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Magnetization of different types of reduced graphene oxide in composites based on polystyrene

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Abstract. The transition from 'the initial graphite material, consisting of multilayer graphene of macroscopic size, to its oxidized form occurring as films, followed by their thermal reduction in an atmosphere of hydrogen, allows for obtaining submicron galleries of reduced graphene oxide with oxygen-containing groups on the surface. Such hydroxyl and carboxyl groups were used to functionalize the surface of graphene nanosheets with methacrylate groups to twist graphene layers relative to each other during in-situ copolymerization with styrene. In such a composite, mechanical stresses and defects are potential in the graphene nanosheets, which may be the reason for local superconductivity at room temperature. A similar effect was also recorded for photoreduced graphene oxide with a perforated surface as a component of a polystyrene-based composite.

Keywords: UV irradiation, reduced graphene oxide, polymeric matrix, percolation, carbon electronics

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Намагниченность различных типов восстановленного оксида графена в композитах на основе полистирола

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Аннотация. Переход от графита, состоящего из многослойного графена макроскопических размеров, к его окисленной форме в виде пленок, с последующим их термическим восстановлением в атмосфере водорода, позволяет получить субмикронные галереи восстановленного оксида графена с кислородсодержащими группами на

поверхности. Такие гидроксильные и карбоксильные группы были использованы для функционализации поверхности графеновых нанолистов метакрилатными группами для скручивания графеновых слоев относительно друг друга при in-situ сополимеризации со стиролом. В таком композите возможны механические напряжения и дефекты в графеновых нанолистах, что может быть причиной локальной сверхпроводимости при комнатной температуре. Аналогичный эффект был также зарегистрирован для фотовосстановленного оксида графена с перфорированной поверхностью в качестве компонента композита на основе полистирола.

Ключевые слова: УФ-облучение, восстановленный оксид графена, полимерная матрица, перколяция, углеродная электроника

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Introduction

Since discovering the superconductivity effect, researchers worldwide have simultaneously focused on creating the theoretical models predicting a high critical temperature (T_c) and synthesizing new superconducting materials with high T_c. Many theoretical studies indicate high-temperature superconductivity up to room temperature in a graphene material due to deformation stresses [1, 2]. According to theoretical models, deformation stresses can radically change the density of electronic states in regions with mesoscopic dimensions and exponentially increase the value of T_c. The assumption of the role of deformation in the appearance of superconductivity is consistent with the experimental results obtained in the composite based on polystyrene (PS) with incorporated mesoscopic size graphene where stresses were created in graphene nanosheets (GNSs) due to covalent bonds between dielectric polymer matrix and conductive carbon filler. Such composite exhibited Josephson $I–V$ characteristics, which can undoubtedly be interpreted as the manifestation of the superconductivity effect [3, 4]. No superconductivity effects were observed in experiments in which graphene was used as a filler in polymer, i.e., without the formation of covalent bonds.

Spintronics can also become an additional stimulus for studying the effect of superconductivity in the composite based on PS with covalent bonded graphene, even on a mesoscopic scale. Indeed, as well known, spintronics uses two essential properties of the electron: charge and spin. Such a superconducting composite could be ideal for spintronics in charge transfer efficiency at room temperature. In addition, it will be possible to realize the ferromagnetic order in the nanoscale filler by the rearrangement of the supramolecular structure of the material during synthesis: The order is realized in the GNSs during in-situ copolymerization with the polymer matrix. Optimism in solving this problem is because the ferromagnetic state can occur in carbon nanomaterials, such as graphene nanoribbons and nanoplates [5], and a composite with graphene needles [6].

Reduced graphene oxide (rGO) is the prospect of fabricating organic-inorganic composites with unique electrical and magnetic properties. Our work aimed to synthesize PS/rGO composites in which the two components are covalently bound together. We show that composite magnetization plots can demonstrate type-II superconductivity without subtracting any diamagnetic and paramagnetic contributions. In addition, we noted that the effect of superconductivity depends on the oxygen-containing residues detected through a paramagnetic signal when measuring static magnetization at low temperature and on covalently binding rGO flakes with the macromolecules of PS.

