



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

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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.

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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], pho-

toassisted 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-

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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 $30 \text{ cm}^2 \text{ min}^{-1}$ 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 ($2.947 \times 10^{11} \text{ dyn cm}^2$).

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

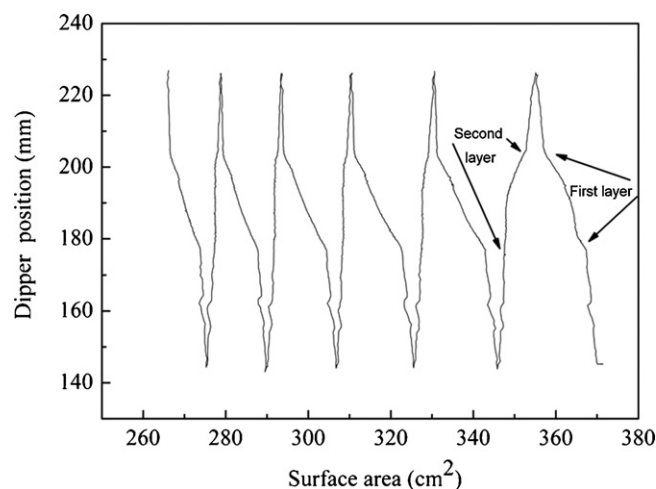


Fig. 1. The number of LB deposition cycles of porp2 thin film at a constant surface pressure value of 15 mN m^{-1} .

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 $20 \mu\text{m}$, 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 (SPIPTM). 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

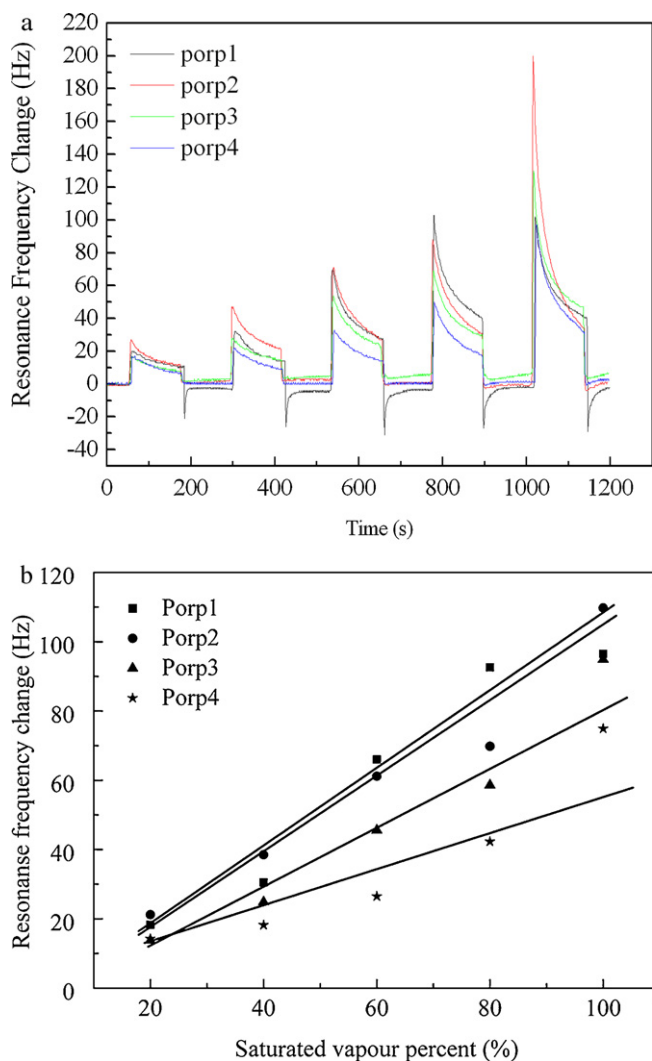


Fig. 2. (a) The kinetic graph in terms of frequency shift versus time in exposure to chloroform vapour. (b) Calibration graph for the chloroform exposure in all thin films.

that similar amount of molecules were deposited onto the quartz in each layer deposition.

