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Efficient core-SiO₂/shell-Au nanostructures for surface enhanced Raman scattering

V.O. Yukhymchuk¹, O.M. Hreshchuk¹, M.Ya. Valakh¹, M.A. Skoryk², V.S. Efanov^{1,2}, N.A. Matveevskaya³

¹*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine;*

41, prospect Nauky, 03028 Kyiv, Ukraine

²*Nanomedtech LLC, 68, Gor'kogo str., 03680 Kyiv, Ukraine*

³*State Scientific Institution of NAS of Ukraine "Institute for Single Crystals",*

60, prospect Lenina, 61178 Kharkiv, Ukraine

Abstract. The efficient SERS (surface enhanced Raman scattering) substrates that are films of nanoparticles (NP) of the "core-shell" type, where the core of SiO₂, and the shell of gold nanoparticles, were developed in this work. Application of scanning electron microscopy and optical absorption enabled to find correlation between surface morphology of nanostructures and position of the plasmon absorption band. It helped to adjust the latter to the wavelength of exciting laser radiation. It has been shown that the designed nanostructures are able to enhance electric field of an emitting dipole not only due to adjustment of the band frequency for plasmon absorption to the wavelength of exciting laser radiation but also due to contribution of the so-called "hot spots" to enhancement of electric field scattering. Analysis of characteristics inherent to SERS substrates with nanostructures of the soil core – Au shell type has shown that they enhance the Raman signal by 5 orders higher as compared with the substrates based on SiO₂ nanospheres not covered with gold nanoparticles.

Keywords: SERS, Raman scattering, optical absorption, core-shell structure, scanning electron microscopy, gold nanoparticle.

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1. Introduction

Spectroscopy of the surface-enhanced Raman scattering (SERS) of light is an efficient analytical method that is intensively developed and, with time, finds wider and wider application for diagnostics of substances in chemistry, materials science, medicine, biology, pharmacology, ecology, and so on [1-5]. Using SERS, they can perform analysis of substances available in super-low concentrations in solutions or after deposition of one or several monolayers on metal nanostructured substrates. Like to ordinary Raman spectroscopy, SERS is a non-destructive method, which allows identifying the component composition of substances as well as features of their molecular structure. It is noteworthy that SERS

spectra of a studied substance can contain vibration modes that are inactive in ordinary Raman spectra, which provides additional information upon its structure.

A key factor for the SERS phenomenon is localization of studied molecules or nanoclusters in direct closeness to metallic nanostructures. There are two possibilities in this case: one with creation of a chemical bond and another without it. Besides, the efficiency of the SERS effect depends on morphology of nanostructured metal surface [6], conditions for deposition of the studied substance, parameters of exciting laser radiation as well as properties of the studied substance itself [7].

To efficiently apply SERS methodology, it is necessary to develop special metal substrates made from

gold or silver, which should possess the following parameters: long-term stability, simplicity of preparation, considerable enhancement of the Raman signal from substances deposited on them. Since it is impossible to theoretically model these real metal substrates, to realize controlled deposition of molecules with creation of definite chemical bonds and to find substantiation of optimal substrate characteristics for the SERS effect, it seems topical to search efficient methods for preparation of these substrates.

It should be noted that up-to-date methods for preparation of SERS substrates have both their advantages and deficiencies. For example, electron-beam nano-lithography allows creating ordered metal nanostructures with preset dimensions, shapes and distances between elements. However, this method is rather complicated, low-productive, and, as a result, the respective substrates are of high cost [8]. Such a simple method as thermal deposition of gold or silver in vacuum leads to a wide dispersion of nano-islands by their sizes and shape, which results in considerable widening the band of plasmon absorption as well as lowering the efficiency of enhancement of the Raman signal [9].

A new efficient type of substrates for SERS diagnostics is related with “core-shell” technology, where the role of cores is played by spherical particles of amorphous silicon dioxide, while their shells are gold nanoparticles [10]. On the one hand, the spherical shape allows to considerably increase the effective surface where gold nanoparticles are placed, and on the other hand, to enhance electric field of the emitting dipole not only due to adjustment of the band frequency for plasmon absorption to the wavelength of exciting laser radiation but also due to contribution of the so-called “hot spots” that are superposition of electric fields from several closely located gold nanoparticles.

This work is aimed at investigation of processes providing synthesis of these nanostructures, studying their properties and ascertaining the relationship between their morphology and plasmon characteristics as well as the value of SERS signal versus conditions for deposition of analytes.

