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GAS SENSING CHARACTERISTIC OF COBALT (II)-PORPHYRINS THIN FILMS PREPARED USING LANGMUIR-BLODGETT DEPOSITION TECHNIQUE

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ABSTRACT

This paper reports the study of the effect of surface morphology of cobalt (II) tetraphenyl porphyrins thin films on its sensing sensitivity toward the presence of an organic vapors; cyclohexane. The thin film was deposited on glass substrate using Langmuir-Blodgett deposition technique. The annealing process was performed to modify the thin film surface morphology. The thin films samples were annealed in several temperatures; 50, 100 and 150°C, in air atmosphere for one hour, each. The sensing sensitivity of the films samples was studied based on the change on the optical absorption characteristic upon exposure toward gas which was measured at a particular wavelength of the light source; 626 nm. It was found that the sensing sensitivity of the thin film toward a particular vapor sample depended on the surface morphology of the thin film surface. The optimum sensing sensitivity was found for the thin films with a large number of hills and valleys on the surface which was given by the as prepared thin films.

Keywords: Porphyrins, Surface Morphology, Optical sensing, Organic vapor, Langmuir-Blodgett film

INTRODUCTION

Recently, the exploitation of materials properties which was related to the sensitivity, stability and the selectivity in the detection of gas turned in to be the main research objectives of many researchers [1]. Several materials from the class of transition metal oxide [2] and the organic chemicals [3] have been intensively studied and their property was determined. Porphyrins and their related compounds are a class of organic chemicals that became a prospective candidate as sensitive materials for gas detection [4]. These chemicals feature intriguing electrical and optical properties and these entire characteristic may be adjusted by a simple modification on the structure of the central molecule and the structure of the ring through substitution of atoms or ligands [5]. Their rich chromophoric behaviors which depend on the molecular structure have been intensively exploited to develop versatile optical gas sensor systems that showed a large range selectivity nature [6].

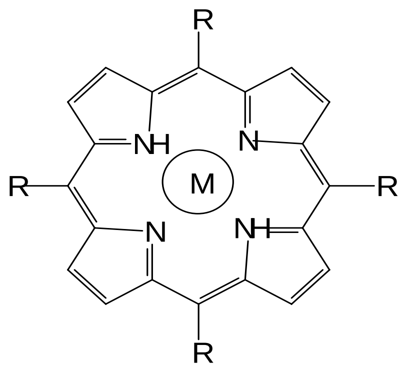

Figure 1. The molecular structure of the metallotetraphenyl porphyrins with M = cobalt (II) atom.

In a complex gas sensor system, such as electronic nose, the sensing elements must demonstrate a large difference on the sensing sensitivity amongst the sensing element towards a particular gas sample [7]. Many techniques have been employed to increase the variation on the sensing sensitivity amongst them to vary the type of materials that attached in the sensor system. However, this technique features several disadvantages which the system may be much un-effective in cost and bulky in size. One approach which may be used to increase the performance of a gas sensor system is to modify the sensing sensitivity of particular sensor towards gas sample through the modification on the surface morphology of sensing elements. In our previous work, the sensitivity of a particular sensing element towards a gas sample can be improved through the annealing process and the optimum condition of the sensing element which demonstrates a high sensitivity can be determined [8]. This paper reports the use of a derivative of metallo-tetraphenyl porphyrins, 5, 10, 15, 20 tetraphenyl 21H,23H-porphine cobalt (II) Langmuir-Blodgett films, as sensing element to detect the presence of saturated vapor of cyclohexane. The sensing sensitivity was based on the change on the optical absorption of the films upon exposure towards the vapor sample which was measured at a particular wavelength, 626 nm, of the light source. The annealing technique was used to improve the sensitivity of the films towards this sample. It was found that the annealing technique modified the sensing sensitivity and the optimum condition was obtained. The surface morphology-sensitivity relationship will be discussed.

