Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded $500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.

Wisconsin Initiative for Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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MOLECUAR MONOLAYERS FOR ATTACHING ELECTROACTIVE MOLECULES TO VERTICALLY ALIGNED CARBON NANOFIBERS

By

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Introduction for the General Public

Scaffolds for catalysis

As we try to move away from fossil fuels and toward renewable energy sources, chemical tools called catalysts are becoming increasingly important because they are essential for better fuel cells and some types of solar cells. Our research on attaching catalysts to carbon nanofibers could have far-reaching results for building more efficient fuels cells or converting excess CO_2 to useful products instead of contributing to global warming. It could also reduce the release of toxic materials from industry.

Catalysts are substances that make chemical reactions happen or speed up without destroying the catalyst itself. Without them, some key materials can't be made at all or cost so much that it isn't practical to make them. Catalysts are already used in many industrial processes. For example, adding a catalyst based on the element antimony to a mixture containing molecules known as esters will cause the esters to link together to form polyester, the synthetic fiber used in shirts and socks.

Generally, catalysts convert chemical reactants into products while keeping their original structure: Antimony remains in the polyester product mixture after the esters have all been converted to polyester. Most catalysts can be extracted and reused many times, so a small amount of catalyst can be used to make a very large amount of the product. This efficiency is one reason materials such as polyester are so inexpensive even though catalysts themselves are often expensive.

Catalysts have the practical disadvantage that molecules such as the antimony polyester catalyst must be separated from the reaction products in order to be reused.

This is often difficult and complete removal is important because many catalysts contain either expensive or toxic metals. One way to overcome this difficulty is to attach the catalyst to some surface, so the raw ingredients can flow in and the products can flow out without taking the catalyst with them.

Nanoscale materials are excellent candidates for catalyst support systems because they have very large surface areas for catalysts to adhere to. The effect is similar to the way the bristles of a toothbrush have much more surface area to hold toothpaste than the same amount of solid plastic would.

Nanoscale materials are measured in nanometers (nm), which are one billionth of a meter long. Nanoscale materials make human hairs look enormous. A hair is about 25,000 nanometers thick. Nanoscale carbon is a particularly attractive material for attaching catalysts because it is very stable.

Graphite, the material in pencil lead is formed from carbon atoms arranged in sheets. While each sheet is quite strong, the sheets are not strongly connected to each other. Sheets can slide along one another and flake off, making graphite a good material for writing. It is also possible to form sheets of graphite into nanomaterials. A sheet of graphite can be rolled into a tube to form a carbon nanotube. These nanotubes present the sheet surface along their length, with the sheet edges showing only at the tube ends.

It is also possible to form carbon sheets into cones. The cones can be stacked, like a stack of cupcake wrappers, to form a cylinder. That's called a carbon nanofiber. Figure1 shows two scanning electron microscope images of carbon nanofibers, one from the sides showing that they stand up like toothbrush bristles, and one from above showing how closely they are packed together. Like the cupcake wrappers, the nanofibers have

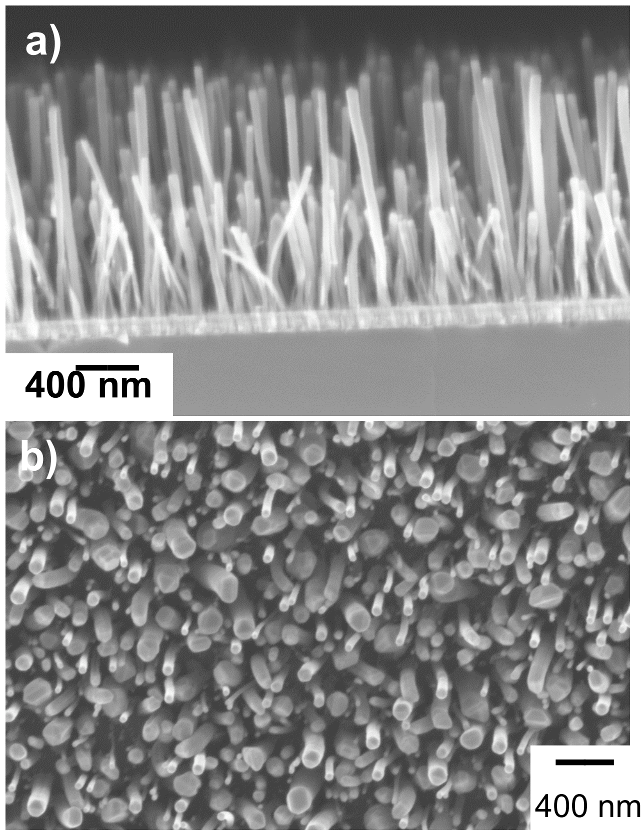

Figure 1: a) Side view of the carbon nanofibers showing their high surface area b) Top down view of the carbon nanofibers showing their close packing on the surface.

many exposed edges down their sides. That gives them a great number of edges on the surface.

