On the synthesis of the carboxylated graphene via graphene oxide liquid-phase modification with alkaline solutions

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Abstract. In this work we present a facile method for the synthesis of the carboxylated graphene derivat. The resulting material contains up to 10.9 at.% of carboxyl groups and with negligible content of other oxygen-containing groups. Moreover, formation of large round-shaped nanoscale holes is observed due to the applied synthesis process. The synthesized graphene derivat is of high interest for the sensing applications due to combination of its conductive nature and chemical reactivity provided by the attached carboxyl groups.

1. Introduction

Nowadays, a large number of methods for the graphene synthesis have been developed, such as chemical vapor deposition (CVD) [1], epitaxial growth on silicon carbide [2], and chemical reduction of graphene oxide (GO) [3]. Among them, the latter one is considered as a cost-effective and facile approach that does not require complex and expensive equipment and allows to obtain graphene materials in a large scale [4-5]. However, the structural quality and properties of the graphene layers obtained via GO chemical reduction still far from the desired ones and those inherent to the CVD graphene [1]. This is due to the fact that GO reduction never proceeds completely and 3-10 at.% of oxygen-containing groups remain, as well as defects, such as rips and nanoscale holes, are commonly introduced into the graphene layer during the process [5]. Nevertheless, regarded from another perspective, these features can be used in an advantageous way – to produce functionalized graphenes [6,7]. Graphene functionalization has become a prominent topic in the field of graphene studies, since it allows to tune properties of graphene materials, such as its electrical resistance [8], luminescence spectra and quantum efficiency [9,10], the material’s band gap value [11,12]. The latter one is of great interest for electronic and optoelectronic applications, such as light-emitting diodes (LEDs), field-effect transistors (FETs), etc. From a chemical point of view, functionalization provides the changes in the materials’ chemical activity, significantly improving the performance of graphene-based sensors, particularly, increasing their sensitivity and selectivity [13]. In addition, chemical functionalization allows to overcome the limitations of the graphene dispersability.
in various polymer matrices, which is one of the key issues in composites manufacturing. Many papers on the functionalized graphenes obtained via GO modification have been published [14-16] up to now. For instance, Wang, et al. [17] showed that amine derivate of graphene oxide, containing 3.2% of amines, can be synthesized and further used for the lead ions detection with a detection limit comparable to atomic absorption spectroscopy. Moreover, aminated graphene derivative, containing up to 4 at.% primary amines with verified chemical reactivity, was obtained via simple consecutive GO treatment with hydrobromic acid and ammonia solution [18] Chua et al. reported the synthesis of graphene layers via the conversion of epoxy and hydroxyl groups on GO through the reaction with thiourea and HBr, followed by treatment with NaOH [19]. The obtained graphene derivative demonstrated a heterogeneous electron transfer rate, being promising highly active electrocatalysts. Caliman et.al. [20] investigated the electrochemical behavior of the graphene oxide modified with different nitrogen-containing species via microwave-assisted reaction with the use of several types of amines. The best results were shown for samples synthesized using pipyridine and diisopropylamine, with the specific capacities estimated to comprise 290 F*g⁻¹ and 260 F*g⁻¹, respectively. Graphene subsequent functionalization by the use of “click” chemistry was shown by Sofer et al. through the application of series of Grignard reagents including simple alkyl chains, vinyl groups, ethynyl, and propargyl group [21].

Within graphene chemical derivatives family, carboxylated (C-xy) graphene and GO are ones of the most actively studied ones, owing to the high reactivity of carboxyl groups for the covalent bonding and strong effect on the graphene electronic structure. Additionally, carboxyl groups deprotonate more strongly than any other functional groups and, thus, have a higher bond strength with respect to either cations or molecules with an induced positive charge. The authors in [22] used a suspension of the reduced and carboxylated GO, prepared via reaction with sodium hydroxide and chloroacetic acid, as an adsorbent for methylene blue. In [23] Ziółkowski et. al. noted that analogous graphene material can be used to adsorb ionic dyes. In [24] authors showed that the sensor system based on carboxylated graphene synthesized in the same way as in the last two works, for the detection of uranyl UO²⁺ ions in water can be manufactured using this kind of graphene chemical derivatives. We earlier have demonstrated nanoscale perforation and carboxylation of graphene layer upon GO photoreduction, allowing the formation of C-xy graphene layers containing up to 10 at.% carboxyl groups for sensing applications [25,26]. At the same time, the investigation of new facile approaches for the C-xy graphene synthesis as well as its application still is of high interest. In this study, we present our results on the synthesis, analysis of physical properties, and possible application of C-xy graphene.

