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Atomic luminescence of Ag during single-bubble sonolysis of silver nanoparticles aqueous suspension

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For the first time, luminescence of Ag atoms was recorded during moving single-bubble sonolysis of silver nanoparticles aqueous colloidal suspension. This glow is caused by the entry of nanoparticles into a bubble deformable during motion and their decomposition to atoms with collisional excitation in the nonequilibrium plasma of the bubble. Nanoparticles were obtained by multibubble sonolysis of an $AgNO_3$ solution with the addition of honey. This method was used to synthesize a stable suspension of Ag nanoparticles with an average size of ~ 10 nm. By comparing the experimental spectrum of this suspension and simulated spectra of Ag, the electron temperature in the bubble plasma was found to be $\sim 10\,000$ K.

Keywords: single-bubble sonoluminescence, silver nanoparticles, electron plasma temperature.

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The vigorous motion of cavitation bubbles produced in liquids under ultrasonic irradiation leads to injection of micro- and nanodroplets of liquid into these bubbles. Dissolved nonvolatile compounds contained in droplets also enter the bubbles [1]. This is the reason why luminescence of atoms, ions, and molecules was observed in the process of sonolysis of solutions of semivolatile compounds. Among these are salts of alkaline and alkaline-earth metals (Na, Mg, K, Li, Ca, Mn, Ba) [2–6], lanthanide ions Ln^{3+} (Ln = Gd, Tb, Dy) [7,8], uranyl (UO_2^{2+}) [9], and polyaromatic luminophores [10]. Volatile carbonyl complexes of transition metals ($Me(CO)_n$, Me = Fe, Mo, Cr, W) enter bubbles via simple evaporation from the liquid–gas interface and also yield atomic metal luminescence [11]. These cases of sonoluminescence are attributable to the formation of inequilibrium plasma in gas-vapor cavitation bubbles under acoustic oscillations [12]. Collisional electron excitation in plasma subsequently induces luminescence of ionic [7–9] or molecular organic luminophores [11] and atoms of metals that are produced as a result of thermal decomposition of compounds of these metals [2–6,10].

The detection of characteristic emission lines or bands of various substances in sonoluminescence spectra allows one to identify these substances, find intensifying and quenching additives by examining their influence on the intensity of spectra, and analyze plasma-chemical processes in cavitation bubbles. It has been demonstrated recently that this sonoluminescence spectroscopy may be performed both in solutions and in fine suspensions of insoluble substances. If nanoparticles of these substances in suspensions are sufficiently small, they enter moving bubbles without disrupting them. This was confirmed in experiments with colloidal suspensions of chromium carbonyl nanoparticles (less than 50 nm in size) in water and inorganic acids and suspensions of porous SiO_2 nanoparticles saturated with ruthenium dodecacarbonyl and elemental sulfur. Molecular SiO lines and atomic Cr, Ru, or S lines were observed in moving single-bubble sonoluminescence (MSBS) spectra of these suspensions [12,13].

In order to expand the range of spectroscopically studied insoluble substances involved in bubble plasma-chemical reactions, we examined the sonoluminescence of a colloidal suspension of silver nanoparticles that was prepared by reducing silver nitrate in an aqueous solution.

A number of ways to perform this procedure with the use of different organic compounds as reducers, which produce suspensions of nanoparticles 2–100 nm in size, are known [14–16]. The method of reduction with natural honey [16] turned out to be the best suited for synthesis of a suspension with aggregation-resistant nanoparticles less than 50 nm in size that is transparent to luminescence emission. In accordance with this method, 20 ml of an $AgNO_3$ (chemically pure, 50 mmol) solution were mixed with 20 ml of a 10% aqueous solution of natural honey. This mixture was subjected to ultrasonic dispersion, which was performed using a UZDN-2T (22 kHz, 20 W) setup for 45 min, and a nanoparticle suspension was prepared. The obtained nanoparticles were separated by centrifuging, and rinsed five times with bidistilled water (40 ml) to remove the residual unreacted mixture. This rinsing prevented the penetration of soluble honey components into a suspension of silver nanoparticles. Since the concentration of insoluble components (metal sols included) in honey does not exceed 0.17% [17], the overall content of nanoparticles of other metals, which are potentially produced in synthesis, may be estimated at less than 2% of the content of silver nanoparticles. Thus, the possible influence of unstandard-

