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# Polymer Sensitive Elements for Gas Sensors of Ammonia

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*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. We proved that the thin-film structure of PANI / PEDOT significantly extends the spectral range of sensitivity to ammonia of individual PANI n 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. The results can be used to optimize ammonia gas sensors for monitoring biotechnological processes in food industry and the environment.*

***Keywords:*** *gas sensor, polyaniline, poly-3,4-ethylenedioxythiophene, ammonia, optical absorption, sensitive element, thin film.*

# Полімерні чутливі елементи для газових сенсорів аміаку

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*Досліджено вплив аміаку на спектри оптичного поглинання тонких плівок поліаніліну (PANI), полі-3,4-етилендіоксітіофену (PEDOT), їх сумішей, а також плівкових структур на їх основі, отриманих електрохімічним методом. Вивчено кінетику змін оптичного поглинання досліджуваних структур під дією аміаку в спектральному діапазоні 350…900 нм. Доказано, що тонкоплівкові структури PANI/PEDOT суттєво розширюють спектральну область чутливості до аміаку окремо взятих плівок за рахунок суперпозиції високої газочутливості плівок PANI і PEDOT в областях довжин хвиль 500…700 нм і 350…550 нм відповідно. Показано, що площа під спектрами змін оптичного поглинання для тонкоплівкової структури PANI/PEDOT в 1,45 раз більша за аналогічну площу окремих складових шарів, що є запорукою збільшення чутливості газових сенсорів. Отримані результати можуть бути використані для оптимізації газових сенсорів аміаку для моніторингу біотехнологічних процесів харчової промисловості та стану довкілля.*

***Ключові слова:*** *газовий сенсор, поліанілін, полі-3,4-етилендіоксітіофен, аміак, оптичне поглинання, чутливий елемент, тонка плівка.*

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# Полимерные чувствительные элементы для газовых сенсоров аммиака

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*Исследовано влияние аммиака на спектры оптического поглощения тонких пленок полианилина (PANI), поли-3,4-етилендиокситиофена (PEDOT), их смесей, а также пленочных структур на их основе, полученных электрохимическим методом. Изучена кинетика изменений оптического поглощения исследуемых структур под действием аммиака в спектральном диапазоне 350 ... 900 нм. Доказано, что тонкопленочные структуры PANI / PEDOT существенно расширяют спектральную область чувствительности к аммиаку отдельно взятых пленок за счет суперпозиции высокой газочутливости пленок PANI и PEDOT в областях длин волн 500 ... 700 нм и 350 ... 550 нм соответственно. Показано, что площадь под спектрами изменений оптического поглощения для тонкопленочной структуры PANI / PEDOT в 1,45 раз більше за аналогичную площадь отдельных составляющих слоев, что является залогом увеличения чувствительности газовых сенсоров. Полученные результаты могут быть использованы для оптимизации газовых сенсоров аммиака для мониторинга биотехнологических процессов пищевой промышленности и состояния окружающей среды.*

***Ключевые слова:*** *газовый сенсор, полианилин, поли-3,4-етилендиокситиофен, аммиак, оптическое поглощение, чувствительный элемент, тонкая пленка.*

## Introduction

To date, a wide variety of sensor devices and systems for controlling gas environments have been developed. The films of oxides, as well as various inorganic and organic semiconductors have been exploited as sensitive elements in these sensors. In recent years, an interest in the use of polymer films (Reemts et al., 2004; McGovern et al., 2005; Sandberg et al., 2005; Kukla et al., 2005; Ameer and Adeloju, 2005; Ram et al., 2005; Xu et al., 2006; Nohria et al., 2006; Athawale et al., 2006; Bai and Shi, 2007; Tsizh and Aksimentyeva, 2016; Tsizh et al., 2016; Olenych et al., 2016) sensitive to different gases increased due to the better adaptability, easiness of synthesis and use, lower cost, and in some cases better performance for the polymer films. Alternatively, despite of successful development and use of «artificial nose» systems and other gas-sensitive devices, there is high need of cheap portable sensors for operational observation of environmental and industrial processes, monitoring of gaseous media in food, especially, control of freshness for food (meat, fish, dairy and other products) in the process of the storage and other purposes. In particular, the loss of freshness (putrefaction damage) in protein containing food results in detachment of volatile substances, especially ammonia, due to a degradation of proteins and other nitrogenous compounds. The intensity of detached ammonia corresponds to a level of degradation for proteins, polypeptides and free amino-acids, and thus, the ammonia concentration is the most accurate reliable criterion of freshness for protein contained food at different stages of the storage (Tsizh et al., 2009). In this regard, there is an urgent need for simple, reliable, cheap and accessible sensors of ammonia, and their development is extremely 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) (Reemts et al., 2004; McGovern et al., 2005; Ram et al., 2005; Nohria et al., 2006; Xu et al., 2006; Bai and Shi, 2007). 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 (Bai and Shi, 2007; Tsizh et al., 2009; Tsizh et al., 2014; Tsizh and Aksimentyeva, 2016; Tsizh et al., 2016). However, the needs of modern processing industries and other fields of human activity require constant improvement of operational parameters 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.

## Materials and methods

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 (Reemts et al., 2004; Athawale et al., 2006; Nohria et al., 2006; Bai and Shi, 2007; Tsizh and Aksimentyeva, 2016). 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·cm$^{-2}$ during 2 – 10 minutes as described early.

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 polaron-bipolaron state 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 (Bai and Shi, 2007). As alternative way to obtain PANI/PEDOT composition film a simultaneous electrochemical polymerization of 0.05M aniline and 0.05M EDOT mixture solution was carried out at constant current density 0.20 mA·cm$^{-2}$ during 10 minutes.