3.2. QCM results and gas sensing properties

In Fig. 2(a) the kinetic gas response of the porphyrin thin films in exposure to different concentrations of chloroform vapor in terms of the change in resonance frequency (Δf) with time is given. The analyte gas was injected into the gas cell for 2 min at diluted amounts of saturated vapor concentration followed by 2 min recovery with dry air. The concentration of analyte vapor was arranged as 20%, 40%, 60%, 80% diluted saturated gases with dry air for consequent exposures respectively and at the last cycle saturated concentration of analyte vapor was injected. The decrease in resonance frequency of the quartz crystal resonator is proportional to the increase in mass due to presence of vapor adsorbed on its surface. All porphyrin thin films give very fast response to the analyte vapor chloroform in the range of a few seconds. The thin films recover themselves to their initial values after they are flushed with dry air which means that they can be used multiple times. Fig. 2(b) shows the dependence of the resonance frequency change (Δf) to the percent of saturated vapor, namely calibration graph. It is clear that all thin films have a linearly increasing response with

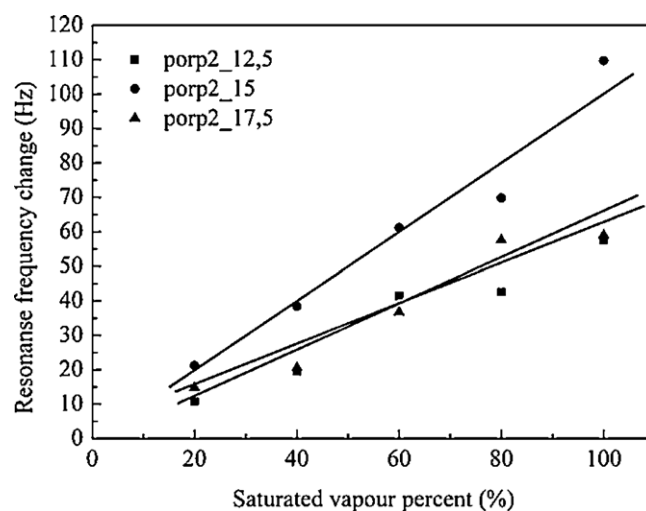


Fig. 3. Calibration graph for the chloroform exposure for porp2 thin film fabricated in different fabrication surface pressure values of 12.5 mN m^{-1} , 15 mN m^{-1} and 17.5 mN m^{-1} .

the increasing concentration of the vapor. Three different vapors: benzene, toluene and chloroform are used and similar results have been recorded. All of the results have been listed in Table 1.

The main aim of this work is to verify the dependence of gas sensor performance of the thin films on their surface properties. To better understand this phenomenon thin films have been fabricated using different values of fabricating surface pressure ranging between 12.5 mN m^{-1} and 17.5 mN m^{-1} forming different surface textures. The calibration curves for porp2 thin film fabricated at surface pressure values of 12.5 mN m^{-1} , 15 mN m^{-1} and 17.5 mN m^{-1} have been given for chloroform exposure in Fig. 3. The complete data can be observed in Table 1. As it is seen both in Table 1 and Fig. 3 the maximum response of the thin films due to the exposure has been recorded for the thin films fabricated at a surface pressure value of 15 mN m^{-1} . Additionally, highest response has been observed for chloroform vapor among the tested analytes.

3.3. Atomic Force Microscopy (AFM) results

In Figs. 4–7, the AFM images of 11 layers of porphyrin thin films fabricated onto glass substrates at different fabrication surface pressure values have been given. As seen from the images the thin films fabricated at different deposition surface pressure values have different textures on their surfaces.

It is well known that the parameters that affect the strength of gas interaction of the porphyrin thin films include central metal atom [2,6,20,24] and the molecular size of the analyte gas molecules [5]. Another possible mechanism affecting the interaction between the gas molecules and thin films may be the surface morphologies of the thin films as appropriated that the interaction of the gas molecules firstly starts with the interaction of the active adsorption sites on the surface of the thin film and continues with diffusion into the bulk. This makes surface morphology important in terms of sensing capabilities. In order to understand the relationship between the gas interaction mechanisms and the surface properties of thin films, the surface properties have been analyzed using the SPIP™ program.

The surface roughness characteristics have been analyzed by using one amplitude parameter, root mean square roughness S_q and one hybrid parameter S_{dr} – the surface area ratio that expresses the ratio between the surface area (taking the z height into account)

Table 1
Resonance frequency change values of the thin films due to exposure to analyte gases.

