

Physicochemical Properties of Copper Nanoparticles Synthesized by the Different Methods

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Abstract—The morphology and electronic structure of copper nanoparticles synthesized on the surface of highly oriented pyrolytic graphite by substrate impregnation with a precursor solution and thermoresistive vacuum evaporation have been studied by atomic force microscopy, scanning tunneling microscopy, and scanning tunneling spectroscopy.

Keywords: nanoparticles, copper, scanning tunneling microscopy, atomic force microscopy, synthesis

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INTRODUCTION

Nanoparticles are commonly used in catalysis, microelectronics, medicine, and other fields of science [1]. Since the methods and conditions used for synthesizing nanoparticles largely determine the possibilities of their further application, problems associated with the technology of formation of nanoparticles with a given shape, size, and chemical composition are of current concern [2, 3]. Copper nanoparticles synthesized by various methods are used as catalysts in some processes, such as water–gas shift reaction or gas mixture detoxification [4–6].

The aim of this study is to compare the morphology and electronic structure of copper-based nanoparticles deposited on the surface of highly oriented pyrolytic graphite (HOPG) by substrate impregnation with a precursor solution and thermoresistive vacuum evaporation. Modern analytical methods of atomic force microscopy (AFM), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS) are used.

EXPERIMENTAL

Deposition of Nanoparticles

Synthesis of copper nanoparticles by the impregnation method was conducted directly in the chamber of an Omicron STM instrument (Germany). An aqueous solution of copper(II) nitrate $\text{Cu}(\text{NO}_3)_2$ with a concentration of 3×10^{-5} mg/L was used as a precursor. The precursor solution was deposited on a cleaned surface of HOPG (AIST-NT, Russia), which had a form of extensive atomically smooth C(0001) terraces. After drying of the solution, the sample was placed in

the chamber of the STM instrument, where it was calcined under ultrahigh vacuum conditions (residual gas pressure of no more than 5×10^{-10} Torr) at a temperature of 470 K for 40 h. During calcination, the precursor solution undergoes decomposition to form copper(II) oxide and gaseous nitrogen(IV) oxide and oxygen, which are pumped out of the chamber. The decomposition of copper(II) nitrate occurs as follows:



This calcination temperature (470 K) was selected taking into account the fact that, at atmospheric pressure, the decomposition of anhydrous copper nitrate begins at a temperature of 440 K.

Thermoresistive vacuum evaporation of copper on the graphite surface was implemented in two versions, namely, by the evaporation of a weighed portion of copper from a tantalum boat and the evaporation of a copper wire clamped between two current leads. The vacuum system for thermoresistive vacuum evaporation developed at our laboratory makes it possible to change the vacuum evaporation conditions by varying the source temperature, the sample temperature, and the geometric parameters of the system, namely, the distance from the source to the sample and the angle of incidence of the evaporant beam relative to the sample surface. In addition, the design of the system provides the use of various types of grids and accelerating potentials. Vacuum evaporation was conducted in a vacuum chamber at a residual gas pressure of no more than 2×10^{-6} Torr.

