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Photochemical Synthesis of Silver and Gold Nanoparticles in Polyhydric Alcohols

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Abstract—A procedure was developed for the synthesis of gold and silver nanoparticles in the presence of polyols like ethylene glycol, diethylene glycol, triethylene glycol, and 1,2-propylene glycol. Spectral characteristics of the obtained nanocomposites were mesured and kinetics of the formation of the colloidal phase was studied. The influence of the polyol nature and concentration on the photoinitiated formation of silver and gold nanoparticles was studied. The 1,2-propylene glycol is shown to exhibit maximal stabilizing effect.

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Scientific and practical interest to the silver and gold nanoparticles is due to their specific properties that distinguish them from the compact metal: the presence of intense plasmon absorption bands in the visible spectral range, the highly developed surface, high capacity of the electric double layer, the unique electrical, optical, catalytic, and antibacterial properties. Therefore the transition metal nanoparticles are widely used in medicine, optics, electronics, and serve as material for creating modern sensor devices of new generation.

There are several methods for producing gold and silver nanoparticles in the presence of different stabilizers: chemical reduction of metal ions [1], biochemical synthesis, synthesis in reverse micelles [2], electrochemical, radiochemical [3], cryochemical [4] and photochemical methods [5, 6]. The main disadvantage of most methods is the contamination of formed metal nanoparticles with by-products and impurities and the necessity to use a number of expensive organic compounds (mostly polymers) for their stabilization. The photochemical method is distinguished by the simplicity of equipment, the absence of by-products, and the possibility of monitoring the degree of dispersion, size, and shape of the nanoparticles. Earlier by the photochemical method stable nanoparticles of copper, silver, gold, nickel, platinum, and palladium were synthesized in the aqueous solutions of monohydric alcohols and polymers, on the surface and in the bulk of matrices of diverse stiffness [7–9].

The aim of this work is the photochemical synthesis of gold and silver nanoparticles in the presence of polyols of different nature and viscosity.

The use of polyols, like ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, and glycerol as stabilizers is due to their high viscosity, which prevents oxidation of obtained nanoparticles, and to the capability to form organic radicals and compounds acting a reducing agent of the silver and gold ions.

Figure 1 shows the absorption spectra of solutions containing 5×10^{-4} M solution of $AgNO_3$ and 1,2-propylene glycol in a ratio of 1:9.

Irradiation of solutions containing silver ions and 1,2-propylene glycol leads to the formation of silver nanoparticles, as evidences by the appearance in the spectrum of unstructured absorption band with a characteristic minimum at 320 nm. After 5 min exposure, in the absorption spectra the formation of the plasmon absorption band is observed at a wavelength of 430 nm. During the 30 min irradiation the plasmon band maximum position does not change, indicating the formation of monodisperse particles. The optical density increases to values $D > 2$ relative units. Based on the published data, the estimated size of formed nanoparticles is 20–25 nm [10].

