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# Synthesis of graphite oxide by electrochemical oxidation in aqueous perchloric acid

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ABSTRACT

In this research a graphite oxide (GO) was synthesized by electrochemical oxidation of natural graphite in aqueous solution of perchloric acid. The process of anodic oxidation of graphite was performed by linear sweep voltammetry (LSV) from the rest potential of electrode to 1.4 V. In consequence of the electrochemical treatment graphite was fully transformed yielding GO. Formation of GO was proved by X-ray diffraction (XRD) and Raman spectroscopy analysis. The synthesis product was also characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

## 1. Introduction

Graphite oxide (GO) can be obtained using different synthesis techniques, i.e. chemical and electrochemical methods. From the literature data, it is known that chemical methods are the most widely used. For the first time GO was synthesized by Brodie [1] in the nineteenth century. Other methods of GO preparation were developed by Staudenmaier [2] and Hummers [3]. Each of mentioned methods of GO formation based on graphite immersion in a strong acid and its chemical oxidation in the presence of strong oxidants. Several modifications of these methods were employed [4–9]. Depending on the method, graphite precursor and the reaction conditions used, the resulting GO is characterized by different level of oxidation.

Alternatively, there are literature reports about formation of GO through electrochemical oxidation of graphite in aqueous acids [10–16]. Contrary to the chemical methods electrochemical synthesis is highly controllable, therefore the obtained material is characterized by the desired properties as well composition. However the electrochemical synthesis of GO can be recognized as an attractive method from the environmental as well as economical point of view. The amount of used reagents can be significantly reduced and the entire process is carried out at ambient conditions [17]. GO can be formed by anodic oxidation of graphite in aqueous solutions of sulfuric [11,13], perchloric [10–12,14,15] and nitric acid [16]. The commonly used method employed to the GO formation is galvanostatic oxidation. Beck et al. [13] have proposed a zone model of the GO formation based on the galvanostatic overoxidation of graphite in aqueous solution of sulfuric acid. Within the first stage of the mentioned oxidation graphite intercalation compound with sulfuric acid ($H_2SO_4$–GIC) is synthesized. Layered structure of graphite and large distance between the neighboring graphene layers enable insertion of ions or molecules (intercalate) between the interlayer spaces of the graphite lattice. This process is known as intercalation, whereas the product of this reaction is called graphite intercalation compound (GIC) [18]. Depending on the direction of electron transfer during the formation of chemical bonds between the graphite matrix and intercalate, GICs can be divided into acceptor-type (an intercalate accepts an electron from graphene layer) and as a donor-type (an electron is transferred from the intercalate to graphene layer) [19]. In the next stage, water molecules are co-intercalated into the $H_2SO_4$–GIC. Further oxidation of GIC leads to the formation of oxygen functionalities and finally the GO is synthesized. The level of graphite oxidation depends on many factors, such as the amount of water within the acid solution, type of acid used, the features of graphite precursor and the applied conditions [11–16]. However some works have been performed to characterize the process of GO formation by graphite oxidation in perchloric acid, still there is no unequivocal conformation that the graphite matrix was fully transformed to GO.

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Process of GO synthesis by graphite oxidation in 71% $HClO_4$ using cyclic voltammetry method was investigated by Jiang [10,14]. These works were focused on the reversibility and thermodynamic state of the considered process. The detailed description of reversal and non-reversal formation of GO are not enriched in the particular analysis of its structure and properties by such methods as XRD, Raman and XPS spectroscopy. Besenhard et al. [11] have investigated the hydrolysis of perchloric acid accompanied by the disappearance of $ClO_4^-$ ions. Resulted GO was not subjected to the examination of structural properties (e.g., by XRD, Raman spectroscopy) as well as chemical composition (e.g., by XPS analysis). Some valuable information on the structure of GO being synthesized by galvanostatic oxidation of graphite in 4.6, 9.2 and 11.6 M $HClO_4$ are revealed by Nakajima and Matsuo [12]. According to the Authors, there is a correlation between the concentration of perchloric acid and intercalation stage of GIC which allows the GO formation. The structure of graphite oxide was investigated indirectly by its fluorination at elevated temperatures and directly by XRD analysis.

