

FUNCTIONALIZATION OF CARBON NANOTUBES BY DIFFERENT BIOMOLECULES FOR STABLE DISPERSION IN WATER

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To select the effective methods for functionalizing carbon nanotubes and to compare the ability of a number of biological molecules (plasmid DNA, ATP, mix of deoxyribonucleoside triphosphates, bovine serum albumin, compounds of vitreous humor extract and sodium humate) to interact non-covalently with carbon nanotubes and mediate their dispersion in an aqueous medium was the aim of the work. Properties of carbon nanotubes-biomolecules conjugates were characterized using ultraviolet, visible and near infrared spectroscopy, Raman spectroscopy, transmission electron and atomic force microscopy. Formation of stable aqueous polydisperse colloidal systems of single-walled and multi-walled non-covalently functionalized carbon nanotubes was shown. The appearance of extended functionalization coating consisting of biomolecules on the surface of carbon nanotubes was demonstrated. Changes in morphology and structure of carbon nanotubes, namely shortening and the appearance of defects in sp²-hybridized surface caused by functionalization were revealed. As a result, the range of molecules of biological origin suitable for noncovalent functionalization of carbon nanotubes was chosen, with correspondence to the specific use in plant biotechnology and the properties of formed conjugates were characterized.

Key words: single- and multi-walled carbon nanotubes, noncovalent functionalization, biomolecules.

Growing use of carbon nanotubes (CNTs) in biotechnology requires the development of methods to modify them in order to overcome hydrophobicity, improve biological compatibility and specificity as well as introduce various properties of interest to CNTs [1, 2]. CNTs earn great interest in terms of their promising applications for imaging in biological systems [3], constructing supersensitive sensors [4] and targeted delivery of different molecules into living cells [5–14]. CNTs have already been successfully used to deliver DNA [7, 15, 16], small interfering RNA [8, 9], proteins [10, 17] and therapeutic agents [6, 11, 12–14] into animal cells. CNTs were used to carry DNAs for genetic transformation of bacterial [18–20] and mammalian cells [7, 15, 16, 21]. The involvement of CNTs into the development of novel approaches for genetic transformation

in plant biotechnology is associated with a number of benefits including increased efficiency, wide taxonomic applicability together with no need to use excess energy and toxic compounds [22]. Several studies have demonstrated the ability of CNTs to deliver molecular cargos in protoplasts [23, 24] and walled plant cells [25, 26].

The exceptional properties of CNTs for use in biotechnology are determined by a combination of their physical, chemical characteristics and nanosize. CNTs are rolled into a seamless tube graphene layers in which carbon atoms form a hexagonal lattice. Depending on the number of walls (layers) CNTs are classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [27, 28]. SWCNTs consist of a single graphene cylinder with diameters varying within a

range of 0.4–2 nm. Depending on how the two-dimensional plane of graphene is rolled about its hexagonal lattice SWCNTs are divided into three types, namely “armchair”, zig-zag and chiral which differ in structure and properties. MWCNTs consist of several nested coaxial graphene cylinders. Depending on the number of walls outer diameter of MWCNTs can vary from 2 nm to 100 nm, while their inner diameter is about 1–3 nm. Lengths of CNTs range from hundreds of nanometers to tens of microns. In the structure of CNTs two functionally different areas are distinguished: tube with hexagonal carbon atoms placement and the end zone (cap), built of alternating five- and six-membered cycles similar to a hemisphere of the fullerene molecule [29]. Binding of functional groups during chemical modification process primarily occurs in the end zones and in the defects of sidewalls (pentagon-heptagon couples, sp^3 -hybridized carbon atoms, vacancies in the lattice of nanotube, “open” ends etc.) which have increased reactivity compared to an ideal polyaromatic surface of CNTs [2, 30].

