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PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Effect of Various Factors on the Dispersity of Copper Nanopowders Produced by Reduction of Copper Salts with Glycerol

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Abstract—Effect of the nature of a copper salt and initiators on the dispersity of copper powders was studied. The dispersity was determined by electron microscopy, X-ray phase analysis, and method of small-angle X-ray scattering, as well as from the specific surface area found by the BET technique.

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Of considerable recent interest in view of the intensive development and wide introduction of computer technologies and various electronic equipment in all fields of science, technology, and industries is the replacement of noble metals with composites based on ultradispersed copper nanopowders, because the latter are nearly as good in electrical and heat conductivity, but are substantially less expensive and more accessible. Therefore, development of techniques for production of nanosize copper particles and materials based on these powders is a topical task of indubitable importance.

Electronic engineering for the most part uses powders produced by explosion of conductors, condensation techniques, and electrolysis, which requires specialized equipment and involves gross energy expenditure. The most economically efficient are chemical techniques for production of copper powders by reduction of copper salts. This enables wide variation of the size and shape of powder particles and of the impurity content and, consequently, allows purposeful control over their properties.

Previously, methods for production of ultradispersed copper powders by reduction of various copper(II) salts with glycerol, ascorbic acid, and sodium hypophosphite have been developed [1–3]. It has been shown that chemical modification of ultradispersed copper powders can yield composites with increased stability (epoxy composites, >10 years; novolac composites, >6 years) and electrical conductivity (10^{-6}–10^{-7} Ω m) [4]. The influence exerted by the nature of a reducing agent on the dispersity, stability, and electrical conductivity of copper powders has been analyzed [5].

In this study, the influence exerted by the nature of a copper(II) salt and initiators on the dispersity of copper powders produced by reduction of copper salts with glycerol was examined. New dispersity data were compared with data on the electrical conductivity of novolac composites based on these powders, reported in [4, 6].

EXPERIMENTAL

Copper nanopowders (NPs) produced by reduction of copper salts with glycerol were used in the study. As starting copper compounds served salts of both inorganic (sulfate, basic carbonate) and organic (formate, acetate) acids. As initiators of the process of copper sulfate reduction with glycerol were used various organic acids-reducing agents (ascorbic, acetylsalicylic, and citric acids). The procedures used were described in [4].

Copper nanopowders were studied using high-resolution transmission electron microscopy (HRTEM,

Table 1. Physicochemical properties of copper nanopowders produced by reduction of various copper salts with glycerol

Sample no.	Copper(II) salt	τ_{decomp}, min	T_{decomp}, °C	D_{Cu}, nm	S_{sp}, m^2 g^{-1}
1	$Cu(HCOO)_2$	30	135–140	29±1	2.90±0.14
2	$Cu(CH_3COO)_2 \cdot H_2O$	40	145–155	38±2	2.00±0.12
3	$CuCO_3 \cdot Cu(OH)_2$	14	155–160	44±2	1.40±0.07
4	$CuSO_4 \cdot 5H_2O$	180	180–185	51±3	0.50±0.03

PEM-125), X-ray phase analysis (XPA, DRON-3.0, CuK_α radiation, $\lambda_{Cu} = 0.15418$ nm), and small-angle X-ray scattering method (SAXS, KRM-1). The specific surface area of the powders was determined by the BET method from the argon adsorption. The average particle size D_{Cu} was calculated by the Warren method with allowance for the instrumental width of the diffractometer, found by analyzing a well-annealed homogeneous copper powder with particle sizes of 1–10 μm [7].

The particle size distribution was determined from small-angle X-ray scattering curves [8].

It is known [9] that, in the general case, the chemical reduction of metal salts in solutions occurs with acceleration and, as a rule, includes three characteristic transformation regions: induction period and stages of acceleration and decay of the transformation.

