# Ultrasound-assisted formation of composites of carbon nanotubes with nanosilver

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In the present work a method of manufacturing of a nanocomposite of single-walled carbon nanotubes with silver nanoparticles (SWNT–AgNP) by ultrasound treatment of SWNT and $AgNO_3$ mixture in aqueous medium is tested, anticipating the advantage of avoiding reducing chemicals employment. Transmission electron microscopy inspection of the objects obtained showed the presence of the nanotubes or relatively small SWNT bundles with inclusion of AgNPs of 5–20 nm in diameter. Laser desorption/ionization mass spectrometric analysis revealed the sputtering of small silver clusters $Ag_n$ ($n = 2, 3, 5, 7, 9$) from the nanotubes surface, which may serve as nucleus for the nanoparticles growth. Possible mechanisms of the SWNT–AgNPs composite formation under ultrasound treatment due to cavitation-induced processes and sonochemical reactions are discussed.

**Keywords**: nanocomposites, single-wall carbon nanotubes, silver nanoclusters, ultrasound treatment, transmission electron microscopy, mass spectrometry, cavitation.

Опробован метод приготовления нанокомпозита одностенных углеродных нанотрубок с наночастицами серебра (ОУНТ–АgНЧ) путем ультразвуковой обработки смеси ОУНТ и $AgNO_3$ в водной среде, преимуществом которого является отсутствие необходимости работы с химическими восстанавливающими агентами. Исследование с помощью просвечивающей электронной микроскопии объектов, полученных таким способом, показало наличие в них нанотрубок или небольших снопов ОУНТ с вкраплениями наночастиц серебра размером от 5 до 20 нм. С помощью масс-спектрометрического анализа методом лазерной десорбции/ионизации обнаружено распыление с поверхности нанотрубок малых кластеров серебра $Ag_n$ ($n = 2, 3, 5, 7, 9$), которые могут служить зародышами для роста наночастиц. Обсуждаются возможные механизмы формирования композита ОУНТ–АgНЧ под действием ультразвука в ходе кавитационного процесса и сонохимических реакций.

**Про формування композитів вуглецевих нанотрубок з наносріблом за допомогою ультразвуку**. *О.А.Боряк, В.С.Шелковський, М.В.Косевич, В.В.Орлов, О.М.Вовк, В.О.Карачевцев.*

Випробувано метод виготовлення нанокомпозиту ОВНТ–АgНЧ шляхом ультразвукової обробки суміші ОВНТ і $AgNO_3$ у водному середовищі, перевагою якого є відсутність необхідності роботи з хімічними відновниками. Дослідження за допомогою трансмісійного електронного мікроскопа об'єктів, отриманих у такий спосіб, показало наявність у них нанотрубок або невеликих снопів ОВНТ з вкрапленням наночастинок срібла за розміром від 5 до 20 нм. За допомогою мас-спектрометричного аналізу методом лазерної десорбції/іонізації виявлено розпилення з поверхні нанотрубок малих кластерів срібла $Ag_n$ ($n = 2, 3, 5, 7, 9$), які можуть бути зародками наночастинок. Обговорюються можливі механізми формування композиту ОВНТ–АgНЧ під дією ультразвуку впродовж кавітаційних процесів та сонохімічних реакцій.

## 1. Introduction

Combination of unique properties of components along with the acquisition of qualitatively new features is expected from the composite materials. Integration of useful properties of carbon nanomaterials and metal nanoparticles predetermines the prospects of applications of carbon nanotubes (CNT) composites with nanosilver or silver nanoparticles (AgNPs) in various devices and technology in nanoelectronics, biosensorics, heterogeneous catalysis, biomedicine [1–3]. Although the CNT–Ag nanocomposites were obtained more than a decade ago [4–6], the interest in these materials has not waned because of need in tailoring of their properties for certain functions and expansion of its application to new areas [7–11].

