Анотація

Рідкокристалічні речовини, леговані вуглецевими нанотрубками, як чутливе середовище датчика CO2

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https://doi.org/10.1080/15421406.2023.2236374

Анотація

Актуальною проблемою є створення високочутливих оптичних датчиків CO_2 в повітрі, які дозволяють контролювати вміст CO_2 як у приміщенні, так і в навколишньому повітрі, де його рівень зазвичай становить 600…1000 ppm. Як чутливий елемент сенсора CO_2 пропонується використовувати рідкокристалічну речовину (холестерично-нематичну суміш на основі 5ЦБ з холестеричними домішками), доповнену багатошаровими вуглецевими нанотрубками. Досліджено спектральні характеристики рідкокристалічної суміші в діапазоні 400…600 нм. Вміст вуглецевих нанотрубок становив від 0,1 до 0,5 мас.%. Встановлено, що зі збільшенням концентрації в діапазоні 10…100 мг/м^3 мінімум пропускання зміщується в довгохвильову область спектра. Максимальна спектральна чутливість у цьому діапазоні становить 6 нм ⁄ мг ⁄ м3. Досліджуваний матеріал може бути використаний як чутливий елемент оптичного датчика CO_2 . Подальші дослідження слід проводити в напрямку дослідження взаємодії такого композиту з іншими газами, а також пошуку можливостей для покращення властивостей композиту. Можливо використання багатошарових вуглецевих нанотрубок.

Ключові слова:

- БЛО-61
- вуглецеві нанотрубки
- 5СВ
- СО
- датчик газу

- оптичний датчик

Liquid crystalline substances doped with carbon nanotubes as a sensitive medium of the CO2 sensor

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Liquid crystalline substances doped with carbon nanotubes as a sensitive medium of the CO2 sensor

The creation of highly sensitive optical CO2 sensors in air is an urgent problem, as it allows monitoring the content of CO2 both indoors and in ambient air, where its level is usually 600...1000 ppm.

As a sensitive element of the CO2 sensor, it is proposed to use a liquid crystal substance (cholesteric-nematic mixture based on 5CB with cholesteric impurities), supplemented with multi-layered carbon nanotubes. The spectral characteristics of the liquid crystal mixture in the range of 400...600 nm were studied. The content of carbon nanotubes ranged from 0.1 to 0.5 wt.%. It was established that with an increase in concentration in the range of 10...100 mg/m3, the transmission minimum shifts to the long-wave region of the spectrum. The maximum spectral sensitivity in this range is 6 nm⁄mg⁄m3. The researched material can be used as a sensitive element of an optical CO2 sensor.

Further research should be conducted in the direction of investigating the interaction of such a composite with other gases, as well as finding opportunities to improve the properties of the composite. Perhaps the use of multi-walled carbon nanotubes.

Keywords: optical sensor, gas sensor, carbon nanotubes, 5CB, BLO-61, CO_2

1. Introduction

To determine the concentration levels of various gases in biotechnology, medicine, ecology, pharmacology, food production, and other industries, the development, development, and wide implementation of modern portable sensors are necessary, as well as the creation and selection of highly sensitive materials for them.

Among such materials, the class of liquid crystals and liquid crystal mixtures can be singled out. Along with their classic use as an active medium in information display devices, more and more research is focused on the possibility of their use as sensitive gas sensors [1-4].

Liquid crystalline mixtures are promising materials for the detection of harmful gases due to the sensitive reaction of the light flux to the change in their molecular order under external influence. Such changes can be easily detected optically since liquid crystals have high optical anisotropy [5]. In recent years, special attention has been paid to composite systems based on liquid crystal mixtures. Such systems have unique electrical and magneto-optical properties. The introduction of nano-sized particles with high gas adsorption into an anisotropic medium is promising. Due to the interaction with gases, nanoparticles change their physical properties, which leads to a change in the optical properties of the liquid crystal substance [6, 7].