EXPERIMENTAL

A derivative of metalloporphyrins was used as sensing element for VOC detection. Figure 1 shows the molecular structure of 5, 10, 15, 20-tetraphenyl 21H, 23H-porphine cobalt (II). This chemical is commercially available and is used directly without some further process. This material was prepared in the form of thin films using Langmuir-Blodgett (LB) technique. At first, 0.16 mg/ml solution of the chemical was mixed with arachidic acid with the composition of 1:3 by weight. The addition of acid to the solution was meant to improve the transferability of the monolayer to the substrate. Before being deposited on to the substrate, the stability of the floating monolayer was characterized using the isotherm experiment. Then, a suitable surface pressure for the dipping experiment was determined which in this experiment, a surface pressure as high as 20 mN/m was selected. In order to form a monolayer, the solution of this chemical was spread on pure water subphase. Then, the floating monolayer was compressed until the surface pressure was 20 mN/m. The thin film was deposited on glass substrate by lifting up the substrate which has been dipped earlier in the subphase, through the monolayer at the speed of 5 mm/min and the surface pressure is maintained. Multilayer LB films of z-type deposition [9] up to 16 layers were prepared.

The structure of the thin films samples were studied using the x-ray diffraction technique at low diffraction angle. The prepared thin films were annealed at three different annealing temperatures, 50, 100 and 150°C for one hour each, to obtain a different surface morphology structure. And, the surface morphology of the thin films samples was studied using Atomic Force Microscopy (AFM) technique. The sensitivity of the prepared films towards saturated vapor of cyclohexane was studied. The experimental mechanism of the optical detection technique has been described elsewhere [4].

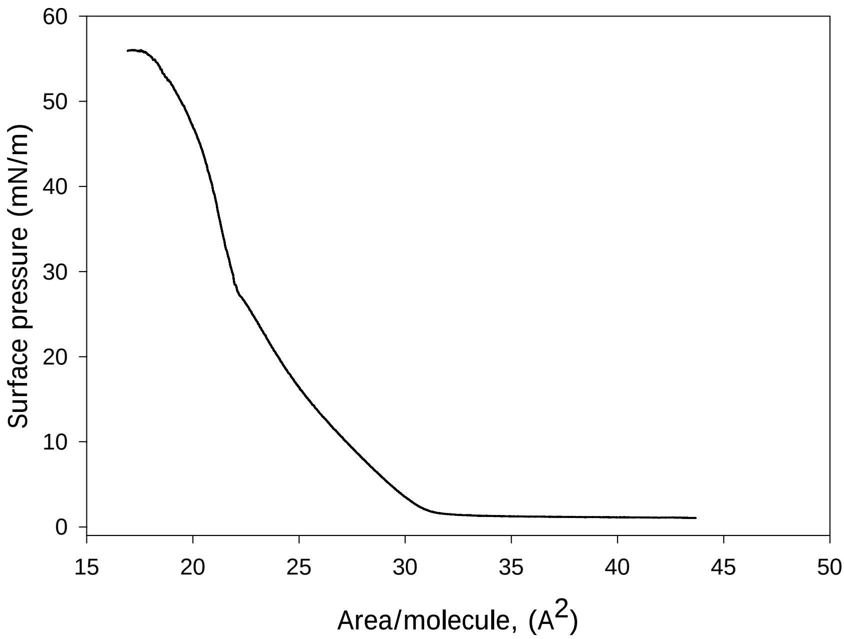

Figure 2. The isotherm curve of CoTPP LB monolayer.

