Synthesis of graphene foams and their sorption properties of n-hexane

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Abstract

The influence of preparation conditions of the graphene foams on their physicochemical properties is shown. Different graphene aerogels were obtained from various graphene oxide water suspensions using the hydrothermal method (with or without the addition of acrylic microemulsion and varying in drying time—24 and 48 h). Prolonged drying of the hydrogels resulted in smaller pores in the foams. The composition of graphene oxide (GO) and acrylic polymer water suspensions leads to the smallest surface area which is due to the closing of the pores of the composite structure. Thermal treatment of samples at 950 °C removed the polymer residues. The heating process increased the surface area and the total pore volume of all samples, which were used to test the graphene foams (GFs) for adsorption of n-hexane. These tests have shown that the most effective samples for n-hexane adsorption were the samples where for the preparation of the composite GO and acrylic resin were used. The best of obtained samples adsorbed 415 mg g⁻¹ of n-hexane which is a better result than for activated carbon manufactured from natural cork. Further preparation and modification of graphene foams could result in a significant increase in their sorption properties and could be used for contaminated air purification in the nearest future.

Keywords Graphene · Graphene foam · Surface area · Acrylic resin · n-Hexane

1 Introduction

Graphene gained a lot of attention in recent years due to its unique properties, such as high mechanical strength, electrical and thermal conductivity or high specific surface area (up to 2630 m² g⁻¹) [1]. There are many different methods for obtaining graphene, such as mechanical graphite exfoliation [2] or oxidation of graphite [3, 4]. Graphite oxidation using Hummers', Brody's or Staudenmaier's method leads to formation of graphite oxide with high amount of oxygen functional groups, such as hydroxyl, carboxyl, or epoxide. Graphite oxide exfoliation by the ultrasonic treatment leads

to a few layers graphene oxide (GO) with covalently bonded functional oxygen groups which can further be reduced to obtain reduced graphene oxide (rGO) [5, 6]. Due to its high surface area, graphene materials could be used as adsorbents for many different pollutants, such as dyes or volatile organic compounds (VOCs).

The emission of volatile organic compounds (VOCs) is a serious global environmental problem. The problem is regulated in the European Union by the Paints Directive [7] and the Industrial Emissions Directive [8]. In the EU, VOCs is defined as “any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard atmospheric pressure of 101.3 kPa.” [7].

In general, sorbents with high surface areas and high pore volumes are good candidates for VOCs adsorption. Three-dimensional (3D) porous graphene-based materials have a potential to meet these conditions as shown in the following examples. Adsorbent with surface area up to 3100 m² g⁻¹ was produced by KOH activation of microwave exfoliated graphene oxide [1]. Similar results were reported for thermally exfoliated GO after KOH activation [9]. The produced graphene-based material showed surface area of

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3240 m² g⁻¹ and total pore volume of 2.23 cm³ g⁻¹. Adsorbents with surface areas up to ~1900 m² g⁻¹ and total pore volume up to 1.65 cm³ g⁻¹ were also fabricated using the same method of KOH activation of exfoliated GO in another work [10]. These examples demonstrate significant potential of graphene-based materials in the field of environmental protection.

Despite the great potential of graphene-based materials, there are only a limited number of papers reporting on their adsorption properties of VOCs. To date, the following VOCs have been studied: acetaldehyde [11], acetone [12], benzene [13–16], butanone [14], ethanol [13], methane [10, 16–19], methylene chloride [20], toluene [11, 15]. Hexane is an aliphatic saturated hydrocarbon obtained from petroleum with a boiling point 68.73 °C [21]. In contrary to the polycyclic aromatic hydrocarbons (PAHs), n-hexane has no aromatic rings that could interact with graphite layers. Hexane is mainly used as a solvent, formulation additive in glues for shoes and leather products and can be found in petroleum and gasoline products [22]. Thus, it can be released to the environment through different pathways. It is very important to control the amount of hexane in the environment, because exposure to it may result in different health effects, such as vertigo, nausea, peripheral neuropathy or headaches [23].

