A NONSTATIONARITY OF SILVER HYDROSOLS FORMATION AND CHANGES OF NANOPARTICLES SHAPE AFTER «FREEZING»

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Abstract

Among the other elements the dispersed silver holds a special place because of its protective biocidal effect and specific physicochemical characteristics depending on the particle size and shape. Absorption spectra of silver hydrosols were monitored in processes of Ag nanoparticles (Ag-NPs) formation due to reducing reaction of Ag^+ ions by tannin with $AgNO_3$ or Ag_2SO_4 as precursors. The dependence of the optical absorption on the wavelength in the long-wavelength range of plasmon spectra has been analyzed in framework of Mie theory by an original method. Several parameters may be estimated, such as the volume fraction of NPs (NV), the effective concentration of conduction electrons (Ne), and the damping factor of the metal electron plasma vibrations (γ). The changes in γ are the most interesting because γ includes surfaces` defects of metallic nanoparticles. It was found that in case of $AgNO_3$ precursor the increase of NV leads to γ decrease with oscillations for both parameters when the reaction $Ag^+_n \rightarrow Ag^0_n$ proceeds. Low temperature treatment of the stable silver particles (10 nm in diameter) undergo aggregation (rearrangement) because silver NPs surface becomes defective. At 77 K changes in NV and γ may be explained by tunnel mechanism of surface defects formation. These defects include mobile small surface clusters $H^+(H_2O)_n$ and $OH^-(H_2O)_n$. We compare the influences of precursor and Ag-NPs concentration on NV and γ parameters before and after freezing.

Keywords: Silver nanoparticles, freezing of Ag hydrosols, plasmon spectra, surface defects

1. INTRODUCTION

Metal nanoparticles (NPs) of 1-20 nm range attracted significant attention of researchers because of the wide range of applications and extraordinary optical and electronic properties [1-3]. Localized plasmons are the collective oscillations of free electrons in metal nanoparticles. The optical properties of silver clusters and NPs largely depend on their sizes [4,5]. In [6,7], it has been found that the peak width Δ of the surface plasmon spectrum linearly depends on 1/r (r is the radius of a Ag-NPs) and that the peak shifts to the lower frequencies with a decrease in the particle size. The dependence of the optical density on the wavelength in the long-wavelength range (see **Figure 1a**) has been analyzed in terms of the Mie theory in [8,9] and its representation corresponded by equation (1).

$$\frac{l}{2{,}3Abs} = \frac{\theta_2}{\theta_1} + \frac{1}{\theta_1}\left(\frac{\lambda_{max}^2}{\lambda} - \lambda\right)^2 \ (1), \quad \theta_1 = \frac{9\pi NVc\,m_0^3}{\sigma} \ (2), \qquad \theta_2 = \frac{e^4\lambda_{max}^4 N_e^2}{4\pi c^2 m_e^2 \sigma^2} \ (3).$$

The parameters θ_1 (cm) and θ_2 (cm^2) defined by formulas (2) and (3) are used to estimate the volume fraction *NV of* metal particles, the effective concentration N_e *of* conduction electrons, and the damping factor γ of the metal electron plasma vibrations. The latter factor is related to the particle conductivity (formulas 4).

$$\sigma = \frac{e^2 N_e}{m_e \gamma} \ (4), \quad \lambda_{max}^2 = \frac{(2\pi c)^2 m_e(\varepsilon_0 + 2m_0^2)}{4\pi N_e e^2} \ (5), \qquad \gamma = \gamma_{ee} + \gamma_{ef} + \gamma_{ed} = \widetilde{\gamma_0} + n_d \sigma_S V_F \ (6), \ \widetilde{\gamma_0} = \gamma_{ee} + \gamma_{ef}$$

The wavelength at the absorption peak λ_{max} is related to *Ne* by (formula 5), where ε_0 is the λ-independent dielectric constant of silver; *e* and m_e are the charge and effective mass of electron, respectively; *c* is the velocity of light; m_0 is the refractive index of the medium. The coefficient γ determines the half-width of the absorption band and includes the coefficients of conduction electrons scattering by electrons (γ_{ee}), by phonons (γ_{ef}), and by crystal lattice defects (γ_{ed}) (formula 6), where $\widetilde{\gamma}_0$ denotes the constant at given temperature, n_d the defect concentration in the near-surface layer of a metallic particle, σ_S the effective section of electron scatter by defects, and V_F the electron speed at the Fermi level.

