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ENHANCEMENT OF LUMINESCENCE FROM A CARBON NANOTUBE AQUEOUS SUSPENSION AT THE CYSTEINE DOPING: INFLUENCE OF THE ADSORBED POLYMER

We have studied the enhancement of the luminescence intensity from semiconducting carbon nanotubes with the adsorbed polymer (DNA) in an aqueous suspension due to the doping with amino acid cysteine. The intensity increase is caused by the presence of a thiol group in the cysteine structure, which allows a reduction of defects on the nanotube surface that quench the emission. It is observed that the initial nanotube/polymer weight ratio affects the dependence of the luminescence intensity on the cysteine concentration so that it is shifted toward greater concentrations in case of the 1 : 1 ratio comparing to the dependence obtained for a suspension with the 1 : 0.5 ratio. Such shift can be explained by a greater surface coverage with the polymer that restricts the access of cysteine molecules to nanotube defects. We have also noted that the obtained dependences vary for nanotubes with different chiralities, which can be attributed to different densities of a polymer coverage on their surfaces.

Keywords: luminescence, exciton, cysteine, DNA, carbon nanotube, structure defect.

1. Introduction

Single-walled carbon nanotubes possess many unique mechanical, electrical, and optical properties. The luminescence from semiconducting nanotubes is of particular interest among optical properties of this nanomaterial, because it has unusual spectral characteristics and is described within the exciton model with unique parameters [1, 2]. The nanotube luminescence is characterized by narrow bands at room temperature, is free of an essential background, and is time-stable (without photobleaching and blinking) [3, 4, 5]. It is also of importance that the nanotube emission is located in the near infrared (NIR) range, where living tissues have a transparent “window.” This fact extends the possible applications of nanotubes to the sphere of nanomedicine, including luminescent diagnostics and photodynamic/photothermal therapy [6]. Excitons in carbon nanotubes have a huge binding energy (Coulomb interaction) between electron and hole (0.3–0.4 eV) [2]. This makes excitons very mobile along the nanotube, the diffusion length being over 100 nm [7]. Such high mobility is accompanied by the high sensitivity of the nanotube luminescence to a local environment and to the adsorption of various organic and biological molecules or nanoparticles on the nanotube surface. Such high sensitivity toward the external environment can be exploited to create various luminescent sensors [8].

The high mobility of excitons also leads to a small quantum yield of the nanotube luminescence in an aqueous environment (not above 1% [5]). This is caused, along with other reasons, by the creation of defects in nanotubes that quench the nanotube luminescence through the trapping of excitons followed by their nonradiative relaxation [9, 10]. In work [10], it was shown that the luminescence quantum yield can be enhanced by the interaction of nanotubes with small molecules that have redox activity (dithiothreitol, mercaptoethanol, trolox). It is assumed that they neutralize the impact of defects on the luminescence owing to their chemical properties. Specifically, dithiothreitol (DTT) [10, 11] and mercaptoethanol [10] show reducing properties due to the presence of thiol (–SH) groups in the structure.

We have shown [12] that the addition of cysteine to nanotubes also leads to an enhancement of the nanotube luminescence. This increase of the emission was explained by a reduction of defects, because this amino acid also contains the thiol group. We also note that, in these experiments, the water-soluble biopolymers were used for the solubilization of nanotubes to prepare their aqueous suspensions. In the mentioned experiments, DNA/RNA were used as such polymers, and their influence on the nanotube luminescence should be also considered. In our experiments concerning the influence of dithiothreitol on the nanotube emission [11], we have shown that the degree of polymer coverage of the nanotube surface influences strongly the efficiency of the reducing agent addition. It was assumed that a more complete coverage of the nanotube surface with a polymer, on the one hand, will enhance its luminescence, because it hinders the access of defect- making molecules [13] (for example, oxygen). On the other hand, such tighter coverage hinders the access of a reducing agent to already existing defects and decreases its impact on the luminescence.