In this paper we proposed the use of 3D graphene foams for n-hexane adsorption tests. We studied different preparation processes and their effect on the structure, chemical composition, surface area and hexane sorption properties of the obtained graphene foams. The novelty of the proposed materials is connected to the use of polymer microemulsion to stabilize the graphene foam structure and increase the surface area. The preparation process of these materials is simple and scalable, which means it could be applied commercially for adsorption of VOCs, especially n-hexane.

2 Experimental

2.1 Materials

For the preparation of graphene oxide the following materials were used.

Sodium nitrate p.a. potassium permanganate p.a., sulfuric acid p.a. 98%, hydrogen peroxide p.a. 30% were purchased from Alchem Grup sp. z o.o., Poland and graphite powder ≥ 99.5% purchased from Acros Organics. Acrylic microemulsion used for preparation of graphene foams was purchased from CTS Srl, Italy.

Nitrogen 6.0 (Messer, Poland) and helium 6.0 (Multax, Poland) were used to perform analyses in a surface characterization analyzer. For vapor analyses, n-hexane (CAS: 110-54-3; purity ≥ 99%), purchased from Chempur (Poland),

was used. A separate nitrogen gas cylinder (purity 5.0) was used with a degasser unit.

2.2 Sample preparation

2.2.1 Synthesis of graphene oxide

Graphene oxide was prepared using modified Hummers method [3] from pure graphite powder. In this method 4.7 g of sodium nitrate and 30 g of potassium permanganate were added to 10 g of graphite powder and 230 ml of concentrated sulfuric acid (98%) at the temperature below 10 °C. Then the mixture was heated up to 35 °C and kept under stirring for 2 h. In the next step, 100 ml of water was added, and the mixture temperature reached ~100 °C. Finally, the mixture was treated with 10 ml of H₂O₂. For purification, the slurry was filtrated and washed with deionized water till the pH of the filtrate reached ~6.5.

2.2.2 Preparation of graphene foams

The sample GF 24 h was prepared by hydrothermal method in stainless steel autoclave (Carl Roth) of 250 ml 1 wt% graphene oxide water suspension. The reaction was carried out for 2 h under the pressure of 20 bar and the temperature reached 250 °C. Obtained hydrogel was dried for 24 h at 20 °C. After that the hydrogel of partially reduced graphene oxide was frozen at –20 °C. The sample GF 48 h was prepared in the same way as sample GF 24 h but the hydrogel after synthesis was dried for 48 h at 20 °C and then was frozen at –20 °C.

The sample denoted as Acrylic/GF 24 h was prepared by mixing 242 ml of 1 wt% graphene oxide water suspension and 8 ml of 32 wt% acrylic microemulsion. The mixture was transferred to the glass reactor and placed in a stainless-steel autoclave. The reaction was carried out for 2 h under the pressure of 20 bar and the temperature reached 250 °C. The sample was dried for 24 h at 20 °C and frozen at –20 °C and was denoted as Acrylic/GF 24 h.

All of the hydrogels (GF 24 h, GF 48 h, Acrylic/GF 24 h) were lyophilized using vacuum pump to obtain graphene foams.

2.2.2.1 Thermal treatments of the foams Lyophilized samples were transferred to the tube furnace and sintered at 950 °C for 1 h in an argon atmosphere. After the heating process the samples were additionally denoted as 950C.

2.2.3 Graphene foams characterization

The obtained graphene foams were analyzed by scanning electron microscopy (SEM), Raman and FT-IR spectroscopy.

Raman spectroscopy measurements were performed on an InVia Raman microscope (Renishaw) using 514 nm laser. For each sample, the spectra were collected from 5 different spots, from which I_D/I_G ratio was calculated and the average value is presented in Table 1. The samples were measured as prepared.

FT-IR measurements were performed on a Nicolet iS10 (Thermo Scientific) spectrometer. Before the sample measurement “dry air” background was recorded, which was subtracted automatically during registration of spectra for the investigated samples. The samples were mixed with KBr at a ratio of 1/300 mg, then compressed at 7 MPa cm^{-2} to form a pellet and the transmission spectrum was recorded. The spectra were collected in the range 400–4000 cm^{-1} .

The electron microscope images were taken on a Hitachi S-5500 scanning electron microscope in secondary electrons (SE) mode.

