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Photochemical Synthesis of Gold Nanoparticles in Aqueous Dispersions of Carboxylated Polystyrene

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Abstract — Photochemical synthesis of gold nanoparticles in aqueous dispersions of carboxylated polystyrene with microsphere sizes of 100, 300, 500, and 1410 nm under the action of monochromatic light with an excitation wavelength of 254 nm was studied. Preliminary irradiation of the polymer dispersion induces formation of gold particles under dark conditions. Dependences of gold nanoparticles formation on the duration of preliminary polymer irradiation and concentration of introduced $HAuCl_4$ aqueous solution were determined. A mechanism of the polystyrene-assisted formation of gold nanoparticles was proposed. The size and structure of gold nanoparticles were determined.
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Hybrid structures of the nucleus–shell type with a metal deposited in one or another way can be obtained on the basis of polymer microspheres. Such systems find application in catalysis, optics, and immunochemical research in experimental biology and medicine. Metal layer is deposited on the surface of polymer microspheres by vacuum metal spraying [1] or by electrostatic precipitation of preliminarily obtained metal nanoparticles [2]. In the laboratory practice, metal shell is most often formed from nanoparticles obtained by chemical reduction of metal ions in aqueous solutions in the presence of polymer microspheres [3, 4]. The main problem limiting practical usage of such systems consists in nonuniform distribution of metal particles on the surface of microspheres, their high polydispersity, and low degree of filling of polymer surface. The problem can be solved, first, by engrafting to the surface of polymer microspheres of functional groups, for example, carboxy [3], amide [5], thiolic [6, 7], and other groups capable of forming donor–acceptor bonds with metal ions and of functioning as centers of metal nucleation [8], or, second, by modifying the surface of microspheres by surface-active materials, such as 2-aminoethanethiol hydrochloride [9, 10], which bind metal particles with microsphere surface.

The highest effectiveness is reached on sequential alternate deposition of metal nanoparticles [11- 13]. Rather satisfactory results in the formation of bimetallic shells on the surface of polystyrene microspheres were obtained by its activation with Sn^{2+} ions [14]; earlier this technique was used for activation of silica surfaces. The use of photosensitive metal-containing compounds and polymers [15, 16] allows the photochemical method to be applied for metal plating. However, we found [17, 18] that the reduction of metal ions takes too long time (as a rule, the induction period of nanoparticle formation is 1–2 h) and the degree of coating of microsphere surface with metal is low. An increase in the content of the solid polymer residue shortens the induction period, implying that metal ions are reduced with the participation of polymer and/or stabilizer macromolecules sensitive to the UV light, as well as of their photolysis products whose fraction increases as the polymer solid residue increases.

The aim of this work was to perform photochemical synthesis of gold nanoshells on the surface of carboxylated polystyrene microspheres and to study the role of the polymeric support in the formation and growth of gold nanoparticles.

The participation of the polymer in the reduction of Au(III) ions on photochemical preparation of gold nanolayers on the surface of polystyrene microspheres was studied by preliminary irradiating carboxylated polystyrene with subsequent dark introduction of $HAuCl_4$. The presence of a characteristic plasmon band in the absorption spectrum of gold particles allowed us to use spectrophotometry as a convenient method for monitoring nanoparticle formation. Figure 1 shows typical absorption spectra of samples obtained on introduction of a 2×10^{-4} M aqueous

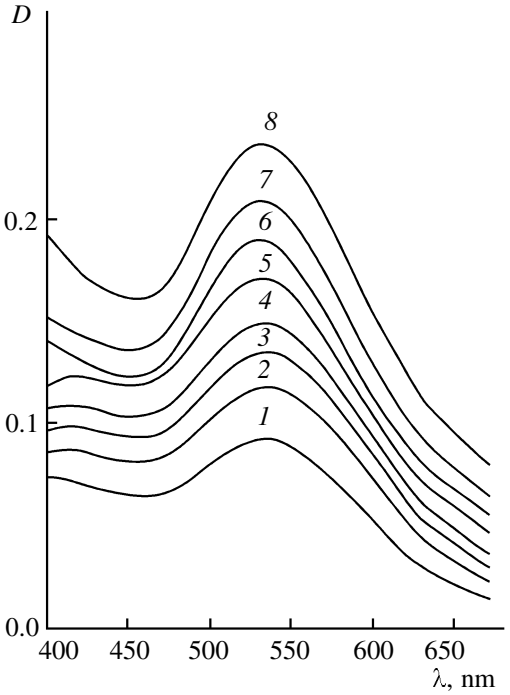

Fig. 1. Change in the absorption spectrum of a 2×10^{-4} M solution of $HAuCl_4$ in preliminarily irradiated (λ_{exc} 254 nm) aqueous dispersion of carboxylated polystyrene with a microsphere size of 100 nm in dark conditions within: (*1*) 2, (*2*) 13, (*3*) 24, (*4*) 34, (*5*) 63, (*6*) 162, (*7*) 313 min, and (*8*) 24 h.

