

CATALYST DYNAMICS DURING SURFACE-BOUND CARBON NANOTUBE NUCLEATION

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The exceptional electronic, mechanical and optical properties of low dimensional carbon allotropes are closely related to the underlying sp^2 carbon honeycomb lattice. Graphene ribbons and single-wall carbon nanotubes (CNTs) can be metallic or semiconducting depending on their edge determination or “roll-up”, respectively. The properties of multi-walled CNTs and carbon nanofibres (CNFs) depend on the number of walls and the angle of graphene layer stacking.

Generally CNT nucleation requires the presence of a catalyst, typically a 3d transition metal, the detailed role of which, however, is not completely understood [1]. At present, neither single-wall CNT chirality nor CNF layer stacking can be sufficiently controlled, which limits their technological impact.

We have combined atomic-scale environmental TEM (ETEM) and in-situ time-

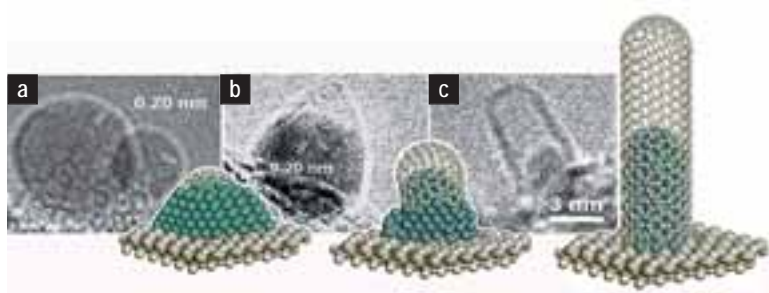
resolved X-ray photoelectron spectroscopy (XPS) to study dynamic effects before and during catalyst assisted CVD of CNFs and single walled CNTs (SWNTs) [2]. We used a model catalyst system based on <10 nm Ni and Fe films evaporated onto oxidised Si, and transformed into a series of isolated nano-particles (Figure 1a). CNTs are nucleated by subsequent exposure to acetylene (Figures 1 b, c).

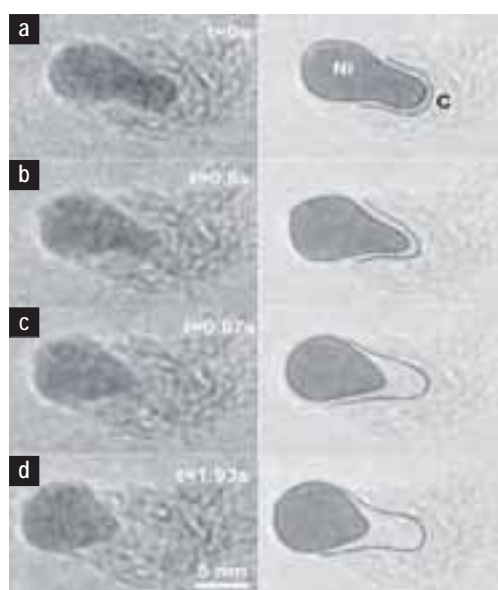
Our ETEM videos show that the formation of graphitic carbon leads to the dynamic reshaping of the catalyst particle. It is this reshaping that during further growth of the graphitic layer(s) defines the morphology of the carbon nanotube.

SWNTs nucleate by the lift-off of a carbon cap (Figures 1 b, c). The carbon cap appears to initially replicate the shape of the apex of the triangular/pyramidal metal particle. The carbon network expands by lifting off from the catalyst particle, which itself is thereby restructured. The growing nanotube forces its shape onto the Ni cluster. The contact angle of the Ni particle to the SiO_x substrate increases to approx. 90° , whereby the nanotube constrains the Ni particle to a more cylindrical shape. Growth terminates when the tangential graphitic lattice encapsulates the catalyst particle down to its support interface.

The catalyst particle reshaping is even more dramatic for CNFs. The Ni particle

Figure 1. ETEM images of Ni catalyst nano-particles on a SiO_x membrane at $615^\circ C$ (a) in vacuum (10^{-6} mbar), (b) after exposure to 8×10^{-3} mbar C_2H_2 . (c) HRTEM image of SWNT root growth. The ball and stick models indicate the different SWNT growth stages.





continually elongates until it suddenly contracts into a rounder shape, and the sequence recurs (Figure 2). Typically, the substrate anchorage is overcome during the first contraction, the catalyst crystal lifts off the substrate, resulting in a tip growth mode.

