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Conditions for the Formation of Copper Nanoparticles by Reduction of Copper(II) Ions with Hydrazine Hydrate Solutions

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Abstract—Optimal conditions were found for the preparation of copper nanoparticles in aqueous solution via reduction of copper(II) ions with hydrazine hydrate. The effects of ligand environment of copper(II) in the initial solution (hydrate, ammonia, citrate, and glycine complexes), concentration, pH, surfactants, temperature, and mode of heating were examined. The obtained colloidal systems were studied by optical spectroscopy, X-ray photoelectron spectroscopy, X-ray powder diffraction, and atomic force microscopy. The examined colloids were found to contain generally spherical copper nanoparticles with a diameter of about 10 nm, which were coated with a copper(I) or copper(II) oxide and hydroxide film.

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Copper nanoparticles attract interest from the viewpoint of their potential wide application as catalysts in various large-scale chemical processes, such as conversion of heavy petroleum fractions [1], transformation of alcohols into aldehydes [2], oxidation of carbon(II) oxide, transformation of solar energy [3], and isomerization of chlorolefins [4], as well as in microelectronics [5] and for the design of liquid- and gas-phase transducers and sensors [6]. Antibacterial properties of copper nanoparticles may be useful in the manufacture of medical equipment and materials and equipment for food industry [7]. Copper nanoparticles can also be used for the preparation of up-to-date lubricants [6], composite materials [8], etc.

Copper nanoparticles are obtained most frequently by chemical reactions in solution, which do not require special equipment, and the size and morphology of the resulting nanoparticles may be controlled. In keeping with the standard electrode potential [9], copper(II) in aqueous solution should be reduced to copper(0) with most commonly used reducing agents; however, in many cases copper(I) oxide Cu_2O is formed. In particular, oxidation of Cu(0) may be promoted by the presence of oxygen in the initial solution even in a small concentration. Presumably, the reduction with hydrazine hydrate, which is accompanied by evolution of nitrogen, could provide synthesis of copper nanoparticles without prolonged deoxygenation of solution. On the other hand, hydrazine hydrate itself could act as oxidant under some conditions, which could result in dissolution of copper nanoparticles or formation of surface oxide layer.

Analysis of published data showed that copper(II) species are generally reduced with hydrazine hydrate to Cu_2O [10–11]; metallic copper nanoparticles were obtained in aqueous solution only in a few cases, and these nanoparticles were characterized as a rule by a considerable extent of surface oxidation [12]. To avoid intermediate formation of copper(I) oxide (or hydroxide), it is advisable to carry out the reaction in weakly acidic medium, but under these conditions the efficiency of reducing agents is appreciably lower. Another approach is based on the reduction in alkaline medium in the presence of complexing agents that retain copper ions in solution.

The goal of the present study was to find optimal conditions for the preparation of copper nanoparticles

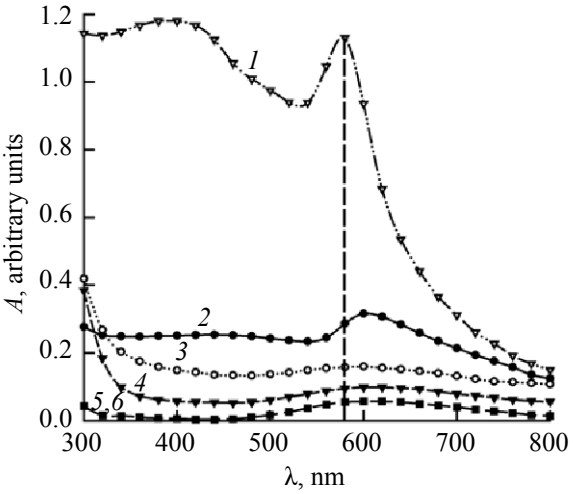

Fig. 1. Effects of temperature and mode of heating on the electronic absorption spectra of copper-containing sols: (*1*) microwave activation (100°C); conventional heating at (*2*) 100, (*3*) 80, (*4*) 60, and (5) 20°C; (*6*) initial copper(II)–ammonia complex, c[Cu(II)] = 1×10^{-3} M, pH 12, $c(N_2H_4\cdot H_2O)$ = 0.11 M.

