Gas sensing properties of mixed stearic acid / phthalocyanine LB thin films investigated using QCM and SPR

İ. ÇAPAN*, B. İLHAN
Balıkesir University, Faculty of Art and Sciences, Department of Physics, Cagis Campus, 10145 Balikesir TURKEY

Metal free 2,3,9,10,16,17,23,24-Octakis(Octyloxy)-29H,31H Phthalocyanine and its derivatives containing zinc and copper have been used to fabricate thin films through the Langmuir-Blodgett (LB) Thin Film Fabrication technique. These highly ordered homogeneous, nanoscale thin films' characterization has been investigated using UV-Visible Spectrophotometer. The gas sensing properties of these thin films has been investigated using both Surface Plasmon Resonance (SPR) and Quartz Crystal Microbalance (QCM) Techniques. Several groups of volatile organic compounds including benzene and toluene (aromatic hydrocarbon) methanol and ethanol (alcohol) and chloroform, dichloromethane and carbon tetrachloride (chlorinated aliphatic hydrocarbons) have been used as analyte molecules. The sensor response of the thin films through interaction with the gas molecules has been analyzed in terms of dipole/dipole interaction or hydrogen bonding. It is seen that the analyte gas molecules with high refractive index show a higher response in the SPR technique compared to QCM. Also, a central metal atom effect on gas sensing has not been observed by the SPR technique while the experiments performed using the QCM technique showed that the central metal atom enhances the gas response.

(Received September 29, 2014; accepted March 19, 2015)

Keywords: Langmuir Blodgett (LB) Thin films; Phthalocyanine; Surface Plasmon Resonance (SPR); Quartz Crystal Microbalance (QCM); gas sensing mechanism

1. Introduction

Phthalocyanines have unique chemical and physical properties owing to their thermal stability, ability to form very well ordered thin films and their conjugated π-electron system. They have potential technological applications such as photovoltaic and solar cells [1-2], molecular electronics [3-4], electrochromic display devices [5-6], liquid crystals [7], photosensitizers in photodynamic cancer therapy [8-9]. Another possible application of phthalocyanines is in the field of gas sensing where the phthalocyanines are used as sensing elements in the form of thin layers that interact with analyte gases due to their physical and chemical properties. Several techniques are used to form these layers such as spin coating, vacuum sublimation, drop casting, Langmuir Schäfer (LS) and LB thin film fabrication techniques.

LB thin film fabrication technique is well known for its excellent efficiency in fabrication of well ordered, nanoscale, defect free layers in desired architecture [10]. These properties of the LB thin films make them appropriate for many applications, one of which is gas sensing. The gas sensing capability of phthalocyanines has been investigated by many researchers for more than 25 years using several techniques such as electrical [11-12], optical [13-15] or gravimetric [16-17]. It is found that the phthalocyanines interact with both inorganic and organic gases. Gas response times to inorganic gases are much longer than response times to organic gases. It is also found that response to inorganic gases is obtained only in an appropriate temperature range which is above room temperature [18-20]. On the other hand, response times for organic gases were expressed in terms of seconds and the working temperature was in the range of room temperature [21-22].

In this study, three classes of organic gases namely aromatic hydrocarbons, alcohols and chlorinated aliphatic hydrocarbons have been used to investigate the gas sensing properties of mixed stearic acid / phthalocyanine LB thin films using the QCM and the SPR techniques. The gas sensing mechanism has been discussed in terms of the molecular interactions between the thin films and the analyte gas molecules.

2. Experimental Details

2.1. Chemicals

2,3,9,10,16,17,23,24-Octakis(octyloxy)-29H,31H, Zinc 2,3,9,10,16,17,23,24-Octakis(octyloxy)-29H,31H and Copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29*H*,31*H* phthalocyanines, coded as OcPc, ZnOcPc and CuOcPc respectively, were purchased from Sigma Aldrich and used without further treatment to fabricate LB Thin Films. The chemical structures of the phthalocyanines have been given in Fig.1. Stearic acid used in thin film fabrication was also purchased from Sigma Aldrich. The analyte gas molecules selected were, benzene, toluene,

methanol, ethanol, chloroform, dichloromethane and carbon tetrachloride because of their toxicity and harmful effects on human health. All were purchased from Sigma Aldrich.

