Gas-Sensing Fluorescent Nanostructured Composites with Coumarin Dyes and CdTe Semiconductor Nanoparticles for Non-Invasive Medical Diagnostics

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The paper presents the results of the study of the spectral-luminescent properties of solutions and nanostructured composites, which include some coumarin dyes (coumarin 4, coumarin 7), semiconductor nanocrystals (CdTe quantum dots), as well as values of their spectral shifts depending on the medium. The effect of enhancing the fluorescence intensity of coumarin dyes by CdTe quantum dots through nonradiative energy transfer is revealed. The fluorescence sensitivity of the synthesized systems to ammonia and acetone vapours in the air is shown, that manifests itself by means of the decrease in the fluorescence intensity proportional to the analyte concentration. For ammonia, the response to a vapour concentration of 10 p.p.m. is $13.2 \pm 0.6\%$, and for 5000 p.p.m., it is $74.0 \pm 1.1\%$. For acetone, the response to a vapour concentration of 33 p.p.m. is $0.56 \pm 0.08\%$; for 67 p.p.m., it is $1.2 \pm 0.1\%$, and for 133 p.p.m., it is $2.2 \pm 0.1\%$. Recovery of sensory properties of such systems after desorption of analytes' molecules is revealed. The created nanostructured composites are promising as sensor elements of devices for non-invasive medical diagnostics of several pathologies, such as lung cancer, liver and kidney diseases, diabetes mellitus, heart failure, pancreatitis, by determining the concentrations of their biomarkers in human exhaled air: ammonia and acetone.

У статті наведено результати дослідження спектрально-люмінесцентних властивостей розчинів і наноструктурних композитів, що включають ряд кумаринових барвників (кумарин 4, кумарин 7), напівпровідникових нанокристалів (квантових точок CdTe), а також величини їхніх спектральних зсувів в залежності від середовища. Виявлено ефект підсилення інтенсивності флюоресценції кумаринових барвників квантовими точками CdTe шляхом безвипромінювального переносу енергії. Показано флюоресцентну чутливість синтезованих систем до парів аміяку й ацетону в повітрі, що проявляється у пониженні інтенсивности флюоресценції, пропорційному концентрації аналіту. Для аміяку відгук на концентрацію парів у

10 p.p.m. складав $13,2 \pm 0,6\%$, на 5000 p.p.m. — $74,0 \pm 1,1\%$. Для ацетону відгук на концентрацію парів у 33 p.p.m. складав $0,56 \pm 0,08\%$, на 67 p.p.m. — $1,2 \pm 0,1\%$, а на 133 p.p.m. — $2,2 \pm 0,1\%$. Виявлено відновлення сенсорних властивостей таких систем після десорбції молекул аналітів. Створені наноструктурні композити є перспективними як сенсорні елементи приладів для неінвазивної медичної діягностики ряду патологій, таких як рак легенів, захворювання печінки та нирок, цукровий діабет, серцева недостатність, панкреатит, шляхом визначення концентрацій їхніх біомаркерів у видихуваному повітрі людини — аміяку й ацетону.

1. INTRODUCTION

Studies in the field of molecular spectroscopy and luminescence have received new pulls in connection with the development of works on optical sensorics of chemical compounds [1]. The development of fluorescent gas sensor systems is becoming increasingly important to solve a wide range of problems that require determining the concentrations of various components of the gaseous environment: environmental monitoring (living and working areas), detection of biomarker molecules in human exhaled air, and others. Such sensor systems can be created using micro- and nanotechnology, which will provide miniature, reliable, and relatively inexpensive detectors and sensor systems.

Nanosensors based on nanoparticles and molecules of organic fluorophores placed in organic or inorganic matrices are used to detect gases. Fluorescent optical chemosensors in which the output signal is a change in the fluorescence properties of the sensor material are among the most promising, due to the high sensitivity of the fluorescence signal to certain agents, and as a consequence, the ability to detect ultra-low concentrations of analytes [1−4].

