Fabrication of Langmuir–Blodgett thin films of porphyrins and investigation on their gas sensing properties

İ. Capan [a],[*], Ç. Tarımcı [b], R. Capan [a]

[a] Balikesir University, Science and Arts Faculty, Physics Department, 10145 Balikesir, Turkey
[b] Ankara University, Faculty of Engineering, Department of Engineering Physics, 06100, Tandoğan, Ankara, Turkey

ARTICLE INFO

ABSTRACT

In the present study, we report about the Langmuir–Blodgett thin film fabrication and gas sensing properties of metal free 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine and its derivatives containing iron chloride, cobalt and magnesium. The isotherm graphs are recorded to investigate the optimum conditions for the thin film deposition. Gas sensing performances of these thin films for volatile organic compounds (VOCs) including chloroform, benzene, toluene and ethyl alcohol are studied using quartz crystal microbalance (QCM) technique. The experimental results showed that these materials are suitable to produce a sensing layer for VOCs compounds. The best response was recorded against toluene vapour for all thin films where the dominating effects for gas sensing mechanism was considered as interaction between the central metal atom and conjugated π electron system.

1. Introduction

Developments in gas sensing technology became a serious aspect because of the need to control the air quality as an important environmental issue. The need to improve the performance of the gas sensing devices mostly depends on the sensitivity and the selectivity of the sensing materials. In the last decade the use of organic materials as gas sensing materials has increased because of their simple and low cost synthesis, wide range of physical and chemical properties that can be tailored by changing their composition. Porphyrins are known as promising organic gas sensing materials because of their strong π–π^* interactions which helps to increase aromatic compounds adsorption [1,2]. Optical properties of porphyrins have also attracted great interest in gas sensing studies [3–5].

The thin film fabrication can be made using several techniques including spin coating, spray coating, vacuum sublimation, self-assembly and Langmuir–Blodgett (LB) thin film deposition technique [6]. Among these techniques LB thin film deposition technique is one of the most convenient method which enables to fabricate high quality films with significantly improved molecular order and a uniform surface [7,8]. It is well known that the introduction of gas molecules towards porphyrin thin films may cause some changes in their physical properties such as optical or electrical in the case of inorganic gas interactions and this aspect has been used to investigate the gas sensing properties of these thin films [3,9,10]. However to the best of our knowledge gas sensing properties of porphyrin thin films towards volatile organic compounds have not been investigated as extensively as inorganic vapours due to their low response compared with the inorganic ones.

In this work thin films of metal free, iron (III) chloride, magnesium and cobalt derivatives of octaethyl porphyrins have been fabricated using LB thin film fabrication technique. Their characterisations have been made using atomic force microscopy (AFM) and gas sensing properties towards saturated vapours of some volatile organic compounds (VOCs) such as chloroform, benzene, toluene and ethyl alcohol have been investigated using quartz crystal microbalance (QCM) technique. The gas sensing responses through LB thin films of porphyrins were investigated and the dominating effects on gas sensing mechanism were proposed. It is found that central metal atom and conjugated π electron system interaction effects are important in the interaction mechanism of porphyrin thin films with the VOCs in the investigated concentration range.

2. Experimental

Four different porphyrin chemicals as 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine iron(III) chloride, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine magnesium(II) and 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine cobalt(II) were purchased from Sigma–Aldrich and used without further purification. The chemical structures of them are given in Fig. 1 and coded as porp1,

