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A. I. Mantel

L.N. Gumilyov Eurasian National University, Kazakhstan

A. E. Yensebayeva

L.N. Gumilyov Eurasian National University, Kazakhstan

S. B. Smatov

L.N. Gumilyov Eurasian National University, Kazakhstan

I. S. Irgibayeva

L.N. Gumilyov Eurasian National University, Kazakhstan,

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Decreasing of the concentration quenching of fluorescent dye in a solution by introducing it to nanoparticles of silicon dioxide

A.I. Mantel*, A.E. Yensebayeva, S.B. Smatov, I.S. Irgibayeva

L.N. Gumilyov Eurasian National University, Astana, Kazakhstan
**e-mail: wunderucho@mail.ru*

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The technique of introduction a fluorescent dye Tris(bipyridine)ruthenium (II) chloride into nanoparticles of silicon dioxide in isopropyl alcohol was tested. The preparation of nanoparticles was carried out by means of the Stober method. The optimal reaction conditions were determined. It was found out that the penetration of a dye into silicon dioxide nanoparticles reduced the effect of concentration quenching of the dye and made it possible to achieve an increase in fluorescence intensity in the solution more than twofold. An attempt was made to functionalize the obtained particles by introducing amino groups onto the particle surface. Fused silver nanoparticles were seeded with silver nanoparticles.

Keywords: nanoparticles of silicon dioxide; concentration quenching; functionalization; fluorescence; absorption.

Introduction

Fluorescent dyes are very popular in science and technology due to a wide range of their applications. They are used in solar energy [1], scintillation technology [2], as spectrum shifters [3], biosensors [4], etc.

Fluorescent dyes are often used in the form of their solutions in organic solvents or polymer matrices. At the same time, science and technology are constantly confronted with a single problem – concentration quenching [5,6], which leads to a significant decrease in the fluorescence intensity of the entire system due to the formation of aggregates between the dye molecules in the solution [7]. For this reason, it is not always possible to obtain a sufficient concentration of the dye or the required luminescence intensity in the final product. In some cases it does not allow to achieve the required sensitivity of different detectors [8].

Very interesting is the possibility to reduce the effect of the concentration quenching of a fluorescent dye is to incorporate it into mesoporous silica nanoparticles (SNPs) [9-11], obtained by the Stober method [12]. The dye inside SNPs is in the molecular form and chemically bound to the crystal lattice of silica, which prevents its aggregation and reduces the probability of self-absorption [9].

The purpose of this work is to study the possibility of reducing or even completely eliminating the effect of concentration quenching of a fluorescent dye by

introducing it into silicon nanoparticles, and also testing the possibility of functionalizing the resulting nanoparticles to make them suitable for further chemical transformations [13, 14].

Experimental part

Reagents

Tris(bipyridine)ruthenium (II) chloride (Cat #: 224758); tetraethoxysilane $\geq 99.0\%$ (Cat #: 86578); (3-Aminopropyl)trimethoxysilane, 97% (Cat #: 281778); Sodium citrate tribasic dehydrate BioUltra, $\geq 99.5\%$ (Cat #: 71402); Tetrakis(hydroxymethyl)phosphonium chloride solution 80% in H₂O (Cat #: 404861); Silver nitrate, ReagentPlus®, $\geq 99.0\%$ (Cat #: S6506); Hydrochloric acid, 37% (Cat #: 07102); Ammonium hydroxide solution $\approx 25\%$ NH₃ basis (Cat #: 30501) was purchased from Sigma-Aldrich.

Equipment

Fluorescence spectra were measured on a spectrofluorimeter Fluorat-02 Panorama from Lumex.

The absorption spectra were measured on a UV-Vis spectrophotometer Specord 250 Plus from Analytic Jena.

Images of nanoparticles were obtained on a scanning electron microscope JSM-7500F from JOEL

Preparation of fluorescent silicon nanoparticles (1)

In 50 ml of isopropyl alcohol was added 1 ml of a solution of Tris(bipyridine)ruthenium(II) chloride (RuBpy) in isopropyl alcohol with a mass fraction of 0.16% and mixed with a magnetic stirrer at 1100 rpm. for 30 minutes. 40 μ l of TEOS and 20 ml of distilled water were added to the resulting solution and stirred for 10 minutes, after which 1 ml of aqueous ammonia was added to the solution. The addition of all the reagents was carried out without stopping the stirring of the solution.

