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Nucleic acid interaction and interfaces with single-walled carbon nanotubes

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The discovery of the carbon nanotubes has opened up a new field in biomedical research. Indeed, the recognition of carbon nanotubes by DNA, DNA assisted separation of carbon nanotubes, DNA immobilization on carbon nanotubes surfaces have been demonstrated. The knowledge of carbon nanotubes-DNA interaction is of fundamental importance for using carbon nanotubes/biomechanical complexes. In this study experimental and theoretical study of the DNA-interface coupling is performed to achieve better understanding of the properties of many carbon nanotubes - based biosystems, as well as novel phenomena caused by the interaction of carbon nanotubes with biomolecules. This paper is focused on the study of interactions between single walled carbon nanotube (SWCNT) surfaces with DNA, poly-A, and individual nucleotides, to clear up the conformation changes in these complexes. New spectroscopic technique based on the effect of enhancement of infrared (IR) absorption by rough metal surface (SEIRA) together with surface enhanced Raman spectroscopy (SERS) and atomic force microscopy (AFM) for registration of structural changes in carbon nanotubes and DNA/carbon nanotubes complexes were applied. SEIRA spectroscopy data was compared with *ab initio* quantum-chemical calculations performed for thymine and adenine adsorbed on carbon nanotubes. A possible model of interaction between nucleic acid bases, double and single nucleic acid strands and the carbon nanotube surfaces is derived from the experiments and calculations.

1. Introduction

The discovery of carbon nanotubes in 1991 (Iijima, 1991), and afterwards, the production of bulk quantities (Dresselhaus, 1996) have paved the way to exploration of the physical and chemical properties of these quasi-one dimensional graphite structures. Carbon nanotubes have been envisioned in a variety of applications such as gas and battery devices, as efficient

energy storage elements, sensors and electromechanical systems, biocompatible agents and recognition elements, and more (Dresselhaus et al., 1996), (Dresselhaus et al., 2000).

In regard to the above mentioned carbon nanotubes application, one of the most promising and interesting properties is the ability of the carbon nanotubes to interact with biological molecules providing to new properties of the carbon nanotubes/biomolecule complex.

The discovery of carbon nanotubes has opened up a new field in biomedical research as well. Indeed, functional bio-nanosystems, which are formed by functionalizing inorganic nanostructures with biochemical molecules, utilize unique properties of biochemical species recognition, DNA recognition, drug delivery systems, DNA transfection and more. The use of carbon nanotubes in this regard is of particular importance. The functionalization of carbon nanotubes with proteins, nucleic acids, DNA and RNA has been pioneered. More specifically, the DNA recognition of carbon nanotubes (Williams et al., 2002), DNA assisted separation of carbon nanotubes (Zheng et al., 2003 (a)), DNA immobilization on CNT surfaces (Guo et al., 1998) have been demonstrated.

In connection to using carbon nanotubes/biomechanical complexes, the knowledge of carbon nanotubes/DNA interaction is of fundamental importance. Today several models on DNA interaction with carbon nanotubes are known. The most popular model is a DNA wrapping around carbon nanotubes proposed by Smalley (O'Connell et al., 2001). In (Zheng et al., 2003 (a)) a molecular modeling have suggested that single stranded DNA (ssDNA) can bind to carbon nanotubes through π-stacking via bases. The authors of (Zheng et al., 2003 (a)) have demonstrated the poly-T wrapping around carbon nanotubes and concluded about many ways in which short ssDNA strands can interact with nanotube surface, namely, wrapping with right-handed turns, wrapping with left-handed turns, (absorb) on the surface with a linearly extended structure. In other paper (Zheng et al., 2003 (b)) the authors concluded that ssDNA can adopt many different modes of binding to carbon nanotubes with little difference in binding free energy. These modes include helical wrapping with different pitches and forming a fever allowed conformation than ssDNA.

However, due to complexity, full comprehension of the mechanism of interaction of carbon nanotubes and nucleic acids (NA) has not been established up to date. That is why we did the experimental measurements and theoretical modeling of the DNA/interface couplings to achieve better understanding of the properties of the carbon nanotubes-NA, as well as the induced novel phenomena. It will also help us to establish new concepts of controlling and tuning the performance of such systems and facilitate the design and optimization of DNA/carbon nanotubes based functional devices. *The goal* of our paper was to study the interaction of single walled carbon nanotubes with the double stranded DNA dsDNA), Poly-A in double and single strands, thymine and adenine with modern sensitive methods - surface enhanced infrared absorption (SEIRA) and surface enhanced Raman scattering (SERS), as well atomic force microscopy (AFM) and *ab initio* calculation.

2. Methods and Materials

2.1 SEIRA and SERS spectroscopy

The enhancement of optical process by a factor $10^2...10^6$ near rough surface of a metal is already known for optical transitions in adsorbed molecules and the processes which do not depend on the presence of the molecules on the metal surface. These processes are SERS, SEIRA, metal enhanced fluorescence, second harmonics generation. For the first time an

enhancement of IR signal from molecules chemisorbed on Au and Ag surface by factor up to 10^3 has been registered by Harstein and colleagues in 1980 (Harstain et al., 1980). Only in the beginning of the nineties the scientists came back to study of the enhanced IR effect, mainly due to very low limit of the molecules that could be detected by IR and its some advantages (non-destructivity, higher signal-noise ratio, less distorted spectra) in comparison with SERS. In 1991 the effect was named as SEIRA by Osawa and Ikeda (Osawa & Ikeda, 1991). The effect can not be explained in a simple way, it includes several mechanisms, such as: 1) increase of electromagnetic field near the rough metal surface or metal film, 2) increase of dipole transition moment of adsorbed molecules; and was theoretically described by V. Kosobukin (Kosobukin, 1983; Kosobukin, 1985).

The advantages of SEIRA compared to other spectroscopic methods show that SEIRA is desirable when biological complexes are studied. This is dictated by the fact that when one works with biological complexes, usually very small amounts with desirable properties are available. SEIRA provides a mechanism for enhancing the biological substances' spectroscopic properties. In addition, biological molecules are with very complicated structures and many properties from different constituents of the biological compound entangle and mix. SEIRA provides an opportunity to monitor specific parts of the biological compound and its conformations. Therefore, the surface enhancement methods has very attractive features which will be useful when DNA/carbon nanotubes conformations are described. SEIRA spectroscopy was applied to study a conformation of DNA, Poly-A, at the single-walled carbon nanotubes (SWCNT) interface for an ensemble of SWCNT/biological molecule with of the use of a special SEIRA support (Dovbeshko, 2004 (a); Dovbeshko, 2004 (b)). The SEIRA application for the study of nanotubes gives a possibility to increase a sensitivity of IR spectroscopy by 3-10 times and enhances the absorbance of biological molecules adsorbed on the nanotube surface located on the rough gold surface (Fig. 1).
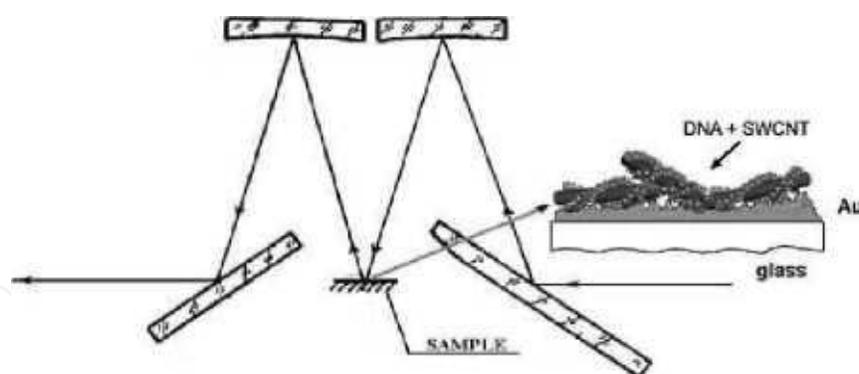

Fig. 1. Scheme of SEIRA experiment in reflectance geometry

A drop from the transparent part of the solution was then taken for SERS, AFM, and SEIRA studies. The characterization of individual nanotubes wrapped by Poly-A, as well as the Poly-A conformation on the separated nanotubes, was probed and enhanced with a conventional Klarite SERS support. The factor of enhancement in SERS experiments on the Klarite support was equal to 10^4-10^6 for different vibrations in comparison with a conventional Al support. The spot of the field for SERS and AFM study was taken as 1x1 µm. SERS spectroscopy give us a possibility to register a signal from 1-2 nanotubes and Poly-A adsorbed on the nanotubes.