For different applications the surface properties of CNTs are modified using covalent and non-covalent functionalization approaches. Covalent functionalization of CNTs is widely used. It usually generates numerous breaks in continuous π -network and significant change or loss of specific mechanical, optical and electronic properties of CNTs. Commonly covalent functionalization includes chemical treatment (using nitric, sulfuric, perchloric and other acids, esters, aldehydes, amines, thiols, aryldiazonium cations, carbenes, ozone, osmium tetroxide, chromates). It is frequently combined with the use of microwaves, ultrasound, pulsed discharge, cryogenic destruction, γ -irradiation [1, 30–32], etc.

Noncovalent functionalization of CNTs is based on van der Waals and π - π -interactions between the molecules of aromatic substances, surfactants, polymers of different nature and the surface of CNTs [2, 30–34]. In particular, for noncovalent functionalization of CNTs such substances as sodium dodecyl sulfate, dodecane-1-sulfonate, sodium 4-dodecylbenzene sulfonate, bromides of tetraalkylammonium, hexadecyltrimethylammonium, cetyltrimethylammonium, Triton, Pluronic are widely used. Noncovalent functionalization, unlike covalent, does not change significantly the intrinsic properties of CNTs [35]. However, noncovalent functionalization as well as covalent can be a basic step for further attachment of desirable molecules onto the surface of water-dispersed CNTs [36, 37].

Water is the environment and solvent in all biological systems. Therefore hydrophobicity of CNTs poses the main limiting factor for their use in biotechnological approaches [38]. Commonly, in an aqueous media hydrophobic CNTs form dense clusters due to strong van der Waals interactions. This hinders direct application of unmodified CNTs in biological systems. Numerous methods of functionalization of CNTs for dispersing them in water are presented largely by the technologically complex energy- and time-consuming procedures that also involve use of critical reaction conditions (temperature 500–600 °C) and hazardous toxic reagents (concentrated acids, alkalis, etc.) [1, 2, 27–32]. These factors may limit the applicability of CNTs-based strategies in biotechnology due to their complexity, high cost as well as associated toxicity concerns [39].

Thus, the important issue for the introduction of CNTs into plant biotechnology is the development of technologically adapted, fast, simple and safe methods for functionalizing CNTs capable of generating hydrophilic biologically compatible product. In this respect it is necessary to search for and select suitable and effective functionalizing procedures. The aim of the study was to analyze and compare the ability of a range of biological molecules to interact non-covalently with pure CNTs and subsequently mediate their dispersion in water as well as to investigate properties of formed conjugates. The work was carried out using a number of biological compounds of different chemical structure, selected according to the following two criteria: 1) permissible in view of the chemical structure ability to interact with the surface of CNTs and mediate their dispersion in water; 2) non-toxicity, non-specificity, accessibility. The efficiency of ultrasound-mediated noncovalent functionalization of SWCNTs and MWCNTs using double-stranded DNAs, deoxyribonucleoside triphosphates (dNTPs), ATP, bovine serum albumin (BSA), commercial vitreous humor extract, obtained from eyes of livestock animals, L-proline, peptone, spermidine and sodium humate was estimated.

Materials and Methods

For the study commercial SWCNTs and MWCNTs synthesized by chemical vapor deposition method were used (Table 1). On the basis of double distilled water obtained using the system for water treatment Barnstead

Table 1. Characteristics of used carbon nanotubes

| Product | SWCNTs | MWCNTs |
|-------------------------------------|------------------------|-----------------------------|
| | ARS002 “Arry”, Germany | 698849 “Aldrich”, USA |
| Length, μm | 5–20 | 2,5–20 (10 — average) |
| Diameter, nm | 1–2 | 6–13 — outer 2–6 — inner |
| Purity, wt. fraction, % | 90 | 99 |
| Surface area, m^2/g | 400 | 220 |
| Number of graphene layers in wall | 1 | 7–13 |

Note: SWCNTs — single-walled carbon nanotubes; MWCNTs — multi-walled carbon nanotubes.