The resulting solution was left to stir at 1100 rpm. Over time, nanoparticles of silicon dioxide with the RuBpy dye embedded in them were formed in the solution. The completeness of dye penetration into the silica was determined by centrifugation. Full implementation was achieved 90 minutes after the addition of aqueous ammonia. 0.8 ml of concentrated hydrochloric acid was added to the resulting suspension of fluorescent silica nanoparticles. From the suspension, ammonia residues and most of the solvent were distilled off in vacuum until the total volume of the 10 ml suspension was reached. The resulting concentrated suspension was centrifuged and the resulting precipitate was separated from the solvent.

The precipitate was washed twice with water and twice with isopropyl alcohol. Then dispersed in a mixture of 40 ml of ethanol + 10 ml of water. The pH of the obtained suspension was adjusted to 4.

Preparation of aminated fluorescent silicon dioxide nanoparticles (2)

To the suspension of fluorescent nanoparticles prepared by the procedure described above was added 1.2 ml of APS solution in isopropyl alcohol (20 μ l of APS + 10 ml of alcohol) with stirring. The suspension was left stirring overnight, after which a large portion of the solvent was distilled from the suspension in vacuum to a total volume of 10 ml. The resulting concentrated suspension was centrifuged; the precipitate was separated and washed with isopropyl alcohol.

The resulting precipitate was dispersed in 50 ml of isopropyl alcohol.

The inoculating of silver nanoparticles on the surface of fluorescent silica nanoparticles

14 ml of a suspension of fluorescent silica nanoparticles (1) were divided into two equal portions of 7 ml. In the first part was added 1 ml of a colloidal solution of silver nanoparticles in distilled water. In the second part – 1 ml of distilled water.

14 ml of a suspension of aminated fluorescent silicon dioxide nanoparticles (2) were also divided into two equal portions of 7 ml. In the first part was added 1 ml of a colloidal solution of silver nanoparticles in distilled water. In the second part – 1 ml of distilled water.

The resulting four solutions were stirred overnight.

Results and discussions

For studying the spectral-luminescent properties of the RuBPy dye, several solutions were prepared in isopropyl alcohol with concentrations of RuBPy 2×10^{-5} mol/l, 1×10^{-5} mol/l, 5×10^{-6} mol/l, 2.5×10^{-6} mol/l and 1.25×10^{-6} mol/l. Different concentrations were prepared in order to determine the optimum concentration, the increase of which would lead to concentration quenching. The absorption and fluorescence spectra of the dye are shown in Figures 1 and 2.

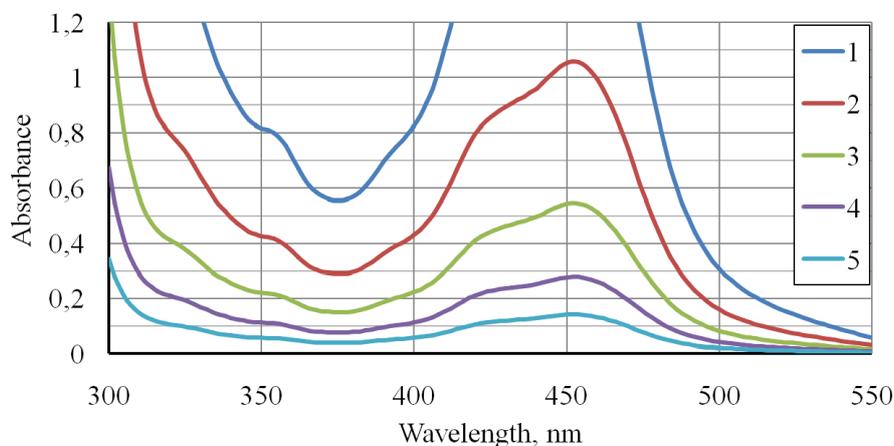


Figure 1. Absorption spectra of RuBPy solutions in isopropyl alcohol.
Concentration of RuBPy in the legend:
 2×10^{-5} mol/l, 1×10^{-5} mol/l, 5×10^{-6} mol/l, 2.5×10^{-6} mol/l, 1.25×10^{-6} mol/l.

