Electrically conductive CNT networks formed by laser

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Abstract. Materials containing conductive CNT networks were investigated in this work. Binding of CNTs to each other was carried out using laser radiation in scanning mode. As a result of experimental studies, radiation energy density at which the effect of SWCNT binding occurred was found – 0.061 J/cm². Mechanism by which formation of porous materials with SWCNTs in composition takes place has been established. Materials from CNTs and biopolymers with controllable pore sizes that make up more than 60% of nanocomposite volume have been made.

1. Introduction

Nowadays laser radiation is widely used for modification of nanomaterials made of metals, dielectrics, and semiconductors. One of laser radiation applications is to improve the characteristics of materials for bioelectronics, namely, electrically conductive materials for biointerfaces. Such materials can be used for targeted stimulation of cells and tissues with high spatial resolution. One of the promising materials is carbon nanotubes (CNT) [1]. They are durable [2] and have high biocompatibility [3].

It is known that laser radiation in pulsed and continuous modes can bind carbon nanoparticles (carbon nanotubes, graphene) with each other [4]. This effect is achieved due to two main mechanisms: sublimation of the most defective nanotubes or graphene sheets under the influence of laser radiation and subsequent condensation of sublimation products at nanotubes and graphene junctions; and due to the formation of covalent bonds in defect regions of nanoparticles during laser heating. Defective areas of nanoparticles have the least thermal conductivity and they are the most chemically active. This leads to appearance of chemical bonds in defective areas [5,6]. It is known that carbon nanoparticles have semiconductive and electrically conductive properties. When nanotubes and graphene are bonded to each other, electrically conductive nodes (percolation nodes) appear. It is necessary to create a complex of percolation nodes in given area or in given volume for fabrication of electrically conductive compounds for nanoelectronics or functional 3D materials in bioelectronics [7,8].

Materials such as biopolymers are used to enhance the biocompatibility of interface materials [9]. Albumin under the action of laser forms a nutrient-rich matrix for cell growth. Collagen increases flexibility of biointerface, chitosan has an antibacterial effect [10, 11]. Networks made of nanotubes in matrix, formed under the laser action, imparts electrical conductivity to matrix materials.
In this work, fabrication of SWCNT networks based materials was carried out by depositing disordered system of single-walled carbon nanotubes (SWCNT) on a substrate. Forming of SWCNT network inside its structure helps to achieve high strength and electrical conductivity of material. This is of great relevance in the field of creating bioelectronic devices, for example, when creating electrically conductive implants. In this regard, we have developed technology for creating electrically conductive biopolymer nanocomposites consisting of SWCNT network in biopolymers matrix: albumin, collagen and chitosan.

2. Materials and methods
First stage in preparation of samples was creation of homogeneous dispersion of SWCNT in solvent (dimethylformamide - 90% and methylethylketone - 10%). Resulting dispersion was applied using a nitrogen sputtering system onto a polished silicon wafer for nano- and microelectronics located on a heating stage for solvent evaporation. Application was carried out layer-by-layer. After that, disordered system of SWCNTs, consisting of 500 layers up to 2 nm thick each was treated with laser action in scanning mode. Laser setup consisted of irradiation system represented by pulsed Yb laser with wavelength 1064 nm, pulse frequency 30 kHz. Positioning of laser beam was carried out using scanner with two mirrors and focusing lens. Sample was uniformly coated with laser pulses with the same energy density. Laser scanning was carried out using computer program along given trajectory.

Nanocomposites with biopolymers were created by the action of same Yb laser radiation on homogeneous dispersion made of albumin, collagen, chitosan and with SWCNTs. Dispersions were prepared from distilled water and nanotubes with concentration 0.01%. Components were mixed on magnetic stirrer for 30 minutes, then agglomerates of nanotubes were separated using ultrasonic homogenizer and ultrasonic bath. Biopolymers were added to the resulting dispersion, treatment was performed with magnetic stirrer for 1 hour and with ultrasonic bath for 1 hour. Biopolymers concentrations were 25% of albumin, 1% of collagen, and 2% of chitosan. Dispersion was deposited layer-by-layer on silicon substrate using the similar method as for SWCNT depositions, but they were irradiated with pulsed laser radiation immediately after each deposition.

All the obtained samples were examined in detail using scanning electron microscope (SEM) FEI Helios NanoLab 650. Accelerating voltage of electron column was 2 kV, electron probe current was 21 pA.

