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Chemical routes to materials

Energetically efficient and electrochemically tuneable exfoliation of graphite: process monitoring and product characterization

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ABSTRACT

In this work, graphene oxide was prepared by electrochemical exfoliation of graphite in sodium dodecyl sulphate and sodium dodecylbenzene sulphonate aqueous solution. Two different working electrodes were investigated: an electrode prepared from natural graphite flakes and a commercial natural graphite rod. The working electrode was polarized in a two-electrode system by using platinum counter electrode and by a multistep change of polarity or by single anodic and cathodic polarization. The voltage value ranged from 2.5 to 3.2 V. By monitoring the current transients and the colour of the resultant solutions, it was shown that the exfoliation process depends on the type of working electrode, surfactants and applied voltage value. The multistep change of polarity was more effective compared to single polarization. The ultraviolet–visible spectrophotometry and Raman spectroscopy indicated the presence of defects within the graphene structure, while FTIR spectroscopy indicated the presence of oxygen functional groups, which is characteristic of graphene oxide (GO). Dynamic light scattering revealed that the solutions obtained in this work contained GO sheets within the size of 10–600 nm. Atomic force microscopy measurements proved that the obtained product contains multilayer sheets. The energy consumption for the process carried out in this work ranges from 0.084–0.038 kWh g^{-1}, and therefore this process is considered to be a low-energy and cost-effective process.

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Introduction

Graphene is a material that was first isolated in 2004 [1] and since then fills the pages of scientific journals. Strictly speaking, graphene is an allotrope of carbon, whose structure consists of one-atom-thick planar sheets of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice [2]. It has fascinating properties, such as excellent electrical [3] and thermal conductivity [4], large specific surface area [5], high mechanical strength [4, 6] and absorption of 2% of the light passing through it [7]. These properties render graphene suitable for an array of applications, for instance supercapacitors, batteries, composite materials, fuel cells, solar cells, molecular gas sensors and biosensors [2, 8, 9]. Although various methods have been developed for graphene production so far, they all possess certain disadvantages. Micromechanical exfoliation of graphite, chemical vapour deposition and epitaxial growth of graphene films on substrate by vacuum graphitization result in high-quality graphene layers. However, a high cost and low yield limit their applications [1, 10–12]. Chemical oxidation of graphite followed by chemical reduction relies on harsh oxidants, and the obtained graphene sheets show many structural defects that cannot be completely removed [13].

Apart from the aforementioned methods, the electrochemical method is simple, operates at ambient temperature and pressure and can be easily scaled up [14–18]. Moreover, when using the electrochemical method, it is possible to obtain graphene of relatively high quality, with minimal hole defects and tuneable level of oxidation [17, 19–22].

The electrochemical process includes application of anodic or cathodic polarization causing intercalation of ions within the graphite structure. This process is based on graphite intercalated compound (GIC) chemistry developed in the field of batteries. One of the most interesting anions for GIC formation is sulphate anion, and intercalation of sulphuric acid into graphite is a well-known process [23–25]. It was also reported that anion intercalation takes place in the solutions containing perchlorate, sulphate or nitrate anions, while it is aggravated in the phosphate-containing solution. The oxidizing power of H_2SO_4 can be used even for direct intercalation of sulphate ion without application of voltage [24]. Additional processes important for the electrochemical exfoliation are carbon oxidation and oxygen or hydrogen evolution in aqueous medium [19, 20]. By controlling potential, it is possible to control the number of layers and surface properties of graphene [2, 9, 21, 26]. The procedure time varies, from several minutes to several hours in order to be fully completed and to obtain monolayer or multilayer structures. Parvez et al. [27] demonstrated the exfoliation of graphite in H_2SO_4 aqueous solution. They prepared graphene with a sheet size from 5–10 µm, low oxygen content (7.5%) and C/O ratio 12.3, as well as excellent electronic properties. In this work, the authors have obtained a black dispersion by applying high voltage value (10 V) between the two graphite electrodes. After the isolation, the product was dispersed in *N*,*N*-dimethylformamide in order to exfoliate it completely and to obtain graphene layers. Later, in 2014. Pervez et al. [16] reported the electrochemical exfoliation of graphite in aqueous solutions of different inorganic salts, including $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, NH_4Cl, $NaNO_3$ and $NaClO_4$. It was found that sulphate ions showed a better exfoliation efficiency than other ions. They obtained graphene with a high yield, large lateral size, low oxidation degree and a remarkable hole mobility of 310 $cm^2\ V^{-1}\ s^{-1}$.

Anodic polarization was utilized in the above-mentioned electrochemical methods. However, Morales et al. [28] used cathodic treatment in aqueous perchloric acid in order to avoid oxidation of the graphite. Cathodic polarization resulted in proton intercalation and hydrogen gas evolution that lead to electrode expansion. Nonetheless, the electrode polarization was pretreatment for the microwave-assisted expansion and ultrasonic exfoliation of the graphite. Wang et al. [29] reported the exfoliation of the graphite in propylene carbonate (PC). They used $LiClO_4$/PC as electrolyte and by applying 15 V expanded the graphite foil. By further ultrasonification, highly conductive few-layer graphene sheets were successfully obtained with a high yield (> 70%). Successful expansion of the graphite foil was also obtained by Zhong et al. [30] by applying lower voltage value of 5 V in $LiClO_4$/PC in the first step and tetra-n-butylammonium perchlorate/PC in the second step.

Reports on the graphite exfoliations carried out in aqueous solutions frequently include two steps. The first one is a low potential pretreatment for the purpose of ion intercalation that is followed by the second step related to ramping to the high potential values causing the graphite to exfoliate [20, 31, 32]. However, it is possible to significantly decrease the potential value by using surfactant, such as sodium dodecyl sulphate (SDS), sodium dodecylbenzene sulphonate (SDBS), poly(sodium-4-styrene-sulphonate), cetyltrimethylammonium bromide (CTAB) or sodium cholate (SC) [2, 33]. Also, by using surfactants, it is possible to avoid additional treatments, for example microwave treatment or ultrasonification. Surfactants are amphiphilic molecules with a polar head at one end, and a long hydrophobic tail at the other. Dissociation of polar head enables involvement of surfactant in double-layer charging, and hydrophobic tail enables adsorption of surfactant on the graphite structure [34]. Additional advantage of using surfactants is that graphene sheets remain dispersed after the exfoliation, rather than self-associated into aggregates or stacked into more graphitic layers structures. Due to the fact that sulphate groups shows notable intercalating power, the surfactants containing sulphate or sulphonate groups also represent an anion with a significant potential for intercalation [22].

A successful exfoliation of the graphite was carried out by using different graphite electrodes, such as highly orientated pyrolytic graphite (HOPG) [17, 19], graphite foil [4, 27, 29], graphite rod [14, 16, 35–37] and natural graphite flakes (NGF) [16, 19, 35, 38–40]. Natural graphite flakes [41, 42], in comparison with synthetic graphite, have a larger crystallite size, which makes it a suitable precursor for graphene production [34]. Nonetheless, although it possesses satisfying structural properties and it is the cheapest precursor, there are only few reports on electrochemical exfoliation of NGF in $HClO_4$, H_2SO_4 or sulphate salts solutions when compared with a greater number of reports on exfoliation of synthetic graphite rod, graphite foil or HOPG.

The aim of this work was electrochemical exfoliation of natural graphite flakes in the presence of surfactants by applying low voltage values. This process is considered to be an efficient and a low-cost method. In order to increase the exfoliation efficiency, the graphite electrode was consecutively polarized at positive and negative potentials. The resulting product was successfully characterized by employing Raman spectroscopy, ultraviolet–visible spectrophotometry (UV/Vis), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and dynamic light scattering (DLS). The exfoliation process was characterized by using chronoamperometry, cyclic voltammetry and scanning electron microscopy (SEM) techniques.

