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The Texture, Structure, and Nanotexture of ToF-CVD-Prepared Carbon Micro-/Nano-Cones

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Keywords

Scroll texture, Growth mechanisms, Identification of defects

INTRODUCTION

Carbon conical morphologies exhibit interesting geometrical features (*e.g.*, needle-like shape, small apex) and excellent physical properties (*e.g.* mechanical resistance, electrical, thermal conductivity) that make them excellent candidates for many applications such as electron emission, and near-field microscopy probes, with better performances than other carbon materials such as nanotubes (CNTs). Individual micro-/nano-cones (CnCs) were grown onto CNTs as individual supports using a Time-of-Flight Chemical Vapor Deposition (ToF-CVD) process (Allouche, 2003; Paredes, 2020). CnCs are all-graphenic micro-/nano-objects, made of a rough-surface fibre-segment with protruding smooth-surface conical parts at both ends (Figure 1a).

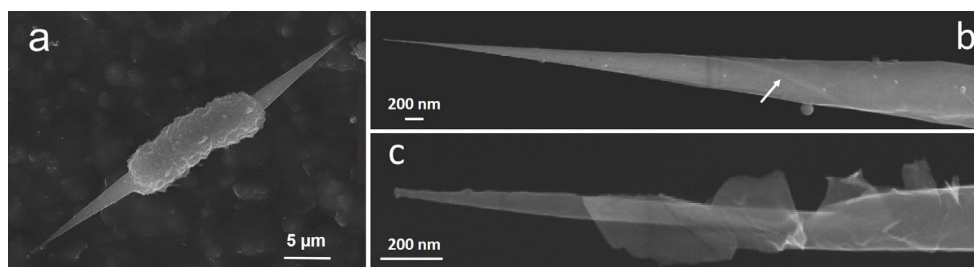


FIGURE 1. Scanning electron microscopy (SEM) images. (a) Example of an as-grown CnC morphology. (b) close-up on a cone end; the arrow designates a step at the cone surface, presumably a graphene edge; (c) the same cone surface as in (b) after passing a current, and showing the unwrapping of the graphene layers.

The very first steps of CnC formation were shown to be dominated by the physical behaviour of a short-lifetime polyaromatic hydrocarbon (PAH)-rich liquid wetting the CNTs (Paredes, 2021). Afterwards, the fibre-segment mostly grows from the PAHs while the conical parts mostly grow from the radicals, as both species are present in the gas phase (Paredes, 2021). The nanotexture and texture of CNCs have been partially studied, suggesting that the cones might follow a Russian-doll model with concentric graphenes parallel to the cone axis, in which many graphenes could present the same helicity (Allouche, 2005; Paredes, 2022). Consequently, the conical shape makes that the cone surface exhibits many graphene edges (which are chemisorption sites for the radicals).

However, a systematic study regarding the graphene arrangement, in particular at the cone apex, which can be a crucial aspect when considering potential applications, was still needed. In this work, we investigated the texture, structure and nanotexture of CnCs, by analysing their behaviour when passing a current through it, and by performing multiple characterization studies such as high-resolution transmission electron microscopy (HRTEM), HR-SEM, Raman spectroscopy, and molecular dynamic modelling, in order to show how actually these cones look like, particularly at the apex.

RESULTS AND DISCUSSION

Concentric Versus Scroll Growth

SEM images of the cone surface (Figure 1b) show faint, oblique lines suggesting that the graphene edges at the cone surface could adopt a spiral display, indicating a scroll configuration of the graphenes. This was confirmed by conducting a scaled-down duplicate of the experiment carried-out by Bacon (1960) to reveal the way graphenes were displayed in carbon whiskers. For doing so, a current of 2 nA at 1,1 V and then of 5 nA at 0,25 V was passed through the carbon cones. An unwrapping phenomenon of the cone surface was observed (Figure 1c), thereby demonstrating that the cone texture is preferably scroll-like, with the scroll turns being parallel to the cone axis as for Bacon's carbon whiskers. This explains why many of the concentric graphenes (actually scroll turns) were found to exhibit the same helicity vector. Such a spiral growth is a common way for crystals to grow rapidly when starting from a screw dislocation. However, calculations showed that the cones are made with hundreds or thousands of concentric graphenes, making unlikely that a single cone could be formed by a single, wrapped graphene. A texture as shown in Figure 2 is proposed, involving multiple intricate concentric scrolls combined with a Russian-doll model for the earliest growth step, which is consistent with the distinct roles of the radicals and the PAHs previously mentioned.