It can be seen from Figure 1 that in the absorption spectra of the RuBPy dye there is a maximum at a wavelength of 452 nm. At this wavelength the samples were excited to measure the fluorescence spectra shown in Figure 2, as well as all subsequent samples containing the RuBPy dye. It is seen from Figure 2 that the wavelength of the maximum of the dye fluorescence is 616 nm. This wavelength was subsequently used to record the excitation spectrum. As can be seen from Figures 1 and 2, the optimal concentration of the dye corresponding to the maximum fluorescence intensity of the solution is the concentration of solution # 2, which is 1×10^{-5} mol/l. In the preparation of SNPs, this concentration in the solution was intended to be exceeded in three times in order to assess how fully

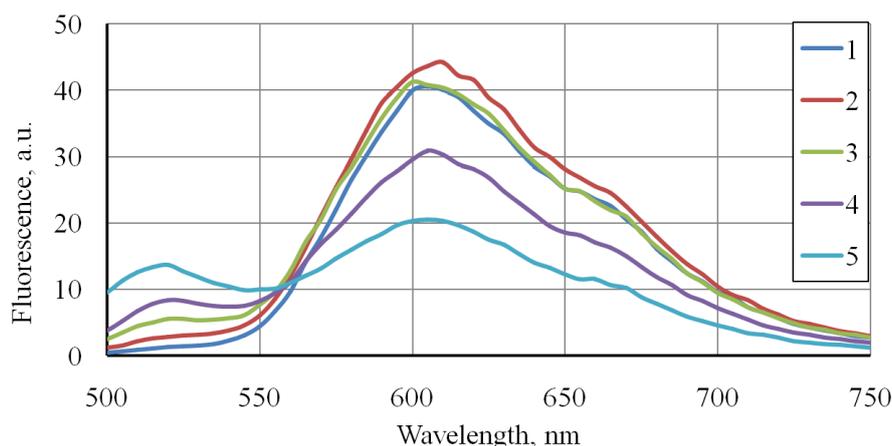


Figure 2. Fluorescence spectra of RuBPY solutions in isopropyl alcohol. The excitation wavelength is 450 nm.
 Concentration of RuBPY in the legend:
 2×10^{-5} mol/l, 1×10^{-5} mol/l, 5×10^{-6} mol/l, 2.5×10^{-6} mol/l, 1.25×10^{-6} mol/l.

the dye from a highly concentrated solution (showing a clear quenching of fluorescence) will be fully penetrated and how its introduction into SNPs will reduce the probability of aggregation.

The formation of SNPs is due to the alkaline saponification of the TEOS ether, while the resulting SiO₂ molecules build up the crystal lattice of the growing particle, which always has a negatively charged oxygen atom at the end. The RuBPY dye represents chloride dissociates into chlorine anions and cations of tris (2,2'-bipyridine) ruthenium (2+) ion [15].

Owing to the presence of a positive charge, tris (2,2'-bipyridine) ruthenium (2+) ion cations easily attach to the negatively charged oxygen of silicon dioxide, thereby penetrating into the growing particle. In this case, the dye is consumed in the solution and, as a consequence, its concentration is reduced. Due to this, the effect of concentration quenching falls down to a complete absence.

In the procedure for obtaining SNPs (1), the ratio of volumes of TEOS, water and aqueous ammonia was chosen so that the diameter of the produced nanoparticles was not more than 50 nm [12]. Ammonia, which serves as the catalyst in this reaction, was added last, so that the dispersion of nanoparticle sizes was minimal.

