Thermal deoxygenation of graphite oxide at low temperature

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Abstract
Synthesis of graphene via the deoxygenation of the graphite oxide (GO) is a method for the large-scale production of this nanomaterial possessing exceptional mechanical, electrical and translucent properties. Graphite oxide sheet contains at least four different oxygen atoms connected to the C\text{sp}^3 and C\text{sp}^2 atoms of the sheet in the form of hydroxyl, epoxy, carboxyl or carbonyl groups. Some of these functional groups are located at the surface but others situated at the edges of the platelets. To obtain the graphene nanoplatelets or the few-layer graphene the oxygen functionalities must be removed. Exfoliation and deoxygenation can be accomplished by the use of chemical reductants or heat. Thermal deoxygenation as greener and simpler approach is more preferable over chemical reduction approach. Usually a considerable mass loss of GO observed upon heating at temperatures starting at 200 °C and is attributed to the deoxygenation process. In order to avoid the defects of the obtained graphene sheets it is very important to find the methods for lowering the deoxygenation temperature of GO. Herein, we have investigated the way treatment of the Hummer’s synthesis product with acetone and methyl tert-butyl ether under ultrasonication in order to lower the thermal stability of the graphite oxide and its deoxygenation temperature. The obtained results indicate that treatment of the graphite oxide with solvents mentioned above substantially reduces the reduction and exfoliation temperature (130 °C) under ambient atmosphere. The investigation of the composition of evolved gases by hyphenated Pyr/GC/MS method at different experimental conditions under helium atmosphere shows that without the expected H\textsubscript{2}O, CO and CO\textsubscript{2} also sulphur dioxide and acetone has been released.

1. Introduction
Graphene is defined as sheets of sp\textsuperscript{2}-hybridized carbon, where the number of stacked sheets is lower than 10 [1]. The properties of graphene materials depend on the number of graphene layers in stack. Exceptional mechanical, electrical and translucent properties of the single and few layer graphene cause a great interest to this nanomaterial [2, 3] and make it attractive for a wide range of potential applications [4-8]. For example, the optical transmittance, high electrical conductivity and good stability allow to replaces the indium tin oxide by graphene for production of transparent electrodes of different devices [9]. Many fields of the potential application request to develop a market for this nanomaterial, therefore the elaboration of new methods for the commercial mass production of graphene is very important. Currently, there are few fundamentally different methods used for the graphene production: micromechanical cleavage of highly oriented graphite (top-down method), the growth the graphene sheets on different substrates (bottom-up methods), and thermolysis of structurally defined precursors and chemical exfoliation of...
graphite. Described methods have different variations, but remain suitable only for the fundamental investigation. High quality graphene films were grown on nickel and copper substrates as catalysts by chemical vapour deposition (CVD) at the temperature around 1000 °C by use of the reduced pressure and methane or other volatile carbon precursor [10]. Unfortunately, the CVD process is time and resource consuming and thus can’t be commercially viable for the mass production [11]. Similar assessment can be done for the Arc-Discharge method [12]. Another process (chemical solid deposition, CSD) for the fabrication of high quality graphene sheets on SiC wafer can be done with the use of the epitaxial growth and annealation of SiC at temperatures around 2000 °C [13], but it is also considered as not commercially feasible. Different bottom-up approach for the synthesis of graphene can be done by the thermolysis of structurally-defined precursors [14], but the synthesis of the precursors is complex and time and resources consuming. Solvothermal-assisted exfoliation of the edge-selectively functionalized graphite (EFG) also has various problems for the practical use [15, 16]. Synthesis of graphene from graphite oxide (GO) is widely investigated and practically used top-down method [17], considered as one of the possible for the large-scale synthesis of graphene. The oxidation of graphite breaks up the sp²-hybridized carbon sheets into nanoscale graphitic sp² domains surrounded by oxidised sp³ domains as well as defects the carbon vacancies [18]. The oxidation product of the graphite has a layered morphology with -OH (phenols and alcohols) and >O (epoxide) functionalities on the hexagonal basal planes and carbonyl groups on the periphery. Although the oxygen functionalities wearing the attractive forces between layers, the graphite oxide retains stacked similar to the graphite but with much wider spacing, enabling facile exfoliation. The sonication in polar solvents is often used for the exfoliation of GO. After exfoliation or during the exfoliation the obtained GO shall be reduced in order to restore the sp²-hybridized carbon sheets of graphene. It is known that the oxidation process of graphite followed by restoration of the sp²-hybridized carbon sheets, proceeds with the introduction of some defects into the graphene structure [18, 19], therefore the obtained product usually is termed as reduced graphite oxide (rGO). Elaboration of the new methods of high quality rGO production produces a great interest [18]. Thermal reduction and exfoliation of GO is considered as most promising strategy for the employment in mass production of rGO materials and has potentially lower costs and higher quality material. During the thermal reduction of GO some of the partially oxidised sp³ carbon atoms become fully oxidised to carbonaceous gases such as CO₂ and the rest is reduced to the sp² graphene product [18] The temperature for successful exfoliation is of great importance. Thermal analyses show that most of the functional groups can be removed at a temperature lower than 300 °C [20]. If the temperature is low, the thermal deoxygenation of GO is less complicated and more controlled. The low exfoliation temperature (as low as 200 °C) is a breakthrough for the mass production of rGO, which might result in low cost and sustainable energy consumption [20]. In order to lower the deoxygenation temperature we performed the additional treatment of GO prior the use, which later is synthesized accordingly to the modified Hummer’s method [17], with MTBE and acetone by ultrasonification.