Recently, carbon nanotubes have been widely studied as adsorbents of various gases, in particular H2, N2, CO2, SO2, NO2, NH3, and alkanes [8-10]. Significant interest in the use of nanotubes as gas adsorbents is due to their properties, in particular, extremely small size, high specific surface area, hollow structure, and high structural and chemical stability. Numerous studies have shown higher adsorption of gases in carbon nanotubes compared to other sorbents [10]. Therefore, the study of the influence of gases on the change in the optical properties of liquid crystal mixtures doped with carbon nanotubes is a good opportunity to improve the sensitivity of liquid crystal optical gas sensors to inorganic gases, in particular CO2.

Optical sensors are based on optoelectronic devices consisting of a light source, a photoreceptor, and an optically active medium [11, 12]. A change in the optical properties of the medium in the presence of a certain gas in it affects the output signal of the photodetector, which is used to detect gas in the medium. The creation of such devices is relevant because it makes it possible to solve the complex problem of monitoring the atmosphere, control of technological environments, and safety of industrial production using electronic devices.

The concentration of carbon dioxide in the premises can significantly exceed the norms due to insufficient ventilation and the presence of a large number of people. In particular, a constant elevated level of CO2 in the air can cause an increase in blood acidity - acidosis [13]. It arises due to the interaction of carbon dioxide and water with the formation of carboxylic acid. The first signs of acidosis are strong excitement, rapid heart rate, and a moderate increase in blood pressure.

However, today, in addition to the negative factors of influence that have appeared as a result of human progress, we have also received means to temporarily solve such problems. Among them, is the development of accurate and easy-to-use infrared gas sensors, absorbents for carbon dioxide, and other resources, which, if desired, will allow the authorities to make control systems for the level of CO2 in the premises.

2. The structure of a liquid crystal sensor based on a liquid crystal mixture and a CO2 mixture doped with nanotubes

The general concept of the sensor corresponds to other developed optical liquid crystal gas sensors with measurement of the spectral characteristics of the light passing through the sensitive liquid crystal element. Similar sensors are presented in works [14-18]. The main feature of the developed sensor is the sensitive element created on the basis of a liquid crystal mixture and a mixture doped with carbon nanotubes. Liquid crystals are promising materials for detecting dangerous gases due to their high sensitivity to changes in molecular order under external influence.

As the basis of the sensitive element, a mixture of cholesteric liquid crystals of the MERK© company - BLO-61 was chosen, which is characterized by a minimum of selective transmission at a wavelength of 420 nm (Fig. 1) [19]. The choice is due to the main advantage of this liquid crystal mixture, namely, chemical inertness and stability of mesophase existence in the temperature range of 10-70 °C. The chemical composition of this mixture combines nematic liquid crystals with cholesteric liquid crystals.

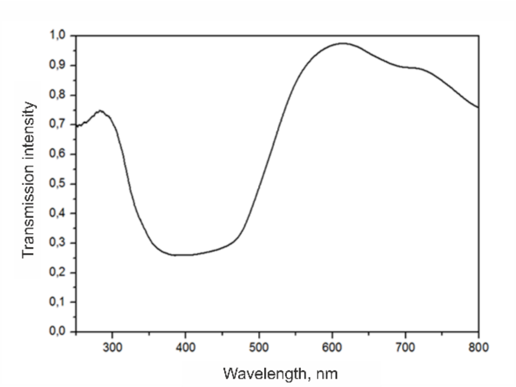

Figure 1 Spectral characteristics of BLO-61 cholesteric liquid crystal

Another component of the mixture is nematic 5CB, which is 4-n-pentyl-4-cyanobiphenyl [20].

Carbon nanotubes (CNTs) have the ability to adsorb and desorb materials of a certain chemical composition, which makes them promising for the development of sensors based on them [21, 22]. The use of carbon nanotubes as an impurity in the mixture of a sensitive liquid crystal element can significantly increase the sensitivity of the sensor due to the adsorption of gases. Due to the large specific surface, carbon nanotubes have unique advantages in terms of detecting environmental pollutants and are widely used in gas chemical sensors, NH3, NO2, SO2, and CO2 [23]. Compared to other sensors, gas sensors based on carbon nanotubes are characterized by fast response, high sensitivity, small size and low operating temperature [24]. That is why a nanocomposite based on CNM doped with single-walled carbon nanotubes was created to study the effect of CO2 on the optical properties of nanocomposites.