* Corresponding author. Tel.: +90 266 612 1000; fax: +90 266 612 12 15.
 E-mail addresses: inci.capan@gmail.com, ibasaran@baikesir.edu.tr (İ. Capan).
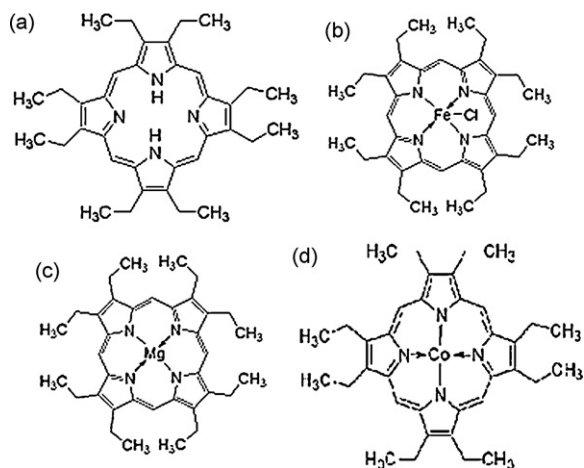
Fig. 1. Chemical structures of (a) free porphyrin and its (b) iron(III) chloride, (c) magnesium(II) and (d) cobalt(II) derivative.

Fig. 3. Π–A isotherm graphs of the porphyrins with the porp3 isotherm in the inset.

porp2, porp3 and porp4 respectively. Other chemicals: chloroform, toluene, benzene and ethyl alcohol were also purchased from Sigma–Aldrich and used without further purification.

Alternate layer Nima 622 model LB film trough provided with a filter paper Wilhemly balance has been employed to record the surface pressure–area (Π–A) isotherm graphs and to fabricate the thin films. The porphyrins have been dissolved in chloroform with the concentration of 0.2 mg ml^{-1}. 500 μl of these solutions 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 the constant surface pressure value of 15 mN m^{-1}. Transfer speeds for both downstroke and upstroke deposition were 15 mm min^{-1} with a transfer ratio value of approximately 0.95. Ten layers of porphyrins have been deposited onto quartz crystal substrates for gas sensing experiments and onto glass substrates for AFM measurements.

An in-house built QCM has been employed to investigate the gas sensing properties of the thin films. The block diagram of the QCM system is shown in Fig. 2. The alternating voltage applied across to quartz crystal oscillator electrodes by the power supply provides the quartz crystal oscillator to oscillate in its oscillation frequency. Function generator is used to monitor the changes in the resonance frequency where the oscilloscope is used to see the changes in the system. The sensitivity of the QCM system was 1–2 ng/Hz. Detailed information can be found elsewhere [11,12]. The AT-cut quartz crystal with a nominal frequency of 3 MHz sandwiched between two metal electrodes and coated with the porphyrin thin film was
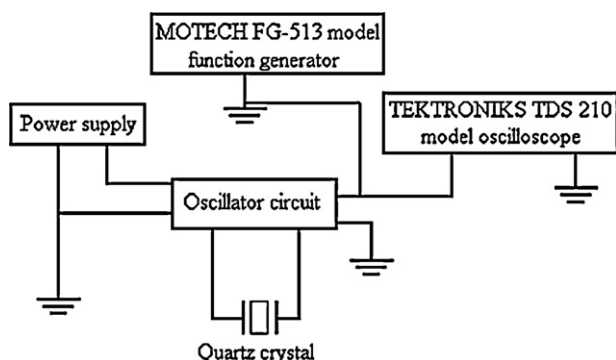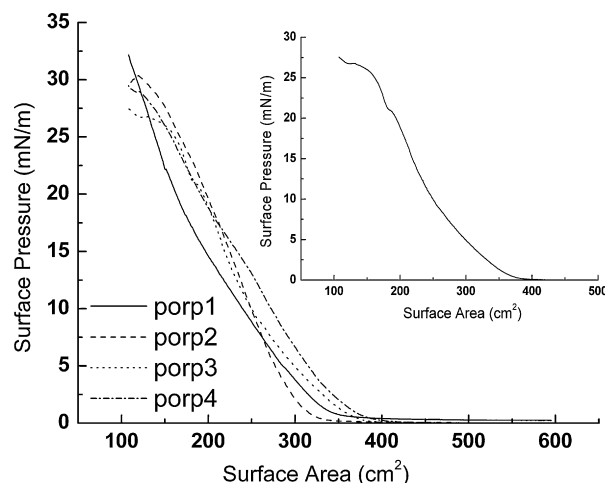
inserted into the QCM system which is connected to the oscillator circuit. The frequency was monitored using the function generator during exposure to toxic gas and its recovery. Diluted amounts of saturated toxic gas ranging between 20% and 100% was introduced into the gas cell for 2 min followed by flushing with dry air for 2 min. All measurements were made at room temperature.

