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Graphene Oxides for Application in Non-Faradaic Supercapacitors

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ABSTRACT

Graphene oxide (GO) was the precursor of graphene, which is the material with unique properties how electrical conductivity, thermal conductivity, mechanical etc. Graphene presents the high specific surface of $2,965 \text{ m}^2 \cdot \text{g}^{-1}$, and your electric conductivity has been increased by thermo treatments with elevated temperature, and a consequence has been obtained increase the specific surface and low resistance intern, which is favorable for energy storage. Nevertheless, graphene oxide (GO) has attractive properties by energy storage due to your compatibility with different electrolytes due to functional groups present on the surface of carbon structure.

In the literature, have been reported different methods for the obtained of graphene oxide. However in this work, the synthesis of graphene oxide (GO) was realized by Hummer's modified method, because is a method of obtaining at great scale. The process of synthesis consist of four steps: 1.-Pre-thermal oxidation with oxygen flow, 2.- Chemical oxidation of precursors, 3.- Chemical oxidation for the obtainment of graphite oxide and 4.- Exfoliation of graphite oxide by ultrasonic to obtaining the sheets of graphene oxide (GO).

GO obtained was characterized physically and chemically by SEM, EDAX and RAMAN. Also, the GO was evaluated electrochemically by voltammetry cyclic as different scanning rates at 5, 10, 20, 30 and 50 mV/s and limit potential of 0 to 1 V. For realize to the electrochemical characterization of material, this was deposited on carbon cloth electrode of 1 cm^2 .

Keywords: Supercapacitors, (GO) Graphene Oxide.



1. INTRODUCTION

Electrochemical capacitors (EC) are often called supercapacitors or ultracapacitors as a result of having a high capacitance in a small amount of area. These devices have been used as energy storage and are classified by mechanism of energy storage, devices; there are two kinds of supercapacitors: the electric double layer capacitors and redox pseudocapacitors [1].

The Electric Double Layer Capacitors (EDLC's) works by accumulation of the electrostatic charges on the surface of electrode-electrolyte, by separation or deposition of electrons in anodes and cathodes, which in turn induced by an applied potential across the device [1]. The positive or negative charge on the surface is balanced by an accumulation of counter ions (ions of opposite charge) of the solution, forming a double-layer of positive or negative charges (or vice versa), these devices employ carbon to generate a load double Layer [2], development of these devices emphasizes the importance of designing new materials to improve the power delivered and the energy storage EDLCs, which include nanostructured materials of carbon aerogels, carbon nanotubes and graphene, etc.

The mechanism by storage energy in the case of pseudocapacitors, is due to both processes EDL and faradic or redox, in conditions thermodynamics defined potentials and the electrode surface and are responsible for accumulation and release a capacitive charge which depends on the repulsive forces between electrolyte absorbed or intercalated ions which performance an important role in extending the operating potential for the development of capacitive charges, on the contrary a force weak repulsive or attractive between ions severely limits the useful operating window [3]. Pseudocapacitive materials generated a significant attraction due to the number of electrons transferred in the redox process which can be compared with the capacitive charge of the EDL; between these materials may be mentioned intrinsically electro-conductive polymers, and metal oxides[1].

The performance of a supercapacitor too dependent on the materials you choose to build their anode and cathode electrodes, between the characteristics of the materials must meet to satisfy the conditions of the electrodes can be found graphene. The graphene is sheet monatomic carbon atoms attached through bonds covalent sp² (monolayer of graphite) [4], until 2004 did not believe it is possible existence as an isolated sheet, as it is supposed to strictly two-dimensional crystals are thermodynamically unstable. Graphene is a special case of semimetal and has a zero gap metal, having the peculiarity that the density of states at the level of Fermin is zero. Graphene tends to adsorb molecules on its surface, this coupled with its high specific surface area (2600m²g⁻¹) , mechanical strength and high conductivity postulated as a possible successor as electrodes of supercapacitors EDLC[5]

Nevertheless, the graphene in reduced state presents weak interaction with electrolyte. The graphene oxide (GO) is one of the most crucial derivatives of graphene, and it exhibits a layered structure with oxygen functional groups bearing the basal planes and edges. The existing functional groups such as carboxyl and hydroxyl groups tend to improve the hydrophobicity of basal planes. The ECs fabricated with the graphene-based electrodes display an exciting potential with high rate capability and reversibility[6].