3. Nanocomposite for a sensitive sensor element

The creation of a liquid crystal nanocomposite began with the creation of the actual cholesteric-nematic mixture. The concentration of the nematic liquid crystal was selected to obtain the maximum selective reflection in the visible region and varied from 25 to 35%. Experimental mixtures were obtained by heating the components in a thermostat to a temperature that is 5-7 degrees higher than the temperature of the phase transition to the isotropic state. This temperature was maintained for 1 hour with periodic mixing of the samples. Experimental cholesteric-nematic mixtures were obtained in this way.

The obtained mixture was doped with single-walled carbon nanotubes with concentrations of 0.15%, 0.3, and 0.5 wt. %. The maximum concentration of nanotubes is limited by the optical transparency of the studied samples. To obtain a homogeneous suspension, the nanotubes were introduced into a cholesteric-nematic mixture (CNM) in the isotropic phase with subsequent mixing in an ultrasonic bath for 1 hour. Effective mixing of nanotubes in the liquid crystal mixture layer was observed precisely in the isotropic phase of the liquid crystal.

In fig. 2 shows the spectral characteristics of the cholesteric-nematic mixture and nanocomposites based on CNM with a 5CB concentration of 25 wt. % and an admixture of carbon nanotubes 0.15; 0.3 and 0.5 wt.%.

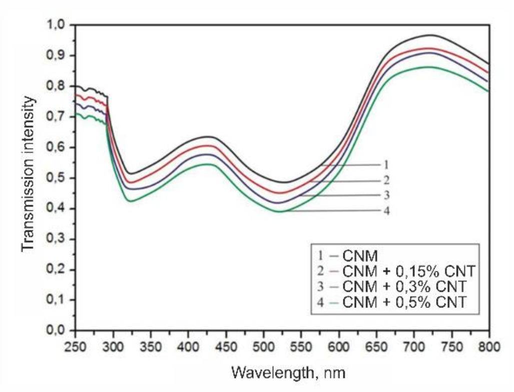

Figure 2 Spectral characteristics of cholesteric-nematic mixture and nanocomposite based on it

4. Experimental part

To study the effect of gases on the nanocomposite, a device for measuring the spectral characteristics of nanocomposites under the action of gases was used, the functional diagram of which is shown in Figure 3. This device makes it possible to obtain spectra in real time in an atmosphere of harmful gases, and also ensures the temperature stability of measurements.

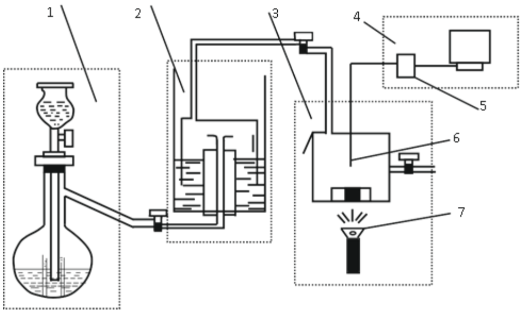

Figure 3 Functional scheme of the experimental setup for studying the influence of harmful gases on the LC-nanoparticle system: 1- reactor; 2- laboratory gas holder; 3- experimental box; 4- spectrum analyzer; 5- spectrometer; 6- optical fiber; 7- light source

The prepared nanocomposites were applied in a thin layer on a transparent cover glass and placed in the experimental setup. Gas is supplied to the installation and artificial circulation of the mixture of gas and air in given concentrations takes place. Carbon dioxide is produced based on the reaction of CaCO3 calcium salt with hydrochloric acid HCl. The measured parameter was the position of the absorption minimum of the samples at room temperature, which changed depending on the gas concentration in the air atmosphere of the chamber.

Adsorption of CO2 by liquid crystal nanotubes is much smaller than, for example, NO2 and SO2. The nature of the change in the wavelength of the absorption minimum under the influence of CO2 for the cholesteric-nematic mixture with single-walled nanotubes is shown in Figure 4.

