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Bacterial Synthesis of Silver Sulfide Nanoparticles

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Abstract—The metal-reducing bacterium *Shewanella oneidensis* MR-1 has been employed to obtain Ag_2S nanoparticles from an aqueous solution of $AgNO_3$ and $Na_2S_2O_3$ at an ordinary temperature and pressure. The nanoparticles vary in size within 2–16 nm, and the fraction 6 to 12 nm in size constitutes about 70%. The maximum yield of nanoparticles in silver equivalent is 53%. Being visualized by transmission electron microscopy, the particles look like spheres with average diameters varying from 7 ± 2 nm to 9 ± 2 nm. The elemental composition of synthesized nanoparticles has been analyzed by energy-dispersive X-ray spectroscopy, and the estimated silver to sulfur atomic ratio is 2 : 1. The presence of living bacterial cells is mandatory for the formation of Ag_2S nanoparticles in the aqueous salt solution. Changes in the reaction conditions (reagent concentrations, temperature, and cell-incubation time in the reaction mixture) influence the yield of nanoparticles dramatically, but have little influence on their size.

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INTRODUCTION

Silver sulfide nanoparticles possess unique semiconducting, optical, and electrical properties and are highly stable. Owing to these features, they are broadly used in solar-cell batteries [1], thermoelectric sensors, etc. [2]. The recently obtained Ag_2S/graphene nanocomposite is promising for the development of supercapacitors [3]. The great potential of practical applications of Ag_2S nanoparticles brought into existence numerous protocols for their preparation. The thermolysis of silver xanthates with long aliphatic chains at 200°C brings about egg-shaped particles with a narrow range of sizes [4]. Rod-shaped Ag_2S nanocrystals have been obtained from silver nitrate and thioacetamide [5]. Leaf-shaped Ag_2S nanolayers can be produced by autoclaving an ethanol solution of silver nitrate and carbon disulfide at 160°C [6].

We consider only methods for the preparation of Ag_2S nanoparticles from aqueous solutions not requiring high temperatures. The simple mixing of silver salt solutions with sodium or ammonium sulfides yields aggregated irregularly shaped crystals [7]. Egg-shaped Ag_2S nanoparticles can be obtained by mixing $AgNO_3$ and Na_2S with the presence of 1-thioglycerol under strictly anoxic conditions [8]. Unfortunately, their size distribution is not reported. Nanoparticles Ag_2S 25–50 nm in size have been obtained by reaction of aqueous $[Ag(NH_3)_2]^+$ with thioacetamide with the presence of in-house prepared surfactant 2-undecyl-1-dithioureido-ethyl-imidazoline (SUDEI) [9]. The reaction of $AgNO_3$ with thioacetamide with the presence of denatured bovine albumin yields Ag_2S nanoparticles 65 nm in size [10].

An alternative approach to nanoparticle production under mild conditions can be a biotechnological process with microbial cells [11]. Common requirements imposed on nanoparticles include reproducibility, narrow shape and size distribution, stability (the absence of aggregation), a simple protocol, and the absence of toxic substances. Many of these parameters are inherent in the biotechnological nanoparticle industry.

Bacteria of the genus *Shewanella* are commonly used in the preparation of nanoparticles of metals, oxides, and sulfides. These bacteria can reduce many substances, including metal oxides, nitrates, sulfates, etc. They have been employed in the synthesis of gold nanoparticles [12], arsenic sulfide nanotubes [13], and uranium dioxide nanoparticles [14]. The preparation of Ag_2S nanoparticles in a solution of $AgNO_3$ and sodium thiosulfate with *Shewanella* is described in [15]. The authors of the referred study obtained Ag_2S nanoparticles with a narrow size range (9.0 ± 3.5 nm) in a very simple process with nontoxic reagents in aqueous solutions at a low temperature under aerobic conditions.