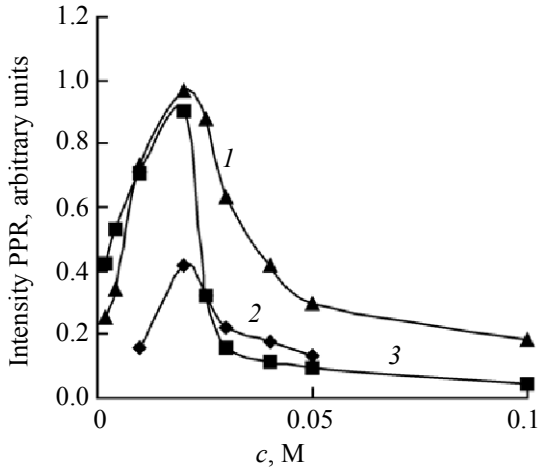

Fig. 2. Effect of ligand nature and its concentration on the intensity of surface plasmon resonance of copper-containing sols: (*1*) sodium citrate (pH 11), (*2*) sodium tartrate (pH 11), and (*3*) aminoacetic acid (pH 4.4); c[Cu(II)] = 5×10^{-4} M, $c(N_2H_4\cdot H_2O)$ = 0.02 M.

from copper(II) species in aqueous solution using hydrazine hydrate in the presence of complexones and detergents, as well as to examine the resulting colloid solutions by atomic force microscopy (AFM), X-ray powder diffraction (XPD), and X-ray photoelectron spectroscopy (XPS).

Effects of temperature and mode of heating. Metal nanoparticles were identified by the presence of so-called surface plasmon resonance (SPR) maxima in the optical spectra, their shape, intensity, and position (570 nm for spherical copper nanoparticles with a diameter of 2 to 10 nm) [13]. These parameters were set as target while optimizing the conditions of synthesis in the present work. The spectra of the products obtained at 20–80°C (Fig. 1, curves *3–5*) were characterized by a broad absorption maximum at λ 600 nm, which is typical of initial copper complex with ammonia. On heating to 90–100°C (Fig. 1, curve *2*) we observed formation of a red colloid with an SPR maximum at λ 590 nm, indicating the presence of metallic copper.

The use of microwave activation with a power of 700 W (Fig. 1, curve *1*), other conditions being equal, shortens the reaction time from 60 to 15 min and ensures higher yield of copper nanoparticles with a smaller size, as follows from increases SPR intensity and its displacement to λ 580 nm. We also found that microwave activation ensures good reproducibility of the results, so that this procedure was used in our subsequent experiments.

Effect of complexing agent. Preliminary experiments showed that the reduction of copper(II) aqua or hydroxo complexes in the pH range from 5 to 13 leads to formation of Cu_2O and that copper nanoparticles could be obtained in ammonia solution. On the other hand, elevated temperature (see above) induces appreciable loss of ammonia, so that the equilibrium is displaced toward formation of Cu_2O. Therefore, in some experiments ammonia was partly replaced by organic complexones which are capable of forming copper(II) coordination compounds with approximately the same stability as that of ammonia complexes {pK[Cu$(NH_2)_2$] = 12.03}: citrate [pK(CuCit) = 14.21] and tartrate ions {pK[Cu(OH)Tart] = 12.44} and glycine {pK[Cu$(Gly)_2$] = 15.1} [14, 15]. In addition, these anions are frequently used to stabilize metal nanoparticles [16].

Addition of organic complexones (Fig. 2) increases the yield of copper nanoparticles (the SPR intensity considerably rises). Simultaneously, absorption in the red region of the spectrum, which is typical of copper(I) oxide [17], becomes weaker. The dependences of the SPR intensity versus concentration of citrate and tartrate ions and glycine have extremal character with a maximum at about 0.02 M regardless of the complexone nature. Presumably, higher ligand concentration favors stabilization of copper(II), and the rate of its reduction decreases.

