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Thermostimulated Formation of Silver and Gold Nanoparticles in Porous Silicon Dioxide Matrices

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Abstract—Manifestations of thermostimulated formation and subsequent transformation of silver and gold nanoparticles in porous opal and Vycor glass matrices are studied using optical spectroscopy. Two temperature ranges for silver nanoparticles are revealed, where first-type particles transform into another type of particles. With gold nanoparticles in these matrices, a temperature range in which one type of particles transforms into another type is established. An effect of complete blackening of Vycor glass samples, caused by their annealing, is revealed, and a rationalization of this effect is given.

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INTRODUCTION

Porous silicon oxide matrices containing nanoparticles of noble metals are nanocomposite materials having a lot of potential practical applications. Such materials can be used as nanoreactors, where organic catalytic reactions are much accelerated [1]. For example, the use of aerogels containing silver nanoparticles as catalysts of ethylene glycol oxidation into glyoxal has been reported [2]. Voluminous opal matrices and opal films with the pore size less than 100 nm, including silver or gold nanoparticles, can be used as wafers in experiments on the generation of giant Raman scattering, for instance, from tested organic molecules [3]. At present this field of research is making the greatest progress (see, for example, [4–6]). The information on thermostimulated processes associated with the formation of noble metal nanoparticles in such matrices would be useful in any case.

At the same time, the synthesis of metal nanoparticles in porous matrices at elevated temperatures provides a prominent example of phenomena which involve both the processes of self-organization of metal atoms in material voids and conditions which impose constraints on such processes, as well as the transformations of already formed nanoparticles, associated with their melting and oxidation. The physicochemical process of nucleation and growth of nanoparticles and their subsequent transformation passes through a sequence of interrelated stages: thermochemical transformation, mass-transfer processes (temperature-dependent diffusion, transport of condensing particles into the assembly zone), sorption processes (sorption–desorption, reactions of particles of the surface of nuclei), destruction of the formed nanoparticles and formation of new ones [7]. Furthermore, quite an important role here belongs to thermochemical oxidation of surface nanoparticle layers [8] due to the open nature of interconnected matrix pores. Clearly, the complicated, multistage character of such processes in a matrix is to a great extent dependent on its synthesis conditions, specifically, intrinsic morphology, type of precursors, method of metal reduction, etc.

The aim of the present work was to study the mechanism of formation of gold and silver nanoparticles in nanoporous silica matrices. The matrices were modified by impregnation with alcoholic solutions of

these metals with subsequent thermal treatment of the impregnated samples. Comparative study of the formation of noble metal nanoparticles in two SiO_2 matrices (Vycor nanoporous glasses and artificial opal matrices) was performed. These processes are considered in terms of the effect of the type of precursors embedded in matrices. Comparative analysis of the transformations of silver and gold nanoparticles in the same matrices upon successive annealing of the obtained nanocomposite samples was also performed.

EXPERIMENTAL

For the silver and gold-containing precursors for impregnation of matrices we used $AgNO_3$, Ag(hfac)COD {(hfac)COD = 1,5-cyclooctadiene 1,1,1,5,5,5-hexafluoroacetylacetonate}, and $H[AuCl_4]\cdot 4H_2O$.

Silver nitrate $AgNO_3$ appears as transparent rhombic crystals decomposing at temperatures above 300°C. It is well soluble in water, ethanol, pyridine, and other organic solvents.

For the second precursor we chose a compound of the β-diketonate series Ag(hfac)COD {where COD = 1,5-cyclooctadiene and hfac = 1,1,1,5,5,5-hexafluoro 2,4-pentanedionate}, purchased from Aldrich (USA). The compound appears as light gray fine crystals, decomp. point ~124°C, well soluble in organic solvents; a solution of Ag(hfac)COD in ethanol gives a strong UV absorption band near 315 nm, which is associated with intraligand transitions [9].

The gold precursor was hydrogen tetrachloroaurate $H[AuCl_4]\cdot 4H_2O$. It appears as yellow needle-like crystals, decomp. point 120°C, soluble in water, alcohols, and diethyl ether.

