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Josephson type current-voltage characteristics of chemically modified graphite at room temperature and normal pressure

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This work shows that Josephson type current-voltage characteristics are observed up to room temperature at normal pressure for hybrid particles based on polystyrene and multilayer reduced graphene oxide. The deformation of sheets of multilayer reduced graphene oxide during its functionalization with methacrylate groups, copolymerization with styrene and exposure to a toluene solution in the cross-linked structure leads to the appearance of superconductivity in the resulting hybrid flakes. Moreover, with an increase in the magnetic field or temperature above the critical one, the Josephson type of current-voltage characteristics for them reversibly changes to ohmic.

Keywords: Reduced graphene oxide, superconductivity, hybrid material, polystyrene.

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The synthesis and study of novel materials with a high critical temperature of transition to a superconducting state is one of the priority lines of research in solid state physics, which is relevant both to the development of superconductivity theory and to practical applications of such systems. Numerous, but completely random observations of superconductivity in highly oriented graphite at room temperature and normal pressure, which have been reported by different research groups over a wide time interval [1–9], are of particular interest in this context. The stochastic (uncontrolled) nature of observed superconductivity effects is the exact reason why these works did not receive due attention from the scientific community. As a consequence of this, a theoretical model predicting the emergence of high-temperature superconductivity in highly oriented graphite has not been developed yet.

A new approach involving chemical modification and copolymerization of graphene sheets may be effective in solving this problem. The formation of covalent bonds between surface-functionalized graphene and polymer chains leads to geometric distortion of its sheets, inducing microstresses and structural defects in them. Local regions similar to Landau levels, which are known to arise in strong magnetic fields, emerge in this case in the density of states of graphene [10,11]. This is the reason why such deformation fields are called pseudomagnetic in scientific literature.

Graphene is a flat one-monolayer-thick honeycomb mesh of sp^2-hybridized carbon atoms bound by covalent bonds into a two-dimensional hexagonal crystal lattice. Structural defects forming in the graphene crystal lattice due to sp^3-hybridization bend graphene planes and induce the formation of pseudomagnetic fields. In the present case, a pseudomagnetic field was established in the course of *in situ* radical copolymerization of 3-(trimethoxysilyl)propyl methacrylate bound covalently to the surface of graphene sheets with styrene. Experiments have indeed demonstrated that chemically oxidized, exfoliated, and thermally reduced graphite in hybrid materials, where its sheets are bound to polystyrene by covalent bonds instead of being just a simple filler, had Josephson-type current–voltage characteristics (CVCs) [12,13] and magnetization dependences on magnetic field characteristic of type II superconductors [14–16] measured after soaking the samples in a toluene solution for 24 h at room temperature.

In the present study, a hybrid material based on multilayer reduced graphene oxide and polystyrene was examined. Its preparation procedure was discussed in detail earlier [16]. The results of application of a set of physicochemical analysis methods in the study of its structure were also reported in [16]. Let us highlight the following important points related to the procedure of composite preparation. The synthesis of a hybrid material based on polystyrene and multilayer graphene oxide reduced thermally in a hydrogen atmosphere included several stages. The first one was surface modification of multilayer reduced graphene oxide sheets with 3-(trimethoxysilyl)propyl methacrylate [15]. Multilayer reduced graphene oxide particles functionalized with methacrylate groups were then dispersed in a toluene solution of a monomer with an initiator and copolymerized with styrene in an inert atmosphere at 70°C for 24 h. Following rinsing and drying, hybrid flakes $\sim 8 \times 13\,\mu$m in size with a thickness up to several hundred nanometers were obtained. These flakes based on polystyrene with covalently bound particles of multilayer reduced graphene oxide were then soaked in a toluene solution for 24 h.

Figures 1, *a*, *b* show (with different scales) typical fragments of surface relief of such hybrid aggregates imaged with an Integra Aura (NT-MDT SI, Zelenograd) atomic force microscope (AFM). AFM measurements were carried out in the hybrid mode [17]. The measurement results were processed using the Gwyddion 2.55 program for visualization and analysis of scanning probe microscopy data.

Figure 1, *c* presents the section of a scan by the AFM cantilever along the line shown in Fig. 1, *b*. It is evident that the surface of graphene in the hybrid material is very uneven, which suggests the presence of a deformation field in graphene.