One of the important practical applications of such sensors can be a non-invasive diagnosis of diseases by analysis of exhaled air, which can be an alternative to blood and urine tests. The connection between some pathologies and the increase in the concentration of certain biomarker molecules is well established. Today, some of the most studied and most important biomarkers in exhaled air are ammonia and acetone [5]. Ammonia is a marker of liver and kidney dysfunction, lung cancer, *etc.*, and acetone is a marker of diabetes, pancreatitis, heart failure, lung cancer, *etc.* [5−8].

The use of coumarin dyes as fluorophores is promising, which is based on information about their spectral-luminescent properties, as well as the ability to intermolecular interactions and the formation of proteolytic forms [9]. There are many reports of studies of coumarin fluorophores in sensors that are sensitive to ammonia vapour [1, 9], but due to several disadvantages (low selectivity, low sensitivity limit, *etc*.), they have not yet found practical application. In [10, 11], it was shown that some coumarin dyes show fluorescent sensitivity to the presence of acetone in liquids, but there are no data on the study of their sensor properties to acetone vapours currently. Therefore, it is important to further study coumarin dyes to create highly sensitive fluorescent sensors of ammonia and acetone in a gaseous medium.

To increase the sensitivity of such fluorescent sensors, it is of interest to investigate the use of the effects of enhancing the fluorescence of organic dyes located near nanoparticles. According to the works [12−16], nanoparticles of metals or semiconductors (quantum dots) near fluorophores can significantly increase the intensity of their radiation due to non-radiative, so-called Förster resonance energy transfer (FRET) from nanoparticles to fluorophores molecules. When two objects (donor and acceptor) converge to the distance of the Förster radius (approximately, of 10 nm) and the fluorescence spectrum of the donor overlaps with the absorption spectrum of the acceptor, the probability of energy transfer without radiation increases significantly between them.

This paper is concerned with the creation of gas-sensing fluorescent nanostructured composites with coumarin dyes and semiconductor nanoparticles CdTe and the study of their optical properties and sensory sensitivity to acetone and ammonia vapours.

2. EXPERIMENTAL

We used such materials and reagents: ethanol 96%, acetone ('extra pure'), ammonia solution 10% (aqueous), coumarin 4 (chemical formula 7-Hydroxy-4-methylcoumarin, produced by Avocado), coumarin 7 (chemical formula 3-(2-Benzimidazolyl)-7-N,N-(diethylamino)−coumarin, Alpha-Aconis), CdTe quantum dots (produced by BukNano-Tech) with a particle size of 2.3 nm, a quantum yield of 30%, and luminescence at wavelengths of 530−535 nm, stabilized by the surfactant thioglycolic acid (TGA), pH = 11; silica gel 60 (pore size 6 nm) with a specific surface area of 500 ± 50 m^2/g and a particle size of 37−63 μm (UkrOrgSyntez), hydrophilic pyrogenic silica 'Aerosil' brand A-380 with a specific surface area of $3.8 \cdot 10^2$ m^2/g, polymer ethylene-vinyl acetate (EVA). The materials of the sorbents were selected due to their developed surface, which determines their high sorption properties.

Recording of absorption spectra and fluorescence excitation spec-

tra were performed on the Specord M40 UV-VIS spectrophotometer (manufactured by Carl Zeiss Jena). Fluorescence spectra were measured using the SL40-2 spectrometer (Solar TII). Kinetics of fluorescence was obtained on the FLx800T fluorimeter (BioTek Instruments) and on the Specord M40 UV-VIS. The Justor 1100DG (manufactured by Nichiryo) and the Research (Eppendorf) manual pipettes were used to dispense a given volume of liquid substances. Reagents were weighed on the electronic scales AD50 (Axis).

The semiconductor laser with a wavelength of 405 nm and the ultraviolet 370–375 nm LED were used as sources of fluorescence excitation for measuring fluorescence spectra.

