MODULATING THE DEGREE OF STRUCTURAL ORDERING OF CARBON GELS

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Introduction

Synthetic carbons with very well controlled porous structure can be obtained from polymerization of resorcinol (R) and formaldehyde (F) through a sol-gel process. Varying the synthesis conditions, mainly amount of precursors and pH of the precursor solution, carbons with different textural properties are obtained. The synthesis conditions lead to a three dimensional network of interconnected clusters of RF polymer. The size of the clusters and the crosslinking degree determine the mean pore size of the resultant carbon in the meso or macropore range. These materials present an amorphous carbon structure, but for certain applications it would be necessary to develop graphitic structures in order to increase the electrical conductivity, to decrease microporosity, to improve the mechanical resistance or just to minimize the chemical reactivity of the carbon materials, besides the controlled porosity performed during the polymerization process. That could be achieved by different approaches such as (i) adding some additives to the precursor solution prior synthesis that provide ordered structures in the RF polymeric matrix, (ii) high temperature post-treatment of the RF polymers or (iii) a combination of both approaches. In this work the different approaches were performed and evaluated in terms of electrical conductivity, structural order degree and porosity of the final carbons.

Materials and Methods

RF gels were obtained from polymerization of resorcinol and formaldehyde in water under microwave heating. Control of the porous structure of the RF gels was performed by tuning synthesis variables such as R/F ratio, dilution ratio D, pH of the precursor solution, etc[1]. It is also possible to incorporate any additive to the precursor solution of the RF polymer as long as it is a stable suspension in water. Thus, graphene oxide can be added to this initial mixture and due to its reactivity it can be incorporated to the polymeric network[2].

Samples were carbonized at 1000ºC in order to eliminate all oxygen functionalities, and further thermal treatments were performed at 2800ºC for reorganization of the carbonaceous structure and increasing the structural order. Porous properties were evaluated by helium density, mercury porosimetry and N_2 adsorption-desorption isotherms at -196ºC. The carbonaceous structure was characterized by XRD, SEM and HRTEM. Electrical conductivity was also determined by the four-point probe technique.

Samples carbonized (i.e. treated at 1000ºC) were denoted as C and samples graphitized (i.e. treated at 2800ºC) were denoted as G, followed by GO (only if graphene oxide was added to the precursor solution) and the mean pore size of the sample. Thus, sample G-GO-1000 stands for a sample treated at 2800ºC, obtained with graphene oxide in the precursor solution, with a final mean pore size of 1000 nm.

Results and Discussion

Samples with different pore size in the range of meso and macropores can be easily obtained by means of microwave heating in a one-pot process of ca. 5 hours. Carbonization of these samples at 1000ºC leads to carbon gels with certain microporosity and the meso/macroporosity designed by the previous synthesis conditions. Further treatment at higher temperatures (i.e. 2800ºC) induces a reorganization of the carbonaceous structure that results in the considerably decrease of the microporosity of the resultant samples. This means that although carbon gels are amorphous materials, the graphitization process brings about certain order to the carbon structure with the coexistence of amorphous and graphitic structures. The latter ones are favoured by the size of the polymeric clusters, which implies that the bigger the clusters the wider the pores and the higher the graphitic degree of the resulting materials. The incorporation of graphene oxide to the precursor solution implies an increase of conductivity in the carbonized samples. However the graphene structures imbibed in the polymeric network are exfoliated at high temperature and wide pores are obtained.

Table 1. Characterization parameters of the samples studied

Sample	Graphitic degree (%)	S_{BET} (m^2/g)	Conductivity (S/m)
CX-10	-	610	100
CX-100	-	591	200
CX-GO-10	-	605	300
G-100	8	71	1600
G-300	23	22	1700
G-GO-1000	33	29	1500
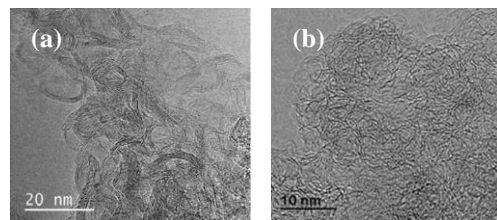
Figure 1. HRTEM images of some of the samples studied (a) G-GO-1000 (b) CX-100

Conclusions

There is an influence of the polymeric cluster size (and thus the pore size) on the graphitization degree of the RF gels. It seems that the bigger the cluster, the higher the graphitic degree of the sample. However, there is always co-existence of amorphous and graphitic structures in RF polymers. Graphene oxide may induce a higher graphitization degree, but also wider pores and both properties have an opposite influence on the electrical conductivity in the final sample.

References

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