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Highly sensitive active medium of primary converter S sensors based on cholesteric-nematic mixtures, dop by carbon nanotub

Abstract. *The spectral characteristics of cholesteric-nematic mixture intercalated with one-, double- and manywalls nanotubes under the SO_2 are presented in the paper. It has been demonstrated the possibilities of using the nanocomposites based on a cholesteric nematic mixtures by carbon nanotubes for material of primary transducer of sulfur dioxide optical sensor. It has been optimized the nanocomposite structure in to achieve a maximal coefficient of spectral sensitivity which is 6.66 nm/ppm for nanocomposites on the base of cholesteric-nematic m intercalated by 0.5% double-walled carbon nanotube.*

Streszczenie. *W artykule zaprezentowano charakterystyki widmowe mieszanki cholesteryczno-nematycznej interkalowanej z jedno-, d wielowarstwowymi warstwami nanorurek pod wpływem działania SO_2. Wykazano możliwości wykorzystania nanokompozytów na bazie mies cholesteryczno nematycznej domieszkowanej przez nanorurki węglowe na materiał przetwornika pierwotnego dwutlenku siarki czujnika optycznego. K ten został zoptymalizowany w celu uzyskania maksymalnego współczynnika czułości widmowej która wynosi 6,66 nm/ppm dla nanokompozytów na mieszaniny cholesteryczno-nematycznej interkalowanej przez 0,5% dwuściennych nanorurek węgla. (Bardzo czuły aktywny nośnik w czujnik głównym przetwarzaniem SO_2 opartych na mieszaninach cholesteryczno-nemotycznych domieszkowanych nanorurkami węglowymi).*

Keywords: optical gas sensor, transmittance spectra, nanocomposite, sulfur dioxide. carbon nanotubes, cholesteric nematic mixtures
Słowa kluczowe: optyczny czujnik gazu, widmo transmitancji, nanokompozyty, dwutlenek siarki, nanorurki węglowe, cholester mieszaniny nematyczne

Introduction

Sulfur dioxide is a toxic substance with an abrupt smell which causes irritation of mucous membrane, muscle spasms and a narrowing of the upper respiratory system. This gas causes coughing, wheezing, laryngeal spasm and stuffiness in great concentrations. The presence of sulfur oxides in the environment is marked both by direct damage to plants and by altering water and soil composition. SO_2. Therefore, it is important to analyze the content of SO_2 in the air[1]. The traditional fixed methods of such analysis, including gas chromatography and spectrophotometry, are quite effective, but they can not be used for rapid analysis, and in relation to this the development of portable gas sensors [2] is the urgent problem.

The problems of sensors creation for analysis of air composition are current in the region of environmental control. Recently different types of gas sensors are developed, mostly it is resistive type, in which thin films of semiconductor inorganic and organic materials are used as gas sensitive material. The optimum composition of gas sensitive materials usually is determined experimentally with selection of material components. The resistive sensors have some significant drawbacks, one of which is the need to reheat an active medium [3, 4]. The cholesteric liquid crystals doped by carbon nanotubes are used in the proposed work for the creation of gas sensitive material.

Experimental objects and methods

The cholesteric nematic mixtures based on cholesteric liquid crystal BLO-61 and nematic liquid crystal 5CB (25%, and35%) were used in the work. The resulting mixtures were doped by single-, double- and multiwalled carbon nanotubes with concentrations from 0.1% to 0.5%. The highest concentration of nanotubes is limited by optical clarity of the analyzed samples. The measurement appliance, that was described in the work [5], was used to measure spectral characteristics and their changes under the influence of SO_2. The gas sensitivity of the resulting samples was measured at room temperature. The wavelength of minimum transmission of template, which value was changed from the gas concentration, was a measured parameter. The sensitiv the sensor was estimated by the value of the coeffici spectral sensitivity that was calculated by the formula

$$S = \Delta\lambda / \Delta C \qquad (1)$$

where Δλ – interval of change of wavelength mini transmission LC mixture under effect of gas, nm, ΔC – in of change of the gas concentration,%.

During the interaction of molecules sulfur dioxide nanocomposite for 5–10 sec the process of gas sorpti occurred, due to that its concentration changes some This is a result of change of the wavelength min transmission. The process of sorption is stabilized after sec, the evidence is the lack of change in the sp transmission. At this time the measuring of sp characteristics is performed.