For SWNT as well as CNF growth we observe crystalline phase contrast from the transition metal catalyst nano-particles. For most nanocrystals, only one set of lattice fringes is visible, which can make the analysis of their chemical state solely based on lattice assignments ambiguous. The 0.20 nm reflection is expected for metallic fcc Ni(111), but also for Ni₂O₃(200) and Ni₃C(113). We therefore included XPS measurements to describe the chemistry related to the particle surface.

Nanotubes were nucleated by exposing nominally 0.5-nm-thick Fe films to undiluted C₂H₂ at 580°C in the end-station of the SuperESCA beamline. Figure 3 shows the evolution of the C 1s core level spectrum during acetylene exposure at a background pressure of $\sim 2 \times 10^{-7}$ mbar C₂H₂. The appearance of a peak at ~ 282.6 eV precedes an intermediate peak at ~ 283.2 eV and the increase of a very strong peak at ~ 284.5 eV, which saturates after ~ 150 s (Figure 3, inset). We interpret this chemical shift in the C 1s binding energy as a transition from chemisorbed carbon (~ 282.6 eV), to carbidic carbon (~ 283.2 eV) and to an sp²-bonded carbon network (~ 284.5 eV). The

C-C bond starts to appear after ~ 90 s of acetylene exposure, at saturation of the chemisorbed C signal. The catalyst is active in its metallic state; Fe and Ni films that were deliberately oxidised before annealing showed a lower/no nanotube yield on C₂H₂ exposure.

In conclusion, we have highlighted some of the progress made towards an atomistic CNT growth model by combining in-situ TEM and XPS. Selective acetylene chemisorption and the formation of a carbon-rich surface layer were observed on otherwise crystalline transition metal nano-particles. Structural selectivity is determined by the dynamic interplay between carbon network formation and catalyst particle deformation.

References

- [1] S. Hofmann et al, *Phys. Rev. Lett.* **95** (2005) 036101.
- [2] S. Hofmann et al, *Nano Letters* **7** (2007) 602.

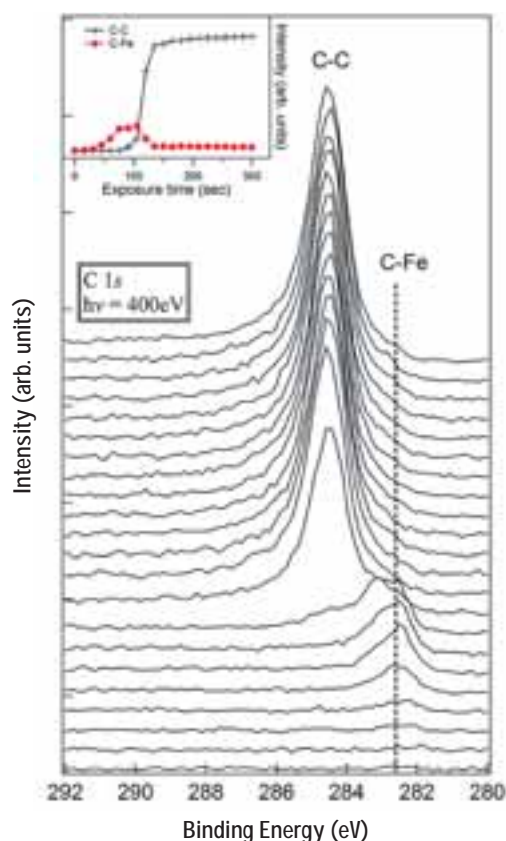


Figure 3. Time-resolved evolution of C 1s core level during Fe exposure to $\sim 2 \times 10^{-7}$ mbar (background pressure) C₂H₂ at 580°C. The inset shows the evolution of the chemisorbed (dots) and graphitic (crosses) carbon peaks.

Figure 2. (a)-(d) ETEM image sequence showing a growing CNF in 3:1 NH₃:C₂H₂ at 1.3 mbar and 480°C. The video was recorded at 30 frames/s, and the time of the respective stills is indicated. Drawings (right column) indicate schematically the Ni catalyst deformation and C-Ni interface.