Proven methodology for production of CNT composites with silver is traditionally used, which is based on reactions of silver ions reduction in the presence of a chemical reducing agent [6, 12, 13]. A drawback of such methods is the necessity of purification of the material obtained from the remains of chemical reagents. Furthermore, chemical reactions occur in the bulk liquid medium (as opposed to the reactions at the CNT surface), which cause the loss of the nanoparticles not bound with the nanotubes. Ultrasound was harnessed in such technologies mainly for CNT dispersion in liquid medium. At the same time, a vast field of sonochemistry [14–18] investigates ultrasound-induced chemical transformations. Thereafter a question concerning the role of ultrasound *per se* in the technological process of CNT–Ag composite formation emerges. In this connection, the aim of the present work is to verify a possibility of production of CNT–Ag composite by ultrasound treatment only, that is without use of any chemical reducing agents, followed by discussion of possible mechanisms of AgNPs formation on the CNT surface.

## 2. Experimental

The process of preparation of single-wall CNT (SWNTs) composite with silver nanoparticles was as follows: portions of SWNTs and $AgNO_3$ salt were placed into deionized water in a glass vessel and subjected to ultrasound in cylindrical resonator of UZDN-1 U4.2 ultrasonic disperser (AP "Electron", Sumy, Ukraine) operating at 22 kHz frequency and 1 W power.

To avoid noticeable heating, three sessions of sonication 10 min each were alternated by 10 min breaks. After sonication the resulting samples were transferred to Eppendorf plastic vessels for further storage.

The selection of the components concentrations and their ratios was performed. Absolute concentration of salt was varied from 2 mg/mL to 20 mg/mL; weight ratio $SWNT:AgNO_3$ was changed from 1:40 to 1:200. Composites produced from the mixtures containing the highest silver content (20 mg/mL $AgNO_3$ and 1:200 $SWNT:AgNO_3$ ratio) were selected for further studies as the specimens characterized by higher probability of AgNPs formation on single nanotubes.

Transmission electron microscopy inspection of the nanomaterials obtained, visualization and evaluation of size of AgNPs were performed with the help of analytical complex "Transmission electron microscope EM-125" (AP "Electron", Sumy, Ukraine) operating at the Centre for collective use of scientific equipment of the Institute for Single Crystals of the NAS of Ukraine. For sample preparation a drop of water suspension of SWNT–Ag was deposited on a copper grid and dried.

Mass spectrometry characterization of the nanomaterial using laser desorption/ionization (LDI) technique was conducted at the Centre for collective use of mass spectrometer Autoflex II LRF 20 (Bruker Daltonics GmbH, Germany) located at the Institute for Surface Chemistry of the NAS of Ukraine. Parameters applied for mass spectra recording were as follows: nitrogen laser with $\lambda = 337$ nm was used, laser power attenuation was set at 50–60 % of maximum value (the energy of 100 % laser pulse was 64 µJ [19]); 20 kV accelerating voltage, laser pulse 3 ns long and 40 ns delay in time for ion extraction were applied; the results of 10 laser shots were summarized in linear and reflectron modes. A drop of the sample was loaded at the standard steel target plate and dried at ambient conditions.

Single-wall carbon nanotubes (Carbon Nanotechnologies Inc., Houston, TX, USA), synthesized by HiPCO method and further purified to 99 % [20], and $AgNO_3$ (≥99.0 %, Sigma-Aldrich) were used for the nanocomposite manufacturing. Deionized water was used for preparation of solutions and suspensions.

## 3. Results and discussion

Visual inspection of water suspensions of SWNT–Ag nanocomposites produced by ultrasound treatment of a mixture of SWNT and AgNO$_3$ in aqueous medium permitted us to make some preliminary conclusions as to the characteristics of the material obtained. Firstly, the samples evaluated right after the sonication looked like turbid suspensions in black and white coloring (Fig. 1a), which distinguished them from suspensions colored in shades of yellow, obtained during chemical reduction of silver in the presence of reducing agents. Secondly, SWNT–Ag suspensions remained visually unchanged during several hours, which differentiated them from the sonicated aqueous suspensions of neat nanotubes, characterized by rapid sedimentation of the nanotubes after termination of sonication. Thirdly, gradual aggregation of the suspension components with time was observed, which resulted in formation of visible aggregates (Fig. 1b) after one day of storage; such aggregation behavior of the composite also differed from the rapid precipitation of the neat nanotubes to the bottom of a vessel. These three features will be further accounted during the discussion of the mechanisms of formation of SWNT–Ag nanocomposite under ultrasound treatment in the absence of the chemical reducing agents.

