

Optical properties of the porous glass composite material

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Spectrum absorption and luminescence methods were used to investigate the peculiarities of optical properties of compound material consisting of nanoporous silica with impregnated gold nanoparticles soaked in rhodamine 6G ethanol solution. One possible explanation for the phenomenon of increasing of absorption near plasmon resonance frequency and rhodamine 6G absorption band is given.

Keywords: porous silica, gold nanoparticles, dye, absorption, luminescence, rhodamine 6G.

1. Introduction

Metal nanoparticles impregnated into nanoporous silica attract attention of modern scientists because of their unique properties: chemical and thermal stability, optical translucency. In addition, such systems are extremely easy to make; thermal decomposition of some salt of metal leads to the forming of nanoparticles, and a change in optical properties. Metal nanoparticles have very high electrical field near their surface, and this can dramatically change optical properties of properly selected material which is in contact with the metallic surface. In this article such material is rhodamine 6G.

2. Experimental

2.1. How to obtain the Au nanoparticles

There are many methods of obtaining gold nanoparticles. One of the most common methods is based upon the thermal decomposition [1] of HAuCl_4 at approximately 1000 K. If the crystals are spread within nanopores, their decomposition will lead to the creation of the nanoparticles of Au. This method was used for our sample preparation. Dry samples of nanoporous silica (13 nm average pores size; 1 mm thickness) were soaked in the HAuCl_4 solution, then dried and annealed at 1000 K in the air for 1 hour. The color of obtained samples became pink.

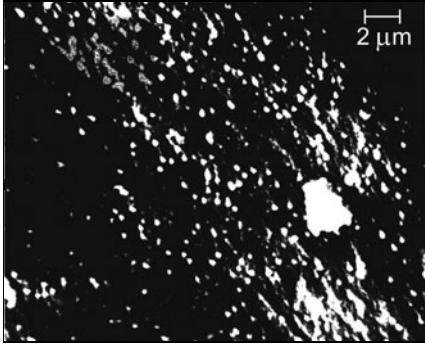


Fig. 1. Electron microscope photography.

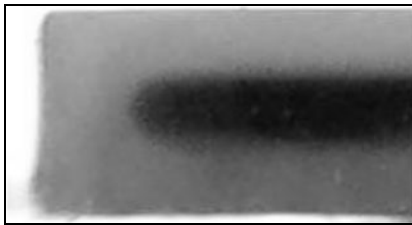


Fig. 2. A look at the flat end of nanoporous silica, 2 mm of thickness, 50 nm average pores diameter.

One proof that nanoparticles do exist is the electron microscope photography shown in Fig. 1. Although porous material was not the same as the one we used for gold nanoparticles, we can assume that nanoparticles also exist in smaller pores of nanoporous silica. The average pore diameter of the silica used for electron microscopy was 50 nm. The typical look of it with impregnated nanoparticles is shown in Fig. 2.

2.2. Samples holder design

For further luminescence investigations we designed a special holder for the samples, shown in Fig. 3. It consists of thin translucent glass plates (1) (0.2×24×24 mm), an aluminium limiting diaphragm (3) of 0.4 mm thickness, with three 2.0 mm diameter through holes each (2a). Two identical samples of nanoporous glass, both 1 mm thick, 13 nm average pores diameter, one with nanoparticles (4a), another one as the referent

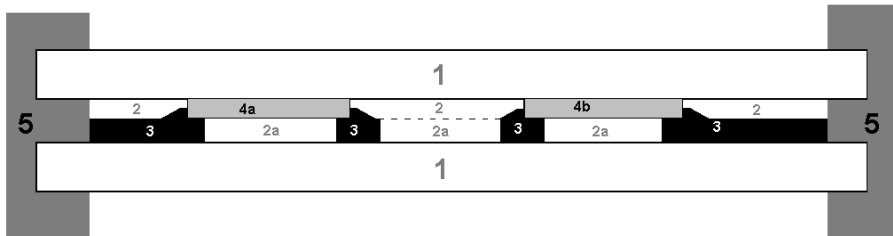


Fig. 3. The samples design; 1 – thin glass plates; 2, 2a – voids; 3 – aluminium limiting diaphragm; 4a – nanoporous silica plate with impregnated Au nanoparticles, 4b – reference clean nanoporous silica plate; 5 – sealing compound.

sample without them (4b), are fixed by glass plates (1) and sealed by means of a sealing compound (5). Such design firstly allows us to eliminate scattered light by limiting the diaphragm (3) and secondly gives us the possibility to fill this cell with liquids. When the cell is filled with a liquid and sealed, the liquid fills the pores of the samples and voids (2) and (2a).

