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COMPOSITE FILM STRUCTURES WITH FLUOROPHORES AND CdTe QUANTUM DOTS FOR SELECTIVE FLUORESCENT DETECTION OF AMMONIA MOLECULES AT ULTRA-LOW CONCENTRATIONS

The work presents the results of the synthesis and investigation of the spectral-fluorescence characteristics of gas-sensing film composite structures based on ethylene vinyl acetate (EVA), microporous silicate sorbent SiO_2, colloidal quantum dots of CdTe, and fluorescently active dyes of the coumarin group. An increase in the fluorescence intensity of the alcohol solution of the coumarin 7 dye is revealed upon the addition of a solution of colloidal CdTe quantum dots ($\lambda = 530$ nm) due to the Förster resonance energy transfer (FRET). It is experimentally established that the synthesized gas sensor structures had a fluorescent response to volatile ammonia molecules in a steam-gas sample in trace concentrations (0.5–10 ppm). Created gas sensor material demonstrates the ability to restore the initial sensor properties at the end of each measurement cycle. The proposed polymer structures have prospective in use as sensitive elements of fluorescent sensors of ammonia trace concentrations in air.

Keywords: ammonia, quantum dots, sensor films, coumarin dye.

1. Introduction

Individual molecules detection under the real conditions of the multicomponent gas medium, including volatile endogenous metabolites, is a complex analytical problem, where a lot of research and developments were devoted to its solution [1–4] and *etc.* In particular, there is a problem of determining the ammonia concentration in gas mixtures for biomedical diagnostics, environmental monitoring, prohibited substances detection *etc.* [2, 3].

Endogenous ammonia is volatile ammonia molecules that are a product of complex cell-molecular processes. As their result, the body releases NH_3 molecules into the environment through breathing or transcutaneously (through the skin) with different activity depending on the protein metabolism processes, the amino acid deamination reaction *etc.* Concentration of endogenous ammonia in exhaled air is quite low and lies in the interval of 100–150 ppb for healthy people [4], whereas, for patients, it is 700–3 ppm [5]. Ammonia elevated level indicates the presence of pathological processes and diseases, such as liver and kidneys dysfunctions; acute and chronic radiation sickness; lung cancer; Reye's syndrome, and many congenital metabolism pathologies [6]. On the other hand, since ammonia is toxic to most animals and persons even in trace amounts, it is of great interest for environmental monitoring.

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All existing methods and means of ammonia control can be divided into three groups: traditional chemical-analytical methods, instrumental methods, methods with applying sensors, and sensor technologies [7].

Traditionally, instrumental methods include gas chromatography [8], spectrophotometry [9], mass spectrometry combined with gas chromatographic separation [10], laser diode methods, UV-chemoluminescence, and IR spectroscopy [11]. Though the above-mentioned methods have a number of disadvantages and problems of applying them. For example, a system of pre-concentration of samples is required for ammonia determination by the gas chromatographic method. Although such equipment has high sensitivity, it is usually of a stationary type and is characterized by the complexity of the design, relatively high energy consumption, high cost, and requires qualified maintenance.

Chemical analytical methods include analysis using liquid absorbers, reagents, indicator and caloristic tubes, indicator strips and strip gas analyzers. In most cases, the disadvantage of these methods is the impossibility of including them in automated monitoring systems, and the as necessity for a long-term process to pump a certain sample volume through gas analyzers to carry out the analysis itself [12].

Among sensor methods, the most common are: electrochemical ammonia sensors, which are made on a porous base with a developed surface of inert conductive material made of powders (Ti, Zr, Nb), on which a film of catalytically active metal oxide (Mn, Co, Pb) is applied; thermochemical, thermocatalytic sensors (metal oxide), TGS type semiconductor sensors doped with SnO_2 ceramics; organic semiconductors: phthalocyanines, metal porphyrins and other organometallic compounds, highly conductive polymers and polymer-based composites, in particular, filled with heteropoly-compounds; piezoquartz resonators of volume and surface types.