The completeness of the dye penetration into the silica was determined by precipitation of SNPs, for which 1.5 ml of the sample of the reaction mixture was centrifuged at 14.000 rpm for 2 minutes. The complete penetration of the dye was indicated by the absence of color, complete transparency of the solution and the formation of a bright orange precipitate, which was achieved 90 minutes after the start of the reaction. To interrupt the reaction, hydrochloric acid was added to the resulting suspension to neutralize the ammonia present in the reaction and thereby stop the growth of the nanoparticles, as well as various side processes such as the formation of new reaction centers, agglomeration of the particles obtained, and so on.

In the process of neutralizing ammonia with hydrochloric acid is formed ammonium chloride salt, which is avoided by washing the precipitate with distilled water. The precipitate is washed with isopropyl alcohol to remove unreacted starting reagents.

The resulting washed precipitate was dispersed again in a mixture of 40 ml of

isopropyl alcohol + 10 ml of water. For sufficient dispersion, the suspension was stirred for 1 hour at 1100 rpm, and then filtered through filter paper with pore sizes from 1.5 to 5 μm . Filtration is carried out to remove the largest particles of silicon dioxide, as well as to get rid of dust and other fine contaminants. The obtained suspension was used to measure the absorption spectra before and after filtration. Absorption spectra are shown in Figure 3.

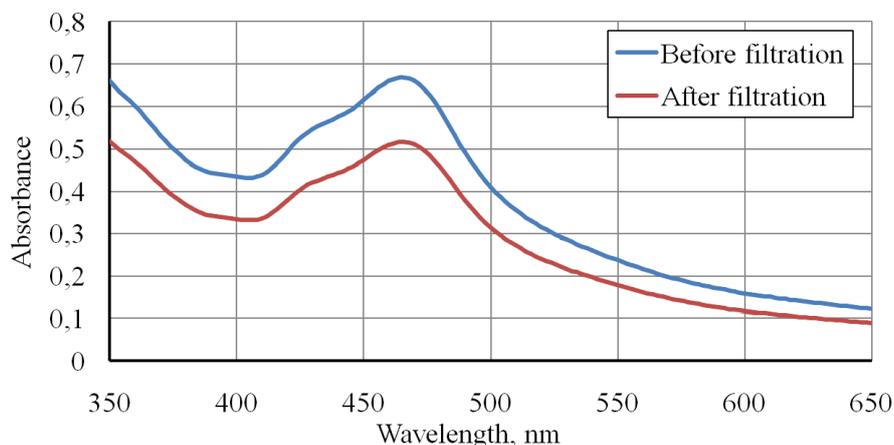


Figure 3. Absorption spectra of a suspension of fluorescent SNPs before and after filtration.

Figure 3 show that the suspension showed a decrease in the absorption intensity after filtration from 0.6 to 0.5, while maintaining the shape of the spectrum. From the nanoparticles of silica, images of the electron scanning microscope were taken (Figure 4).

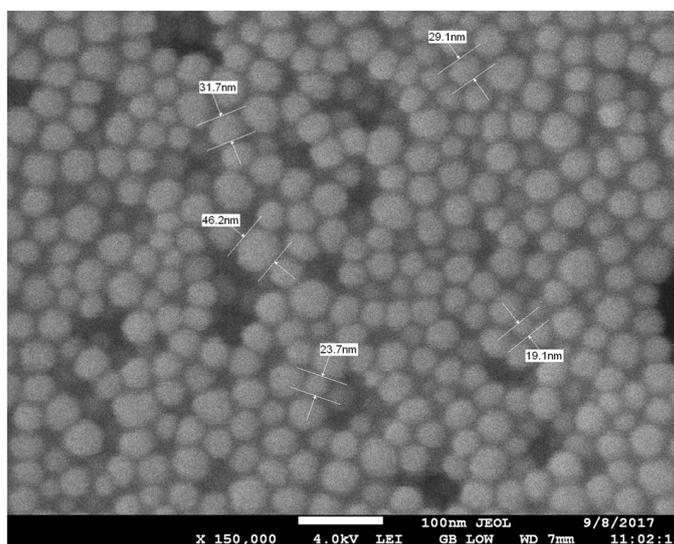


Figure 4. SEM image of fluorescent silica nanoparticles.

