

Analysis of Silver Nanoparticles Produced by Chemical Reduction of Silver Salt Solution

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In the present research silver colloid was produced by chemical reduction of silver salt (silver nitrate AgNO₃) solution. As a reducer sodium citrate was used. UV-VIS spectrometry indicated formation of nanoparticles. The surface plasmon resonance peak in absorption spectra of silver colloidal solution showed an absorption maximum at 450 nm. Comparison of theoretical (Mie light scattering theory) and experimental results showed that diameter of silver nanoparticles in colloidal solution is about 100 nm. Silver nanoparticles were deposited on two substrates: silica (SiO₂) and polyethylene terephthalate (PET) modified with various polymers (polycarbonate (PC), polymethyl methacrylate (PMMA), polystyrene (PS)). The colloidal silver was incorporated by dip-coating to the polymer-substrate structures. X-ray fluorescence spectroscopy (XRFS) and atomic force microscopy (AFM) results indicate that produced structures include silver nanoparticles. It was found that during deposition, silver nanoparticles forms aggregates on the surface. The size of aggregates varied from 240 nm to 400 nm.

Keywords: silver, surface plasmons, absorption spectrum.

1. INTRODUCTION

Colloidal particles are increasingly receiving attention as important starting points for the generation of micro- and nanostructures [1]. These particles are under active research because they possess interesting physical properties differing considerably from that of the bulk phase. It comes from small sizes and high surface/volume ratio [2].

Silver nanoparticles have received considerable attention due to their attractive physical and chemical properties. Metallic silver colloids were first prepared more than a century ago. Ag nanoparticles can be synthesized using various methods: chemical, electrochemical [3], γ -radiation [4] photochemical [5], laser ablation [6] etc. The most popular preparation of Ag colloids is chemical reduction of silver salts by sodium borohydride or sodium citrate. This preparation is simple, but the great care must be exercised to make stable and reproducible colloid. The purity of water and reagents, cleanliness of the glassware are critical parameters. Solution temperature, concentrations of the metal salt and reducing agent, reaction time influences particle size. Controlling size and shape of metal nanoparticles remains a challenge [7]. The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics and so on.

Silver nanoparticles exhibit new optical properties, which are not observed neither in molecules nor in bulk metals. One example is presence of absorption band in visible light region. This band appears due to the surface-plasmon-oscillation modes of conduction electrons which

are coupled through the surface to external electromagnetic fields [8]. The surface plasmon resonance and large effective scattering cross section of individual silver nanoparticles make them ideal candidates for molecular labeling, where phenomena such as surface enhance Raman scattering (SERS) can be exploited [9]. In addition, silver nanoparticles have recently been shown to be a promising antimicrobial material [10].

In this research, Ag nanoparticles were synthesized by silver salt (AgNO₃) reduction with sodium citrate and transferred onto polymer modified silica (SiO₂) and polyethylene terephthalate (PET).

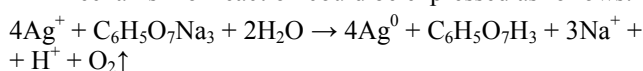
2. EXPERIMENTAL

2.1. Preparation of Ag colloid

Silver nitrate AgNO₃ (Sigma Aldrich, UK) and trisodium citrate C₆H₅O₇Na₃ (Sigma Aldrich, UK) of analytical grade purity, were used as starting materials without further purification.

The silver colloid was prepared by using chemical reduction method according to the description of Lee and Meisel [11]. All solutions of reacting materials were prepared in distilled water. In typical experiment 50 ml of 1·10⁻³ M AgNO₃ was heated to boiling. To this solution 5 ml of 1 % trisodium citrate was added drop by drop. During the process solution was mixed vigorously. Solution was heated until color's change is evident (pale yellow). Then it was removed from the heating element and stirred until cooled to room temperature.

