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REVIEW

Thin Films of Polyanilines and Polymer Nanocomposites for the Development of Chemical Sensors

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Abstract

The control and monitoring of humidity levels and the concentration of hazardous gases in the atmosphere are subjects of significant interest across various fields. Consequently, current research focuses primarily on the advancement of sensitive materials tailored for humidity and toxic gas sensors, aiming to achieve heightened performance and sensitivity while operating efficiently at ambient temperatures. Investigative efforts delve into exploring thin film compositions comprising polyanilines and their derivatives, as well as polymer nanocomposites, with the intention of fabricating chemical sensors. Diverse configurations of chemical sensors, manifesting as thin-film electronic devices such as resistive and transistor structures, are under scrutiny. The surface morphology of these thin films is meticulously examined through scanning electron microscopy. Furthermore, the electrical characteristics, as elucidated by the current-voltage profiles, of resistive and transistor structures utilizing thin films of polyanilines and their derivatives alongside polymer nanocomposites, are analyzed in relation to variations in ambient humidity levels and concentrations of hazardous gases such as ammonia vapors. The outcomes of this investigation underscore the potential utility of organic compound-based thin films in the realm of chemical sensor development.

Keywords: Polyanilines, Nanocomposites, Sensors, Humidity, Ammonia

1. Introduction

The discovery in 1977 of the electrical conductivity of polyacetylene, modified with halogens and close to metals conductivity, became the starting point for the development of organic electronics, i.e. electronics based on the use of organic semiconductors. Organic electronics have undeniable advantages over inorganic (silicon): low cost of starting organic materials, inexpensive, environmentally friendly production of organic electronic devices through printing technologies. Light weight, flexibility, transparency, long shelf life and reliability make organic materials extremely promising for electronics [1].

The wide spread of organic electronics is also hampered by various disadvantages. First of all, the low mobility of charge carriers in organic semiconductors (mainly electrons). As a result, designers can only handle low currents and must tolerate the low conductivity of semiconductor devices and devices. Therefore, researchers face a primary task: the search for new effective organic materials with high charge carrier mobility. In addition, there is no definitive understanding of the mechanisms of charge carrier transport in organic materials. The influence of the structure of a polymer layer on its transport properties is well known. An analytical model suitable for describing the nonequilibrium hopping transport of charge carriers in

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a disordered organic medium is developed in the works of Nikitenko V.R. and H. Bässler [2,3]. Experimental studies of charge carrier transport in thin films of organic compounds were carried out in the following works [4,5]. Including in Refs. [6—8], the values of the Schottky barrier are determined for charge injection through the metal-polymer film boundary. Based on the temperature dependence of the conductivity of polymer films, the values of the HOMO — LUMO interval were determined for soluble forms of polyanilines [8] and fullerene-containing derivatives [9,10].

The studies carried out to elucidate the characteristics of charge carrier transport are important from the point of view of selecting the necessary organic compounds and the technology for producing thin films of these compounds with high charge mobility. And this, in turn, opens up great prospects for their practical application, including in electronic chemical sensors, which are described below in this review.

The significance of monitoring and controlling toxic gases like ammonia, nitrogen oxides, and various volatile organic compounds across industries ranging from environmental monitoring to automotive, defense, aviation, chemical, medical, and food cannot be overstated. Presently, researchers are actively engaged in the development of toxic gas detection sensors that possess attributes of high selectivity, cost-effectiveness, operability at ambient temperatures, and rapid response times.

Ammonia, being a widely utilized compound in industries encompassing industry, agriculture, household cleaning, plastics, petrochemicals, and explosives, plays a pivotal role. It is water-soluble, colorless, and emits an unpleasant odor. Household cleaning products containing ammonium salts or derivatives stand as the primary sources of ammonia contamination. Inhalation of this toxic gas can result in various respiratory ailments [11].

The development of ammonia gas sensors, particularly those based on polyaniline (PANI) composites, presents a significant challenge. For instance, researchers in Ref. [12] demonstrated the efficacy of PANI nanorods for NH3 sensing, while Kumar et al. [13] synthesized a flexible NH3 sensor employing pure polyaniline, showcasing a response time of 4.29 s at 25 ppm.

Graphene oxide (GO), characterized by its exceptional electronic, electrophysical, and mechanical properties alongside high flexibility and surface area, emerges as a promising material [14]. Its hydrophilicity is particularly noteworthy in gas sensors, offering enhanced gas sensitivity and selectivity, as explored by Garcia et al. [15] in investigating the adsorption capacity of PANI/GO nanocomposites for CO2 capture.

Polyaniline garners significant attention due to its intrinsic properties such as low synthesis cost, tunable electrical conductivity, and chemical stability. Moreover, its surface morphology, charge characteristics, and physical attributes can be readily modified through various dopants and templates during synthesis [16].

This study comprehensively investigates the influence of graphene oxide on the sensitivity of polyaniline to NH3 and CO gases at room temperature. PANI/GO nanocomposites were synthesized via chemical oxidative polymerization in the presence of GO. Optical, spectroscopic, and structural analyses of the resulting materials were conducted using UV, FTIR, Raman spectroscopy, and X-ray diffraction, while atomic force microscopy (AFM) facilitated topological studies. Sensors were fabricated by drop casting from pure PANI and PANI/GO nanocomposites using a low-cost copper interdented electrode (IDE) design. Notably, sensors based on PANI/GO exhibited superior sensitivity to NH3 compared to those made solely from PANI. These findings underscore the high sensitivity (9.6% - 70 ppm), rapid recovery time (23 s), low detection limit (30 ppm), and linear dynamic range (30—230 ppm) of PANI/GO sensors, alongside exceptional repeatability, reproducibility, long-term stability, and selectivity for NH3 detection. Hence, PANI/GO-based sensors hold promise for applications necessitating high-throughput sensing [17].

In a recent study [18], researchers showcased the integration of organic (polyaniline, PANI) and inorganic (carbon nanotubes (CNT), SnO2, TiO2) materials within gas sensors, utilizing nanocomposite layers that exhibit notable sensitivity, temperature stability, and reversibility, all while functioning at room temperature. Findings from another investigation [19] highlight PANI-NO2 and PANI-C6H5 derivatives as promising candidates for enhancing chemical sensor performance.

Conductive polymer nanocomposites commonly incorporate various nanofillers such as conductive nanostructures (e.g., metals, graphene, carbon nanotubes), metal oxides, and insulating ceramic nanoparticles [20]. Leveraging interfacial interactions and synergistic or complementary effects, these nanocomposites demonstrate intriguing properties that could be harnessed for novel applications. Specifically, their enhanced electroactivity and redox characteristics render them conducive to catalyzing redox reactions within sensors [21].

A gas sensor array based on polyaniline nanocomposites was explored for the selective detection of ammonia (NH3), nitrogen dioxide (NO2), carbon oxides (CO2 and CO), acetone ((CH3)2CO), and toluene (C6H5CH3) [22].