In this work we study the effect of reaction conditions on the yield and size of Ag_2S nanoparticles pro-

Silver sulfide nanoparticles

Sample no.	Reaction parameters and yield of Ag_2S nanoparticles			
	Salt concentrations in the reaction mixture $AgNO_3 : Na_2S_2O_3$, mM	Temperature of cell incubation in the reaction mixture, °C	Incubation time, h	Nanoparticle yield in Ag equivalent, %
1	1 : 1	24	96	53.7
2	1 : 1	24	48	17.3
3	2 : 2	24	96	20.4
4	1 : 1	30	48	38.5
5	1 : 1	37	24	8.0
6	1 : 1	37	48	12.2
7	1 : 1, cells inactivated by heating	30	72	–
8	1 : 1, no cells (control)	24	96	–

duced by *Shewanella oneidensis* MR-1 bacteria in an aqueous solution of $AgNO_3$ and $Na_2S_2O_3$. The conditions tested are temperature, reagent concentrations, time of microbial cell incubation in the reaction mixture, and presence of living or inactivated cells.

MATERIALS AND METHODS

Shewanella oneidensis MR-1 bacteria were received by the Russian National Collection of Industrial Microorganisms (VKPM), GosNIIGenetika, from the collection of microorganisms of Institut Pasteur, France, accession CIP106686.

The strain was grown in a Luria–Bertani agar medium (LBA) at 30°C for 24 h. Individual colonies were picked from LBA, inoculated to 100 mL of LB broth in a 750-mL flask, and stirred in an orbital shaker at 30°C and 220 rpm for 18 h. Cells were harvested by centrifugation at 6000 rpm for 20 min, washed twice with sterile Milli-Q water, and resuspended in 2 mL of Milli-Q water. The titer of living cells was determined by inoculating serial dilutions of cells onto LBA. The optical density of the cell suspension was also measured. One milliliter of the suspension was transferred into a 750-mL flask with 100 mL of aqueous 1 mM $AgNO_3$ and $Na_2S_2O_3$ 1 mM. The mixture was incubated in an orbital shaker at 30°C and 220 rpm for 48 h. Cells were centrifuged as above, and the supernatant was filtered through a sterile Nucleopore filter 0.2 μm. Nanoparticles were sedimented from the filtered supernatant by high-speed centrifugation at 100000 g (that is, at the gravity 100000 times as large as terrestrial gravity) for 1 h and washed twice with Milli-Q water with centrifugation under the same conditions. The control experiment was done with the same 1 mM $AgNO_3$ and $Na_2S_2O_3$ 1 mM solution without the addition of microbial cells. With this exception, all manipulations with the control sample were the same.

The experimental conditions reported in [15] were supplemented in our study: temperature (24 and 37°C), reagent concentrations (2 mM $AgNO_3$ and 2 mM $Na_2S_2O_3$), incubation time of *Shewanella* cells in the reaction mixture (24, 72, or 96 h), and the presence of living or inactivated cells.

The yield of Ag_2S nanoparticles was determined gravimetrically. Here we present a calculation of the nanoparticle yield in silver equivalent in Sample 1 as an example. Sample 8 is the control experiment without cells. A volume of 100 mL of 1 mM $AgNO_3$ was taken for each sample in the experiment. The volume of each nanoparticle sample obtained after the last high-speed centrifugation was 2.0 mL. One hundred microliters of nanoparticle suspensions from samples 1 and 8 (Table 1) were placed onto completely desiccated cover glasses, dried to constant weight, and weighed. The measurement was done in triplicate for each sample. The difference between the mean values for the experimental and control samples was 0.32 mg. This weight of Ag_2S contains 0.29 mg of Ag. Hence, the 2 ml of the Ag_2S nanoparticle suspension contains 5.8 mg of silver. Because we took 100 mL of 1 mM $AgNO_3$ solution, the total amount of the silver involved in the experiment was 10.8 mg. Thus, the yield of nanoparticles in silver equivalent was 53.7%.

The thermal inactivation of living *S. oneidensis* MR-1 cells was done by a single heating of cell suspension in a water bath at 50°C for 40 min. The cell titer in the starting suspension was 1.5×10^8 cfu/mL. The survival of heat-inactivated cells was tested by inoculation on an LBA. All cells died under these conditions.