2. The method for synthesis of structures

Mono-disperse spherical particles of silicon dioxide with the diameter close to 170 nm were prepared using alkaline hydrolysis of tetra-ethyl-ortho-silicate (TEOC) [11, 12]. To synthesize SiO₂, absolute ethanol (99.9%) was mixed in a flask with 25 % water solution of ammonia for 10 min, which was drop-by-drop added with TEOC. The obtained mixture was thoroughly agitated for 5 hours. After finishing the reaction, SiO₂ nanospheres were separated by centrifuging, washed with bi-distilled water and dispersed using ultra-sound in ethanol up to creation of lasting dispersion. Our investigations showed that colloid solutions of SiO₂ nanoparticles keep their aggregate lasting for 6 months.

In what follows, to form gold nanoparticles on SiO₂ surface, it was modified with bi-functional organic molecules of 3-amino-propyl-3-etoxy-silane (APES) that creates covalent chemical bonds with core silanol groups, and due to amino-groups provides combination between SiO₂ core and metallic shell.

The process providing formation of outer shell from Au nanoparticles on functionalized surface of SiO₂ spheres was performed using the method for their controlled growth on nucleation centers. At the first stage, isolated negatively charged Au nanoparticles with diameters 1 to 2 nm were fixed on the surface of modified SiO₂ due to electrostatic interaction with positively charged ammonia groups. Au nanoparticles containing up to 100 atoms served as nucleation centers for their following directional growth on the core surface.

To prepare SiO₂/Au nanoparticles, the suspension of SiO₂ particles modified with organosilane was agitated with colloid solution of Au nanoparticles with diameters 1 to 2 nm that were obtained by reducing with HAuCl₄·3H₂O (in the concentration 2.5·10⁻² M) tetrakis-hydroxy-methyl-phosphonium chloride (1 % water solution) [13]. The following growth of Au nanoparticles with a set size and degree of filling the template surface was provided via reducing HAuCl₄·3H₂O in water solution. As reducing agents, we used hydroxyl-amine muriatic NH₂OH·HCl and sodium borohydride NaBH₄.

To obtain the plasmon absorption peak at the vicinity of the wavelength for exciting laser radiation, mean sizes of Au nanocrystals formed on SiO₂ surface were varied between 5 up to 15 nm. The nanoparticles formed in this manner were deposited on glass substrates. As can be seen from Fig. 1, diameters of SiO₂ nanospheres lie within the range 160 to 210 nm, while gold nanoparticles covering their surface have diameters from 10 to 15 nm. The nanospheres with gold nanoparticles deposited on the surface of glass substrate are localized rather densely, which results in closing the Au nanoparticles and formation of the so-called “hot spots”.

3. Experimental methods

Morphology of the prepared SiO₂/Au nanostructures after deposition on glass substrates was studied using the scanning electron microscope (SEM) Tescan Mira 3 LMU. Transmission and reflection spectra of the nanostructures were registered using the two-beam spectrophotometer UV-VIS-IR Shimadzu UV-3600. Raman spectra were registered at room temperature by using the spectrometer (double monochromator) equipped with a CCD camera of the firm Andor. To excite Raman spectra, we used radiation of a solid-state YAG:Nd³⁺ laser with the wavelength 532 nm. In the role of analyte, we used solution of Rhodamine 6G in bi-distilled water. Its concentration was 10⁻⁵ M. To prepare a thin film of Rhodamine 6G molecules on SERS substrates, this solution was deposited onto the surface with a doser providing distribution of the same amount of substance over the equal area. Then the samples were dried in air flow.