3. Results and discussion

3.1. Fabrication of the thin films

The isotherm graphs which give information on the behaviour of the monolayers on the air–water interface are given in Fig. 3 for all porphyrins. Isotherm graphs show that the porphyrins form regular monolayers on the water subphase with three of the phases as gas, liquid and solid phases are seen in the graph. The surface pressure values corresponding to these three phases are given in Table 1. Similar results on the behaviour of porphyrin monolayers at the air–water interface have been observed and already have been reported [13–15]. The surface pressure value of 15 mN m^{-1} is a common value for the solid phases for all porphyrins therefore it is suitable to be selected as the fabrication pressure value. Collapse has been observed for 3 of the porphyrin monolayers except porp1. Moreover a phase transition value for porp3 has been observed at 21 mN m^{-1} which has been pointed out in the inset of Fig. 3.

The reduction in the surface area of the monolayer versus dipper position during the deposition of the LB layers onto the substrates are known as deposition graphs which give information on the quality of the monolayers. In Fig. 4 the deposition graph of porp1 monolayer onto quartz substrate for 10 layers is shown. The average reduction in surface area of the monolayer due to its transfer onto substrate is similar for all layers where for the last 4 layers it starts to be less than the first layers. The deposition graphs for other 3 thin films are similar to those shown in Fig. 4 and they are not reported in this work.

Fig. 2. Block diagram of the quartz crystal microbalance system.

Table 1
The Π–A isotherm data.

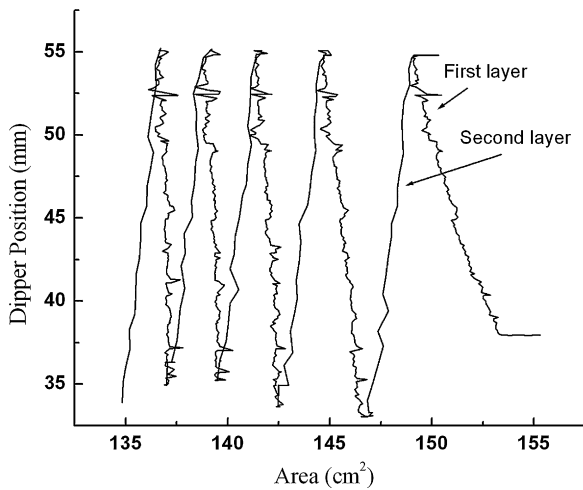| Surface pressure (mN m^{-1})	Gas phase	Liquid phase	Solid phase	Collapse
Porp1	0–1	1–14	14–30	Not observed
Porp2	0–1	1–14	14–30	30
Porp3	0–1	1–10	10–21	25
Porp4	0–1	1–14	14–28	28

Fig. 4. Deposition graph of 10 layers of porp1 thin film.

3.2. Atomic force microscopy results

AFM is an excellent tool to obtain information on surface morphology which is an important parameter on the interaction between the thin film and the gas molecules. The roughness, pore size and surface area of the thin film can influence the gas sensing performance when the gas molecules interact with the surface. The AFM results of 10 layers of porp1 thin film fabricated onto glass substrate have been given in Fig. 5(a) and (b). Fig. 5(a) shows a larger surface area with the dimensions of 10 μm × 10 μm. In this image it is clearly seen that the thin film fabrication is successfully made onto the substrate. The pores observed on the surface may be a result of aggregated porphyrin groups on the surface [16]. A detailed investigation can be made using the image shown in Fig. 5(b) which shows a selected part of the first image with a smaller area with the dimensions 3 μm × 3 μm. The average height on the surface and the rms value have been calculated as 24.83 nm