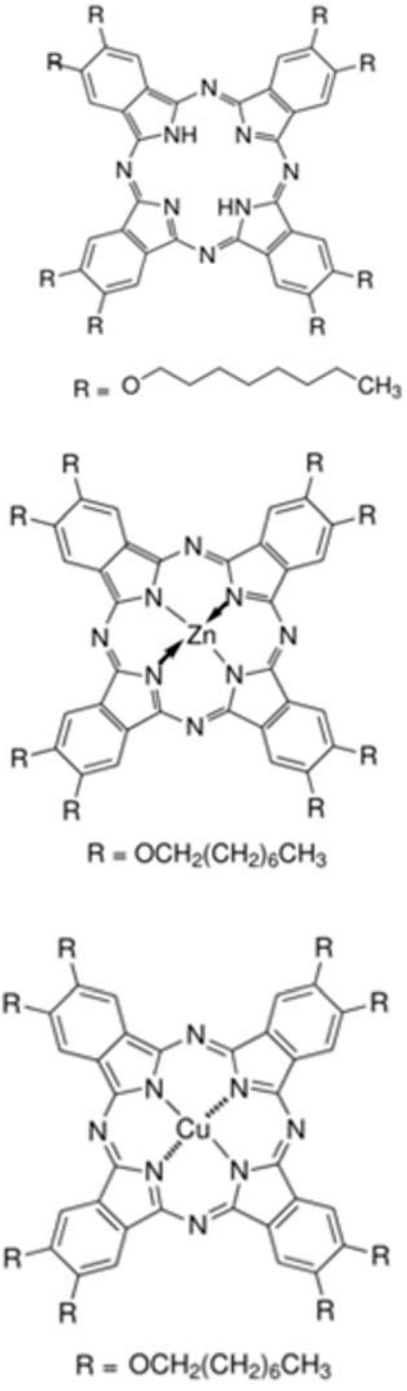

Fig. 1. The chemical structure of the phytalocyanine molecules (a) OcPc (b) ZnOcPc (c) CuOcPc

2.2 LB Thin Film fabrication and characterization

Nima 622 model Alternate Layer LB film trough has been employed for the fabrication of the LB thin films. For the surface pressure measurements a filter paper Wilhemly balance was employed. The phthalocyanine and stearic acid solutions prepared using chloroform as solvent have been spread onto the clean water subphase. The concentrations of all solutions were 0.2 mg ml^{-1}. Y-type LB films at a constant surface pressure of 25 mN m^{-1} were fabricated by using a mixed monolayer of phthalocyanine and stearic acid where their solutions were mixed with a volume ratio of 1:3. The transfer ratio which is defined as the ratio between the decrease in monolayer area during a deposition stroke and the area of the substrate were calculated with a value of approximately 0.90. The transfer speeds for both downstroke and upstroke deposition were 5 mm min^{-1}.

For gas sensing measurements using the SPR technique LB thin films were fabricated onto glass slides with the dimensions 20 mm × 20 mm × 1 mm which were coated by a very thin (50 nm) homogeneous layer of gold on top. For gas sensing investigations with the QCM technique, the LB films were fabricated onto quartz crystals with a nominal frequency of 3MHz which were sandwiched between gold electrodes.

2.3 Gas sensing experiments

The QCM technique provides a quartz crystal which is sandwiched between two metal electrodes to oscillate in its oscillation frequency. This is achieved through an in-house built electronic circuit. A block diagram of the QCM system can be found in previous publications [23]. The sensitivity of the QCM system was 1-2 Hz. The AT-cut quartz crystal with a nominal frequency of 3 MHz sandwiched between two metal electrodes is coated with the phthalocyanine thin film. The gas sensing properties are investigated by monitoring the resonance frequency during the exposure of the analyte gases into the gas cell and later flushing with dry air.

The SPR technique measures the light intensity versus the angle of incidence between two media which consists of a metal and a dielectric. To investigate the gas sensing properties a resonance is obtained on the plasmons that has been formed on the surface. Around this resonance angle value, by fixing the angle of incidence, the change in the light intensity in exposure to analyte gases are monitored. Biosuplar 6 Model spectrometer with a low power laser diode (630–670 nm) light source was employed to monitor the SPR spectra with an angular resolution of about 0.003°. A glass prism (n = 1.62) was mounted within a holder and a compatible transparent plastic flow cell with an inlet and outlet connected to silicone tubes was used for organic vapor measurements. All measurements were performed at room temperature.

