

# Laser-induced synthesis of hybrid C-Au-Ag nanostructures: nanoparticles, nanoflakes, nanoflowers

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## ABSTRACT

Metallic silver-gold nanoparticles (1–5 nm) encapsulated into carbon nanospheres (20–30 nm), or carbon flakes and flowers were synthesized via laser-induced chemical liquid phase deposition. The obtained carbon-silver-gold nanostructures are characterized by high specific surface area and demonstrated high sensitivity as a material for surface-enhanced Raman scattering and adsorption properties allowing analyte extraction from a dilute solution for quantitative monitoring of low concentration components.

**Keywords:** metal-carbon composites, carbon-encapsulated bimetallic nanoparticles, SERS activity, adsorption properties

## 1 INTRODUCTION

The modern trend in the design of novel functional materials consists in combination of different matters in a single species to give so-called hybrid materials. A special attention is focused on the carbon-metal nanostructures because of their unusual properties for different application areas such as chemistry, surface science, spectroscopy, catalysis, biomedicine, etc. For example, Ag, Ag-Ag, and Au-Pd nanoparticles dispersed in spherical carbon particles demonstrate excellent efficiency as a Raman tag for quantitative immunoassays and high catalytic activity [1]. This is why a lot of efforts are contributed into development of efficient preparation methods of the hybrid material with controlled properties (composition, structure, morphology).

Laser-induced synthesis is now considered to be the most attractive approach which makes possible convenient routes of matter formation/reconstruction. An appropriate choice of laser radiation parameters may provide novel routes for preparation of new materials and structures. Our latest studies demonstrated that a promising way of the bimetallic-carbon nanostructures synthesis can be based on laser-induced liquid phase deposition (LCLD) method [2], which was used to prepare the composite materials from photosensitive organometallic complex  $[\text{Au}_{13}\text{Ag}_{12}(\text{C}_2\text{Ph})_{20}(\text{PPh}_2(\text{C}_6\text{H}_4)_3\text{PPh}_2)_3](\text{PF}_6)_3$  (**1**) [3]. We have found that the variation of deposition parameters (concentration of organometallic complex, solvent,

substrate) allows for the preparation of different C-Au-Ag structures with controlled morphology: nanoparticles (NPs), flakes (mono-crystalline structures) and flowers (poly-crystalline structures).

## 2 EXPERIMENTAL

NPs, flakes and flowers were deposited from the solutions of supramolecular complex  $[\text{Au}_{13}\text{Ag}_{12}(\text{C}_2\text{Ph})_{20}(\text{PPh}_2(\text{C}_6\text{H}_4)_3\text{PPh}_2)_3](\text{PF}_6)_3$  in dichloroethane, acetophenone and acetone of analytical grade purity. It was prepared concentration series of solutions by dissolving of 2, 3, 4, 5 and 10 mg of the supramolecular complex in 1 ml of solvent. To remove the undissolved components, the solutions were centrifugated at 10000 rpm for 5 min. Then the aliquot of solution was placed into a cuvette and covered by chemically cleaned substrate. As substrate we used microscope-cove glass, microscope-cove glass with ITO film and silicon nanowires (SiNWs). The deposition of the nanostructures was carried out with He-Cd laser (CW,  $\lambda=325$  nm,  $P = 0.1$  W/cm<sup>2</sup>). The choice of He-Cd laser was determined by the strong absorption band of the organometallic complex at 328 nm. Unfocused laser beam irradiated the substrate-solution interface from the substrate side; the diameter of laser spot was 3 mm, exposure time for all the experiments – 10 min. Low laser intensity was used to eliminate thermal-induced chemical processes. After deposition process the substrate was washed with acetone and dried using an air flow.

## 3 RESULTS AND DISCUSSION

It was found that both the concentration parameters of the solution and the used solvent determines the morphology of the structures formed under the laser irradiation onto the substrates surface. Table 1 summarizes variety of deposited structures onto the surface of the microscope-cove glass with ITO film. The deposition of nanoparticles (NPs) which are more or less agglomerated can be obtained almost for all the solutions parameters. It is interesting to note that in the case of acetophenone solution formation of regularly shaped flakes was observed along with NPs deposition in all the concentration range. High concentrated dichloroethane solution allowed deposition not only NPs and flakes, but also flowers. For the acetone

solution formation of flowers was observed for concentrations 3 and 4 mg/ml. The SEM photos of deposited structures (NPs, flakes and flowers) are presented in fig.1.

