

The low-temperature specific heat of thermal reduced graphene oxide

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Measurements of heat capacity at constant pressure of thermally reduced graphene oxide (trGO) and graphite oxide (GtO) were performed in the temperature range from 1.8 to 275 K by thermal relaxation method. Above 15 K, the specific heat values of trGO and GtO are close to each other within 20%. Below 10 K, the ratio of the specific heat of trGO to the specific heat of GtO increases with decreasing temperature and reaches 5 at 2 K. It was found that the temperature dependence of the specific heat of trGO is of a complex character. There are temperature ranges in which of the specific heat of trGO is close to either linear or $T^{2.5}$.

Keywords: graphene oxide, graphite oxide, heat capacity, low-dimensional systems.

Introduction

The discovery of the family of carbon nanomaterials (fullerenes, single-walled carbon nanotubes and multi-walled carbon nanotubes, graphene) aroused great interest in these objects both in basic science and for applied purposes. This interest is due to their unique physicochemical properties. Graphene occupies a special position in this family [1]. Graphene consists of a monolayer of carbon atoms which are linked by strong covalent sp^2 bonds into a close-packed hexagonal two-dimensional (2D) crystal lattice. Other carbon nanosystems can be obtained from it by some kind of modification (see Fig. 1 in Ref. 2). The variety of unique chemical and physical properties is due to the crystal structure and π -electrons of the carbon atoms that make up graphene. Graphene itself can be obtained using various methods, in particular, by modifying graphite oxide [3]. Graphene oxide is an important precursor of graphene [4]. Graphene oxide is a chemically modified graphene obtained by oxidation and exfoliation of graphite, which is accompanied by an extensive oxidative modification of the basal plane [5]. Graphene oxide is a single layer material with a high oxygen content, which is usually characterized by an atomic C/O ratio of less than 3 and usually closer to 2. To diminish the oxygen content, graphene oxide can be reduced by various methods: chemical, thermal, microwave, photo-

chemical and others. To obtain reduced graphene oxide, mostly graphite oxide is used.

Graphite oxide was first obtained by Benjamin Brody in 1859 [6]. 100 years later, Hammers and Offeman [7] proposed a faster and relatively safe method for the synthesis of graphite oxide, which is still widely used. During the oxidation of graphite, oxygen-containing functional groups (epoxide, carbonyl, hydroxyl and carboxyl) are attached to carbon atoms in the basal planes of graphite in various ratios. The structure and properties of graphite oxide depend on the specific synthesis method and oxidation state. Layers are retained in graphite oxide, as in graphite, but the distance between them increases approximately twofold (~ 0.7 nm) as compared to graphite. The thickness of graphene oxide layers is about 1.1 nm [8,9]. Graphite oxide is easily hydrated, resulting in an increase of inter-planar distance (up to 1.2 nm in a saturated state). Graphite oxide exfoliates and decomposes when heated at moderately high temperatures (~ 280 – 300 °C) with the formation of finely dispersed amorphous carbon. That “soot” consists of the finest graphite flakes, the diameter of which can reach up to several hundredths of a millimeter. Flakes consist of several layers of reduced graphene oxide. During the preparation process, vacancies and other defects can appear in the lattice layers of graphene.

The main interest in these oxides is due to the fact that the reduced graphene oxide (rGO) resembles graphene, but may contain residual oxygen, as well as structural defects (vacancies, Stone–Wales defects, functional groups, and others). The complexity of the structure of graphene oxide is due to the presence of functional oxygen-containing groups located on both sides of the monatomic layer (epoxy, carbonyl, and hydroxyl) and along its edges (hydroxyl, carboxyl). A large number of models have been proposed to describe the structure of graphene oxide (see, for example, [10]). Much of them are associated with an indefinite, amorphous arrangement of oxygen-containing functional groups.

The theoretical curves of the temperature dependence of the specific heat of graphene, presented in the works of Hone [11] and Popov [12], are linear at low temperatures. In the work of Gospodarev *et al.* [13], the phonon part of the specific heat of bigraphene and trigraphene was described. An analysis of the nature of the bending stiffness of graphene monolayers allowed these authors to determine the temperature ranges in which the form of the temperature dependence of the heat capacity is determined by the competition between the contributions of bending, longitudinal, and transverse vibrations.