2.2.4 Degassing

Degassing was performed in the Smart VacPrep (Micromeritics, USA). The samples of about 100 mg were degassed under vacuum (about 10^{-2} mmHg) using a two-stage temperature program: (1) 90 °C for 1 h, and (2) 300 °C for 24 h. Degassing removed moisture and other volatile contaminants from the samples.

2.2.5 Surface characterization

The 3Flex Surface Characterization Analyzer (Micromeritics, USA) was used to examine the surface characteristics of GFs. All calculations were performed using the nitrogen adsorption isotherms determined at -196 °C. The BET surface area was calculated from a BET plot in the relative pressure range between 0.03 and 0.3535 that was determined using a procedure proposed by Rouquerol [24]. The micropore surface area was calculated using the t-plot method [25]. Porosity distribution was calculated using the Non-Local-Density-Functional Theory (NLDFT) with density-independent weights. The N2-DFT model was employed in the calculations assuming a slit-like pore geometry with the pore size range covered from 4.0 to 4000 Å [26].

2.2.6 Vapor adsorption

A vapor source container (Micromeritics, USA) filled with n-hexane was used to carry out vapor adsorption on the degassed GF samples. The vapor source temperature was set at 40 °C and was controlled by the 3Flex with the heating mantle. Adsorption of n-hexane was performed at the temperature of 31 °C.

3 Results and discussion

3.1 Sample characterization

3.1.1 Scanning electron microscopy

The microscope images obtained for the graphene foams show that the surface of the samples is different for the materials before and after heating. In the sample GF 24 h (Fig. 1a, b) it can be seen that the surface of the sample is covered with small wrinkles. After heating (Fig. 1c, d) the surface of the sample becomes more rough, sharp edges of the graphene flakes become more visible and small spherical particles appear. This might be due to a partial reduction of graphene oxide during heating at 950 °C. Reduced graphene oxide has lower oxygen group content which leads to a decrease in hydrogen bonding between separate flakes and the structure is not as ordered as for GO and it becomes more brittle. Small particles visible after heating can be also a result of GO reduction, during which oxygen groups are removed from bigger flakes leaving smaller carbon particles. A similar effect is observed also for samples GF 48 h (Fig. 1e, f) and Acrylic/GF 24 h (Fig. 1i, j) before and after heating (Fig. 1g, h and k, l respectively) of the graphene foams.

3.1.2 Raman spectroscopy

In Fig. 2, there are two exemplary Raman spectra presented for sample GF 24 h before (Fig. 2a) and after heating at 950 °C (Fig. 2b). For the other samples, the spectra were similar as for GF 24 h and GF 24 h–950C and were deconvoluted the same way. The obtained results allowed to specify the D and G modes position and I_D/I_G ratio. The results are presented in Table 1. Raman spectra analysis exhibits, that the heating of the samples at 950 °C leads to the increase of the I_D/I_G ratio. This might suggest an increase of the defect (carbon with sp^3 hybridization) concentration in the graphene foams after heating. Heating of the foams at 950 °C leads to pyrolysis of the polymers used for the preparation of Acrylic/GF graphene foams and might also result in the removal of oxygen functional groups present in the GO structure. Pyrolysis of the polymers leads to formation of mostly carbon with sp^3 hybridization (amorphous structure, which in Raman spectra will indicate a higher intensity of the D mode comparing to G mode which is observed for sp^2 carbon structures). Removal of oxygen groups not necessarily will restore the graphene structure and change the hybridization of carbon atoms (leaving sp^3 hybridization) present in the structure leading to a higher intensity of the D mode comparing to G mode. These results are in good agreement with the scanning electron microscopy measurements,

Fig. 1 SEM pictures of graphene foams: GF 24 h (a, b), GF 24 h after heating at 950 °C (c, d), GF 48 h (e, f), GF 48 h after heating at 950 °C (g, h), Acrylic/GF 24 h (i, j) and Acrylic/GF 24 h after heating at 950 °C (k, l)

where the images show that after heating graphene foams have rougher structure indicating a higher defect density in the obtained samples.

