Annealing effect on composition and functional properties of hybrid C-Au-Ag nanoparticles

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ABSTRACT

Here we present a novel approach to the synthesis of hybrid C-Au-Ag nanoparticles which were found to be 20 - 30 nm carbon nanospheres containing dispersed Au-Ag bimetallic nanoparticles (1-5 nm). It was also revealed that annealing of C-Au-Ag NPs at various temperatures in the 100-600 ^{0}C temperature range allows for the variation of NPs' morphology and composition. This makes possible tuning of the surface plasmon resonance characteristics that opens an efficient way of the NPs functional properties control, like for example Surface-Enhanced Raman Scattering (SERS). It was found that the obtained hybrid C-Au-Ag NPs display pronounced SERS activity with the enhancment factor (EF) ca. 10^5.

Keywords: hybrid C-Au-Ag nanoparticles, surface plasmon resonance, SERS

1 INTRODUCTION

Synthesis of hybrid nanoparticles with controllable properties is one of the key tasks of modern science and technology, which determines the rate and directions of further progress in chemistry, surface science, spectroscopy, catalysis, sensing technologies, etc. Hybrid materials like metal-dielectric composites (nanoparticles (NPs), nanotubes, multilayer films) especially metal-carbon composites are now widely used because the combination of carbon with the metal NPs increases functionality of these materials, due to plasmon effect of metal nanophase [1]. The most striking example of metal NPs' properties is the Surface-Enhanced Raman Scattering (SERS). SERS spectroscopy analysis have experienced fast progress in the last few decades since it was recognized as a powerful tool in many research areas especially in biomedicine and toxin detection. Here we present a novel approach to the synthesis of carbon-encapsulated bimetallic nanoparticles with controlled composition, morphology and pronounced functional properties (SERS) which can be tuned by annealing protocol.

2 EXPERIMENTAL

The carbon nanospheres with dispersed silver-gold nanoparticles were prepared by one-step laser-induced chemical deposition method [2] from solution of photosensitive organometallic complex $[Au_{13}Ag_{12}(C_2Ph)_{20}(PPh_2(C_6H_4)_3PPh_2)_3](PF_6)_3$ [3].

Nanoparticles were deposited from dichloroethane solution of the supramolecular complex onto the surface of silica-based (microscope-cover) glass. The deposition of the nanoparticles on the surface of the substrate was carried out with He-Cd laser (CW, λ=325 nm, P = 0.1 W/cm^2). The choice of He-Cd laser was determined by the strong absorption band of the organometallic complex at 328 nm. The substrate-solution interface was irradiated with unfocused laser beam from the substrate side; the diameter of laser spot was 3 mm, exposure time for all experiments – 10 min. Low laser intensity was used to eliminate thermal-induced chemical processes. As a result of the deposition a spot of NPs layer with diameter ca. 3mm was formed. After completion of the experiment the substrate with precipitated particles was washed with acetone and dried at 40 ^{0}C for 50 min. The NPs obtained were then annealed for 20 min at various temperatures in the 100 – 600 ^{0}C range.

3 RESULTS AND DISCUSSION

The SEM, TEM and EDX analyses demonstrated that irradiation of the supramolecular complex solution results in formation of the C-Ag-Au NPs. The deposited hybrid NPs were found to be carbon nanospheres (20–30 nm) containing dispersed Au-Ag bimetallic nanoparticles (1–5 nm). Figure 1(a) shows a high resolution transmission electron microscopy (TEM) image (Zeiss Libra 200FE with the energy dispersive X-Ray detector X-Max) of a single nanoparticle, the fast Fourier transform (FFT) image is presented in the inset. The presence of fringed facet implies the crystalline structure of the deposited NPs. It should be noted that inhomogeneous contrast of the 30-nm nanoparticle demonstrates that it comprises at least six sphere-like crystalline structures of about 5 nm in diameter.

This structure of deposited NPs provides highly developed surface area. Figure 1(b) presents the result of energy

dispersive X-Ray spectroscopy (EDX) analysis, which shows that the deposited NPs consist of carbon, silver, and gold [4].

