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Optical and electrochemical properties of a composite material based on PEDOT:PSS and oriented nickel fibers

G.R. Nizameeva [1, 2] ✉, E.M. Lebedeva [1], I.R. Nizameev [1, 3]

[1] Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia;
[2] Kazan National Research Technological University, Kazan, Russia;
[3] Kazan National Research Technical University named after A.N. Tupolev-KAI, Kazan, Russia
✉ guliya.riv@gmail.com

Abstract. The paper presents the results of electrochemical and conductometric studies of poly (3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) and composite material PEDOT:PSS/oriented nickel fibers in the presence of carbon dioxide. It has been shown that the introduction of oriented nickel fibers into the PEDOT:PSS polymer matrix improves the electrochemical properties of the polymer. The nickel fibers in the polymer bulk act as a catalyst and thus shift the PEDOT:PSS reduction peak towards positive potentials. Gas sensing elements for a conductometric sensor were fabricated by depositing PEDOT:PSS and composite films PEDOT:PSS/oriented nickel fibers on the surface of a glass substrate with interdigitated gold electrodes., Special equipment was designed to study the sensory properties of gas-sensitive elements. Using this equipment, we measured the sensory response R_r and the response time $\tau_{0.9}$ of finished gas-sensitive elements in a carbon dioxide environment. Conductometric studies have shown that the response time $\tau_{0.9}$ of the composite material to CO_2 is shorter, and the sensory response R_r is twice as long as compared to a pure PEDOT:PSS film. As a result of the generalization of the experimental data, the possibility of using the composite material PEDOT-PSS/oriented nickel fibers to create electrochemical and conductometric sensors for carbon dioxide was shown.

Keywords: gas sensor, PEDOT:PSS, electrochemical cell, band gap, sensor response, response time

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Оптические и электрохимические свойства композитного материала на основе PEDOT:PSS и ориентированных волокон никеля

Г.Р. Низамеева [1, 2] ✉, Э.М. Лебедева [1, 2], И.Р. Низамеев [1, 3]

[1] ИОФХ им. А.Е. Арбузова, ФИЦ КазНЦ РАН, г. Казань, Россия;
[2] Казанский национальный исследовательский технологический университет, г. Казань, Россия;
[3] Казанский национальный исследовательский технический университет им. А.Н. Туполева, г. Казань, Россия
✉ guliya.riv@gmail.com

Аннотация. В работе приведены результаты электрохимических и кондуктометрических исследований поли(3,4-этилендиокситиофен):полистиролсульфоната (PEDOT:PSS) и композитного материала PEDOT:PSS/ориентированные волокна никеля в среде диоксида углерода. Показано, что введение ориентированных волокон никеля в полимерную матрицу PEDOT:PSS улучшает электрохимические свойства полимера. Волокна никеля в объеме полимера действуют как катализатор и, тем самым, смещают пик восстановления PEDOT:PSS в сторону положительных потенциалов. Путем нанесения PEDOT:PSS и композитных пленок PEDOT:PSS/ориентированные волокна никеля на поверхность стеклянной подложки со встречно-штыревыми золотыми электродами были изготовлены газочувствительные элементы для кондуктометрического сенсора. Для исследования сенсорных свойств газочувствительных элементов сконструирована специальная установка. С помощью данной установки были измерены сенсорный отклик R_r и время отклика $\tau_{0.9}$ готовых газочувствительных элементов в среде диоксида углерода. Кондуктометрические исследования показали, что время отклика $\tau_{0.9}$ композитного материала на CO_2 меньше, а сенсорный отклик R_r в 2 раза больше, по сравнению с чистой пленкой PEDOT:PSS. В результате обобщения экспериментальных данных была показана возможность использования композитного материала PEDOT:PSS/ориентированные волокна никеля для создания электрохимических и кондуктометрических сенсоров на диоксид углерода.

Ключевые слова: газовый сенсор, PEDOT:PSS, электрохимическая ячейка, ширина запрещенной зоны, сенсорный отклик, время отклика

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Introduction

Studies of composite materials based on a polymer matrix and various functional materials dispersed in this matrix [1], such as metal oxide nanoparticles, graphene, carbon nanotubes, etc., have been widely developed in recent years. The increased interest in such materials is associated with the possibility of their application in supercapacitors [2], in catalysis, and also as an active element in greenhouse gas sensors (such as carbon dioxide, nitrogen dioxide, and carbon dioxide) [3].

