535. Influence of pH on intensity of luminescence of one layer carbon nanotubes in water environments

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Abstract. Monitoring of sewages by using carbon one layer nanotubes (OLNT) for the exposure of the toxic troop landing revealed the possibility of their use for the express-analyses [1]. At the same time the OLNT intercommunication with the hydrogen index of rN solutions is of special interest, including the luminescence. Luminescence of semiconductor one layer carbon nanotubes was discovered in 2002 [2], right after it was obtained their firm water suspension in surroundings superficially of active matter [3]. Plaits of nanotubes at which they are found at ordinary terms, it was succeeded to slit by means of ultrasonic activation in an aqueous environment. The radiation of nanotubes takes place as a result of annihilation of electron-hole pair which appears in semiconductor nanotubes as exciton at absorption of quantum of light.

Keywords: nanotubes, luminescence, monitoring, water suspension.

Introduction

Theoretical computations of the area structure OLNT testify that as a result of single dimensionality of nanotubes, both in the area of conductivity, and symmetric to the lances of closeness of the states (Fig. 1), which got the Van't Hoff singularities, appear in a valency area [4].

By the pointer E^S22 transition with absorption of photon between the second pair of Van't Hoff singularities (v2, c2) is marked, and pointer E^S11 indicates transition with the radiation between the first pair of peaks (v1, c1) after relaxation of excitation (the transition c2>s1).

Between the proper lances located in different areas, there are electronic transitions with absorption of photon, which result in absorption of light. Researches [2] demonstrated that the first inter-area transition in semiconductor nanotubes was found in a near infra-red range 0,8-1,3 eV, the size of energy of transition relies on chirality of nanotubes, that is on their diameter. Thus, the nanotubes of small diameter have the most width of the forbidden region, and the nanotubes of greater diameter count for little energy. Other inter-area transition between the second pair of Van't Hoff singularities has approximately 2 times larger values of energy (1,5-2,5 eV), and is observed in a visible range. The third transition has energy approximately 3 times higher in comparison to the first transition, and is found in ultraviolet range, and etc.

As nanotubes of different diameters appear at the synthesis, in a spectrum the absorption of light there is the row of separate peaks, answering separate electronic transitions. Each of these peaks has wings which are conditioned by electron-photon co-operation. At absorption of light in a visible range there is transition between the second pair of Van't Hoff singularities (Fig. 1). Rapid relaxation of excitation on the lower level of energy, from which there is the radiation of quantum of light, having energy which answers the first inter-area transition of nanotubes of definite diameter.

By means of such method, analyzing spectrum of absorption or luminescence, it is possible to define nanotubes chirality and their diameter.

Detection of luminescence of nanotubes opened a wide spectrum of experimental possibilities for study of both nanotubes and implementation of researches of cooperation of nanotubes on conditions of different external surroundings, for example in solutions with different pH. Already the first publications on research of luminescence of nanotubes demonstrated influence of pH on intensity of their luminescence (radiation) [2].

These research works are significant since until now there are many unanswered questions, for example, as luminescent properties of nanotubes depending on the type of superficial-active matter will change that is contained in solution.

In the present work we investigated luminescence of two water-suspended carbon nanotubes, which contained the superficial-active matters (FALLING) of different type. Influence of pN solution on luminescence of nanotubes was studied as well.

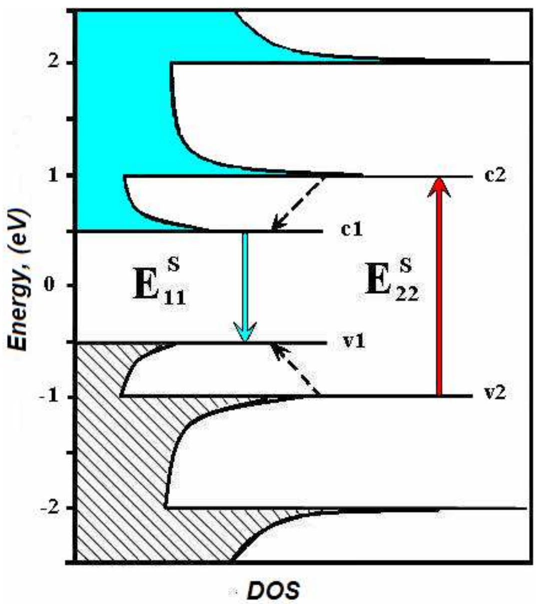

Fig. 1. Power diagram of closeness of the states of semiconductor nanotubes in which lances in the area of conductivity (top) and valency area (bottom) show up, refereed to as Van't Hoff singularities

Details of experiment

OLNT, which was used in the current research, was obtained by means of recently developed method in US that allows to rear, mainly, the semiconductor nanotubes of definite chirality. In the explored standards gravimetric part of nanotubes made 90%, here part of semiconductor nanotubes was evened 90%, from them no less than a half was on the nanotubes of definite chirality (6,5).