Easypure II (Thermo Scientific, USA) a series of solutions for the functionalization were prepared using following substances: double-stranded plasmid DNA (0.5 mg/ml), previously isolated by method described in [40] from transformed *E. coli* strain DH5 α cells; equimolar mixture of four deoxyribonucleoside triphosphates (dNTPs), namely sodium salts of deoxyadenosine triphosphate, deoxyguanosine triphosphate, deoxycytidine triphosphate and thymidine triphosphate with total concentration of 1 mg/ml (Sigma, USA); bovine serum albumin (BSA) at a concentration of 10 mg/ml (Sigma, USA); sodium humate at a concentration of 10 mg/ml (Humintech GmbH, Germany); L-proline at a concentration of 10 mg/ml (Sigma, USA); peptone at a concentration of 10 mg/ml (Alfarus, Ukraine). Sodium salt of adenosine triphosphate (ATP- Na_2) at a concentration of 10 mg/ml (Darnitsa, Ukraine) and vitreous humor extract (Biopharma, Ukraine) were used as ready-made commercial aqueous solutions. As a control bidistilled water was used.

Plasmid DNA pGreen 0029 [41] was amplified in *E. coli* strain DH5 α cells. Preparation of competent cells of *E. coli* DH5 α and their genetic transformation with plasmid pGreen 0029 was performed by the method [42]. DNA concentration was determined spectrophotometrically using the device BioPhotometer plus (Eppendorf, Germany).

CNTs were added in a series of functionalizing solutions in the amount of 1 mg/ml and stirred for 3 minutes using a centrifuge Vortex Microspin FV-2400 (BioSan, Latvia), and then treated with ultrasound at a frequency of 22 kHz at a temperature of 25 °C (UM-4, Unitra Unima Olsztyn, Poland, 40 W) for 120 minutes. After ultrasonic treatment samples were centrifuged for 10 min at 16 000 rpm at a temperature of 10 °C in a

centrifuge 5417R (Eppendorf, Germany) to remove agglomerates of non-dispersed CNTs. Prepared samples were stored at a temperature of 4 °C and used for further analysis.

Absorption spectra of samples were recorded in the wavelength range of 190–1100 nm using spectrophotometer SPECORD 210 (Analytik Jena AG, Germany) and WinASPECT 2.3.1.0 (Analytik Jena AG 1998-2000, Germany) software. Transmission electron microscopy (TEM) was performed on microscope JEM-200A (JEOL, Japan) at a bright field imaging mode and acceleration voltage of 200 kV. Samples were prepared on copper mesh with holes size of 100 microns covered with 5 nm thick carbon film by “ultrasonic mist” method [43]. Atomic force microscopy (AFM) study was performed on the AFM NanoScope IIIa (Digital Instruments, USA). 50–100 nm thick sample films on silicon substrates were obtained by centrifugation (spin-coating) and successive application of 3–5 layers. Micro-Raman spectra were obtained at room temperature using spectrometer T64000 (Horiba Jobin Yvon, Japan), equipped with a confocal microscope BX-41 (Olympus, Japan) (long focus 50 \times lenses, aperture of 0.60) and registered using 1024 \times 256 cooled CCD detector (Andor, Ireland). Samples were excited with continuous Ar-Kr laser 2018-RM (Spectra-Physics, Germany) with excitation energy 2.54 eV (488.0 nm). The accuracy of determination of the frequency of phonon lines was $\leq 0.2 \text{ cm}^{-1}$.

Results and Discussion

The dispersion of SWCNTs and MWCNTs in an aqueous medium via ultrasound-mediated non-covalent functionalization using plasmid DNA, dNTPs mixture, ATP- Na_2 , BSA, vitreous humor extract and sodium humate was shown

(Fig. 1, *b–g*). Commercial pharmaceutical ready-made substances ATP- Na_2 and vitreous humor extract as well as sodium humate were used for noncovalent functionalization of CNTs for the first time. In aqueous solution and in samples containing heterocyclic amino acid L-proline, the product of incomplete enzymatic hydrolysis of proteins of various origin, which is a mixture of peptides and amino acids — peptone and biogenic polyamine spermidine, dispersion of CNTs under the used conditions was not observed (Fig. 1, *a, h–j*).

Obtained colloidal aqueous systems of functionalized CNTs were stable over various time periods (Table 2). Ultrasound treatment used for dispersing CNTs also provided decontamination of samples allowing their further use in aseptic *in vitro* objects.