2.2 FTIR and Raman spectra evaluation

A Bruker IFS-66 instrument with a reflection attachment (the incidence angle of 16.5°) was used for the registration of IR spectra in the reflectance mode in the region of 400-4000cm^{-1}. Spectra of DNA, Poly-A, adenine, thymine and their complexes were collected in reflectance mode. Evaluation of the spectra has been done with Opus 5.5. The position of the bands has been estimated with the use of the method of second derivative and/or standard method. The intensity of the bands was normalized to the band with maximal intensity in each spectrum, namely, to OH-NH-CH stretching vibration in the region 3340-3400 cm^{-1}. The bands have been assigned to the certain molecular groups in DNA, poly-A, according to references: (Taboury et al., 1985; Taillandier et al., 1985; Tajmir-Riahi et al., 1995; Schrader, 1995; Parker, 1983; Litvinov, 1991; Dovbeshko, 2008, Dovbeshko, 2009). Reproducibility of the frequency in the IR spectra was equaled to ±0.5 cm^{-1} and for absorption ±0.0005 a.u.). Earlier we studied the validity of the use of the effect of enhancement of infrared absorption by metal surface for nucleic acids, lipids, amino acids and albumin (Dovbeshko et al., 2002; Dovbeshko et al., 2004, Dovbeshko et al., 2006 (a); Dovbeshko et al., 2006 (b)) deposited onto Au substrate in the reflectance experiments. The results show that when using the SEIRA method for the study of IR absorption of nucleic acids (and for other molecules), no deformation of contour of the absorbance bands is observed as compared with the spectrum on neutral CaF$_2$. Some frequency shifts are present, but for the most part of the bands they are small (1-2 cm^{-1}).

In our experimental conditions we registered the DNA with 60% humidity and poly-A with 65% humidity. The microscope experiment was done using a Via Raman Microscope (Renishaw) instrument with laser excitation at 785 nm with 0.3-60 mW power.

2.3 AFM imaging

The microphotograph of the Au substrate for SEIRA, Klarite support for SERS as well as Poly-A adsorbed on nanotubes placed on Klarite support was obtained by atomic force microscopy (AFM). We used the tapping mode under AFM imaging of the gold surface of home-made support with a commercial Nanoscope IIIa (Digital Instrument, Santa Barbara, CA). Tapping force mode scans were performed using commercially available AFM tips (silicon nitride). The scanning frequency was approximately 1 Hz in all experiments.

AFM microscopy with a Park Scientific Instrument Auto Probe LS was used to analyze the nanotube-Poly-A interface. We have obtained images on a SWCNT in the contact mode with a silicon nitride ultra sharp tip (all images are obtained in air).

2.4 Au home-made support for SEIRA and Klarite support for SERS

Au home-made support for SEIRA was produced in the Institute of Physics of NASU (Kiev, Ukraine) (Dovbeshko et al., 2004 (b)). Gold thin layer was obtained by vacuum deposition of 99.999% pure Au upon glass supports (TF-1 glass, 20x20 mm) via an intermediate adhesive Cr layer. Before Au deposition, glass surface was cleaned by NH$_4$OH:H$_2$O$_2$:H$_2$O and HCl:H$_2$O$_2$:H$_2$O solution subsequently, both 1:2:2 by volume concentration during 5 minutes at boiling temperature. Then it was rinsed in bidistilled water and dried in a flow of pure nitrogen. The gold was evaporated from molybdenum heater and deposited at a rate of 1.0-1.5 nm s^{-1} on room temperature substrate. The thickness of gold surface was within 300-350 Å in the different experiments. The Cr interlayer does not exceed 10-20 Å. The gold surface just

after deposition looks like hydrophobic surface with wetting angle close to 80° and random roughness about 50 Å (Fig. 2).
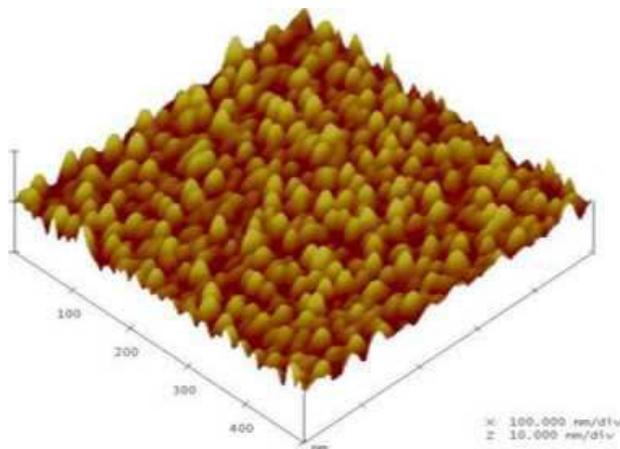

Fig. 2. AFM image of gold surface of home made support used in SEIRA
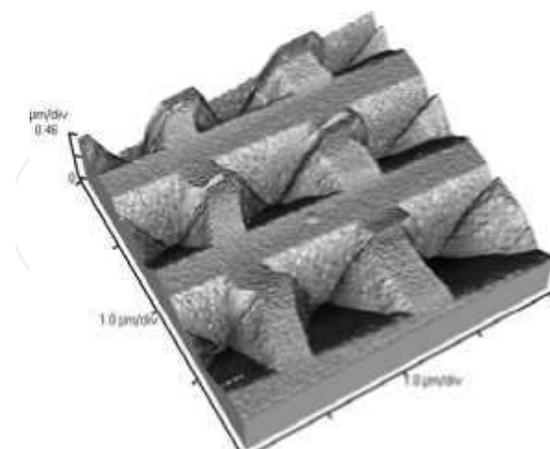
Fig. 3. AFM Image of gold surface of Klarite support used in SERS

We used standard Klarite support for SERS produced by Mesophotonics (Fig.3).

2.5 Principal component analysis

Principal component analysis was applied to SEIRA spectra of DNA. As one principal component was chosen a relative intensity of phosphate asymmetrical band (at 1240 cm^{-1}) to intensity of maximum in the 3400 - 2300 cm^{-1} region assigned to OH stretching vibration. According to (Shie, 1977), this component characterizes the number of water molecules per 1 nucleotide. The second principal component was ratio of intensity at 1712 cm^{-1} and 1700 cm^{-1} that is a characteristics of conformation state of DNA relating to A, B or Z-form. Earlier we have estimated the contribution of above-mentioned components in principal components and found that they have shown the preferential contribution (Dovbeshko et al, 2004 c). The amount of the molecules of water per nucleotides in DNA was estimated according to a formula:

$$W_w^\alpha = \frac{N_{H_2O}}{N_{\text{nucleotide}}} = \frac{\mu_{H_2O}^\alpha}{\mu_{\text{nucleotide}}} = \frac{D_{3400}^\alpha}{D_{1228_{cm}^{-1}}^{97\%\text{relative humidity}}} \cdot \frac{\varepsilon_{1228cm^{-1}}}{\varepsilon_{3420cm^{-1}}}; \qquad (1)$$

$\varepsilon_{3420cm^{-1}}$ = 101 ± 7 L·M^{-1}·cm^{-1} (value obtained by averaging the data from different authors) $\varepsilon_{1228cm^{-1}}$ = 530 ± 9 L·M^{-1}·cm^{-1}. Then we obtained:

$$W_w^\alpha = 5,25 \frac{D_{water}}{D_{\text{phosphate}}} \qquad (2)$$

The error of calculation of amount of molecules of water was calculated as a square root from the sum of squares of standard errors averaged by all multipliers in a formula 1. Standard averaged error is determined as: $\sqrt{\dfrac{\sigma^2}{n}}$, where σ is standard deviation, n-amount of experimental points. Standard deviation for $\varepsilon_{3420cm^{-1}}$ equaled to 6,9%, for $\varepsilon_{1228cm^{-1}}$

cm^{-1} =1,7%. Then standard averaged error for $\varepsilon_{3420cm-1}$ cm^{-1} equaled to 3,2 %, for $\varepsilon_{1228cm-1}$ cm^{-1} =0,8%. An error for D is determined by systematic instrumental errors and is 0,1%. Then a total error of calculation of amount of molecules of water equaled to 3,3%.