Materials and Methods

Colloidal suspensions of multilayer graphene oxide (GO) were obtained from natural crystalline graphite using a modified Hummers method [7]. GO films, extracted at suspension evaporation, were reduced thermally or under the action of ultraviolet (UV) radiation in an inert atmosphere. The rGO differed from that obtained from graphite by mechanical scotch splitting [8]. In particular, after the reduction, the oxygen content in rGO decreases significantly but does not disappear completely [9]. It was found that during thermal reduction of GO in an argon atmosphere, the content of oxygen-containing groups is lower than in a hydrogen environment. In the case of UV photo-reduction of GO films and the removal of hydroxyl and carboxyl groups, the surface of graphene sheets is perforated with the formation of micron-sized holes [10]. The rGO surface was functionalized with methacrylate groups by alkaline hydrolysis of methoxyl groups of 3-(trimethoxysilyl)propyl methacrylate (TMSPM, CAS Number: 2530-85-0, Aldrich) and the subsequent condensation between them and the surface hydroxyls of graphene sheets [11, 12].

The composite systems contained 1–3 wt.% rGO assemblies with several microns long/wide and up to 200 nm thick, according to scanning electron microscopy (Zeiss EVO 50 instrument) [11]. Magnetic measurements of the samples were performed on the vibration magnetometer of the PPMS9 (Quantum Design) complex in the temperature range of 2–400 K and magnetic fields from 0 to 8000 $A \cdot m^{-1}$

Results and Discussion

The temperature (Fig. 1, curve *1*) and field dependences (Fig. 2, *a*) of static magnetization measured on a vibration magnetometer for a composite based on GO reduced in an argon atmosphere, modified with TMSPM, and in-situ copolymerized with the macromolecules of PS (System 1) exhibit only the magnetization of the diamagnetic type, which as well-known does not depends on temperature. In comparison, PS containing thermally-reduced in a hydrogen atmosphere and covalently-bound rGO flakes (System 2) gives a gradually increasing paramagnetic response at low temperature, suppressing the diamagnetic behavior (Fig. 1, curve *2*).

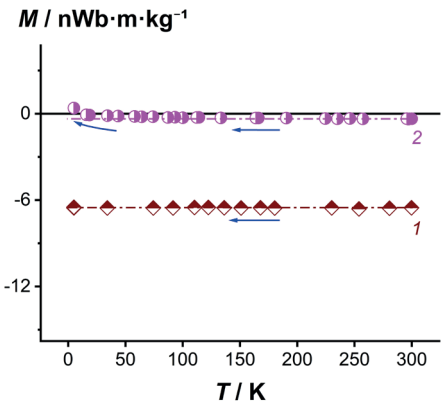

Fig. 1. Temperature dependence of the static magnetization for Systems 1 (*1*) and 2 (*2*) in cooling at $H = 40$ $kA \cdot m^{-1}$

According to elemental analysis and X-ray photoelectron spectroscopy, a significant paramagnetic contribution is associated with the large content of oxygen-containing groups, which depends on the reduction conditions of rGO.

Fig. 2, *b* shows the field dependence of static magnetization for System 2. This type of hysteresis is not observed in ferromagnets but is characteristic of granular type-II superconductors [13]. As the magnetic field increases, the anomalously high magnetization component is suppressed, as observed in superconductors [14]. Only diamagnetism manifests in the composite in strong magnetic fields due to PS and the rGO (300 K). It should be noted that in weak magnetic fields, an abnormally high increase in magnetization with a small hysteresis turned counterclockwise is observed [15].

To prove our hypothesis, we have the film of GO reduced by UV irradiation (UV-rGO) according [16, 17]. In an argon atmosphere, the UV irradiation procedure is also accompanied

