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Proceeding Paper

Polyaniline Derivatives for Chemical Sensors of Ammonia Vapor †

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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

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1. Introduction

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 us to receive, register, process, and transmit information about the state of various systems [1–5].

Modern sensors have high requirements for sensitivity, accuracy, linearity, response speed, and interchangeability. The sensors must have high reliability, a long service life, and be trouble-free during operation. Devices must be technologically advanced, have small dimensions and weight, be simple in their design, and have a low 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 polyaniline (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. Experiments

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 the following specific parameters: a cylindrical chamber with a length of 25 mm and an inner diameter of 4 mm. The operational temperature varied within the range of 400–650 K, with the deposition occurring at temperatures of 500–550 K.

The structure of the 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]).

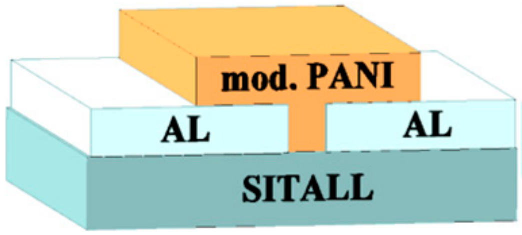


Figure 1. Structure of sensors.

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

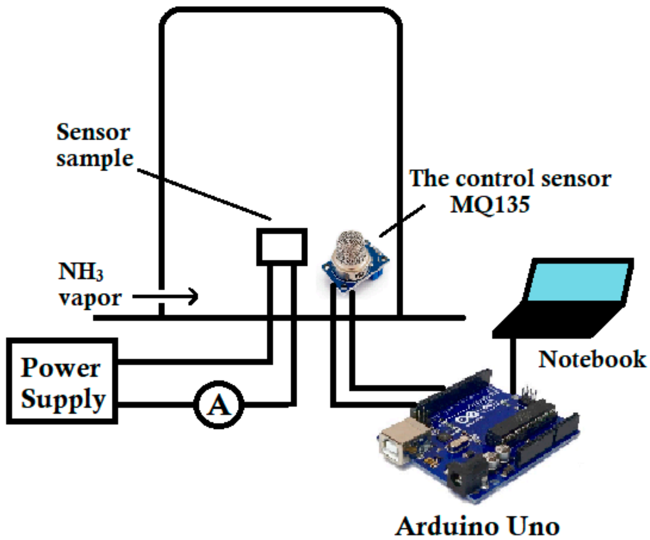


Figure 2. Experimental setup for studying the effect of ammonia vapors on the electrophysical properties of films of polyaniline derivatives.

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

3. Results and Discussion

The relationships between the current flow across the sensor film specimen and the concentration of ammonia vapors were quantified and are illustrated in Figure 3. The data demonstrate 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 detection sensors developed using polyaniline films exhibit several merits, notably high sensitivity and minimal hysteresis.

The variations in the current passing through the sensor film sample, in response to differing concentrations of ammonia vapors, were meticulously recorded (see Figure 3). The plotted curves illustrate that the 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.