Currently, scientific research is focused on monitoring the environment, in connection with climate change as a result of an increase in the greenhouse effect of the atmosphere [4]. The release of carbon dioxide (CO_2) into the atmosphere is the main cause of global warming and sea level rise [5]. A significant proportion of CO_2 emissions are related to human activities such as the burning of fossil fuels for transport and energy production. Developing efficient methods for measuring and detecting CO_2 is critical to mitigating the negative impacts of climate change. Over the past few years, the use of conductive polymers as gas-sensitive sensors due to their unique properties has attracted considerable attention. One promising among such polymers is poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS). This is due to its excellent thermal and air stability, high conductivity, flexibility, and optical transparency, as well as a well-developed and relatively simple synthesis technology that allows printing and production on a large scale [6,7]. PEDOT:PSS has been widely researched and used due to its versatility in various applications such as electronics, energy storage (supercapacitors, batteries), and sensors to detect changes in pH, humidity, hazardous gases [8].

However, the use of the PEDOT:PSS as a sensor has limitations. The pure PEDOT:PSS film has low greenhouse gas sensitivity. In addition, the material has been reported to be sensitive to humidity and other environmental factors, which can affect its accuracy. Recently, research has been actively carried out to improve the gas-sensitive characteristics of the PEDOT:PSS to CO_2 by dispersing various functional materials (polymer-carbon composites, graphene, metal or semiconductor nanoparticles, etc.) into the PEDOT:PSS polymer matrix, that is, creating a composite material. For example, in [9], the authors synthesized a CO_2 sensor based on PEDOT:PSS and graphene on a PET substrate. It is assumed that the graphene layer can act as a protection against moisture. Chuang et al. [10] developed a material with high moisture selectivity using PEDOT:PSS and polyaniline (PANI). The combination of these polymers improved the conductivity and sensitivity of the material to CO_2.

In this paper, to increase the detection of carbon dioxide CO_2, it is proposed to create a composite material based on PEDOT:PSS with oriented nickel (Ni) fibers dispersed in its polymer matrix [11–13]. Ni is a metal with high conductivity and high surface area and can act as a catalyst capable of increasing the sensitivity and selectivity of PEDOT:PSS.

Materials and Methods

Cyclic voltammetry (CV) was used to study the electrochemical properties of PEDOT:PSS and the composite material PEDOT:PSS/oriented nickel fibers in the presence of carbon dioxide. Electrochemical studies were carried out in a glass three-electrode cell in an environment of the study gas. A fluoroplastic cylindrical tube with 3 mm glassy carbon was used as the working electrode. A platinum electrode was used as a counter electrode, and a silver chloride electrode (Ag/AgCl) was used as a reference electrode. A solution of 0.1 M $KHCO_3$ in water was used as an electrolyte. The potential sweep rate when taking cyclic voltammograms was 50 mV/s. To obtain stable cyclic voltammograms, the potential sweep was cycled three times.

For carried out of the electrochemical studies, a thin layer of PEDOT:PSS was applied to the surface of the working electrode and dried at a temperature of 60 °C for 1.5 hours. Composite films PEDOT:PSS/oriented nickel fibers were obtained by depositing submicron nickel fibers on the electrode surface in the presence of a magnetic field, followed by depositing a thin layer of PEDOT:PSS on the surface of the oriented fibers. The resulting composite material was also dried at a temperature of 60 °C for 1.5 hours.

To create a gas-sensitive element of the conductometric gas sensor based on PEDOT:PSS and PEDOT:PSS/oriented nickel fibers, glass substrates were preliminarily prepared. As is known, conductometric sensors operate based on a change in the electrical conductivity of the gas-sensitive element before and after the adsorption of the detectable component. Interdigital electrodes were obtained to measure the resistance of the gas-sensitive element before and after exposure to the test gas on the surface of glass substrates by sputtering gold onto a photoresist template. Next, a PEDOT:PSS film was deposited on the surface of the substrates with gold electrodes by centrifugation. To obtain a composite material, freshly prepared nickel fibers were deposited on the surface of finished substrates in the presence of a magnetic field. The magnetic field was used to create an oriented network of fibers on the surface of the substrates. Next, a thin film of PEDOT:PSS was applied to the finished mesh.