A significant disadvantage of electrochemical sensors is poisoning of the electrolyte and, as a result, temporary degradation of sensor characteristics and high operating temperatures (more than 200 °C). Thermocatalytic sensors' disadvantages include almost complete no selectivity: any molecules that enter the reaction zone and enter into an oxidation reaction with oxygen at the catalytic center at high operating temperatures affect this sensor's indicators. The main problems of the practical use of semiconductor sensors are related to insufficiently good temporal stability of their sensitivity and low selectivity [13, 14].

Most of the above-mentioned sensor methods for detecting ammonia in gas mixtures do not have the necessary sensitivity and are unsuitable for the real-time diagnosis.

Optical sensors [15] are well established, among which fluorescent sensors should be noted, because the fluorescent method of analysis is very sensitive. It allows detecting substances in concentrations down to 10^{-9} mol/l and can be used in a wide range of analyte concentrations. This method is suitable both for the detection of cations and anions and for the detection of neutral molecules. Fluorescent sensors are easy to be used and have good selectivity and fast response to analytes [16]. The undoubted advantage of choosing them is also a low cost and small size as compared to other known sensors [17].

Optical sensors, regardless of their design, always have a sensitive layer in which analytical reagents molecules (or their active fragments) are introduced at the molecular or phase level, which interact with gas molecules controlled by the sensor. Since one of the important characteristics of the sensor is the reproducibility of the sensor parameters over time with many cycles of measurement/regeneration, so, in recent years, preference has been given to sensitive materials with chemical covalent or ionic bonding of analytical reagent molecules to inert material of the sensitive matrix [18].

There are two types of optical ammonia sensors: sensors for detecting ammonia in liquids and in gaseous media.

Different types of fluorescent sensors are used to detect ammonia in aqueous solutions: based on liquid crystals doped with luminogen [19], based on BF_2-chelate tetraarylazadipyrromethane (aza-BODIPY) dye placed in a polymer matrix with a hydrophobic membrane [20], based on lead-free perovskite $Cs_2AgInCl_6:Bi$ [21].

Work [22] reported on ultrasensitive sensor based on covalently bonded lattices for detecting ammonia in organic solvents (Covalent organic frameworks (COFs)) of TAPA-TPD-COF fluorophores. Basis of such sensors functioning is the principle of nonlinear amplification of a weak signal response to the analyte using the so-called domino method: when ammonia interacts with one dye molecule, a specific catalytic reaction is started which covers the entire fluorophores' configuration. Gaseous ammonia is also detected by the method of pumping air with ammonia through a liquid in a miniature scrubber, where ammonia was highly efficiently absorbed by the liquid from the air and a fluorescent substance was formed, the fluorescence intensity of which had been measured using a photodiode [23]. This ammonia sensor is quite sensitive (30–100 ppm) and inexpensive, but, obviously, this method requires constant addition of reagents, because the formation of chemical reactions with the fluorescent substance formation are occured. Therefore, the main disadvantage of such methods, based on passing ammonia through a liquid, is the use of complex systems of pumping and air dosing at a certain speed, solvent evaporation, and inconvenience of such facilities operating. Optical fluorescent ammonia detection sensors that directly adsorb ammonia from air have usually no such drawbacks.

Research work [24] describes an optical sensor based on luminescent $\mathrm{ZnO:Eu^{2+}}$ nanoparticles, which determines the ammonia presence in a sample based on fluorescence quenching. This sensor has following advantages: high sensitivity (20 ppm) and ease of fabrication. However, the specified sensor sensitivity is not sufficient for application in exhaled air sensors. Developed fluorescent sensor [25] for ammonia detection based on curcumin derivatives incorporated into the polyvinylpyrrolidone matrix, which was formed using electrospinning technology, showed high sensitivity (0.5–10 ppm) due to improved dye modification and use of nanofiber with high specific surface area as matrix.

However, till now, there are only single examples of creating highly sensitive fluorescent ammonia sensors in the air, and its detection in the gaseous medium remains an actual problem. Nowadays, there are practically no methods and devices for measuring ammonia concentration in exhalation in real time.

