Materials Science-Poland, 33(2), 2015, pp. 292-300
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.1515/msp-2015-0042

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Synthesis and modification of reduced graphene oxide aerogels for biofuel cell applications

IZABELA KONDRATOWICZ[1]*, KAMILA ŻELECHOWSKA[1], DOMINIKA MAJDECKA[2], RENATA BILEWICZ[2]

[1]Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland

[2]Division of Inorganic and Analytical Chemistry, Faculty of Chemistry, University of Warsaw, Pasteura St. 1, 02-093 Warsaw, Poland

We have carried out the preparation of reduced graphene oxide aerogels using eco-friendly method that is based on the Hummers method of graphite oxidation without the use of $NaNO_3$ that produces toxic gases. To obtain a porous 3D structure of reduced graphene oxide, we performed the hydrothermal reduction at elevated temperature. We also prepared the rGO aerogel/CNT composite using multiwalled carbon nanotubes as linkers. The rGO aerogels are promising materials as they possess good electrical conductivity (up to 100 S/m) and high surface area and porous structure ($\sim$500 m^2/g). The main goal was to obtain the material for electrodes in enzymatic biofuel cells. Thus, the proper modification was performed using free radical functionalization. It was shown that in order to synthesize rGO aerogels modified with anthracene, the proper order of reactions needs to be provided. The morphology of anthracene modified electrodes was analyzed using scanning electron microscopy, which confirmed their porous structure with non-uniform pore size distribution that ranged between few nanometers to microns. Data obtained by Raman spectroscopy confirmed the successful oxidation and reduction of analyzed materials. UV-Vis spectra revealed the presence of anthracene moieties in examined materials. We also recorded preliminary cyclic voltammograms that confirm an electric conductivity of the obtained structures.

Keywords: *graphene oxide; reduced graphene oxide; graphene aerogel; functionalization of graphene; biofuel cell*

1. Introduction

Carbonaceous materials have been used widely so far as the electrode materials. The major advantages are their good electrical conductivity, high specific surface area, porous structure and good biocompatibility. Up to now graphite, glassy carbons, carbon black or activated carbons have been the most common [1, 2]. Their applications are of particular interest in the electronic devices that store and convert energy, such as supercapacitors, batteries, fuel and solar cells. After the discovery of carbon nanotubes and graphene, the scientists focused on utilizing these new materials. Graphene aerogels are a new class of materials that may be produced using different methods. These three-dimensional porous structures are formed by the self-assembly of graphene sheets [3]. It is worth mentioning that in most methods chemicals are used to firstly oxidize graphite to graphene oxide (GO) and then reduce GO thermally, chemically or electrochemically under specific conditions to obtain 3D porous structures. Reduction of graphene oxide leads to the so called reduced graphene oxide (rGO) that is not a pure graphene as it still possesses some residual oxygen-containing functional groups. However, in the graphene literature, hydro- or aerogels nomenclature is used, even though these structures are not composed of pure graphene, but reduced graphene oxide. In this paper graphene aero- or hydrogel term is used when it is cited after other authors, but in case of our experiments rGO aero- or hydrogel phrase is used to describe obtained materials.

Several approaches leading to 3D graphene-type structures can be found in the literature.

*E-mail: ikondratowicz@mif.pg.gda.pl

One of the methods is resorcinol-formaldehyde (RF) sol-gel synthesis [4, 5]. RF acts as a binder that helps to cross-link individual graphene oxide sheets with sodium carbonate as a catalyst. Firstly, authors prepared a suspension of graphene oxide using the Hummers method [6], where the graphite powder is oxidized with the use of $NaNO_3$, H_2SO_4 and $KMnO_4$. Then the mixture of resorcinol-formaldehyde (with a molar ratio 1:2) was added. The molar ratio of resorcinol to Na_2CO_3 was 200:1. The mixture was kept in vials at 85 °C and after gelation the GO-RF gel was thermally reduced at 1050 °C to obtain graphene aerogel (GA). It possessed high electrical conductivity (102 S/m) and surface area (584 m^2/g). Xu et al. [7] reported a method in which reduction of graphene oxide could be obtained under lower temperatures than it was described above. They carried out one-step hydrothermal process by heating the graphene oxide aqueous dispersion in a Teflon-line autoclave at 180 °C for 12 h. They managed to produce GA with high specific capacitance (175 F/g) that could be used as a supercapacitor electrode material. Another research conducted by Nguyen et al. [8] showed that it was possible to perform GA synthesis at 95 °C without the use of any binders. They took graphene oxide water dispersion and reduced it using L-ascorbic acid. The electrical conductivity of such structure was 0.04 S/m and its surface area was 394 m^2/g. The density was 0.042 g/cm^3.