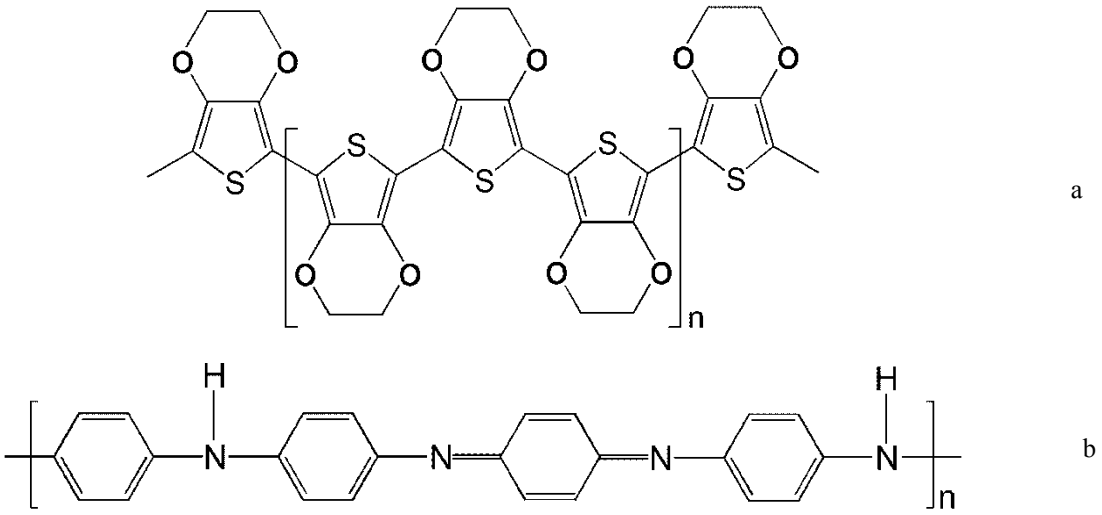


**Fig. 1. Chemical structure of PEDOT (a) and PANI (b) films**

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 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 0.5M 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.

## Results and discussion

During the electrochemical deposition of PANI films from solutions of monomers in proton acids a series of physical and chemical processes are occurring. In results of electron transfer at the electrode/solution interface is occurs an oxidation of the monomer with the formation of cation radicals of aniline. Follow isomerization of cation-radicals and oxidative coupling reactions leading to a formation conjugated polymer chains and deposition of

conductive polymer layer. Formation of the polymer is bimolecular reaction complicated by heterogeneous conditions of the chain growth, when the reaction product formed near the electrode is not soluble in the reaction medium and forms a film on the electrode surface. A high conductivity of polyaniline permits to synthesize the film with various thickness. The obtained polymer layer has a bright green color being a feature of acid-doped form of PANI, emeraldine salt. The surface morphology of the films is shown in Fig. 2.

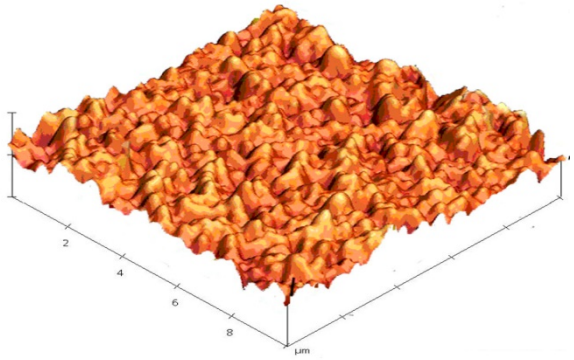


**Fig.2. ACM image of surface of PANI film (d = 0,3μ), made on $SnO_2$ electrode with electrodeposition method from 0.1M aniline solution in 0.5M sulfuric acid solution**

In previous publications (Tsizh et al., 2009; Tsizh et al., 2014; Tsizh and Aksimentyeva, 2016; Tsizh et al., 2016; Olenych et al., 2016) 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 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.

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 . 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. These spectra show that the bilayer film structure of PANI / PEDOT, and the films based on mixtures of PANI + PEDOT are sensitive to ammonia in a wide spectral range. 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 long-wave region of spectrum and therefore, integrated optical absorption changes for them are smaller, than for PANI / PEDOT structures.

Spectral dependence of optical absorption presented in Fig. 3 allows doing more detailed comparative analysis of different types of gas sensitive elements. It can be seen from Fig. 3 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).

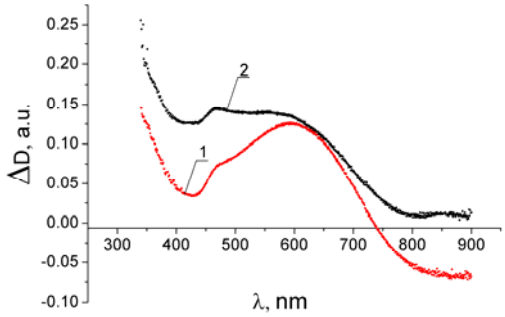


**Fig. 3. Spectra of absolute change of optical absorption of polyaniline film (1) and of thin-film structure PANI / PEDOT (2) under influence of ammonia during 2 min, P $NH_3$ = 6.2 Pa.**

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 $\Delta D(\lambda)$ is kind of coefficient spectral sensitivity. From spectra presented in Fig. 3 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.

## Conclusions

We proved that the thin-film structure of PANI / PEDOT significantly extends the spectral range of sensitivity to ammonia of individual PANI n 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.

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