PHYSICS AND CHEMISTRY OF SOLID STATE
V. 22, No. 3 (2021) pp. 426-431

Section: Technology

DOI: 10.15330/pcss.22.3.426-431

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ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 22, № 3 (2021) С. 426-431

Технічні науки

UDC 681.325.2

ISSN 1729-4428

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Highly Sensitive Active Medium of sensor NO_2, Based on Cholesteric Nematic Mixture with Impurities of Carbon Nanotubes

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The paper presents the results of the study of the parameters of the highly sensitive active medium of the NO_2 sensor based on a cholesterol-nematic mixture with an admixture of carbon nanotubes. The dependences of the change in the wavelength of the two transmission minima on the NO_2 concentration for cholesterol-nematic mixture with single-walled, double-walled and multi-walled nanotubes at different concentrations of nanotubes and two concentrations of nematically liquid crystal 5CB were obtained. It is established that by changing the ratio between the concentrations of nanotubes and nematic liquid crystals, it is possible to obtain mixtures that have the maximum spectral sensitivity coefficient in a given range of gas concentration.
Keywords: NO_2 sensor, active medium, cholesterol-nematic mixture, carbon nanotubes.

Received 28 May 2021; Accepted 30 June 2021.

Introduction

Nitrous oxide (NOx) is one of the most harmful gaseous environmental pollution. Nitrous monoxide oxidizes in the atmosphere to nitrogen dioxide (NO_2), which is one of the main components of surrounding air pollution that affects the human health. NO_2 engages with the particles of soot and forms HNO_2 that cause the global environmental problems. For instance, photochemical smog, ozone holes, acid rains and corrosion of the metals [1]. It was also established that the concentration of NO_2 rapidly increases during combustion [2]. Therefore, NO_2 is an early indicator of heat that is more efficient than current detectors of fire.

Let's note, that recently, a demand on reliable as well as rapid systems for detection of explosive substances because of the increasing of the terroristic threat. Their molecules are mainly organic compounds that can be classified under pressure and concentration of the steam. Carbon (C), hydrogen (H), oxygen (O) and nitrogen (N) are the main elements in the chemical structure of the explosive substances. However, most explosive substances also contain a nitro groups (-NO2) [3, 4].

Sensors with resistive type and optical sensors are used to detect NO_2. Semiconductor thin films of organic and inorganic materials [5-7] are used as gas sensitive element of sensors with resistive type. The drawbacks of most common resistive methods are the relatively low sensitivity and selectivity, high energy consumption and the need of heating the active environment. Optical methods have several advantages, including high sensitivity, low time of response resistance to the environment [8-10].

The formation of informational signal in optical sensors NO_2 are predetermined the selective reflection of optical radiation from the active medium.

A great number of nanocomposites is formed from liquid crystals doped with nanoimpurities to modify the optical properties of the LCs [11.14].

As the carbon nanotubes are highly sensitive to NO_2 and have the ability to change the properties from the sorbed gas [15], so it serves for the investigation of the impact of nitrous dioxide on the spectral properties of nanocomposites based on cholesteric nematic mixture (CNM) doped as single, double and multi-walled carbon nanotubes. Carbon nanotubes absorb NO_2 and as the result the optical characteristics of CNM are changed.

I. Experimental Method

Cholesteric-nematic mixtures based on cholesteric liquid crystal BLO-61 and nematic liquid crystal 5SV (25% and 35%) are used in the work. The concentration of NLC in the mixture is chosen in order to spectrum of transmittance was in the visible region. NLC is characterized by a minimum transmittance per a wavelength of 350 nm and the HLC has a minimum transmittance per a wavelength of 427 nm [16]. The position of a minimum transmittance NLC in the mixture is sheared to the short-wave region and is 322 nm and a minimum of transmittance HLC in the mixture sheared to the long-wavelength region.

Also, let's note that, spectrum characteristics of gas NO_2 was received in the works [17-19]. The characteristic show that gas has its own minimum transmittance wavelength of 400 nm.