To characterize the material obtained its electron microscopic inspection was performed. On the photos in Fig. 2 single nanotubes and bundles of nanotubes up to 30 nm in diameter (which corresponds to aggregates of SWNTs from several to tenth of units) are visible in light grey color. There are more dark species of rounded form on the SWNTs surface, which correspond to nanoparticles of 5–20 nm in diameter (Fig. 2c). In Fig. 2b a site containing aggregates of AgNPs on nanotubes mesh is shown. The method of sample preparation for microscopy, consisting in deposition of the analyzed suspension onto the copper grid, provides the absence of nanoparticles not bound to SWNT in the microscopy field.

Next, the material was characterized by LDI mass spectrometry. LDI mass spectrum (Fig. 3) of the sample obtained by drying of the drop of SWNT–AgNPs suspension on the standard metal target plate contains sets of peaks corresponding to silver nanoclusters along with a row of peaks in the small mass region. The latter correspond to low mass impurities present as a back-
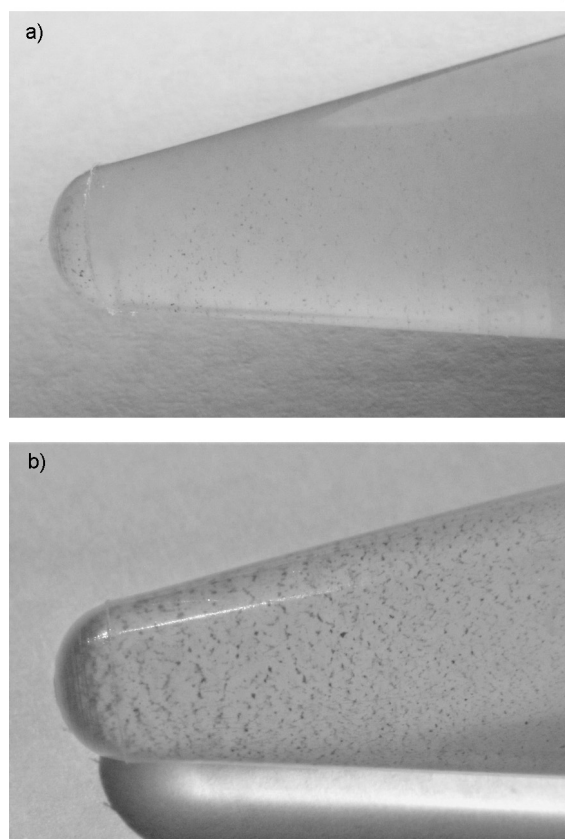


Fig. 1. Aqueous suspensions of the SWNT–Ag nanocomposite obtained by ultrasound treatment of 1:200 mixture of SWNT and AgNO$_3$: a — photographed right after the sonication; b — after one day of storage. (The container is an Eppendorf vessel of 1.5 mL.)

