THE INFLUENCE OF SUPERPARAMAGNETIC Fe₃O₄ NANOPARTICLES ON SPECTRAL AND LUMINESCENT PROPERTIES OF MESOSTRUCTURED SiO₂/P123/Rh6G/Fe₃O₄ FILMS FORMED IN STATIONARY MAGNETIC FIELDS

*V.N. Grebennikov* , E.A. Leonenko , P.A. Manorik , N.I. Romanovska, N.G. Kobylinska **, A.V. Shulzhenko

The effect of superparamagnetic Fe₃O₄ nanoparticles (NPs) on the spectral luminescence properties of homogeneous optically transparent mesostructured silica films of SiO₂/P123/Rh6G/Fe₃O₄, containing {P123 (Rh6G)} micelles consisting of Pluronic 123 with encapsulated Rh6G, and formed in stationary magnetic fields (MF) with an induction of less than 500 mT, was investigated. It was shown that, unlike SiO₂/P123/Rh6G, the spectral and luminescent properties of SiO₂/P123/Rh6G/Fe₃O₄ films depend on the MF used during their formation, and a gradual decrease in the band intensities in Rh6G spectra and quenching of luminescence with increasing of MF induction was observed. It is associated with a decrease in the monomer fraction and an increase in the fraction of non-luminescent Rh6G H-aggregates in micelles due to the interaction intensifying in the MF (formation of Fe³⁺-O bonds) of superparamagnetic NPs with micelles {P123 (Rh6G)}, oriented in the MF, which leads to a gradual deformation of micelles and accumulation in them of H-aggregate. The dependences of the changes in the absorption bands intensity and fluorescence of the monomeric form of Rh6G in the spectra of the films on the changes in the magnetic induction of the MF are described by an exponential function, and the ratio of the fluorescence intensities of the SiO₂/P123/Rh6G films to the fluorescence intensities of the SiO₂/P123/Rh6G/Fe₃O₄ films linearly depends on the induction of MF, which they are able to "remember", which is manifested in the values of fluorescence intensities.

**INTRODUCTION.** Interest in nanostructured materials is due to a noticeable change in
their physical and physico-chemical properties compared to the bulk material. In this regard, nanocomposites from two or more phases and hybrid materials with a certain spatial mesostructure are attracting attention. From the practical point of view, the condensed mediums in the form of hybrid organo-inorganic mesostructural films containing molecules of fluorescent dye [1, 2] and follow-up firmware nanodimensional particles of subgroup of iron and their oxides as a magnetic component of such hybrid materials [3, 4] capable to interact with the constant magnetic fields (MF) with an induction < 500 mT are interesting. The use of such NPs as the magnetic component of a hybrid material is due to their unique properties associated with a change in the domain structure of such magnetically ordered systems, acquisition of superparamagnetic properties that appear when particle sizes are reduced [5, 6], and also with the presence of a hysteresis curve, which plays an important role in magnetization of reversal processes.

The influence of an external magnetic field is manifested in changes in several physical and physicochemical properties of hybrid materials. Thus, the introduction of NP γ-Fe oxide into the matrix of mesoporous SiO₂ allows obtaining materials with different structural and magnetic properties [7]. The use of MP makes it possible to improve the sensory characteristics of some composite materials with nickel NPs [8] and to propose a sensitive element for a magnetically controlled sensor. When studying the photophysical properties of some organic fluorescent probes [3], an increase in the luminescence intensity was detected in the presence of an external constant magnetic field with an induction of 1–20 mT.

The influence of local magnetic fields of superparamagnetic magnetite NPs on the spectral-kinetic properties of the triplet excitation of Rh6G dye molecules embedded in the polyvinyl alcohol polymer matrix was shown in [4]. Changes in the absorption and luminescence spectra of the dye are explained by the formation of charge-transfer complexes.

The choice of magnetite as one of the components of such hybrid materials is because magnetite particles behave like ferromagnetic only at temperatures below the blocking temperature TB, which depends on the particle volume and anisotropy value. A decrease in the particle size to a single-domain level at a temperature higher than TB allows the magnetization vector of a single-domain particle to fluctuate from one direction of the easy magnetization axis to another, by analogy with an ideal paramagnet [9, 10]. Fe₃O₄ nanoparticles with sizes less than 24 nm at a temperature T = 300 K, which is somewhat higher than TB and characterized by a small relaxation time (<5·10⁻² s), acquire superparamagnetic properties [9, 10] and behave like paramagnet. Thus, in the absence of an external magnetic field at room temperature, such a system of nanosized particles of magnetite behaves like an ensemble of paramagnetic atoms with zero resulting magnetization.

At the stages of preparation and formation of thin hybrid mesostructured films containing fluorescent dye molecules, the introduction of magnetic NPs can affect the spectral-luminescent and magnetic properties of such materials, giving them new properties.
that can change under the influence of an external magnetic field.

The aim of this work was to study the effect of superparamagnetic Fe$_3$O$_4$ NPs on the spectral luminescence properties of homogeneous optically transparent mesostructured silica SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ thin films containing \{P123 (Rh6G)\} micelles consistent of Pluronic 123 (R126) and encapsulated Rh6G dye molecules and formed in stationary magnetic fields with an induction of less than 500 mT.

EXPERIMENT AND DISCUSSION OF THE RESULTS. The following reagents were used in the work: Iron chloride tetrahydrate (FeCl$_2$·4H$_2$O; 98,0 %, Merck), Iron chloride hexahydrate (FeCl$_3$·6H$_2$O; 99,0 %), tetraethoxysilane (TEOS), triblock copolymer Pluronic P123 (Sigma-Aldrich), hydrochloric acid (HCl 37%), EtOH (ethanol, anhydrous), Rh6G (Rhodamine 6G for microscopy), distilled water.