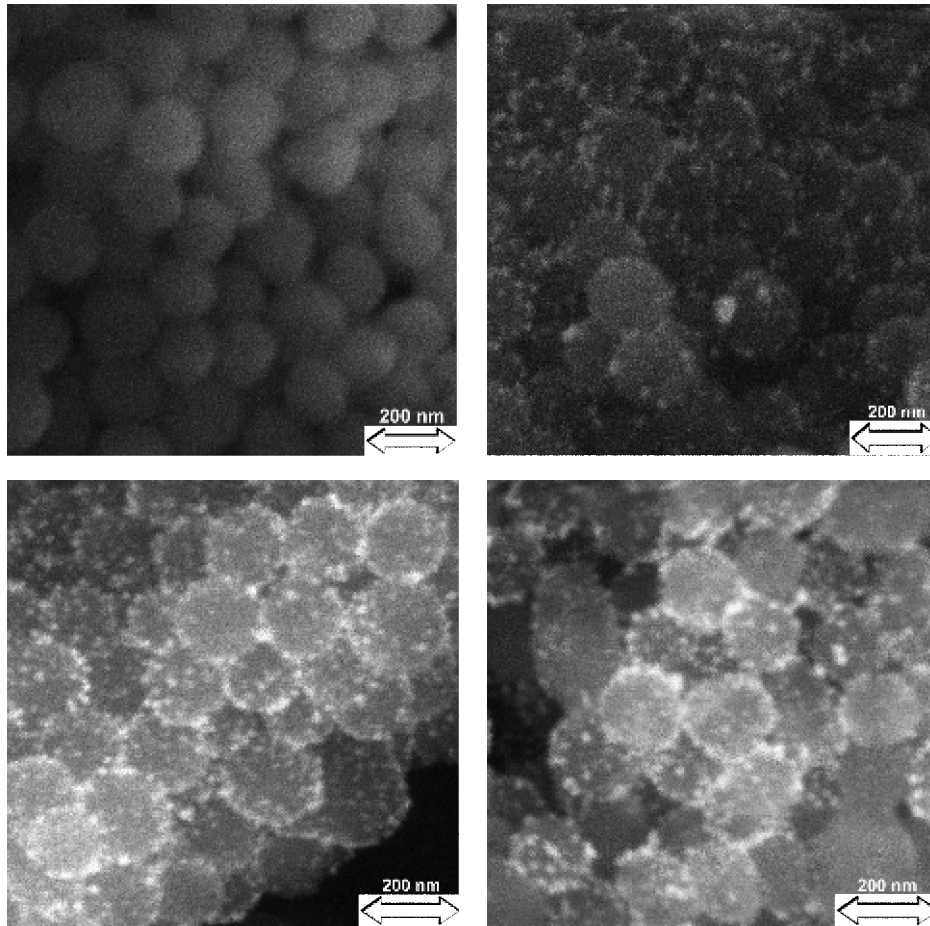


Fig. 1. SEM images of nanoparticles: SiO₂ spheres (1) and nanoparticles SiO₂-Au of the core-shell type, with various geometrical parameters of cores and shells (2-4).

4. Results and discussion

As it was stated above, enhancement of a SERS signal due to a special substrate is considerably increased in the case of coincidence or closeness between the frequency of exciting laser radiation and that of plasmon absorption peak inherent to metal substrates. To reach this coincidence, it is more reasonable to adjust substrate parameters, in particular, sizes of gold nanoparticles and their surface density, since the wavelengths of lasers for SERS have fixed values. Therefore, one of important characteristics for SERS substrates is their absorption spectrum. It is the plasmon band peak position and its half-width that define the spectral range where considerable surface enhancement of the Raman signal can take place under respective choice of exciting laser radiation.

Shown in Fig. 2 are absorption spectra of four different samples, which peak positions for plasmon absorption bands are changed between 530 to 536 nm that is very close to the laser wavelength ($\lambda = 532$ nm). At the same time, the half-width values of plasmon absorption bands possess considerably higher dispersion: from 73 up to 90 nm, which is caused by different

distributions of Au NP by their sizes and variation of their surface density. Intensities of plasmon absorption bands are also different, however, these depend, first of all, on the amount of nanoparticles related to the core-shell type, which were deposited on glass substrates. Positions of plasmon absorption peaks in the studied nanostructures are not random – sizes of Au NP varied in the process of their synthesis for the coincident or closeness to the exciting wavelength (532 nm).

To study the enhancement efficiency for the Raman signal from SERS substrates, they were covered with identical volumes of the solution of Rhodamine 6G with the concentration 10^{-5} M, distributed approximately equally over the same surface areas.

When estimating the enhancement coefficient for SERS signals, we took into account growth of the Raman signal caused by an increase in the surface area. To realize it, we deposited the same amount of solution on SiO₂ spheres that were not covered with gold nanoparticles (Fig. 1, image 1). It is known that the coefficient of SERS enhancement can be determined using the formula [14]:

$$k = (I_{\text{SERS}}/N_{\text{SERS}})/(I_{\text{RS}}/N_{\text{RS}}), \quad (1)$$

where I_{SERS} , I_{RS} are intensities of the SERS signal and of the ordinary Raman signal; N_{SERS} , N_{RS} – amounts of molecules that contribute to SERS signals and to the ordinary Raman signal, respectively. Since these amounts are very close in our case, then the enhancement coefficient can be determined through the ratio of band intensities for two different type substrates.