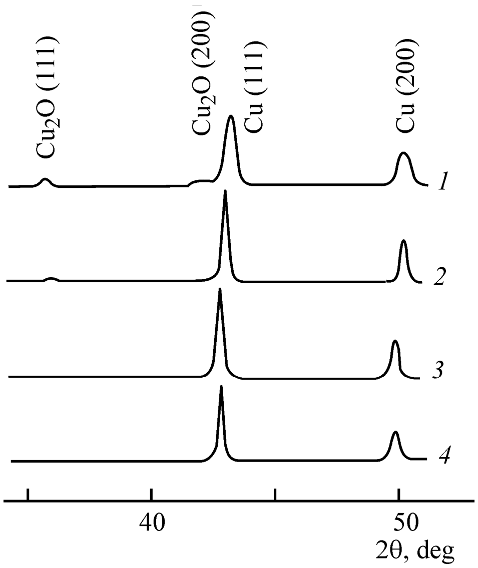

Fig. 1. X-ray diffraction patterns of copper nanopowders produced by reduction of various copper(II) salts with glycerol. (2θ) Bragg angle; the same for Fig. 3. (*1–4*) Sample numbers in Table 1.

The aim of this study was to determine the specific surface area and average crystallite sizes of the copper nanopowders obtained. The results are listed in Table 1.

It can be seen that, in reduction of readily decomposing salts, it is possible to raise severalfold the specific surface area of powders, compared with copper sulfate, and to make substantially smaller the constituent crystallites. As the decomposition temperature of a complex decreases, the specific surface area grows and the average crystallite size becomes smaller (according to XPA data). X-ray diffraction patterns of copper NPs produced by reduction of various copper salts with glycerol are shown in Fig. 1.

It was found that, in the case of copper(II) sulfate reduction with glycerol, the duration of the induction period is several hours. Further, the reaction rate noticeably increases because, presumably, the metallic clusters being formed catalyze this process, in agreement with the concepts accepted in the literature.

It can be assumed that introduction of reducing agents, such as various organic acids, into the reaction mixture makes shorter the induction period of the reduction process and raises the dispersity of the powders obtained.

It has been shown previously that organic acids-reducing agents (*L*-ascorbic, oxalic, citric, formic, or acetylsalicylic), added in small amounts, initiate the reduction of copper sulfate by glycerol. Introduction of these acids enables the reaction to proceed at lower temperatures, makes the process substantially faster (with acetyl-salicylic acid, the process duration becomes 7 times shorter), leads to an increase in the dispersity of copper powders, and raises the electrical conductivity and stability of their composites with novolac resin, which is confirmed by HRTEM and XPA data (Figs. 2, 3).

It can be seen in Fig. 2 that, compared with copper NPs produced by copper sulfate reduction with glycerol in the absence of initiators (*1*), the NPs

