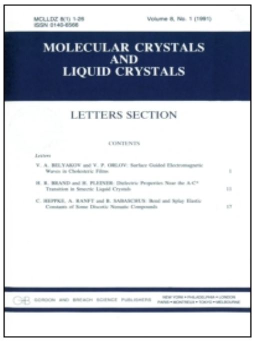

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Recovery processes of optical properties of polymer sensor films

B. Tsizh[a,b], M. Chokhan[b], and M. Olkhova[b]

[a]Kazimierz Wielki University in Bydgoszcz, Bydgoszcz, Poland; [b]Stepan Gzytsky Lviv Natoinal University of Veterinary Medicine and Biotechnologies, Lviv, Ukraine

ABSTRACT
We study process of recovery of optical properties of thin polyaniline (PANI) films, obtained by electrochemical deposition method after ammonia impact on it. We show, that heating of sensitive element of the gas sensor based on PANI films with simultaneous air blowing leads to their effective regeneration and provides multi-reversibility of the sensor performance. We find that optimal temperature value for recovery of the optical absorption at wave length 600 nm of thin PANI films after ammonia impact is equal to 80°C.

KEYWORDS
Gas sensor; polyaniline thin film; sensitive element; optical absorption

1. Introduction

Organic films, properties of which change under influence of the different gaseous media are basis for modern gas sensor industry. Among them PANI films are one of the most perspective sensitive elements due to their high sensitivity, selectivity and reversibility and relative simplicity of synthesis and low price [1–21].

We have already reported on high-tech possibilities of ammonia-sensitive PANI films and structures bases on them, obtained by electrochemical deposition method, and on ways to increase their sensitivity and expand the spectral range of action [3, 4, 6–9]. For practical multiple use, the possibility of repeated reversible changes in physical properties, caused by the action of the test gas environment is needed in gas sensors. This is possible with effective restoring processes of the original physical properties of the sensitive elements of sensors after the action of certain natural gas. In od known, that in case of electrochemicaly deposited thin PANI films partical recovery of the properties, in particular, optical absorption after ammonia impact, is obtained by their short-term exposition in water solution of 0.5M sulfuric acid, washing with distilled water and drying in dry air for 3 – 5 min, and also by heating [3, 8, 21]. However, there was no detailed studies of recovery physical properties of the PANI film, and information about optimal parameters of their regeneration is absent. In this paper we provide the results of such studies, and also give the optimal technological parameters of recovery of sensitive elements of ammonia optical gas sensors based of thin PANI films.

CONTACT B. Tsizh tsizhb@ukw.edu.pl
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2. Experiments

Thin PANI films were obtained by electrochemical deposition, because by the sum of its benefits and features it seems to us the most optimal, including for following practical usage and mass production of sensor devices.

In particular, in comparison with such methods of obtaining conjugated polymers, as vapor deposition polymerization, thermal evaporation, dip-, drop- and spin-coating, Langmuir-Blodgett and layer-by-layer technique, and others [1–20], method of electrochemical deposition is one of the simplest and cheapest one, which allows at the same time to effectively manage the properties of the films through process parameters of obtaining. PANI film formation was performed at room temperature in a glass electrochemical cell, with glass plate as working electrode ($10 \times 20 \times 0.3$ mm) with transparent conductive coating (SnO_2), the antielectrode was a platinum lattice. PANI films of thickness 0.3 …2.0 mkm where deposited from 0.1M solution of anilyne (monomer) in 0.5M solution of sulfuric acid at a current density 0.05 – 0.20 mA·sm^{-2} during 2 – 10 min., as it was discribed in previous papers [3, 6 – 9]. This method of deposition has allowed us to widely vary the composition, topology, thickness and other parameters of the synthesized layers and optimize them effectively and achieve high stability and reproducibility for different parties of synthesis. Recovery of the properties of PANI films was performed by blowing air with a standard fan with a power of 75 W in temperature range 20 …130°C. The simplicity of method allows to predict its future practical usage for creating reversible sensing elements for gas sensors.