2. FIGURES, SCHEMA, TABLES

Silver hydrosols (0.001 and 0.002 wt.%) were prepared by reduction of $AgNO_3$ (sol$_1$, sol$_2$) or Ag_2SO_4 (sol$_3$) (reagent grade) with tannin ($C_{76}H_{52}O_{46}$, high-purity grade, Germany) as reducing agent and stabilizer in the presence of a sodium tetra borate buffer (reagent grade, pH 9.0). Sols which were synthesized this way showed high stability and reprodusibility of absorption spectra during two years. The absorption spectra were recorded at room temperature from 300 to 750 nm on an SK-101 spectroscopic complex (Russia) at 25°C before and after cryotreatments, with an accuracy of optical density determination Abs ± 0.002. Freezing was performed by holding a sol (4 ml) in a low-temperature bath for 15-120 s. The baths were cooled with mixtures of liquid nitrogen with pentane (142 K), toluene (178 K), octane (217 K), and butanol (230 K). Dewar flask and special thin-walled test tubes with a ~1.5 mm interval gap were used. This excluded gradients across the layer of the colloidal solution to be cooled. After freezing a sample was rapidly (1 min) heated up to room temperature and its absorption spectrum was recorded. The optical path was 1 cm, water was in reference channel. It was preliminarily checked that freezing treatment has no effect on the state of tannin/buffer solution.

Figure 1b demonstrates the spectral controlling synthesis of Ag hydrosol ($AgNO_3$). This routine procedure is applied by many researchers. The rate of Ag-NPs formation in different conditions can be defined. The particularity of our approach consists in the analysis of Ag-NPs absorption curve that permits to clarify the changes in the states of forming Ag-NPs.

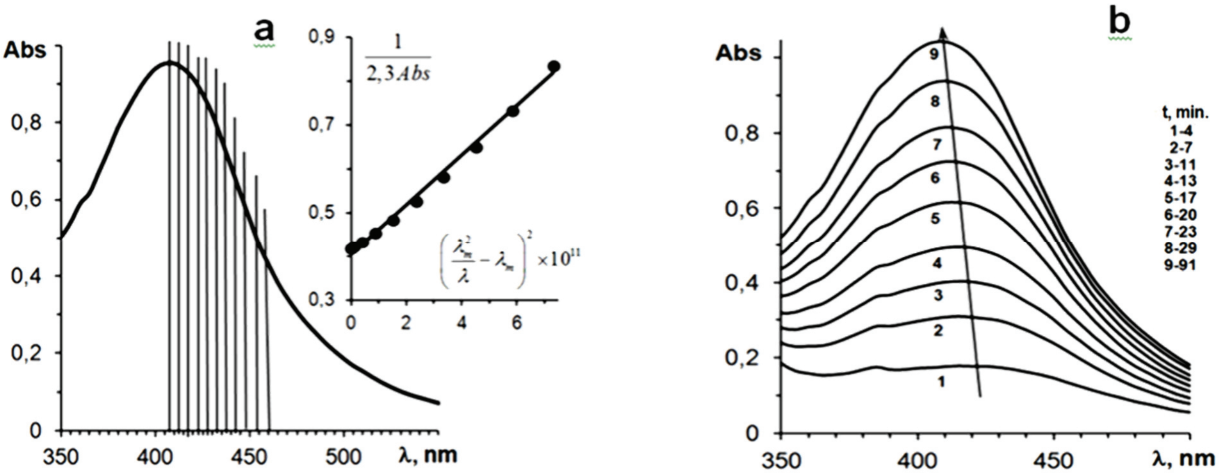

Figure 1 Absorption curve analysis (a) and AgNPs absorption spectra in Ag sol$_1$ synthesis (b)

It is seen from **Figure 2** that the volume fraction of the dispersed phase NV and γ coefficient of plasma-resonance vibrations vary during the synthesis of hydrosols. The time dependencies of NV and γ are antisymbatic: the growth of NV is accompanied by a decrease in γ, that is, a decrease in the defectiveness of the surface of the emerging particles (healing of biographical defects). On the kinetic curves we can see a nonstationary period with oscillations for both parameters NV and γ. Nonstationary phenomena plays an important role in chemistry and self sustained oscillations are known for different heterogeneous catalytic reactions [10,11]. The appearance of nonstationarity mode in Ag NPs formation processes is a very interesting result. To explain the parameters of NV and γ oscillations we considered the auto catalytic way of ions-metal NPs complex formation in the schema of reduction reaction $Ag^+ \rightarrow$ Ag-NPs.