Materials and methods

Chemicals and materials

The following analytical-grade chemicals were purchased: graphite rod containing natural graphite flakes (GR) from (Tup d.d., Croatia), natural graphite flakes, polyvinylidene fluoride (PVDF), *N*-methyl pyrrolidone (NMP), sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulphonate (SDBS) (Sigma-Aldrich). All solutions were prepared by using bidistilled water.

Working electrode was GR or laboratory-made electrode containing natural graphite flakes (GE).

GE was prepared by mixing natural graphite flakes with a PVDF (10%) and by addition of NMP. The NMP was added in an amount that is sufficient to produce a paste. Homogenized paste was applied on platinum support, which was previously polished by Al_2O_3 slurry, washed by bidistilled water and degreased in ethanol. Natural graphite flakes were grained by mill (IKA M20) prior to mixing with a PVDF. The electrode was dried 24 h at 40 °C in a vacuum oven prior to use. The working area of the GR electrode was 2.55 cm^2 and of the GE electrode was 2.44 cm^2.

Electrochemical exfoliation of natural graphite flakes

Electrochemical exfoliation was carried out in a one-compartment two-electrode system by using chronopotentiometry method. Different voltage values were applied by means of Potentiostat/Galvanostat PAR model 263A. GE or GR electrode was used as working electrode and the counter electrode was a Pt foil ($A = 1$ cm^2). The solution of 0.1 mol dm^{-3} SDS or 0.1 mol dm^{-3} SDBS was used as supporting electrolyte. Graphite electrode was polarized at positive or negative potentials by applying appropriate voltage between graphite electrode and platinum electrode and by changing polarity of the electrodes. The following procedures were used during electrochemical exfoliation in two-electrode system:

Procedure 1

Anodic polarization of graphite electrode was carried out by first applying voltage of 3.2 V during 360 min, and after that, cathodic polarization of graphite electrode was carried out by applying voltage of 2.8 V at an interval of 120 min. This procedure was based on previous investigations of the similar system [2]. Figure 1a illustrates voltage change during exfoliation process for Procedure 1.

Procedure 2

Anodic polarization of graphite electrode by applying voltages of 2.5, 2.8, 3.0 or 3.2 V during 30 min was carried out, and after that, cathodic polarization of graphite electrode by applying voltage of 2.8 V during 30 min was also carried out. This process was repeated throughout 12 cycles in order to achieve 360 min of overall anodic polarization. Figure 1b illustrates voltage change during exfoliation process for Procedure 1. Schematic illustration of electrochemical exfoliation of natural graphite is presented in Fig. 2.

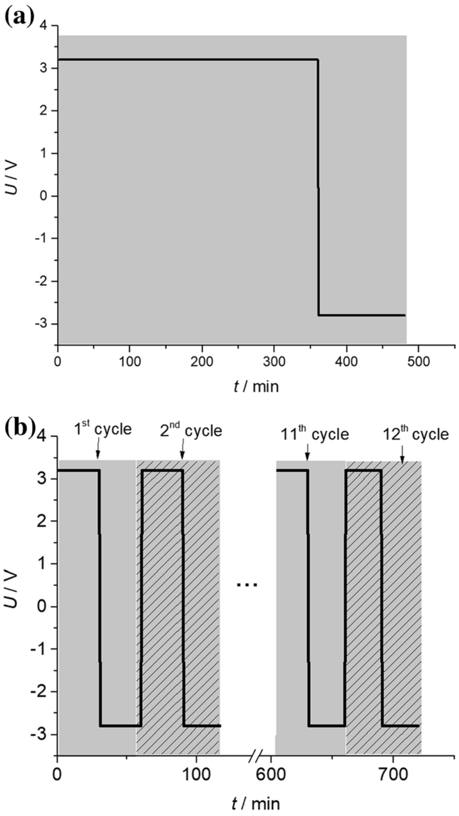

Figure 1 Polarization of working electrode according to **a** Procedure 1 and **b** Procedure 2.

The relative concentration of graphitic structure within the surfactant solutions was determined by using UV/Vis spectroscopy with regard to chemically prepared graphene oxide equivalent. The absorption coefficient value (ε) was obtained to be 36.4 $\mathrm{dm^3\ g^{-1}\ cm^{-1}}$.

The mass of the graphitic structure obtained in SDS solution was calculated by using mass concentration and volume of used electrolyte, which was 5 ml. The energy consumption was calculated by integrating the responses recorded by the chronoamperometry method, according to Eq. (1):

$$\text{energy consumption} = \frac{U\left(\sum_{i=1}^{12}\int_{0}^{t=30\,\text{min}} I_{A,i}\mathrm{d}t + \sum_{i=1}^{12}\int_{0}^{t=30\,\text{min}} I_{K,i}\mathrm{d}t\right)}{m} \tag{1}$$

where U/V is applied voltage, I_{A}/A is anodic current, I_{K}/A is cathodic current, t/s is time during which polarization is applied, m is mass of the product obtained in SDS solution.

Electrochemical characterization of GR electrode in three-electrode system was carried out by using GR as working electrode, Pt foil as counter electrode and saturated calomel electrode (SCE) as reference electrode.

Characterization methods

SEM measurements

The SEM morphology analysis of all samples was performed by VEGA 3 SEM TESCAN at an acceleration voltage of 10–20 kV, with a detector of secondary electrons.

AFM measurements

The AFM measurements were performed with Flex AFM (Nanosurf) in tapping mode. The set point was 60%, and the used AFM tips were AppNano (ACLA-SS) super sharp type with tip radius less than 5 nm, a nominal force constant of 58 N/m and a nominal frequency of 190 kHz. All of the AFM data analysis was performed in the WSxM software [43].

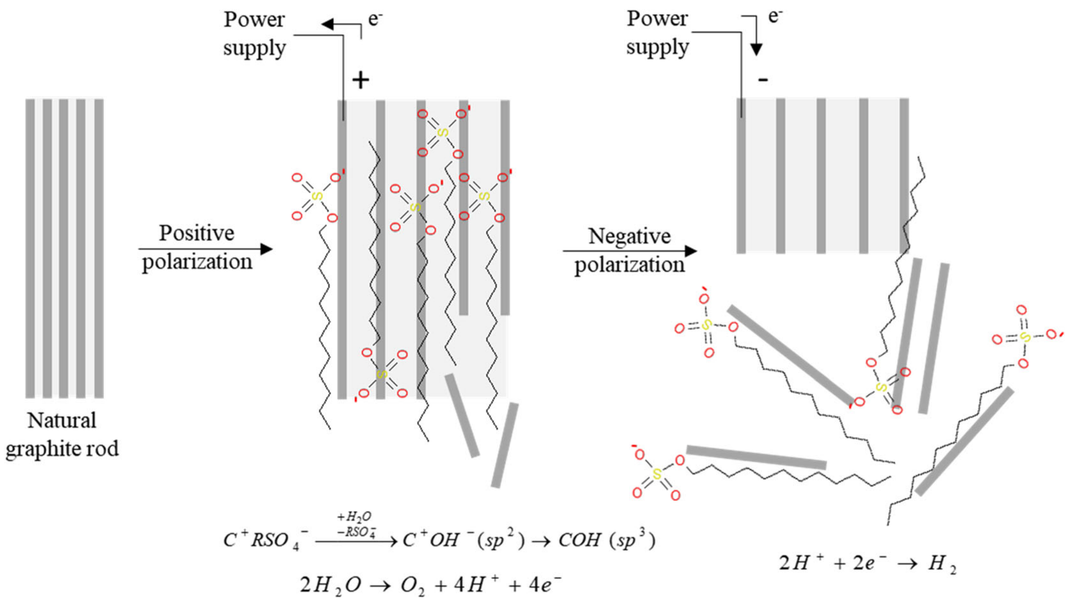

Figure 2 Schematic illustration of electrochemical exfoliation mechanism when SDS is used as electrolyte. The mechanism includes positive polarization of graphite electrode followed by negative polarization; the processes such as anion intercalation, graphite oxidation, oxygen evolution and hydrogen evolution result in electrode expansion and graphene sheets exfoliation.