ground practically for any sample due to high sensitivity of the LDI technique; in the mass region above ~500 Da the background peaks are absent or negligibly small. It should be noted that carbon nanotubes are not transferred to the gas phase by UV laser irradiation and thus cannot be detected in mass spectra. A series of Ag$_n^+$ clusters recorded in the LDI mass spectra of the SWNT–AgNPs material has a peculiar pattern: the highest intensity is observed for clusters with $n = 2, 3$; they are followed by smaller in abundance clusters with odd $n$ values equal to 5, 7, 9. Reliable coincidence of the recorded isotopic distributions in the peaks envelopes of each Ag$_n^+$ cluster (see example for Ag$_7^+$ cluster in the insert in Fig. 3) with the calculated one [21] confirms the attribution of the peaks to silver nanoclusters. The absolute abundances of the clusters with $n > 3$ are of the same order of magnitude. Such a pattern of Ag$_n^+$
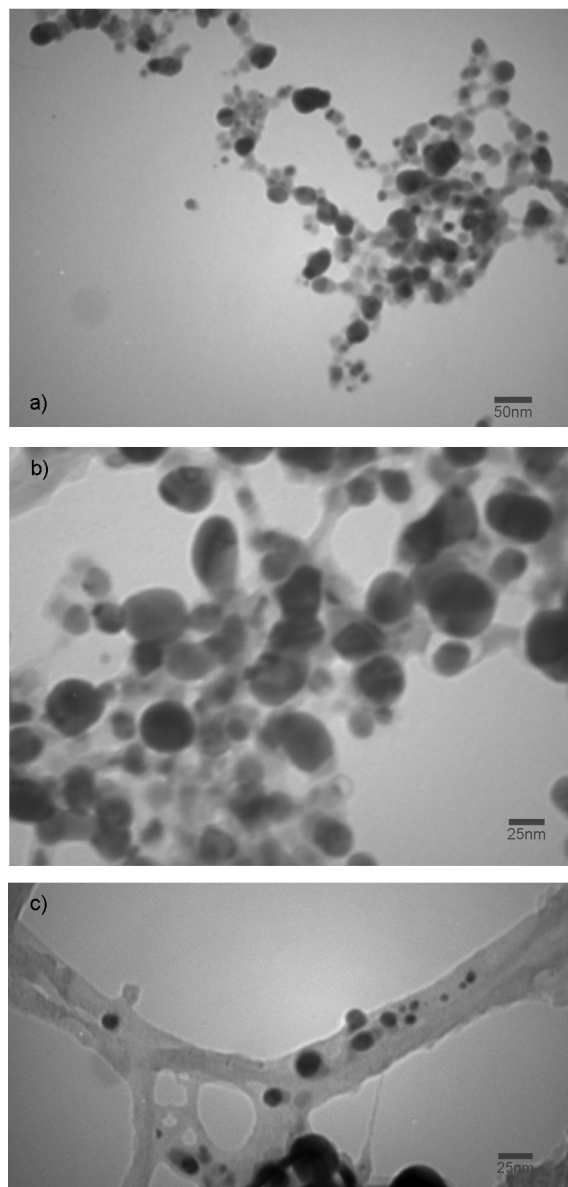
Fig. 2. Transmission electron microscopy image of SWNT–Ag nanocomposite obtained by ultrasound technique (scale bar corresponds to 50 nm (a) or 25 nm (b, c)).
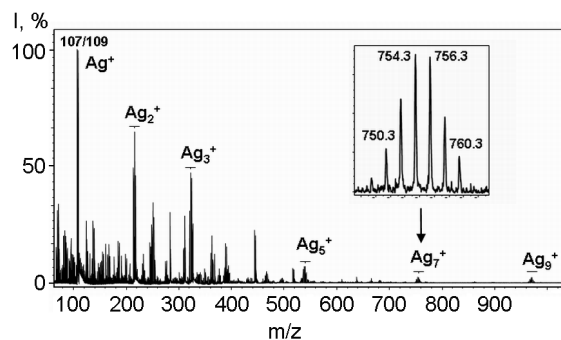
Fig. 3. LDI mass spectrum (reflectron mode) of dried drop of SWNT–Ag nanocomposite suspension obtained by ultrasound technique. In the insert the enlarged fragment of the spectrum demonstrates isotopic distribution for $Ag_7^+$ cluster.

nanoclusters of interest in the mass spectrum in Fig. 3 coincides qualitatively with the pattern of $Ag_n^+$ set in the LDI spectrum recorded at the same instrument for the silver nanoclusters synthesized by a chemical method described in work [21]. At the same time, it differs from the patterns of $Ag_n^+$ clusters generated by various mass spectrometric desorption/ionization methods from other silver-containing objects (metal, foil, salts, colloids, performed nanoparticles). For example, the pattern of a set of $Ag_n^+$ ($n$ up to 60) clusters sputtered from the surface of metallic silver by accelerated ions

