Chemistry for Sustainable Development **21** (2013) 403–409

UDC 544.77

Synthesizing Highly Concentrated Hydrosols of Copper Nanoparticles *via* Reduction by Ascorbic Acid in the Presence of Gelatose

S. V. SAIKOVA[1], K. S. MURASHEVA[1], S. A. VOROBYEV[1], K. YU. KOCHMAREV[1], E. E. KARIMOV[1], A. D. EREMINA[1] and YU. L. MIKHLIN[2]

[1]*Siberian Federal University,*
Pr. Svobodny 79, Krasnoyarsk 664041 (Russia)

E-mail: ssai@mail.ru

[2]*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences,*
Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)

(Received April 17, 2013; revised June 3, 2013)

Abstract

A simple and environmentally safe method has been proposed for producing highly concentrated (about 0.01 mol/L) hydrosols containing copper nanoparticles with the size of 30–40 nm. The method is based on the reduction of Cu^{2+} ions in aqueous solution of ascorbic acid in the presence of high molecular mass gelatose stabilizer, the product of high temperature hydrolysis of gelatin.

Key words: copper nanoparticle synthesis, hydrosols, gelatose, ascorbic acid, guar, carrageenan

INTRODUCTION

Copper nanoparticles have proven serve as excellent catalysts of industrial processes [1–8], they are used in the production of materials for electronics [9, 10] as well as in producing liquid and gas phase detectors and sensors for some chemical substances (NO, H_2S, *etc.*) or for some biological objects (Hepatitis B virus) [11–13]. The antibacterial properties of copper are also widely known, whereby the nanoparticles of copper could be used to develop medical supplies and equipment for the food industry, as well as for obtaining antibacterial media [14]. One could use copper nanoparticles in designing modern lubricating substances [11], "skeletons" for composite materials with different properties [15], and so on.

Traditionally, in order to obtain copper nanoparticles one carries out a controlled chemical reaction of reducing the copper (II) ions in solutions. The method of chemical synthesis does not require complicated equipment and any significant investment thus it can be easily incorporated into industrial technology. Moreover, it allows controlling the particle size and morphology of the products formed *via* maintaining certain reaction parameters. However, contemporary methods for copper nanoparticle synthesis require for the use of organic solvents as well as strong and toxic reducing agents such as hydrazine [16–18], or sodium borohydride, [19–22], those are potentially hazardous with respect to the environment.

Another problem consists in the fact that in most cases achieving a high concentration of nanoparticles in the final solution is not possible (only about 10^{-3}–10^{-4} mol/L) owing to the sedimentation the instability of colloidal systems. At the same time, the use of the sols with a high content of nanoparticles ($(1–10) \cdot 10^{-2}$ mol/L) allows significantly increasing the productivity of the processes. Moreover, owing to a high reactivity of nanosized copper which is oxidized in the presence of even small amounts of oxygen in the solution, the nanoparticles formed should be protected from oxidation. These problems are solved with the use of special materials, stabilizers; most of tose are hazardous with respect to the environment.

The attention of researchers is increasingly attracted to chemical processes those are aimed at avoiding or minimizing any use of hazardous substances. This trend is most clearly formulated by Anastas and Warner in the form of 12 principles of green chemistry [23].

In this paper, we propose a simple and environmentally safe (green) method for the synthesis of highly concentrated dispersions of copper nanoparticles, wherewith there is ascorbic acid used as a reducing agent, and gelatose or a polysaccharide (guar, carrageenan, gammaksan) used as a stabilizer.

EXPERIMENTAL

In this work we used analytical grade and chemical purity grade reagents with no further purification. In addition, compounds with a high molecular mass were used: food gelatin (State Standard GOST 11293–89), xanthan biopolymer "Gammaksan" (xanthan gum), technical regulations TU 2458-002-50635131–2003 (Gammakhim JSC, Tatarstan, Russia), carrageenan (technical regulations TU 9284037-02698170–99), guar (guar gum) (technical regulations TU 2458-019-57258729–2006).

