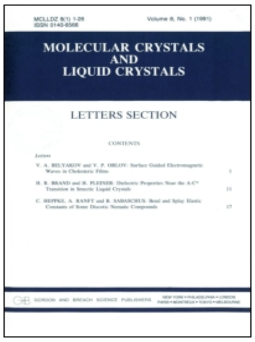

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B. Tsizh & O. Aksimentyeva

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Organic high-sensitive elements of gas sensors based on conducting polymer films

B. Tsizh[a,c] and O. Aksimentyeva[b]

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

ABSTRACT
The influence of ammonia on the optical absorption spectra of thin films of polyaniline (PANI), poly-3,4-ethylenedioxythiophene (PEDOT), mixtures thereof, and the bilayer film structures based on PANI and PEDOT obtained by electrochemical method were studied. The kinetics of changes in the optical absorption of these structures under the action of ammonia was explored in the spectral range of 350 … 900 nm. It was shown that thin film bilayer structure PANI / PEDOT significantly broaden the range of spectral sensitivity to ammonia compared to individual films.

KEYWORDS
Gas sensor; polyaniline; poly-3,4-ethylenedioxythiophene; ammonia; optical absorption

1. Introduction

In modern gas sensors the organic materials are used more and more widely for creating sensitive elements. Ones of the most promising of them are gas-sensitive polymer films, which is caused by their high fabricability, simplicity of the synthesis and usage, lower prime cost and in some cases by better exploitation parameters [1–8].

For today precision sensor systems and separate gas sensors are developed, which are successfully used for monitoring gaseous mediums in manufacturing, transport, environment control, quality of food production control and for other purposes. Nevertheless, despite the successful design of such devices there is a need in simple, reliable, cheap and reasonable sensors of ammonia, and their development is very important.

Typical trends of evolution of modern gaseous sensors can be seen in the development of ammonia sensor, among which chemical, electrochemical, biological, semiconductor and other types are present. Ones of the most perspective of them are optical gas sensors, and as a gas-sensitive material are well-proven thin films of conjugated polymers, in particular, layers of polyaniline (PANI) and poly-3,4-ethylenedioxythiophene (PEDOT) [1–5, 7–11]. To date, the mechanisms of interaction of ammonia molecules with the organic polymer films PANI, PEDOT and their derivatives is proposed, the features of changes of their properties, including optical, under the action of ammonia are studied, the ways of their usage in industrial manufacturing devices are suggested and working model of optical ammonia sensors based on them are made [1–4, 12,13]. However, the needs of modern processing industries and other fields of human activity require constant improvement of operational parameters

CONTACT B. Tsizh ✉ tsizhb@ukw.edu.pl
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of gas sensors. This article presents ways to improve and optimize the thin film gas sensitive elements of ammonia for using in optical gas sensors.

2. Experimental

Among the numerous methods of obtaining thin polymer films, the most widespread are thermal evaporation, electrochemical deposition, dip-, drop- and spin-coating, Langmuir-Blodgett and layer-by-layer technique, vapor deposition polymerization and other [1,2,4,5,8,11–13]. For obtaining layers of PANI and PEDOT on the transparent surface we used method of electrochemical polymerization. This deposition technique has allowed us to vary in high extent the composition, topology, thickness and other parameters of the synthesized layers and to optimize them effectively towards achieving high stability and reproducibility for different batches of samples.

Deposition of PANI films was performed at room temperature in a glass electrochemical cell in which as a working electrode served glass plates (10 × 20 × 0.3 mm) with a transparent conductive coating (SnO_2). Counter electrode was a platinum mesh. Thin PANI films was deposited by electrochemical polymerization of a 0.1M aniline (Aldrich) in 0.5M aqueous sulfuric acid at constant current density 0.05–0.20 $mA{\cdot}cm^{-2}$ during 2–10 minutes as described early [4–6].

The polymer films of PEDOT on the SnO_2 surface were obtained by the electrochemical polymerization of a 0.1M solution of monomer (3,4-ethylendioxythiophene /EDOT/, Aldrich) in acetonitrile – 0,5M sulfuric acid mixture (1:1) under the potential cycling between 0 and 1.5 V at the sweep rate $v = 20$ mV/s. The sweep cycle number regulated the film thickness. The glass plates (10 × 20 × 0.3 mm) coated by SnO_2 were used as a working electrode. The counter electrode acted as a platinum mesh, whereas Ag/AgCl (in saturated KCl) was used as a reference electrode. The PEDOT films of a controlled thickness (280–320 nm) were electrodeposited on the electrode surface as a result of 15–20 cycles of the potential scanning between -0.2 and $+1.2$ V. The chemical structure of PEDOT and PANI films is presented in Fig. 1.