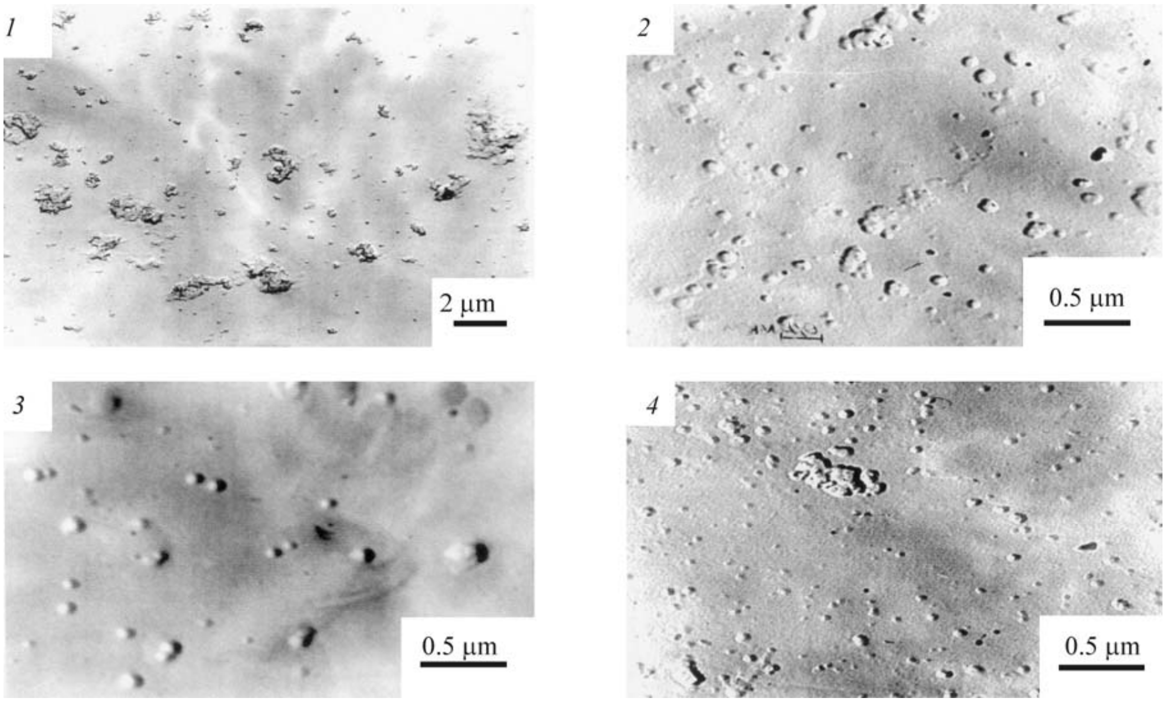

Fig. 2. Electron micrographs of copper NPs produced by reduction of copper(II) sulfate with glycerol in the presence of initiators, organic acids. (*1*–*4*) Sample numbers in Table 2; the same for Figs. 3, 4.

obtained with initiators (*L*-ascorbic, acetylsalicylic, and citric acids) have a higher dispersity. The highest dispersity is observed in the cases of citric (*4*) and acetylsalicylic (*3*) acids. The minimum particle sizes in Fig. 2 are 10–40 nm. As a rule, aggregates of the particles are not larger than 100–200 nm. With *L*-ascorbic acid (*2*), the amount of aggregates with sizes of 100–200 nm is somewhat larger than that with citric acid. The powders obtained without initiators are more aggregated (*1*) and contain aggregates up to 1–2 μm in size, composed of finer particles.

Figure 3 shows X-ray diffraction patterns of copper powders produced by copper(II) sulfate reduction with glycerol without an initiator (sample no. 1) and in the presence of initiators: *L*-ascorbic (sample no. 2), acetylsalicylic (sample no. 3), and citric acids (sample no. 4). Apparently, the powders obtained with ascorbic and citric acids as initiators contain almost no copper oxide impurities. If, however, the role of initiator is played by acetylsalicylic acid decomposing below the reaction temperature (T_{decomp} = 140°C), copper(I) oxide is present in the powders.

The peak broadening in the X-ray diffraction patterns was used to calculate the average crystallite size by the Warren method. The data obtained are listed in Table 2.

Apparently, the introduction of organic acids-initiators results in the decrease of crystallite size and the growth of specific surface area, compared with a sample obtained without an initiator. The smallest crystallite size and largest specific surface area are

Table 2. Physicochemical properties of copper nanopowders produced by reduction of copper(II) sulfate with glycerol in the presence of initiators

Sample no.	*c*	Indicator (acid)	T_{decomp}, °C	τ_{decomp}, min	D_{Cu}, nm	S_{sp}, m^2 g^{-1}
1	1:10.0	–	180–185	180	51±3	0.50±0.03
2	1:7.5:0.020	*L*-Ascorbic	140–145	40	49±2	0.70±0.03
3	1:10.0:0.050	Acetylsalicylic	155–160	25	44±2	1.80±0.10
4	1:7.5:0.060	Citric	170–175	100	31±1	2.70±0.13

