

MECHANICAL PROCESSING OF GRAPHENE OXIDE, ITS REDUCED FORM AND BIOCHAR

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Abstract

This paper describes the performance of the chemical-mechanical processing of GO, rGO and biochar (ball mill grinding in $(\text{NH}_4)_2\text{SO}_4$) to obtain a nanomaterial for application as a supercapacitor. The synthesis of carbon nanomaterials, including their characterization according to available measurement techniques, is presented in this paper as well. The experimental part is devoted to the specification of ball milling conditions. Subsequently, elemental analysis and TGA analysis were determined for the ground samples. This is followed by a discussion of the results and a comparison of the obtained results with those from scientific publications.

Keywords: Graphene oxide, reduced graphene oxide, biochar, doping, supercapacitor

1. INTRODUCTION

Recently, there has been a growing interest in the use of graphene-based materials in biosensing applications. Graphite oxide (GO) is an example. This interest is due to the high output signal and the potential for industrial development. Graphene has many attractive properties, such as excellent conductivity and mechanical resistance (e.g., toughness and flexibility). High reactivity towards chemical molecules is also another notable advantage of this material. Waves on the surface (either intrinsic or induced) are also an important variable that offers enormous potential when used correctly. [1]

GO is one of the suitable nanoparticles for increasing the hydrophilicity of the membrane. The Hummer method is the traditional way to prepare GO. [2] Because it contains functional groups, it is better dispersed in the polymer solution. When GO is incorporated into membranes, better results and properties can be achieved in water purification technologies such as immersion and wetting, layer-by-layer assembly, or vacuum filtration. [3] Increased mechanical strength and thermal stability can be observed in membranes with added GO. In low-pressure applications, improved water transport can occur. A fundamental feature of GO nanocomposites is the ability to protect against fouling during operation due to a negative charge and significant hydrophilicity. [4] It can be expected that by incorporating GO into membranes, we can achieve greater fouling resistance through a reduction in surface roughness and an increase in hydrophilic properties. [5] It can also be observed that the resulting membranes with GO demonstrate high water permeability in, for example, nanofiltration and reverse osmosis processes. [6] However, despite the many advantages offered by GO, the work is very costly and mass production is a challenge. It is therefore crucial to thoroughly optimize production processes to reduce costs and simplify production. [7]

The use of graphene oxide is possible, for example, in the environment. Here, one of the key threats is air pollution caused by emissions of harmful gases from industrial sources (CO_2 , CO , NO_2 and NH_3). Due to the oxygen groups present on the basal plane and edges, GO has the ability to form both covalent and non-covalent interactions with various molecules. GO can be used in catalytic processes for the transformation of

pollutant gases during industrial operations. The neutralization of these unwanted gases can be achieved through their capture and subsequent storage, through catalytic gas transformation reactions, or by their direct utilization. [8]

2. PREPARATION OF CARBONACEOUS MATERIALS

2.1. Graphene oxide (GO)

GO was prepared by oxidating finely ground graphite (0.025 mm) according to the classical Hummers method (H_2SO_4 , NaNO_3 , H_2O_2 , KMnO_4 , HCl). The oxidation product was repeatedly centrifuged until a negative reaction to sulphate ions was obtained.

2.2. Reduced graphene oxide (rGO)

In graphene oxide, the reduction of oxygen groups can be carried out by a series of reactions. More than 50 different reducing agents have been described in the literature. The most commonly used agent was hydrazine hydrate, which was replaced by NaBH_4 or HI due to its toxicity and ascorbic acid was found to be optimal.

In our case, ascorbic acid was used as reducing agent in the reaction ratio 1 graphene oxide: 1.6 ascorbic acid. The reaction was carried out on a water bath at 55-60 °C for 2 hours. After cooling, the contents were filtered, the cake was washed with H_2O and $\text{C}_2\text{H}_5\text{OH}$, and the cake was dried at 55 °C for 24 hours.

