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Formation of molecular clusters of silver by polymer-salt method in porous glasses

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A methodology for the formation of molecular clusters of silver in silicate nanoporous glasses has been developed. Composite materials containing molecular clusters of silver, silver nanoparticles and zinc oxide have been synthesized. The synthesis was carried out by impregnation of porous glasses in aqueous solutions of silver and zinc nitrates stabilized with high-molecular polyvinylpyrrolidone, followed by heat treatment of samples for decomposition of metal nitrates and polymer. Spectral-luminescent properties of composites have been investigated.

Keywords: porous glass, zinc oxide, silver molecular clusters, silver nanoparticles, spectral-luminescent properties.

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Introduction

It is known that porous glasses have a developed porous structure [1], which allows them to be used as matrices to create various functional composites based on them [2–7]. Molecular clusters of silver, consisting of a small number of atoms and ions, are an intermediate product in the formation of Ag nanoparticles from silver atoms and ions [8–10]. The structure and optical properties of silver molecular clusters differ significantly from the structure and properties of the nanoparticles of Ag [11] . Molecular clusters of small sizes absorb light in the UV range and exhibit high luminescent properties [6,11], which allows them to be used in various sensor applications. Since the molecular clusters of silver interact with each other and with the environment, the task of stabilizing them becomes urgent [12]. One of the possible solutions to this problem may be the formation of molecular clusters of silver inside nanoporous glasses that play the role of a matrix using the polymer-salt method.

The aim of paper was the polymer-salt synthesis of nanocomposites based on porous glasses containing ZnO-Ag nanoparticles and the study of their spectral-luminescent properties.

Materials and methods

A porous glass of the MAP type [13] was used as the basis for the composite, characterized by a total porosity of 59%, a specific pore surface of 73 m^2/g and having a mean pore size of 25 nm.

For the synthesis of ZnO-Ag nanopowders used to modify porous glass, a polymer-salt method was used, similar to the method described earlier in [14] and used by us in [7] to create composites „porous glass (powder) — ZnO-Ag“ and studies of their adsorption and photocatalytic activity. An aqueous solution containing $Zn(NO_3)_2$, $AgNO_3$, was used as the starting materials for the synthesis and high molecular weight ($M_w = 1300000$) polyvinylpyrrolidone (PVP). Porous glass (samples in the form of plates with a thickness of 1 mm) was impregnated with this solution for 48 h at 20°C. After extraction from the solution, the samples were subjected to two-stage heat treatment in an electric furnace. The sample was heated to 200°C, after which the sample was kept at this temperature 2 h, then the temperature was increased from 200 to 550°C with access to this temperature for 3 h and subsequent exposure for 2 h. This heat treatment mode avoids the destruction of the sample and ensures the complete decomposition of metal nitrates and PVP and the removal of gaseous products.

The absorption spectra were recorded using a Perkin Elmer Lambda 900 spectrophotometer in the spectral range 200−800 nm. A Perkin Elmer LS-50B fluorescence spectrophotometer was used to study photoluminescence spectra.

Results and discussion

On the absorption spectra (Fig. 1, *a*) there is a band with $\lambda_{max} = 300-305$ nm. In freshly prepared solution (Fig. 1, *a*, curve *1*), absorption in this spectral region can only be associated with light absorption by nitrate anions present

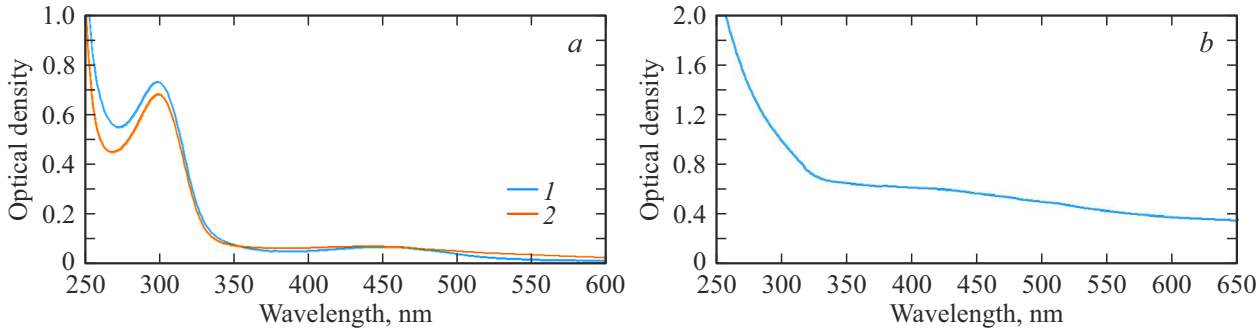

Figure 1. (*a*) Absorption spectra of freshly prepared solution (*1*) and solution after 2 days of impregnation (*2*), (*b*) absorption spectrum of porous glass after impregnation and heat treatment.