Porous SiO_2 matrices were impregnated by ethanol solutions of precursors with concentrations varied from 10 mg mL^{-1} for Ag(hfac)COD to 50 mg mL^{-1} for inorganic silver and gold compounds; the impregnation time was several days. For the porous SiO_2 matrices we used artificial opal matrices and Vycor nanoporous glasses.

Artificial opal matrices possess unique properties, in particular, they can form nanocomposites, when materials with enhancing, nonlinear, sensory, and magnetic properties are embedded in their regular voids [10, 11]. The structure of opal matrices and their synthesis have been described in [11, 12]. These matrices are composed of SiO_2 nanospheres 200–600 nm in size, arranged in ordered cubic or hexagonal packings. In [12] we used matrices with SiO_2 spheres about 200 nm in size, and the size of intersphere voids varied, depending on the packing density, from 40 to 80 nm. The absorption spectra of all the samples used in our experiments showed a band at 570 nm, associated with the photonic band gap in the opal matrix [10]. The intensity of this band points to an ordered structure of the matrix, while variations in the intensity and maximum position depend on the filling of intersphere voids with precursors and the conditions of thermal treatment of the samples.

Vycor glasses, like opal matrices, represent a system of open monodisperse 4–6-nm pores interconnected by narrow channels. In our experiments we used glasses purchased from Bioanalytical Systems (USA). All the matrix samples looked like plates 0.5–1 mm thick, and Vycor glass plates were polished.

The absorption spectra were registered on a Carl Zeiss Specord M40 UV/Vis double-beam spectrophotometer. To prevent partial light scattering by opal matrices, samples were exposed in an immersion liquid immediately before measurements.

Annealing was performed in air for 5–10 min in a specially designed oven with programmed temperature.

In certain experiments, in particular, in the light-induced fabrication of metal nanoparticles in a Vycor glass matrix, a KLM-473-50 solid-state semiconductor laser (λ_{em} 473 nm, output power 50 mW). Laser beam was directed through a narrow lateral face (width 1 mm) of the plate, in parallel to a wide polished face.

RESULTS AND DISCUSSION

Figures 1 and 2 show the absorption spectra of the Vycor glass and opal matrices, impregnated by the precursors and annealed in air at various temperatures.

The spectra of the annealed samples contain characteristic absorptions bands with their maxima at 400–500 nm, which belong to the plasmon resonance of silver nanoparticles. In general, analysis of the resulting spectral data revealed a certain difference in the behavior of plasmon resonance spectra of the annealed samples impregnated by different precursors. With silver nitrate–impregnated samples and at a relatively higher temperature of thermochemical decomposition, the plasmon resonance bands first rise and then steeply fall in intensity in the range 300–400°C. With silver β-diketonate and at a lower temperature of thermal decomposition, this effect is observed starting from 200–300°C. With annealed samples, attenuation of the plasmon resonance band is accompanied by a blue shift of its maximum. These phenomena are