In this paper we investigated a GO synthesis by electrochemical treatment of graphite in 8 M perchloric acid. In our research the GO was synthesized form natural graphite flakes by simple one–step anodic oxidation. For the first time to obtain GO the linear sweep voltammetry method was used. In specific conditions of electrochemical oxidation the second-stage $HClO_4$–GIC is formed. Further oxidation of $HClO_4$–GIC allows us to perform entire transformation of graphite giving the final product – GO. To confirm the GO formation X-ray diffraction and Raman spectroscopy were used. While the SEM observation and XPS analysis were performed to characterize the obtained product.

## 2. Experimental

### 2.1. Synthesis of GO

GO was synthesized from natural graphite flakes (purity 99.5%, flake size 170–283 μm, Graphit Kropfmühl, Germany) by electrochemical treatment using a linear sweep voltammetry (LSV) technique. Measurements were carried out in a three-electrode system. 100 mg of graphite, playing a role of working electrode, was closed in platinum mesh (purity 99.9%, 120 openings per inch, Goodfellow, United Kingdom) and immersed in 8 M $HClO_4$ (purity 71%, Merck, Germany). Platinum wire (purity 99.9%, 1 mm diameter, Goodfellow, United Kingdom) was used as a counter electrode. Working electrode was separated from the counter electrode by sintered glass frit. $Hg/Hg_2SO_4$/1 M $H_2SO_4$ playing a role of reference electrode. LSV measurements were performed with scan rate equal to 0.01 mV $s^{-1}$ in the potential range from the rest potential of electrode ($E_R$) to 1.4 V. After the synthesis the material was washed with distilled water and dried in desiccator for 24 h.

### 2.2. Instrumentation

Morphology of the synthesized GO was characterized by scanning electron microscope (SEM) JSM-7001F (Jeol, Japan). To confirm the GO formation the X-ray diffraction (XRD) and Raman investigations were done. XRD analysis was carried out on a Empyrean diffractometer (PANalytical, Netherlands) using Cu Kα radiation (1.54 Å), reflection-transmission spinner (sample stage) and PIXcel 3D detector, operating in the Bragg–Brentano geometry. The 2 Theta scans were recorded at room temperature (300 K) in angles ranging from 4 to 60 °2Theta with a step size of 0.006 °2Theta and continuous scan mode. Raman spectra were recorded using inVia Raman Microscope (Renishaw, United Kingdom) with 514 nm laser excitation source. In order to investigate the oxidation level of the obtained material X-ray photoelectron spectroscopy (XPS) was performed. XPS spectra were obtained with Sphera II photoelectron energy analyzer (Scienta Omicron, Germany) with the monochromatized Al Kα X-ray source mounted inside the UHV system. LSV measurements were carried out using Autolab PGSTAT 302N potentiostat/galvanostat (Metrohm, Netherlands).

## 3. Results and discussion

### 3.1. Electrochemical oxidation of graphite

The voltammetry curve for graphite electrochemically oxidized in 8 M $HClO_4$ is presented in Fig. 1. Graphite was oxidized up to the five different potentials: 1.2, 1.225, 124, 1.255, and 1.4 V.

To omit the partial decomposition of GO to $CO_2$ and electrochemical decomposition of water, when the potential of 1.4 V was reached the process was interrupted. When the respective potential was reached, the measurement was stopped and the obtained sample underwent XRD analysis (Fig. 2). The curve recorded during the process of graphite oxidation can be divided into two parts. Within the first the small anodic peak appears at the potential 1.14 V. This peak illustrates the intercalation of $ClO_4^-$ ions into graphite matrix forming GIC with perchloric acid [15]. During the anodic polarization graphite is electrochemically oxidized giving the $C_x^+$ lattice. When the potential of graphite electrode is equal to 0.68 V, the intercalation of $ClO_4^-$ ions between the positively charged graphene layers starts thus forming GIC of $C_x^+ClO_4^-$ formula [19]. According to the XRD analysis (Fig. 2) the intercalation finished up to the potential 1.2 V results in formation of 2-stage $HClO_4$-GIC.