Fig. 2 Exemplary Raman spectra of foam GF 24 h before (a) and after (b) heating at 950 °C

Table 1 Raman spectra analysis of the D and G modes position and I_D/I_G ratio

	D position (cm ⁻¹)	G position (cm ⁻¹)	I_D/I_G
GF 24 h	1353	1585	1.45
GF 24 h–950C	1349	1593	1.79
GF 48 h	1349	1584	1.21
GF 48 h–950C	1349	1595	1.64
Acrylic/GF 24 h	1345	1586	1.17
Acrylic/GF 24 h–950C	1344	1581	1.42

3.1.3 FT-IR spectroscopy

As can be seen on the FT-IR spectra in Fig. 3, graphene oxide used for the preparation of the foams contains many functional groups. Mainly, they are hydroxyl (–OH) groups found around 3500 cm⁻¹, C–H bonding found near 2900 cm⁻¹, C=O groups around 1700 cm⁻¹, C=C bonding around 1600 cm⁻¹, and C–O bonding near 1100 cm⁻¹. It can be observed that the autoclave process for samples GF 24 h reduced most of the functional groups present in graphene oxide. The GF 48 h sample (spectrum not presented) exhibits the same chemical composition as sample GF 24 h. On

Fig. 3 FT-IR spectra of (a) graphene oxide, GF 24 h before and after heating, (b) graphene oxide, Acrylic/GF 24 h before and after heating

the FT-IR spectrum for the sample Acrylic/GF 24 h many functional groups are visible. This is due to the acrylic resin used for the preparation of this foam: mainly C–H bonds can be observed in the range 2800–3000 cm^{-1} and around 1450 cm^{-1} , C=O groups are seen at around 1700 cm^{-1} , C–O–C groups are visible at around 1100 cm^{-1} . For all samples heating at 950 $^{\circ}\text{C}$ lead to defunctionalization of the obtained GFs.

3.1.4 Surface characterization

Figure 4 shows a comparison of the nitrogen isotherms performed at $-196\text{ }^{\circ}\text{C}$ for the tested GFs. This analysis allows for determination of the porous structure of obtained GFs, especially micro- and mesopores, which are crucial for the adsorption of n-hexane. Interestingly, all presented isotherms, except that for Acrylic/GF 24 h sample, have similar shape. The adsorption branches are a composite of types I and II according to the IUPAC classification [27]. On the other hand, the adsorption branch of the Acrylic/GF 24 h sample resembles type II isotherm. Note that a true type II isotherm is reversible in the whole range of relative pressures. The pseudo-type II isotherms recognized for the tested GFs are reversible only

in the lower relative pressure range. Similarly, the type H4 hysteresis loop has been identified for all GFs, except that for Acrylic/GF 24 h sample [27, 28]. Regarding the Acrylic/GF 24 h sample, the type H3 hysteresis loop has been found. In summary, with one exception regarding the Acrylic/GF 24 h sample, the initial reversible filling of micropores ($< 2\text{ nm}$) is followed by multilayer adsorption and capillary condensation taking place in meso- (2–50 nm) and macropores ($> 50\text{ nm}$). Capillary condensation occurring in meso- and macropores can be seen as a hysteresis loop with a sharp increase of the adsorbed amount close to the saturation pressure. On the other hand, a pseudo-type II isotherm linked to the Acrylic/GF 24 h sample is characteristic for materials with pore diameters larger than micropores. Note also that only the Acrylic/GF 24 h-950C sample has the typical steep region of the desorption branches closing the hysteresis loops at $P/P^0 \sim 0.42$. This is characteristic for the nitrogen hysteresis loops [27]. The other samples, except the Acrylic/GF 24 h sample, exhibit low pressure hysteresis which can be connected to the swelling of a non-rigid porous structure of GFs. In turn, the steep desorption branch at $P/P^0 \sim 0.85$ for the Acrylic/GF 24 h sample reveals that the biggest pores can be expected. This might be connected to the fact

Fig. 4 Nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ on the GFs

that acrylic polymer is still present in the graphene foam and is filling the pores. Both types H3 and H4 hysteresis loops are similar. The former has the adsorption branch being a pseudo-type II isotherm, while the latter has the adsorption branch being a composite of types I and II. The slit-like pores are associated with the H3 and H4 hysteresis loops.