Mechanism of reaction could be expressed as follows:



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2.2. Preparation and modification of substrates

Substrates were cleaned chemically (only silica) and with oxygen plasma (glass and PET). Silica substrate was boiled for 10 minutes in dimethylformamide and 10 min in isopropyl alcohol. Then substrates were cleaned using oxygen plasma ($RF = 13.56$ MHz, $P = 0.3$ W/cm², $t = 60$ s – 120 s) [12].

Substrates were modified with various polymer solutions. Polymer solutions were prepared by dissolving polystyrene (PS), polycarbonate (PC) and polymethyl methacrylate (PMMA) (Sigma Aldrich, UK) in chloroform. The concentration of the solutions is expressed as percentage of weight/volume (% w/v). We used 5 % PS, 5 % PC and 2.5 % PMMA solutions. Polymer films were made according to spin coating technique, using centrifuge “Dynapert Prisma”. The following parameters were chosen: rotation speed – 3000 rpm, formation time – 20 s, dried in room temperature (20 °C), humidity – 60 %.

2.3. Deposition of silver nanoparticles

Deposition of silver nanoparticles was performed in Langmuir-Blodgett trough (Microtestmachines Co, Belarus), in dipper unit. Substrates were vertically dipped into silver colloid solution, pulled down in 10 s – 20 s and then pulled out very slowly for 15 minutes. This technological regime was chosen according to colloid drying speed. The process was repeated for 10 times to increase sorption of silver nanoparticles.

2.4. Analysis technique

The optical properties (absorbance) of colloidal solution were evaluated with UV/VIS/NIR spectrometer (Avantes-2048), light source – combined deuterium-halogen (AvaSpec-Dhc), wavelength range: 200 nm – 1100 nm. Thickness of polymer films was measured with a laser ellipsometer (Gaertner L115), wavelength $\lambda = 632.8$ nm. Morphology of silver – polymer structures was investigated with an Atomic force microscope (NANOTOP–206) operating in a contact mode (cantilever force constant 3 N/m). Image processing and analysis of the scanning probe microscopy data was performed with a program “Surface View version 2.0”. The amount of silver as element in the polymer structure was measured with an X-ray fluorescence spectrometer (VRA-20) operating X-ray source voltage 35 kV and current 26 mA. Registration time was 30 s and the investigated area was 78.5 mm².

3. THEORETICAL MODEL

Theoretical predictions of the surface plasmon resonance peak (nanoparticle size) were made using Mie calculations, performed with software “MiePlot v.3.4” [13]. The algorithm of this software is based on Mie scattering from a sphere calculations. Mie theory describes the scattering of light by particles. “Particles” are defined as aggregates of material that constitutes a region with refractive index (n_p) that differs from the refractive index of its surroundings (n_{med}). Mie’s classical solution is described in terms of two parameters, n_r and x :

$$n_r = \frac{n_p}{n_{med}}, \quad (1)$$

where n_r – mismatch between refractive indexes of particle and medium.

The size of the surface of refractive index mismatch is expressed as a size parameter x :

$$x = \frac{2\pi n_{med}}{\lambda}. \quad (2)$$

According to the Mie theory calculation, efficiency of scattering is expressed this way:

$$\sigma_s = Q_s A, \quad (3)$$

where Q_s – scattering coefficient, $A = \pi r^2$ – true geometrical cross-sectional area of the spherical particle.

Scattering and extinction coefficients are expressed in this way:

$$Q_s = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2); \quad (4)$$

$$Q_{ext} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) R(a_n + b_n), \quad (5)$$

where a_n and b_n are Mie coefficients, which may be complex. The expressions of these coefficients are discussed further in [14].

Program “MiePlot” calculates scattering efficiencies (Q_{ext} – extinction, Q_{abs} – absorption, Q_s – scattering) as functions of wavelength. In general, light absorption dominates in the extinction (extinction = absorption + scattering) spectrum for particles relatively small radius (<20 nm), and light – scattering becomes the dominant process for large particles [15].

