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Interaction of laser radiation with carbon nanotubes for the creation of biocompatible media

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Abstract. The paper describes the process of carbon nanotubes structuring as a result of their interaction with laser radiation. Mechanisms of the formation of biocompatible media with single-walled carbon nanotubes (SWCNTs) under the action of laser radiation were proposed. An investigation of the temperature field distribution in the defect region of two nanotubes contact after laser heating showed that the defect region had a temperature of ~ 50 % higher than the temperature of the defect-free regions of the structure. The formation of four covalent C-C bonds occurred in 2-2.5 ps at an effective binding distance of SWCNTs 3-5 Å. The interaction energy of the tubes ranged from -7.43 to -7.36 eV/atom at the formation of bonds between SWCNTs. The distribution of the maximum values of the electromagnetic field over the SWCNTs volume was in good correlation with the SEM images of the branched nanoscaffold in the protein matrix. The scaffold provided a hardness of biocompatible media up to 400 MPa. Topography study of the media surface led to the conclusion that an increase of SWCNTs concentration helps to reduce the number of pores and increase their size. Created biocompatible media can be used as tissue-engineered matrixes that promote cell proliferation.

1. Introduction

Currently, regenerative medicine makes extensive use of biocompatible media with an internal nanoparticle scaffold. Optical prototyping is significant among methods for obtaining scaffold media. With the development of lasers, the directions of optical sintering, stereolithography and polymerization of three-dimensional objects, including nanoscale, have gained popularity [1]. Since the resulting voxel size depends on the size of the focus of laser radiation in the medium when it is translated into a solid state.

Materials, which have nanometer-sized particles as a reinforcing component, more successfully mimic the structure of the natural matrix for cell growth, which favorably affects their biocompatibility [2]. Carbon nanotubes (CNTs) are perspective nanoparticles for the scaffold media formation, due to their unique optical, electrical and thermal properties. CNTs have dimensions close to those of the main components of the natural cellular matrix, their mechanical properties are similar to those of protein structures [3-5].

There are many works describing the mechanisms of CNTs rotation and movement under the influence of an electromagnetic field by laser radiation [6]. With strong local heating of nanotubes by
laser radiation, CNTs are bonded to each other in defective areas of the carbon surface [7]. In this paper, the mechanisms of carbon nanotubes structuring under laser evaporation of a liquid medium based on the water-protein dispersion of CNTs are studied.

2. Materials and methods

Single-walled carbon nanotubes (SWCNTs) with an average diameter of 1.8 ± 0.2 nm were used for theoretical and experimental studies. SWCNTs were synthesized by an electric arc method on a Ni-Y catalyst. Raman spectroscopy was used to determine the level of the tubes defectiveness. The value of the ratio of the diamond scattering peak intensity to the graphite peak was 0.116. The level of the tubes defectiveness turned out to be below average. The main defects of nanotubes were single, double vacancies and Stone-Wells defects in various concentrations and configurations.

The approach of molecular dynamic modeling was used to study the formation mechanism of an ordered structure from an ensemble of carbon nanotubes under the action of laser radiation. At the same time, the laser radiation energy was converted into thermal energy of the structural atoms motion. Since carbon nanotubes have high thermal conductivity and elasticity, even with very strong heating they do not collapse, and thermal energy is distributed evenly throughout the entire length. Except for areas of the carbon structure with defective regions, in which a considerable heating is observed when exposed to a laser beam, because of the low thermal conductivity [3].

In theoretical studies, two cases of the bonds formation between nanotubes in an aqueous box were considered. That allowed them to freely move relative to each other as a result of laser action and a significant increase in temperature. The first case described the perpendicular interaction of the open end of one nanotube with the another tube lateral surface. In the second case, cross-contact of two SWCNTs was considered. Molecular dynamic modeling was carried out using a reactive empirical potential of the bonds order with a time step of 0.1 fs.

As the protein matrix, an aqueous dispersion of albumin (25 wt.%) and collagen (2 wt.%) was used. A semiconductor laser (1) with a wavelength of 810 nm was used to structure the protein media with a carbon nanoscaffold (figure 1). The laser beam (2) moved along a layer of the dispersion (3) on the substrate (4) until the liquid component evaporated. The laser radiation path was set using a computer 3-D model (5).

![Figure 1. Scheme of creating biocompatible media under the laser evaporation of water-protein-SWCNTs dispersion on a substrate.](image)

The structure of the obtained biocompatible media was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Instrumental scanning probe indenting method was used to study nanohardness of solid state biocompatible media.
3. Results

As a result of laser heating of the contact perpendicular to and cross-contacted SWCNTs, it was determined that the defect area had a temperature of ~ 50% higher than those of the defect-free regions of the carbon structure (figure 2). This temperature redistribution effect was observed during the first picoseconds.

![Figure 2. Temperature distribution for laser heating perpendicular (a) and cross (b) contact SWCNTs.](image)

Thus, the temperature distribution along the nanotubes in the ensemble was continuously changing, due to the regular heat dissipation. The dynamics of perpendicular nanotubes (12,12) binding with one defect of a double vacancy is shown in Figures 3 a and b. The figure shows two time intervals after laser exposure in the contact region of SWCNTs through 1.8 ps (a) and 2 ps (c) with the formation of four C-C bonds. The maximum temperature was observed near the defect area and was 1600-1700 K. The binding time of nanotubes was determined by the laser radiation power and the initial distance between the tubes, which was 3.2 Å. After a time of 2 ps, the temperature became practically uniformly distributed throughout the nanostructure of the tubes.

