Plasmon enhancement of Raman scattering and fluorescence for rhodamine 6G molecules in the porous glass and PVA films with nanoparticles of silver citrate hydrosol

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Abstract. The study of Raman and fluorescence spectra for Rhodamine 6G molecules in a film of polyvinyl alcohol on the modified by silver nanoparticles (NPs) porous glass and without the porous glass has been done. The gain of the scattering intensity and fluorescence emission has been obtained in the presence of silver nanoparticles. The gain order was obtained as ~ 10¹¹

1. Introduction

The nanoparticles of noble metals due to the surface plasmon resonance [1], arising on the surface of NPs under photoexcitation, are promising to create a variety of devices and biophysical sensors for diagnosis and destruction of cancer cells. Today, gold and silver NPs are investigated for the possibility of sensor elements creation based on nonradiative dipole-dipole energy transfer of plasmon excitation in molecular systems [2-4], and for detecting various compounds using fluorescent markers [5].

Raman spectroscopy has a special place in the study of biological structures and organometallic compounds, in case of its possibility to identify distinct groups of biological molecules and the interactions between them in a condensed media and on a solid surfaces. Therefore, the attention of researchers is attracted to use various nano- and microstructures like porous and mesoporous silica [5] ZnO nanorods [6], gold nanorods and nanoholes [5, 8], porous glass [9], etc. The porous glass - the unique material having both high biocompatibility and abundance, making it a very economical biosensor application. In addition, the production technology of porous glass allows us to control the size and the degree of porosity.
In the present study of the Raman scattering and fluorescence of rhodamine 6G (R6G) molecules, amplified by generation of surface plasmons of silver NP in a film of polyvinyl alcohol (PVA) and on porous glass were investigated. The main objective of the paper was to study non-radiative processes of electronic energy transfer between molecule adsorbates R6G and Ag NPs on porous glass in order to create an optical sensor.

2. Method of the sample preparation

2.1. Synthesis of Ag NPs

The Turkevich citrate method was used for the synthesis of silver NP [10-12]. The sodium citrate Na$_3$C$_6$H$_5$O$_7$ was added dropwise, up to 5.8·10^{-4} mol/l concentration, into the boiling aqueous solution of silver nitrate at the concentration $C$(AgNO$_3$) = 5.3·10^{-4} mol/l. The resulting solution was boiled during one hour to obtain a yellow-green color. Citrate-ion acts both as a stabilizer and a reducing agent, therefore the ions concentration determines both the rate of recovery and the growing processes of metal particles. Total recovery of silver citrate reaction can be expressed by the following equation:

$$6\text{AgNO}_3+3\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \rightarrow 6\text{Ag}+3\text{Na}_2\text{C}_6\text{H}_5\text{O}_6+3\text{CO}_2+3\text{NaNO}_3+3\text{HNO}_3$$

Borohydride silver sol was synthesized by reduction of silver nitrate by sodium tetraborohydride (borohydride) [13]. The solution of silver nitrate at the concentration $C$(AgNO$_3$) = 10^{-3} mol/l was added dropwise, with vigorous stirring, into the cooled to 0°C aqueous solution of sodium borohydride at the concentration of $C$(NaBH$_4$) = 2·10^{-3} mol/l. The process of recovery of silver can be expressed by the following equation:

$$\text{AgNO}_3+\text{NaBH}_4+\text{H}_2\text{O}\rightarrow \text{NaNO}_3+\text{B(OH)}_3+\text{H}_2+\text{Ag}.$$

2.2. Preparation of PVA films with R6G on a surface of porous glass modified by silver NP

Glass used for the experiments has the following chemical composition (%): SiO$_2$ - 72.2; Na$_2$O - 14.3; K$_2$O - 1.2; CaO - 6.4; MgO - 4.3; Al$_2$O$_3$ - 1.2.