Results and discussion

We observe two minimums of wavelength transmi the first of which (I) is placed in the short-wave spectrur the second (II) in the long-wave spectrum, on the sp dependences of cholesteric nematic mixtures (Fig. 1).

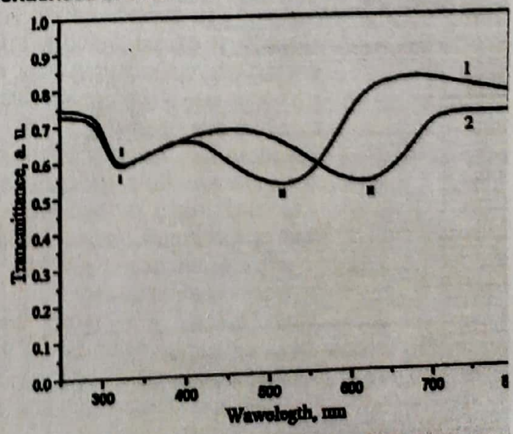

Fig.1. The range of transmission CNM with carbon nan 1 – 5CB concentration – 25%, 2 – 35% 5CB concentration

The short-wave minimum is caused by nematic liquid crystal, which occurs at a wavelength of 322 nm, the long-wave minimum depends on the concentration of nematic liquid crystal – a direct correlation, it is caused by cholesteric liquid crystal.

At the interaction the gas sensitive medium with SO_2 gas at the concentration changing from 0 to 50 ppm the wavelength shift of long-wave minimum transmittances in short-wave range of spectrum and shortwave minimum in to longwave vice versa is observed. Moreover, the maximum changes are observed for nanocomposite based on 5CB with 35% and 0.5% double wall nanotubes. On the figure 2 the spectral characteristics for the above composite versus of the SO_2 concentration is shown. As can be seen from these dependencies, during such interaction the minimal shift of two transmissions in the opposite direction is occurred, and finally, at high gas concentrations, they form a common minimum of wavelength transmittances.

The mechanism of sorption of sulfur dioxide on the surface of carbon nanotubes considered in [6 – 12]. Fig. 3 shows a side and top views of most stabilized structures SO_2 adsorbed on pure carbon nanotubes. The shortest distance of the atom S and the nearest vacant atom C is 3,445 Å. As adsorption energy and energy of charge transfer are -0,062 eV, -0.032 – it is feeble electrostatic interaction. Similarly, the time of interaction is relatively long, the changes of charge transfer and electronic interactions are poor so we can say that the adsorption between the CNT and SO_2 is a physical adsorption [6].

For all the studied nanocomposites increase the concentration of SO_2 leads to an increase of the wavelength of the first minimum transmission. Figure 4 shows the dependence of short-wave and long-wave minimum of SO_2 concentration, which is the maximum for CNM with the impurities of single-, double- and multi-walled carbon nanotubes. Maximum sensitivity observed in the range of 7–30 ppm for mixtures with a 5SV concentration of 35% and with the impurity of double-walled nanotubes with 0.5% concentration. The coefficient of spectral sensitivity for the sample is 6.25 nm/ppm.

Let us consider the character of the molecular interaction of SO_2 with cholesteric-nematic mixture doped with nanotubes.The shift of wavelength to long region is observed when inject nematic liquid crystal in cholesteric-nematic crystal indicating the increase in pitch of cholesteric spiral.Adding nanotubes does not lead to a significant shifts of minimum transmission of wavelength and the pitch of spiral. In the mixture they are considered only as defects.

As a consequence of the action of SO_2 adsorbed by nanotubes the change of intermolecular interactions occurs.In sorption of SO_2 by nanotubes, they alter their electrical parameters such as conductivity.

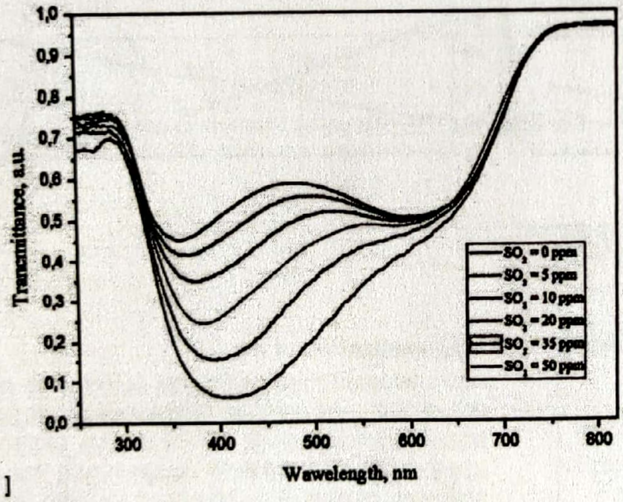

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Fig.2. Transmittance spectrum of cholesteric-nematic mixtures based on 35% concentration 5CB and 0.5 % of double wall carbon nanotubes at SO_2 gas influence