4. RESULTS AND DISCUSSIONS

4.1. Optical properties of Ag colloid

UV-VIS absorption spectra have been proved to be quite sensitive to the formation of silver colloids because silver nanoparticles exhibit an intense absorption peak due to the surface plasmon (it describes the collective excitation of conduction electrons in a metal) excitation [16]. The absorption spectrum of isolated spherical particles is characterized by the Mie resonance occurring at a frequency w_0 such that:

$$\varepsilon_{1s}(w_0) = -2\varepsilon_m, \quad (6)$$

where $\varepsilon_s(w)$ is the dielectric function of the silver spherical particles and ε_m is the dielectric function of the surrounding medium [17].

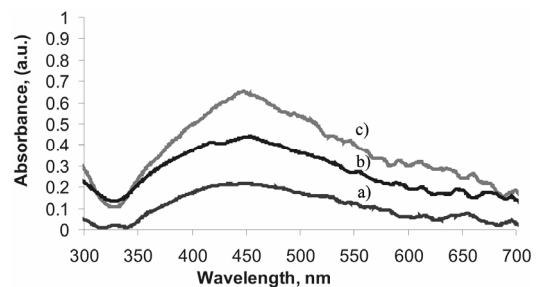


Fig. 1. The UV-VIS spectra of Ag colloid. Time after synthesis: a – 1 hour, b – 2 weeks, c – 3 weeks

Figure 1, a, shows the UV-VIS spectra of the silver colloid in the range 300 nm – 700 nm. The absorption band in visible light region (350 nm – 550 nm, plasmon peak at 445 nm) is typical for silver nanoparticles. The plasmon peak and the full-width of half-maximum (fwhm) depends on the extent of colloid aggregation [18]. To monitor stability of the silver colloid, we have measured the absorption of the colloid after different periods of time. The evolution of UV-VIS spectra is shown in Figure 1 (b and c curves). There was no obvious change in peak position for three weeks, except for the increase of absorbance. As the particles increase in size, the absorption peak usually shifts toward the red wavelengths [15]. Increase of absorption indicates that amount of silver nanoparticles increases. The stable position of absorbance peak indicates that new particles do not aggregate. One can understand that since the silver colloidal particles possessed a negative charge due to the adsorbed citrate ions, a repulsive force worked along particles and prevented aggregation.

To determine the particle size we performed several calculations changing the radius of particles and compared absorption dependencies on wavelength with the experimental UV-VIS absorption spectrometry results. In theoretical calculations the radius of particle was changed from 5 nm to 100 nm. We have chosen scattering from many spheres, because there was possibility that particles in colloidal solution aren't uniform. The standard deviation used in simulation was 10 %.

We found that the best fit between the experimental and theoretical results was when for theoretical absorption dependence calculations radius of particle 50 nm was used. Both absorbance curves (theoretical and experimental) are shown in Fig. 2.

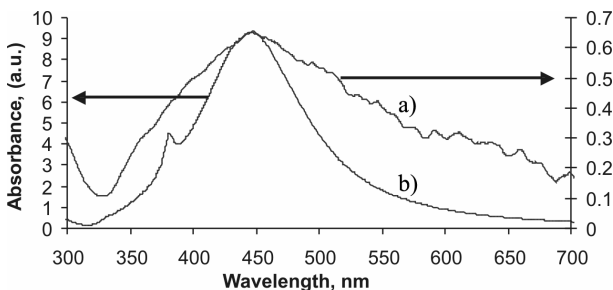


Fig. 2. Comparison of theoretical and experimental absorption dependence on wavelength: a – UV-VIS measurement of colloidal solution, b – theoretical curve when radius of particle is 50 nm

These results are in good agreement with other studies [11].

4.2. Amount of silver in polymer-substrate structures

Amount of silver in produced structures silver-polymer-silica detected by XRFS is presented in Table 1. No silver was detected with XRFS on PET substrates modified with polymers because concentration was too small. There is a great difference of absorbed amount of silver on substrates (Table 1). Depending on the used treatment this can be explained in difference of sample morphology due to different modification by polymer.