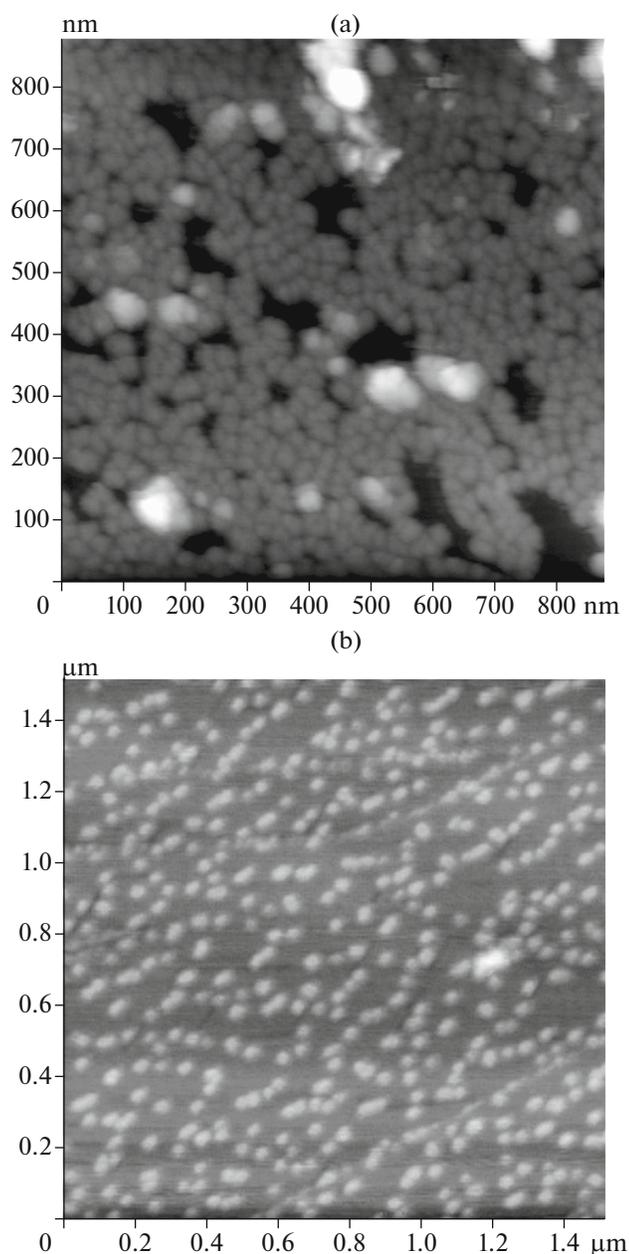


Fig. 1. Topographic image of the HOPG surface with copper nanoparticles deposited by thermoresistive vacuum evaporation: (a) the multilayer coating and (b) the degree of surface coverage of 15%.

Experimental Setup

The state of the graphite surface with copper nanoparticles deposited by thermoresistive vacuum evaporation was controlled using a Solver AFM instrument (NT-MDT, Russia). Scanning of the sample surface was conducted in a tapping mode of the microscope with a high-precision cantilever with a silicon tip (Etalon NT-MDT, Russia).

The morphological and electronic properties of the prepared samples were determined by STM and STS.

STM probes were tungsten needles prepared by the electrochemical etching of a tungsten wire with a diameter of 0.2 mm in a 0.1 M aqueous KOH solution and platinum–iridium needles prepared by the mechanical cutting of a platinum–iridium wire.

RESULTS AND DISCUSSION

Thermoresistive Vacuum Evaporation Method

The thermoresistive vacuum evaporation method makes it possible to synthesize coatings composed of individual nanoparticles on a graphite surface. No fundamental difference was found between the evaporation of a weighed portion of copper from a tantalum boat and a copper wire clamped between two current leads; the samples synthesized by these methods were similar.

Coatings with varying degree of surface coverage were obtained. For example, Fig. 1a shows an AFM image of a graphite surface with a multilayer coating of nanoparticles, while the degree of surface coverage in Fig. 1b does not exceed 15%. This parameter is determined by the evaporant flow density and the time of exposure of the sample to this stream. A fairly short exposure time provides the formation of isolated copper nanoparticles with a narrow size distribution range on the graphite surface. The nanoparticles have the form of “washers” with a characteristic diameter of 40–50 nm and a height of 5–15 nm. The fact that the resulting coating is composed of individual nanoparticles suggests that the particles exhibit low mobility on the graphite surface at room temperature. An increase in the substrate temperature to 570 K during deposition leads to an increase in the mobility of the nanoparticles and leads to the formation of agglomerates.