Raman spectroscopy

Raman spectra were acquired on the optical setup built around 532 nm single-mode laser (Coherent Sapphire SF) and Andor Shamrock 303i spectrometer with Idus420 camera. Laser power was kept below 500 µW to avoid heating effects.

Dynamic light scattering

Measurement of particle size distribution was performed by dynamic light scattering (DLS) on a ZetaPlus instrument (Brookhaven, NY, USA). Particle size distribution range for this instrument falls between 40 and 2.500 mm.

UV/Vis measurements

UV/Vis absorption spectra of solutions obtained in the presence of SDS were collected with an Ocean Optics 200 UV/Vis spectrophotometer (Model D 1000 CE, Analytical Instrument Systems Inc.) by using 1 cm quartz cuvettes.

FTIR spectroscopy

FTIR spectroscopy was applied to identify the characteristic peaks of oxygen-containing groups within the graphene structure. FTIR spectra were recorded using a Perkin Elmer Instruments, Spectrum One. The sample was isolated by using nitrocellulose filter paper (Pall Corporation).

Results and discussion

In order to obtain graphene or graphene oxide by the electrochemical exfoliation process, it is crucial to select an appropriate electrolyte, a graphite electrode, as well as to apply appropriate potential value. In our experiments, natural graphite flakes were used as precursor, and aqueous surfactant solution as supporting electrolyte. The exfoliation process was carried out by consecutive positive and negative polarization of working graphite electrode according to Procedure 1 or Procedure 2. During this process, the colour of the solution became brown, which may indicate the presence of graphene oxide (GO) and a successful exfoliation of the graphite (Fig. 3) [17, 27]. Positive polarization was carried in the voltage range from 2.5 to 3.2 V. By applying 5 V positive polarization, only the black dispersion containing large size particles was obtained, indicating that the working electrode was crumbled without the exfoliation process. On the other hand, by applying voltage value lower than 2.5 V, the process became too slow. Therefore, it was concluded that optimal voltage for

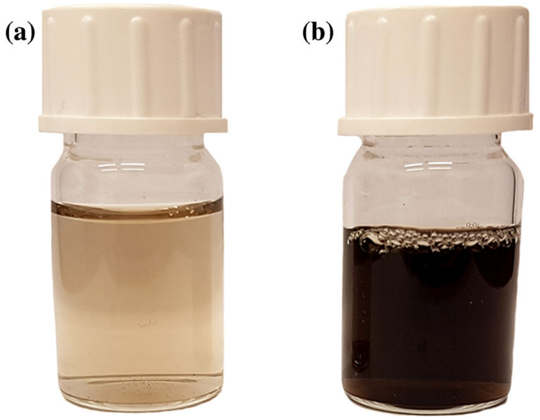

Figure 3 Solutions obtained after exfoliation of GR electrode in SDBS solution by using **a** Procedure 1 and **b** Procedure 2.

positive polarization during exfoliation of NGF, in the presence of surfactant, ranges from 2.5 to 3.2 V. Negative polarization of the working graphite electrode each time was carried out at 2.8 V, which was selected based on the previous research [2].

The electrochemical exfoliation is a result of different processes taking place at the polarized graphite electrode [19]. The positive polarization of graphite in the first step included oxidation of the edge plane surface of graphite through the attack by hydroxyl and oxygen radicals. These radicals are generated from the oxidation of water molecules at the anode [22, 44]. Indeed, brown colour obtained in this work indicates graphite oxidation process (Fig. 3). The oxidation process increased the distance between graphitic layers and assisted the intercalation of anionic surfactants (Fig. 2), as well as water intercalation and oxygen evolution [9, 19, 23, 24, 45–47]. Negative charge of sulphate or sulphonate groups drives surfactant intercalation during the anodic process. This conclusion is in accordance with the previous investigations, which have shown that different amphiphilic molecules with sulphate or sulphonate groups can be intercalated within a graphite structure [22, 48]. Gas accumulation during the oxygen evolution increased the pressure between the layers, which resulted in graphite exfoliation. Additionally, the exfoliation was facilitated by interactions between graphite and hydrophobic tail of the surfactant. Finally, the obtained product was easily dispersed in a solution by the help of a hydrophilic group.

In this work, it was shown that a more intensive exfoliation is obtained when, in addition to anodic polarization, cathodic polarization of the graphite at 2.8 V is carried out [47]. The process that takes place during cathodic polarization is hydrogen evolution [2] as illustrated in Fig. 2. Therefore, two different approaches were tested, Procedure 1 and Procedure 2, both including consecutive anodic and cathodic polarization. However, Procedure 2 included a multistep change of polarity, while Procedure 1 incorporated a single anodic and single cathodic polarization. By a simple process of monitoring the colour change of the solution, it was evident that the exfoliation was more efficient in the case of Procedure 2 (Fig. 3). This can be explained by the fact that a long-time anodic polarization accumulates an oxidized product at electrode surface due to which cell overvoltage increases and exfoliation efficiency decreases. By applying cathodic potentials, oxidation products will be removed through either hydrogen evolution or graphite oxide reduction [28, 47]. It is also expected that the oxidation products will be removed by oxygen evolution. However, due to the continuous accumulation of oxidation products, in anodic process, additional cathodic treatment will certainly increase overall efficiency. Procedure 2 included a removal of oxidized products more frequently, whereas in the case of Procedure 1, the oxidized products were removed only at the end of anodic polarization. For this reason, the overall efficiency was higher in the case of Procedure 2, and therefore, this method seems to be more suitable for the purpose of graphene production. Positive influence of the intercalation/deintercalation process, during the graphite exfoliation in 0.1 mol dm^{-3} (NH4)$_2$SO$_4$ solution, was also noted by Zhan et al. [21]. The intercalation/deintercalation improved both the quality and the yield of the product. In our work, an additional effect of hydrophobic tail might also have occurred during deintercalation process. This effect is tail withdrawing of graphitic structure from the bulk of material into the solution, and this could increase overall exfoliation efficiency.

The cyclic voltammogram in Fig. 4a illustrates the response obtained for the two-electrode system containing GR and platinum electrodes. The cyclic voltammogram was monitored by anodic polarization of GR from 0 V to 3.2 V and its cathodic polarization from 0 V to − 2.8 V at a scan rate of 20 mV s^{-1}. This voltage range relates to the voltage values of the graphite exfoliation process. A continuous current increase is obtained between 0.5 V and

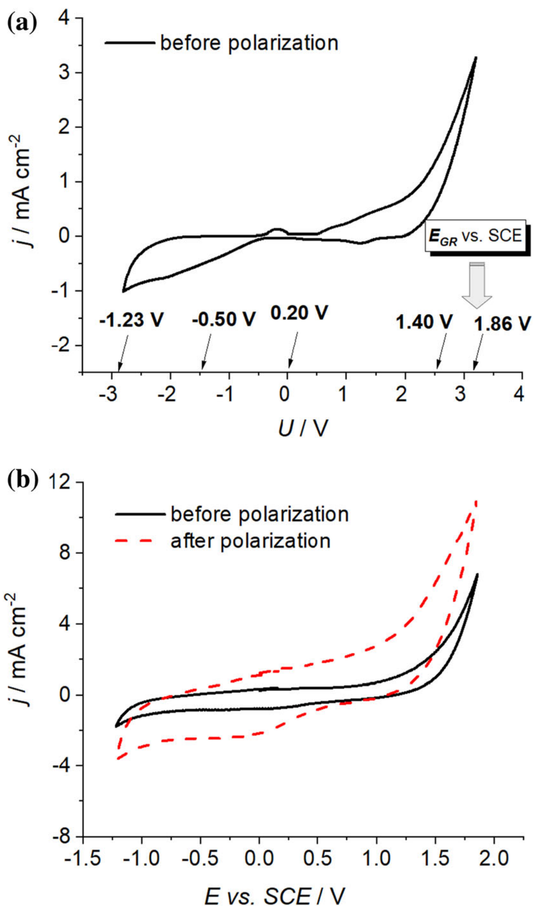

Figure 4 Cyclic voltammograms recorded before and after anodic polarization* of GR in 0.1 mol dm^{-3} SDBS at scan rate 20 mV s^{-1} for **a** two-electrode system containing GR and Pt electrode and **b** three-electrode system; *anodic polarization was carried out in two-electrode system at 3.2 V during 30 min.

