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ABSTRACT

The article presents the results of the SERS study of fluorine-containing dye 6G (R6G) adsorbed onto quartz surfaces modified with gold nanoparticles (NPs). A new technique for quartz glass modifying with hydrosols of gold NPs of various shapes has been developed. The possibilities of its application to implement SERS effect for R6G molecules have been shown. In this work, we synthesized hydrosols of spherical gold NPs (nanospheres) and rod-shaped NPs (nanorods (NRs)) and studied their optical and morphological properties. The SERS spectra of R6G molecules on NP modified quartz glasses have been obtained as well as the SERS enhancement factor has been calculated.

Keywords: nanoparticles, nanorods, plasmon enhancement, SERS

1. INTRODUCTION

Since the SERS effect was discovered in 1974 [1], SERS spectroscopy has been widely used as an effective non-destructive, sensitive and accurate technique [2] for wide range of analytes analysis, varied from complex chemical compounds to single molecules. SERS effect is implemented through the excitation of surface plasmons (SPs) near the surface of metal NP. Surface plasmons can appear near the interface of the media (metal-dielectric) when electron density is excited by an external electromagnetic source [3]. When the frequency of the external field is equal to the frequency of SPs, a surface plasmon resonance (SPR) occurs, which leads to a strong electromagnetic field amplification near the particle surface and it causes absorption cross section increase. Silver and gold are widely used as a basis for SERS structures [4]. Copper [5], platinum NPs [6], as well as bimetallic NPs [7,8], rough surfaces [9] and thin films [10] are also used in SERS applications. Various advanced methods are used to fabricate SERS active substrates, such as electron beam lithography [11], focused ion beam deposition [12], nanoimprinting [13], block copolymer matrix [14], inclined deposition angle [15], chemical etching and galvanic redox reaction [16]. As a result, nanostructured surfaces provide an effective Raman signal amplification from $10^1$ to $10^{10}$. However, most of the existing technologies applied for the SERS active media manufacture are quite complex, time-consuming and require high-tech equipment. Nowadays, the search for new solutions for obtaining the SERS effect using plasmon field-inducing NPs remains a hot topic. The article describes novel methods for the manufacture of SERS active substrates with adsorbed gold NPs of various shapes and sizes. The proposed methods are quite simple and do not require specialized equipment. Chemical reagents used in the synthesis are available. In order to study the ability to raise the SERS effect on the created substrates, we used an aqueous solution of Rhodamine 6G dye (R6G). The SERS intensity detected from the dye was up to 30,944 counts. The maximum amplification of the SERS signal was $3 \cdot 10^4$.

2. EXPERIMENTAL METHODS

2.1 Reagents

We used chemically pure reagents for the study: Tetrachloroaurate (III) trihydrate (HAuCl₄, 99%, LTD Aurat (Russia)), ascorbic acid (AA) (C₆H₇O₆, Sigma-Aldrich), Cetyltrimethylammonium Bromide (CTAB) (99%, BioChemica), citric acid (C₆H₈O₇, 99%, LTD LenReactiv (Russia)), Sodium borohydride (NaBH₄, 98%, LTD LenReactiv (Russia)).
2.2 Synthesis of colloidal gold NPs

2.2.1 Synthesis Au NPs. Spherical gold NPs were synthesized according to the Turkevich method [17] with minor modifications. To perform the process 0.02 g of HAuCl₄ was added to a pre-washed with acetone and boiled Erlenmeyer flask with 190 ml of Milli-Q water (18.2 MΩ). The resulting solution was heated on a magnetic stirrer with vigorous stirring (~ 1100 rpm) to a boil. Then 5 ml of 1% citric acid was rapidly added dropwise to it. In 3 minutes after mixing the reagents, the clear solution quickly began to change color from blue to purple. The resulting sol was boiled for another 20 minutes; during that time the solution turned a burgundy color with a purple hue. The NPs hydrosol was cooled to room temperature and used within 30 – 120 minutes after preparation.