A number of results suggest that the formation of the nanoparticles occurs directly on the sample surface. Thus, a decrease in the evaporant flow density caused by the introduction of grids into the flow (characteristic cell size, 50 μm; weaving wire diameter, 30 μm) led to a decrease in the degree of surface coverage; however, it did not affect the nanoparticle size. In addition, STM and STS studies of the sample surface revealed the presence of regions of pure graphite in the interstices between the particles. Figure 2 shows an image of the graphite surface with copper nanoparticles and current–voltage characteristics measured in the regions of graphite (dashed curve) and copper nanoparticles (solid curve) marked in Fig. 2a. These results indirectly indicate that the nanoparticles are formed on the surface by the Volmer–Weber growth mechanism [7]. At the initial stage, copper clusters are formed on the graphite surface. Metastable clusters, which are in equilibrium with the adsorption layer, form critical nuclei, which grow owing to the diffusion-induced addition of neighboring clusters. The nuclei grow to three-dimensional islands. Individual small islands can migrate over the surface, as evi-

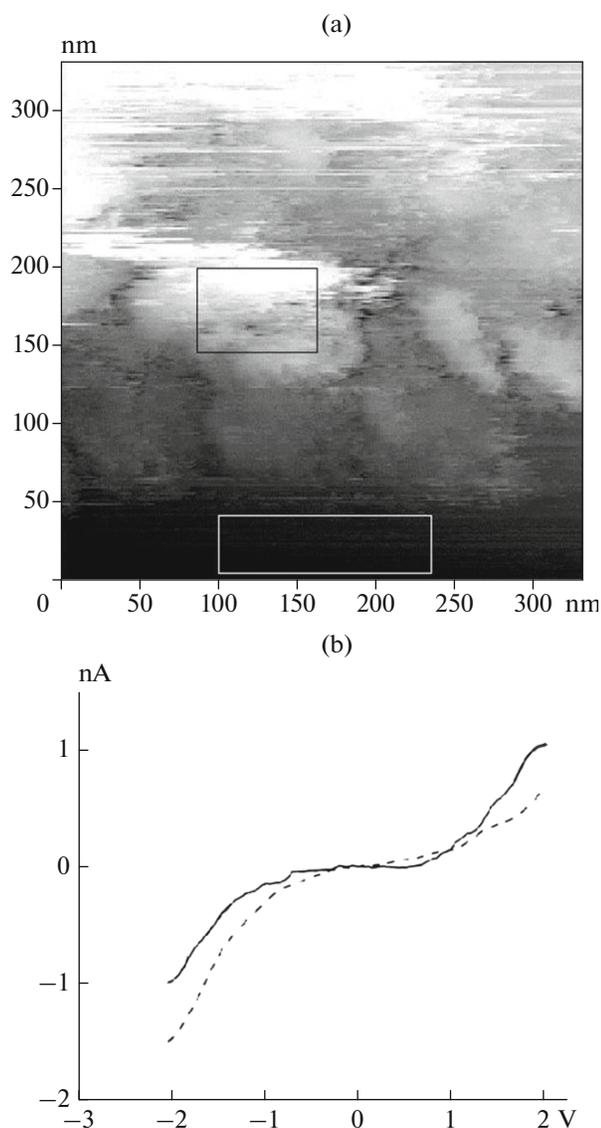


Fig. 2. (a) Topographic image of the HOPG surface with copper nanoparticles deposited by thermoresistive vacuum evaporation and (b) current–voltage characteristics measured in the regions of (dashed curve) graphite and (solid curve) copper nanoparticles.

denced, for example, by the formation of copper nanoparticles along the boundary of the graphite terraces (Fig. 3).

The current–voltage characteristics shown in Fig. 2 also make it possible to draw some conclusions about the chemical composition of the nanoparticles. It is evident that the curve corresponding to a nanoparticle has a zero-conductivity region with a width of about 1.3 eV. According to the published data for various copper oxides, the band gap is 1.7 eV for CuO and 2.1 eV for Cu₂O. In this case, the width of the zero-conductivity region within one nanoparticle varies from point to point and cannot be identified with any particular

