

Graphene-like carbon synthesized from popcorn flakes

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Abstract. The synthesis of graphene-like carbon using popcorn kernels as a renewable resource is presented. In a first step popcorn kernels were heated to produce popcorn flakes with a spongy appearance consisting of a polygonal cellular structure. In a second step, the flakes were treated at high temperature in an inert atmosphere to produce carbonization. Raman spectroscopy shows graphene-like structure with a high degree of disorder.

1. Introduction

Since the first report on graphene, a one layer of carbon atoms arranged in a hexagonal structure, there is plenty of reported work on this system and related materials. One of the main characteristics is its high electrical mobility, which makes graphene a good candidate for high frequency electronics [1]. Other related materials, such as graphene oxide or porous carbons have great interest due to their possible applications in the purification of water [2], or for electrodes in supercapacitors and batteries [3].

One of the main concerns is the use of renewable resources as the precursor of carbonaceous materials, such as porous carbon [4] and graphene [5]. In the present work we explore the possibility of the use of corn as a renewable precursor to synthesize graphene-like carbon. Specifically we use popcorn kernels to make popped flakes which have a foamed appearance with a volume roughly 30 times the volume of the original kernel. The visualized physical process is as follows. When the popcorn kernel is heated, the temperature and the internal pressure increase due to the evaporation of water moisture; at a temperature around 180°C the pressure is around 9 atmospheres and the hull of the kernel breaks producing the explosion (“popping”) of the endosperm. The final flake is a foam with polygonal cellular structure [6]. The majority of the flake is expanded starch and a careful examination of the foam reveals that the cells are separated by thin planar walls. The main idea of the present work is that the planar structure of the cell walls may transform to graphitic structures under thermal treatments.

2. Experimental Section

Popcorn kernels were heated in a home microwave oven (650 W) during several minutes until the popping process is concluded. The white foam is separated from the residual hull and loaded into a fused quartz tube in the interior of a horizontal furnace. In an atmosphere of nitrogen, the temperature was raised to 1000°C or 800°C and maintained during a period of one hour, the resultant material has a black color and is named CORNBON1000 and CORNBON800,



respectively. Originally we selected 1000°C for the heat treatment because this is the temperature for the synthesis of graphene using the Chemical Vapor Deposition (CVD) technique [7], but a lower temperature was also used for comparison. Samples were characterized by scanning electron microscopy (SEM), X-ray diffraction and Raman spectroscopy.

3. Results

In figure 1 SEM images of the worked material are presented. The pristine popcorn flake shows an overall porous morphology (figure 1a) and in a close up a polygonal cellular structure is clearly revealed with an average diameter of 20 microns (figure 1b). After the heat treatment the morphology changes, such as is observed in figure 1c and figure 1d for temperatures of 800°C and 1000°C, respectively.