Our aim was to produce porous graphene materials that can be used as electrodes in enzymatic biofuel cells. The working principle of such cells is similar to that of traditional fuel cells. Instead of metallic catalysts they use biocatalysts (enzymes), whereas as the fuel, glucose and oxygen are usually used. They are promising power sources for miniaturized, implantable electronic devices, such as cardiac pacemakers, drug dispensers or artificial organs which need power densities in the range of several mW/cm^2 to several W/cm^2 [9]. At the beginning, platinum electrodes were used, but because of their cost they were quickly replaced by carbonaceous materials. As mentioned before glassy carbon has been the most commonly used material. At the moment the electrodes modified with carbon nanotubes, which are also properly modified, seem to have the best performance reported so far [10]. The main goal in producing electrode materials for biofuel cells is to provide good electrical conductivity along with the relevant pore size distribution. At the same time the immobilization of enzymes on the electrode surface, that impacts their stability and orientation, is a very important issue to achieve the good electron exchange [1, 10, 11]. To increase the output of such devices, the loading of enzymes on the electrode surface should be as high as possible. Thus, the suitable pore size within the new electrode is required. Bayne et al. [12] reviewed the published data and estimated that the optimum pore size for the enzyme immobilization should be in the range of 10 to 80 nm for the enzyme diameter usually between 2 to 10 nm. Fig. 1 shows the relationship between pore diameter and protein loading. In the case of pore sizes below 10 nm and above 80 nm protein loading drops dramatically.

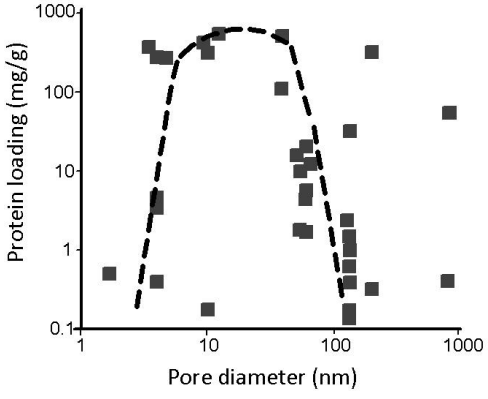

Fig. 1. Optimum pore size for protein loading. (Reproduced from [12] with permission of The Royal Society of Chemistry).

To provide high enzyme loading and long lifetime of biofuel cells the proper modification of the electrode surface can be helpful. The chemical modification seems to be a proper approach for the future development of biofuel cells. Blanford et al. [13] attached anthracene residues to the surface of pyrolytic graphite. It facilitated the electron transport between the active center of the enzyme and the electrode surface due to the high hydrophobic interactions. Anthraquinone residues

were used by Sosna et al. [14] for the immobilization of laccase to the glassy carbon electrode. The system was found to adsorb laccase easily and to provide a good electrical path between the enzyme and the electrode. In recent years, carbon nanotubes (CNTs) were shown to provide an attractive, versatile and simple route for the development of the bioelectrical devices, because of their significant mechanical strength, excellent electrical conductivity, large surface area and good chemical stability. As was shown earlier, chemical functionalization of carbon nanotubes may increase the stability and efficiency of the biofuel cell [15–17]. Due to the presence of hydrophobic pocket, laccase exhibits affinity to aromatic groups attached to the carbon nanotubes. It is directed onto the carbon nanotubes covered electrode in favorable orientation to achieve an efficient biocathode. The functionalized CNTs studied by Bilewicz group [18–20] cover phenyl, naphthyl, anthryl, biphenyl, terphenyl and other moieties attached chemically to CNTs by direct carbon to carbon bond or by amide bonds. Świetlikowska et al. [21] reduced graphene oxide sheets electrochemically and found that residual hydroxyl groups were able to physically adsorb laccase molecules. However, to the best of our knowledge there are no reports on the modification of rGO aerogels using aryl groups. Thus, the method of preparation and performance of such functionalized electrodes is studied in this work.

