

## X-Ray Diffraction Evaluation of the Average Number of Layers in Thermal Reduced Graphene Powder for Supercapacitor Nanomaterial

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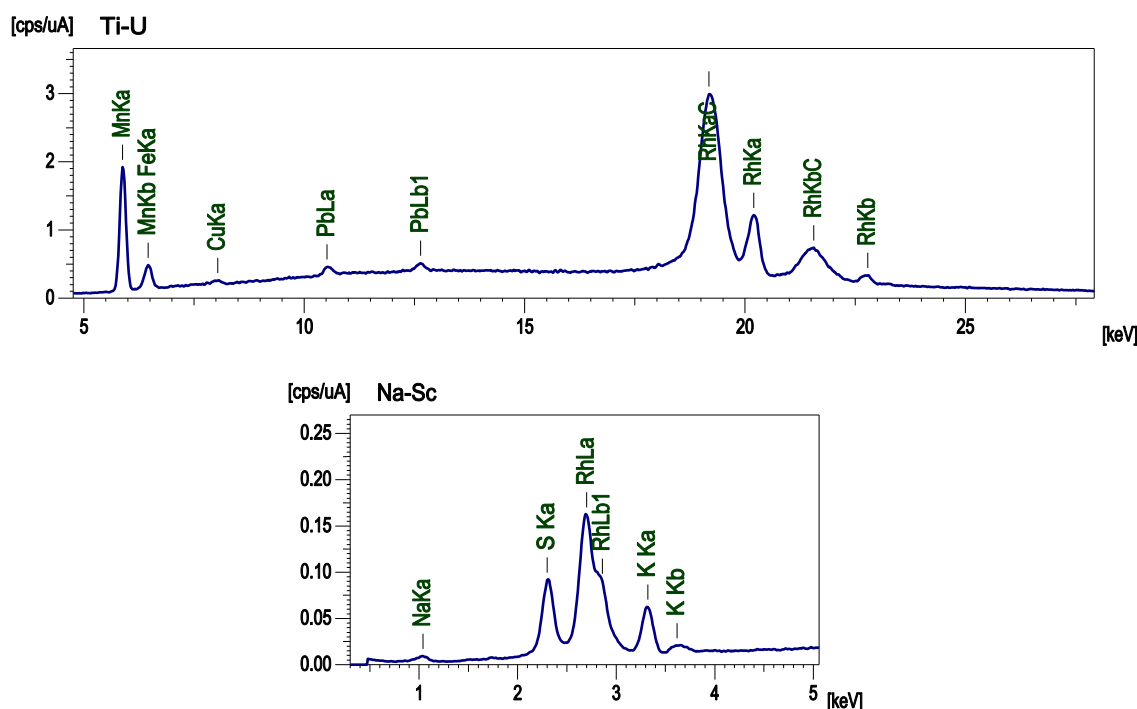
**Abstract.** Graphene oxide (GO) can be partially reduced to graphene-like sheets by removing the oxygen-containing groups and recovering the conjugated structure. In this work, the thermal reduction of GO powder has been carried out using back pumping vacuum pressures and investigated employing X-ray diffraction analysis. The experimental results of estimating the number of graphene layers on the reduced powder at various temperatures (200 – 1000 °C) have been reported. Electrical changes have been produced in a graphene oxide with the vacuum reduction process. This study has shown that the ideal processing temperature for reducing graphene oxide nanomaterial was about 400 °C. It has also been shown that at 600 °C the number of layers in the reduced nanomaterial increased. The internal series equivalent resistance (ESR) has been improved substantially with the vacuum thermal treatment even at temperatures above 400 °C. ESR was reduced from 95.0 to about 13.8  $\Omega$  cm<sup>2</sup> with this processing. These results showed that the process can be applied to the reduction of graphene oxide to produce supercapacitor nanomaterials. The advantage of employing this method is that the processing is a straightforward and low cost thermal treatment that might be used for large amount of nanocomposite material.

### Introduction

Graphene oxide (GO) has been reported to have a high electrical conductivity [1]. However, GO must be reduced in order to improve the electrical conductivity for practical supercapacitor applications [2]. GO materials are typically reduced using a chemical reagent or by thermal annealing, although many other methods have been employed [3-5]. Vacuum reduction, preferentially at lower temperatures, is an essential step for producing supercapacitors using graphene oxide as starting nanomaterial. Recently, thermal reduction of GO under a highly controlled atmosphere was reported; however, the cost of the high vacuum pumps and gas atmosphere controller might result in an extremely high price for reduced graphene oxide (rGO) in larger quantities. In this research, we propose an inexpensive route for the production of rGO under a back pumping vacuum at a variety of temperatures (200–1000°C). Supercapacitors have been prepared using a Na<sub>2</sub>SO<sub>4</sub> electrolyte and the electric properties measured in a computerized analyzer. X-ray diffraction (XRD), X-ray fluorescence (XRF) and thermogravimetric analysis (TGA) have also been employed in this investigation.

