

The influence of the oxidation method on the size of reduced graphene oxide

Łukasz Drewniak,* and Sabina Drewniak

*Department of Optoelectronics, Faculty of Electrical Engineering, Silesian University of Technology,
2 Krzywoustego St. 44-100 Gliwice, Poland*

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Abstract—Derivatives of graphene have become important materials due to their excellent properties. Graphene oxide and reduced graphene oxide are especially interesting because they are relatively easy, cheap and quick to produce. Among many possible applications, reduced graphene oxide is a good candidate for sensor applications. Its properties can be controlled at the production stage. The precursor used and the method of oxidation have a significant influence on its properties. Therefore, it is worth taking a closer look at them. In this paper we analyse the influence of the oxidation method on the size of the reduced graphene stock, which determines the sensitivity of the rGO layer. We used AFM microscopy for this purpose.

Graphene and derivatives of graphene are of great interest due to their unique chemical and physical properties [1–4]. However, derivatives of graphene such as graphene oxide (GO) or reduced graphene oxide (rGO) are more suitable for sensor applications. It is because, pristine graphene has not dangling bonds, defects and additional functional groups which have a significant influence on gas adsorption [1]. High cost of graphene fabrication and low capacity of production are an additional problem [1]. Considering GO and rGO, rGO is more suitable for sensor applications due to its much higher conductivity (GO shows insulating or semi-conducting behavior whereas rGO has electrical conductivity of $\sim 6300 \text{ S cm}^{-1}$) and richer sorption sites (specific surface area of GO is $890 \text{ m}^2 \text{ g}^{-1}$ whereas rGO is $\sim 2600 \text{ m}^2 \text{ g}^{-1}$) [5–6].

Reduced graphene oxide (Fig. 1) is a p-type semiconductor that is obtained from the graphite by oxidation and further reduction (chemical, thermal, electromechanical, or other method). This process, generally, reduces the GO oxygen content, removes functional groups and defects in an atomic-scale lattice [7–8]. Thus, it allows to obtain a material similar in structure to pristine graphene but much cheaper. The choice of oxidation and reduction method is important because it significantly affects the properties of the reduced graphene oxide [9]. For example, it determines the number and type of functional groups as well as the size of rGO affecting the sensitivity of the sensor [10–12]. So, rGO produced by various methods will have various chemical and physical properties.

In this paper we analyze the influence of the oxidation method on the size of the rGO stack. To measure these parameters, we used the atomic force microscopy (NT-MDT, NTEGRA Prima platform).

AFM is a powerful tool for the acquisition of topographic data of the surface of various materials and their analysis. The basic parameters that can be determined from AFM measurements are max and min height of the surface, roughness, average roughness, x and y dimensions of the selected area, root-mean-square coefficient (RMS), and etc. The principle of the AFM operation is presented in [13]. Generally, AFM can operate in three modes: contact, non-contact and intermittent contact mode. We used in our investigation the intermittent-contact mode, which eliminates the disadvantages of those previously mentioned. The measurements were performed with the following parameters: frequency: 1 Hz, number of points per line: 256. The obtained data (AFM images) were analyzed using Nova Software.

To investigate how different oxidation methods affect the size of the reduced graphene oxide, we fabricated a few samples.

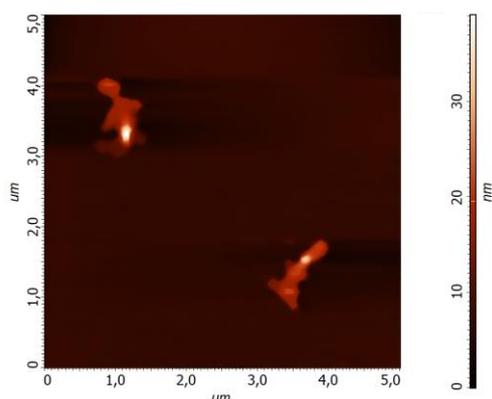


Fig. 1. Exemplary AFM image of rGO stacks.