3. Results and discussion
3.1. SWCNT network, formed by laser
As a result of laser exposure, SWCNT network was formed. Experimental studies have made it possible to determine the energy density that led to formation of networks. It was 0.061 J/cm². Figure 1a shows optical scheme of laser setup for influencing SWCNT and for creating nanocomposites. An ordered network of connected SWCNTs is shown on pictures, made by scanning electron microscopy (figure 1b-e).
Figure 1. Optical scheme of laser setup for SWCNTs irradiation and for creating nanocomposites (a): 1 – Yb laser, 2 – scanner mirrors, 3 – focusing lens, 4 – SWCNT, 5 – Si substrate, 6 – area of laser influence with laser beam trajectory, SEM images of SWCNT networks (b,c) and places where SWCNTs are welded together (d,e).

It is known that high temperatures promote destruction of nanotubes and C-C bonds, but also leads to subsequent formation of new bonds. High-intensity laser radiation heats nanotubes to high temperatures around 1800 °C. This facilitates the formation of welded SWCNT networks. In addition to nanowelding effect, new chemical bonds are forming on the contact surfaces of heated nanotubes. Formed SWCNT network had high electrical conductivity. In table 1, data on electrical conductivity of obtained SWCNT networks, formed with different modes of laser exposure, are presented.

Table 1. Electrical conductivity of SWCNT network formed by laser action.

| Laser energy density, J/cm² | Number of passes | Electrical conductivity, S/m |
|-----------------------------|------------------|-----------------------------|
| Disordered SWCNTs | SWCNT network, obtained by laser irradiation with energy density E/S |
| 0.002 | 0.028 | 0.044 | 0.061 |
| 2.3×10⁴ | 3.8×10⁵ | 6.5×10⁵ | 8.7×10⁵ | 1.1×10⁶ |

3.2. Nanocomposite consisting of SWCNT network and biopolymers

It is known from nonlinear optical studies of materials with carbon nanotubes that nonlinear absorption and nonlinear scattering of radiation occur in liquid dispersed medium exposed to pulsed laser radiation (with high pulse energy). In this case, energy of laser pulse is absorbed by carbon nanotube and converted into heat. Further, gas bubbles appear around the carbon nanotubes because of heating. The resulting bubbles scatter the rest of the pulse and subsequent laser pulses. Nonlinear processes in dispersion with carbon nanotubes are triggered if laser pulse has sufficient threshold energy density. At the same time, threshold energy density was established, at which formation of nanocomposites with a given structure (porosity) took place.

By determining the threshold radiation energy density, it is possible to control pore size in solid composite. The energy density at which porosity of biopolymer composites is more than 60% was determined in this work. Biopolymer composites of albumin, collagen, and chitosan with SWCNT had clearly visible porosity, the sizes of pores were 1-5 μm and 100-200 μm at the threshold energy densities of 0.051, 0.054, and 0.057 J/cm², respectively. Large pores should promote cell adhesion and
proliferation. Small pores are necessary for vascularization and innervation processes. Created nanocomposites can be used as electrically conductive interfaces for restoration of nerve and muscle tissues of the body. Figure 2 shows SEM images of nanocomposites structure, formed by laser radiation with different energy densities: 0.051 J/cm² (figure 2a) and 0.057 J/cm² (figure 2b).

Morphology of nanocomposite layer based on SWCNT network can be seen in figure 2c,d. Yellow arrows show the areas of SWCNT connections in network, formed under the influence of laser radiation.

![Figure 2. SEM images of nanocomposites structures formed by laser radiation with different energy densities: 0.051 J/cm² (a), 0.057 J/cm² (b), SWCNT network based on nanocomposite layer with biopolymers (c,d).](image)

It can be seen from the images that the size of network elements exceeds the diameter of single nanotubes. An increase in the diameter of SWCNTs may be due to their coating with biopolymers. Under the influence of laser radiation, elongated biopolymer molecules unfold and attach to SWCNT due to side amino groups [7]. When water molecules are removed, biopolymers completely cover the walls of nanotubes.

4. Conclusion
Materials based on conductive CNT networks were investigated in this work. Creating of CNTs to each other was carried out using laser radiation in scanning mode. As a result of experimental studies, radiation energy density at which the effect of SWCNT binding occurred was found – 0.061 J/cm². Mechanism by which formation of porous materials with SWCNTs in composition takes place has been established. Materials from CNTs and biopolymers with controllable pore sizes that make up more than 60% of nanocomposite volume have been made. Materials can be created in various forms to create independent implantable structures or coatings for cardiovascular or neural devices.

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