2.2.2 Au NRs Synthesis. Au NRs was synthesized according to [18] with minor modifications.

Seed Solution. In order to form a seed solution, 5 ml of 0.2 M CTAB was added to 5 ml of 0.0005 M HAuCl₄. Then 0.6 ml of 0.010 M NaBH₄ freshly prepared in an ice bath was added to the resulting and stirred solution, which led to a gray-beige colloidal mixture. The seed solution was actively mixed for 2 minutes at 1100 rpm/min. Then it was kept at room temperature for 30 minutes before utilization.

Growth of Au NRs. For NRs synthesis, 5 ml of 0.2 M CTAB was added to 0.15 ml of a 0.004 M AgNO₃ solution. Then 5.0 ml of 0.001 M HAuCl₄ was added to this solution, and after gentle mixing 70 μl of 0.0788 M ascorbic acid was added. Ascorbic acid is a mild reducing agent, which leads to a growth solution color change from brown-yellow to colorless. The final step was an addition of 12 μl seed solution to the growth mixture. The color of the solution changed gradually. After 1 hour, the resulting colloid finally took on a blue color.

2.3 Samples

2.3.1 Modification of the quartz surface with Au NPs

Before the experiment, the optically transparent high quality quartz glass was cleaned with isopropyl alcohol, then in an ultrasonic bath with distilled water and dried in an oven for 10 – 15 min at a temperature of 60°C. After cooling, a polyvinyl chloride film was attached to the edges of quartz glass to form edges along the perimeter of the glass. After the film was fixed around the perimeter, the sample was washed once again with isopropyl alcohol and Milli-Q water. Then, 3 ml of the previously prepared Au NPs hydrosol was applied dropwise onto a purified substrate. After a uniform distribution of the hydrosol on quartz glass, the sample was placed in a furnace at 40°C. The hydrosol was evaporated for 3 hours, forming a cluster surface of spherical gold NPs on quartz glass. After complete drying, the substrate was cooled for 10 minutes. 5 μl of R6G (C = 10⁻³ M) was applied to the cooled surface for further investigation.

2.3.2 Modification of the quartz surface with Au NRs

The quartz surface was cleaned according to the procedure in paragraph 2.3.1. After cleaning, the glass was placed on a magnetic stirrer and heated to a certain temperature. The tiles and quartz glass heating degree was carried out using a temperature sensor and a thermometer, respectively. Upon reaching a temperature of 40°C, three drops were sequentially deposited onto the surface of the substrate, 10 μl each, of the previously synthesized Au NRs hydrosol. After drying of the hydrosol, a solution of R6G (10⁻⁵ M) with a volume of 5 μl was adsorbed on the first drop while second and third layers of colloid NRs were formed on the same procedure and R6G solution was also applied on it.

3. RESULTS AND DISCUSSION

3.1 Optical properties of gold NPs

The prepared NPs hydrosols of the were investigated using UV-adsorption and photon-correlation spectroscopy. In order to determine the NPs size, the Photocor-Complex (LTD «PhotoCorr», Belarus) experimental unit was used (Fig. 1). Absorption spectra (Fig. 2) were obtained by means of UV-2600 double-beam spectrophotometer (Shimadzu, Japan). The calculation of the NPs concentration was carried out according to the formula:

Absorption spectra (Fig. 2)
\[ C = \frac{3m}{4\pi r^3 \rho N_a V} \quad (1) \]

The resulting values were 3.7 nM for spherical gold NPs and 4.9 fM for NRs. Concentration of NRs was calculated using micron NR radius.

![Figure 1](https://example.com/figure1.png)

A) B)

Figure 1. The hydrodynamic radius of gold spherical NPs (A) and gold NRs (B).

The NPs size estimation showed that the hydrosol with spherical gold NPs was polydisperse and the size distribution range was varied from 5 nm to 100 nm. However, the number of gold NPs with a hydrodynamic radius of 30 nm has the maximum value. This radius was taken as the average NPs size of in a colloid. The estimated average length of gold NRs in a hydrosol was 1.98 \( \mu \)m.