Thin films	Deposition surface pressure (mN m ⁻¹)	Analyte gases	Resonance frequency change Δf (Hz)				
			%20	%40	%60	%80	%100
Porp1	15	Benzene	8.8	14.4	18.5	36.8	40.3
		Toluene	70.3	13.2	21.16	26.6	29.4
		Chloroform	18.3	30.15	66	92.6	96.5
	17.5	Benzene	5.2	7.5	16.2	25.6	54.3
		Toluene	3.2	7.1	8.5	22.1	27.2
		Chloroform	21.5	27.16	52.7	62.7	101.05
Porp2	12.5	Benzene	3.03	7.76	14.02	17.9	27.9
		Toluene	3.3	4.9	8.3	11.3	19.1
		Chloroform	10.8	19.5	41.5	42.66	57.6
	15	Benzene	13.6	23.08	36.86	44.72	70.06
		Toluene	9.4	12.7	24.1	36.9	53.2
		Chloroform	21.2	38.5	61.18	69.8	109.76
	17.5	Benzene	5.7	10.09	16.01	20.34	40.79
		Toluene	4.1	8	11	14.4	23.8
		Chloroform	14.8	20.6	36.8	57.6	59.01
Porp3	12.5	Benzene	11.2	13.2	18.4	21.3	32.9
		Toluene	6.7	8.1	12.4	15.05	23.3
		Chloroform	10.8	19.04	31.2	35.3	45.3
	15	Benzene	7.8	9.8	15.8	20.24	36.7
		Toluene	8.5	15.2	21.9	25.9	34.6
		Chloroform	13.8	24.9	45.6	58.6	94.9
	17.5	Benzene	6.3	10.15	15.05	13.8	10.9
		Toluene	6.4	10.8	11.4	8.6	6.9
		Chloroform	18.6	24.9	40.5	54.5	70.8
Porp4	12.5	Benzene	10.4	13.2	18.11	21.5	32.2
		Toluene	8.3	16.4	23.1	26.4	45.2
		Chloroform	16.9	37.9	62.1	91.6	112.3
	15	Benzene	4.9	8.6	13.9	15.3	28.06
		Toluene	1.9	3.5	6.3	10.2	17.7
		Chloroform	14.2	18.2	26.5	42.3	74.9
	17.5	Benzene	8.1	11.4	18.3	20.2	36.4
		Toluene	3.7	7.3	12.1	15.7	29.4
		Chloroform	16.9	28.7	50.7	67	109.2