The purpose of this work was to create polymer composite structures with fluorophores, that had the ability to selective fluorescent detection of volatile ammonia molecules in trace concentrations.

Organic dyes can be used as such fluorophores, which must satisfy a number of requirements, the most important of which is a clear optical response to the presence of foreign molecules or ions, which manifests itself as a significant change in their spectral-luminescent properties [26].

Fluorescent dyes such as coumarin, rhodamine, Nile red *etc.* can be used as signal organic molecules, the molecular structure of which ensures a change in their spectral-luminescent properties depending on the molecular environment. Our previous experimental studies have shown that the best spectral and luminescence characteristics for studying the ammonia molecules' concentration can be obtained by using coumarin dyes, in particular, coumarin 7, which significantly changes its intensity in the presence of ammonia [7].

Sensor sensitivity can be intensified by using so-called fluorescence amplifiers, as which inorganic fluorophores – semiconductor nanocrystals – quantum dots with different fluorescence wavelengths can be used [27]. Amplification occurs from one fluorophore to another as a result of the non-radiative, so-called Förster resonance energy transfer (FRET) [28].

2. Samples and Experimental Technique

High-molecular polymer ethylene vinyl acetate (EVA) was used as a matrix, which was applied to glass substrates heated to 80 °C to create polymer composite structures. EVA is a good film former that has good gas permeability and high chemical resistance to acids, alkalis and inorganic solvents.

The sorbent layer – microporous silicon dioxide $\mathrm{SiO_2}$ with particle sizes of 37–63 microns and a specific surface area of 500 ± 50 m^2/g ("UkrOrgSyntez", Ukraine) – was applied to the heated layer of EVA.

A dry sample of the coumarin 7 dye with an absorption wavelength of $\lambda = 435$ nm and fluorescence emission of $\lambda = 493$ nm ("Alfa-Akonis") was mixed with ethanol by using the M5 magnetic stirrer to obtain ethanol solutions of various concentrations 10^{-2}–10^{-3} M. An aqueous solution of CdTe colloidal quantum dots was added to the prepared mixture. Quantum dots (manufactured by "BukNANOtech", Chernivtsi), stabilized by the surfactant thioglycolic acid (TGA), had following parameters: particle size of 2.3 nm, quantum yield of 30%, and luminescence at wavelengths of 530–535 nm, pH = 11.

The received mix was applied to a layer of silicon dioxide $\mathrm{SiO_2}$. Next, the composite was dried at a temperature of 65–70 °C. The dimensions and thickness were determined by the microscopic object-micrometer method. Translucent samples of polymer composite structures with a matte surface of 7×35 mm^2 and a thickness of 20–60 μm ± 5 μm were obtained.

Absorption spectra and fluorescence excitation spectra of the synthesized samples were measured on a Specord M40 UV-VIS spectrophotometer with an attachment for automated fluorescence measurement. Fluorescence spectra were measured on a SL 40-2 spectrometer (Solar TII). The fluorescence kinetics of the samples and their fluorescence response to ammonia were obtained by the Flx-800T fluorometer (BioTek Instruments), which was modified for measurements in a gaseous medium with quartz cuvettes, optically transparent to the radiation source of the device.

Polymer composite structures on the substrate were placed in a quartz gas cuvette, which was then placed in the compartment of the Flx-800T fluorimeter. The fluorescence intensity of the sample was measured at a wavelength of $\lambda = 528$ nm, and the fluorescence of the sample was excited at a wavelength of $\lambda = 485$ nm.

Calibration gas mixture with given ammonia content was prepared according to the static volumetric method of preparing gas mixtures, then a prepared gas sample with a definite ammonia concentration was injected into the cuvette with the sample by using a syringe. During the measuring interval, the fluorescent response of the sample was recorded and analyzed; processing of the received data was carried out using a PC. While measuring the sensor properties of the created gas-sensing material, the fluorescence intensity change of the sample as a result of its interaction with NH_3 ammonia molecules in the gas sample was taken as the analytical signal.

