

Interaction of Silver Nanoparticles with Ozone in Aqueous Solution

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Abstract—The interaction between ozone and silver nanoparticles stabilized with sodium polyphosphate is studied in aqueous solutions. The process of ozone decomposition is established to have a chain character. The oxidation of one silver atom initiates the decomposition of about three ozone molecules. The stability of colloidal silver decreases upon the oxidation, which leads to its partial aggregation.

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INTRODUCTION

It is known that, because ozone is a strong oxidizer, it actively interacts with organic and inorganic substances in aqueous solutions. The efficiency of its practical application, which is significantly limited by the selectivity of corresponding reactions, may be enhanced by using catalysts of ozone decomposition, which yields hydroxyl radicals that, in turn, are nonselective and more efficient oxidizers. These catalysts comprise both water soluble substances (transition metal ions [1, 2] and hydrogen peroxide [3, 4]), which enable one to implement homogeneous catalytic processes, and solid catalysts (activated carbon [5], transition metal oxides [6, 7], etc.).

The mechanism of ozone decomposition in aqueous colloidal solutions of metals draws much interest. In this process, nanoparticles can be oxidized with ozone and/or initiate the chain process of its decomposition. In this case, the selection of an object for study is of principle importance because nanoparticles of chemically reactive metals (copper, cadmium, etc.) are oxidized even by oxygen [8, 9], which results from ozone decomposition or is introduced into a solution with an ozone–oxygen gaseous mixture. Moreover, the production of stable colloidal solutions of metal nanoparticles implies the use of stabilizers (surfactants), the majority of which are organic compounds that actively interact with ozone.

This work is devoted to investigating the interaction of ozone with silver nanoparticles in aqueous solutions. This system satisfies the aforementioned requirements imposed on the objects of the study; these nanoparticles are resistive to oxygen, while polyphosphate, which is used as their stabilizer, is not oxidizable with ozone.

EXPERIMENTAL

Ozone was obtained in an ozonizer equipped with a capillary discharge chamber (OOO LOT), which

produces an ozone–oxygen mixture (OOM), in which ozone concentration is regulated over a range of 5–180 mg/l. The concentration of O_3 in the gaseous mixture was determined with a Medozon-254/5 detector. Silver colloidal solution was prepared by reducing 1×10^{-4} M $AgClO_4$ (Aldrich) with molecular hydrogen in the presence of 1×10^{-3} M sodium polyphosphate (extra-pure grade) with an average molecular mass of 2100 g/mol as a stabilizer of nanoparticles being formed. Silver nanoparticles were oxidized by OOM bubbling through a 100-ml thermostated cell under stirring at $20.0 \pm 0.2^\circ C$; the flow rate of the gaseous mixture was 0.1–0.5 ml/s, and ozone concentration was 5–10 mg/l. Before the experiments, residual hydrogen was removed from the solutions by deaeration, which was followed by saturation with air. The optical spectra of periodically taken samples were measured with a Cary Varian 50 spectrophotometer.

The size characteristics of nanoparticles were determined using a Philips EM 301 transmission electron microscope (TEM) operating at an accelerating voltage of 100 keV. Copper grids, which were coated with a thin carbon film by thermal deposition, were applied as substrates. The examined nanoparticle-containing solutions were applied onto the substrates and dried in vacuum.

Micrographs of nanoparticles taken with TEM were processed with the help of a personal computer employing the Origin 7.5 software package (Originlab) and the ImageJ program (Broken Symmetry Software). The particle sizes, size distributions, and the character of the distributions were determined from the micrographs using the statistical applications of these programs.