As can be seen from Figure 4, the dimensions of the nanoparticles are not more than 50 nm with a relatively small spread. A slight drop in the absorption of the suspension after filtration (Figure 4) may be due to the screening of particles larger than five μm . However, in this case, a particle of five μm or less should have been present, whereas the average particle size is 30 nm. This decrease in intensity can be explained by the slight electrostatic attraction of SNPs to the filter material.

The resulting fluorescence spectrum was measured after filtration of the suspension. The fluorescence spectrum of the suspension in comparison with the fluorescence spectrum of the RuBPY solution with a concentration of 3.6×10^{-5} mol/l is shown in Figure 5.

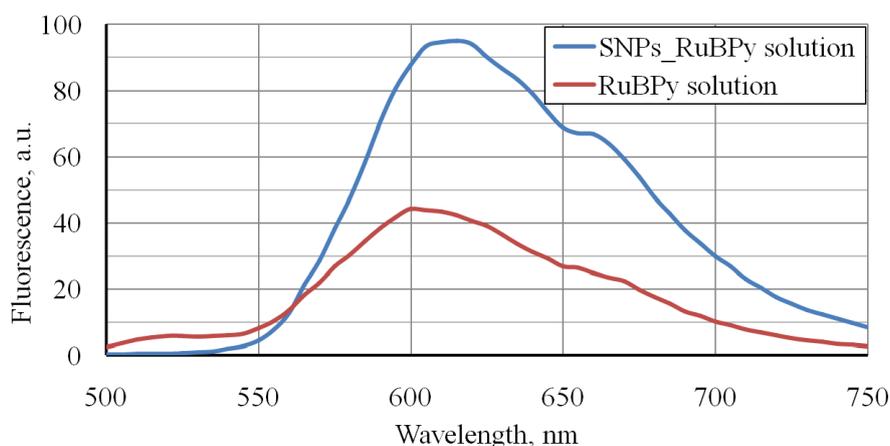


Figure 5. Fluorescence spectra of a suspension of fluorescent silica nanoparticles and a RuBPY dye solution. The excitation wavelength is 450 nm.

It can be seen from Figure 5 that the fluorescence intensity of SNPs is more than 2 times higher than that of the dye solution. This indicates the absence of aggregation and concentration quenching of the dye implanted in the SNPs, since otherwise the intensity would have to be much lower than that of the RuBPY dye solution in Figure 5.

Since the particles obtained are of great practical interest, it was interesting to modify their surface by inoculating an amino group on their surface according to the procedure (2) described above.

The resulting aminated fluorescent SNPs (aSNPs) do not differ from the unaminated spectra from the absorption and fluorescence spectra.

To test whether the modification was successful, an attempt was made to sow AgNPs on the surface of aSNPs. AgNPs were obtained according to the previously described procedure. A photograph of the scanning electron microscope of the obtained AgNPs presented in Figure 6. The absorption spectrum of AgNPs shown in Figure 7.

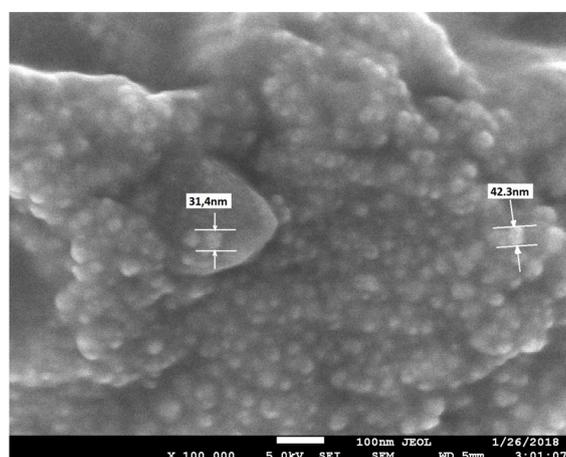


Figure 6. SEM image of AgNPs.