2.3. Optical absorption measurement

We performed three series of spectrum absorption measurements. The first one was performed with dry samples, the second one with ethyl alcohol, and the third one with rhodamine 6G ethyl alcohol solution. Measurements were carried out with an upgraded spectrophotometer C115-M1 [2]. We worked in transmitted light with a stabilized halogen lamp (12 V, 4.5 A) as the source of light. The optical train of measurements is shown in Fig. 4. The Spectrum was taken in the step mode. Firstly, C115-M1 set a wavelength, *e.g.*, 500 nm. Then, the sample holder (3) set consecutively in *B*-position

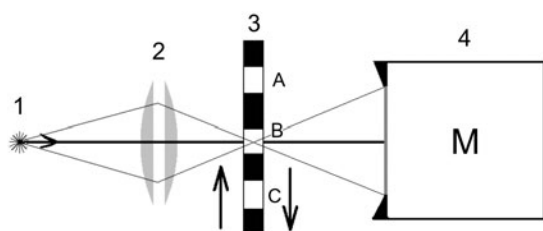


Fig. 4. The optical absorption measurement train; 1 – source of light; 2 – collimator; 3 – computer controlled step motor drive with the sample holder; A, B, C – measurement positions of sample holder; 4 – receiving aperture of spectrophotometer C115-M1.

in the sample holder (void space), then *A*-position (referent nanoporous silica) and at last *C*-position (nanoporous silica with gold nanoparticles). The diaphragm inside the sample holder was at the side of the receiving aperture to eliminate incorrect measurements. To obtain the absorption spectrum in optical density units of metal nanoparticles we had to eliminate spectral characteristics of the lamp, the photomultiplier inside C115-M1 and the clean nanoporous glass. This can be done by means of the simple formula: $D = \ln(I_A) - \ln(I_C)$, where I is the intensity of light inside the aperture.

2.4. Optical luminescence measurement

The optical setup used in luminescence measurements was the same as it was in the absorption measurements. The only difference was the source of light. We used laser (ILGI-101) with copper vapors as the laser medium. It has the following parameters: it generates simultaneously two lasing lines (*i.e.*, 510.6 nm and 578.2 nm), it generates in pulse mode with average CW power is 4.5 W, the pulse duration is 20 ns and repetition rate is 8 kHz, beam divergence is 10 mrad, diameter of the beam is

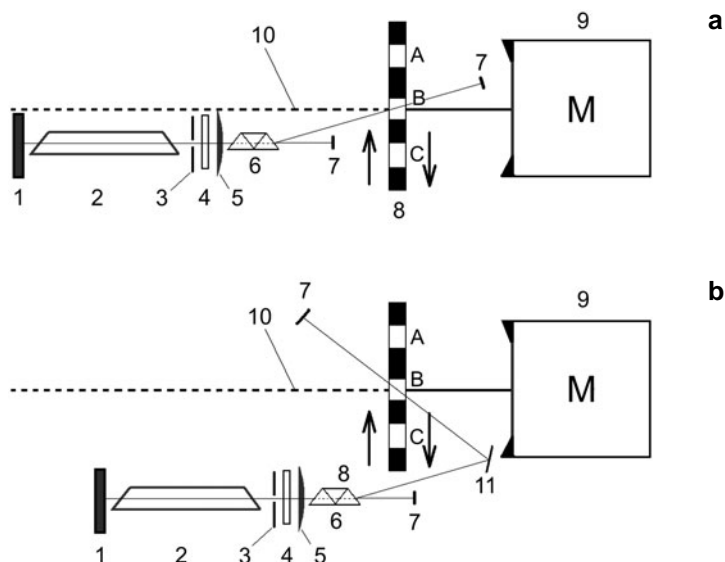


Fig. 5. Optical train of luminescence measurements: “transit” (a) and “reflection” (b). 1, 4 – laser’s mirrors; 2 – discharge laser tube; 3 – diaphragm; 5 – long-focus lens; 6 – direct-vision prism; 7 – absorber for unused laser beam; 8 – computer controlled step motor drive with the sample holder; 9 – receiving aperture of spectrophotometer C115-M1; 10 – direction of maximum sensitivity of C115-M1; 11 – mirror.

