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Effect of light on the disperse composition of silver hydrosols stabilised by partially decarboxylated polyacrylate

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Spherical silver nanoparticles prepared by the reduction of $AgNO_3$ with sodium borohydride in an aqueous solution of partially decarboxylated poly(acrylic acid) coalesce under exposure to light in the course of additional photoreduction of Ag^+ cations to form coarse non-spherical particles and their aggregates.

High-molecular-weight compounds from various classes are widely used for the stabilization of nanosized metal particles.[1,2] Polyelectrolytes, in particular, poly(acrylic acid) (PAA), occupy a prominent place among them. The polyacrylate (PA) anion can bind metal (*e.g.*, silver[3–5]) cations into complexes and serve as a photoreducing agent[5] and stabiliser of metal clusters and nanoparticles.[4–6] Previously, we found that the participation of PA at all steps of the formation of nanoparticles opens up new opportunities for controlling the particle growth. For example, stable nanosized rods up to 500 nm long were obtained in the photoreduction of Ag^+ in the presence of PA decarboxylated by at least ~30%.[7]

Reasons for changes in the disperse composition of metal sols under the action of radiation of various types were discussed in detail in the literature.[2,8–10] We believe that the formation of nanosized rods, which was observed in the course of photochemical reduction of Ag^+ cations, can also result from light-induced coalescence. The aim of this work was to demonstrate that the ability of PA-stabilised spherical silver nanoparticles to coalesce increases with increasing degree of decarboxylation of the stabilizer polyanion. For this purpose, we studied the action of light on silver hydrosols prepared by the reduction of $AgNO_3$ with sodium borohydride in the presence of PA with different degrees of decarboxylation γ (PA_γ). PA_γ was prepared from PAA (Aldrich, $M_w = 450000$) according to a published procedure.[7] Hydrosols were obtained by adding an excess of $NaBH_4$ (1.2×10^{-3} mol dm^{-3}; Aldrich) to a solution containing $AgNO_3$ (6×10^{-4} mol dm^{-3}) and initial or partially decarboxylated PA (2×10^{-3} mol dm^{-3}; pH 9.0) with intense stirring. Afterwards, the reaction mixtures were allowed to stand for ~10 h until the completion of spectral changes accompanying the formation of nanoparticles and take off their cathodic polarization caused by borohydride-to-silver electron donation.[11]

Figure 1 shows the absorption spectra of the resulting sols stabilised with PA_γ. The occurrence of an intense band at 400 nm in the spectra results from the excitation of surface plasmon resonance of spherical silver nanoparticles. As γ was increased from 0 to 65%, the absorption band maximum shifted to the short-wave region from 420 to 404 nm and the band intensity increased. At a constant silver content of the investigated sols, the former effect could be attributed to a decrease in the nanoparticle size.[8] However, in this case, the adsorption band intensity would decrease rather than increase, as was observed experimentally. In our opinion, the observed spectral changes can be attributed to a decrease in the carboxylate group content of the adsorption layer of PA_γ because similar spectral changes were also observed on the desorption of anions from the surface of silver nanoparticles.[8,11]

Immediately before irradiation, 3×10^{-4} M $AgNO_3$ was added to the prepared sols. Thus, the conditions approached those for the production of elongated silver particles by the photoreduction of Ag^+ in the presence of $PA_{\gamma > 30\%}$, when up to 50% of cations present in the system occurred in equilibrium with the $Ag^+{\cdot}PA_\gamma$ complex.[7] Irradiation in quartz cells ($l = 2$ mm) was performed in air at 20 °C for 30 min. The light source was a 250 W high-pressure mercury lamp. Figure 2 demonstrates the absorption spectra of irradiated sols. A comparison between Figures 1 and 2 shows that, in the cases of $PA_{\gamma = 0\%}$ and $PA_{\gamma = 22\%}$, the addition of $AgNO_3$ followed by irradiation resulted in an increase in the absorption band intensity. In our opinion, this is due to an increase in the volume fraction of nanoparticles upon the photoreduction of Ag^+ ions. The shapes and positions of absorption bands in the spectra of sols with $PA_{\gamma = 0\%}$ and $PA_{\gamma = 22\%}$ (Figure 2, curves *1* and *2*) are indicative of the presence of only isolated spherical particles. In the sols with $PA_{\gamma = 35\%}$ and $PA_{\gamma = 57\%}$ (Figure 2, curves *3* and *4*), the spectral pattern is qualitatively