Nanomaterials have revolutionized various fields, particularly biotechnology, owing to their facile modification and advantageous properties. They offer significant advancements in sensitivity and selectivity, particularly in diagnostics, surpassing traditional methodologies. Nanomaterials, especially carbon-based ones, exhibit exceptional electrical, thermal, chemical, and biological attributes [23,24]. Derived composite materials find applications in diverse areas such as energy storage, sensors, drug delivery, field emission, and nanoelectronics [25—28], encompassing nanotubes, graphite, carbon nanofilms, carbon fibers, and fullerenes [29]. Notably, fullerenes have gained increasing prominence due to their distinctive structure and properties.

In recent years, sensing and biosensor technologies have experienced rapid evolution, with nanomaterials assuming crucial roles as immobilization materials for detecting analyte molecules. While fullerenes have garnered attention, research focusing on them remains relatively limited compared to other carbon-based nanomaterials [30].

Recent research progress reports fabrication of conducting polymer nanostructures/composite, and their excellent hydrogen sensing performance (detect 5 ppm of Hydrogen gas) in the following works [31—33].

2. Organic materials and nanocomposites

The focus of the investigation lies in the examination of various material groups. A novel polymer, poly-2-(1-methylbut-2-en-1-yl)aniline, was synthesized through the utilization of doping and oxidizing agents. The impact of preparation conditions on the physicochemical properties of these materials is under scrutiny. Morphological analysis of the polymers was conducted via scanning electron microscopy. Subsequently, the synthesized polymers were evaluated as active constituents in humidity sensors.

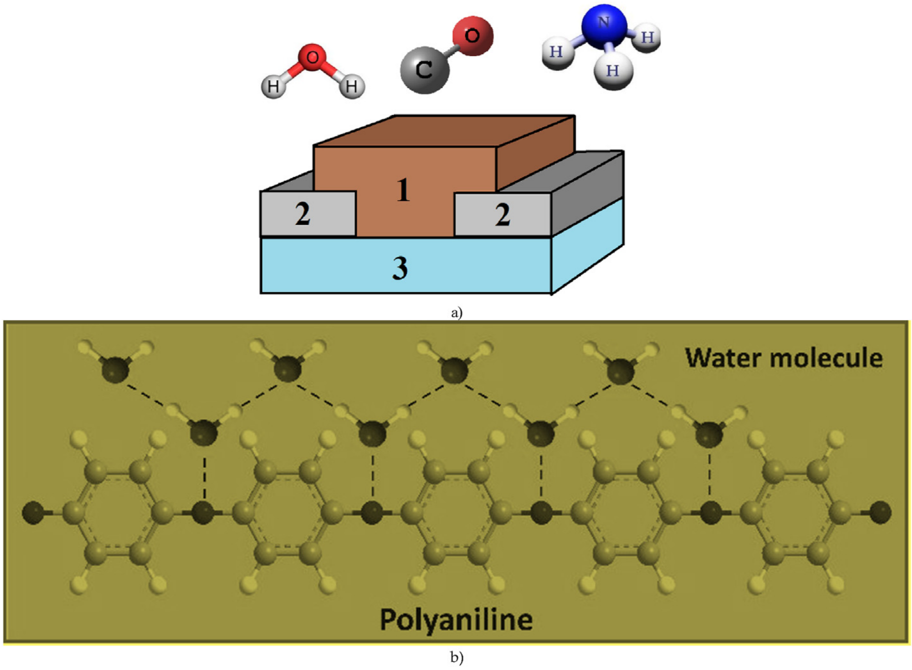
There are various analytes that need to be analyzed, the structure and scheme of humidity sensing of PANI are shown in Fig. 1.

All polymer samples underwent synthesis following a standardized procedure. Specifically, a solution comprising 2-(1-methylbut 2-en-1-yl)aniline (1 g, 6.2 mmol) dissolved in 50 ml of an aqueous solution containing 0.2 moL/l acid was subjected to gradual addition of an oxidizing agent solution in 50 ml of 0.2 moL/l acid (as outlined in Table 1) at room temperature, under continuous stirring.

Samples of synthesized polyaniline derivative, namely poly[2-(2-chloro-1-methylbut-2-en-1-yl)aniline] (referred to as PClPA) and poly(2-ethyl-3-methylindole) (abbreviated as 2E3MPIn), were employed as the sensitive constituents in resistive humidity sensors. Notably,

Table 1. Sample synthesis conditions [34].

Sample	Acid (0.2 mol/L)	Oxidant (7.75 mmol)	Yield, %
1	HCl	FeCl3	21
2	H2SO4	(NH4)2S2O8	62
3	H2SO4	FeCl3	29
4	HNO3	(NH4)2S2O8	74
5	HNO3	FeCl3	42
6	HClO4	(NH4)2S2O8	53
7	HClO4	FeCl3	55
8	HCl	(NH4)2S2O8	72



a)

b)

Fig. 1. (a) Structure of the resistive sensor (1- polyanilines or its nanocomposites, 2- aluminum, 3- glass or ceramic glass) and (b) scheme of humidity sensing of PANI.

2E3MPIn exhibited superior sensitivity to environmental humidity fluctuations compared to PClPA [35].

The research focused on investigating the relationship between the current passing through resistive structures based on thin films of polyaniline derivative (Poly[2-(2-chloro-1-methylbut-2-en-1-yl)aniline] (PClPA-NA), Poly[2-(2-chloro-1-methylbut-2-en-1-yl) aniline] (PClPA-HA), Poly[2-(2-chloro-1-methylbut-2-en-1-yl)aniline] (PClPA-SA), Poly[2-(2-chloro-1-methylbut-2-en-1-yl)aniline] (PClPA-PA), and the neutral form Poly[2-(2-chloro-1-methylbut-2-en-1-yl)aniline] (PClPA — ND)) and relative air humidity. Results indicated the potential utility of thin polymer films in chemical sensor design [36].

Furthermore, the impact of polyaniline (PANI) and its copolymers' morphology on the electrical conductivity and sensitivity to air humidity of thin-film structures derived from them was explored. Synthesis efforts yielded three new copolymers: poly(aniline-co-ortho-toluidine), poly{aniline-co-2-(cyclohex-2-en-1-yl)aniline}, and poly{aniline-co-2-(cyclopent-2-en-1-yl)aniline} [37].

Examination of the electrical conductivity of films at varying air humidity levels revealed their potential use as relative air humidity sensors. Notably, films exhibited optimal electrical conductivity at maximum relative humidity (90%), aligning well with morphological findings. Utilization of poly[2-(cyclohex-2-en1-yl)aniline] as a sensing material in resistive sensors demonstrated high sensitivity of electrical conductivity to fluctuations in humidity (% relative humidity) and ammonia concentration in the ambient environment. Table 2 presents data on the yields of poly[2-(cyclohex-2-en-1-yl)aniline] obtained under different alloying acids and oxidants.