3. Results and Discussion

Appropriate deposition surface pressure values for the monolayer was necessary for the fabrication of LB thin films from phthalocyanines. After the preparation of the phthalocyanine solutions, the π–A isotherm graphs of the phthalocyanine monolayers have been recorded. It has been observed that these materials were not suitable to form a stable monolayer at the air-water interface as already has been reported previously by other researchers [24]. Therefore the monolayer has been mixed with an amphiphilic compound which has also been implemented by previous research groups [25-26]. Stearic acid which is well known with its elegant monolayer behavior forming precise monolayers at the air-water interface has been mixed with phthalocyanine. The isotherm graphs of the mixed monolayers of phthalocyanine and stearic acid with a volume ratio of 1:3 has been given in Fig. 2 for all derivatives of the phthalocyanine materials used. It is seen from the Fig. 2 that all depositions under investigation were forming stable monolayers at the air-water interface. The gas, liquid and solid phases can be clearly seen in the isotherm graphs which are recorded during the compression of the monolayers. The thin film fabrication has been selected to be performed at a surface pressure value of 25 mN m^{-1} which falls in the solid phase region for all monolayers.

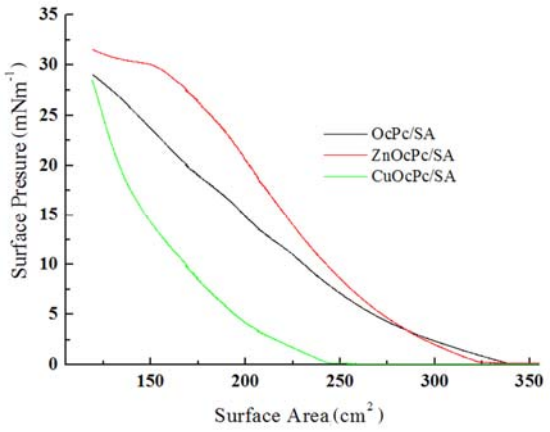

Fig. 2. Isotherm graphs of the mixed phytalocyanine/Stearic Acid monolayers with a volume ratio of 1:3.

The UV-Visible Spectrums of the thin films were collected after deposition of definite layers and the quality of the thin films were evaluated. Fig. 3 shows the UV-Visible spectrums of the CuOcPc/SA thin films with different layers. This result can be considered as a typical phthalocyanine spectrum where two distinct regions are observed. The major absorbance band, which is devoted to the visible colour properties of phthalocyanines is located between 500 and 700 nm and it is known as the Q band. The second region where significant light absorption occurs due to interactions with highly energetic photons in the UV region is observed below 400 nm [27]. In Fig.3 the UV-Visible spectrum given for CuOcPc/SA shows that the two regions described above can be observed which is consistent with the literature [28-29]. The UV-Visible spectrums obtained for OcPc/SA and ZnOcPc/SA also show similar results which are not presented here.

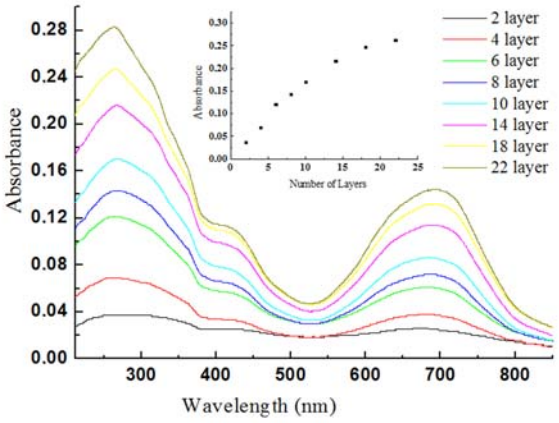

Fig. 3. The UV-Visible spectrum of the CuOcPc/SA LB thin films

It is seen that the absorbance values increased with the number of layers deposited which indicates that in all cycles of deposition an amount of monolayer is transferred onto the solid substrate. To better evaluate the situation, the dependence of the absorbance value at 270 nm with the number of layers deposited is given in inset of Fig. 3. It is seen that the amount of material deposited for each layer is similar to each other which indicates a successful deposition.

