GROWING A CARBON NANOTUBE ATOM BY ATOM: "AND YET IT DOES TURN"

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The key issue for realizing the potential of CNTs has always been, and still remains, a better control of CNT growth. Measurement techniques, models and control are needed at the atomic scale as this is the size of the critical growth zone. Though important progress is now being made by growing CNTs in transmission electron microscopes[1], this does not yet show how individual atoms integrate into a growing CNT. Ding, et al.[2] have recently proposed that atoms may simply repetitively stick to the edges of growing single wall nanotubes (SWNTs) by a 'screw-dislocation-like' (SDL) mechanism. Such a mechanism is attractive because it points towards controlled growth by a sort of epitaxy, as for bulk single crystals, and connects the growth speed to helicity. However to test this theory and find the experimental conditions over which it is applicable, an experimental method that can measure growth with an atomic resolution is needed. Here we show that field emission (FE) permits such "atomic" resolution by observing the growths of individual carbon nanotubes (CNTs); from the nucleation stage, directly in a field emission microscope (FEM)[3]. As we explain below, our results lend direct support to the SDL model.

Ni was first deposited on a sharp W tip in an ultrahigh vacuum FE system and formed into nano-particle catalysts by de-wetting. The CNTs were then grown by chemical vapour deposition (CVD) in 10^{-7} Torr acetylene at 800°C, during FEM imaging. Electrons emitted from the caps of individual, growing CNTs formed circular FEM patterns on a phosphor viewing screen. A series of typical FEM images during the growth of a CNT are shown in Fig. 1. The voltage necessary for FE progressively decreased and the pattern increased in diameter which by FE principles means that a CNT grew radially from the W support tip.

A more interesting type of growth was when in addition to strengthening and widening, the FE pattern rotated axially during growth. In one case the CNT rotated ~180 times during its 11 min growth cycle (see Fig. 2). This immediately suggests growth by the SDL mechanism where the integrating atoms don't simply extrude the CNT, but force it to simultaneously rotate about the catalyst particle.

More striking and in-depth information was obtained by a frame by frame analysis of the video. This showed that the rotation proceeded by discrete steps with about ~24 per rotation, half the number of atoms on the circumferences of common SWNTs (see Fig. 3). We conclude that each step is the direct observation of the SDL growth of a SWNT, one carbon dimer at a time.

This work brings new insights to the three elements needed for advancing controlled CNT growth: measurement, model and control. The striking observation by FEM of the fabrication

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References:

[1] See for examples, Helveg, S., López-Cartes, C., Sehested, J., Hansen, P. L., Clausen, B. S., Rostrup-Nielsen, J. R., Abild-Pedersen, F., Nørskov, J. K. *Nature* **2004**, *427*, 426. and Yoshida, H., Takeda, S., Uchiyama, T., Kohno, H., Homma, Y., *Nano Lett.* **2008**, *8*, 2082.
[2] Ding, F., Harutyunyan, A. R., Yakobson, B. I. *PNAS* **2009**, *106*, 2506.
[3]Mickaël Marchand, Catherine Journet, Dominique Guillot, Jean-Michel Benoit, Boris I. Yakobson, StephenT. Purcell (in review, coming soon).

atomic brick by atomic brick of a molecular system is a new measurement technique at the atomic scale.

Figures:

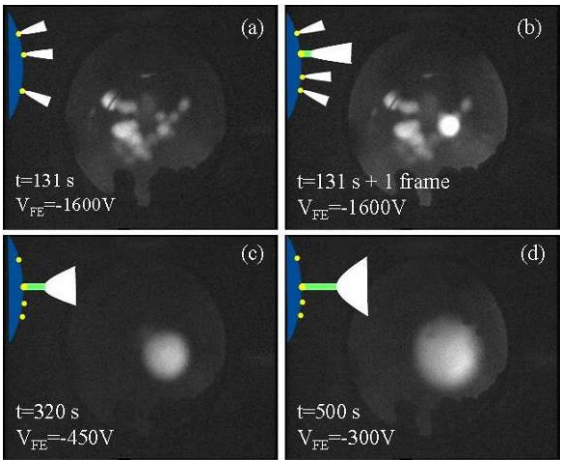

Figure 1: Evolution of the FEM pattern with time during CNT growth in acetylene at 800°C. (A) FEM pattern from Ni particles before acetylene. (B) FEM pattern showing a bright circular spot one frame after the CNT nucleation. (C)(D) Enlarging CNT-FEM pattern as the CNT lengthens.