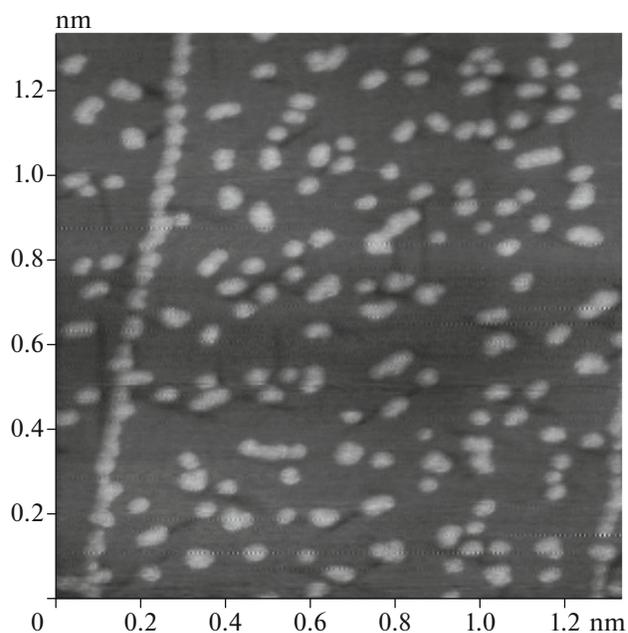


Fig. 3. Topographic image of the HOPG surface with copper nanoparticles deposited by thermoresistive vacuum evaporation.

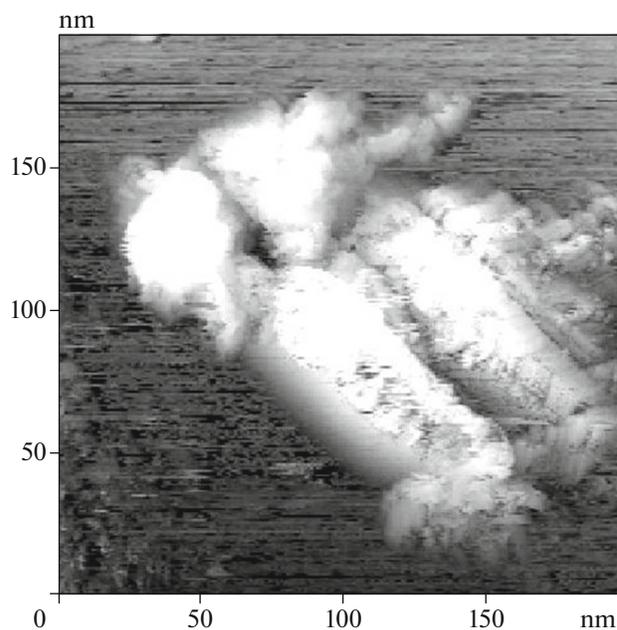


Fig. 4. Topographic image of the HOPG surface with copper nanoparticles deposited by the impregnation method.

oxide. Results of [8] suggest that the nanoparticle surface is coated with a nonstoichiometric copper oxide formed under the action of atmospheric oxygen.

Impregnation Method

The samples prepared by the impregnation method are fundamentally different from the samples synthe-