3. The Results

At the first stage, experiments are conducted to establish the effect of enhancing the coumarin 7 dye fluorescence by CdTe quantum dots. A donor-acceptor complex was formed between the coumarin 7 molecule, with a maximum absorption band at a wavelength of 430 nm, and a CdTe quantum dot with a maximum fluorescence band at a wavelength of 530 nm [4].

Figure 1 shows the overlap of the absorption spectrum of coumarin 7 (energy acceptor) with the fluorescence spectrum of CdTe quantum dots (energy donor), which indicates the possibility of Förster Resonance Energy Transfer (FRET). It is shown that, when quantum dots were added to solution (in a ratio of 1 : 1), a significant increase in the band fluorescence intensity (by ∼57%) with a maximum of 492 nm (coumarin 7 band fluorescence) was observed. The inclusion of fluorescent quantum dots in the sensor leads to improve sensory sensitivity of the sensors, because the increase in the effective fluorescence intensity of the sensor's sensing element increases the signal-to-noise ratio, which simplifies receiving the optical response of the sensor to ammonia.

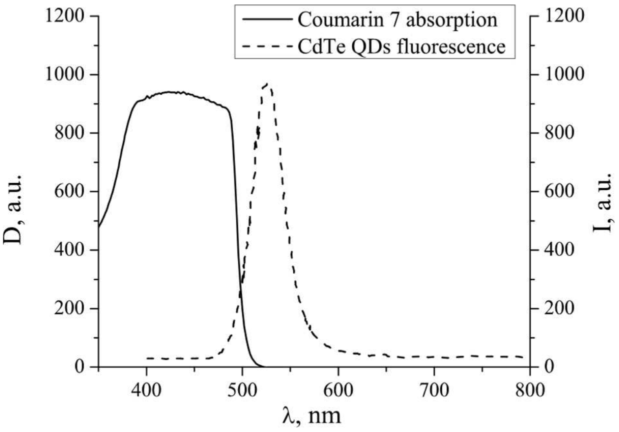
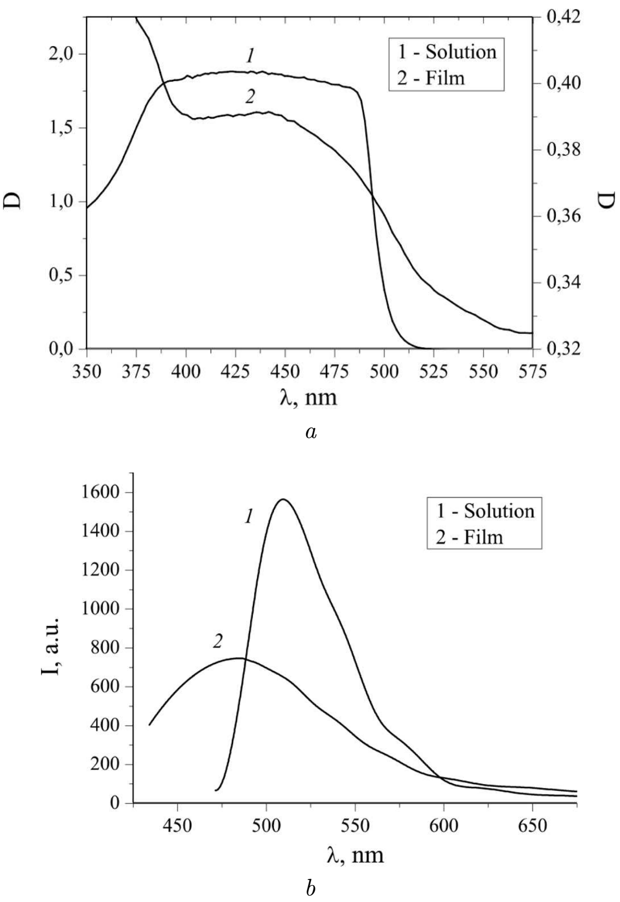