2 V, while a significant current increase is registered at a voltage value higher than 2 V. The cathodic polarization indicates a continuous current increase from – 0.5 to – 2.8 V. The anodic current increase from 0 V to 1.5 V corresponds to double-layer charging and redox reactions of oxygen functional groups, while a current increase above 2 V corresponds to oxygen evolution and graphite oxidation reactions. The cathodic current increase at negative voltage values indicates that processes related to double-layer charging and reduction of oxidized form of graphite take place. The beginning of a sharp current increase at – 2.8 V indicates that the hydrogen evolution process progresses slowly. [49, 50]. From the obtained results, it can be concluded that the features of the cyclic voltammogram support the proposed mechanism for graphite exfoliation (Fig. 2).

The similar response was obtained for the three-electrode system investigation, which additionally confirms previous conclusions about the reactions that take place. The potential window for the three-electrode system investigation was determined by monitoring GR potential (E_{GR}) vs. saturated calomel electrode in a two-electrode system measurement. By comparing the cyclic voltammogram registered before and after the GR positive polarization (Fig. 4b), it is evident that current values increase after the anodic polarization, which is most probably a consequence of the graphite electrode expansion [29].

Although it is frequently reported for conventional electrolytes that a graphite sample macroscopically swells [19], in this work, the inspection of electrode during and after the exfoliation process did not show a significant expansion of the graphite (Fig. 5).

Additionally, electrode surface was analysed by SEM, where it can be noticed that the graphite structure after the exfoliation was changed, which can be related to swelling of very thin surface layer (Fig. 6), and for this reason, it is not possible to notice it by visual observation. This conclusion is supported by the previous observations that SDS and SDBS show limited mobility within the graphite because of its structure that contains a relatively bulky hydrophobic tail with a single anion [22]. Such a disadvantage was successfully overcome in the previous investigation by increasing the number of ionic groups of the surfactant.

The exfoliation of the graphite could be followed by monitoring current transients, which was not

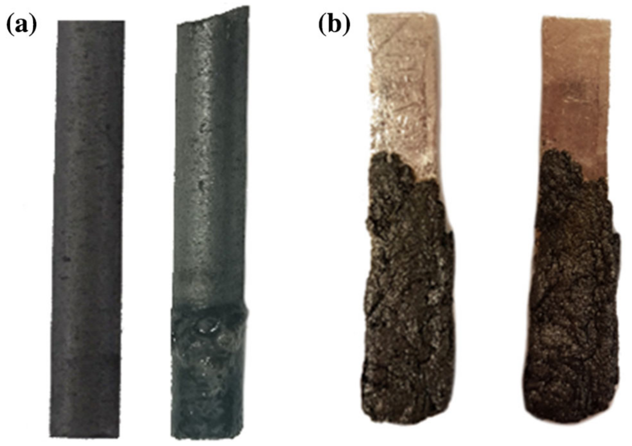

Figure 5 Different working electrodes **a** GR and **b** GE before and after exfoliation.

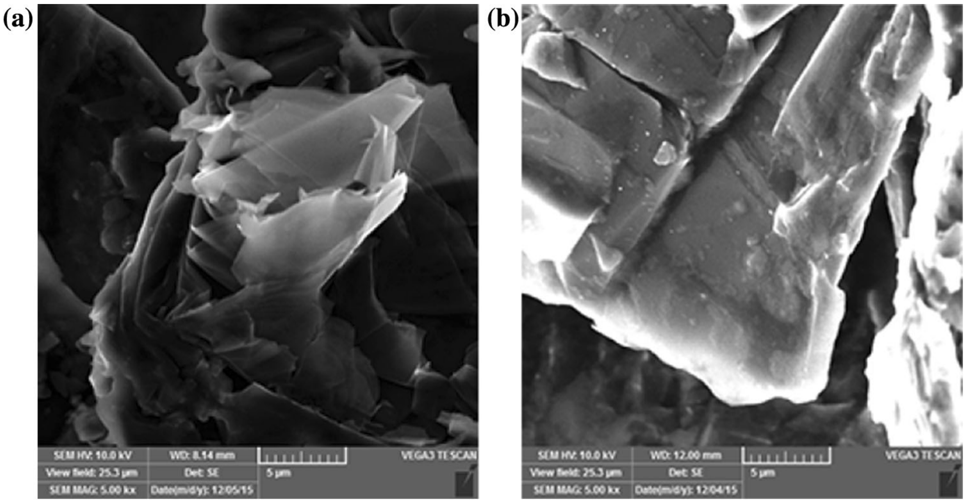

Figure 6 SEM images of GE electrode **a** before and **b** after exfoliation.

reported in the previous works that studied the exfoliation process. Figure 7 illustrates current transients obtained for GR electrode at positive potentials. At the beginning, the current rapidly increases due to the double-layer charging which is followed by a decrease in current. The current registered during the time is a consequence of the processes that were described before and that take place on the surface and within the bulk of the material. From the obtained transient, it is evident that the current value depends on the type of surfactant and applied voltage value. Anodic currents registered during time period of 360 min (Procedure 1) proved to be much higher in SDBS, compared to SDS solution that showed a more intensive exfoliation in the presence of SDBS (Fig. 7).

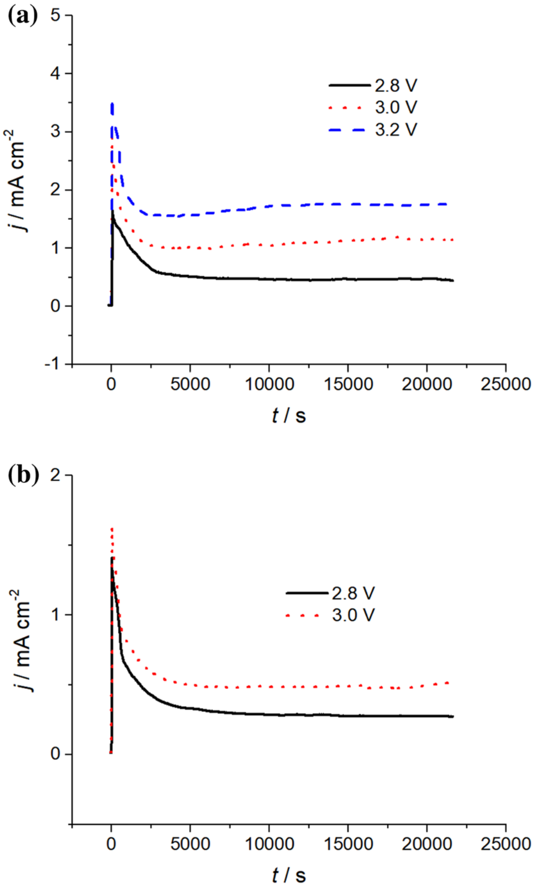

Figure 7 Chronoamperometry responses obtained by using GR electrode and Procedure 1 in **a** SDBS and **b** SDS electrolyte at different applied voltage values.