Ultra-violet, visible and near-infrared spectroscopy of samples of functionalized CNTs

The analysis of the absorption spectra (in a range of 190–1100 nm) revealed the irregular growth of absorbance along analyzed wavelength range in all samples of functionalized CNTs. Generally, for each used functionalizing agent increase in absorption within its typical spectrum was shown. But equally greater increase in optical density for all samples was fixed in the range of 250–900 nm. However, spectra of functionalized using vitreous humor extract and sodium humate CNTs demonstrated a significant reduction in the absorption intensity in a range of 190–210 nm wavelengths. This may be due to the bounding of separate faction of minor compounds from the used solutions onto the surface of CNTs. Generally, similar

processes of interactions between minor biogenic substances and CNTs introduced into biological systems can lead to masking of the toxicity and subsequent changes in behavior and biological effect of CNTs.

Also we found that the optical absorption in the tested range of wavelengths for SWCNTs-based colloidal systems was generally higher than that for MWCNTs-based systems. The latter may be due to better capacity of lighter SWCNTs to come into dispersed state than that of the MWCNTs which appear to be larger and heavier. Generally, formation of the stable colloidal aqueous polydisperse systems by CNTs-biomolecules conjugates is considered to be a result of dual hydrophobic-hydrophilic properties of used functionalizing agents. It is known that hydrophobic domains of biomolecules are able to come into π - π -stacking and van der Waals interactions with the surface of CNTs [15, 22, 30, 31, 35]. In turn, the distal orientation of hydrophilic domains of adsorbed onto the surface of CNTs biomolecules mediate dispersion in water of formed conjugates. Organizing role in these interactions belongs to triggering mechanical effect of ultrasound treatment and to the coordinating effect of the aqueous environment. In particular, on the one hand it is known that ultrasound treatment enables overcoming the van der Waals interactions between the hydrophobic surfaces of CNTs thus disaggregating the latter [44]. On the other hand, ultrasonication induces conformation changes in functionalizing molecules enabling their interactions with hydrophobic surface of CNTs [45].

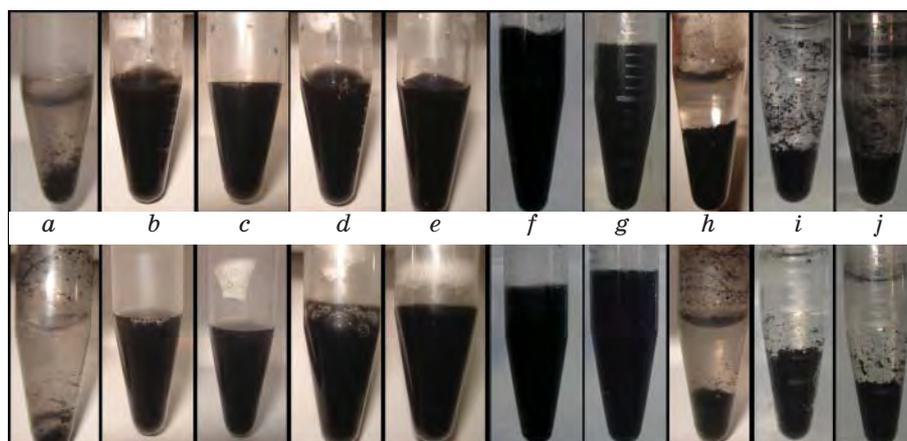


Fig. 1. Comparative results of noncovalent functionalization of SWCNTs (top row) and MWCNTs (bottom row) using compounds of biological origin:

a — control (H_2O); *b* — plasmid DNA; *c* — dNTPs; *d* — ATP- Na_2 ; *e* — BSA; *f* — vitreous humor extract; *g* — sodium humate; *h* — L-proline; *i* — peptone; *j* — spermidine

Table 2. Stability of functionalized carbon nanotubes in time (months)

| Type of CNTs | Type of functionalizing coating | | | | | |
|--------------|---------------------------------|-------|-----|-----|------------------------|---------------|
| | DNA | dNTPs | ATP | BSA | Vitreous humor extract | Sodium humate |
| SWCNTs | 6 | 6 | 6 | 10 | 6 | 3 |
| MWCNTs | 6 | 6 | 6 | 10 | 6 | 3 |

Transmission electron microscopy of samples of CNTs functionalized using double-stranded DNA

TEM study of functionalized CNTs has made it possible to establish the presence of extended functionalizing coating on the surface of spatially separated nanotubes (Fig. 2). The coating possessed high affinity to the CNTs surface, combined with the ability to act as an interim bifunctional hydrophobic-hydrophilic phase.