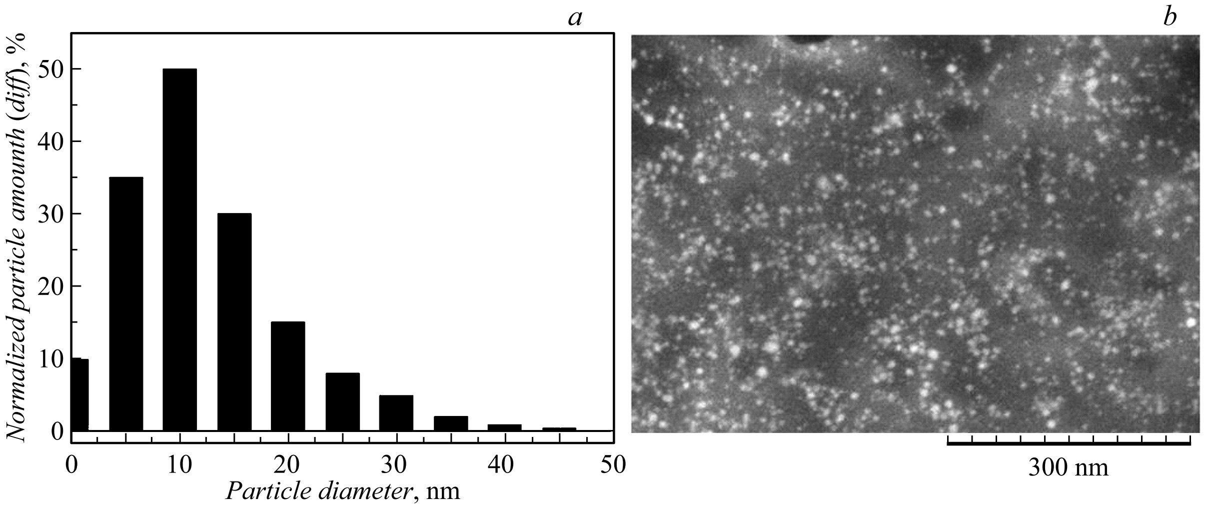

Figure 1. Morphological characteristics of silver nanoparticles. *a* — Size distribution of synthesized nanoparticles in an aqueous suspension (determined by photon cross-correlation spectroscopy performed using a Nanophox instrument); *b* — nanoparticles on a solid substrate imaged with a Hitachi SU8000 scanning electron microscope.

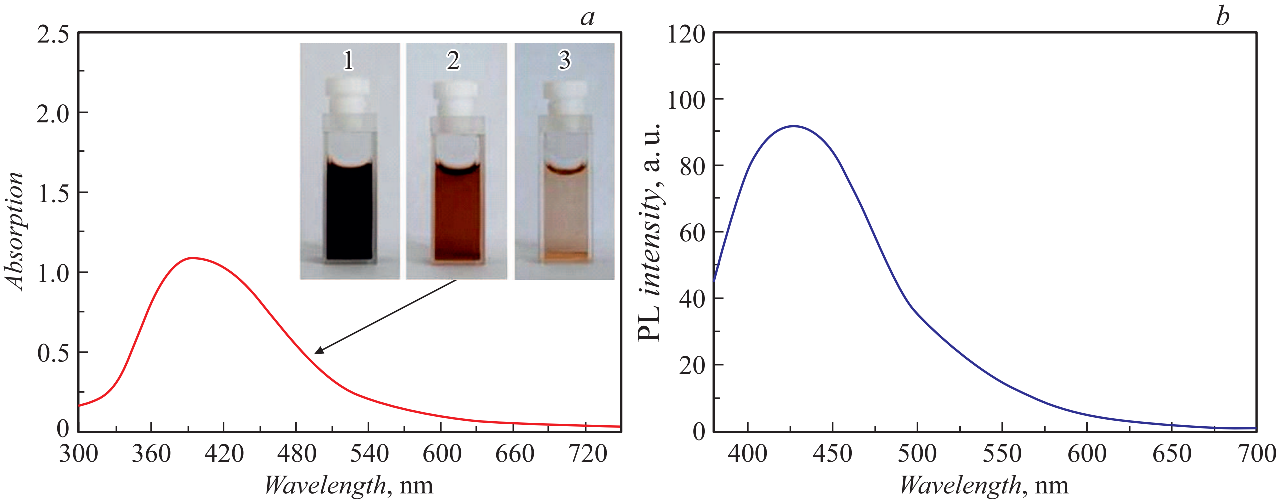

Figure 2. Optical characteristics of silver nanoparticles. *a* — Absorption spectrum (Shimadzu SU 1800, $l = 1$ cm); *b* — photoluminescence spectrum of sample No. 2 (Fluorolog 3, $\lambda_{ex} = 360$ nm).

ized composition of honey on the data presented below is reduced to a minimum.