2.3. Biochar

Biochar (brand name, Biochar 4073) from Biouhel s.r.o. Zlín was prepared by pyrolysis at 470 °C from a digestate containing 60% wood and 40% corn silage, with a pyrolysis time of 25 min. The Biochar was subsequently milled three times for 2.5 h on a high-speed pin mill through several passages; pyrolysis was carried out by Biouhel s.r.o. Zlín. All the details of the preparation of the Biochar are not listed due to the protection of the patent number PV 2016–555, from the company Aivotec s.r.o

3. EXPERIMENTAL PART

3.1. Mechanical treatment of GO, rGO and Biochar in $(\text{NH}_4)_2\text{SO}_4$ environment

A TPR-D950-FU-EA ball mill (**Figure 1A**) with a GT 13746 timer (**Figure 1B**) was used for the experiment and the mixing of the aforementioned substances with ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ under predetermined conditions for all mixing. The materials were taken from a publication [9] where GO, rGO, and Biochar were ground with $(\text{NH}_4)_2\text{SO}_4$ at a ratio of 1 : 5 using agate balls (3 x 20 mm, 60 x 15 mm, 145 x 6 mm) at a grinding speed of 300 rpm for 3 h. [9]



A



B

Figure 1 Ball mill (A) with timer (B)

The mass ratio of the substances before mixing (0.5 g : 2.5 g $(\text{NH}_4)_2\text{SO}_4$) was maintained for the purpose of this test. The mixing was achieved using stainless steel balls in similar proportions (3 x 20 mm, 60 x 15 mm and 145 x 9 mm) with a grinding time on the ball mill of 3 hours and a maximum speed of 5 liters: 33-110 rpm. The resulting products after milling were washed from the balls and repeatedly decanted in distilled water (**Figure 2**) until a negative reaction for sulfate ions (Ba^{2+}) occurred and then dried at 55-60 °C for 15 hours.



Figure 2 N,S-doped decantation products from the left (GO, rGO, Biochar)

3.2. Elementary analysis

Elemental analysis was performed on 1) CHN 628 SC, model 3277 from LECO and 2) 628 S, model 622-000-600 from LECO.

Elemental analysis showed the following composition of nitrogen and sulfur in the products, see **Table 1**.

Table 1 Results of elementary analysis of samples

Sample number	Sample description	N^a (%)	S^a (%)
		Nitrogen (analytical sample)	Sulfur (analytical sample)
1.	rGO	0.55	0.18
2.	GO	1.05	0.40
3.	Biochar	0.86	0.11

In our case, the N content of all products was higher than that of S. Nevertheless, in our case the detected values were much lower than in the cited publication [9], where their detected contents for graphene oxide were 5.82 % of N and 1.33 % of S.

To the products from the first milling was added $(\text{NH}_4)_2\text{SO}_4$ in a ratio of 1 : 5 to the weight of the product. The mixture thus prepared was milled under the same conditions except the milling time, which was 24 hours.

3.3. TGA analysis

The lowest increase in nitrogen content was after the long-term grinding of graphene oxide. In thermal analysis, mass loss was observed for GO as early as 150 °C and was terminated at about 650 °C with a broad exoeffect with a maximum at 492 °C. After thermal decomposition, the residue was about 30 % of the original mass (**Figure 3a**). For rGO, the TDA plot shows a mass loss from 160 °C onwards and goes into a broad exoeffect with a maximum at 543 °C (**Figure 3b**). Again, there is a 14 % residue. An even larger residue of 32 % was found for Biochar, where the plot covers the exoeffect course with a maximum at 548 °C (**Figure 3c**). The measurements were carried out on the TGA/DSC2 Mettler – Toledo.