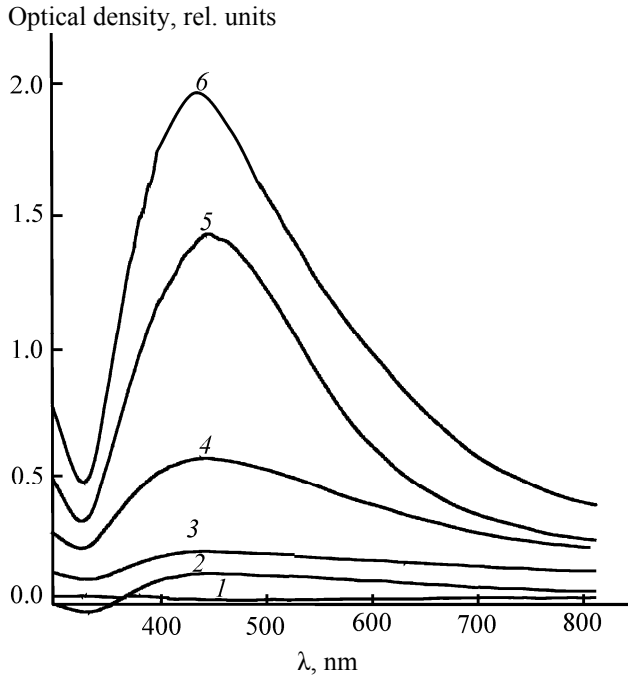

Fig. 1. Evolution of the absorption spectra of a solution containing $AgNO_3$ 5×10^{-4} M and 1,2-propylene glycol (1:9 ratio) at the photolysis with the monochromatic light (λ_{excit} = 254 nm). Exposure time, min: (*1*) 0, (*2*) 3, (*3*) 5, (*4*) 15, (*5*) 30, (*6*) 45.

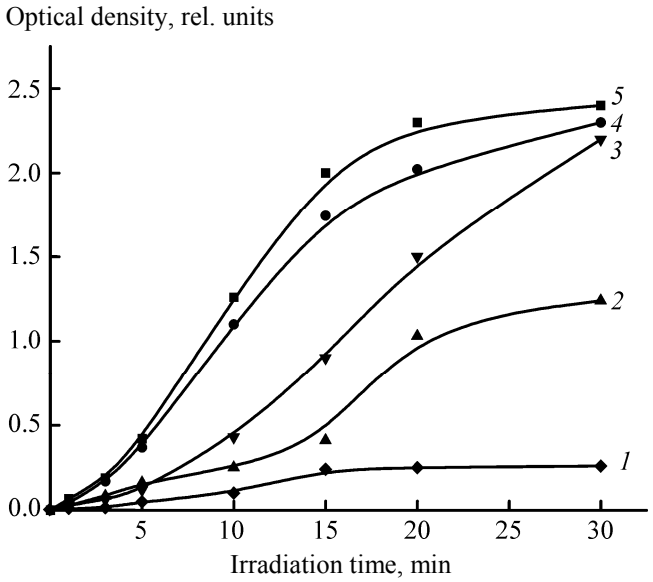

Fig. 2. Kinetic curves of formation of silver nanoparticles in the presence of 1,2-propylene glycol, depending on the concentration of $AgNO_3$, M: (*1*) 1×10^{-2}, (*2*) 5×10^{-3}, (*3*) 5×10^{-4}, (*4*) 2.5×10^{-4}, (*5*) 5×10^{-5}.

The analysis of the effect of the concentration of $AgNO_3$ in the 1,2-propylene glycol on the average size and the degree of monodispersity of nanoparticles showed the following (Table 1). With increasing concentration from 5×10^{-4} to 1×10^{-2} M the plasmon absorption peak shifts toward longer wavelengths (from 430 to 450 nm), which is due to the change in the size of the silver nanoparticles. The uncontrolled process of a colloidal phase formation at high concentrations of silver ions reduces the degree of the particles monodispersity. The 200 times increase in the concentration results in reducing the induction period from 13 min to 3 min and increasing the rate 8-10-fold (Fig. 2). At low concentrations of silver ions (5×10^{-5} M) the induction period increases, the rate of the colloidal phase formation is reduced significantly, the degree of monodispersity of the nanoparticles decreases. The best option is the introduction of $AgNO_3$ in concentration in the range of 5×10^{-4} to 5×10^{-3} M that provides short induction period and good monodispersity of the produced particles.

Table 1. Dependence of the wavelength of maximum absorption (λ_{max}), the degree of monodispersity (δ), and the optical density (D^{15}) of silver nanoparticles on the $AgNO_3$ concentration after 15 min irradiation

c, M	λ_{max}, nm	δ, %	D^{15}, rel. units
1×10^{-2}	450	0.22	2.03
5×10^{-3}	440	0.27	1.75
5×10^{-4}	430	0.16	0.92
2×10^{-4}	430	0.11	0.41
5×10^{-5}	430–480	0.06	0.24

Similar experiments were carried out with the ethylene glycol, diethylene glycol, and triethylene glycol matrices. The use of ethylene glycol and diethylene glycol leads to the formation of silver nanoparticles with absorption band 430–440 nm (Table 2). Optical density did not exceed the value of $D > 1$ rel. units even after prolonged exposure.