RESULTS AND DISCUSSION

The Langmuir-Blodgett films

The thin films of 5, 10, 15, 20-tetraphenyl 21H, 23H-porphine cobalt (II) has been successfully deposited on glass substrate using Langmuir-Blodgett technique up to 16 layers. The average transfer ratio of the deposited monolayer was 0.95. Before being transferred on to the substrate, the isotherm experiment was performed to find the mechanical characteristic of the monolayer. At the air-water interface, the floating monolayer exhibited a high stability against the change of the increasing of the surface pressure. It was found that the collapse pressure of the monolayer was 57 mN/m. Figure 2 shows the isotherm curve of the CoTPP monolayer at the air-water interface. It was observed that until the average molecules area approached 33 A°/molecule, the monolayer did not exhibit to increase its surface pressure. At this circumstance, the monolayer may be still in gas phase. After the molecule area slightly below 30 A°, the monolayer showed to response linearly growth of its surface pressure towards the reducing of the average molecules area. At this point, the monolayer could be in the liquid phase. The reducing of the average molecule area has been responded by the monolayer through exponentially growth of its surface pressure. This case was continued until the average molecule area was approaching the value of 18 A°, which at this circumstances, the monolayer was going to collapse with the surface pressure was 57 mN/m. These results indicated that the monolayer feature a good stability against the change of the external force by showing a high collapse pressure point.

Figure 3 shows the pattern of the x-ray diffraction curve which was taken in the region $2° < 2\Theta < 15°$, of diffraction angles. It was found that the pattern show the appearance of some Bragg peaks with the average distant between two adjacent peaks was 2.3°. This conveyed that the thin film of CoTPP has been formed on the substrate in a very well ordered structure. Using the Bragg equation, it can be calculated the thickness of the thin films assemblies. The average thickness of 16 layers of CoTPP LB films was 45.56 nm. When the annealing process performed on the thin films, the pattern of the curve was changed. It was observed that the intensity of all the first two peaks was decreased, but the peak at the region of $2\Theta = 7°$, the intensity of the peak increased sharply when the annealing temperature was increased. This indicated that there was the re-organization of the CoTPP molecules in the layer to form a different structure when the film was annealed. From these results, it can be concluded that the annealing technique can be used to modify the orientation of the molecular layer on the substrate.

The surface morphology characterization has been performed on the as prepared, annealed at 50, 100 and 150°C LB films using atomic force microscopy (AFM) technique. Figure 4 shows the AFM image of the four LB film samples which were recorded in the area of 14 x 14 μm^2. It was found that the surface morphology of the thin films changed when the annealing process performed on the LB films. For the case of the as prepared thin films, the surface exhibited to have a low peaks and valleys and the surface showed a rather smooth structure. The surface roughness of the thin film was 18.21 nm. When the thin films samples were annealed, the morphology of the thin films

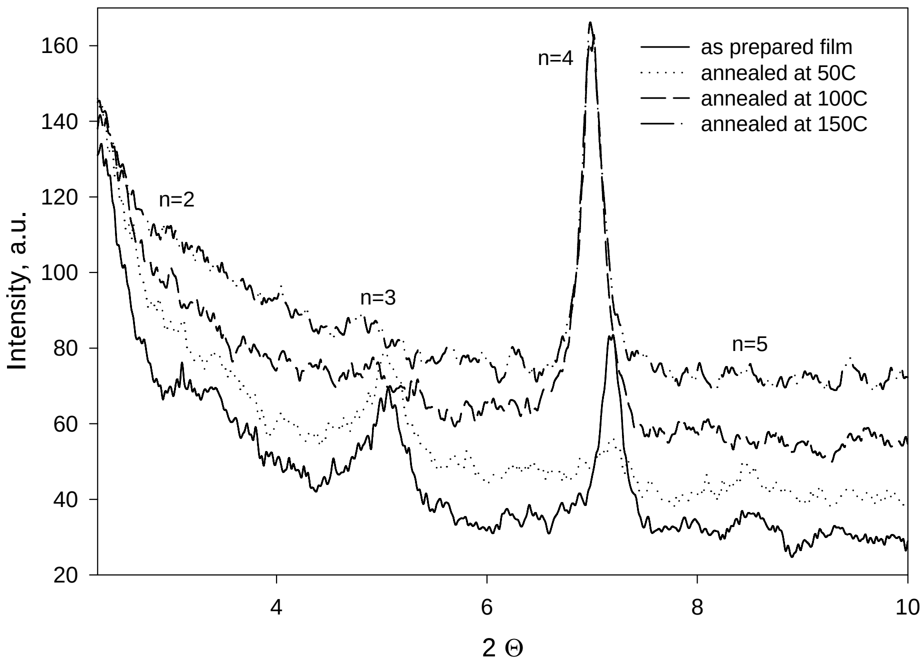

Figure 3. The XRD pattern of the thin films samples; the as prepared, annealed at 50, 100 and 150°C.