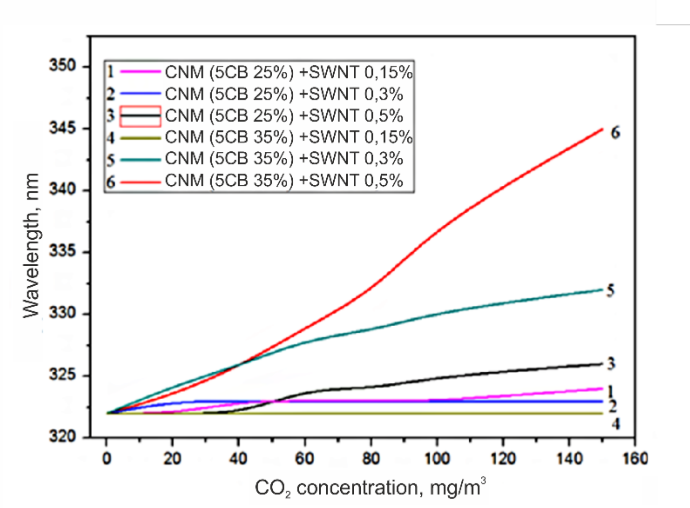

Figure 4 Dependence of the change in the wavelength of the light transmission minimum on the concentration of CO2 for single-walled nanotubes (SWNT)

The coefficient of spectral sensitivity in this range is 1.2 nm/mg/m3. In the range of 60-150 mg/m3 for this nanocomposite, a decrease in sensitivity is observed (the coefficient of spectral sensitivity is 0.152 nm/mg/m3), after which saturation is observed. The graph of the spectral dependence under the influence of CO2 for the nanocomposite based on CHN doped with single-walled nanotubes with different concentrations is shown in Fig. 5.

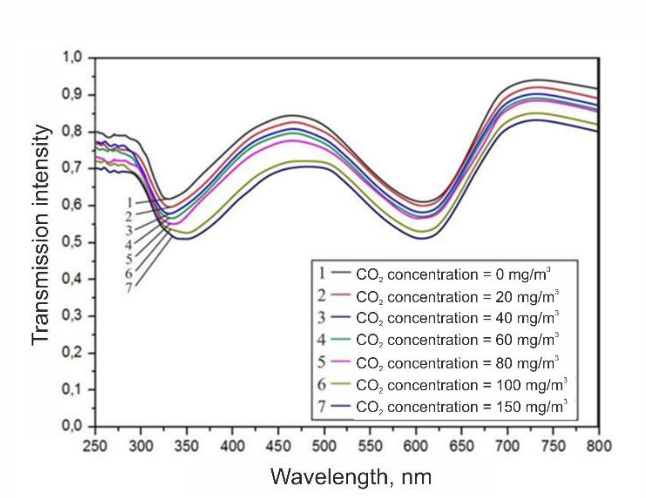

Figure 5 The transmission spectrum of a nanocomposite with a concentration of 5CB of 35% and an admixture of single-walled nanotubes of 0.5% (b) under the influence of CO2

In order for a sensor based on HNS doped with carbon nanotubes to be commercially attractive and competitive, it is necessary that the active medium be characterized by a short relaxation time and the possibility of repeated use without replacing the active medium. That is why the research was conducted on the relaxation properties of the studied nanocomposites.

After the gas was removed from the experimental setup, a change in the spectral characteristics was recorded for 1-2 minutes depending on the time the nanocomposites were left without gas.

For the investigated nanocomposites, after interaction with CO2, a rapid return of the spectral characteristics to the initial position is observed (Fig. 6).

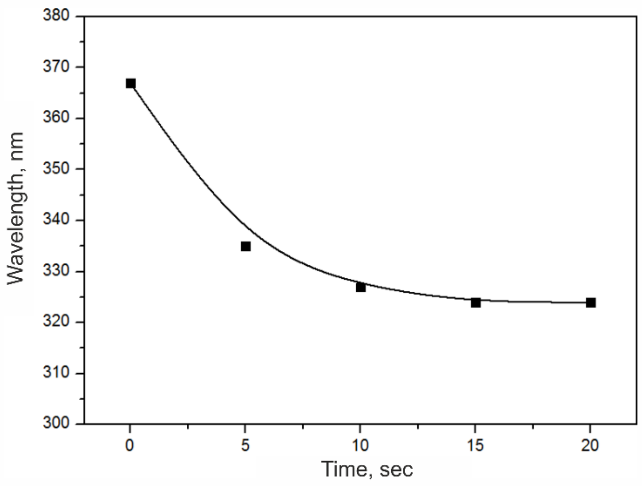

Figure 6 Relaxation characteristics for a nanocomposite based on CNM with a concentration of 5CB of 25% and an admixture of 0.5 % of SWNT after interaction with CO2 for the short-wave minimum