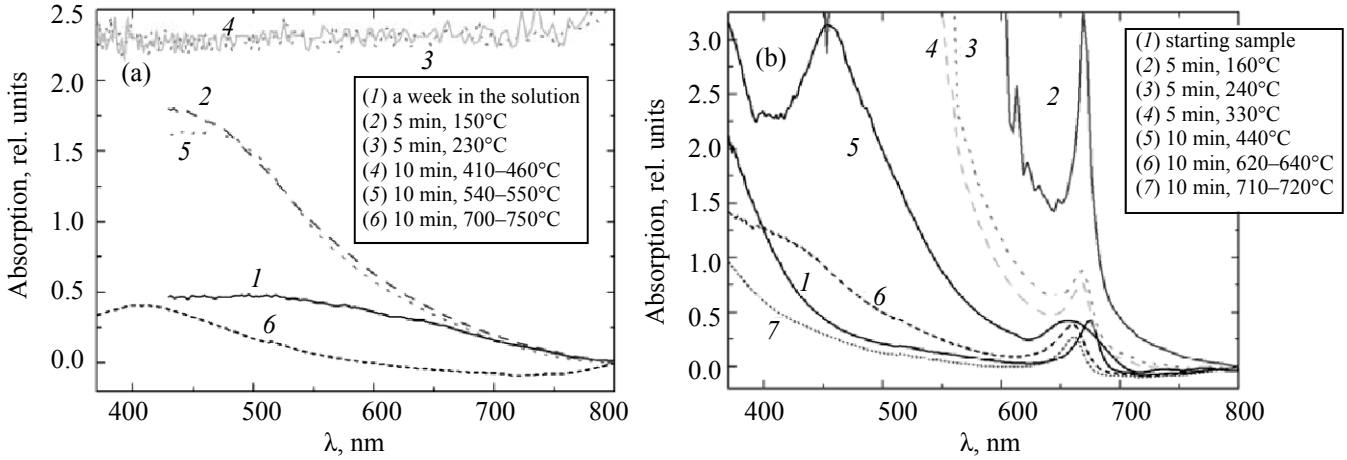

Fig. 1. Absorption spectra of the (a) Vycor glass and (b) opal matrix, impregnated by an alcoholic solution of $AgNO_3$ and annealed in air.

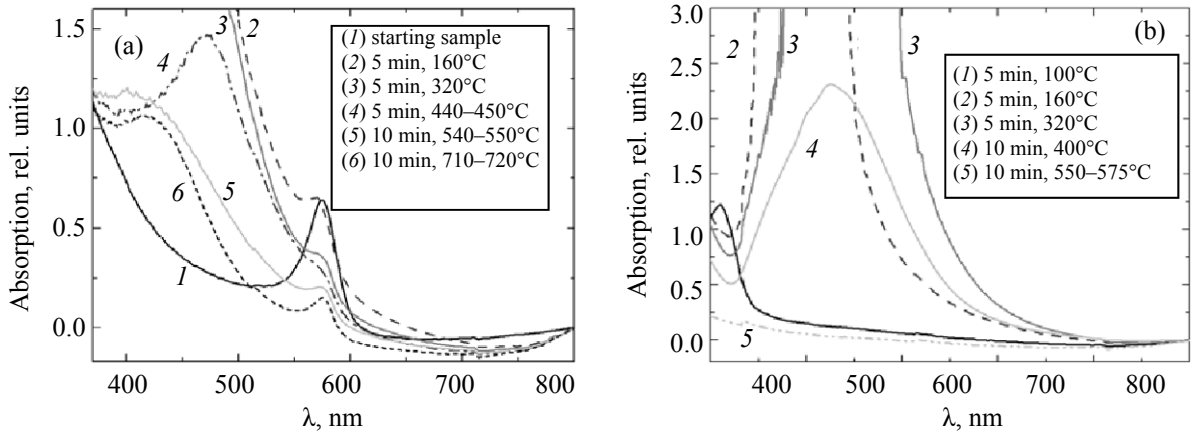

Fig. 2. Absorption spectra of the (a) opal matric and (b) Vycor glass, impregnated by an alcoholic solution of Ag(hfac)COD and annealed in air.

indicative of thermal oxidation processes on the surface of silver nanoparticles in a system contacting with atmospheric oxygen [8]. During oxidation the particles are getting smaller (the blue shift of the spectral band) until they degrade completely.

Comparison of the transformation processes of silver nanoparticles in both matrices reveals some specific features of these processes in Vycor glasses. First, the absorption spectra of the samples annealed at temperatures above 200°C show continuous and stepwise enhancing absorption over the entire spectral range, thus providing evidence for complete blackening of the samples. This effect in Vycor glasses is observed not only with silver precursors, but also with $H[AuCl_4]\cdot 4H_2O$.

Second, in the temperature range, where the intensity of plasmon resonance bands falls due to thermal oxidation, transformation of nanoparticles from one form to another is also initiated. The latter process is evidenced by a broadening of the plasmon resonance band of these samples compared to samples annealed at lower temperatures. The same effect we observed in [12] with Vycor glasses impregnated by a silver compound dissolved in supercritical CO_2 rather than in alcohol. A possible explanation for this effect is that silver nanoparticles are formed not only inside glass pores, but also in interpore channels.