surface changed. This was indicated by the change of the surface roughness of the thin films to the value of 40.99, 26.90 and 18.88 nm for the thin films annealed at 50, 100 and 150°C, respectively. The roughness was determined by the presence of the peaks and valleys on the surface where it was defined as the root mean square of the highest and the lowest part differences on the surface. The roughness determined the morphology of the surface which represented as the appearance of hills and valleys or pores and voids. For this reason, it can be concluded that the annealing technique may be used to modify the morphology of the surface. Therefore, the optimum condition on the surface morphology can be obtained.

Optical sensing of gas.

The detection of VOC vapor samples using CoTPP films was performed by introducing the vapor into the chamber. The light source at a particular wavelength was transmitted to one arm of the two arms fiber reflectance probe and then, and the reflected intensity of the light from the thin films at the peak wavelength was recorded. The sensing sensitivity of the films toward the vapor was calculated based on the change in the light intensity after being reflected. In order to find whether the response was repeatable, the vapor which has been flowed into the chamber was, then, cut off and the remaining vapors were removed by sucking them using an electrical pump. The reversibility of the films was determined by recording its response; at least three cycles at once measurement and repeated this procedure at the other time to make sure its stability against the VOC

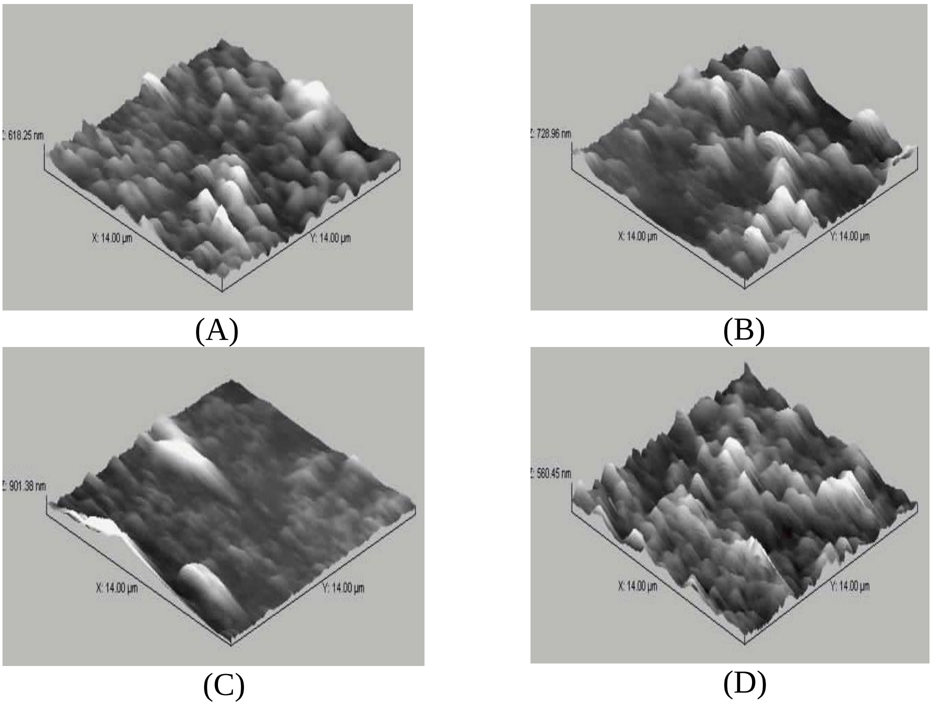

Figure 4. The AFM image of the thin films samples, (A) the as prepared, (B) annealed at 50°C, (C) annealed at 100°C and (D) annealed at 150°C.