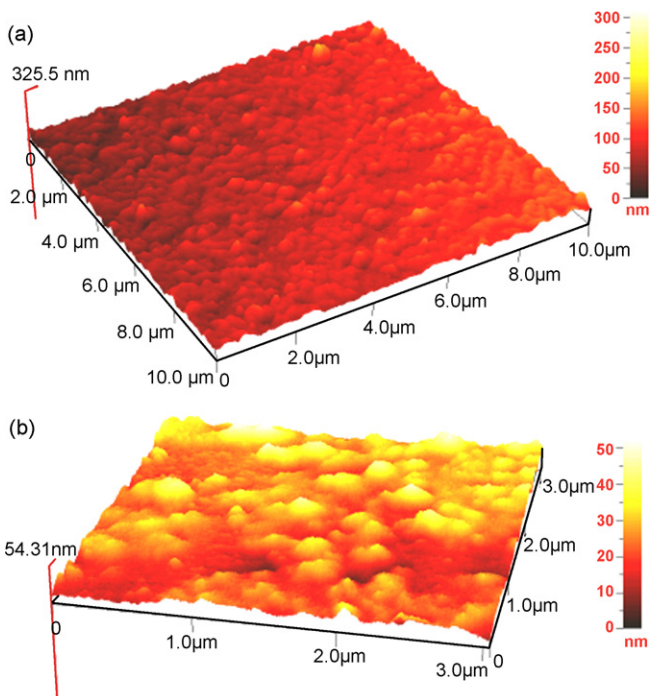**Fig. 5.** AFM image of 10 layers of porp1 thin film (a) 10 μm × 10 μm and (b) 3 μm × 3 μm.
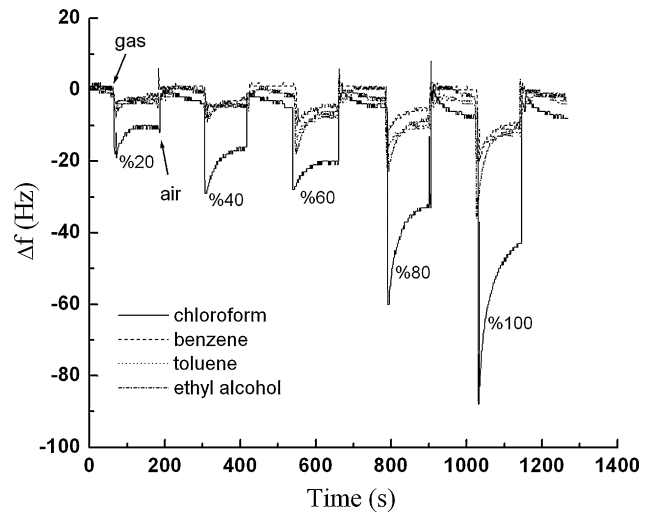

Fig. 6. Kinetic gas response of the porp1 thin film in exposure to different concentrations of organic vapours.

and 7.067 respectively. The pores that have been observed in the larger image also exists in this smaller image which can be considered as an advantage for gas sensing capability of the surface where in this situation the surface gives more active area for the gas molecules to interact [17].

3.3. Film sensing properties using QCM

The quartz crystal microbalance system is well known with its gravimetric sensitivity in terms of nanograms. The piezoelectric behaviour of the quartz crystal was firstly described by Sauerbrey [18] and the resonance frequency shift (Δf) on a quartz crystal against a mass change per unit area (Δm) is given by;

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

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

The resonance frequency change of the quartz crystal after thin films were 158, 102, 176 and 121 Hz for porp1–4 deposition thin films respectively. Assuming that equal amounts of material have been deposited onto the quartz crystal during the deposition process the mass deposited onto the quartz crystal is calculated as 262 ng for each layer for porp1 material. For porp2–4 materials the deposited mass value for each layer is calculated as 169, 285 and 200 ng respectively.