The highest SPR intensity, the absorbance in the red region being relatively weak, was observed in the

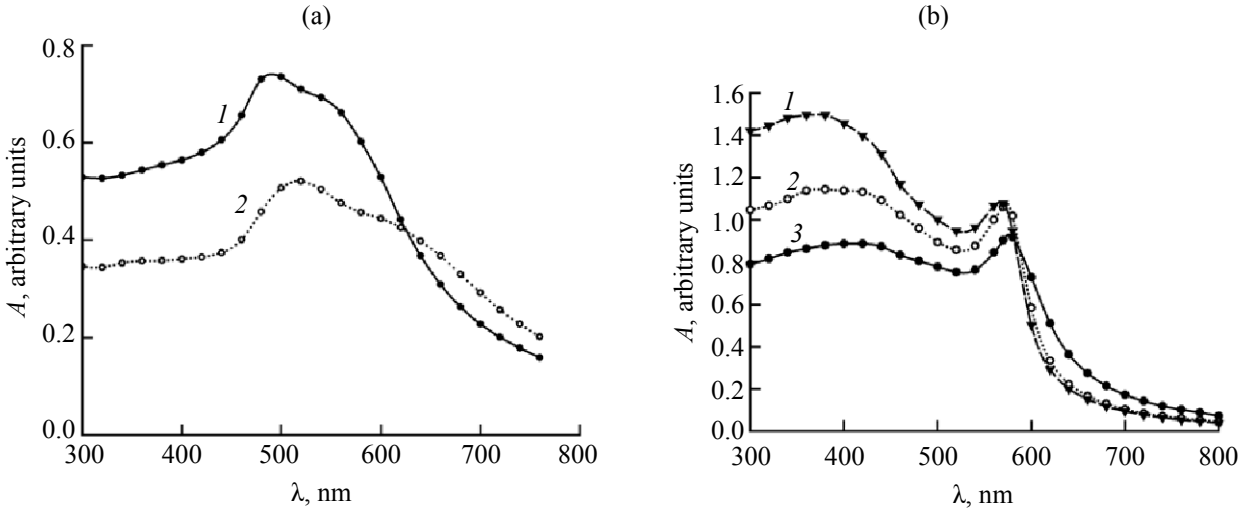

Fig. 3. Effect of base on the electronic absorption spectra of copper-containing sols: (a) NaOH: (*1*) pH 12, (*2*) pH 11; (b) $NH_3 \cdot H_2O$: (*1*) pH 12, (*2*) pH 11.5, (*3*) pH 11; c[Cu(II)] = 5×10^{-4} M, $c(N_2H_4 \cdot H_2O)$ = 0.01 M.