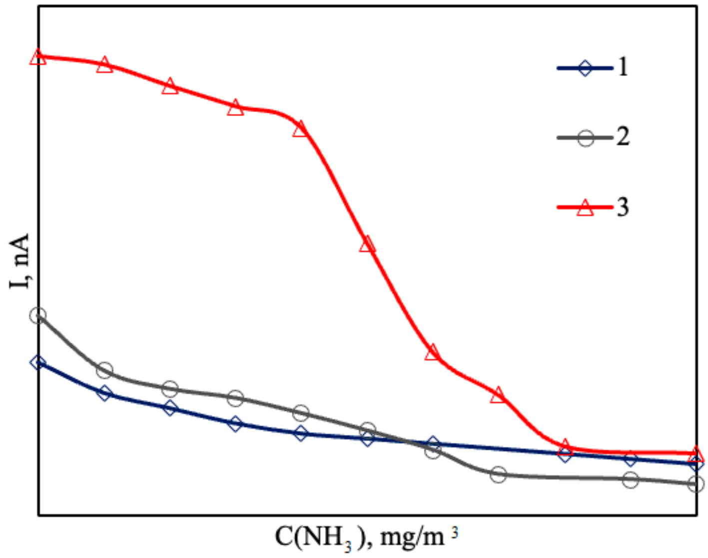
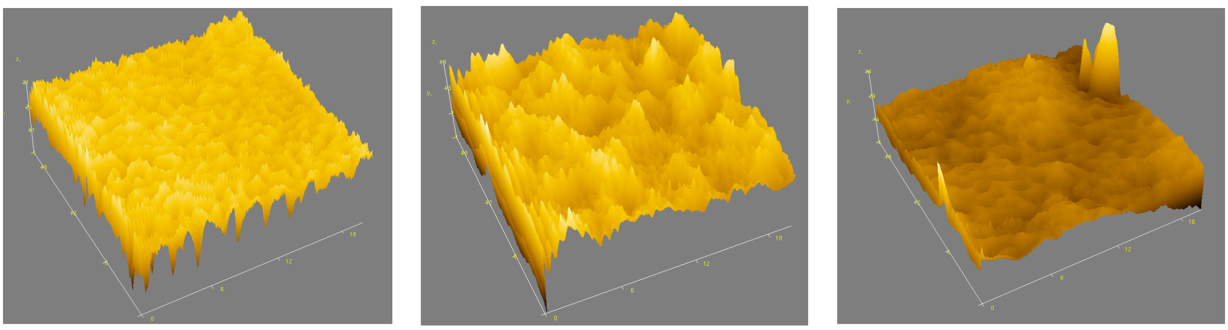


Figure 3. The relationship between the current passing through the PANI derivative film (1-PA, 2-PC, 3-PB) and the concentration of ammonia vapors within the air volume.

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



(**a**) (**b**) (**c**)

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

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 and roughest surfaces. 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 the PB film samples.

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

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.

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

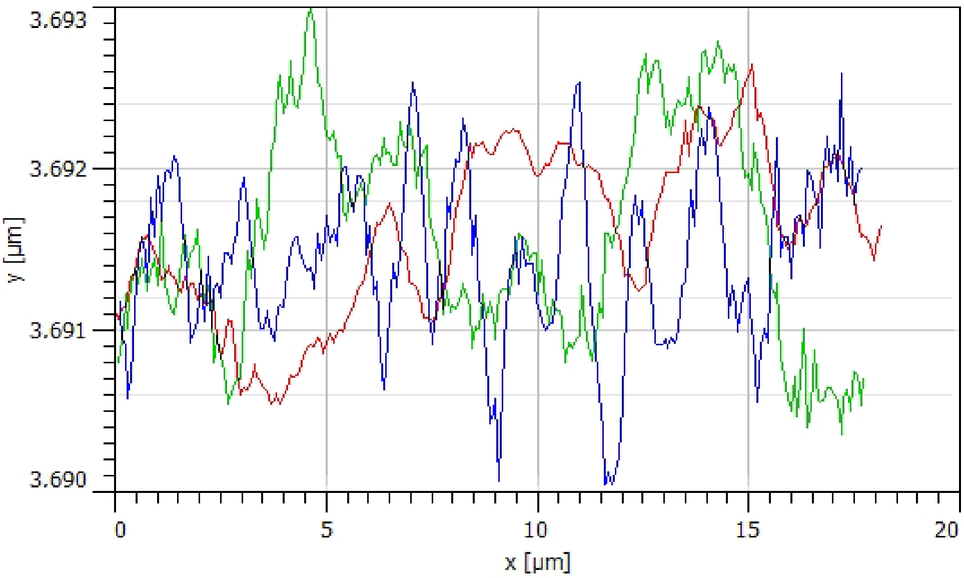


Figure 5. Surface profiles of films. Red profile—PA. Blue profile—PC. Green profile—PB.

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 presented work shows that thin films of the studied polyaniline derivatives are promising for use as sensitive elements of ammonia vapor sensors.

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