

Exploiting Environmental Transmission Electron Microscopy Approaches to Understand the Origin of Carbon Nanotube Growth Termination

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The growth of dense, vertically aligned single-walled carbon nanotube (SWNT) ‘carpets’ is of intense interest in the field of nanotechnology. A pioneering advance was made by Hata and colleagues [1], who demonstrated that the addition of a small, controlled amount of water vapor into the growth ambient led to dramatically improved nanotube yield and longer carpet heights. Despite this, it is still not possible to grow ‘infinitely long’ nanotubes, as growth terminates after the nanotubes reach some finite length (usually of order millimeters).

Here we present a systematic study of the growth termination mechanism of SWNT carpets, by combining measurements of carpet height obtained from in-situ growth experiments in a water-assisted CVD apparatus and measurements of catalyst size distributions using both ex-situ and in-situ transmission electron microscopy.

These observations allow us to determine mechanisms by which deactivation of the catalyst population occurs, and relate these to the terminus of nanotube growth. Specifically, we observe that both Ostwald ripening and subsequent sub-surface diffusion result in catalyst loss, and find from our in-situ observations that this can be correlated directly with growth termination. [2] The presence of H₂O is found to inhibit the Ostwald ripening process, perhaps due to changes in the diffusion rate of catalyst atoms on the surface caused by differences in surface structure in the presence of oxygen and hydroxyl species. [3]

Our results point to a strong interaction between the type of catalyst (Fe) and the catalyst support material (alumina). We have investigated how the population of Fe catalysts evolves on a variety of alumina supports, created by a number of different deposition methods, namely (a) sputter deposited alumina films, (b) e-beam deposited alumina films, (c) annealed e-beam deposited alumina films, (d) alumina films deposited by atomic layer deposition and (e) single crystal (0001) sapphire. The catalytic behavior, Ostwald ripening, and subsurface diffusion rates of Fe catalyst are strongly influenced by the support porosity, with the catalytic activity increasing in the following order: sapphire/Fe < annealed e-beam/Fe < ALD/Fe < e-beam/Fe < sputtered/Fe.[4] These observations clearly indicate that there is a strong connection between catalyst activity and changes in the catalyst size distribution. We will suggest methods by which these observations can be used to further guide catalyst / support designs to maximum nanotube yield.

References

- [1] K. Hata, et al., *Science*, 306 (2004) 1362.
 [2] S.M. Kim, et al., *J. Phys. Chem. Lett.*, in press, 2010.
 [3] P. Amama, et al., *Nano Lett.*, 9 (2009) 44.
 [4] P. Amama, et al., *ACS Nano*, ASAP: DOI: 10.1021/nn901700u, February 2010.
 [5] Support from AFOSR is gratefully acknowledged. CLP and RHH acknowledge partial support from the Lockheed Martin LANCER program. SMK and EAS acknowledge support from the Air Force Research Laboratory.

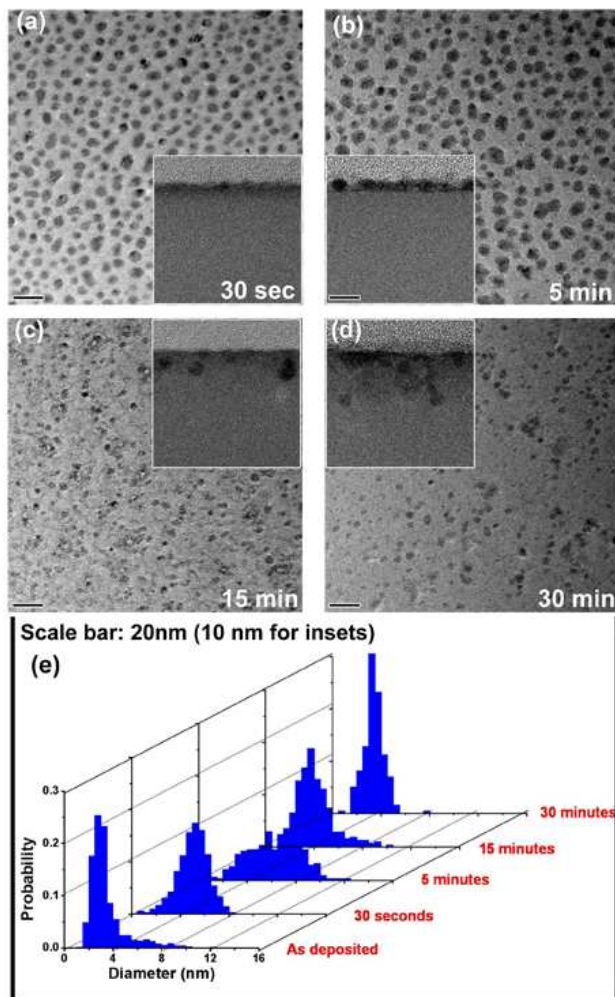


Figure 1: Plan-view TEM images of annealed Fe/Al₂O₃ catalyst layers at 750°C for various labeled times (a) 30 seconds, (b) 5 minutes, (c) 15 minutes, and (d) 30 minutes. Insets are cross sectional views demonstrating sub-surface diffusion of Fe into the Al₂O₃ layer. (e) Statistical representation of the catalyst particle size distribution for the four cases shown in (a)-(d) and the as-deposited Fe sample.

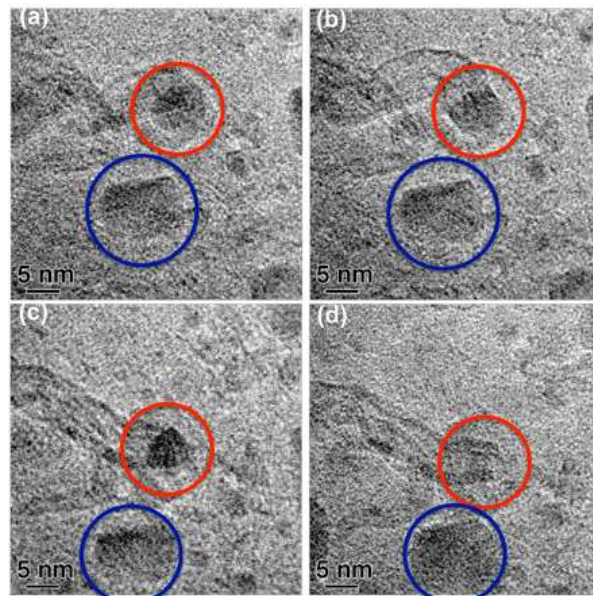


Figure 2: Four subsequent snapshots (a)-(d) from growth at 650°C in 2.5 mTorr of C₂H₂ and 7.5 mTorr of H₂ in-situ with TEM showing stages of catalyst morphological evolution and its effect in growth termination for an individual growing few-walled CNT.