From the results obtained by consecutive anodic (2.8–3.2 V) and cathodic polarization (2.8 V) (Procedure 2), it follows that anodic current registered during the first cycle for SDBS is lower than anodic current registered during the 12th cycle, indicating that the electrode surface was changed with increasing number of cycles (Fig. 8a). The difference between electrode surface at the beginning and after exfoliation process is also supported by Figs. 5 and 6. In the case of SDS, different current declines in the first and 12th cycles were registered (Fig. 9a), which was not observed for SDBS. The significant current decrease at prolonged times for SDS (12th cycle) as well as lower currents in the case of SDS could be a consequence of a lower degree of interaction between SDS and graphite in comparison with SDBS and graphite. The lower degree of interaction resulted in the accumulation of oxidized products on the electrode surface, which increased the electrode resistance and decreased the current value. Therefore, different electrochemical behaviours registered for SDBS and SDS point out that surfactant tail structure

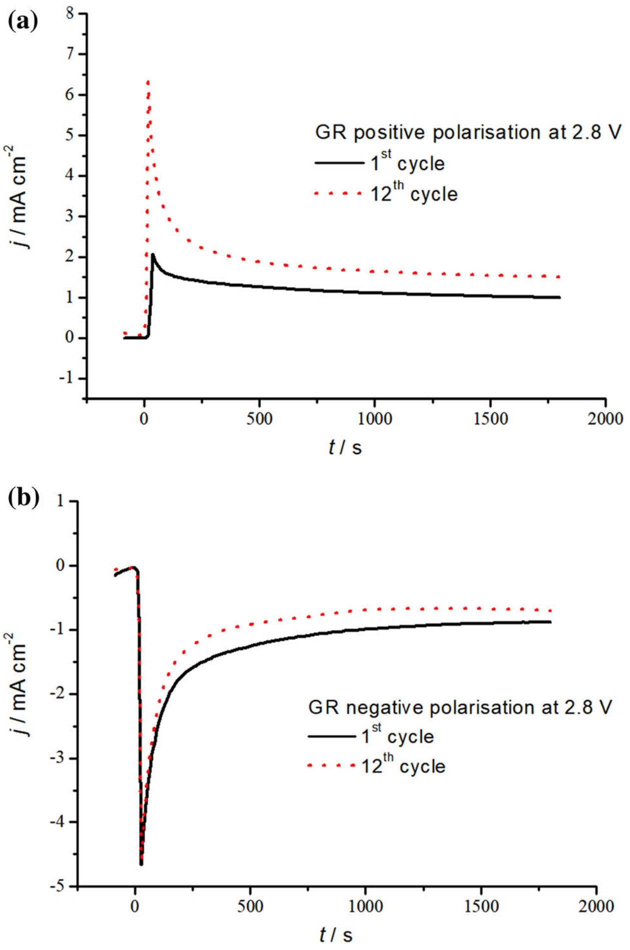

Figure 8 Chronoamperometry responses of GR electrode obtained by using Procedure 2 and 2.8 V during first and 12th cycle of GR electrode polarization in SDBS electrolyte at **a** positive and **b** negative polarization.

significantly influences the overall exfoliation process. Cathodic currents do not indicate significant differences between the first and 12th cycles (Figs. 8b and 9b).

The colour intensity of the solution obtained after the exfoliation (Fig. 10) also supports higher exfoliation efficiency in the presence of SDBS, compared to SDS. SDBS contains an aromatic ring, and therefore, besides nonpolar interactions there are π–π interactions between the graphite and SDBS surfactant. These π–π interactions facilitate the intercalation process and withdrawing of graphitic structure from the bulk of the material. This observation is in accordance with the previous investigation where it was proven that the surfactant chain structure and branching of the tail will affect interactions of the surfactant and graphite, as well as electrochemical exfoliation efficiency [48].

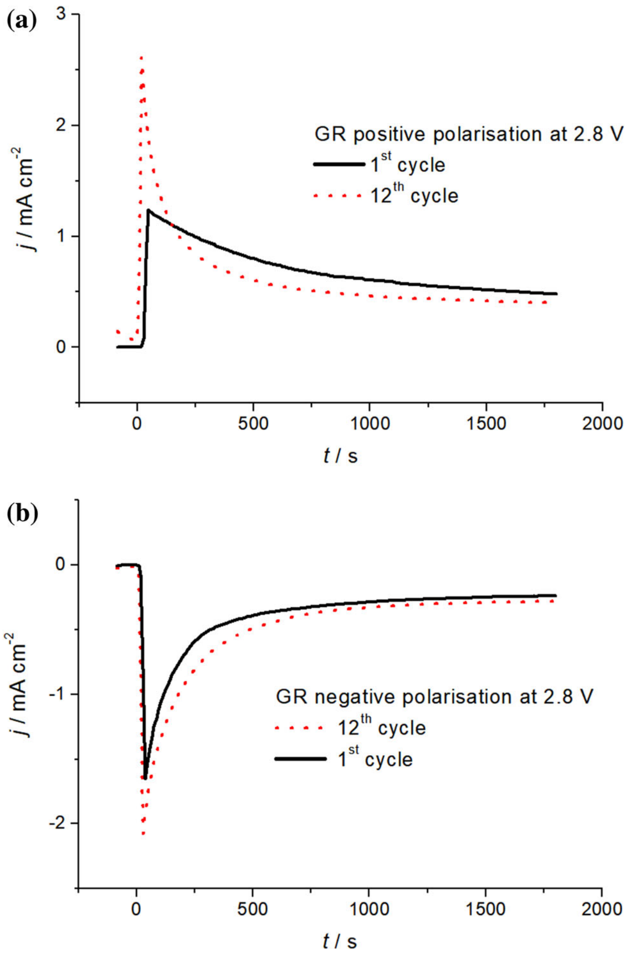

Figure 9 Chronoamperometry response of GR electrode obtained by using Procedure 2 and 2.8 V during first and 12th cycle in SDS electrolyte at **a** positive and **b** negative polarization.

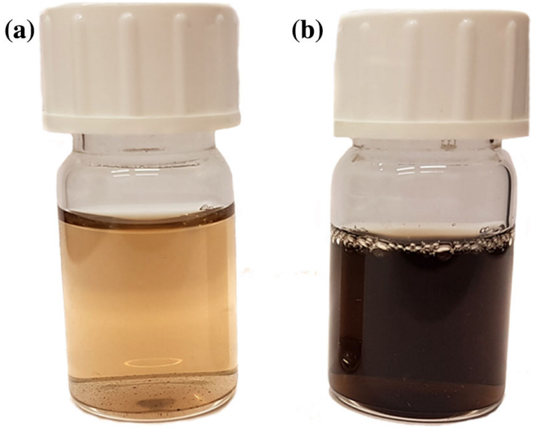

Figure 10 Solutions obtained after exfoliation of GR electrode by Procedure 2 at 2.8 V in **a** SDS and **b** SDBS electrolyte.

It is also apparent that the exfoliation is more efficient at high voltage values, which can be explained by the fact that the basic processes important for the exfoliation will be more intensive if the voltage increases (Fig. 11). However, a significant gas evolution could destroy the electrode without the exfoliation process.

In this article, two different types of electrode containing NGF were tested, a commercial electrode (GR) (Fig. 5a) and the electrode prepared in laboratory (GE) from natural graphite with addition of PVDF binder (Fig. 5b). Two different electrodes were used in order to investigate the influence of GR production process on exfoliation efficiency. From Fig. 12, it is evident that the exfoliation efficiency depends on the type of electrode and better efficiency was obtained for GR. It can be explained by different conductivity of each electrode, GR was more compact and therefore it has lower contact resistance between graphite particles and better conductivity.