Propylene and triethylene glycol that have high viscosity promote the formation of the most monodisperse silver particles (Table 2), which is associated with the stabilizing effect of these glycols forming a rigid matrix and inhibiting proliferation of silver nanoparticles.

The analysis of the kinetic curves (Fig. 3) showed that at the use of 1,2-propylene glycol after 15 min irradiation the absorption of the reaction mixture

increases 5 times compared to the reaction in triethyleneglycol, 2.5 compared to diethylene glycol and 1.7 compared to ethylene glycol. The study showed that the use of 1,2-propylene glycol as a stabilizer is characterized by the highest viscosity, the generation at the action of light of stronger organic reducing agents, a significant acceleration of the formation of silver nanoparticles with a narrow particle size distribution and a higher content in the solution.

The irradiation of 1,2-propylene glycol with UV light leads to the formation of the strongest reducing agents due to the presence of the donor CH_3 group. An indirect proof of the effectiveness of 1,2-propylene glycol in the reduction of metal ions was obtained by its preliminary exposure resulting in the generation in the solution of a high concentration of reducing agent (organic radicals and compounds), in contrast to other investigated polyols. The organic radicals formed in the first stage of the 1,2-propylene glycol photolysis reduced metal ions, creating more nucleus of the metal particles. Thus, the introduction of $AgNO_3$ solution to the pre-irradiated aqueous solution of 1,2-propylene glycol leads to instantaneous formation of silver nanoparticles, as evidences the appearance of the plasmon band of silver particles (λ_{max} = 460 nm) with initial value D = 0.07 relative units increasing further to 0.66 relative units for 90 min of keeping in the dark. Apparently, at the irradiation the 1,2-propylene glycol is oxidized to 2-hydroxypropanal, which later turns into pyruvic acid that promotes the reduction of silver cations and stabilizes them.

Study of the effect of 1,2-propylene glycol concentration showed that its increase reduces the induction period of the formation of silver particles from 60 and 30 minutes at a ratio of 1:1 and 1:4, respectively, to 3 min at a ratio of 1:9 (Fig. 4). In addition, at this ratio the relative rate of nanoparticles formation increases 25 times. At 10-fold increase in the ethylene glycol concentration the rate of formation of silver nanoparticles increases 2.5 times. Increasing the concentration of glycol in the system increases the stability of intermediates, which in turn causes shortening of the induction period and an increase in the concentration of metal particles per unit volume.

When storing the samples in the dark for 2 weeks the following pattern was observed. The 1,2-propylene glycol shows the greatest stabilizing effect at a ratio of 1:9 and 1:4. The value of the optical density and peak shape of the plasmon absorption during storage remained virtually unchanged. The silver nanoparticle dispersions produced using ethylene glycol, di-, and triethylene glycol are unstable on storage due to coagulation of nanoparticles with subsequent sedimentation.

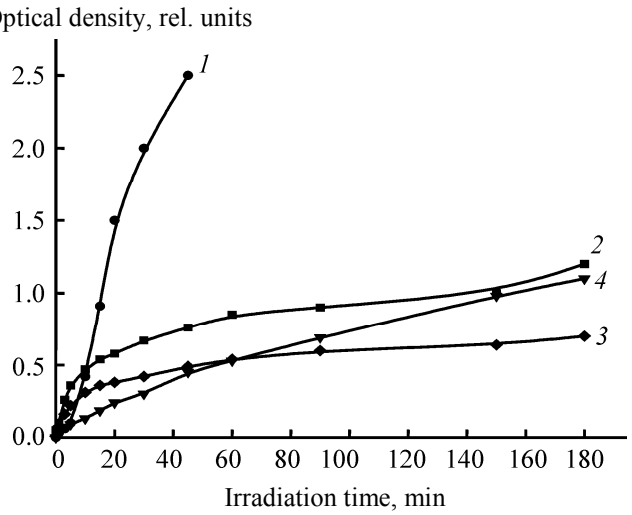

Fig. 3. Kinetic curves of the formation of silver nanoparticles from solutions containing $AgNO_3$ 5×10^{-4} M and propylene glycol (*1*), ethylene glycol (*2*), diethylene glycol (*3*) and triethylene glycol (*4*) (the ratio of $AgNO_3$ solution : glycol = 1: 9) .