It means that the two neighboring layers of intercalate are separated by the two graphene layers. Peaks associated with the *d* spacing of 1.69 Å and 3.40 Å being attributed to the formation of 2-stage $HClO_4$-GIC can be observed on XRD pattern for graphite oxidized to 1.2 V (Fig. 2, curve b) [12,20]. It is well known, that an application of lower concentrations of acids makes impossible to form 1-stage GIC, while GIC with lower stages can be successively obtained [13]. The second part of voltammetric curve (Fig. 1) spread over the potential 1.2 V represents the process of graphite oxide formation. Between the potentials 1.2 and 1.4 V, a huge asymmetric peak with two maxima at 1.24 and 1.255 V, and one prepeak at 1.225 V can be observed. The XRD patterns (Fig. 2) for samples oxidized up to the potentials 1.225 (Fig. 2c), 1.24 (Fig. 2d) and

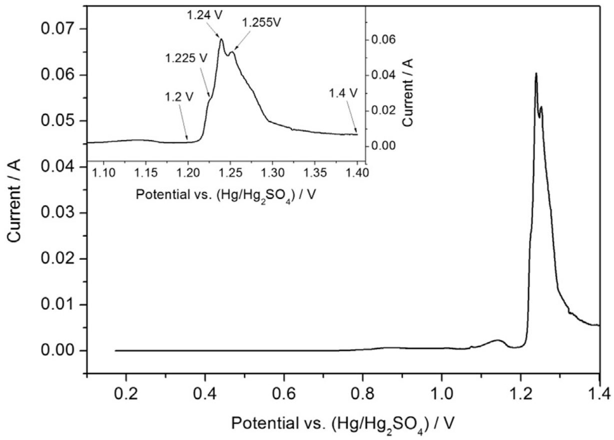

**Fig. 1.** Linear sweep voltammetry curve recorded in 8 M $HClO_4$ during anodic oxidation of graphite. Potential range: $E_R \rightarrow 1.4$ V. Scan rate: 0.01 mV $s^{-1}$.

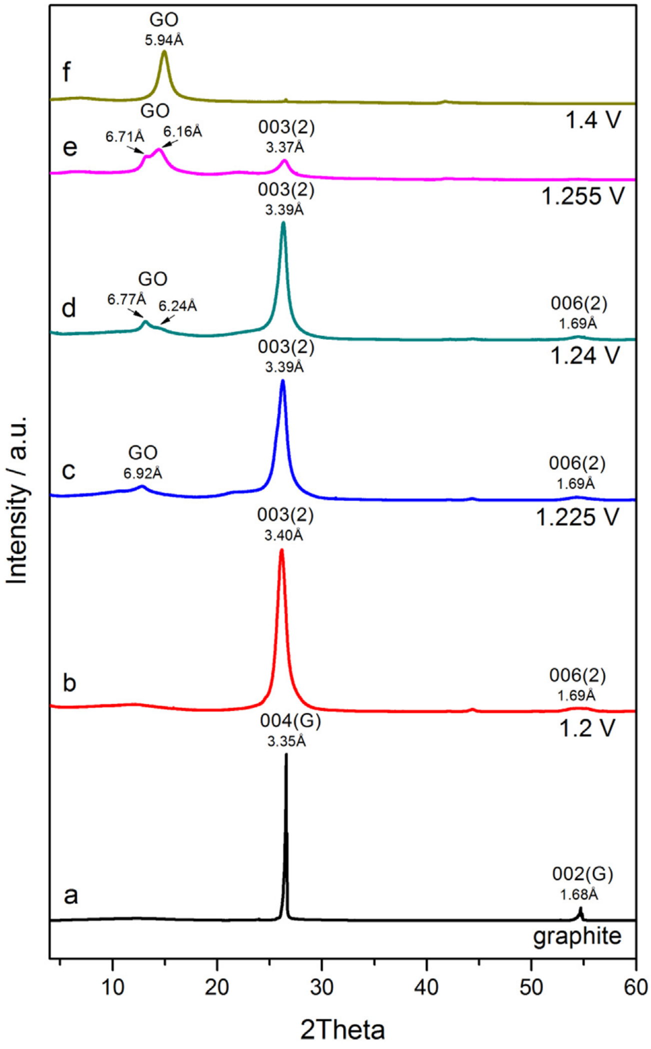

**Fig. 2.** XRD patterns of graphite (a) and graphite electrochemically oxidized in 8 M $HClO_4$ to the potentials: 1.2 (b), 1225 (c), 1.24 (d), 1.255 (e) and 1.4 V (f). (A colour version of this figure can be viewed online).