Alcohol solutions of coumarin dyes at concentrations of 10^{-3} M and 10^{-4} M were prepared by dissolving in ethanol a dry portion of the dye. Samples of composite structures of two types were created. In the first case, the formation of composite structures involved the layer-by-layer application of their components. On a heated to 80°C glass substrate, EVA polymer was applied, after that, on the polymer layer, a layer of silica gel 60 was immobilized. On the resulting two-layer composite, the mixture of the solution of coumarin 7 in ethanol (concentration 10^{-3} M) with the aqueous solution of colloidal quantum dots CdTe in the ratio (1:1) was applied. The resulting composite was dried at a temperature of 65–70°C. The obtained samples were translucent with a matte surface and had a size of $7 \times 35 \pm 2$ mm and a thickness of 80 ± 5 μm (without substrate). In the second case, samples were created by applying a layer of Aerosil A-380 with immobilized coumarin 4 to the glass substrate. Immobilization of coumarin 4 on Aerosil was performed by sorption from the ethanolic solution of the dye with concentrations of 10^{-3} M and 10^{-4} M, followed by drying at room temperature.

Air mixtures with the required concentration of the analyte (acetone or ammonia) were obtained by the static volumetric method of preparation of gas mixtures, similar to that described in the international standard ISO 6144:2003 [17].

Measurement of the fluorescence response of nanostructured composite samples to the presence of certain concentrations of analytes in the gas samples was performed as follows. The synthesized samples were fixed in the quartz gas cuvette, which was placed in the measuring compartment of the fluorimetric device. Next, the fluorescence intensity kinetics of the samples was recorded. A certain volume of the prepared air mixture with the given concentration of analyte was cyclically pumped through the cuvette for a definite time at the first stage of the measurement. On the second, there was a pumping of clean air through the cuvette. The difference in the fluorescence intensity of the sample before pumping the gas mixture and at the end of pumping was considered the fluorescent response

of the sample. All data were registered in automatic mode with further processing on PC. Fluorescence excitation was performed at 485 nm and registration was at 528 nm for the samples with coumarin 7. Fluorescence excitation was performed at 340 nm and registration was at 360–600 nm for the samples with coumarin 4.

3. RESULTS AND DISCUSSION

We investigated the spectral-optical properties of ethanolic solutions of fluorescent dyes, aqueous solutions of quantum dots, as well as their donor-acceptor mixtures. The absorption spectra and the fluorescence spectra of ethanolic solutions of coumarin 7 and coumarin 4 dyes are presented in Fig. 1 and Fig. 2. Absorption (D) was measured in absolute units of optical density, and fluorescence (I) was measured in relative units of intensity.

The absorption spectrum of the ethanolic solution of coumarin 7 (Fig. 1 (*1*)) has a wide band in the range of 370–480 nm with a maximum near $\lambda_{max} = 430$ nm. The fluorescence spectrum (Fig. 1 (*2*)) has a band with a maximum at $\lambda_{max} = 508$ nm. The widths of the bands (full width at half maximum—FWHM) were $\Gamma = 150$ nm and $\Gamma = 51$ nm, respectively. The concentration of the dye coumarin 7 in ethanol was 10^{-3} M; the excitation of fluorescence was at $\lambda = 405$ nm.

The absorption spectrum of the ethanolic solution of coumarin 4 (Fig. 2 (*1*)) has a band in the range of 260–400 nm with a maximum $\lambda_{max} = 324$ nm. The fluorescence spectrum (Fig. 2 (*2*)) has a band with a maximum at $\lambda_{max} = 453$ nm. The widths of the bands were $\Gamma = 45$ nm and $\Gamma = 57$ nm, respectively. The concentration of the coumarin 4 dye in ethanol was 10^{-4} M; the excitation of fluorescence was at $\lambda = 370$–375 nm.

We have performed experiments to detect the effect of CdTe quantum dots on the fluorescence of the ethanolic solution of coumarin 7. The results showed an increase in fluorescence of coumarin 7 in ethanol by 57% when it mixed with the solution of CdTe quantum dots in a ratio of 1:1. This evidences that FRET takes place because there is an overlap of the fluorescence band of quantum dots and the absorption band of coumarin 7.

We will use the obtained spectra of coumarin 7 and coumarin 4 in ethanol solutions to compare with the spectra of composite structures, which include these dyes. It will allow us to study the spectral behaviour of molecules of these dyes depending on the molecular environment. It should be noted that our experimental data on ethanolic solutions of the studied dyes coincide with the known spectra [18] that indicates the reliability of our results.