![Figure 3. Temperature distribution at the contact point SWCNTs after laser heating of nanotubes with defect of the 2V type and with an open end through 1.8 (a), 2 (b) and 1.4 (c) and 2.5 (d) ps.](image)

When cross-contact SWCNTs with defects of a double vacancy, maximum heating was observed through 1.4 (c), and complete cooling with formation of 4 covalent bonds through 2.5 ps (d). In the
course of numerical simulation, it was found that inhomogeneous temperature heating leads to the
formation of covalent bonds between the tubes at a distance of 3.2 to 3.7 Å. This was confirmed by the
experimental data of a branched scaffold structure in organic matrices studied by SEM and its high
mechanical strength (figure 5b).

The time dependences of the covalent C-C bonds formation between SWCNTs on their number
during laser heating were determined. Based on the averaging results of ten numerical experiments, a
number of temporal regularities were revealed at different distances between the tubes 3 - 3.7 Å (figure 4a).

![Figure 4](image1.png)

**Figure 4.** Dependence of the C-C bonds formation time between SWCNTs (12,12) on the number of
bonds at different tube spacing (a), the temperature field distribution in the nanotube contact region (b)

For the case of binding two SWCNTs (12,12) having defects of a double vacancy, the dependence
of the system energy change on the bonding time is shown (figure 5a). The energy graph confirms the
stability of the formed nanosystem from SWCNTs through 1.7 ps. Points 1 to 4 show the moments of
time forming the bonds between nanotubes. Energy after the formation of four bonds has reached a
constant value. This value did not change with further electromagnetic field energy absorption by
nanotubes. The change in energy during the formation of bonds in time varied in the range -7.43 – -
7.36 eV / atom.

![Figure 5](image2.png)

**Figure 5.** Dependence of the SWCNTs contact formation energy (a), the model of the nanocarbon
scaffold with the maxima of the electromagnetic field (b), the SEM of the biocompatible medium (c)

Using the finite-difference method in the time domain, the patterns of the electromagnetic field
distribution over the SWCNTs volume with the maximum values of the intensity were obtained (the
red areas in figure 5b).
Figure 5c shows a SEM image of a laser-structured medium with scaffold of carbon nanotubes in a protein matrix. As a result, a solid nanomaterial with a branched scaffold structure was obtained. The figure shows the binding sites of SWCNTs.

Laser structuring and scaffold formation under the action of covalent bonding were confirmed by high values of the material nanohardness. The experimental data demonstrated a high hardness of nanomaterials of 380-410 MPa at a load of 1 µN – 1 mN and a maximum loading depth of 350-850 nm. Hardness for biocompatible media created by the thermostatic method (without laser radiation) of a liquid dispersion to a solid phase state demonstrated lower hardness values from 70 to 120 MPa.

These biocompatible media are intended to provide the cells proliferation of various biotissues. Consequently, the medium must have a surface structure that will ensure a high adhesion of the cells to itself. Due to this, the topography of the media surface in a flat (film) form on a silicon substrate was studied.

![AFM images of the biocompatible media surfaces with a concentration of SWCNTs of 0.01 wt.% and 0.1 wt.%](image)

**Figure 6.** AFM images and corresponding profiles of biocompatible media with concentrations of SWCNTs 0.01 wt.% (a) and 0.1 wt.% (b).

AFM images of the biocompatible media surfaces with a concentration of SWCNTs of 0.01 wt.% and 0.1 wt.% are shown in figure 6. The images visualize the porous structure of the samples. The structure was formed due to the water boiling during the laser evaporation of the protein dispersion with nanotubes. Both images have pores of different diameters and depths. A greater pore density (pore number on the area of 10 µm²) is observed on for samples with low concentration of SWCNTs (0.01 wt.% than for samples with a high concentration (0.1 wt.%). This may be due to the uniform formation of SWCNTs contacts in the carbon scaffold and the most uniform distribution of the temperature field when the liquid part of the sample evaporates. The pore diameter on the samples...
surface with low concentration of SWCNTs was less than 1 μm, and for samples with high concentration, the pore diameter was <1.8 μm. The pore depth for both samples reached 300 nm.

4. Conclusion

Mechanisms of the formation of biocompatible media with single-walled carbon nanotubes under the laser radiation influence were developed. The processes of temperature field distribution in the defect area of two nanotubes contact during perpendicular- and cross-linking were described. The effect of temperature redistribution in a carbon nanoscaffold was observed for several ps. As a result of laser SWCNTs contact heating, it was determined that the defect area had a temperature of ~ 50 % higher than those of the defect-free regions of the carbon structure. The formation of four covalent C-C bonds occurred in 2 ps for perpendicular contact between the open end of one nanotube and the defect surface area of another nanotube. The distance between the tubes was 3.2 Å in this case. The formation of four CC bonds occurred in 2.5 ps for cross-contact between two tubes with the defects of the double vacancy. The heating of the contact site to a temperature of 1700 K was observed in 1.4 ps at a temperature of the defect-free tube region of ~ 500 K. According to the results on the time dependence of the formation of contact between tubes, the effective linking distance of the defective SWCNTs regions were determined (3 – 5 Å). The change in energy during the formation of bonds in time varied in the range -7.43 – -7.36 eV/atom.

The energy pattern of the electromagnetic field distribution over the SWCNTs volume with the maximum values of the intensity was in good correlation with the SEM image of the branched tubes nanoscaffold in the protein matrix. This scaffold provides hardness of biocompatible media up to 400 MPa. The study of the samples surface topography led to the conclusion that an increase of SWCNTs concentration reduces the number of pores and also increases their size.

The porous structure of created biocompatible media helps to increase the adhesion of various biological tissues cells. Such media can be used as tissue-engineering matrixes that promote cell proliferation.

Acknowledgments

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