## Experimental

Graphene oxide was prepared using a modified Hummers' method [6]. Graphite powder,  $\text{NaNO}_3$ , and  $\text{H}_2\text{SO}_4$  were briefly stirred in an ice bath.  $\text{KMnO}_4$  was then gradually added, and the temperature was kept at about  $35\text{ }^\circ\text{C}$  for one hour. The addition of deionized (DI) water followed by  $\text{H}_2\text{O}_2$  (30 %) generated a change in the color of the solution from dark brown to yellow. The product was washed with DI water,  $\text{NaOH}$  (1 M), and  $\text{HCl}$  (1 M) until the solution reached pH 7. The sample was then centrifuged at 12000 rpm for 10 min. The resultant GO samples were dispersed in ethanol, exfoliated using ultrasonication, and then dried for further analysis. Fig. 1 shows the X-ray fluorescence of the GO powder material obtained from modified Hummers' method. The chemical analysis of this starting material investigated using X-ray fluorescence is presented in Table 1.



**Fig. 1.** XRF energy spectrum of GO powder obtained from modified Hummers' method and used as the starting nanomaterial.

**Table 1.** Semi-quantitative X-ray fluorescence analyses of the prepared GO nanomaterial.

Analyte	Amount (%)	Standard Deviation	Line – Intensity (cps/ $\mu\text{A}$ )
<b><math>\text{Na}_2\text{O}</math></b>	72.64	2.00	(NaK $\alpha$ ) 0.06
<b><math>\text{SO}_3</math></b>	12.47	0.06	(S K $\alpha$ ) 1.07
<b><math>\text{MnO}</math></b>	8.37	0.04	(Mn K $\alpha$ ) 15.40
<b><math>\text{K}_2\text{O}</math></b>	5.28	0.04	(K K $\alpha$ ) 0.62
<b><math>\text{Fe}_2\text{O}_3</math></b>	0.55	0.02	(Fe K $\alpha$ ) 1.22
<b><math>\text{PbO}</math></b>	0.53	0.02	(Pb L $\beta$ 1) 1.86
<b><math>\text{CuO}</math></b>	0.16	0.01	(Cu K $\alpha$ ) 0.67

To reduce graphene oxide, the GO material was placed in a reactor chamber in 200 mg batches. The pressure of the chamber was reduced to  $10^{-2}$  mbar using a mechanical pump and the chamber was then heated. The temperatures investigated ranged from 200 to  $1000\text{ }^\circ\text{C}$  in order to elucidate the thermal reduction of graphene oxide employing thermogravimetric analysis.

The supercapacitor electrodes were prepared by mixing 100 mg of reduced powder with 40 mg PTFE binder and 12.5 mg carbon black conducting agent. The mixture was homogenized in isopropyl alcohol by being stirred for 30 min, and then dried for one hour at oven at 100 °C. The mixture uniaxial pressed (2 t) to produce two electrodes (10 mm diameter).

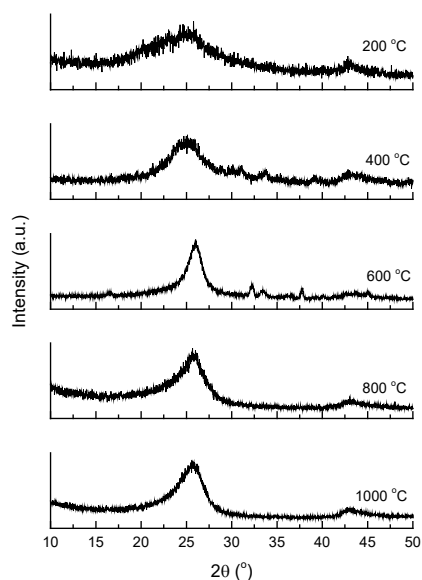
Electrical measurements were carried out at a BT4 Arbin analyzer with Swagelok-type cells in aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte (1 M). Specific capacitance was calculated using de mass of only one electrode ( $I_s=25 \text{ mA g}^{-1}$ ). The series equivalent resistance (ESR) was determined by discharging the fully charged supercapacitor at  $1 \text{ mA F}^{-1}$  for 10 s and reducing the current to zero. The resistance was calculated using this initial potential and the potential after 5 s of null current [6]. All electrical measurements were carried out at room temperature.