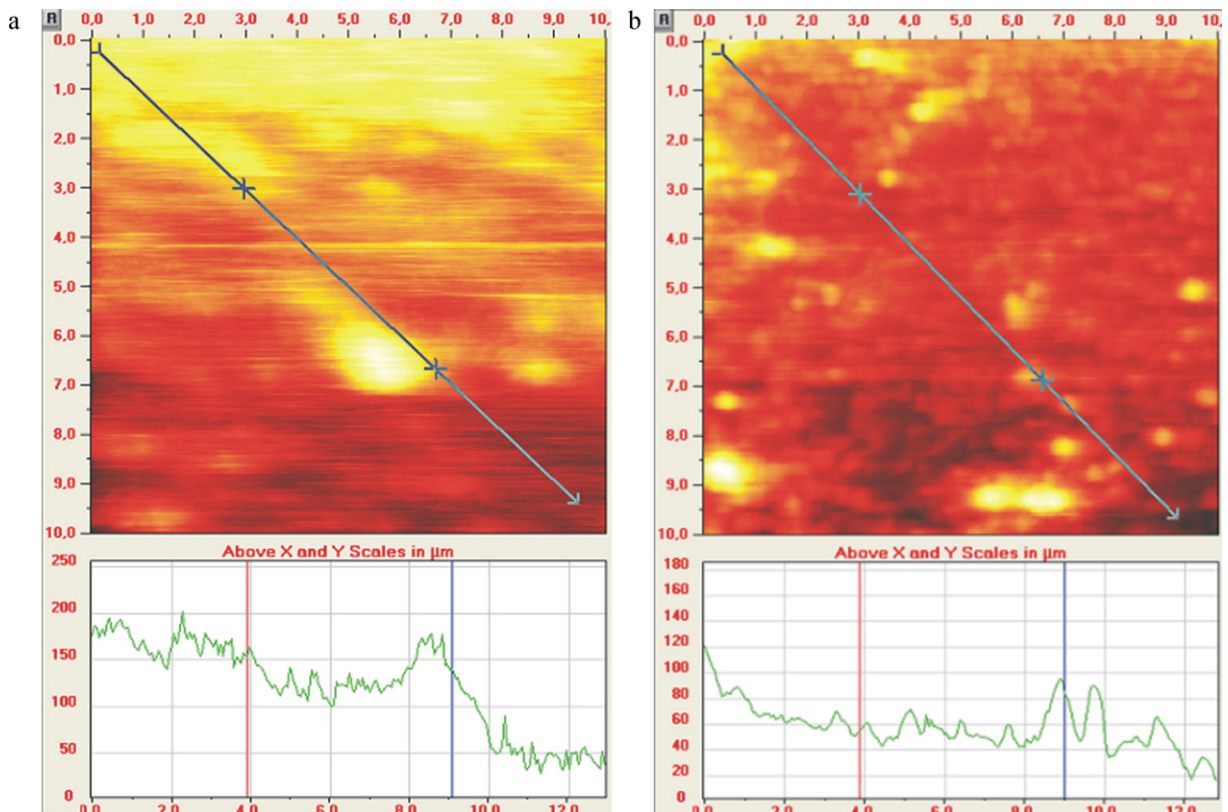


Fig. 4. 2D AFM images of porp1 thin film fabricated at a fabrication deposition pressure of (a) 15 mN m⁻¹ and (b) 17.5 mN m⁻¹ at a scale of 10 μm × 10 μm.

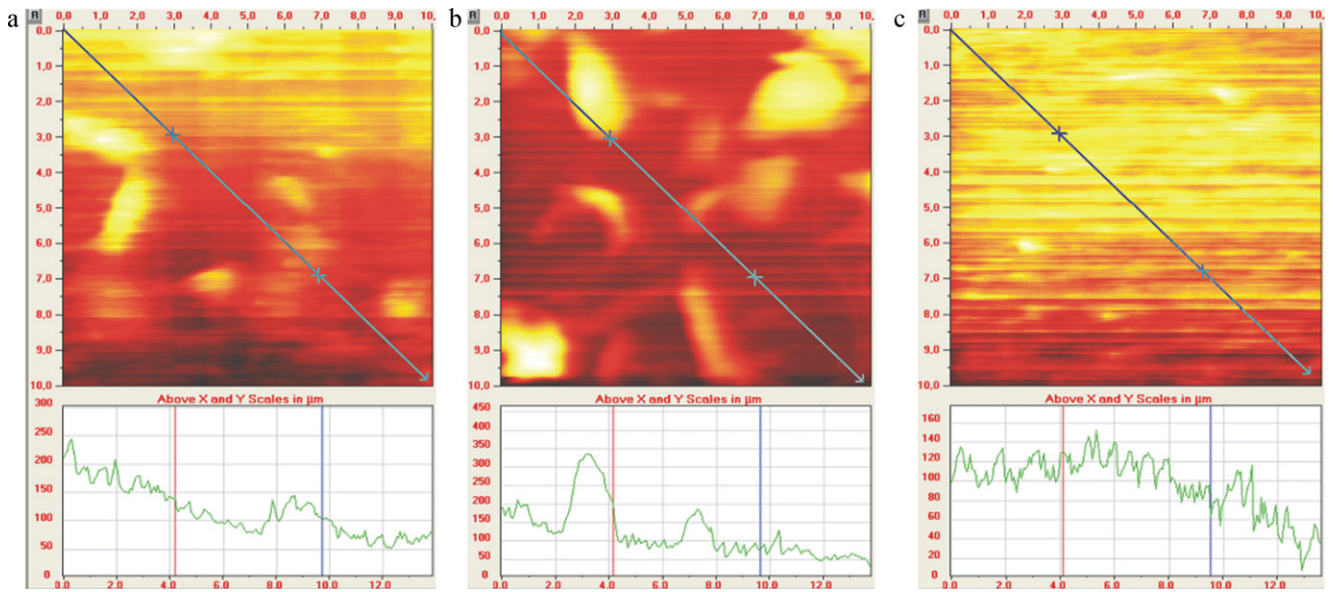


Fig. 5. 2D AFM images of porp2 thin film fabricated at a fabrication deposition pressure of (a) 12.5 mN m^{-1} , (b) 15 mN m^{-1} and (c) 17.5 mN m^{-1} at a scale of $10 \mu\text{m} \times 10 \mu\text{m}$.

and the area of the flat x, y plane. For a rectangular image $M \times N$, the parameters are defined as:

$$S_q = \sqrt{\frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [z(x_k, y_l) - \mu]^2} \quad (2)$$

where μ is the mean height which is expressed below.

$$\mu = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} z(x_k, y_l) \quad (3)$$

S_{dr} – the surface area ratio is expressed as

$$S_{dr} = \frac{\left(\sum_{k=0}^{M-2} \sum_{l=0}^{N-2} A_{kl} \right) - (M-1)(N-1)dxdy}{(M-1)(N-1)dxdy} 100\% \quad (4)$$

where A_{kl} is given below.