A study of the spectral-optical properties of the samples was performed in order to determine the spectral ranges for the experi-
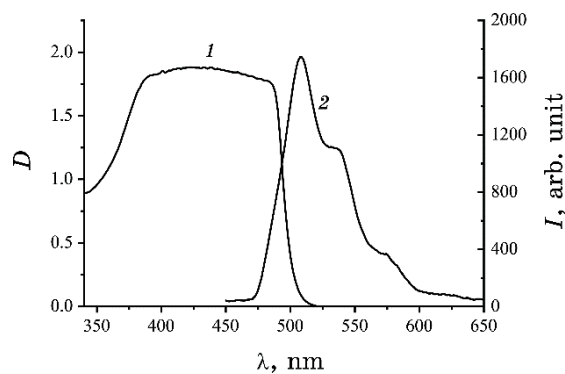
Fig. 1. Spectra of optical absorption (*1*) and fluorescence (*2*) of ethanolic solution of coumarin 7 with a concentration of 10^{-3} M.
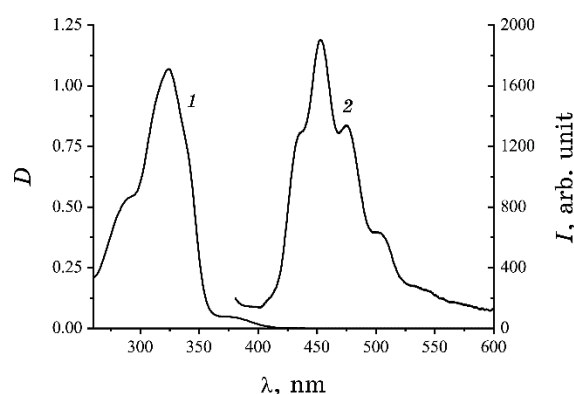
Fig. 2. Spectra of optical absorption (*1*) and fluorescence (*2*) of ethanolic solution of coumarin 4 with a concentration of 10^{-4} M.

mental study of the sensory properties of the synthesized samples of nanostructured composites based on coumarin dyes, CdTe quantum dots, and silicate matrices.

The spectra of matrices without fluorophores (polymer ethylene-vinyl acetate (EVA) with a layer of silica gel 60 as well as Aerosil A-380) obtained by us showed the practical absence of their own fluorescence at the wavelengths of the fluorescence range of coumarin dyes and quantum dots. This indicates that the fluorescence of the synthesized samples is due to the fluorescence of coumarin 4 or coumarin 7 molecules and CdTe quantum dots, and not the matrix material.

Figure 3 shows the absorption and fluorescence spectra of the synthesized composite structures with coumarin 7. As can be seen in Fig. 3 (*1*), the sample based on EVA and silica gel 60 with coumarin 7 and quantum dots of CdTe has a wide absorption band of 404–550 nm, with
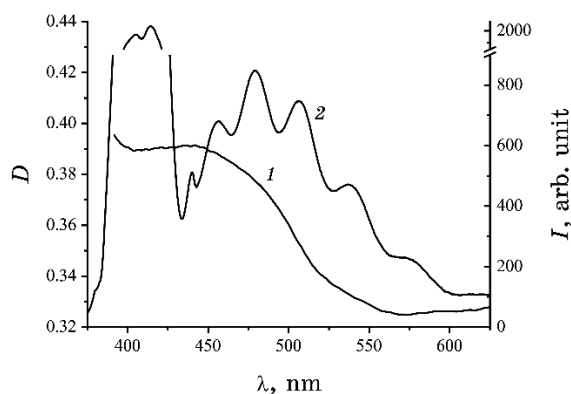
Fig. 3. The spectra of optical absorption (*1*) and fluorescence (*2*) of the sample of composite structures based on EVA and silica gel 60 with coumarin 7 and CdTe quantum dots.

a maximum of about $\lambda_{max} = 441$ nm. After 550 nm, the absorption spectrum reaches a value of approximately $D = 0.33$, due to the scattering of light by the sample. The fluorescence spectrum of the sample (Fig. 3 (*2*)) has a band with a maximum $\lambda_{max} = 478$ nm. The fluorescence bandwidth was $\Gamma = 118$ nm. The intense band in the range of 385–430 nm corresponds to the excitation radiation of the laser $\lambda = 405$ nm. The width of the absorption band because of the shape of the spectrum could not be determined exactly, it is approximately 80 nm. For such samples, a bathochromic (red) shift of the absorption band is observed in comparison with the ethanolic solution of coumarin 7 (Fig. 1) by 11 nm, while for the fluorescence band, a hypochromic (blue) shift of 30 nm.