The suspension was tested for the presence of Ag_2S nanoparticles by transmission electron microscopy (TEM). To analyze the elemental composition, TEM was combined with energy-dispersive X-ray spectroscopy (EDS). The ED spectra were recorded from a cluster of nanoparticles and from a site with particles.

Samples for TEM were completed as follows: 3 μL of a suspension were loaded onto a copper grid with a holey carbon support covered by an ultrathin carbon layer (Ted Pella Inc, United States). After 30-s incubation, the excess of the liquid was removed with a filter paper and the grids were dried.

The local elemental analysis of nanoparticles was done by EDS with scanning transmission electron microscopy (STEM). An individual particle was scanned with an electron beam about 1–5 nm in diameter.

Measurements were done with a JEM2100 transmission electron microscope with a lanthanum hexaboride (LaB_6) cathode (JEOl, Japan) equipped with an X-Max detector controlled by INCA software (Oxford Instruments, United Kingdom). The accelerating voltage was 200 kV. Energy-dispersive spectra were recorded from clusters of particles and individual particles in the range from 0 to 10 keV.

Particle sizes were analyzed with Image J software by measuring the least linear size of particles in TEM images. About 100 particles were measured for each sample. Bar graphs of the particle size distribution were constructed with Origin 8.5.

RESULTS AND DISCUSSION

Eight silver sulfide nanoparticles samples were obtained by microbial synthesis in an $AgNO_3$ and $Na_2S_2O_3$ solution with the *S. oneidensis* MR-1 metal-reducing electrogenic bacterium. The samples differed in synthesis conditions (Table 1).

It is known that *S. oneidensis* MR-1 can live in a broad temperature range, from 15 to 45°C. The optimum range for the common production of their biomass is 25–30°C. The same temperature is favorable for the bacterium-mediated reduction of metal salts. For example, it is optimal for the reduction of Cr(VI) cells by *S. oneidensis* MR-1 [16]. However, this strain shows reduction ability at lower temperatures as well. It successfully reduces graphene oxide to graphene at room temperature [17]. No comparative analysis of the efficiency of nanoparticle production by *S. oneidensis* MR-1 at various temperatures has been done hitherto. It became one of the objectives of the present study. Our results shown in Table 1 demonstrate a correlation between the temperature of reaction-mixture incubation and the amount of nanoparticles (determined as sediment weight), the presence of nanoparticles in the field of EM view, and the nanoparticle yield in silver equivalent. It follows from the data in samples 2, 4, and 6, incubated at 24, 30, and 37°C, respectively, for 48 h in salt solutions of identical compositions that the largest nanoparticle yield is achieved at 30°C (the optimum temperature for the strain), whereas the yields at 24 and 37°C are lower. The decrease in nanoparticle yield at 24°C is likely related to the lower rate of particle bioproduction than at 30°C. The decrease at 37°C is related to the faster death of cells at the elevated temperature. We showed that the growth of the strain in liquid medium at 37°C produced 10–100 times lower titers than at 30°C. However, cells grown under optimum conditions, 30°C, were added to all reaction mixtures. It appears that the further incubation of cells in the reaction mixture at 37°C causes faster cell death than at 24 and 30°C and thereby decreases the nanoparticle yield.

The nanoparticle yield depends on the incubation time even at near-optimum temperatures (24°C). At equal temperatures (24°C) and salt concentrations (1 mM each), the yield after 96 h of incubation was higher than after 48 h (samples 1 and 2, respectively). This observation indicates that cells remain viable at 24°C and serve as nanoparticle production sites for a long time. Note that the maximum amount of nanoparticles is obtained at salt concentrations 1 mM and temperature 24 h for 96 h (sample 1). The gravimetrically determined nanoparticle yield in sample 1 was 53.7%. No direct correlation between the time of cell incubation and particle yield at equal temperatures and salt concentrations (samples 1 and 2) was noted. Similar results have been obtained in the study of the kinetics of Ag_2S nanoparticle formation in the $AgNO_3$ and $Na_2S_2O_3$ solution with *S. oneidensis* MR-1 cells [15]. The increase in solution color within 0–48 h has been measured by spectrometry in the visible and UV regions. This increase, associated by the authors of [15] with nanoparticle formation, shows no direct correlation with the incubation time.

The reduced yield of silver sulfide nanoparticles at $AgNO_3$ and $Na_2S_2O_3$ concentrations elevated to 2 mM may be related to the toxic action of Ag^+ on the cells. Silver sulfide particles themselves are toxic to neither bacterial nor animal cells [15].

Our work pioneers the demonstration of the necessity of living *S. oneidensis* MR-1 cells for the formation of Ag_2S nanoparticles in the salt solution. The possibility of obtaining nanoparticles with living cells or living cell-free extracts is disputed by scientists. This dispute concerns the question of whether or not the bacterial reduction of metals from salts is an active energy-dependent process or passive adsorption on membrane support, or a combination of both. In most studies, the synthesis occurs with the presence of living cells. However, it has been shown that nanoparticles also form with cells inactivated by heating or with extracts containing no living cells. Spherical nanoparticles have been obtained by the interaction of the blue-green alga *Plectonema boryanum* UTEX 485 with aqueous platinum(IV) chloride at temperatures ranging from 25 to 100°C for 28 days and at 180°C for 1 day, whereas no nanoparticles form in experiments conducted under the same conditions for the same time but without cells [18]. Silver nanoparticle synthesis has been demonstrated under the influence of sun-

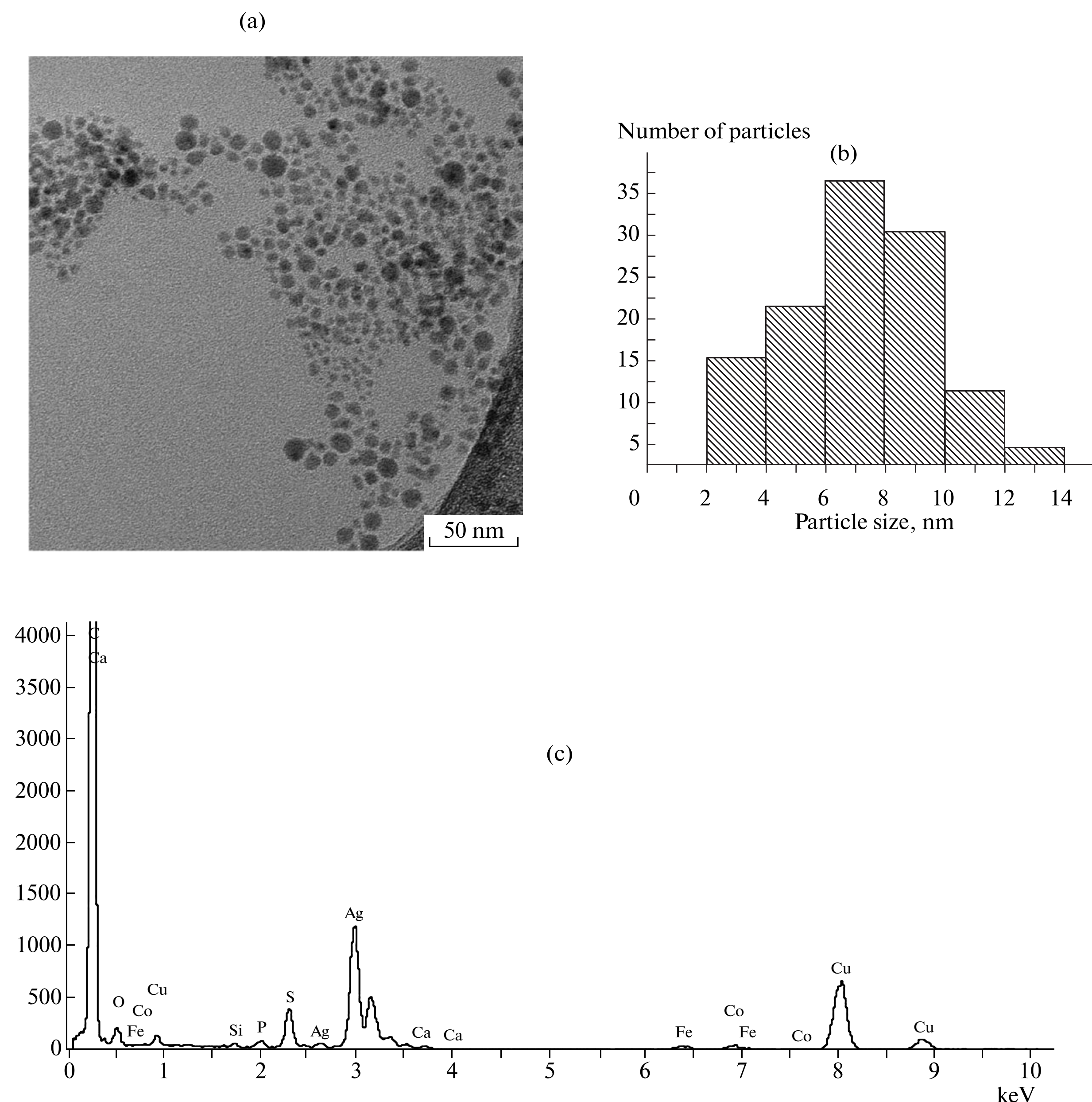

Fig. 1. Analysis of nanoparticles from sample 4 by transmission electron microscopy combined with energy-dispersive X-ray microscopy: (a) TEM image of nanoparticles, (b) size distribution of particles, and (c) ED spectrum obtained from a nanoparticle cluster.

light on $AgNO_3$ solution with a cell-free extract of *Bacillus amyloliquefaciens* inactivated by heating [19]. The authors of [19] suggest that enzymatic reactions are unlikely to participate in silver nanoparticle synthesis. Similar results have been obtained in selenium nanoparticle production with cell-free *Microbacterium* sp. ARB05 extract [20]. This poses the question as to whether the presence of living *S. oneidensis* MR-1 cells is essential for Ag_2S nanoparticle synthesis or the synthesis can occur with nonviable cells. We performed an experiment on Ag_2S nanoparticle production by heat-inactivated *S. oneidensis* MR-1 cells. A heated cell suspension containing no living cells was added to the reaction mixture with 1 mM $AgNO_3$ and 1 mM $Na_2S_2O_3$. All subsequent manipulations were conducted as with living cells. It was shown that the incubation of inactivated cells in the reaction mixture of salts did not yield Ag_2S nanoparticles (Table 1, sample 7). It appears that the formation of Ag_2S nanoparticles in our case demands the reduction of the sulfur of $Na_2S_2O_3$, which may be mediated by various proteins with redox activity located on the inner and outer surfaces of the *S. oneidensis* MR-1 cell mem-

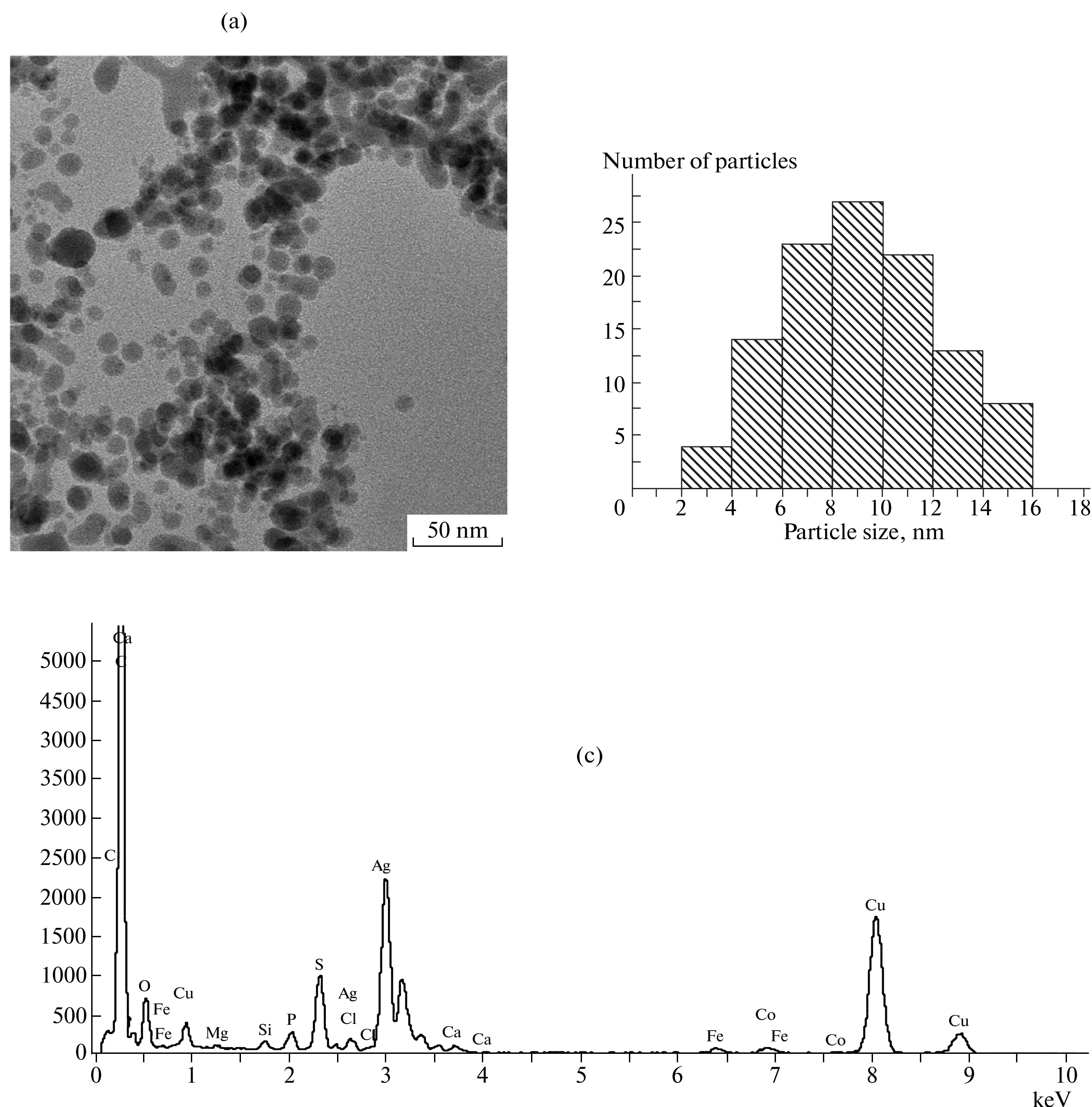

Fig. 2. Analysis of nanoparticles from sample 1 by transmission electron microscopy combined with energy-dispersive X-ray microscopy: (a) TEM image of nanoparticles, (b) size distribution of particles, and (c) ED spectrum obtained from a nanoparticle cluster.

brane. In this case, the presence of living cells is a prerequisite for nanoparticle biosynthesis.

The particle size was found to depend little on reaction conditions. This is proven by the data reported by other authors, e.g., in uraninite nanoparticle synthesis [14]. However, nanoparticle sizes can vary broadly depending on the microbial producer species [21]. The maximum difference is observed in our study between samples 4 and 1, where particle sizes are 7 ± 2 and 9 ± 2 nm, respectively (Figs. 1a, 1b, 2a, 2b). The ED spectra of the particles (Figs. 1c, 2c) show K-series peaks of sulfur, the most intense being $K\alpha1$ (2.308 keV), and L-series of silver, where the most intense peaks are $L\alpha1$ (2.984 keV) and $L\beta1$ (3.15 keV). Peaks of carbon, oxygen, and Cu copper originate from the support material, and the minor peaks of iron, cobalt, and silicon are instrumental. The presence of minor Ca, Mg, Cl, and P peaks may be associated with the presence of their salts in the cell matter. The atomic Ag : S ratio calculated with INCA software from the intensity of K-series peaks of sulfur and L-series peaks of silver is 2 : 1. Thus, the chemical composition of the nanoparticles corresponds to the formula Ag_2S. To test this statement, we conducted a

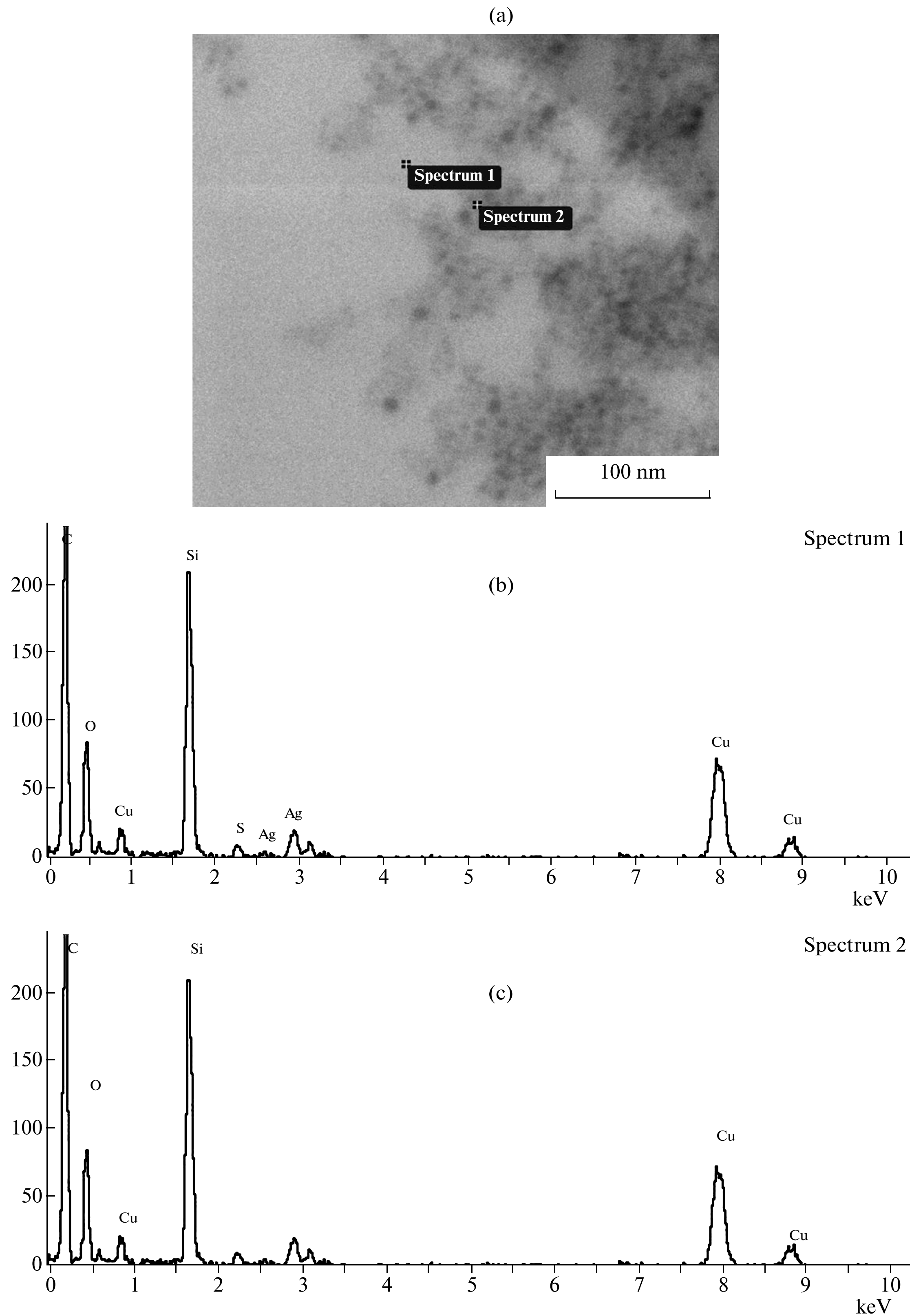

Fig. 3. Analysis of nanoparticles from sample 4 by scanning transmission electron microscopy combined with energy-dispersive X-ray microscopy: (a) STEM image of nanoparticles, (b) ED spectrum obtained from a site with particles, and (c) ED spectrum obtained from a particle-free support site.

local analysis of the elemental composition of nanoparticles by EDS combined with STEM. The resolution of the images was worse than in TEM (Fig. 3a), but this approach made it possible to obtain spectra from particular sites of the sample. Point spectra were obtained from a site with particles (Spectrum 1) and from a particle-free site on the support (Spectrum 2). Unlike the spectra from clusters of particles (Figs. 1c, 2c), the analyte is scarce and the signal is weak. Nevertheless, L-series peaks of Ag and a K-peak of S are clearly identified in the spectrum from the site with particles (Fig. 3b). Quantitative analysis is hampered by the small number of detected X-ray photons in the spectrum, but the atomic Ag : S ratio determined with INCA is 2 : 1. It is seen that the spectrum from the support has peaks of carbon, oxygen, copper, and silicon, the last being instrumental (Fig. 3c).

It is still poorly understood how bacteria are involved in nanoparticle synthesis. Apparently, in our study bacteria participate in thiosulfate sulfur reduction to S^{2-}. Then it is conceivable that positive silver ions Ag^+ are adsorbed on the bacterial cell surface. These adsorbed ions may be seeds for silver sulfide crystallization. As a rule, the bacterial cell surface is negatively charged. It has been reported that living *Shewanella* cells adsorb Cu^{2+} and Zn^{2+}, whereas autoclaved cells bind these ions severalfold worse [22]. It is known that Ag_2S particles have negative charges [15]; hence, they are expected to be repulsed from cell surface. This repulsion probably determines