

ECO-FRIENDLY METHODOLOGY FOR THE SYNTHESIS OF GRAPHENE-BASED CATALYTIC MEMBRANE REACTORS

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INTRODUCTION

Carbon-based structures characterized by a polygonal cell distribution are commonly named random networks [1,2]. On the other hand, well defined, molecular and therefore nanometric networks such as fullerenes [3], nanotubes [4] and graphene [5] have been some of the most remarkable discoveries in the area of carbon research in recent years. Another ill-defined type of randomly carbon network is that corresponding to the microporous structure of activated carbons (AC). So, three carbonaceous network structures can be considered according to the dimension: the molecular (fullerenes, nanotubes, graphene), the micro (microporous carbon), and the macro (macroporous carbon). Although in the case of carbon materials, synthetic routes for both molecular-networks and micro-networks have been extensively investigated [3,6], few studies exist regarding the synthesis and characterization of random networks of carbon [7-11]. This work presents the synthesis and characterization of 2D and 3D polygonal random networks of carbon (RNC) from the controlled pyrolysis of saccharose in absence or presence of KOH.

METHODOLOGY

The synthesis, the topological definition, the activation and characterization of RNC have been reported in previous works [7-10]. In a typical synthesis 2 g of D(+)-saccharose was placed inside a 50 mL Pyrex beaker and dissolved in 1 mL of water or in 1 mL of aqueous solution (34 wt%) KOH and stirred at 80°C until a viscous and light brown solution was observed. The solution is left in rest until achieving the recrystallization of the saccharide. Then, the sample was submitted to two consecutive heat treatments. First, at low temperature inside a vacuum oven at 130°C, for 10 min. The second one in a ceramic muffle under N₂ flow at 450°C. The carbonaceous macro-networks were denoted as A_{NW-1} and A_{NW-2}, for the saccharose dissolved in water or in KOH solution, respectively. Different temperatures and times under N₂ or CO₂ flow were used for the activation of porous framework [9]. Characterization of A_{NW-1} and A_{NW-2} was performed by N₂ adsorption-desorption isotherms, XRD, XPS, RAMAN, FTIR, EPR, SQUID, NEXAFS and XANES.

RESULTS AND DISCUSSION

Fig. 1 shows the optical images of the bi-dimensional (2D) macroscopic RNC obtained in presence of KOH (A_{NW-2}). The topological properties of the 2D-RNC are significantly different from other 2D cell structures [7,8]. The polygonal distributions of the macro-networks from the A_{NW-1} (Saccharose + H₂O) and A_{NW-2} (Saccharose + KOH) showed the pentagon was found to be the most abundant polygon in the 2D RNW. In previous works [8,9] we showed the activation of the present RNC can be easily achieved by physical activation under CO₂ flow or by pyrolysis under N₂ flow, with BET surface areas up to 850 and 981 m².g⁻¹ [9].

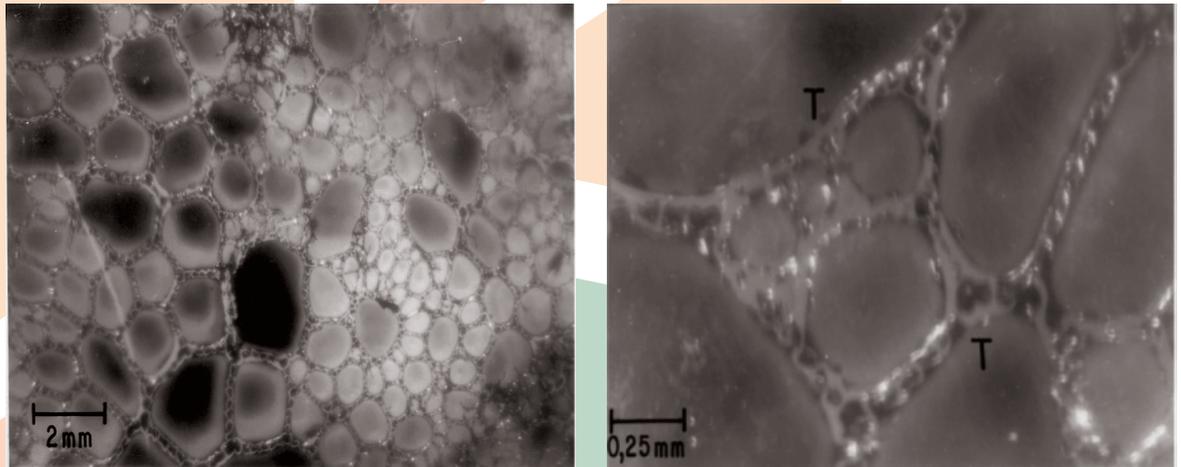


Fig. 1. Images of the 2D carbonaceous macro-network film from the A_{NW-2} sample adhering to the pyrex beaker. (Left): Typical random pattern showing the predominance of five-sided cells. (Right): A subsection showing the presence of "T" type vertices with internal angle $\theta = 180^\circ$.