Fig. 6 shows the kinetic gas response of the porp1 thin film in exposure to different concentrations of organic vapours in terms of the change in resonance frequency (Δf) with time. The analyte gas was injected into the gas cell for 2 min followed by 2 min recovery with dry air. Here the concentration of analyte gas was 20%, 40%, 60%, 80% and 100% diluted saturated gas with dry air in a sequence of exposures respectively. The resonance frequency of the quartz crystal resonator decreases with the introduction of gas vapour into the gas cell where increasing gas concentration leads to higher response as can easily be predicted.

Although the interaction of gas molecules with the thin film is not fully understood there are a number of hypothesis made to explain the mechanism of interaction. We can summarise these interactions as:
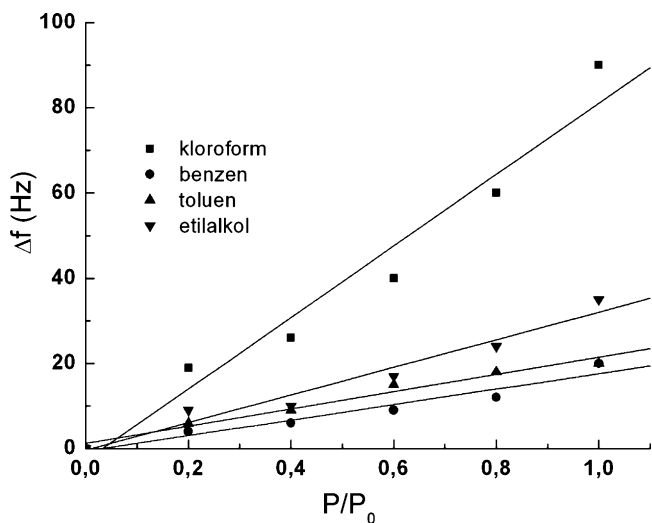
Fig. 7. Calibration curve for the porp1 thin film.

Fig. 8. Calculated sensitivity values of each thin films in exposure to analyte vapours.

(a) Central metal atom effect which is believed to effect the sensitivity of the porphyrins through different gases [3,4].
(b) Molecular size effect of the gas molecules where it is evident fact that the smaller size of the gas molecule enables the interaction in terms of diffusion into the thin film matrix [16].
(c) Interaction with the conjugated π electron system which leads to a charge transfer between interacting sites [19].
(d) Condensation of organic vapours in the nanoporous cavities within the film matrix which is more descent in the case of high concentrations [20].

In the case of interaction with the VOCs, the adsorption and desorption of gas molecules onto the thin film during exposure and flushing with dry air respectively can be an additional information for the gas sensing mechanism [21,22]. During the exposure, gas molecules are believed to interact with the adsorption sites on the thin film surface; moreover, the diffusion into the thin film matrix may also be possible at high concentrations till the interaction reaches the equilibrium (number of absorbed an desorbed molecules reach equilibrium). In Fig. 6 the fast response that takes place over the first few seconds for all analyte gas vapours which is believed to be a result of fast adsorption and the equilibrium is reached after 30–40 s. The kinetic studies for porp2–4 thin films gives similar kinetic graphs which are not given in this article.

The calibration curves which give the dependence of the change in resonance frequency with the increasing gas concentration are shown in Fig. 7 for porp1 thin film. The linear dependence is seen in the graph for all analyte gas vapours where the deviation from linearity is seen in the low concentration region for some gases. The calibration curves for the other 3 thin films give similar behaviour providing the linear dependence.

