Perspectives

Nucleation and growth of carbon nanotubes and nanofibers: Mechanism and catalytic geometry control

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A B S T R A C T

Carbon nanotubes and nanofibers with certain shape, size and structure are desired. The study of the kinetics of nucleation and growth of carbon nanotubes and nanofibers is an important key to understand and control the growth process. That knowledge will greatly improve our capacity to optimize structural shapes and increase growth rates. This Perspectives article draws from the literature on carbon nanotube growth and analyzes them to reveal some aspects underlying reaction mechanisms. In each catalyst nanoparticle a constant carbon bulk diffusion flux operates between two distinct catalytic areas with different roles: 1) Surface catalysis producing carbon atoms in some areas; 2) Graphene nucleation and growth, in other areas. Preliminar solid-state changes — obeying 2nd Fick's law — may take place. Subsequent kinetic linearity is the sign that a steady-state 1st Fick's law controlled growth process has been established. Data from the literature on diverse crystal orientations activity are discussed. Catalyst duality may be based on different crystal faces or on solid-state phases prevailing during steady-state growth. Growth of carbon nanotubes from Ni nanoparticles usually described as "octopus" carbon offers evidence of the role of geometry, pentagon formation "catalysis" and *catalyst duality* operating at low temperatures.

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1. Introduction

There is pressure nowadays to produce nanotubes efficiently and with a given geometry due to its expanding multiple uses [1–9]. But the mechanism is not well understood: "*The central problem of nanotube science is still the mechanism*" [3]. The early proposals for the mechanism of catalytic carbon formation involving bulk diffusion of carbon atoms through the catalyst were based on detailed thermogravimetric kinetic studies of carbon formation from hydrocarbons on metals: on Ni in the range 200–350 °C [10], at 1,000 °C [11] and on Ni, Co and Fe and other transition metals in the range 350 °C and 700 °C [12]. Based on the kinetics observed all those authors concluded that C diffusion through Ni was a step in the carbon growth process and calculated the respective activation energy, based in operating conditions where that step was assumed to be rate controlling (Table 1).

Most of the studies on catalytic carbon formation in the period 1970–1990 aimed at minimizing the problem of catalyst poisoning in several processes, particularly steam reforming. Since the 1990's

the scientific interest in understanding carbon formation aims at optimizing the shape, the rate and the density of carbon nanotubes and nanofibers, initially grown mostly at high temperatures - up to 2,000 °C. Several alternative routes of carbon formation are known. The mechanisms of 3 alternative routes in carbon formation have been discussed in a recent paper [14]. Table 2 lists and briefly describes the 3 routes.

The routes of carbon nanotubes (CNTs) formation may be initiated *pyrolytically* or *catalytically*. We call *hybrid route* the formation of carbon particles pyrolytically in the gas phase, impinging on the surface of a catalyst, dissolving carbon atoms and nucleating and growing graphite elsewhere on the surface of the catalyst.

In the nucleation and growth of CNTs by a catalytic route, three factors must be accounted for [14]:

1) The *dual catalyst*: different and separate areas, some active in gas decomposition (or carbon black solubilization, in pyrolysis) and others active in carbon nucleation and growth;
2) The meaning of *kinetic linearity* under steady-state, both in catalytic carbon formation and catalytic carbon gasification;
3) The need to form *6 pentagons* to get perpendicular CNTs growth, after initial graphene nucleation.

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Table 1
Early thermogravimetric studies of C formation on Ni (assuming carbon bulk diffusion).

Year	Authors	Ref.	Gases	T °C	E_a
1967	Baggioni, Eyraud	[10]	C_2H_2, C_2H_4	200–350 °C	22,5
1968	Lafiteau, Jacque	[11]	CH_4	1,000 °C	37
1971	Lobo, Trimm	[12,13]	C_2H_2, 4 olefins	350–800 °C	33

E_a: exponential dependence on temperature of C diffusion in Ni, Kcal/mole.

Table 2
Three alternative kinetic routes in carbon formation [12].

3 Routes	Process description	Remarks
Dual catalyst route	Carbon formation by surface catalysis decomposition, carbon bulk-diffusion, nucleation and growth — in different surface areas of the catalyst	Initial solid-state changes (2nd Fick's law) followed by steady-state linear growth (1st Fick's law).
Hybrid route	Pyrolytic decomposition, particle impingement, dissolution in catalyst, selective graphite nucleation/growth.	Initial solid-state changes followed by steady-state growth; risk of encapsulation.
Pyrolysis route	Pyrolytic decomposition, forming carbon black particles, usually in layers - sometimes spheres (C60) or tubes.	Various particle shapes: laminar, spherical, tubular.

