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Formation and Electrical Conductivity of Low-Dimensional Copper Structures in Porous Glass

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Abstract—Metallic copper nanostructures were synthesized in porous glass membranes by reduction of two-dimensional copper(II) oxide layers. The frequency and temperature dependences of the electrical conductivity, combined with X-ray diffraction data, evidence the fixation of a 2D copper layer on the walls of the through channels of the support. The possibility of formation of planar metallic structures depends on the degree of surface coverage by the oxide precursor. The amount of copper resulting from copper oxide reduction in porous glass determines its resistance to oxidation in air.

Keywords: porous glass, copper nanostructures, electrical conductivity, size dependences

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Formation mechanisms, structural characteristics, and size-dependent properties of metallic nanostructures account for a considerable part of the total body of research in the field of nanochemistry. The main research task is still the development of methods for directed production of metallic nanostructures with *controllable size* and, just as important, sufficient stability. The latter presents a particularly challenging task due to excess surface energy and pronounced tendency to aggregate, exhibited by metal nanoparticles. In this context, of particular importance are the nature of the forces that hold the particles together in the medium and the strength of their fixation in the support bulk or on the surface, essential for the stability of the size of metal clusters and of the structure of their associates.

Much research has been done on small copper particles ([1–6], just to mention a few selected recent publications), whereas only sporadic publications were dedicated to the formation and studies of electrically conducting small-dimensional copper structures. Features of formation of conductive chains of copper nanoparticles deposited onto the silicon and glass surface by laser ablation were considered in [7, 8]; the factors determining the electrical conduction include the packing density and the degree of the particle surface oxidation. The percolation phenomenon revealed in [7, 8], well known for thin metal films [9, 10], is manifested as a drastic increase in conductivity during the formation of multiple contacts between the particles distributed in the support bulk or on the surface. Along with the "through" conduction via the resultant metal channels, activated electron tunneling between adjacent spatially separated particles is possible. The number of contacts typically decreases sharply with decreasing effective thickness of the films [9, 10], whereby the possibilities of producing well conducting ultrathin metal layers are significantly limited.

Sequential "stepwise accumulation" of copper(II) oxide on the walls of the through channels in porous glass membranes involves an increase in size of the planar clusters with 2D-structure in the tangential direction, culminating in the formation of a monolayer structure [11, 12]. The 2D structure of small-dimensional metallic copper forms may well be associated with the use of encapsulated 2D-oxides as precursors. The formation and persistence of conductive metallic structures upon oxygen "removal" from the planar distributed oxide is the more probable the higher their continuity and extension. The delocalized state of electrons in the conjugated copper structures may be energetically more favorable that their state in 3D metal particles ("islands"). An important role is played by the silica skeleton of porous glass with its pronounced electronegative character [13, 14],

therefore copper formation via copper oxide reduction proceeds under a strong polarization effect exerted by the support surface, promoting fixation and distribution of atoms as conjugated 2D-structures.

Porous glasses with pore radius r_p of 4.5 nm and specific surface area S_{sp} of 80 m^2/g served as supports in our experiments [15]. Copper(II) oxide was synthesized by the "small step" route [11, 12] through which its amount in the support could be monotonically increased. The formation of an oxide monolayer was concluded, as previously [11, 12], from a sharp decrease in resistivity of the CuO–porous glass samples, observed at the "accumulated" oxide amount Q_{CuO} of 1.310 mmol/g (hereinafter, the deposit amount is given per gram of the support). Further increase in the oxide content to above monolayer level (Q_{CuO} 1.618 and 1.946 mmol/g) was accompanied with a slight increase in conductivity which is consistent with the data from [11, 12]. Highly illustrative is the ratio of the specific surface area of the porous glass support, 80 m^2/g, to the amount of the oxide introduced, corresponding to its monolayer 2D-distribution (Q_{CuO} 1.310 mmol/g). In this case, one [CuO_4] structural unit has a "landing pad" of ~0.1 nm^2, which is close to the packing density of the chains of polyhedra in the crystal lattice of CuO [16].

In preliminary experiments we determined the conditions of hydrogen reduction of the CuO–porous glass samples with monolayer (1.31 mmol/g) and supermonolayer (1.618 and 1.946 mmol/g) copper oxide coverages. The reduction was monitored by measuring the transverse ohmic resistance of the plates. The onset of its noticeable decrease as compared to the initial level $R \sim 10^4$ Ω is observed only at the reduction temperature of ~200°C. Close to 250°C the resistance of all the samples decreases sharply to few ohms; with further increase in temperature by 20–30°C the resistance remained unchanged, indicating that the reduction is complete. With increase in the oxide amount the yield of well conducting plates increases from 40 to 75%.