The thin films fabricated for the investigation of their gas sensing properties have also been characterized using the SPR system. The SPR curve of all thin films were recorded which gives the reflected light intensity (at an individual wavelength λ) versus the angle of incidence. The minimum in reflected light intensity indicates a resonance of the surface plasmons. The value of the resonance angle is given as

$$\theta_{SPR} = \sin^{-1}\left(\frac{\varepsilon_M}{\varepsilon_P(\varepsilon_M + 1)}\right)^{1/2} \quad (1)$$

where ε_M the dielectric constant of the metal film which is sandwiched between a glass prism of dielectric constant ε_P [30]. A shift in the resonance angle θ_{SPR} occurs when a thin film with a thickness of d and dielectric constant of ε is fabricated onto the metal film. This shift of Δθ has been formulated [31] and given as follows

$$\Delta\theta = \frac{(2\pi/\lambda)(|\varepsilon_M|)^{3/2} d}{\sqrt{\varepsilon_P}\cos\theta(|\varepsilon_M - 1|)^2\varepsilon}(\varepsilon - 1) \quad (2)$$

where $|\varepsilon_M|$ is the modulus of the real part of the dielectric constant of the metal film. It is clear that the shift in the resonance angle is dependent on the thickness and the dielectric constant of the fabricated thin film.

The SPR curves of gold coated solid substrate, OcPc/SA thin film of 16 layers, its exposure to saturated vapor of chloroform vapor and recovery with dry air is given in Fig. 4. The shift in θ_{SPR} is around 1.17^0 with respect to gold coated substrate is observed in the case of OcPc/SA thin film of 16 layers. Similar experiments have been performed to record the SPR curves for the other two thin films. The shift in SPR angle due to the thin film fabrication was 0.79^0 and 1.18^0 for the ZnOcPc/SA and CuOcPc/SA thin films respectively. Although the thin film fabrication conditions were identical in all cases, a difference in the $\Delta\theta$ values has been observed for ZnOcPc/SA thin film with respect to the other two thin films which may be due to differences in the thin film thickness which is connected to the molecular weights and the dielectric constant values of the phthalocyanines as easily can be referred to Eq. 2 [31]. The mechanism which causes a shift in θ_{SPR} in the case of fabrication of the thin film also takes place when the thin film is exposed to gas molecules. The interaction of the thin film with the gas molecules are believed to be occur as a surface interaction followed by a diffusion into the bulk of the thin film. This interaction will cause a change in the thickness and/or the dielectric constant of the thin film which will result with a shift in resonance angle . The $\Delta\theta$ value obtained when the saturated chloroform vapor is injected into the gas cell is monitored in Fig. 4 with a value of 0.42^0. This experiment has been performed for chlorinated aliphatic hydrocarbons and the shift in resonance angle has been observed between the range 0.15^0 and 0.45^0. The changes in the $\Delta\theta$ value may be a result of differences in the thickness and dielectric constants of the thin films which have been fabricated using different phthalocyanines. The recovery of the thin film can also be observed in Fig. 4 when the dry air is exposed into the gas cell to remove the analyte gas. The SPR curve was returned to its initial state during recovery without a shift of resonance angle.

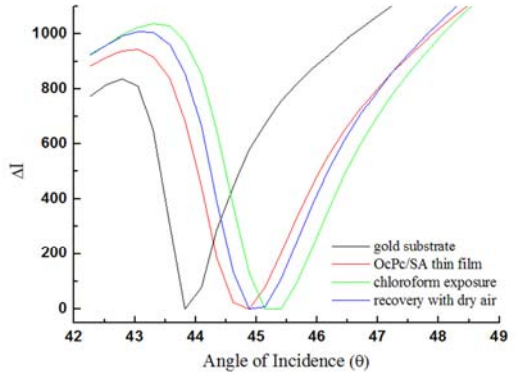

Fig. 4. The SPR curves of gold coated solid substrate, OcPc thin film of 16 layers, its exposure to saturated vapor of chloroform vapor and recovery with dry air.