1. $\mathrm{Ag_V^+ \rightleftarrows Ag_S^+}$ (Adsorption of Ag+-ions)

2. $\mathrm{red_V \rightleftarrows red - s}$ (Adsorption of reducing agent)

3. $\mathrm{Ag_S^+ + (Ag_n^0)^* \rightleftarrows Ag_S^+ - Ag_n^0}$ (Formation of the complex Ag+-NPs)

4. $\mathrm{Ag_S^+ - Ag_n^0 + red - s \rightleftarrows Ag^0 - Ag_n^0 - ox \longrightarrow Ag_{n+1}^0 + ox}$ (Reduction step: the interaction of the adsorbed reducer and a complex to form a product Ag0n+1)

5. $\mathrm{Ag_S^+ - Ag_n^0 + Ag_S^+ \rightleftarrows Ag_S^+ - Ag_n^0 - Ag_S^+}$ (Inhibiting of complex Ag-ion on the second adsorption stage).

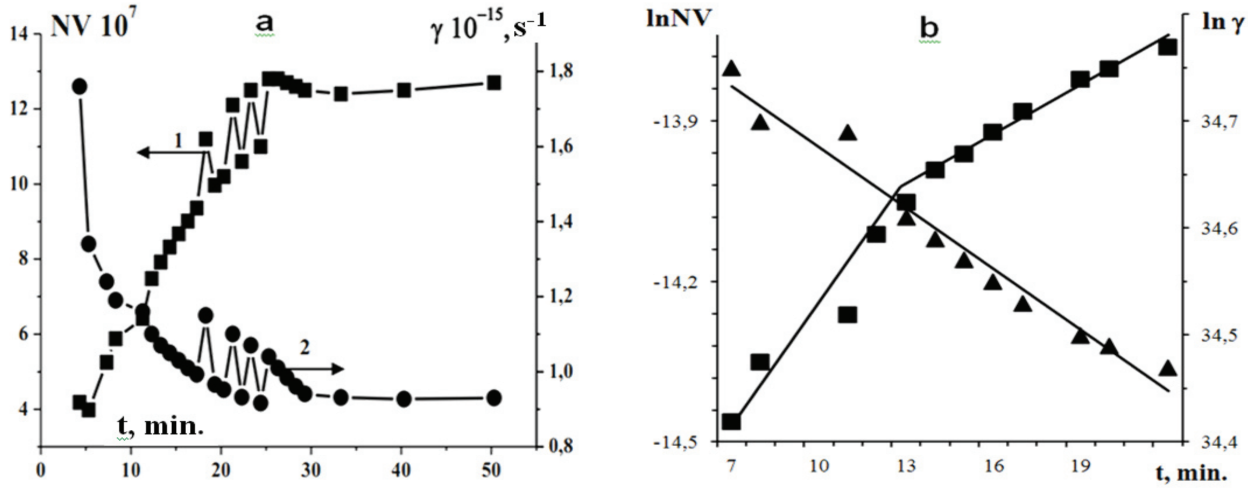

Figure 2 Nonlinear time dependences of Ag-NPs parameters in silver hydrosol ($AgNO_3$) synthesis processes with NV and γ self oscillations (**a**) and its linear plots in first kinetic order coordinates (**b**)

The kinetic of formation of Ag-NPs corresponds to first order. The rate constant values K_{NV} and K_γ were calculated from semilogarithmic plots (**Figure 2b**). Only for *NV-time* dependence two periods of AgNPs formation were observed with diminishing in 2 times of K_{NV} as it can be seen from data in the **Table 1**.

Table 1 Constant rates (min.$^{-1}$) of optical parameters changes for Ag hydrosols formation

Ag sol ($AgNO_3$) 0.001 % wt.			Ag sol (Ag_2SO_4) 0.002 % wt.	
k_γ	k_{NV} (1)	k_{NV} (2)	k_γ	k_{NV}
0.02	0.06	0.03	0.01	0.06

Figure 3a *illustrates the spectra monitoring in situ for synthesis of Ag-hydrosol with* Ag_2SO_4 precursor (sol$_3$*).* The unusual shape of the spectrum line and red shift of Abs_{max} are associated with the formation of unstable aggregated Ag-NPs and clusters Ag^+_n (sharp peaks below 380 nm). After mixing and dispersion stabilization we see the shift of peak maximum in a short wave area and typical plasmon spectra of isolated stable AgNPs of 8-10 nm in diameter that appearance due to disintegration of unstable agglomerates and incorporation of unstable Ag^+_n in NPs. As in the case of Ag-sol ($AgNO_3$) at the initial stage (up to 20 minutes) the parameters NV and γ change also antisymbiatically and in the final stage we see its synchronous decrease due to disaggregation of initially formed associated AgNPs with weak oscillations (**Figure 3b**).

