Metal-carbyne clusters for SERS realization

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Abstract. Metal-carbyne materials, synthesized by laser irradiation of colloidal systems consisting of carbon and noble metal nanoparticles, are promising objects to realize surface-enhanced Raman scattering. The dependence of the Raman scattering intensity of the material composition has been investigated. The possibility of detecting of the organic dye Rhodamine 6G Raman spectrum was demonstrated.

1. Introduction
Hybrid carbon-based nano- and composite materials have a unique place in modern nanoscience owing to their exceptional electrical, thermal, chemical and mechanical properties. This type of materials have found application in areas diverse as nanoscale electronic components, energy storage and conversion, sensors, drug delivery and etc. Carbon quantum dots are a newly developed class of carbon nano-materials that have attracted much interest and attention thanks to demonstrate a promising optical properties depending on the degree of crystallization, size and shape. The amplification of the observed phenomena can be realized by the addition of the noble metal nanoparticles, which have a plasmon resonant peaks in the visible region. The linear carbon chain (carbyne) is the promising carbon material for the creation of the hybrid and composite materials. Carbyne is an allotrope of carbon composed of sp-hybridized carbon atoms. It is an n-type semiconductor with an energy gap vary from as little as 0.2 eV to more than 4 eV, in which electronic transport properties are structurally sensitive. Carbyne has a chain of covalently bonded carbon atoms with sp-hybridization of orbitals of two possible types: alternation of n single and triple bonds (–C≡C–)n, or alternation of n double bonds (≡C≡C≡)n. Optical and electrical properties of carbyne depend on its morphology [1-3]. Thus, the synthesis of carbyne with a variable structure of bonds has a considerable interest not only from a fundamental point of view, but also this material is applicable in the development of new integrated circuits of advanced, next-generation hybrid electronic devices. The strategy to incorporate metal nanoparticles in a carbon matrix is a great method to integrate the different properties to various materials, enabling to realize multifunctional composites. Such materials may be used in advanced applications like nanobiotechnology, optoelectronics, etc. In particular, a widely used approach is given by the combination of linear carbon chains and metals. In effect, linear carbon chain is the one of the most promising materials because of its unique physical and chemical properties and wide potential applications in nanophotonics. The possibility to obtain
composites with large visible photoluminescence spectra for optoelectronic devices becomes especially interesting.

In this paper, we report the results of studying the formation of metal–carbyne clusters under laser irradiation of colloidal systems, consisting of shungite carbon and noble-metal nanoparticles. It was shown that this irradiation leads to the formation of clusters, in which metal nanoparticles are interrelated by carbyne chains. The Raman spectra of these structures exhibit SERS and depend significantly on the variation of metal particles concentration in colloidal system.

2. Laser synthesis of metal-carbyne material
In our experiments, the proposed method is based on the laser irradiation of colloidal systems consisted of shungite carbon [4] and noble metal (Au and Ag) nanoparticles [5]. Such colloidal system was placed under Yb-fiber laser (1.06 μm) with a pulse duration of 100 ns and a pulse energy of up to 1mJ. This process resulted in the fabrication of long linear carbon chains (LLCC) in liquid. Such mechanism proceeds because of the homogeneous symmetry interaction in liquid for the carbon system that stabilizes the linear structure [6]. In this study, we have analyzed the possibility of control over the properties of fabricated composites by changing the irradiation conditions and the particle concentration in colloid. The laser irradiation of the colloidal system was performed by scanning a focused laser beam (focal spot diameter 50 μm) in a cuvette volume with a scanning speed of 50 μm/s; the total irradiation time was about 15 min.

![Figure 1. SEM-image of formed metal-carbyne materials.](image)

In the processes of laser irradiation the metal nanoparticles decorate the carbyne fiber. The variation of a laser radiation and concentration on metal nanoparticles in colloidal system allow to change the morphology of metal-carbyne clusters syntheses [5]. The UV-Vis absorption spectra of the colloidal systems presented on the figure 2. The absorption peaks around 400 and 530 nm are the plasmon bands due to pure Ag and Au nanoparticles, respectively. The UV-Vis spectra for the C-Au-Ag systems showed a blue shift of the absorption peak around 500 nm. The absorption band near 290 nm corresponds to the carbon phase.
The more detailed study of the carbon material structure reconstruction under laser irradiation was performed by using Raman spectroscopy.

After the irradiation we have detected the peaks in the area of 1900-2200 cm\(^{-1}\). This area corresponds to carbyne spectra [6, 7]. The D-peak for all samples was reduced and forming of the LLCC-peak [8] was observed. Cumulene structure (=C=\(-C=\)) was found by the absorption lines 1950 cm\(^{-1}\) and 1070 cm\(^{-1}\). Polyyne structure of carbon atomic chains was determined by the lines of the triple bond stretching vibrations in area of 2100-2300 cm\(^{-1}\). The change of chain length resulted in the frequency shift towards the shortwave area during the irradiation of colloidal system. This kind of structures can be also modified under the laser radiation. In this case, the irradiation of the metal-carbon colloidal system can result in the obtaining of the more complicated C:Au:Ag systems (as in analogy [5, 6]). The variation of spectra in area of 1900-2200 cm\(^{-1}\) corresponded to the formation of the carbon chains with different length.

3. Deposition of metal-carbon films

For the deposition, we have used ytterbium fiber laser (\(\lambda = 1.06 \, \mu\)) with a pulse duration of 100 ns, pulse repetition rate of 100 kHz, and a pulse energy up to 0.1mJ. The diameter of the laser beam in the focal plane was 30 \(\mu\)m. Periodic array formation on the surface substrate was performed by scanning the laser beam with 60\(\mu\)m step (in XY dimension) with irradiation time about 3s for each step.

Depending on the conditions of laser exposure for a single pulse, the value of the absorbed energy was 10\(^{-9}\)J. Under the conditions of multi-pulse exposure the local heating may occur, resulting in the stability loss of the colloidal system [9]. In addition, agglomerates can be formed due to particles heating. This happens when particles absorb a larger volume of laser energy and move thermally in the colloid. The local heating of the liquid results in the formation of convective currents, providing particle motion to the substrate surface (fig 3).
4. SERS research
The SERS research using deposited films was performed at Senterra spectrometer (Bruker), with the pump laser wavelength of 532 nm, the power of 0.1 mW and the focal spot diameter of 2 µm.

In experiments we have determined a limit of sensitivity of metal-carbon films. To obtain this value, we deposited the solution of dye Rhodamine 6G with different concentration on the surface of metal-carbon films. The SERS investigations (see figure 5) had demonstrated, that the sensitivity limit was about $10^{-7}$M.

![Raman spectra of deposited dye Rhodamine 6G with concentration: a) $10^{-6}$M; a) $10^{-7}$M.](image)

The use of films with variable composition as a substrate for metal-carbon nanostructures under the same measurement conditions allowed to detect and identify the dye, its Raman spectra can be clearly seen in Figure 4. The changing of the gold and silver nanoparticles ratio results in changes of the amplification degree of different bands in the dye spectrum. The peaks of plasmon resonances for silver and gold are in the range of 410 and 540 nm, thus, different vibration modes are amplified by gold and silver particles, and with different gain.

5. Conclusion
The results of laser synthesis of a metal-carbon clusters and complexes are shown in this work. The laser with nanosecond pulse duration allows to modify the structure of carbon bonds and creates best conditions for obtaining the linear carbon chains with different hybridization. The obtained structures can be used for the SERS effect registration with the possibility of the sensitivity control in different areas of the spectra because of the changing of the initial component concentration and morphology.

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