The porous surface was created by mechanical rubbing. The degree of porosity was controlled by the transmission spectra of porous glasses. Random error, calculated from the intensity, was 7%. Samples were washed thoroughly with distilled water and dried at 60°C. Silver NPs of borohydride sol at Ag concentrations (cm$^{-2}$): 0.23·10^{12}, 0.6·10^{12}, 1.1·10^{12} were added to surface. After sol drying samples were thermally treated (T = 350°C) in a muffle furnace. During the heat treatment on the glass surface chemical processes were following:

$$2\text{NaNO}_3\rightarrow 2\text{NaNO}_2+\text{O}_2,$$
$$2\text{B(OH)}_3\rightarrow\text{B}_2\text{O}_3+3\text{H}_2\text{O}.$$

PVA films with R6G was applied to the porous glass with Ag NPs by adding aqueous solution containing R6G (C = 5·10^{-4} M) and PVA ($\omega$= 4%) on the surface of porous glass. After drying at T = 60°C on the porous surface of the glass the film of R6G d≈3 microns thick was formed.

2.3. Preparation of films with R6G and NPs of silver citrate sol on the polished surface of the glass

Films on a smooth glass was made by adding of an aqueous solution containing R6G, Ag NPs and PVA onto the surface. The concentration of components in the solution: R6G (C = 5·10^{-4} M) and PVA ($\omega$= 4%) on the polished glass. After drying at T = 60°C the film of R6G d≈3 microns thick was formed.

3. Experimental results

The synthesized Ag NPs were investigated by photocorrelation spectroscopy with Photocor Complex unit. The dimensions of NPs were 1.0 nm and 16.0 nm (for borohydride sol), and 15.0 nm and 64.0 nm (for citrate sol). Measurement error was 5%.

The morphology of Ag NPs on the glass surface and inside the film was studied using a fluorescence microscope Olympus of M319/12-OG BX43F model. The agglomeration nature of NPs distribution appeared as dark areas on porous glass (Figure 1a) and in PVA films (Figure 1b).
Figure 1. The morphology of the porous glass surface (a) and for PVA film with Ag NPs (b), the topology porous glass surface (c), and for the PVA film cut (d).

Raman spectra were obtained by CENTAUR U unit with diode-pumped solid-state laser (DPSS) excitation ($\lambda = 632$ nm, radiation power of 50 mW). Raman spectra were recorded using a CCD detector matrix with 5 s signal accumulation.

The porosity of the glass was investigated by using the SPM Certus Standart module with optical registration system (Russia), using tapping mode atomic force microscopy (AFM). MikroMasch cantilever probes with a curvature radius less than 10 nm were used for scanning. The obtained surface images (Figure 1c) showed the average pore size equal $\sim 0.5 \mu$m. However, it had been shown that the surface had nanometer sized pores.

Also, by using techniques of AFM with tapping mode scanning, crosscut image of PVA film was taken (Figure 1d). Determined crosscut thickness of the film was equal 12 microns and it is fully correlates to the theoretical calculation.

IR spectra were obtained on Shimadzu IRPrestige-21 (Japan) in the range of 500-4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Background noise was detected in the range of 1300-2000 cm$^{-1}$, therefore, this area has been removed from PVA result spectra.

The absorption spectra were recorded on a double-beam spectrophotometer Shimadzu UV-2600 in the range of 200-800 nm. Fluorescence spectra were recorded on an optical module unit Fluorolog-22 Horiba (France).
3. Results and discussion

Ag NPs melting temperature depends on their size [14], decreasing from 950 °C to ~ 450 °C for 40 nm sized NPs or less. Presence of 1nm and 15 nm sized NPs in hydrosols, gives us the reason to believe that the heat treatment of porous glasses with NPs leads to NPs caking with the glass matrix. The absorption spectrum of the porous glass with Ag NPs after heat treatment (Figure 2) shows the spectral broadening and long-wavelength shift of surface resonance peak, which indicates the increasing of NPs size.