The sensory properties of the finished samples were studied on specially designed equipment, consisting of a sealed capsule, a detector with an embedded gas-sensitive element, a target gas cylinder, a pressure-reducing valve, a personal computer, and a potentiostat for controlling a given voltage and measuring current. The tests were carried out at room temperature and relative air humidity of 45%. Carbon dioxide was used as the target gas.

Results and Discussion

Electrochemical studies of the working electrode modified with a pure PEDOT:PSS film in 0.1 M aqueous $KHCO_3$ solution were carried out in the cycling range from -1.5 V to 1.5 V. Figure 1 shows the results obtained.

As can be seen from the CV curves for the PEDOT:PSS films, a typical quasi-rectangular pseudocapacitive response is observed, which was previously observed in [14]. As can be seen from the CV curves during repeated cycling in the potential range of $-1.5 \div 1.4$ V, a stable behavior of PEDOT:PSS films is observed. With a further increase in the cycling limit, the electrical properties of the film begin to deteriorate, and at a potential of -1.5 V, a sharp decrease in the anode current is observed, which is associated with degradation and irreversible oxidation of a pure PEDOT:PSS film. In the region of negative potentials, PEDOT:PSS behaves stably.

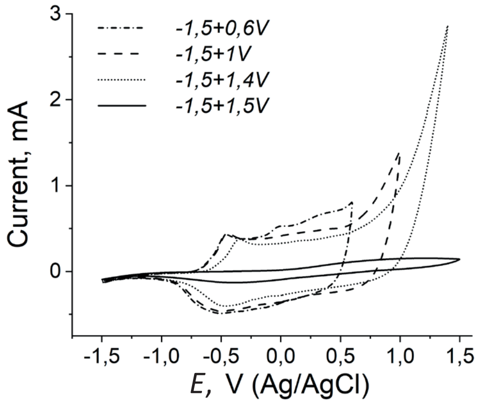

Fig. 1. CV-curves of the PEDOT:PSS in the cycling range from -1.5V to 1.5V

Considering this fact, in the future, all electrochemical studies were carried out in the range from -1.5 V to 1 V.

Next, electrochemical studies of PEDOT:PSS films were carried out in carbon dioxide. Figure 2, *a* shows the results obtained in comparison with the results obtained in an inert gas environment – argon. In the CO_2 environment, a pronounced reduction peak appears on the PEDOT:PSS CV curve at a potential of -1 V, which is absent in the argon environment. The presence of this peak indicates that the PEDOT:PSS film has an electrochemical response to carbon dioxide.

Similar electrochemical studies in the presence of carbon dioxide were carried out for composite films PEDOT:PSS/oriented nickel fibers. According to the results obtained (Fig. 2, *b*), the reduction peak for the composite material, compared to a pure PEDOT:PSS film, shifts towards positive potentials and appears at -0.75V. The shift in the reduction peak can be explained by the fact that nickel fibers, which have high conductivity and large surface area, act as a catalyst in the bulk of the polymer and reduce the electron transfer energy. The appearance of a reduction peak for PEDOT:PSS and composite film PEDOT:PSS/oriented nickel fibers indicates the potential for their application as an electrochemical CO_2 sensor.

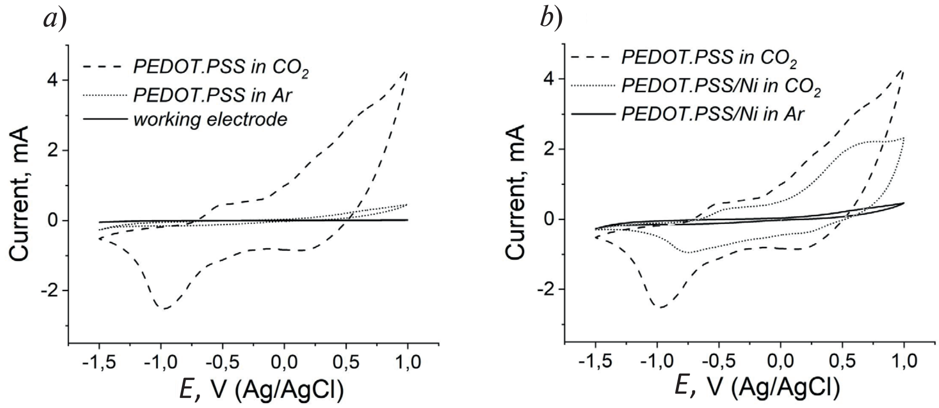

Fig. 2. CV-curves of the PEDOT-PSS film (*a*) and composite material (*b*) in carbon dioxide and argon environment