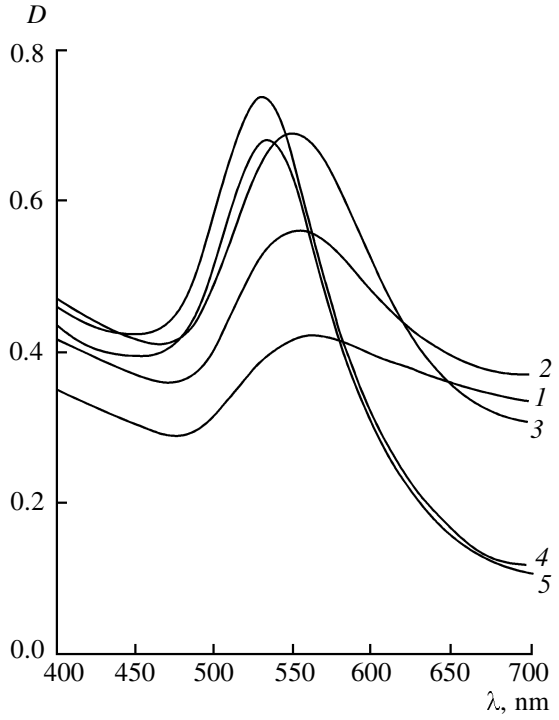

Fig. 2. Absorption spectra of a 2×10^{-4} M solution of $HAuCl_4$ as functions of the time of preliminary irradiation of an aqueous dispersion of carboxylated polystyrene with a microsphere size of 100 nm. Irradiation time, min: (*1*) 10, (*2*) 20, (*3*) 30, (*4*) 45, and (*5*) 60 min.

$HAuCl_4$ solution into a dispersion containing 0.005 wt% of carboxylated polystyrene preliminarily irradiated for 45 min. On addition of the $HAuCl_4$ solution the latter immediately changes color from yellow to wine-red. Therewith, the plasmon absorption band characteristic of colloidal gold appears in the spectrum at λ_{max} 525 nm.

The rate of the dark reduction of Au(III) ions, the size of gold particles, and their dispersity depend on the duration of irradiation. The irradiation of the polystyrene dispersion for 45 min (Fig. 2) and subsequent $HAuCl_4$ introduction increases the intensity of the gold plasmon absorption band and shifts it hypsochromically from 560 nm (10-min irradiation) to 525 nm, which points to a stronger monodispersity of forming metal particles and to their smaller average size. The irradiation of the polymer for more than 45 min gives rise to broadening of the plasmon band, its bathochromic shift to 535 nm, and decrease in the optical density, implying formation of a polydisperse gold colloid.

Centrifugation of the dispersion and spectral analysis of the mother solution showed that gold particles not only precipitate on the surface of polymer microspheres, but also form in bulk solution. According to electron microscopy, the average size of nanoparticles precipitated on the surface of microspheres after 45-min preliminary irradiation of polystyrene is 15 nm. The particles are of the icosahedral shape, are evenly distributed on the surface of microspheres, and the degree of surface filling reaches 25%. The particle size in the solution is, too, 15 nm, the particles are aggregated due to interaction with the polystyrene dispersion stabilizer, sodium dodecyl sulfate. For comparison, on irradiation of an $AuCl_4^-$–polystyrene system gold nanoparticles are mainly precipitated on the surface of polymer microspheres, and the degree of surface filling is 30%.

