chemistry proceedings

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Proceeding Paper

#Polyaniline Derivatives for Chemical Sensors of Ammonia Vapor †

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† Presented at the 27th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-27), 15–30 November 2023; Available online: https://ecsoc-27.sciforum.net/.

Abstract. This study considers the possibility of using thin films of new soluble modified polyaniline derivatives in the creation of chemical sensors. The study involves an examination of how the current passing through resistive structures, which are constructed using thin films of polyanilines, is influenced by varying concentrations of ammonia vapors present in the surrounding air.

Keywords: sensors; polyaniline; thin films; ammonia vapors

Citation: Salikhov, R.B.; Gaskarova, A.A.; Salikhov, T.R.; Ostaltsova, A.D.; Yumalin, T.T. #Polyaniline Derivatives for Chemical Sensors of Ammonia Vapor. *Chem. Proc.* **2023**, *70*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s):

Published: 15 November 2023

1. Intorduction

Due to the annual increase in the level of air pollution every year, the monitoring of the environment and the air in it becomes an increasingly urgent task. The use of various sensors allows you to receive, register, process and transmit information about the state of various system [1–5].

Modern sensors have high requirements for sensitivity, accuracy, linearity, response speed, and interchangeability. The sensors must have high reliability, long service life and be trouble-free in operation. Devices must be technologically advanced: have small dimensions and weight, be simple in design and have a low-cost price [6,7].

A very common air pollutant that forms on livestock and poultry farms, as well as in the production of mineral fertilizers, is ammonia. In the modern world, the most promising devices for monitoring gaseous media are chemical sensors-small, high-speed sensors with a fairly low cost. On the basis of thin polymer films, such gas sensors can be manufactured, including those for ammonia vapors [8–11].

In recent studies, there has been extensive exploration into the sensory attributes of both PANI and composite configurations derived from it [12–15]. Specifically, emphasis has been placed on comprehending the potential of organic thin-film sensors for ammonia gas (NH_3). Such sensors are deemed crucial in various facets of daily human life, notably in the analysis of breath composition. Moreover, they hold promise for non-invasive diagnostics concerning conditions such as kidney disease and hepatitis [16,17].

2. Experimental

Aluminum contacts, spaced at 50 μm intervals, were applied onto a glass-ceramic substrate through thermal spraying within a vacuum chamber. Within this gap area, a thin film of a polyaniline derivative was generated using centrifugation, exhibiting an approximate thickness of 300 nm. Additionally, we investigated insoluble polyaniline derivatives, depositing thin films of these materials into the gap using vacuum deposition through a Knudsen cell. The Knudsen cell was characterized by specific parameters: a cylindrical chamber with a length of 25 mm and an inner diameter of 4 mm. The operational temperature was varied within the range of 400–650 K, with the deposition occurring at temperatures of 500–550 K.

Structure of sensors is shown in Figure 1. New modified derivatives of polyaniline forms were used as a sensitive layer: PA (poly[2-(1-methylbut-1-en-1-yl)aniline]), PB (poly[2-(1-methylbutyl)aniline]) and PC (poly[2-(2-aminophenyl)pentan-2-ol]).

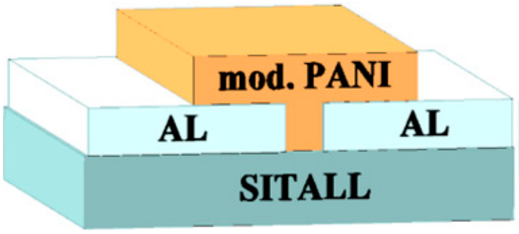

Figure 1. Structure of sensors.

For measurements, a setup was created (Figure 2), with the help of which the sensory properties of film samples were investigated. The experiments used: DC POWER SUPPLY HY3005D-2 power supply, DMM4020 multimeter as an ammeter, Arduino Uno programmable controller, laptop, MQ135 sensor.

In this setup, the MQ135 sensor was used to determine the actual concentration of ammonia vapor.

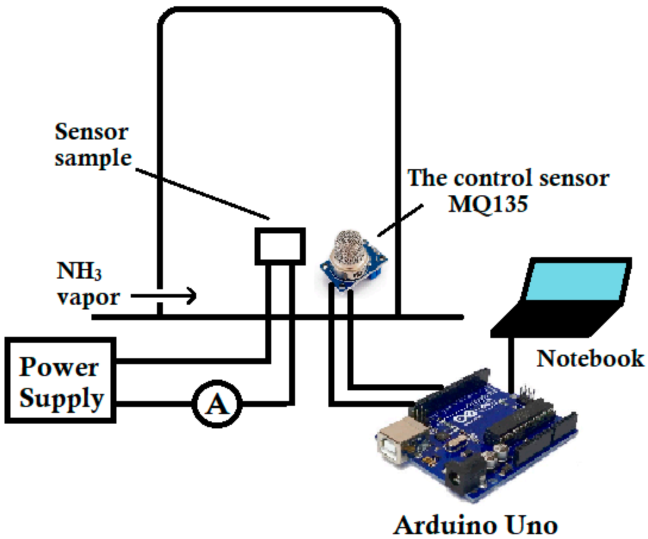

Figure 2. Experimental setup for studying the effect of ammonia vapors on the electrophysical properties of films of polyaniline derivatives.