* E-mail: lukasz.drewniak@polsl.pl

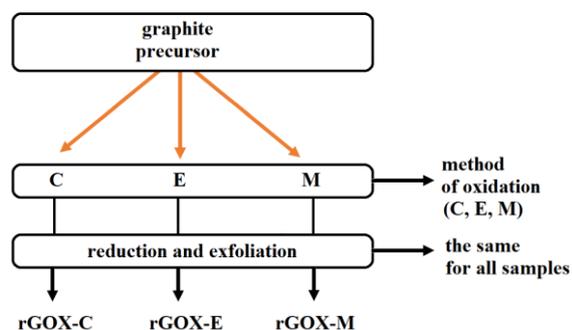


Fig. 2. Scheme of samples preparation.

Firstly, we took 3 samples (1 g) of flake graphite (F). Secondly, we oxidized each of them using one of the three methods (C, E, M). Method C is the modification of the Hummers' method while methods E and M are the modification of the Tour's method. The parameters of the oxidation process were selected in such a way that the obtained graphite oxide was characterized by the highest possible degree of oxidation. The parameters of the oxidation process are shown in Table 1.

Table 1: The parameters of the oxidation process

	Method		
	C	E	M
acid base	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄ H ₃ PO ₄
oxidizing mixture	HNO ₃ KMnO ₄	NaNO ₃ , KMnO ₄	KMnO ₄ , KNO ₃
time	24h	2h	5h

In that way, we obtained 3 samples of graphite oxide (GOF-C, GOF-E and GOF-M, depending on the oxidation method). Further processes were exactly the same for all graphite oxides: we performed thermally reduction (900°C, 0.5h) and sonic exfoliation. We called the obtained samples as: rGOF-C, rGOF-E and rGOF-M. The general scheme of preparation of reduced graphene oxide is shown in Fig. 2. The obtained materials were not single-layered, they contained a few layers arranged in a stack. For such materials, we performed the AFM measurements and compared the sizes of reduced graphene oxide stacks. The summary of the results is shown in Fig. 3. Finally, based on this data, we drew the conclusions. To check whether our conclusions were reproducible for reduced graphene oxides obtained from the other graphite precursors (scaled, synthetic), we repeated the entire preparation process for other precursors (scaled and synthetic). The samples obtained in this way were called: rGOS-C, rGOS-E, rGOS-M for a scaled precursor and rGOE-C, rGOE-E, rGOE-M for a synthetic precursor.

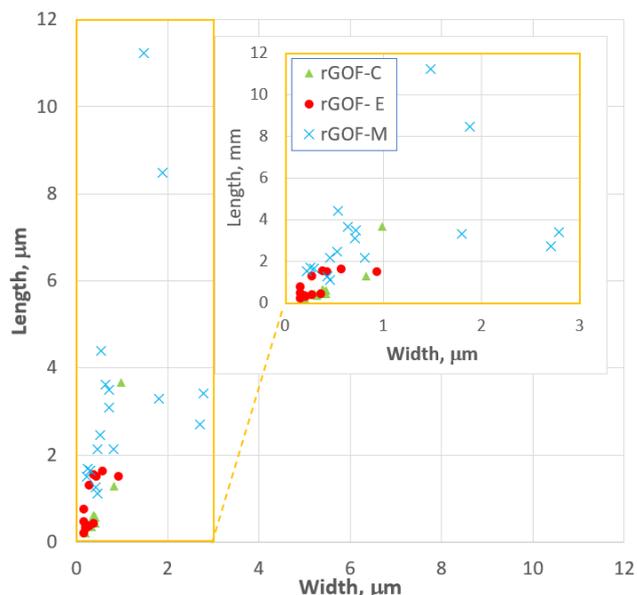


Fig. 3. The size of reduced graphene oxides obtained using flake graphite and various oxidation method.