TEM results also confirmed that ultrasound treatment have led to significant shortening of major fraction of CNTs. Thus, truncated CNTs lengths varied in a range of few hundreds of nm to few microns. These changes, in turn,

are known to be favorable for further use of CNTs as delivery vectors for living cells and subcellular structures [23, 26, 46–49]. Generally, in case of use DNA, dNTPs mixture and ATP solutions for functionalization, during the process of formation of conjugates with CNTs nitrogenous bases come into π - π -stacking interaction with the surface of nanotube while sugar-phosphate hydrophilic moieties turn towards the water environment [16]. One important moment is that for biotechnological practice use of ready-made pharmaceutical ATP solution for dispersing CNTs may be easy and cost-saving, instead of using expensive dNTPs or DNAs if latter both are not prescribed in study as necessary.

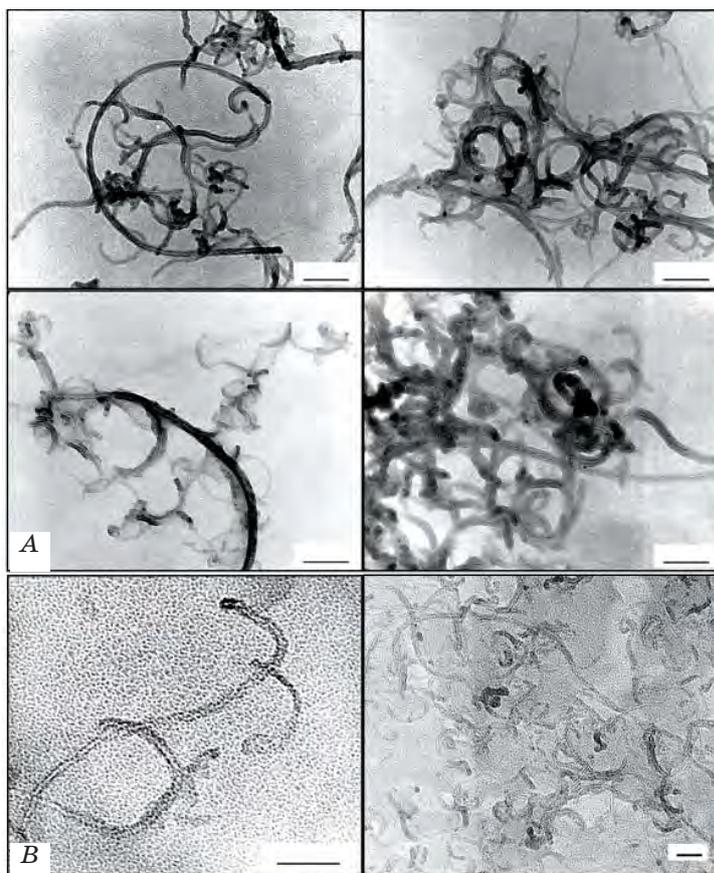


Fig. 2. Transmission electron microscopy image of MWCNTs:

A — nanotubes functionalized using double-stranded DNAs (DNA forms an amorphous coating);
 B — pure nanotubes after ultrasonic treatment. Scale bar — 300 nm