Comparison of the plasmon resosnance bands of porous matrices impregnated by silver precursors (Figs. 1 and 2) with the spectra of the same samples impregnated by a gold precursor (Fig. 3) allows us to reveal one more specific feature.

The intensity of the plasmon resonance band in the spectra of gold-containing samples annealed in air at temperatures of up to 700°C varies only slightly. However, at temperatures above 200°C, the band exhibits

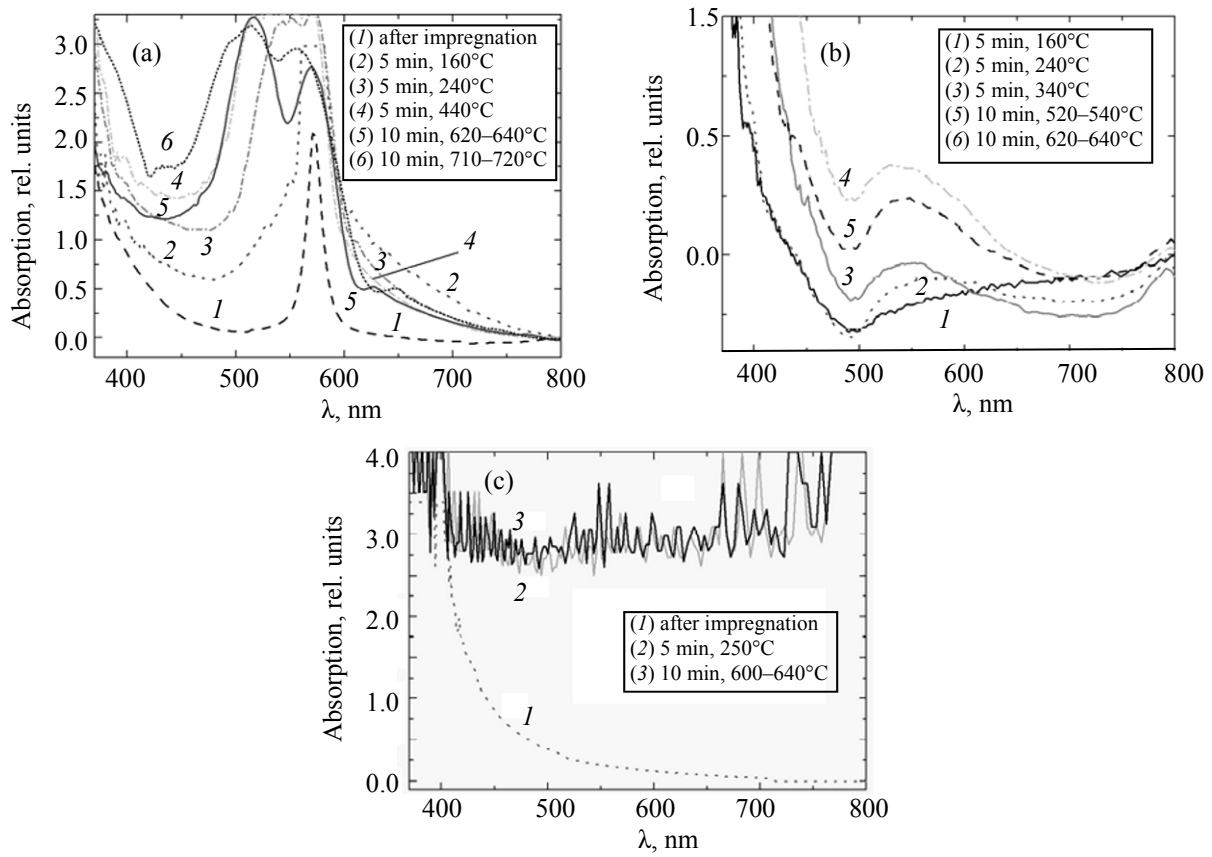

Fig. 3. Absorption spectra of the (a) opal matrix and (b, c) Vycor glass, impregnated by an alcoholic solution of $H[AuCl_4]\cdot 4H_2O$ and annealed in air. Concentration of the impregnating solution for Vycor glass, mg/mL: (b) 15 and (c) 50.

a well-defined spitting, with the appearance of a short-wave component.