10 mm and the length of discharge tube is 150 cm. We used the angular mode selector (3) to improve the divergence. Then we used the direct-vision prism (6) to eliminate the non-used lasing line (578.2 nm) by the absorber (7) and focused the laser beam (510.6 nm) with the help of the long-focus lens 5 in the dislocation of the maximum sensitivity of the receiving aperture of C115-M1. We conducted two experiments: firstly, we used the transmitted light method, where the laser beam spread to the receiving aperture almost directly, and, secondly, the laser beam spread from the side of the receiving aperture to the samples. As in the previous absorption measurements, there were three positions of measurements (Fig. 5.): A, B, C.

3. Results and discussions

3.1. Optical absorption properties

The first interesting result in this section is the plasmon resonance shift. As we showed in our previous work [1, 3], the Mie scattering theory [4] can be used for average diameter measurements of the nanoparticles. Detailed analysis of spectra for different soaking mediums can give us some information on how the nanoparticles are distributed inside the nanoporous silica. If we apply the analysis presented in detail in our previous works [3], we can obtain such parameters of gold nanoparticles as their size and their total mass and even more – the average dielectric constant of media. Figure 6 represents the analysis of spectra of the dry samples:

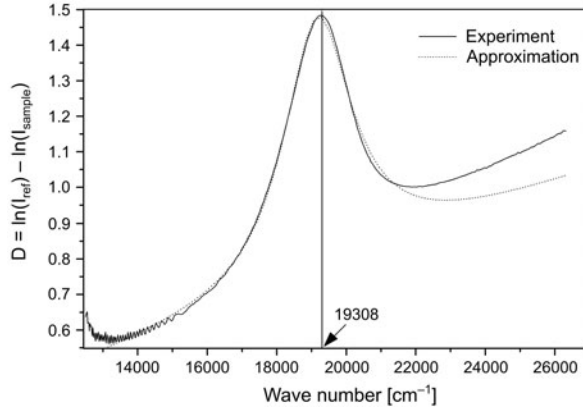


Fig. 6. Experiment and approximal spectra of absorption of dry sample with gold nanoparticles.

Nonlinear regression was performed on experimental data from 16000 cm^{-1} to 22000 cm^{-1} to eliminate non-plasmon resonance spectral peculiarities. That is why experimental and approximation results diverge at $> 22000\text{ cm}^{-1}$ region. The obtained parameters from this approximation are: the average diameter of the particles is $6.14 \pm 0.06\text{ nm}$, the surface density of impregnated particles is $9.8 \pm 0.1\text{ mkg/cm}^2$, the effective dielectrical constant is 2.202 ± 0.003 . The absolute error is taken from the statistical analysis and, evidently, it does not take into account the systematic error. The same method was applied to the spectra of absorption of the silica soaked in ethanol. The only parameter which changed significantly is the effective dielectric constant: its value became 2.450 ± 0.004 . These data allow us to roughly estimate the value of the influence of ethylene alcohol on the effective dielectric constant. Let a and b be the fractions of influences of silica and ethanol accordingly to the total dielectric constant $\varepsilon_m = a\varepsilon_{\text{silica}} + b\varepsilon_{\text{void}}$, where ε_m is the effective dielectric constant. Thus, we have two equations: $1.48 = a\varepsilon_{\text{silica}} + b$ (dry silica); $1.56 = a\varepsilon_{\text{silica}} + 1.36b$ (silica soaked in ethanol) and normality condition $a + b = 1$. From here we obtain $a = 0.78$, $b = 0.22$; so, a rough estimation shows that nanoparticles are impregnated into silica quite strongly. The change in the effective dielectric constant leads to the plasmon resonance red shift. This is shown in Fig. 7.