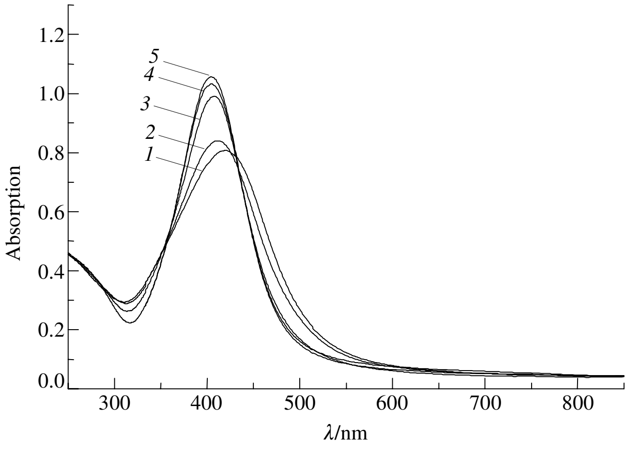

Figure 1 Absorption spectra of silver sols prepared by the reduction of 6×10^{-4} M $AgNO_3$ with 1.2×10^{-3} M $NaBH_4$ in the presence of 2×10^{-3} M PAA with the degrees of decarboxylation equal to (*1*) 0%, (*2*) 22%, (*3*) 35%, (*4*) 57% and (*5*) 65%.

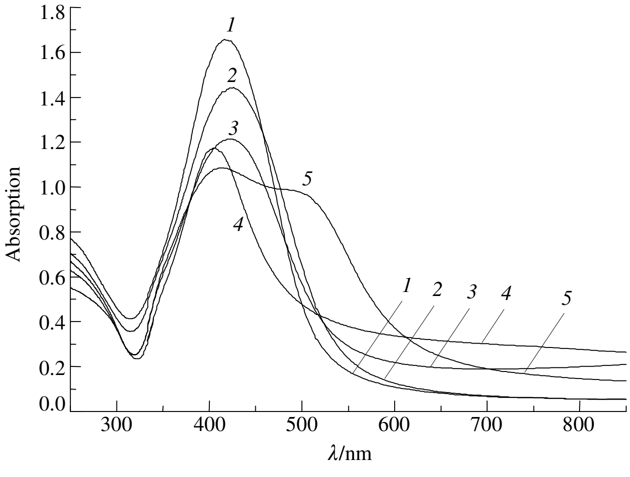

Figure 2 Absorption spectra of silver sols prepared in the presence of PAA with the degrees of decarboxylation equal to (*1*) 0%, (*2*) 22%, (*3*) 35%, (*4*) 57% and (*5*) 65%, after the addition of 3×10^{-4} M $AgNO_3$ followed by irradiation for 30 min.