bombardment is characterized by monotonous decrease of cluster abundance with $n$ increase and systematic superiority of abundance of odd-$n$ species over the neighboring even-n ones [22]. In a work on laser ablation of silver colloids [23] noticeable dependence of small clusters $Ag_n^+$ ($n = 1–3$) abundance on the laser type and the wavelength was reported. As to the LDI from AgNPs, the relevant information was provided in the work [24] devoted to application of silver nanoparticles (~160±20 nm) as a matrix for LDI of peptides. No silver cluster ions with $n > 3$ overlapped with the reported LDI mass spectra of peptides at laser parameters being the same as in our investigation (337 nm wavelength and 20 keV accelerating voltage). Similarly, in work [25] small species only with $n \leq 3$ were observed under LDI of separate spherical silver nanoparticles, while larger clusters were produced from silver nanoislands film. These pattern features reported in the literature [24, 25] allow us to propose that odd-$n$ $Ag_n^+$ ($n = 5, 7, 9$) clusters recorded for our composite samples are not generated from larger AgNPs, but exist as individual species in the nanocomposites.

Laser desorption of such small $Ag_n^+$ ($n = 3, 5, 7, 9$) clusters from the nanotubes evidences that, along with nanoparticles detected by electron microscopy, there are much smaller entities of several silver atoms at the SWNT surface, which may serve as nucleus for further growth of nanoparticles [26]. Experimental observation of small silver clusters on nanotubes is a new fact which should be accounted in determination of the properties of SWNT–AgNPs nanocomposite.

To check a probability of silver nanoclusters formation under laser effect on possible remains of silver nitrate in the sample, the control LDI experiments for a neat $AgNO_3$ salt were performed. While $Ag^+$ ion was sputtered from the salt, no silver clusters were observed at the laser parameters applied in this study.

Further, control experiments on ultrasound treatment of water solution of silver nitrate using the same sonication scheme as for the composite production, did not show nanosilver formation in the absence of SWNT, since no differences were observed in the UV-vis spectra of the salt solution recorded before and after sonication. Note that the conditions required for silver nanoparticles formation on sonication of salt solutions were reported in the literature [27, 28].

Absence of the yellow coloring of the liquid water suspension containing SWNT–AgNPs, marked at the beginning of this section, points to difference in the processes proceeding on chemical reactions in the presence of reducing agents and on sonochemical reactions. The main reason for these distinctions may be in spatial parameters: chemical reactions with a reducing agent (as a source of electrons) proceed over the whole volume of bulk solution; while a set of discreet reaction zones confined to cavitation bubbles is present in the system at a given moment during the ultrasound treatment.

Since ultrasound is the only factor affecting our system in which, as we have shown above, the composite SWNT–AgNPs is formed, it can be anticipated that all processes resulting in nanoparticles formation at the nanotube surface must proceed at its region which fall into a cavitation bubble. In this connection it is necessary to consider possible mechanisms of nanoparticles formation in the ultrasound-induced processes [14−18].

While in the majority of works devoted to technology of CNT handling the function of ultrasound is limited to purely mechanical separation of CNT from bundles and their dispersion in water medium, in the works devoted to synthesis of nanocomposite it is necessary to account the interplay of nanotubes with ultrasound and sonochemical reactions. In particular, the role of nanotubes in development of cavitation processes in liquid medium, their role as centers of heterogeneous nucleation of nanoparticles growth and their involvement in sonochemical reactions, as well as corre-

lation between geometrical parameters of nanoobjects and reaction zones created by ultrasound should be evaluated. Further estimates are based on literature data related to these subjects.

Let us briefly describe the processes induced in liquid by ultrasound [14–18]. The most significant process is acoustic cavitation which consists in nucleation, growth and implosive collapse of cavitation bubbles. The existence of such cavitation bubbles determines primary sonochemistry consisting in gas phase reactions inside the collapsing bubble, secondary sonochemistry connected with reactions in a limited layer outside the bubble and physical processes caused by super sound jets and shock waves emerging during the collapse of a bubble. As to sonochemical reactions extensively studied for a variety of objects, in the framework of a problem in question we are interested in defining of reducing agents required for reduction of silver ions to neutral constituents of metal nanoparticles. Such agents generated in the cavitation process are solvated electrons [29] and hydrogen radical $H^*$ (atomic hydrogen) [30] formed on splitting (sonolysis) of water molecules [31].