3. Results and Disscution

The relationships between current flow across the sensor film specimen and the concentration of ammonia vapors were quantified and illustrated in Figure 3. The data demonstrates that as the concentration of ammonia vapors increases, the conductivity of the films diminishes. Notably, this reduction is notably pronounced in the PB films. Conversely, the PC samples exhibit a gradual and nearly linear decline in conductivity throughout the complete spectrum of changes in ammonia vapor concentration.

The NH_3 absorption sensors developed using polyaniline films exhibit several merits, notably high sensitivity and minimal hysteresis.

Aluminum contacts, separated by a 50 μm distance, were deposited onto a glass-ceramic substrate through thermal spraying within a vacuum chamber. Within the gap area, a thin film of the polyaniline derivative was created using a centrifugation process, with a thickness of approximately 300 nm. Additionally, investigations were conducted on insoluble polyaniline derivatives, and thin films of these derivatives were deposited into the gap region through vacuum deposition using a Knudsen cell. The Knudsen cell specifications encompass a cylindrical chamber length of 25 mm, an inner diameter of 4 mm, and a variable working temperature range of 400–650 K, with a deposition temperature set at 500–550 K. An experimental setup was devised for measurements (Figure 2). The variations in current passing through the sensor film sample in response to differing concentrations of ammonia vapors were meticulously recorded (Figure 3). The plotted curves illustrate that PB polymer films exhibit the highest sensitivity to ammonia vapors. However, these curves, representing PB polymer films, bifurcate into two nearly linear segments, each characterized by distinct slope angles, spanning from 0 to 20 mg/m^3 and from 20 to 50 mg/m^3. Conversely, though the curves for PA and PC polymers possess smaller slopes, they remain consistent across the entire range of measurements. Notably, polyaniline PA films demonstrated the lowest sensitivity to ammonia vapors.

The NH_3 absorption sensors devised using polyaniline films offer the advantage of minimal hysteresis.

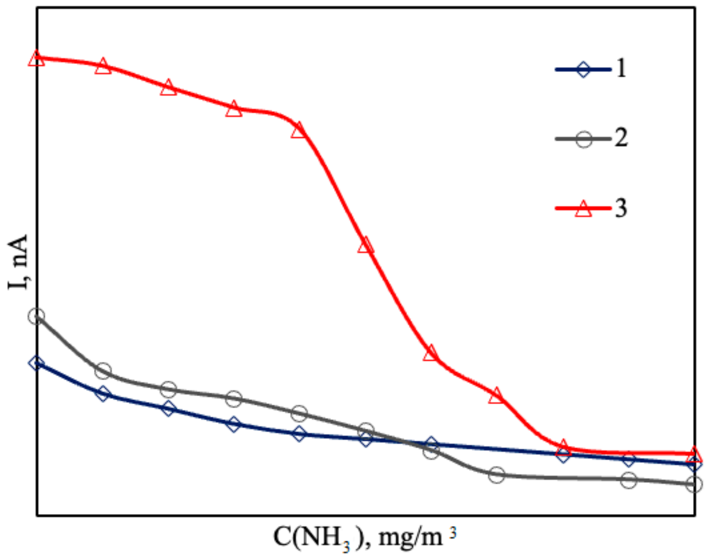

Figure 3. The relationship between the current passing through the PANI derivative film (1-PA, 2-PC, 3-PB) and the concentration of ammonia vapors within the air volume.

Employing the educational suite of scanning microscopes Nanoeducator II, surface images of the examined polymer films were acquired (Figure 4). Surface profiles of films, calculated from AFM images, are shown on Figure 5

Figure 4 shows fragments of the surface of films with dimensions of 20 • 20 μm^2. The color scale of the surface relief is shown to the right of the image. Comparative analysis of AFM images shows that P-MB polymer films have the most uneven rough surface. The root-mean-square roughness of these films reaches 11 nm.

Comparative analysis of the surface profiles shown in Figure 5 shows the strongest fluctuations in height and the greatest roughness have curves related to film samples PB.

The profiles and roughness values were obtained using the Gwyddion AFM image processing program. The average roughness Ra and root mean square roughness Rs of the obtained PA, PC films are shown in Table 1.

Table 1. Roughness of PANI derivatives thin films.