2. Experimental

2.1. Methods and materials

Natural graphite rock was used as a source of graphite. Potassium permanganate ($KMnO_4$), L-ascorbic acid, 98 % sulfuric acid (H_2SO_4), 85 % phosphoric acid (H_3PO_4), 30 % hydrogen peroxide (H_2O_2), 35 % hydrochloric acid (HCl), and ethanol were purchased from POCh (Gliwice, Poland). 2-aminoanthracene, isoamyl nitrite were purchased from Aldrich. They were used directly without further purification. During the experiments the magnetic stirrer Heidolph MR hei-standard with hot plate was used and the centrifugation of all samples was done using Chemland model P3032 centrifuge with the speed 15000 rpm for 10 min.

UV-Vis spectra were measured using Lambda 10, Perkin Elmer. Raman spectroscopy was done using Micro Raman Renishaw InVia with a 514 nm laser. Samples were put on a glass without any solvent. The morphology of reduced graphene oxide aerogels was observed with a scanning electron microscopy (ESEM Quanta Feg 250, FEI). Cyclic voltammetry measurements were conducted in three electrode arrangement with calomel electrode as the reference electrode, platinum foil as the counter electrode and aerogel as the working electrode.

2.2. Synthesis of graphene oxide

Graphene oxide (GO) was prepared using modified Hummers method that was described in [22]. First, a piece of graphite rock was crushed using a sandpaper and the obtained powder was grinded thoroughly in a mortar. Then, 0.2 g of graphite powder was mixed with 0.6 g of $KMnO_4$ which is a strong oxidant. Then the mixture of H_2SO_4/H_3PO_4 (12 ml:3 ml) was slowly added. This procedure allowed us to avoid the use of $NaNO_3$ that releases toxic gases, such as NO_2 and N_2O_4. Contrary to the authors of [22], we used an ice bath to keep the temperature below 20 °C and provide the safety of the experiment. The suspension was left for 24 h with the magnetic stirring. Then 3 % of hydrogen peroxide was added in order to stop the reaction. It resulted in a color change of the suspension to dark yellow and a production of graphite oxide (GrO). The suspension was centrifuged at 15000 rpm for 10 min and washed several times with deionized water, 3 % of HCl and with water once again. It was left to dry at room temperature to avoid the detachment of functional groups. To obtain graphene oxide, the suspension of GrO powder in water (0.1 mg/ml) was ultrasonicated for 4 h. The solids were separated by centrifugation and left to dry at room temperature.

2.3. Synthesis of modified graphene aerogels

In order to obtain modified reduced graphene oxide aerogels, two approaches were adopted. The scheme of used procedures is depicted in Fig. 2.

Starting from graphene oxide our aim was to first modify GO with anthracene radicals (left branch of the scheme) and then reduce it hydrothermally to the modified aerogel. In the second way (right branch) the hydrothermal reduction of graphene oxide in the first step was achieved and then modification of obtained 3D structure with anthracene was performed. The relevant nomenclature of each structure was denoted in brackets.

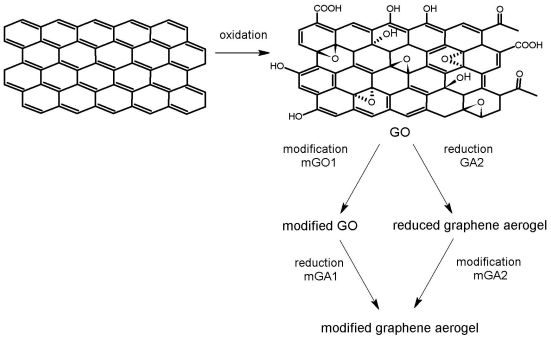

Fig. 2. Scheme of modified graphene aerogels preparation.

