Laser-deposited hybrid Au-Ag@C nanoparticles as efficient SERS & adsorption material

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Abstract. In this work, we present an approach to the synthesis of hybrid multifunctional nanomaterials with pronounced functional properties (SERS, adsorption properties). One-step laser-induced deposition method was used to synthesize hybrid Au-Ag@C nanoparticles. Physicochemical and functional properties of obtained nanostructures were studied using various experimental techniques. Adsorption properties were studied via Raman spectroscopy using organic chromophore – rhodamine 6G.

1. Introduction
Carbon/metal hybrids are regarded as a new family of multifunctional nanomaterials, which are highly promising for multifarious applications thanks to enhanced characteristics resulting from synergetic effect of components, mutual influence of their electronic structures, their physical and chemical interaction. The main impact of nanometal phase of such hybrid materials is typically governed by localized surface-plasmon resonance to give surface-enhanced Raman scattering (SERS) [1-3]. Silver nanoparticles show the largest effect in these phenomena but gold is also considered as a prospective component due to chemical stability and compatibility with various target materials (especially biological), that stimulates growing attention to bimetallic Au-Ag nano-aggregates and associated expansion of the application areas [4,5]. The carbon phase functionality is determined by its electronic structure related to both allotropic form and morphology. These observations clearly point to various ways of bimetallic (in particular Au-Ag)/carbon hybrid nanomaterials applications, which can cover a wide range of sensing technologies.

The method used for obtaining of multiphase nanomaterials is laser-induced self-organization processes. Unlike other known techniques for synthesizing multiphase nanomaterials [6,7], this approach is a one-step process based on the effect of laser irradiation at the interface between the solid substrate and a solution, resulting in the formation of hybrid nanostructures (metallic particles embedded in a carbonaceous matrix) of well-defined morphology and structure. The laser irradiation influences to molecules of organometallic complex dissolved in a chosen solvent, and as a result, the organometallic molecules destruct with formation of hybrid nanoparticles. In dependence on experiment geometry the nanoparticles may be deposited onto different types of substrates: cover glass, ITO films, anodic aluminium oxide nanoporous membranes, silicon, etc [8,9]. The morphology...
of obtained nanostructures mainly depends on choice of solvent as well as time of laser deposition procedure. The composition of nanostructures is determined by type of used organometallic complex. The metal loading of nanostructures depends on the solubility of complex in a chosen solvent and deposition time.

2. Experimental part

The experimental work included two main steps: synthesis of hybrid nanoparticles and investigation of their functional properties. Both of them are discussed below.

2.1. Laser-induced deposition of hybrid Au-Ag@C nanoparticles

The solution of the organometallic complex \([\text{Au}_{12}\text{Ag}_{12}(\text{C}_2\text{Ph})_{18}\text{Cl}_3(\text{PPh}_3(\text{C}_6\text{H}_4)\text{PPh}_2))(\text{PF}_6)_3]\) in dichlorethane was used for the laser-induced deposition procedure. The methodology of the organometallic complex synthesis is presented in [10]. The concentration of organometallic complex was 4 mg/ml that is close to the solubility limit. To enhance the dissolving process the ultrasonic bathing of the solution for 5 min was utilized. The undissolved species were removed with centrifugation of the solution for 5 min at 10000 rpm. Then the cuvette with the organometallic solution was covered with substrate and illuminated with laser beam. Figure 1 shows the laser-induced deposition procedure. As a light source He-Cd laser (CW, \(\lambda = 325\) nm and \(P = 15\) mW) was chosen as the laser wavelength coincides with the organometallic complex absorption band [11]. The laser-deposition time was varied from 5 to 15 min.

![Figure 1. Scheme of experimental procedure for the laser-induced deposition process](image)

2.2. Characterization of NPs

The morphology and composition of obtained nanostructures were investigated by scanning electron micrographs (SEM) and energy-dispersive X-ray spectroscopy (EDX) on Zeiss Merlin Scanning Electron Microscope with Field Emission cathode, GEMINI II electron-optics column, oil-free vacuum system. As the synthesized samples could contain carbon, the SEM images were obtained with charge compensation to avoid the preliminary carbon spattering of the studied sample.

To study the availability of the deposited NPs for the SERS analysis the solution of rhodamine 6G was chosen as a model substance. The concentration of rhodamine 6G in acetone was \(10^{-6}\) M. The SERS spectra presented in this paper were obtained with confocal express Raman spectrometer Senterra (Bruker) with 50 \(\mu\)m iris aperture set and spectral resolution about 3 cm\(^{-1}\). The Stokes part of Raman spectra was recorded in the region 80-4500 cm\(^{-1}\). Solid-state laser with 532 nm wavelength and 0.2 mW power was used for excitation of Raman scattering. The adsorption properties were also studied by Raman spectroscopy. The substrate with hybrid nanoparticles was immersed in rhodamine
6G solution for defined time. Then the Raman spectrum was measured. After that, the immersion process and Raman spectrum measurement were repeated for several times.

3. Results and discussion

3.1. Characterization of hybrid Au-Ag@C nanostructures

The irradiation of the interface of the substrate and organometallic solution results in formation of the agglomerated nanoparticles that form rather porous layer (Figure 2a). It is important to note that the deposition time increase effects the number of the deposited nanoparticles and the morphology of the layer on the whole. The most porous structure is formed as a result of 10 min irradiation, further increase of the irradiation time results in formation of denser packed nanoparticles.