Raman spectroscopy of samples of CNTs functionalized using double-stranded DNA

Comparison of Raman spectra of functionalized CNTs with spectra obtained from untreated CNTs revealed changes in presence, shape and intensity of characteristic bands. In particular, for spectrum of SWCNTs functionalized using DNA significant changes in the spectral region of the radial breathing mode (RBM) are shown in Fig. 3. RBM is a characteristic band for SWCNTs, whereas in MWCNTs radial oscillations of carbon atoms are limited by the presence of adjacent walls [50]. In the spectrum of functionalized SWCNTs RBM band was not detected obviously due to the presence of functionalizing coating on the surface of nanotubes. The D/G bands intensities ratio in the spectrum of CNTs characterizes the ratio of the materials with disordered and ordered structure in sample [50]. For spectrum of SWCNTs functionalized using DNA an increase in D/G ratio in comparison with a D/G ratio of untreated SWCNTs was recorded (0,625 against 0,125). This is thought to be due to the appearance of defects in normal sp^2 -hybridized structure of CNTs which *per se* present sites for initial binding of functionalizing molecules. Another reason for observed changes in D/G ratio appearance is supposed to be an increase of the fraction of short CNTs after functionalization. D-band in the range of $1250\text{--}1450\text{ cm}^{-1}$ in Raman spectra of carbon materials is caused by oscillatory mode of boundary effects in

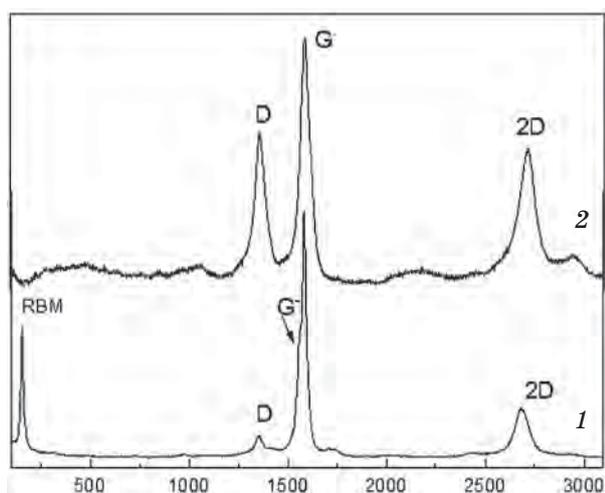


Fig. 3. Raman spectrum of untreated (1) and functionalized using DNA (2) SWCNTs

Vertical axis: intensity, arb. units.;
horizontal axis: Raman shift, cm^{-1} .
The bands of the spectrum: RBM — radial breathing mode, D-band, G-band and 2D-band

graphene. Reported increase in intensity of this band in the spectrum of functionalized CNTs may be due to the appearance of sp^3 -hybridized structures and a high fraction of truncated nanotubes with “open” ends and, as a result, increased edge effects [51]. These data are consistent with results from samples testing using TEM.

Atomic force microscopy of samples of CNTs functionalized using double-stranded DNA

AFM study (in contact mode) revealed the increased diameter of obtained CNTs-based structures due to adsorption of functionalization coating on the surface of nanotubes. In particular, on the topographic profile shown in Fig. 4 diameter of truncated functionalized MWCNT is of about 30 nm, while the maximum nominal diameter of pure MWCNTs used in the study was 13 nm (Table 1). Generally, with different functionalizing agents used the thickness of conjugates varied, but in most cases diameter was in range of 15–25 nm for MWCNTs and 4–10 for SWCNTs. It should be noted that thickening had irregular mode along the tube length.

Functionalization of CNTs using bovine serum albumin

Among all used agents in the study BSA-mediated functionalization was associated with the highest stability over time of dispersed SWCNTs as well as MWCNTs (Table 2). Interactions of CNTs with water-soluble proteins, hydrophobic domains of