RESULTS AND DISCUSSION

Figure 1 demonstrates the optical absorption spectrum of colloidal silver obtained by reducing silver ions with hydrogen in a neutral medium [10] and its disap-

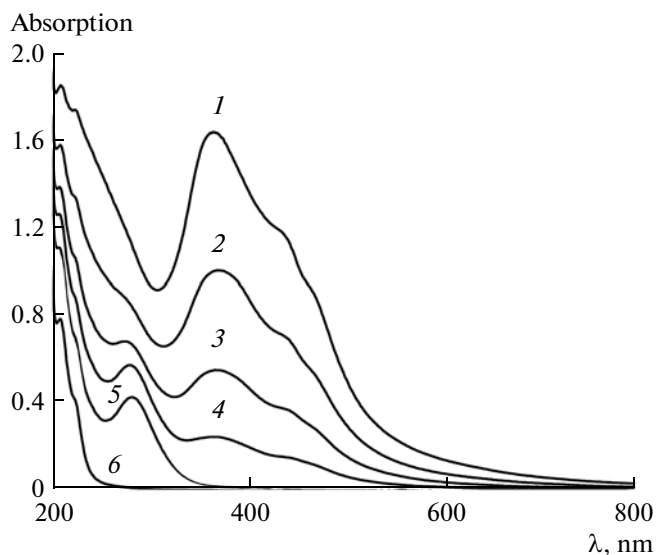


Fig. 1. Variations in the absorption spectrum of silver nanoparticles during their oxidation with OOM: (1) initial absorption spectrum and (2–6) spectra measured 10, 20, 30, 50, and 90 min after the onset of OOM bubbling, respectively; initial solution composition is AgClO_4 , 1×10^{-4} M and sodium polyphosphate, 1×10^{-3} M; volume flow rate of OOM is 0.25 ml/s; $[\text{O}_3] = 6$ mg/l.

pearance during OOM bubbling. The absorption with a maximum at 380 nm corresponds to the plasmon absorption of silver nanoparticles. The broadening of the spectrum in a range of 420–480 nm is explained by the presence of silver nanoparticles of different shapes [10]. In the course of the solution ozonolysis, the optical density uniformly diminishes in a range of 350–800 nm, which indicates that the oxidation rate of silver nanoparticles is almost independent of their size and shape. The composition and flow rate of OOM were selected such that ozone traces were not detected at the outlet of the mixing reactor to ensure its complete decomposition during the interaction with silver nanoparticles.

Silver nanoparticle oxidation, which is judged by the decrease in the absorption, is accompanied by the appearance of a new band with a maximum at $\lambda = 280$ nm (Fig. 1, curves 3–5), which declines at a noticeably lower rate, as compared with the absorption assigned to silver nanoparticles, and is relatively stable in the spectrum of the solution after the latter disappears. The nature of the product corresponding to the band at 280 nm remains as yet unclear. It may be assumed to be poorly soluble Ag_2O and/or AgO particles, which are slowly dissolved as the solution is further saturated with OOM.

If a solution that occurs at an intermediate stage of silver nanoparticle oxidation is kept in vacuum at room temperature, its optical properties remain almost unchanged for several days. Moreover, it was established (see Fig. 2) that the absorption intensity of

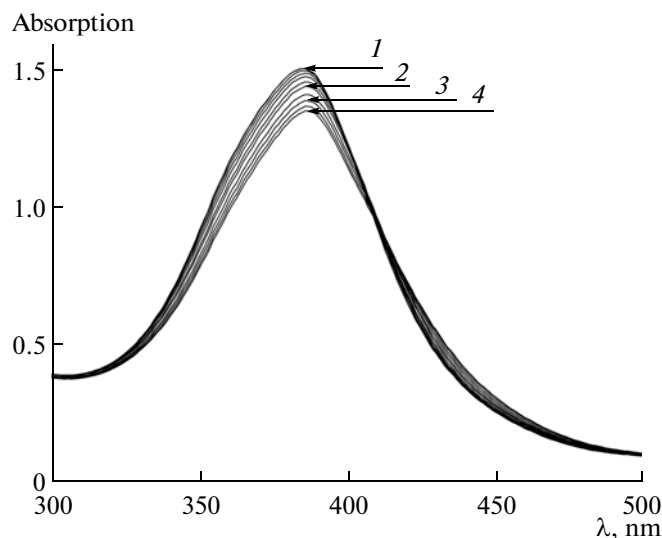


Fig. 2. Variations in absorption spectrum of silver nanoparticles in an aqueous solution with the duration of oxygen bubbling: (1) 0, (2) 1, (3) 2, and (4) 3 h; initial solution composition is AgClO_4 , 1×10^{-4} M and sodium polyphosphate, 1×10^{-3} M; volume flow rate of O_2 is 1.0 ml/s.