Fig. 1. Overlap of the absorption spectrum of coumarin 7 (energy acceptor) with the fluorescence spectrum of CdTe quantum dots (energy donor)

The spectral-luminescent properties are found to vary significantly in ethanol solutions and in polymer film structures. In Fig. 2 absorption spectra (*a*) and fluorescence excitation spectra (*b*) of coumarin 7 dye in ethanol solution and a polymer film structure based on EVA (ethylene vinyl acetate), SiO_2 sorbent, quantum dots (CdTe/TGA) ($\lambda = 530$ nm) are presented, which were obtained at Specord M40 UV-VIS spectrophotometer, and fluorescence spectra – on the SL40-2 spectrometer.

The absorption spectrum of the solution *1* (Fig. 2, *a*) has the form of a broad band in wavelength interval of 370–480 nm and a maximum at wavelength of $\lambda = 430$ nm. In contrast to this, the film structure *2* (Fig. 2, *a*) has a wide absorption band in the wavelength interval of 404–490 nm, for which a bathochromic (red) shift is observed compared to the ethanol solution of coumarin 7 dye.

Fluorescence spectra are also different. The luminescence spectrum of a sample of film structures with coumarin 7 based on EVA and SiO_2 sorbent doped with QD CdTe ($\lambda = 530$ nm) *2* (Fig. 2, *b*) has a



a

b

Fig. 2. Absorption (*a*) and fluorescence (*b*) spectra of coumarin 7 in an ethanol solution (*1*) and in a film structure (*2*)

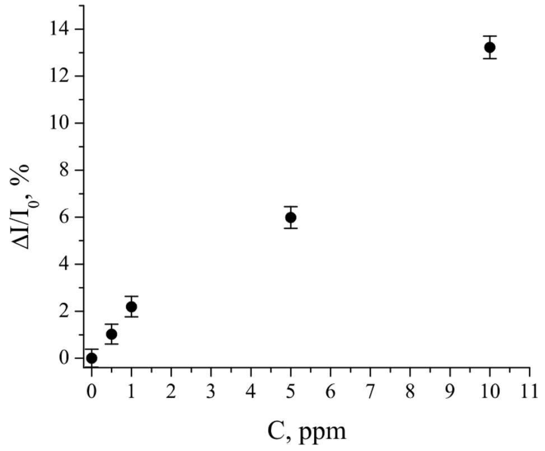


Fig. 3. Dependence of the fluorescence response (fall in fluorescence intensity) of the synthesized film composite structures on the ammonia concentration in the pure air

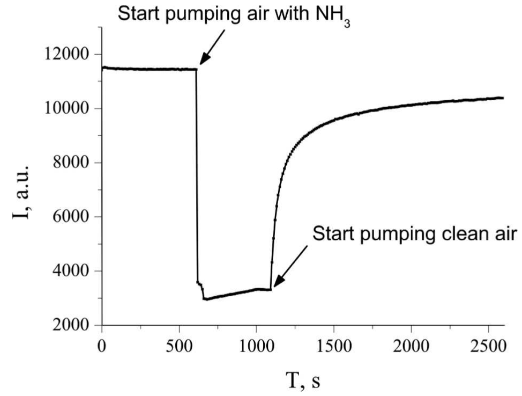


Fig. 4. The dynamics of recovery of the fluorescence signal intensity of a sample of polymer composite structures based on EVA, SiO_2 sorbent, quantum dots (CdTe/TGA) ($\lambda = 530$ nm) and coumarin 7 dye after interaction with ammonia at concentration of 5000 ppm

maximum at wavelength of $\lambda = 480$ nm. It is shifted relative to the fluorescence spectrum of coumarin 7 in ethanol *1* (Fig. 2, *b*), which has a maximum at wavelength of 508 nm, by 28 nm in the blue area (hypsochromic shift). Research has shown that the polymer ethylene vinyl acetate (EVA) does not have its own fluorescence in this wavelengths' interval.