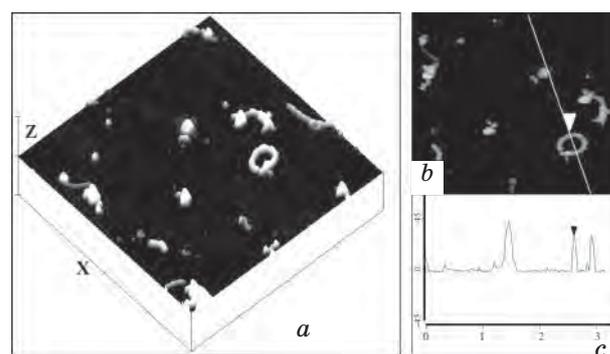


Fig. 4. The results of atomic force microscopy study of samples of MWCNTs functionalized using DNA:

a — three-dimensional image, scale interval for *x* axis — 1000 nm, for *z* axis — 200 nm; *b* — two-dimensional image with a line of topographic cross section perpendicular to the plane; *c* — two-dimensional topographical section, units on *x* axis — nm, on *y* axis — μm . The triangle indicates CNT

which normally stay in folded state, and the subsequent formation of water-dispersible conjugates is associated with conformational changes such as unfolding and refolding of protein molecules under the influence of ultrasonic treatment [52, 53]. Therefore, various studies have shown the effectiveness or unsuitability of different proteins for noncovalent functionalization of CNTs in aqueous media [30, 31, 52]. There is evidence that the presence of amino acids such as histidine containing heterocyclic regions, and tryptophan, which is composed of aromatic ring and heterocyclic regions, largely affects the ability of proteins to mediate dispersion of CNTs in water [54]. In addition, we can assume an important role in this process of aromatic amino acids such as phenylalanine and tyrosine. More than 10% of 583 amino acid residues of BSA globular protein molecule are histidine, tryptophan, phenylalanine and tyrosine [55, 56] and about 40% of its amino acid residues contain nonpolar radicals. This, obviously, together with a favorable change in the conformation of protein molecules under the influence of ultrasonic treatment results in a high stability of aqueous dispersions of non-covalently functionalized using BSA CNTs.

Functionalization of CNTs using vitreous humor extract

The major compounds of vitreous humor aqueous extract that obviously are involved in the dispersion of CNTs in water are fibrillar protein collagen, proteoglycans and hyaluronic acid. While hydrophobic sites of the protein constituent of the proteoglycan molecules bind to the surface of CNTs, hydrophilic hydrocarbon constituent of proteoglycan is supposed to “anchor” formed conjugates in water. Thus hyaluronic acid — highly hydrophilic glycosaminoglycan [57] — is able to provide additional stabilization for dispersed in aqueous environments CNTs. Collagen has high content of L-proline residues, 3-hydroxyproline and 4-hydroxyproline [58]. However, pure L-proline when used in the study was not efficient for the dispersing of CNTs. Given this, we can assume that dispersion of CNTs in an aqueous media using vitreous humor extract is the result of complex action of different compounds of protein and carbohydrate nature.

Functionalization of CNTs using humic acids

Humic acid molecules contain numerous aromatic nuclei, hydrophilic carboxyl and

carbonyl groups, alcohol and phenolic hydroxyls [59]. In our study complex action of these regions obviously mediated the formation of water dispersed conjugates of humate-functionalized CNTs. Water systems of CNTs functionalized using sodium humate demonstrated the lowest stability over time among effective functionalizing agents tested. However, humic acids and their derivatives are important for ecosystems organic compounds that are widely distributed in the environment. Hence, on the one hand, our results show one possible way of spontaneous modification of CNTs when they are released into the environment. On the other hand, CNTs conjugated with humic acid derivatives may be investigated to examine their plant growth enhancement activity as well as ability to serve as nutrients delivery system for plants.

It should be noted that with the increase in number of integrated interdisciplinary research, numerous reports were published regarding the obtaining of CNTs conjugates with proteins, carbohydrates, nucleic acids and other biological molecules for applications in physics, electronics, material science, biology and medicine [8–10, 17, 30, 31, 49–53, 60, 61]. However, in many cases biomolecules are bound onto the CNTs that are covalently pre-modified using physical and chemical methods [62]. Introduced on the surface of CNTs chemical groups interact with biological molecules and mediate the formation of the conjugates. Sometimes after the 1st-step generating chemical groups on the carbon skeleton of CNTs the 2nd-step bounding of intermediate compounds is conducted, such as polyelectrolyte poly(diallyldimethylammonium chloride), polymers as poly(allylamine hydrochloride), polyethyleneimine, polyethylene glycol, which, in turn, on the 3rd-step bind biological molecules of interest [7, 16, 17, 18, 21, 31, 63]. However, due to existing need to develop technologically adapted, smart and environmentally friendly nano-based approaches for biotechnology, investigation of biological molecules as priority compounds for functionalization of CNTs remain an important issue.