In the present work, we have experimentally studied how the polymer coverage influences the nanotube luminescent properties, by using the doping with cysteine as a probe. The different polymer coverages of nanotubes were achieved through the preparation of two nanotube aqueous suspensions with different initial weight ratios of nanotubes/single stranded DNA (ssDNA). It is shown that this weight ratio has a great influence on characteristics of the nanotube luminescence and allows one to tune the dependence of the luminescence intensity on the cysteine concentration. It is also shown that the nanotube luminescence intensity increase that occurs upon the addition of cysteine into the suspension can be used for the detection of cysteine including the range of physiological concentrations.

2. Materials and Methods

Single-walled carbon nanotubes produced by the CoMoCAT method (SouthWest Nanotechnologies, USA) were used without additional purification. Nanotubes with (6,5) chirality prevailed in the starting material. Single-stranded DNA (ssDNA) obtained from natural double-stranded DNA [14] was used for the preparation of nanotube aqueous suspensions. Initial weight ratios of nanotube bundles and ssDNA were selected as 1 : 1 and 1 : 0.5 (300 μg of SWNTs in 1 mL of the aqueous suspension). For the preparation of ssDNA-wrapped nanotubes, a buffer solution (0.005 mol/L Na^+ cacodylate with 0.005 mol/L NaCl) was used. After the mixing of ssDNA and nanotubes, their aqueous suspension was sonicated using the water bath method during 30 min (22 kHz, 0.7 W) with the following ultracentrifugation (70000 g, 60 min).

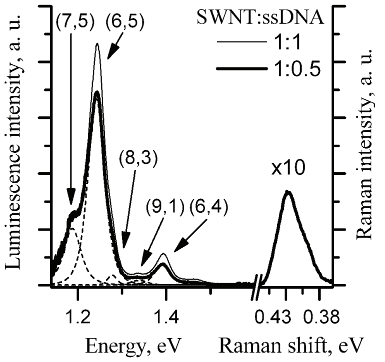

Fig. 1. Luminescence spectra of nanotube aqueous suspensions with different initial weight ratios of nanotubes and DNA (1 : 1 and 1 : 0.5, shown by thin and thick solid lines, respectively). Luminescence spectra are normalized to the intensity of the O–H stretching band ($\sim$3400 cm^{-1} or $\sim$0.42 eV) in Raman spectra observed simultaneously with the luminescence

The aqueous solutions of amino acid cysteine (Realab, Russian Federation) with concentrations of 10^{-6}–5×10^{-2} mol/L were prepared for the titration of nanotube suspensions. The minimal addition was 2 μL of a cysteine solution (10^{-6} mol/L concentration). The time delay between additions and the luminescence spectrum observation was 5 min.

The nanotube luminescence was excited using a diode-pumped solid state (DPSS) laser ($\lambda_{\text{exc.}} = 532$ nm, 5 mW). The luminescence was analyzed, by using a spectrometer, and detected by applying a thermocooled CCD-camera (spectral range 400–1150 nm). The NIR absorption spectra of SWNTs were obtained, by using a NIR spectrometer with a cooled InGaAs detector (900–1600 nm). Quartz cuvettes were used in all spectroscopic experiments (2-mm path length for the absorption registration).

3. Results and Discussion

Luminescence spectra of two ssDNA-wrapped nanotube aqueous suspensions with different initial weight ratios of nanotubes and the biopolymer (1 : 1 and 1 : 0.5) are shown in Fig. 1 in the 1.1–1.6 eV spectral interval. These suspensions will be further denoted as SWNT : ssDNA 1 : 1 and SWNT : ssDNA