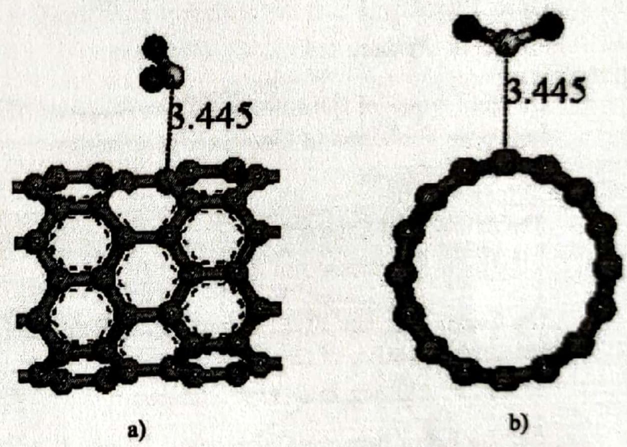

Fig.3. Appearance of the system of carbon nanotube – SO_2 side view (a) and top view (b) [6]

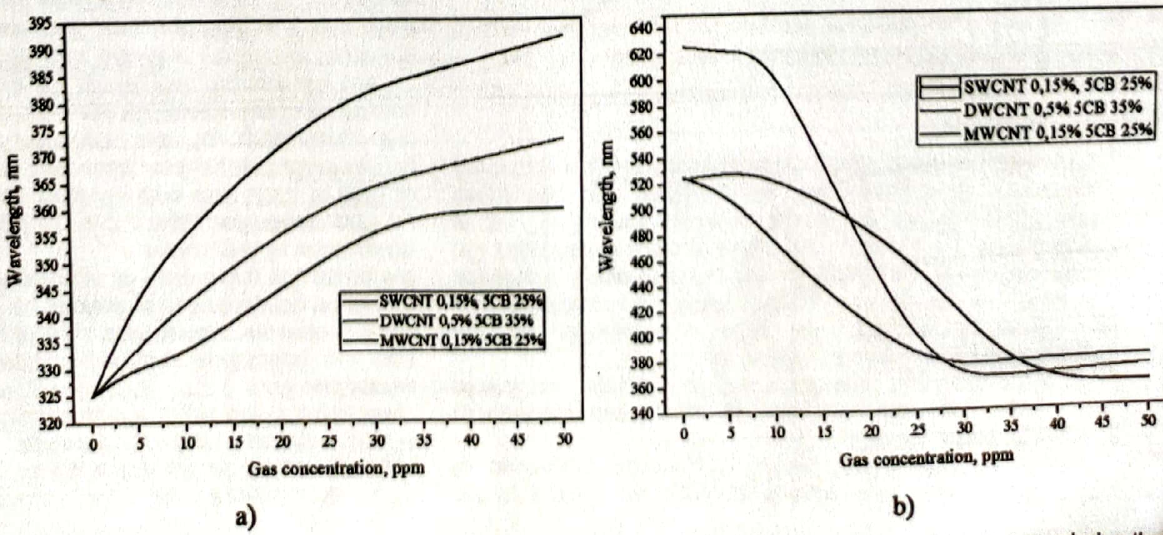

Fig.4. Dependence of change of wavelength of short-wave minimum transmission (a) and long-wave minimum transmission the from the concentration of SO_2 for CNM with nanotubes

As a result some charge appears on surface of the nanotubes [13], which attract highly-polar molecules of nematic liquid crystal.

Since the molecules size of nanotubes significantly exceeds the liquid crystal molecules it makes possible to attract a large number of molecules of 5CB.

Because of this the 5CB concentration in the cholesteric-nematic mixture decreases with increasing SO_2 concentrations and therefore the pitch of spiral decreases and a minimum transmission shifts to short wavelength. On the Figure 4a at a certain concentration of SO_2 it is observed the saturation at sorption by nanotubes molecules, resulting that a minimum transmission shift does not changed.