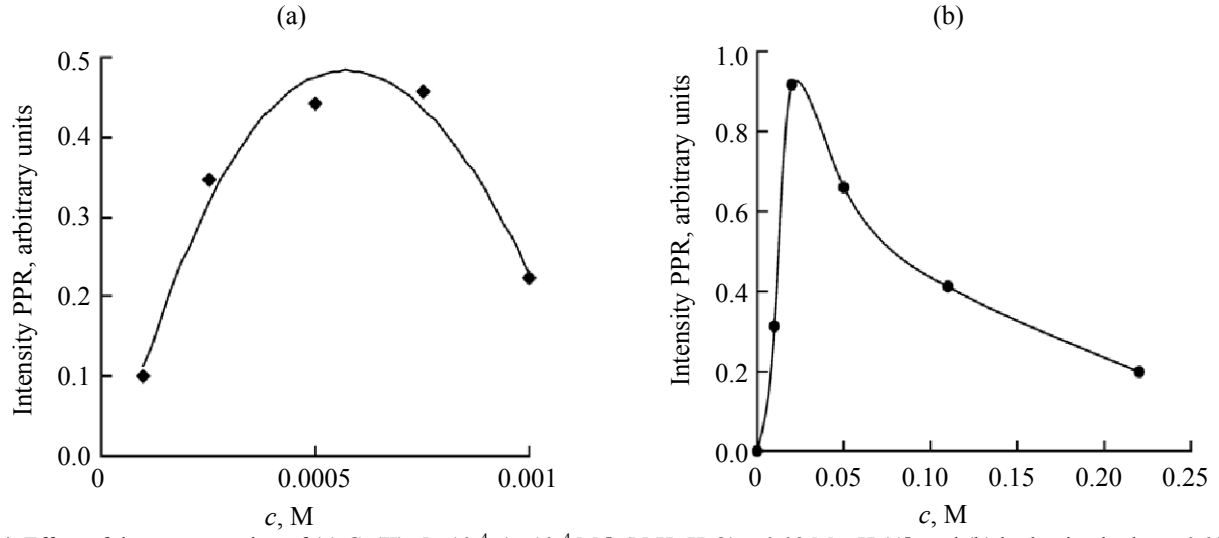

Fig. 4. Effect of the concentration of (a) Cu(II), 5×10^{-4}–1×10^{-4} M [$c(N_2H_4 \cdot H_2O)$ = 0.02 M, pH 11], and (b) hydrazine hydrate, 0.02–0.22 M {c[Cu(II)] = 5×10^{-4} M, pH 11} on the intensity of surface plasmon resonance of copper-containing sols [$c(N_2H_4 \cdot H_2O)$ = 0.01 M, pH 11].

presence of tartrate ions, and the latter were used as additional ligand in our subsequent experiments.

Effect of pH. The reactions in the presence of tartrate ions were performed in alkaline medium, taking into account that only mixed tartrate hydroxo copper(II) complexes are stable and that pK(CuTart) is equal to 3.03 [14]. However, addition of a strong alkali (Fig. 3a) even to a relatively low concentration (pH 11) leads to the formation of yellow copper(I) oxide (hydroxide) colloid rather than mixed coordination compound, presumably as a result of local oversaturation; this follows from the lack of SPR assignable to copper nanoparticles and the presence of an absorption band at λ 500 nm [18]. Therefore, alkaline medium was created using ammonia solutions. Figure 3b shows that variation of the concentration of $NH_3 \cdot H_2O$ in the examined range only insignificantly affects the intensity of SPR; on the other hand, rise in the $NH_3 \cdot H_2O$ concentration is accompanied by increase in the intensity of absorption in the "blue" region, but the reason for the observed variation remains unclear.

Effect of copper(II) and hydrazine hydrate concentrations. The dependence of the yield of copper nanoparticles versus initial concentration of $CuSO_4$ has a maximum at about 5×10^{-4} M (Fig. 4a). At higher concentration of copper(II) ions the SPR intensity falls

down due to formation of copper mirror on the walls of the reaction vessel and probably due to oxidation of copper nanoparticles (the absorbance in the red region considerably increases). The plot of the yield of copper nanoparticles versus hydrazine hydrate concentration (Fig. 4b) also has a maximum at 0.02 M, whereas no copper nanoparticles are formed at a concentration of 0.22 M (obviously, they undergo oxidation immediately after formation).

Effect of the nature and concentration of detergents. Various surface-active substances at concentrations excluding micelle formation are often used to protect nanoparticles from oxidation and aggregation, as well as to control their shape. As a rule, particular additive and its concentration are selected on the basis of experimental results obtained separately for each system. We examined the effect of detergent concentration and nature on the formation of copper nanoparticles using anion-active sodium dodecyl sulfate, cation-active cetyl(trimethyl)ammonium bromide, and nonionogenic poly(vinylpyrrolidone). Increased concentration of sodium dodecyl sulfate favors formation of smaller nanoparticles and appreciably reduces the fraction of oxidized species, as follows from shift of the SPR from λ 580 to 560 nm and decrease in the absorption in the long-wave region. On the other hand, addition of cation-active cetyl(trimethyl)ammonium bromide sharply reduces the intensity of SPR and hence the yield of copper nanoparticles. Obviously, unlike sodium dodecyl sulfate, cetyl(trimethyl)ammonium bromide is adsorbed on the surface of copper(I) oxide particles, thus hampering their further reduction.