The transmission spectra of porous glass (Figure 3) in the range of 2500-2800 cm\(^{-1}\), show both reducing the intensity from 40% to 16% and a frequency split of SiH deformation vibrations groups at 2900 cm\(^{-1}\) into two: 1) - 2920 cm\(^{-1}\) and 2) - 2980 cm\(^{-1}\). The presence of two bands in this range of the spectrum is typical for silicon nanoclusters [15, 16]. Ag NPs, fixed on the porous surface of the glass reduce transmission rate on another 3.5%, as a result of the heat treatment.

NP on the porous glasses Raman spectra (Figure 4a) display 1333 cm\(^{-1}\) and 1577 cm\(^{-1}\) maxima which are characteristic of bridge-oxygen in B-O-Si group asymmetric vibrations and bridge hydrogen bonds in B-Si-H group [16]. Intense wide band (70 – 1000 cm\(^{-1}\)) with the 127 cm\(^{-1}\) peak, which appears at the maximum NP concentration (curve 1), can be associated with Ag\(_2\)O (96 cm\(^{-1}\) and 146 cm\(^{-1}\) [17]), Na\(_2\)O (298 cm\(^{-1}\) [18]) and NaNO\(_2\) (186 cm\(^{-1}\) [19]) groups vibrations. The presence of the above mentioned groups’ wavenumbers in confirmed by Gaussian spectra analysis (Figure 4b). The good fitting of experimental spectrum with Gaussian spectra allows to identify a 434 cm\(^{-1}\) band, which can be associated with Si stretching vibrations in SiO\(_2\) group (484 cm\(^{-1}\) [15]). The analysis of the middle-range of the experimental spectrum (Figure 4c) displays the following bands: 1153 cm\(^{-1}\) (Si stretching vibrations in -Si-O-Si- group), 1346 cm\(^{-1}\) (B stretching vibrations in B-O group), 1234 cm\(^{-1}\), 1517 cm\(^{-1}\) and 1602 cm\(^{-1}\) (NO\(_2\) group symmetrical stretching vibrations) [20, 21]. All the identified vibrational bands are shifted by 5 – 25 cm\(^{-1}\) to the low-wavenumber region compared with literature data for “clean” compounds. The observed shift was assumed to be caused by phase decomposition in the system “porous glass – borohydride sol Ag NP”. The shift decrease to the NaNO\(_2\) and SiO\(_2\) groups evidence of the strengthening bonding between the phases.
Figure 4. Ag NP on the porous glass experimental Raman spectra at various NP concentrations (cm$^{-1}$): 1 – 1.1 $\cdot$ 10$^{12}$, 2 – 0.6 $\cdot$ 10$^{12}$, 3 – 0.23 $\cdot$ 10$^{12}$, 4 – without Ag NP (a); Raman spectra Gaussian analysis at low- (b) and middle-wavenumbers (c) spectral ranges.

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Shift and vibrational bands intensity selective increase in Raman spectra indicates of light scattering plasmon enhancement by borohydride sol products on the porous glass surface. In this
regard, it was interesting to study Raman spectra of R6G doped to PVA film on the porous glass surface.

According to the experimental spectra (Figure 5), the bands defying R6G [21], appeared to be the following: 602 cm$^{-1}$, 770 cm$^{-1}$, 1180 cm$^{-1}$, 1349 cm$^{-1}$, 1507 cm$^{-1}$ and 1644 cm$^{-1}$.

Gain coefficient can be obtained by the formula [21]

$$SE = \frac{I_{SERS}}{I_{RS}} \cdot \frac{C_{RS}}{C_{SERS}},$$

where $I_{SERS}$ and $I_{RS}$ denote SERS and Raman scattering intensities on the defined wavenumber, respectively; $C_{SERS}$ and $C_{RS}$ denote agent concentrations in SERS- and Raman scattering experiments, respectively. SE estimated value was equal to $10^{11}$. Light scattering enhancement by R6G molecules in PVA film doped with Ag NP constituted approximately $10^{13}$.