2.Experimental
The graphite flakes and other reagents were purchased from “Sigma-Aldrich” and used without further purification. IR-spectra were recorded on “Perkin-Elmer Spectrum 100” spectrometer by using “Universal attenuated total reflectance” accessory with 3 bounces. The X-ray powder diffraction (XRD) patterns were
recorded on a „Bruker D-8 advanced” diffractometer with the “LynxEye” detector using the monochromatic CuKα radiation. The experimental data were collected over the 2θ range of 5 – 60 °. The thermal properties were characterised by thermogravimetric analyser “STA 6000” with sample mass 30 mg in a pure nitrogen flow of 20 ml/min and hyphenated Pyr-GC-MS system. In Pyr-GC-MS system the samples of graphite oxide were pyrolyzed using “CDS Analytical Inc. Pyroprobe 5200” pyrolysis rig at different experimental conditions. Gas chromatograph GC -2010 Plus “Shimadzu” with FID detector was connected with mass spectrometer “GCMS-QP2010 Ultra, Shimadzu” to obtain the analysis results of the gases evolved. The chromatographic separation was carried out with the use of “Restek” capillary column – “Rtx-XLB” (60 m, 0.25 mm ID, film thickness 0.25 μm) with helium as a carrier gas. The ion source temperature was set at 220 °C, the injection temperature was 300 °C, the oven temperature program was 10 min at 30 °C, 40 °C/min to 270 °C, and 5 min at 270 °C.

The graphite oxide has been prepared according to the modified Hummer’s method [21] by the use of 10 g of graphite flakes. Molten graphite flakes were mixed with conc. H2SO4, then KMnO4 and NaNO3 were gradually added with continuously stirring and cooling and the oxidation process at temperature 30 – 35 °C during 2h was performed. After them the 25% H2O2 solution was slowly added. The mixture was filtrated and then using centrifugation (9000 rpm) washed several times with 5 % HCl solution. The obtained by centrifugation tar-like graphite oxide was washed with de-ionized water repeatedly until the filtrate became neutral and don’t contain the chloride ions. The obtained tar-like sediment after centrifugation was twice suspended in acetone and twice in MTBE by the use of the laboratory ultrasonic cleaner over 5 minutes. After centrifugation and drying at room temperature for 24 h following 4 h in vacuum at 50 °C, 22.8 g of a black coal-like product was obtained. CHNS microanalysis was performed using “Euro Vector EA 3000”.