The yield of copper nanoparticles considerably increases upon addition of poly(vinylpyrrolidone) to a concentration of 0.0001 M; however, raising its concentration to 0.0005 M leads to reduction in the yield of copper nanoparticles, which may be due to fairly strong coordination of the oxygen atoms in poly (vinylpyrrolidone) to copper(II) ions.

Parameters of nanoparticles. Figure 5 shows a typical view on nanoparticles immobilized on mica surface, which was obtained by atomic force spectroscopy. Nanoparticles have spherical shape and, in keeping with the size distribution diagram (Fig. 5b), more than 80% of nanoparticles are smaller than 25 nm in diameter, though some amount of larger particles or their aggregates with a diameter of up to 100 nm is present. The lateral dimension of nanoparticles may be overestimated due to restrictions

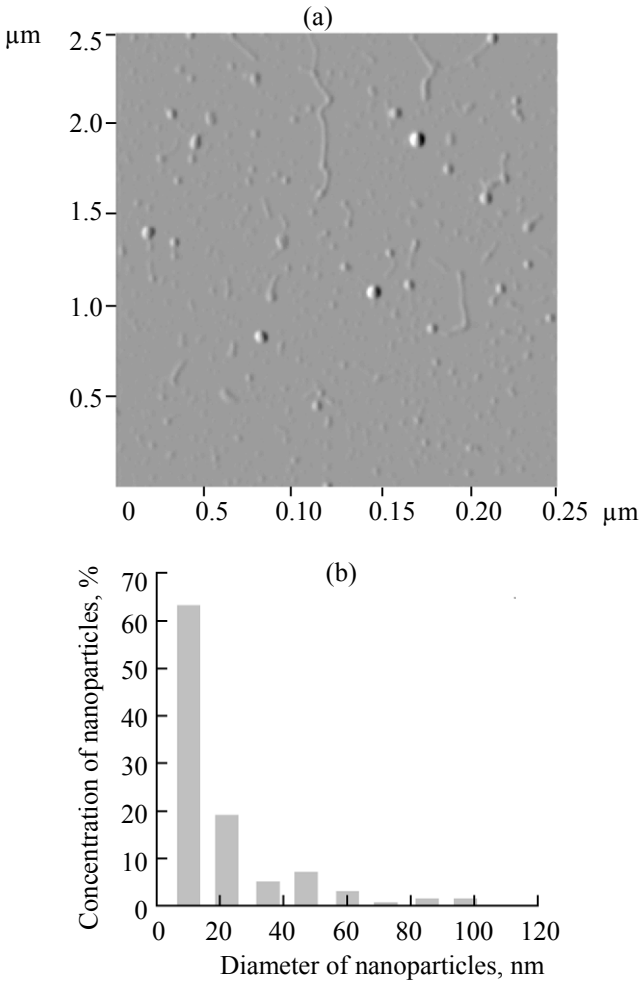

Fig. 5. (a) Typical AFM pattern (semi-contact mode) of copper nanoparticles immobilized on mica surface and (b) size distribution diagram of copper nanoparticles (a sample consisting of 130 species); c[Cu(II)] = 5×10^{-4} M, $c(N_2H_4\cdot H_2O)$ = 0.02 M, $c(KC_2H_4O_2)$ = 0.02 M, pH 11.