![Figure 5](image_url)

**Figure 5.** Raman (a), absorption (curves 5 – 8) and fluorescence (curves 9 – 12) spectra of R6G molecules in PVA film on the porous glass modified by Ag NP at various concentrations of Ag NP (cm$^{-2}$): 1, 5, 9 – without Ag NP; 2, 6, 10 – $0.23 \cdot 10^{12}$; 3, 7, 11 – $0.6 \cdot 10^{12}$; 4, 8, 12 – $1.1 \cdot 10^{12}$. Curves 3 and 4 are weighted by the factor of $10^{2}$.

Significant increase of light scattering by R6G molecules with Ag NP on the porous glasses is caused by the presence of scattering centers which participate in both scattering and fluorescence. The spatial restriction that takes place due to surface pores leads to the molecular complexes formation. With Ag NP concentration increase, due to nonradiative energy transfer, R6G molecules absorbance increase, as shown in their absorption spectra (Figure 5b). However, in the time range between molecule excitation and deactivation there may be relaxation, recombination and inter-conversion processes leading to fluorescent molecules number decrease. For R6G molecular clusters localized in glass pores, due to their proximity to each other, the transfer to the triplet state probability can change, resulting in delayed fluorescence and phosphorescence emission along with that the number of singlet molecules decreases. This statement will lead to the further investigations of photoprocesses occurring in porous media with the presence of NP.

Ag NP doped into the polymer matrix tend to form centers which enhance light scattering of nearby dye molecules. As shown on Figure 4, Raman spectra of these matrices allow to obtain detected R6G molecules. The main bands (612 cm$^{-1}$, 1370 cm$^{-1}$, 1518 cm$^{-1}$ and 1664 cm$^{-1}$) shift of R6G in PVA Raman spectra to the “clean” compounds range is minimal, which explains strong bonding of the polymer and dye in the CO- and OH-groups deformational vibrations range. The polymer-porous glass bonding formation occurs at these groups wavenumbers (Figure 5a).

Scattering intensity drastic increase bands occurs in Raman spectra of dye molecules adsorbed on NP surface, which is not observed for R6G molecules doped into polymer (Figure 5a and Figure 6a). This can be associated with energy redistribution while bonding formation with polymer.
R6G in polymer film with the presence of Ag NP absorption and fluorescence increase (Figure 6b) which is caused by local surface plasmon resonance in NP occurring on excitation [22, 23].

Figure 6. Raman (a) and absorption (curves 3, 4) and fluorescence (b) spectra of R6G molecules in PVA film with the presence of Ag NP: curves 1, 3, 5 – R6G in PVA film; 2, 4, 6 – R6G with Ag NP in PVA film

5. Conclusion
It was shown that the optical spectroscopy of dye molecules adsorbates and Ag NP in PVA films on the porous glasses surface allows to obtain and evaluate the efficiency of the energy exchange between electron-excited and unexcited molecules. It was found that electron and vibrational energy absorbance and scattering centers are formed in the presence of Ag NP and dye molecules which is shown in SERS and Raman spectra. FRET, plasmon excitation in Ag NP and R6G fluorescence enhancement was found to occur in these conditions. It is difficult to conclude which process is predominant due to the investigated processes complexity: the additional experiments are needed. In addition, porous glass modifying by Ag NP results in appearance of new properties (molecular fluorescence enhancement), which allows to use these systems as optical sensors. R6G fluorescence intensity detection in PVA film showed that fluorescence weak red shift was due to surface plasmons generation in Ag NP, while Ag NP Raman spectra Stokes shift was well detected. We suggest that Raman spectra of R6G molecules in PVA near glass surface is due to interaction between polymer chains and dye on the CO- and OH-groups vibrations wavenumbers range.

Thus, modified porous glasses allow to enhance Raman scattering on R6G molecules by Ag NP surface plasmons and detect polymer-dye system features.

The results obtained in the framework of the State task of Russian Ministry of Science and Education. Nr. 3.809.2014/K.

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