X-ray diffractometry of the NPs was carried out using a Panalytical X’Pert Pro powder diffractometr with CuKα-radiation (λ = 1.540598 Å), monochromatized Ni-filter, at room temperature in the range of angles 2θ 5-120° in increments of 0.040. The crystalline phases were identified using the JCPDS (Joint Committee on Powder Diffraction Standards) file cabinet. The morphology of the NPs samples was studied using a JSM-6610 LV scanning electron microscope (JEOL, Japan) at a voltage of 20 kV with an increase of up to 50.000 times. To enhance the optical contrast, the samples were sprayed with gold using the JFC-1600 Auto Fine Coater (JEOL, Japan), an ultra-thin spraying device.

FTIR-spectra of NPs and films as films coated on KBr crystal plate were recorded on spectrometer Perkin-Elmer Spectrum One.

The absorption and luminescence spectra of the films before and after exposure to an external magnetic field were recorded on a Specord 210 spectrophotometer (Analytic Jena) and a spectral setup in the "photon counting" mode, respectively (wavelength of exciting light 406 nm). The thickness of the films was measured by the results of AFM studies on atomic force microscopy (Nanoscope IIIa (Nanoscope Digital Instrument, USA). The magnitude of the magnetic induction of the magnetic field was measured using a universal device Teslameter 43205/1 (Ukraine).

Synthesis of Magnetit (Fe$_3$O$_4$) nanoparticles were obtained by chemical coprecipitation of FeCl$_2$ and FeCl$_3$ salts in an ammonia medium according to the modified previously described method [11] by mixing the salt solutions in the ratio 1:2 at a temperature of 55°C and the subsequent addition of 25% ammonia solution. The resulting precipitate was separated by magnetic separation and washed thoroughly with EtOH. The obtained magnetite nanoparticles were stored in an ethanol solution without drying.

Preparation of film-forming sol Hybrid silica films received by method of single-stage sol-gel synthesis by the technique described earlier [1]. To film-forming sol with a molar ratio of reagents: TEOS : Pluronic P123 : HCl : EtOH : H$_2$O = 1 : 6∙10^{-3} : 0.2 : 30 : 9.2 the calculated amount of Rh6G dye (1∙10^{-3} M) and a magnetite (7.5∙10^{-3} g/ml) was added. For dispersion of components the sol was subjected to ultrasonic processing (10 min.), aged for 72 hours. Films were obtained by applying a film-forming sol
on a pre-cleaned substrate (glass 25 mm×20 mm) by spin-coating at a substrate rotation speed of 1800 rpm⁻¹ for 5 s. Films formed in a constant magnetic field with the known induction. Thickness of the prepared films according to the atomic forces microscopy (AFM) was 200 ± 5 nanometers.

The magnetic field at which silica hybrid mesostructured films of the composition SiO₂/P123/Rh6G and (#)SiO₂/P123/Rh6G/Fe₃O₄ were formed was created using N38 (Ni) permanent magnets made of NdFeB alloy with the characteristics listed in Table 1, in the form of a magnetic composite module of a cylindrical shape (Fig. 1 a). To visualize the lines of magnetic induction around the magnetic module the program Vizimag 3.18 was used. In Fig. 1 a shows the locations of the formed hybrid mesostructured (#) SiO₂/P123/Rh6G/Fe₃O₄ films, where # is the number of the sample that corresponds to the position (Fig. 1 a) of the film in the field during its formation. Samples of hybrid films of (0) SiO₂/P123/Rh6G/Fe₃O₄ and (4) SiO₂/P123/Rh6G were obtained outside the field (B₀ = 0).

Characterization of the obtained nanoparticles to investigate the phase content of the Fe₃O₄, as well as to determine the average crystallite size, the method of XRD was applied (Fig. 1 b).

| Residual induction, T | 1.24 |
|----------------------|-----|
| Induction coercive force, kA/m | 915 |
| Magnetization coercive force, kA/m | 955 |
| Diameter of a disk, mm | 60 |
| Height of disk, mm | 15 |

The diffraction patterns identified seven peaks at: 18.4 (111), 30.2 (220), 35.6 (311), 43.3 (400), 53.7 (422), 57.7 (511) and 62.9 (442). These peaks are typical for a phase like spinel of the composition Fe₃O₄, i.e., for magnetite (250540-JCPDS). Iron oxides nanoparticles are prone to oxidation, but the absence of g-Fe₂O₃ (40142-JCPDS) peaks and the intense black color of the powders in the diffractogram indicate the absence of significant impurities of this oxide in the phase of the obtained Fe₃O₄.

On the diffractograms of the obtained magnetite, there is a slight decrease in intensity and broadening of the peaks, but no additional peaks observed (Fig. 1 b). The average crystallite size of the obtained magnetite calculated by the Scherrer formula [12] is 10 nm. In Fig. 1 c,d shows the data of electron microscopy and the corresponding size distributions of the NPs of the obtained magnetite. It is known that iron oxide nanoparticles are prone to aggregation due to the high surface energy inherent in finely dispersed structures, which is confirmed by transmission microscopy (Fig. 1 d).

An analysis of CEM microphotographs of Fe₃O₄ (Fig. 1 c) indicates that the synthesized materials, after drying are aggregates consisting of smaller particles. The magnetite NPs were obtained at a reaction solution temperature of 55 °C and stored in an ethanol suspension. They are characterized by an average particle size of ~ 9–11.0 nm (Fig. 1 d), which is consistent with the calculation data from XRD data.