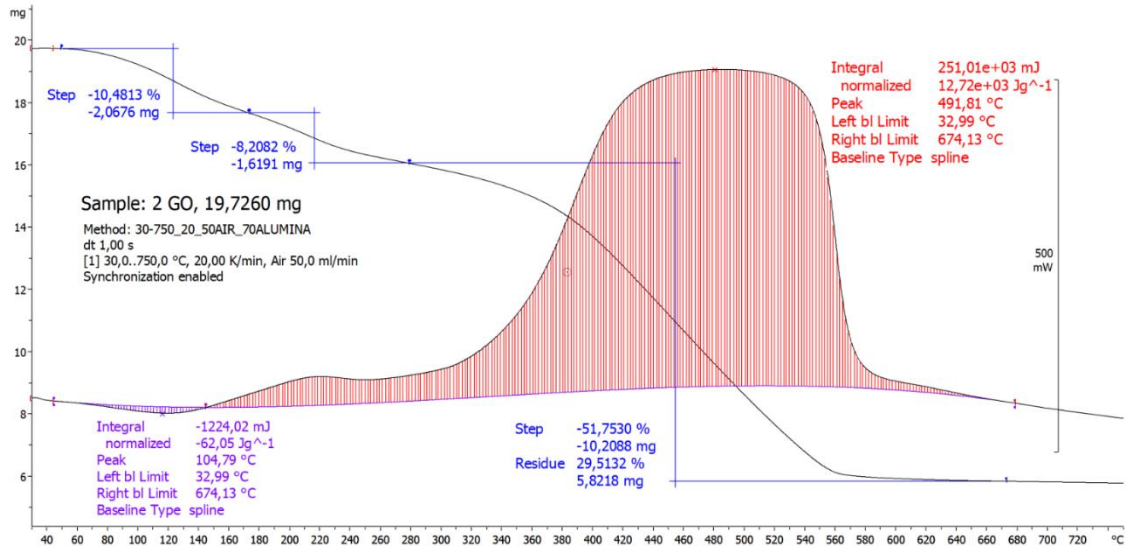


Figure 3a TGA and DC analysis of doped products after ball milling of GO

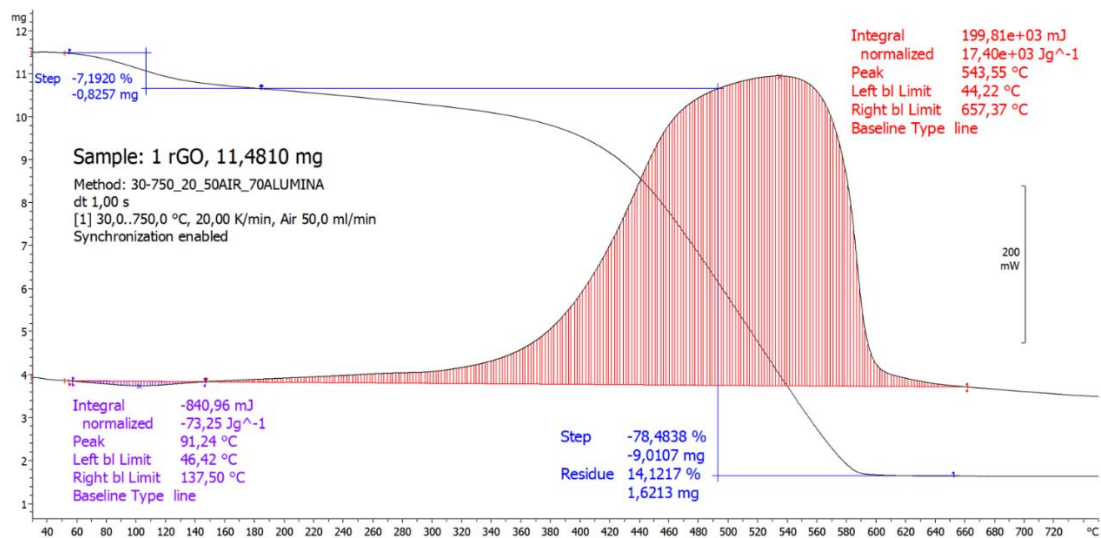


Figure 3b TGA and DC analysis of doped products after ball milling of rGO

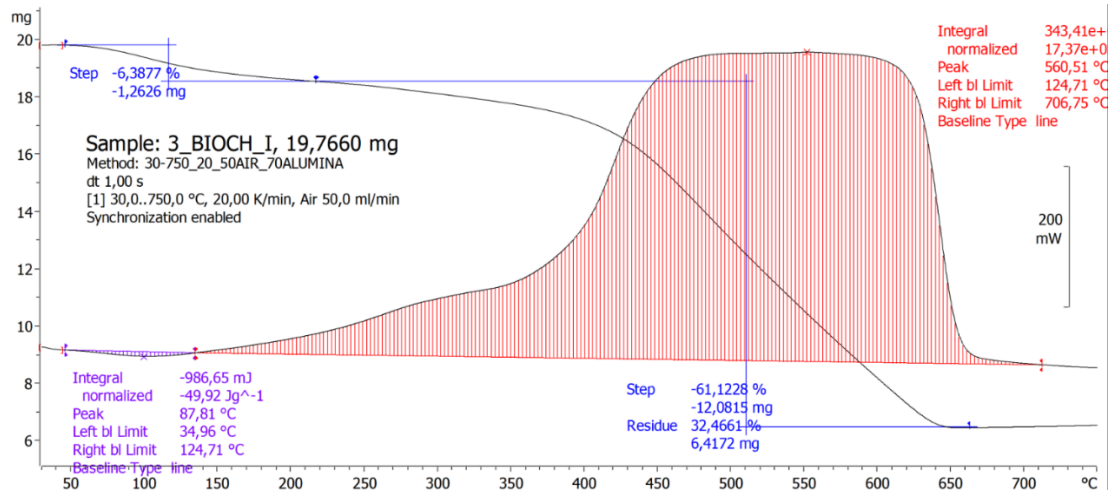


Figure 3c TGA and DC analysis of doped products after ball milling of Biochar

4. THE RESULTS

In our case, the N content of all products was higher than that of S. Nevertheless, in our case the detected values were much lower than those of the cited publication [9], where their detected contents for graphene oxide were 5.82% N and 1.33% S.

The results of the TGA analysis showed that all 3 ground compounds were accompanied by exothermic processes in which weight losses were recorded in the intervals of about 150 °C - 650 °C with the largest weight loss recorded for the N,S doped Biochar product.