Carbon nanotubes (0,05 mg/ml) in water solution with maintenance of superficial-active matter was suspended by ultrasonic homogenizer, performing the disperging for 40 minutes (20 Vt, 44 kGts). As a superficial-active matter we used the following detergents: sodium dodecylbenzene sulfonate (SDBS, $CH_3(CH_2)_{11}C_6H_4(SO_3)^-Na^+$) and sodium dodecyl sulfate (SDS, $CH_3(CH_2)11(SO_4)^-Na^+$), the structural formulas of which are presented in Fig. 2.

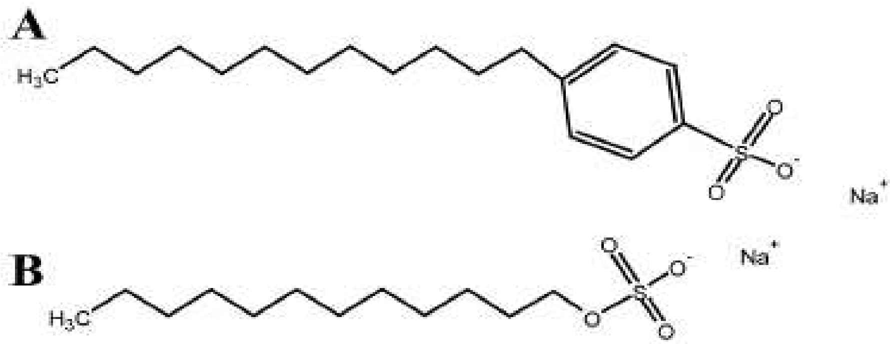

Fig. 2. Structures of sodium dodecylbenzene sulfonate (SDBS) (A) and sodium dodecyl sulfate (SDS) (B)

Concentration of PEAHENS in aqueous solutions was evened 1%. The unsplit plaits of nanotubes were deleted by means of centrifugation (30 000 g) during 1 hour.

Luminescence of semiconductors UONT, which was heated by a diode laser with a wave-length generation 2,33 eV ($\lambda_в$=532 nm), selected by means of double monohromator (9000-12000 sm^{-1}) and registered by means of cooled FEU-83-83.

Results of researches

In Fig. 3 the spectrums of luminescence of water suspension of semiconductor nanotubes are represented, that contain SDBS and SDS.

Spectrums of luminescence of the explored standards at excitation by a diode laser with $\lambda_в$=532 nm (2,33 eV) are located in near IR-range with energy from 0,8 to 1,5 eV. For them there is the characteristic presence of a few peaks which correspond to luminescence of nanotubes of definite chirality. Approximation of spectrums was executed by the sum of ten functions Lorentt, from which we selected 3 for the consideration, which have the most integral intensity and correspond to nanotubes with chirality: (6,5) - diameter 0,757 nm, peak position - 1.24 eV; (7,5) - diameter 0,829 nm, peak position 1,19 eV; and (9,4) - diameter 0,916 nm, peak position 1,09 eV [5]. Integral intensity of bar corresponds to the nanotubes with chirality (6,5) and approximately equals the sum of integral intensity of other bars.

During approximation was definitely semiwidth of bars that correspond to separate nanotubes of definite chirality, which made 40-50 meV. In an experimental spectrum the width of bars is a bit greater. Approximation showed that the width of bars in this spectrum is conditioned by superposition of a few lines.

We will emphasize that for the given standards there is characteristic maintenance of semiconductor nanotubes of small diameter.