Hybrid material flakes dried after soaking in a toluene solution were introduced into a capsule made of a dielectric material with the following internal dimensions: a diameter of 2.0 mm and length of 10 mm. With a movable current electrode, the hybrid material flakes were pressed into an assembly under a low external pressure (below 1 kg/cm^2). Two probe electrodes were inserted into the capsule in advance to monitor the voltage drop across them. DC electrical measurements of the assemblies were carried out using the four-point probe method in accordance with the standard procedure for materials with metallic conductivity. The voltage drop across the probes was measured using Shch-300 and Hewlett Packard 3457A digital voltmeters (with an accuracy up to 0.1 μV) and a V2-36 voltmeter (with an accuracy up to 0.01 μV).

The CVCs measured for the hybrid material by the four-point probe method at $T = 300$ K in zero external magnetic field are denoted with squares in Fig. 2, *a*. It is evident that the CVCs are of the Josephson type, which agrees completely with the results obtained earlier in [13,14] and is indicative of superconductivity at currents $I < I_c$ ($I_c \approx 2\,\mu$A is the critical current of transition to the normal state).

To verify the presence of a Josephson contact, CVCs were measured in magnetic field $H = 3.0$ kOe. A uniform magnetic field was produced by an electromagnet with a pole diameter of 60 mm. Field magnitude $H = 3.0$ kOe was chosen in view of the results reported in [16], where the similarity of magnetizations of a hybrid material (a composite) and a type-II superconductor was revealed and it was demonstrated that superconductivity should be suppressed completely in a magnetic field of this strength. Our experiment did indeed show that Josephson-type CVCs give way to ohmic (metallic) conductivity (circles in Figs. 2, *a*, *b*). The effect did not depend on the orientation of the magnetic field relative to the sample assembly and was reversible (i.e., when the magnetic field was turned off, the CVCs reverted back to the Josephson shape). The same behavior of CVCs was observed when the temperature was increased to 110°C: the CVCs then also became ohmic. This effect also was reversible; i.e., when the hybrid material was cooled to room temperature, the Josephson-type CVC was restored again. These experiments and earlier data from [12–16] are consistent with each other and indicate clearly that hybrid structures may have superconducting properties.