silver nanoparticles present in an aqueous solution bubbled with oxygen for 3 h decreases insignificantly (by 10–15%). In this case, the band somewhat shifts toward longer wavelengths (from 380 to approximately 390 nm, while the isobestic point is observed at 415 nm). This change in the absorption results from the sorption of oxygen on the surface of nanoparticles and a corresponding decline in the electron gas density [11]. Thus, it may be concluded that, during the oxidation of silver nanoparticles with OOM (the time of ozonolysis is 60 min) the effect of oxygen is insubstantial and silver nanoparticles are oxidized namely with ozone.

Extinction coefficient related to one Ag^0 atom, which appeared to be nearly $1.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, was calculated from the optical density of a silver colloidal solution at a wavelength of 380 nm after the complete reduction of 1×10^4 M Ag^+ ions (see Fig. 1). The stoichiometric ratio between the amounts of oxidized colloidal silver and consumed ozone was found by measuring silver concentrations in the course of nanoparticle oxidation with ozone. It was established that the stoichiometric ratio $\Delta_{\text{st}} = [\text{O}_3]/[\text{Ag}^0]$ is independent of the initial concentration of Ag^0 and equal to $\Delta_{\text{st}} = 2.8 \pm 0.3$ (see Fig. 3); i.e., the oxidation of one silver atom initiates the decomposition of about three ozone molecules. This finding shows that the decomposition of ozone has a chain character.

The addition of *tert*-butyl alcohol, which slowly interacts with ozone and is an efficient acceptor of hydroxyl radicals ($k = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [12], which are

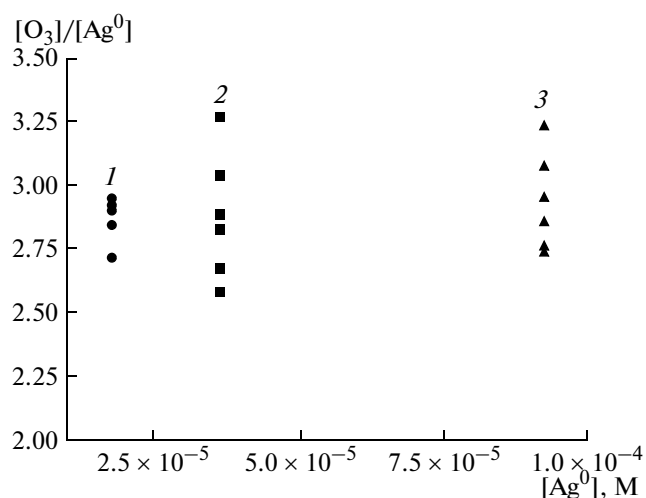
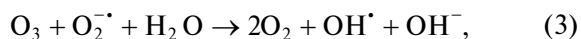
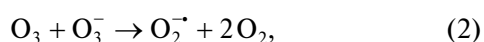


Fig. 3. Stoichiometric ratios between oxidized silver atoms and decomposed ozone molecules at different initial Ag^0 nanoparticle concentrations: (1) 1.8×10^{-5} , (2) 3.6×10^{-5} , and (3) 9.2×10^{-5} M.

the main intermediate products of ozone decomposition in aqueous media, to the initial solution does not decrease Δ_{st} . This fact unambiguously indicates that hydroxyl radicals are not involved in the development of the chain decomposition of ozone. In our opinion, the mechanism of the ozone–silver interaction comprises the following reactions of chain initiation and propagation:



as well as the following chain termination reaction:



According to the scheme proposed for the ozone–silver interaction, one event of silver atom oxidation initiates subsequent decomposition of three ozone molecules, which corresponds to the experimental observations.

