Etchant-induced shaping of nanoparticle catalysts during chemical vapor growth of carbon nanofibres: supplementary data

Z. B. He,[a] J.-L. Maurice,[a,*] C. S. Lee,[a] A. Gohier, D. Pribat,[a,b] P. Legagneux[c] and C.-S. Cojocaru,[a]

[a] Laboratoire de Physique des Interfaces et Couches Minces, LPICM, UMR 7647, École Polytechnique-CNRS, Route de Saclay, 91128 Palaiseau Cedex, France

[b] Departement of Energy Science, Sungkyunkwan University Suwon 440-746, Korea

[c] Thales Research and Technology France, 1, Avenue Augustin Fresnel, 91767 Palaiseau Cedex, France

Finding growth axis and facet orientations with TEM

As TEM provides projections of 3-dimensional objects, a single image is generally not sufficient to characterise a given axis as the growth axis, or a given flat in the image as a facet. A means, to check whether a given flat in the image is a planar facet viewed in cross-section or an edge, is to look at the contrast of the particle: dark and slowly varying for a planar surface, it should be bright at an edge, with equal-thickness fringes in zone axis illumination. However, tilting the sample about different axes remains the only way to make sure that a given facet exists [1]. Figure S1 gives an example of that procedure, where we have tilted the nanofibre, first around its axis, and then around an axis perpendicular to it (adapted from ref. [1]).

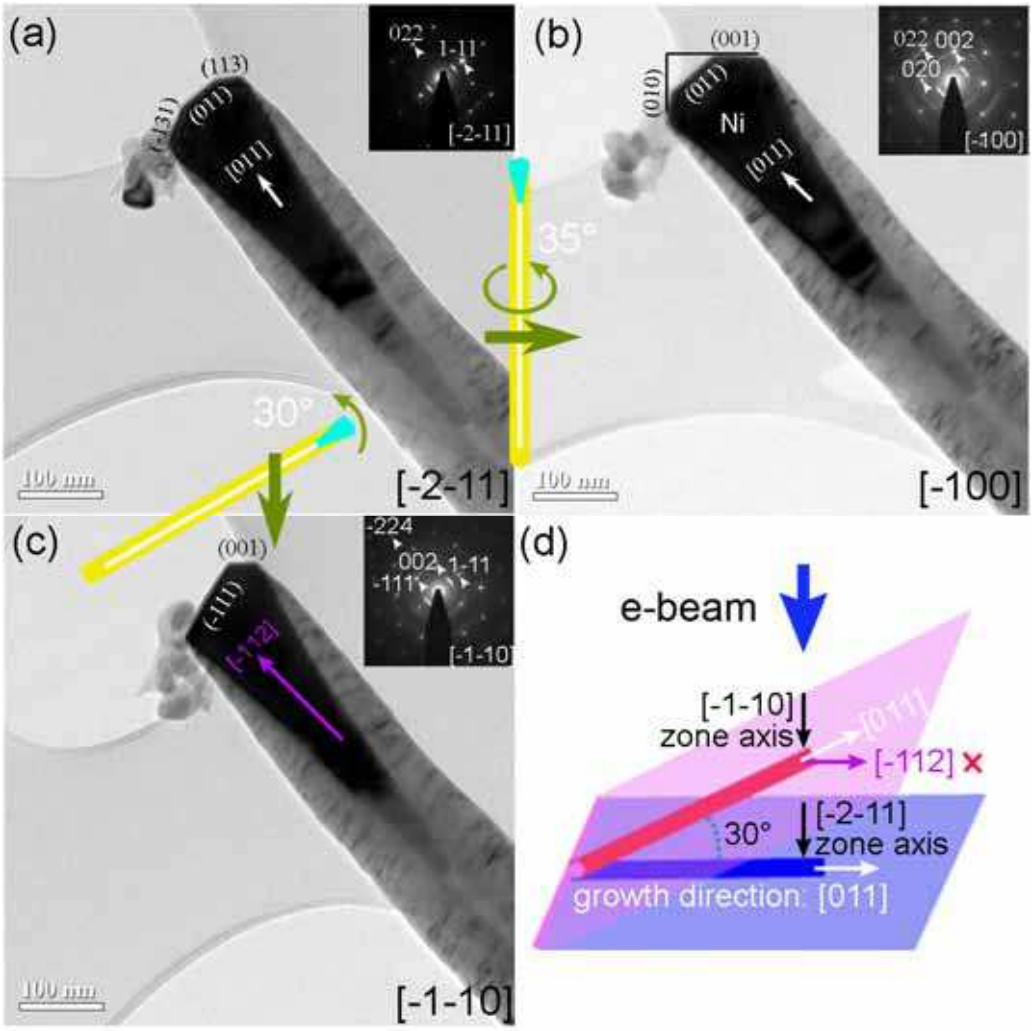

Fig. S1. (a-c) A series of TEM bright-field images of the same Ni particle taken at the same magnification, but viewed along different zone axes (adapted from ref. [1]): (a) [-100]; (b) [-1-10]; and (c) [-2-11]; (d) schematics of the tilt angle from (a) to (c). The growth direction of the CNF is determined as [011] from (a) and (b). Note that if the CNF is tilted by a large angle from the horizontal, the growth direction deduced from the corresponding diffraction pattern is not the real value, e.g. [-112] in (c). Actual facets of the present particle have {111}, {100} and {110} orientations. The {311} "facets" in (a) actually correspond to edges between the former [1]. Nanofibre grown in H2O:IPA (isopropyl alcohol) at 600°C.