Gelatin was used for obtaining an aqueous gelatose solution *via* microwave hydrolysis. For this purpose, 10 g of dry gelatin was poured with 200 mL of distilled water in a 250 mL flask with further heating on a 1 L water bath r in a microwave oven at 350 W during 40 min. To prevent evaporation we used a backflow condenser. The resulting gelatose solution with the concentration of 50 g/L was diluted with distilled water before use to obtain a required concentration value.

For the synthesis of copper hydrosol, to 10 mL of an aqueous solution of copper (II) sulphate ($C = 0.01–0.60$ mol/L) were added equal volumes of a stabilizer solution with preset concentration (gelatose, gammaksan, carrageenan, guar), and sodium ascorbate or ascorbic acid with different pH value (2.8–11.5). Sodium ascorbate was prepared *via* adding a certain amount of NaOH 1 M solution of ascorbic acid (0–0.45 g per 10 mL of the ascorbic acid solution). The resulting solution was heated on a water bath (0.5–0.6 L) in a microwave oven with 750 W power during 10 min. In this case the solution changed its colour from pale yellow to saturated maroon-red colour.

The hydrosols obtained were studied spectrophotometrically within the wavelength range of 300–800 nm (Specol 1300 and Thermo Scientific Evolution 300 spectrometers). In the course of the process, we sampled 1 mL of the sol from the reaction medium with the further 10-fold dilution thereof because of too great initial values of the optical density of the dispersions, caused by a high concentration of nanoparticles. Then, the solution was placed in a cell with an optical layer length equal to 1 cm. It was preliminary found that the difference in light absorption of the cells with distilled water is equal to zero. The data obtained are presented as average value of three to six parallel experiments.

The atomic force microscopy (AFM) investigation was performed in a tapping mode using a NTegra Aura multimode scanning probe microscope (NT-MDT, Moscow) in air at a room temperature. A silicon cantilever having a typical resonance frequency of about 150 kHz was used as the probe. A drop of the reaction solution, 5–10 μL in volume was applied onto a freshly renewed mica surface with further drying at a room temperature. In a similar manner, we dealt with the sol washed from excess gelatose by the solution of sodium ascorbate.

The sol, prior to the investigation by means of transmission electron microscopy (JEOL JEM-2100, the accelerating voltage of 200 kV) were centrifuged during 5 min at a rotation speed equal to $1.6 \cdot 10^4 \text{ min}^{-1}$ with trice washing from gelatose. A drop of the washed sol was applied onto a copper grid coated with an amorphous carbon film, and dried in air.

The precipitate obtained by centrifugation of the initial hydrosol was placed on a silicon single crystal to perform XRD phase analysis using an X'Pert PRO PIXcel diffractometer (PANalytical), CuK_α radiation.

RESULTS AND DISCUSSION

It is known that the optical spectra of hydrosols containing metallic nanoparticles are characterized by the presence of so-called surface plasmon resonance maxima (SPR) those appear when the frequency of the incident electromagnetic wave and the natural oscillations of the electrons in the nanoparticle coincide. The type, intensity and position of SPR maxima are determined by size, shape and degree of oxidation of the nanoparticles. For spherical copper nanoparticles (2–10 nm in size) the position of SPR maximum position corresponds to 570 nm [24]. With increasing the thickness of the oxide film on the surface of the copper nanoparticles, as well as the aggregation level, the SPR maximum intensity decreases and the absorption within the wavelength range 700–800 nm exhibits an increase [25]. In our opinion, the difference between the intensity (b) of the SPR maximum (I_{SPR}) and the intensity of optical absorption in the “red” region of the spectrum at 750 nm (in the middle of this range, I_{750}), determined as

$$b = I_{SPR} - I_{750} \quad (1)$$

should characterize both the product fraction (copper nanoparticles) with respect to the initial amount of copper in the system (yield of nanoparticles), and the degree of oxidation thereof. This parameter was chosen in order to optimize the process of producing copper nanoparticles in this study.