exposure. Figure 5 shows three cycle's responses of the CoTPP film toward the saturated vapor of cyclohexane at 626 nm, the peak wavelength of the light source. This film was found to be sensitive to the vapor with the average response times to reach the maximum change in the reflected light intensity was within 10 seconds. The response recovered back to the original state when the vapor was removed from the film chamber within 10 seconds. Despite the drift on the original measurement, the thin films exhibited a high stability to the presence vapor sample. The detection of this vapor was continued using the annealed films at 50, 100 and 150°C. Figure 6 shows the comparison of the thin films responses towards the presence of cyclohexane vapor. It was found that there was a significant change on the sensing sensitivity when the films were annealed, which the sensing sensitivity was tend to decrease when the annealing temperature was increased. This could be caused by the transformation of the thin films structure to the un-organized state upon exposure towards higher temperature. Therefore, the response decreased.

The change on the sensing sensitivity of the CoTPP LB films towards a particular vapors sample if annealed can be directly correlated to the change of the surface morphology structure of the thin films [8]. It was found that the annealing process may modify the surface morphology of the films where the change on the structure depended on the annealing temperature applied. From the experimental results, it was obtained that the thin films which features a large number of peaks and valleys on the surface morphology, as shown by the as prepared thin films, demonstrated a high sensing sensitivity towards the gaseous molecules. This can be understood that the larger the number of peaks and valleys on the surface will provide a larger surface area for the interactions with the gaseous molecules. Hence, the sensing sensitivity increased. For the case of the thin films annealed at 150C, the thin films showed the lowest sensing

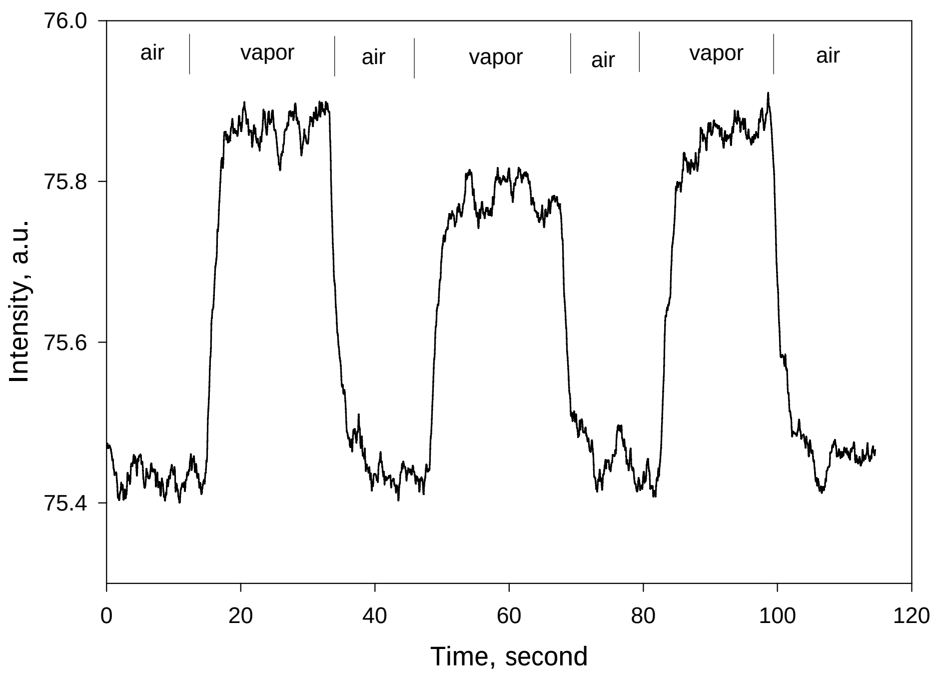

Figure 5. The sensing sensitivity of the CoTPP films towards the presence of saturated vapor of cyclohexane which was recorded at the wavelength of 626 nm, the light source.