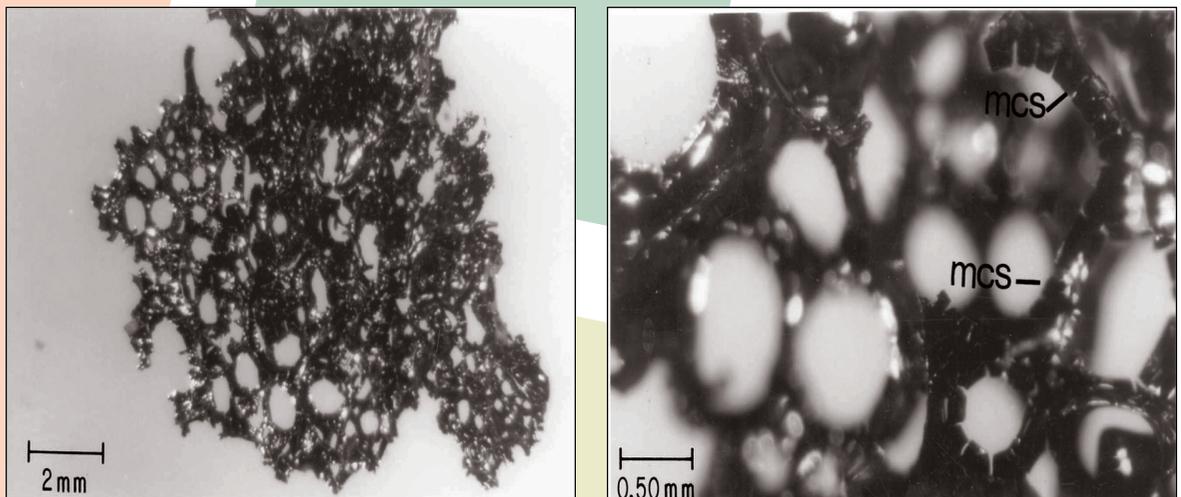


Fig. 2. Image of bulk carbonaceous macro-network from the A_{NW-2} sample. (Left): 3D random structure of a subsection of the sponge. (Right): Subsection showing macrocoil shapes (mcs).

In addition, a similar randomly structure to that in the films was found in the three-dimensional (3D) random network of carbons in the shape of irregular sponge balls were obtained as shown the Fig. 2. An assembly of carbonaceous grains with different sizes composed the sponges where the carbon grains developed into a continuous of 3D-RNC in the form of tubes with coiled shapes. The formation of coils was attributed to the diffusion of K_2O nanoparticles within the carbonaceous matrix. It can be seen from Fig. 3 (left) that filaments interconnect the structure in the 3D-RNC. An interesting resemblance with exfoliated graphite or graphene oxide can be seen from the SEM image in Fig. 3 (right) for the A_{NW-2} .

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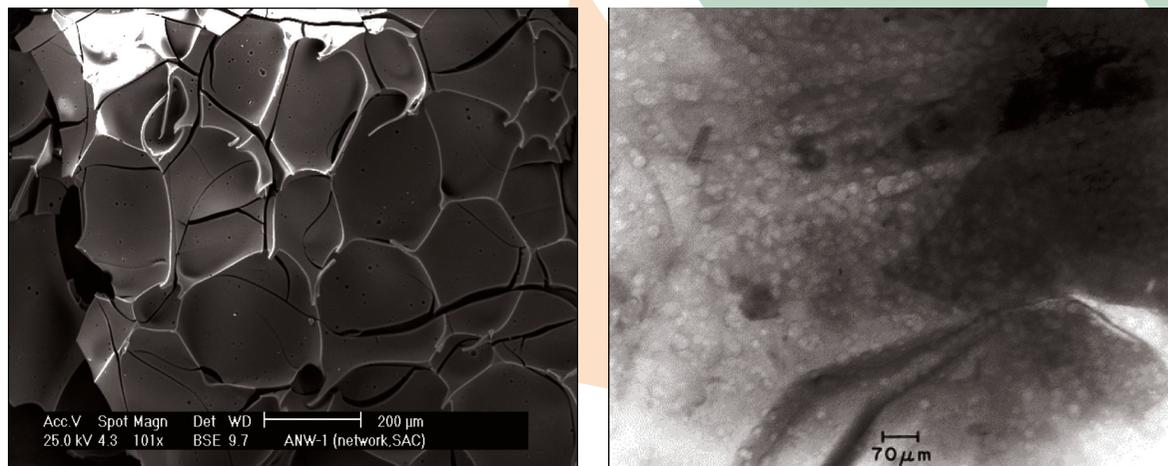


Fig 3. SEM images of random networks of carbon (RNC). (Left): A_{NW-1} (Right): A_{NW-2} .