5. CONCLUSION

New methods for the preparation of doped carbon-based nanomaterials by ball milling promise great applications, e.g., as electrode materials, capacitors or supercapacitors, see **Figure 4**. Our products GO, rGO and Biochar were milled on a ball mill in an ammonium sulfate (NH_4SO_4) environment. The elemental analysis and thermal stability of the N,S-doped carbon nanomaterials were determined using TGA/DSC curves. The pilot products of N and S doping inside the carbon structure have great application potential in the future. The experiments will have to be repeated and further analyses (SEM, XRD, XPD) will have to be performed on them to accurately characterize the starting nanomaterials.

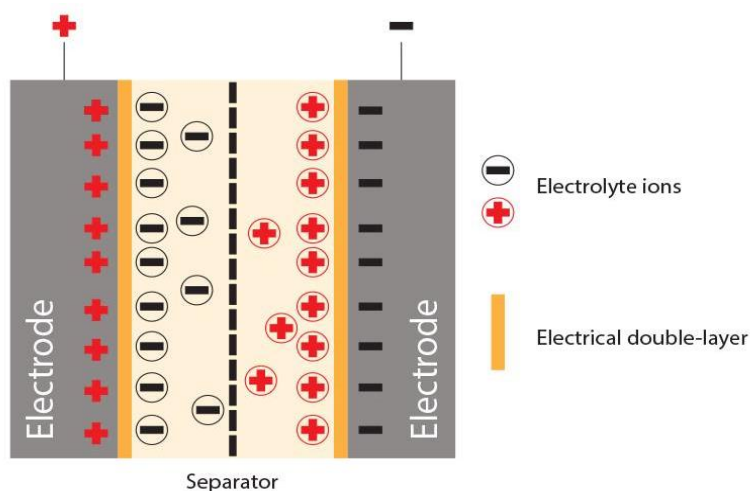


Figure 4 Potential applications of doped carbon nanomaterials

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