Utilizing poly-2-[(2E)-1-methyl-2-buten-1-yl]aniline (referred to as P1) and poly-2-(cyclohex-2-en-1-yl)aniline (designated as P2) as the basis, resistive thin-film structures were fabricated, and their electrical conductivity's dependence on relative air humidity, as well as the current response to varying concentrations of ammonia vapor, were assessed. Experimental observations elucidated the impact of film surface morphology on sensor sensitivity to air humidity, showcasing the potential utility of the investigated films in humidity sensors [39].

Table 2. Conditions for the synthesis of [2-(cyclohex-2-en-1-yl)aniline] (C1—C8) [38].

Polymer	Acid (0.2 M)	Oxidant	Yield, %
C1	H2SO4	FeCl3	39
C2	HNO3	(NH4)2S2O8	83
C3	HCl	FeCl3	18
C4	HCl	(NH4)2S2O8	61
C5	H2SO4	(NH4)2S2O8	48
C6	HClO4	FeCl3	21
C7	HNO3	FeCl3	48
C8	HClO4	(NH4)2S2O8	54

A series of novel polyaniline derivatives (PANI) derived from an ortho-substituted aniline derivative, 2-(1-methylbut-2-en-1-yl)aniline, were synthesized and characterized. The research outcomes underscored the potential of thin polymer films in chemical sensor design. Specifically, the utilized polyaniline derivatives included Poly[2-(1-methylbut-1-en-1-yl)aniline] (denoted as P-PA), Poly[2-(1-methylbutyl)aniline] (abbreviated as P-MB), and Poly[2-(2-aminophenyl)pentan-2-ol] (referred to as P-AP) [40].

This subsection delves into the investigation of nanocomposite thin films formed by the polyelectrolyte complex of chitosan and chitosan succinamide (PEC), incorporating single-walled carbon nanotubes (SWCNTs) as fillers. Utilizing these nanocomposite materials as a foundation, resistive thin-film structures were fabricated, and their current response to changes in relative air humidity and ammonia vapor concentration were measured [41].

The development of a highly sensitive electronic gas sensor tailored for detecting carbon monoxide at ambient temperature is detailed in this section. Films were produced by casting a polymer solution containing graphene oxide and carbon nanotubes. Morphological analysis of the resulting thin polymer films, alongside spectral chemical assessments, and measurement of current-voltage characteristics of the sensors were conducted. Additionally, an IoT (Internet of Things) solution for remote monitoring was devised. The results showcased favorable response and repeatability at room temperature, positioning polymer-CNT-graphene oxide composite thin films as promising materials for electronic CO detection sensors [42].

3. Surface morphology

The sensor sensitivity of thin films is highly dependent on the surface morphology. To study the surface morphology of thin films, various methods are used, such as scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), etc. These methods provide detailed information about the shape and structure. film surface. In this review, the study was carried out using a Tescan Mira 3 LMH high-resolution scanning electron microscope (SEM).

The microstructure of the nanoparticles was studied using high-resolution scanning electron microscopy. The morphology of the samples differs significantly from the PANI and PPA structures studied previously (Fig. 2).

Fig. 3, sample 1 has a fibrous nanostructure, and in Fig. 3 b large hollow spheres were obtained. Products 3 and 4 show nanostructures with smaller globules

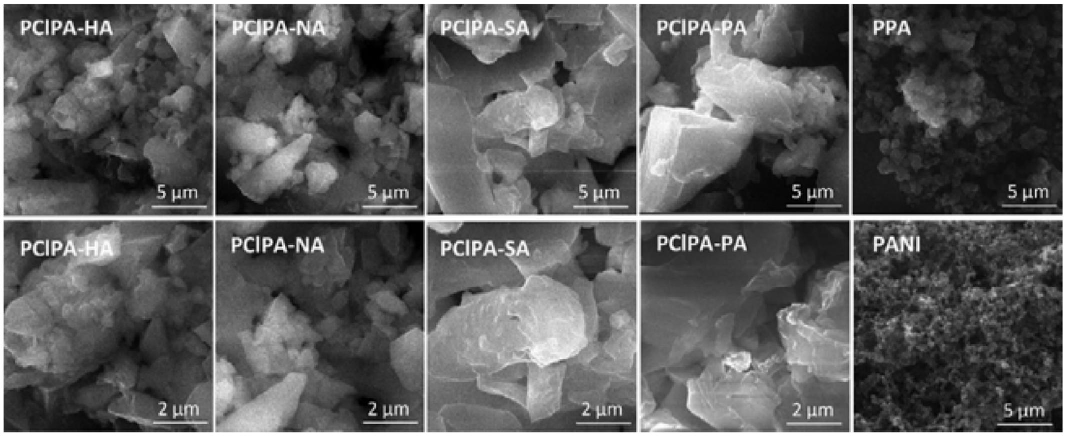


Fig. 2. SEM images of polymers [37].

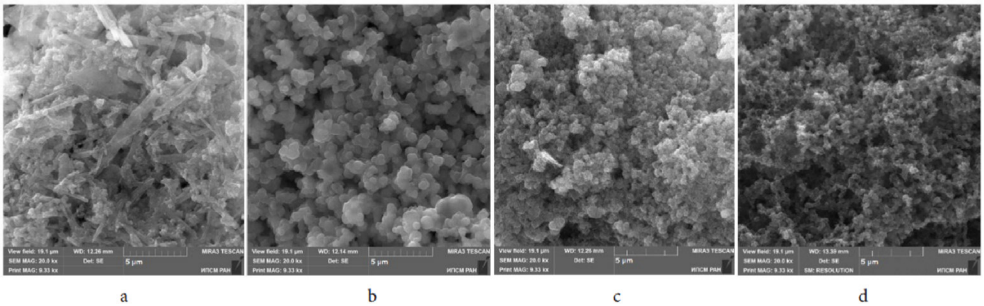


Fig. 3. SEM images of samples of the obtained (co)polymers: 1 (a); 2 (b); 3 (c); 4 (d) [37].

(Fig. 3c and d). A study of the morphology of PANI films shows that the conductivity of the latter is affected by the size of their globules [43—48]. Next, in accordance with the purpose of this study, we measured the dependence of the current flowing through films of PANI and its derivatives on humidity and relaxation time (recovery of the sample).

Images of the surface of the studied polymers were obtained (Fig. 4).

The morphology of the P2 surface is ragged, heterogeneous, with large dips in depth, which reduces the surface area available for molecules of the analyzed gas. The surface of P1 has a uniform spherical globular structure, which facilitates the access of a larger number of gas molecules compared to P2.

Fig. 5 shows the scanning electron microscopy results.

Images of the surface of the studied polymer PEC and PEC-SWCNT-3 were obtained (Fig. 6).

Unlike the surface of pure PEC, the surface of the PEC nanocomposite structure with SWCNTs is covered with filament-like formations. It can be assumed that these threads are complex formations formed by carbon nanotubes.