2.6 Method of the dispersion of SWCNT

SWCNTs have been synthesized by arc discharge between two graphite electrodes in a He atmosphere at the Moscow Institute of Physics (Obraztsova et al., 1999). The nanotube content in the raw material was about 30-40 wt%. The contaminants are amorphous carbon, metallic catalyst particles, soot, etc. The material has been certified by high resolution transmission electron microscopy and Raman scattering (Dovbeshko et al., 2003; Dovbeshko et al., 2008,). The length of SWCNTs was 1-2 µm, and the diameters are 0.9-1.6 nm with preferential fraction of 1.4-1.5 nm. The probe of SWCNTs was mixed with DNA and/or Poly A aqueous solution (0.25-0.5mg/ml) (0.1-1 weight part of nanotubes to 1 weight part of Poly-A) by an ultrasonic mixer Sonorex TK52 (60 W, 35 kHz) during 60 min (Fig. 1) with a subsequent centrifugation under 30 000 turn/min during 30-60 min. Na-salt of calf thymus DNA was purchased from Servo; Polyadenilic acid potassium salt (polyA), Adenine (Ade) was purchased from Fluka (Germany), Thymine (Thy) was purchased from Sigma and used without additional purification. Aqueous solution of DNA (0.25 mg DNA/ 0.5 ml H$_2$O) was heated up to 100 °C, then 0.5 mg SWCNT was added. Compounds of the solution were mixed, stirred and then precipitated onto quartz substrate covered with gold layer. The concentration of adenine and thymine solutions in SEIRA experiment was 1 mg/ml. In the experiment first we isolated the nanotubes with aqueous (alcoholic) solution of Thy (Ade) (1:1 weight ratio) by ultra-sound mixing (UZDN-A, Sumy, Ukraine) for 1 hour. Then we have deposited a drop of the solution of Ade (Thy) with carbon nanotubes on gold and CaF$_2$ substrate. The output of nanotubes during the process was 2-8%, the concentration of poly-A in different experiments was 10^{-3}-10^{-4} M, and the concentration of nanotubes was 10^{-4}-10^{-5}M as estimated according to (Dai, 2005). This procedure separates nanotubes from a bundle for their further individual characterization and usage (Fig. 4). After the treatment, the inhomogeneous solution contained 3 parts of different densities. The upper and bottom parts contained a black dust with nanotubes and contaminations such as soot, metallic particles, etc., while the mid transparent part (Fig. 4) contained a solution with isolated nanotubes.
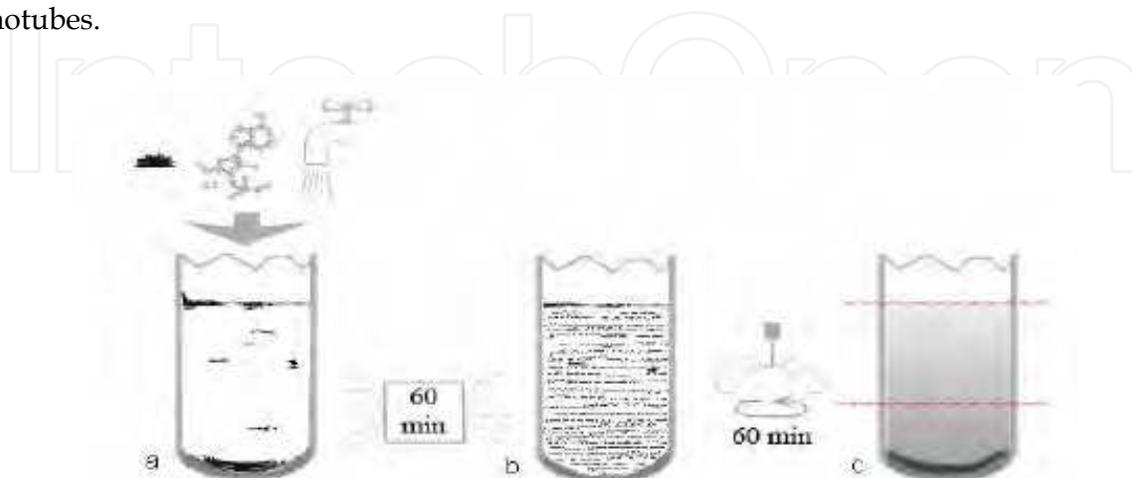
Fig. 4. Scheme of the nanotube-Poly-A solution: (a) before mixing in an ultrasonic mixer, (b) bottom and (c) top part of the solution after centrifugation

The pH of the solution was measured with a pH-150 M (Belorussia, Gomel) instrument with 0.01 accuracy.

2.7 Method of Calculation

The method for this work will be based on Density Functional Theory (DFT) (Hohenberg & Kohn, 1964)] electronic structure calculations. The calculations were done utilizing the Vienna Ab Initio Simulation Package (VASP)**.** This is state of the art Projection Augmented Wave (PAW) simulation methods which use exact valence wave functions improving the reliability of the potential (Kresse & Joubert, 1999). The code is available and supported at the USF computing facility.

This code uses a plane wave basis and a periodic supercell method with Vanderbilt pseudopotentials or a projector-augmented wave method to account for the electron core. The adsorption on the metallic SWCNT (6,6) with length of 12,25 Å, and the adsorption of thymine on the semiconducting (8,0) SWCNT with length of 17,035 Å, were considered with nonspin-polarized LDA (local density approximation) for the exchange-correlation functional. DFT is known to be suitable for the description of short ranged strong forces and to give an imperfect description for long range interactions as the local density approximation (LDA) tends to overestimate and the generalized gradient approximation (GGA) for the exchange correlation energy tends to underestimate the binding (Shtogun et al., 2007), (Woods et al., 2007). DFT gives a better description of these systems than empirical models or classical molecular dynamics models and it has proven to be a powerful tool in the adsorption description of carbon nanotubes (Girifalco & Hodak, 2002).

3. Result and Discussion

3.1. Characterization of carbon nanotubes

Carbon nanotubes are extended cylindrical structures with a diameter from one to a few ten of nanometers and length of a few centimeters (Iijima, 1991; Dresselhaus et al., 2000). They consist of one or more hexagonal graphene planes rolled up in a tube with a hemispheric head. Characterization of the carbon-based materials could be done with Raman spectra being a fingerprint of it.

The main feature of the Raman spectra of graphite structure is, so called G mode (1589 cm^{-1}) according to the theory characterizes the tangential vibrations of carbon atoms of graphene layer of E_{2g}, E_{1g}, A_{1g} symmetry in the Γ point of Brillouin zone and correlates with the ordering of crystal lattice of graphite structure. Frequency shift in high frequency region means reduction of the areas of coherent scattering of the materials under study (Saito & Dresselhaus, 1998). The second characteristic modes of graphite-like materials, so called D-mode, with A_{1g} symmetry that characterizes the disorder of lattice of graphene layer. It refers to breathing vibrations of rings of graphene layer in the K point of Brillouin zone (Saito & Dresselhaus, 1998) and has been registered at 1291 cm^{-1} for nanotubes (Fig.5). The second order mode of this vibration (so called D_1) well registered at 2568 cm^{-1} in SWCNT and they have the intensity which usually exceeds the intensity of second-order vibrations (Fig.5). The last fact could be the evidence that nanotubes consist of similar structures that manifest a strong electron-phonon interaction and strong dispersion dependence of D-mode. Other carbon-like materials don't have such peculiarity.

SWCNT have a low frequency mode of significant intensity that is assigned to the breathing vibration of a whole tube (Saito & Dresselhaus, 1998).
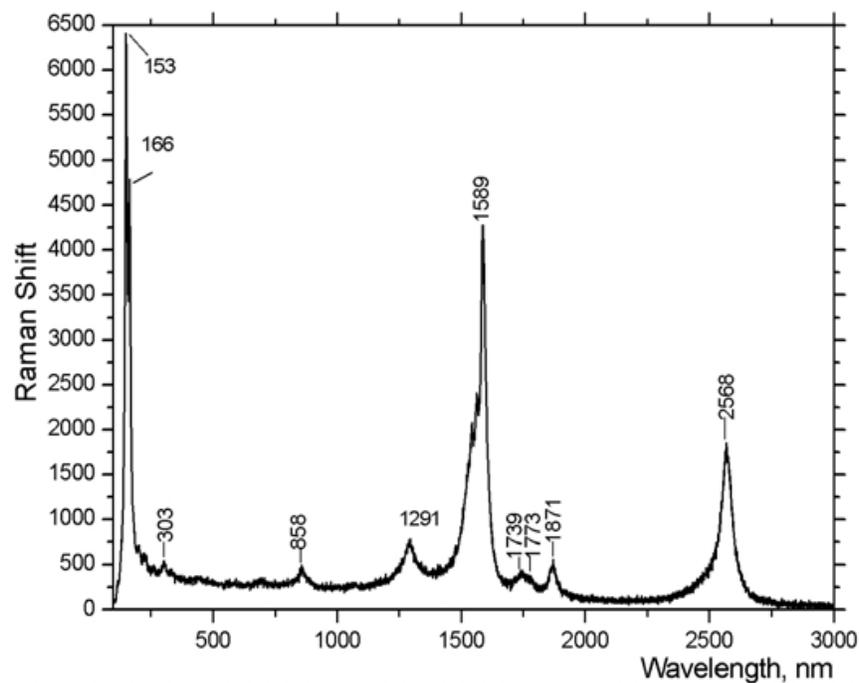

Fig. 5. Raman spectra of initial fraction of nanotubes

The wavenumbers, halfwidth and relative intensity of above mentioned bands could be used for characterization of type of allotropic forms of carbon, the nanotubes and their diameters.