To study the sensory properties (fluorescence response) of the created film composite structures in the interaction with ammonia (NH_3) molecules, the samples were placed in the gas cuvette of the fluorimeter and ammonia's steam-gas mixture of different concentrations was pumped through it.

Changing the sample's fluorescence intensity under the ammonia action in steam-gas mixture was measured when it was exceeded in air by 0.5, 1, 5, 10 ppm regarding the basic one (Fig. 3). The ammonia concentration in the pure air was considered as a baseline.

Figure 3 shows the concentration dependence of the fluorescence intensity change of the synthesized composite upon ammonia sorption. While ammonia pumping, the fluorescence intensity decrease is observed, which indicates the presence of chemical interaction of ammonia molecules with the organic dye – coumarin 7 anions, and the formation of coumarin anion – ammonium cation complexes and other processes. In the synthesized EVA/SiO_2/C7 samples, when interacting with ammonia, a significant fluorescence intensity decrease was observed for the specified interval of microconcentrations. For the maximum concentration (10 ppm), the film composite response is 14%; and, for the minimum (0.5 ppm), the response is 1%.

As the experiment showed, when pumping a steam-gas mixture with the content of even quite significant ammonia concentrations (5000 ppm), the sample can be recover pure air pumping. Figure 4 shows the fluorescence intensity dropping while pumping of the air-ammonia mixture and the recovery dynamics. Ammonia injection with a concentration of 5000 ppm causes a decrease of over three-fold in the sample fluorescence intensity.

While pumping pure air through the cuvette with the sample for 20 minutes, the sample's fluorescence intensity was recovered by almost 90%, due to desorption of ammonia molecules from the composite surface. As can be seen from Fig. 4, the processes described by this curve cannot be accurately described by a single exponential function, since they are more complex (there are several of them, and they have different physical natures).

At the beginning, the fluorescence intensity decays relatively quickly – within a very short time (∼10 s), the fluorescence value decreased by a factor of 5. However, since the measurement frequency in the experiment was 1 measurement every 10 s, we have an insufficient number of data points in this segment of the curve for an accurate analysis of its nature. Therefore, based on approximate estimations (made visually from the graph), the characteristic decay time of the fluorescence is 10 s.

The decay in fluorescence intensity is explained by fluorescence quenching processes of the fluorophore complex in the sensor by the quencher, which, in this case, is gaseous ammonia. Typically, both types of quenching, dynamic and static, are present, which causes a complex kinetic curve.

The part of the curve corresponding to the fluorescence intensity recovery process is described in the first approximation by the graph of the exponential function of the form $I = I_0 + A_1 e^{(-(t-t_0)/\tau)}$ with an accuracy of $R = 0.976$ and a characteristic recovery time of $\tau = 135$ s.

In order to detect selectivity of the samples to ammonia, experiments were conducted on the change of samples' fluorescence during air pumping, which contained other gases of the main groups of molecules, such as pentane and acetone, which are presented in the ambient air and human exhalation (Fig. 5).

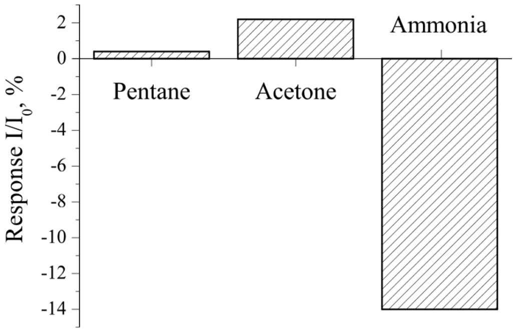


Fig. 5. Fluorescent responses of the EVA/SiO$_2$/coumarin 7/QD(CdTe) sample to pentane and acetone vapors as compared to ammonia vapors with concentrations of 10 ppm in the air sample

The diagram (Fig. 5) shows that, when we use to pentane, the sample reacts to its presence in the air sample at a concentration of 10 ppm with a relatively weak increase in the intensity of the fluorescence signal by 0.4%; and if acetone at a concentration of 10 ppm is involved, the sample's fluorescence intensity increases by 2.2%. While the sample reacts to a similar concentration of ammonia (10 ppm) with a significant falling of fluorescence intensity by 14% relative to the initial fluorescence intensity of the sample, which indicates the sensitivity of the sample to ammonia 6.5 times greater than to acetone, and 35 times greater to ammonia than to pentane. Therefore, the created film composite structures have a significantly greater sensitivity, and hence a certain selectivity to ammonia compared to acetone and pentane.