Note that the types H3 and H4 hysteresis loops do not have a plateau at high relative pressures. Therefore, the pore size distribution in the mesopore range cannot be evaluated using classical methods based on the modified Kelvin equation, such as the Barrett–Joyner–Halenda (BJH) method. Instead, microscopic methods using statistical mechanics such as the NLDFT or Grand Canonical

Fig. 5 Pore size distributions for the GFs calculated with the N₂-DFT model

Monte Carlo can be applied. Using these methods an accurate pore size analysis over the complete micro- and mesopore size range is possible.

Figure 5 shows a comparison of the pore size distributions for all tested GFs. The distributions cover a wide range of the pore sizes from micropores up to the meso-macropore range

(> 500 Å). Again, all presented distributions, except that for Acrylic/GF 24 h sample, have some similarities. They display the porous structures in a wide range of pore widths. The presence of microporous structure is very beneficial for adsorption of small VOC molecules (critical diameter of n-hexane molecule is 4.9 Å). On the other hand, the presence

of mesoporous structure can be critical for adsorption of larger molecules. In addition, mesopores are needed to provide adsorbates with access to the smallest pores. Regarding the Acrylic/GF 24 h sample, no micropores are identified and mesopores are practically absent. As stated earlier, this is possibly due to the filling of the pores with acrylic polymer. For the samples GF 24 h and GF 48 h there are slight differences in the amount of micro- and mesopores. Sample GF 24 h has a higher content of mesopores and lower of micropores comparing to GF 48 h, which can be explained that due to extended drying the pores start to collapse from the hydrogen bonding between GO functional groups.

Table 2 summarizes the results on BET surface area, t-plot micropore area and total volume in pores for all GFs. As can be seen in Table 2, the BET surface area is higher for the heated GFs than the raw ones. This might be connected to partial reduction of graphene oxide forming a rougher structure, as can be seen from microscopic images. For the Acrylic/GF 24 h–950C sample, the polymer was pyrolyzed revealing the micro- and mesopores present in the structure. Additionally, pyrolyzed polymer residues could form new porous structure increasing the surface area of the sample.

Nitrogen isotherms at $-196\text{ }^{\circ}\text{C}$ for different graphene-based adsorbents have been reported in the literature [10, 11, 14, 15, 17, 18, 20, 29]. Remarkably, their shape and the shape of the isotherms obtained for our pyrolyzed GFs is the same. This reveals that such materials generally possess porous structure in a very wide range of sizes extending from micro- to macropores.

3.1.5 Adsorption of n-hexane vapor

Based on the surface characterization results adsorption of n-hexane was performed for graphene foams after heating at $950\text{ }^{\circ}\text{C}$. Figure 6 shows a comparison of n-hexane isotherms determined at $31\text{ }^{\circ}\text{C}$ for the pyrolyzed GFs. The Acrylic/GF 24 h $950\text{ }^{\circ}\text{C}$ sample demonstrates the best performance among the three samples. There is full agreement with the results presented for nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ in Fig. 4. The surface area and total volume

of pores of the Acrylic/GF 24 h–950C sample is the highest amongst the three analyzed samples. The Acrylic/GF 24 h–950C sample shows the maximum amount adsorbed of 415 mg g^{-1} (after converting units from $\text{cm}^3\text{ g}^{-1}\text{ STP}$ to mg g^{-1}). Comparing to the literature data this result is better than the maximum amount adsorbed for activated carbon derived from cork powder waste by KOH activation [30]. This activated carbon showed about 390 mg g^{-1} for the best sample (C800) prepared by mixing 1 g of KOH per 1 g of pretreated cork waste and calcinated at $800\text{ }^{\circ}\text{C}$. Another example where adsorption of n-hexane was also investigated was for metal–organic frameworks (MOF)/graphene oxide composites [31]. For this material the n-hexane uptake at $25\text{ }^{\circ}\text{C}$ was 1042 mg g^{-1} , which is a higher value compared to our GFs. This is due to very beneficial textural properties of this material—BET surface area of $3502\text{ m}^2\text{ g}^{-1}$ and total pore volume of $1.75\text{ cm}^3\text{ g}^{-1}$.