Metal nanoparticles obtained by reducing silver ions and then subjected to oxidation with ozone were examined by TEM. The data on the particle size distribution are presented in Fig. 4. Nanoparticles resulting from the reduction of silver ions are spherical and have an average diameter of about 9.1 nm. When nanoparticles interact with ozone, which is bubbled through a colloidal solution, the sizes of nanoparticles gradually increase. After ozone bubbling for 10 and 30 min, the average particle diameter enlarged from $9.1 \pm$

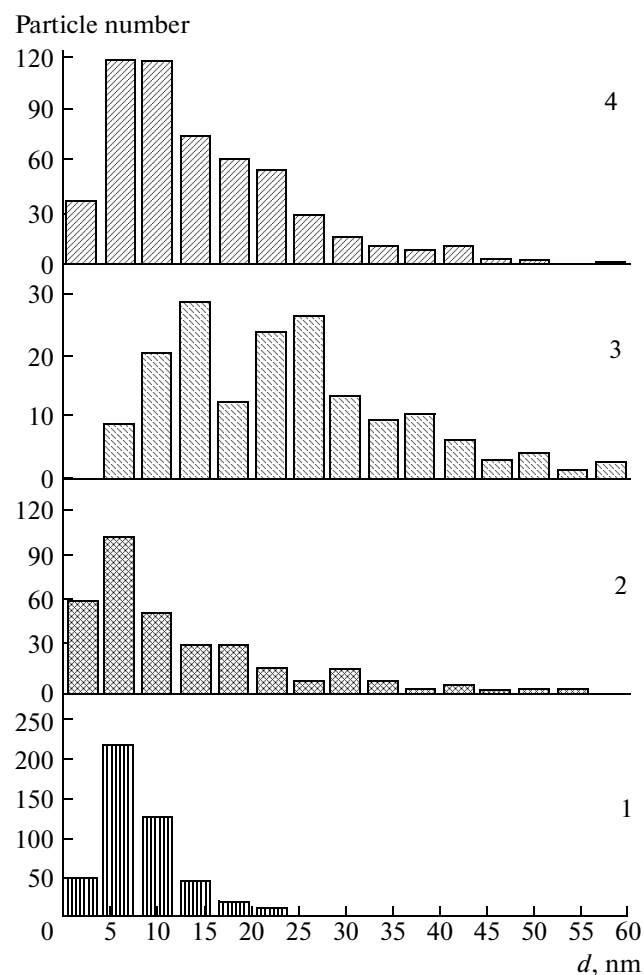


Fig. 4. Variations in the size distribution of silver nanoparticles during their oxidation with ozone: (1) before OOM bubbling and (2–4) 10, 30, and 50 min after the onset of OOM bubbling, respectively; distribution (4) refers to the fraction of small particles alone; initial solution composition is the same as in Fig. 1.

0.3 to 17.7 ± 1.5 and 24.4 ± 1.0 nm, respectively (Fig. 4, distributions 1–3). These results testify that, while silver nanoparticles are oxidized, they lose aggregation stability and enlarge. At the final stage of oxidation, large silver agglomerates are formed, among which branched structures are observed with characteristic sizes on the order of several micrometers (Figs 5a–5c). However, along with the latter, small spherical silver particles are also present (Fig. 5d); their average size is 16.6 ± 0.8 nm, i.e., the size distribution for the fraction of small silver particles turns out to be close to the particle size distribution observed at the previous stages of colloidal silver treatment with ozone (compare distributions 2, 3, and 4 in Fig. 4).

An increase in the average size of silver nanoparticles was observed upon the interaction with ozone in both the absence and presence of gelatin, which was

