Metal-carbon nanoclusters for SERS

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Abstract Metal–carbon materials exhibiting surface-enhanced Raman scattering have been synthesized by laser irradiation of colloidal systems consisting of carbon and noble metal nanoparticles. The dependence of the Raman scattering intensity on the material composition has been investigated. The possibility of detecting of the Raman spectrum of organic dye DCM and rhodamine 6G is demonstrated.

1. Introduction
The formation of new photonic materials is a promising area in laser physics. Bimetallic complexes of noble metals with particle sizes from 1 to 100 nm in carbon matrix are widely used as materials for implementing surface enhanced Raman scattering (SERS) [1]. The application of carbon as a matrix, stabilizing metal nanoparticles and preventing their degradation in environment, is interesting and promising [2]. The metal-carbon materials based on carbyne are of particular interest. Carbyne is a carbon polymer material [3]. The distance between neighboring atoms in a carbyne chain is 0.128 nm and the distance between chains is 0.295 nm; these values are much smaller than the distances between atoms and between layers in graphite: 0.142 and 0.335 nm, respectively. Carbyne has a unique of the optical and electrical properties [4].

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

2. Laser-induced carbon chains
We presented a new experimental realization by the two-stage laser-induced synthesis of long linear carbon chain – LLCC [5]. In our experiments, the proposed method is based on the laser irradiation of colloidal systems composed of nanoparticles shungite. The substance is a mixture of various carbon allotropes: natural origin of fullerenes and carbon nanostructured forms whose small lattices are connected by amorphous carbon). This a two stage technique boils down to the following:
(1) a colloidal system prepared beforehand by laser ablation from target shungite in distilled water using YAG:Nd³⁺- laser (1.06 μm) with a pulse duration of 1 ms and a pulse energy of up to 10 J;
(2) next, such colloidal system is placed under Yb-fiber laser (1.06 μm) with a pulse duration of 100 ns and a pulse energy of up to 1mJ, and the process results in the fabrication of LLCC in liquid. The mechanism for that is due to the homogeneous symmetry interaction in liquid for the carbon system that stabilizes the linear structure [6].

On the other hand, when exposed to fluids, the stabilization of long linear carbon chains (carbyne allotropic form) can be achieved by laser ablation in the presence of, e.g. gold nanoparticles, which
leads to the consolidation of the ends of linear chains on the surface of gold particles, and prevents them from instabilities/destruction: twisting further into tangles [7].

The Raman spectra of both the original colloidal systems and systems obtained by us after irradiation by nanosecond laser radiation intensity $10^6 \text{W/cm}^2$ (stage 2) are shown in Figure 1 (with the laser exposure time from 5 to 15 minutes).

![Figure 1](image1.png)

**Figure 1.** Raman spectra of synthesized substance with different electron orbital configurations in the experiment with shungite (for irradiated colloidal system).

We have the following specific characteristics for spectral bands: graphite $G(1580 \text{ cm}^{-1})$ and disorder $D(1380 \text{ cm}^{-1})$ lines for carbon substance; 2100-2300 cm$^{-1}$ – polyene chain with the carbon chain (–С≡С–)$_n$; 1900-2200 cm$^{-1}$ – cumulene connection with the carbon chain (=С=С= )$_n$; 600-900 cm$^{-1}$ – probably, mechanical stress, deformation and distortion of linear carbon chains.

The next approach is to stabilize the linear chain of carbon by external forces from metallic particles Au and Ag doped in the colloidal system.

### 3. Laser synthesis of metal-carbyne material

The carbon, gold and silver colloidal solutions were prepared by the intense mixing with changing mass ratio in water, then the ultrasonic bath was used for about 10 minutes for particle decoagulation (see Figure 2, where we show the results for different concentration in composition C:Au:Ag).

![Figure 2](image2.png)

**Figure 2.** The Raman spectra of colloidal systems with variable composition in concentration of the mixture (C:Au:Ag) system. Laser energy $W=5J$; irradiation time $T=5$ min.
After the irradiation in similar condition [8] we have detected the peaks in the area of 1900-2200 cm\(^{-1}\). This area corresponds to carbyne spectra [6-9]. The D-peak for all samples was reduced and forming of the LLCC-peak [7, 10] was observed. Cumulene structure (\(=\text{C} = \text{C} = \text{C} =\)) is shown by the absorption lines 1950 cm\(^{-1}\) and 1070 cm\(^{-1}\). Polyyne structure of carbon atomic chains is shown by the lines of the of stretching vibrations of triple bonds \(\text{C} \equiv \text{C}\) in area of 2100-2300 cm\(^{-1}\), and deformation oscillations at 800 cm\(^{-1}\). The chain length change results in the shift of the line in shortwave area during the irradiation of colloidal system. The absorption line in the area of 1600 cm\(^{-1}\) can be compared with fundamental absorption line for the cumulene state of carbine (regular zigzags with straight parts consist of 4 carbon atoms). This kind of structures can be also modified under the laser radiation. According to the [11] the formation of carbon linear chains can result in the \(\text{sp}^3\)-hybridization structure formation (example: the carbine chain binds two fullerenes). 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 [6]). The variation of spectra in area of 1900-2200 cm\(^{-1}\) corresponds to formation of the carbon chains with different length. There is a dramatic spectra modification. The change of the metal concentration results in the variation of the spectral lines.

4. Research of SERS

Thin metal-carbon films were formed on the surface of the glass substrate using a drop deposition technique [12]. Small droplets deposited on the surface of the substrate at room temperature using a glass capillary with an inner diameter of 50 \(\mu\)m. Evaporation drops occurred under normal conditions.

The SERS research by deposited films was performed using Senterra spectrometer (Bruker), with the pump laser wavelength of 532 nm, the power of 0.1 mW and the focal spot diameter of 2 microns.

In the first experiments we determined a limit of sensitivity of metal-carbon films. For that we deposited the solution of dye DCM with different concentration on the surface of metal-carbon films. The Raman investigations (Figure 3) are demonstrated, that limit sensitivity of our material is \(10^{-6}\)M.

![Figure 3. Raman spectra of due DCM with various concentration.](image)

In the next experiments the standard dye Rhodamine 6G was used as a test molecule. The dye solution in ethanol \((10^{-6}\text{M})\) was placed on a metal-carbon structures using a micropipette. The metal-
carbon surfaces are formed on an oxide glass substrates with different composition of metal nanoparticle. The Raman spectra of molecules of Rhodamine 6G on various substrates are shown on Figure 4.

![Figure 4](image)

**Figure 4.** Raman spectra due Rhodamine 6G with variable composition of metal-carbon films.

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

5. Conclusion

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

Raman and UV/VIS absorption spectra were measured at Center for Optical and Laser Materials Research, St. Petersburg State University.

The reported study was also supported by the Ministry of Education and Science of the Russian Federation (state project no. 2014/13), RFBR grants № 16-42-330531, №14-02-97506

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