The effect of freezing treatment was studied for two *Ag-hydrosol obtained from* $AgNO_3$. Sol$_1$ was a freshly prepared sample and the sol$_2$ was the sol$_1$ stored for a year. It was found preliminarily that low temperature treatment (LTT) did not influence the state of tannin/buffer system: UV spectra were reproducible after LTT. The spectra of sols had one absorption maximum at about 416 nm. According to literature data and our TEM images, the Ag particles diameters with plasmon spectra maximum 410-430 nm is about 8-10 nm.

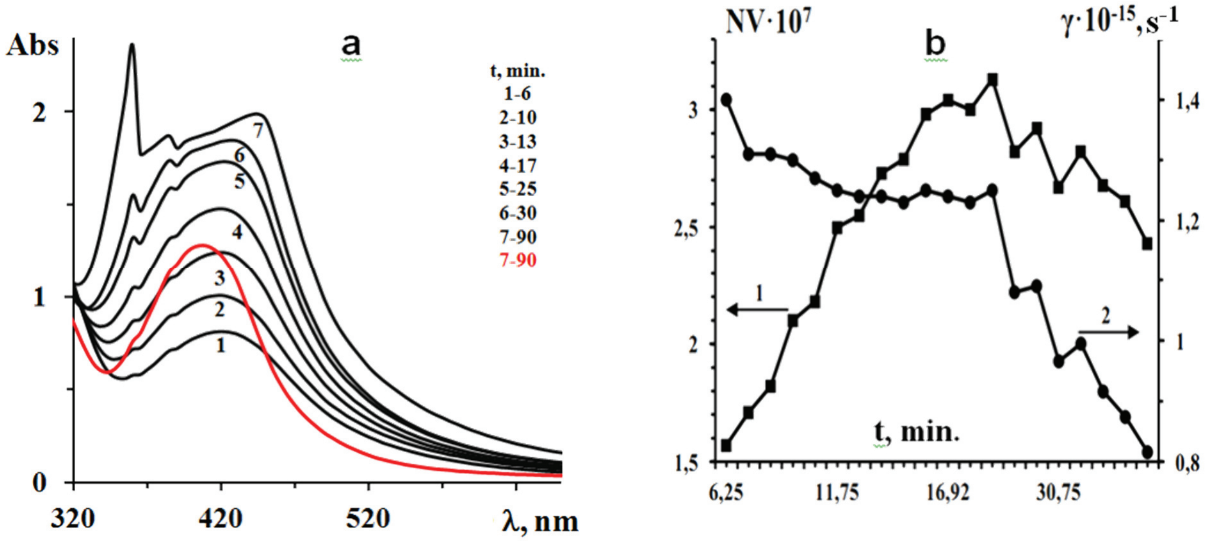

Figure 3 Absorption spectra of Ag-sol$_3$ formation (a) and time dependences of Ag-NPs parameters volume fraction of metallic particles *NV* and damping factor of electron plasma vibrations γ (b)

For example, spectra obtained before and after silver hydrosol treatment at 77K for 20 s are shown in **Figure 4**. We found that the absorption maximum did not shift as the temperature decreased, while the optical density at the maximum Abs$_m$ lowered (**Table 2**). However, Abs$_m$ values for T=77 K fell out of this dependence. Absorption peak at 500-550 nm appeared at T < 182 K and related to the formation of a new fraction of larger Ag particles and/or nonspherical anisotropic NPs and their aggregation [12]. Holding sols subjected to low-temperature treatment at room temperature for 48 h additionally decreased Abs$_m$ and increased absorption in the long-wave region, that is, changes in degree of dispersion also occurred after LTT.

Table 2 Influence of cryotreatment temperature (duration 20 s) on γ (s^{-1}) and NV of Ag hydrosols

№	**T, K**	**Sample 1**				**Sample 2**			
		Abs$_m$	**ΔAbs*, %**	$\gamma \cdot 10^{-15}$,	**NV·10^6**	**Abs$_m$**	**ΔAbs*, %**	$\gamma \cdot 10^{-15}$,	**NV·10^6**
1	298	0.94	100	0.72	1.09	1.01	100	0.50	0.79
2	230	0.91	85	0.70	1.02	0.95	94	0.54	0.82
3	207	0.77	82	0.74	0.92	0.74	73	0.63	0.80
4	182	0.66	70	0.81	0.87	0.72	71	0.64	0.74
5	142	0.50	53	0.93	0.75	0.52	51	0.72	0.70
6	77	0.86	92	0.71	0.99	0.63	62	0.64	0.68

The hexagonal ice structure with a disordered arrangement of protons transforms into a denser structure with an ordered arrangement of H^+ as the temperature decreases to 77 K [13]. Explanation of this effect is discussed in detail in [14] for gold hydrosols by means of tunnel mechanism for “cryodefects” formation from positively charged surface complexes $X^+(H_2O)_n$-Au (or Ag), e.g., $H^+(H_2O)_n$ and $Au^{+\delta}(H_2O)_n$ (n = 1-100).