The obtained graphene solution can be characterized by using UV/Vis spectroscopy [2, 51]. Since the response of the aromatic ring in SDBS overlaps with graphitic structure, it is hard to accurately determine the presence of graphene structure in solution containing SDBS. Thus, only the solution prepared in the presence of SDS was analysed using UV/Vis spectroscopy (Fig. 13). The characteristic absorptions maximum occurred for all samples between 200–250 nm. It corresponds to π–π^* transition in delocalized graphitic structure, and it is evident that in the case of electrochemically obtained graphene, absorption is moved to shorter wavelength compared to the one registered for chemically obtained graphene oxide [51–53] (Fig. 13a). Shorter wavelength means higher energy barrier for π–π^* transition and smaller conductive domains in the sample obtained by the electrochemical exfoliation. From Fig. 13b, it can also be concluded that the absorption maximum moves to higher wavelengths with voltage decrease. This could indicate a different oxidation degree of products obtained at different potential, which is in accordance with the previous reports [2, 54]. High-wavelength absorption maximum at 300 nm corresponds to n–π transition characteristic for oxygen functionalities, and it proves the presence of oxygen within the graphene structure. This maximum was obtained for chemically prepared GO, while for electrochemically prepared sample, it was not evident; only the absorption in wide wavelength range was obtained. Strong absorption in wide range was reported previously for structures containing sp^2 bond [53, 55].

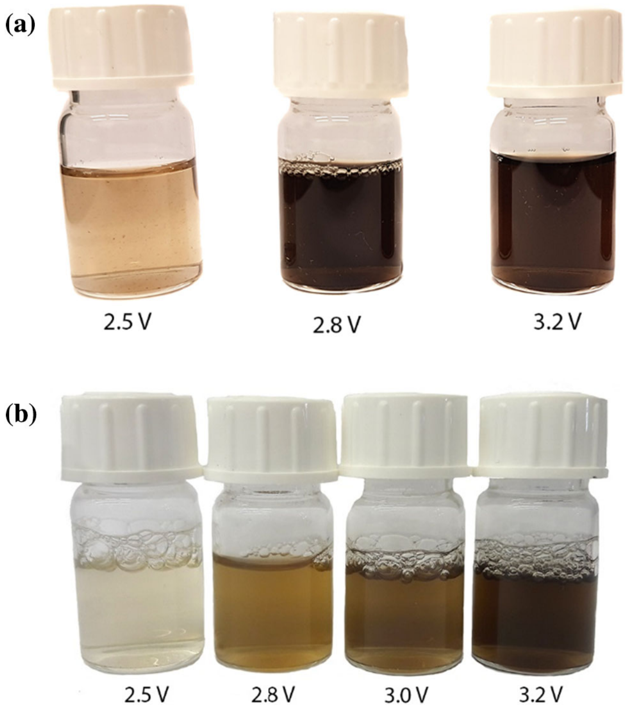

Figure 11 Solutions obtained after exfoliation of GR electrode by Procedure 2 at potentials that range from 2.5 to 3.2 V in **a** SDBS and **b** SDS electrolyte.

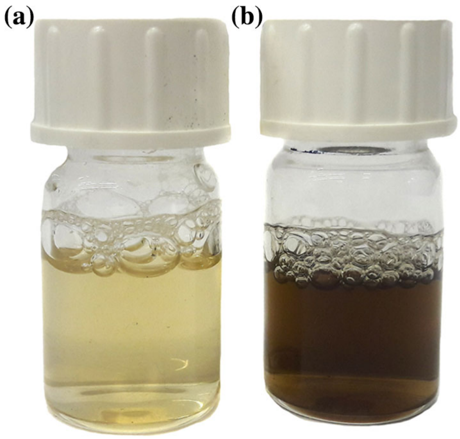

Figure 12 Solutions obtained after exfoliation of **a** GE and **b** GR electrode by Procedure 2 in SDS electrolyte at 3.2 V.

UV/Vis spectroscopy could be useful to determine a concentration of graphitic structure present within the solution. For this purpose, a calibration curve was obtained by using a chemically prepared graphene oxide solution of a known concentration. The results

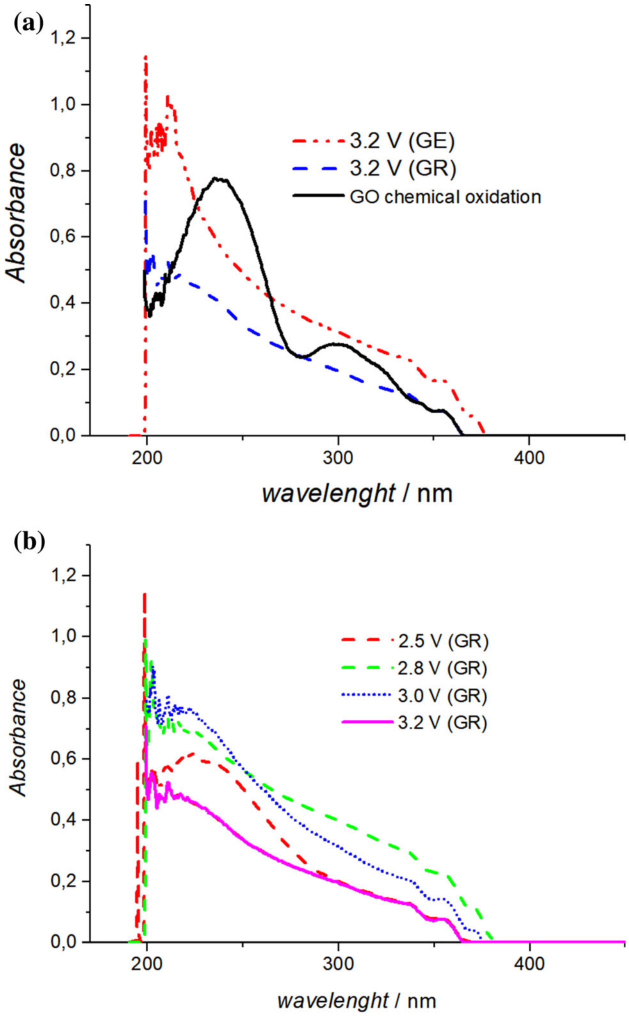

Figure 13 UV/Vis spectra of the SDS solution containing **a** sample obtained by electrochemical exfoliation of GR and GE at 3.2 V and GO obtained by chemical exfoliation; **b** sample obtained by electrochemical exfoliation of GR at different voltage values.

are presented in Table 1., and it is in accordance with the previous conclusions considering the influence of the applied voltage and type of electrode. The concentration of product increased with voltage increase. Also, a higher exfoliation degree was obtained for GR compared to GE, which is in accordance with Fig. 12. In previous publications, it was reported that after electrochemical exfoliation of graphite, in a similar electrolyte solution, flakes concentrations from 0.01 to 6.25 mg ml^{-1} were obtained [2] that is consistent with our data. It is important to point out that concentration in this manuscript was determined by UV/Vis spectroscopy, while in other paper, concentration was determined from the mass of isolated graphene flakes. Also, there are other reports where solution containing graphene was prepared by electrochemical exfoliation and subsequent treatment in dimethylformamide where solution containing flakes in concentration from 0.084 to 2.5 mg ml^{-1} was obtained [56].