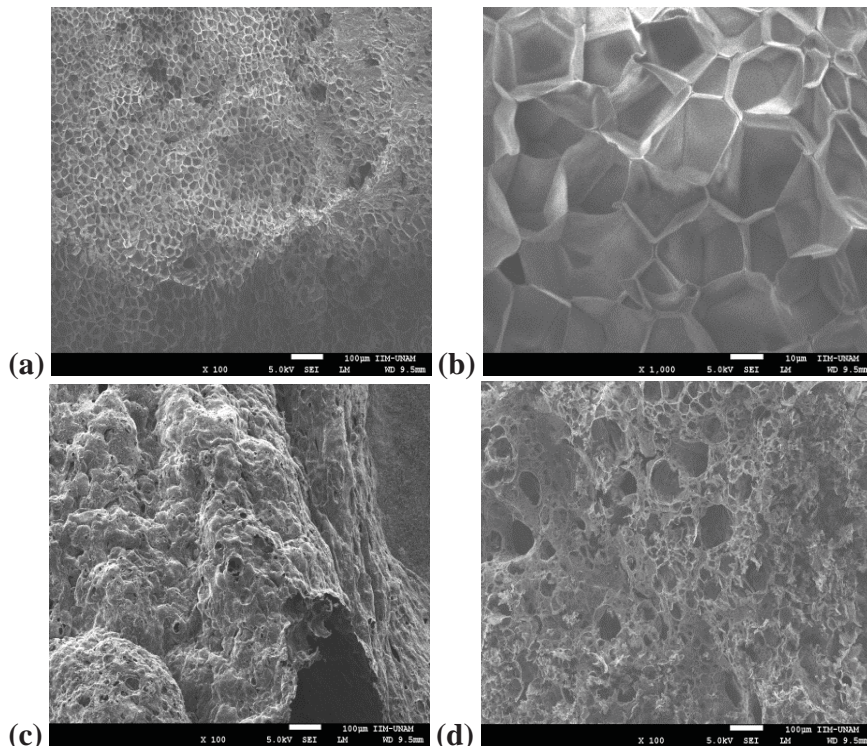


Figure 1. (a), (b) SEM images of the popcorn flakes, in the close up in (b) the cellular polygonal structure is observed, note the lamellar form of the intercell walls. Carbonaceous material after the heat treatment at 800°C (c) and 1000°C (d).

X-ray diffraction indicates that the carbonaceous samples are highly disordered (figure 2), showing a broad peak around 27° which is related to (002) diffraction peak of graphite and other broad peak around 43° that is associated to turbostratic graphite, in which the planes stack in a very disordered manner [8].

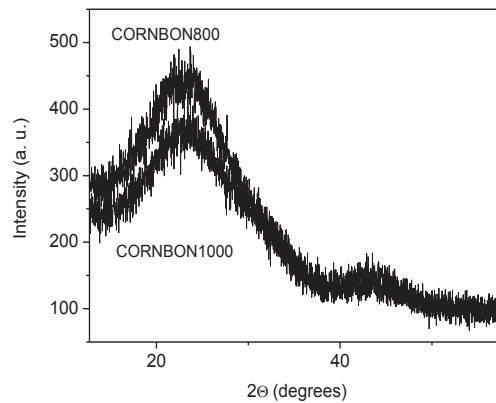


Figure 2. X-ray diffractograms of samples with heat treatment at 800^oC (CORNBON800) and at 1000^oC (CORNBON1000). The carbonaceous material shows two broad bands centered around 27^o and 43^o. The first band is more noticeable in sample treated at 1000^oC as a shoulder, the highest broad band centered around 23^o is due to the glass container of the carbonaceous powder.

Raman spectroscopy of the samples shows two intense bands centered around 1330cm⁻¹ and 1583cm⁻¹ for the sample treated at 800^oC, and 1320cm⁻¹ and 1580cm⁻¹ for sample treated at 1000^oC; both samples show a very broad band between (2400-3200)cm⁻¹ (see inset in figure 3a). The main difference between these two kinds of samples is that a higher stage of graphitization at the higher temperature is observed.

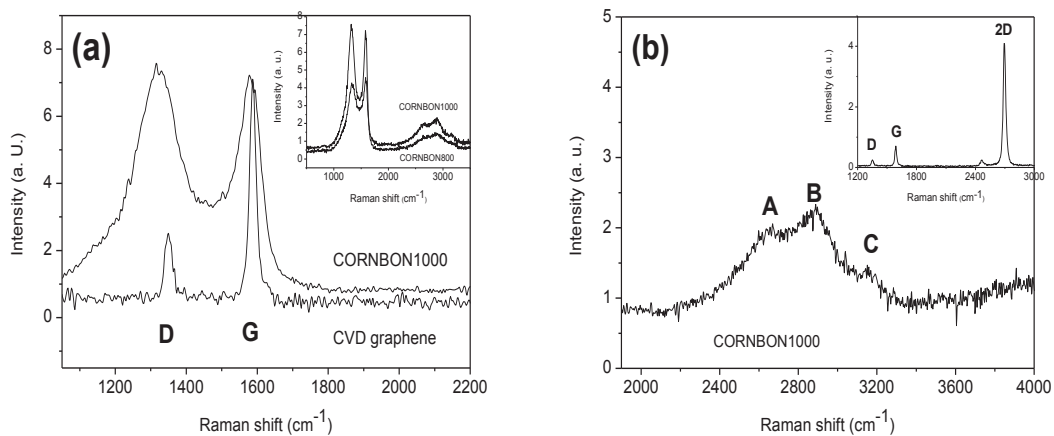


Figure 3. Raman spectra of the graphene-like material with heat treatment at 800^oC (CORNBON800) and at 1000^oC (CORNBON1000). (a) Comparison with graphene obtained by CVD technique showing the D and G bands, in the inset the overall spectra of the synthesized samples are shown. (b) Close up of the zone around the 2D band showing three bands labeled A, B and C discussed in the main text, the inset show the total spectrum of graphene obtained by CVD.