According to the results of previous studies [26–28], for the synthesis of copper nanoparticles in aqueous solutions we chose a “green” reducing agent such as ascorbic acid. Dry pure crystalline ascorbic acid is stable with respect to atmospheric oxygen, but in aqueous solution the ascorbic acid enters into an oxidation reaction (electrode potential at pH 4 and 35 °C being equal to +0.166 V, whereas in alkaline medium and in the presence of atmospheric oxygen this value amounts to +0.08 [29]), the composition of the oxidation products depending on the conditions of the process. The most part researchers believe that with no alkalizing there are furfural and oxygen formed, whereas in an alkaline medium the formation of 2,3-diketo-*L*-gulonic acid is observed (with a subsequent destruction into oxalic acid and *L*-treonic acid):

$$C_6H_8O_6 + CuSO_4 + 2NaOH \rightarrow Cu + Na_2SO_4 + C_6H_8O_7 + H_2O \quad (2)$$

The oxidation process could be accelerated by heavy metal ions, especially copper and iron. Thus, the reduction process is to a considerable extent determined by the reaction conditions. For efficiently producing copper nanoparticles it is important to determine the character and the degree of influence of each parameter of the reaction, the ratio required between the reagents, as well as other optimal conditions of the process in order to avoid adverse interactions in the system, resulting in the destruction of the product formed.

Choosing a stabilizer

Figure 1 presents electronic absorption spectra for copper nanoparticle hydrosols obtained using the stabilizers under investigation. The reduction process was performed using a water bath, in a microwave oven during 10 min. After adding the ascorbic acid, the solutions immediately got yellow colour, which colour in the course of the reaction changed into green, then into black and then into red. The completion of the reaction is indicated by the formation of a maroon-red collared colloid.

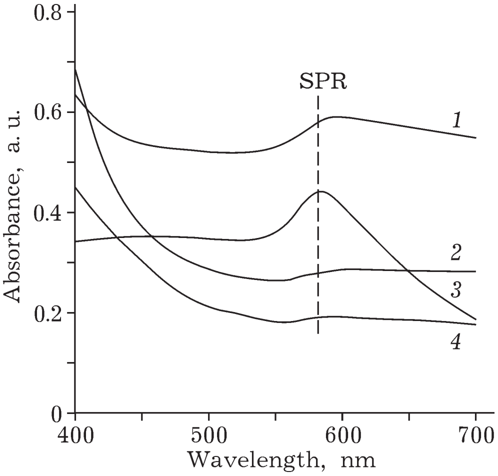

Fig. 1. Effect of the stabilizer nature on the type of optical spectra inherent in copper nanoparticles: *1* – guar, *2* – carrageenan, *3* – gelatose, *4* – gammaksan (xanthan gum); process conditions: initial concentration of $CuSO_4$ 0.01 mol/L (10 mL), ascorbic acid 1 mol/L, stabilizer 3 g/L, duration 10 min.

The SPR maxima within the wavelength range of 580–590 nm indicate the presence of nanoparticles in the sols. However, judging from a low intensity of the maxima in the case of all the polysaccharides used (except for gelatose) and a significant absorption within the region of high wavelength value, the amount of nanosized particles is small and they are profoundly oxidized. In this connection, all the further experiments were performed using the solution of gelatose as a stabilizer.

Effect of pH

From equation (2) it follows that the equilibrium of copper reduction process is shifted to the right under alkalizing the reaction solution. The acidity of the initial copper solution was varied with the help of NaOH within the pH range from 2.8 to 11.5. The number of nanoparticles formed (Fig. 2) increases with increasing the pH value up to 10.3, which is consistent with decreasing the value of ascorbic acid electrode potential in an alkaline medium. However, further increasing the pH value is accompanied by some decrease in the number of copper nanoparticles formed, which, to all appearance, could be associated with decreasing the activity of copper (II) ions as the result of the hydrolysis process.