2. EXPERIMENTAL



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To synthesize graphite oxide proceeded to weight 20 g of graphite flakes by Sigma Aldrich with a percentage purity of 70%, the sample was heated to 250 ° C in oxygen saturated atmosphere, this temperature was maintained for 4 hours to remove impurities[4]. Posterior, was applied the method of. Hummer's to synthesize graphite oxide[7] and then graphene oxide (GO). This method employs two stages, first to remove ions and acids with a pre-oxidation thermal of graphite using 2 L of hydrochloric acid solution ratio at 1:10 and the second step is to wash the sample with 2 L of deionized water to remove residual acid for a week in an ultrafiltration cell by Millipore Amicon, after the sample is dried at 60 ° C for 48 hours.

Following, 20 mg of graphite oxide obtained is carried out by chemical reduction by adding 20 ml of a 0.1M solution of sodium boron hydrate; the reduction is realized when the graphite oxide changes your coloration from brown to black, then is begins the hydrogen secondary reaction [8, 9]. The mixture was stirring by ultrasonic bath during one hour for reduced graphene sheets (CRG), and posterior were washed with deionized water and filtered with Millipore Amicon ultrafiltration cell. The sample was dried of vacuum oven at 60 ° C for 24 hours to remove residual water. Finally, 2 mg of reduced graphene was placed in 20 ml of ethylene glycol and was stirred inside an ultrasonic bath for one hour.

The samples were characterized by Raman spectroscopy is a technique which can be inferred in several material properties such as chemical and structural, the depth of analysis extends only a few nanometers in the sample by which is considered a non-destructive technique surface [10, 11]. 2 samples were prepared for spectroscopy Raman, depositing on a microscope slide 100 μ L of a solution graphene oxide concentration of 5mg in 20ml of ethylene glycol and 100 μ L of graphene reduced, which were heated to 190 ° C to evaporate all the ethylene glycol.

For the evaluation of the performance electrochemical of these materials, there materials were characterized by cyclic voltammetry was used a cell of three electrodes, the work electrode (WE) was the carbon cloth electrode of 1cm² of area and this was deposited 400 μ L of reduced graphene solution as the concentration of 2mg/20mL in ethylene glycol. The counter electrode (CE) was a graphite rod with 0.5mm of diameter and as the reference electrode (RE) was used a saturated calomel electrode (SCE). For the tests, was used a solution 0.05 M of H₂SO₄, as the electrolyte, and the window potential of 0 to 0.9 V vs. SCE x 5 cycles at different sweep rates.

3. RESULTS AND DISCUSSION

Morphology changes of graphite oxide by oxidation process, was realized by SEM analysis and by EDAX was determined by elemental analysis. In the figure 1a shows the morphology of graphite flakes by Sigma Aldrich at 70% of purity. Figure 1b shows the morphology of graphite oxide. In this case, the graphite oxide shows mayor irregularity and mayor roughness with respect to graphite (figure 1 a) due to the process of oxidation; this is confirmed with the percent of oxygen present in the sample (Table 1). By means of EDAX analysis was obtained an



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average percentage of elements for the two samples, the average was obtained taken six different areas and the values are presented in the Table 1.

There values show differences between graphite and graphite oxide, correspondent to contain of carbon and oxygen, principally. For the case of graphene oxide is observed an increase of contained of oxygen and diminished of carbon, this is possible of the formation of oxygen functional groups.