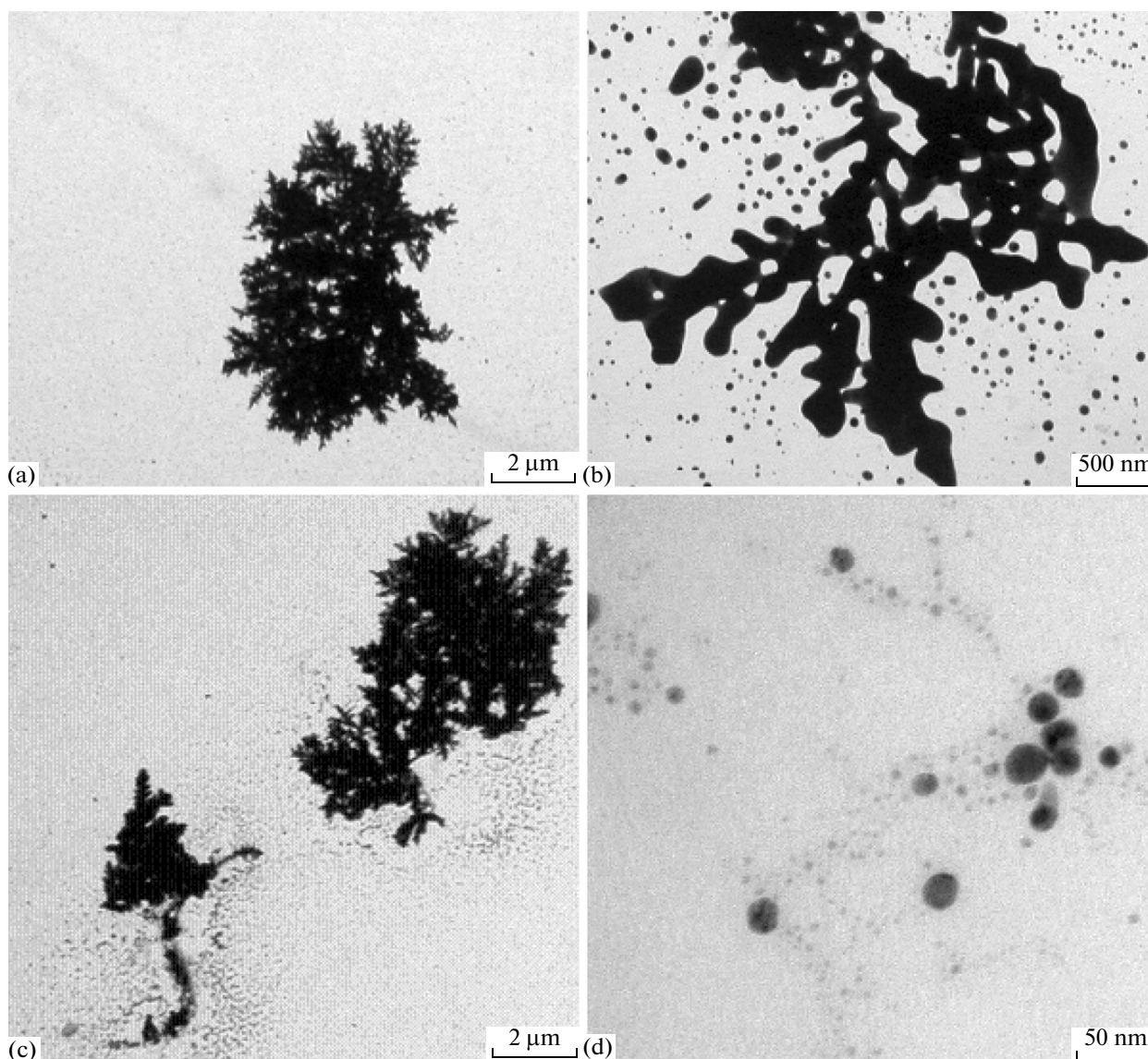


Fig. 5. TEM images of silver nanoparticles after 50-min oxidation with ozone in an aqueous colloidal solution. Initial solution composition is the same as in Fig. 1.

applied as a stabilizer [13]. However, in the cited work, ozone was not directly introduced into a solution, but rather diffused through an interface. The loss of the aggregation stability of colloidal silver upon its interaction with ozone seems to be caused by the oxidation of metal nanoparticle surface and a decrease in the stabilizing effect of polyphosphate. Thus, ozone oxidizes colloidal silver stabilized with polyphosphate in an aqueous solution. The process is of a chain character, and the oxidation of one silver atom initiates the decomposition of three ozone molecules. During oxidation, the stability of colloidal silver diminishes, which leads to its partial aggregation.

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