Another four spectra are shown in Fig. 8. They represent the interaction of rhodamine 6G absorption and plasmon resonance absorption. The first spectrum, marked as Au:EtOH:PG, represents the absorption of gold nanoparticles soaked in ethanol: $D = \ln(I_{A_Eth}) - \ln(I_{C_Eth})$. The second spectrum, marked as EtOH:PG:Rh6G, shows how clean nanoporous silica changes the optical properties of rhodamine 6G. The corresponding formula for this spectra is $D = \ln(I_{B_Rh}) - \ln(I_{A_Rh})$. The third one, marked as Au:EtOH:PG:Rh6G is the spectrum of the optical density of nanoporous silica with the nanoparticles soaked in rhodamine normalized upon the referent silica soaked in the same solution of rhodamine: $D = \ln(I_{A_Rh}) - \ln(I_{C_Rh})$. At last, the fourth one is the sum of the first and the second spectra and it represents the estimated

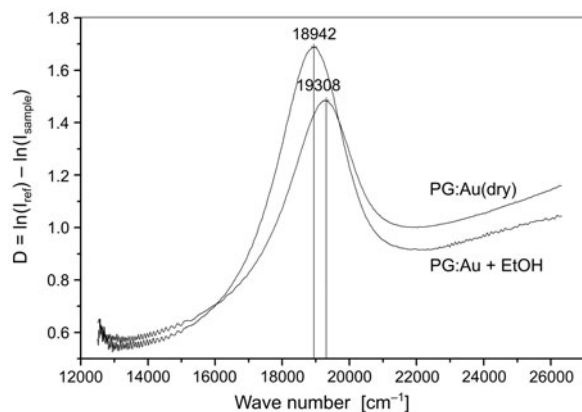


Fig. 7. Dry versus soaked in ethanol absorption spectra of gold nanoparticles.

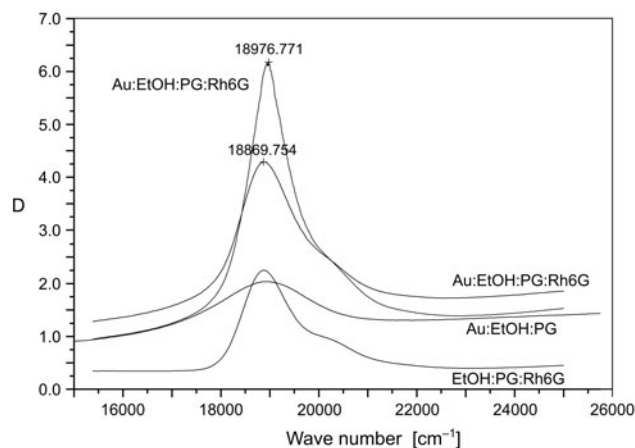


Fig. 8. Plasmon spectra that represent the interaction of rhodamine 6G with nanoparticles.

absorption of the composite material consisting of nanoporous silica, gold nanoparticles and rhodamine 6G ethanol solution. The corresponding formula for this spectrum is $D = \ln(I_{A_Eth}) - \ln(I_{C_Eth}) + \ln(I_{B_Rh}) - \ln(I_{A_Rh})$. As one can see, the total amount of absorption in the case when nanoparticles are soaked in rhodamine is greater than in the case when the spectra are added. This is quite a peculiar result. Theoretically, when any two oscillators (in our case nanoparticles and rhodamine) are bound, their absorption peaks push apart, which has to lead, at least, to a flatter peak than the sum of spectra taken separately, or even a two-peak absorption curve in case of a strong interaction. But we may observe an even stronger sharpening of the peak of absorption instead. We can assume that this is caused by the nanoinhomogeneity and the role of the adsorption on the surface of silica with nanoparticles, which increases the effective absorption cross-section. If we compare the spectra of

the absorption of silica without nanoparticles soaked in rhodamine to the rhodamine solution (both of the same thickness, Fig. 3), we can see the same effect. Another possible explanation is based upon the discussion given above: the nanoparticles are quite strongly impregnated or even fused into the nanoporous silica and that is why the interaction between nanoparticles and rhodamine is not as strong as suspected.