The formation of a two-component plasmon resonance band (annealing at 620°C) with its maxima at 510 and 570 nm is much better defined in the spectrum of the opal matrix (Fig. 3a). Increasing contribution of the short-wave component with simultaneous decrease of the intensity of the long-wave component is also observed with Vycor glasses (Fig. 3b). Here this process is less pronounced in view of the low intensity of the bands at low precursor concentrations. The observed effect can be considered to result from high-temperature transition from one type of gold nanoparticles to others. Such transitions can occur, for example, due to melting of particles of one specific form [7] at corresponding temperatures of thermal treatment. According to [4, 13], we can suggest that the short-wave plasmon resonance bands belong either to smaller particles or, most likely, to more regularly shaped ones, say, spheres.

Let us analyze the spectra in Figs. 1a and 3c, which show a stepwise developing complete blackening of Vycor glasses impregnated by inorganic precursors. Such annealed glasses acquire an absolutely black color, i.e. they get virtually nontransparent.

The effect of complete optical blackening of annealed Vycor glasses impregnated by inorganic compounds of silver and gold ($AgNO_3$ and $H[AuCl_4]\cdot$

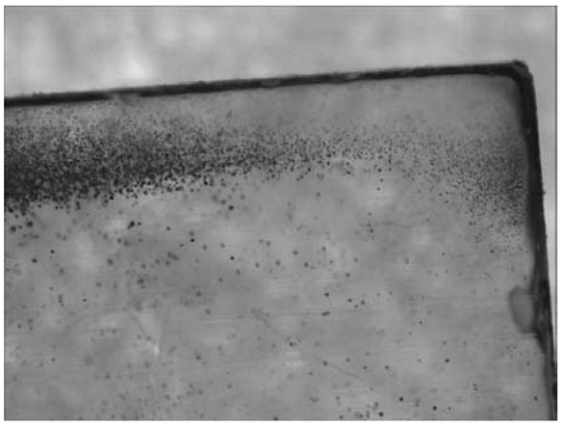

Fig. 4. Photograph of a laser-irradiated (λ_{em} 473 nm) Vycor glass impregnated by $H[AuCl_4]\cdot 4H_2O$. Irradiation along the sample plane.

$4H_2O$) can be explained in the following way. Apparently, Vycor glasses intrinsically contain microdomains with increased concentration of pores which can be filled, together with interpore channels, by small precursor molecules. The linear molecular dimensions of silver nitrate and gold tetrachloride are much smaller compared to those of the organic silver compound Ag(hfac)COD (linear dimensions ~1 nm). Thermal decomposition of the inorganic molecules first forms separate metal nanoparticles and then aggregates of those nanoparticles in microdomains with increased pore concentration. According to theoretical computations in [14], when metal nanoparticles reside at a short distance from each other (about one particle size), such aggregates absorb and scatter light in an almost entire observed wavelength range. A more detailed interpretation of this effect is given in [15]. The effect will be initiated beginning with certain concentrations of precursors introduced in the glass matrix.

Note that such formations looking like separate black dots a few micrometers or larger in size we more directly observed in a different situation, in particular, on the photolysis of $H[AuCl_4]\cdot 4H_2O$ molecules under the action of continuous radiation from a solid-state laser source (λ_{em} 473 nm). Figure 4 shows a micrograph of a Vycor glass sample irradiated along the surface for 10 min.

As seen from Fig. 4, a dark trace associated with the formation of gold nanoparticles appears along the propagation direction of the laser beam and then splits into a multitude of black dots.

Taking into account that gold is much more resistant to atmospheric oxygen than silver, we can now understand why blackening does not disappear in gold-containing glasses annealed at temperatures of up to 640°C and disappears under the same conditions in silver-containing samples.

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