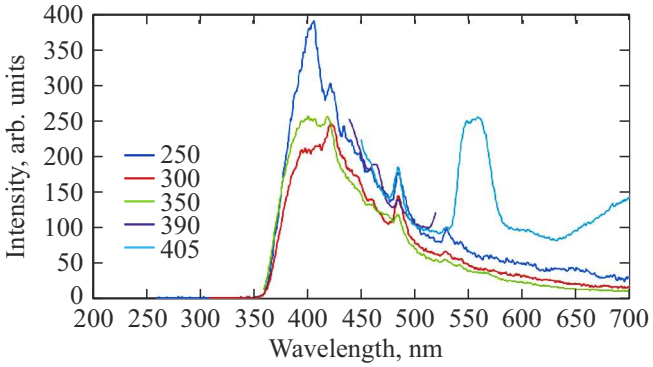

Figure 2. Luminescence spectra of a synthesized composite based on porous glass after heat treatment (see text).

in solutions having a characteristic absorption band with $\lambda_{max} = 305$ nm [14].

After mixing solutions of metal nitrates with a PVP solution and with a temporary exposure of the resulting mixture, even in the absence of external UV irradiation, the processes of reduction of Ag^+ ions begin to occur, which leads to the formation of silver nanoparticles in solutions of [15–17]. The intermediates in this photochemical process are neutral atoms and various molecular clusters of silver. The small molecular clusters Ag_n ($n < 5$) formed in solution have absorption bands in the spectral range 270–405 nm [18]. Therefore, in the mixed solutions studied by us, light absorption in the UV region of the spectrum ($\lambda = 250–350$ nm) (Fig. 1, *a*, the curve *2*) can consist of light absorption by nitrate anions NO_3^-, having an absorption band with $\lambda_{max} \sim 305$ nm, and light absorption by various molecular silver clusters Ag_n ($n < 5$) [19,20].

Fig. 1, *b* shows the absorption spectrum of porous glass impregnated with a solution of metal nitrates and PVP.

In the 450–500 nm region, a band characteristic of plasmon absorption of Ag nanoparticles [21,22] appears. The appearance of this band in the absorption spectra indicates the formation of silver nanoparticles in the resulting sample.

Fig. 2 shows luminescence spectra with excitation wavelengths of 250, 300, 350, 390 and 405 nm. Several luminescence bands in the range from 370 to 500 nm and a luminescence band with a maximum of 555 nm are observed on the spectra. The presence of different luminescence bands on the spectrum is explained by the formation of various forms of silver [19]. The luminescence band at $\lambda_{ex} = 250$ nm with a maximum at $\lambda = 400$ nm is mainly associated with Ag^+ ions. Also, luminescence in this region with an increase in the excitation wavelength to 300 nm can be attributed to the same ions and luminescence of atomic silver (Ag^0). Luminescence bands with maxima of 480 nm can be attributed to Ag_2^+ silver molecular clusters and Ag_3^{2+}, which correlates with the results presented in [19]. The formation of ZnO [14] nanocrystals and the presence of a porous matrix contribute to the stabilization of molecular clusters.

Conclusion

The polymer-salt method makes it possible to form in a matrix of nanoporous glass and preserve after heat treatment the molecular clusters of silver Ag_n ($n < 5$). Photoluminescence of these clusters is observed in the visible range of the spectrum when excited by UV (250–405 nm). Water-soluble organic polymer — polyvinylpyrrolidone — plays the role of a low-temperature stabilizing agent in solutions. At high temperatures, the stabilization of small luminescent molecular clusters Ag_n is achieved due to their spatial separation using a porous matrix, as well as the emerging oxide nanocrystals ZnO as nanobarrier layers.

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Conflict of interest

The authors declare that they have no conflict of interest.

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