Obtained results extend the available set of biological compounds that can be used for noncovalent functionalization of CNTs for biotechnology. In addition, the study of noncovalent interactions of biomolecules with CNTs forms the basis for predicting their behavior in living organisms and the environment.

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ФУНКЦІОНАЛІЗАЦІЯ ВУГЛЕЦЕВИХ НАНОТРУБОК РІЗНИМИ БІОМОЛЕКУЛАМИ ДЛЯ СТАБІЛЬНОГО ДИСПЕРГУВАННЯ У ВОДІ

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Метою роботи був підбір ефективних методів функціоналізації вуглецевих нанотрубок та порівняння здатності низки молекул біологічного походження (плазмідна ДНК, АТФ, дезоксирибонуклеозидтрифосфати, бичачий сироватковий альбумін, компоненти екстракту склоподібного тіла і гумат натрію) нековалентно взаємодіяти з вуглецевими нанотрубками та опосередковувати їх диспергування у водному середовищі. Властивості отриманих полідисперсних кон'югатів було охарактеризовано за допомогою спектроскопії ультрафіолетового, видимого та ближнього інфрачервоного діапазону, Раманівської спектроскопії, трансмісійної електронної та атомно-силової мікроскопії. Показано формування стабільних водних полідисперсних колоїдних систем одношарових та багатшарових вуглецевих нанотрубок. Продемонстровано утворення на поверхні вуглецевих нанотрубок протяжного функціоналізуючого покриття з біомолекул. Встановлено зміни морфології та структури вуглецевих нанотрубок, спричинені їхньою функціоналізацією, зокрема такі, як вкорочення і поява дефектів sp^2 -гібридизованої поверхні. У результаті проведеного дослідження відібрано молекули біологічного походження, придатні для нековалентної функціоналізації вуглецевих нанотрубок, й охарактеризовано властивості утворених комплексів.

Ключові слова: одношарові та багатшарові вуглецеві нанотрубки, нековалентна функціоналізація, молекули біологічного походження.

ФУНКЦИОНАЛИЗАЦИЯ УГЛЕРОДНЫХ НАНОТРУБОК РАЗЛИЧНЫМИ БИОМОЛЕКУЛАМИ ДЛЯ СТАБИЛЬНОГО ДИСПЕРГИРОВАНИЯ В ВОДЕ

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Целью работы был подбор эффективных методов функционализации углеродных нанотрубок и сравнение способности ряда молекул биологического происхождения (плазмидная ДНК, АТФ, дезоксирибонуклеозидтрифосфаты, бычий сывороточный альбумин, компоненты экстракта стекловидного тела и гумат натрия) нековалентно взаимодействовать с углеродными нанотрубками и опосредовать их диспергирование в водной среде. Свойства полученных полидисперсных конъюгатов были охарактеризованы с помощью спектроскопии ультрафиолетового, видимого и ближнего инфракрасного диапазона, Рамановской спектроскопии, трансмиссионной электронной и атомно-силовой микроскопии. Показано формирование стабильных водных полидисперсных коллоидных систем однослойных и многослойных углеродных нанотрубок. Продемонстрировано образование на поверхности углеродных нанотрубок протяженного функционализирующего покрытия из биомолекул. Установлен ряд изменений морфологии и структуры углеродных нанотрубок, вызванных их функционализацией, в частности таких, как укорочение и появление дефектов sp^2 -гибридизованной поверхности. В результате проведенного исследования отобраны молекулы биологического происхождения, пригодные для нековалентной функционализации углеродных нанотрубок, и охарактеризованы свойства образованных комплексов.

Ключевые слова: однослойные и многослойные углеродные нанотрубки, нековалентная функционализация, молекулы биологического происхождения.