First approach

To functionalize GO with anthracene, we used the procedure that was described in [23, 24]. To 10 mg of graphene oxide, 10 mg of 2-aminoanthracene and 7 µl of isoamyle nitrite were added according to the stoichiometry of the reaction. The reaction was performed in a round-bottom flask in acetonitrile as a solvent. The mixture was magnetically stirred and heated at 75 °C for 2 h. After the reaction completion, the mixture was washed several times with different solvents (DMF, isopropanol, ethanol) until the supernatant was colorless. During the reaction aryl diazonium salts are produced which decompose under elevated temperatures, releasing nitrogen and aryl radicals. The radicals attach to the surface of graphene oxide (to sp^2 carbons present on a sheet) and release nitrogen molecules [23]. As an excess of aromatic amine is used, the bonded anthryl residues can react with other anthryl radicals or diazonium salts, leading to highly branched structures [24], which is schematically presented in Fig. 3.

In the next step reduction of modified graphene oxide (mGO1) was performed in order to form 3-dimensional porous structures. The hydrothermal method of reduction, analogous to that found in [25] was used. Briefly, 8 mg of modified GO in 4 ml of distilled water was sonicated for 3 h. Afterwards, 32 mg of ascorbic acid was added to the suspension and sonicated for additional 15 min. The used amount of the reducing agent was in excess accordingly to the stoichiometry of reaction proposed in [25, 26] and it was four times the amount of the carbonaceous material. The flask was then closed and the suspension was brought to 95 °C in an oil bath. After 5 h we observed an aggregate on the bottom of the flask and no hydrogel was formed. Therefore, we extended the time to 12 h but without any success. The sample was dubbed mGA1 but it should be pointed that using this method we did not obtain an aerogel.

Second approach

In the second approach, graphene oxide was reduced using the analogous hydrothermal method described in the previous section. Similarly, 8 mg of GO in 4 ml of distilled water was sonicated for 3 h, followed with addition of 32 mg of ascorbic acid. The formed suspension was heated in a closed vial using an oil bath. In contrary to the first experiment, in this case hydrogel started to form after half an hour since the sample reached 95 °C. It was left for 5 h to complete the hydrogel formation. The hydrogel was carefully taken out from the reaction medium and put into deionized water. In order to remove reactants and by-products from the hydrogel pores it was left in deionized water for three days, replacing the solvent two times per day. Produced hydrogel was dried at room temperature for a few days to obtain an aerogel. This sample was denoted as GA2 and used for further experiments.

Additionally, we prepared the rGO aerogel/multiwalled carbon nanotubes composite, using analogous procedure as described in [25]. Multiwalled carbon nanotubes were oxidized using a standard method found in [27] and then frequently used by us in previous studies [28, 29]. Oxidized multiwalled carbon nanotubes are denoted in this paper as CNT. In two separate vials 40 mg of GO

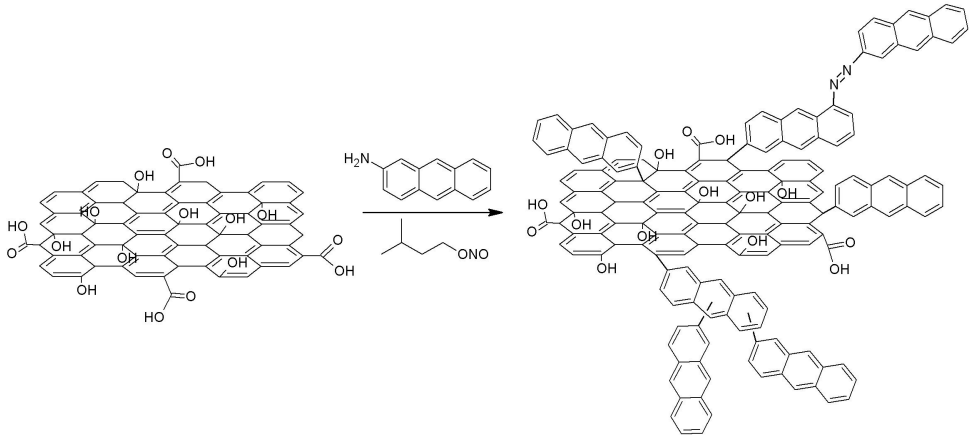

Fig. 3. The scheme of GO modification with anthracene residues.

in 10 ml of water and 10 mg of CNT in 10 ml of distilled water were sonicated for 30 min. After that time, samples were mixed and sonicated together for additional 1 h. To obtain carbonaceous hydrogel 200 mg of ascorbic acid was added to the GO/CNT suspension and the vial was closed and kept at 90 °C. After several minutes GO/CNT three-dimensional hydrogel started to form. After 5 h the hydrogel was carefully removed from the reaction vial and washed with water. Finally it was dried at 60 °C. This sample was denoted GA2-CNT.