The saturated vapour concentrations for different analyte vapours are not the same in ppm. Taking this into account to make a comparison between the sensing performances of the thin films towards analyte gas molecules sensitivities have been calculated. The sensitivity of a thin film towards an analyte vapour has been defined as the response corresponding to 1 ppm of this individual gas vapour. Fig. 8 shows the sensitivity values of the thin films towards different gas vapours calculated using the slope of the calibration curves in terms of Δf/concentration (Hz/ppm). It is obvious in Fig. 8 that toluene has shown the highest response on exposure to all four types of thin films. It has already been shown that the sensitivity of porphyrin and phthalocyanine LB films increases during interaction wi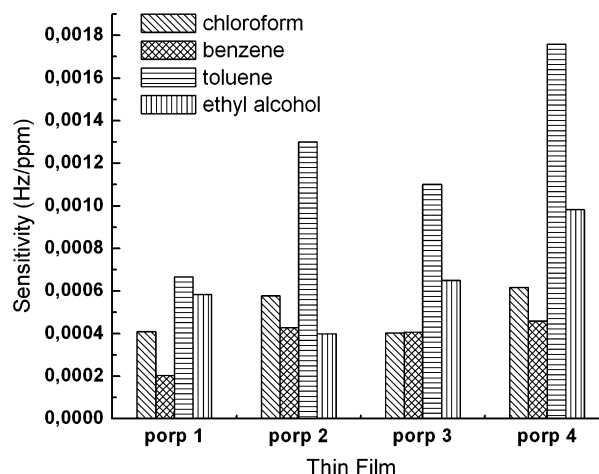th gas molecules having planar structure with conjugated double bonds and high degree of symmetry [2]. These molecules are believed to make optimum interaction with porphyrins due to large portion of their molecular body contacting with the porphyrin molecules and enable high sensitivity [23]. The high sensitivity of toluene demonstrates the importance of this claim.

Benzene molecule however has a similar planar structure as toluene molecule, lowest sensitivity of all porphyrins to benzene molecules due to interaction with thin films may be explained by the fact that the polarizability and dipole interactions are not sufficient to compete with both the coordination to the metal atom and the hydrogen bond interactions [1]. This effect is believed to be more effective in the case of benzene interaction. The results in Fig. 8 also suggest that the higher sensitivity values of the metallated porphyrins' as compared with the metal-free porphyrins'. It is clearly seen that for all analyte vapours the sensitivity has the lowest values for the porp1 thin film which is metal free indicating the importance of metal atom effect on sensitivity [24]. The highest response among metallated porphyrins (porp2, porp3 and porp4) has been obtained for porp4 thin film. This behaviour may be attributed to the highest electron affinity of Co atom in porp4 porphyrin compared with the Fe and Mg atom in porp2 and porp3 thin films respectively [25].

4. Conclusion

In this paper the LB thin film fabrication of the four different chemicals: metal free porphyrin and its three metallated derivatives have been used to fabricate Langmuir–Blodgett thin films. The thin film fabrication process has been monitored using quartz crystal microbalance technique and surface morphology of the thin films has been investigated using atomic force microscopy. These investigations showed that the transfer of the porphyrin monolayers onto suitable substrates has been successfully carried out. The surface morphology investigations showed that the thin films surface is suitable for gas sensing experiments with randomly scattered aggregated porphyrin groups on it.

The interaction of VOCs with the LB thin films have been investigated using QCM technique. The entire interaction of gas molecules with the thin films however is a complicated phenomena with a number of predicted mechanisms, metal atom effect and conjugated π electron system interaction effect are found to be dominating effects in gas sensing mechanism.

Finally these results clearly show the promising gas sensing capabilities of the selected porphyrins. Porp1–4 thin films can find extensive utilization in electronic nose applications. Future work

will be on the thickness dependence of gas sensing properties of these thin films.

Acknowledgement

This work has been partially funded by the Balıkesir University Scientific Research Projects department within the project BAP 2006/07.