As can be seen from the figures, the recovery time of spectral characteristics after interaction with CO2 is 20 s. This speed of recovery of the nanocomposite is due to the fact that the main role in the change of characteristics under the influence of gases is played by the interaction of gases with carbon nanotubes. As is known, such an interaction is physical absorption, which enables gases to easily bind to nanotubes and quickly detach from them.

5. Conclusions

In the paper, we studied the developed nanocomposites based on HNS with different concentrations of nanotubes under the action of CO2. Based on the research, the optimal composition of the sensitive nanocomposite was determined. Thus, the maximum sensitivity to CO2 in the range of 0–60 mg/m3 is observed for the nanocomposite based on HNS doped with nanotubes with a concentration of 0.5 wt.%. Due to the use of carbon nanotubes for doping the liquid crystal mixture, it was possible to significantly increase the interaction of such a sensor with CO2. This happens due to the interaction of nanotubes with CO2 and its direct absorption.

The recovery time of nanocomposites after interaction with gases was established, which is 20 s for SO2 and CO2 and 40 s for NO2. Given the short response time and recovery time of nanocomposites, they can be used as an active element of an optical gas sensor. Therefore, by optimizing the signal processing system, it is possible to obtain a highly sensitive optical gas sensor for multiple use.

Further research should be conducted in the direction of investigating the interaction of such a composite with other gases, as well as finding opportunities to improve the properties of the composite. Perhaps the use of multi-walled carbon nanotubes.

4. References

(1) Nazemi, H., Joseph, A., Park, J., & Emadi, A. (2019). Advanced micro-and nano-gas sensor technology: A review. Sensors, 19(6), 1285.

(2) Schelski, K., Reyes, C. G., Pschyklenk, L., Kaul, P. M., & Lagerwall, J. P. (2021). Quantitative volatile organic compound sensing with liquid crystal core fibers. Cell Reports Physical Science, 2(12).

(3) Pschyklenk, L., Wagner, T., Lorenz, A., & Kaul, P. (2020). Optical gas sensing with encapsulated chiral-nematic liquid crystals. ACS Applied Polymer Materials, 2(5), 1925-1932.

(4) Agra-Kooijman, D. M., Robb, C., Guan, Y., Jákli, A., & West, J. L. (2021). Liquid crystal core polymer fiber mat electronic gas sensors. Liquid Crystals, 48(13), 1880-1887.

(5) Hanson, E. G., & Shen, Y. R. (1976). Refractive indices and optical anisotropy of homologous liquid crystals. Molecular Crystals and Liquid Crystals, 36(3-4), 193-207..

(6) Li, T., Yin, W., Gao, S., Sun, Y., Xu, P., Wu, S., ... & Wei, G. (2022). The combination of two-dimensional nanomaterials with metal oxide nanoparticles for gas sensors: a review. Nanomaterials, 12(6), 982.

(7) Wang, Y., & Yeow, J. T. (2009). A review of carbon nanotubes-based gas sensors. Journal of sensors, 2009.

(8) Zhao, J., Buldum, A., Han, J., & Lu, J. P. (2002). Gas molecule adsorption in carbon nanotubes and nanotube bundles. Nanotechnology, 13(2), 195.

(9) Santucci, S., Picozzi, S., Di Gregorio, F., Lozzi, L., Cantalini, C., Valentini, L., ... & Delley, B. (2003). NO 2 and CO gas adsorption on carbon nanotubes: experiment and theory. The Journal of chemical physics, 119(20), 10904-10910.