The thermal properties of graphene were discussed in the review [14]. The effect of thermal reduction on the low-temperature sorption of hydrogen, helium and other gases was studied in Refs. 15–18. In [19], the influence of the degree of reduction on the electrical properties of functionalized graphene sheets obtained by thermal exfoliation and reduction of graphite oxide was studied. The effect of oxygen-containing groups on the infrared (IR) absorption spectra of graphene oxide was investigated using Fourier-transform infrared (FTIR) spectroscopy and quantum mechanical modeling in [20].

Materials of the graphene family, in particular, graphite and graphene oxides, are of great interest for use in new materials and applications, such as: nanoelectronics, polymer composite materials, energy storage, biomedical applications, sorption materials, etc. Especially, it is important to study the heat capacity of thermally reduced graphene oxide at low temperatures.

We are not aware of any direct measurements of the heat capacity of graphene, graphene and graphite oxides.

In this paper, we present the results of the first measurements of the heat capacity of thermally reduced graphene oxide.

Experiment

Calorimetric studies of thermally reduced graphene oxide (trGO) and graphite oxide (GtO) have been carried out in the temperature range from 1.8 to 275 K. Their specific heats were determined using the method of thermal relaxation on a commercially available Physical Properties Measurement System (PPMS, Quantum Design Inc.) [21]. Investigated samples were prepared as follows: The graphite

powder (GSM-2) with a mass of 5 g was used as a starting material, having the composition: carbon (not less than 99.5%), ash (not more than 0.5%), humidity (not more than 0.2%). The initial graphite oxide (GtO) was obtained from graphite powder using the modified Hummers method [7]. Sodium nitrate NaNO_3 , sulfuric acid H_2SO_4 , and potassium permanganate KMnO_4 were used as oxidizing agents.

The synthesis of graphite oxide consisted of several stages. Concentrated sulfuric acid H_2SO_4 (170 ml) was added to a mixture of graphite flakes (5.0 g) and sodium nitrate NaNO_3 (3.75 g). The mixture was cooled in an ice bath and stirred for 30 min. Then potassium permanganate KMnO_4 (25 g) was slowly added and the resulting mixture was stirred for 30 min. The resulting product was warmed to 35 °C and stirred for 2 h. Then water (250 ml) and 30% hydrogen peroxide H_2O_2 (20 ml) were slowly added. After stirring for 1 h, the mixture was filtered. The filtered graphite oxide powder was washed several times with 10% aqueous hydrochloric acid HCl (400 ml) and dried in air for 3 days at a temperature of about 90 °C.

To obtain reduced graphene oxide, thermal exfoliation of graphite oxide powder was carried out in vacuum with gradual heating (not more than 5–7 degrees per minute) to 300 °C. After reaching 300 °C, the temperature was stabilized for 15 min, after which the cell was cooled to room temperature for one and a half hour under vacuum.

The structure and morphology of thermally reduced graphene oxide (trGO) obtained in this way was studied using scanning and transmission electron microscopy. SEM images of the trGO sample are presented in Fig. 1, with magnification $\times 3000$ (Fig. 1(a)), TEM — $\times 50000$ (Fig. 1(b)). It can be seen from Fig. 1 that the product obtained as a result of thermal exfoliation contains conglomerates consisting of several layers of graphene oxide. The distances between graphene layers in such composites exceed two or more times the distance between the layers in graphite.

The elemental composition of the samples was studied using energy dispersive x-ray spectroscopy (EDS). Analysis of the EDS spectrum indicated that the samples of thermally reduced graphene oxide consist mainly of carbon and oxygen. As impurities, the samples contain small amounts of sodium, aluminum, silicon, sulfur, chlorine, potassium, manganese, and iron, in total not exceeding 2.4 at. % (see Table 1). The error in the EDS measurements of the trace element composition was approximately 10–20%. The ratio of carbon atoms and oxygen C/O is ≈ 6 due to the reduction of oxygen-containing groups during heat treatment. That value [$C/O \approx 6$] indicates the presence of electric conductivity in GO [8]. In the case of complete oxidation of GO, this ratio is approximately equal to 1.3 [22] and GO is an insulator.