Carbon formation on foils or catalyst layers is also being used to produce graphene layers. The geometry is a key factor in this type of reactions, both in nucleation and in the growth process. This will be discussed below. The duality required to get a sustained growth may be based on different crystal orientations or on distinct solid-state phases (one in equilibrium with graphite and a different one in equilibrium with the reacting gas).

The case of octopus carbon nucleation and growth help illuminate the geometry requirements for CNTs growth [15–19]. The recent paper by Saavedra et al. is of particular interest in view of the detailed observations and statistics presented [18]. Spheroid metal particles are nowadays deposited on substrates to produce CNTs by CVD (chemical vapor deposition): understanding the initial changes in shape, the crystal nano-faces prevailing and the geometry of carbon nucleation and growth is essential to optimize the process.

The metals active in the dual catalyst route are Ni, Co and Fe. For the hybrid route there is no need for surface catalysis. Pt, Pd, Cu and many other transition metals are active.

It is important to understand the differences in the growth mechanism of carbon tubes (perfectly cylindrical, with one or several graphene walls) and carbon fibers (graphene structure arranged *apparently* as stacked cones). This will be discussed below, at point 4.

2. CNT growth initiation: 6-pentagon rule and pentagon forming catalysis

Iijima et al. [20–22] observed nanotube caps of different shapes and based their analysis on Euler's theorem concerning polyhedrons and their number of faces (F), vertices (V) and edges (E): $F + V = E + 2$. A consequence is the fact that a hexagonal lattice of any size or shape can only form a closed structure by the inclusion of 12 pentagons. They showed how 6 pentagons could explain the structure of hemispherical caps at the end of nanotubes. The context of Ijima's work was an apparently non-catalytic arc discharge process, but the CNTs grew at the negative end of the electrode. The carbon nucleation stage must be selective. If nucleation took place over the entire surface, the catalyst would be poisoned and growth would stop. Best catalysts should exhibit selective *duality*, with certain areas enabling nucleation and other areas (most of the surface) catalyzing carbon formation (or receiving pyrolytic carbon black deposition - hybrid route).

In a spheroid single crystal nano-particle various low index flat surfaces will appear and high index areas may predominate. The discussion about the catalytic particles being solid or liquid does not apply in surface catalysis: liquids do not have the solid-state crystal structure that is the essence of surface catalysis.

We will try to explain how nanotubes can nest on flat solid surfaces of appropriate metal catalysts using Euler's law and local geometry. High selectivity in nucleation is the key to get various particular growth processes. The formation of a graphene layer may be seen as a series of hexagon rounds expanding from an initial hexagon, in successive rounds of 6, 12, 18, 24, etc. hexagons (Fig. 1-b). The "next round" has always 6 more hexagons. When two pentagons are formed, the next round will have only 4 hexagons more (two less than in a planar expansion). The growth will in fact include from then on only 4 hexagons more in each successive round, instead of 6 more each time. But when a total of six pentagons are formed, the next round (and all subsequent ones) will have the *same stable number of hexagons*: a hollow *graphene tube* with a stable number of hexagons is then growing. So the graphene growth orientation is turned 90° in relation to the initial flat growth. A drawing describing CNT nucleation and growth is shown in Fig. 1-a,c.

The bending of the initial layer takes place at the edges of that nano surface, as the neighboring carbon atoms coming from the bulk of the metal are at a lower level (Fig. 1-c). The "pentagon formation catalysis" of Ni(111) nano faces can be explained in the following way: Assuming a nanoparticle with 100 nm, the 8 Ni(111) hexagonal facets may be 5–10 nm across and hexagonally shaped. When the growing graphene reaches the border of the facet the next carbon atoms coming from the bulk will be at lower level. Along the zigzag graphene borders the extension will be a range of hexagons slightly bended downwards. But at each corner of the Ni(111) hexagonal facet there is one armchair hexagon. A rehybridization of sp^2 σ and p π-orbitals, as discussed by Haddon [23] will be induced by geometry/topology. The best fit is then a pentagon not a hexagon with an adequate pyramidalization angle. The 6 corners of the Ni hexagon facet will then "catalyze" the formation of the 6 pentagons needed for the growth to proceed as a nanotube exactly in a perpendicular direction.

Discussions of the role of pentagons in other carbon structures, including C60, can be found in the books by Peter Harris [3] and by Kroto and Walton [24]. The work of Ijima mentioned above stimulated the study of these structures. The main differences to the catalytic route discussed here are: 1) Non-catalytic nucleation and growth in the gas phase require much higher temperatures (up to 2000–3000 °C; 2) The two catalytic carbon formation processes (dual catalyst route and hybrid route) involve carbon bulk diffusion through the catalyst, graphene nucleation and sustained growth, but the initiation process is substantially different as discussed elsewhere. "Pentagon catalysis" on Ni (111) nanofacets does in fact enable growing nanotubes at temperatures up from 350 °C. In the