Optical absorption spectra of PANI films were obtained with help of modified two-beam optical spectrometer Specord M400 with following parameters of measurement: spectral range – 200 …900 nm, slit width – 1 nm, integration time – 1 s, step of scanning – 1 nm, speed of recording – 10 nm/s. To measure optical spectra of sensor films in an atmosphere of ammonia the sealed quartz chamber of volume 50 sm^2 was used, where needed quantity of gas (ammonia) was added. All measurements were carried out under standard conditions of temperature and pressure. Analysis of results was carried out using standard correlation program, in which on the entire range of measurement relative error does not exceed 1.5%, and also with using methods described in [22, 23].

3. Results and discussion

Under the action of ammonia there is a significant increment in optical absorption of PANI films in spectral range 460 …680 nm, maximum of changes are recorded in the vicinity of wavelengths $\lambda = 600$ nm (Fig. 1). These changes are caused by the interaction of ammonia with protonated nitrogen atoms, the charge which is delocalized on the coupling chain and compensated by anionic dopants with formation of new unstable complex. A more detailed analysis of changes in optical absorption of PANI films under the action of ammonia and description of the mechanisms of their occurrence is represented in our works [3, 6, 9].

The processes of restoring the original optical properties of the PANI films for their repeated use in gas sensors have to ensure their maximum practical applicability and adaptability, besides effective film regeneration. From this point of view the described above recovery of properties of PANI films by exposure to sulfuric acid solution is not optimal, because it requires additional operations and material costs.

We propose to carry out the recovery process of optical properties of gas sensitive PANI films without the usage of additional materials and with minimal cost. The main factors of films regeneration processes are thus heating and blowing air.

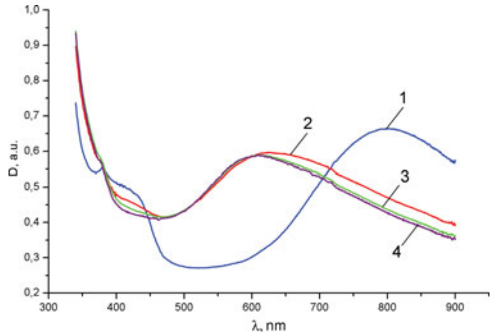

Figure 1. Spectral dependences of intensity of optical absorption of thin PANI films with ammonia action on it (P_{NH3} = 6.2 Pa): 1 – without ammonia; 2 – ammonia action during 1 min; 3 – 2 min; 4 – min.

In Fig. 2 the spectra of optical absorption of PANI films regenerated after ammonia impact at different temperatures with simultaneous air blowing are presented. From the comparising of spectra in Fig. 2a – 2d once can see, that difference between lines 3 and 4, that is before and after the regeneration, increases with increasing of temperature. Obviously, during heating of PANI films which previously had adsorbed ammonia, its desorption is intensified with destruction of unstable donor-acceptor complexes of ammonia and aniline.

To determine the optimal temperature of regeneration of the studied films we examined the dependence of reverse changes in their optical absorption on temperature of recovery process at a wavelength 600 nm, that is in the region of the spectrum where the observed absorption