References

[1] A. Macagnano, E. Sgreccia, R. Paolesse, F. De Cesare, A. D'Amico, C. Di Natale, Sorption and condensation phenomena of volatile compounds on solid-state metalloporphyrin films, Sens. Actuators B, Chem. 124 (2007) 260–268.
[2] H. Ding, V. Erokhin, M. Kumar Ram, S. Paddeu, L. Valkova, C. Nicolini, A physical insight into the gas-sensing properties of copper (II) tetra-(*tert*-butyl)-5,10,15,20-tetraazaporphyrin Langmuir–Blodgett films, Thin Solid Films 379 (2000) 279–286.
[3] T.H. Richardson, C.M. Dooling, L.T. Jones, R.A. Brook, Development and optimization of porphyrin gas sensing LB films, Adv. Colloid Interface 116 (2005) 81–96.
[4] Akrajas, M. Mat Salleh, M. Yahaya, Enriching the selectivity of metalloporphyrins chemical sensors by means of optical technique, Sens. Actuators B, Chem. 85 (2002) 191–196.
[5] T.H. Richardson, C.M. Dooling, O. Worsfold, L.T. Jones, K. Kato, K. Shinbo, F. Kaneko, R. Tregonning, M.O. Vysotsky, C.A. Hunter, Colloid Surf. A 198–200 (2002) 843–857.
[6] A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-Assembly, Academic Press, Boston, 1991.
[7] G.G. Roberts (Ed.), Langmuir–Blodgett Films, Plenum Press, New York, 1990.
[8] T. Richardson (Ed.), Functional Organic and Polymeric Materials, John Wiley and Sons, Ltd., West Suxxes, 2000.
[9] A. Dunbar, T.H. Richardson, A.J. McNaughton, W. Barford, J. Hutchinson, C.A. Hunter, Understanding the interactions of porphryin LB films with NO$_2$, Colloid Surf. A 284–285 (2006) 339–344.
[10] B. Wang, X. Zuo, Y.Q. Wu, Z.M. Chen, Preparation, characterization and gas sensing properties of lead tetra-(*tert*-butyl)-5,10,15,20-tetraazaporphyrin spin-coating films, Sens. Actuators B, Chem. 125 (2007) 268–273.
[11] J. Schröder, R. Borngraber, F. Eichelbaum, P. Hauptmann, Advanced interface electronics and methods for QCM, Sens. Actuators A 97–98 (2002) 543–547.
[12] J.M. Beeley, C. Mills, P.A. Hammond, A. Glidle, J.M. Cooper, L. Wang, D.R.S. Cumming, All-digital interface ASIC for a QCM-based electronic nose, Sens. Actuators B, Chem. 103 (2004) 31–36.
[13] V.V. Borovkov, S. Casilli, S. Conoci, Y. Inoue, S. Sortino, L. Valli, Molecular organization and *synanti* conformational equilibria in ethane-bridged bis(zinc porphyrin) floating films at the air–water interface, Thin Solid Films 572 (2004) 66–76.
[14] X. Li, W. Xu, T. Itoh, A. Ikehata, B. Zhao, B. Li, Y. Ozaki, Effects of a central metal on the organization of 5,10,15,20-tetra-(p-chlorophenyl)-rare earth porphyrin hydroxyl compound at the air/water interface and in Langmuir–Blodgett films, J. Colloid Interface Sci. 284 (2005) 582–592.
[15] F.J. Pavinatto, A.F. Gameiro Jr., A.A. Hidalgo, L.R. Dinelli, L.L. Romualdo, A.A. Batista, N.M. Barbosa Neto, M. Ferreira, O.N. Oliveira Jr., Langmuir and Langmuir–Blodgett (LB) films of tetrapyridyl metalloporphyrins, Appl. Surf. Sci. 254 (2008) 5946–5952.
[16] A.A. Umar, M. Mat Salleh, M. Yahaya, Self-assembled monolayer of copper(II) meso-tetra(4-sulfanatophenyl) porphyrin as an optical gas sensor, Sens. Actuators B, Chem. 101 (2004) 231–235.
[17] A. Macagnano, E. Zampetti, B.R. Pistillo, S. Pantalei, E. Sgreccia, R. Paolesse, R. d'Agostino, Double layer sensors mimic olfactive perception: a case study, Thin Solid Films 516 (2008) 7857–7865.
[18] G. Sauerbrey, Verwendung von Schwingquarzcn zur Wagung d nner Schichten und zur Mikrowagung, Z. Phys. 155 (1959) 206.
[19] S.A. Brittle, T.H. Richardson, J. Hutchinson, C.A. Hunter, Comparing zinc and manganese porphyrin LB films as amine vapour sensing materials, Colloid Surf. A 321 (2008) 29–33.
[20] A.V. Nabok, A.K. Hassan, A.K. Ray, Condensation of organic vapours within nanoporous calixarene thin films, J. Mater. Chem. 10 (2000) 189–194.
[21] Y. Açıkbaş, M. Evyapan, T. Ceyhan, R. Çapan, Ö. Bekaroğlu, Characterisation of Langmuir–Blodgett films of new multinuclear copper and zinc phthalocyanines and their sensing properties to volatile organic vapours, Sens. Actuators B, Chem. 123 (2007) 1017–1024.
[22] M. Penza, et al., Metalloporphyrins-modified carbon nanotubes networked films-based chemical sensors for enhanced gas sensitivity, Sens. Actuators B, Chem. (2009) 060, doi:10.1016/j.snb.2008.12.
[23] A.A Umar, M. Mat Salleh, M. Yahaya, Optical gas sensing selectivity property of ruthenium (II)-metalloporphyrins Langmuir–Blodgett films, Curr. Appl. Phys. 8 (2008) 53–56.
[24] A.P. Filippov, P.E. Strizhak, V.G. Il'in, Quartz crystal microbalance modified with Cu(II) stearate and octadecylamine co-ordination chemical compounds for detection of volatile organic compounds, Sens. Actuators B, Chem. 126 (2007) 375–381.
[25] R. Paolesse, C. Di Natale, A. Macagnano, F. Davide, T. Boschi, A. D'Amico, Self-assembled monolayers of mercaptoporphyrins as sensing material for quartz crystal microbalance chemical sensors, Sens. Actuators B, Chem. 47 (1998) 70–76.