Further, gas-sensitive elements for a conductometric sensor based on PEDOT:PSS and composite film PEDOT:PSS/oriented nickel fibers were fabricated. The sensory properties of the finished gas-sensitive elements were studied on specially designed equipment at room temperature. The sensor response was calculated by the formula: $R_r = (R_{gas} - R_0)/R_0$, where R_{gas} is the sensor resistance in the presence of the test gas, R_0 is the sensor resistance before exposure to the test gas. In addition to the sensor response, the concept of response time $\tau_{0.9}$ is used in practice as a parameter characterizing the speed of the gas-sensitive elements. This is the time during which the sensor response reaches a value equal to 0.9 of the maximum possible value $(R_{gas} - R_0)/R_0$. The calculated values of R_r and $\tau_{0.9}$ are shown in Table.

Table

Sensor properties of gas sensitive elements

	Types of gas-sensitive element	
	PEDOT:PSS film	PEDOT:PSS / Oriented nickel fibers composite film
R_r	0.28	0.57
$\tau_{0.9}$	1192 min	1038 min

According to the results obtained, both PEDOT:PSS and the composite film have a conductometric response R_r to carbon dioxide, which manifests itself in a decrease in resistance. However, as expected, the sensor response R_r of the composite material is larger and equals 0.57, which is 2 times higher than that of the PEDOT:PSS film. Such a good response of the composite material can be explained by the fact that the introduction of nickel fibers into the PEDOT:PSS polymer matrix improves the conductivity and, accordingly, the sensitivity to the target gas. The results obtained demonstrate the possibility of using the composite films PEDOT:PSS/oriented nickel fibers in a conductometric CO_2 sensor.

It is known that PEDOT:PSS is a transparent conductive polymer with a wide bandgap. The band gap of the PEDOT:PSS film was calculated from the CV curves. It turned out to be equal to 1.56 eV, which is in good agreement with the literature data. For the composite film PEDOT:PSS/oriented nickel fibers, the band gap remained unchanged. This suggests that this material can be used not only as a conductometric sensor but also as an optical sensor for the express analysis of greenhouse gases.

Conclusion

The composite material was obtained by introducing oriented nickel fibers into the PEDOT:PSS polymer matrix. Electrochemical studies of the PEDOT:PSS film showed that at potentials above 1.4 V the polymer is overoxidized, which leads to degradation and loss of its functional properties. It has been established that the introduction of oriented nickel fibers into the PEDOT:PSS polymer matrix shifts the polymer reduction peak from -1 V to -0.75 V, i.e. reduces the electron transfer energy in the electrochemical reaction. The CV curves of PEDOT:PSS and PEDOT:PSS/oriented nickel fibers recorded in carbon dioxide showed that the films have an electrochemical response to CO_2. Conductometric studies carried out in specially designed equipment showed that the sensor response R_r of the composite material is 2 times greater than that of pure PEDOT:PSS films and is equal to 0.57. The band gap for PEDOT:PSS and PEDOT:PSS/oriented nickel fibers was calculated from the CV curves, the value of which for both materials is 1.56 eV. Summarizing the obtained data, we can conclude that a composite material based on PEDOT:PSS and oriented nickel fibers can be used as an active element in conductometric CO_2 gas sensors, as well as in optical sensors for express analysis.

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THE AUTHORS

NIZAMEEVA Guliya R.
guliya.riv@gmail.com
ORCID: 0000-0002-4991-0502

NIZAMEEV Irek R.
irek.rash@gmail.com
ORCID: 0000-0002-5420-6181

LEBEDEVA Elgina M.
elgina.lebed@mail.ru
ORCID: 0000-0003-0095-5205

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