Complementary data on the sensitivity of growth rate on the nature of etchant

Figure S2 compares the results of growing CNFs at 650° with the two gas mixtures CH_4:H_2:H_2O (2:2:1) (fig. S2a), and C_2H_2:NH_3 (1:4) (fig. S2b). Although the growth time was one third longer with the former (dewetting period excluded), the final nanotubes are more than twice longer, which shows that C_2H_2:NH_3 is not as efficient, in terms of growth rate, as CH_4:H_2:H_2O, while acetylene has been shown to accelerate growth with respect to methane when the same ammonia is used as etchant [2]. The hydrogen-water vapour mix appears to have not only annihilated the handicap of methane, but also brought an additional speeding factor.

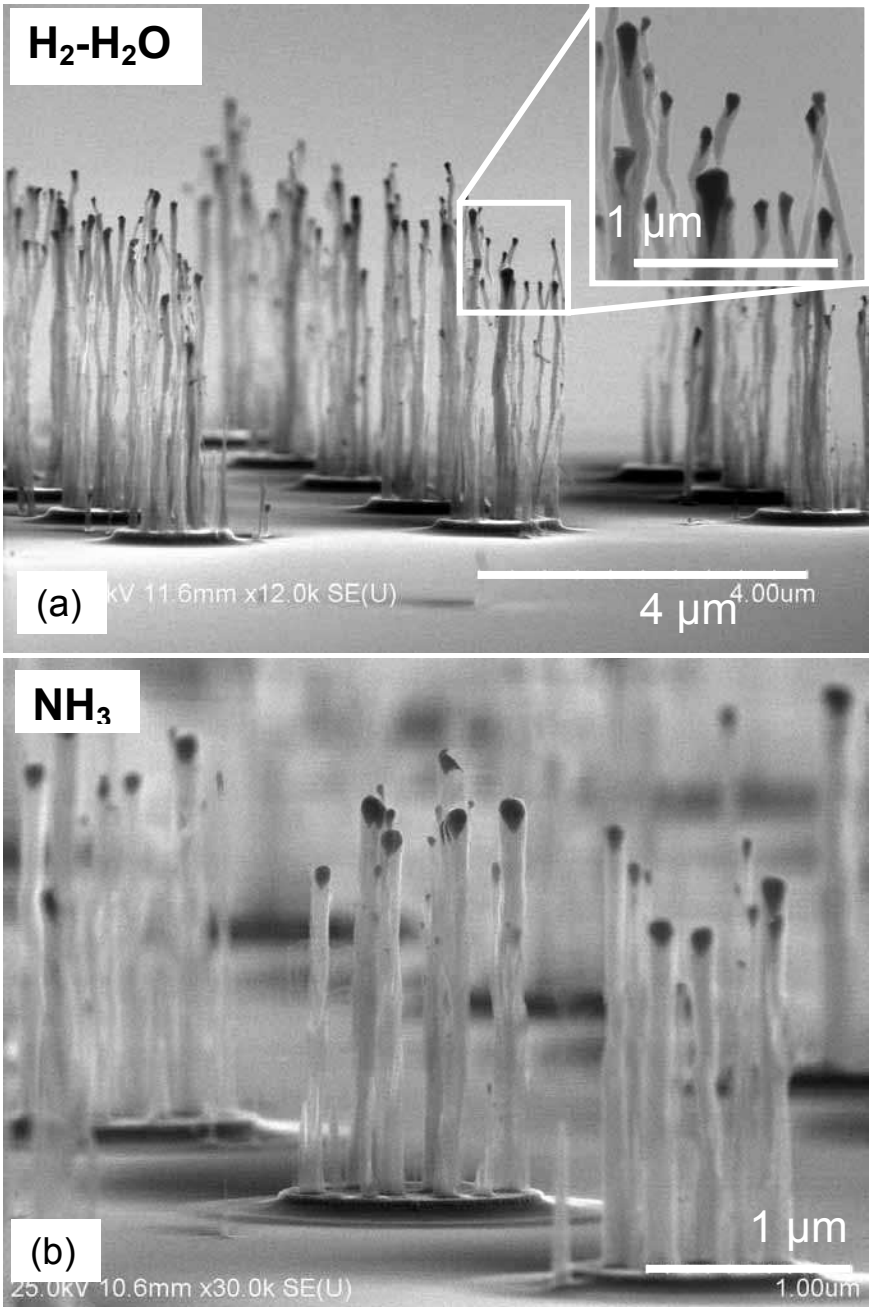

Figure S2. SEM images of vertically aligned top-type CNFs grown for 30 min at 650°C in hydrogen-water (H_2-H_2O) and ammonia (NH_3). Note the different scales: the H_2O fibers are approximately twice as long as the NH_3 ones (the inset in H_2O is at the same scale as NH_3). The Ni particles have facets in the case of H_2O, and rounded shapes in the case of NH_3.

---

[1] He ZB, Maurice J-L, Lee CS, Pribat D, Cojocaru CS, to appear in the Arabian Journal for Science and Engineering, Theme Issue on "Science and Engineering at the Nanoscale".

[2] Hofmann S, Kleinsorge B, Ducati C, Ferrari AC, Robertson J, Low-temperature plasma enhanced chemical vapour deposition of carbon nanotubes. Diamond and Related Materials 2004;13:1171-1176.