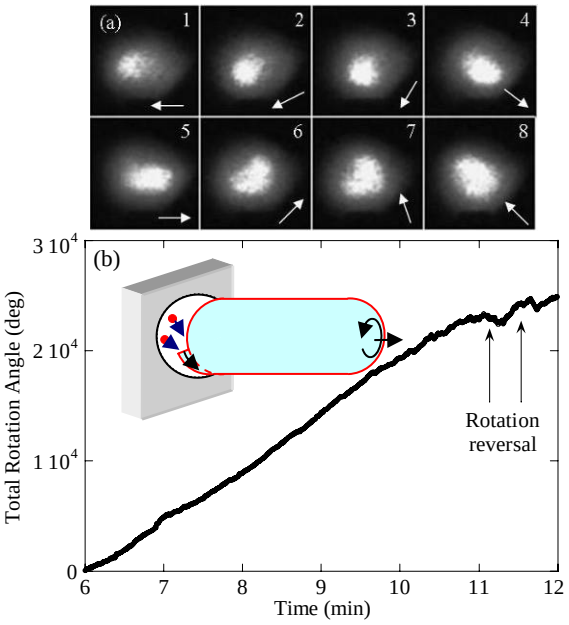

Figure 2: (a) Sequence of FEM patterns from a growing CNT that follows a single revolution as the CNT lengthens (in order 1 to 8). (b) Angle of the pattern as a function of time during a large part of the growth. Inset: schema of the rotating CNT growth.

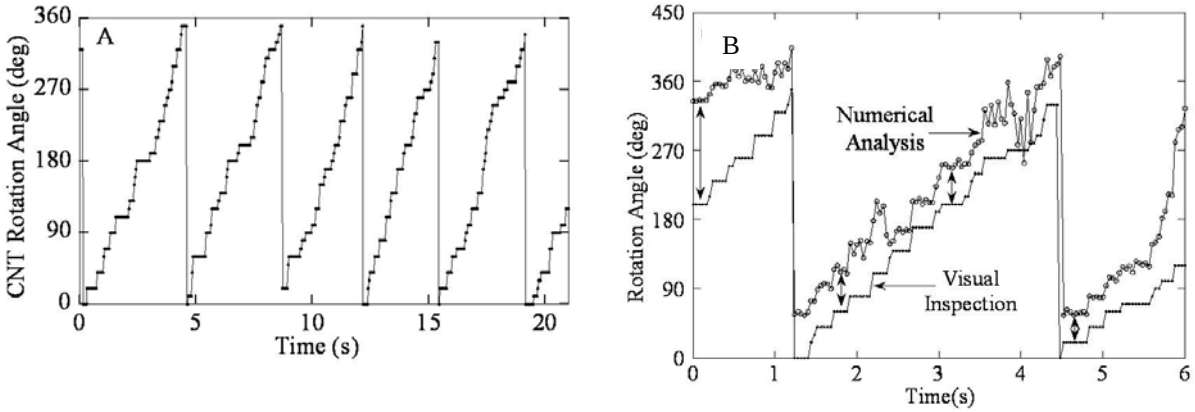

Figure 3. (A) Frame by frame measurement of the rotation angle of the FE pattern showing that it proceeded by discrete steps. The number of the steps for the 5 cycles were {25, 25, 21, 21, 25}, varying because steps of one or less frames are difficult to tabulate. (B) Detail of the fourth cycle. Two types of analysis have been made which are displaced by 60° for clarity.