The surface morphology of thin films obtained from a polymer solution with CNT and graphene oxide additives by casting onto glass-ceramic substrates was studied (Fig. 7).

In addition, the chemical composition of the surface of the thin film was determined, which naturally consists mainly of carbon (Fig. 8). The surface morphology is torn, loose, heterogeneous, with small dips in depth, which facilitates the access of more molecules of the analyzed gas. The response of a gas sensor is directly dependent on the surface roughness and the surface-to-volume ratio of the sensitive materials.

Thus, we see that the surface morphology of thin films is an important area of research to understand the properties and behavior of these materials. They have their own unique and inimitable structure that affects sensory sensitivity.

4. Sensory sensitivity

Below are experimental studies of various thin-film structures when exposed to water vapor, ammonia and carbon monoxide molecules. As a rule, changes in electrical conductivity were recorded, and in some cases, the magnitude of the electric current passing through the thin-film structure when the concentration of ammonia vapor, carbon monoxide and relative air humidity changed.

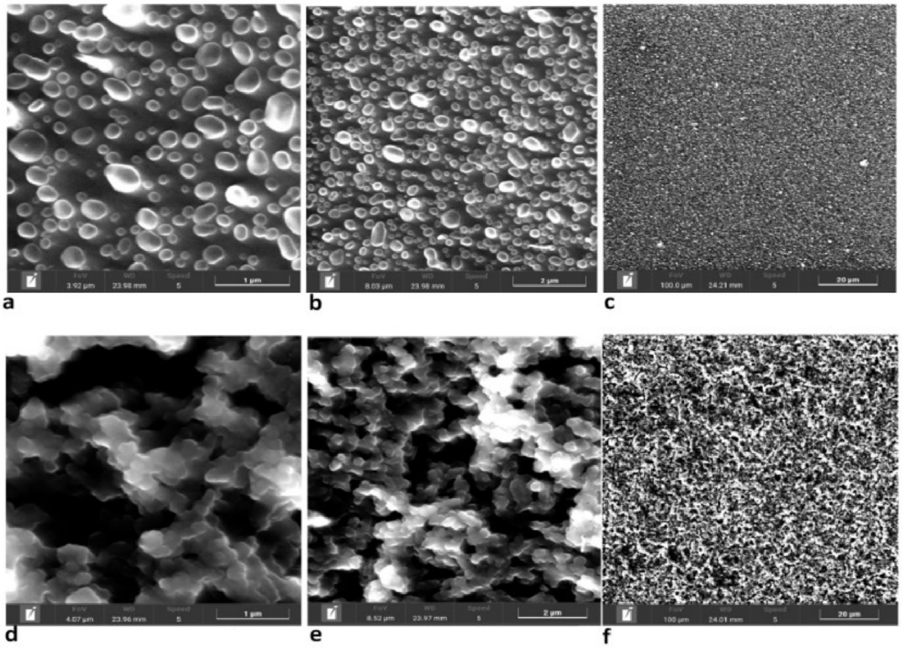


Fig. 4. SEM images of microstructures of film samples. Size of the scanning area of sample P1 (film thickness 500 nm): a — 4 µm, b — 8 µm, c — 100 µm; sample P2 (film thickness 400 nm): d — 4 µm, e — 8 µm, f — 100 µm [39].

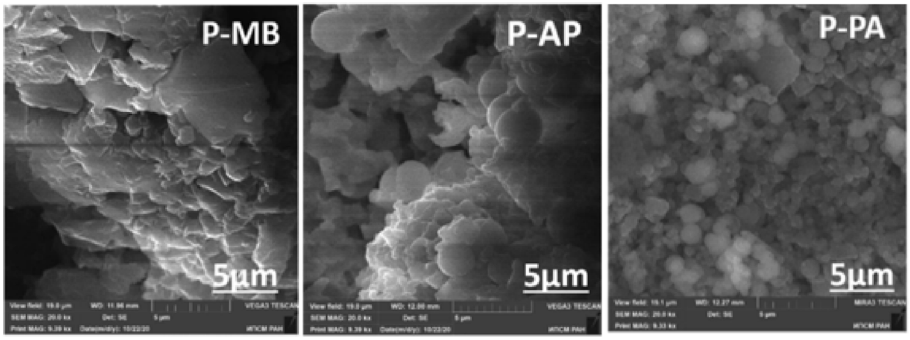
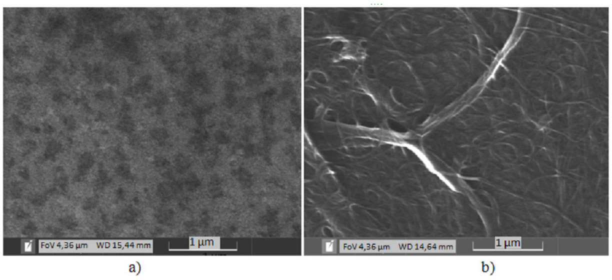


Fig. 5. SEM images of the polymers [40].

Fig. 9a shows the dependence of electrical conductivity σ on humidity for resistive sensors based on thin films of PANI derivatives. Fig. 9b shows graphs of current versus humidity for resistive sensors based on thin films of PANI derivatives. The conductivity of the samples increases (i.e., the resistivity decreases) with increasing humidity of the surrounding atmosphere.



a) b)

Fig. 6. SEM images of microstructures of film samples a) pure PEC b) PEC-SWCNT-3 [41].

Recent investigations into polymers utilized in humidity sensors employing thin-film resistive structures have highlighted the controllable sensitivity of PANI derivatives through judicious dopant selection.

Comparatively, resistive sensors incorporating C60 exhibit a more pronounced current increase in response to humidity variations when contrasted with PANI. Nevertheless, C60 films do not exhibit responsiveness to the presence of NH3 vapor within the ambient environment. Noteworthy advantages of NH3 absorption sensors crafted from polyaniline films include minimal hysteresis.

Polymer films were synthesized via centrifugation from polymer solutions in DMF. This study scrutinized

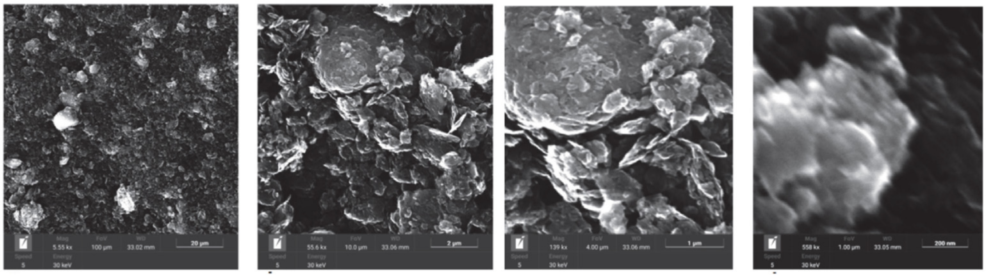


Fig. 7. SEM images of microstructures of film samples. Sample scanning area size (film thickness 700 nm) [42].