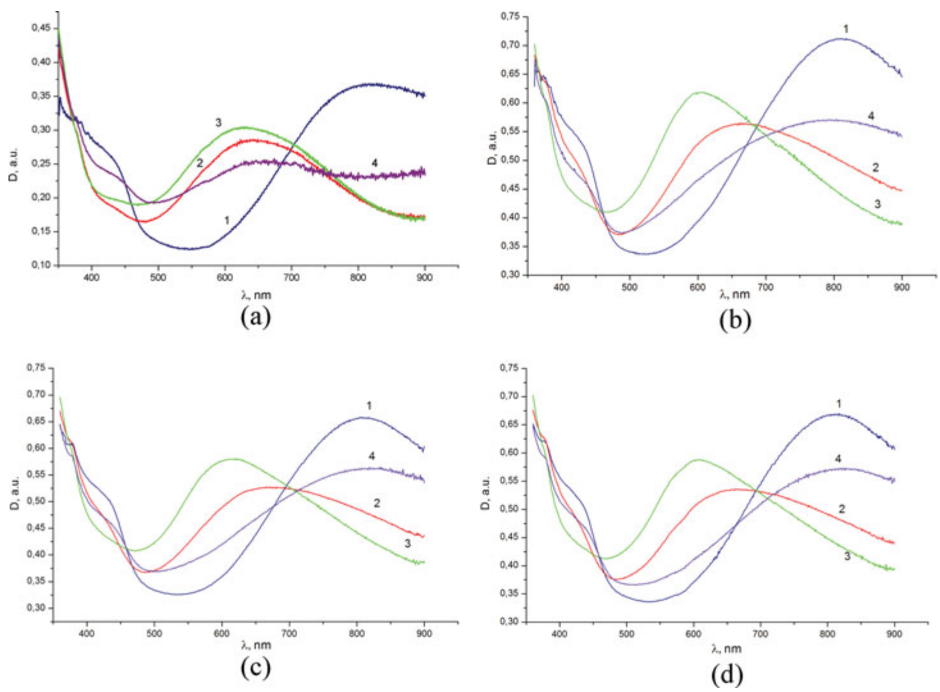

Figure 2. Spectral dependences of intensity of optical absorption of thin PANI films on time of exposition in ammonia atmosphere (P_{NH3} = 6.2 Pa) and following recovery: 1 – without ammonia; 2 – ammonia action during 1 min; 3 – ammonia action during 5 min.; 4 – after air blowing during 10 min. at 60°C (a), 80°C (b), 110°C (c), 126°C (d).

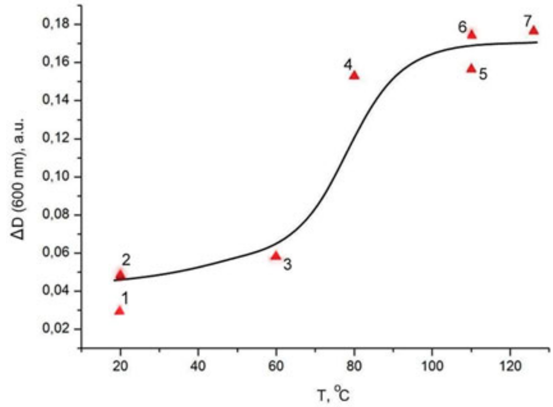

Figure 3. Change of PANI film optical absorption at a wavelength 600 nm after 10 min. after previous exposition to ammonia ($P_{NH3} = 6.2$ Pa, 5 хв.) for different conditions of the recovery: 1 – in air without blowing at 20°C, after air blowing at temperature 20°C (2), 60°C (3), 80°C (4), 110°C (5,6), 126°C (7).

changes were maximal (Fig. 3). From Fig. 3 one can see, that air blowing significantly intensifies these recovery processes, which is seen from comparising of points що 1 and 2. From Fig. 3 it is also seen, that in temperature range 70 …80°C there is significant escalation of recovery processes of PANI films, and in case of increasing temperature to higher values there is stabilisation of these changes, which can be seen from plato at T > 80°C. This dependence allows to suggest that optimal temperature for recovering of sensitive elements of optical gas sensors based on PANI films is 80ºC, because in case the further growth of temperature the changes do not exceed several percent.

The described above method of regeneration of gas sensitive sensor elements is suitable for practical use, because of blowing surface of film uses the same system for gas injection which was used for the analysis. And for low-temperature heating it is convenient to use transparent conductive coating SnO_2, which served as the working electrode in the synthesis of gas sensitive PANI films. Sketch of the sensor gas sensor is shown in Fig. 4.

For possibility of heating, narrow bands (1 …2 mm) of low-resistance metal contacts (Fig. 3, 4) are applied at the edges of the conductive transparent layer SnO_2 (Fig. 2, 4), for example, made from Cr – Cu – Ni layers, which provides homogeneous passage of heating current on all SnO_2 surface. Thus, without removing the sensor from the measuring cell the restoring the physical properties of gas sensitive PANI films can be made, while providing multiple reversibility. Our research showed that the multiplicity of effective recovery is not less than 10^2 cycles.

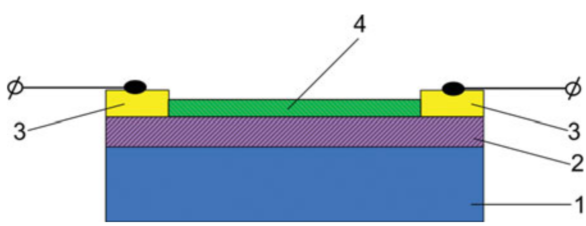

Figure 4. Sensitive element of optical gas sensor: 1 – glass padding, 2 – SnO_2 layer, 3 – metallic electrodes, 4 – PANI layer.