Since direct monitoring of the interaction of CNT with cavitation bubbles is hampered by the instability (rapid time variability) of the ultrasound-treated system and small (nano) sizes of the objects, the related experiments were reported in the literature for more stable systems and conditions [32, 33]. The process of boiling of liquids incorporating CNT was examined as a special case of phase transitions of first order; the relevancy of the dimension of a nanotube surface to phase separation boundary was considered. Investigations of bubbles growth directly at the CNT surface were performed using laser irradiation [32] and resistive heating [33]. In the site of a nanotube heating by the laser ($\lambda = 1064$ nm, 100 mW power) growth of bubbles with radius of 5−6 µm was observed; separation of the bubble from the tube did not happen [32]. On resistive heating by permanent current of the CNT-contaning conductive medium, CNTs served as bubble nucleation centers as well; maximal bubble diameter was 400 µm [33]. In the notions on ultrasound induced sonochemical processes it is accepted that there are two types of "chemical reactors": gas phase inside the cavitation bubble with mean radius 150 µm and a thin layer of liquid adjacent to the collapsing bubble of ~200 nm width and lifetime

after the bubble collapse smaller than 2 μs. The above information permits the following estimates to be done.

The role of CNT in formation of silver nanoparticles under sonications of the system is predetermined by the fact that during the growth and collapse of a bubble near the nanotube surface, the nanotube (or its part) may be located in the liquid reaction zone, where electrons and radicals required for silver reduction are available due to sonochemical transformations of water. Furthermore, when the average linear dimensions of a CNT exceed the thickness of the liquid reaction zone (500 nm vs 200 nm), the conducting CNT can provide transport of electrons to noticeable distances towards its part in the bulk liquid. Thus, the probability of silver ions reduction at the CNT sites remote from the boundary of a single bubble is increased. This means that the CNT with the sonochemical bubble at its surface increases the cross section of sonochemical reactions. On the other hand, linear dimensions of the gas phase reaction zone significantly exceed an average length of a nanotube (0.5 μm CNT vs 150 μm bubble radius). At such ratio, the nanotube occupies only a small part of the gas phase reaction zone and, virtually, can play a catalytic function in gas phase reactions.

Physical factors affecting CNT under sonication determine mechanical behavior of CNT in the instant velocity fields near the cavitation bubble and thermodynamic parameters of formation of vapor bubble in liquid. In a number of works devoted to theoretical description of CNT behavior near the cavitation bubble in the sonicated liquid different forces acting on CNT and CNT orientation are considered. In work [34] forces affecting elongated nanostructures directed radially in relation to the collapsing bubble are described and a model for description of the cavitational splitting of single mesoscale fibers (carbon nanotubes, protein fibrils, silver nanowires) is proposed. In work [35] the dispersion of CNT under ultrasound treatment is described as a power function of time $t^m$ (where $m = 0.2{-}0.5$). On the bubble collapse short CNT are oriented radially and more long are bent. It is obvious that both stretching and bending can expose the defects on the CNT surface for contacts with the redox active environment. The defects of various nature at the nanotubes surface can serve as centers for heterogeneous nucleation for AgNPs growth [14, 36].

Analysis of the SWNT–AgNPs nanocomposite structure at the electron microscopy photographs in Fig. 2 permits to express some propositions as to improvement of technology of nanocomposite manufacturing. It follows from the image that AgNPs are located mainly at the nanotubes bundles (not at single nanotubes). Obviously, within the procedure applied, using of aqueous solution of silver nitrate provides simultaneous splitting of the CNT bundles and nucleation of nanoparticles. The latter may bound several adjacent nanotubes, thus preventing them from separation from the bundle. Thus, to obtain single nanotubes decorated with AgNPs it is necessary to perform dispersion of the initial CNT sample in pure water as the first stage, and add silver nitrate solution at the next step.