The resistance of the Cu–porous glass samples, achieved in our experiments, is indicative of the formation of well-conjugated copper structures. The reduction is apparently not complicated by metal aggregation. At a small amount of copper in the porous glass its islands inevitably would have been disconnected and significantly separated from one another, which is inconsistent with a decrease in resistivity of the samples by several orders of magnitude. The

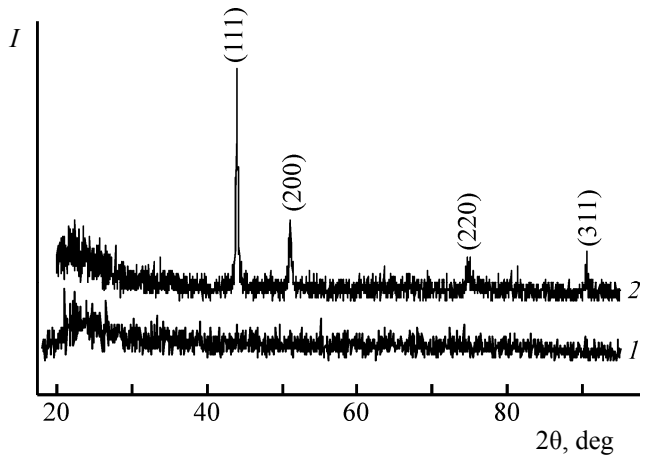

Fig. 1. XRD patterns of the CuO–porous glass samples (Q_{CuO} 1.946 mmol/g) reduced by hydrogen at (*1*) 250 and (*2*) 350°C.

predominantly two-dimensional structure of the metal assembly is indicated by the lack of reflections in the X-ray diffraction patterns taken from cleaved Cu–porous glass surfaces (Q 1.946 mmol/g) (Fig. 1).

At the same time, in the case of identical amount of copper in porous glass, its directed aggregation can be caused by increasing the reduction temperature above 300°C. The 3D copper particles formed under these conditions are reliably identified from the X-ray diffraction pattern (Fig. 1), and the lack of contacts between them is confirmed by a high resistance $R > 10^6$ Ω exhibited by an overheated Cu–porous glass samples. There are reasons to believe that complete reduction of the CuO–porous glass oxide monolayer and thermodynamic stability of the resultant 2D-structure of copper are limited to a narrow temperature range of 250–300°C.

The planar distribution of copper is also apparent from the estimated area occupied by one copper atom on the surface of the through channels of porous glass: $\omega_{Cu} = S_{sp}N_A/Q_{Cu}$, where N_A is Avogadro's number. For the Cu–porous glass samples with the copper content Q_{Cu} of 1.31, 1.618, and 1.946 mmol/g, ω_{Cu} was estimated at 0.102, 0.082, and 0.068 nm^2, respectively. The last-named value is virtually identical to ω_{Cu} ~0.066 nm^2 corresponding to a copper atom (r_{Cu} 0.128 nm [17]) in a densely packed monolayer. Hence, the planarity of the oxide layers in the CuO–porous glass precursors is presumably "inherited" primarily by the 2D-structures of copper, and the degree of coverage of the porous glass surface with copper γ in the three cases considered exhibits an increasing sequence 0.67, 0.83, 1.0.

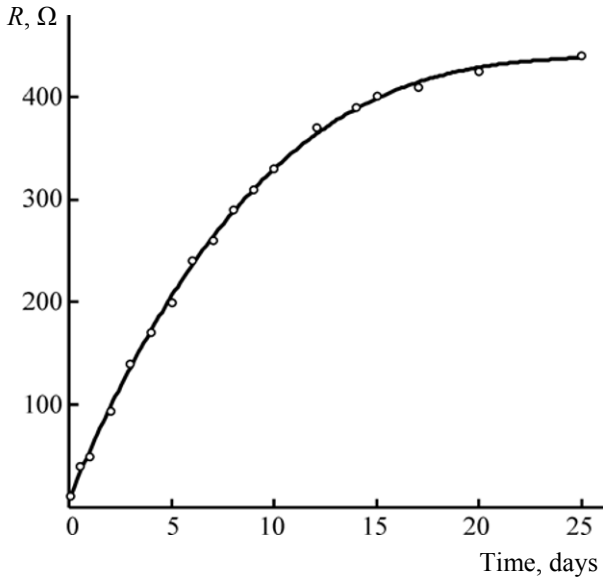

Fig. 2. Electrical resistance of the Cu–porous glass sample (Q_{Cu} 1.946 mmol/g) vs. air exposure time.

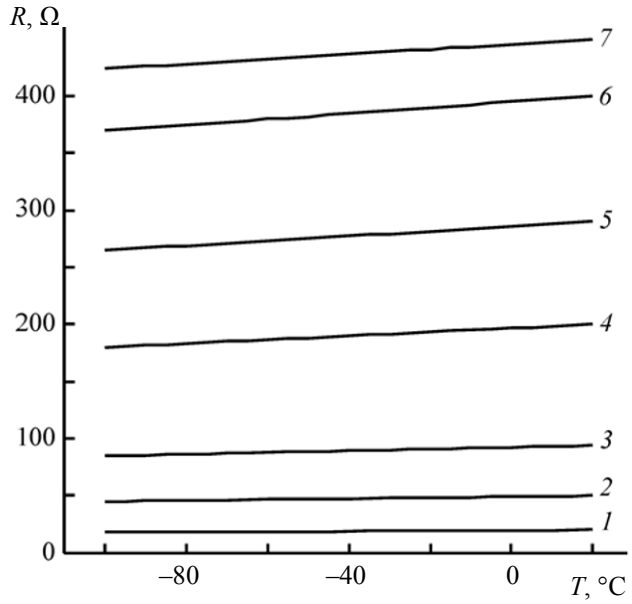

Fig. 3. Temperature dependences of the resistance of the Cu–porous glass sample (Q_{Cu} 1.946 mmol/g); air exposure time, days: (*1*) 0.2, (*2*) 1, (*3*) 2, (*4*) 5, (*5*) 8, (*6*) 15, and (*7*) 30.