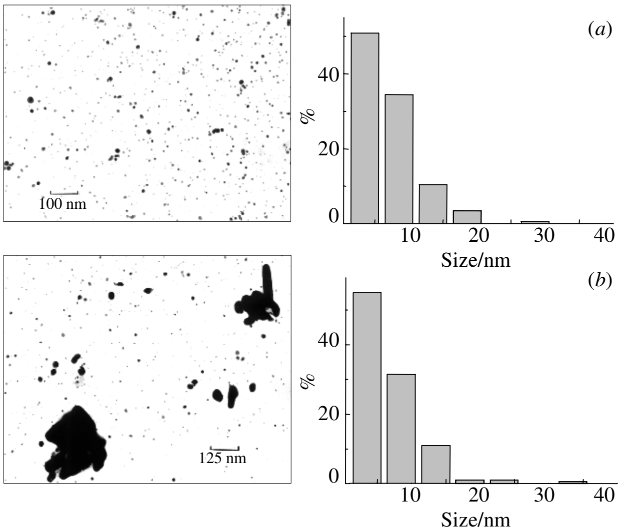

Figure 3 Electron micrographs of silver nanoparticles and the particle-size distribution in sols prepared in the presence of PAA with the degree of decarboxylation 57%: (*a*) initial sol; (*b*) after the addition of 3×10^{-4} M AgNO$_3$ and irradiation for 30 min. For the irradiated sol (*b*), the particle-size distribution corresponds to a fraction of small spherical particles.

changed. The band intensity at ~400 nm insignificantly changed with γ, whereas the absorbance at $\lambda > 600$ nm noticeably increased, which is characteristic, in particular, of systems containing coarse non-spherical particles.[8] The formation of such particles was supported by electron microscopy. As examples, Figure 3 shows micrographs and bar diagrams which characterise the disperse composition of a sol with PA$_{\gamma = 57\%}$ before and after irradiation. It can be seen that in the starting sol [Figure 3(*a*)] the particle shape is close to spherical, and the average particle size is 7±4 nm. Figure 3(*b*) indicates that the irradiation of the sol resulted in the formation of irregularly shaped coarse particles. In this case, the average particle size of coexisting small particles was 7±4 nm, *i.e.*, equal to the particle size of the starting sol, and the particle concentration decreased by ~30%. This approximate evaluation was made by the spectrophotometric analysis of the supernatant obtained after separating coarse particles by the centrifugation of the irradiated sol. The action of light on a sol with PA$_{\gamma = 65\%}$ (Figure 2, curve *5*), in addition to an increase in absorption at $\lambda > 600$ nm, resulted in the appearance of a shoulder at ~500 nm in the spectrum; this shoulder is indicative of the coagulation of particles.[8]

Thus, we found that the ability of silver nanoparticles stabilised with PA to coalesce under exposure to light appears at the degrees of decarboxylation of the polyanion higher than ~30%. It manifests itself only upon additional photoreduction of added Ag$^+$ ions. In the absence of the additive, the disperse composition of irradiated sols remained almost unaffected. Note that the threshold degree of decarboxylation is consistent with the value found previously in the single-step photochemical synthesis of nanosized rods.[7]

In the general case, it is essential for coalescence that, first, particles should come within short distances of each other at which attractive forces are greater than repulsive forces and, second, firmly bonded surface layers that hinder close contacts between particles should be absent.[8,12] In this context, let us consider the roles of Ag$^+$ cations, PA decarboxylation, and light. At a pre-irradiation stage, the bonding of added Ag$^+$ ions to PA would decrease the total negative charge of the polyanion and hence weaken the electrostatic repulsion of particles coated with an adsorption layer of PA. The ability of Ag$^+$ ions to form cationic cross-linking bridges between PA[3] suggests the appearance of PA-coated particle microaggregates, which can serve as the centres of subsequent condensation.[10] Under exposure to light, the mutual attraction of silver particles will increase because of the enhancement of the dipole–dipole interaction between them[9] and (or) electron photoemission from the metal, which can result in the generation of oppositely charged particles.[10] It is evident that the effective photoreduction of added Ag$^+$ cations, which results in the additional formation of silver and in a decrease in the stabiliser-to-metal ratio, is responsible for an additional decrease in the stability of particles. The consumption of carboxylate groups[13] in the course of photoreduction weakens the interaction of PA with the surface of nanoparticles[14,15] and the electrostatic repulsion of adsorption layers. The above factors result in the approach and close contacts between particles and in coalescence.

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