On the other hand, another recent article on similar hybrid materials reports quite different adsorption capacities of n-hexane. Namely, rGO and three-dimensional graphene network (3DGN) were combined with ZIF-8 (ZIFs—zeolitic imidazolate frameworks) and UiO-66 (zirconium-based metal–organic frameworks) to increase their adsorption capacities [32]. Although these hybrid materials performed much better than pure ZIF-8 and UiO-66, they still had poorer n-hexane adsorption capacities than our Acrylic/GF 24 h $950\text{ }^{\circ}\text{C}$ sample. While the best ZIF-8/3DGN sample adsorbed 4.26 mmol g^{-1} (367 mg g^{-1}) of n-hexane at 40 bars, the n-hexane adsorption capacity was lower than about 40 mg g^{-1} at 1 bar as follows from Fig. 1e in [32]. A comparison of separate results showing N_2 uptake at $-196\text{ }^{\circ}\text{C}$ on ZIF-8/3DGN (Fig. 2b in [32]) and the Acrylic/GF 24 h $950\text{ }^{\circ}\text{C}$ sample (Fig. 4) confirms better n-hexane adsorption capacity of our sample. Note also that the use of metal–organic frameworks increases the cost of such materials, which makes it difficult to commercialize. Having that in mind, GFs prepared and studied in this paper have good adsorption of n-hexane with much lower costs compared to other studied adsorbents.

Table 2 Textural properties of the tested GFs

Run no.	Sample name	BET surface area ($\text{m}^2\text{ g}^{-1}$)	t-Plot micropore area ($\text{m}^2\text{ g}^{-1}$)	DFT	
				Pore size ($\text{\AA}$)	Total volume in pores ($\text{cm}^3\text{ g}^{-1}$)
1	GF 24 h	240.0268	48.5221	≤ 4003.09	0.28811
2	GF 24 h–950C	244.9433	25.7369	≤ 4003.09	0.32546
3	GF 48 h	238.1401	63.8178	≤ 1475.96	0.15249
4	GF 48 h–950C	314.8579	30.6792	≤ 1720.79	0.27307
5	Acrylic/GF 24 h	15.3572	–	≤ 1475.96	0.06329
6	Acrylic/GF 24 h–950C	319.0186	13.4942	≤ 1858.04	0.98202

Fig. 6 n-Hexane adsorption at 31 °C on the GFs

4 Conclusions

Various graphene foams were obtained from graphene oxide suspensions using different methods of foam preparation. Manufacturing conditions influenced the properties of the obtained graphene foams. The preparation conditions resulted in different structures of prepared graphene

foams. Prolonged drying process of the hydrogel (sample GF 48 h) resulted in higher amount of micropores and lower of mesopores. Addition of the acrylic polymer to GO suspension (Acrylic/GF 24 h) resulted in the smallest surface area which was due to filling the pores with the polymer. Annealing the samples at 950 °C was responsible for defunctionalization of the obtained foams and pyrolyzation of the acrylic

polymer. This resulted in an increase of the defects present in the carbon structure. The heating process increased the surface area and total volume in pores also in all the samples, which was used to test the graphene foams for adsorption of n-hexane. The tests have shown that the best sample for n-hexane adsorption was the sample where for the preparation of the hydrogel acrylic resin was used. Sample Acrylic/GF 24 h-950C adsorbed 415 mg g⁻¹ of n-hexane. The use of the acrylic microemulsion can lower the production costs of the graphene foams due to the fact that it is much cheaper than pure graphene and leads to a significant decrease of the used graphene for the preparation of the final product and its adsorption properties are enhanced. Comparing to the granular activated carbon graphene foams prepared with acrylic resin can be formed in desired shapes and have better mechanical properties, which makes them good candidates for preparing air filters with a large surface area. Additionally, these materials have also good acoustic and thermal insulation properties, which could be used for production of novel insulating materials with air purifying possibilities. Further tests on the preparation and modification of graphene foams could result in a significant increase of their adsorption properties and could be used for air purification in the future.

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