Then the functionalization step was performed for both samples using the same method with aryl diazonium salts as described before. 30 mg of 2-aminoanthracene was added to GA2 or GA2-CNT pellets, weighing 22 mg and 26 mg, respectively. Then 20 µl of isoamyl nitrite was added with acetonitrile as a solvent. Both samples were heated to 75 °C and kept for 2 h in this temperature without stirring which could destroy the 3D structure of the aerogels. After that time, the pellets were removed from the reaction medium and washed with different solvent for several days. The aminoanthracene and its derivatives are colorful and many of them show also fluorescence, thus, purging was continued until the washings become clear, colorless and not fluorescing. Firstly, washing with DMF was performed, observing brown-reddish color of the solvent due to the presence of aminoanthracene and its derivatives. After several washings, the color fainted, but liquids still showed fluorescence. The washing with DMF was repeated till no fluorescence was observed and in the last stage ethanol was used to remove DMF from the pores. Finally, the samples were dried at 60 °C. The samples were labeled mGA2 and mGA2-CNT.

3. Results and discussion

We presented two approaches to obtain modified graphene aerogels. After the synthesis of graphene oxide we modified GO with anthracene residues and then reduced it hydrothermally. This resulted in failure as we did not obtain 3D structures. The second way started with the reduction of graphene oxide and then the modification using anthracene. The mechanism of hydrogel formation described by author of [26] involves the hydrogen bonds formation between oxygen containing groups present in the graphene oxide and water molecules. As the reduction proceeds, the hydrophilic character of GO changes to hydrophobic nature of reduced graphene oxide, which helps in the encapsulation of water molecules and making pores. In case of anthracene modified GO, the hydrophobic nature of anthryl moiety and steric hindrance of branched structures, that are likely formed in the reaction, hinder hydrogen bonding formation, thus, no hydrogel is formed. Fig. 4 shows the scheme of hydrogen bonds created between

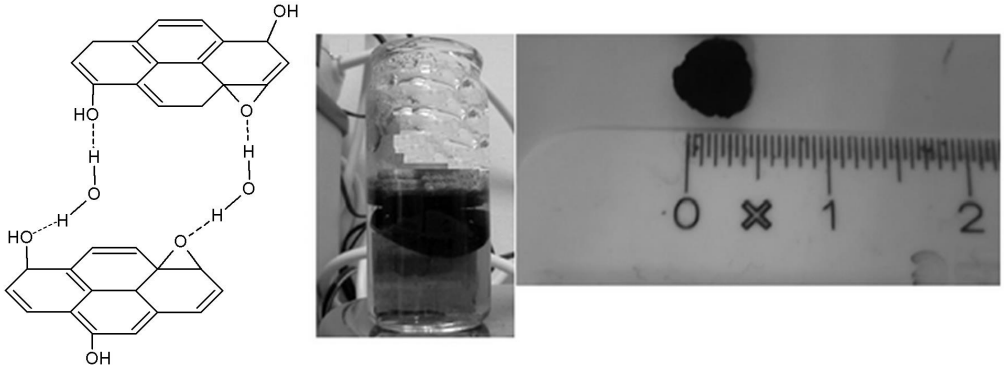

Fig. 4. Left: Formation of hydrogen bonds between rGO sheets. Middle: Graphene hydrogel formed at 95 °C from 2 mg/ml of GO. Right: Aerogel (GA) after drying at room temperature.

reduced graphene oxide sheets (left) proposed by author of [26] and the pictures of the obtained hydro- (middle) and aerogel (right) in our laboratory.