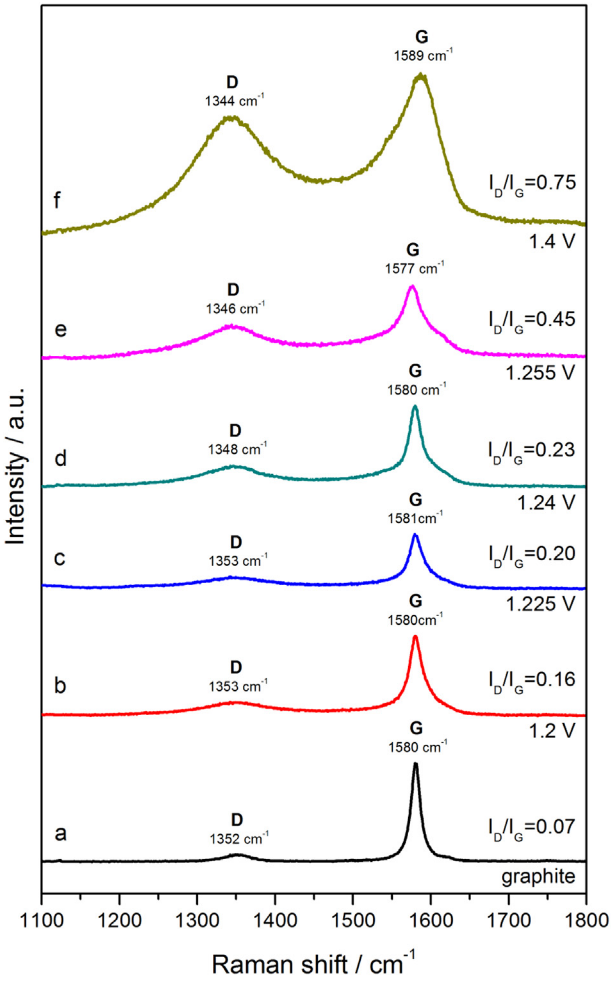

**Fig. 3.** Raman spectra of graphite (a) and graphite electrochemically oxidized in 8 M $HClO_4$ to the potentials: 1.2 (b), 1225 (c), 1.24 (d), 1.255 (e) and 1.4 V (f). (A colour version of this figure can be viewed online).

1.255 V (Fig 2e) shows that the intensity of peaks attributed to $HClO_4$-GIC decrease with increasing of oxidation potential. On the other hand the intensity of peaks with *d* spacing of 6.92 Å (Fig. 2c), 6.24 and 6.77 Å (Fig. 2d), 6.16 and 6.71 Å (Fig. 2e) related with the appearance of GO increases noticeably [12]. The shift in *d* spacing associated with GO formation may be caused by the increase in concentration of oxygen functionalities due to electrochemical oxidation of graphite matrix. It can be assumed that the mentioned asymmetric peak on voltammetric curve illustrates a gentle transformation of GIC into GO. Its asymmetric shape indicates the multistep character of the conducted process. According to the literature data, within the regarded potential range, the reactions of water co-intercalation, vicinal OH groups formation and their transformation into epoxy rings take place [13,14]. When potential 1.4 V is reached GIC is fully transformed into the GO. Peak at 14.9 °2Theta (Fig. 2f) corresponding to *d* spacing of 5.94 Å for final product indicates that graphite oxide structure is formed [9]. The disappearance of the signal at 26.6 °2Theta (Fig. 2f) associated with the graphite structure (Fig. 2a) indicates the oxidation of graphite matrix, thus forming GO.