4. Conclusions

The research paper proposes a new gas-sensor material for the optical quantitative detection of ammonia in air, synthesized on the basis of a complex of fluorescent coumarin 7 dye with QD (CdTe) quantum dots and ethylene vinyl acetate EVA polymer matrices with a SiO$_2$ sorbent layer. The samples were obtained through layer-by-layer application on glass substrates, which made it possible to create a thin-layer composite material (∼60 μm), which was easy to be fabricated and had stable sensory properties, and good photostability.

Changing the fluorescence intensity of the gas-sensing material after the interaction with ammonia in air in the interval of 0–10 ppm has a linear dependence on the NH$_3$ concentration. The smallest experimentally determined sensitivity of the obtained material to ammonia (achieved at the present moment) is 0.5 ppm.

It is possible for the obtained composite structures to recover the fluorescence intensity and, therefore, its sensory properties after a full cycle (injection of an ammonia-air mixture – regeneration). In addition, there is a possibility of multiple using the same sample.

Created gas-sensing composite material shows a selectivity of response to ammonia in the presence of other gases of the main group of volatile molecules-biomarkers, namely acetone and pentane.

While examining synthesized material samples upon contact with ammonia molecules, a decrease in fluorescence intensity was registered, which is probably explained by the fluorescence static quenching phenomenon of coumarin 7 with QD (CdTe) complex. This complex, in its turn, at interaction with ammonia molecules, forms a complex of ammonium cation – coumarin anion.

Created gas-sensing composite material allows one to detect the presence of ammonia in air at the concentration level of 0.5–10 ppm by fluorescent method, which meets the sensitivity requirements for the detection of ammonia low concentrations and its quantitative determination in human exhalation and can be applied to create compact optical sensors or ammonia sensors for non-invasive diagnosis of diseases in medical institutions.

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КОМПОЗИТНІ ПЛІВКОВІ СТРУКТУРИ З ФЛУОРОФОРАМИ ТА КВАНТОВИМИ ТОЧКАМИ CdTe ДЛЯ СЕЛЕКТИВНОГО ФЛУОРЕСЦЕНТНОГО ВИЯВЛЕННЯ МОЛЕКУЛ АМІАКУ НАДНИЗЬКОЇ КОНЦЕНТРАЦІЇ

В роботі наведено результати синтезу та дослідження спектрально-флуоресцентних характеристик газосенсорних плівкових композитних структур на основі етиленвінілацетату, мікропористого силікатного сорбенту $\mathrm{SiO_2}$, колоїдних квантових точок CdTe та флуоресцентно активних барвників групи кумаринів. Виявлено підсилення інтенсивності флуоресценції спиртового розчину барвника кумарин 7 при додаванні розчину колоїдних квантових точок CdTe ($\lambda = 530$ нм) за рахунок ферстерівського безвипромінювального перенесення енергії. Експериментально встановлено, що синтезовані газосенсорні структури мають флуоресцентний відгук на молекули леткого аміаку в парогазовій пробі в слідових концентраціях (0,5–10 ppm). Створений газосенсорний матеріал демонструє здатність відновлювати початкові сенсорні властивості по завершенні кожного вимірювального циклу. Запропоновані нами полімерні структури мають перспективність при їх використанні в ролі чутливих елементів флуоресцентних сенсорів слідових концентрацій аміаку у повітрі.

Ключові слова: аміак, квантові точки, сенсорні плівки, кумариновий барвник.