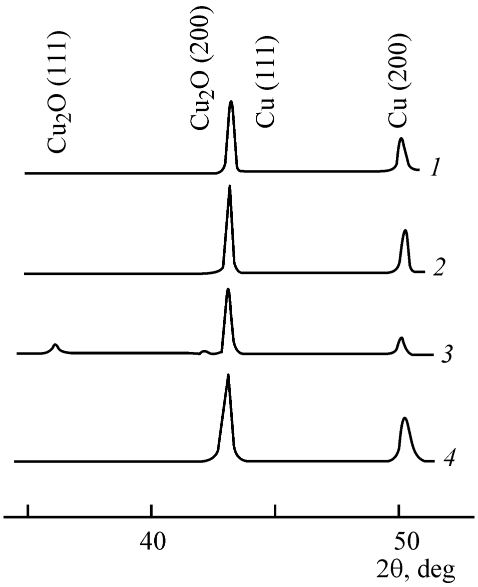

Fig. 3. X-ray diffraction patterns of copper nanopowders produced by reduction of copper sulfate with glycerol.

observed for powders produced by reduction with glycerol, with citric acid as initiator. In addition, these powders contain no admixtures of copper(I) oxide.

Figure 4 shows weight particle size distributions calculated from small-angle scattering curves. Apparently, a bimodal particle size distribution is observed for almost all powders, with the first peak at 5–10 nm, and the second, at 60–100 nm. It can be seen that, with initiators used, the peak maxima are shifted to smaller particle sizes. For example, the maximum of the main (second) peak lies at 100–110 nm for the copper powder produced without initiators (Fig. 4, sample no. 1), at 80–85 nm for the powder produced in the presence of *L*-ascorbic acid as initiator, and at 60–70 nm for acetylsalicylic acid, with the second peaks beginning at 40–50 nm in the first two cases. With acetylsalicylic acid, the second peak is very broad (from 10 to 200 nm) and has an almost constant intensity in the range from 50 to 90 nm. The only exception is the powder produced with citric acid as initiator. In this case, only a single peak is clearly seen, with the maximum at 25–30 nm.

Separately are the first peaks presented of the distribution functions (Fig. 4b), calculated using a special procedure [10]. It can be seen that for all the powders the maximum of the peak is at 5–6 nm. For powders produced in the presence of ascorbic and citric acids, the maximum is shifted to the left. The peak has the highest intensity for the copper powder produced by reduction in the presence of citric acid as initiator.

X-ray data (XPA, SAXS) are in good agreement with results obtained using electron microscopy. Apparently, the highest dispersity is observed with citric acid used as initiator.

Comparison of the dispersity data obtained in this study with previously reported data on the electrical conductivity and stability of the composites [4, 6] suggests that introduction of organic acids-reducing agents not only intensifies the reduction process and raises the NP dispersity, but also enables synthesis of composites with prolonged stability (>6 years) and high electrical conductivity even with a novolac resin. The highest stability is observed for the composites produced with an organic acid that is the most stable against decomposition (at the temperature of the reaction of copper sulfate reduction by glycerol), citric