Disorder in $sp^2$ carbon materials can be characterized by Raman spectroscopy commonly used to investigate of carbon material structure. Fig. 3 shows typical Raman spectra of graphite and GO formation. The Raman spectrum of graphite (Fig. 3a) shows characteristic peak of G band around 1580 $cm^{-1}$ [21,22]. The G band is a radial C—C stretching mode of $sp^2$ bonded carbon. The D band peak with a very low intensity can be also observed on Raman spectrum recorded for graphite. Such a behavior results from the appearance of structural defects, edges as well as partial oxidation of graphite surface [23,24]. The process of deep anodic oxidation of graphite in 8 M $HClO_4$ leads to the disordering of graphite structure. This effect is revealed on Raman spectra as an increase in intensity of the D band peak (around 1350 $cm^{-1}$). Curves b—f depicted in Fig. 3 show a consecutive increase in $I_D/I_G$ ratio (intensity of D band peak/intensity of G band peak) from 0.16 to 0.75 for the samples underwent oxidation up to 1.2 and 1.4 V, respectively. For sample being oxidized up to 1.4 V, the G band peak becomes flattened and shifts to 1589 $cm^{-1}$. Such a behavior is caused by the formation of oxygen functionalities within the graphite matrix thus decreasing the $sp^2$-hybridized C—C bonds concentration in synthesized GO [21,25–27].

### 3.2. Characterization of synthesized graphite oxide

The morphological properties of GO synthesized by electrochemical treatment in 8 M $HClO_4$ are depicted in Fig. 4. SEM images shown in Fig. 4a and b were recorded under the same

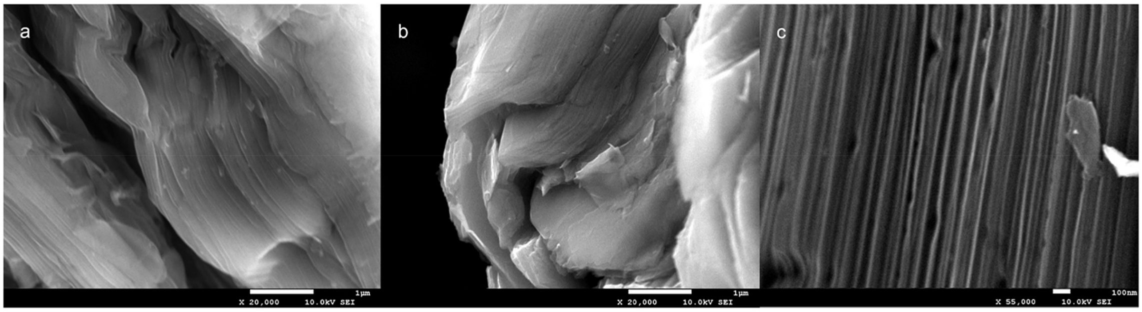

**Fig. 4.** SEM micrographs of GO synthesized by anodic oxidation of graphite in 8 M $HClO_4$.

magnification, whereas Fig. 4c displays an image acquired with higher resolution. The graphene layers of GO have many defects and are partially creased (Fig. 4a,b). Process of $HClO_4$ intercalation into the graphite accompanied by the deep oxidation brought about the significant delamination of a graphene layers. Some destroyed layers are also present on the surface and edges of graphite flakes. As can be seen from the Fig. 4c, despite the above mentioned defects and delamination of graphene layers within the GO, the layered structure is preserved.

Chemical composition of the surface of examined material was performed by XPS analysis. Fig. 5a and 5b–f show deconvoluted XPS spectra of C1s region recorded for graphite and graphite underwent anodic oxidation in 8 M $HClO_4$, respectively. The detailed information on oxygen, carbon and chlorine content, deconvoluted peak positions and the concentration of oxygen containing groups formed due to graphite oxidation are shown in Table 1. According to our expectations, oxidized graphites gathered due to electrochemical treatment in 8 M $HClO_4$ up to the potentials of 1.2, 1.225, 1.24, 1.255 and 1.4 V. (Fig. 5b–f) are significantly much more oxidized compared to starting graphite (Fig. 5a) (Table 1). The oxidation degree grows with extension of upper potential of graphite oxidation. Simultaneously, the concentration of chlorine gradually decreases. For sample underwent anodic oxidation up to 1.4 V, chlorine completely disappears. Such a behavior corresponds to the process of gradual GO formation demonstrated by the increase in oxygen concentration accompanied by the release of chlorine compounds from graphite matrix. The obtained results are in coincidence with the mechanism of electrochemical oxidation of graphite proposed by Beck et al. [13].