3.2 Characterization of complex SWCNT/Poly A

Visualization of the separate nanotubes with poly-A was done with AFM (Fig. 6). According to AFM, size of nanotubes after separation was 4.3 nm in vertical axis and 10 times more- 40.31 nm in horizontal axis (Dovbeshko et al. , 2008). It is known that probe method, AFM included, does not give real object image, it is the product of probe only. Due the fact that curvature of probe is much more than size (diameter) of the object under study, we should expect that lateral size of the object is much more than its real size. In the same time the height of the object keeps real size as the nanotube is single object and method is valid for height estimation without error. So, shows that height of nanotube is equaled to 4 nm, and its lateral size 40 nm estimated with big error (Dovbeshko et al., 2008). According to this data we could suppose that 1 or 2 nanotubes have been separated from the bundle and registered by AFM (Fig.6).
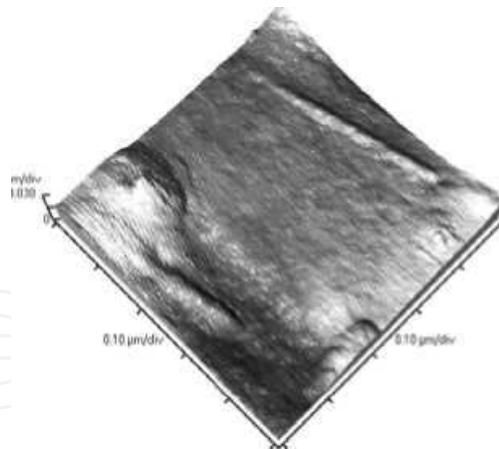
Fig. 6. AFM image SWCNT

Breathing mode in RS spectra is sensitive to diameter of nanotubes and density of states and depends on frequency of excited light. Linear dependence between reverse diameter and position of breathing mode is expressed by the formula:

$$v\,(cm^{-1}) = \frac{223.75}{D_1\,(nm)} \tag{3}$$

(Chen et al., 1998) that obtained from *ab initio* calculation. In the most cases nanotubes in the bundle are studied by scientists, so Van der Waals interaction between nanotubes in the bundle are realized and determined by the diameter of nanotubes and number of nanotubes in the bundle, that is why additional constant are appeared in the formula or coefficient in the term of fraction are changed. Different formulas are applied by different authors for calculation of diameter of nanotubes. We estimated a diameter of nanotubes in initial fraction of nanotubes as well in solution, accordingly, with the formula in the following form:

$$v\,(cm^{-1}) = \frac{234}{D_2\,(nm)} + 10 \tag{4}$$

(Bokova et al., 2003) and/or

$$v\,(cm^{-1}) = \frac{248}{D_6\,(nm)} \tag{5}$$

(Jorio et al., 2001) that is in the good agreement with data of electron microscopy.
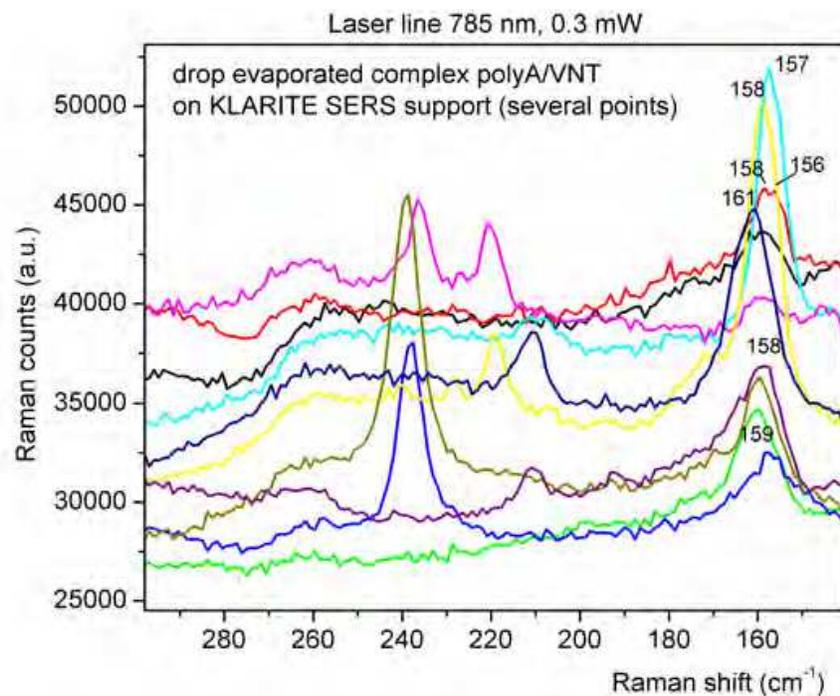
Fig. 7. SERS of isolated nanotubes in the region of «breathing modes» in the different points of the support

Fit peaks for breathing modes was done with Peak Fit Program. The nanotubes have a number of "breathing modes" with the frequency: 136, 148, 156, 162, 169, 177, 219, 233, 264 cм⁻¹ (Dovbeshko et al., 2006(c)). Diameter of isolated single wall carbon nanotubes wrapped by poly-A has been estimated by formula (3) and (5) that is used for estimation of diameter of isolated nanotubes (Dovbeshko et al. , 2008). For isolated nanotubes by poly-A (Fig.7) the frequencies of breathing modes are 157, 158, 159, 161, 221, 236, 238 cm⁻¹ and diameter of this nanotubes are in the range 0,94-1,58 nm with preferential fraction of diameter about 1 nm (Dovbeshko et al. , 2008).

3.3 DNA conformation under SWCNT interactions

DNA is the basic building block of the cell. Hereditary information is encoded in the chemical structure of DNA and reproduced in all living organisms. In Fig. 8 we show dsDNA although, other forms exist, such as ssDNA, B-DNA, A-DNA, Z-DNA, etc. with various stretching and twists (Saenger, 1988; Strick et al., 2003). The common structure to all of them is special combination of bases, sugar and phosphorous groups. Describing adsorption of different complexes on CNT surfaces in general, is a complex process, which stems from different adsorption mechanisms possible (Bruch et al., 1997). The adsorption can occur through a chemical bond between the CNT and the compound, which is a chemisorption process and it is a result from strong short range forces. The adsorption can also be physisorption where no chemical bond is formed and it is due to long range dispersive forces such electrostatic, Van der Waals, dipolar forces. The last type of adsorption will be discussed here. No functionalization nanotubes will be done in the experiment. In the case of DNA-SWCNT complex, we obtained the changes of the vibrational modes in comparison with reference DNA according to the marker bands of the conformational state of DNA (Schrader, 1995; Liquier et al., 1991). It is known (Schrader, 1995; Liquier 1991), that marker