$$A_{kl} = \frac{1}{4} \left(\sqrt{dy^2 + (z(x_k, y_l) - z(x_k, y_{l+1}))^2} + \sqrt{dy^2 + (z(x_{k+1}, y_l) - z(x_{k+1}, y_{l+1}))^2} \right) \times \left(\sqrt{dx^2 + (z(x_k, y_l) - z(x_{k+1}, y_l))^2} + \sqrt{dx^2 + (z(x_k, y_{l+1}) - z(x_{k+1}, y_{l+1}))^2} \right) \quad (5)$$

The S_{dr} values, S3A values which is the real area of the sample and rms (root mean square roughness) values of the surfaces have been listed in Table 2 for the images recorded with the dimensions $10 \mu\text{m} \times 10 \mu\text{m}$. The highest surface area ratio leads to the largest

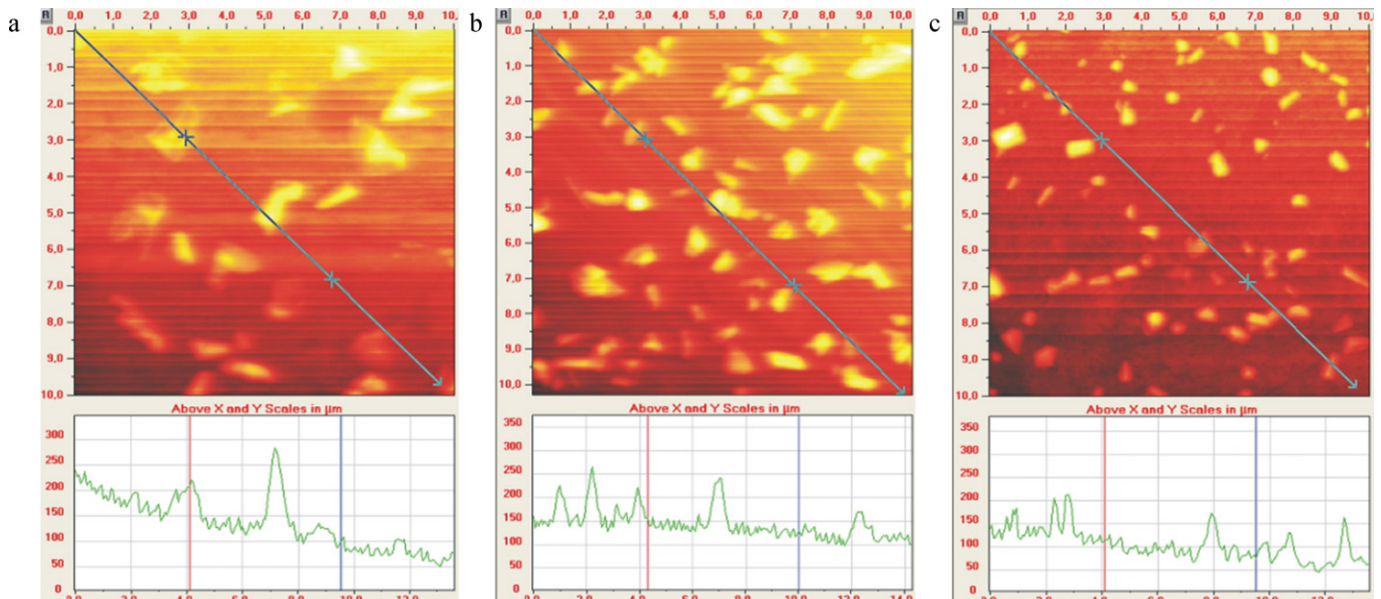


Fig. 6. 2D AFM images of porp3 thin film fabricated at a fabrication deposition pressure of (a) 12.5 mN m^{-1} , (b) 15 mN m^{-1} and (c) 17.5 mN m^{-1} at a scale of $10 \mu\text{m} \times 10 \mu\text{m}$.