Table 1. Amount of silver detected with XRF

Structure	Amount of silver, μg
Ag/PS/SiO ₂	0.12
Ag/PMMA/SiO ₂	0.015

4.3. Morphology of substrates after deposition of silver nanoparticles

Firstly deposition of silver nanoparticles was performed on primary substrates (after surface preparation). But there was no evidence of silver nanoparticles sorption. Then substrates were modified with polymer solutions. Modification and deposition of silver nanoparticles essentially changed roughness of the surface. Statistical characteristics are summarized in Table 2. Statistical analysis was performed for (3 × 3) μm area of substrates. The roughness of silica and PET substrates has changed after modification and deposition of silver nanoparticles. One can understand, that intense decrease of roughness in structure PET+PMMA+Ag is because silver nanoparticles filled cavities which appear on the substrate after modification with polymer takes place.

Table 2. Statistical parameters of substrates

Structure	Z, nm	R _a , nm	R _q , nm	d, nm
SiO ₂	4.2	0.2	0.4	–
PET	3.4	0.4	0.5	–
SiO ₂ +PC	12.9	0.4	0.6	140.8
SiO ₂ +PC+Ag	58.5	5.8	7.8	–
SiO ₂ +PS	17.9	2.0	2.6	179.4
SiO ₂ +PS+Ag	82.0	11.4	14.3	–
PET+PS	26.8	2.6	3.4	106.6
PET+PMMA	912.6	158.9	218.0	274.4
PET+PS+Ag	52.7	2.3	3.5	–
PET+PMMA+Ag	125.6	12.3	16.7	–

Abbreviations: Z – maximum height, R_a – roughness average, R_q – root mean square roughness, d – thickness of polymer film, measured with an ellipsometer.

AFM pictures of silica and PET substrates before and after deposition of silver nanoparticles are presented in Fig. 3.

From the pictures made in torsion mode (Fig. 3, d and f) interface between two different materials (polymer and silver nanoparticle) can be seen. This confirms that silver nanoparticles are sorbed onto the substrates modified with polymers.

As it was mentioned earlier, size of the silver nanoparticles was determined to be 100 nm. After deposition, from the AFM pictures we can see that the size of nanoparticles is bigger. Silver nanoparticles tend to form aggregates on the surface during deposition. Size of the detected aggregates is summarized in Table 3.

According to the scattering theory, any variation in refractive index of the surface layer will lead to some changes in the intensity and/or position of surface plasmon