Once again, the stabilization of planar metallic structures is achieved via the extension of electronic conjugation. Insufficient surface coverage (γ 0.67) in the Cu–porous glass membranes with the copper content Q_{Cu} of 1.310 mmol/g is responsible for a pronounced instability of the resultant 2D-assembly, preserved only in a hydrogen or inert gas atmosphere. Under air at room temperature, already within 10–15 min the sample exhibits a sharp increase in ohmic resistance to $R > 10^6$ Ω, well above that of the oxide precursor CuO–porous glass. Apparently, intensive copper oxidation in this case is accompanied by the degradation of the 2D-structure and the formation of disconnected copper oxide islands.

Nevertheless, there are reasons to expect that the stability of the planar metallic structure will increase with increasing number of atoms in the layer. Under air the Cu–porous glass sample (Q_{Cu} 1.618 mmol/g, γ 0.83) exhibits a significant slowdown in resistance increase, and R~10^6 Ω is achieved only after 30–40 h. The lack of structural reflections in the X-ray diffraction patterns of the oxidized samples can be explained by both a small size and a low degree of crystallinity of the resultant island structures. A convincing demonstration of stabilization is provided by the formation of a copper monolayer (Q 1.946 mmol/g, γ 1.0). In this case, the resistance of the Cu–porous glass sample slowly increases during 25–30 days until relatively low, close to stationary, resistance R ~450 Ω (Fig. 2) is reached. Thus, even dense coverage of the porous glass surface with copper atoms does not provide sufficient stability of the planar copper structure. Growth slowdown and gradual stabilization of resistance in this case are apparently associated with selective oxidation of structurally strained metal layer segments possessing excess energy, with the results being the formation of dielectric barriers hindering the electron transfer.

The copper monolayer formed in porous glass can preserve its planarity under local oxidation as well. A characteristic feature of metallic conductivity of not only the initial but also of the partially oxidized Cu–porous glass sample (γ 1.0) is the invariance of the measured resistance over a broad frequency range of 10–10^6 Hz. The persistence of the conducting 2D-structure under conditions of its gradual oxidation can also be revealed by examining the temperature dependences of the resistance. These dependences (Fig. 3) were recorded in the mode of cooling to –100°C under nitrogen stream, which prevents oxidation of the sample in the course of measurements.

At all initial resistances, a decrease in temperature causes a monotonic increase in conductivity, as typical of metals. A specific feature of the copper layer planarity is a weakly pronounced slope of the *R–T*

dependences: The corresponding temperature coefficient of resistance lies within 0.0005–0.0008 deg^{-1}, being substantially lower than that for bulk copper (0.004 deg^{-1} [18]). The resistance of the Cu–porous glass plates (Q_{Cu} 1.946 mmol/g, γ 1.0) varies within ~5–450 Ω (Fig. 2), which corresponds (at the porous glass thickness of 10^{-2} m and surface area of 10^{-4} m^2) to high resistivity ρ of 0.5–45 Ω m. The more characteristic seems a metal-like behavior of the Cu–porous glass system. Thus, the dielectric gaps resulting from partial oxidation of the 2D copper layer cause an increase in resistance, while the conjugated segments responsible for metallic conductivity are preserved.

EXPERIMENTAL

The CuO–porous glass system samples were synthesized in accordance with the regulations [11, 12]. The porous glass plates were impregnated with a copper(II) nitrate solution (*c* 0.15 M) for 30 min; excess solution was removed from the external surface of the plates with compressed air. The dehydration and thermal decomposition of the salt in the pore space were performed under conditions of linear heating at the rate of 5 deg/min from room temperature to 400°C. Gradual buildup of the oxide in the porous glass was achieved by multiple repetitions of the impregnation–decomposition cycles. Series of the CuO–porous glass samples with copper oxide content of 1.310, 1.618, and 1.946 mmol/g were placed in a tubular resistance furnace and reduced in a hydrogen stream (15 cm^3/min) at a temperature >200°C. The transverse electrical resistance of the samples was measured with a Novocontrol Concept 41 dielectric spectrometer at frequencies of 10–10^6 Hz and temperatures from 20 to –100°C. To reduce the contact barriers, the Cu–porous glass plates were coated with a ~1-mm-thick layer of graphite powder having an average particle size of 10–20 μm and mounted between planar graphite pressure electrodes (constant load of 200 g cm^2) with copper shunts therein. The X-ray diffraction patterns of the samples were recorded on a DRON-7 diffractometer with a copper anode (λ 1.5406 Å).

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