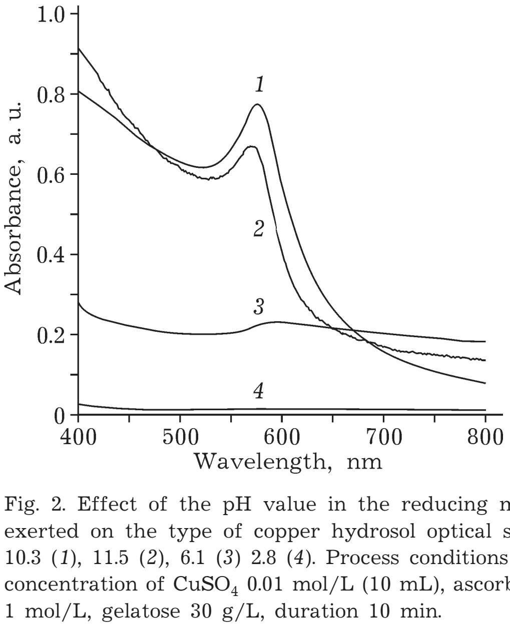

Fig. 2. Effect of the pH value in the reducing medium exerted on the type of copper hydrosol optical spectra: 10.3 (*1*), 11.5 (*2*), 6.1 (*3*) 2.8 (*4*). Process conditions: initial concentration of $CuSO_4$ 0.01 mol/L (10 mL), ascorbic acid 1 mol/L, gelatose 30 g/L, duration 10 min.

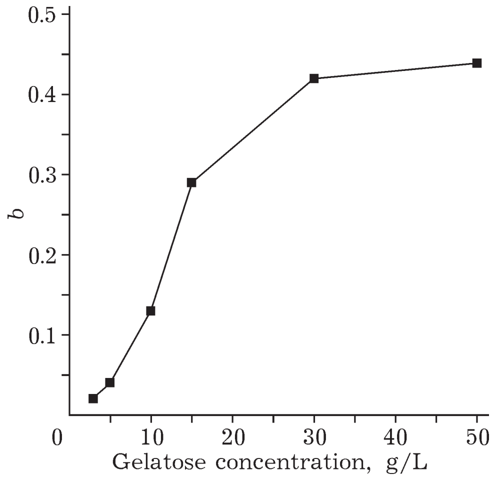

Fig. 3. Effect of gelatose concentration on the synthesis of copper nanoparticles (parameter *b*). Process conditions: initial concentration of $CuSO_4$ 0.01 mol/L (10 mL), ascorbic acid 1 mol/L, pH 10, duration 10 min.

Effect of gelatose concentration

The number of nanoparticles formed (Fig. 3) increases with increasing the stabilizer concentration up to 30 g/L, and then goes “to the plateau”. To all appearance, at higher concentrations values the formation of nanoparticle is complicated by the solution viscosity, whereas a lower concentration causes decreasing the gelatose stabilizing effect exerted on nanoparticles, which could lead to agglomeration and oxidation thereof. In the further experiments, we used gelatose concentration amounting to 30 g/L.

Effect of the concentrations of ascorbic acid, copper (II) ions and the molar ratio between them

The comparison of optical spectra for hydrosols with different initial concentration of copper (Fig. 4, *a*) revealed that with increasing the initial concentration the amount of copper nanoparticles in the system does not vary monotonically. First, there is a maximum observed at 0.01 mol/L and then a decrease is exhibited within the range of 0.03–0.06 mol/L. However, there are neither precipitate nor “copper” mirror observed to form on the walls of the reaction vessel. Therefore, the decrease of the yield of nanoparticles could be associated with an insufficiency of the reducing agent. This can be confirmed by the data presented in Fig. 4, *b*,