3. Results and discussion
FTIR spectrum of the synthesized GO significantly differs from the spectrum of the graphite and has absorption bands characteristic to oxygen functionalities (Fig.1).

![FTIR spectrum of GO](image)
There are absorption bands of stretching vibration of different OH and C-H groups in 3000 - 3400 and 2800 cm\(^{-1}\) region respectively. Stretching vibration of carboxyl groups and carbon-carbon double bonds at 1736-1710 and 1620 cm\(^{-1}\), respectively. Also the characteristic C-O-C absorption and C-O bands at 1200 and 1045 cm\(^{-1}\). The chemical oxidation of the graphite flakes causes the essential change of the XRD patterns (Fig. 2) of the graphite. The obtained sample has a new intensive peak at 2\(\theta = 9.66^\circ\) (d002) together with the weak peak at 2\(\theta \approx 4^\circ\). The intensive peak at 2\(\theta = 9.66^\circ\) corresponds to the layered structure with an interlayer distance approximately at 0.915 nm and confirms the graphite-like stacked morphology of the GO. A bit larger basal spacing than usual [21, 22] by approximately 0.1 nm shall weaken the attractive forces between layers and enable the exfoliation.

It is known that the recovery of the graphene structure has been made by the deoxygenation of the graphite oxide after or simultaneously with the exfoliation. The removal of the oxygen functionalities from the graphite oxide and employment of the obtained colloidal suspension of the reduced graphene oxide is one of the most promising techniques to produce electrically conductive graphene-based platelets on a large scale [22]. The deoxygenation often has been performed utilizing chemical reductants [22, 23]. It is known that the reduced graphene oxide can also be produced from the GO by the thermal exfoliation and reduction [20]. As in the case of chemical reduction the properties of the product of thermal deoxygenation depends on the methods of preparation of the graphite oxide as well as of the realization of the thermal treatment, but the thermal deoxygenation is likely to be easier to implement and more sustainable process.

![Figure 2. The XRD patterns of GO before and after the deoxygenation.](image)

In order to investigate the thermal deoxygenation process we had begun with the thermogravimetric investigation of the synthesized GO. Thus, to the data reported [20, 24] considerable mass loss of the graphite oxide occurs at temperatures close to 200°C.
and is accompanied by the release of CO₂, CO and H₂O. By employing solvents or dispersion in propylene carbonate the deoxygenation temperature has been decreased to 150 °C [25]. Our experiments showed that in all the cases when heating rate exceeds 1 °C/min an explosion like mass loss at 130 °C occurs indicating spontaneous exfoliation and deoxygenation of GO (Fig. 3). Analogous decomposition of GO obtained without the treating with acetone and MTBE proceed at 193 °C.

The data obtained from FTIR spectra of the products thrown out from the sample pan do not show the presence of oxygen containing functional group and the X-ray spectra show a weak and wide band in the region 22-26 °, while the peak at 2θ = 10.5 ° is absent (Fig. 2). The broad and weak peaks of reduced graphene oxide correspond to interlayer distances of 0.35 – 0.46 nm and can be related to the non-exfoliated part of reduced GO, obtained after the removing intercalated water molecules, carboxyl, hydroxyl and epoxide groups.

Figure 3. TG curve of mass loss of the synthesised GO at heating rate 5 °C/min.