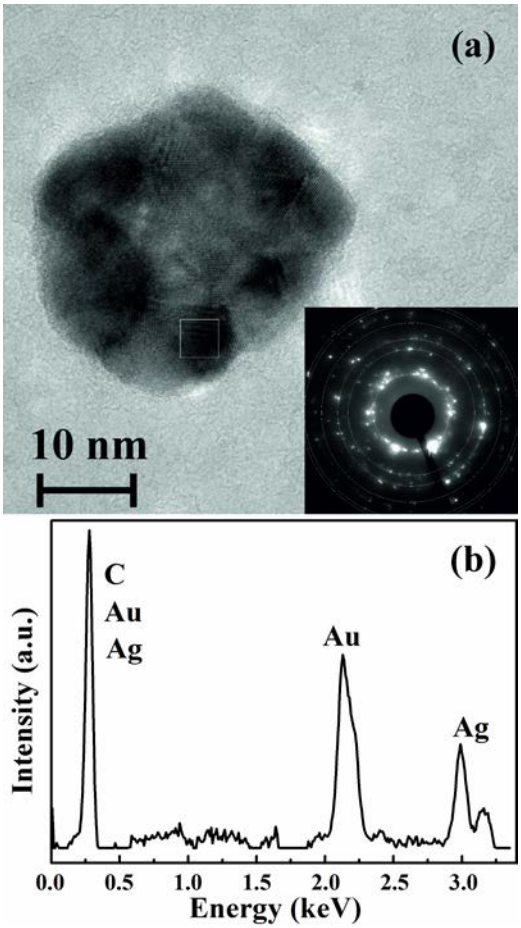

Figure 1: (a) Typical TEM image of an Au-Ag-C nanostructure. (b) EDX spectrum recorded from the region marked in (a).

The annealing procedure was found to have strong effect on both NPs morphology and composition. Fig 2 presents SEM images of as prepared NPs, as well as annealed at temperatures in the range 100 – 500^{0}C. Annealing at temperature 600^{0}C results in complete evaporation of deposited NPs. The EDX spectra were recorded using an Oxford Instruments Inca X-act detector. All measurements were performed with uncoated samples, charging was compensated by local injection of nitrogen. Quantitative analysis of NPs composition was performed by the PAP (Pouchou and Pichoir) procedure described in [5]. First approximation was obtained by simplified XPP-procedure. Final concentration was calculated using iterative technique: concentrations were corrected by thin film factor described in [5]. Then the concentrations of elements in the NPs under study were normalized (presented in Tab. 1).

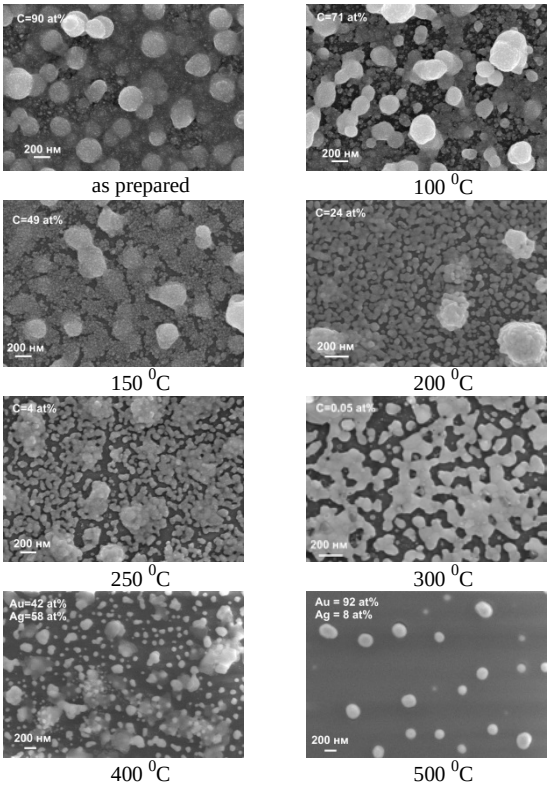

Figure 2: SEM images of NPs annealed at at temperatures over the range 100 – 500^{0}C.

	C, at%	Ag, at%	Au, at%
initial	90	6	2
100	71	20	7
150	49	37	12
200	24	55	19
250	4	70	24
300	0	74	25
400	0	58	42
500	0	8	92

Table 1: The composition of as prepared NPs (initial), as well as annealed at temperatures over the range 100-500^{0}C.

Analysis of the results presented in Fig.2 and Tab. 1 demonstrates that the annealing procedure leads to the change of NPs' morphology – decrease of NPs' aglomeration degree in the temperature range 100-150^{0}C folowed by NPs sintering at 200-300^{0}C. Simultaneously with morphology modification the variation of NPs' composition was also found. The carbon content dropped from 90 to 0.05 at% with the increase in annealing temperature up to 300^{0}C, at the same time Ag/Au ratio was found to be kept at ca. 3/1 in this temperature range. Futher temperature increase up to 500^{0}C results in gradual Ag evaporation and formation of isolated Au-enriched NPs.

