[*n*]arene molecules with different numbers [*n*] of 4-tert-butyl units within the calix ring were chosen which were 4-tert-Butylcalix[4]arene (C4), 4-tert-Butylcalix[6]arene (C6) and 4-tert-Butylcalix[8]arene (C8). They were used as supplied from Fisher Scientific UK Ltd. Fig. 1 also shows the chemical structures of PMMA and the calix[*n*]arene molecules. The EHO, PMMA and calixarene molecules were dissolved in chloroform at concentrations of $\sim 0.5\,\mathrm{mg\,ml^{-1}}$, $\sim 0.1\,\mathrm{mg\,ml^{-1}}$ and $\sim 0.3\,\mathrm{mg\,ml^{-1}}$, respectively. Langmuir films were made by spreading the solutions from a Hamilton microliter syringe onto an ultrapure water sub-phase (ElgaPURELab Option >15 MΩ cm) in a NIMA Model 601 BAM Langmuir trough. A time period of 15 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced by moving the trough barrier. In order to investigate the behavior of monolayer at the air–water interface, surface pressure–area (Π–A) isotherm graphs were obtained using a barrier compression speed of $200\,\mathrm{cm^2\,min^{-1}}$ (this correlates to the speeds of 9×10^{-3}, 8×10^{-3}, 12×10^{-3}, $16 \times 10^{-3}\,\mathrm{nm^2\,s^{-1}\,molecule^{-1}}$ for EHO, calix-4, calix-6 and calix-8 respectively. The PMMA rate corresponds to $4 \times 10^{-3}\,\mathrm{nm^2\,s^{-1}\,monomer^{-1}}$). Π–A isotherm graphs were recorded during the barrier closing process. All experiments were performed in a cleanroom and at a temperature of ~18 °C.

The LS thin film transfer process was used to transfer the films from the Langmuir trough onto supporting substrates. Glass slides and small squares of Si wafer were used as supporting substrates. These were cleaned by refluxing in isopropyl alcohol for several (>3) hours, followed by exposure to 1,1,1,3,3,3-hexamethyldisilazane (HMDS) vapors for >12 h in order to render the surface of the substrate hydrophobic prior to deposition of the LS films. LS film deposition was performed by bringing a horizontally oriented substrate into contact with the floating monolayer. Upon contacting the floating monolayer, the monolayer adhered to the substrate such that when it is raised vertically a single layer of the floating film is subsequently lifted off from the water surface. In order to produce a multilayer LS film this process was repeated the required number of times, whilst ensuring that a new region of the floating film was selected for each step of the multilayer LS film deposition in order to ensure that uniform LS layers were transferred. The LS deposition procedure was performed at the selected surface pressure with a substrate speed of $10\,\mathrm{mm\,min^{-1}}$ and every LS layer was dried for 5 min after each lift off before any subsequent layers were added.

2.2. Atomic Force Microscopy (AFM)

In order to use AFM to investigate their surface morphologies, LS films nominally identical to the sensor layers were deposited on Si substrates. Si substrates were used because the Si surface is considerably flatter than glass. $2\,\mu\mathrm{m} \times 2\,\mu\mathrm{m}$ AFM images of the LS porphyrin films were taken using an Extended Multimode AFM (Veeco Ltd., Santa Barbara, USA) with a Nanoscope IIIa controller operated in tapping mode [18]. The same LS films on Si substrates were used for the SE experiments.