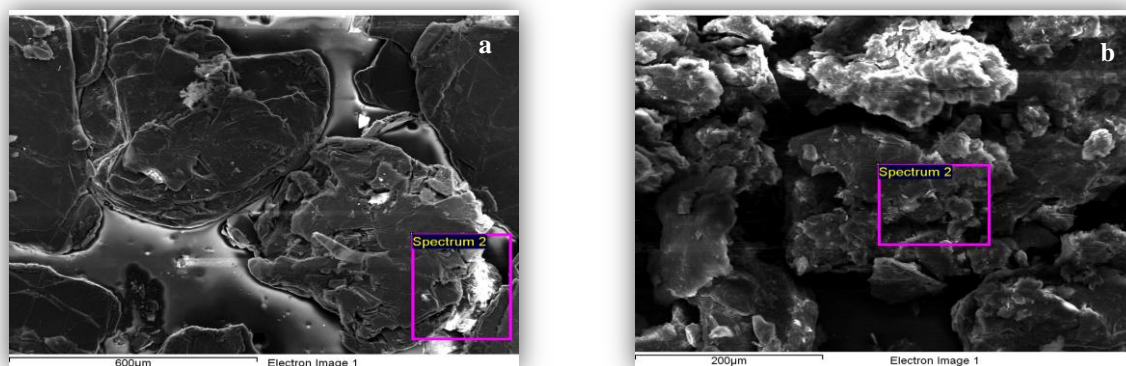


Figure1: SEM images obtained for two different samples: a) graphite flakes at 70% of purity and b) graphite oxide obtained.

Table 1: EDAX analysis for elements present in the samples.

Flake graphite		Graphite oxide	
Element	%	Element	%
C	88.97	C	59.77
O	9.78	O	37.75
Mg	0.05	Si	0.986
Si	0.55	S	0.416
Ca	0.10	Cl	1.022
Fe	0.22	Al	0.054

By mean of Raman spectroscopy can be confirm the obtained of graphene reduced and graphene oxide. However, the equipment used to perform the analysis in this occasion is limited, therefore only be observed the first-order spectrum. For the case of perfect graphite, the first-order of spectrum Raman includes a very narrow and intense peak around of 1580cm^{-1} , this band is called G and its relationship with the graphitic order. This band is shown at 1580 cm^{-1} of Raman shift for highly ordered pyrolytic graphite (HOP) [10], (see Figure 2) which was used as background to compare with the obtained graphene.

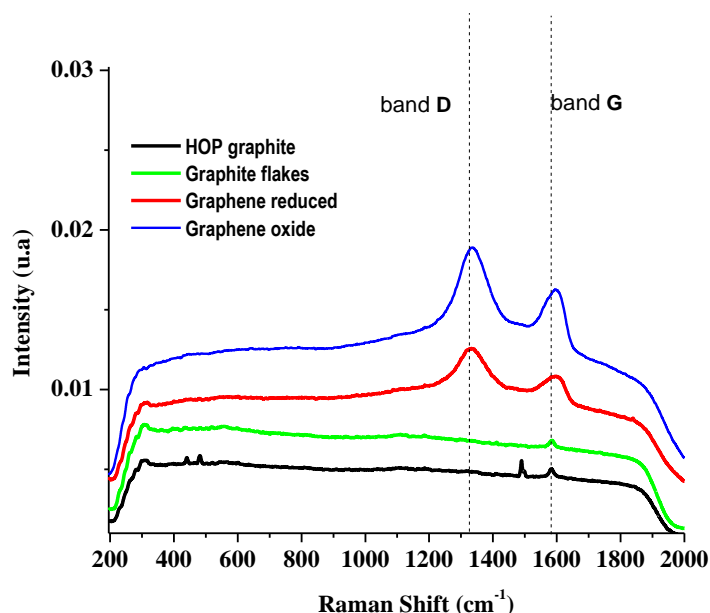


Figure 2: Spectra Raman of graphite flakes (green), HOP graphite (black), graphene oxide (blue) and graphene reduced (red)

Conform the graphite loses its structural order by the introduction of defects caused by oxidation processes, shows the apparition of a band located around 1360cm^{-1} called D [11]. In the figure 2 is showed the appears in the curve of graphene oxide this band at 1339cm^{-1} ; in graphene reduced this band appears at 1333cm^{-1} . One of the parameters employed by determined the graphitic order is the ratio of the intensity of the band D with respect to the band G (I_D / I_G). However there comes a point at which the ratio I_D/I_G decreases with increasing the disorder, due to the disappearance of the aromatic rings, which leads to decreasing the intensity of the band D. Table 2 shows the relationship between the intensity of these two bands characteristics obtained from Raman spectra by different samples prepared.