As follows from the Fig. 1 e, curve 1) in NPs spectra Fe₃O₄ together with the bands, which can be attributed to valence and banding vibrations of ethanol’s different groups.
The influence of superparamagnetic Fe₃O₄ nanoparticles on spectral...
there are a few bands (640,589,565 cm⁻¹) forming summary contour in region 500-700 cm⁻¹, which according to [13, 14] may be attributed to Fe-O valence stretching bands (O of ethanol and in Fe₃O₄).

Analysis of the absorption spectra of aqueous solutions of Rhodamine 6G and the obtained films (Fig. 2) shows that in the concentration range from 1·10⁻⁶ M to 1·10⁻⁴ M, the dye is in monomeric form. At the used concentration of Rhodamine 6G (>1·10⁻⁴ M) both in solution and when its molecules included in the solid matrix, two main types of dimers formed as a result of dimerization of dye molecules: H-dimer and J-dimer [15]. The configuration of H-type dimers is energetically more favorable than the configuration of J-type dimers [16] with a relatively small difference in energy ≤ 3 kT, which indicates the joint presence of these configurations at room temperature. The aggregation mechanism during the formation of H dimers is explained by π-π interaction of aromatic π systems of two Rhodamine 6G molecules [2].

The influence of the aggregation of Rhodamine 6G dye molecules (Rh6G) and the concentration of Pluronic 123 in the film-forming sol (SiO₂ + P123 + Rh6G) on the spectral-luminescent properties of the formed silica hybrid films without magnetite NPs is studied in [17].

Fig. 2 shows the absorption and fluorescence spectra of a film without NPs magnetite (SiO₂/P123/Rh6G), as well as the spectra of thin hybrid films of the same composition (SiO₂/P123/Rh6G/Fe₃O₄), formed by different MF induction in the places shown in Fig. 1a.

As follows from the Fig. 2 a, the absorption spectra of hybrid films correspond to the monomeric form of Rh6G, which are characterized by a vibronic shoulder [18] at λ₁ = 501 nm [2,15,19,20] and the central maximum at λ₂ = 534 nm, the intensity of which depends on the amount of dye. The fluorescence spectra of hybrid films (Fig. 2 2Гр c) are characterized by a band at λ = 562 nm, which corresponds to the monomeric form of the Rh6G molecule.

It follows from the experimental data that an increase in the induction of the external MF, in which films are formed, leads to a sequential decrease in the intensity of the absorption and fluorescence bands (Fig. 2 a, Fig. 2 c and Table 2). However, in the presence of MF, such changes in the spectra of samples of hybrid SiO₂/P123/Rh6G films without NPs were not observed, which indicates the presence of interaction of Rh6G molecules with superparamagnetic magnetite NPs in samples of hybrid SiO₂/P123/Rh6G/Fe₃O₄ films.

Differential absorption and fluorescence spectra of samples of hybrid films in Fig. 2 b and fig. 2 d obtained by subtracting from the spectrum of a SiO₂/P123/Rh6G film the corresponding spectra of SiO₂/P123/Rh6G/Fe₃O₄ films formed at different values of magnetic induction. On differential absorption spectra, as shown in Fig. 2 b, bands appear at λ₁ = 501 nm and λ₂ = 534 nm.

The numerical values for the difference in the intensities of the absorption bands in the electronic spectra of the film samples at these wavelengths are given in Table 2, from which it follows that the magnitudes of the difference increase in the series under consideration without changing the position of the maxima of the absorption bands. An
The influence of superparamagnetic Fe₃O₄ nanoparticles on spectral...
Fig. 3. The effect of magnetic induction of MF on the difference in band intensities (No. 0, No. 1, No. 2, No. 3, see Fig. 2 b and Fig. 2 d) in the absorption spectra (ΔA) and luminescence (ΔI) of samples of hybrid films with magnetite NPs; Changes in the absorption intensity A at λ = 534 nm (c) and the fluorescence intensity I at λ = 562 nm (d) of the samples of hybrid mesostructured SiO₂/P123/Rh6G/Fe₃O₄ films as a function of magnetic induction (No. 0, No. 1, No. 2, No. 3, see Fig. 2 b and Fig. 2 d).

of MF, the intensity of the bands in the differential fluorescence spectra of the film samples decreases.

Fig. 3 shows the results of measurements of the difference in the intensities of the bands (No. 0, No. 1, No. 2, No. 3, see Fig. 2 b and Fig. 2 d) in the absorption spectra (ΔA, Fig. 3 a) and luminescence (ΔI, Fig.
The influence of superparamagnetic $\text{Fe}_3\text{O}_4$ nanoparticles on spectral...

Table 2
The band intensities in the absorption and fluorescence spectra of hybrid films in MF and the difference between the band intensities in the spectrum of the $\text{SiO}_2$/P123/Rh6G film and the band intensities in the spectra of $\text{SiO}_2$/P123/Rh6G/$\text{Fe}_3\text{O}_4$ films.