Since the samples based on Aerosil A-380 with coumarin 4 were opaque due to high light scattering by Aerosil, instead of absorption spectra, fluorescence excitation spectra were measured, which generally essentially correspond to the absorption spectra of fluorescent substances [19]. Figure 4 shows the fluorescence and fluorescence excitation spectra of the synthesized composite structures with coumarin 4. The sample has a fluorescence excitation band of 310–360 nm with a maximum $\lambda_{max} = 340$ nm (Fig. 4 (*1*)). The fluorescence excitation bandwidth was $\Gamma = 45$ nm. The fluorescence spectrum of the sample (Fig. 4 (*2*)) has a band of approximately 400–600 nm. The intense band in the region of 360–450 nm corresponds to the excitation radiation of the laser $\lambda = 405$ nm (horizontal section $I = 2168$ corresponds to the 'upper counts' of the device). The position of the maximum and the width of the fluorescence band are difficult to establish due to the illumination of the excitation radiation in this area. For such samples, a bathochromic shift of the fluorescence excitation band by 16 nm is observed in comparison with the absorption band in the ethanolic solution of
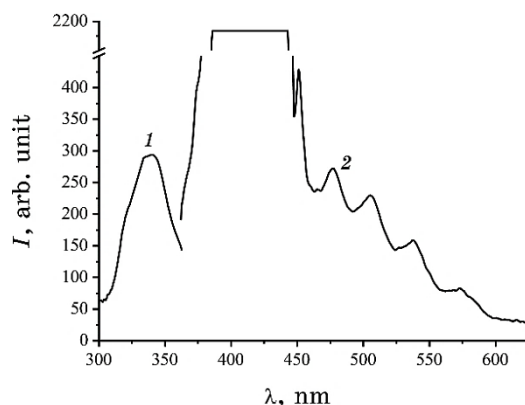
Fig. 4. The spectra of fluorescence excitation (*1*) and fluorescence (*2*) of the sample of composite structures based on Aerosil A-380 with coumarin 4.

coumarin 4 (Fig. 2).

The presence of shift of fluorescence bands of coumarin dye molecules in SiO_2 matrices (silica gel 60 and Aerosil A-380) relative to ethanol is explained by us that the medium of the matrixes has a higher polarity because the spectral behaviour of coumarin dyes depends on the polarity of the medium [20].

The study of the sensory properties of the created composite structures to ammonia and acetone was carried out, that is the fluorescence response of the samples interacting with analyte molecules in the air. The concentration of ammonia and acetone in the air was considered as the base, *i.e.*, equal to zero, because in pure air the concentrations of these VOCs were much lower than those studied. Our experiments showed the presence of an evident sensory response of samples with coumarin 7 to ammonia and with coumarin 4 to acetone (in air medium), which corresponds to a decrease in fluorescence intensity.