X-ray measurements were carried out using Cu Ka radiation. The Scherrer equation was used for estimation of number of 002 planes stacked,  $2\theta$  and the FWHM of the 002 reflection was determinate by Origin software to fitting of peak shape, which was used a Pearson 4 and a Pseudo-Voight 1 function for  $2\theta$  and FWHM, respectively [7-10].

## Results and Discussion

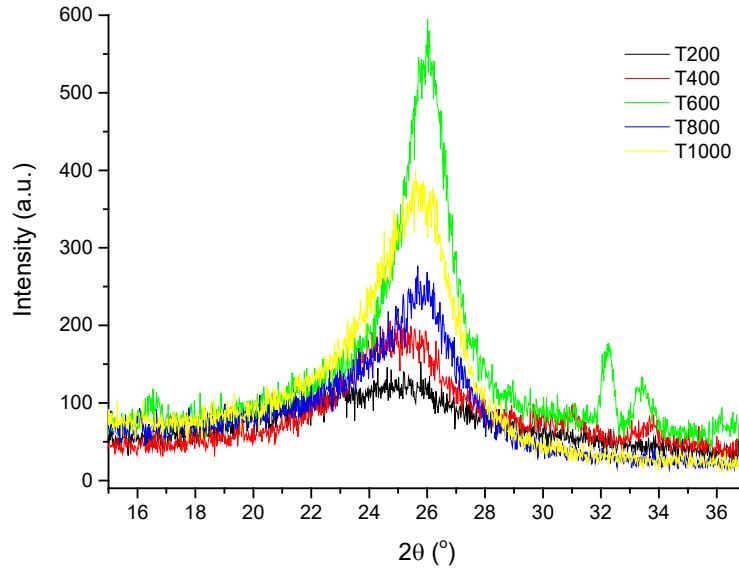
XRD patterns of the GO starting nanomaterial and after thermal reduction at various temperatures are shown in Fig. 2. Vacuum thermal treatment at 600 °C changed somewhat the X-ray pattern. The magnified peak region is shown in Fig. 3. at 600 °C the peak intensity was also somewhat higher.

Table 2 presents the estimated crystallite size ( $L_{002}$ ) and number of planes 00L stacked (N). It can be noted that the highest number of planes was found for processing the GO nanomaterial at 600 °C. On the other hand, the GO nanomaterial showed the smallest number of planes. The number of planes on the nanomaterial processed at 600 °C ( $N=14$ ) was more than twice that of the GO nanomaterial processed at 400 °C ( $N=6$ ).



**Fig. 2.** XRD patterns of the GO starting nanomaterial before and after thermal treatment at different temperatures.

Table 3 presents the electrical properties of the prepared supercapacitors using the processed nanomaterial at distinct temperatures. The GO nanomaterial has been included for a comparison. The specific capacitance diminished substantially for the nanomaterial processed at 600 °C, indicating that a lower temperature is appropriate for reducing the GO nanomaterial. On the other hand, the internal series resistance was consistently improved with higher processing temperatures. This improvement was much less significant as the process temperature was increased from 400 °C to 600 °C, confirming that the ideal processing temperature for supercapacitor applications is about 400 °C.



**Fig. 3.** Detailed view of the analyzed peak region.

**Table 2.** Crystallite size ( $L_{002}$ ) and number of planes 00L stacked (N).

Sample	$L_{002}$	N
GO	13,20	3
200	10,06	4
400	18,65	6
600	43,36	14
800	21,75	7
1000	22,92	8

Thermogravimetric analysis (TGA) plots of GO and GO after thermal processing are shown in Fig. 4. A considerable change on the curves profile can be observed with the vacuum thermal processing at various temperatures. In the GO (black) sample, the major weight was lost between 100 to 300 °C, indicating water desorption from the surface at 100 °C and the gradual decrease in weight from 200 °C to 300 °C is due to the pyrolysis of hydroxyl, epoxide, and carboxyl groups [11-13]. This weight loss diminished with thermal treatment. These features became much less pronounced as the treatment temperature increased.

