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Comments on "Structure evolution mechanism of highly ordered graphite during carbonization of cellulose nanocrystals" by Eom et al., Carbon 150 (2019) 142-152

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This is a comment on the conclusions of the paper by Eom et al. mostly because they could introduce a confusion in the understanding and right use of the vocabulary specific of carbon materials and the carbonization mechanisms.

From a study of cellulose carbonised at temperature ranging from 400°C to 2500°C combining high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, wide-angle X-ray diffraction (WAXD), and X-ray photo-electron spectroscopy (XPS), the main result is claimed to be that the carbonization process undergoes three distinctive stages of structural changes:

- (1) Formation of turbostratic graphitic structure below 1500°C
- (2) Conversion to polycrystalline graphite between 1500 and 2000°C
- (3) In-plane of homogenization to highly ordered graphite above 2000°C

All the terms used here need revision based on the following comments:

1st stage: "Turbostratic" is enough to describe the structure of graphene stacks in which piled-up graphenes are rotationally misoriented. "Graphitic" is enough to describe the structure of graphene stacks in which piled-up graphenes are superimposed while adopting the ABAB... sequence of genuine (pristine) graphite (although "genuine", here, is useless as graphite is graphite, period). Therefore, a carbon material can be either turbostratic OR graphitic, but cannot be both turbostratic AND graphitic as both are structural terms which describe exclusive structures. However, by using the word "graphitic", it can be guessed that the authors wanted to describe the material, not the structure, in order to point-out that the carbons involved are sp^2 hybridised, not sp^3 . In such a case, "turbostratic" is enough to describe the material because, as far as carbon materials are concerned, only graphenes can be turbostratically stacked. On the other hand, it is right that it is of common use to combine

words with overlapping meanings to insist on an important aspect, as I just did by writing “genuine graphite”. But in that case, “graphitic” should not be used as it is a structural term, and “graphenic” should be used instead, as recommended in a previous editorial [1].

2nd stage: “polycrystalline graphite”?? The use of the term “graphite” here is not appropriate and misleading. None of the results shows that graphitization has even started. The occurrence of the graphite structure (hence the conversion of the turbostratic stacking sequence into the ABAB... stacking sequence) is usually confirmed by XRD, by following the splitting of the *hk* peaks into *hk0* and *hkl* peaks. No such a conversion is shown to have started, even at the ultimate temperature of the series, i.e. 2500°C.

Also, what was the material even during the first stage already, if not polycrystalline?? At the end of primary carbonisation, once the material has become brittle solid and has acquired the local anisotropy, nanosized graphene stacks with the turbostratic structure (so-called Basic Structural Units according to Oberlin’s model) have developed. They exhibit lattice periodicities, hence they are nanosized crystals, yet bidimensional, and their association within the anisotropic domains makes the material intrinsically polycrystalline from the very beginning of secondary carbonization; and the material remains so all along the carbonization process which makes the BSUs gradually coalesce.

3rd stage: the group of terms “highly ordered graphite” is redundant in general, and again not appropriate to describe the material obtained in the paper. Graphite is intrinsically highly ordered. If it is not, it is no longer graphite. And actually, the material studied here is NOT graphite, even at the highest temperature of the heat-treatment (2500°C). As mentioned above, the turbostratic to graphitic conversion has even not started.

Generally speaking, cellulose is known as a non-graphitizable material, because of its high oxygen content which generates cross-linking and thereby prevents the occurrence of long-range anisotropy during the primary carbonization. Hence, cellulose cannot transform into graphite upon regular carbonization/graphitization conditions. The contradiction between this basic knowledge and the terms of their conclusion should have been noticed by the authors. All the WAXS data demonstrate the persistence of the turbostratic structure, as expected for a non-graphitizable material. Even the d_{002} value shown in Figure 9c does not go down beyond ~0.344 nm, which actually is the exact shortest intergraphene distance for the turbostratic structure. Raman data are consistent with this observation as a D band is always

present, yet decreasing with the increasing temperature, as expected. In fact, it comes out that the comments regarding the occurrence of the “graphitic” order, “graphite”, and “highly ordered graphite” are mostly based on the fact that the graphenes gradually become linear and stiff as observed by TEM lattice fringe imaging. This misinterpretation suggests that the authors are probably unfamiliar with graphenic carbons and the graphitization processes. Graphenes do not need to be stacked according to the Bernal (ABAB...) sequence to look defect-free. Graphenes come out to look perfect (hence they may look quite linear and stiff in HRTEM images) because of the removal of most of the in-plane defects, independently from their interaction with the neighbouring superimposed graphenes. This means that the stiffening event depends on the heat-treatment temperature, not on the material graphitizability. Consequently, at 2500°C, all the graphenes from any carbon material look straight, despite the structure is still turbostratic, or possibly not more than partially graphitized in the case of graphitizable materials. Indeed, for the latter, reaching higher temperatures in the range of 2800-3000°C is necessary to achieved the full conversion into graphite.

Once the conclusion is corrected by using the right words, the three steps mentioned in the paper and the conclusion only describe the well-known structural changes upon increasing heat-treatment in any carbon material, although 1500°C has not been shown to be a key temperature valid for all types of carbon materials:

- Far before 1500°C, the graphenization takes place and proceeds, resulting in a polycrystalline material made of turbostratic graphene stacks.
- At 1500°C, all the heteroatoms have been eliminated, making the material pure carbon. For other precursors, this step can be achieved for different temperatures than 1500°C, below 2000°C.
- At 2000°C, the overall stiffening of the graphene layers and merging between the turbostratic graphene stacks become significant, as a result from the removal of the defects previously located between the stacks.

The other conclusion of the paper is the observation that the fibrillar morphology of the starting cellulose crystals is lost upon carbonization, but can be maintained upon previous mild oxidative treatment at 250°C in air. The former is the expected consequence of the softening which occurs in any organic precursor at some point during the primary carbonization,

although the extent of the softening (i.e., whether the material just softens or becomes a liquid, or any state in-between) depends on the elemental composition. On the other hand, maintaining the fibrillar morphology by oxidative stabilization is merely a rediscovery of the effect of the stabilization process which is currently used at industrial scale for preventing carbon fibre precursors (either polymeric such as PAN, or colloidal, such as pitch) to melt once the spun precursor is subjected to the carbonization process.

To summarize, the paper reveals that the authors need to carefully revise (1) the structure of graphite; (2) the characteristics used to reveal the turbostratic to graphitic conversion; (3) the basics of the carbonisation/graphitization processes; (4) the proper use of the dedicated vocabulary; (5) the effect of oxidative stabilization treatments for maintaining the morphology of organic materials upon heat-treatment; which all are information which can be found in the literature.

The paper as such provides a thorough study by WAXD, HRTEM, Raman, and XPS of the structural evolution upon thermal treatment up to 2500°C of a cellulose material before and after having been subjected to mild oxidation. In this regard, the paper could be a reference paper for other researchers interested in this material. But the readers should merely consider the data, not the terms of the conclusion.

References

[1] Bianco A., Cheng H.-M., Enoki T., Gogotsi Y., Hurt R. H., Koratkar N., Kyotani T., Monthioux M., Park C.-R., Tascon J. M. D., Zhang J. *All in the graphene family – A recommended nomenclature for two-dimensional carbon materials*. **Carbon** 65 (2013) 1-6