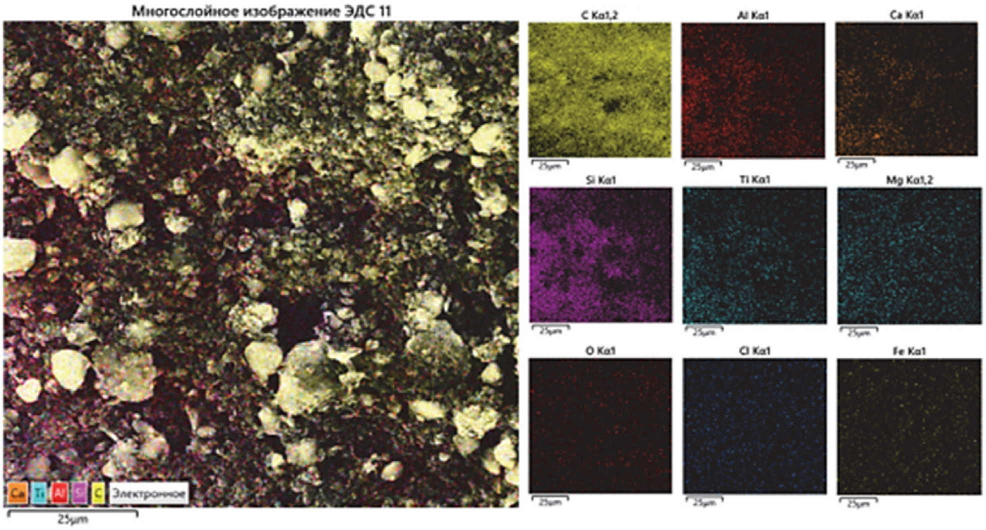
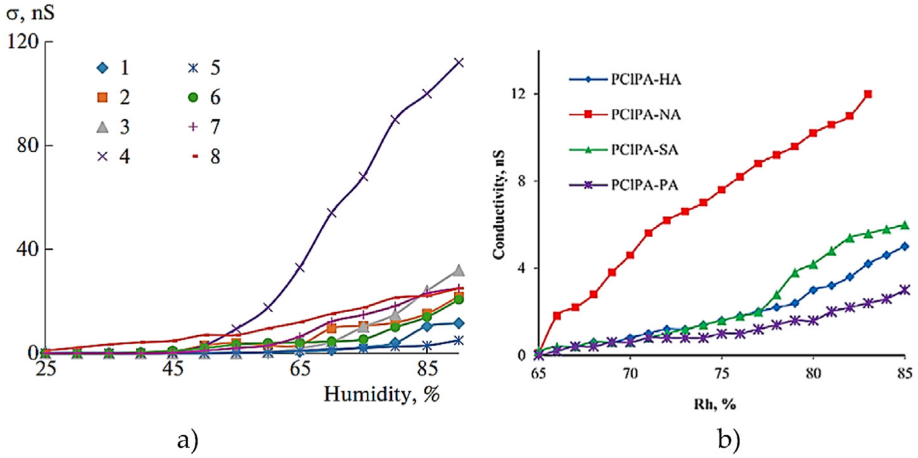


Fig. 8. Total chemical spectral composition of a polymer film with carbon nanotubes and graphene oxide [43].



a) b)

Fig. 9. (a) Electrical conductivity of film samples 1—8 depending on relative humidity [34] and (b) dependence of electrical conductivity of films on relative humidity [36].

the correlation between the current passing through resistive structures formed by thin films of PANI and its derivatives and relative air humidity. Additionally, the response time of these structures was estimated (refer to Fig. 10).

Consequently, the synthesized derivatives discussed in Ref. [49] exhibit potential utility as active components in rapid-response humidity sensors, wherein resistance modulation can be achieved through appropriate dopant selection.

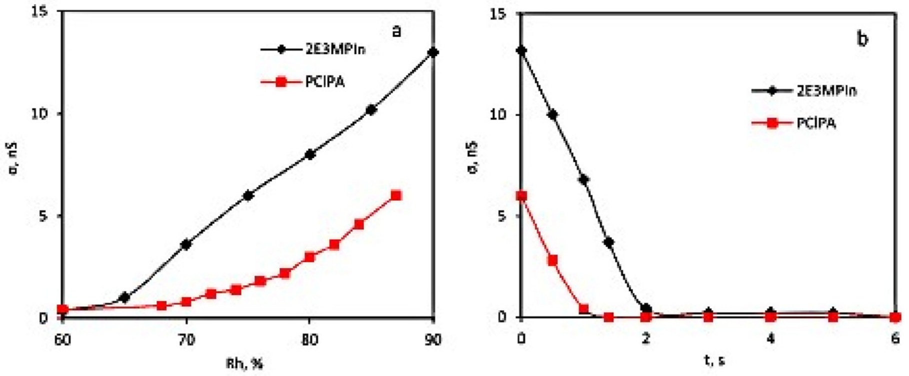


Fig. 10. (a) Dependence of the electrical conductivity of polymer films on relative air humidity; (b) relaxation time was measured at room temperature and normal atmospheric pressure [35].

A notable enhancement in solubility was observed across the presented series of polymers P(Ani-co-ClpA) 1—P(Ani-co-ClpA)5 by blending solutions of ClPA and Ani in 1 mol L—1 HCl, with varied Ani:ClPA ratios of 5:1, 3:1, 1:1, 1:3, and 1:5. This facilitated the fabrication of homogeneous thin films, which were then utilized as an active layer in resistive gas sensors. Discrepancies in the data stem from errors in the reference ammonia sensor and heightened atmospheric humidity due to the utilization of a 10% aqueous ammonia solution (see Fig. 11). Subsequently, the electrical conductivity of PANI derivatives reached a saturation point and remained constant thereafter. A subsequent reduction in ammonia concentration in the medium corresponded to an increase in sample electrical conductivity. However, this effect was transient, with a subsequent decline in electrical conductivity attributed to PANI film degradation. On average, PANI films retained their electrically conductive properties for a duration of 24 hours, beyond which the conductivity diminished.

This research also investigated the relationship between the electrical conductivity of polymers and relative air humidity (refer to Fig. 12a). Previously, an extensive examination was conducted to analyze the impact of diverse structural factors on the sensory attributes of numerous PANI derivatives. It is established that incorporating substituents into the PANI polymer chain induces alterations in sample morphology, electrical conductivity, and solubility, consequently influencing material sensitivity [50,51].

The electrical conductivity of these compounds depends on the structure and nature of the substituents. In general, ortho-substituted PANI derivatives have low electrical conductivity because their molecular structure does not facilitate the free movement of electrons. However, some substituents can increase electrical conductivity, especially if they contain electron-donating or electron-withdrawing groups. Fig. 12b shows the response of polymers with different chemical structures to changes in air humidity.