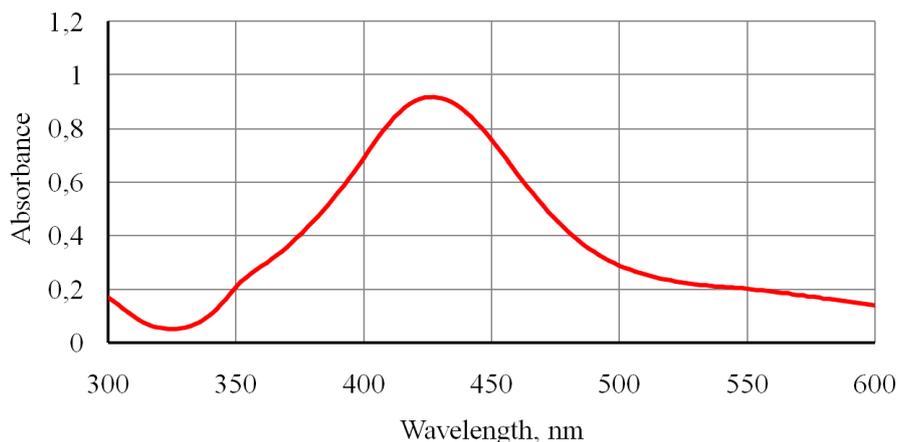


Figure 7. Absorption spectra of a suspension of AgNPs.

In the course of the research, a comparison was made of the processes of silver nanoparticles on the surface of SNPs and on the surface of aSNPs. Four suspensions of 7 ml each were prepared with the same concentration of SNPs or aSNPs.

1 ml of colloidal AgNPs solution was added to the first suspension containing SNPs.

1 ml of distilled water was added to a second slurry containing SNPs. This sample served as the standard of comparison of the first sample.

In a third aSNPs containing suspension was added 1 ml of a colloidal AgNPs solution. In a fourth aSNPs containing suspension was added 1 ml of distilled water. This sample served as a comparison standard for the third sample. The absorption spectrum was taken from the obtained samples (Figure 8).

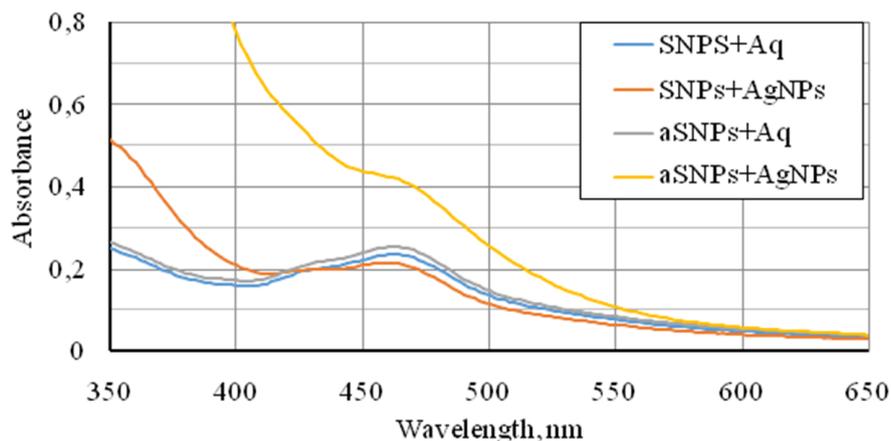


Figure 8. Absorption spectra of a suspension of fluorescent silica nanoparticles before and after filtration.

It is seen from Figure 8 that the absorptions of samples 1 and 3 are practically identical. Sample 2 shows an increase in absorption compared to sample 1 in the shortwave region to 400 nm, and a slight decrease in absorption is observed in the long-wave region. Sample 4 shows a noticeable increase in absorption over the entire wavelength range compared to sample 3. This confirms that only in this sample, the inoculating of AgNPs on the aSNPs surface was successful, whereas in the case of a sample with SNPs, this cannot be said.

Figure 9 shows the excitation spectra of the obtained samples. As it was mentioned earlier, the wavelength 616 nm was used for registration, since the dye has

a maximum of luminescence at this wavelength.