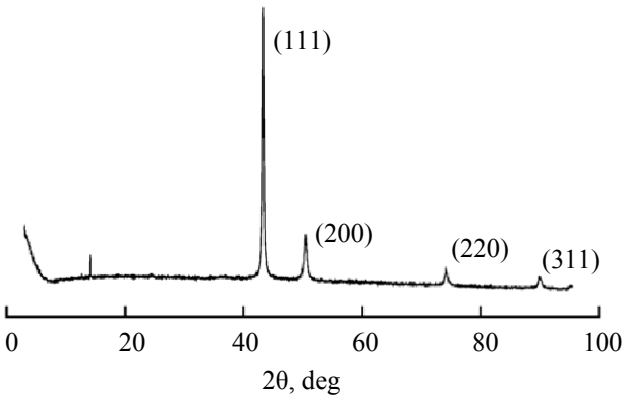

Fig. 6. X-Ray powder pattern of copper nanoparticles; c[Cu(II)] = 0.01 M, $c(N_2H_4\cdot H_2O)$ = 0.11 M, $c(KC_2H_4O_2)$ = 0.02 M.

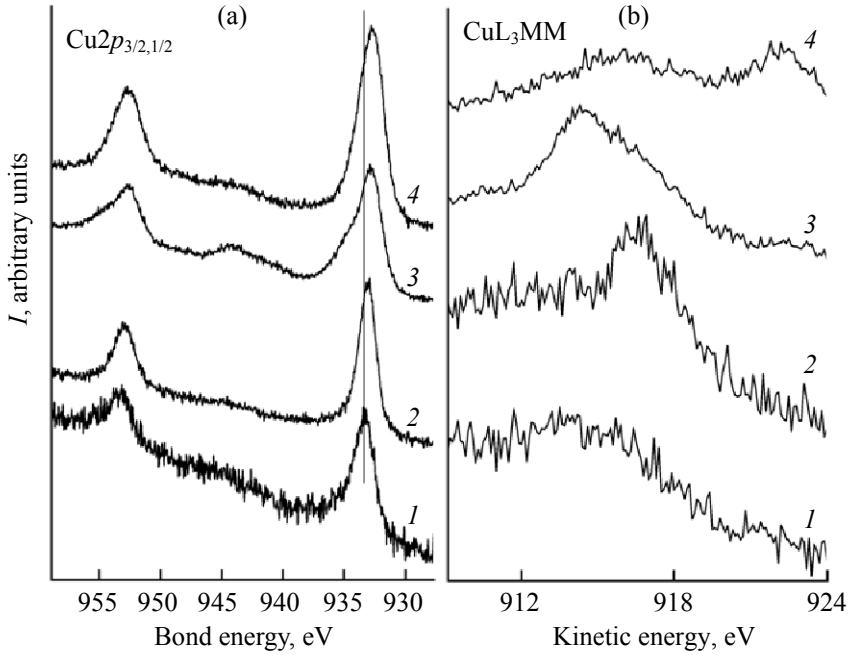

Fig. 7. X-Ray photoelectron spectra of copper nanoparticles (a) obtained by reduction with hydrazine hydrate (*1*, *2*) in the absence and (*3*, *4*) in the presence of sodium tartrate and (b) immobilized on pyrographite (*1*, *3*) before and (*2*, *4*) after etching with Ar^+ ions (5 keV, 30 μA) over a period of 2 min; c[Cu(II)] = 5×10^{-4} M, $c(N_2H_4 \cdot H_2O) = c(KC_2H_4O_2)$ = 0.02 M, pH 11.0.

intrinsic to atomic force spectroscopy; but the cross section (is not given) shows that the height of nanoparticles as a rule does not exceed 10 nm.