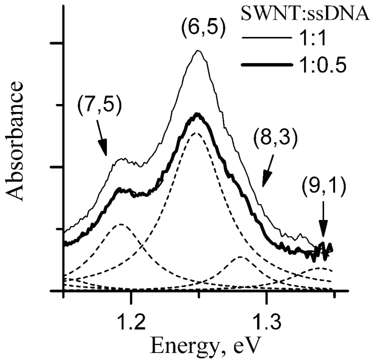

Fig. 2. NIR absorption spectra of nanotube aqueous suspensions with different initial weight ratios of nanotubes and DNA (1 : 1 and 1 : 0.5, shown by thin and thick solid lines, respectively). Spectral bands of individual nanotubes are shown for the suspension SWNT : ssDNA 1 : 0.5 and denoted by the corresponding chirality

1 : 0.5. We have performed the decomposition of spectra into bands corresponding to certain nanotube species. The superposition of these bands gives the resulting spectrum, which was fitted to the experimental one. Bands assigned to nanotube species are shown in Fig. 1 with thin dashed lines for SWNT : ssDNA 1 : 0.5 suspension, numbers in brackets denote the chirality of corresponding nanotubes [11, 15]. Both luminescence spectra were normalized to the intensity of the Raman band corresponding to the O-H stretching mode of water molecules ($\sim$3400 cm^{-1} or $\sim$0.42 eV), which was observed simultaneously with emission.

For both nanotube suspensions, the NIR absorption spectra were obtained in the spectral interval 1.15–1.35 eV (Fig. 2). The absorption bands were associated with nanotube species (7,5), (6,5), (8,3), (9,1) [15] (also observed in luminescence spectra).

It follows from Figs. 1 and 2 that both luminescence and NIR-absorption spectra of the suspension SWNT : ssDNA 1 : 1 have greater intensity comparing to corresponding spectra of the suspension SWNT : ssDNA 1 : 0.5. It is explained by the fact that the larger amount of the polymer suspends the greater amount of nanotubes in water. In addition, the different degrees of the polymer coverage of a nanotube surface in two suspensions should be taken into account, when the spectra are compared. It is known that, even upon an invariable amount of nanotubes in a suspension, a change of the polymer (DNA) coverage of their surface influences the luminescence intensity [13]. The assumption of different polymer coverages is also supported by the observation that the integral intensity of the emission spectrum of the SWNT : ssDNA 1 : 1 suspension does not exceed twice the intensity of the SWNT : ssDNA 1 : 0.5 one. We revealed that the integral intensity of the SWNT : ssDNA 1 : 1 spectrum (both luminescence and NIR absorption) is larger by only about 30% of the SWNT : ssDNA 1 : 0.5 spectrum. This experimental observation allowed us to assume that the surfaces of individual nanotubes in the SWNT : ssDNA 1 : 0.5 suspension are covered by a smaller amount of polymer than those in the SWNT : ssDNA 1 : 1 suspension. This is also confirmed by the fact that a noticeable amount of nanotubes in the SWNT : ssDNA 1 : 0.5 suspension aggregated into bundles and precipitated after 4 months of storage. For the suspension SWNT : ssDNA 1 : 1, no similar precipitation of nanotubes was observed, which indicates their greater stability. In other words, a greater amount of the adsorbed polymer provides the better temporal stability of nanotubes in a suspension.

To understand better the influence of the polymer coverage on the emission properties of nanotubes, we compare the observed spectra of two suspensions in more details. Bands in the emission spectrum of the SWNT : ssDNA 1 : 0.5 suspension are slightly (not more than 2 meV) red-shifted comparing to similar bands in the SWNT : ssDNA 1 : 1 spectrum. We assume that such shift occurs due to a smaller degree of polymer coverage of nanotubes in the first suspension, so that their surface is more exposed to water. It is known that the spectral position of bands in the nanotube luminescence spectrum depends on the dielectric constant of a medium [16]. The smaller value of this constant means that the nanotube surface is more isolated from water. As a result, the nanotube bands are shifted toward higher energies in the spectrum. As for the NIR absorption spectra, the spectral shift for certain bands is smaller (not above 1 meV), and the shift is not observed at all for some bands. The smaller spectral shift for these spectra can be related to a greater width (at half of the height) of bands (by $\sim$10%) comparing to the luminescence one. A greater spectral width for the absorption can appear due to the contribution of small nanotube bundles, which may not be observed in the emission spectra, for example, because of the presence of metallic nanotubes quenching the luminescence in such bundles. Although the amount of nanotubes with metallic conductance is small (not above 10%) in the investigated samples, nevertheless, one such nanotube can quench the luminescence of all semiconducting nanotubes in a small bundle.