A hybrid film structure PANI/PEDOT was obtained by electrochemical polymerization of EDOT on the electrode coated with PANI film near 120–150 nm thickness. Polymerization of EDOT on the PANI modified electrode proceeds in the interval of potentials corresponding to PANI electrochemical activity. In this potential range, a polymer is in a highly conductive

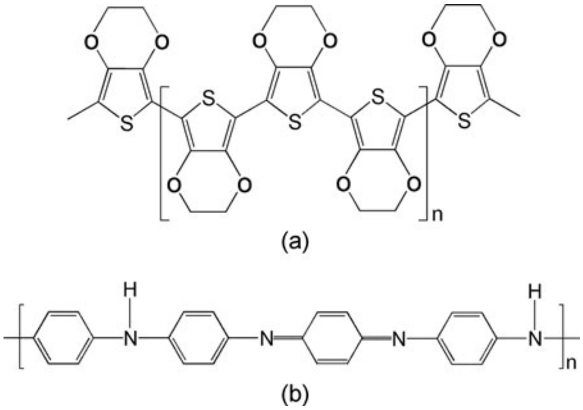

Figure 1. Chemical structure of PEDOT (a) and PANI (b) films.

polaron-bipolaron state [14] and serves as a mediator of the electron transfer between electrode surface and EDOT monomer molecules. An electrocatalytic action of polyaniline layer leads to a reduced oxidative potential of EDOT and flowing the polymerization in the potential range from 0.5 to 1.0 V. It may be suggested that, as a result of the EDOT chemisorption on a PANI layer and the electron transfer between the electrode surface with the conductive PANI layer and EDOT monomer molecules, the graft copolymerization is leading to the formation of a PANI/PEDOT bilayer structure [15]. As alternative way to obtain PANI/PEDOT composition film a simultaneous electrochemical polymerization of 0.05 M aniline and 0.05 M EDOT mixture solution was carried out at constant current density 0.20 mA·cm^{-2} during 10 minutes.

Optical absorption spectra of PANI, PEDOT and PANI/PEDOT films were obtained using the modified two-beam optical spectrometer Specord M400 applying the following measurement parameters: spectral range – 200–900 nm, slit width – 1 nm, integration time – 1 s, scan step – 1 nm, scan speed – 10 nm/s. To measure the optical spectra of the films in ammonia atmosphere, a sealed quartz chamber with volume of 50 cm^3 was used, in which the necessary volume of gas (ammonia) was supplied. All measurements were performed at the temperature of 293 ± 1 K. Analysis and processing of experimental data was done using methods described in [16, 17]. Analysis of the results was performed using standard correlation program, in which the relative error did not exceed 1.5% in entire range of measurements.

Recovery of gas sensing in the films has been achieved by short time exposure in 0.5 M aqueous solution of sulfuric acid, rinsing with distilled water and drying in a stream of dry air for 3–5 min. Process of relaxation of gas sensitive films also was carried out by exposition these films in air under normal conditions, or by blowing with air in temperature scale 293 …423 K.

3. Results and discussion

In previous publications [2,4,5] we have already reported about the change of optical absorption of PANI films under ammonia influence, in particular, about the fact that the most significant changes occur in the optical absorption spectral range 500 … 700 nm (Fig. 2) and gas sensitivity of film is defined exactly by this spectral range. It is logical to predict that the expansion of the spectral sensitivity region will lead to an increase of performance of gas sensors.

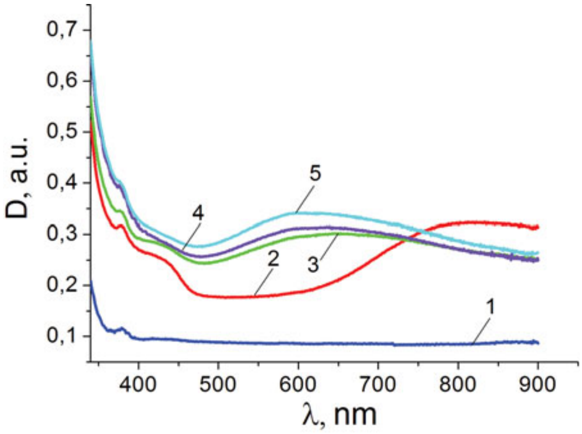

Figure 2. Spectra of optical absorption of polyaniline film before (2) and after contact with ammonia during 1 min (3), 2 min (4), 5 min (5), P NH$_3$ = 6.2 Pa, (1 – without sample). Film thickness 305 nm.

