Supplementary Material

Decoding structural complexity in conical carbon nanofibers

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1. Number of edge carbon atoms in a graphitic cone

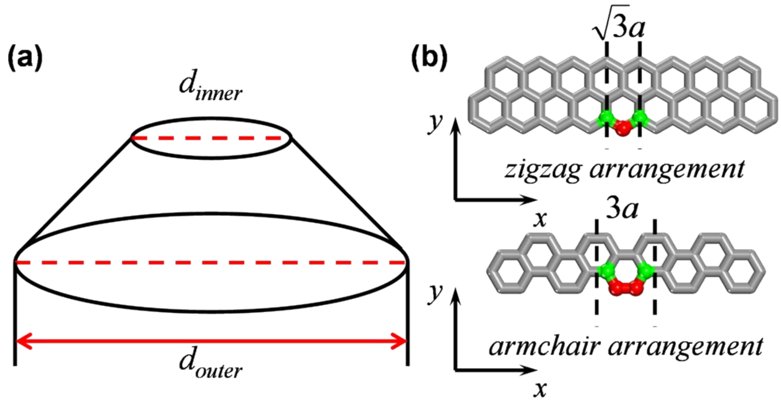

Fig. S1 – Schematic representation of (a) a graphitic cone and (b) edge carbon atoms in "zigzag" and "armchair" arrangements.

A graphitic cone with d_{inner} and d_{outer} is schematically represented in Fig. S1a. The sum of the arc length around the cone tip and that around the exposed outer edge can be written as

$$L_{arc,overall} = \pi \cdot (d_{inner} + d_{outer}) \tag{1}$$

From Fig. S1b, one can see that there are two and four edge atoms in a repeating unit of the "zigzag" and "armchair" arrangements, respectively, and the average interatomic distances along the *x*-axis are quite close in these two cases ($\frac{\sqrt{3}}{2}a$ *vs.* $\frac{3}{4}a$, where a is the carbon-carbon bond length in graphene sheets and takes the value of 0.142 nm). If we assume to a first approximation that the "zigzag" and "armchair" arrangements contribute equally to the termination of interior and exterior facets of conical CNFs, then the number of edge atoms (n_{edge}) in a helical cone can be expressed as

$$n_{edge} = \frac{L_{arc,overall}}{2 \cdot \left(\frac{\sqrt{3}}{2} \cdot a \right)} + \frac{L_{arc,overall}}{2 \cdot \left(\frac{3}{4} a \right)} = \frac{\left(2 + \sqrt{3}\right) \pi \cdot (d_{inner} + d_{outer})}{3 \cdot a} \tag{2}$$

2. Surface area of a graphitic sector

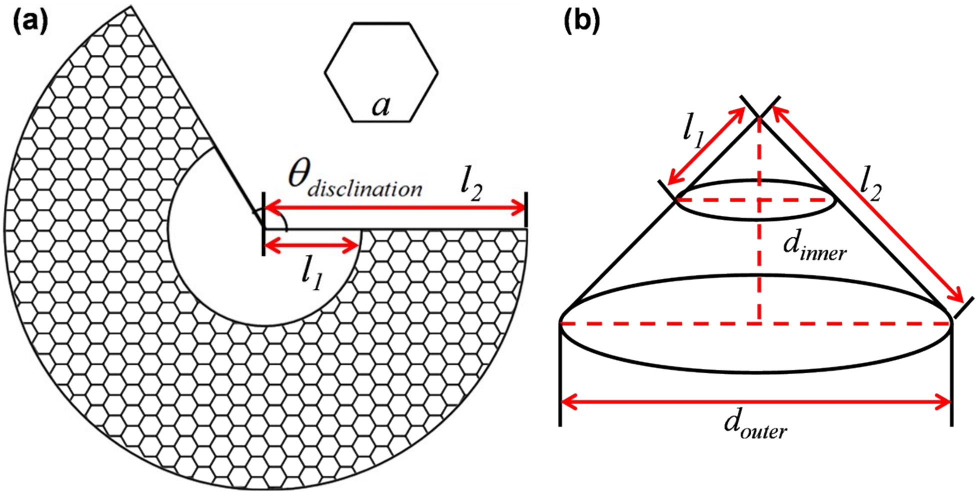

Fig. S2 – Schematic representations of (a) a graphitic sector with $\theta_{disclination}$ and (b) a resultant graphitic cone.

A graphene sheet that is used to form a graphitic cone is shown in Fig. S2a, and its surface area can be expressed as

$$S_{area} = \frac{2\pi - \theta_{disclination}}{2\pi} \cdot \pi \cdot (l_2^2 - l_1^2) \tag{3}$$

From the geometric relationship between sides and angles of the right triangle given in Figs. S2b, it follows that

$$l_1 = \frac{d_{inner}}{2 \cdot \sin \frac{\theta_{apex}}{2}} \tag{4}$$

and

$$l_2 = \frac{d_{outer}}{2 \cdot \sin \frac{\theta_{apex}}{2}} \tag{5}$$

and therefore we have

$$S_{area} = \frac{2\pi - \theta_{disclination}}{2\pi} \cdot \pi \cdot \frac{d_{outer}^2 - d_{inner}^2}{4 \cdot \sin^2 \frac{\theta_{apex}}{2}} \tag{6}$$

Furthermore, because the arc length of the graphitic sector holds constant before and after the transformation, one can write

$$\frac{2\pi - \theta_{disclination}}{2\pi} = \sin\frac{\theta_{apex}}{2} \tag{7}$$

Substituting Eq. (7) into Eq. (6) gives

$$S_{area} = \frac{\pi \cdot (d_{outer}^2 - d_{inner}^2)}{4 \cdot \sin\frac{\theta_{apex}}{2}} \tag{8}$$

3. Number of six-membered carbon rings in a helical cone

Given the fact that an unfolded graphitic cone is in essence six-membered carbon rings aligned in a close-packed (hexagonal) array (see Fig. S1a), we therefore write the number of six-membered carbon rings (n_{ring}) involved as

$$n_{ring} = \frac{S_{area}}{S_{ring}} \tag{9}$$

where S_{ring} is the surface area of the constituent six-membered carbon rings and can be expressed as

$$S_{ring} = \frac{\sqrt{3}}{4} \cdot a^2 \cdot 6 \tag{10}$$

Hence, we have

$$n_{ring} = \frac{S_{area}}{S_{ring}} = \frac{\pi \cdot \left(d_{outer}^2 - d_{inner}^2\right)}{\sqrt{3} \cdot a^2 \cdot 6 \cdot \sin\frac{\theta_{apex}}{2}} \tag{11}$$

4. Number of bulk carbon atoms in a helical cone

As half of the edge carbon atoms are possessed by one hexagonal carbon ring while the other half are shared by two six-membered carbon rings, the amount of bulk atoms (n_{bulk}) can be expressed as

$$n_{bulk} = \frac{6n_{ring} - \frac{n_{edge}}{2} \cdot 2 - \frac{n_{edge}}{2}}{3} \tag{12}$$

Upon substitution of Eqs. (2) and (11) into Eq. (12), we obtain

$$n_{bulk} = \left(\frac{\sqrt{3}\pi \cdot \left(d_{outer} - d_{inner}\right)}{9a^2 \cdot \sin\frac{\theta_{apex}}{2}} - \frac{\left(2 + \sqrt{3}\right)\pi}{6a} \right) \cdot \left(d_{inner} + d_{outer}\right) \tag{13}$$