

Building from the Ground up: Nanostructures to microstructures



Steven Noyce

American Fork High School, E-mail: steven.noyce@gmail.com

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Creativity is at the heart of existence. Throughout history, humankind has sought to create, whether it is a painting, a piece of architecture, or a machine. Incredible feats have been realized, with increasing complexity and diversity, as technology has enabled us to create larger buildings, more vibrant images, and smaller electronics. Although countless enabling discoveries have been made, there is a common theme that has sparked the technological explosion of the last century: the utilization of the small. Miniaturization has led to everything from our advanced electronics to our convenient microfiber couches that easily wipe clean after a spill. We have seen amazing advances, but as a whole have not come anywhere near utilizing the possibilities that small scales provide. The research now presented deals not only with the creation of nano-scale structures such as Carbon Nanotubes (CNTs), but also on the assembly and use of these components in micro and macro scale devices, such as MicroElectroMechanical Systems (MEMS).

When I began my 2009 International Science and Engineering Fair (ISEF) research project, I knew exactly what I wanted to work with: Carbon Nanotubes. I was blown away by the countless unique features of these molecules; ballistic electron transport, variable semiconductivity, tensile strength greater than any other material except the related Graphene molecule, impermeability to gaseous hydrogen, Van Der Waals radii allowing huge macroscale forces, and countless other properties

made CNTs seem like a molecule of dreams.

And dream, I did, but for quite some time it seemed like that was all I would ever do. You see, I was working in a High School chemistry room, with extremely limited resources, and in these conditions I feared that I would never create even one measly nanotube. I worked tirelessly, however, and in time, success came. By doing extensively modified replications of experiments I had seen in journal articles, I first began synthesizing amorphous carbon product, then impure CNT/carbon compound, and eventually, a pure Carbon Nanotube product.

As my replications began to work, I started to realize ways that the processes could be improved upon. I used my physics and chemistry background to work out the math and build models for some of the ideas I was having, and then I started to try them out, again dealing with very limited supplies and apparatus.

One of the first improvements that I made was adding chlorine gas (generated from the controlled electrolysis of salt water and used with stringent safety precautions) to the flame synthesis setup I had running. The basic idea of the setup was to take a hydrocarbon gas, such as methane, mix it with hydrogen gas and combust it in a controlled flame with a chemically isolated, catalytically activated metal mesh slicing through the flame. The high thermal conductivity of the mesh transferred a large amount of heat from the combustion region on the

outside of the flame to the inner gas cone, where oxygen was not present (a necessary requirement for CNT growth). Some great chemistry then had a chance to occur in the localized high temperature regions on the surface of the mesh. First, the iron salt which the isolated mesh had been coated with experienced a heat decomposition, leaving only a mix of iron and iron oxide behind. It then became diffusively mobile, conglomerated into small nanoparticles, and was reduced to porous iron metal by the hydrogen gas. Next the hydrocarbon gas was cracked at the catalytic iron sites, often yielding carbon atoms which went into a solid state steel solution, eventually causing the iron particles to become saturated with carbon solute. Finally supersaturation and crystallization occurred, with the "crystal" being a carbon nanotube that emerged and "grew" from the iron clumps. The reason that the addition of chlorine was helpful to this process is twofold. Not only did the chlorine remove the undesirable contaminant of amorphous carbon more readily than the CNTs, but it also forms intermediate chlorocarbons that are more prone to donating carbon atoms to the iron catalyst. This improvement synthesized better quality nanotubes with less impurities with less reactant in less time.

Without going into great detail, some of the other processes that I improved upon were Hot Wire Generator synthesis (which I rigged up using tungsten filaments from old light bulbs in various arrangements), synthesis in fused sodium chloride using an exfoliated graphite precursor (pencil "lead" in a blender with some chemicals), high voltage arc synthesis, and carbon electrode arc synthesis in various media. These methods were all great, and I was thrilled with the success that I was having with them, but I sensed that there was something missing. The end result of all of these procedures was a powdery black mess of CNTs, which, although having many incredible applications, did not seem, like the highly ordered nanostructures I had wanted to create.

I began to realize the source of my dissatisfaction. Although the nanotubes themselves had low entropy with their precise arrangements of atoms, they had no order with respect to one another as they lay jumbled together. It seemed to me that although CNT composites and the like had an incredible amount of potential, the most exciting properties of nanotubes were at either the individual or highly organized

level. My goal became to create ordered arrays of nanotubes, and so I set out, shooting for the stars.

The only technique I had found in the literature that gave me a hint as to how I would go about accomplishing this goal was that of patterned, plasma-enhanced chemical vapor deposition. I had no idea how I could possibly get something similar to work in my meager High School lab, so I went into overdrive trying to reason out what simplifications I could make in order to set up a functional apparatus.