Addition of colloidal gold obtained by the reduction of $HAuCl_4$ with formaldehyde [19] to preliminarily irradiated polymer dispersion followed by keeping in dark conditions for 24 h resuled in no precipitation of gold nanoparticles on microsphere surface. This fact suggests that the formation of gold particles begins with a chemical reaction of polymer

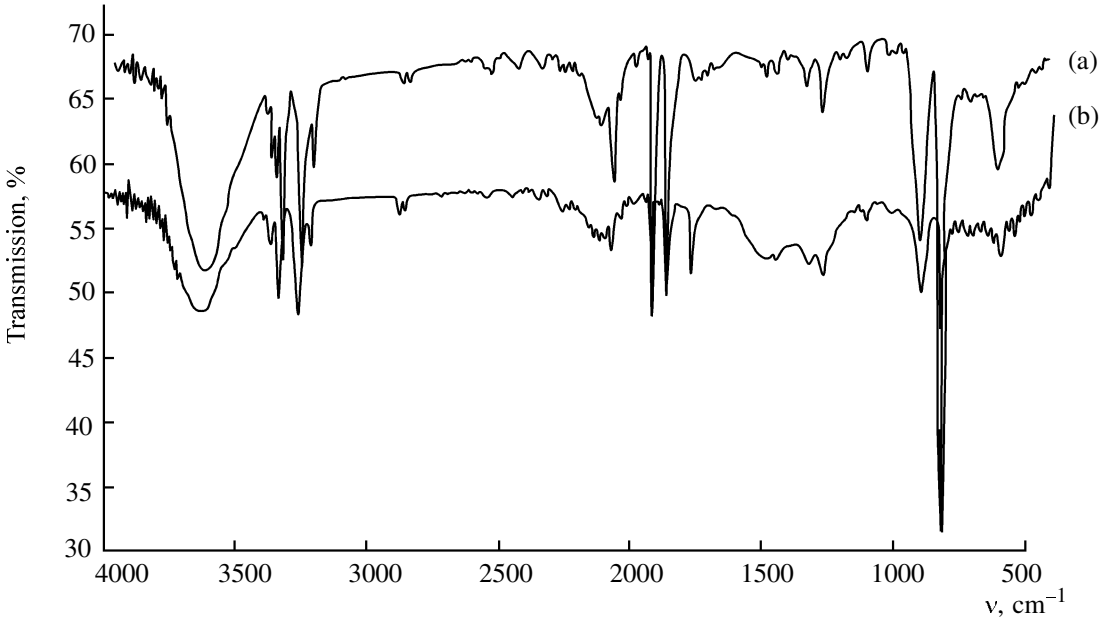

Fig. 3. IR spectra of carboxylated polystyrene with a microsphere size of 100 nm: (a) nonirradiated and (b) irradiated within 120 min.

functional groups with intermediates, low-valent and clusters forms of gold, arising during synthesis.

The above results provides evidence showing that carboxylated polystyrene is directly involved in the formation of gold nanoparticles. Under the action of the UV light in aerated conditions polymers can be oxidized, which is accompanied by the formation of carbonyl compounds [20] capable of effectively reducing Au(III) ions. However, the IR spectra (Fig. 3) of non-irradiated and irradiated carboxylated polystyrene samples revealed no changes in its chemical composition even under prolonged (120 min) irradiation. Almost all aromatic systems tend to form donor–acceptor complexes in the ground (charge-transfer complexes) and excited (exciplexes and excimers) states, and polystyrene is not an exception. The light with an excitation wavelength of 254 nm is actinic for polystyrene (λ_{max} 260 nm). Light absorption results in formation of excimers [21, 22] which give a characteristic fluorescent emission at 335 nm (358 kJ). Hence it follows that the photochemical synthesis may well involve energy transfer from polystyrene on $AuCl_4^-$ ions diffusing to microsphere surface and absorbing at 323 nm (371 kJ). This assumption requires a more detailed study.

In this context the formation of metal nanoparticles can be presented as follows. Under prolonged irradiation of a polystyrene dispersion (PD), gradual energy accumulation due to intramolecular transfer in polystyrene occurs, which is accompanied by increase in the concentration of excimers in a microsphere. When $HAuCl_4$ is added, Au(III) ions in the near-surface layer of the polymer microsphere absorb excimer radiation and are reduced to Au(II).

$$PD^* + Au_3^+Cl_4^- \longrightarrow (Au_3^+Cl_4^-)^* + PD, \quad (1)$$

$$(Au_3^+Cl_4^-)^* \longrightarrow Au_2^+Cl_3^- + Cl. \quad (2)$$

The unstable Au(II) form rapidly disproportionates into Au(I) and Au(III) ions.