UV-Vis measurements were carried out in order to confirm the anthracene functionalization of graphene materials. Fig. 5 shows the spectra of (a) mGA1, which corresponds to the modified graphene oxide that was subsequently reduced (precipitate on the bottom of the vial) and (b) mGA2 that corresponds to the reduced graphene oxide aerogel which was then modified. For this measurement the samples were crushed and prepared as a water dispersion of equal concentration (1 mg/ml). The both spectra show the evident maximum absorption peaks around 260 nm that confirm the reduction of GO and are related to π-π^* transition of carbon-carbon bonds. Additional peaks around 300 to 400 nm correspond to anthracene molecules attached to the surfaces. By comparing the relative ratio between the peak at 260 nm and anthracene signal we can assume that more anthracene radicals were attached to the mGA2 sample. It may be due to the greater amount of sp^2 carbons on the rGO plane that are more likely to bind radicals. This observation is in accordance with other report [23].

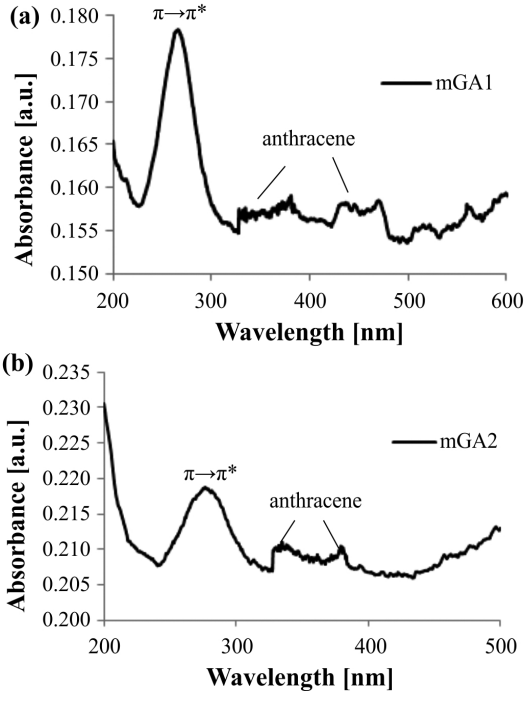

Fig. 5. UV-Vis spectra of (a) mGA1 and (b) mGA2 modified with anthracene.

Raman spectroscopy was used as it is a versatile tool to study carbon nanomaterials. Fig. 6 shows the spectra for pure graphite, graphene oxide (GO), modified graphene oxide (mGO1) and graphene aerogel (GA2), respectively. The Raman spectrum for graphite exhibits three characteristic modes, namely D (1355 cm^{-1}), G (1579 cm^{-1}) and 2D (2720 cm^{-1}). For graphite, 2D mode is lower and wider as compared to G mode. Typical Raman spectrum for a single-layer graphene sample (data not shown here) reveals presence of sharp G mode and mode 2D, whose intensity is higher than G. The first-order D peak itself is not visible in pristine graphene because of crystal