Shown in Fig. 3 are Raman spectra of Rhodamine 6G molecules deposited onto the SERS substrates that are nanostructures SiO_2/Au of the core-shell type (curves 2 – 4) and the substrate with SiO_2 spheres of the same diameter (curve 1) as that chosen for the SERS substrate. It is seen from these curves that the most intense spectrum corresponds to the nanostructure of the SiO_2/Au type (curve 3). At the same time, it is noteworthy that essential enhancement of the Raman signal is typical for all the three structures containing gold nanoparticles, the enhancement coefficient being different for these samples by only several times.

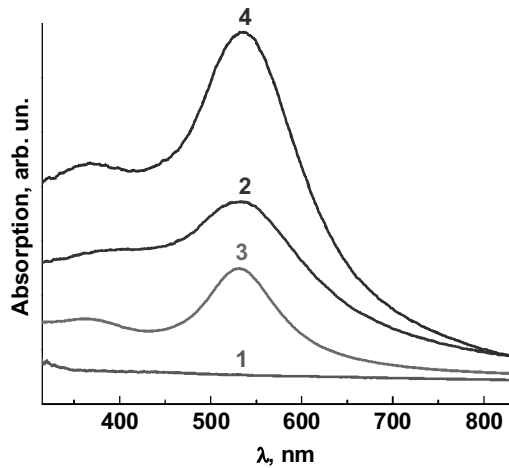


Fig. 2. Absorption spectra of nanostructures: SiO_2 spheres (1) and nanoparticles SiO_2/Au of the core-shell type, with various geometrical parameters of cores and shells (2-4).

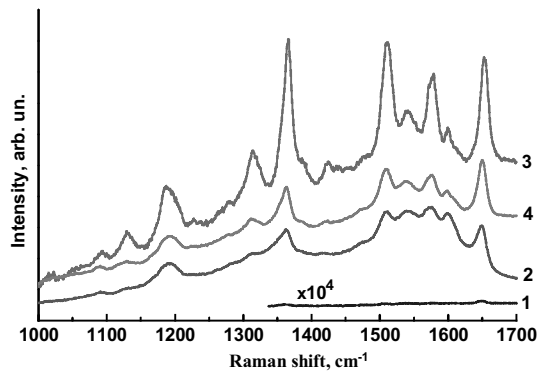


Fig. 3. Raman spectra of Rhodamine 6G solution deposited on various SERS substrates (2-4) and on the film with SiO_2 nanoparticles (1). Numbers of the curves correspond to SEM images in Fig. 1.

This result is understandable, since structure morphology is rather similar, and the respective bands of plasmon absorption lie within the same spectral range. As it was stated above, amplitudes of plasmon peaks and their half-widths are different to some extent, which influences on the enhancement efficiency of Raman scattering. Another factor that influences on the intensity of Raman signal is the surface density of gold nanoparticles on SiO_2 spheres. The higher the surface density, the higher is the Raman band intensity, which is clearly observed for the sample 3. Besides, a dense array of gold nanoparticles can demonstrate enhancement due to superposition of electric fields from several closely situated nanoparticles, which corresponds to the case of a hot spots.

The obtained Raman spectra enabled us to estimate the enhancement coefficient by using the formula (1). It is approximately equal $5 \cdot 10^6$.

5. Conclusions

The efficient SERS substrates in the form of films consisting of nanoparticles of the core-shell type, where cores are SiO_2 nanospheres covered with the shell of gold NP, were developed and investigated. The latter are present in the form of nano-islands on SiO_2 surface. This nanoisland structure enhances electric field of emitting dipoles due to not only adjustment between the frequency of the plasmon absorption peak but to the presence of hot spots, too. In addition, SiO_2/Au nanostructures are characterized by direct contact of adsorbed molecules with gold nanoparticles, which results in chemical enhancement. Our analysis of the Raman spectra inherent to Rhodamine 6G molecules deposited on SERS substrates showed that the latter are 5 orders more efficient in Raman signal enhancement than the substrates with SiO_2 nanospheres not covered with gold nanoparticles.

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