4. Discussion

Raman spectroscopy is a very useful technique to study the great variety of carbon structures, in particular, the graphene-based materials [9, 10]. Graphene is characterized by three bands: G band around 1580cm^{-1} related with in plane stretching carbon-carbon bonds, D band $\sim 1350\text{cm}^{-1}$ associated with structural disorder, and the 2D band located $\sim 2700\text{cm}^{-1}$ and considered as an overtone of the D band. In the process to excite the 2D band, two phonons with opposite wave-vectors are involved, hence it is not necessary the existence of disorder or defects and always is present in the graphene spectrum [10]. It is also possible to quantify the number of graphene layers using the intensity ratio $I(2D)/I(G)$ and the local structure of the 2D band which can be modeled with different sub-bands depending on the number of graphene layers. Respect to the peaks intensity, the general rule is that for graphene (monolayer), $I(2D)/I(G) > 3$ to 4, and for many graphene layers the peaks intensity ratio is less than one [9].

For comparison purposes, in the inset of figure 3b the overall spectrum of graphene synthesized by CVD technique [11] is presented. The characteristic of this kind of material is the existence of the D band compared to graphene obtained by exfoliation of graphite crystals where D band is almost absent [12]. In figure 3a the comparison of CVD graphene and the material synthesized at 1000°C is presented, clearly we can associate the prominent bands located at 1320cm^{-1} and 1580cm^{-1} with D and G bands, respectively. Although the two bands are well defined, they are very broad and we propose it is due to structural disorder (recall: X rays diffraction shows high degree of disorder).

In a systematic study on ion bombardment of graphene and few layer graphene, Martins, et al. [13] show the evolution of the Raman spectrum. In the case of monolayer graphene, G and 2D are the original bands, as the dose of ions increases D band appears, and finally the three bands deform. At the final stage, Raman spectra of graphene and few layers graphene are very similar to that presented in the inset of figure 3a of the present work. This process is explained in terms of disorder induced by ion bombardment [13]. It should be noted that at the higher ions dose (high disorder), the 2D band changes to a very broad and complex band, very similar to that shown in figure 3b for our material. The broad bands labeled A, B and C are identified as overtones: 2D, D+G and D'+G, respectively; where D' band (around 1620cm^{-1}) is also related to disorder but involucres intravalley scattering processes.

The carbonaceous material obtained by our method has a high degree of disorder but it also resemble the structure of graphene and few layers of graphene, this is the reason for which we denominated this material as graphene-like carbon. We suppose there are small zones or crystallites that are similar to graphene with defects. We can estimate the size L of these crystallites using the following relation [10]: $I(D)/I(G) \sim 5\text{nm}/L$, valid for wave length excitation of 532 nm, which is our case. From figure 3a we can see that D and G bands have similar intensities, hence the average size of the graphene nanocrystals is around 5 nm, which explains the absence of crystalline peaks in the X-ray pattern and also the overall structure of the Raman spectrum.

Finally, taking advantage of the foam structure of the popcorn flake, this material can be used as a template to generate other materials. As a preliminary result, in figure 4 the formation of silver particles is shown. In this case, the white flakes were immersed into a silver nitrate-water solution which is readily absorbed by the popcorn flake. After drying, the material is heated to 500°C during one hour in a nitrogen atmosphere. We believe that choosing the appropriate conditions, it would be possible to control the size of the silver particles.

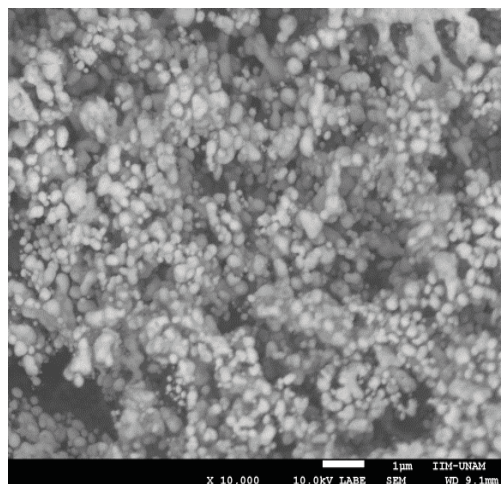


Figure 4. Silver particles grown on popcorn flake after a heat treatment at 500°C using silver nitrate as the precursor.

5. Conclusion

Using corn kernels as a renewable resource we synthesized carbon with a graphene-like structure with a high degree of disorder. We envisage that the obtained material may be useful as electrodes for supercapacitors and batteries due to its porous and spongy structure.

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