Comparison of integral intensity of radiation of two suspensions of nanotubes which were got approximately on conditions of identical gravimetric correlations of reagents and at identical pH=7 was executed. Measuring for both standards was executed in the same optical cuvette with saving of all optical position of devices and at identical power of laser. On the basis of comparison, it was determined that integral intensity of standard of nanotubes, which contains SDBS, is approximately 8 times higher than intensity of standard of nanotubes with the SDS maintenance. Most probably, it is related to different efficiency of maintenance of nanotubes in water suspension for two used superficial-active matters, which is determined by their co-operation with the surface of nanotubes. SDBS and SDS are is the superficial-active matters of anionic type, however the first connection, unlike the second, has a benzol ring (Fig. 2). It is known that π-electronic structure of such hetero-system effectively co-operates with the surface of nanotubes [6, 7]. In addition, it follows to take into account also the additional deposit of energy of hydrophobic cooperation which appears in water surroundings and is instrumental in reduction of area of hydrophobic surfaces [8]. As a benzol ring and surface of nanotubes are hydrophobic, the contact between them gives increase in hydrophobic energy exactly due to reduction to the area of hydrophobic surfaces that contact by water.

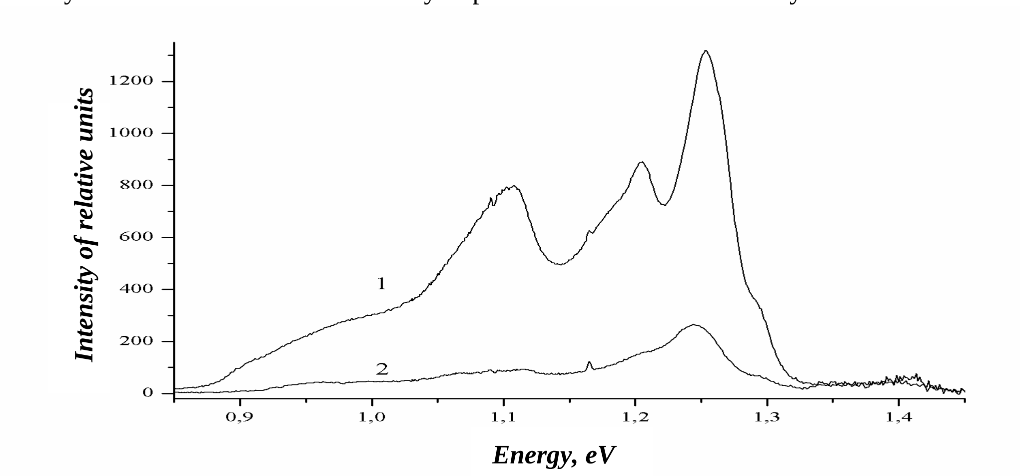

Fig. 3. Spectrums of luminescence of water suspension of semiconductor nanotubes with the use of (1) SDBS (intensive) and (2) SDS (weak). Luminescence was obtained at excitation by a diode laser with $\lambda_в$ =532 nm (2.33 eV)

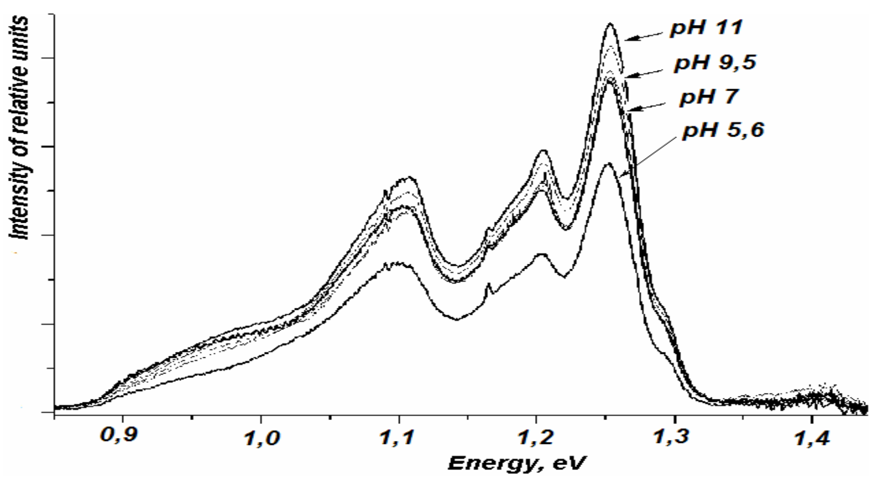

Fig. 4. Spectrums of luminescence of water suspension of semiconductor nanotubes with SDBS at different pH. Luminescence was heated by light of diode laser with $\lambda_в$=532 nm (2,33 eV)

Thus, the SDBS co-operation with the surface of nanotubes will be prepotent in comparison to case of SDS. As a result, the quantity of nanotubes in water suspension will be higher in a standard from the first detergent. Thus, the larger quantity of nanotubes will result in luminescence of nanotubes with greater integral intensity.