The detailed analysis of spectra (Figs. 1 and 2) has shown that the intensity increases differently in spectral bands, when we pass from the SWNT : ssDNA 1 : 0.5 spectrum to SWNT : ssDNA 1 : 1 one. Note that the luminescence spectra demonstrate a more essential difference in the band intensity increase. For example, the band attributed to (7,5) nanotubes shows only a small rise of the emission integral intensity (3–4%). We can also note that namely this band does not show any spectral shift under comparison of the spectra of two suspensions. As for the bands assigned to (6,5) and (6,4) nanotubes, the spectral shift is about 1.5 meV, and their integral intensity differ in the luminescence spectra by 23% and 40%, respectively. These differences for bands attributed to various nanotubes suggest that the biopolymer can adsorb differently on nanotubes with different chiralities. The heterogeneous adsorption can be caused by the different interaction energies between DNA and nanotubes of different chiralities. The observed difference in the luminescence intensity increase for various spectral bands cannot be explained by the transfer of excitons between adjacent semiconducting nanotubes (from nanotubes with greater band gap to those with smaller one) [17]. In the experiments, on the contrary, we observe a stronger luminescence intensity increase (upon comparison of two suspensions) for nanotubes with greater band gap [17].

The relative contents of (7,5), (6,5), and (6,4) nanotubes in two suspensions can be approximately estimated from the comparison of the intensities of their bands. If we denote the integral intensity of (7,5) band as 1, the ratio of the integral intensity of three mentioned bands for the SWNT : ssDNA 1 : 1 suspension is 1 : 3.7 : 0.44, while this ratio for the SWNT : ssDNA 1 : 0.5 one is 1 : 3 : 0.32. From these ratios, it follows that the content of (6,5) and (6,4) nanotubes is higher in the SWNT : ssDNA 1 : 1 suspension. We can also assume (considering the spectral shifts of these bands in two emission spectra) that they have more adsorbed DNA on their surface comparing to the SWNT : ssDNA 1 : 0.5 suspension.

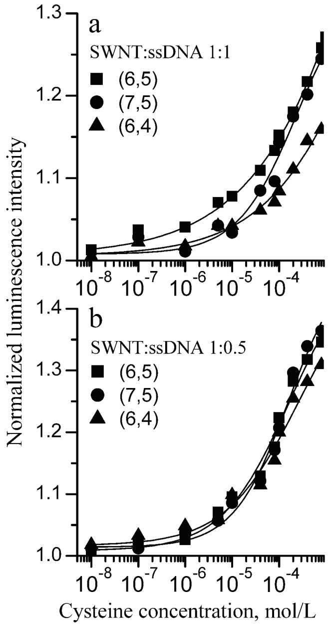

Fig. 3. Dependences of normalized integral luminescence intensities of (6,5), (7,5), and (6,4) nanotubes on the cysteine concentration in two aqueous suspensions: SWNT : ssDNA 1 : 1 (*a*) and SWNT : ssDNA 1 : 0.5 (*b*)

The influence of the nanotube polymer coverage on the luminescent properties was further studied by the titration of a nanotube aqueous suspension with cysteine, which acts, in fact, as a molecular probe. The titration with cysteine was performed for two aqueous suspensions, so that its concentration ranged from 10^{-8} to 10^{-3} mol/L. The concentration dependences of emission integral intensities for (7,5), (6,5), and (6,4) nanotubes are presented in Fig. 3. In each case, the normalization on the integral intensity of the corresponding band in the spectrum of a suspension without cysteine was performed. We note that the cysteine addition into a nanotube aqueous suspension did not affect their NIR absorption spectrum.

