

Using environmental electron microscopy to elucidate the mechanisms of chirality selection during carbon nanotube growth

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Carbon nanotubes have long received significant attention for their interesting electronic properties, which depend directly on their chiral angle. This is especially true in the last several years, with metallic tubes being strongly considered as vias in electronic devices [1] and seeing renewed interest as conducting channels in logic circuits. [2] At present, however, it is not possible to sufficiently control chiral selection of nanotubes during the nucleation stage: this represents a significant limitation to their eventual utilization in technological applications.

Environmental transmission electron microscopy provides an ideal tool for imaging carbon nanotube nucleation and growth in real time and at high spatial and temporal resolutions. Specifically, it is possible to follow the dynamic evolution of how the nanoparticle catalysts responsible for mediating nanotube growth change as a function of temperature, time and gaseous environment. In this presentation, I will review our observations of three specific phenomena that appear to influence chiral selection.

We have found that through careful control of both carrier gas and residual water vapor pressure it is possible to growth carbon nanotubes with a strong selectivity for metallic conductivity, specifically in the presence of small, but significant H₂O pressure and a He carrier gas. [3,4] Our in-situ transmission electron microscopy observations point to two key effects of gaseous ambient on the nanoparticles. The first effect of this ambient is to significant retard the coarsening / Ostwald Ripening rate of the Fe catalysts, leading to a narrower size distribution (Figure 1).[5,6] The second effect is that the presence of H₂O / He is to create nanoparticles with sharp facets. (Figure 2). These two phenomena are in fact related, as highly faceted nanoparticles are known to coarsen at a lower rate. [7]

The remaining question, of course, is which of these is the more important phenomenon? Is simply maintaining a more narrow size distribution key to creating predominantly metallic nanotubes? Or does the presence of strong facets lead to the selection of particular chiral angles? We have been investigating this later question by working the problem in reverse and trying to understand whether or not there is strong tendency towards epitaxy between Fe and carbon nanotubes. Recent results of Fe nanoparticle nucleation on graphene demonstrate that the drive to epitaxy is strong at each stage of the nanoparticle nucleation. These results will be discussed in the broader context of the field, and a case will be made that nanotube chiral selection can be further improved.

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3. Hata, K., et al., *Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes*. *Science*, 2004. 306: p. 1362-1364.
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5. Amama, P.B., et al., *Role of Water in Super Growth of Single-Walled Carbon Nanotube Carpets*. *Nano Lett.*, 2009. 9(1): p. 44-49.
6. Kim, S.M., Pint, C.L, et al., *Evolution in catalyst morphology leads to carbon nanotube growth termination*, *J. Phys. Chem. Lett.*, 1, 918-922, 2010.

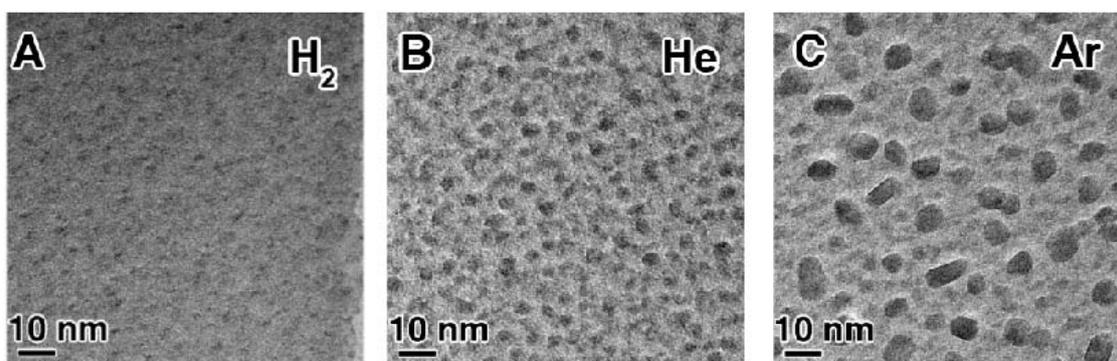


Figure 1. Plan-view TEM images of catalyst nanoparticles formed on the substrate after annealing (A) in H_2 / 4 mTorr of H_2O for 30 min, (B) in He / 4 mTorr of H_2O for 30 min and (C) in Ar / 4 mTorr of H_2O for 30 min. It is clear that the presence of different carrier gases strongly affects the rates of Ostwald ripening in the nanoparticle array.

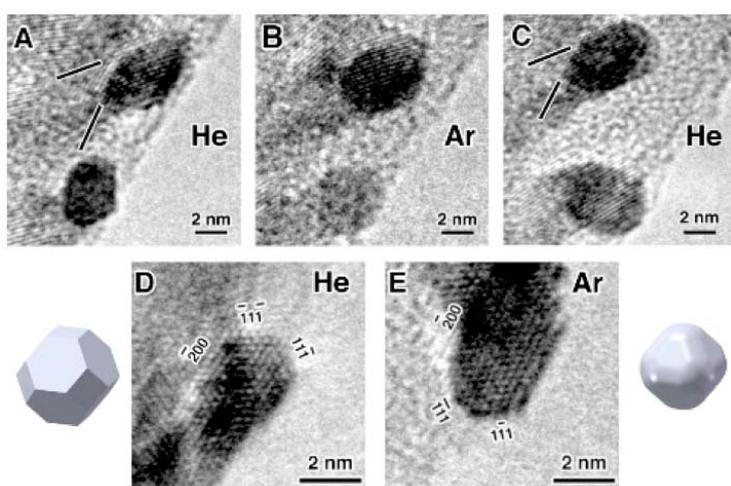


Figure 2: Frames extracted from in-situ video of Fe nanoparticles at 500 °C and in the presence of either He / 4 mTorr H_2O or Ar / 4 mTorr H_2O as noted. Strong faceting is observed for nanoparticles in He, while those in Ar show significant rounding.