For the gas sensing experiments two different techniques has been used. SPR and QCM techniques are used to investigate the gas sensing performances of the LB thin films due to exposure to 3 groups of analyte gas molecules; i) aromatic hydrocarbons (benzene and toluene) ii) alcohols (methanol and ethanol) and iii) chlorinated aliphatic hydrocarbons (chloroform, dichloromethane and carbon tetrachloride). In Fig. 5 the kinetic graphs for saturated vapors of all analyte gases during interaction with the OcPc/SA LB thin film have been given for the investigation made via a) QCM system b) SPR system. It is seen that in both techniques the response is obtained in just a few seconds for all vapors which is very fast. The recovery of the OcPc/SA LB thin film for all vapors under examination has been achieved. The intensity of the response for all vapors was different denoting the selectivity of the various classes of gases. It can generally be concluded that the interaction of the thin film with the chlorinated solvents are higher with respect to that of the other groups. Similar behaviour also been observed during the experiments performed using ZnOcPc/SA and CuOcPc/SA thin films where the kinetic graphs have not been plotted.

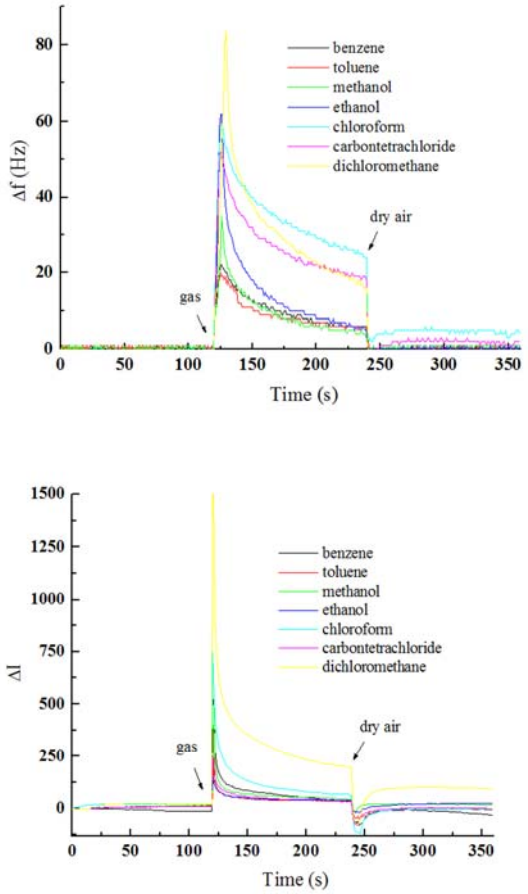

Fig. 5. The kinetic response graphs of 16 layered OcPc/SA LB thin film of phytalocyanine obtained using a) QCM system b) SPR system for all saturated vapors of analyte gases.

The kinetic responses of all 16 layered phthalocyanine / stearic acid LB thin films investigated using both techniques has been listed in Table 1 in terms of the change in light intensity (ΔI) and change in resonance frequency (Δf). It is clearly seen that the relatively high values obtained in both techniques for chlorinated aliphatic hydrocarbons especially for dichloromethane and chloroform is noteworthy. The interaction of these gases with the LB thin films is believed to be a physical absorption through a dipole/dipole interaction or hydrogen bonding [32]. The highest response that is seen in Table 1 for dichloromethane is followed by chloroform for all cases in both QCM and SPR experiments. This may be explained by the high dipole moment values of dichloromethane (1.60 D) and chloroform (1.04 D) which explains this effect as previously been reported by other research groups [33-34]. The relatively lower response observed for carbontetrachloride can also be explained with this aspect since this gas has no dipole moment at all. The interaction with carbontetrachloride is believed to be originated from the electrostatic interactions where the relatively high molecular weight of carbontetrachloride (153.82 gr/mol) with respect to dichloromethane (84.93 gr/mol) and chloroform (119.38 gr/mol) should be taken into account. It is known that it is harder for the bigger the gas molecules to penetrate into the bulk of the thin film [32].

The responses obtained for the alcohols usually follow the highest response of the chlorinated aliphatic hydrocarbons in most cases as can be seen from Table 1. It is known that the interaction of hydrophilic molecules such as alcohols with the organic molecules may be due to strong hydrogen bonding, besides C-H … π interaction [35]. The hydrogen bonding ability of the alcohol gases are highest among the investigated analyte gases.