Although I didn't have the means, the first simplification I knew I needed to make was to set up a proper RF coil. Because of my limited access to scientific literature, I did not know if it would be possible to do the same process thermally, but I took a guess and hoped that it would, and worked out the thermodynamics so that I could sleep at night. I scavenged for materials, trying with all my might to find things that would be chemically inert, thermally stable, geometrically workable, and most of all, obtainable. I never did find an ideal solution to all those problems for the reaction chamber, since I didn't have access to quartz or porcelain tubing, but I was able to work things out with some carefully oxidized aluminum. For the substrate, I had similar troubles and settled on aluminum again, this time an alloy with a high enough melting point. For the iron catalyst, I needed precise control over the thickness, composition, and pattern. I used a Sharpie marker to replicate the photolithography process, drawing simple patterns on the substrate. I then used an electroplating technique to put down an extremely thin layer of iron on the areas where Sharpie was not preventing conductivity. Once again I used natural gas and hydrogen obtained from the electrolysis of water as my reactant gases, and a combination of an old ceramics kiln and the grills from a toaster for the heat source. After a lot of work and more luck, I had finally produced true carbon nanotube microstructures!

At this point my chemistry teacher decided he could use the work I had done to get me involved with a university research group. I had previously contacted a local university, but they had turned me down, telling me that no professors were interested in working with High School students. At this point, however, my teacher brought a faculty member from

the university over to my school and had him take a look at what I was doing. He seemed impressed with what I had done, and gave me the contact information of a professor who led a CNT research group. I started attending group meetings, and discovered that the work being done by the group was nearly identical to the setup I had recently finished throwing together. They informed me of their process of filling the CNT microstructures with silicon in order to make MEMS, or MicroElectroMechanical Systems, and I was immediately enthralled with the idea, as it provided a simple method of making MEMS from any material with aspect ratios tens of times higher than previous fabrication methods.

I was thrilled to finally have access to high quality equipment, and started doing research into the specifics of CNT synthesis so that I could get a better framework in anticipation of my future in MEMS fabrication. I studied how various conditions, such as ethylene flow rate, hydrogen flow rate, reactant composition, argon dilution, and other variables affected the growth rate, dynamics, and maximal height. I reasoned that a likely limitation on the growth height was the coating of the iron nanoparticles with amorphous carbon, but I knew that adding an oxidizer would etch the CNTs, so I devised a phased water vapor incorporation method that increased the maximal growth height by a factor of 3. I studied nanotube oxidation rates and increased the efficiency of synthesis throughput. I researched the process of iron diffusion that occurs during growth, found several easy methods of determining the post-synthesis location of the iron, and looked into the practicality of substrate reusability. The findings from these projects were great additions to the CVD (chemical vapor deposition) process, making it more efficient, extensible, and usable.

At this point, I was almost ready to start making CNT MEMS, but before I began, I wanted to learn more about CNT properties, and I did so by finding interesting ways to use them. My first investigations were making CNT/polymer composites of various composition. These materials have a wide range of applications, yet I focused on how strength and conductivity vary with CNT concentration. I then moved on to creating conductive CNT sheets and wires, and from them I was able to make several useful items. The first was that of incandescent light bulbs

that neither require vacuum conditions to operate nor suffer from evaporative filament degradation. A second item was a much less than paper thin speaker that operates by thermoacoustical methods and thus has no moving parts and can be bent or stretched into any shape. A final item that I made was that of a non sticky, extremely strong adhesive tape that is stable under fairly high temperatures and is able to support very high forces. After assembling these items, I explored CNTs further by suspending them in various solutions and running time series dynamic conductivity tests that provided information about their properties and how they interact with other molecules.

I was finally ready to use the information I had gained in an effort to improve upon the CNT MEMS fabrication process. My first project dealing with this was the "RIE-less Process," in which I worked out some of the details of using a thermal oxidation step in order to avoid the expensive and cumbersome Reactive Ion Etch that had previously been used to remove the floor layer so that MEMS devices could be released. The problem then arose that the small amount of iron at the base of the CNT forest precluded our samples from entering some semiconductor processing machinery, so I worked on a gas phase iron removal process that was not harmful to the CNTs, but would steal the iron out from under them. After that, I became interested in using different materials for the sacrificial layer, instead of silicon or silicon dioxide. I tried chromium, aluminum, nickel, iron, and copper with some success, but it was difficult to get as good of growth atop these materials. After those attempts, I became interested in whether the number of walls on the multi-walled CNTs could be adjusted during a growth by changing reactant gas compositions. I experimented with this briefly, and found first that by stopping reactant flow for a short time during growth, a line could be drawn across the forest, and if reactants were turned back on at different flow rates afterward, then the change in growth rate made a very slight alteration to the side-wall angle, so that by repetition of this process, a limited amount of three dimensional control over the forest structure was possible.

Through all of the above methods and others not mentioned, I was able to improve upon many aspects of engineering structures on both the

nanoscale and the microscale. I may not have made one end all, incredible discovery, but I was able to effectively feed my creative spirit and love of learning by doing many separate experiments, which all blended together as contributions to

the singular goal of designing simple methods of advanced microfabrication through organization of nanoscale precursors. The experience I had through doing research was enlightening, and life changing.

About the Author

Motivated. That's how I would describe myself. My desire has always been to learn more, to do more, and to be more. I have sought improvement, both of myself and those around me. Although I have put forth great effort in this regard, it has been only through divinely given strength that I have had any capacity to achieve. When I was young my learning was disabled, yet I never allowed my future to appear dark. My life has been one filled with hope, and I yearn for my story and research to instill such in others and improve the world in which we live.

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