Investigation of the core and edge structure of carbon cones and discs

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A rather peculiar polymorph of carbon; carbon cones, were first reported by Ge and Sattler in 1994 [1]. The cones they described exhibited an apex angle of ~19^{o}. However, in 1997 cones with five distinct apex angles were discovered as a product of the Kvaerner Carbon Black and Hydrogen Process (CB&H) [2]. Krishnan et al. reported that the material resulting from the CB&H process contained 10% carbon black like particles, 70% flat carbon discs and 20% carbon cones [3]. Most importantly, they showed that the multiwalled cones exhibit discrete apex angles of 112.9˚, 84.6˚, 60˚, 38.9˚ and 19.2˚, corresponding to the incorporation of 1- 5 60˚ disclinations in a hexagonal graphitic sheet [3]. Note that the discs can be considered as cones with an apex angle of 180°. Both cones and discs exhibit sets of facets with angles $\theta_1 = 22 \pm 1°$ and $\theta_2 = 60.0° - \theta_1$, which has been explained by a shift of ± 21.8° between graphene layers yielding the most stable configuration [4, 5].

Due to the unique topography of the cones, they are promising for applications in hydrogen storage, sensors and electrodes [6]. Yu et al. have shown that hydrogen adsorbs on the surfaces of cones and discs produced by the CB&H process and suggest that electronic and adsorption properties at the edges might differ significantly from the rest of the surface of the particles [7]. Thus, it is of utmost importance to know the edge structure if any effect of edges on hydrogen storage is to be determined.

In the present study, '*as-produced*' and heat treated (HT) samples from the CB&H process have been studied in detail by combining different transmission electron microscopy (TEM) techniques; high resolution imaging (HREM), bright field (BF) and dark field imaging (DF), selected area electron diffraction (SAED), and energy filtered TEM imaging (EFTEM). HT of the sample was done at 2700°C for 3h in an argon atmosphere. The powder samples were suspended on holey carbon grids, while microtome sections were prepared (at Diatome AG) by embedding the carbon powder in an epoxy resin, cutting with a feed of 50nm and subsequently suspending sections on holey carbon grids. All samples were investigated with a Jeol JEM2010F microscope; equipped with an ultra high resolution pole piece and Gatan Image Filter (GIF200), operated at 197kV. HREM micrographs were obtained quickly in order to minimize irradiation damage to the samples.

The focus of the present study is on structure of the edges, graphitisation and domains. SAED patterns of as produced carbon carbon discs (Figure 1A) exhibit both diffuse rings and a set of distinct reflections. This suggests that carbon discs contain a graphitic core surrounded by more disordered carbon in agreement with [5]. Due to the relative intensities of the diffracted spots, it has been suggested that a graphitic core comprises of approximately 10-30% of all the material in a disc. BF images of microtome cross sections (Figure 1B) confirm the existence of a core within 'as produced' carbon discs. Here, the darker contrast of the central region indicates a denser (i.e. more graphitic) structure. The width of the core is ~8.5 nm thick and represents ~15% of the total volume of the disc, which is in agreement with calculated core size estimate of Næss et al. [5]. By SAED, EFTEM, HREM and DF micrographs, carbon cones and discs were determined to exhibit a closed curved edge structure, as can be seen for the open end of a HT cone in Figure 2. Here, the closed edge exists throughout the cone and the initial core cannot be distinguished from the rest of the cone. Although HT significantly increases the graphitic order, the curved edge topography was found for all cones and discs independent of treatment. Micrographs of HT cones and discs (not shown here) exhibit Moiré fringes consistent with crystalline domains within the particles. Here, domains are several hundred nanometres in diameter, which is inconsistent with the previously reported coherence length of 20nm [5]. [8].

