TUNING GRAPHENE PROPERTIES BY A MULTI-STEP THERMAL REDUCTION PROCESS

Patricia Álvarez[a*], *Clara Blanco*[a], *Ricardo Santamaría*[a], *Patricia Blanco*[a], *Zoraida González*[a], *Laura Fernández-García*[a], *Uriel Sierra*[a], *Marcos Granda*[a], *Antonio Páez,*[b] *Rosa Menéndez,*[a]* .

[a]Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain.

[b]REPSOL, Centro de Tecnología, Carretera de Extremadura, km 18, 28935 Mostoles, Madrid

ABSTRACT. A multi-step thermal reduction process to produce graphene from graphite oxide was developed to optimize the degree of reduction, its BET surface area and its suitability as electrode in electrochemical energy storage devices. The procedure combines an initial flash pyrolysis to a temperature below 460ºC and a subsequent ramp-heating treatment up to the selected final temperature. With this methodology, the morphology of the graphene materials obtained, which have a great influence in its properties as electrodes, is controlled.

Graphene is a sp^2-hybridized carbon monolayer that has attracted a great deal of interest in recent years due to its inherent electronic and mechanical properties[1]. The chemical methods for producing graphene materials via the formation of graphite oxide are among the most suitable due to their simplicity and easy scalability[2]. The methodology comprises an initial graphite oxidation step followed by exfoliation and reduction to obtain the final graphene. Alternatively, thermal exfoliation/reduction of graphite oxide[3] can be applied, rather than other types of reduction (chemical, electrochemical, etc.)[4] to prepare graphene materials for applications such as energy storage, composites or biomedicine. The efficiency with which graphene sheets are produced by the thermal exfoliation/reduction of graphite oxide depends on the degree of oxidation of the graphite. One of the requirements is that a sufficient amount of pressure is built up in the initial stages of the heat treatment.[5] The characteristics of the graphene materials obtained, which will determine the applications for which they are best suited, are greatly affected by the experimental conditions. Most of the studies in this field are focused on controlling the degree of reduction of graphene materials by means of temperature. The majority of the treatments described in the literature involve the thermal heating of the graphite oxide sample up to the desired temperature in a single step to obtain graphene materials with different structural properties. An example of this is the rapid heating of graphite oxide (on a hot plate) up to a temperature of 400 ºC in a single step to produce bulk quantities of single functionalized graphene sheets

* *Corresponding authors*: E-mail: rosmenen@incar.csic.es (Rosa Menendez). E-mail: par@incar.csic.es (Patricia Alvarez)

from a flake graphite oxide, a method that gives rise to problems in certain applications.[6] Another example is the thermal exfoliation/reduction of graphite oxide at different temperatures ranging from 127 ºC to 1000 ºC at a slow heating rate. [7] In general terms, the sheets experience less alteration but the resultant graphene materials have been reported to have low BET surface areas. With thermal flash heating up to 1050ºC in a sealed tube[5,8], graphene materials with high BET surface areas are reported to have been obtained by some authors. However, there is no mention about other properties (e.g. processability for subsequent applications). In any case, the use of single-step thermal treatment does not allow the properties of the materials to be tuned as, once the final temperature has been fixed, the resulting properties (C/O ratio, BET surface area, processability…) are also fixed.

In an attempt to prepare graphene materials with controllable characteristics, a multi-step exfoliation/reduction procedure was investigated by Zhang et al.[9] These authors made use of a sequential thermal treatment consisting of an initial stage of low thermal temperature exfoliation at 700ºC using a fast heating ramp (a heating rate of 100 ºC/min) followed by a second thermal treatment where the reduced graphene oxide sheets were annealed at 1500 ºC and 40 MPa uniaxial pressures were applied for 5 min under vacuum. The graphene materials obtained showed a high electron mobility and no appreciable oxygen content (i.e., no D peak was detected on the Raman spectrum). However, for certain applications (e.g., active electrode materials in vanadium redox flow batteries), a certain amount of residual oxygen might be desirable. [10]