There also exists another possible reason that causes change of intensity of luminescence. This is charge screening by the superficial-active matter of electronic closeness on nanotubes. In the ideal case at the continuous location of detergent on the surface of nanotubes negative charges will be remote from a tube, however, at the uncontinuous filling of surface of nanotube some of charged „tails" of detergent can be found near-by or in contact to the surface of nanotubes. At that rate, localization of electrons, which will be removed on filling of area of conductivity of nanotubes and which will result in reduction of probability of absorption of photon by nanotubes, will occur in this point of surface.

For the study of influence of pH on intensity of luminescence of semiconductor nanotubes a standard with SDBS was chosen, to which the largest intensity radiation is inherent. As measurements showed, intensity of spectrum of illumination of nanotubes changes depending on pH water suspension (Fig. 4). So, maximal intensity of luminescence is observed at pH=7-9, and at reduction, or increase of pH (from this interval) intensity of luminescence diminishes. The spectrums of radiation at different pH were the approximation sum Lorentt. Dependence of change of intensity of luminescence in these bars from pH is represented in Fig. 5.

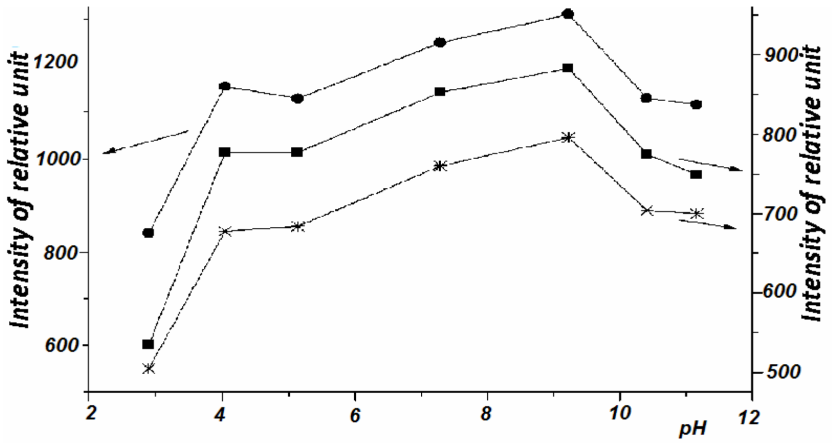

Fig. 5. Dependence of intensity of peaks of luminescence of nanotubes on pH (● - peak on 1,24 eV, ■– peak on 1,19 eV, ж - peak on 1,09 eV). Experimental points are connected by lines

As visible from the Fig. 5, more considerable weakening of intensity of luminescence takes place in a sour environment, at the small values of pH. So at reduction of pH from 7 to 4 intensity of luminescence diminished by 30-40%, and at the increase of pH from 7 to 11 intensity of luminescence diminishes by 15-20%. In the range of pH from 4 to 10 change of intensity has a reverse character. At the values of pH less than 3 there is an aggregation of nanotubes, which becomes noticeable visually. The aggregates of nanotubes in few hours fall out in sediment and intensity of luminescence falls. These supervisions are indicated, formed by the SDBS molecules round nanotubes, collapse at deviation from neutral pH, thus in a sour environment, at pH<3 the changes carry an irreversible character.

Conclusions

Intensity of luminescence of water suspension of semiconductor nanotubes with the use of SDBS detergent is considerably higher in comparison to SDS application. It is related to a more effective maintenance of the SDBS separate nanotubes in a water environment.

Spectral studies of standards of nanotubes as water suspension demonstrated that at pH less than 7, and at pH more than 9, there occurs weakening of intensity of luminescence of semiconductor nanotubes by 30-40% and 15-20% respectively. At pH<3 the changes of intensity of radiation become irreversible, as there is aggregation of nanotubes that results in their sedimentation.

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