The sample isolated from the solution (GR electrode, 2.8 V) was analysed by Raman spectroscopy (Fig. 14). The band at 1603 cm^{-1} (G band) is related to the E2g phonons of C *sp*^{2} atoms, and band at 1365 cm^{-1} (D band) is related to breathing mode of k-point phonons of A1g symmetry, corresponding to the defects and disorder in the hexagonal graphitic layers [13]. These results indicate that graphene obtained by exfoliation contains structural defects. In order to prove whether graphene contains oxygen functional groups in addition to defects, the product isolated at cellulose nitrate filter paper was characterized by FTIR spectroscopy. The obtained spectra at Fig. 15 correspond to graphitic structure and nitrocellulose filter paper, and therefore filter paper was also analysed in order to estimate the part of the spectrum related to the sample. The filter paper with sample shows some additional absorption bands at 1724, 1545, 1175 and 1031 cm^{-1}. Absorption band at 1724 cm^{-1} corresponds to carbonyl stretching vibrations, the band at 1175 cm^{-1} to C–OH or C–O–C stretching vibrations, the band at 1545 cm^{-1} to in plane (C=C) stretching and 1031 cm^{-1} to C–O stretching vibrations. This result indicates that sample isolated at filter paper contains oxygen

Table 1 Concentrations of product obtained in supporting electrolyte solution after exfoliation of GR and GE at different voltage values

Electrode	Voltage/V	Concentration/mg ml^{-1}	Concentration*/mg ml^{-1} cm^{-2}
GR	2.5	0.089	0.035
GR	2.8	0.186	0.073
GR	3.0	0.275	0.108
GR	3.2	0.460	0.180
GE	3.2	0.134	0.055

*The concentration normalized per electrode surface area

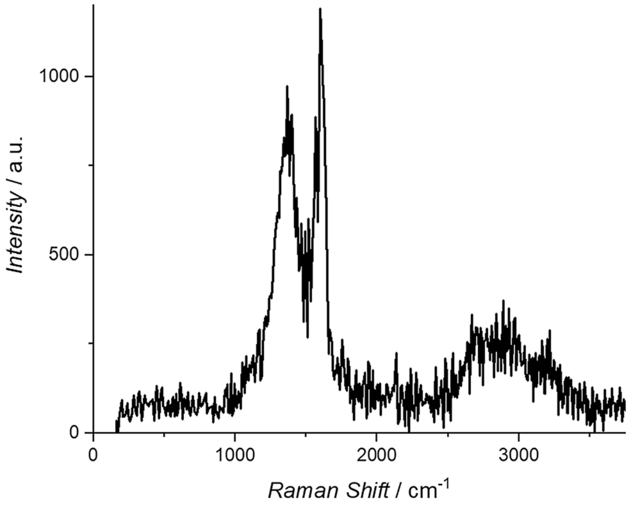

Figure 14 Raman spectra of the carbon structure obtained by electrochemical exfoliation of GR electrode at 2.8 V.

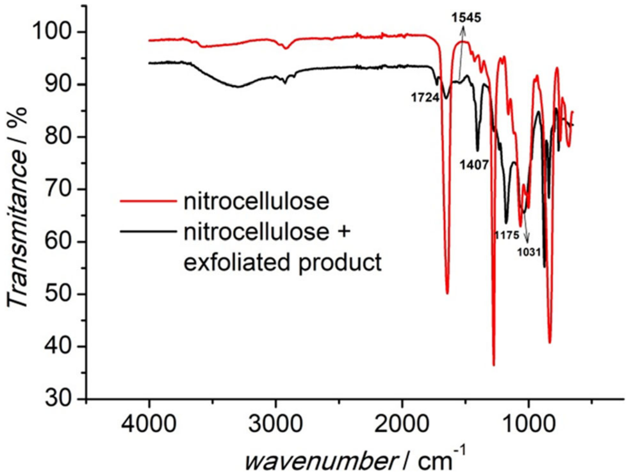

Figure 15 FTIR spectra of the carbon structure obtained by electrochemical exfoliation of GR electrode at 2.8 V.

functionalities, and therefore, it was concluded that obtained product is GO [57].

The product obtained from GR electrode at 2.8 and 3.2 V and from GE electrode at 3.2 V in SDS solution was analysed by DLS (Fig. 16). The solution obtained at 3.2 V from GR mostly contained small sheets (9–11 nm) with a small portion of large size sheets (25–50 nm) and only the traces of sheets from 500 to 1500 nm (Fig. 16a). A solution obtained at the same voltage value from GE electrode was also tested, and Fig. 16b unmistakeably shows that in the case of GE solution a sheet size was distributed between 25 and 60 nm. The difference can be explained by different preparation method for two different electrodes. Although larger sheets were registered for the case of GE, the difference was not significant. The obtained sheet size corresponds to the dimensions of graphene quantum dots (GQD) [58]. This is in accordance with previous publications where it was reported that electrochemical exfoliation can be effective method for GQDs preparation [59].

In the case of GR electrode and 2.8 V, the sheets size was from 200 to 600 nm and for small amount of sheets 1000 nm. For the last sample, a successful analysis was conducted by AFM method. Figure 17 depicts the product isolated from SDS solution. It is apparent that elongated formations up to 500 nm wide and around 2 µm in length are present within the solution. The thickness of the obtained sheet is 3 nm, which implies that the sample is not completely exfoliated and few sheets are stacked together, which is in accordance with the results obtained in H_2SO_4 or Na_2SO_4 [9, 16, 19, 60]. It is well known that graphene monolayer has thickness of 0.34 nm. The thickness that was mostly reported for the oxidized form of graphene is around 1 nm due to the presence of oxygen, as well as due to the hydration. Stankovich at all. [61] reported that for "dry sheet" GO thickness of 0.63 nm was obtained, while for hydrated sheet the thickness of 1.2 nm was obtained. Z. Xia et al. [60] by electrochemical oxidation of graphite obtained few-layer "sandwich-like" structure consisting of bilayer graphene stacking that is partially oxidized. The thickness of the one bilayer graphene stacking was 8 ± 2 Å, and according to it, our sample should contain three bilayer structures. On the other hand, S. Yang at all. [47] obtained 0.72 nm for one layer and according to it our sample should contain ~ 4 layers. However, it is hard to compare the results and to estimate the number of layers since the layer thickness depends on degree of oxidation. AFM analysis of the samples containing mostly small dimensions products (< 100 nm) was not successful.

From the DLS and AFM results, it follows that in this work the sheets with lateral size smaller than the one reported for chemically [55, 61] and electrochemically [56] prepared graphene or GO were obtained. This observation is also supported by UV/Vis spectroscopy where characteristic absorptions maximum occurred at shorter wavelength indicating smaller conducting domains.

The experiments carried out in this work have shown that it is possible to prepare a GO/surfactant solution by one-step electrochemical method. This is