The investigation of the process of photochemical formation of gold nanoparticles in the matrices of polyols showed that the use of ethylene glycol as a stabilizer leads to the formation of spherical monodisperse gold particles. The plasmon absorption band shape and its maximum position at 520 nm do not depend on the exposure duration (Fig. 5a). The dispersion color varies at the irradiation from light yellow to pink.

The irradiation of 1×10^{-4} M of $HAuCl_4$ solution in 1,2-propylene glycol (1:9) includes the following steps of the process. At the initial stage of irradiation (τ_{irr} =

Table 2. Dependence of the wavelength of maximum absorption (λ_{max}), the degree of monodispersity (δ) and the optical density (D^{15}) of silver nanoparticles on the nature of the polyol after 15 min irradiation

Alcohol	λ_{max}, nm	δ, %	D^{15}	Viscocity at 20°C, MPa s
1,2-Propylene glycol	430	0.45	1.3	56.1
Ethylene glycol	430	0.15	0.54	20.9
Diethylene glycol	440	0.08	0.36	35.6
Triethylene glycol	430	0.24	0.18	49

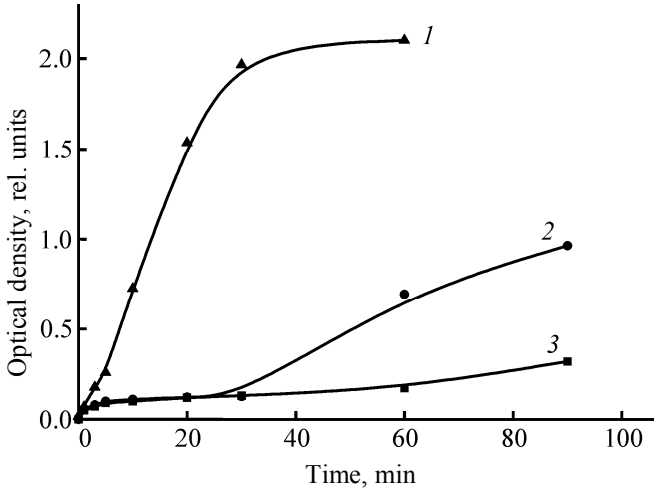

Fig. 4. Kinetic curves of the formation of silver nanoparticles in aqueous glycol solutions containing $AgNO_3$ 5×10^{-4} M and propylene glycol (*1*), ethylene glycol (*2*), diethylene glycol (*3*).

5 min) in the absorption spectrum contains the plasmon absorption band at 520 nm (Fig. 5b). Further irradiation for 10 min leads to the formation of a weakly expressed maximum at 650 nm, which at the irradiation for 60 minutes is shifted to longer wavelengths up to 730 nm with a simultaneous increase in the absorption intensity. The color of the solution changes from yellow to purple. The results obtained in conjunction with published data [11] showed that the obtained nanoparticles have anisotropic shape. The appearance of second absorp-tion maximum (at 650 nm) and its shift to the long-wavelength region indicate the transformation of spherical gold nanoparticles to rods followed by their elongation.

Reducing the $HAuCl_4$ concentration does not affect the shape and nature of the absorption of gold nanoparticles, and results in a decrease of the optical density to 0.4 and 0.2 relative units at 2- and 4-fold decreased concentration, respectively. The formation of gold nanoparticles of is also confirmed in the presence of di- and triethylene glycols.

Thus, the influence of the nature and concentration of the polyol in the photoinitiated formation of silver and gold nanoparticles was studied and it was found that the best matrix for the synthesis of monodisperse particles is 1,2-propylene glycol. By varying the nature of the glycol gold particles of spherical or anisotropic shape can be produced.