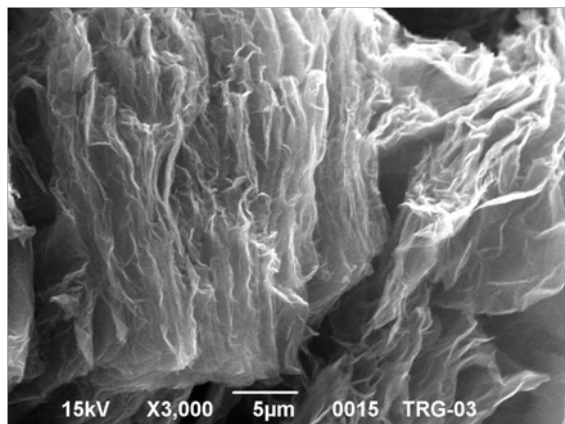
Samples were cut from tablets with the diameter of 10 mm and thickness of 2–3 mm. The tablets were obtained by pressing powders of thermally reduced graphene oxide and graphite oxide under the pressure of 1.1 GPa [23]. Two samples were studied: thermally reduced graphene oxide

Table 1. The chemical composition of the trGO sample

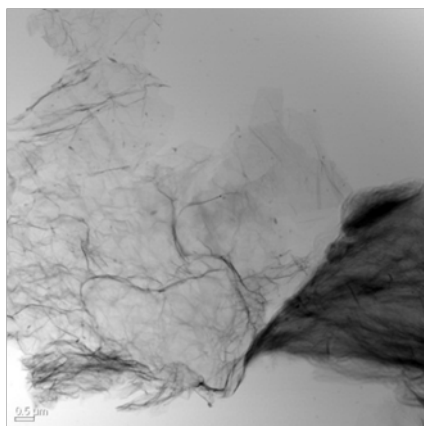
Element	at. %
C	83.64
O	14.02
Na	0.10
Al	0.25
Si	0.05
S	0.78
Cl	0.45
K	0.34
Mn	0.25
Fe	0.13

(sample s1) and graphite oxide (sample s2). The mass of the samples was (4.36 ± 0.01) mg (sample s1) and (7.47 ± 0.01) mg (sample s2).

The sample under test was mounted on a PPMS measuring platform. Apiezon grease was used to improve thermal contact between the platform and the sample. Heat exchange gas was not used to cool the calorimeter down to low temperatures.



(a)



(b)

Fig. 1. (a) SEM image of a trGO sample (magnification of $\times 3000$); (b) TEM image (magnification of $\times 50000$).

For each sample, two series of measurements were performed. During the first series, measurements were made from 150 to 2 K, and in the second series, from 2 to 275 K. The temperature of the sample was measured with a Cernox (Lake Shore Cryotronics) resistive thermometer. The random error in the measurement of heat capacity did not exceed 2–3%. Other details of the experiment were described elsewhere in Refs. 24–26.

Results and discussion

The specific heat at constant pressure of thermally reduced graphene oxide and graphite oxide has been measured in the temperature range from 1.8 to 275 K. The temperature dependence of the specific heat of the samples under study is plotted in Fig. 2.

The specific heat for these samples varies 10^3 – 10^4 times in the temperature range of 2–250 K. At 250 K, the specific heat of the oxides exceeds the specific heat of graphite and is less than classical limit (Dulong and Petit law) more than two times. Above 10 K, the heat capacity curves of the oxides are close to each other within 10–20%. The specific heat curves of reduced graphene oxide deviate upward from the specific heat curve of graphite oxide below 10 K. This discrepancy increases with decreasing temperature. At 2 K, the specific heat of reduced graphene oxide exceeds the specific heat of graphite oxide by more than 5 times. This situation resembles the behavior of temperature dependences of the heat capacity of multi-walled carbon nanotubes (MWCNTs) [12,26], bundles of single-walled carbon nanotubes (SWCNTs) [12,27] and graphite below 10 K. With a decrease in the number of walls in MWCNTs and the number of tubes in bundles of SWCNTs, their heat capacities increase and the difference