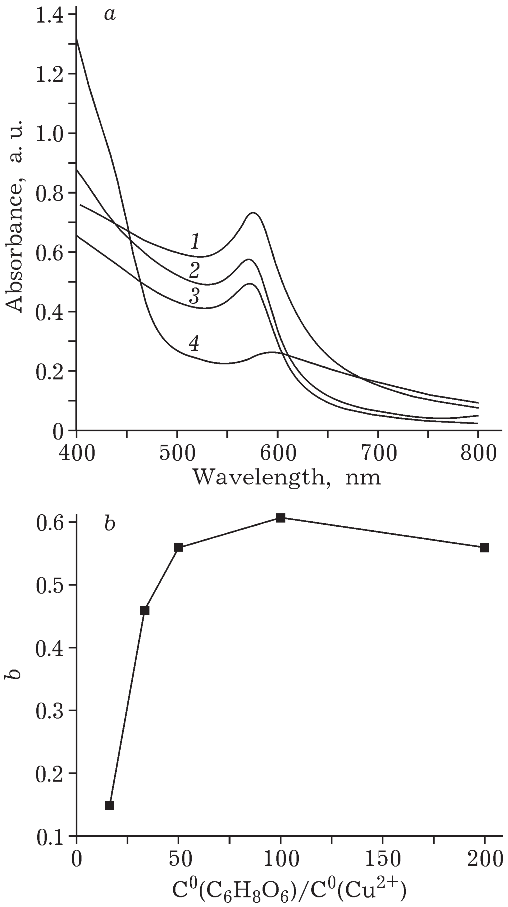

Fig. 4. Optical absorption spectra of copper-containing hydrosol with different initial concentrations of Cu^{2+} (*a*) and changing the *b* parameter depending on the ratio between the concentrations of ascorbic acid and Cu^{2+} (*b*). The initial concentration of copper ions (mol/L): 0.01 (*1*) 0.005 (*2*) 0.03 (*3*) 0.06 (*4*); process conditions: initial concentration of $CuSO_4$ 0.005–0.006 mol/L (10 mL), ascorbic acid, 0.5–1.0 mol/L (10 mL), gelatose 30 g/L (10 mL), duration 10 min.

whereby the optimum ratio between the number of moles of ascorbic acid (at the initial concentration equal to 1 mol/L) and that of copper ions amounts to approximately 100, in spite of the stoichiometry of the reaction (2). To all appearance, a considerable excess in the reductant is requires in order to prevent oxidation of the nanoparticles formed. It should also be noted that in the case of decreasing the concentration of ascorbic acid down to 0.5 mol/L the duration of the synthesis doubly increased. Accordingly, as the optimum molar ratio we have chosen 100, the initial concentration of the copper (II) salt is equal to 0.01 mol/L, and the ascorbic acid concentration amounting to 1 mol/L.

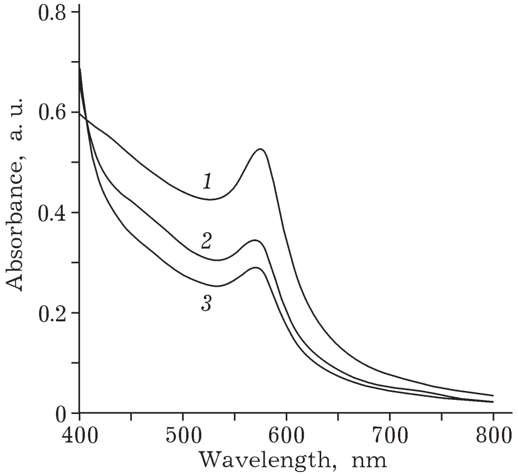

Fig. 5. Changing the optical absorption spectra of copper-containing hydrosol under contacting between copper nanoparticles and air. Contact time, h: 0 (*1*), 72 (*2*), 120 (*3*); process conditions: initial concentration of $CuSO_4$ 0.01 mol/L (10 mL), ascorbic acid 1 mol/L, gelatose 30 g/L (10 mL), duration 10 min.

Stability of hydrosols in air

We investigated the oxidative and sedimentation stability of copper nanoparticle dispersions produced *via* contacting with atmospheric oxygen during 120 h under optimal conditions chosen: the concentration of copper sulphate, sodium ascorbate and gelatose 0.01 mol/L, 30 g/L and 1 mol/L, respectively, pH 10.3. There is a maximum decrease in the intensity of SPR observed (Fig. 5), which could be, to all appearance, caused by a decrease of the amount of nanoparticles due to dissolving the most small among them in the course of oxidation. Thus, gelatose can not completely prevent the oxidation of the nanoparticles, but protects the sols from aggregation and sedimentation.