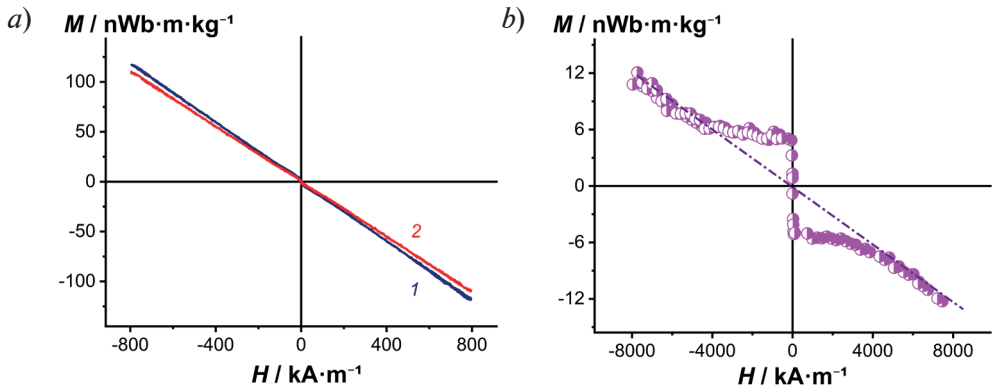

Fig. 2. The field dependence of the static magnetization for System 1 (*a*) at $T = 50$ (*1*) and 300 K (*2*), and System 2 (*b*) at $T = 300$ K

by many submicron holes in graphene flakes, just as after proton irradiation [8]. We tested this hypothesis by purposefully synthesizing and investigating a PS-based composite (System 3). For that, TMSPM was covalently bonded to the surface of UV-rGO flakes having typical dimensions of several microns in width and up to 200 nm in thickness, and then was cross-linked with PS chains in the process of in-situ radical polymerization of styrene. Two types of styrene were used: giving or not ferromagnetic ordering. As a result, polystyrene was obtained with magnetic impurities (PS_{Ferro}) and without them (PS) [10].

As a specified outcome, the photoreduction has many submicron holes distributed within the UV-rGO flakes, containing defective edge structures comprising carboxyl and hydroxyl groups. The impact of UV irradiation on GNSs is like irradiation with high-energy protons. Under the model [18], it should cause a defect-induced magnetic order (ferromagnetic-like loop) in UV-rGO flakes on the mesoscopic scale (Fig 3, curve *1*). The PS_{Ferro}/UV-rGO composite (System 3 in Fig 3, curve *3*) has a hysteresis loop of the same size as PS_{Ferro} (curve *2*), and it is much smaller than the one for UV-rGO (curve *1*). Consequently, introducing a magnetic component to the PS-based composite suppresses the hysteresis magnetization loop for UV-rGO as a part of the composite because of the internal magnetic field emerging in a system. This result is exclusively characteristic in type-II superconductors [19].

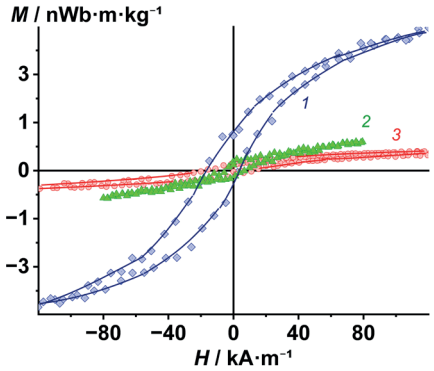

Fig. 3. Magnetic field dependence of the specific magnetic moment for UV-rGO flakes (*1*), PS_{Ferro} (*2*), and System 3 (*3*) at $T = 200$ K

Conclusion

In this paper, summarizing our earlier studies, we can conclude that the registered magnetization graphs for composites based on PS with covalently attached rGO flakes have a form characteristic of type II superconductors. The anomalously low resistivity of sheets twisted in the process of copolymerization with styrene is due to the concentration of oxygen-containing residues on their surface. These groups allow the creation of defects and additional mechanical stresses in the GNSs and provide displacement of the sheets relative to each other when they are included in the polymer chain, which leads to the formation of magnetic order in this kind of composites.

By the example of the composite with UV-rGO, it is demonstrated that the magnetization of the carbon filler flakes has a ferromagnetic hysteresis type. However, the experiment with the inclusion of a ferromagnetic impurity in System 3 did not increase the ferromagnetic magnetization according to the additivity principle, and the hysteresis loop was more pronounced for PS-based composites without ferromagnetism than for UV-rGO flakes. This observation questions the long-range magnetic order model caused by point defects in mesoscopic graphite samples with ferromagnetic loop behavior. Guided by the above, we can conclude that the hysteresis observed in the UV-rGO flakes at high temperatures may be due solely to type II superconductivity rather than ferromagnetic ordering.

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