$$2Au_2^+Cl_3^- \longrightarrow Au_1^+Cl_2^- + Au_3^+Cl_4^-. \quad (3)$$

The formation of gold particles on microsphere surface and in the solution is caused by the reaction of the Au(I) ions with carboxy groups grafted to polystyrene surface and with sodium dodecyl sulfate present both on the surface of microspheres and in the solution. The reaction products play the role of nanoparticle nucleation centers. The conversion of Au(I) to Au(0) requires one more quantum of light, and, therefore, the dark formation of nanoparticles probably mainly occurs via disproportionation of Au(I) ions.

$$3Au_1^+Cl_2^- \longrightarrow Au_3^+Cl_4^- + 2Au^0 + 2Cl^-. \quad (4)$$

As seen from the kinetic curve (Fig. 4), particles are formed effectively within the first 3–5 min, and then the process is essentially decelerated to reach equilibrium in a day. During this day the intensity of the gold plasmon absorption band increases, preserved and the Au(III) absorption band increases. The optical densities reach 0.25 units. This is caused by the dark formation of particles with a size most stable under the given conditions, due to concurrent disproportionation of Au(I) ions [reaction (4)], oxidation of gold clusters by accumulated Au(III) ions [reaction (5)], and autocatalytic growth of small gold particles (Au_N) or their coalescence into larger particles [reaction (6)].

$$3Au^0_n + Au^{3+}_{(solution)} \quad Au^0_{n-1(col.)} + 3Au^+_{(solution)}, \quad (5)$$

$$Au_N + Au_N \longrightarrow Au_m. \quad (6)$$

The average size of particles formed during the day of dark reduction is 20 nm (Fig. 5a). The degree of filling of microsphere surface by particles increases to 30–35% due to the sorption of particles stabilized by sodium dodecyl sulphate from the solution. Increased time of preliminary irradiation of polystyrene favors reactions (2) and (3) and, as a consequence, decreases the concentration of Au(III) ions which are strong oxidizing agents with respect to clusters formed in the solution and to metal nanoparticles. This creates conditions for formation of larger particles in the system with a wide size range. The average size of particles obtained on preliminary irradiation of the polymer within 60 min is 25 nm; the particles form agglomerates of up to 100 nm in size.

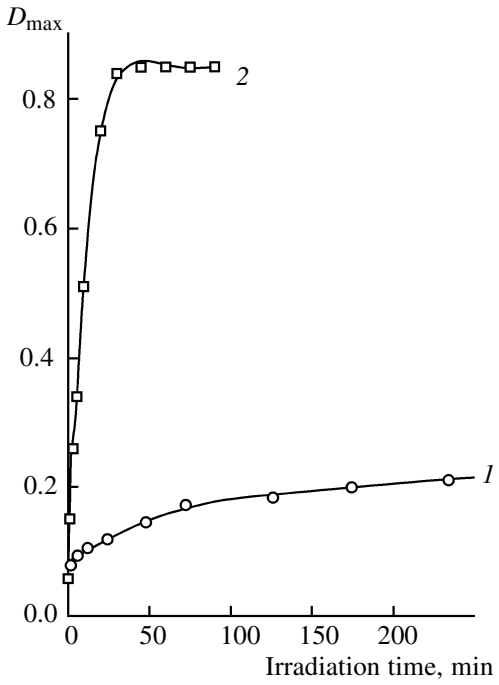

Fig. 4. Kinetics curves of the formation of gold nanoparticles in carboxylated polystyrene preliminarily irradiated for 45 min (*1*) in dark conditions and (*2*) with subsequent irradiation (λ_{exc} 254 nm).

(a) (b)