Table 1: Response of LB thin films in terms of the change in reflected light intensity and resonance frequency change due to exposure to saturated vapors of analyte gases.

Gases	OcPc/SA		ZnOcPc/SA		CuOcPc/SA	
	ΔI	**Δf (Hz)**	**ΔI**	**Δf (Hz)**	**ΔI**	**Δf (Hz)**
Benzene	223	18	259	21	57	29
Toluene	111	14	75	18	32	14
Methanol	178	20	96	27	33	21
Ethanol	93	36	175	35	26	19
Chloroform	384	51	210	69	103	54
Carbontetrachloride	135	43	92	65	47	50
Dichloromethane	762	59	269	92	221	51

When the gas interaction results from the two different techniques are compared, it is noteworthy that in both techniques the highest interaction is observed for dichloromethane and chloroform. The response obtained for benzene interaction using the SPR technique is observed to always have a higher value compared with the results obtained using the QCM technique. The response obtained for benzene in QCM technique has a lower magnitude. At this point it should be remembered that the gas sensing detection in SPR system relies on the thickness, dielectric constant and/or refractive index change in the thin film during interaction with the gas molecules. When the gas molecules interact with the thin film a change in the above mentioned parameters may occur due to the penetration of the gas molecules into the thin film matrix therefore the refractive index of the gas molecules are important. It has been noted that the highest refractive index among all the analyte gases belongs to benzene molecule with a value of 1.501. This aspect has been considered as the main reason for the high response associated with benzene molecules in experiments performed using the SPR technique [36].

The results also showed that the gas response of the thin films were independent of central metal atom for the investigations performed using the SPR technique. Any relationship between the gas responses and the central metal atom could not be observed. On the other hand, as can be analyzed from Table 1, investigations performed using the QCM technique showed that the central metal atom plays an important role on the gas sensing response.

4. Conclusion

It is found that the response to chlorinated aliphatic hydrocarbons is higher than that of the other analyte gases.

The response has been attributed to dipole/dipole interaction or hydrogen bonding between the thin films and the gas molecules. Differences have been observed between two different analyzing techniques for the detection of the analyte gases. It is found that the detection of the high refractive index gas was easier with the SPR technique. The central metal atom effect was obvious with the QCM technique while the SPR technique failed to detect it. Our future work will concentrate on improving also the selectivity of the gas sensing thin films.

Acknowledgements

We thank to the Balıkesir University Scientific Research Projects Unit for their financial support (Project number 2011/24).