Table 1 Morphology of the structures deposited onto the surface of the microscope-cove glass with ITO film

Concentration of supramolecular complex, mg/ml	Solvent		
	Aceton	Acetophenon	Dichloroethane
2	NPs	NPs	No deposition
		Flakes	
3	NPs	NPs	No deposition
		Flowers	
4	Agglomerated NPs	NPs	NPs
		Flowers	
5	NPs	NPs	NPs
		Flakes	
10	Agglomerated NPs	No deposition	Agglomerated NPs
			Flakes
			Flowers

The typical size of NPs was found to be about 30 – 50 nm for all the solvents used, the NPs' agglomeration degree is determined by the concentration of supramolecular complex in solution and grows with concentration. One can see that flakes are extremely regular right-angled structures that testifies to their crystalline nature. The dimension of flakes varies in the range 0.6 – 1.8  $\mu\text{m}$  in width and 2 – 7  $\mu\text{m}$  in length. Thickness of flakes is about 40 – 90 nm. Flowers are more complex 3D structures with average size ca. 5 – 7  $\mu\text{m}$  which are in all probability the agglomerates of the flakes.

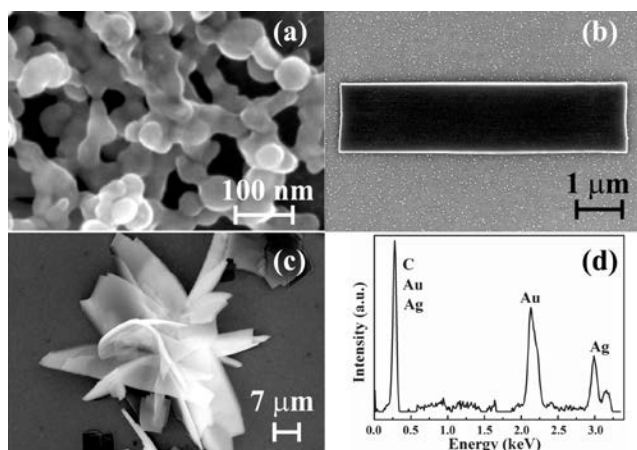


Fig.1. The SEM photos of (a) NPs, (b) flakes (c) flowers and (d) EDX spectrum.

The EDX analysis of all the deposited structures shows that they consist of carbon, silver, and gold with components ratio about 90/5/5 at. %. (Fig. 1 (d)).

Analysis of the deposited structures (NPs, flakes and flowers) with transmission electron microscopy (TEM) (Zeiss Libra 200FE with energy dispersive X-Ray detector X-Max) demonstrated inhomogeneous contrast of the species under investigation – presence of crystalline 1–3nm inclusions which are characterized by the (111) lattice planes with spacing of 0.23 nm. The observed lattice parameters correspond either to the Ag or Au metal phases. Fig. 2 shows TEM images of NPs (a) and flake (b, d), and the fast Fourier transform (FFT) images in the inset (a, d).

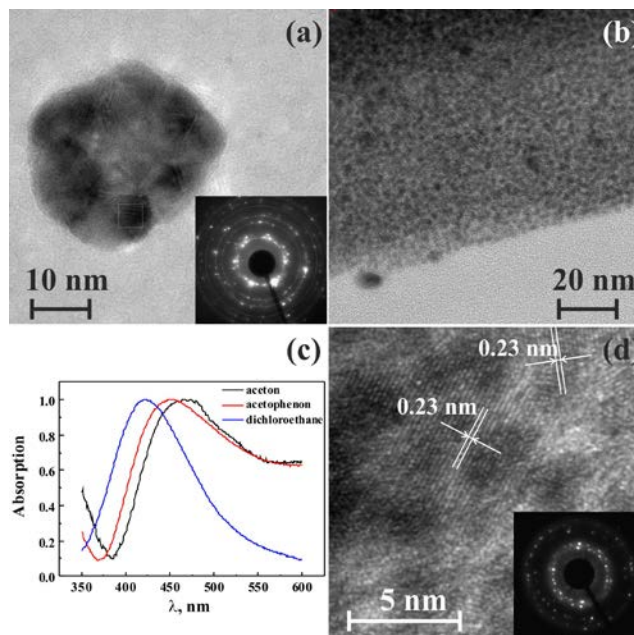


Fig. 2 TEM images of NPs (a) and flake (b, d), and the fast Fourier transform (FFT) images in the inset (a, d).