Biographies

İnci Çapan received MSc degree in 2003 and her PhD in 2008 at the Balikesir University Physics Department, Balıkesir, Turkey. Her main interests are fabrication of thin films, gas sensors for environment applications and the electrical and optical properties of organic thin film materials. Dr. Capan was appointed as research assistant at the Balıkesir University between 2000 and 2008 and she has been working as assistant professor since 2008 at the Balıkesir University in Turkey.

Çelik Tarımcı received MSc degree and PhD at Pittsburgh University, USA. His main interests are investigation on molecular structures of the potential materials that can be used as effective material in medicine and in biology, vacuum systems and thin film fabrication techniques. Dr. Tarımcı was appointed as research assistant in Pittsburg University between 1972 and 1975 and lecturer in Ege University between 1976 and 1977 and in Ondokuzmayıs University between 1977 and 1980. He has worked as research expert in Turkish Atomic Energy Agency between 1980 and 1984, in Turkish The Scientific and Technological Research Council of Turkey (TUBİTAK) between 1984 and 1986. He started to work at Ankara University as Associate Professor. He has been working as full professor since 1998 in Department of Engineering Physics at the same university.

Rifat Çapan received MSc degree at Hacettepe University Physics Engineering Department in 1991, Ankara, Turkey and his PhD at the University of Sheffield (UK) in 1998. He established first Langmuir–Blodgett Thin Film Research Group in Turkey. He had a PhD scholarship from Turkish High Education Council between 1993 and 1998 and had Oversea's Research Student Award (UK) from 1995 to 1998. His main interests are pyroelectric heat sensor, gas sensor for environment applications, the electrical and optical properties of organic thin film materials. Dr. Capan was appointed assistant professor between 1999 and 2002 and associate professor from 2002 to 2007 at University of Balıkesir in Turkey. He became a deputy of Head of Physics Department in 2001 and was the Head of Physics Department between 2003 and 2006. He has been working as a professor and the Head of Department at the University of Balıkesir since 2007.