From Fig. 5a it can be noticed that the starting material has slightly oxidized surface. 1Cs spectra for all samples are deconvoluted into five peaks at the binding energies of: 284.5 and 285.2 eV (non-oxygenated C $sp^2$ and C $sp^3$, respectively) [28–30], 286.4 eV (C–O bond for epoxy and alkoxy groups) [28,29], 288.1 eV (C=O in carbonyl groups) [28–31], 289.3 eV (COO carboxyl groups) [28–31] and at 291.2 eV (π–π transitions in aromatic rings) [29–31]. Data

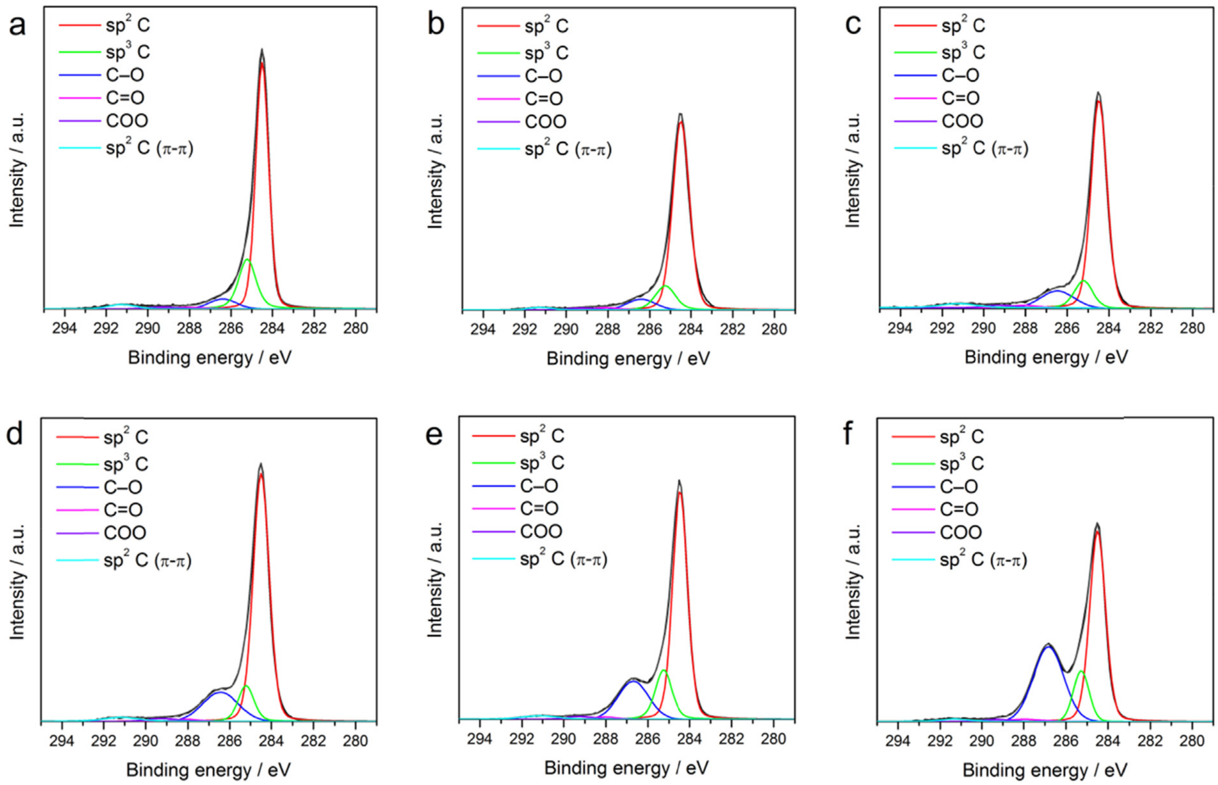

**Fig. 5.** C1s XPS spectra of graphite (a) and graphite after anodic oxidation in 8 M $HClO_4$ up to the potentials 1.2 (b), 1.225 (c), 1.24 (d), 1.255 (e) and 1.4 V. (f). (A colour version of this figure can be viewed online).