The received mixtures doped as single-, double- and multi-walled carbon nanotubes with concentrations 0,15% 0,3% and 0,5%. Maximum concentration of nanotubes is restricted of optical transparency of analyzed samples. Mixture is processed in hypersonic bath of 50W capacity during 10 minutes for the progress of homogeneous division of the nanotubes.

Nitrous dioxide was received according to the reaction:

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O.$$

Measuring installation, which is described in work [20], is used for metering spectrum characteristics and their changes under the influence of nitrous dioxide. Concentration dependence of position of the minimum transmittance was received due to covering increase of nitrous dioxide concentration from 0 to 100 mg/m^3 with the move of 20 mg/m3. After the gas is received to the camera its sorption of liquid crystal substance occurs, as a result the concentration of gas in the camera changed a bit. Process of sorption takes 5-10 seconds, then the interaction of the gas with LCD stops, the proof is a region of saturation on the dependence of a minimum transmission on the time.

The spectral characteristics are obtained from the spectrophotometer USB-2000 in the range of 200-1100 nm. The processing of experimental results was carried out by means of the software OriginPro 8. The received spectral dependencies were approximated by Gaussian functions that makes it possible to determine the wavelength by the position of the minimum transmission of the light.

The position of minimum transmittance of samples at room temperature was a measured parameter, which was changing depending on the concentration of nitrous dioxide in the air atmosphere camera. The sorption properties of the films were assessed by means of spectral sensitivity factor S, which is determined by the ratio:

$$S = \Delta\lambda / \Delta C,$$

where $\Delta\lambda$ – the interval of changing of the wavelength of minimum transmission of LCD mixtures under the gas effect, nm, ΔS – interval of changing of the gas concentration,%.

Figure 1 shows the spectral characteristic of the mixture HLC BLO-61 and NLC 5CB for two concentrations 5CB-25 and 35 %.

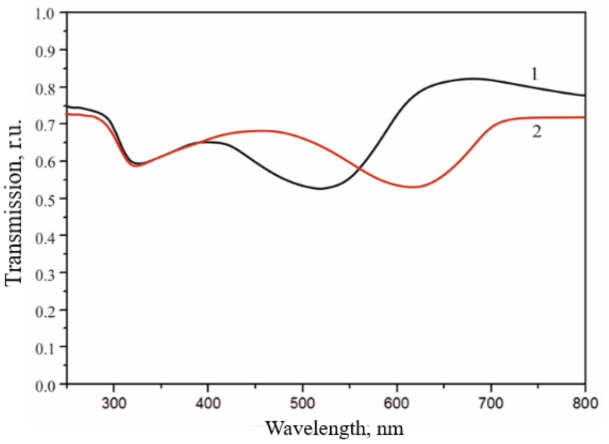


Fig. 1. The spectrum of transmission CNM (with the impurity of carbon nanotubes: 1 – concentration 5CB 25 %; 2 - concentration 5 CB 35 %).

The mechanism of sorption of nitrous dioxide on the surface of carbon nanotubes was discussed in the works [21- 23]. The absorption of molecules NO_2 by means of nanotubes in different positions of molecule in relation to the axis of nanotube was considered to find the most stable configuration [9]. The abstinence of molecules NO_2 on the surface of nanotubes is determined by Van der Waals forces (physical adsorption).

II. The results and discussion

The researches showed that the short-wave minimum of transmission with increasing of concentration of NO_2 is shifted to long-wave region for all samples, moreover the maximum displacement is observed for multi-walled nanotubes with their concentration 0.5 % (concentration 5CB is 35 %) (Fig.2).

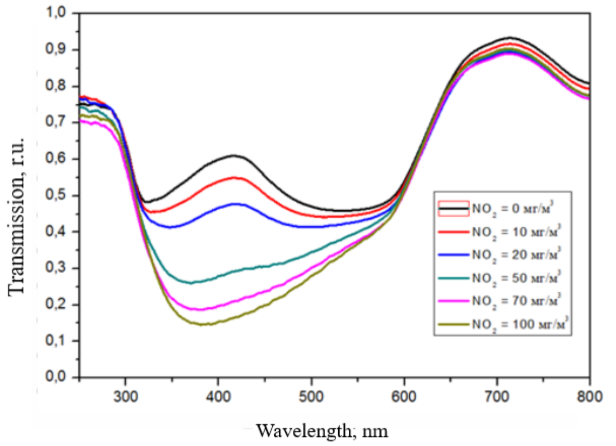


Fig. 2. The spectrum of transmission of cholesteric nematic mixture with concentration 5CB 25 % and impurity of multi-walled carbon nanotubes under effect of NO_2.