| Sample of the film | magnetic induction $B$, mT | Bands intensity characteristics in the spectra of the films in magnetic field: |
|-------------------|--------------------------|---------------------------------------------------------------|
|                   |                          | absorption ($A_{\lambda}, \text{MFE}, \Delta A_{\lambda}$)      |
|                   |                          | fluorescence ($I_{\lambda}, \text{MFE}, \Delta I_{\lambda}$)     |
|                   | $\lambda_1$=501 nm       | $\lambda_2$=534 nm                                            |
|                   | $\lambda_3$=562 nm       |                                                               |
| №0 (c $\text{Fe}_3\text{O}_4$) | $B_0=0$ | $0,092$ | 0 | $0,009$ | $0,147$ | 0 | $0,009$ | 15,624 | 0 | 2,69 |
| №1(c $\text{Fe}_3\text{O}_4$) | $B_1=15$ | $0,091$ | 1 | $0,010$ | $0,140$ | 5 | $0,016$ | 14,392 | 7,9 | 3,92 |
| №2(c $\text{Fe}_3\text{O}_4$) | $B_2=100$ | $0,088$ | 4 | $0,013$ | $0,132$ | 10 | $0,024$ | 12,304 | 21,2 | 6,01 |
| №3(c $\text{Fe}_3\text{O}_4$) | $B_3=300$ | $0,085$ | 8 | $0,016$ | $0,125$ | 15 | $0,031$ | 11,600 | 25,8 | 6,72 |
| $\text{SiO}_2$/P123/Rh6G | $B_0=0$ | $0,101$ | - | - | $0,156$ | - | - | 18,312 | - | 0 |

3 b) samples of hybrid films with NP magnetite depending on the magnitude of the magnetic induction. As can be seen from fig. 3, these curves tend to reach the shelf.

The magnitude of the magnetic field (MFE) influence was estimated according to the approach proposed in [3] by changing in the intensity of the bands in the absorption and fluorescence spectra of the formed hybrid films, which is caused by the magnetic field. The MFE value was determined as $\text{MFE} = (F_\lambda - F_u) \cdot 100\% / F_u$, where $F_\lambda$ and $F_u$ are the intensities of the bands in the spectra of the hybrid film in the magnetic field and at $B = 0$, respectively.

Moreover, for the intensity of the bands in the absorption spectra of the hybrid film $F_\lambda = A_\lambda$, $F_u = A_u$, and for the intensity in the fluorescence spectra $F_\lambda = I_\lambda$, $F_u = I_u$. The calculated MFE values are shown in table 2.

The observed effect of the influence of external MF induction on the change in the absorption intensity and luminescence intensity
Table 3
Parameters of the approximating curves describing the experimental data on the changes in the maximum of absorption and fluorescence intensities in the spectra of hybrid mesoscopic SiO2/P123/Rh6G/Fe3O4 films formed in MP.

| λ, nm | A0     | An-A0 | kA×10^3 | λ, nm | I0     | In-I0 | kI×10^3 |
|-------|--------|-------|----------|-------|--------|-------|----------|
| 501   | 0.084±0.001 | 0.008±0.001 | 7.0±0.9  | 562   | 11.68±0.19 | 3.86±0.24 | 20.8±4.6 |
| 534   | 0.124±0.001 | 0.021±0.001 | 12.0±0.9 |       |        |       |          |

of magnetite-containing mesostructured films can be described by a general differential equation: \(-dF_\lambda/dB = k_F(F_\lambda - F_0)\) in which \(dF_\lambda\) is the change in the intensity of the band (absorption, fluorescence), \(F_0\) is the limiting value of the change in intensity.

Integration of the differential equation from the initial value \(F_u\) (at \(B = 0\)) to \(F_\lambda\), at the current value of \(B\), gives a logarithmic response function \(\ln[(F_\lambda - F_0)/(F_u - F_0)] = -k_F B\) that depends linearly on the magnitude of the induction \(B\), in which the coefficient \(k_F\) characterizes the sensitivity of magnetite-containing hybrid mesostructured films to the influence of an external MF.

By potentiating, we obtain general expressions for changing the band intensity in the absorption and fluorescence spectra \(F_\lambda = F_0 + (F_u - F_0) \exp(-k_\lambda B)\), which describe the experimental data in Fig. 6 with the corresponding parameters of the approximating curves. The numbers of film samples in Fig. 3 c and d correspond to their location in a magnetic field during their formation, according to Fig. 1 a. The calculated parameters of the approximating curves are shown in Table 3. Since for these films \(k_I\) are larger \(k_A\), the sensitivity of the SiO2/P123/Rh6G/Fe3O4 hybrid film to the influence of an external MF is maximum under fluorescence (MFE = 25.8%).

Dependence of the ratio of the fluorescence intensity of a film without magnetite NPs in experimental value of the fluorescence intensity of SiO2/P123/Rh6G/Fe3O4 films on the magnitude of magnetic induction is shown in Fig. 4. It can serve as a characteristic of the degree of quenching of the fluorescence of these films by magnetite nanoparticles.

As shown from the above results, superparamagnetic magnetite NPs significantly affect the spectral and luminescent properties of mesostructured SiO2/P123/Rh6G/Fe3O4 films formed in stationary magnetic fields with an induction of less than 500 mT.

The observed effect of the magnetic field used in the formation of hybrid (#) SiO2/P123/Rh6G/Fe3O4 films on their spectral-luminescent properties is due to the presence of Fe3O4 NPs in the films interacting with magnetic field, since significant differences in the spectral-luminescent properties of the SiO2/P123/Rh6G films, formed in the MF and outside MF were not observed.

To understand the above facts and explain the possible mechanism of the effect of the increasing magnitude of magnetic induc-
The influence of superparamagnetic Fe₃O₄ nanoparticles on spectral...
tion of Fe$^{3+}$ ions (which in an amount of about 15 are present on the surface of magnetite NPs with an average size of 10 nm [21]), for example, with amine nitrogen of Rh6G look-like observed interaction of magnetite NPs with humic acids [22] upon their adsorption, then a shift in the maximum of the dye absorption band observed. However, as it is evidenced by the results of the experiment, this does not happen. Direct interaction of Fe$_3$O$_4$ NPs with dye molecules encapsulated in a micelle with P123 seems unlikely.