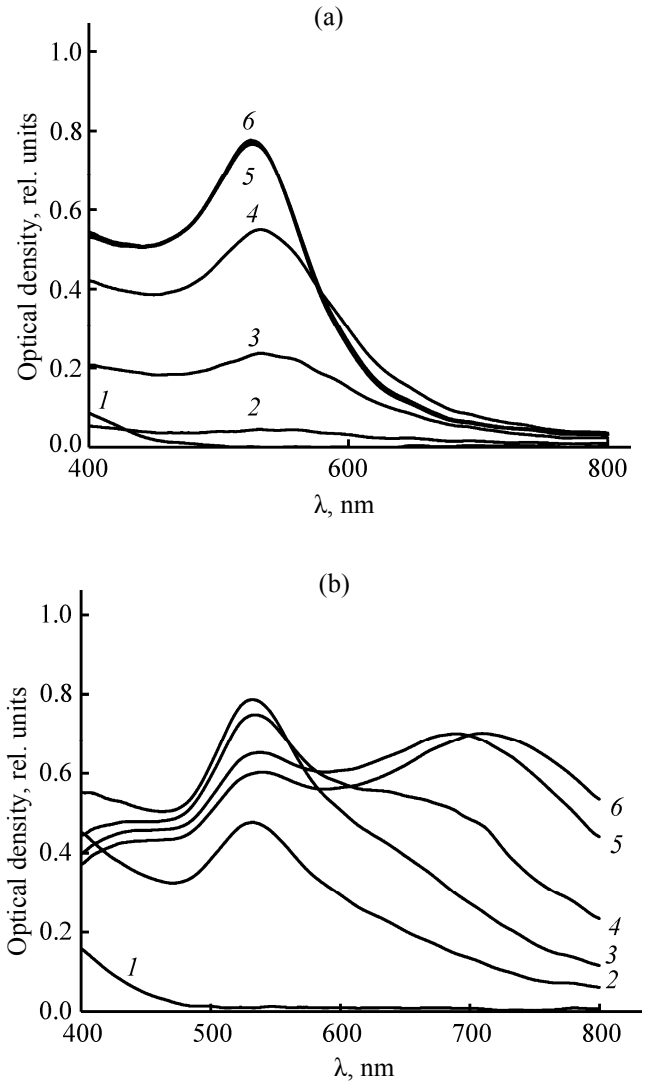

Fig. 5. Evolution of the absorption spectra of solutions containing $HAuCl_4$ 1×10^{-4} M and ethylene glycol (a) and 1,2-propylene glycol (b) in a ratio of 1:9 at the photolysis with monochromatic light ($\lambda_{excit.} = 254$ nm). Exposure time, min: (*1*) 0, (*2*) 3, (*3*) 5, (*4*) 15, (*5*) 30, (*6*) 60.

EXPERIMENTAL

As a source of metal ions for the preparation of silver and gold nanoparticles silver nitrate of analytical grade from Reakhim and chloroauric acid of chemically pure from Aurat were used. The $AgNO_3$ concentration ranged from 1×10^{-2} to 5×10^{-5} M, in the synthesis of gold nanoparticles 1×10^{-4} M solution of $HAuCl_4$ was used.

As the gold and silver nanoparticles dispersions stabilizers the polyols: ethylene glycol, diethylene glycol, triethylene glycol, and 1,2- propylene glycol from Vekton were used.

The prepared samples were irradiated with monochromatic UV light with the excitation wavelength 254 nm produced by the mercury lamp Philips TUV 4W/G4 05, while recording absorption spectra at each step of radiation. The intensity of incident light was 4.8×10^{16} quant cm^{-2} s^{-1}. The irradiation was carried out in quartz cells with optical path length of 1 cm. The quartz cells were preliminary degreased in a solution of chromic mixture, boiled for 10 min in concentrated solution of hydrogen peroxide, washed thoroughly with distilled water, and dried.

The formation of nanostructures in the photolyte bulk were recorded spectrophotometrically by a characteristic absorption in the wavelength range of 200–800 nm (spectrophotometer SF-2000).

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