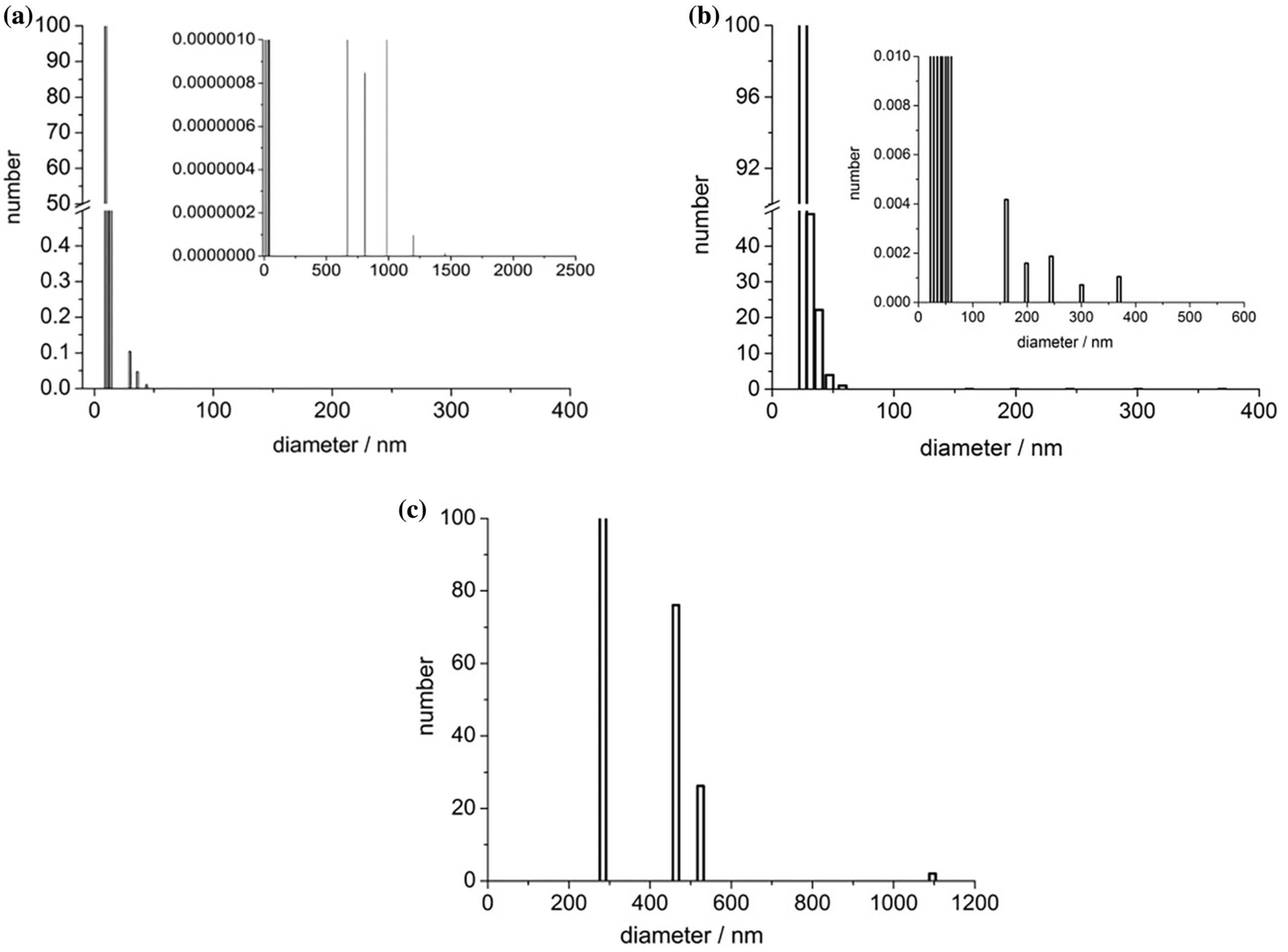

Figure 16 Dynamic light scattering size distribution for the solutions obtained by using **a** GR electrode at 3.2 V, **b** GE electrode at 3.2 V and **c** GR electrode at 2.8 V.

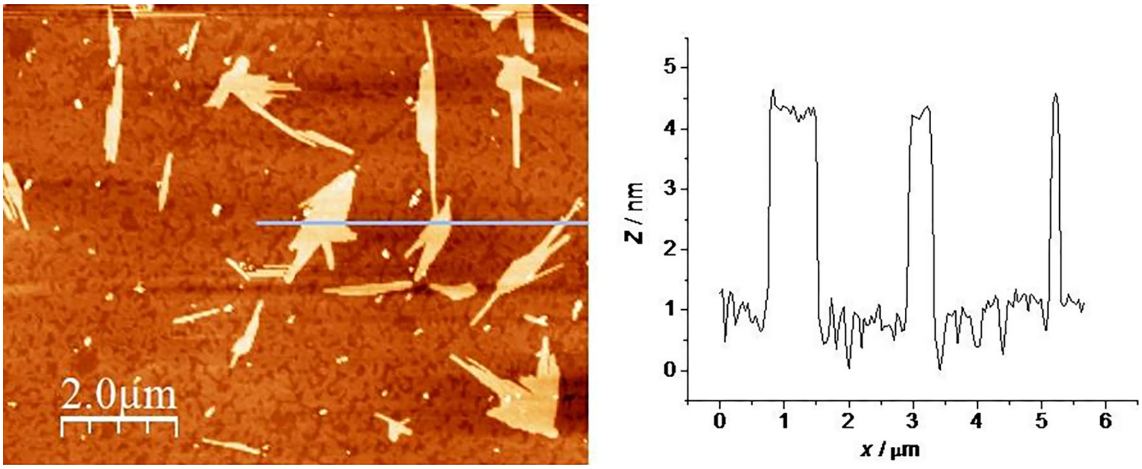

Figure 17 AFM topography image of graphitic structure obtained by electrochemical exfoliation of GR electrode at 2.8 V. Figures on the right present a line scan taken across the blue line marked on the corresponding topography image.

a simple, fast and cheap way to prepare a solution containing the graphene structure. The disadvantage of this method is the fact that surfactant is strongly absorbed on the carbon structure and it is hard to be entirely removed. However, this solution could be directly used as supporting electrolyte for conductive polymer/GO composite synthesis [62]. Additionally, it can be used as suitable electrolyte for graphene / metal catalysts formation [22, 63] or it can be used to remove a pollutant containing an aromatic structure from aqueous solutions [48].

It is important to emphasize that the exfoliation process was conducted successfully by applying the low voltage values (2.5–3.2 V), and therefore, it is considered to be a low-energy process. In the previous reports, voltage values amounted to 10 V or even above 10 V, which significantly increased the energy consumption. Finally, graphene production at high voltage values has disadvantages as it demands both additional ultrasound treatment and appropriate equipment. Herein, for the first time we have calculated energy consumption for the electrochemical exfoliation of the graphite. In order to express consumed energy per mass of the obtained product, only SDS solutions of the known concentrations of graphene structure were considered. The calculated values indicate that energy consumption ranges from 0.084 to 0.038 kWh g^{-1}, depending on the applied voltage and type of electrode. For GR electrode at 3.2 V, the obtained value was 0.038 kWh g^{-1}, whereas for GR electrode at 2.5 V, the value was 0.067 kWh g^{-1}. By comparing energy consumption for different electrodes at 3.2 V, it was evident that the value has changed from 0.038 kWh g^{-1} for GR to 0.084 kWh g^{-1} for GE, most likely due to the increased contact resistance between graphite particles in the case of GE. If we take into account that nonhousehold electricity prices in the EU, during the second half of 2019, ranged from 0.18 to 0.07 EUR per kWh [64] and that the reduced graphene oxide current price is 83 EUR per gram [65], it can be concluded that electrochemical exfoliation at low voltage is a quite cost-effective process.

Conclusions

The experiments carried out in this work showed that it is possible to exfoliate natural graphite flakes in surfactant solutions by applying voltage values from 2.5 to 3.2 V. The solution obtained after exfoliation at 3.2 V mostly contained small sheets (from 9 to 60 nm), with a small portion of large-dimension sheets, while the solution obtained at 2.8 V contained sheets from 200 to 600 nm. AFM measurements proved that the obtained product consisted of few sheets stacked together. Raman indicated the presence of structural defects and UV/Vis spectroscopy indicated that small conductive domain is present within the sample, whereas oxygen functionalities were proved by FTIR spectroscopy.

The exfoliation was more effective in the presence of SDBS, compared to SDS, most probably due to the π–π interactions between the graphite and SDBS surfactant. The efficiency of this process was enhanced by a multistep change of polarity. The applied voltage value and the type of the electrode were additional parameters which influenced the process. The energy consumption indicated that this is a low-energy and cost-effective process that provided surfactant/GO solution.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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