It can be seen in Fig. 3 that the size of rGOF-E and rGOF-C is the smallest and does not exceed the size of (2×1) μm. The rGOF-M stack is bigger than the others (average 3×1 micrometers). The similarly situation is observed for reduced graphene oxides obtained from scalar graphite (Fig. 4). The biggest size is registered for rGOS-M stack. For rGO obtained from scalar precursor, the sizes of rGOS-E stack are the most homogeneous and the smallest (max. 0.8×0.5 μm) while the sizes of rGOS-M and rGOS-C stacks are more varied. Their sizes do not exceed a few by a few micrometres.

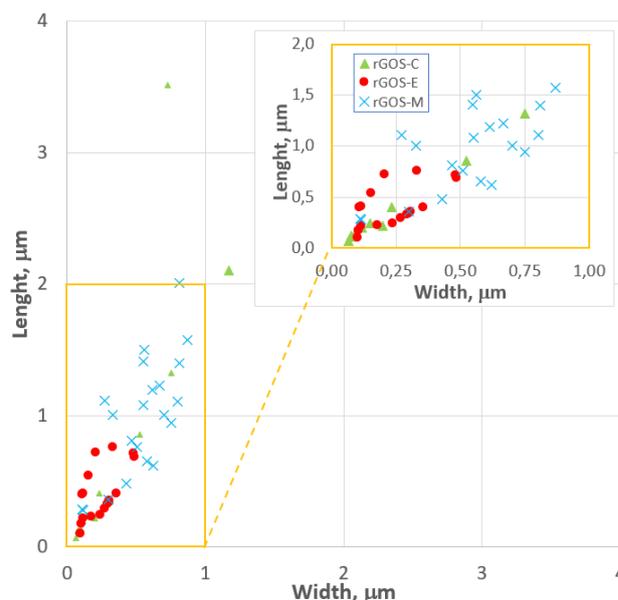


Fig. 4. The size of reduced graphene oxides obtained using scalar graphite and various oxidation method.

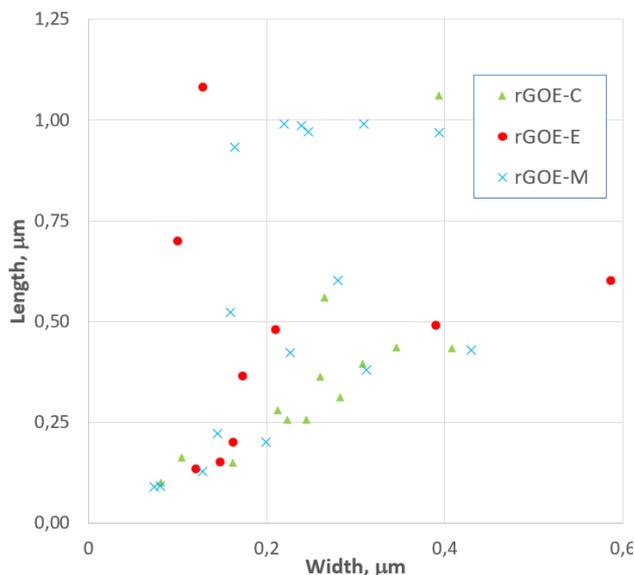


Fig. 5. The size of reduced graphene oxides obtained using synthetic graphite and various oxidation method.

Figure 5 presents the size of the rGO stack obtained from synthetic graphite and oxidized using various (C, E, M) methods. All stacks (independent from the type of oxidation method) are small in size and mostly do not exceed $(1 \times 0.5) \mu\text{m}$. It allows us to conclude that for the samples obtained from synthetic graphite, the oxidation method does not have much influence on the rGO stack size.

Summarizing, the reduced graphene oxides obtained using the E oxidation method are the smallest, while those obtained by the M method are the most heterogeneous. In our opinion, among the analyzed materials, the most suitable for sensor purposes seem to be those oxidized using the E method (based on [14–17], the size of rGO's grains used as a sensing layer are about 1 or a few micrometers). However, this requires additional research including FT-IR measurements, gas and response testing. Such investigations are currently in progress.

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