It should be noted that TEM image (Fig. 2 (a)) of the 30-nm nanoparticle demonstrates that it comprises at least six sphere-like crystalline structures. In accordance with TEM image of flake (fig. 2 (b)), it contains large number of uniformly distributed crystalline nanostructures with lattice planes spacing of 0.23 nm fig. 2(d) corresponded to Ag or Au which are located at distance 1 – 3 nm. Figure 2. (c) shows the absorption spectra of nanoparticles deposited from acetophenone, dichloroethane and acetone solutions of supramolecular complex. The spectra display a single absorption band in the 400-500 nm range generated by the surface plasmon resonance (SPR). The position of the absorption band is typical for the Au-Ag structures and is indicative of the heterometallic nature of the deposits.

The data obtained with SEM, TEM, and absorption spectroscopy demonstrate the formation of structures that can be called hybrid nanoparticles as they consist of carbon matrix (with architecture of particles, flakes, flowers) with dispersed bimetallic Au-Ag nanoclusters.

It should be noted that in the case of deposition onto the microscope-cove glass without ITO film formation of

exclusively NPs (without other structures like flakes and flowers) was found at any solutions parameters. However use of silicon nanowires (SiNWs) as substrates allowed deposition of flowers with architecture following the local field geometry of the used substrate (Fig.3).

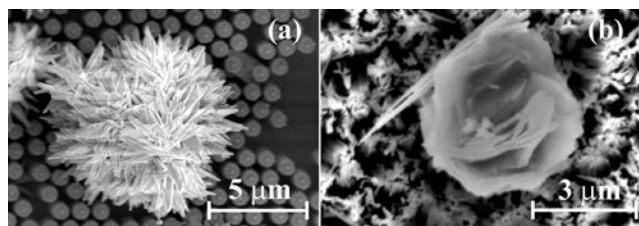


Fig.3 The SEM photos of flowers deposited onto the SiNWs.

The obtained results testify to the strong effect of media parameters (density, viscosity of solvent as well as local field of the substrate) on the mechanism of nanostructures formation under the laser irradiation of solutions of supramolecular complex. A special emphasis should be made on sensitivity of deposits architecture on substrate's local field – in the case of amorphous substrate exclusively NPs can be obtained; crystalline substrate (microscope-cove glass with ITO film,  $\text{LiNbO}_3$ ,  $\text{Al}_2\text{O}_3$  wafers) allows the deposition of not only NPs, but flakes and flowers; use of nanostructured crystalline substrate results in formation of bulk complex flowers. All the obtained nanostructures are characterized by high specific surface area.

As the synthesized nanoparticles contain carbon (about 90%), which is well known as an efficient adsorbing material, the adsorption properties of the C-Au-Ag nanoparticles were studied [4]. The substrate with C-Au-Ag nanoparticles (NPs density  $20 \times 10^3 \mu\text{m}^{-2}$ , diameter of spot 3 mm) was immersed into ethanol solution of anthracene ( $10^{-6}\text{M}$ ), which is a polycyclic aromatic hydrocarbon (PAHs) included in the Environmental Protection Agency's (EPA) priority pollutant list. Then, the substrate was taken out from the solution, and the luminescence spectrum from surface of deposited NPs was recorded with Modular spectrofluorimeter Fluorolog-3 at excitation wavelength of 340 nm. Fig. 4(a) shows the luminescence spectra measured at various immersion times from 2 to 12 min. The spectra obtained are typical for anthracene and demonstrate luminescence intensity increase on immersion time (Fig. 4(b)) that is indicative of effective adsorption properties of C-Au-Ag NPs and their ability to extract the analyte from solution. At immersion time above 12 min, the absorbency saturation was observed. The anthracene Raman spectrum detected from the 12 min immersed C-Au-Ag nanoparticles is presented in Fig. 4(c).