In the absence of MF at room temperature, the magnetic moments of spherical magnetite nanoparticles (10 nm) located in a film-forming sol with micelles \{P123 (Rh6G)\} are randomly oriented due to thermal fluctuations.

Taking into account the above considerations, the reasons for the changes in the spectral-luminescent properties of the (0)SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ film as compared to the (4)SiO$_2$/P123/Rh6G film that does not contain magnetite NPs (Fig. 2 a, curves 0 and 4), Fig. 2 c, curves 0 and 4; Fig. 2 b, curve No. 0, Fig. 2 d, curve No. 0) become clear. It should be noted that the intensity of the vibronic shoulder (or the band corresponding to the H-dimer) and the band corresponding to the monomer (Fig. 2 b, No. 0), in contrast to the spectra for (4)SiO$_2$/P123/Rh6G (Fig. 2 a, No. 4) and (0)SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ (Fig. 2 a, No. 0) are comparable.

The formation of new Fe$^{3+}$ - O bonds, in which Fe atoms on the surface of Fe$_3$O$_4$ NPs and oxygen donor atoms of P123 micelles with Rh6G molecules encapsulated in them in monomeric form participate, can cause micelle deformation and contribute to the formation of both intermediate and H- dimers. This is consistent with a decrease in the intensity of both bands (vibronic and related to the monomeric form) both in the differential absorption spectra (Fig. 2 b, No. 0) and in the differential fluorescence spectra (Fig. 2 d, No. 0).

However, in contrast to the differential absorption spectra (Fig. 2 b, curve No. 0), where $\Delta A (\lambda_{\text{max}} \approx 562 \text{ nm}) \approx \Delta A (\lambda_{\text{max}} \approx 604 \text{ nm})$, in the differential fluorescence spectra (Fig. 2 d, curve No. 0) $\Delta I (\lambda_{\text{max}} \approx 562 \text{ nm}) < \Delta I (\lambda_{\text{max}} \approx 604 \text{ nm})$ and the observed decrease in the intensity of the vibronic band is very insignificant in contrast to the decrease in the intensity of the monomer band.

This may indicate that, against the background of a noticeable decrease in the content of the Rh6G monomeric form, the so-called “oblique” dimers (with angles of $0^\circ < \theta < 90^\circ$) are formed in the system [15,19,20], having fluorescence spectrum. The formation of these dimers instead of H-dimers occurs apparently due to insufficiently strong deformation of the micellar structure.

When a film-forming sol with superparamagnetic magnetite particles is placed in a MF, NPs acquire additional potential energy, and their magnetic moments tend to orient themselves along the lines of magnetic field induction.

As a result of the orienting action of the constant magnetic field in the film-forming ash (in the process of film formation), the number of magnetite NPs with a smaller angle formed between the magnetic induction vectors and the magnetic moment increases, as well as the number of NPs for which the directions of the vectors coincide.
The formation of a hybrid mesostructured SiO₂/P123/Rh6G/Fe₃O₄ film ends with a “freezing” of the magnetic moments of the NPs, which are oriented under the action of the magnetic field, not randomly, but in a certain direction. The formation of a hybrid mesostructured film with a larger magnetic induction also ends with “freezing”, but with a larger number of NPs oriented along the lines of magnetic field induction.

Thus, the number of magnetite NPs in the film-forming sol, for which the directions of the vectors coincide, should increase with increasing of magnetic field induction. In the presence of a weak permanent MF at the formation of a hybrid film from a film-forming sol, a small part of the magnetite NPs is magnetized, being oriented and aligned along the lines of magnetic induction.

Considering the fact that, apparently, Fe₃O₄ NPs are connected via surface iron atoms to donor oxygen atoms of P123 micelles, such an orientation of NPs and their increasing “aggregation” in the magnetic field with increasing magnetic induction should lead to increasing micelle deformation, which should contribute to a decrease in fractions of Rh6G monomers and their dimerization.

According to the calculations, the number of micelles in the reaction mixture was 1.4 × 10¹⁶ (the calculation used the concentration of P123 and the known [23] content (250 molecules) of P123 in one micelle), and the amount of magnetite NPs was 6.16 × 10¹⁶ (in the calculation we used a weight of Fe₃O₄ NPs, its density (5.17 g / cm³) and average size (10 nm) of NPs). That is, in the resulting reaction mixture, 4.4 NP Fe₃O₄ are accounted for one micelle. Despite the fact that this value is an estimate, it gives an idea of the ratio of the numbers of NPs and micelles in the film. It follows that, with the formation of “linear aggregates” of NPs and an increase in their linear dimensions with increasing magnetic field induction, micelle deformations can be enhanced by increasing z, q and p in the resulting complexes {{(NP) q} Fe z ... O p [Pluronic123 (Rh6G) n] m}. According to the results of FTIR- spectra (Fig. 1e), the interaction of iron atoms on the surface of Fe₃O₄ NPs with P123 oxygen atoms (curve 2) leads to redistribution of the band intensities observed in the spectrum of Fe₃O₄ NPs (curve 1). The band in the region of 1200-950 cm⁻¹ with a maximum of about 1107 cm⁻¹ is, according to [24], the total contour, consisting of a group of bands that can be attributed to ν₁ and ν₂ CO-С and С-O of the ether group P123. The band in the region of 500–700 cm – 1 with a maximum of about 590 cm – 1 consists of three bands (640.589, 565 cm – 1), which according to [13,14] can be attributed to the Fe – O stretching vibrations with the participation of O in Fe₃O₄ and P123. With a twofold increase in the ratio of NPs to P123, the magnitude of the ratio of the intensities of the bands with maxima near 590 cm⁻¹ and 1107 cm⁻¹ (Fig. 3, curves 2 and 3) increases from 0.15 to 0.18. In the spectra of SiO₂ {Pluronic123 (Rh6G)} Fe₃O₄ films obtained outside the magnetic field (curve 4) and in the magnetic field (curve 5), the ν (Fe-O) band with a maximum of about 590 cm⁻¹ is retained, however, with insignificant changes in its total contour due to the redistribution of the intensities of its constituent bands. Moreover, comparing its intensity with the band intensity in the region of 1200–950 cm⁻¹ with a maximum of about