Stability (absence of precipitation) of SWNT–AgNPs suspension during at least several hours can be explained by mechanical repulsion between "Protrusions" created by AgNPs on a smooth surface of CNT or CNT bundles, which prevents their adhesion or, otherwise, by temporary preservation of positive charge at the surface of metallic nanoparticles, which cause repulsion of the modified bundles. Note that destabilization of the suspension with time proceeds not via sedimentation, but by aggregation of the composite fibers in the bulk suspension. The last question is related to the way of the AgNPs fixation at the CNT surface either by chemical immobilization or physical adsorption. In assumption that the centers of heterogeneous nucleation of nanoclusters and nanoparticles are defects, i.e. distortions in the native carbon structure on the surface of a nanotube, the nanoparticles grown on such defects may be electrostatically attached to the surface. The above estimates of the relation of geometrical sizes of nanotubes and cavitation bubbles permit to consider tentatively one more attachment mechanism connected with welding of silver nanoparticles to the carbon surface. From the sonochemistry basics [15, 18] it is known that the effective temperatures of the gas and liquid reaction zones of cavitation bubble may reach 5200 K and 1900 K, respectively. While the melting temperature of metallic silver is 961.8°C (~1234 K) [37], a known manifestation of nano-effects is decrease of melting temperature of nanoparticles, which correlates with the particle size decrease [38]. The lowest reported melting temperature for AgNPs is 112°C recorded for particles of 3.5 nm size [39]. Thus,

when the segment of a nanotube containing a grown nanoparticle finds itself in the reaction zone of a cavitation bubble, there appears an opportunity of the silver nanoparticle melting and welding to the CNT surface. Note that an average size of nanoparticles being 5–20 nm is an order of magnitude smaller than the length of the liquid reaction layer of the collapsing bubble being ~200 nm. Shock waves arising during the cavitation bubble collapse [40] can cause AgNPs implantation into the CNT surface. This kind of effects were reported in the literature: melting of AgNPs under ultrasound procession of fabrics sprinkled by nanoparticles was observed in work [41]; anchorage and implantation of AgNPs into the glass surface on ultrasound treatment of glass slides immersed in AgNPs aqueous suspension was achieved [42] as well as paper coating by AgNPs was described [43].

Obtained in this work SWNT–AgNPs nanocomposite match the condition set in the task of the investigation, namely, it does not contain reducing agents. Naturally, various reducing chemical agents and dispersants are selected and tested to control the sizes and shapes of the growing nanoparticles; however, in the absence of special requirements to the size and shape merely ultrasound treatment is sufficient for production of CNTs composite with silver nanoparticles. In the framework of further developments of technological processes thus obtained nanocomposite may be directly deposited from its water suspension to some carrier, e.g. to a surface to be covered by the composite film or to a fabric with bactericidal properties.

### 4. Conclusions

SWNT–AgNps nanocomposite is produced as an aqueous suspension of nanotubes decorated by silver nanoparticles applying ultrasound-assisted technique. Presence of silver nanoparticles with average diameter 5–20 nm at the surface of nanotubes bundles is demonstrated by transmission electron microscopy. Laser desorption/ionization mass spectrometry shows presence of small $Ag_n$ clusters in the system, which may serve as nucleation centers for further growth of nanoparticles. Possible mechanisms of formation of SWNT–AgNps nanocomposite under ultrasound treatment in the course of cavitation process and sonochemical reactions is discussed. Comparison of geometrical sizes of cavitational bubbles and nanotubes shows that segments of CNT (or not

separated bundles) may occur either in gas phase or liquid phase reaction zones of the collapsing bubble. Defects on CNT surface, either initially existing or induced by ultrasound, may serve as centers for heterogeneous nucleation of AgNPs growth. The agents for silver ions reduction are available in the system as solvated electrons or hydrogen atoms (radicals) generated due to sonochemical solvolysis of water molecules. Possible mechanism of nanoparticles anchorage at the CNT surface which accounts ultrasonic welding is proposed. An advantage of the proposed ultrasound-assisted procedure of SWNT–AgNps composite production as compared to conventional chemical reduction methods is in the avoiding of the laborious stage of the sample purification by removing of reducing agents. The composite obtained may be deposited directly from water suspension onto various carriers for further applications.

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