bands of DNA in B-helix conformation are the following: 1715-1710 cm^{-1} (base pairing), 1228-1220 cm^{-1} (phosphate asymmetric band), 1088-1085 cm^{-1} (phosphate symmetric band), 890 and 835 cm^{-1} ($C_{2'-endo/anti}$ conformation). A-helix of DNA has characteristic features at 1705-1700 cm^{-1} (base pairing), 1240-1230 cm^{-1} (phosphate asymmetric band), 1092-1090 cm^{-1} (phosphate symmetric band), 890,878,860 and 805 cm^{-1} ($C_{3'-endo/anti}$ conformation). It is known (Schrader, 1995), that marker bands of DNA in Z conformation are the following: 1700-1692 cm^{-1} (base pairing), 1434 cm^{-1} (A-T pairs), 1215 cm^{-1} (phosphate asymmetric band), and 925-929 cm^{-1} (C-O-C deoxyribose), 867-864 and 838-834 cm^{-1} ($C_{3'-endo}$ conformation).
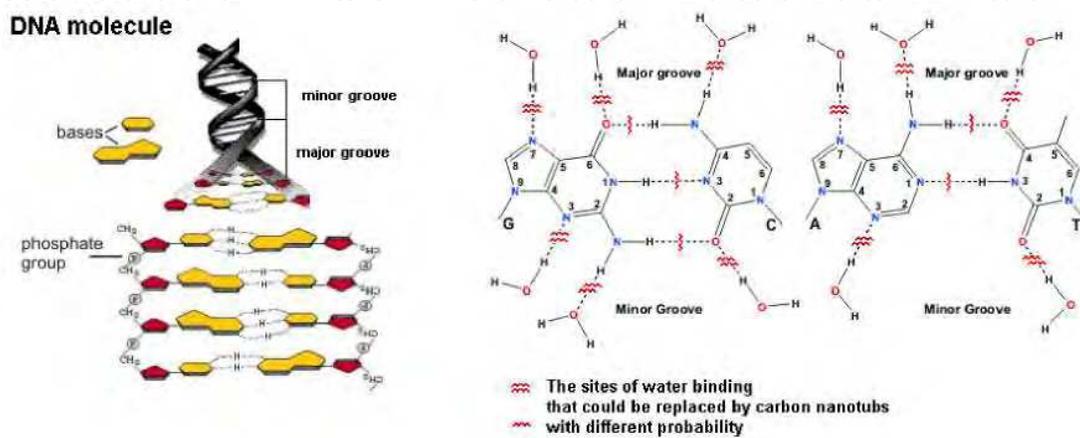
Fig. 8. DNA structure, minor and major grooves with water molecules
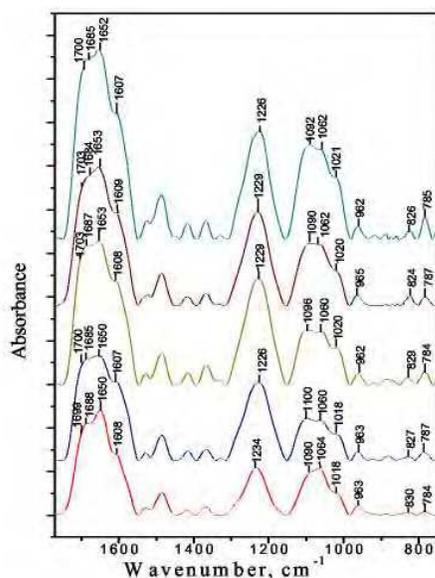
Fig. 9. SEIRA spectra of different parts of the DNA-SWCNT sample in comparison with the reference DNA (bottom spectra).
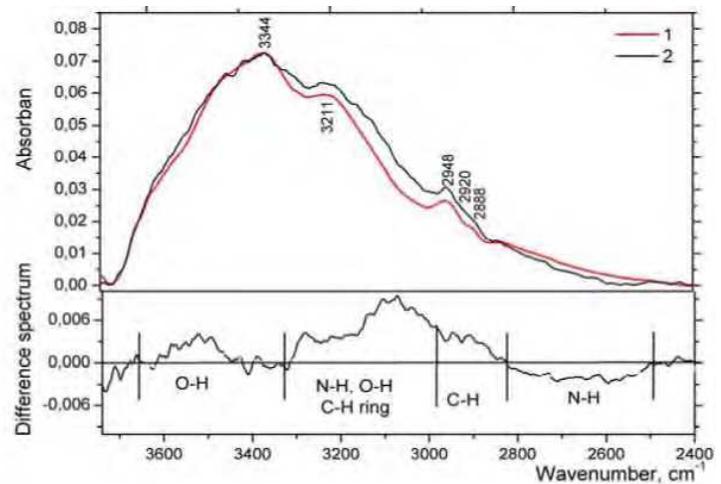
Fig. 10. SEIRA spectra of reference DNA (curve 1), DNA with carbon nanotubes (curve 2) on the gold substrate in the region 2400–3800 cm^{-1} and its difference spectrum. Both spectra was normalized to intensity of the maximum of the band in the 2400-3700 cm^{-1} region.
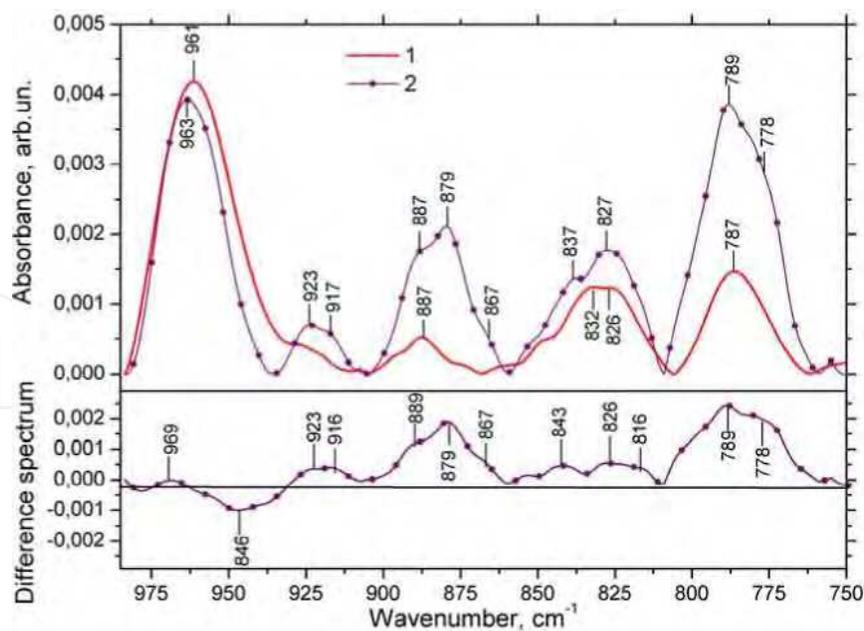
Fig. 11. SEIRA spectra of reference DNA (curve 1), DNA with carbon nanotubes (curve 2) on the gold substrate in the region 750-1025 cm-1. Difference spectrum - DNA with carbon nanotubes-reference DNA

As it could be seen from Fig.9, the spectra of different DNA-SWCNT parts of the same sample changed drastically in comparison with the reference DNA (bottom spectra). The phosphate I band shifts in high frequency region from 1090 cm-1 in reference DNA to 1100, 1096 (non-A- or B-form or Z-form), 1092 cm-1 (A-form) in the DNA-SWCNT, the phosphate II band has low-frequency shift from 1234 cm-1 in reference DNA to 1226, 1229 cm-1 (B-form) in the DNA-SWCNT. The most contribution in phosphate asymmetrical band in DNA (1220-1240 cm-1) is assigned to PO_2^- vibration. The phosphate symmetrical band (1085-1092 cm-1) is more complex and deoxyribose (C-O, C-C) gives a great contribution and influences the shape of this band. However, no known forms of DNA with the position of phosphate I at 1100 cm-1. It says about drastic curvature of DNA backbone as well about restoring of helix structure in DNA (frequency moves from 1064 to 1060 cm-1). So, the changes in phosphate backbone along with sugar moieties could be induced by SWCNT and explain the position of phosphate symmetrical band that is not A- or B-form in the case of DNA- SWCNT. In the case of DNA-SWCNT complex, the essential increase of the absorption of C=O molecular groups at 1712, 1700, 1685 cm-1 and C=N at 1608 cm-1 was registered. The base bands show the presence of a high-frequency shoulder at 1700 cm-1 (A-form) - 1712 cm-1 (B-form) (in comparison with 1699 cm-1 in reference DNA). Abovementioned data indicates the strengthening of interaction between the DNA with SWCNT and restoring the helix form of DNA. The integral intensity of the base band has been increased by factor of 6.24 for the DNA-SWCNT complex. Some of the features shows that in the case of DNA-SWCNT complex the B-helical structures DNA are restored. By the way, we registered an increase of absorbance in 1600-1700 cm-1 in comparison with reference DNA that could indicate to changes in base-pairing as well specific interaction with carbon nanotubes. This could be connected with enhancement of SEIRA signal of DNA under their adsorption on carbon nanotube and/or decreasing of stacked basis, etc. The increase of the bands in the sugar region (900-750 cm-1) (Fig. 11) and shift of sugar vibration at 830 cm-1 (reference DNA) to 827,

829, 824, 826 cm⁻¹ in DNA-SWCNT is an evidence of some changes in conformations of sugar and bases in DNA under SWCNT interaction. Registration of the band at 925 cm⁻¹ (deoxiribose in Z-conformation), 784 cm⁻¹ (syn-form of dG- marker of Z -conformation) indicates to the existence of DNA in Z-form. That is why we could suppose that SWCNT causes to B-A and B-Z transitions in DNA sugar-phosphate backbone.

Some transformation of H-bonds in the region of OH-, NH- and CH-vibrations was observed (Fig.10). The increase (about 50 cm⁻¹) of the halfwidth of H-bonded O-H and N-H stretching vibration has been registered for DNA-SWCNT complex. Thus, for reference DNA the halfwidth of the OH-NH-CH band is equal to 478 cm⁻¹, for DNA-nanotubes complex this parameter is equal to 527 cm⁻¹. This halfwidth increase in DNA-SWCNT is due to increase of shoulder in the 2950-3200 cm⁻¹ region. This indicates the formation of strongly H-bonded NH and OH molecular groups (Badger & Bauer, 1937; Semenov et al., 1994; Maleev et al., 2003) in DNA with SWCNT and could be seen from the difference spectra in Fig. 10.

We registered a drastic decrease of water molecules in DNA-SWCNT. Number of water molecules per nucleotide for reference DNA is equaled to 17.5, for DNA-SWCNT - 10.5, 7.9, 8.9, 7.6 for different points. So, we suppose that nanotube replaces the water molecules from their cites under interaction with DNA Seems, that the cites of DNA interaction with CNT is bases due to their hydrophobic properties. The nanotubes could be inserted in major and/or minor grooves of DNA (Fig.8). The authors of (Li et al., 2006) consider that minor groove of G-C has preference for interaction with carbon nanotubes than A-T minor groove. The interaction of nanotube with G-C pairs is stronger than those for A-T. We think that this point is connected with appearance of additional cites of interaction in the case of G-C-SWCNT binding in comparison with A-T-SWCNT binding. Indeed, in DNA-SWCNT complex a number of water molecules bound with DNA became less 7-9 molecules that is in coincidence with a total number of the sites occupied of water molecules in DNA bases in the major and minor grooves., see Fig.8.
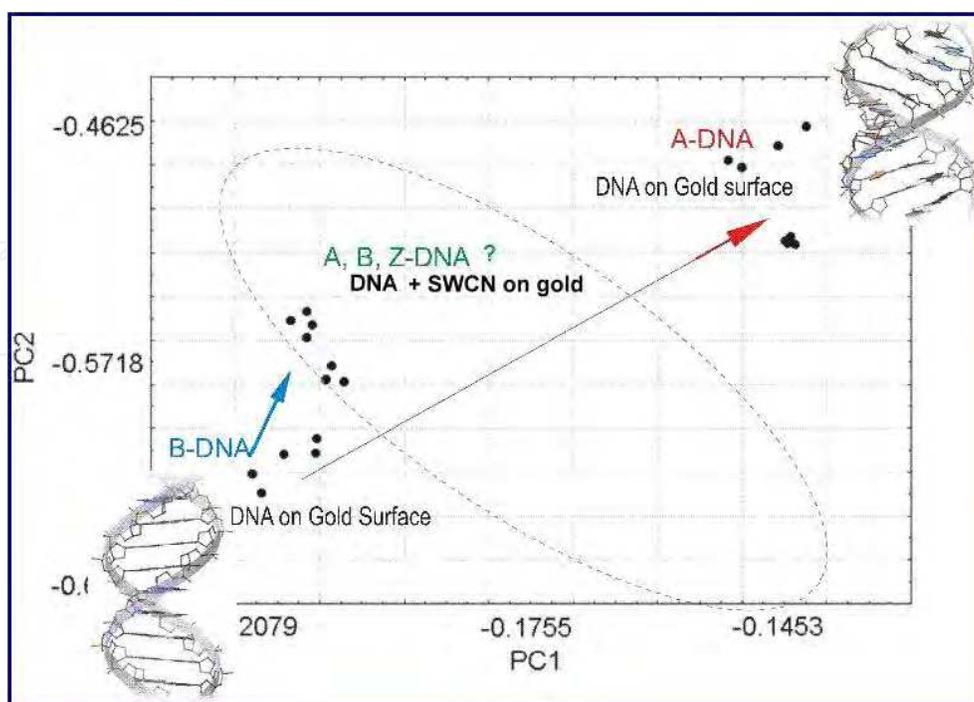