Surface attachments on nanoscale carbon

Nanoscale carbon does have a limitation: it is a very stable material, which means it doesn't react with most other chemicals. Stable, unreactive materials are a good starting point for catalyst scaffolds, but it's difficult to get other materials to attach to them. To make nanoscale carbon more useful, our lab is finding ways to attach molecules to it.

Not much is known about attaching molecules to carbon nanofibers. They were only developed in the 1990s, so many aspects of their surface behavior at the atomic level have not been studied. Ideally, our attachment method could be very general so we could attach many different kinds of molecules for a variety of applications. For example, if we were attaching polymer-making catalysts, we would want a surface that could be tuned to make many polymers, such as PET, the polymer in soda bottles, not just polyester.

On this project, we first investigated attaching molecules to carbon nanofibers utilizing ultraviolet light. This reaction works for liquids with a particular reactive group at one end of the molecules. To attach the molecules, we coated the nanofiber surface with the liquid and then illuminated it with a UV light to give the molecules the energy needed to attach them to the surface. Covering the surface takes about 16 hours.

To understand how the molecules bind to our carbon nanofibers, I studied whether the molecules were binding at the graphite surface sites or at the edges. I found that the molecules were binding at the edges – like the cupcake wrapper edges, which form rings regular at intervals along the nanofiber surface. That showed that our molecules are spaced out along the nanofiber surface, because we only have graphite sheet edges about every 2 nanometers and the molecules are about 1.5 nanometers long.

One of the ways we figured out where the molecules were binding was through a collaboration with scientists working at Oak Ridge National Lab who are experts in carbon nanofiber growth. They could control the density of the edge plane rings on the carbon nanofibers (similar to controlling whether you have a squashed down stack of cupcake wrappers or a stack that has been fluffed apart). We could measure how many molecules were on the different types of nanofiber and see that there were more molecules on nanofibers with more edge plane sites.

Understanding electron movement

We wanted to use this ultraviolet attachment method to attach catalysts to the carbon nanofiber surface. Figure 2 shows a diagram of the surface we were trying to assemble, with the catalyst molecules attached to the carbon nanofiber surface through a molecular linkage. For many catalysts to work while attached to a surface, our ability to move electrons back and forth between the surface and the catalyst is essential. To understand how a catalyst could work on the surface we needed to understand how electrons transferred through the molecular linker attaching it to the surface. Since catalyst molecules are often quite complex in structure and in electronic activity, I started to study electron movement through the molecular layers by attaching a simple compound, ferrocene, to the surface. Ferrocene is a small, simple molecule that contains one iron atom so its behavior is easy to understand. By studying how to add and remove an electron from ferrocene I could learn how electrons moved through the molecular

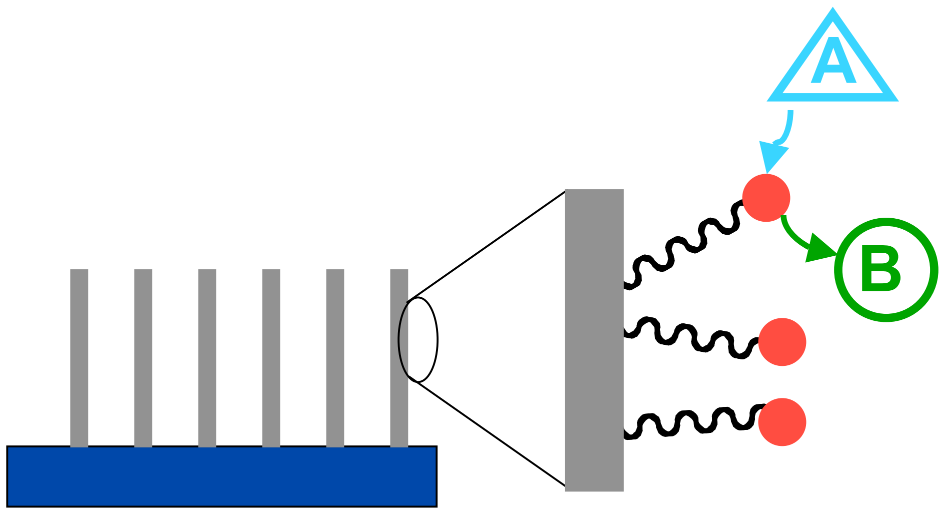

Figure 2: Diagram of the target assembly. The carbon nanofibers are depicted in grey. In the expanded section, the catalyst molecules are depicted as red circles, attached to the nanofibers by the black squiggles, which represent the molecular linker. The catalyst on the surface would take reactants (A) and convert them to products (B) while remaining immobilized.

layers. