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Preparation and Study of Concentrated Hydrosols of Copper Nanoparticles Using of Weak Reducing Agents

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Abstract—We propose a facile and environmentally friendly method to prepare concentrated copper nanoparticles dispersion via reduction of aqueous copper(II) sulfate solution with ascorbic acid or glucose in the presence of gelatin as stabilizer. The so synthesized hydrosols have been examined using a set of physicochemical methods (ex situ and in situ) in order to determine the nanoparticles features.

Keywords: copper, nanoparticle, hydrosol, gelatin, ascorbic acid, glucose, UV spectroscopy, X-ray photoelectron spectroscopy, X-ray phase analysis, small-angle X-ray scattering, X-ray absorption near edge structure spectroscopy, transmission electron microscopy, Auger spectroscopy

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Copper-based nanoscale materials have attracted considerable attention due to the broad range of their potential application in science and technology. Copper nanoparticles are among key components of catalysts, chemical sensors, lubricants, antibacterial agents, and other materials [1–6].

Metal nanoparticles can be synthesized via a number of methods, chemical reduction in aqueous media being probably the most used and promising. This method requires very simple equipment; the process can be easily controlled to yield the particles with desired parameters (size, shape, and structure). However, a significant drawback of chemical reduction is that it does not afford high concentration of the nanoparticles in the final dispersion (it is generally $<10^{-4}$ mol/L M^0) because of the particles instability towards aggregation and sedimentation. Furthermore, high reactivity of the resulting material leads to oxidation of the formed nanoparticles with dissolved or air oxygen.

Much effort has been recently put into development of the approaches to improve the metal sols stability against aggregation and oxidation as well as to increase the upper limit of the accessible nanoparticles concentration. The latter issue is important, since the ability to prepare metal sols with high nanoparticle content of 0.01–0.1 mol/L M^0 will extend the range of their applications in production of thin films, coatings (in particular, "inks" for printing the electrically conductive patterns), and catalysts [7–10]. Targeted synthesis of metal nanoparticles possessing long-term stability and the desired properties involves different stabilizers. Selected studies of the coordination interactions between the nanoparticles and the stabilizer molecules have been reviewed in [11].

This study aimed to synthesize stable concentrated hydrosols of copper nanoparticles using weak reducing agents (ascorbic acid and glucose) and to examine the products via ex situ and in situ methods: optical and X-ray photoelectron (XPS) spectroscopy, X-ray absorption spectroscopy (XANES), small-angle X-ray scattering spectroscopy, X-ray diffraction analysis (XRD), transmission electron microscopy (TEM).

The size and morphology of the growing particles can be efficiently controlled using weak reducing agents because of the lower process rate. Moreover, ascorbic acid and glucose are environmentally friendly reducing agents. Ascorbic acid is capable of reducing oxygen dissolved in aqueous solutions, thus improving the oxidative stability of copper nanoparticles [12].

A number of reports have been published on preparation of copper nanoparticles using weak reducing agents [13–18]; however, the issue of the process optimization has been rarely touched upon, and the data are often contradictory. For example, the products obtained under similar conditions are reported as copper, copper oxide, or mixed nanoparticles. In our opinion, this can result from artifacts of the specimen preparation for the ex situ analysis, including the chemical changes induced in the sample. Therefore, we performed a comprehensive study of the prepared nanoparticles combining ex situ and in situ methods.

Reduction of the copper(II) ions with ascorbic acid can be described by Eq. (1).

$$C_6H_8O_6 + CuSO_4 + 2NaOH \rightarrow Cu^0 + Na_2SO_4 + C_6H_8O_7 + H_2O. \quad (1)$$

The composition of the organic products of reaction (1) depends on the medium pH: Ascorbic acid is oxidized into 2,3-diketo-L-gulonic acid which is further decomposed into oxalic and L-threonic acids in alkaline solutions; furfural is the reaction product in the absence of alkali [12]. The reductive power of ascorbic acid and the process rate reach maximum at pH = 10.5. Electrode potential of ascorbic acid at pH = 4 is of 0.166 V and of 0.08 V in alkaline medium [19]. Oxidation of ascorbic acid is accelerated by heavy metal ions, especially by copper(II).

Oxidation of glucose in acidic medium yields dicarboxylic saccharic acid ($C_6H_{10}O_8$); gluconic acid ($C_6H_{12}O_7$) is the oxidation product in alkaline medium. Redox potential of glucose at pH 5 is of –0.05 V, decreasing upon alkalization to reach –0.24 V at pH 9–10 [20]. However, copper reduction is accompanied by the formation of insoluble in water copper(I) oxide (hydroxide) in alkaline medium (2); these products cannot be reduced to Cu^0 with glucose [$E^0(Cu_2O/Cu)$ = –0.36 V) [19].

$$C_5H_{11}O_5–COH + 2Cu(OH)_2 = C_5H_{11}O_5–COOH + Cu_2O\downarrow + 2H_2O. \quad (2)$$

At the same time, the standard electrode potential of reaction (3) is of –0.01 V under conditions of complexation with ammonia, meaning that reduction of copper with glucose is possible using ammonia as the alkalinizing agent.

$$[Cu(NH_3)_4]^{2+} + e^- = [Cu(NH_3)_2]^+ + 2NH_3. \quad (3)$$

We have earlier shown that the highest yield of copper nanoparticles via reduction with ascorbic acid is achieved in slightly alkaline medium (pH = 9) in the presence of a 100-fold excess of ascorbic acid and 30 g/L of gelatin as stabilizer using a water bath and microwave heating [21]. The similar optimized conditions were employed in this work for copper nanoparticles preparation via reduction with glucose. The resulting copper hydrosols were examined by in situ (UV spectroscopy, small-angle X-ray scattering spectroscopy) and ex situ (XPS, Auger spectroscopy, XANES, XRD, TEM) methods.

In situ study. Fig. 1 illustrates the overall stability (against oxidation, aggregation, and sedimentation) of copper nanoparticles hydrosols obtained via reduction with ascorbic acid and glucose, as examined by electronic absorption spectroscopy. The spectra were recorded after incubation of the sols under atmospheric oxygen exposure during several predefined times (0.5–120 h).

The electronic spectra of sols containing metal nanoparticles revealed the so called surface plasmon resonance peaks at the electromagnetic radiation frequency corresponding to that of the natural oscillations of electrons in nanoparticles. Parameters of surface plasmon resonance peak are generally determined by size, shape, and the oxidation state of the nanoparticles. The surface plasmon resonance peak has been found at 570 nm in the case of 2–10 nm spherical copper nanoparticles [22–24].

The sample prepared via reduction with glucose (Fig. 1b), initially red, turned black and partially precipitated within 8 h, thus indicating the formation of copper(II) oxide. The similar sample prepared via reduction with ascorbic acid revealed the surface plasmon resonance peak getting stronger during the first day after preparation (Fig. 1a). That was apparently caused by the ongoing reduction process and efficient protection of the nanoparticles against oxidation due to the presence of ascorbic acid.

Synchrotron small-angle X-ray scattering experiment allowed determination of the size and shape of the nanoparticles in the sol. Fig. 2 presents the scattering curves of the sols; irrespectively of the reducing agent nature, the scattering curves were similar in shape and corresponded to spherical particles, possibly partially agglomerated. Processing of the scattering data using the Guinier method gave the radius of gyration R_g related to the radius of the spherical particles as

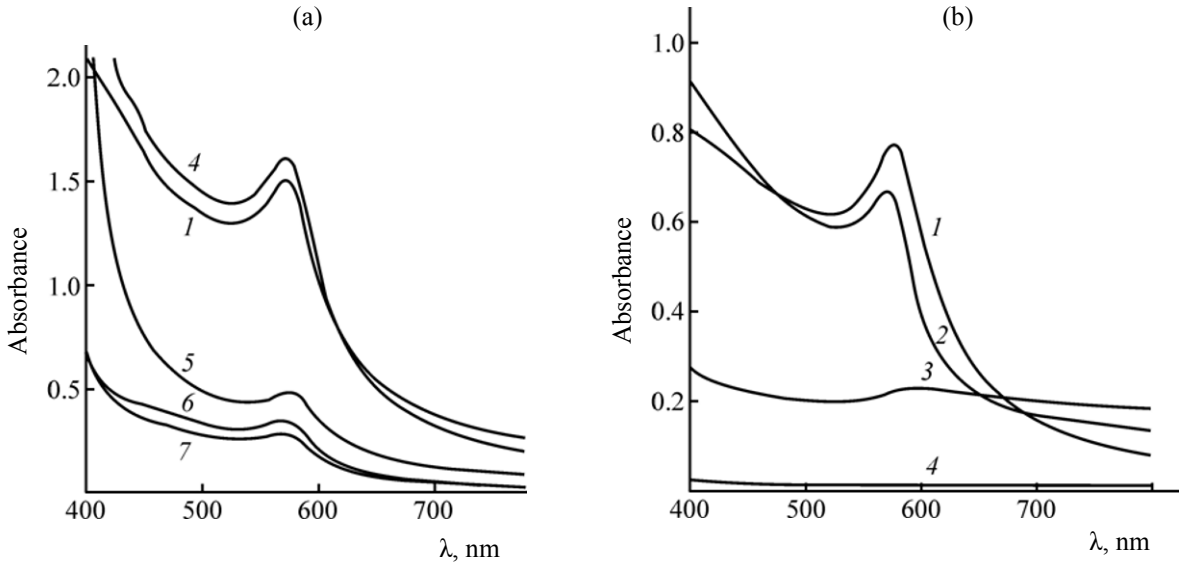

Fig. 1. Evolution of the electronic absorption spectra of the copper hydrosols obtained via Cu(II) reduction with (a) ascorbic acid and (b) glucose and exposed to air during (*1*) 0.5, (*2*) 3, (*3*) 8, (*4*) 24, (*5*) 48, (*6*) 72, and (*7*) 120 h.

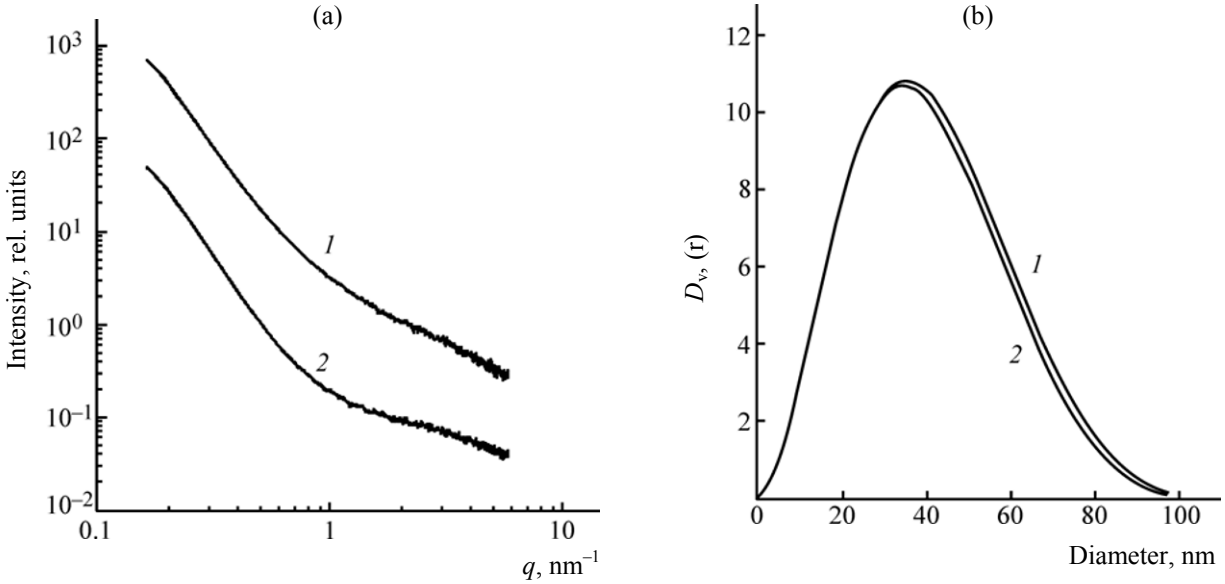

Fig. 2. (a) Small-angle X-ray scattering curves and (b) mean interparticle distance for the copper sols obtained via Cu(II) reduction with (1) ascorbic acid and (2) glucose.

$$R_g = \sqrt{0.6R.} \quad (4)$$

The radius of gyration was of ≈12 nm irrespectively of the nature of the reducing agent used, and the nanoparticles diameter was of ≈30 nm.

Ex situ study. X-ray diffraction analysis was applied to examine the precipitates obtained via centrifugation and air-drying of the copper nanoparticle sols (Fig. 3). The both samples consisted of metal copper particles [25].

The shape of the X-ray photoelectron spectra of the nanoparticles surface (Fig. 4) was virtually independent of the reducing agent nature. The Cu2$p_{3/2}$ line could be decomposed into two components with the binding energies of 934.7 and 932.5 eV. The former weak peak was assigned to Cu(II) oxide or hydroxide [26], the conclusion being confirmed by the presence of weak shake-up satellites at 940–945 eV due to the unoccupied Cu 3*d* orbital. The peak at 932.5 eV could not be unambiguously assigned, since the binding

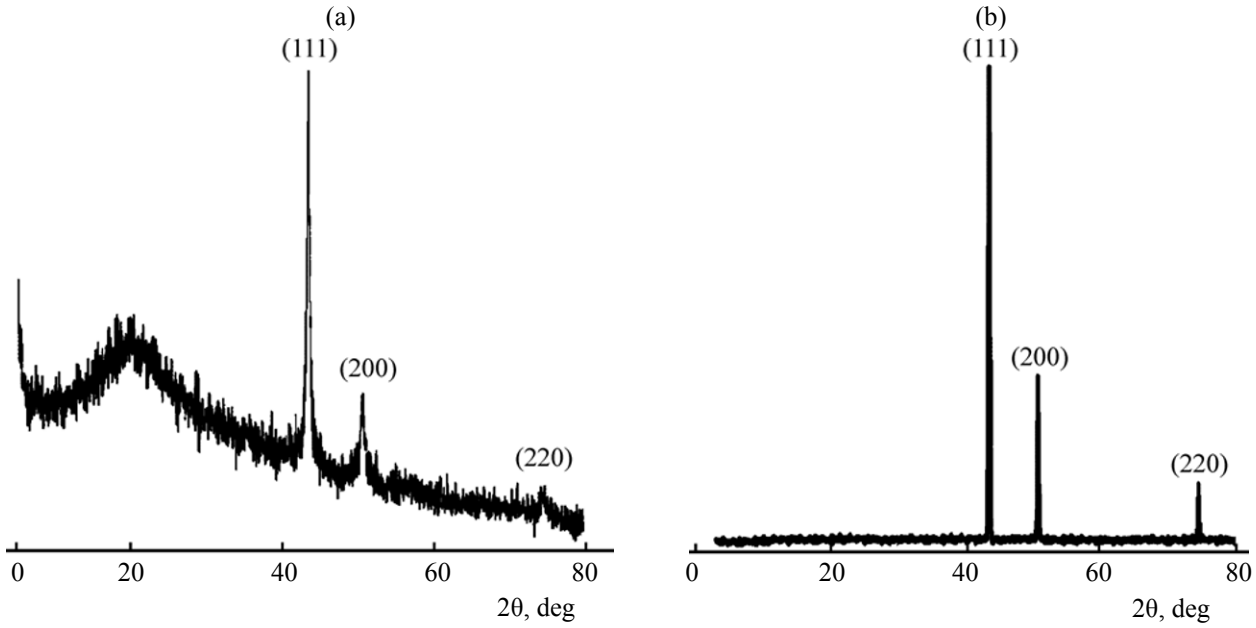

Fig. 3. X-ray diffraction patterns of the precipitates obtained via Cu(II) reduction with (a) glucose and (b) ascorbic acid.

energies of Cu(I) and metal copper were virtually identical (932–933 and 932.6 eV, respectively).

The peak at 934.7 eV was significantly weakened and the shake-up satellites disappeared after etching with argon ions, thereby indicating that the copper(II)-containing phase was exclusively present in the particle surface and was removed via the ion etching.

In order to elucidate the chemical state of copper, the Auger spectroscopy data (CuL_3MM line) was used (Fig. 4b). The complex shape of the spectra could be described with several maxima in the E_{kin} range of 910–920 eV, apparently corresponding to a mixture of Cu(II), Cu(I), and Cu(0) species. Kinetic energy of the electrons corresponding to the main peak was of 918.5 eV [Cu(0)] and 916.5 eV [Cu(I)]. Prior to the ion etching, Cu(I) and Cu(II) were the major species (Fig. 4b, curves *1* and *3*). However, the Cu(I) peaks sharply decreased and the Cu(0) peaks were enhanced after the etching. The particles obtained via the reduction with glucose revealed the stronger peak associated with metal copper as compared to that in the spectrum of the sample prepared via reduction with ascorbic acid.

To conclude, the XPS and Auger spectroscopy data confirmed that the resultant particles contained Cu(0) coated with thin layer of Cu(I) and Cu(II) oxygen-containing species, appearing due to oxidation by air and/or dissolved oxygen. The oxidation was apparently an artifact of the sample preparation for ex situ examination.

The XPS analysis probed the 1–2 nm surface layer of the specimen; the XANES technique enabled analysis of the deeper (>5 nm) layers of the nanoparticles. Fig. 5 shows the XANES spectra of the studied sols along with these of the reference pure compounds. It is to be seen that the reduction with ascorbic acid (curve *1*) yielded the nanoparticles containing mainly Cu(0), as confirmed by the similarity between the sample and the reference spectra. The spectrum of the particles produced via the reduction with glucose was similar to those of the Cu_2O and CuO phases, contradicting the Auger spectroscopy data. In our opinion, the particles were oxidized during the preparation for the analysis. That indicated the nanoparticles instability, coinciding with the data of the electronic absorption spectroscopy (Fig. 1).

After removal of the excess gelatin, the prepared hydrosols were examined via transmission electron microscopy coupled with local electron diffraction (Fig. 6). It was found that the reduction with ascorbic acid yielded spherical 60±20 nm copper metal nanoparticles coated with a thin (2–3 nm) gelatin film apparently preventing the particles oxidation and aggregation. The sample obtained via the reduction with glucose contained larger (100–500 nm) aggregates of copper metal particles containing Cu_2O

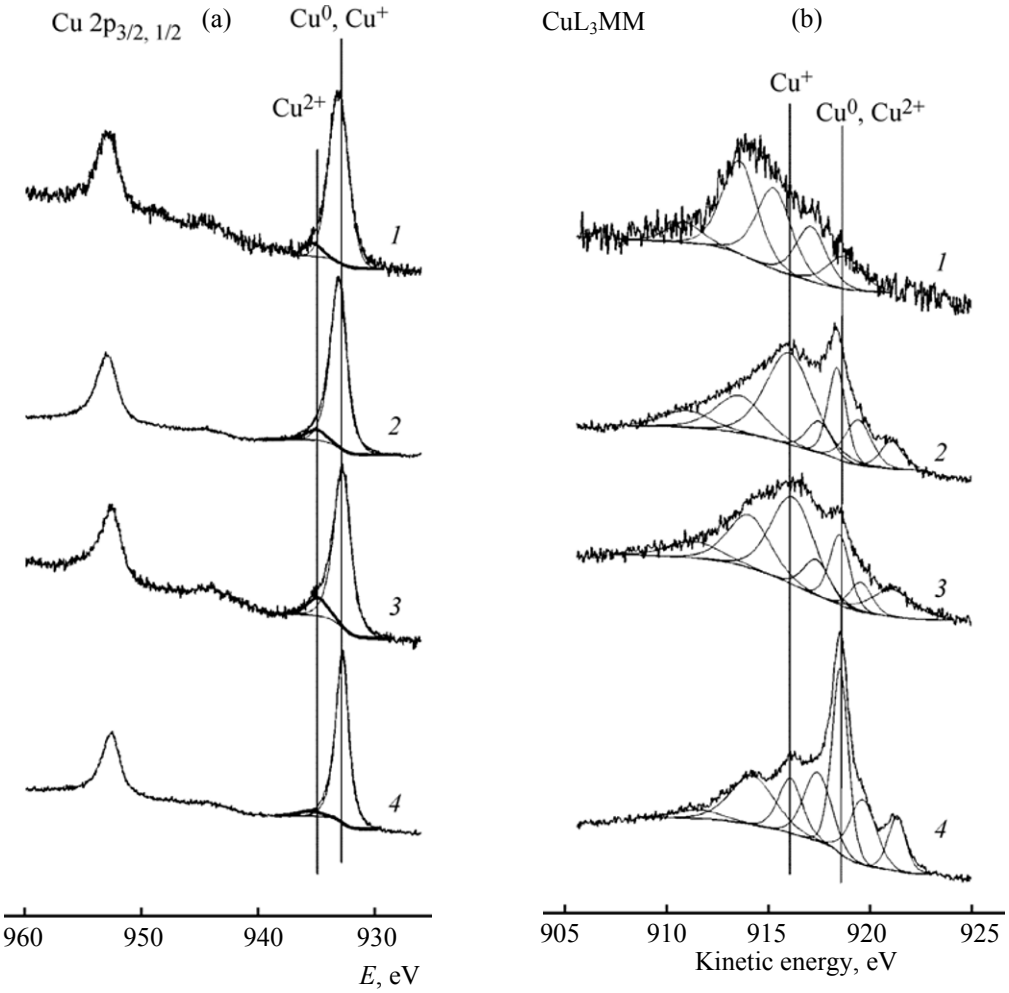

Fig. 4. (a) X-ray photoelectron and (b) Auger spectra of the samples obtained via Cu(II) reduction with (*1, 2*) ascorbic acid and (*3, 4*) glucose: (*1, 3*) before and (*2, 4*) after the ion etching.

admixture (Fig. 6d). The discrepancy between TEM and small-angle X-ray scattering data could be explained by the specimen changes during removal of gelatin from the sol via centrifugation, specifically by enrichment of the thickened product with larger particles and by their possible aggregation during washing [27].

In summary, the method used in this study (reduction with ascorbic acid or glucose using a high-molecular-weight stabilizer gelatin) allowed preparation of concentrated hydrosols of copper nanoparticles, stable against sedimentation and oxidation. Comprehensive examination of the products revealed that the nanoparticles composition was virtually independent of the reducing agent nature; however, their size and resistance to air oxygen was different. Reduction with glucose yielded the agglomerated 100–

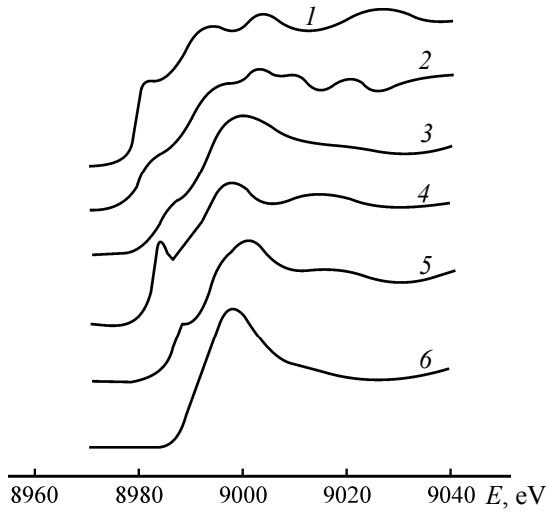

Fig. 5. CuK-edge XANES spectra of (*1*) Cu (foil), (*2, 3*) copper hydrosols obtained via Cu(II) reduction with (*2*) ascorbic acid and (*3*) glucose, (*4*) Cu_2O, (*5*) CuO, and (*6*) Cu^{2+}.

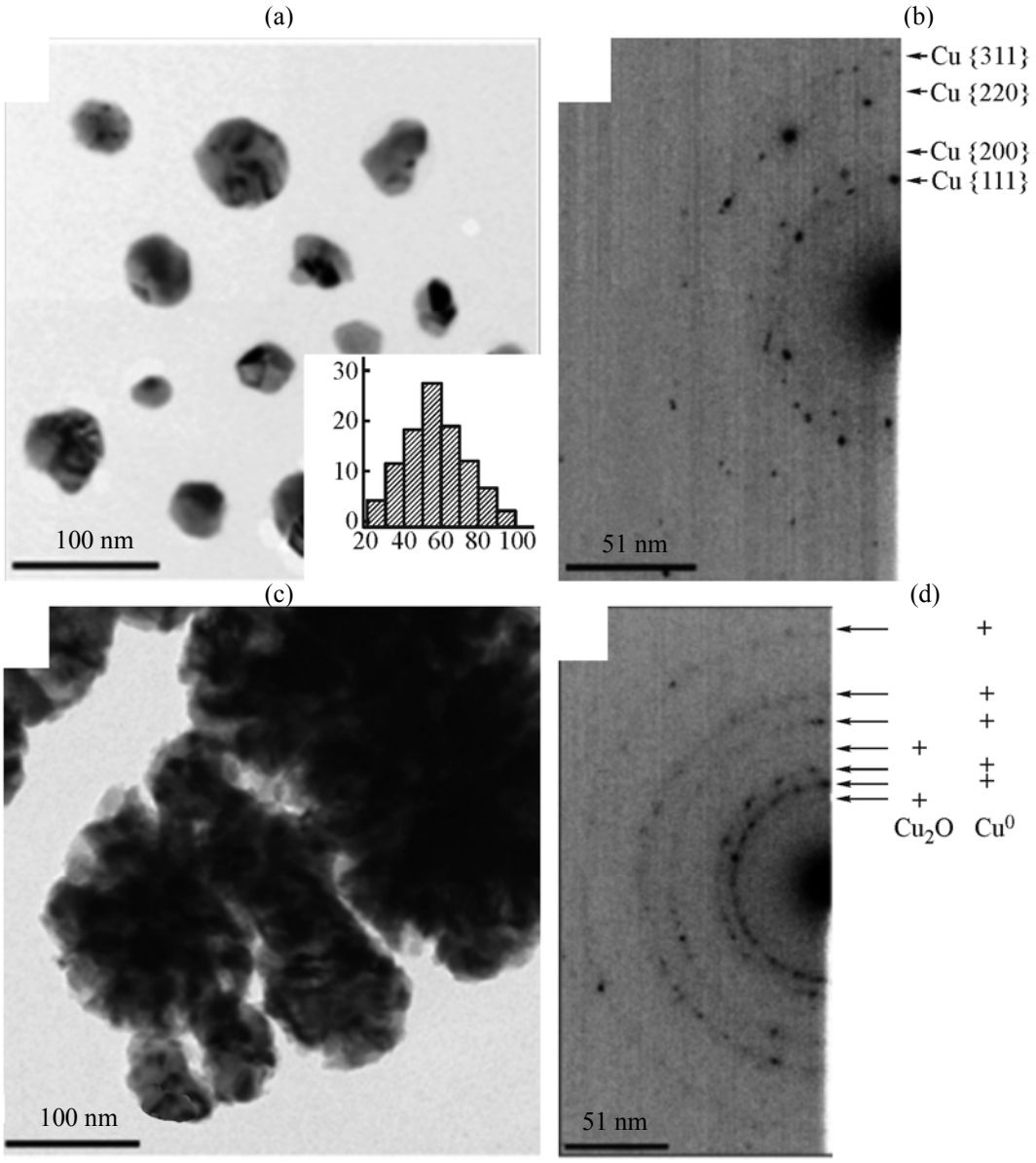

Fig. 6. (a, c) TEM images and (b, d) the electron diffraction patterns of the copper nanoparticles obtained via Cu(II) reduction with (a) ascorbic acid and (b) glucose.

500 nm metal particles coated with a thin layer of oxides or hydroxides. The particles obtained via the reduction with ascorbic acid were of 60±20 nm.

The study revealed possible sources of the errors associated with the sample preparation for ex situ observation. In particular, washing the immobilized particles with water caused their oxidation and dissolution. Thickening via centrifugation or sedimentation led to agglomeration and enrichment of the precipitate with larger metal particles, the fluid being enriched with smaller oxidized particles.

EXPERIMENTAL

The reagents of "chemical pure" or "analytical pure" grade were used as received. Gelatin (GOST 11293–89) was used as a high-molecular-weight stabilizer. The gelatin solution was prepared by dilution of 3 g of gelatin with 100 mL of distilled water and heating on a water bath in a microwave oven (350 W) during 5–10 min.

Synthesis of copper nanoparticle hydrosols. 10 mL of gelatin solution (30 g/L), 10 mL of 1 mol/L

aqueous solution of the reducing agent (glucose or sodium ascorbate, pH = 10), and 4–5 drops of 17 mol/L ammonia solution (in the case of the reduction with glucose) were added to 10 mL of 0.03 mol/L copper(II) sulfate solution. The mixture was heated on a water bath with a microwave oven (750 W, 15–30 min). The mixture color changed from pale yellow to deep maroon-red in the course of the reaction.

The reaction course was monitored by electronic absorption spectroscopy (300–800 nm, Spekol 1300 and Perkin Elmer Lambda 35 spectrometers, 2–10 dilution with distilled water, 1 cm quartz cell, distilled water as reference). The final products were studied similarly.

Photoelectron and Auger spectra were recorded using a SPECS spectrometer equipped with a PHOIBOS MCD-9 energy analyzer. The sols were centrifuged during 4 min at 9000 rpm (Eppendorf Centrifuge 5415 D) and twice washed with distilled water to remove excess of gelatin prior to the examination. Next, a droplet of the sol was dried on a pyrographite substrate under vacuum of the lock chamber of the spectrometer. The spectra of the samples were excited with non-monochromatic MgK_α radiation of the X-ray tube at the threshold energy of the analyzer of 8 eV. The pressure in the sample chamber was below 10^{-9} mbar. The C1*s* line of highly-oriented pyrographite (284.45 eV) was used as internal reference to account for the electrostatic charging. The XPS spectra were processed using CasaXPS software. The Ar^+ ion etching was performed at a rate of about 2 nm min^{-1} (accelerating voltage 5 kV, emission current 30 μA).

XRD analysis of the powder obtained via centrifugation and air-drying of the sol was performed on a silicon single crystal using an X'Pert PRO PIXcel PANalytical diffractometer (CuK_α radiation).

The specimens for XANES examinations were prepared via deposition at a pyrographite substrate and air-drying. The $CuL_{3,2}$ spectra were recorded in the total electron yield (TEY) mode at room temperature using the equipment of the Russian-German Laboratory at the BESSY II synchrotron radiation facility (Berlin, Germany) under the following conditions: scan step 0.05 eV, pressure in the analytical chamber no lower than 10^{-8} Pa, X-ray beam diameter 0.2 mm. The monochromator transmission was accounted for by normalization of the measured spectra with a gold foil spectrum (TEY mode). The energy scale was calibrated using the Ne K-edge.

Small-angle X-ray scattering spectra were collected at the 7T-WLS-μSpot beamline of the BESSY II synchrotron radiation facility (Berlin, Germany) using a Si(111)-monochromator with an energy resolution $\Delta E/E$ of 2×10^{-4}. The monochromator transmission was accounted for by normalization of the measured spectra with a gold foil spectrum (TEY mode). In the experiment, an aliquot of the sol was placed in a quartz capillary (inner diameter of 1.5 mm) and transferred into the chamber. The radiation energy was of 11.5 keV; a MarMosaic 225 CCD-detector was used. The averaging and normalization procedures afforded the scattering intensity as function of the wave vector; the nanoparticle size was estimated via indirect Fourier transformation.

The resulting particles were visualized with transmission electron microscopy (a JEOL JEM-2010 microscope) at accelerating voltage of 200 kV. A drop of the washed sol was deposited onto an amorphous carbon film-coated copper grid and air-dried.

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