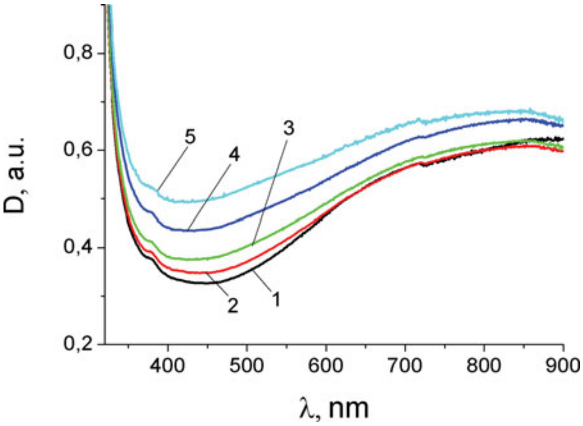

Figure 3. Spectra of the optical absorption of PEDOT films before (1) and after a contact with ammonia during 1 min (2), 2 min (3), 3 min (4) and 5 min (5), P $NH_3 = 6.2$ Pa. Film thickness 320 nm.

For expansion of the spectral sensitivity region we proposed to use films, which are characterized by maximal gas sensitivity to ammonia in another spectral region compared to PANI films. For this it was used thin PEDOT films, for which maximal changes of optical absorption under ammonia influence are observed in spectral range of 350 …550 nm (Fig. 3).

In order to create an optimal gas sensitive element we investigated thin film structure with alternately deposited layers of PEDOT and PANI (PANI / PEDOT) and the thin films deposited from solution of monomer mixture (PANI + PEDOT, 1:1). It was studied the effect of ammonia on the optical absorption of mentioned films and corresponding spectra are presented in Fig. 4. These spectra show that the bilayer film structure of PANI / PEDOT (Fig. 4a), and the films based on mixtures of PANI + PEDOT (Fig. 4, b) are sensitive to ammonia in a wide spectral range. From Fig. 4, one can see, that changes of optical absorption under influence of ammonia for PANI/PEDOT structure are more significant, especially for spectral range of $\lambda > 500$ nm. This fact may be explained by the superposition of sensitivity to ammonia of individual films: PANI film in the 470 … 700 nm and of PEDOT films in the 350 … 550 nm which occurs in the bilayer structure PANI/ PEDOT. In the films obtained from a mixture of PANI + PEDOT are likely to form a complex with low gas sensitivity in the

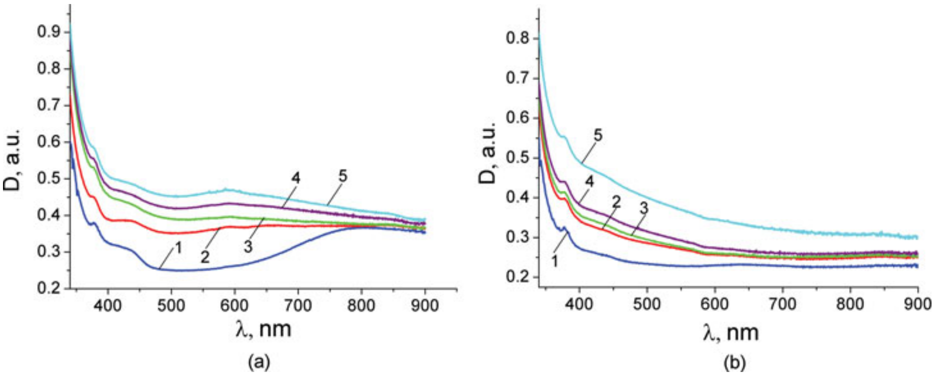

Figure 4. Spectra of optical absorption of thin-film structure PANI / PEDOT (a) and film based on a mixture of PANI + PEDOT (b) before (1) and after contact with ammonia during 1 min (2), 2 min (3), 6 min (4), 10 min (5), P $NH_3 = 6.2$ Pa.