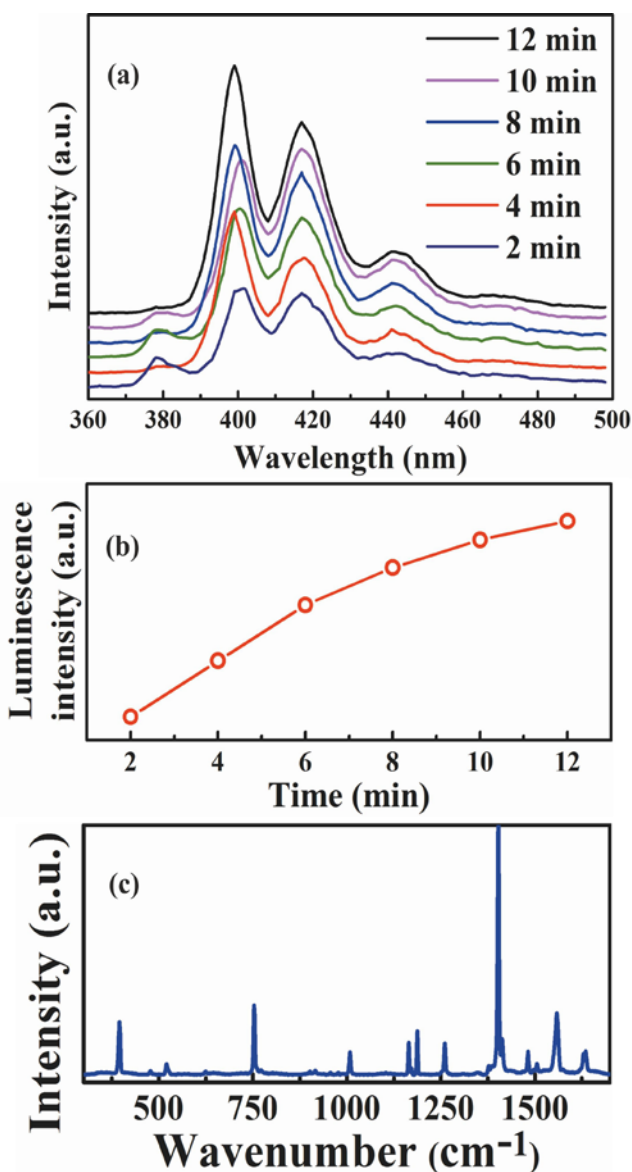


FIG. 4. (a) Luminescence spectra of ethanol solution of anthracene ( $10^{-6}\text{M}$ ) measured at various immersion times from 2 to 12 min; (b) dependence of luminescence intensity on immersion time; (c) Raman spectrum from the 12 min immersed C-Au-Ag nanoparticles.

The other component part of deposited hybrid structures is bimetal Au-Ag nano-inclusions which are characterized by SPR and that is why can be applied as substrates for surface-enhanced Raman scattering (SERS) experiments. SERS spectra were measured for  $10^{-4}\text{M}$  anthracene solution in acetone. A drop of solution was spilled on the substrate surface with and without deposited NPs followed by the substrates drying for 5 min at  $50^\circ\text{C}$ . Figure 5 presents the SERS spectra of anthracene solutions in acetone for a series of concentrations ranging from  $10^{-4}$  to  $10^{-7}$  M. The inset shows the concentration dependence of peak intensity of the anthracene Raman band ( $1400 \text{ cm}^{-1}$ ) in logarithmic scale.

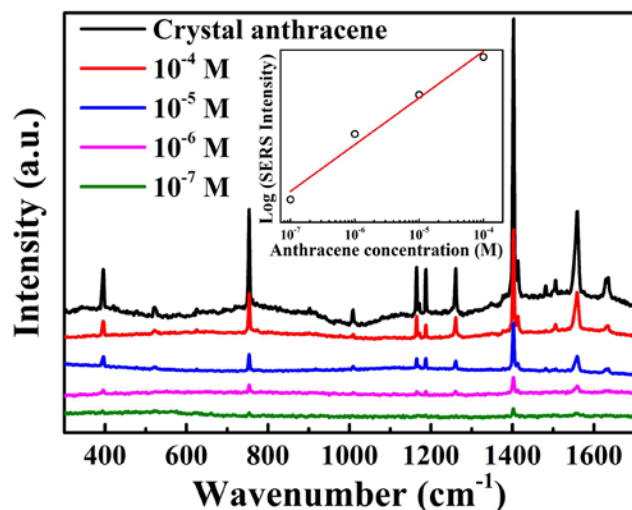


Fig. 5 SERS spectra of anthracene solutions in acetone for a series of concentrations ranging from  $10^{-4}$  to  $10^{-7}$  M.

The results obtained demonstrate that the detection limit of anthracene is  $10^{-7}$  M for the studied C-Au-Ag NPs. These experiments clearly showed that the C-Au-Ag nanoparticles can be used as an extremely efficient adsorbing agent (due to carbon nanosphere properties), which additionally display SERS-activity generated by incorporated Au-Ag nanoparticles.

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