**Table 1**
The results of C1s XPS spectra for graphite and graphite electrochemically oxidized in 8 M $HClO_4$ up to the potentials 1.2, 1.225, 1.24, 1.255 and 1.4 V.

| | Graphite | | 1.2 V | | 1.225 V | | 1.24 V | | 1.255 V | | 1.4 V | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| At. % | | | | | | | | | | | | |
| C | 98.03 | | 92.49 | | 92.18 | | 94.17 | | 94.51 | | 90.75 | |
| O | 1.97 | | 2.15 | | 3.23 | | 4.47 | | 5.06 | | 9.25 | |
| Cl | – | | 5.36 | | 4.59 | | 1.36 | | 0.43 | | – | |
| Surface groups | Peak/eV | Content/% | Peak/eV | Content/% | Peak/eV | Content/% | Peak/eV | Content/% | Peak/eV | Content/% | Peak/eV | Content/% |
| $sp^2$ C ($\pi$–$\pi$) | 291.2 | 2.36 | 291.3 | 1.37 | 291.3 | 3.69 | 291.2 | 2.74 | 291.2 | 2.43 | 291.2 | 1.50 |
| COO | 289.3 | 1.24 | 289.2 | 1.29 | 289.2 | 1.61 | 289.2 | 1.46 | 289.2 | 1.31 | 289.3 | 1.33 |
| C=O | 288.1 | 1.69 | 288.1 | 1.74 | 288.1 | 1.74 | 288.1 | 1.08 | 288.0 | 1.19 | 288.0 | 1.85 |
| C–O | 286.4 | 5.43 | 286.4 | 6.63 | 286.5 | 10.97 | 286.4 | 16.58 | 286.7 | 18.89 | 286.8 | 34.20 |
| $sp^3$ C | 285.2 | 20.64 | 285.3 | 12.39 | 285.2 | 11.34 | 285.2 | 10.21 | 285.3 | 15.35 | 285.3 | 12.38 |
| $sp^2$ C | 284.5 | 68.64 | 284.5 | 76.57 | 284.5 | 70.65 | 284.5 | 67.93 | 284.5 | 60.83 | 284.5 | 48.74 |

included in Table 1 show a continuous increase in concentration of epoxy and alkoxy groups, from 5.43% for original graphite (Fig. 5a) to 34.20% for GO acquired due to graphite oxidation up to the potential of 1.4 V (Fig. 5f). The concentration of carbonyl and carboxyl functionalities remains on practically unchanged level due to graphite oxidation at elevated potentials (Fig. 5 b–f). In contrast, significant decrease in concentration of $sp^2$ C from 68.64% to 48.74% and for $sp^3$ C from 20.64% to 12.38% is noticed. It can be assumed that during the electrochemical synthesis of GO performed in 8 M $HClO_4$, the oxygen atoms are attached to the aromatic rings of graphene layers mainly as epoxy and alkoxy functionalities.

## 4. Conclusions

The synthesis of GO was proved by XRD and Raman spectroscopy. The electrochemical treatment of graphite in 8 M $HClO_4$ using a LSV method leads to GO synthesis through 2-stage $HClO_4$-GIC formation. The deep anodic oxidation of graphite performed up to the potential 1.4 V result in entire transformation of graphite yielding GO. One of the most valuable point of this work is fact that the formation of GO was proved. The XRD results undoubtedly indicate that the GO is gathered. On the basis of SEM observation and XPS analysis it can be concluded that the process of GO formation is selective and the epoxy and alkoxy groups were found to be the main products of this process. The obtained GO has many structural defects, however, the layers of GO are partially oriented, thus forming a quasi-graphite structure. Due to the high control of oxidation potential it is possible to synthesize a GO with a desired degree of oxidation.

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