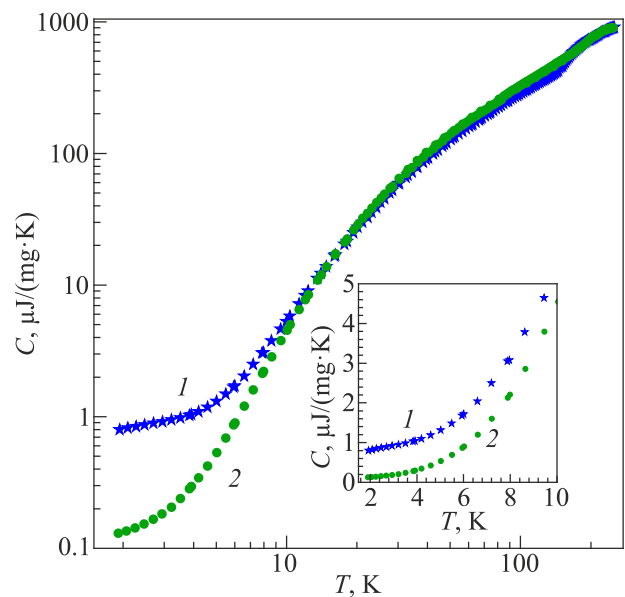


Fig. 2. The specific heat of thermally reduced graphene oxide (1) and graphite oxide (2). On the insert, the low-temperature portion is demonstrated.

monotonically increases between the heat capacities of the tubes and graphite with decreasing temperature.

Figures 3 demonstrate the temperature dependences of specific heat of the investigated materials C/T versus T in linear (a) and logarithmic (b) coordinates. There are temperature regions in which the specific heat is close to either linear or $T^{2.5-3}$ dependence as seen in Fig. 3. In the range of 1.8–4 K, the temperature dependence of the specific heat of reduced graphene oxide is linear. Whereas the linear dependence of the heat capacity of graphite oxide lies slightly below 4 K. Also in Fig. 3, two temperature ranges are observed from 80 to 150 K and 180–240 K, in which the temperature dependence of the specific heat for these samples is close to linear. In the region below 200 K, hysteresis is observed.

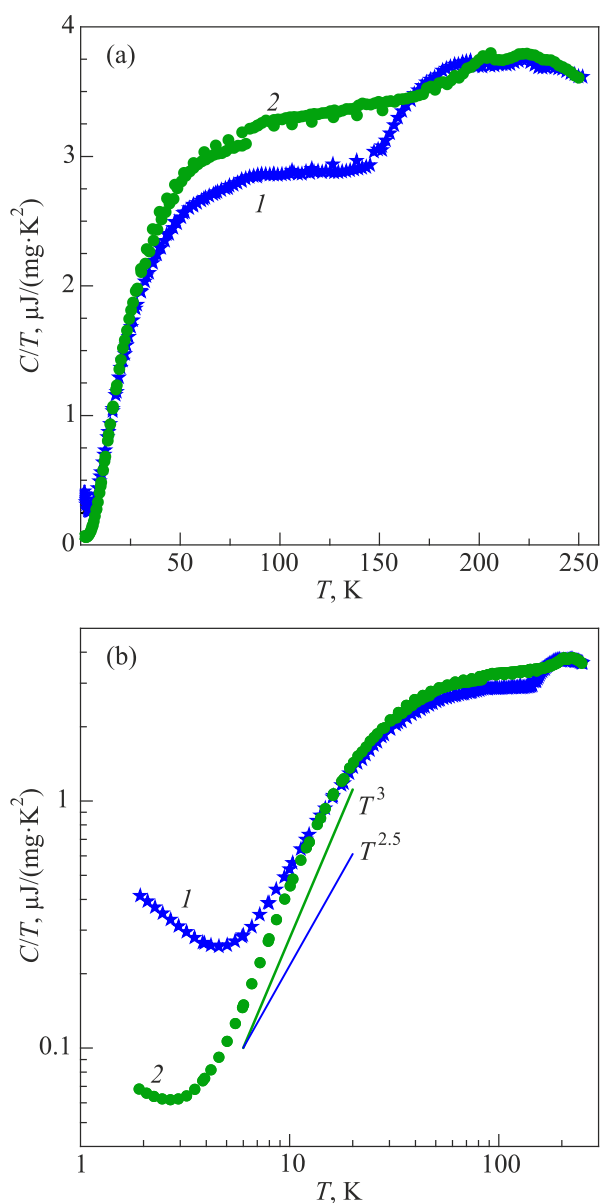


Fig. 3. The specific heat C/T vs T of thermally reduced graphene oxide (1) and graphite oxide (2): in the linear (a) and logarithmic (b) coordinates.