To exclude the concentration influence, we have studied the effect of freezing at 77 K of Ag-sol$_3$ in terms of different Ag-NPs concentration in the dispersions. (**Table 3**, **Figure 4b**).

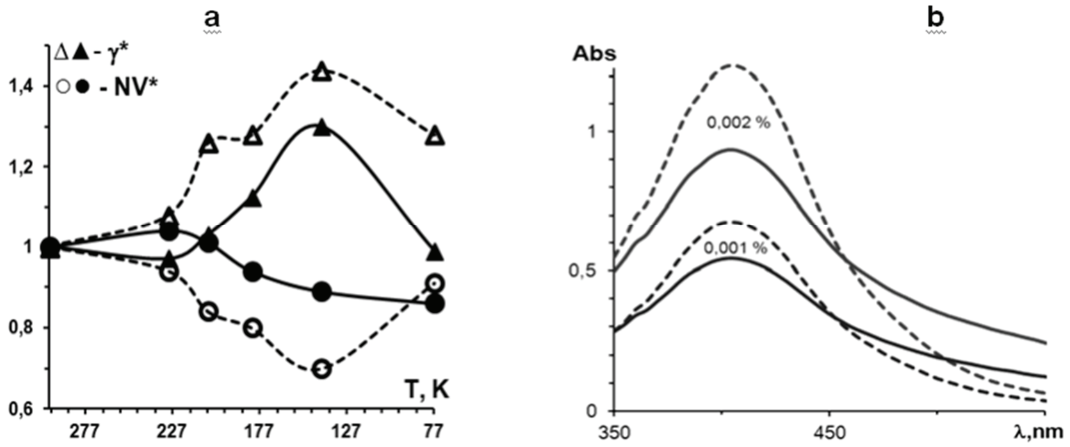

Figure 4 a) Influence of freezing temperature on the relative parameters γ*, and NV* calculated from the spectra of freshly (dashed line) and stored for a year Ag ($AgNO_3$) hydrosols; **b)** Absorption spectra of Ag (Ag_2SO_4) hydrosol before (dashed line) and after freezing at 77 K. Freezing duration is 20 s.

Table 3 Effect of Ag sol concentration in Abs_{max} and $\gamma \times 10^{-15}$ (s^{-1}) after freezing Ag-sol$_3$ (77 K, 20 s)

C, wt. %	**0.001**	**0.0012**	**0.0014**	**0.0016**	**0.0018**	**0.002**
Abs_m before freezing	0.675	0.776	0.910	0.995	1.062	1.237
Abs_m after freezing	0.543	0.591	0.674	0.757	0.794	0.934
ΔAbs_m, %	**–19**	**–24**	**–26**	**–24**	**–25**	**–24**
γ before freezing	1.02	1.03	1.02	0.993	1.04	1.01
γ after freezing	1.3	1.31	1.28	1.23	1.3	1.3
$\gamma\Delta$, %	**+27**	**+27**	**+26**	**+24**	**+25**	**+28**

On the **Figure 4b** it is shown that the absorption in maximum Abs_m after freezing decreases. However, the relative change of ΔAbs_m in this environment remains constant (~25 %). It was found that the freezing of dilute Ag-sols$_3$ does not lead to aggregation of the particles, but the rise of the surface defects is sufficient (~27 **%). Thus freezing effect in relative changes of parameters does not depend on the concentration of the** silver hydrosol.

3. CONCLUSIONS

Our investigation of the kinetics of Ag-hydrosols formation and the effect of sols freezing revealed a changes of optical parameters: a decrease in the effective concentration of unbound electrons and an increase in the imperfections of particles. These leads to formation of small ensembles (floccules) or aggregates depending on LTT duration. Flocculated or aggregated Ag-NPs are formed, respectively, upon short or long expositions. The low activation energy of the cryoaggregation of NPs is dictated by the tunnel mechanism of the formation of "cryodefects" from positively charged surface complexes $X^+(H_2O)_n$-Ag, e.g., $H^+(H_2O)_n$ and $Ag^{+\delta}$ $(H_2O)_n$ (n = 1-100). It is determined that defects on Ag-NPs surface increases with decreasing of temperature of freezing due to its cryoaggregation. **Relative effect of LTT does not depend on the Ag hydrosol concentration.**

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