Figure 5 shows the fluorescence kinetics of the synthesized composite structures with coumarin 7 when they interact with ammonia molecules in the air. 500 ml of the air mixture with 5000 ppm (*i.e.*, million^{-1}) of ammonia was pumped in the time interval of 620–1100 seconds, and a decrease in fluorescence by 72% is observed. The cuvette with the sample was pumped with clean air in the time interval of 1100–2500 seconds, during which the fluorescence intensity of the sample was restored. Already in 1400 seconds, the fluorescence intensity was restored to 90% of the initial level. We interpret these results as follows. When air with ammonia is pumped, the process of sorption of ammonia molecules on the developed pore surface of the matrix element, silica gel 60, takes place. These molecules interact with immobilized molecules of coumarin 7 dye, re-
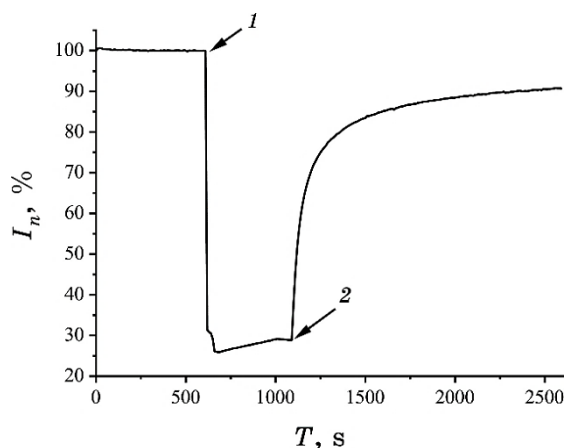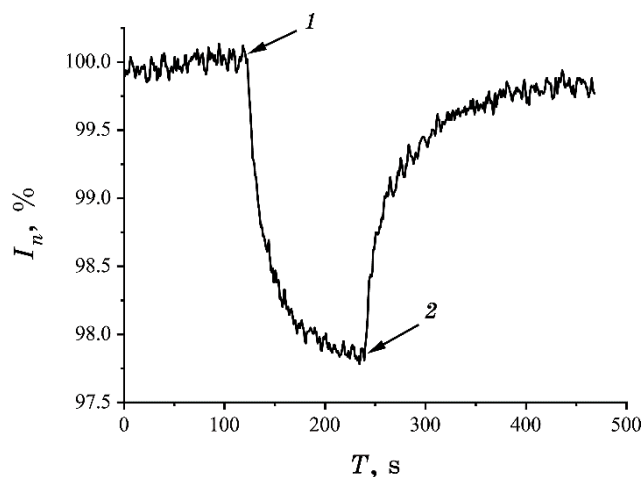
Fig. 5. The kinetics of fluorescence (normalized to 100%) of composite structures based on EVA and silica gel 60 with coumarin 7 and quantum dots of CdTe when interacting with ammonia in the concentration of 5000 ppm in air. *1*—the beginning of pumping the air mixture with ammonia; *2*—the beginning of pumping pure air.

sulting in a decrease in fluorescence intensity. This is due to the presence of a specific chemical interaction of ammonia molecules with coumarin cations and the formation of coumarin anion-ammonium cation complexes [1] that indicates a static mechanism of fluorescence quenching. The reverse process of desorption of ammonia molecules occurs during pumping with clean air, with the fluorescence signal of the sample is restored.

Figure 6 shows the kinetics of the fluorescence of the synthesized composite structures with coumarin 4 when interacting with acetone molecules in air. 1000 ml of the air mixture with 133 ppm of acetone was pumped during a time interval of 120–240 seconds, and the fluorescence was gradually decreased by approximately 2.2%. The cuvette with the sample was pumped with pure air in the time interval 240–470 seconds, and the fluorescence intensity of the sample was restored. Already after 230 seconds of the pumping, the fluorescence intensity was almost completely restored to the value of 99.8% of the initial one. We explain the mechanisms of falling and restoring the fluorescence intensity of such samples similarly: the sorption–desorption processes of acetone molecules on the pore surface of Aerosil A-380 and quenching of the fluorescence of dye molecules take place. However, the quenching of coumarin 4 fluorescence, unlike to coumarin 7, occurs due to the non-radiative de-activation of the excited state of coumarin 4 molecules by acetone molecules, the so-called dynamic quenching of fluorescence [10].