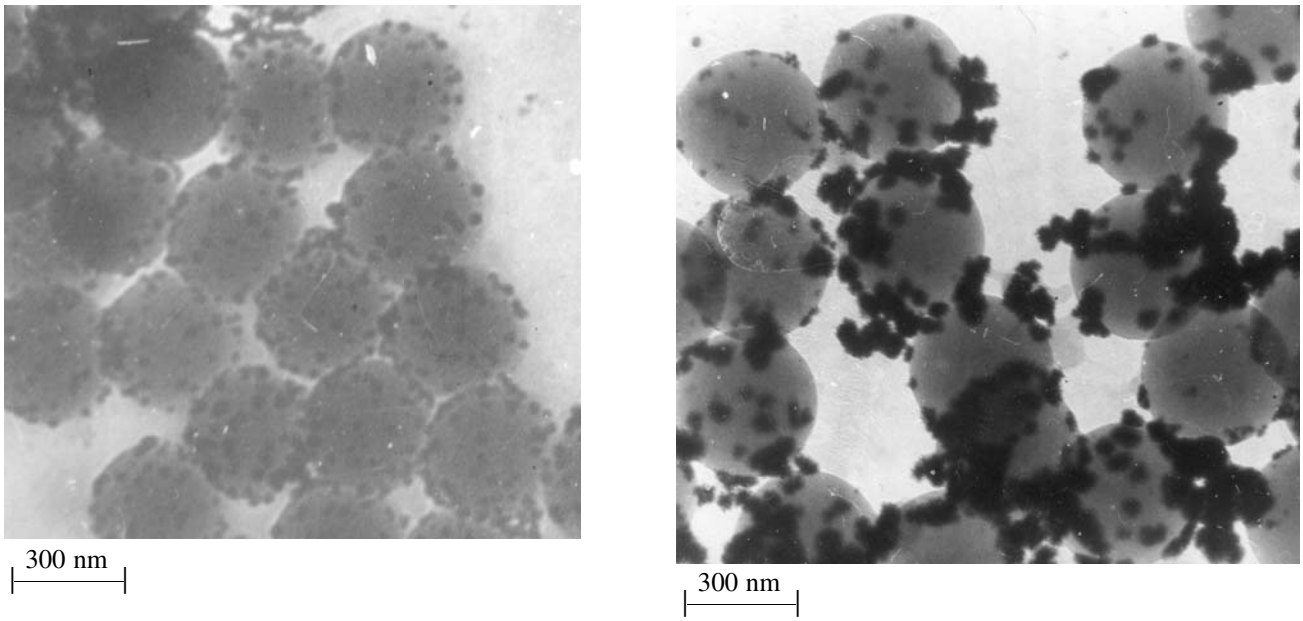

Fig. 5. Microphotographs of gold nanoparticles precipitated on polystyrene microspheres (300 nm) preliminarily irradiated for 45 min. (a) Dark $HAuCl_4$ reduction for one day and (b) additional irradiation for 45 min.

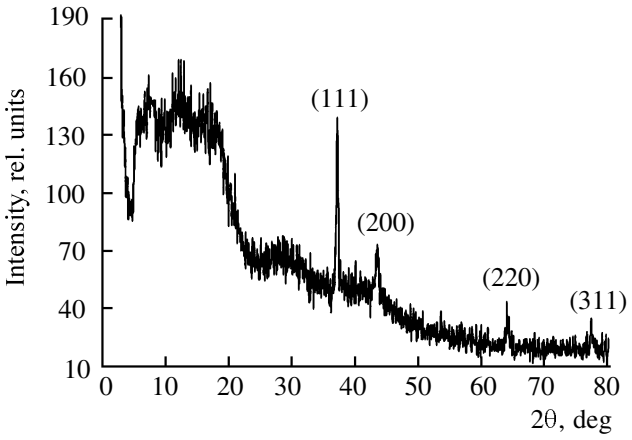

Fig. 6. X-ray diffraction spectrum of the solid residue of polystyrene dispersion containing gold nanoparticles.

The polymer irradiated for 45 min preserves its activity in relation to $HAuCl_4$ for 120 min.

The increase of the concentration of $AuCl_4^-$ ions to 1×10^{-3} M results in the dark formation of smaller particles, as indicated by the shift of the maximum of plasmon bands from 550 up to 535 nm and by the oxidizing action of $AuCl_4^-$ ions on gold particles. According to the electron microscopy data, the average particle size is 25 nm.

Subsequent additional UV irradiation of the systems obtained by dark reduction increases the concentration of gold particles, which is proved by the formation of narrow strong absorption bands. Therewith (Fig. 4), the process rate is higher than the rate of dark reduction in previously irradiated polymer. This fact can be explained by the photochemical reduction of Au(I) ions due to excitation in the region of the ligand-to-metal charge-transfer bands during photolysis by the light with λ_{exc} 254 nm, and also by the presence in the sysem of intermediates and small particles which catalyze formation of metal particles.

$$Au_I^+Cl_2^- \xrightarrow{h\nu} Au^0 + Cl + Cl^-. \quad (7)$$

The position of the plasmon absorption maximum does not vary throughout photolysis, which points to formation of particles of equal size. The optical density reach one unit. Gold particles are formed on the surface of polymer microspheres and in bulk photolyte, and the degree of filling of the surface of polymer microspheres increases in the course of irradiation and subsequent keeping. Upon keeping in the dark for a day almost all particles from the solution are sorbed on the surface of microspheres to form agglomerates (Fig. 5b).