Table 2: Ratio between the intensities of bands D and G

Sample	Intensity D	Intensity G	(I_D/I_G)
Graphene oxide	0.018	0.016	1.1
Graphene reduced	0.012	0.010	1.2

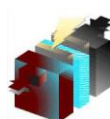


Figure 3 shows the cyclic voltammetry obtained from a sweep rate of 80 mV s^{-1} for the carbon cloth electrodes modified and without modified. The curves correspond to the electrodes with graphene oxides and graphene reduced. The Figure 3 b shows low values of current density for carbon cloth electrodes with and without ethylene glycol.

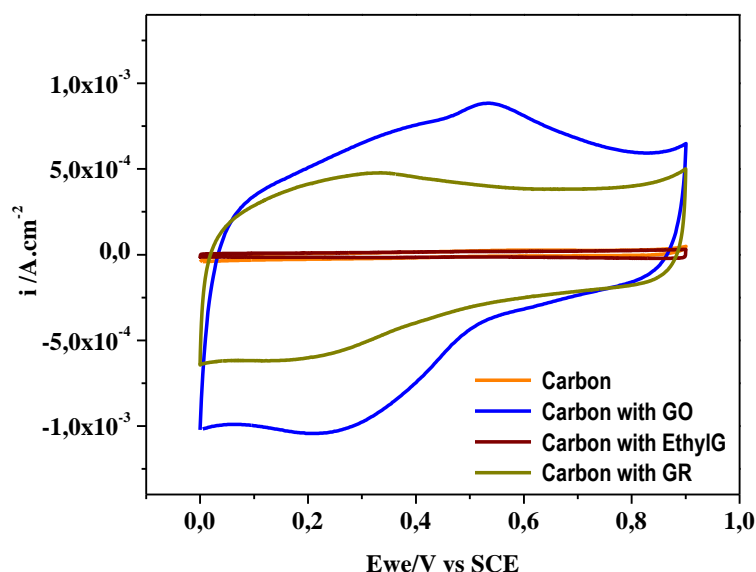


Figure 3: Cyclic voltammetry for electrodes of carbon electrodes with and without ethylene glycol, with graphene oxide and with graphene reduced at 80 mV s^{-1} vs SCE.

In the curve of the electrode graphene oxide shows an increase of values of current density with respect to the other materials, additionally presents a peak at 0.52V which is derived from oxidized graphene, this phenomenon is similar to the processes denominate as pseudocapacitance which is attributed to functional groups of oxidants [11]. With respect to the curve of the graphene reduced is observed decreased values of current density and decreases of the peak around the 0.52V as consequence of the reduction processes of the sample. The curve corresponds to graphene reduced present most rectangular shape and ideally forms by material of supercapacitores. Also was observed what the increase of the current densities depositing the active material (around of $4 \times 10^{-6} \text{ g}$) by electrode. Comparing the curves correspond to graphene reduced and graphene oxide with respect a cloth carbon and cloth carbon with ethylene glycol can be observed what in the two first cases is observed values mayors of current density comparing with the last two cases.

Capacitance values of the electrodes with graphene reduced and graphene oxide was calculated according to

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the following equation, from the curves of cyclic voltammetry [2, 12].

(1)

where C is the specific capacitance based on the mass of material electroactive ($\text{F}\cdot\text{g}^{-1}$), I it is the current density response (A cm^{-1}), v is the sweep rate (mV s^{-1}), m is the mass of electroactive materials in the electrodes (g) y V is the potential applied the device (V). The values of specific capacitance of graphene oxide and reduced graphene are shown in Table 3.

Table 3: Values of capacitance and specific capacitance obtained by graphene reduced and graphene oxide.

Sample	Capacitance (F)	Specific capacitance (F g^{-1})
Graphene oxide	0.0154	3854.5
Graphene reducid	0.0096	2408.7

4. CONCLUSIONS

It can be concluded that the graphite flakes tend to increase the percentage of oxygen after applying oxidation, indicating the effectiveness of the process. Raman spectroscopy confirmed the modified in the structure of graphene reduced and the graphene oxide with respect at the graphite. The curves obtained by cyclic voltammetry of the graphene oxide and the reduced graphene showed specific capacitance around to 2408.7 F g^{-1} with only $4 \times 10^{-6} \text{ g}$ active material, therefore become attractive materials for use as electrodes for supercapacitors.

5. ACKNOWLEDGEMENTS

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