90 ISSN 0041-6045. УКР. ХІМ. ЖУРН., 2020, т. 86, № 2
1107 cm⁻¹ becomes impossible due to the overlapping of the latter with more intense bands, which can be attributed [14] to Si-O stretching vibrations.

With this in mind, and since solvents, including alcohol, are removed during the formation of the film, it can be assumed that at least part of the bands in the region of 500–700 cm⁻¹ is due to stretching Fe – O vibrations involving iron atoms on the NPs surface, bound to ether oxygen donor atoms of P123.

According to experimental data, the use of MF in the preparation of SiO₂/P123/Rh6G/Fe₃O₄ films enhances the manifestation of the influence of NPs on their spectral and luminescent characteristics. As can be seen from the fluorescence spectra (Fig. 2 c) and the differential fluorescence spectra (Fig. 2 d), as the magnetic flux density increases, the intensities of the fluorescence bands (λ₁max≈ 562 nm) and the shoulder (λ₂max≈ 604 nm) decrease.

When using a weak magnetic field of 100 mT (Fig. 2 d, curve No. 1) in the differential fluorescence spectrum, as well as the differential absorption spectrum (Fig. 2 b, curve No. 1), with a slight decrease in the intensity of the vibronic (dimeric, λ₁max≈ 604 nm) band again there is a significant decrease in the band intensity (λ₁max≈ 562 nm) compared to sample No. 0 (Fig. 2 d, curve No. 0) with insignificant changes in the band (λ₁max≈ 604 nm) intensity compared to sample No. 0 (Fig. 2 d, curve No. 0 and Fig. 2 b, curve No. 0 respectively).

Based on this, it can be assumed that a significant decrease in the intensity of the band of the monomeric form of Rh6G in the differential fluorescence spectrum when using a weak (100 mT) MF (Fig. 2 d, curve No. 1) is apparently due to further deformation of micelles containing Rh6G due to an increase in the number of nanoparticles “linear aggregates” oriented in the field with a nonzero magnetic moment and an increase in their size, which leads to a further increase in the number of fluorescent “oblique” dimers due to a decrease in the number of the monomeric form Rh6G.

As can be seen from Fig. 2 d, the observed difference in the intensity of the differential spectra of the samples (No. 0, No. 1, No. 2, No. 3) is significantly larger at λ₁max≈ 562 nm compared to λ₁max≈ 604 nm. However, in this case, with an increase in the magnetic induction of the magnetic field from 100 mT (Fig. 2 d, curve No. 1) to 200 mT (Fig. 2 d, curve No. 2), a sharp drop (jump) in the intensity of the bands (λ₁max≈ 562 nm and λ₂max≈ 604 nm) occurs and starting from sample No. 2 with an increase in the magnetic induction of MF from 200 mT to 300 mT (samples No. 2, No. 3), the decrease in band intensity (λ₁max≈ 562 nm) exceeds the decrease in band intensity (λ₁max≈ 562 nm) ΔΙ(λ₁max≈ 562 nm) < ΔΙ(λ₂max≈ 562 nm) in contrast to samples No. 0 and No. 1, for which ΔΙ(λ₁max≈ 562 nm) < ΔΙ(λ₂max≈ 562 nm). This is apparently due to a stronger deformation of micelles due to an increase in the size and number of “linear aggregates” of Fe₃O₄ NPs oriented in the magnetic field with a nonzero magnetic moment in which surface Fe³⁺ atoms are bonded to oxygen donor atoms in {Pluronic123 (Rh6G)ₙ}ₘ, that is, under these conditions, the formation of complexes [((NP)ₙ)Fe₉…Oₚ{Pluronic123 (Rh6G)ₙ}ₘ] of variable composition (q, z and p), which will depend on the magnitude of the magnet
ic field induction, is possible. This leads to a sharp decrease in the amount of Rh6G monomeric form in the films, which forms “oblique” dimers and, partially, H-dimers.

Thus, in the SiO2/P123/Rh6G film, when it is formed both in MF and without MF, in the absence of magnetite NPs, a certain mutual arrangement of dipoles of dye molecules encapsulated in Pluronic123 micelles incorporated into a SiO2 matrix is “frozen”, which determines the observed spectra absorption (Fig. 2 a, curve 4) and luminescence (Fig. 2 c, curve 4).

During the formation of a (#)SiO2/P123/Rh6G/Fe3O4 film containing magnetite NPs, in the absence of MF, Fe3+ iron ions located on the surface of the nanoparticles form the complexes [(NP)qFez…Op{Pluronic123 (Rh6G)n}m], as a result of which a deformation of the micelle structure can occur, leading to the formation of H-aggregates configuration that are energetically more favorable than a J-type configuration [16]. As a result, the intensity of the absorption and luminescence bands of the film should change (decrease), which is observed in the experiment (Fig. 2 a and Fig. 2 c, spectral curve 0, as well as Fig. 2 b and Fig. 2 d, spectral curve No. 0).