Only when the heating rate is around 1 °C/min it was possible to register the mass loss curve (Table 1) what is with agreement with the reported earlier [25]. The mass loss curve consists of at least four stages of the anticipated H₂O, CO and CO₂ release, but the DTG curve allow established at least three steps of mass loss. The first step is through at 100 °C and can be attributed to the release of the absorbed water. Upon further heating over 100 °C the deoxygenation proceeds with the maximal rate at 158,4 °C.

| No | Temperature interval, °C | Mass loss, % |
|----|--------------------------|--------------|
| 1. | 30-100                   | 16.0         |
| 2. | 100-185                  | 27.4         |
| 3. | 185-300                  | 9.6          |
| 4. | 30 - 750                 | 60.6         |

Using the trapping option of “Pyroprobe 5200” it was possible to register the composition of the gas evolved upon heating at different temperatures. At the
temperatures lower than 100 °C the evolved gas consisted mostly of water (78%), but also included considerable amount of carbon monoxide and carbon dioxide (21%), and acetone (0.7 %) what indicates that the decomposition of the labile oxygen containing functional group starts at unexpectedly low temperatures, however solvent isn’t fully removed upon heating in vacuum at 50 °C. Fig. 4 shows that the evolution of carbon oxides and water proceeds until 800 °C and is part of the complex mechanism of deoxygenation process [23, 26]. The evolution of sulfur dioxide starts at approximately 200 °C reaches the highest rate at 280 °C and proceeds until reaches temperatures close to 800 °C.

Figure 4. Integral peak areas of CO + CO₂ and H₂O in chromatograms obtained by step-by-step heating of GO in the temperature intervals 30-100, 100-130, 130-160, 160-190, 190-230, 230-300, 300-600 and 600-800 °C by heating rate 100 °C/min. Differential characteristics were obtained from thermal desorption and analysis of the gases evolved during each interval.

4. Conclusions
The obtained data indicates that the course of thermal deoxygenation is severely dependent on the pre-treatment of the graphite oxide with the volatile organic solvent. Such pre-treatment reduce the content of adsorbed water and decrease the temperature of thermal deoxygenation and exfoliation, what allows producing the reduced graphite oxide under milder conditions. The temperature of the deoxygenation protocol for the pre-treated graphite oxide is appreciably lower than the characteristic temperatures of deoxygenations of graphite oxide. During the thermal deoxygenation not only the H₂O, CO and CO₂, but also small amounts of sulphur dioxide and acetone has been released, what allow as consider that all parts of process (oxidation, treatment with organic solvents and thermal shock) influenced the chemical composition and structure of reduced graphene oxide.

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6. References
[1] A.K.Geim, K.S.Novoselov. The rise of graphene. Nat. Mater, 2007, 6, 183-191
[2] W.Chi, I.Lahir, R.Seelaboyina, Y.S.Kang. Synthesis of graphene and its applications: a review. Critical Reviews in Solid State and Materials Sciences, 2010, 35, 52-71

[3] K.P.Loh, Q.Bao, P.K.Ang, J.Yang. The Chemistry of graphene. J.Mater.Chem., 2010, 20, 2277-2289

[4] Y.Zhu, S.Murali, W.Cai, X.Li, J.W.Suk, J.R. Potts, R.S. Ruoff. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. Advanced Materials, 2010, 22 (35), 3906–3924

[5] M.D.Stoller, S.Park, Z.Yanwu, J.An, R.S.Ruoff. Graphene-Based Ultracapacitors. Nano Lett. 2008, 8, 3498–3502.

[6] N.Mohanty, V.Berry. Graphene-Based Single-Bacterium Resolution Biodevice and DNA Transistor: Interfacing Graphene Derivatives with Nanoscale and Microscale Biocomponents. Nano Lett. 2008, 8, 4469–4476.

[7] G.Jo, M.Choe, S.Lee, W.Park, Y.H. Kahng, T.Lee. The application of graphene as electrodes in electrical and optical devices. Nanotechnology, 2012, Volume 23 Number 11, doi:10.1088/0957-4484/23/11/112001

[8] Y.Sun, G.Shin. Graphene/polymer composites for energy applications. Journal of Polymer Science Part B: Polymer Physics, 2013, 51 (4), 231-253

[9] K.S.Kim, Y.Zhao, H.Jang, S.Y.Lee, J.M.Kim, J.H.Ahn, P.Kim, J.Y.Choi, B.H.Hong. Large-Scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes. Nature 2009, 457, 706–710.