The significant solubility of the resulting polymers made it possible to form thin films and use them as an active layer in resistive gas sensors.

In accordance with the current value, the electrical conductivity values were calculated, which are indicated on the graphs (Fig. 13 a, b). It can be seen that films of copolymer 2 have the highest electrical conductivity at maximum relative humidity values of 90%. Films 3 and 4 have more than 2 times lower

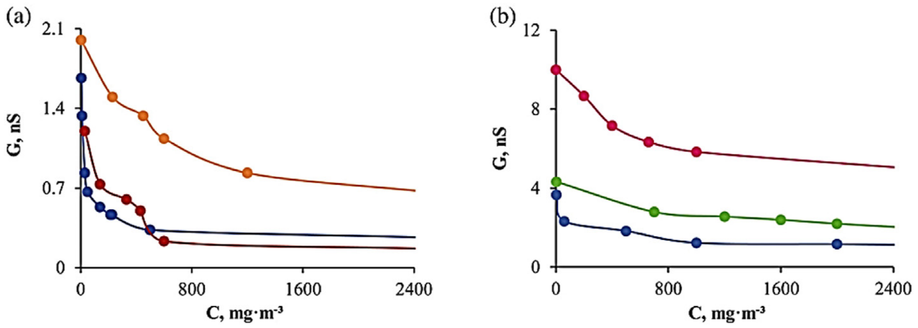


Fig. 11. Plot of conductivity versus NH3 concentration for P(Ani-co-ClPA)1 (a) and P(Ani-co-ClPA)2 (b) [49].

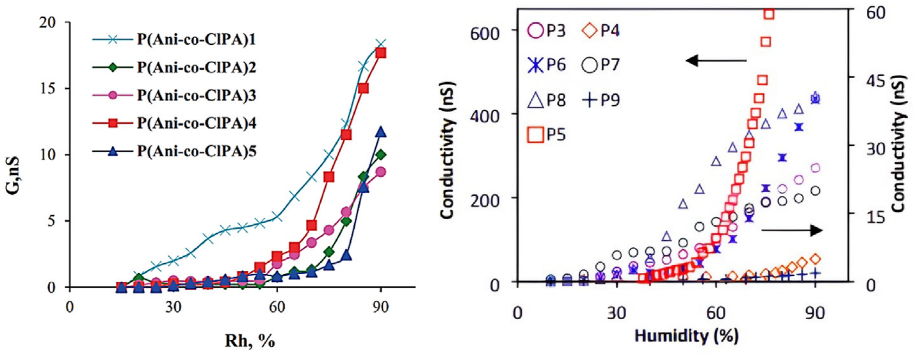
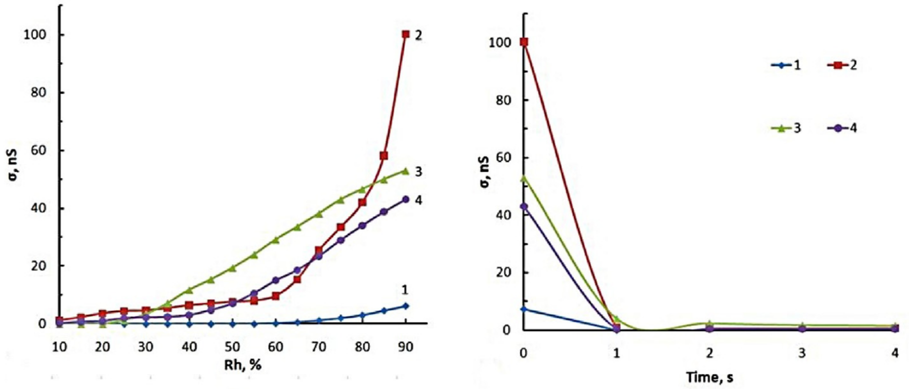


Fig. 12. (a) Plot of conductivity versus humidity for the PANI films and (b) Dependence of electrical conductivity on relative air humidity for resistive sensors based on samples P3 — P9 (at U = 5 V) [50].



a

b

Fig. 13. (Color online) Dependences of the conductivity of films of PANI derivatives on humidity (a); recovery time of samples 1—4 (b) [37].

conductivity. Unmodified PANI samples exhibit the lowest electrical conductivity. It should be noted that resistive sensors on thin films 3 have the most uniform and nearly linear characteristics in the humidity range of 20—90%. The slightly higher conductivity of the film of sample 3 compared to sample 4 can apparently be explained by the difference in the polar properties of the substituents presented in the ortho position and associated with a larger dipole moment of compound 3 than 4.

The impact of relative air humidity on the electrical conductivity of PANI derivatives was investigated. As depicted in Fig. 14a, an increase in ambient humidity correlates with a rise in electrical conductivity. Notably, sample C4, synthesized utilizing (NH4)2S2O8 as an oxidizing agent in an aqueous solution of hydrochloric acid, exhibited the most substantial enhancement in electrical conductivity. Conversely, polymers C2, C3, and C8 displayed minimal alterations in electrical conductivity within each compound series. Noteworthy linearization was observed in the results obtained for sample C7. Subsequently, a series of experiments were conducted with this polymer to assess result reproducibility through ten consecutive environmental humidity sensitivity tests, as illustrated in Fig. 14b.

In addition, samples C1—C8 were investigated as sensing materials in an ammonia sensor (Fig. 14 c). Ammonia vapor was found to affect the conductivity of samples C2, C3, C7 and C8. The time until the previous value of electrical conductivity was restored was about 1—2 s. However, samples C1, C4, C5 and C6 showed no noticeable change in electrical conductivity.

Based on the measurement results, dependences of the current flowing through the PANI films on humidity were plotted (Fig. 15 a), where section 1 is the data taken with increasing humidity in the bench chamber, and section 2 is the data with decreasing humidity. When a material is exposed to moisture, water molecules begin to adsorb on its surface. This leads to a change in the properties of the material, including its electrical characteristics. Adsorption of water molecules can lead to an increase in the electrical conductivity of the material. This happens because some water molecules break up into charged particles - hydrogen ions (H+) and hydroxyl groups (OH-). Hydrogen ions can move within the material, creating an electrical