The temperature dependence character of the specific heat of thermally reduced graphene oxide in the range from ~ 7 to ~ 20 K is close to $T^{2.5}$. In the case of graphite oxide, the temperature dependence of the specific heat is closer to cubic and somewhat shifted toward lower temperatures. Gospodarev *et al.* [13], on the basis of microscopic calculations, note that the contribution of quasi-bending vibrations to the phonon specific heat exceeds the contribution of vibrations in the plane of the layers for graphite, bigraphene, and trigraphene. Their competition determines the linear nature of the heat capacity from above 50–70 K up to the temperatures above room temperature. In the case of graphene and graphite oxides, the character of the temperature dependence of heat capacity is more complicated due to their structure (different number of layers, large distances between layers, topological defects: vacancies, Stone–Wales defects, etc.) and the presence of oxygen-containing functional groups. Note that weakening of interlayer interaction due to an increase in the distance between the layers should lead to an increase in the specific heat capacity of graphene and graphite oxides and its domination over the specific heat capacities of other carbon nanomaterials: multi-walled carbon nanotubes, graphite.

Conclusion

For the first time, the specific heat of thermally reduced graphene oxide trGO and graphite oxide GtO was measured in the temperature range from 2 to 275 K by thermal relaxation method. In this temperature range, the heat capacity of both materials varies by 10^3 – 10^4 times. Above 15 K, heat capacities of trGO and GtO are close to each other in the range of 10–20%. It was found that below 10 K there is a discrepancy in the heat capacity curves of trGO and GtO, which increases with decreasing temperature. At 2 K, the ratio of the specific heat of trGO to the specific heat of GtO reaches 5. It was found that the temperature dependence of the specific heat trGO has a complex character. There are temperature ranges in which of the specific heat of trGO is close to either linear or $T^{2.5-3}$.

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Низькотемпературна питома теплоємність термічно відновленого оксиду графену

В.В. Сумароков, А. Jeżowski, D. Szewczyk, О.В. Долбин, М.А. Вінніков, М.І. Багацький

Вимірювання теплоємності при постійному тиску термічно відновленого оксиду графену (trGO) та оксиду графіту (GtO) проведено методом термічної релаксації в діапазоні температур від 1,8 до 275 К. Вище 15 К значення питомої теплоємності trGO та GtO близькі між собою в межах 20%. Нижче 10 К відношення питомої теплоємності trGO до питомої теплоємності GtO збільшується зі зменшенням температури й досягає 5 при 2 К. Встановлено, що температурна залежність питомої теплоємності trGO має складний характер. Існують температурні діапазони, у яких питома теплоємність trGO або $\sim T$, або $\sim T^{2.5}$.

Ключові слова: оксид графену, оксид графіту, питома теплоємність, низьковимірні системи.

Низкотемпературная удельная теплоемкость термически восстановленного оксида графена

В.В. Сумароков, А. Jeżowski, D. Szewczyk, А.В. Долбин, Н.А. Винников, М.И. Багацкий

Измерения теплоемкости при постоянном давлении термически восстановленного оксида графена (trGO) и оксида графита (GtO) выполнены методом термической релаксации в интервале температур от 1,8 до 275 К. Выше 15 К значения удельной теплоемкости trGO и GtO близки между собой в пределах 20%. Ниже 10 К отношение удельной теплоемкости trGO к удельной теплоемкости GtO увеличивается с уменьшением температуры и достигает 5 при 2 К. Установлено, что температурная зависимость удельной теплоемкости trGO имеет сложный характер. Существуют температурные диапазоны, в которых удельная теплоемкость trGO либо $\sim T$, либо $\sim T^{2.5}$.

Ключевые слова: оксид графена, оксид графита, удельная теплоемкость, низкоразмерные системы.