The aim of this paper is to find a route for the preparation of graphene materials with controllable characteristics from graphite oxide by thermal treatment in order to optimize their degree of reduction and BET surface area and maximize their suitability as electrodes in electrochemical energy storage devices. To this end, we have developed a multi-step procedure that combines both initial flash pyrolysis up to a certain temperature and subsequent thermal treatment up to the final temperature in order to achieve the desired degree of reduction, and we have compared it with the traditional thermal exfoliation/reduction process in a single step (either by ramp or by flash pyrolysis). The graphene materials obtained from the different processes are characterized in terms of BET surface area, reduction degree and suitability for their application as electrodes.

A graphite oxide obtained by a modified Hummers method[11] from one synthetic petrochemical graphite was employed in this study (a detailed characterization of the graphite oxide can be found in the supporting information (S.I.)). Its thermal exfoliation/reduction at 700 and 1000ºC by ramp pyrolysis in a single step gave rise to partially reduced samples (SS-GO-700 and SS-GO-1000), with a C/O ratio, calculated by elemental analysis of 15 and 135 and BET surface areas of 210 and 207 m^2g^{-1}, respectively (Table 1, entries 1 and 7), which directly affected the volume of these samples (see S.I.). Furthermore, their DMSO

suspensions only remained stable for short periods of time (less than 48h, Table 1, see S.I.). The samples were easily processed into disk-shaped electrodes for electrochemical energy storage devices by mixing them with PVDF as binder (30 wt.%), as shown in Figure 1a. The resulting electrodes retained their initial shape after the addition of the corresponding electrolyte (Figure 1b) and were found to be suitable for their application as electrodes in redox flow batteries despite their relatively low surface area (see S.I.).

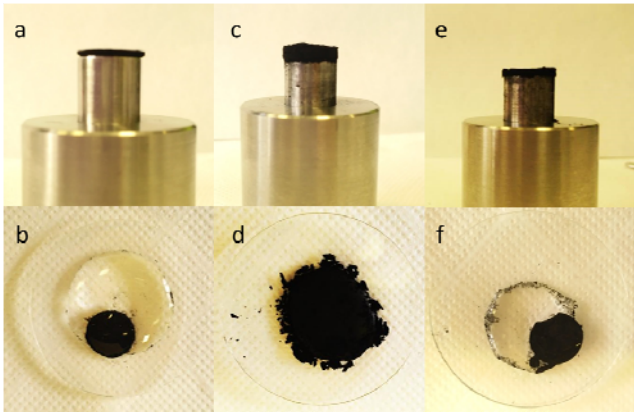

Figure 1: electrodes obtained from thermally reduced graphene oxides SS-GO-700 (a,b) SS-GO-700FP (c,d) and MS-GO-400/700 (e,f)

It is desirable, however, that the thermally reduced graphene materials prepared have an enhanced surface area. In this regard, it was observed that single-step flash pyrolisis of the graphite oxide up to the same final temperature (700ºC, SS-GO-700FP) gave rise to a graphene material with a similar C/O ratio but significantly higher BET surface area, 520 m^2g^{-1} (Table 1 entry 2) than that obtained by a single ramp heating step up to 700ºC, which is in agreement with results previously described in the literature.[5] Furthermore, the corresponding DMSO suspensions were observed to remain stable for long periods of time (Table 1, and see S.I.). Such a high BET surface area might be desirable for certain applications such as that of electrodes in batteries or supercapacitors. However, the disk-type electrodes conformed from SS-GO-700FP (under the same experimental conditions as those mentioned above) were not only found to be thicker than the previous ones (3 mm for SS-GO-700FP instead 1 mm in the case of SS-GO-700, Figure 1c) but also unstable after the addition of the electrolyte (H_2SO_4, Figure 1d). In this case, the adsorption of the electrolyte seems to be too abrupt probably due to the formation of a specific porous structure which leads to disaggregation of the conformed electrode.