The X-ray powder diffraction analysis of the obtained suspension was performed without phase separation. As follows from the X-ray powder pattern shown in Fig. 6 and JCPDS data [19], the examined sample contained only metallic copper. The state of copper on the surface of nanoparticles was studied by X-ray photoelectron spectroscopy (Fig. 7). The Cu2$p_{3/2}$ line consists of the main maximum with a bond energy of 932.5 eV and a weaker line at about 934 eV, which should be assigned to copper(II) oxide or hydroxide. This is also confirmed by the presence of so-called shake-up satellites at about 942–947 eV, indicating the existence of unoccupied 3*d* orbitals. The main line may also be assigned to both Cu^0 and Cu(I), taking into account that the corresponding bond energies are similar. In order to refine the chemical state of copper, the Auger spectra of CuL_3MM were recorded. The Auger spectra displayed a broad band with its maximum at 914–915 eV, which consisted of several overlapping components; this pattern suggests the presence of Cu(II) and Cu(I) compounds and probably metallic copper (Fig. 7b, curves *1*, *3*). After etching with Ar^+ ions over a period of 2 min, which removes approximately 2 nm of the surface layer, copper(II) lines, including shake-up satellites, almost disappeared from the X-ray photoelectron spectrum, whereas the CuL_3MM line became narrower, its maximum being located at about 916.4 eV (Fig. 7b, curves *2*, *4*). The position of lines is more typical of copper(I) [20], but the presence of some amount of metallic copper could not be ruled out; the latter is characterized by a kinetic energy of the CuL_3MM line above 917 eV. Qualitatively the same spectra were obtained for nanoparticles synthesized in the presence of sodium tartrate; however, in this case the amount of copper(II) on the surface is larger.

Comparison of the XPD and XPES data allowed us to conclude that we obtained nanoparticles consisting of metallic copper core coated with a layer of copper(I) oxide. Presumably, surface oxidation of nanoparticles occurred during sample preparation.

Thus we have proposed a fairly simple procedure for the preparation of stable copper(0) hydrosols containing spherical nanoparticles with a size of 7–10 nm. The procedure implies reduction of copper(II) ions in aqueous solution with hydrazine hydrate in the presence of ligands (sodium citrate or tartrate at a concentration of 0.02 M), surface-active substances (sodium dodetcyl sulfate, $c = 1 \times 10^{-3}$ M), or poly(vinylpyrrolidone) ($c = 1 \times 10^{-4}$ M) under microwave activation.

EXPERIMENTAL

All reagents were of analytical grade and were not subjected to additional purification. Hydrazine hydrate was prepared from a saturated solution of hydrazine sulfate (c = 0.22 M) by ion exchange (AV-17-8 anion exchanger, OH form) in a dynamic mode.

According to a typical procedure, a 100-ml heat-resistant beaker was charged with 20 ml of a solution of copper(II) sulfate ($c = 1\times10^{-4}$–1×10^{-3} M), ammonia (pH 11–12), sodium tartrate, sodium citrate, or glycine (0–0.1 M), and surface-active substance [sodium dodecyl sulfate, poly(vinylpyrrolidone), or cetyl(trimethyl)-ammonium bromide, 0–1×10^{-4} M), were added, 20 ml of hydrazine hydrate was then added (c = 0.02–0.22 M), and the mixture was heated at a required temperature (from 20 to 100°C) on a water bath or in a microwave furnace (at a power of 350–700 W). After 3–20 min, the resulting colloidal solutions were examined by spectrophotometry in the λ range from 300 to 800 nm (Spekol 1300).

Sols obtained under optimal conditions were examined by atomic force microscopy in a semi-contact mode using an NTegra Aura multimode scanning probe microscope (NT-MDT, Moskva) in air at room temperature. A silicon cantilever probe with a typical resonance frequency of about 150 kHz was used. A drop of the reaction solution (5–10 μl) was applied onto refreshed mica surface and was allowed to dry at room temperature.

To record photoelectron spectra, a drop of sol was dried on a pyrographite support under reduced pressure (in the transfer chamber of a SPECS spectrometer (Germany). The spectra were recorded upon excitation with nonmonochromatized MgK_α X-ray irradiation; transmittance energy of energy analyzer 8 eV (PHOIBOS 150 MCD-9, narrow scans); pressure in the analytical chamber $<10^{-9}$ mbar.

A concentrated (thickened) suspension of nanoparticles was applied onto a silicon single crystal and was subjected while wet to X-ray powder diffraction analysis (X'Pert PRO PIXcel, PANalytical, CuK_α irradiation).

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