Figures 1, *a* and *b* show the size distribution of synthesized silver nanoparticles in one suspension and the image of these nanoparticles on a dry substrate. It can be seen that nanoparticles are uniform in size and reveal no signs of aggregation. Introduced into water (40 ml), these nanoparticles form a strongly colored dark brown suspension (sample No. 1, inset of Fig. 2, *a*). This suspension was diluted with water by a factor up to 25 to record sonoluminescence spectra (samples Nos. 2, 3, inset of Fig. 2, *a*). The absorption and photoluminescence spectra of a suspension of silver nanoparticles diluted by a factor of 5 (sample No. 2) are shown in Figs. 2, *a* and *b*, respectively. The equipment specified in [12] was used to excite stationary single-bubble sonoluminescence (SSBS) and MSBS in a suspension of silver nanoparticles with an average size of 10 nm. A standing wave was excited at a frequency of ~ 27 kHz by piezoelectric transducers in a spherical flask 57 mm in diameter filled with the prepared suspension. Light from a bubble was transferred via a quartz waveguide 0.2 mm in diameter to the entrance slit of an MDR-206 scanning monochromator. The entrance end of the waveguide was located at a distance of 3 mm from a bubble. The emission of a stationary bubble was observed under an acoustic pressure of 1.2 bar at the flask center, while the pressure in experiments with a moving bubble, which deviated from the flask center by no more than 0.6 mm, was 1.32 bar. Figure 3, *a* presents the high-resolution MSBS spectrum ($\Delta\lambda = 0.9$ nm). It features

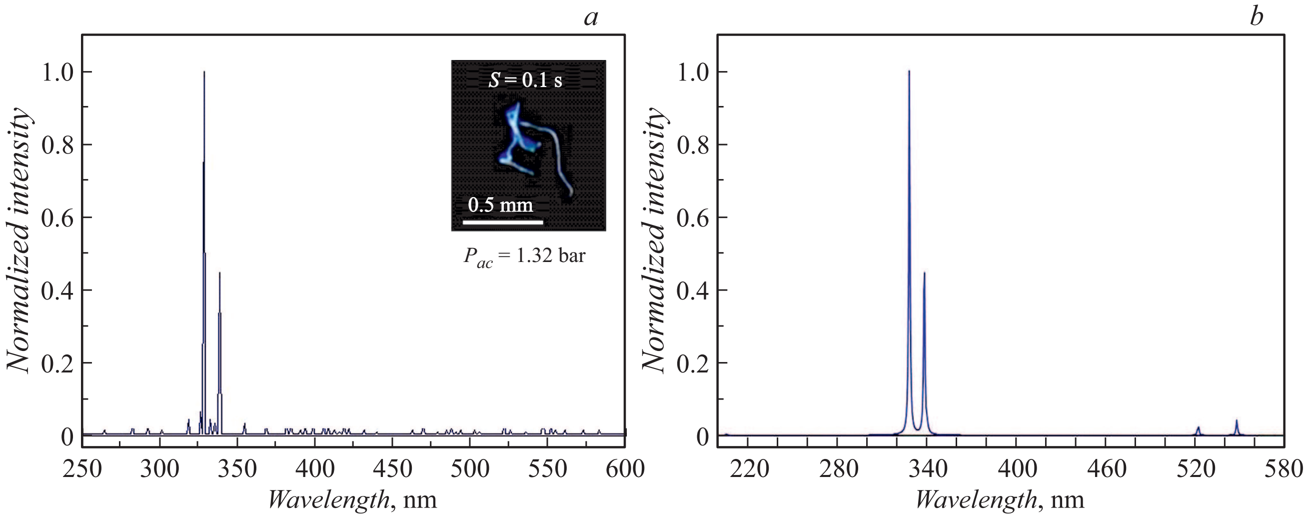

Figure 3. *a* — Photographic image (inset) and MSBS spectrum of an aqueous solution of silver nanoparticles; *b* — simulated spectrum of atomic silver at $T = 10\,000$ K.

intense lines at 328 and 338 nm and a number of less intense lines (520 nm, 546 nm, etc.) that are identified unambiguously as emission lines of atomic silver [18]. In the SSBS mode, a bubble emits light, but atomic lines are not observed in the high-resolution spectrum. The only thing found in the low-resolution spectrum ($\Delta\lambda = 5-10$ nm) is the well-known [1] structureless wideband continuum of the bubble plasma emission in water (not shown here). These continua are the same for SSBS and MSBS.

The electron temperature in the bubble plasma [12] may be determined by comparing the ratios of intensities of various atomic lines in experimental (Fig. 3, *a*) and simulated spectra. In order to find the best-fit temperature value, we used an Excel-based computer program [19] to simulate spectra of atomic silver at temperatures ranging from 1000 to 15 000 K. Figure 3, *b* presents the simulated spectrum for 10 000 K. It follows from a comparison of Figs. 3, *a* and *b* that the simulated spectrum reproduces almost perfectly the experimental one. The obtained result agrees with the values of electron temperature (9500–10 000 K) determined for MSBS of aqueous suspensions of chromium and ruthenium carbonyls [12,13].

Thus, atomic Ag luminescence has been detected for the first time in moving single-bubble sonoluminescence studies of aqueous suspensions of silver nanoparticles. The obtained result confirms that insoluble nanoparticles penetrate into sonogenerated bubbles and verifies the applicability of colloidal suspensions in sonoluminescence spectroscopy of such objects.

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Conflict of interest

The authors declare that they have no conflict of interest.

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