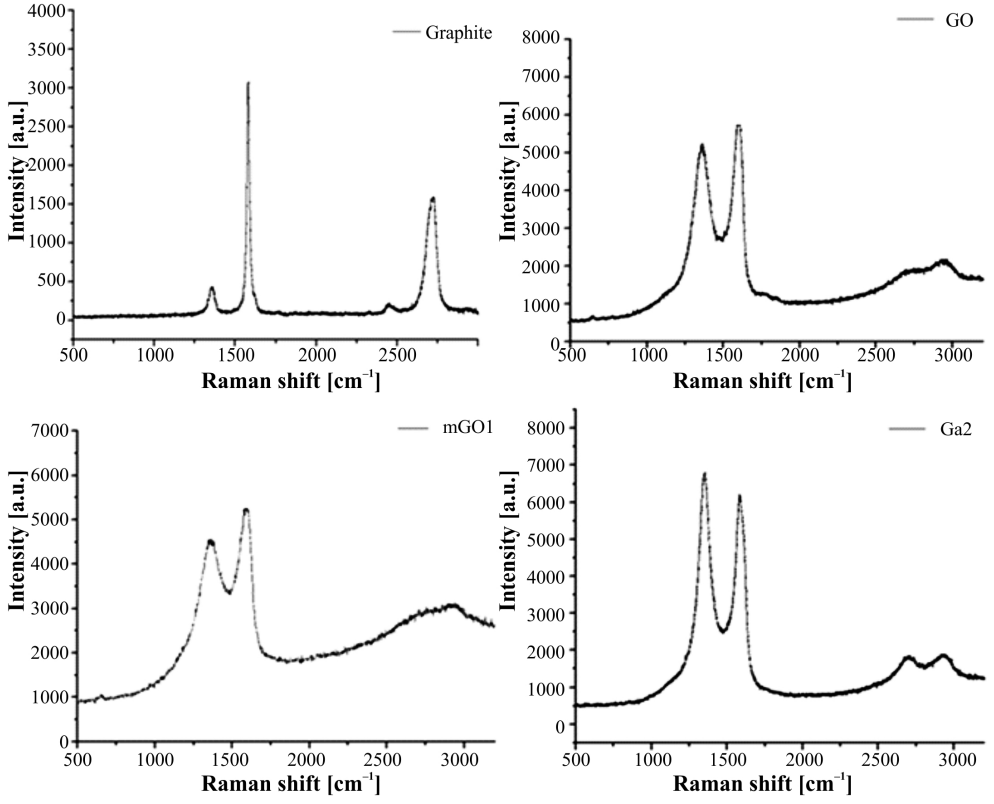

Fig. 6. Raman spectra of (a) pure graphite, (b) graphene oxide, (c) anthracene modified GO, (d) reduced graphene oxide aerogel.

symmetry. The graphene oxide spectrum (Fig. 6b) shows two main modes: a D mode that arises due to the defects in hexagonal carbon network and G mode corresponding to the vibration of carbon-carbon bonds in a basal plane. In the spectrum of GO, the 2D band is substantially lower and wider than G band, suggesting the presence of multi-layered graphene derivatives. For the anthracene modified sample one can notice that the relative intensity ratio between D and G peaks is smaller than for GO, suggesting lower disorder in the modified sample. However, it should be mentioned, that C–C stretching vibration region (1300 to 1650 cm^{-1}), and C–H bending in-plane vibration region (1000 to 1500 cm^{-1}) for anthracene is overlapping with graphene modes. Thus, splitting, widening and tailing of D band can be observed due to anthracene residues presence, and direct D to G peaks intensity comparison is not reliable.

The Raman spectrum of the last analyzed sample, that is reduced graphene oxide aerogel (GA2), reveals that D band intensity (Fig. 6d) is higher than that of G band. It is believed that this results from the longer ultrasonication treatment of the sample which cuts graphene flakes into smaller pieces and produces more edges, which enhance D and 2D intensity.

In order to investigate the morphology of graphene aerogel, scanning electron microscopy (SEM) was used. The porous structure of rGO aerogel (GA2) with the zoom 50.000× is depicted in Fig. 7. The pictures show the highly developed surface area of the sample. Three-dimensional structure of graphene aerogel possesses pore sizes that range from nano- to macropores. Therefore, the controlled method of GA synthesis is required to make a structure with optimal pore size distribution (10 to 80 nm as mentioned in the previous section).

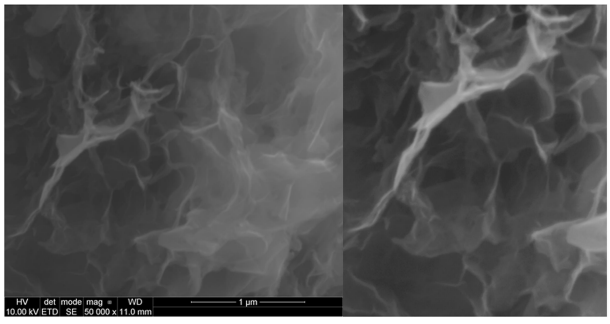

Fig. 7. SEM image of rGO aerogel (GA2) showing the highly developed surface area.

