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LETTERS TO THE EDITOR

Photolysis of Aqueous Solutions of Copper(II) Complexes with Aspartic and Glutamic Acids

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Properties of metal-containing thin films of nanometer thickness essentially differ from properties of large bulk samples which offers wide possibilities of creating fundamentally new materials with enhanced corrosive and wear resistance, and unique electrical, optical, and magnetic characteristics.

The most promising application fields for copper thin films are micro- and nano-electronics. Such films are used as conducting tracks in large and super-large integrated circuits [1]. Solutions of copper nanoparticles and materials modified with their application possess high biocidal and catalytic properties [2]. However, wide practical application of copper nanoparticles is hampered by their high reactivity and strongly expressed dependence of properties on size, composition, and surface admixtures.

The aim of this work was to obtain copper nanoparticles by photochemical decomposition of copper(II) complexes with aspartic and glutamic acids, and to study their optical properties and composition, and also the dependence of effectiveness of the metal phase formation on the nature and concentrations of the complexes.

Earlier we have synthesized photochemically copper nanoparticles and copper-containing films [3–5], an essential condition of the syntheses being the presence of organic solvents (most often alcohols) and (or) stabilizers.

It was found in this work that the irradiation of a thin layer (1 mm) of a 1×10^{-2} M aqueous solution of $K_2[CuGlu_2]$ in the absence of stabilizers results in the formation of a red film with a plasmon absorption maximum at 580 nm (*D* 0.3 relative unit) on a quartz glass surface. Further irradiation up to 210 min results in the *D* increase up to 1.6 relative unit, a red shift of the plasmon absorption maximum (up to 587 nm), and narrowing of the latter. These facts point to the formation of copper nanoparticles and their subsequent coarsening. The application of this complex is distinguished by the copper precipitation exclusively on the quartz glass surface and by the absence of nanoparticles in the photolyte. The quartz glass surface plays a role of a stabilizer for the copper nanoparticles formation.

According to the scanning electron microscopy data, the film consists of copper island spherical particles not exceeding 300-500 nm in size. The energy-dispersive analysis of the film has shown that the sample is characterized by the K_α lines of carbon (15.33 at %), of oxygen (43.97 at %), and of silicon (21.87 at %) at 0.28, 0.53 and 1.74 kV, respectively, and by the L_α line of copper at 0.93 kV (18.84 at %). These values of atomic concentrations of the elements and the belief that oxygen is a part of SiO_2 of a support and carbon is used in spraying allow us to assume that preferentially metallic copper nanoparticles are precipitated on the quartz surface.

The dependence of effectiveness of the formation of copper films on the complex $K_2[CuGlu_2]$ concentration has shown that the concentration range from 5×10^{-2} to 5×10^{-3} M is optimal. The use of $K_2[CuGlu_2]$ with concentrations less than 5×10^{-3} M does not yield copper nanoparticles because of oxidation of clusters and small copper particles by air oxygen in the initial stage of their formation. Application of higher concentrations is not possible because of the $K_2[CuGlu_2]$ poor solubility in water.

The photolysis of a 5×10^{-1} M $K_2[CuAsp_2]$ solution within 10 min results in the formation of copper nanoparticles with an absorption band maximum at 590 nm. After a 60 min irradiation the plasmon absorption band maximum is displaced in the long-wave region up to 600 nm, which points to the coarsening of the formed copper particles, and a maximum at 450 nm (*D* 0.9 relative unit) also appears and increases later, which points to the presence of copper oxide forms. The irradiation within 210 mines leads the increase in the *D* value at 450 nm up to 1.3 relative units and to the complete disappearance of the absorption maximum at 600 nm, which points to the complete oxidation of copper particles up to Cu_2O.

When an 1×10^{-2} M aqueous solution of $K_2[CuAsp_2]$ is irradiated within 10 min, a yellow film with an absorption maximum at 420 nm is formed on a cell frontal side. According to the published data [6], this band corresponds to nanosized Cu_2O particles. Upon further irradiation (240 min) a red shift of the absorption maximum up to 490 nm appears. Independent of the irradiation time, copper nanoparticles are not formed. At a lower concentration of the complex (5×10^{-3} M) Cu_2O nanoparticles are formed preferentially in the bulk photolyte.

The electron microscopy data for the sample obtained by irradiation of the 5×10^{-1} M solution within 210 min point to the fact that an island film consisting of particles of size from 300 up to 600 nm is formed on the quartz surface. According to the results of the energy-dispersive analysis, copper, oxygen, and carbon (49.53, 25.5, and 24.97 at %, respectively) are present in this sample, which confirms the presence of Cu_2O particles in the film.

The complex compounds $K_2[CuAsp_2]$ and K_2 $[CuGlp_2]$ (Asp and Glu are anions of aspartic and glutamic acids) synthesized by the known procedure [7] were used as mother compounds for obtaining copper-containing films.

We irradiated aqueous solutions of the complex compounds with concentrations from 5×10^{-1} up to 1×10^{-3} M by monochromatic UV light with exciting wave length of 254 nm, using a Philips TUV 4W/G4 05 mercury lamp. Absorption spectra (SF-2000) were recorded over the range of 200–800 nm in each stage of the irradiation. The incident light intensity was 4.8×10^{16} quant cm^{-2} s^{-1}. The irradiation was carried out in quartz cells with the path length of 1 mm.

Scanning electron microscopy of copper-containing films obtained upon the irradiation of a complex solution contacting with quartz glass was carried out using a Zeiss EVO 40 scanning electron microscope at the accelerating voltage of 12 kV and a measure current of 175 pA. To exclude accumulation of negative charge on a sample surface, it was covered by a carbon layer 5 nm thick using an SC7620 Mini Sputter Coater installation. Compositions of samples were determined by the X-ray diffraction spectral microanalysis using a Zeiss EVO 40 scanning electron microscope equipped with an energy-dispersive X-ray spectral detector.

REFERENCES

1. Vertoprakhov, V.N. and Krupoder, S.A., *Usp. Khim*., 2000, vol. 69, no. 12, p. 1149.
2. Egorova, E.M., Revina, A.A., Rostovshchikova, T.N., and Kiseleva, O.I., *Vestn. Mosk. Univ., Ser. 2, Khimiya*, 2001, vol. 42, no. 5, p. 332.
3. Boitsova, T.B., Gorbunova, V.V., and Volkova, E.I., *Zh. Obshch. Khim*., 2002, vol. 72, no. 4, p. 688.
4. Isaeva, E.I., Gorbunova, V.V., and Boitsova, T.B., *Zh. Obshch. Khim*., 2009, vol. 79, no. 12, p. 1761.
5. Roslov, I.I., Gorbunova, V.V., and Boitsova, T.B., *Zh. Obshch. Khim*., 2009, vol. 79, no. 12, p. 1958.
6. He, P., Shen, X., and Gao, H., *J. Colloid Interface Sci*., 2005, no. 284, p. 510.
7. Kirschner, S., *J. Am. Chem. Soc*., 1956, vol. 78, no. 11, p. 2372.