4. Conclusions

1. We've established, that optimal values of temperature for recovering of the optical properties of thin PANI films after action of ammonia is 80°C.
2. We've shown, that heating of the sensitive elements of gas sensors based on PANI films with simultaneous air blowing leads to their effective regeneration and provides reversibility of the sensor performance.
3. We've showed, that for heating with purpose of recovery of the optical properties of the gas-sensitive elements based on PANI layers is convenient to use transparent conductive coating, for example SnO_2, which was used as working electrode during synthesis of this films.

References

[1] Bai, H., & Shi, G. (2007) *Sensors*, *7*, 267.
[2] Kunzo, P., Lobotka, P., Kovacova, E. et al. (2013) *Phys. Status Solidi (A)*, *210*, 11, 2341.
[3] Tsizh, B. R., Aksimentyeva, O. I., Vertsimakha Ya. I. et al. (2014) *Mol.Cryst.Liq.Cryst.*, *589*, 116.
[4] Tsizh, B., & Aksimentyeva, O. (2015) *The 4th International Conference on the Physics of Optical Materials and Devices (ICOM 2015). Budva, Montenegro, Proceeding*, 163.
[5] Kukla, A. L., Pavluchenko, A. S., Kotljar, V. A. et al. (2005). *Sens. Electron.and Microsyst. Technol.*, *2*, 42.
[6] Aksimentyeva, O. I., & Konopelnik, O. I. (2005). *Molec. Cryst. Liq. Cryst. 427*. 127.
[7] Aksimentyeva, O. I., Tsizh, B. R., Chokhan, M. I., & Yevchuk, O. M. (2011). *Patent No.65401 (UA), Bull. 23*.
[8] Tsizh, B. R., Aksimentyeva, O. I., Chokhan, M. I., & Gorbenko Yu. Yu. (2015). *Patent No.103496 (UA), Bull. 24*.
[9] Tsizh, B. R., Chokhan, M. I., Aksimentyeva, O. I. et al. (2008). *Mol. Cryst. Liq.Cryst.*, *497*, 254.
[10] Nicolas-Debarnot, D., & Poncin-Epaillard, F. (2003). *Anal. Chim. Acta*, *475*, 1.
[11] Jin, Z., Su, Y. X., & Duan, Y. X (2001). *Sens. Actuators B*, *72*, 75.
[12] Hu, H., Trejo, M., Nicho, M. E. et al. (2002). *Sens. Actuators B*, *82*, 14.
[13] Xu, K., Zhu, L. H., Li, J., & Tang, H. Q. (2006). *Electrochim. Acta*, *52*, 723.
[14] Agbor, N. E., Petty, M. C., & Monkman, A. P. (1995).*Sens. Actuators B*, *28*, 173.
[15] Reemts, J., Parisi, J., & Schlettwein, D. (2004). *Thin Solid Films*, *466*, 320.
[16] McGovern, S. T., Spinks, G. M., & Wallace, G. G. (2005). *Sens. Actuators B*, *107*, 657.
[17] Sandberg, H. G. O., Backlund, T. G., Osterbacka, R., et al. (2005). *Synth. Met.*, *155*, 662.
[18] Prasad, G. K., Radhakrishnan, T. P., Kumar, D. S., & Krishna, M. G. (2005). *Sens. Actuators B*, *106*, 626.
[19] Ram, M. K., Yavuz, O., Lahsangah, V., & Aldissi, M. (2005). *Sens. Actuators B*, *106*, 750.
[20] Nohria, R., Khillan, R. K., Su, Y., et al. (2006). *Sens. Actuators B*, *114*, 218.
[21] Khan, A. A., & Shaheen, S. (2015) *Analytical Methods*. *7*, 2077.
[22] Czerniak, J. (2009) *Fundam. Informat. 92*, 43.
[23] Angryk, R., & Czerniak, J. (2010) *Internat. J. Approxim. Reason. 51*, 895.