![Figure 2](https://example.com/figure2.png)

A) B)

Figure 2. Absorption spectra of gold NPs of spherical shape (A) and gold NRs (B).

The absorption spectra of spherical NPs in a colloidal solution had one wide absorption peak, the maximum of which corresponded to a wavelength of \( \lambda = 533 \) nm, while have two peaks at \( \lambda = 530 \) nm and \( \lambda = 620 \) nm, respectively. It should be noted that the presence of two peaks in the absorption spectrum may indicate spheroidal shape of the nanoparticles in the colloid.

### 3.2 AFM study of a modified quartz surface

To study the morphology of spherical gold nanoparticles on quartz surfaces, atomic force microscopy (Certus, LTD “NanoScanTechnology”, Russia) was used.
Obtained AFM images (Figure 3) show non-uniform nanometer and micron aggregations of Au NPs. The close arrangement of NPs from each other in cluster structures has made it possible to obtain “hot spot” areas. The presence of the R6G molecules in the ‘hot spots’ allowed SERS signal obtaining.

3.3 SERS

SERS spectra were recorded on a Centaur U scientific unit (LTD «NanoScanTechnology», Russia) using Cobolt Samba Diode-pumped solid-state laser (DPSS), with an excitation wavelength of $\lambda = 532$ nm. The SERS spectra of R6G were recorded by means of Andor IDus 401 CCD matrix with a signal accumulation of 30 s at three different points. Spectral preprocessing was carried out by the NSpec instrument software and Origin Pro program.

On the obtained SERS of R6G deposited on modified quartz surfaces with gold NRs demonstrates a decrease in SERS signal intensity with number of layers increasing (Fig. 4B). The main peaks of R6G was detected at frequencies of $310$ cm$^{-1}$, $362$ cm$^{-1}$, $570$ cm$^{-1}$, $615$ cm$^{-1}$, $770$ cm$^{-1}$, $1130$ cm$^{-1}$, $1185$ cm$^{-1}$, $1316$ cm$^{-1}$, $1370$ cm$^{-1}$. Signal had the highest intensity for the one thermally deposited Au NRs hydrosol layer. The intensities SERS signal of R6G deposited on two layers and three layers of the Au NRs hydrosol differs from each other very little. A doublet at a frequency of $770$ cm$^{-1}$
appears in case on NRs substrate. Comparing the SERS spectra of R6G obtained on modified quartz surfaces with spherical gold NPs (Fig. 4A) and gold NRs (Fig. 4B), we observed a higher peak intensity obtained for the evaporated Au NRs hydrosol, which confirmed the calculation of the signal SERS coefficient estimated from the expression

\[
SE = \frac{l_{SERS}}{l_{RS}} \cdot \frac{C_{RS}}{C_{SERS}}
\]

where \(l_{SERS}, l_{RS}\) denote SERS and Raman scattering (RS) intensity, respectively; \(C_{SERS}, C_{RS}\) are R6G concentration for SERS and RS experiment, respectively.

For a modified quartz surface with spherical gold NPs, the SERS enhancement factor appeared to be \(3 \cdot 10^4\). For a quartz surface modified with one, two, and three layers of gold NRs, the SERS coefficient was founded to be \(1.1 \cdot 10^3\), \(5.5 \cdot 10^3\), and \(4 \cdot 10^3\), respectively.

CONCLUSION

A novel technique for quartz glass modifying with hydrosols of gold NPs of various shapes was developed. The possibility of its application to implement SERS effect for R6G molecules has been shown. Hydrosols of spherical gold NPs and rod-shaped NPs were synthesized, their optical and morphological properties have been studied. The SERS spectra of R6G molecules on NPs-modified quartz glasses were obtained, and the SERS enhancement factor was calculated. The perspectives of created SERS media for sensory purposes have been shown.

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