Investigation of sols obtained by means of XRD, TEM and AFM

According to XRD data, the precipitate obtained *via* centrifugation of the initial sol (Fig. 6, *a*), represents metallic copper with crystallite size of about 30 nm [30]. This conclusion is confirmed by electron microdiffraction data (not presented) and micrographs (see Fig. 6, *b*). The particles of the same size, according to AFM, are also detected at the surface of the copper-gelatose composite obtained by drying the origi-

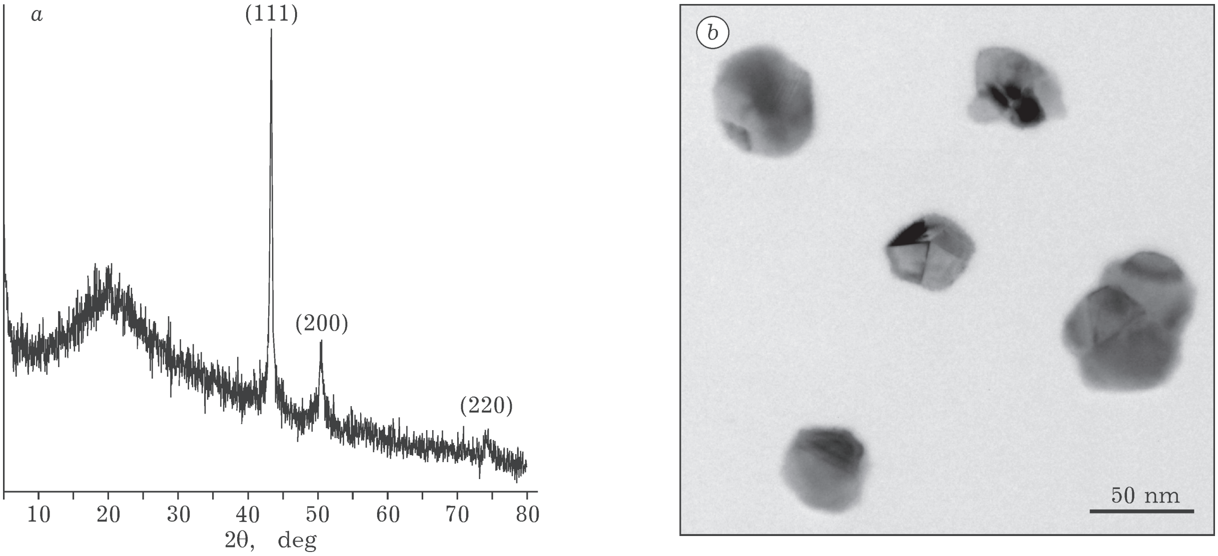

Fig. 6. XRD pattern of precipitate (*a*) and a TEM image of copper nanoparticle hydrosol (*b*).