3.2. Optical luminescence properties

The spectra of luminescence of all three channels *A*, *B* and *C* are shown in Figures 9 and 10.

There are 5 spectra of intensity in arbitrary units in Fig. 9. Silica without nanoparticles demonstrates the most powerful level of luminescence. That is in good

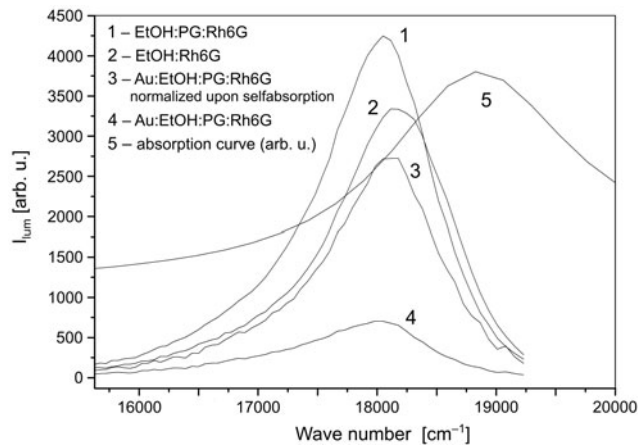


Fig. 9. "Transit" luminescence spectrum.

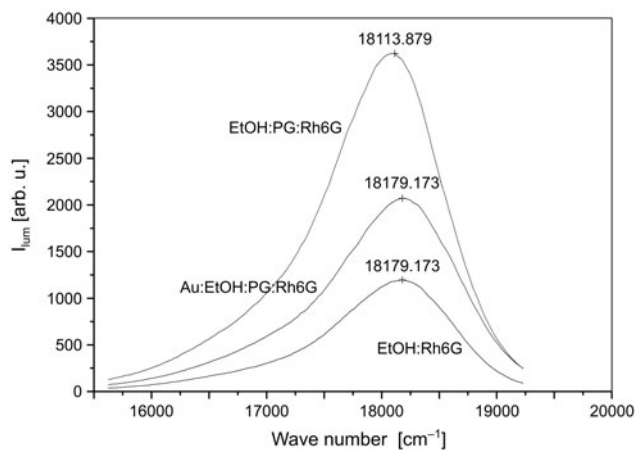


Fig. 10. "Reflection" luminescence spectrum.

a correlation with the previous absorption results: rhodamine inside nanoporous silica shows a better absorption level than the simple ethanol solution. The opposite takes place in case of nanoparticles. As one can notice, the curve 4 in Fig. 9 shows a much weaker luminescence as compared to the luminescence of silica without nanoparticles. This phenomenon cannot be explained just by the self-absorption effect caused only by nanoparticles, when emitted by luminescence light is absorbed by nanoparticles along its path through silica. To demonstrate this we built the curve 3 from the curve 4, which was normalized upon the total absorption of the entire sample of silica measured in the previous experiments with gold nanoparticles inside silica soaked in ethanol without rhodamine (absorption is shown in Fig. 9 as curve 5 in arbitrary units). This simple model of self-absorption gives us the upper level of this effect: every photon of luminescence must propagate through silica with nanoparticles. So, we have to assume that nanoparticles work as a quenching admixture in rhodamine, and not as a phosphor activator. This assumption can also be verified by time-relaxation measurements.

Three spectra in Fig. 10 are the same as curves 1, 2 and 4 in Fig. 9, with a difference in the choice of the optical train used (Fig. 5b). Again, the sample with nanoparticles shows lesser luminescence than the silica without them, but far more powerful than in the previous optical train (Fig. 5a). Again, this can be explained by the self-absorption effect.

4. Conclusions

Although the adsorption and luminescence measurements are in a good correlation with each other, the rhodamine's interaction with nanoparticles leads to quite a peculiar effect of quenching the luminescence. Further investigations are needed to fully explain this effect. The combination of plasmon resonance analysis with soaking nanoporous silica by different liquids appears to be a good method of investigation of the disposition of metal nanoparticles inside the pores of nanoporous silica.

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