C-xy graphene was obtained by one-stage treatment of graphene oxide with sodium hydroxide with the addition of hydrogen peroxide under moderate heating. C-xy graphene obtained by this method contains structural defects, namely large holes with a low population density, decorated with up to 10.9 at.% carboxyl groups. This allows the use of this material for further modification.

2. Materials and methods

2.1. Sample preparation

An aqueous dispersion of graphene oxide was purchased from Graphene Technology (Russia, https://graphtechrus.ru/). During the subsequent processing of GO suspensions sonication was excluded to prevent flake's disruption with retention of their mean lateral size of 20-100 μm.

The synthesis of carboxylated graphene (denoted hereinafter as C-xy) was carried out by treating the GO aqueous suspension with a combination of potassium hydroxide (KOH) and hydrogen peroxide (H₂O₂). All chemicals were of analytical purity (Merck, US). In more detail, 40 ml of the GO suspension with a concentration of 0.3 wt.% was poured into polypropylene capsules, then 15 ml portions of a 60% KOH and 35% H₂O₂ aqueous solutions were added. The resulting mixture was subsequently heated at 80 °C for 24 hours while stirring. Thus obtained suspension of C-xy graphene was cooled to room temperature and centrifuged (Sigma S-16 centrifuge, Germany) at 18200 g for 12 minutes with the rinsing of the precipitate by 30 ml of distilled water. The described procedure was repeated four times to thoroughly purify the synthesized C-xy graphene from the contaminants. To measure the pH values of the suspensions during the synthesis pH meter Fisher Scientific Accumet Basic AB15 (Thermo Fisher Scientific, USA) was used.
2.2. Sample characterization

The studies of chemical composition via X-ray photoelectron spectroscopy (XPS) were performed at the Russian-German beamline of electron storage ring BESSY-II (Helmholtz-Zentrum Berlin) using the beamline ultrahigh vacuum experimental station. The parameters and details of the used experimental setup can be found in [27]. The C 1s and O 1s core-level spectra were acquired and refined by multiple scanning with the subsequent correction of their position in accordance with the Au 4f7/2 line (84.0 eV). The GO core level spectra were additionally aligned to the corresponding one of the C-xy layers to compensate their shift due to the charging effect. To perform deconvolution of the C 1s and O 1s core-level spectra CasaXPS software package was used.

GO and C-xy graphene films for XPS measurement were formed via the drop-casting method. Briefly, 200 μl of aqueous suspensions of GO or C-xy graphene 0.01 wt.% of concentration were dripped onto silica wafers, followed by drying overnight at room temperature (20 °C).

Transmission electron microscopy (TEM) images were acquired using a Jeol JEM-2100F microscope (Jeol, Japan) with the accelerating voltage 200 kV and point-to-point resolution 0.19 nm. TEM samples were prepared by wetting the TEM-grid in an aqueous suspension of the studied material.

3. Result and Discussion

To perform an accurate assessment of the chemical composition of samples, we have carried out XPS measurements. Figure 1 (a) shows the X-ray photoelectron survey spectra of the initial GO and C-xy graphene. The GO survey spectrum contains two dominant peaks, refereeing to C 1s and O 1s core-level lines. At the same time, the core-level lines of other elements, especially sulfur (S 2p at 168 eV) or nitrogen (N 1s at 400 eV), cannot be identified, which indicates the high purity of the initial GO. The C/O ratio for graphene oxide is estimated to be [1.68]. After the modification process was applied, the intensity of the O 1s line has decreased, indicating partial reduction. The C/O ratio of the carboxylated graphene is calculated to be [2.99]. Figure 2 (b) shows C 1s high-resolution spectra of the GO and C-xy graphene after the applied deconvolution process, resulting in the appearance of six discernable components. The ones located near 283.9 eV, 284.7 eV, and 285.1 eV correspond to non-functionalized carbon atoms of the graphene network. The component located at 283.9 eV corresponds to carbon atoms near which defects are located, or to the atoms participating in the formation of C-H bonds. The peak at 284.7 eV unambiguously refers to the sp²-hybridized graphene carbon atoms. The peak at 285.1 eV refers to carbon atoms of the distorted graphene network.