In order to explain these findings, SEM images of the flash-pyrolyzed and ramp-heated samples were analyzed (Figure 2 a,b). The results show in both cases the formation of tridimensional structures derived from the expansion of the graphite oxide on heating, which is the factor responsible for the development of porosity in graphene materials. However, in the case of the flash-pyrolized sample (Figure 2a) cavities with

sizes pertaining to the mesopore range are observed, which cause an increase in the BET surface area (Figure 2a). The fluffy appearance of the graphene obtained by this procedure was previously reported[5]. These structures are not so abundant in the ramp-heated sample which is the reason for its lower BET surface area (Figure 2b)[7].

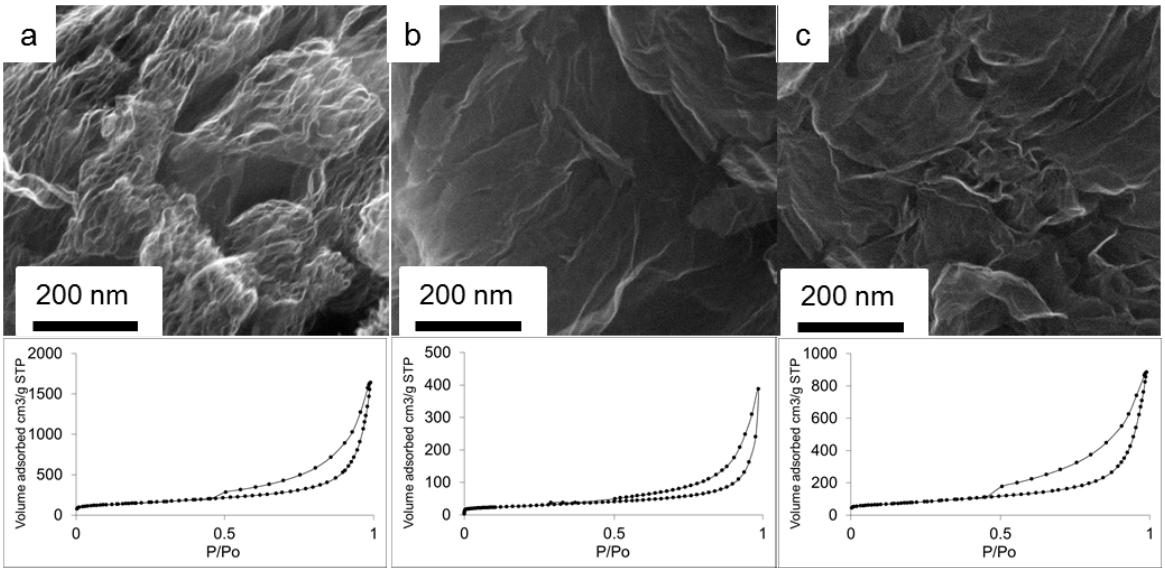

Figure2: SEM image (up) and BET curves (down) of a) SS-GO-700FP, b) SS-GO-700 and c) MS-GO-300/700

To overcome the problems involved in processing these materials into electrodes and to ensure that their BET surface area remained high, we have developed a multi-step procedure (series MS-GO-T1/T2) in which the graphite oxide is first flash-pyrolyzed at a controlled temperature (T1) and then ramp-heated up to the desired final reduction temperature (T2). The degree of reduction achieved in every case (measured as the C/O ratio calculated by elemental analysis) is similar to that obtained by the single step procedure up to the same final temperature (ratios of 15-16 for a T2 of 700ºC Table 1, entries 3, 4 and 5 and 129 for T2 a of 1000ºC, Table 1 entry 9), thus evidencing that temperature is the main factor that determines the degree of reduction of the graphene materials. It needs to be emphasized, however, that the multi-step procedure has a marked effect on the BET surface areas of these graphene materials. That is, they are much larger than those of the samples obtained by the single ramp heating treatment (entries compared: 1 with 3, 4 and 5 and 7 with 9) and similar to, or lower than, those obtained by single flash pyrolysis (entries compared: 2 with 3,4 and 5). Additionally, the DMSO suspensions prepared from these multi-step processed samples remain stable for long periods of time (more than 48h, Table 1), unlike those obtained from the single step ramp heated samples, and they can be satisfactorily processed into disk type electrodes (see as an example MS-GO-400/700, Figure 1 e,f) which exhibit an appropriate thickness, a suitable stability once the electrolyte has been added and improved performance in redox flow batteries than the one obtained by a single step being