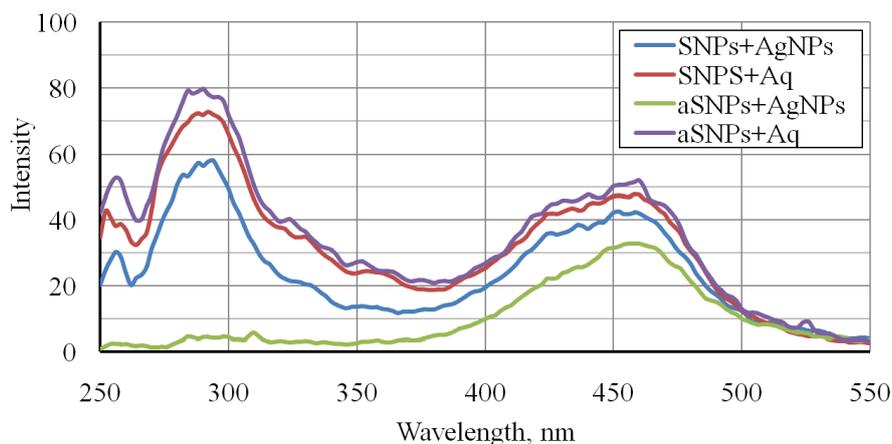


Figure 9. Spectra of excitation of a suspension of fluorescent nanoparticles of silicon dioxide. The registration wavelength is 616 nm.

As it can be seen from Figure 9, the presence of AgNPs causes the quenching of the fluorescence of the samples over the entire range of excitation wavelengths. In the case of sample 4 quenching is most pronounced and it is almost complete up to 350 nm. Spectra of fluorescence were obtained from the obtained suspensions 3 and 4 (Figure 10).

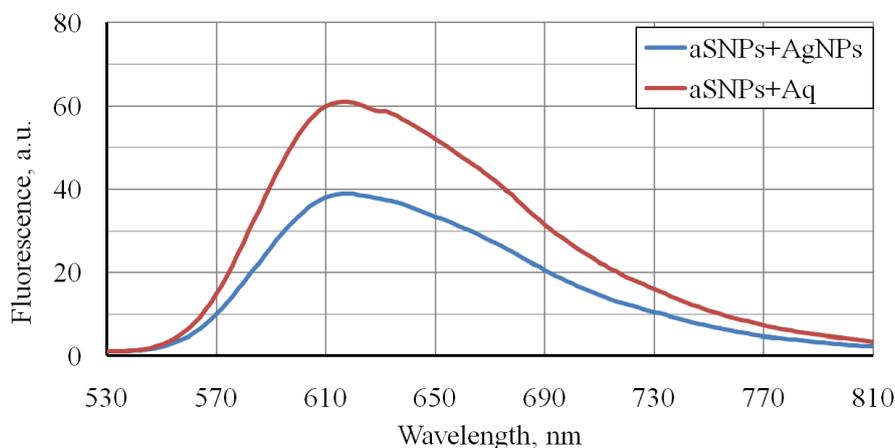


Figure 10. Fluorescence spectra of a suspension of fluorescent silica nanoparticles. The excitation wavelength is 450 nm.

It can be seen from Figure 10 that, as expected, when the samples are excited at a wavelength of 450 nm, a decrease in the intensity of the luminescence is observed in the image shown by AgNPs.

Conclusion

The introduction of the fluorescent dye Tris (bipyridine) ruthenium (II) chloride into silicon nanoparticles was successfully carried out. It is shown that this implantation makes it possible to use the concentration of the dye in solutions that exceeds the optimal concentration by a factor of three, without concentrating quenching. The obtained result is valuable for the preparation of high-brightness polymeric fluorescent materials. A modification of the surface of the obtained

particles was carried out by grafting amino groups to it. The activity of modified particles to adsorption of silver nanoparticles is shown in comparison with unmodified ones.

The seeding of silver nanoparticles onto the surface of modified fluorescent silica nanoparticles causes fluorescence quenching. Especially at the excitation wavelengths from 250 to 400 nm, which is associated, first of all, with an increase in the absorption of the obtained nanoparticles in this region.

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