![Figure 1. Survey (a), C 1s (b) and O 1s (c) X-ray photoelectron spectra of the GO and C-xy.](image-url)
The remaining components correspond to carbon atoms bonded with functional groups. In particular, a peak at 286.2 eV corresponds to phenolic hydroxyl groups, a peak of 286.7 eV to hydroxyls and epoxides on the flake’s basal plane, peaks at 288.1 eV and 289.2 eV correspond to edge-located carbonyl and carboxyl groups. Figure 2 (c) shows the high-resolution spectra of the O 1s region of the GO and C-xy graphene. After the deconvolution process applied three components can be distinguished. Components 531.1 eV, 532.6 eV, and 534.2 eV correspond to a double-bonded oxygen (C=O in carbonyls and carboxyls), to single-bonded oxygen (C-O in hydroxyls, epoxides, and carboxyls), and oxygen in water molecules, respectively.

As can be seen, after the modification process, the functional composition changes significantly. The concentration of basal functional groups decreases; this is evident from the drastic decrease of the peak at 286.7 eV. Particularly, the concentration of hydroxyl and epoxide groups shifts from 53.2 at.% (GO) to 11.9 at.% (C-xy graphene). The diminishing of the 288.1 peaks’ intensity also indicates the decrease in the concentration of carbonyl groups. At the same time, the intensity of the peak centered at ca. ~289.2 eV has increased, which indicates a rise in the carboxyl groups’ concentration. This result is also qualitatively confirmed by the high resolution O 1s spectra: the components at 531.1 eV and 532.6 eV become of the same intensity, pointing out the equality in the number of single- and double-bonded oxygen, what corresponds to carboxyl groups. A more than a three-fold increase of carboxyl groups is seen, from 3 at.% (GO) to 10.9 at.% (C-xy graphene). Besides these changes in the composition of the functional groups, the restoration of the sp2-conjugated graphene structure is observed. This can be seen from the disappearance of 285.1 eV and 283.9 eV peaks.

Such significant changes in chemical composition are usually accompanied by changes in the structure of graphene layers. Particularly, the UV-induced reduction of graphene oxide with the simultaneous carboxylation noted in [23] has led to the formation of arrays of holes. In this case, the holes had an anisotropic and irregular shape, whereas the size varied in the range of 20-100 nanometers. The holes’ formation was associated with the condensation of hydroxyls of basal plane and ketones already present in initial graphene oxide followed by the formation of a carboxyl group. Then, the carboxyl group was cleaved off and the ketone group formed, which means holes’ formation. The size of holes in this case is limited by the amount of hydroxyl group available for condensation. In contrast to this case wet chemistry method that was used in [28] where such condensation is not limited by the amount of hydroxyl groups present in initial graphene oxide. Since, as a result of some reactions, a hydroxyl group can be included in the carbon network near the carbonyl group, a cascade condensation process starts leading to the formation of holes in an isotropic manner. As already written earlier, the modification process was carried via wet chemistry method a kind of similar in parameters to the method used in [28], it was decided to check the structure of the obtained material by the TEM imaging.

![Figure 2. TEM images of (a) GO and (b) C-xy graphene.](image-url)
Figure 2 shows TEM images of a monolayer of graphene oxide and C-xy graphene. As can be seen, the initial GO does not have any rips or tears. However, after the modification process, C-xy graphene demonstrates the presence of holes with a low population density. Calculated population density is 8 holes per 100 nm$^2$ (0.08 nm$^{-2}$). The lateral size of the formed holes range from 5 nm (min) to ~57 nm (max). The average hole size is calculated as 21 nm. At the same time, the shape of holes is isotropic, having almost round shape and is similar to those mentioned in [28].

Summing up, as a result of the modification process, graphene flakes are partially reduced with an increase in concentration of carboxyl groups, located at the edges of formed holes, from 3% to 10.9%.

4. Conclusion
In this work, we presented a simple synthesis method for carboxylated graphene suitable for large-scale production. The carboxylated graphene obtained by this method contains structural defects, namely large holes with a low population density decorated with up to 10.9 at.% of carboxyls. This makes it possible to use this material for further modification. As one of the possible approaches, the modification of carboxylated graphene with aptamers and the formation of reusable, sensitive and selective sensors for the detection of viral diseases, in particular hepatitis B and C.

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