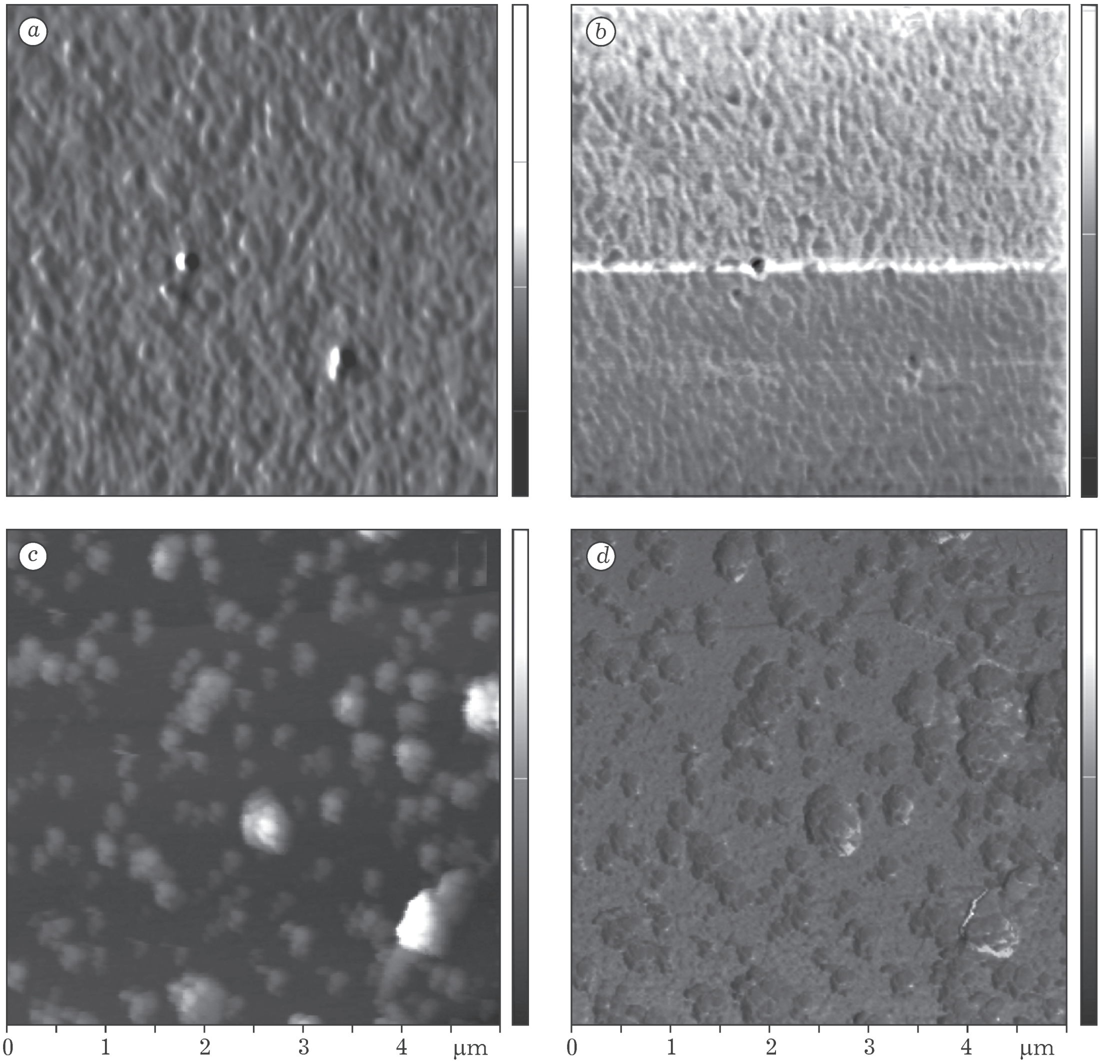

Fig. 7. AFM image for copper nanoparticles immobilized on the surface of highly oriented pyrolytic graphite before (*a*, *b*) and after (*c*, *d*) washing from gelatose: *a*, *c* – height; *b*, *d* – phase contrast.

nal (non-washed) hydrosol on the plate of pyrolytic graphite (Fig. 7, *a*, *b*). It should be noted that the concentration of particles according to the image obtained by AFM, is much higher as compared to electron microscopy data (see Fig. 6, *b*). This could be caused by an agglomeration of the original nanoparticles on the substrate surface in the course of sample preparation for TEM procedure, which consists in washing from gelatose. The aggregates of nanoparticles are not visible in transmitted beam, but they can be visualized well by AFM (see Fig. 7, *c* and *d*).

The studies concerning the antibacterial activity of the sols obtained demonstrated them to exhibit a high efficiency with respect to a strain of *E. coli* (Gram-negative bacteria *E. coli* ATCC 25922), wherewith this method for the synthesis of nanoparticles could be recommended for obtaining antibacterial media.

CONCLUSION

The formation of copper nanoparticles is revealed to depends mainly on the pH value of the reduction medium, on the nature and concentration of the high molecular mass stabilizer, the concentration of reactants and molar ratio between them. Optimal conditions are chosen for obtaining the copper nanoparticles: $CuSO_4$ concentration amounting to 0.01 mol/L (10 mL), ascorbic acid 1 mol/L (10 mL), gelatose 30 g/L (10 mL), pH 10–10.5, heating with the use of a water bath (0.5 L) in a microwave oven at 750 W power for 10 min. The investigation of the hydrosols obtained demonstrated that there are contain copper nanoparticles of approximately 30–50 nm contained therein.