The study of the effect of $HAuCl_4$ concentration showed that the most monodispersed gold particles are formed in a 5×10^{-4} M solution of $HAuCl_4$. The increase of the concentration to 2×10^{-3} M results in formation of polydisperse gold nanoparticles. Particle size increases as the concentration of $AuCl_4^-$ in the photolyte increases, which is confirmed by the bathochromic shift of the plasmon absorption band from 515 nm in 2×10^{-5} M solutions to 550 nm in 2×10^{-3} M solutions. This is caused by the fact that the photochemical reduction of Au(I) ions [reaction (7)] to form nanoparticles occurs in preference to the oxidation of the latter by Au(III) ions [reaction (5)].

The concentration dependence of the rate of colloid formation is analogous to that found earlier for silver [18]: At concentrations lower than 5×10^{-4} and higher than 2×10^{-3} M the rate of photochemical formation of gold nanoparticles decreases, and in the range 5×10^{-4}–2×10^{-3} M it is independent of concentration. It follows from the aforesaid that the most uniform gold particles are formed under additional irradiation of HCl_4 intriduced into irradiated polymer dispersion.

As the size of latex microspheres is increased from 100 up to 1410 nm, the plasmon absorption band shifts bathochromically from 525 to 535 nm, which correlates with increased average size of gold nanoparticles. The average size of gold particles precipitated on polystyrene microspheres of various diameter and the degrees of filling of microsphere surface with gold particles 9%) are presented below.

∅, nm:	100	300	500	1410
r, nm:	20	30	20	35
Degree of filling, %:	25	60	20	65

The optical densities decreased in this case from 0.9 to 0.7 rel. units.

According to X-ray diffraction data, gold particles obtained in aqueous polystyrene dispersions are characterized by a high degree of crystallinity. The presence of a broad maximum at 2θ 15-20° corresponds to an amorphous polymer structure, and the 2θ values of 38, 44.5, 64, and 78° provide evidence for a cubic crystal structure of gold in the points (111), (200), (220), and (311), respectively (Fig. 6).

The dispersions of carboxylated polystyrene with precipitated gold nanoparticles are stable and preserve their optical properties for half a year.

Thus, the developed technique of photochemical precipitation of gold nanoparticles on the surface of polymer microspheres involves initial excitation of the polymer by the UV light and subsequent dark reduc-

tion of $HAuCl_4$. The size of the resulting gold particles and the degree of filling of the polymer surface with them are defined by the duration of preliminary polymer irradiation, the concentration of Au(III) ions in the solution, and the duration of dark reduction.

EXPERIMENTAL

Gold nanoparticles were obtained using analytical grade $HAuCl_4$. All solutions were prepared on the basis of twice-distilled water. Carboxylated polystyrene latexes with microsphere sizes of 100, 300, 500, and 1410 nm were used. The solution of colloidal gold was prepared by the known procedure [19].

Preliminary experiments on the aggregative stability of latex dispersions showed that introduction of $HAuCl_4$ in concentrations exceeding 0.1 M destabilizes the systems, which is evidenced by latex coagulation and sedimentation. To synthesize gold nanoparticles in the presence of latex, $HAuCl_4$ solutions with concentrations from 2×10^{-4} to 2×10^{-2} M were used. The prepared compositions were irradiated by monochromatic light of a TUV 4W/G4 05 Philips mercury lamp (λ_{exc} 254 nm, light flux intensity 4.8×10^{16} quantum cm^{-2} s^{-1}) in quartz cells (l 1 cm). The formation of gold nanostructures was detected spectrophotometrically (SF-2000) by the appearance of characteristic absorption in the range 500–700 nm. The particle size distribution in the bulk latex dispersion was studied by electron microscopy on a Philips CM12 transmission electron microscope (resolution 0.3 nm). The orientation of the axes of crystal textures was determined by X-ray diffraction using a Seifert XRD 3000 TT diffractometer.

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