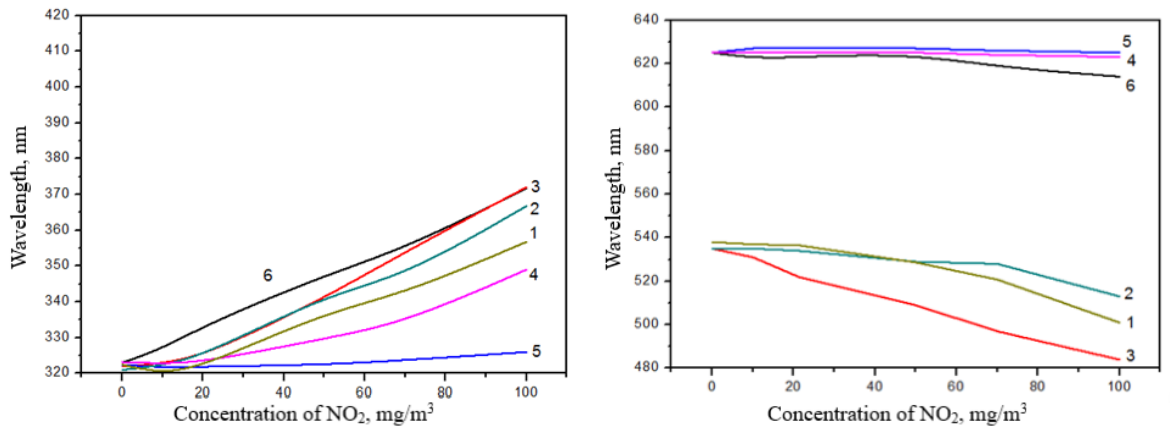
The position of the second minimum of transmission with increasing of concentration of NO_2 is shifted to short-wave region, moreover the maximum displacement is achieved for the sample with impurity of multi-walled nanotubes with concentration 0.5 % and concentration 5CB 35 %.

Analyzing the spectrum of transmission, we can make a conclusion that during the interaction with the gas occurs a displacement of two minimums of passing in the opposite direction, and finally, they form a common minimum of transmission at high concentrations.

Fig. 3-5 show the dependence of changing the wavelength of two minimums of transmission on the concentration of NO_2 for CNM with single-walled, double-walled and multi-walled nanotubes at different concentrations of nanotubes and two concentrations NLC 5CB.

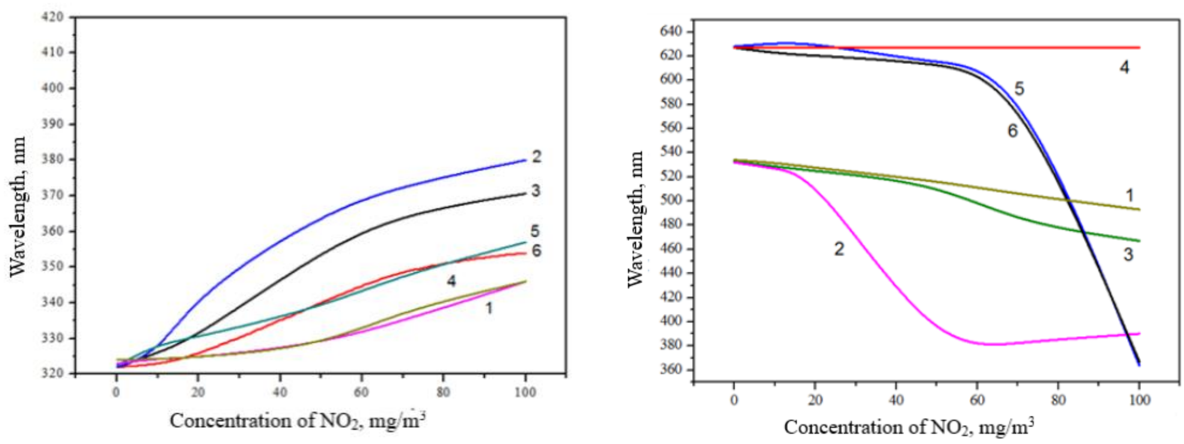
Thus, the maximum sensitivity is revealed by a sample with 5CB concentration of 35% and impurity with multi-walled carbon nanotubes of 0.5%. The coefficient of spectral sensitivity for short wavelength level of 1.46 nm/mg/m^3 on the area of 0-60 mg/m^3, and for long-wave minimum level – 4.7 nm/mg/m^3 on the area of 10-60 mg/m^3. For this sample is constructed the graduation graphs for sensor based on spectral dependence (Figure 6).