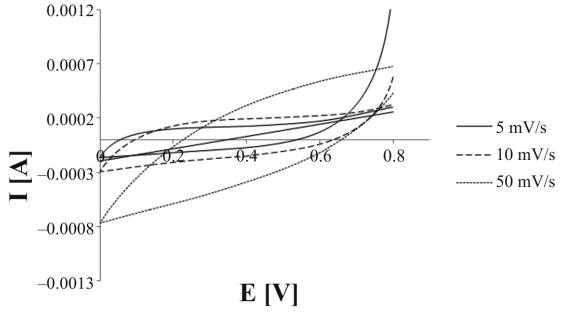

Fig. 8. Cyclic voltammograms recorded for GA2 at different scan rates.

In order to use graphene aerogels as electrodes in biofuel cells the electrochemical experiments need to be performed. The preliminary cyclic voltammetry curves were recorded for GA2, mGA2 and GA with carbon nanotubes (mGA2-CNT) to investigate their electrical conductivity. The cyclic voltammograms are depicted in Fig. 8. All samples were measured in McIlvaine buffer solution (pH 5.3) from 0.2 M $NaHPO_3$ and 0.1 M of citric acid. The samples were used as working electrodes. The surface area of graphene electrodes immersed into the buffer was small and approximately the same for all electrodes, thus, we were able to roughly compare the obtained curves between each other. The exact value of the surface area was difficult to determine due to the non-uniform shapes of each electrode. Firstly, the measurement for GA2 was conducted with different scan rates. As can be seen in Fig. 8 the curve for 5 mV/s exhibits the most rectangular shape (good reversibility), thus, this rate was used for further measurements. It can also be concluded, that the reduced graphene oxide aerogel displays good electrical conductivity.

Fig. 9 shows the voltammograms for GA2 and mGA2 samples. For the anthracene modified sample (mGA2) the area under the curve is smaller which indicates that the lower current has been obtained. For the modified sample with carbon nanotubes (mGA2-CNT) there is a significant increase in the obtained current comparable to mGA2.

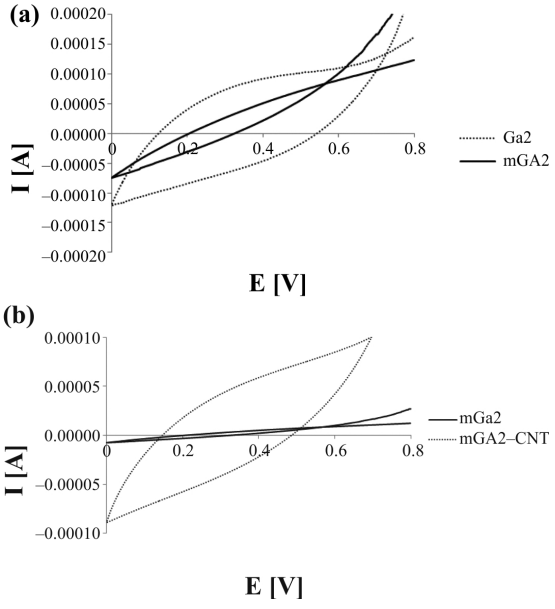

Fig. 9. Cyclic voltammograms for (a) GA2 and mGA2 and (b) mGA2-CNT and mGA2.

4. Conclusions and future prospects

We prepared graphene oxide (GO) that was used as a starting material for the reduced GO production. In the first approach we modified GO with the anthryl groups and then reduced it using the hydrothermal method with an ascorbic acid as a reducing agent. The sample precipitated on the bottom of the vial and no aerogel was obtained. In the second approach GO in form of water dispersion was firstly reduced hydrothermally. In this way the reduced graphene oxide aerogel was formed. In the next step we modified GA using anthryl groups.

Porous graphene-type structures are promising materials for using as bioelectrodes as they are highly conductive and show large surface area. They are very good matrixes for enzyme immobilization, especially after rational functionalization. As was shown in our previous papers, anthracene residues act as bridges between enzyme active center and graphene surface, enhancing the electron transfer. Pore size distribution is not uniform within the structure so the controlled way of the easy and cost-effective chemical synthesis is a key challenge. The more research is then needed to optimize the methods of the synthesis and to investigate the electrical response in the presence of enzymes.

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Received 2014-09-30
Accepted 2015-01-21