Fig. 12. Principal component analysis of DNA

So, according to spectroscopic data and principal component analysis, in the SWCNT-DNA/complex the main marker bands correspond to different conformations of DNA- B, A, Z-forms and un-known form (Fig.12).

3.4 Conformation of poly-A adsorbed on the surface of carbon nanotubes

Poly-A has 2 ordered forms: under neutral and alkaline pH, poly-A shows single strand, a transition in double strand takes place lower pH 5,25 (Scovell, 1978). Under pH 5,25 and lower adenine in poly-A is protonated on N_1 cites. Formation of H-bonding pair with other adenine with participation of N_7 of one adenine and N_{10} another molecules as well as an aggregation of helixes with formation of double strand poly-A occurs. The structure is kept in aqueous solution, under cold temperature and under fiber spinning. Stability of helix form of poly-A is going due to dispersive, vertical stacking interaction for both ordered forms as well as to formation of intramolecular interstrand and intrastrand H-bonds for double strand of poly-A (Zenger, 1987).

Conformation form of poly-A is determined by pH of solution, under pH 5.25-5.75 the poly -A has single strand form. Under protonation from pH 5.27 to 4.62 the poly-A has transition from single strand form to double strand form (Scovell, 1978) and marker bands of poly-A indicate to it.
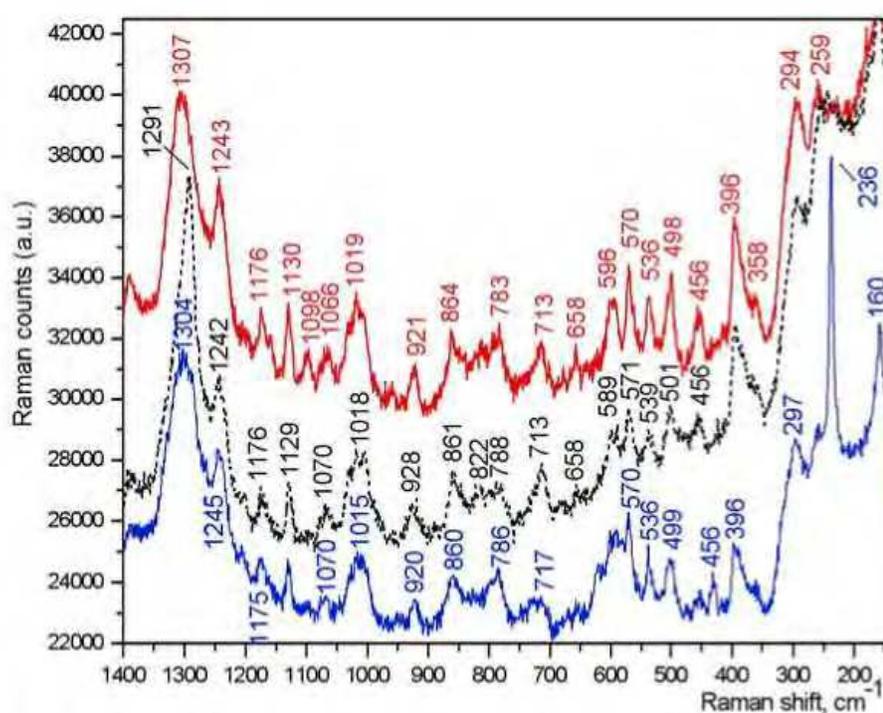

Fig. 13. SERS of poly-A (under pH=5.27) adsorbed at carbon nanotube surface in the region of 1400-400 cm^{-1} in 3 different points

SERS (Fig. 13) and SEIRA (Fig. 14, 15) data was applied for characterization of conformation changes of poly-A at carbon nanotubes surfaces. As a result of interaction between poly-A and nanotubes we have derived the poly-A in single strand conformation (pH=5.27) (Scovell, 1978; Zenger, 1987). With SERS spectroscopy we registered numerous breaks and deformations of poly-A in single strand adsorbed on nanotubes, however the poly-A keeps

their initial form. E.g. sugar conformation in 3 different points has marker bands at 786, 788, 783 cm^{-1} that indicate to backbone of poly-A in helix right hand form. We could registered the signal of poly-A adsorbed on isolated nanotubes (1-3) wrapped by poly-A of concentration of 10^{-3}-10^{-4} M due to usage of Klarite substrate and enhancement of signal about 10^4-10^5 in comparison with Al substrate. We got the selection of nanotubes by poly-A preferentially with diameter size close to 1 nm, meanwhile the diameter of the nanotubes in the bundle was preferentially about 1.4 nm.
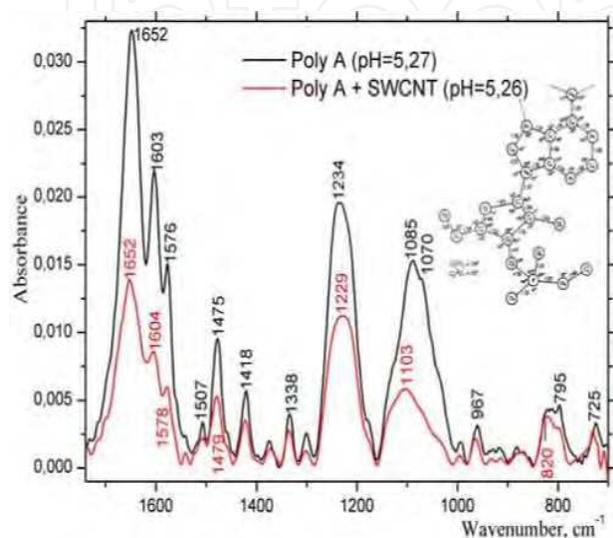
Fig. 14. SEIRA spectra of poly-A and poly-A/SWCNT in neutral solution in the region of 1700-800 cm^{-1}
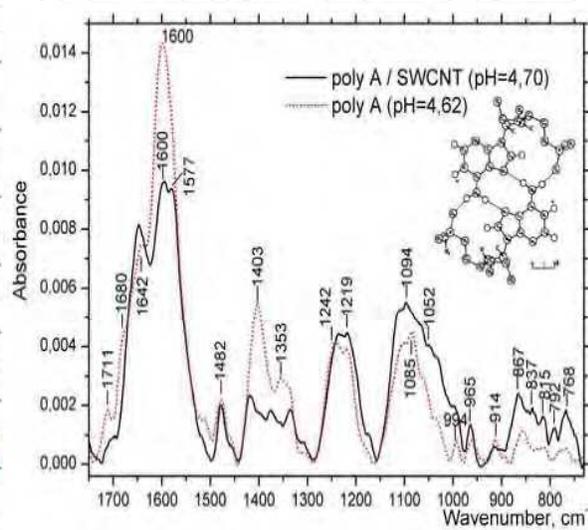
Fig. 15. SEIRA spectra of poly-A and poly-A/SWCNT in acid solution in the region of 1700-800 cm^{-1}

According to SEIRA data we have not observed changes in spectra of poly-A on nanotubes for pH 5.26 in the region of bases 1700-1500 cm^{-1} (Fig.14). However, we have observed strong changes in phosphate bands: symmetrical phosphate shits from 1085 cm^{-1} to 1103 cm^{-1} and asymmetrical phosphate shifts from 1234 cm^{-1} to 1229 cm^{-1} after poly-A adsorption on nanotubes as well as increase of sugar vibration about 4 times. We suppose that the characteristic cites of interaction of poly-A with nanotubes are adenine that induces the curvature of sugar-phosphate backbone.