The dependences of the nanotube luminescence intensity on the cysteine concentration doping demonstrate the emission enhancement with the amino acid increasing concentration in the suspension (Fig. 3). We have assumed earlier that such enhancement can be related to the ability of cysteine to reduce p-defects due to the presence of a thiol group in the structure of this amino acid [12]. These defects can be formed when oxygen binds covalently to carbon atoms in nanotubes [9]. In this case, certain atoms of a nanotube are in the sp^3-hybridized state. At the same time in a defect-free nanotube, the delocalized π-electrons

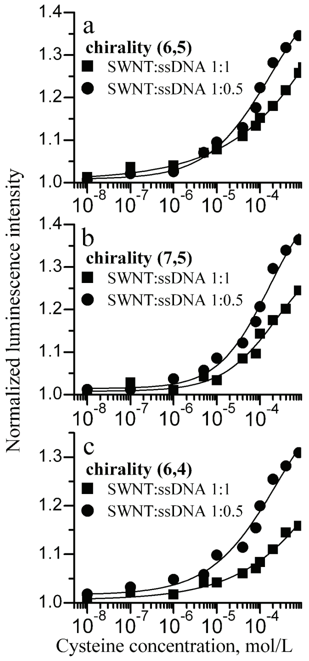

Fig. 4. Dependences of the normalized integral intensity of the nanotube emission on the cysteine concentration for three bands assigned to (6,5) (*a*), (7,5) (*b*), and (6,4) (*c*) nanotubes, which is observed in the luminescence spectra of SWNT : ssDNA 1 : 1 (full squares) and SWNT : ssDNA 1 : 0.5 (full circles)

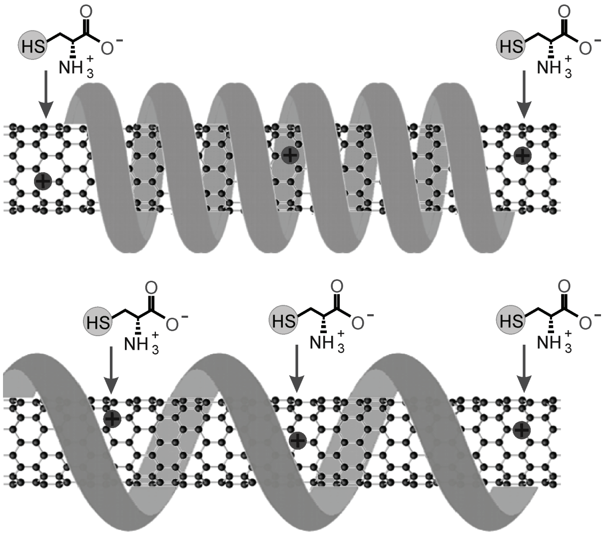

Fig. 5. Schematic picture showing the polymer wrapping around the nanotube with small pitch (top) that restricts the access of cysteine to the nanotube surface sites and wrapping with a larger pitch (bottom) which allows the access of cysteine molecules to the nanotube

(in case of sp^2 hybridization) form a conjugated system. This means that the binding of oxygen results in the formation of defects in the zone structure and the appearance of holes in the valence band, which serve as traps for excitons [10].

Upon comparing the emission intensity increase for two suspensions, we can note that, for (6,5) nanotubes, the final enhancement is ∼25% for the SWNT : ssDNA 1 : 1 suspension and ∼35% for the SWNT : ssDNA 1 : 0.5 one (Fig. 2). As the cysteine concentration was varied by 5 orders of magnitude, the logarithmic scale was used for the concentration axis in the plotted dependences. Experimental values were fitted with sigmoidal curves

$$I(x)/I(0) = A_2 + \frac{A_1 - A_2}{1 + (x/x_0)^p}$$

(where: $I(x)$ is the luminescence intensity of suspensions at the cysteine concentration x; A_1, A_2, x_0, and p are fitting parameters).