[10] X.Li, W.Cai, J.An, S.Kim, J.Nah, D.Yang, R.Piner, A.Velamakanni, I.Jung, E.Tutuc, S.K.Banerjee, L.Colombo, R.S.Ruoff. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils, Science 2009, 324, 1312-1314

[11] S.De, J.N.Coleman. Are There Fundamental Limitations on the Sheet resistance and Transmittance of Thin Graphene Films? ACS Nano, 2010, 4 (5), 2713–2720.

[12] Y.Wu, B.Wang, Y.Ma, Y.Huang, N.Li, F.Zhang, Y.Chen. Efficient and Large-Scale Synthesis of Few-Layered Graphene Using an Arc-Discharge Method and Conductivity Studies of the Resulting Film. Nano Res., 2010, 3, 661-669

[13] J.A.Robinson, C.P.Puls, N.E.Staley, J.P.Stitt, M.A.Fanton, K.V.Emtsev, T.Seyller, Y.Liu. Raman Topography and Strain Uniformity of Large-Area Epitaxial Graphene, Nano Lett, 2009, 9, 964-968

[14] L.Zhi, K.Mullen. A bottom-up approach from molecular nanographenes to unconventional carbon materials. J. Mater. Chem., 2008, 18, 1472–1484

[15] X.Cui, C.Zhang, R.Hao, Y.Hou. Liquid-phase exfoliation, functionalization and applications of graphene. Nanoscale, 2011, 3, 2118-2126

[16] S.-Y.Bae, I.-Y.Jeon, J.Yang, N.Park, H.S.Shin, S.Park, R.S. Ruoff, L.Dai, J.-B.Baek. Large-Area Graphene Films by Simple Solution Casting of Edge-Selectively Functionalized Graphite. ACSNANO, 2011, 5 (6), 4974–4980

[17] X.Zhang , J.Xin, F. Ding. The edges of graphene. Nanoscale, 2013, 5, 2556-2569

[18] W.S.Hummers, R.E.Offeman. Preparation of Graphitic Oxide. J. Am. Chem. Soc. 1958, 80, 1339.

[19] D.Krishnan, F.Kim, J.Luo, R.Cruz-Silva,L.J. Cote, H.Dong Jang, J.Huang. Energetic graphene oxide: Challenges and opportunities. Nano Today, 2012, 7, 137-152

[20] D.W.Boukhvalov, M.I.Katsnelson. Modeling of Graphite Oxide. J. Am. Chem. Soc. 2008, 130, 10697–10701.

[21] H.Jeong, Y.P.Lee, M.H.Jin, E.S.Kim, J.J.Bae, Y.H.Lee. Thermal stability of graphene oxide, Chem.Phys.Lett., 2009, 470, 255-258
[21] K.Yin, H.Li, Y.Xia, H.Bi, J.Sun, Z.Liu, L.Sun. Thermodinamic and Kinetic Analysis of low-temperature thermal reduction of graphene oxide. Nano-Micro Lett., 2011, 3 (1), 51-55
[22] S.Park, J.An, J.R.Potts, A.Velamakanni, S.Murali, R.S.Ruoff. Hydrazine-reduction of graphite- and graphene oxide. Carbon, 2011, 49, 3019-3023
[23] S.Pei, H.Cheng. The reduction of graphene oxide. Carbon, 2012, 50 (9), 3210–3228
[24] H.L.Poh, F.Šaněk, A.Ambrosi, G.Zhao, Z.Sofer, M.Pumera. Graphenes prepared by Staudenmaier, Nanoscale, 2012, 4 (11), 3515-3522
[25] W.Chen, L.Yan. Preparation of graphene by a low-temperature thermal reduction at atmosphere pressure. Nanoscale, 2010, 2, 559–563
[26] M.Acik, Y.J. Chabal. A Review on Thermal Exfoliation of Graphene Oxide. Journal of Materials Science Research, 2013, 2 (1), 101-112