The other important effect of annealing process is strong modification and shift of C-Au-Ag NPs surface plasmon

resonance (SPR). The normalized absorption spectra of the nanostructures obtained at different annealing temperatures are presented in Fig. 3. To measure the absorbance spectra of the deposited NPs, we used the Precision Spectrophotometer Lambda 1050 UV/VIS/NIR. The spectra are characterized by a single absorption band in the 450–550 nm range, which is characteristic of the Au-Ag structures and is indicative of the heterometallic nature of the deposits. The presence of separated monometallic Au and Ag phases typically results in appearance of two bands at 410 nm and 540 nm in the absorption spectra corresponding to Ag and Au SPRs, respectively. Fig. 3a shows the absorption spectra of NPs annealed at temperatures in the 100-300^{0}C range. The data obtained display a monotonous shift of the plasmon resonance peak position from 550 to 460 nm and simultaneous narrowing of the band. Annealing in the temperature range 300-500 ^{0}C results in the opposite plasmon resonance shift from 460 to 540 nm.

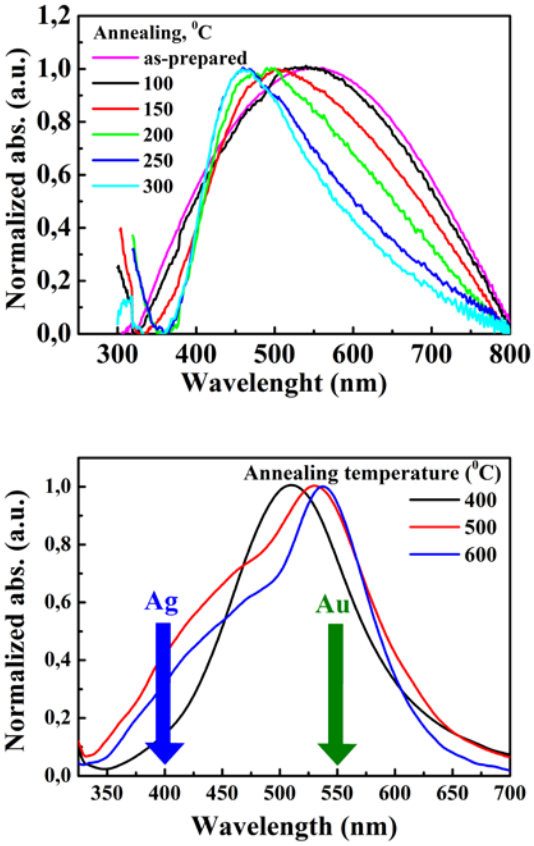

Figure 3: Absorption spectra of NPs annealed at (a) temperatures over the range 100 – 300^{0}C, (b) temperatures over the range 300-500 ^{0}C.

The observed shift of the plasmon resonance band position coincides well with the variation of the NPs' composition calculated using the EDX data. The annealing procedure at 100-300^{0}C leads to gradual carbon vanishing that fits well to the decrease of dielectric function of the Au-Ag NPs environment, to give variations in the SPR spectrum [6]. It should be noted that the opposite SPR shift from 460 to 540 nm in the temperature range 300-500 ^{0}C is also determined by the NPs' composition, namely by the Ag content decrease. Fig 4 presents the variation of NPs' composition and SPR band position with annealing temperature for the 100-300^{0}C range.

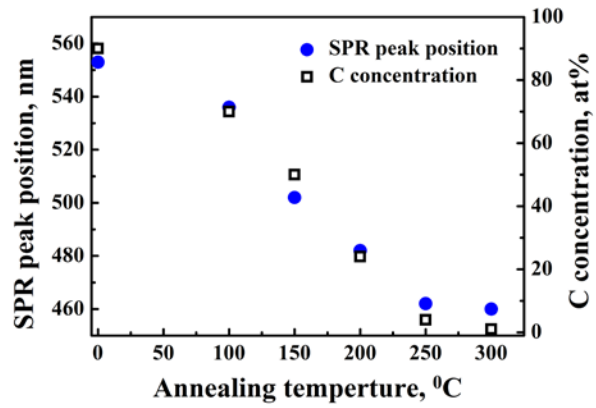

Figure 4: (a) Carbon content and SPR peak position for NPs annealed in the temperature range 100-300^{0}C.