the increased BET surface area one of the main parameters influencing such improved electrochemical behavior (see S.I.). The explanation for this can be found in the SEM images of these samples (Figure 2c) which show the presence of a tridimensional structure with only partial structural development in the mesopore range. The formation of mesopore-range structures is more pronounced at higher initial flash pyrolysis temperatures, confirming that the initial flash pyrolysis step (and more specifically, the difference between the temperature of the flash pyrolysis and the blasting temperature of the graphite oxide) is the main factor that increases the BET surface area (Table 1 entries 2, 10 and 12). In the case of ramp-heated samples, the formation of those structures is not favored leading to low BET surface areas at any temperature above the blasting temperature (Table 1 entries 1, 7 and 11). Furthermore, the sample obtained using the two-step mode but always with ramp-heating in both cases (pseudoMS-GO-460ramp/700**)** showed S_{BET} values similar to those obtained in the single ramp-heating step (Table 1 entries 1 and 6) and the formation of 3-D structures that had not completely developed in the mesopore range. Therefore, in order to optimize the application of these samples as active electrode material, the temperature (T1) of the initial flash pyrolysis must be kept below a certain value (460ºC for this particular GO, see for example MS-GO-700/1000, Table 1, entry 8) to prevent the 3-D structures in the mesopore range from completely developing. If they were allowed to fully develop, they could not be modified in the second thermal treatment, resulting in a sample with a high BET surface area, but quite unsuitable as electrode (leading to disaggregation, as previously observed).

Table 1: Reduction conditions of the graphite oxide studied and main characteristics of the graphene materials obtained

Entry	**Sample**	**Heating ramps**		**BET**	**C/O**	**Dispersion**	**Electrode Conformation**
		1º	2º	(m^2g^{-1})			
1	**SS-GO-700**	5ºC/min	-	210	15	Precipitates	Yes
2	**SS-GO-700FP**	flash	-	520	15	Stable	No
3	**MS-GO-300/700**	flash	5ºC/min	270	15	Stable	Yes
4	**MS-GO-400/700**	flash	5ºC/min	450	15	Stable	Yes
5	**MS-GO-460/700**	flash	5ºC/min	530	16	Stable	Yes
6	**pseudoMS-GO-460ramp/700**	5ºC/min	5ºC/min	200	15	Precipitates	Yes
7	**SS-GO-1000**	5ºC/min	-	207	135	Precipitates	Yes
8	**MS-GO-700/1000**	flash	5ºC/min	480	132	Stable	No
9	**MS-GO-400/1000**	flash	5ºC/min	355	129	Stable	Yes
10	**SS-GO-1000FP**	flash	-	569	127	Stable	No
11	**SS-GO-300**	5ºC/min	-	261	3	Precipitates	Yes
12	**SS-GO-300FP**	flash	-	395	4	Stable	Yes

To summarized, it has been demonstrated that by means of the multi-step procedure developed in this study it is possible to prepare graphene materials with a suitable C/O ratio (depending on the final temperature selected), an increased BET surface area (compared to that of the material prepared by the single-step ramp-heated material) and easily conformable into stable electrodes for electrochemical energy storage devices.

ACKNOWLEDGMENT: The authors thank REPSOL for their financial support. Dr. P. Alvarez also acknowledges MICINN for her Ramon y Cajal contract. Work patented (ref: EP14382352.4)

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