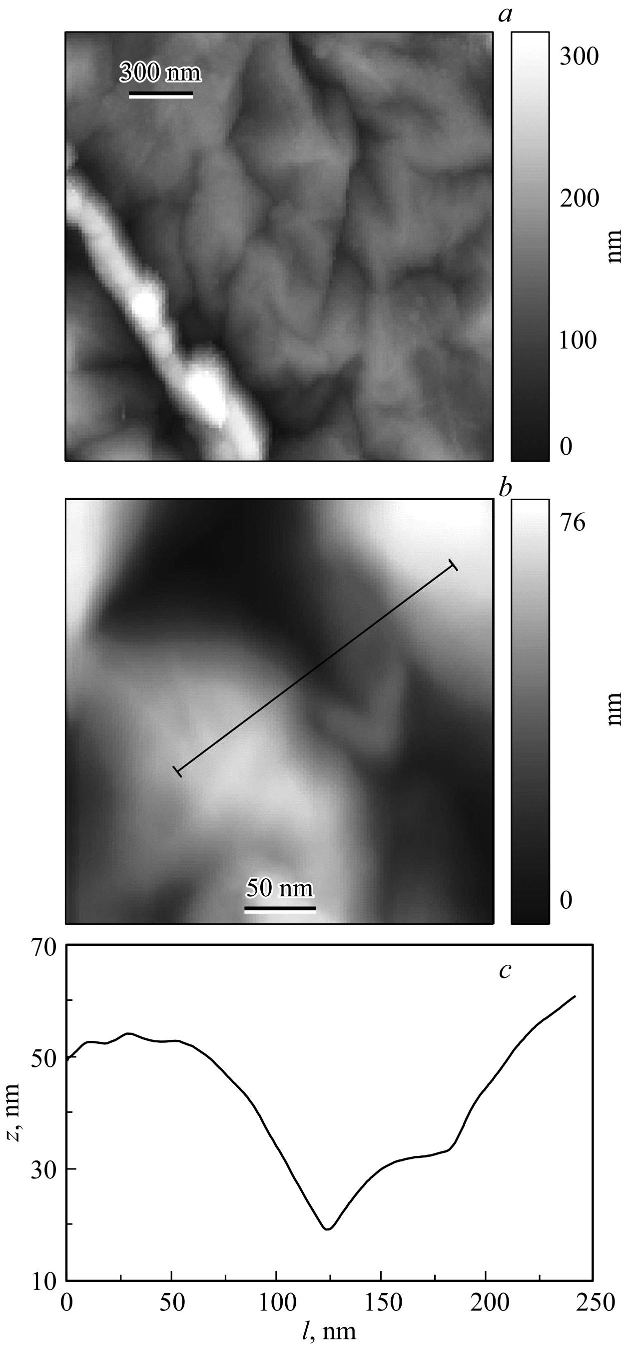

Figure 1. *a*, *b* — Graphene surface in the hybrid material imaged on different scales; *c* — section of a surface scan along the line shown in the middle panel.

A number of theoretical models predicting superconductivity with a high critical temperature (T_c) based on deformation fields in graphene are known. For example, according to the results of theoretical calculations performed in [18], a pseudomagnetic field may induce superconduc-

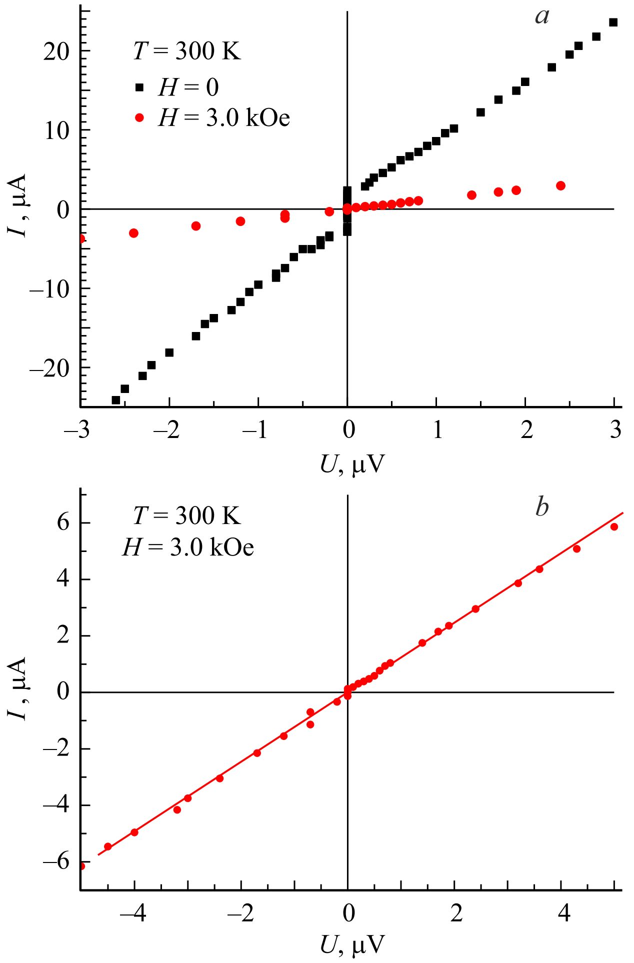

Figure 2. Josephson shape of CVCs at $T = 300$ K and $H = 0$ kOe (squares) and ohmic shape of CVCs at $T = 300$ K and $H = 3$ kOe (circles) for a composite 60 μm in length.

tivity by establishing a discrete spectrum of Landau levels in the density of states. T_c should then depend on the deformation field magnitude and the degree of filling of Landau levels.

However, study [19], which predicts room-temperature superconductivity in linear defects arranged in parallel in layered materials, appears to be the closest to the present case of a hybrid material. If defects are subject to strong fluctuating deformation fields, local pairing of electrons into superconducting droplets may be observed in them. In turn, „one-dimensional" superconductivity emerges for tunnel-coupled droplets in an individual layer of a layered material. However, this is not the superconductivity of independent quantum wires, since, according to the theoretical model, superconducting lines belonging to different layers interact with each other. In the present case, structural defects arising from sp^3-hybridization at the edges of graphene planes may serve as linear defects, since it is there that these defects are first produced during functionalization [20]. The multilayer structure may enable interaction between superconducting lines located at the edges of graphene planes.

Thus, the deformation of graphene planes and the production of structural defects in them in the course of surface modification of graphite, its copolymerization with styrene, and long-term processing in a solvent allow one to synthesize hybrid materials with reproducible room-temperature superconductivity at normal pressure. Macroscopic conductors may be formed from individual superconducting particles of the hybrid material, which is important for practical applications.

Conflict of interest

The authors declare that they have no conflict of interest.

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