Double strand poly-A interaction with nanotubes lead to increase of pH of initial solution of poly-A from 4.62 to 4.7 (Fig.15). Spectroscopic features of double strand poly-A/SWCNT complex are similar to DNA/SWCNT. The addition of nanotubes to poly-A prepared with pH 6.47 lead to decrease of pH complex SWCNT/poly-A to 6.37, conformation of poly-A adsorbed at nanotube surface keep single strand form with minor changes.

In poly-A/ SWCNT complex the most drastic changes are observed in the region of OH band (Dovbeshko et al.,2008). A decreasing of water molecules has been calculated in 2 times. We suppose that in poly-A/SWCNT complex, a formation the possible sites of interaction is similar to those that under process of dehydration. In is known that in Poly-A an adenine bounds 4 H$_2$O molecules, phosphate- 4, ribose -1 (Semenov et al., 1994; Maleev et al., 2003). The sites of H$_2$O in poly-A, seems, are replaced by nanotubes as in DNA.

Thus, the poly-A under SWCNT interaction originating from the data obtained for the ensemble of the molecules keeps the initial conformation with numerous change,

disordering and breaks of backbone derived from the data obtained for separate poly-A molecules. Double strand poly-A in SWCNT complex, seems, could adopt different forms similar to DNA.

3.5 Modeling of DNA Base Interaction with Carbon Nanotubes

It is well-known from calculated data (Shtogun et al., 2007; Meng et al., 2007) that a process of adsorption of nucleobases on carbon nanotubes occurs by π-π stacking between carbon nanotube surface and bases resulting in almost flat-laying thymine (or adenine). We are going to compare the calculation data with experimental data obtained with vibration spectroscopy for Thy and Ade adsorbed on SWCNT.
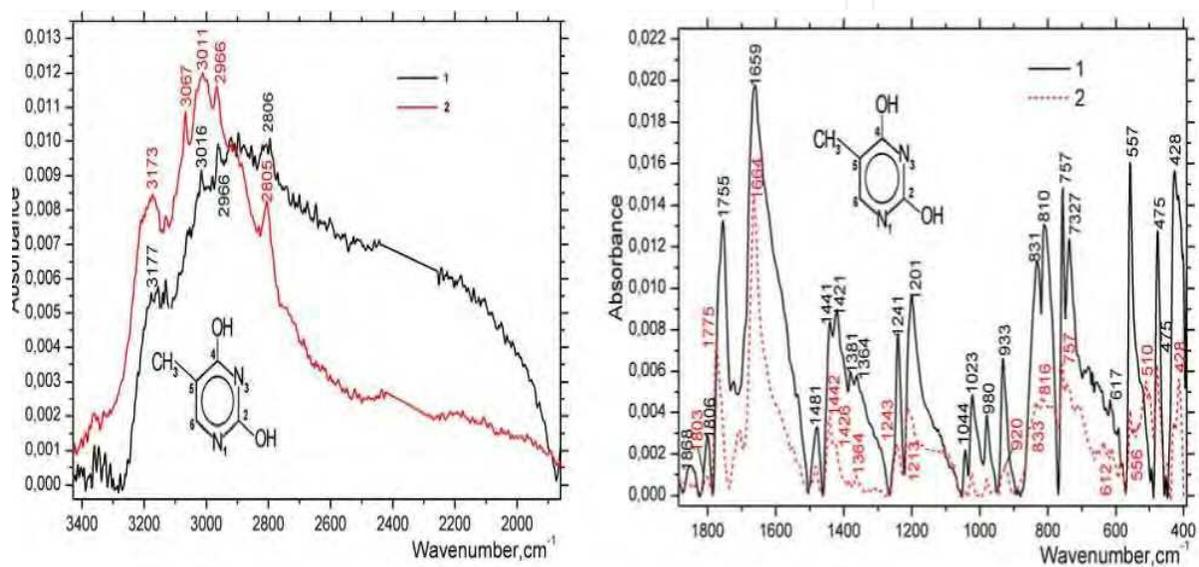
Fig. 16. SEIRA spectra: 1- Thy-SWCNT on gold and 2- Thy on gold
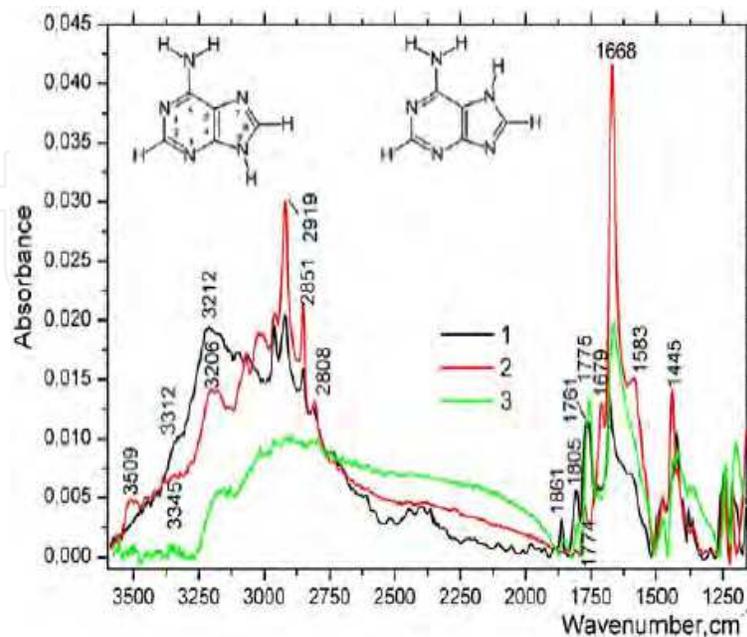
Fig. 17. FTIR spectra: 1 - Thy-SWCNT on CaF_2 and 2 – Thy on CaF_2 , 3 - Thy-SWCNT on gold

Nanotube-Thy interaction resulted to the following spectroscopic features:

1) Widening of H-bonded NH vibrations in the range of 3500-2000 cm^{-1} (Fig.16) and enhance of the intensity of the low-frequency shoulder.

2) Missing of Thy band at 3509 cm^{-1} assigned to N_1H under absorption of SWCNT for both Au and CaF_2 substrates (Fig.17) (Dovbeshko et al., 2009). The last point could be connected with protonation of the Thy ring. We suppose that possible point of Thy interaction with SWCNT is N_1 position.

3) Enhancement of a intensity of the band of NH for the Thy-SWCNT on CaF_2 substrate and a shifting from 3345 (Thy) to 3312 cm^{-1} (Thy-SWCNT) (Dovbeshko et al., 2009). One more NH vibration (seems N_3) shows an increase of the intensity and shift from 3206 (Thy) to 3212 cm^{-1} (Thy-SWCNT).

5) In Thy-SWCNT at Au and CaF_2 we could registered C=O vibrations such as 1861,1805 that could be assigned to C_2=O and C_4=O, respectively, for isolated Thy molecules. We supposed that it connected with adsorption of separated molecules of Thy on carbon nanotubes resulted to film formations due the π-π stacking interaction.

6) Thy-SWCNT on CaF_2 (Fig.17) shows decrease of the intensity of C_4=O vibration and a shift from 1668 to 1679 cm^{-1}, indicating the breaking of some of the inter- or intra-molecular H-bonds with participation of C_4=O.

In Thy-SWCNT (Fig. 17) the C_2=O vibration shows the enhancement of the intensity and a shift is in the low-frequency region from 1774 to 1761 cm^{-1} (Thy-SWCNT on CaF_2) and to 1755 cm^{-1} (Thy-SWCNT on Au) that indicates the formation of new intermolecular H-bonds with C_2=O participation.