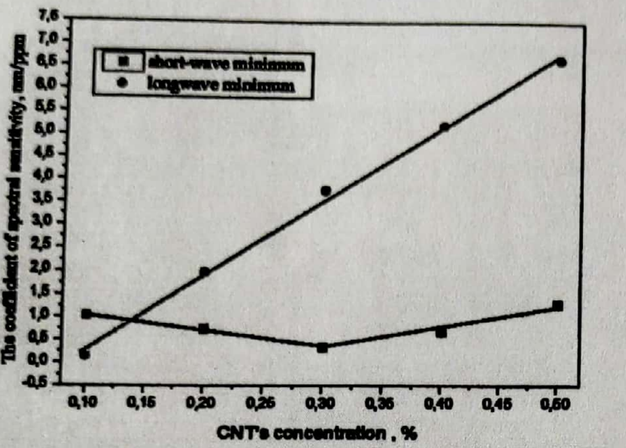

Fig.5. Dependence of the spectral sensitivity of CNM with the 5CB concentration of 35% from the concentration of double-walled nanotubes

The dependence of the spectral sensitivity of nanocomposites to the sulfur dioxide concentrations from single, double and multi-walled carbon nanotubes determined in this work. It was chosen 5 concentrations of nanotubes from 0.1 to 0.5%. In order to get the structure with the nanotubes uniformly distributed nanotubes the limits of concentration should be selected at such way. The maximum concentration of nano-impurity was determined of the possibility conduction of spectral research and minimal coagulation of nanotubes.

The researches have shown that the 5CB concentration of 35% of CNM was only effective sample with impurity of double-walled nanotubes, moreover for long-wave minimum with increasing of the nanotubes concentration the coefficient of gas-sensitivity spectrum increases too (Fig. 5).

For this sample was reveal the maximum coefficient of spectrum sensitivity with the nanotubes concentrations of 0.5% and it is 6.66 nm/ppm. For short-wave minimum the coefficient of spectrum sensitivity obtained the maximum mark nanotubes concentration of 0.5% and it is 1.39 nm/ppm.

As we seen from the figure 6 the maximum coefficient of spectrum sensitivity is observed for long-wave minimum of CNM with concentration multi-walled nanotubes, 0.1%. When the nanotubes concentration increases the value decreases. The biggest coefficient of spectrum sensitivity with nanotubes concentration of 0.3% is observed for all other sample.

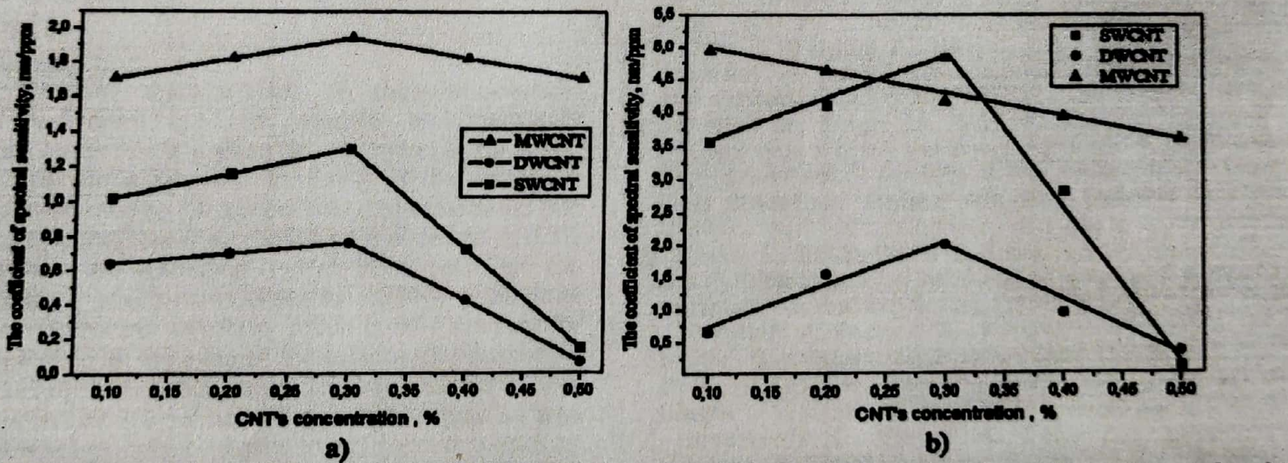

Fig.6. Dependence of the spectral sensitivity of the CNM 5SV concentration of 25% of the concentration of nanotubes on the area from 0 to 30 ppm: a) for short-wave minimum; b) for a double-waved minimum