Substance	PA	PC	PB
Average roughness Ra, nm	1,69	2,51	3,72
Root mean square roughness Rs, nm (by area)	4	8	11

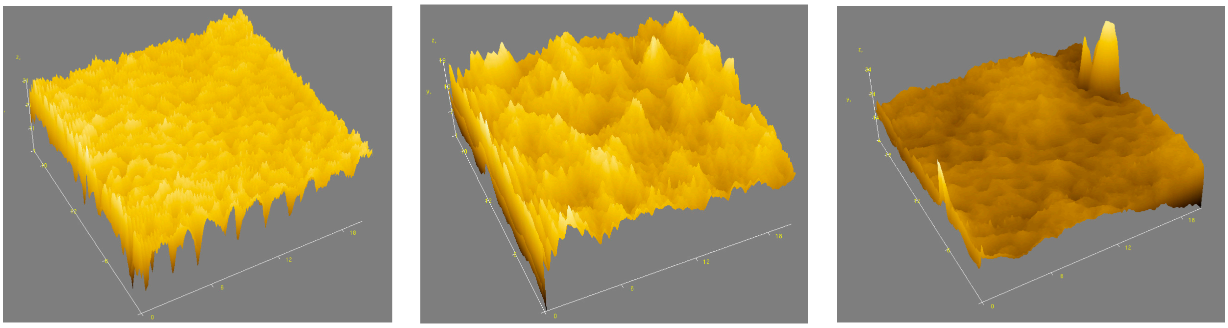

Figure 4. AFM image of the film surface: (**a**) PA; (**b**) PB; (**c**) PC.

Polyaniline derivative films respond to the presence of ammonia vapors in the surrounding environment by a reduction in the current flow. Analysis of the surface morphology of these films reveals a relatively higher current flow through films exhibiting increased surface roughness.

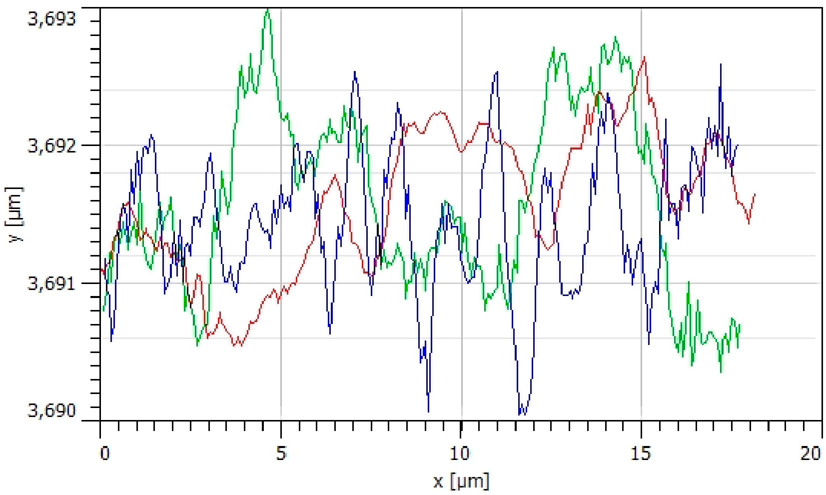

Figure 5. Surface profiles of films. Red profile - PA. Blue profile - PC. Green profile - PB.

The current-voltage characteristics illustrate the substantial impact of a low concentration of ammonia in the air volume on the electrophysical attributes of polyaniline derivative films. To develop sensors with broad sensitivity across various concentrations, further investigations are necessary to enhance the properties of polymers and their corresponding films. The notable sensitivity and minimal inertness observed in a particular polyaniline derivative seem to be linked to distinct aspects of its synthesis.

4. Conclusions

The rapid escalation of environmental contamination has been acknowledged as a critical issue, emphasizing the pressing need for monitoring, which has become a pivotal aspect of human well-being. The development of efficient gas detection devices is imperative to achieve compact, dependable, cost-effective, and portable electronic sensor methodologies for a diverse range of applications, including air quality monitoring, medical diagnostics, food quality control, industrial process safety, and home security systems.

In this study, we investigated the correlations between the current passing through the sensor film sample and the concentration of ammonia vapors. Additionally, we explored insoluble derivatives of polyaniline, and thin films of these derivatives were deposited into the gap using vacuum deposition via a Knudsen cell. The variations in current passing through the sensor film sample in response to different concentrations of ammonia vapors were carefully analyzed. Surface roughness profiles and measurements were obtained using the Gwyddion AFM image processing software. Furthermore, a dedicated measurement setup was devised.

The findings presented in this study underscore the promise of thin films composed of the examined polyaniline derivatives for utilization as sensitive components in ammonia vapor sensors.

Author Contributions: Conceptualization, Data curation, Synthetic investigation, Writing-original draft, and review and editing, R.B.S., A.A.G., T.R.S., A.D.O.; Supervision: R.B.S. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available on request.

Acknowledgments: The research was funded with the support of a state assignment (scientific code FZWU-2023-0002)

Conflicts of Interest: The authors declare no conflict of interest.

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