Functional properties of the obtained C-Au-Ag NPs were studied with surface-enhanced Raman spectroscopy. The SERS measurements were performed using a Raman spectrometer Senterra equipped with confocal microscope. SERS spectra were recorded at room temperature using excitation with helium-neon laser at 532 nm and power 0.2 mW. The laser was focused onto an approximately 10^{-6} cm^2 spot on the sample surface. The spectra were collected over 10 s in back reflection geometry through a 50 x 0.7NA objective and the reflected signal was focused onto a thermo-electrically cooled charge-coupled device (CCD) array. The experimental parameters were kept unchanged for all SERS experiments. The SERS activity of the obtained C-Au-Ag NPs was studied using solutions of rhodamine 6G (RH6G) in acetone. A few drops of the RH6G solution were spilled onto the substrate surface with deposited NPs followed by the substrates drying for 30 min at 50 ^{0}C.

Fig. 5 demonstrates a series of SERS spectra of RH6G solutions in the concentrations range 10^{-4} to 10^{-8} M. The as-prepared C-Au-Ag NPs were used as SERS substrate. Highly intense peaks was observed for the solutions with the 10^{-4} and 10^{-5} M concentrations, less intense bands were also detected at the RH6G concentrations as low as 10^{-7} and 10^{-8} M. The observed detection limit of the RH6G concentration (10^{-8} M) fits well that one found for SERS-optimized Ag dendritic nanostructures [7].

The SERS enhancement factor (EF) of the RH6G solutions obtained using as-prepared C-Au-Ag NPs was calculated with the formula reported by Gupta and Weimer [8] and found to be about 10^5. Further experiments were carried out with the C-Au-Ag NPs annealed in the 100-300 ^{0}C temperature range. The substrates annealed at 400 and

500 ^{0}C were found to be inefficient in the SERS experiments.

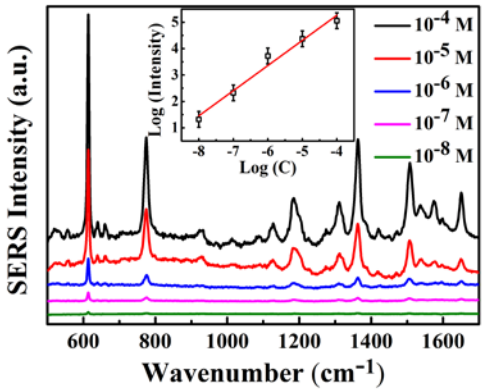

Figure 5: SERS spectra of a series of RH6G solutions with the concentrations ranging from 10^{-4} to 10^{-8} M; inset: the dependence of peak intensity of Raman band (610 cm^{-1}) on RH6G concentration in logarithmic scale.

Fig. 6 presents EF for RH6G solution (10^{-6} M) obtained for the annealed C-Au-Ag NPs. It is clearly visible that the EF demonstrates nonmonotonic variation with annealing temperature, which can be associated with two different factors – NPs' morphology and composition. The NPs annealed at temperature 150 ^{0}C are characterized by more uniform morphology than as prepared and annealed at 100^{0}C with smaller quantity of aggregates that in all probability increase the amount of NPs contributed to SERS process. That is why EF increases up to 4.5 10^5 at annealing temperature 150 ^{0}C.

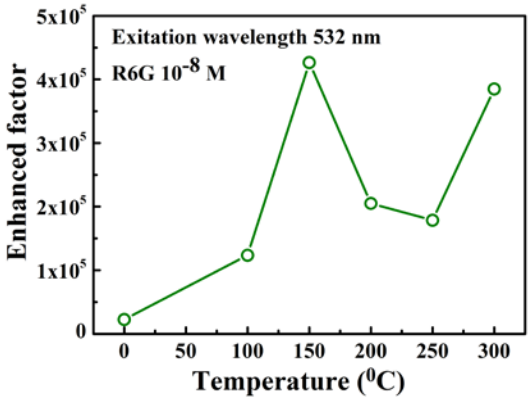

Figure 6: EF for RH6G solution (10^{-6} M) obtained on the C-Au-Ag NPs annealed at various temperatures.

Further annealing temperature increase results in drop of EF up to 2 10^5 in all probability due to NPs' size growth due to sintering process. Carbon content vanishing with annealing process results in the decrease of dielectric function of the Au-Ag NPs environment and increase EF up to 5*10^5.

The results obtained clearly demonstrate a possibility of tuning of the C-Ag-Au NPs plasmon resonance by the variations in annealing procedure. This opens an efficient way to control the functional properties (SERS) of the deposited hybrid structures.

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