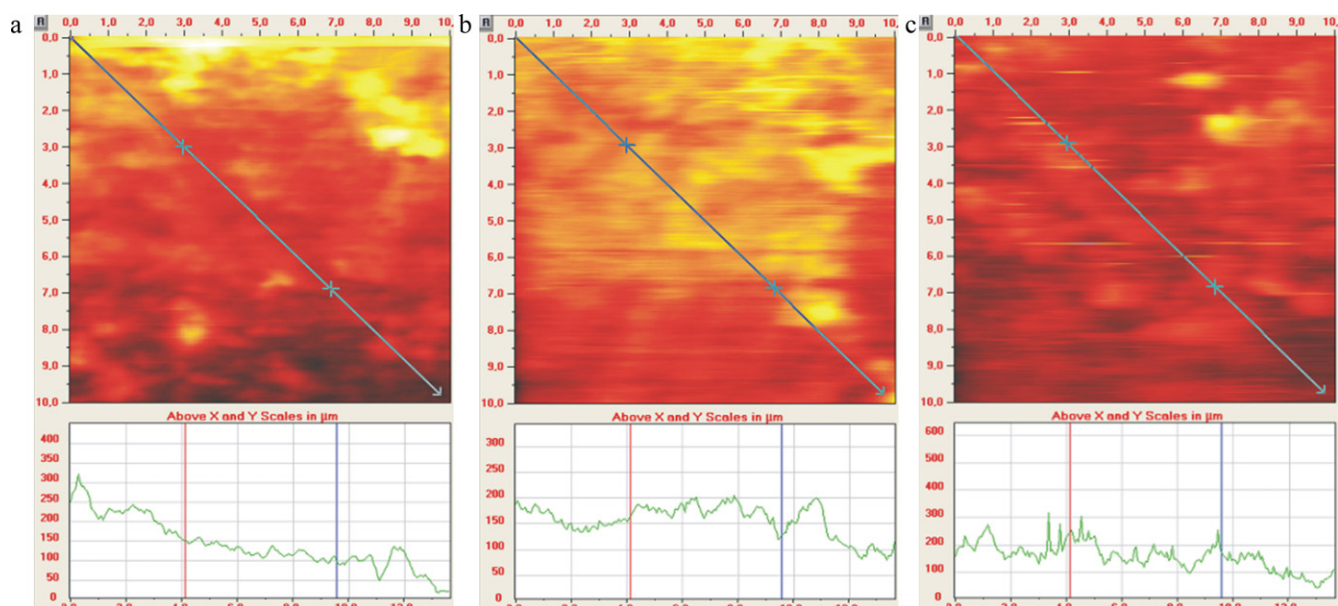


Fig. 7. 2D AFM images of porp4 thin film fabricated at a fabrication deposition pressure of (a) 12.5 mN m⁻¹, (b) 15 mN m⁻¹ and (c) 17.5 mN m⁻¹ at a scale of 10 μm × 10 μm.

Table 2

The root mean square roughness, surface area ratio and real area values of the samples.

Thin films	Deposition surface pressure (mN m ⁻¹)	S _{dr} (%)	S3A (nm ²)	rms (nm)
Porp1	15	9.49	1.09E+8	48.86
	17.5	1.86	1.02E+8	23.42
Porp2	12.5	0.341	1E+8	84.59
	15	2.40	1.05E+8	57.59
Porp3	17.5	0.457	1.01E+8	30.58
	12.5	6.5	1.065E+8	57.13
Porp4	15	7.59	1.08E+8	54.96
	17.5	5.77	1.08E+8	45.70
	12.5	3.6	1.04E+8	76.87
	15	15.72	1.16E+8	41.06
	17.5	26.1	1.26E+8	55.59

surface of the sample. The values are consistent with the images of the thin film surfaces (Figs. 4–7). One can see that for a surface with higher and larger features (as the deposition pressure decreases) the S_{dr} is higher, indicating a rougher surface. There is only one exception in the case of porp4, where the value of rms is higher for 17.5 mN m⁻¹ than for 15 mN m⁻¹.

For porp1–porp3 thin films both the highest S_{dr} (%) values and the highest resonance frequency changes were observed for the thin films fabricated at a surface pressure value of 15 mN m⁻¹. For porp4 thin film similar situation is effective at the surface pressure value of 17.5 mN m⁻¹ where the maximum response for benzene exposure only. It is also our new concern to explore the dependency of the response on the type of the gas molecule and central atom.

4. Conclusion

The gas sensing mechanism for porphyrin thin films has been attracting much interest over the last decade. With this study the effect of the surface morphology of the thin films on the gas sensing properties has been predicated for porphyrin thin films by comparing the surface area and QCM measurements. The idea relies on the possibility of high interaction of the gas molecules when they find a larger surface, and in consequence more sites to bind on the surfaces of the thin films. It has been shown that the gas response

detected using QCM system was high when the surface of the thin film was also high. However there are some other effects which have not been taken under consideration such as central atom and thickness of the thin films. Our future work will concentrate on these factors.

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