References

[1] M Ge and K Sattler, Chemical Physics Letters **220** (1994), p. 192.
[2] JA Bakken *et al*, Pure and Applied Chemistry **70** (1998) p.1223.
[3] A Krishnan *et al*, Nature **388** (1997) p. 451.
[4] T Garberg *et al*, Carbon **46** (2008) p. 1535.
[5] SN Naess *et al*, Science and Technology of Advanced Materials **10** (2009) p. 065002.
[6] J Muller *et al*, Y. Magarshak (ed.), *Silicon Versus Carbon*, Springer Netherlands**,** (2009), p. 285.
[7] X Yu *et al*, Applied Surface Science **255** (2008), p. 1906.
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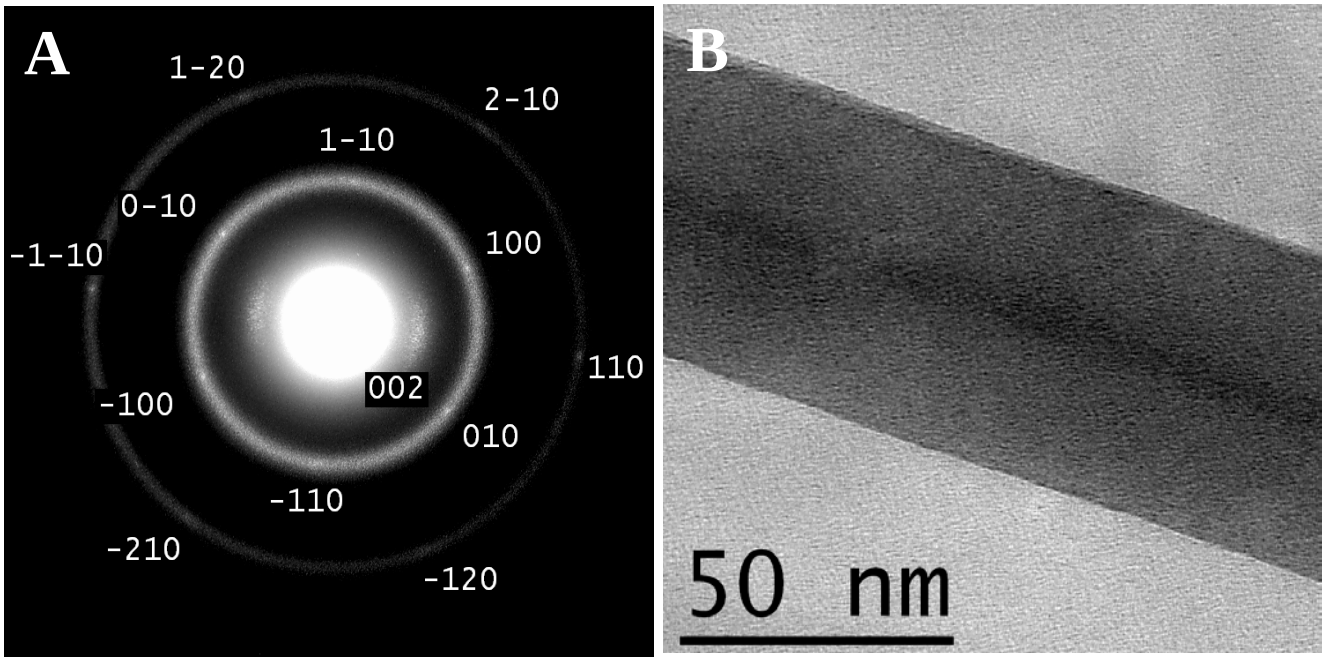

Figure 1A: *SAD pattern of an 'as produced' carbon disc showing a set of discrete reflections corresponding to crystalline region within the C nanodisc.* ***1B:*** *Bright field image of a microtome cross section of a 56 nm thick nanodisc showing direct evidence of the position a crystalline region (8.5 nm) in the core of the nanodisc.*

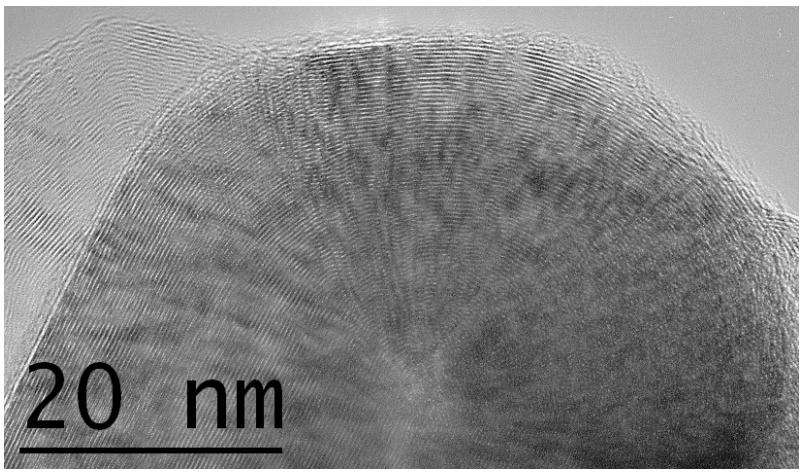

Figure 2*: A HREM micrograph of the open ended edge of a HT carbon cone exhibiting a curved and closed structure throughout the cone.*