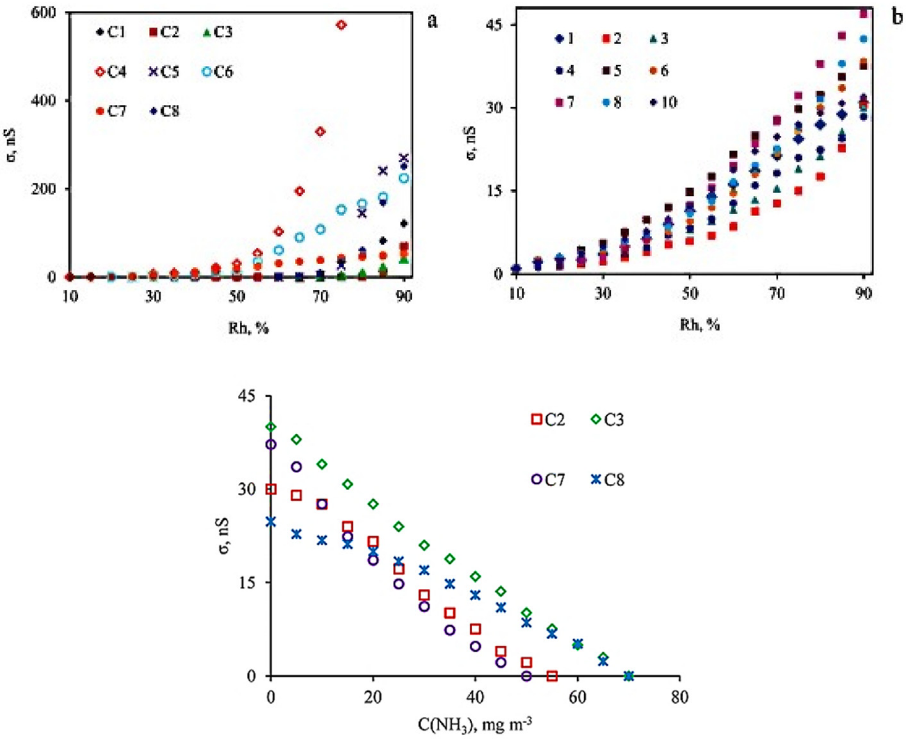
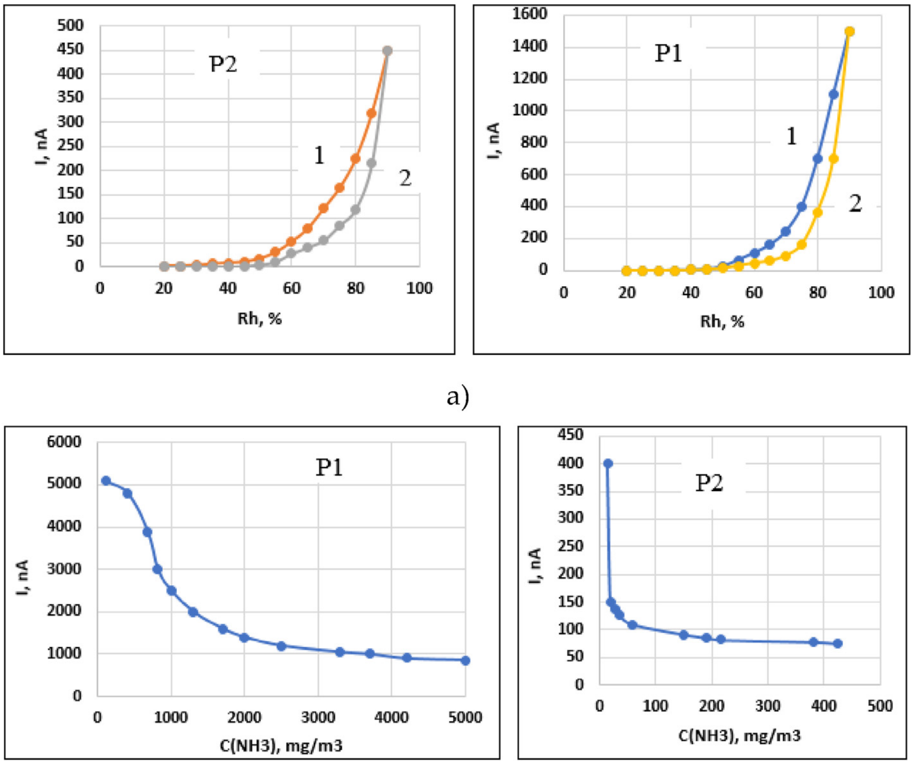


Fig. 14. Dependence of electrical conductivity on the relative humidity of air for resistive sensors based on samples: (a) C1—C8 (at U = 5 V), (b) reproducibility of C7 and (c) C8 on the concentration of ammonia in the environment [38].



a)

b)

Fig. 15. Dependence of the current flowing through the films P2 and P1 (a) on the relative humidity of the air in the air volume and (b) on the concentration of ammonia vapor [39].

current. We see the correlation between the structure of the substance and the values of currents through the films of sensor samples. P2 begins to respond to humidity already at 30% due to its porous structure. The increase in current for samples with P1 begins only at 50%; it is characterized by a sharp increase in current, with the maximum value being 3 times higher than the corresponding value for samples with P2.

Thin films composed of polyaniline derivatives exhibit a response to the presence of ammonia vapor in the surrounding environment, manifested as a reduction in the current flow (refer to Fig. 15b). The observed outcomes are elucidated by the protonation/deprotonation dynamics within the polymer chain. An escalation in the ammonia concentration in the medium induces a decline in the degree of doping. It is postulated that as the polymer interacts with NH3, ammonia molecules sequester protons from PANI, leading to the formation of energetically favorable ammonium (NH4+). Consequently, PANI undergoes deprotonation, resulting in diminished conductivity.

Gas sensors represent one of the promising domains for the utilization of PANI-based polymers [52]. Accordingly, the synthesized polymers were employed as sensitive materials in resistive sensors, with results depicted in Fig. 16 (a,b).

Among materials employed for humidity sensors, electrically conductive polymers emerge as the most promising candidates. This study marks the first instance wherein experimental data encompassing a diverse array of novel substituted polyaniline derivatives (PANI) as sensing materials in sensors is presented. The utilization of PANI derivatives as sensing materials in resistive sensors yielded notable sensitivity of electrical conductivity to humidity variations across a broad spectrum ranging from 20% to 90%.

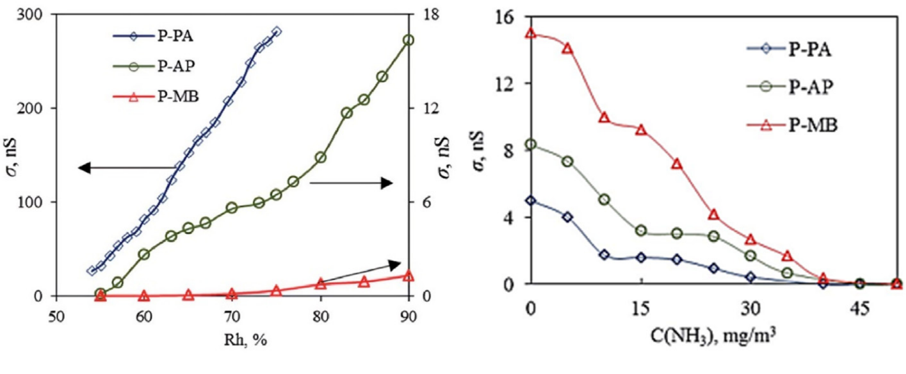
The sensor sensitivity of the PEC-SWCNT-3 film to ammonia vapor in the air was also tested (Fig. 17a).