8) The bands at 1023, 831, 557, 475, 428 assigned to CH_3 and N_1C_2, C_2=O, C_4=O, N_3H, N_3C_4, N_3C_2=O SWCNT for Thy-SWCNT on gold show a 3 to 5 times enhancement of their intensity (Fig. 16). It could be connected with enhancement of local electrical fields in the system SWCNT-gold. In general, one more reason of the enhancement of intensity of vibrations of Thy adsorbed at nanotubes in low frequency region is connected with crystalline packing of Thy molecules. For Ade-SWCNT on gold (Fig.18) the enhancement of intensity of the numerous vibration NH_2, C=C in the region of stretching and deformation bands in the 3400-1100 cm^{-1}, and decrease of many vibrations lower 1100 cm^{-1} up to 400 cm^{-1} were observed also in contrast to Thy adsorption on nanotubes. This fact demonstrates a difference in behavior of the intensity of the bands of Thy in comparison with Ade molecules and, from our point of view, could be connected with different formation of layers by Thy and Ade molecules. Ade, seems, forms the isolated islands and does not cover the nanotube by monolayer or multilayer films as it does Thy by preference.
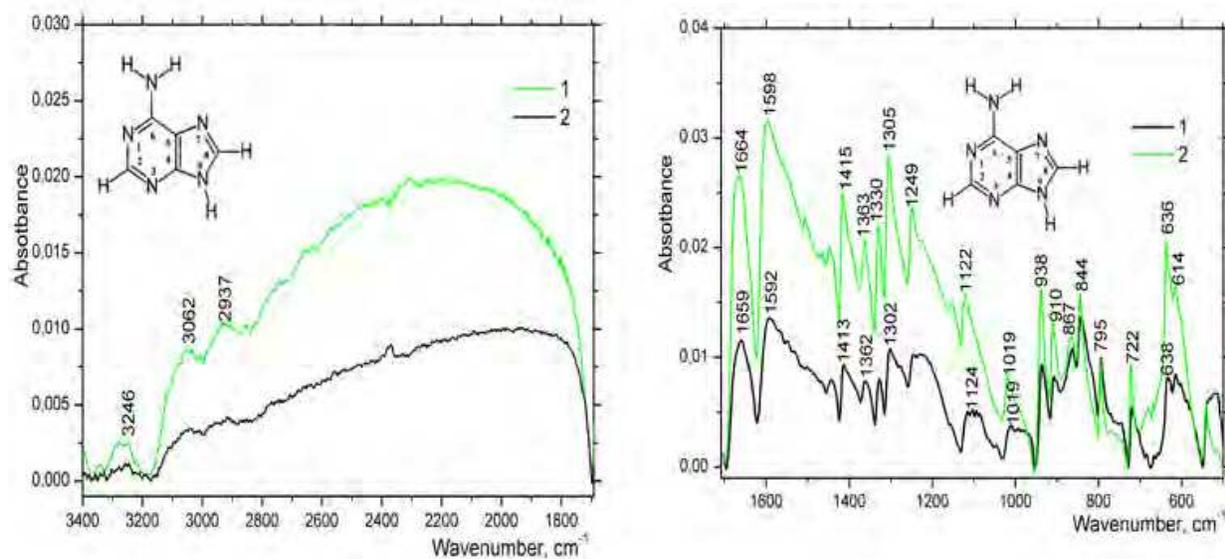
Fig. 18. FTIR spectra on Au: 1-Ade in H_2O, 2- Ade-SWCNT in H_2O
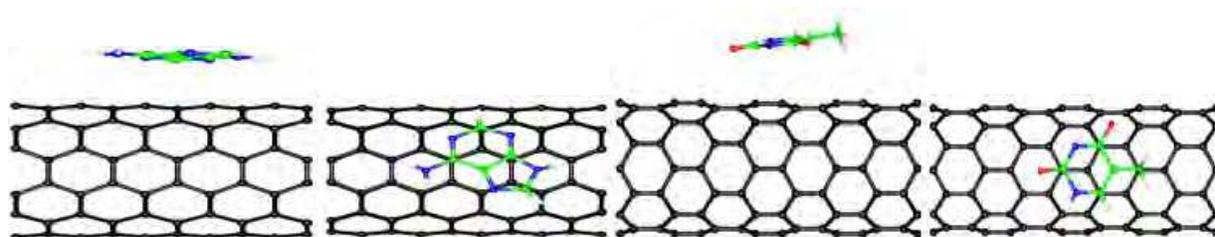
Fig. 19. Possible orientation of a adenine and thymine molecule on surface of SWCNT.
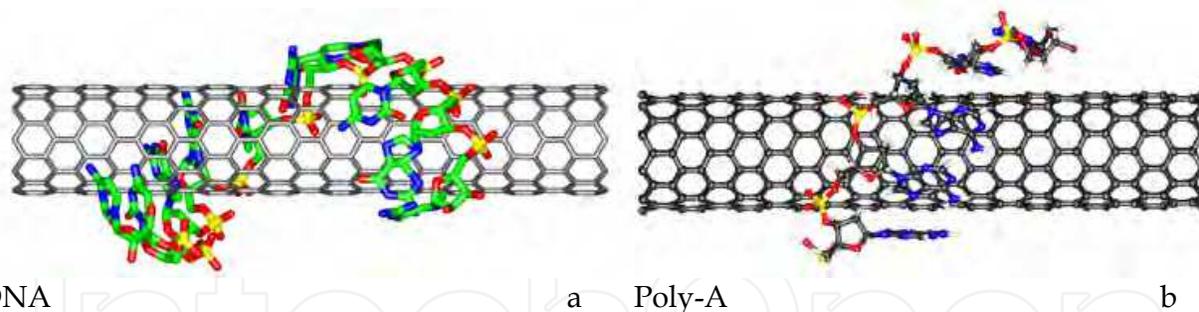
DNA   a   Poly-A   b

Fig. 20.Visualization of possible SWCNT interaction with ss-DNA (a) and Poly-A (b)

Modeling and calculation of the process of the adsorption of thymine on carbon nanotubes have shown the numerous cites of its adsorption on the carbon nanotube surface with weak energy of interaction (Shtogun et al., 2007; Meng et al., 2007; Gowtham et al., 2007). On the basis of the spectral data and the Badger-Bauer rule ($\Delta H = 0,3(\Delta v - 40)^{\frac{1}{2}}$, where ΔH – enthalpy of H-bond formation) (Sokolov, 1981) we have estimated the energy of H-bond formation and break under Thy and Ade interaction with carbon nanotubes. We suppose that break of the H-bonds is due to nanotube interaction with bases, so this energy was accepted by us as an marker for base-nanotube interaction. Data for Ade and Thy in gas phase was taken from (Nowak et al., 1996; Aamouche et al., 1997), respectively correspondingly and in our calculation stretching vibration was taken into account.

Sample	Thy on nanotubes		Thy on graph sheet	Ade on nanotubes		Ade on graph sheet
	Calc. (Shtogun, 2007)	Exp. (our date)	Calc. (Meng, 2007)	Calc. (Meng, 2007)	Exp. (our date)	Calc. (Gowtham, 2007)
Energy, kcal/ mol	5,70-7,29	0,03-3,13	8,16	6,48-7,47	0,09-0,94	10,6
Distance, Å	3,1-3,31	-	3,14	3,05-3,25	-	3,1

Table 1. Energy of interaction of the bases with nanotubes and graphene sheet

Table 1 shows that energy of interaction estimated from SEIRA spectra is less than calculated one. The main reason of non-coincidence of the experimental and calculated data is the fact that more complicated system occurs in the experiment than in calculation. In the calculation we did not take into account an aqueous solution, IR substrate, defects in nanotubes moreover we suppose that covering of nanotube by Thy or Ade is a single molecule as not in the experiment (Fig 19).

Thus, nucleic acid could interact with nanotubes forming the stable complexes by wrapping (Fig. 20), attachment or insertion of NA into SWCNT surface. In the DNA/ SWCNT complex, DNA could adopt left, right helix and un-known forms. The bases are the cites of interaction of NA with SWCNT. The π-π stacking is the main type of interaction in the systems under study that is coincide with data obtained by other scientists (Zheng et al., 2003a ; Zheng et al., 2003b; Gladchenko et al., 2006).

4. Conclusion

1. SERS could be used for characterization of carbon nanotubes and their complexes. SEIRA spectra could effectively indicate the conformation state of nucleic acids in the complex with carbon nanotubes. The analysis of vibrational modes of DNA with SWCNT has shown that the structural changes in DNA occur. They can be interpreted as B-A, B-Z transition and stabilization of DNA structure in some DNA fragments. Un-known conformation forms of DNA induced by SWCNT could be supposed also.
2. The model of DNA wrapping around SWCNT on the basis of replacing of the water molecules by SWCNT is proposed for the process of carbon nanotube interaction with DNA.
3. We developed a technology of selection of nanotubes with diameter of 1 nm by poly-A, meanwhile the bundle has nanotubes of 1.4 nm mostly.
4. We registered a Raman signal from separated nanotubes wrapped by poly-A in single strand as well numerous marker band of poly-A indicated the presence of poly-A on the surface of nanotubes in their initial form. SEIRA data shows the conformation form of poly-A/nanotube in assemble is practically non-changeable in comparison with poly-A.
5. With SERS spectroscopy we registered numerous breaks and deformations of poly-A in single strand adsorbed on nanotubes, however the poly-A keeps their initial form. The characteristic cite of interaction of poly-A with nanotubes is adenine. We could registered the

signal of poly-A adsorbed on nanotubes with poly-A concentration of 10^{-3}-10^{-4} M due to usage of Klarite substrate and enhancement of signal about 10^4 -10^5 in comparison with Al substrate. Nanotubes induces the breaks into double strand in poly-A, redistribution of the H-bond net, break of a number of H-bonds.

6. Ade adsorbed on carbon nanotubes forms mostly islands and Thy forms monolayer or multilayer films by π-π stacking interaction with tilted bases to plane of carbon nanotube.

Acknowledgments

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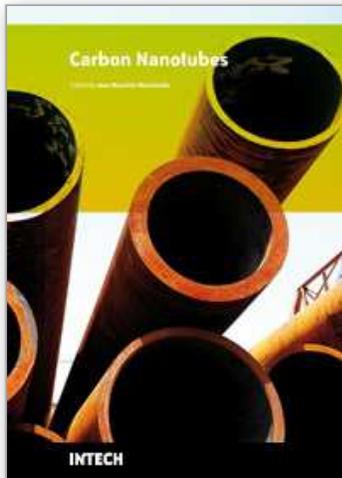
Carbon Nanotubes

Edited by Jose Mauricio Marulanda

This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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