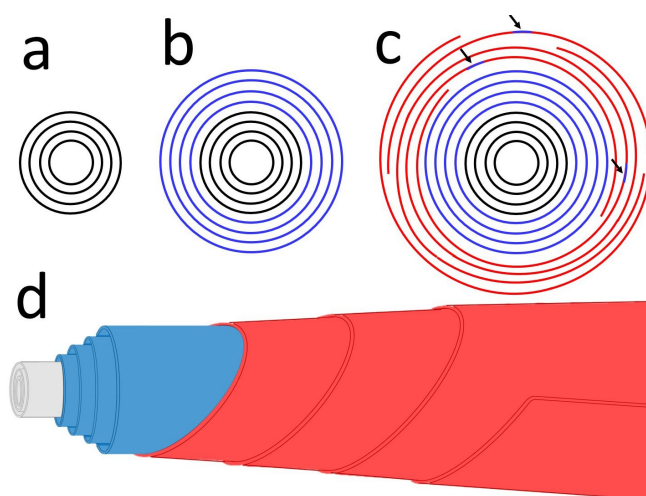


FIGURE 2. Sketches (cross-sections, but (d)) of the way graphenes may display during the cone formation. (a)

The supporting CNT, in which graphenes are concentric (black circles) following the Russian-doll model. (b) Formation of a primary, spindle-like cone, also with the concentric, Russian-doll texture (blue circles), from the carbonisation of PAHs from the liquid phase (Paredes, 2021). (c) The inner concentric graphenes (blue circles) grow in length (perpendicular to the figure) thanks to the chemisorption of species (PAHs or radicals) to the graphene edges; meanwhile, the cone also grows both in diameter and length thanks to physisorbed then carbonised individual PAHs which act as nuclei (arrows) from which graphenes develop as scrolls (red spirals) thanks to the chemisorption of radicals to the edges. (d) Longitudinal view of a cone as seen in (c).

At The Cone Apex

HR-TEM images of carbon cones confirmed that the cone surface exhibits many steps, most of them with a height of a single-layer graphene, although some steps are higher because made of multiple

graphenes, which are those visible by HR-SEM. The graphene nanotexture is perfect all over the cone length, despite they are several-micrometres long. A specific type of double-graphene termination was observed at the cone apex, showing that the edges of two superimposed graphenes close onto each other without exhibiting any curvature (additional to the cylindrical curvature), making the edges looking like they are zipped. It is thus different from the more common "loop" termination which looks like it is made of single graphene heavily folded on itself, and exhibiting negative curvatures at the fold in order to relax the constraints on the C-C bonds. An in-house molecular dynamics (MD) code, operating in the canonical ensemble at the synthesis temperature of the cones (1400 °C), was used to demonstrate that such a zipped graphene closure is plausible and structurally stable. It is made possible by a high number of heterocycles (*i.e.*, aromatic rings with 5, 7, and 8 carbon atoms), which are necessary to accommodate both the cylindrical curvature and the mismatch between the number of carbon atoms available at the edges of the two concentrically superimposed graphene lattices. Simulated HR-TEM images were also performed and matched well the experimental ones. Finally, Raman spectroscopy (wavelength of 632.8 nm, spot size of 0.5 μm and a power of 0.7 mW) was used to analyse cone apices. A $I_D/I_{D'}$ ratio of 1.5 was found, which is the lowest ever reported in the literature., and believed to be the signature of such zip termination. Combining this result with others from the literature, the $I_D/I_{D'}$ Raman ratio appears to be a key parameter to identify 5 different types of graphene defects with values ranging from ~1.5 to ~13.

A detailed version of the work will be published in Paredes (2022).

CONCLUSIONS

Individual carbon micro-/nano-cones produced by ToF-CVD at high temperature are made of perfect concentric graphenes along the cone axis, most of them following a scroll-like model. A growth mechanism involving a primary Russian-doll-type texture subsequently covered with a multiple scroll-type texture is proposed, which accounts for all the observations. A specific kind of double-graphene termination is revealed at the cone apex looking like the edges of a pair of graphenes are zipped to each other without any kind of deformation. Despite they form at 1400 °C, "zip" defects are stable at room temperature, and result from the occurrence of many aromatic heterocycles formed to allow the closing process. A specific Raman signature of zip defects is proposed, corresponding to the lowest $I_D/I_{D'}$ ever reported. Our study confirms the latter ratio as an identification parameter for a variety of defects in graphene systems.

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