Carbon Micro Tubes (CMTs) : Tuning Internal Diameters and Conical Angles

Gopinath Bhimarasetti, Mahendra K. Sunkara,
Chemical Engineering Dept, University of Louisville,
Louisville, KY 40292

John M. Cowley
Dept. of Physics and Astronomy,
Arizona State University, Tempe, AZ 85287

Here, we describe a synthesis strategy for synthesizing carbon micro tubular structures with internal diameters ranging from few nm to several microns and with conical angles from -15^0 (inverted cones) to 0^0 (straight tubes) to 30^0 (diverging cones). The most unique aspect is the fact that the internal channels of these structures are free of any obstructions and should be useful for nanofluidics and electrochemical applications.

Our synthesis strategy is based on our ability to change the wetting behavior of gallium with carbon using *in-situ* gas phase variations. Using this technique, a variety of hollow curved carbon morphologies have been synthesized: cones, tubes, funnels, tube-on-cone, Y-junctions, dumbbells and multi-staged tubules.[1] (Figure 1)

The growth experiments were conducted in a microwave plasma reactor on a substrate covered with molten gallium. Gallium droplets that form during plasma exposure, mediate the growth of carbon shell around the droplet. The contact angle between gallium and the carbon wall determines the conical angle of the structure as shown in Figure 2. The contact angle can now be varied by using different gas phase chemistries. In the presence of oxygen or nitrogen, gallium wets carbon, thus reducing the contact angle. In our synthesis method we adopt various dosing sequences of oxygen and nitrogen at different compositions to vary the morphology of the tubular structures. For example, tubular structures synthesized without any dosing result in conical morphologies with conical angles of about $20\text{-}30^0$. On the other hand, using increasing nitrogen dosing we were able to tune the conical angles from 30^0 to -15^0. With oxygen dosing, we could synthesize straight tubes (conical angle $= 0^0$), as oxygen is more aggressive than nitrogen in changing the contact angle. Adopting an 'n-step' dosing sequence at various stages of growth, we were able to synthesize 'n-staged' morphologies. Seamless tubular Y-junctions were formed during growth when two or more structures impinged on each other, due to spontaneous coalescence of gallium droplets at their tips into one droplet.

The walls of the described morphologies exhibit a very unique structure. Unlike multi-walled carbon nanotubes (MWNTs), the wall is not comprised of graphene sheets rolled into a cylinder. Instead, the wall is comprised of parallel sets of nanocrystals of graphite in the size range of 2-5 nm, as shown in Figure 3. The c-axis of the graphite nanocrystals is always perpendicular to the wall surface. These parallel sets of graphite nanocrystals are oriented with respect to the wall surface, depending on the conical angle of the tube. This orientation corresponds to the angle gallium meniscus makes with the carbon wall. Selected area electron diffraction and nanodiffraction results will be presented to discuss the nanostructure of the wall.

References

1. G. Bhimarasetti, M. K. Sunkara, U. M. Graham, B. H. Davis, C. Suh, K. Rajan, Advanced Materials, 15 (19), 1629 (2003).

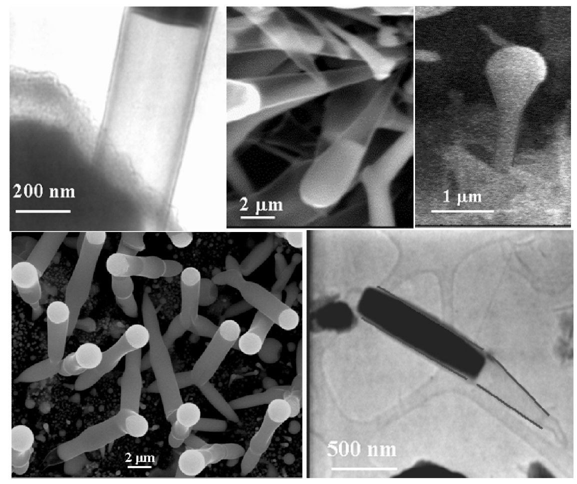

Figure 1. Some of the morphologies that were synthesized by adopting different dosing sequences.

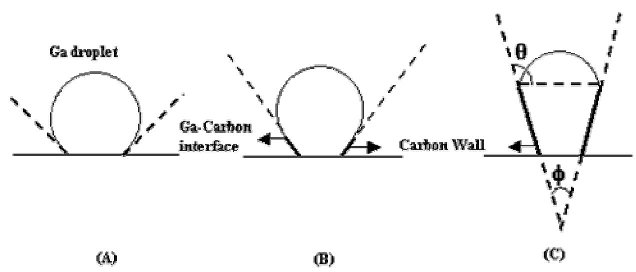

Figure 2. Schematic of the growth mechanism. (A) Initial gallium droplet (B) formation of carbon wall at the base of the gallium droplet. (C) Geometric representation of the relation between the contact angle and the conical angle.

Figure 3. Dark field STEM image of the wall taken using the (00,2) reflection.