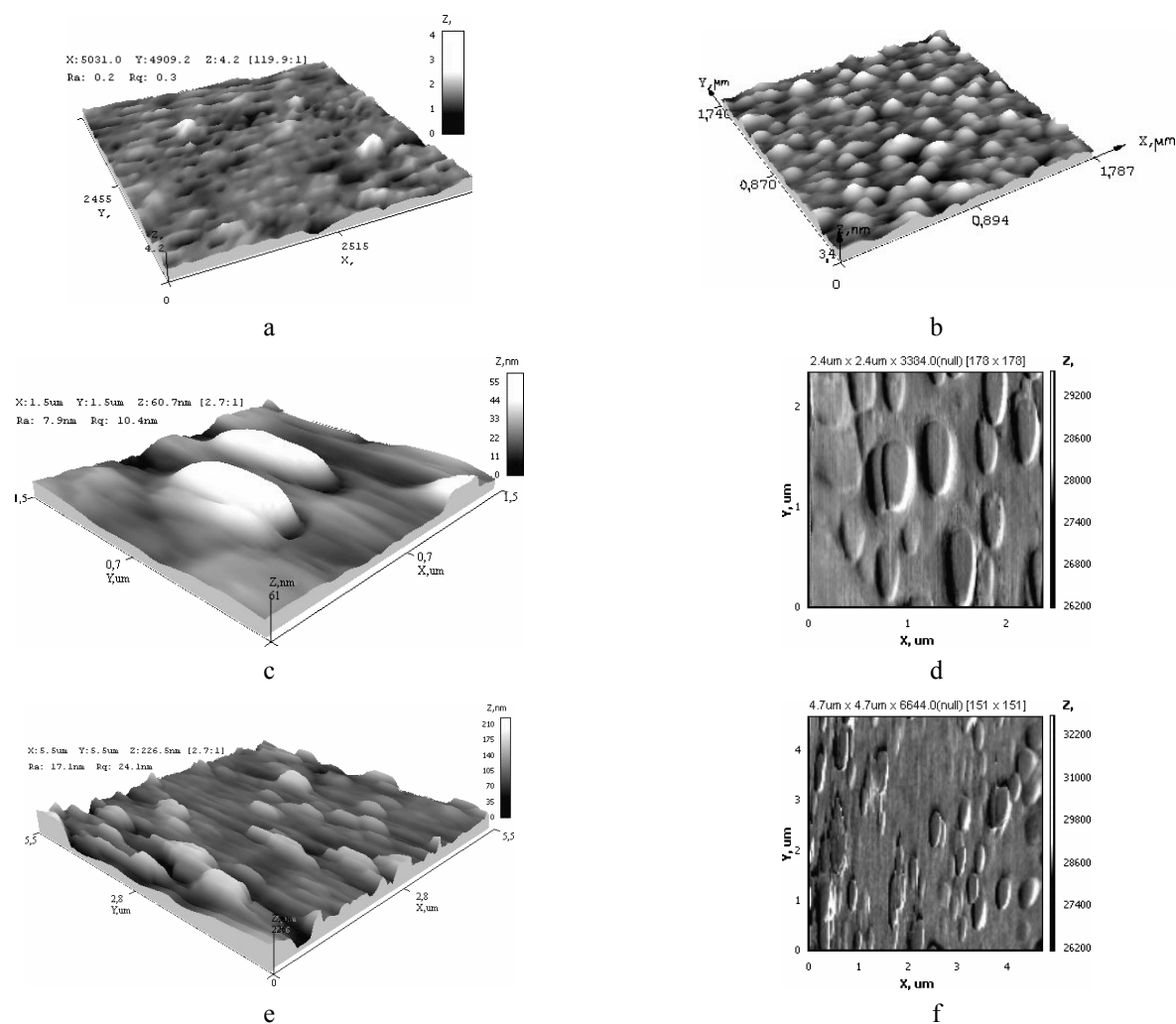


Fig. 3. AFM pictures of substrates: a – initial SiO₂; b – initial PET; c – structure Ag+PC+SiO₂, topography mode; d – structure Ag+PC+SiO₂, torsion mode; e – structure Ag+PMMA+PET, topography mode; f – structure Ag+PMMA+PET, torsion mode

Table 3. Size of silver nanoparticles aggregates on substrates

Structure	Size, nm
SiO ₂ +PC+Ag	400
PET+PS+Ag	240
PET+PMMA+Ag	300

peak [15]. The optical spectrum of silver nanoparticles deposited onto polymer-substrate structures should have different spectrum from the initial colloid spectrum. Theoretically the absorbance peak should have shifted to longer wavelengths according to difference of the surrounding medium (changes in refractive index). In our case, probably the concentration of silver nanoparticles on the substrates was not enough to detect the shift in optical absorbance spectrum.

4. Conclusions

1. UV-VIS absorption results confirmed formation of silver nanoparticles prepared in liquid by chemical reduction method (silver nitrate AgNO₃ reduced by sodium citrate C₆H₅O₇Na₃). Silver nanoparticles were transferred onto polymer-substrate structures using dip-coating technique.

2. Aging UV-VIS measurements have shown that size of the nanoparticles in colloid doesn't change, but with time the concentration slowly increases within few weeks.
3. Size of the nanoparticles determined comparing theoretical (calculations according Mie scattering theory) and experimental UV-VIS absorption spectrum results indicated dispersion of size around estimated value - 100 nm.
4. Silica and PET substrates modified with polymer (PS, PMMA, PC) solutions and can be used to measure sorption of silver particles.
5. AFM measurements have shown that silver nanoparticles stick to substrates and tend to form aggregates. The size of aggregates varies from 240 nm (PET+PS+Ag) to 400 nm (SiO₂+PC+Ag).

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