The above-described features of the effect of magnetic induction of MF used in the process of formation of (#)SiO2/P123/Rh6G/Fe3O4 (# = 1-3) film samples on their luminescence spectra (Fig. 2 c, d) can be considered as a result of a decrease in the fraction of Rh6G monomers (λmax ≈ 534 nm) and the increase in the fraction of “oblique” dimers and H-dimers (λmax ≈ 501 nm) due to the interaction of “linear aggregates” of Fe3O4 nanoparticles oriented in MF associated with Rh6G-containing micelles with MP and formation complexes [(NP)qFez…Op{Pluronic123 (Rh6G)n}m]. Therefore, upon application of a magnetic field, Fe3O4 NPs associated with micelle fragments form “linear aggregates” (chains) consisting of several spherical Fe3O4 NPs with nonzero resulting magnetic moment (unlike individual NPs), sizes of which increase with increasing magnetic induction. This, in turn, leads to more efficient deformation of micelles and their closer contact (between layers) due to the increasing interaction of magnetic fields oriented by superparamagnetic Fe3O4 NPs with micelles (formation of complexes [(NP)qFez…Op{Pluronic123 (Rh6G)n}m]) and, in fact, to a specific orientation of micelles in a magnetic field due to such an interaction. At the same time, part of Rh6G molecules encapsulated in micelles can be forced to come into close contact both inside the micelle and with Rh6G molecules of neighboring micelles. This creates the conditions for the formation of non-fluorescent H-aggregates. However, it should be noted that such a compression effect of micelles and their layers has a limit due to the geometric dimensions of the molecules.

Therefore, in spite of the increasing orientation of magnetite NPs along the lines of force of the applied magnetic field, as the magnetic induction increases, the ratios ΔA/ΔB and ΔI/ΔB should gradually decrease, tending to zero when certain values of magnetic induction are reached. This is consistent with experimental results, namely, the dependences of changes in the difference in band intensities in the absorption spectra ΔA and luminescence ΔI of samples of hybrid
films with magnetite NPs (Fig. 3 a, b), and with changes in the absorption intensity A at $\lambda_2 = 534$ nm and the intensity fluorescence I at $\lambda = 562$ nm of samples of hybrid mesostructured SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ films of magnetic induction (Fig. 3 c, d).

It is important here to note the manifestation of the “memory” effect in mesostructured SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ films formed in magnetic fields with different magnitudes of magnetic induction. The structure of the complexes [{(NP)$_q$}Fe$_z$…O$_p${Pluronic123 (Rh6G)$_n$}$_m$], formed by Fe$^{3+}$ ions located on the surface of oriented in MF magnetite NPs ("linear aggregates") during the formation of a mesoporous film structure in a magnetic field had a total magnetic moment of magnitude significantly superior to the magnetic moment of one nano particle. In these complexes, micelles with a deformed structure retain a certain orientation of the dye molecules incorporated into them.

**CONCLUSIONS.** Optically transparent mesostructured silica films SiO$_2$/P123/Rh6G and SiO$_2$/P123/Rh6G/Fe$_3$O$_4$, containing Fe$_3$O$_4$ NPs with superparamagnetic properties, are formed in stationary magnetic fields with known induction from a film-forming sol mixed with Rhodamine 6G and Pluronic 123.

It was shown that the spectral-luminescent properties of SiO$_2$/P123/Rh6G films are independent of the MF used at their formation. A gradual decrease of the band intensity in the spectra of Rhodamine 6G and quenching of luminescence with an increase in the magnetic field induction in SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ films, is associated with a decrease in the fraction of monomer and an increase in the fraction of non-luminescent H-aggregates of the dye in micelles.

This effect is due to the formation of complexes of variable composition [{(NP)$_q$}Fe$_z$…O$_p${Pluronic123 (Rh6G)$_n$}$_m$], in which the interaction of Fe$^{3+}$ atoms with P123 micelle donor oxygen atoms increases due to the increase in magnetic field induction. It occurs due to an increase in q as a result of the formation of NPs “linear aggregates” with the resulting nonzero magnetic moment in the MF, and hence an increase in z, as well as p. This in turn leads to the gradual deformation of micelles and the accumulation of H-aggregates, which can form both within the micelle and between the micelle layers in the film.

Changes in the intensity of the absorption and fluorescence bands of the monomeric form of Rh6G in the spectra of SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ films depend on changes in the magnetic induction and are described by an exponential function, and the ratio of the fluorescence intensity of the SiO$_2$/P123/Rh6G film to the fluorescence intensities of SiO$_2$/P123/Rh6G/Fe$_3$O$_4$ linearly depends on the magnetic induction of the MF at which they are formed. In this case, the obtained films are capable of “memorizing” these values (in terms of the intensity value), which, apparently, is associated with a sequential increase in the number of magnetite nanoparticles oriented in the MF as the MF induction increases.