The gradual decrease of the hydroxyl, epoxide and carboxyl groups at 600 °C promotes an increase of the crystallite size on the [00L] direction and, consequently, on the number of the planes (00L) stacked. Notwithstanding, at higher temperatures, such as 800 and 1000 °C, the loss of the strongly bound inner groups cause the cleavage of the crystalline structure diminishing the number of staked planes.

**Table 3.** Electrical properties of the nanomaterial prepared supercapacitors.

Nanomaterial Condition	C [F] ( $\pm 10\%$ )	Cs [F/g] ( $\pm 10\%$ )	ESR [ $\Omega\text{cm}^2$ ] ( $\pm 10\%$ )
GO	1.35	59.7	95.0
RGO - 200°C	0.98	46.4	62.8
RGO - 400°C	1.32	58.3	15.7
RGO - 600°C	0.69	29.6	13.8

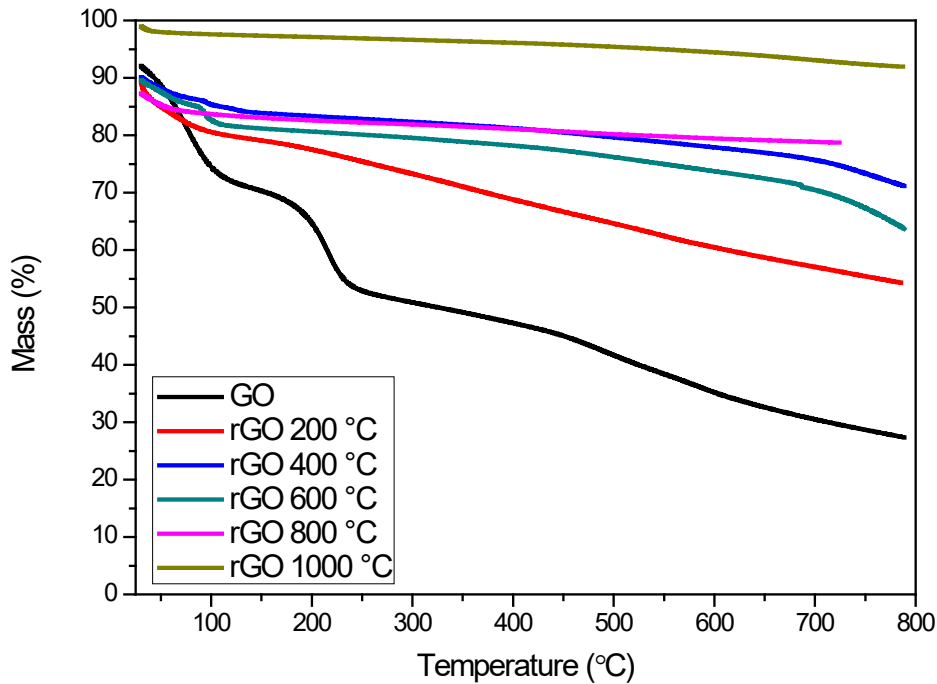


Fig. 4. TGA plots of GO (black) and GO after vacuum reduction.

The reduction of oxygen groups showed at TGA may be explaining the steadily decrease of equivalent series resistance of the supercapacitors. The specific capacitances, before and after thermal processing, are somewhat below to those reported previously [14]. The specific capacitance is influenced by the maximum allowed potential on measurement and organic electrolytes allow higher potential (about 2.7 V) and yield higher capacitances than aqueous electrolytes (~1.23V). Neutral and environmentally compatible electrolytes at low concentration, like the  $\text{Na}_2\text{SO}_4$  electrolyte (1 M) used in the present work, also produces lower specific capacitances than those of toxic organic electrolytes or high concentration corrosive acid/alkaline aqueous ones.

## Conclusion

This study has shown that the ideal processing temperature for reducing graphene oxide nanomaterial was about 400 °C. It has also been shown that higher process temperatures increased substantially the number of layers in the reduced nanomaterial. The highest number of planes (N=14) was estimated for the GO processed at 600 °C. The starting GO nanomaterial showed the smallest number of planes (N=3). ESR has been improved substantially with the vacuum thermal treatment even at temperatures above 400 °C. Vacuum reduction at low temperatures is an essential step for producing supercapacitors using graphene oxide as starting nanomaterial. Thus, the back pumping vacuum process has been considered a promising alternative method of reducing graphene oxide with efficiency and possibly in large scale production. Previously literature reported routes used high (or ultra) vacuum systems, which has a considerable capital, operational and maintenance cost for processing large quantity of nanomaterial.

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