A characteristic feature of the results is that the coefficient of spectral sensitivity for mixtures of carbon multi-wave nanotubes far exceeds the similar coefficient for the mixture of single- and double walled nanotubes. It would seem that as the specific single-walled carbon nanotubes greater than multi-walled, then the density of adsorbed gas molecules single-walled nanotubes should be greater. However, the experiment gives the opposite results. Therefore, the coefficient of spectral sensitivity is determined not only by the specific surface of nanotubes, but also by the curvature of this surface. In multi-walled



a) b)

Fig. 3. The dependence of change of short-wave minimum of transmission (a) and long-wave minimum of transmission (b) of the light on the concentration of NO_2 for CNM with single-walled nanotubes: 1 - nanotubes concentration of 0.15 % and the concentration 5CB 25 %; 2 - 0.3 % and 25 %, 3 - 0.5 % and 25 %; 4 - 0.15 % and 35 %; 5 - 0.3 % and 35 %; 6 - 0.5 % and 35 %.



a) b)

Fig. 4. The dependence of change of short wavelength level (a) and long-wave level (b) light transmittance on the concentration of NO 2 CNM for nanotubes with double walled nanotubes: 1 - nanotube concentration of 0.15 % and the 5CB concentration of 25 %; 2 - 0.3 % and 25 %, 3 - 0.5 % and 25 %; 4 - 0.15 % and 35 %; 5 - 0.3 % and 35 %; 6 - 0.5 % and 35 %.

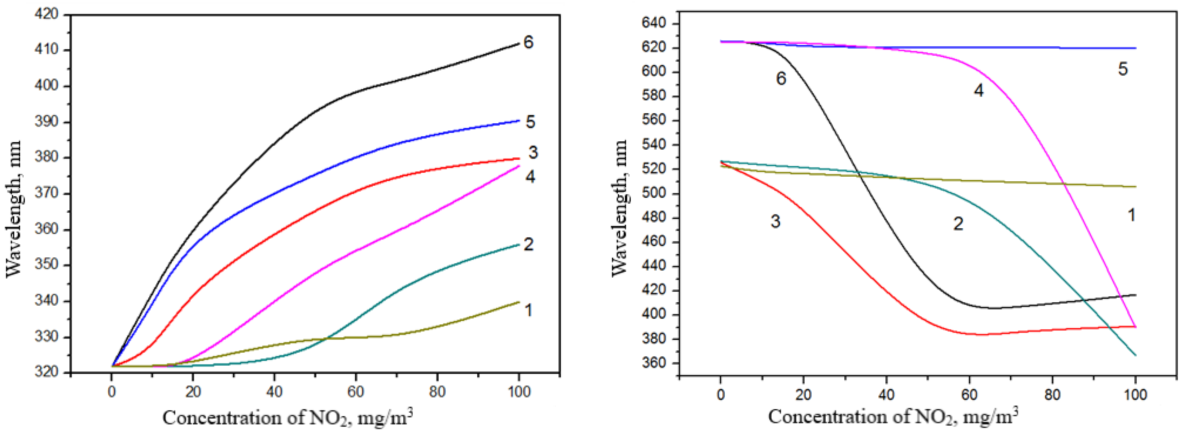


Fig. 5. The dependence of change of short wavelength level (a) and long-wave minimum level (b) depend of the light transmittance of NO_2 concentration for CNM multi-wave of nanotubes 1 - nanotube concentration of 0.15 % and the 5CB concentration of 25 %; 2 - 0.3% and 25 %, 3 - 0.5% and 25 %; 4 - 0.15 % and 35 %; 5 - 0.3 % and 35 %; 6 - 0.5 % and 35 %.