It follows from Fig. 3 that, for the SWNT : ssDNA 1 : 0.5 aqueous suspension, the concentration dependences of the luminescence intensity have approximately the similar behavior for three bands corresponding to (7,5), (6,5), and (6,4) nanotubes. As for the SWNT : ssDNA 1 : 1 suspension, the dependence of the (7,5) nanotube band intensity is more steep in the concentration range of 5×10^{-5}–10^{-3} mol/L of cysteine comparing to those dependences of (6,5) and (6,4) nanotubes.

Further, we carried out a more detailed analysis of the emission dependences on the cysteine concentration for nanotubes with the same chirality, but in different suspensions. Such comparison of the dependences is presented in Fig. 4 for nanotubes with chiralities (6,5), (7,5), and (6,4). It follows from the comparison that, for nanotubes of all three chiralities, the concentration dependences are more steep for the aqueous suspension with the SWNT : ssDNA 1 : 0.5 ratio comparing to the second suspension (with 1 : 1 weight ratio). For (6,5) nanotubes, this trend is observed in the concentration range 10^{-5}–10^{-3} mol/L. We assume that the differences in concentration dependences of the emission of three nanotube bands can appear due to different polymer coverages of their surface in two suspensions, and this difference influences the nanotube defect reducing by cysteine. The less amount of polymer strands on nanotubes in the SWNT : ssDNA

1 : 0.5 suspension makes their surface more accessible for cysteine molecules comparing to the polymer-wrapped nanotubes in the SWNT : ssDNA 1 : 1 suspension. This fact has an effect on the sensitivity of the luminescence of the SWNT : ssDNA 1 : 0.5 suspension to the cysteine molecules and on the concentration dependence behavior so that this suspension shows a stronger enhancement at the same amino acid concentration.

A steeper rise of the concentration dependence for (7,5) nanotubes comparing to (6,5) and (6,4) in case of the SWNT : ssDNA 1 : 1 suspension (in the concentration range of 10^{-5}–10^{-3} mol/L) can appear due to a greater accessibility of defects on the (7,5) nanotube surface to cysteine in this suspension. The greater influence of defects on the luminescence from these nanotubes is also manifested in a small increase of the emission intensity in the spectrum of the initial suspension with a larger polymer amount (3–4%). In the NIR absorption, the intensity of the band corresponding to these nanotubes is increased by 30%, and this value is close to the increase of the absorption of other nanotubes. This means that the amount of (7,5) nanotubes is increased by a third, but they demonstrate a very weak emission. These experimental observations point out that DNA that adsorbs on the surface of (7,5) nanotubes has a disordered conformation. It is possible that wrapped DNA has a large pitch as it is schematically shown in Fig. 5. Less dense polymer coils on the nanotube assist the adsorption of cysteine molecules on its surface between the rare coils, including the adsorption on the defect sites.

We paid a special attention to the comparison of the emission intensity increase at the cysteine addition into two suspensions in the concentration interval 50×10^{-6}–200×10^{-6} mol/L. Exactly in this concentration interval lies the content of cysteine in the healthy human organism. For the comparison, we have chosen the most intense band in the luminescence spectrum at 1.24 eV corresponding to (6,5) nanotubes. Figure 6 shows the linear fits of experimental values, by starting from the 4×10^{-5} mol/L concentration for each suspension. The ranges of physiological concentrations in human urine [18] are also shown in Fig. 6 for healthy men and women. It follows from Fig. 6 that a deviation of the linear fit line from experimental values is not essential and is about ±1.5%.

We indicate that the linear dependence of the emission intensity on the concentration logarithm can be used for the detection of cysteine and for the determination of its concentration. It should be noted that cysteine performs important functions in organism and its abnormal level can be a sign of certain diseases like cardiovascular diseases, Huntington's disease, *etc.* Therefore, the control over its level in human organism is a necessary task. The intensity of the Raman band corresponding to the O–H stretching mode of water molecules (~3400 cm^{-1} or ~0.42 eV) observed simultaneously with the nanotube emission can serve as a checkpoint to normalize the luminescence intensity in future biosensors.