REFERENCES

1 Dhas N. A., Raj C. P., Gedanken A., *Chem. Mater.*, 10, 5 (1998) 1446.
2 Ron H., Cohen S., Matlis M., Rappaport I., Rubinstein I., *J. Phys. Chem. B*, 102, 49 (1998) 9861.
3 Kalidindi S. B., Jagirdar B. R., *J. Phys. Chem. C*, 112, 11 (2008) 4042.
4 Ang T. P., Wee T., Chin S., *J. Phys. Chem. B.*, 108, 30 (2004) 11001.
5 Singh D., Neti N., Sinha A., Srivastava O., Singh D., *J. Phys. Chem. C.*, 111, 4 (2007) 1638.
6 Liu D., Yang S., Lee S.-T. *J. Phys. Chem.* C. 112, 8 (2008) 7110.
7 Padley M., Rochester C. H., Hutchings G. J., King F., *J. Chem. Soc. Faraday Trans.*, 90, 1 (1994) 203.
8 Rostovshchikova T. N., Rostovshchikova T. N., Smirnov V. V., Kozhevin V. M., Yavsin D. A., Zabelin M. A., Yassevich I. N., Gurevich S. A., *Appl. Catal. A*, 296, 1 (2005) 70.
9 Gimenez-Romero D., García-Jaren J. J., Agrisuelas J., Gabrielli C., Perrot H., Vicente F., *J. Phys. Chem. C*, 112, 11 (2008) 4275.
10 Espinos J. P., Morales J., Barranco A., Caballero A., Holgado J. P., Gonzáles-Elipeet A. R., *J. Phys. Chem. B.*, 106, 27 (2002) 6921.
11 Zhou G., Lu M., Yang Z., *Langmuir*, 22, 13 (2006) 5900.
12 Ding R., Jiang J., Wu F., Gong M., Zhu J., Huang X., *Nanotechnol.*, 22, 37 (2011) 375303.
13 Kim D., Yoo S. M., Park T. J., Yoshikawa H., Tamiya E., Park J. Y., Lee S. Y., *Anal. Chem.,* 83, 16 (2011) 6215.
14 Anyaogu K. C., Fedorov A. V., Neckers D. C., *Langmuir*, 24, 8 (2008) 4340.
15 Su X., Zhao J., Bala H., Zhu Y., Gao Y., Ma S., Wang Z., *J. Phys. Chem. C*, 111, 40 (2007) 14689.
16 Dong Y., Li Y., Wang C., Cui A., Deng Z., *J. Coll. Interface Sci.*, 243, 1 (2001) 85.
17 Du F., Liu J., Guo Z., *Mat. Res. Bull.*, 44, 1 (2009) 25.
18 Gui Z., Fan R., Mo W., Chen X., Yang L., Hu Y., *Mat. Res. Bull.*, 38, 1 (2003) 169.
19 Dong T. Y., Wu H. H., Lin M. C., *Langmuir*, 22, 16 (2006) 6754.
20 Mohammed A., Gopakumar G., Shoba T. L., Mulla I. S., Vijayamohanan K., Kulkarni S. K., Urban J., Vogel W., *J. Coll. Interface Sci.*, 255, 1 (2002) 79.
21 Darugar Q., Qian W., Mostafa A., *J. Phys. Chem. B*, 110, 1 (2006) 143.
22 Giuffrida S., Condorelli G. G., Costanzo L. L., Fragala I. L., Ventimiglia G., Vecchio G., *Chem. Mater.*, 7, 16 (2004) 1260.
23 Anastas P. T., Warner J. C., Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.
24 Creighton A. J. and Eadon D. G., *J. Chem. Soc., Faraday Trans.,* 87, 24 (1991) 3881.
25 Johnson R. C., Li J., Hupp J. T., Schatz G. C., *Chem. Phys. Lett.*, 356, 5 (2002) 534.
26 Saikova S. V., Vorobyev S. A., Nikolaeva R. B., Mikhlin Yu. L., *Zh. Obshch. Khim.*, 80, 6 (2010) 952.
27 Saikova S. V., Vorobyev S. A., Mikhlin Yu. L., *Zh. SFU*, 5, 1 (2012) 61.
28 Saikova S., Vorobyev S., Likhatski M., Romanchenko A., Erenburg S., Trubina S., Mikhlin Y., *Appl. Surf. Sci.*, 258, 20 (2012) 8214.
29 Shnaydman L. O., Proizvodstvo Vitaminov, Pishchevaya Promyshlennost', Moscow, 1973.
30 Powder Diffraction File, 2001, JCPDS No. 03-065-9026.