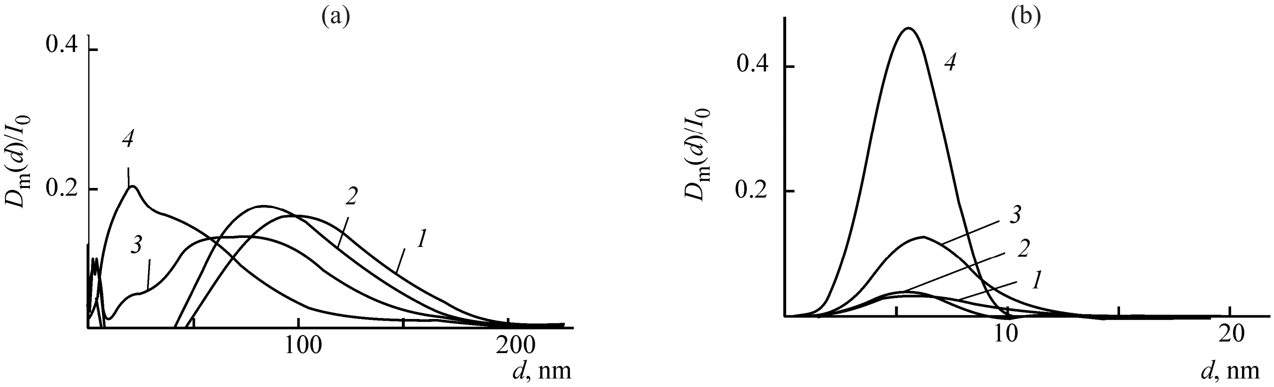

Fig. 4. Mass particle size distribution functions in the ranges (a) 0–200 and (b) 0–20 nm for copper nanopowders produced by reduction of copper(II) sulfate with glycerol in the presence of organic acids. (*d*) Particle diameter and (*I*) intensity of the distribution peak.

acid, as initiator. This is presumably accounted for by stabilization (liganding) of copper particles in the course of the reaction with this acid.

This circumstance makes it possible to synthesize copper nanopowders with high dispersity, stability, and electrical conductivity not only from the expensive copper(II) formate and acetate, but also from a less expensive and more accessible salt, copper(II) sulfate pentahydrate. Moreover, the copper nanopowder produced from this compound in the presence of citric acid is almost as good in dispersity as the powder based on copper formate, but, in contrast to the latter, contains no admixtures of copper(I) oxide and enables fabrication of composites with conductivity stable for more than six years (~4 10–6 Ω m).

CONCLUSIONS

(1) It was shown that, in reduction of readily decomposing copper salts or copper(II) sulfate in the presence of initiators, the specific surface area of the resulting powders can be made larger and the crystallite size can be diminished, with the electrical conductivity and stability of the powders simultaneously raised.

(2) It was found by means of transmission electron microscopy that introduction of initiators leads to a decrease in the size of copper particles. Copper particles with a minimum size of 10–50 nm were shown to be present.

(3) The method of small-angle X-ray scattering was used to demonstrate that introduction of initiators strongly affects the particle size distribution.

(4) The highest dispersity was observed in reduction of copper formate with glycerol and in reduction of copper sulfate in the presence of citric acid as initiator.

REFERENCE

1. Obraztsova, I.I., Efimov, O.A., Eremenko, N.K., and Simenyuk, G.Yu., *Neorg. Mater.*, 1995, vol. 31, no. 4, p. 798.
2. Obraztsova, I.I., Simenyuk, G.Yu., and Eremenko, N.K., *Zh. Prikl. Khim.*, 2004, vol. 77, no. 3, p. 386.
3. Obraztsova, I.I., Simenyuk, G.Yu., and Eremenko, N.K., *Zh. Prikl. Khim.*, 2006, vol. 79, no. 5, p. 717.
4. Obraztsova, I.I., Simenyuk, G.Yu., and Eremenko, N.K., *Zh. Prikl. Khim.,* 2002, vol. 75, no. 11, p. 1772.
5. Obraztsova, I.I., Simenyuk, G.Yu., and Eremenko, N.K., *Zh. Prikl. Khim.*, 2006, vol. 79, no. 10, p. 1626.
6. Obraztsova, I.I., Simenyuk, G.Yu., and Eremenko, N.K., *Neorg. Mater.*, 1999, vol. 35, no. 8, pp. 937.
7. Gusev, A.I., *Nano: materialy, struktury, tekhnologii* (Nano: Materials, Structures, Technology), Moscow: Fizmatgiz, 2005.
8. *Fizika tverdogo tela: Laboratornyi praktikum "Metody polucheniya tverdykh tel i issledovaniya ikh struktury"* (Solid-State Physics: Laboratory Manual "Methods for Production of Solids and for Analysis of Their Structure"), book 1, Khokhlov, A.F., Ed., Moscow: Vysshaya shkola, 2001.
9. Pomogailo, A.D., Rozenberg, A.S., and Uflyand, I.E., *Nanochastitsy metallov v polimerakh* (Metal Nanoparticles in Polymers), Moscow: Khimiya, 2000.
10. Dodonov, V.G., Z. *Kristallogr.,* 1991, no. 4, p. 102.