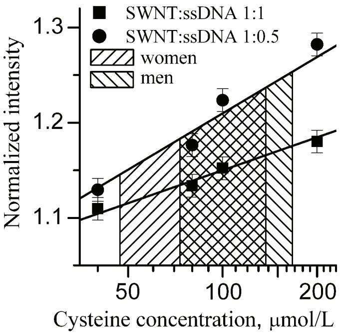

Fig. 6. Experimental values of the normalized integral emission intensity for the most intense band assigned to (6,5) nanotubes at different cysteine concentrations and their linear fits in case of SWNT : ssDNA 1 : 1 and SWNT : ssDNA 1 : 0.5 aqueous suspensions. Two areas with different hatches show the ranges of physiological cysteine concentrations in urine for men and women

4. Conclusions

The addition of cysteine into an aqueous suspension of nanotubes with adsorbed DNA enhances the luminescence of semiconducting nanotubes. This enhancement is explained by a reduction of luminescence-quenching defects on the nanotube surface with the thiol group of cysteine.

The increase of the nanotube luminescence intensity at the cysteine doping of suspensions containing nanotubes depends on the degree of polymer (single-stranded DNA) coverage of the nanotube surface. The different polymer coverages were obtained by the preparation of suspensions using different initial weight ratios of nanotubes : polymer 1 : 1 and 1 : 0.5. It is found that this initial ratio has an essential influence on the dependence of the nanotube luminescence on the cysteine concentration. For the suspension with 1 : 1 ratio, the dependence is shifted to higher concentrations of the amino acid. This can be explained by a greater degree of polymer coverage of the nanotube surface in the suspension with a higher ratio, which restricts the access of a cysteine molecule to nanotube defects. The different concentration dependences of the emission from the nanotubes of different chiralities is also revealed. This observation points out on the different binding energies of DNA with different nanotubes.

The experiments shows that the nanotube luminescence can be used for the detection of cysteine in aqueous solutions, firstly, due to the selectivity of the luminescence enhancement provided by a presence of a thiol group only in the cysteine structure among all amino acids, secondly, due to the linearity of the dependence of the luminescence intensity on the cysteine concentration (on semilogarithmic scale) in the interval of 50–200 μmol/L, which corresponds to the level of cysteine in healthy human organism. We can also note that the level of detection of cysteine due to the nanotube luminescence enhancement is about 10^{-6} mol/L.

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ЗРОСТАННЯ ЛЮМІНЕСЦЕНЦІЇ ВУГЛЕЦЕВИХ НАНОТРУБОК У ВОДНІЙ СУСПЕНЗІЇ ПРИ ДОПУВАННІ ЦИСТЕЇНОМ: ВПЛИВ АДСОРБОВАНОГО ПОЛІМЕРУ

Резюме

Вивчалося зростання інтенсивності люмінесценції водної суспензії напівпровідникових вуглецевих нанотрубок з адсорбованим полімером (ДНК) при допуванні амінокислотою цистеїном. Зростання інтенсивності люмінесценції нанотрубок зумовлене наявністю тіольной групи в структурі цистеїну, за допомогою якої відбувається відновлення дефектів на нанотрубковій поверхні, що гасять світіння. Встановлено, що початкове вагове співвідношення нанотрубки:полімер істотно впливає на залежність інтенсивності люмінесценції від концентрації цистеїну, яка при співвідношенні 1 : 1 зсувається в діапазон великих концентрацій амінокислоти в порівнянні із залежністю, отриманою при співвідношенні 1 : 0,5. Такий зсув пояснюється більш значним покриттям поверхні нанотрубок полімером, який блокує доступ молекул цистеїну до дефектів. Відзначається також відмінність в цій залежності для нанотрубок різної хіральності, яка пов'язана з різною щільністю полімерного покриття поверхні різних нанотрубок.