References

[1] L. Jin, D. Chen, Electrochim. Acta **72**, 40 (2012).
[2] T.T. TLuong, Z. Chen, H. Zhu, Sol. Energ. Mat. Sol. C. **94**, 1059 (2010).
[3] N. Papageorgiou, E. Salomon, T. Angot, J.M. Layet, L. Giovanelli, G.L. Lay, Prog. Surf. Sci. **77**, 139 (2004).
[4] Y. Liu, W. Hu, W. Qiu, Y. Xu, S. Zhou, D. Zhu, Sensor Actuat. B-Chem **80**, 202 (2001).
[5] R.J. Mortimer, A.L. Dyer, J.R. Reynolds, Displays **27**, 2 (2006).
[6] P.R. Somani, S. Radhakrishnan, Mater. Chem. Phys. **77**, 117 (2002).
[7] F. Yakuphanoğlu, M. Durmus, M. Okutan, O. Köysal, V. Ahsen, Physica B **373**, 262 (2006).
[8] P.C. Lo, B. Zhao, W. Duan, W.P. Fong, W.H. Ko, D.K.P. Ng, Bioorg. Med. Chem. Lett. **17**, 1073 (2007).
[9] E. Paszko, C. Ehrhardt, M.O. Senge Dr. rer. nat., FTCD, D.P. Kelleher, J.V. Reynolds, Photodiagn. Photodyn. **8**, 14 (2011).
[10] M.C. Petty. Langmuir Blodgett Thin Films, an introduction, Cambridge University Press, Cambridge (1996).
[11] W. Hu, Y. Liu, Y. Xu, S. Liu, S. Zhou, P. Zeng, D.B Zhu, Sensor Actuat. B-Chem **56**, 228 (1999).
[12] Z. Jie, H.L. Hua, G. Shan, Z. Hui, Z.J. Gui, L. Ning, Sensor Actuat. B-Chem **126**, 588 (2007).
[13] A. Capobianchi, A.M. Paoletti, G. Rossi, G. Zanotti, G. Pennesi, Sensor Actuat. B-Chem **142**, 159 (2009).
[14] A. N. Fernandes, T.H. Richardson, Colloid. Surface. A **284–285**, 335 (2006).
[15] C. Granito, J.N. Wilde, M.C. Petty, S. Houghton, P. J. Iredale, Thin Solid Films **284–285**, 98 (1996).
[16] Y. Açıkbas, M. Evyapan, T. Ceyhan, R. Çapan, Ö. Bekaroğlu, Sensor Actuat. B-Chem **135**, 426 (2009).
[17] L. Valkova, N. Borovkov, O. Koifman, A. Kutepov, T. Berzina, M. Fontana, R. Rella, L. Valli, Biosens. Bioelectron. **20**, 1177 (2004).
[18] L. Valli, Adv. Colloid Interfac. **116**, 13 (2005).
[19] T.V. Basova, E.K. Koltsov, I.K. Igumenov, Sensor Actuat. B-Chem 105, 259 (2005).
[20] I.L. Emelianov, V.V. Khatko, Thin Solid Films **354**, 237 (1999).
[21] G. Gumrukçü, M. Ustun Özgür, A. Altındal, A.R. Özkaya, B. Salih, Ö. Bekaroğlu, Synthetic Met. **161**, 112 (2011).
[22] M. Harbeck, D.D. Erbahar, I. Gürol, E. Musluoğlu, V. Ahsen, Z.Z. Öztürk, Sensor Actuat. B-Chem **155**, 298 (2011).
[23] İ. Capan, Ç. Tarımcı, R. Capan, Sensor Actuat. B-Chem **144**, 126 (2010).
[24] D.P. Arnold, A. Genga, D. Manno, G. Micocci, A. Serra, A. Tepore, L. Valli, Colloid. Surface. A **198–200**, 897 (2002).
[25] V.V. Arslanov, Yu. G. Gorbunova, S.L. Selektor, L.S. Sheinina, O.G. Tselykh, Y.Yu. Enakieva, A.Yu. Tsivadze, Russ. Chem. B+ **53**, 2532 (2004).
[26] S. T. Kang, H. Ahn, J. Colloid Interf. Sci. **320**, 548 (2008).
[27] P. Kluson, M. Drobek, T. Strasak, J. Krysa, M. Karaskova, J. Rakusan, J. Mol. Catal. A-Chem. **272**, 213 (2007).
[28] T.M. Mohan Kumar, B.N. Achar, J. Organomet. Chem. **691**, 331 (2006).
[29] Y. Açıkbas, M. Evyapan, T. Ceyhan, R. Çapan, Özer Bekaroğlu, Sensor Actuat. B-Chem **123**, 1017 (2007).
[30] W. Knoll, Ann. Rev. Phys. Chem. **49**, 569 (1998).
[31] A.K. Hassan, C. Goy, A.V. Nabok, Thin Solid Films **516**, 9006 (2008).
[32] M.M. Ayad, G. El-Hefnawey, N.L. Torad, Sensor Actuat. B-Chem **134**, 887 (2008).
[33] S. Ichinohe, H. Tanaka, Y. Kanno, Sensor Actuat. B-Chem **123**, 306 (2007).
[34] T. Ceyhan, A. Altındal, A.R. Özkaya, M.K. Erbil, Özer Bekaroğlu, Polyhedron **26**, 73 (2007).
[35] Z. Cao, K. Murayama, K. Aoki, Anal. Chim. Acta **448**, 47 (2001).
[36] A. Abdelghani, J.M. Chovelon, N. Jaffrezic-Renault, C. Ronot-Trioli, C. Veillas, H. Gagnaire, Sensor Actuat. B-Chem **38-39**, 407 (1997).

* Corresponding author: inci.capan@gmail.com