(10) Fujiwara, A., Ishii, K., Suematsu, H., Kataura, H., Maniwa, Y., Suzuki, S., & Achiba, Y. (2001). Gas adsorption in the inside and outside of single-walled carbon nanotubes. Chemical Physics Letters, 336(3-4), 205-211.

(11) Massie, C., Stewart, G., McGregor, G., & Gilchrist, J. R. (2006). Design of a portable optical sensor for methane gas detection. Sensors and Actuators B: Chemical, 113(2), 830-836.

(12) Tan, Q., Tang, L., Yang, M., Xue, C., Zhang, W., Liu, J., & Xiong, J. (2015). Three-gas detection system with IR optical sensor based on NDIR technology. Optics and Lasers in Engineering, 74, 103-108.

(13) Dean, J. B. (2010). Hypercapnia causes cellular oxidation and nitrosation in addition to acidosis: implications for CO2 chemoreceptor function and dysfunction. Journal of Applied Physiology, 108(6), 1786-1795.

(14) Mykytyuk, Z. M., Kremer, I. P., Ivakh, M., Diskovskyi, I. S., & Khomyak, S. V. (2021). Optical sensor with liquid crystal sensitive element for monitoring acetone vapor during exhalation. Molecular Crystals and Liquid Crystals, 721(1), 24-29

(15) Vistak, M. V., Dmytrakh, V. E., Mykytyuk, Z. M., Petryshak, V. S., & Horbenko, Y. Y. (2017). A liquid crystal-based sensitive element for optical sensors of cholesterol. Functional Materials. 24(4), 687-691.

(16) Vistak, M., Dmytrah, V., Fafula, R., Diskovskyi, I., Mykytyuk, Z., Sushynskyi, O., ... & Horbenko, Y. (2017, September). Liquid crystals as an active medium of enzymes optical sensors. In 2017 IEEE 7th International Conference Nanomaterials: Application & Properties (NAP) (pp. 04NB13-1). IEEE.

(17) Wójcik, W., Mykytyuk, Z., Vistak, M., Barylo, G., Politanskyi, R., Diskovskyi, I., ... & Kotsun, W. (2020). Optical sensor with liquid crystal sensitive element for amino acids detection. Przeglad Elektrotechniczny, 96(4), 178-181

(18) Sushynskyi, O., Vistak, M., & Dmytrah, V. (2016, February). The sensitive element of primary transducer of protein optical sensor. In 2016 13th International

Conference on Modern Problems of Radio Engineering, Telecommunications and Computer Science (TCSET) (pp. 418-421). IEEE

(19) Orest, S., Iryna, K., Volodymyr, V., Romana, P., Marija, V., & Grzegorz, B. (2018, February). Liquid crystal active medium for quercetin optical sensor. In 2018 14th International Conference on Advanced Trends in Radioelecrtronics, Telecommunications and Computer Engineering (TCSET) (pp. 724-727). IEEE.

(20) Hanemann, T., Haase, W., Svoboda, I., & Fuess, H. (1995). Crystal structure of 4′-pentyl-4-cyanobiphenyl (5CB). Liquid crystals, 19(5), 699-702.

(21) Collins, P. G., Bradley, K., Ishigami, M., & Zettl, D. A. (2000). Extreme oxygen sensitivity of electronic properties of carbon nanotubes. science, 287(5459), 1801-1804.

(22) Chen, B. H. (2015). Quantum effects on adsorption isotherm of hydrogen in strongly confining twisted carbon nanotubes. International Journal of Hydrogen Energy, 40(38), 12993-13002.

(23) Su, F., Lu, C., Cnen, W., Bai, H., & Hwang, J. F. (2009). Capture of CO2 from flue gas via multiwalled carbon nanotubes. Science of the total environment, 407(8), 3017-3023.

(24) Collins, P. G., Bradley, K., Ishigami, M., & Zettl, D. A. (2000). Extreme oxygen sensitivity of electronic properties of carbon nanotubes. science, 287(5459), 1801-1804

Response to Reviewers

Reviewer #2

1) It is required to clarify the value of the maximum sensitivity.

It does not require changes, because the level of maximum sensitivity is already given in the article and even mentioned in the feedback of the first reviewer.

2) The references list is presented in different formats.

   The list of references has been corrected to the APA standard.