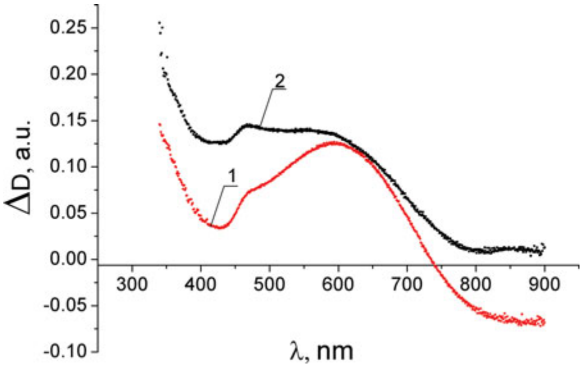

Figure 5. Spectra of absolute change of optical absorption of polyaniline film (1) and of thin-film structure PANI / PEDOT (2) under influence of ammonia during 2 min, P $NH_3 = 6.2$ Pa.

long-wave region of spectrum (Fig. 4, b) and therefore, integrated optical absorption changes for them are smaller, than for PANI / PEDOT structures.

Spectral dependence of optical absorption presented in Fig. 5 allows doing more detailed comparative analysis of different types of gas sensitive elements. It can be seen from Fig. 5 the change in optical absorption under the action of ammonia for film structure PANI / PEDOT (curve 2) is much larger than similar changes in individual PANI films (curve 1).

For quantitative estimation integral spectral changes of optical absorption we evaluate and compare area under the corresponding spectra. Since changes in the optical absorption of optical gas sensor is the main indicator of sensitivity, the area under the curve of the spectral dependence ΔD(λ) is kind of coefficient spectral sensitivity. From spectra presented in Fig. 5 in spectral region 400 …750 nm it was evaluated with numerical integration that values of these areas are equal to $S_1 = 26{,}07$ a.u. and $S_2 = 37.74$ a.u. respectively, and their relation is $S_2/S_1 = 1{,}45$. This gives reason to believe that using film structures PANI / PEDOT as gas sensitive elements increases the sensitivity of ammonia gas sensors up to 1.45.

Kinetics of changes in optical absorption of PANI / PEDOT film structures under the influence of ammonia shows that as for films PANI [2], key changes in the optical properties occur in the first seconds of action of ammonia, what can be seen from Fig. 6. We also see that this kinetics is the same in a wide spectral range 400 … 700 nm, which may be the key to the stability and reproducibility of sensitive elements of gas sensors.

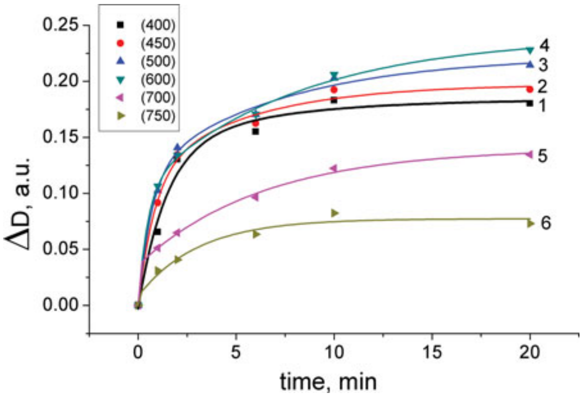

Figure 6. Kinetics of changes of optical absorption of PANI / PEDOT film structure under action of ammonia (P $NH_3 = 6.2$ Pa) at wavelength 400 nm (1), 450 nm (2), 500 nm (3), 600 nm (4), 700 nm (5), 750 nm (6).

4. Conclusions

We proved that the thin-film structure of PANI / PEDOT significantly extends the spectral range of sensitivity to ammonia of individual PANI and PEDOT films by superposition of high gas sensitivity of PANI and PEDOT films in the range of wavelength of 500 … 700 nm and 350 … 550 nm respectively. It was shown that the area under the spectra of change of the optical absorption of thin-film structure of PANI / PEDOT is in 1.45 times larger than the area of the same for individual components of the layers, which is the key to increasing the sensitivity of the gas sensors.

It was established the similarity of the temporal changes of optical absorption of gas-sensitive thin film structures of PANI / PEDOT and individual films under the action of ammonia over a wide spectral range 350 … 900 nm, which allows to recommend those structures for the improvement of sensitive elements of gas sensors.

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