Films of PEC derivatives with SWCNTs respond to the presence of ammonia vapor in the environment by decreasing the flowing current. The current decreases from a value of 260 μA to almost 140 μA when the concentration of ammonia vapor changes from 0 to 1000 mg/m1. The maximum permissible concentration for ammonia is 20 mg/m1. The pattern is nonlinear: up to concentrations of 200 mg/m3, the current decreases quite quickly, then the rate of decrease in the current decreases sharply. Based on the proposed PEC-SWCNT nanocomposite, an air humidity sensor has been developed. Fig. 17 b shows graphs of the dependence of the current flowing through PEC films with SWCNT on the relative humidity of the air in the air volume. The range of humidity changes varied from 20% to 80% under a hood in the working chamber. The current values through the resistive sensor as air humidity increases are shown in the figures above and vary in the range from 450 to 1250 μA. The dependence is not linear; the rate of decrease in the current value is approximately the same over the entire measurement range.

Based on the polymer with the additions of CNTs and graphene oxide, samples of resistive thin-film structures were prepared, the current-voltage characteristics and the dependence of the current passing through the sample (voltage at the contacts 5 V) were measured with a change in the concentration of carbon monoxide, presented in Fig. 18.

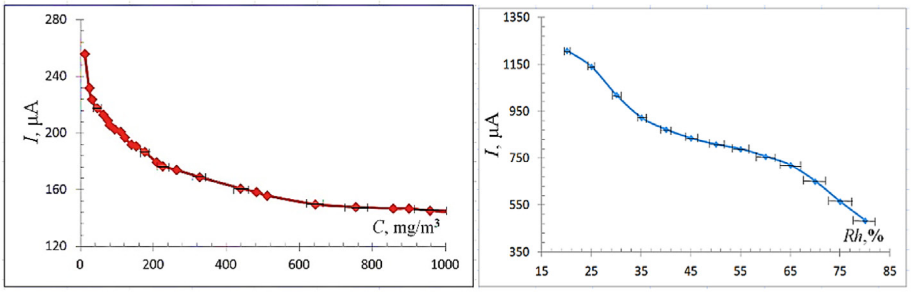
Thus, a thin-film sensor with a sensitive layer of polymer with CNT and graphene oxide additives for determining the concentration of carbon monoxide has been demonstrated [53—58].

The deployment of numerous devices within self-organizing networks has paved the way for the emergence of a novel technology known as wireless sensor networks. In this paper, we will examine an instance of such a network utilizing the Bluetooth Low Energy (BLE) wireless data transfer protocol, which has



a) b)

Fig. 16. Plots of the conductivity of P-PA, P-AP and P-MB films on the air humidity (a) and on the concentration of ammonia vapor (b) [40].



a) b)

Fig. 17. The dependence of the current on the concentration of ammonia vapor in the air (a) and air humidity (b) films PEC-SWCNT-3 [41].

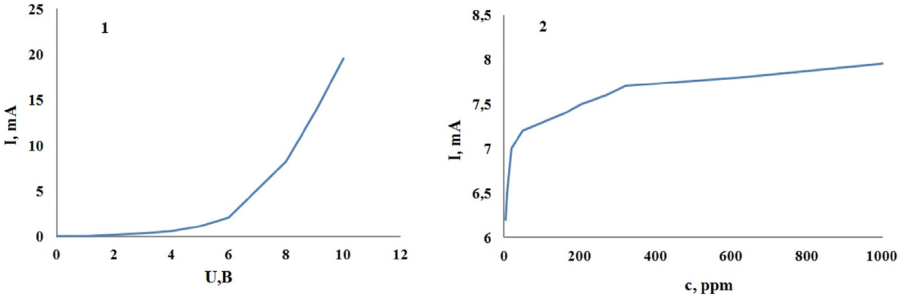


Fig. 18. Current-voltage characteristic of graphene oxide (1), dependence of the current flowing through the films on the concentration of carbon monoxide (2), at Uar = 5V and at room temperature [39].

significantly propelled the advancement of wireless sensors. When combined with organic polymers employed as a sensor layer, this approach enables the attainment of high energy efficiency and selective sensitivity in monitoring [59].

Particular interest should be paid to Bluetooth Mesh works as a connectionless flooding mechanism, where each device broadcasts both its own data and data belonging to other devices. A schematic diagram of a Bluetooth Mesh network is shown in Fig. 19.

There are several accident detection methods in which sensor data is sent to a base station or command post via wireless sensor networks. But this method is not the main one in this study. The focus is on using Bluetooth Mesh technology to create an energy-efficient data transmission system to a mobile receiver. This system can be used in leak detection scenarios or other situations where a mobile device needs to collect information from sensors [60—63].

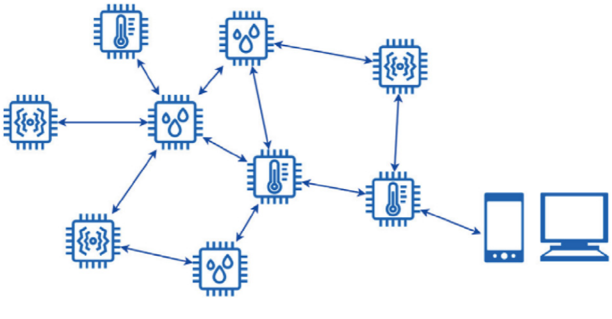


Fig. 19. Diagram of the Bluetooth Mesh network, many sensors (nodes) transmit information to the server device by relaying data [42].

5. Conclusion

Polymer thin film sensors are devices that are used to detect and measure various substances in the environment. They are based on the use of polymer materials that have unique properties that allow them to react to certain substances. Polymers are large molecules made up of repeating structural units called monomers. They can be manufactured with a variety of properties including electrical, mechanical and chemical. This makes them ideal for use in sensors. Thin film sensors are devices in which the sensor material is deposited on a thin film. This allows sensors to be made smaller and lighter, making them ideal for use in a variety of applications, including portable devices and wearable technology. Polymer thin film sensors can be used to detect a variety of substances, including gases, liquids and solids. They can be used to detect toxic substances, explosives, biological agents and more. Polymer thin film sensors can be used in various fields, including medicine, safety, ecology and industry. The sensors can be used to detect harmful gases and can be used to create a wireless environmental monitoring system. Elderly people are susceptible to high blood pressure, increased heart rate and increased temperature, so the development of chitosan-based sensors with the addition of carbon nanotubes, graphene oxide and metal nanoparticles for monitoring human condition in real time is a very promising task. In ecology, they can be used to detect pollutants in air, water or soil. This can help in monitoring environmental quality and preventing pollution. In industry, they can be used to monitor product quality or detect defects during production. This can help improve product quality and reduce production costs. Overall, polymer thin film sensors are a promising technology that can be used in various fields to detect and measure various substances in the environment.

Conflict of interest statement

The authors declare that they have no conflict of interest.

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