![Figure 2. Scanning electron micrographs of hybrid Au-Ag@C nanostructures deposited during (a) 5 min, (b) 10 min, (c) 15 min, (d) typical EDX spectra from area with nanoparticles.](image)

The composition of metal clusters was checked with EDX. The results are presented in Figure 2d. It shows pronounced peaks of C, Au and Ag that originate from the deposited nanoparticles, and in a good agreement with the composition of the organometallic precursor while Ca, Na, Mg and Si signals originate from the glassy substrate. The absorption spectrum of the deposited nanoparticles demonstrate single pronounced peak at 540 nm testifying to the bimetal Au-Ag nanoinclusions in the structure of the deposited nanoparticles, weak absorption band at 470 nm can indicate also presence of some amount of silver nanoinclusions (Figure 3).
3.2. SERS and Adsorption properties of the deposited nanostructures

The chosen for SERS measurements laser wavelength is quite close to the position of surface plasmon resonance of obtained nanostructures. The measurements were carried out for different adsorption times. “0 min” means that substrate with nanostructures was put out of Petri dish immediately after put in. The SERS spectra for different times of adsorption are presented in Figure 4a.

To determine the dynamics of adsorption effect, the dependence of SERS signal at 610 cm⁻¹ (related to C-C-C ring in-plane bending mode [12]) on the adsorption time was examined. This peak has several advantages for quantitative estimations. Among them it has relatively high intensity, comparing with other ones of rhodamine 6G and there are absent of other peaks nearby which can influence on the 610 cm⁻¹ peak intensity. The intensity of SERS signal shows proportional behaviour with adsorption time that seems to be proportional of adsorbed molecules amount. In assumption that in case of such low concentrations (10⁻⁶ M) absorbs monolayer of analyte and there is no interaction between adsorbed molecules, the obtained data was approximated with Langmuir isotherm (Figure 4b).

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I = I_\infty \frac{kT}{1 + kT}
\]  \hspace{1cm} (1)

Figure 3. Absorption spectrum of deposited nanostructures

Figure 4. (a) SERS of rhodamine 6G with different adsorption times; (b) Isotherm of adsorption on hybrid Au-Ag@C nanostructures.
where \( I \) is intensity of 610 cm\(^{-1}\) peak, \( T \) is time (in minutes in our case), \( k \) is adsorption velocity, \( \Gamma_{\infty} \) is adsorption limit value. For the fitted curve presented at figure 4b, the obtained parameters are: \( \Gamma_{\infty}=537, \ k = 0.254 \text{ min}^{-1}. \)

From presented data, we can observe that saturation of SERS-active substrate is achieved after 6 min. Because of uniform distribution of metal clusters in carbonaceous matrix takes place the synergetic effect of adsorption and SERS.

### 4. Conclusion

In conclusion, we have demonstrated that laser-induced deposition method allows depositing of hybrid Au-Ag@C nanoparticles with controlled morphology possessing both adsorption and SERS properties. Optimal time for synthesis of hybrid Au-Ag@C nanoparticles with high-developed surface area was determined to be 10 min. Isotherm of low concentrated rhodamine 6G adsorption on hybrid Au-Ag@C nanostructures was successfully fitted with Langmuir model. Combination of metal and carbon phases is promising for decrease of the detection limit of various chemical substances.

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### References

[1] Fateixa S, Helena N and Tito T 2015 Physical Chemistry Chemical Physics 17(33) 21046.

[2] Wang C, Tang F, Wang X and Li L 2015 ACS applied materials & interfaces 7(24) 13653.

[3] Kolesnikov I E, Ivanov D A, Kireev A A, Mamonova D V, Golyeva E V, Mikhailov M D and Manshina A A 2018 Journal of Solid State Chemistry 258 835.

[4] Wu H, Wang P, He H and Jin Y 2012 Nano Research 5(2) 135.

[5] Kumari M M, Jacob J and Philip D 2015 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 137 185.

[6] Sahay R, Reddy V J and Ramakrishna S 2014 Journal of Mechanical and Materials Engineering 9(1) 25.

[7] Povolotskaya A V, Povolotskiy A V and Manshina A A 2015 Russian Chemical Reviews 84(6) 579.

[8] Bashouti M Y, Povolotckaia A V, Povolotskiy A V, Tunik S P, Christiansen S H, Leuchs G and Manshina A A 2016 RSC Advances 6(79) 75681.

[9] Bashouti M Y, Manshina A, Povolotckaia A, Povolotskiy A, Kireev A, Petrov Y and Christiansen S 2015 Lab on a Chip 15(7) 1742.

[10] Koshevoy I O, Karttunen A J, Tunik S P, Haukka M, Selivanov S I, Melnikov A S, Serdobintsev P Yu and Pakkanen T A 2009 Organometallics, 28(5), 1369.

[11] Manshina A A, Grachova E V, Povolotskiy A V, Povolotckaia A V, Petrov Y V, Koshevoy I O, Makarova A A, Vyalikh D M and Tunik S P 2015 Scientific reports 5 12027.

[12] Hildebrandt P and Stockburger M 1984 The Journal of Physical Chemistry 88(24) 5935.