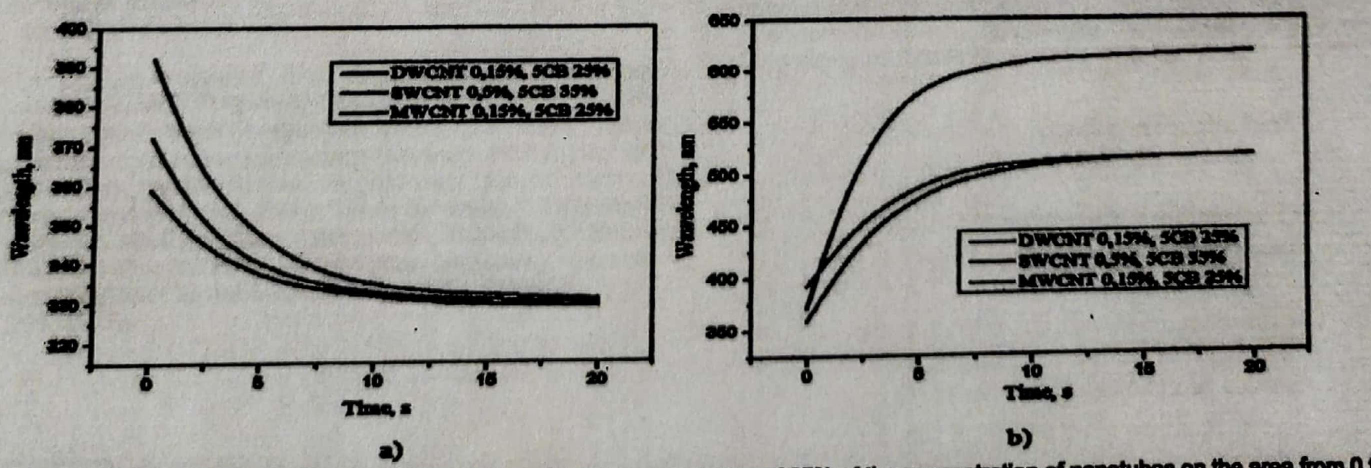

Fig.7. Dependence of the spectral sensitivity of the CNM 5SV concentration of 25% of the concentration of nanotubes on the area from 0 to 30 ppm: a) for short-wave minimum; b) for a double-waved minimum

Thus nanocomposite based on nematic cholesteric mixture doped with carbon nanotubes can serve as a primary converter gas sensitive element of the sensor of SO_2. The output of transformer primary photodiode, which is proportional to the change in wavelength is fed to further processing to a secondary converter.The scheme of a secondary transformer described in papers [14, 15] is used.

Let's consider the relaxation properties of studied gas sensitive materials. The investigation of relaxation characteristics is carried out after SO_2 gas with maximum values of concentration is introduced into chamber and the gas sorption process is occurred. After immediately gas removing from the chamber the minimum of wavelength transmittances with 2 seconds increments is defined. The SO_2 gas desorption process is occurred during the gas removing from chamber, which characterized by the changing of minimum of transmittances wavelength in to initial state [16].

The minimum of wavelength transmittances versus of relaxation time is shown on figure 7 a, b. As can be seen from the figures this process takes place in a certain time range for both short and long-wave minimum of wavelength transmittances, independently for the type and concentration of nanotubes in the mixture. It is also important to note that the transmittances spectrum of the samples did not fully return to its initial state. There are several nanometers in deviation, and if the larger the shift of the minimum of wavelength transmittance under the SO_2 influences than is larger the deviation. But such a deviation is not significant in comparing with the deviation caused by SO_2 influence. But this deviation can be electronically adjusted by the through further processing of the output signal. After the optimization of signal processing system for such deviations can be used for highly sensitive reusable sensor.

Conclusions

The spectral characteristics of cholesteric-nematic mixture intercalated with one-, double- and manywalls nanotubes under the SO_2 effect are presented in the paper. It has been shown how the sensitivity of the composite changes depending on its composition and determined that maximum spectral sensitivity coefficient is observed at 0.3% concentrations of nanotubes. It has been optimized the nanocomposite structure in order to achieve a maximal coefficient of spectral sensitivity which is 6.66 nm/ppm for nanocomposites on the base of cholesteric-nematic mixture intercalated by 0.5% nanotube. It has been established that the interaction of SO_2 with optimized nanocomposites was 10 seconds. It has been proposed to use nanocomposite on the base of cholesteric-nematic mixture intercalated by carbone nanotube as gas sensitive material of primary converter of sensor.

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