The XRD pattern from Fig. 4 (left) shows graphite is the main crystalline phase in the RNC. However, RAMAN spectra in Fig. 4 (center) shows interesting shifts to lower frequency when RNC is prepared in presence of potassium. It can be seen that D-band and G-bands for A_{NW-2} were shifted down to 1361 and 1582 cm^{-1} , respectively. The G peak at 1582 cm^{-1} fits very well with that reported for graphene [12] where G peak is due to the doubly generated zone center E_{2g} mode [13]. So, the present work reports by the first time an easy and eco-friendly alternative methodology to prepare graphene-based materials from the controlled pyrolysis of saccharose in presence of KOH instead of KMnO_4 commonly used by the Hummer method [14].

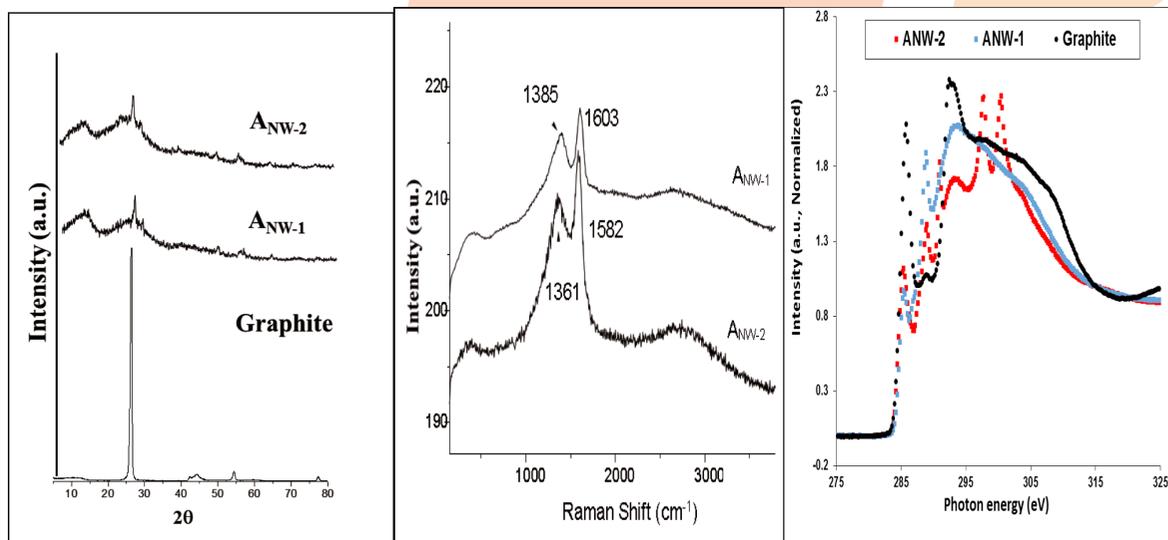


Fig. 4. (Left): XRD patterns. (Center): RAMAN spectra. (Right): C K-edge NEXAFS, for A_{NW-1} and A_{NW-2} samples.

The graphene-based structure in A_{NW-2} sample proposed above has been confirmed by the C K-edge near NEXAFS spectra in Fig. 4 (right). This spectrum showed important differences with respect to high-ordered pyrolytic graphite and with A_{NW-1} . It can be seen that A_{NW-2} samples showed an additional peak about 291.2 eV theoretical predicted [15] and ascribed to the lowest-energy



C 1s \rightarrow s* excitation. It is remarkable to note the appearance of additional resonances between 297.8 and 300.6 eV in the shape of a very symmetric and double peak with 2.8 eV in difference. These peaks can be ascribed to a Stone-Wales structural defect [15,16]. This defect is created by rotating two carbons by 90 degrees, with a formation energy of about 5 eV [16]. The consequence of this rotation is the appearance of two five-rings and two seven-rings in agreement with the polygonal cell distribution in this sample, which showed an important contribution of pentagons and heptagons to the network of carbon [7-11].

Additional characterization by XPS showed important differences with respect to graphite. Finally, EPR and SQUID analysis suggested RNC develop para/diamagnetic behavior that strongly depend of synthesis and activation conditions [10].

CONCLUSIONS

The controlled pyrolysis of saccharose is a single method to obtain simultaneously graphene-based 2D films and 3D sponge balls. These materials can be included within the random networks of carbon (RNC). RAMAN and NEXAFS confirmed the presence of graphene structure, and the presence of structural defects was attributed to the pentagon as the most abundant polygon in the films.

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