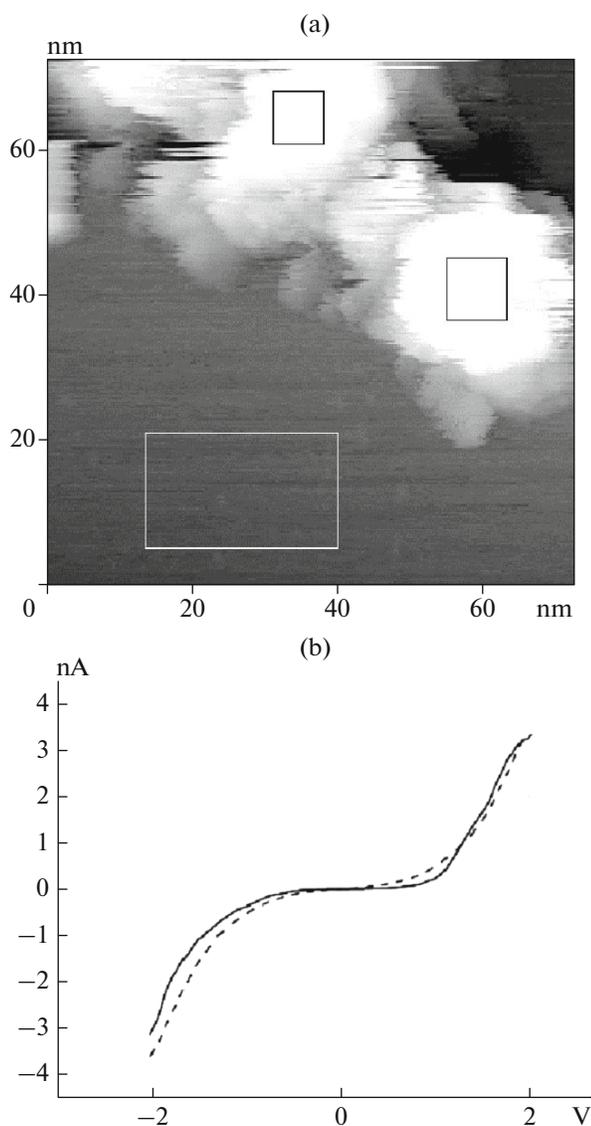


Fig. 5. (a) Topographic image of the HOPG surface with copper nanoparticles deposited by the impregnation method and (b) current–voltage characteristics measured in the regions of (dashed curve) graphite and (solid curve) copper nanoparticles.

sized by thermoresistive vacuum evaporation. STM results show that, after the deposition of a precursor and calcination, fairly large agglomerates of copper nanoparticles with various shapes and sizes are formed on the graphite surface. The topography of the surface of a sample containing copper nanoparticles prepared by the impregnation method is shown in Figs. 4 and 5. It is evident from Fig. 4 that fairly large differently shaped copper particles are formed on the graphite surface. The size of the nanoparticles constituting the agglomerates is 3–6 nm. The results are not in contrast with the known data. Earlier, the authors of [9, 10] showed the possibility of synthesizing copper nanoparticles of various shapes (cubic, tetrahedral,

and rod-like) and characteristic sizes of 5–200 nm. The authors of that study synthesized nanoparticles in reverse micelle solutions at different temperatures. The formation of differently shaped particles was observed in a temperature range of 460–470 K, which is in agreement with our results.

Figure 5 shows results of STS measurements conducted on an STM instrument. In the figure, the dashed curve shows an averaged current–voltage characteristic measured in the region of graphite without nanoparticles; the solid curve represents averaged current–voltage characteristics measured for different nanoparticles.

The current–voltage characteristics measured for the nanoparticles have fundamentally different shapes: some of the curves have a zero-conductivity region with a width of about 1.3 eV and their shape corresponds to that of a semiconductor junction; some of the curves do not have the above region and are more similar to curves corresponding to pure graphite. According to the literature, bulk copper(II) oxide is a *p*-type semiconductor with a band gap of 1.7 eV [11]. According to the general form of the equation for the decomposition of copper nitrate, this oxide should be dominant in the composition of the synthesized nanoparticles. A discrepancy between the values of the band gap of this oxide and the zero-conductivity region can be attributed to a violation of the oxide stoichiometry and defects whose presence essentially destroys the semiconductor pattern of electron energy distribution.

CONCLUSIONS

Copper nanoparticles synthesized by substrate impregnation with a precursor and thermoresistive vacuum evaporation are fundamentally different.

The method based on the impregnation of the substrate with a precursor makes it possible to synthesize large agglomerates of nanoparticles with a size of 3–6 nm on the HOPG surface. The nanoparticles have a semiconductor structure with a band gap of 1.3 eV and, apparently, consist of a nonstoichiometric oxide.

The thermoresistive vacuum evaporation method provides the formation of uniform coatings with varying degree of surface coverage that are composed of individual copper nanoparticles, which are covered with a nonstoichiometric oxide film under the action of atmospheric oxygen. The nanoparticles have the form of washers with a characteristic diameter of 40–50 nm and a thickness of 5–15 nm. Apparently, the formation of nanoparticles on the HOPG surface occurs by the Volmer–Weber growth mechanism.

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