The detected ability of magnetite-containing mesostructured films to “memorize” the magnitude of magnetic induction after they are formed in a permanent magnetic field can find practical application in sensor technologies, as well as in the development of new multifunctional organo-inorganic...
The influence of superparamagnetic Fe$_3$O$_4$ nanoparticles on spectral...
ных наночастиц (НЧ) Fe₃O₄ на спектрально-люминесцентные свойства однородных оптически прозрачных мезоструктурных кремнеzemных пленок SiO₂/P123/Rh6G/Fe₃O₄, содержащих мицеллы {P123 (Rh6G)}, состоящие из Pluronic 123 (P123) с инкапсулированными молекулами красителя родамина 6Ж (Rh6G), и сформированных в стационарных магнитных полях (МП) с индукцией менее 500 мТл. Показано, что в отличие от SiO₂/P123/Rh6G, спектрально-люминесцентные свойства пленок SiO₂/P123/Rh6G/Fe₃O₄ зависят от использованного при их формировании МП, а наблюдаемое для них постепенное уменьшение интенсивности полос в спектрах Rh6G и тушение люминесценции с увеличением индукции МП связано со снижением доли мономера и увеличением доли не люминесцирующих Н-агрегатов Rh6G в мицеллах вследствие усиливающегося в МП взаимодействия (образования Fe³⁺-O связей) ориентированных в МП суперпарамагнитных НЧ с мицеллами {P123 (Rh6G)}, что приводит к постепенной деформации мицелл и накоплению Н-агрегатов. Зависимости изменений интенсивности полос поглощения и флуоресценции мономерной формы Rh6G в спектрах пленок SiO₂/P123/Rh6G/Fe₃O₄ от изменений величины магнитной индукции МП описываются экспоненциальной функцией, а отношения интенсивности флуоресценции пленок SiO₂/P123/Rh6G/Fe₃O₄ к интенсивностям флуоресценции пленок SiO₂/P123/Rh6G линейно зависят от использованных величин магнитной индукции МП, которые они способны «запоминать», что проявляется в величинах интенсивностей флуоресценции.

Ключевые слова: гибридные мезоструктурные кремнеземные пленки, спектрально-люминесцентные свойства, родамин 6Ж, Pluronic 123, наночастицы, магнетит, магнитное поле.

REFERENCES

1. Telbiz G, Leonenko E, Goer D, Manorik P. Optical manifold of spatial localization of dyes molecules self-organized in the body of silica thin films // Springer Proc Phys. - 2013.- 146.- P. 83–91.
2. De Queiroz T. B., Botelho M. B. S., De Boni L., [et al.] Strategies for reducing dye aggregation in luminescent host-guest systems: Rhodamine 6G incorporated in new mesoporous sol-gel hosts // J. Appl. Phys. - 2013 -113, 113508.
3. Zhang M., Chen J., Gao J., Wang Z., Xu H., [et al.] Magnetic-Field-Enabled Resolution Enhancement in Super-Resolution Imaging // Phys. Chem. Chem. Phys. 2015. - 17. - P. 6722-6727.
4. Zarezin A., Samusaev V., Alexandrov K. Investigation of the interaction of supermagnetic nanoparticles with molecules of Rhodamine 6G in polymeric matrix // Issues KLGTU. – 2011. - № 20. – P. 25-31.
5. Hernando A. and Gonzalez J.M. Soft and hard nanostructured magnetic materials // Springer. Hyperfine Interact. 2000. - V. 130. – P. 221-240.
6. Massart R. Preparation of aqueous magnetic liquids in alkaline and acidic media // IEEE Trans. Magn. - 1981, Mag-17, 2. P. 1247-1248.
7. Kharlamova M., Sapoletova N., Eliseev A., Lukashin A. Magnetic properties of γ-iron oxide nanoparticles in a mesoporous silica matrix // JETP Lett. – 2007. – 85 № 9. - P. 439-443.
8. Semko L., Kruchek O., Gorbyk P., Shevlyakov Yu. Influence of magnetic field on sensor characteristics of composite materials on a basis of nanocrystalline nickel // Chem. Phys. Technol. Surface. – 2008. – 14. – P. 398-406.
The influence of superparamagnetic Fe₃O₄ nanoparticles on spectral characteristics of hybrid mesostructured silica films // Theor. Exp. Chem – 2015. - 50 № 6. - P. 358-363.
18. Lasio. B., Malfatti L., Innocenzi P. Photodegradation of rhodamine 6G dimers in silica sol–gel films / Journal of Photochemistry and Photobiology A: Chemistry -2013. -271. - P. 93–98.
19. Anedda A., Carbonaro C.M., Corpino R., Ricci P.C., Grandi S., Mustarelli P.C. Formation of fluorescent aggregates in Rhodamine 6G doped silica glasses // J. Non-Cryst. Solids - 2007.- 353.- P. 481-485.
20. Innocenzi P., Kozuka H., Yoko T. Dimer-to-monomer transformation of Rhodamine 6G In sol-gel silica films // J. Non-Cryst. Solid- 1996.- V. 201. -P. 26-36.
21. Nikiforov V., Ignatenko A., Irhin V. The influence of size and surface on the magnetism of nanoparticles of magnetite and maghemite // JETP. – 2017. – 151 №2. – P. 356-363.
22. Kokorin A., Kulyako L., Degtyarv E., Kovarskii A., Patsaeva S., Dzhardimalieva G., Yurishcheva A., Kyrdaliev K. Structure and properties of nanosized composites based on Fe₃O₄ and humic acids // R. J. Phys. Chem. B. – 2018. – 12 №1. – P. 172-178.
23. Y. Zhao, X. Chen, C. Yang, G. Zhang Mesoscopic Simulation on Phase Behavior of Pluronic P123 Aqueous Solution. J. Phys. Chem. B 2007, 111, 13937-13942.
24. T. Bala, R. Gunning, M. Venkatesan, J. Godsell, S. Roy, K. Ryan Block copolymer mediated stabilization of sub-5 nm superparamagnetic nickel nanoparticles in an aqueous medium Nanotechnol. -2009, 20, 415603, 11 pages.

Received 16.12.2019