Fig. 6. The kinetics of fluorescence (normalized to 100%) of composite structures based on Aerosil A-380 with coumarin 4 when interacting with acetone in the concentration of 133 ppm in air. *1*—the beginning of pumping the air mixture with acetone; *2*—the beginning of pumping pure air.
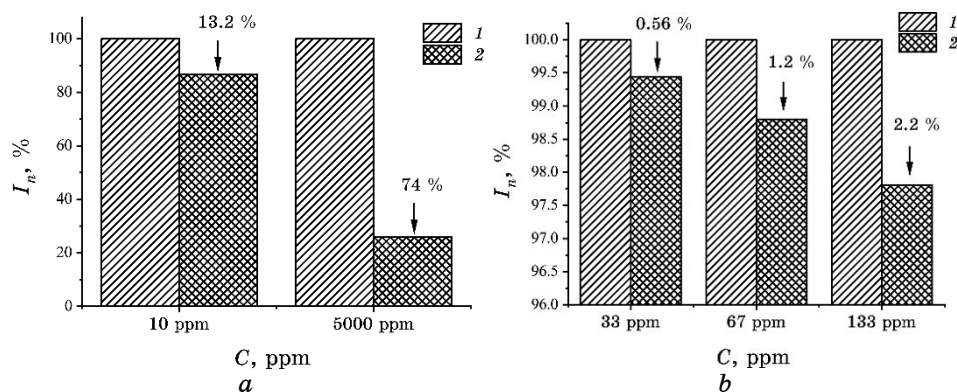
Fig. 7. Bar charts of the fluorescent responses (normalized to 100%) of the composite structures with coumarin 7 (*a*) for ammonia concentrations of 10 ppm and 5000 ppm, and with coumarin 4 (*b*) for acetone concentrations of 33 ppm, 67 ppm, and 133 ppm. *1*—the initial fluorescence intensity of the sample; *2*—the fluorescence intensity after interaction with the analyte.

Figure 7 shows the fluorescent responses of the composite structures with coumarin 7 (Fig. 7, *a*) and coumarin 4 (Fig. 7, *b*) for different concentrations of ammonia and acetone in the air, respectively. As can be seen in Fig. 7, *a*, the response to 10 ppm of ammonia was $13.2 \pm 0.6\%$, and to 5000 ppm was $74.0 \pm 1.1\%$. The response to 33 ppm of acetone was $0.56 \pm 0.08\%$, to 67 ppm was $1.2 \pm 0.1\%$,

and to 133 ppm was $2.2 \pm 0.1\%$ (Fig. 7, *b*). For both samples, the correlation of the value of the fluorescent response with the value of the concentration of analyte molecules in the air is observed.

Thus, we have shown the presence of a significant fluorescent response of the samples, as well as we demonstrated an evident correlation between the value of the fluorescence signal decrease of the samples and the change in analyte concentration in the air and the ability to restoring after ventilation. All this suggests that the composite structures created by us have a significant sensory sensitivity to ammonia molecules (composite with coumarin 7) and acetone molecules (composite with coumarin 4).

4. CONCLUSIONS

The spectral-optical properties of ethanolic solutions of fluorescent dyes of coumarin 7 and coumarin 4 as well as synthesized nanostructured composites, which include these dyes, are obtained. The presence of a significant shift of the spectral bands of coumarin dyes in the matrices of the synthesized samples in relation to the spectral bands of these dyes in ethanol has been demonstrated. This indicates a significant effect of matrix molecules on the electronic structure of the energy levels of coumarin dyes molecules. It was found that when mixing the CdTe quantum dots (fluorescence band position $\lambda_{max} = 530$ nm) with the ethanolic solution of coumarin 7 dye, the fluorescence intensity of the dye increased by 57%. This made it possible to increase the fluorescence intensity signal of the synthesized samples with coumarin 7 as well as to increase the sensory sensitivity of such samples to ammonia molecules. It has been shown that the composite structures with coumarin dyes developed by us show fluorescent sensitivity to molecules of ammonia (concentrations range 10–5000 ppm) and acetone (concentrations range 33–133 ppm) in the air. This sensitivity is due to static fluorescence quenching of QD (CdTe)—coumarin 7 complexes or dynamic fluorescence quenching of coumarin 4 molecules by molecules of the analytes.

The presence of a significant response of the synthesized by us nanostructured composites to ammonia and acetone molecules, as well as the ability to repeatedly restore the signal after aeration of samples with clean air, gives prospects for the use of these materials in portable sensors for non-invasive disease diagnosis, environmental monitoring.

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