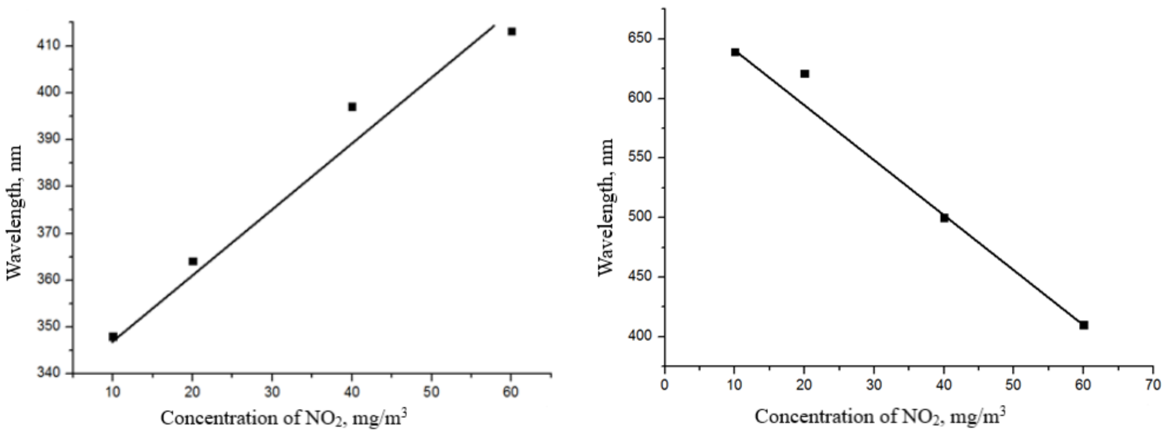


Fig. 6. Graduation graph of gas sensitive element of optical sensor NO $_{2:}$ a - for short wavelength minimum, b - for long-wavelength minimum.

nanotubes curvature of the cylinder is much smaller than single-walled so that molecules more easily absorbed in them, that causes increase of the spectral sensitivity.

The spectral characteristics and its changes under the action of nanocomposites based on HLC doped with carbon nanotubes tracked by the signal converter optical sensor. The main problem of creating signal converter of optical sensors discussed in work [24-29].

Conclusions

Short wavelength minimum of transmission with increasing concentrations of NO_2 shifts in the long-wavelength region for all samples, and long-wavelength contrary – in the short-wave region, namely, a shift of two minimum of transmission is occur in the opposite direction.

The maximum shift of the minimum of transmission observed concentration of CNM 5CB concentration of 35% and with MWCNT impurity of 0.5%. The coefficient of spectral sensitivity makes 4.7 nm/mg/m^3 on the area of 10-60 mg/m^3.

By changing the ratio between the concentrations of nanotubes and NLC, we can obtain mixtures which have a maximum coefficient of spectral sensitivity in a given range of gas concentration.

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Високочутливе активне середовище сенсора NO_2 на основі холестерико-нематичної суміші з домішкою вуглецевих нанотрубок

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В роботі наведено результати дослідження параметрів високочутливого активного середовища сенсора NO_2 на основі холестерико-нематичної суміші (ХНС) з домішкою вуглецевих нанотрубок. Отримано залежності зміни довжини хвилі мінімуму пропускання від концентрації NO_2 для холестерико-нематичних сумішей з одно-, дво- та багатостінковими нанотрубками за різних концентрацій нанотрубок для різних концентрацій нематичного рідкого кристала (НРК) 5СВ. Встановлено, що зміна співвідношення між концентраціями нанотрубок та нематичних рідких кристалів, дає змогу отримати суміші з максимальним коефіцієнтом спектральної чутливості для досліджуваного газу.

Ключові слова: сенсор NO_2, активне середовище, холестерико-нематична суміш, вуглецеві нанотрубки.