the formation of the silver sulfide nanoparticle dispersion obtained in our study. According to this model, the *Shewanella* cell surface acts as a catalyst and adsorption sites of metal cations (sites of silver sulfide priming) are used repeatedly. This assumption can be verified by calculation. With the Ag_2S nanoparticle yield 53.7%, the spherically approximated mean particle diameter 8 nm, $AgNO_3$ concentration 1 mM, and cell titer 1×10^8 cells/ml, each cell produces 3.2×10^7 Ag_2S particles. A single cell has room for no more than 8×10^5 particles located on its surface in a monolayer. Thus, the produced cells can cover the cell surface in 40 layers. In practice, this means that reaction conditions can be improved to produce large amounts of nanoparticles with a small numbers of cells.

CONCLUSIONS

It is found for the first time that the bacterial synthesis of silver sulfide nanoparticles by the metal-reducing electrogenic bacterium *S. oneidensis* MR-1 is a biocatalytic process demanding the presence of living cells in the reaction mixture of salts $AgNO_3$ and $Na_2S_2O_3$. It is shown that nanoparticle yield increases with the incubation time of cells in the reaction mixture at 24°C. The maximum nanoparticle yield, 53% in silver equivalent, is achieved by the incubation of cells in a solution of 1 mM $AgNO_3$ and 1 mM $Na_2S_2O_3$ at 24°C for 96 h. The elevation of the incubation temperature to 37°C and concentration increase to 2 mM decrease the nanoparticle yield. It is demonstrated that a change on the conditions of nanoparticle synthesis changes their yield but insignificantly affects their size, varying from 7 ± 2 to 9 ± 2 nm in various samples. An analysis of particle clusters and individual particles by STEM combined with EDS shows that the atomic Ag : S ratio in the particles is 2 : 1, which is in agreement with the formula Ag_2S.

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