sensitivity even tough it possessed a large number of peaks and valleys on the surface. At this circumstance, the thin film may undergo the damage on the surface morphology structure because of a high heating temperature. Therefore, the sensing sensitivity towards the presence of the gaseous molecules decreased. The change on the sensing sensitivity due to the surface morphology change can also be explained in the perspective of the interactions of gas and the thin films. The change on the surface morphology could be attributed to the modification of the interaction activation energy between these two systems. Such energy may depend directly on the morphology of the thin films surface and the properties of the gaseous molecules. An appropriate surface morphology structure may provide high activation energy of the interaction. For the case of the properties of the gas molecules, such as molecular structure and the electrical properties, play an important role in the interaction with the thin film surface. These properties determined the type of interaction which may be occurred between the two systems. For the case of cyclohexane vapor with polar-planar structure molecule, the interaction with the porphyrins molecules may be attributed to the columbic binding activity with the molecular plane of the porphyrins. At this stage, the optimum sensitivity may be given by the thin film with low surface roughness in order to facilitate more interaction between molecular plane of porphyrins and the cyclohexane molecules.

The interactions of the metalloporphyrins film and various kinds of gases have been widely studied [10]. There are two particular sites in the porphyrins molecule which is responsible for the interactions, namely at the peripherals position and at the center of the ring. The interactions of porphyrins with analytes pertaining to the interaction at one particular site causes rearrangement of the electrical dipole in the bulk thin films. This creates the change on the electronic energy state in the porphyrins compounds, particularly the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Metalloporphyrins films before interacting with the

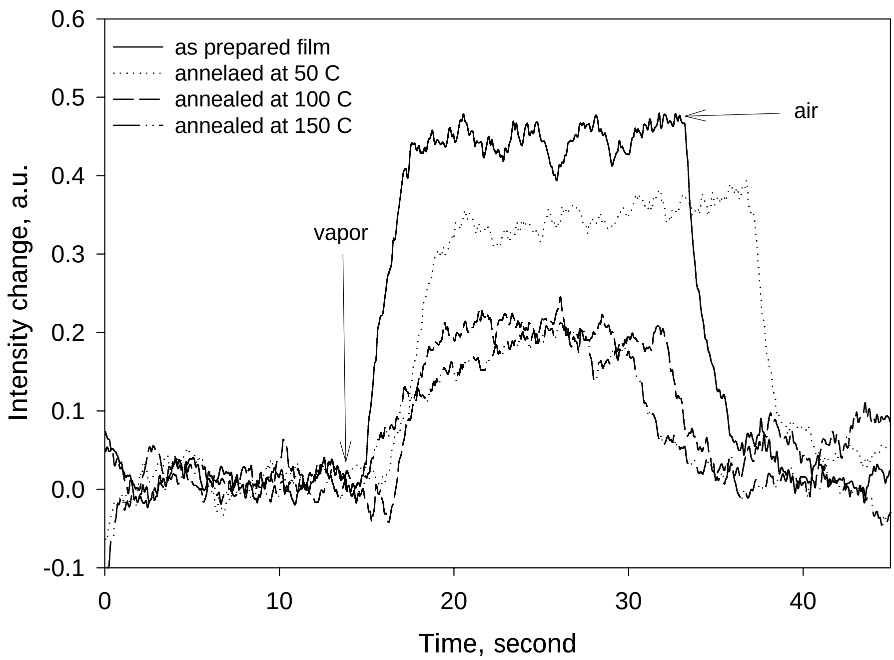

Figure 6. The comparison of the sensing sensitivity of the as prepared thin film and the annealed films.

molecules of gases possess a gap between these two orbitals which determines its initial absorption upon the light radiation [5-6]. When a light source with a certain wavelength radiates and passes through the film, which has already interacted with analytes, the light may undergo the decreasing or increasing of the intensity and the shift on the peak wavelength. The change of the light intensity could be caused by the addition or reduction of the amount of the light energy absorbed by the dipole system to excite to the excited level due to the broadening and narrowing the gap energy between the ground and the excited state, respectively. This case was considered as the transduction mechanism.

CONCLUSION

The Langmuir-Blodgett films of CoTPP was found to be sensitive to the presence of saturated vapor of cyclohexane. Its sensing sensitivity was found to depend on the morphology of the thin film surface. These results indicated that the modification of the surface morphology structure of the thin films surface can be obtained an optimum condition on the surface to provide the highest sensing sensitivity towards the gaseous molecules.

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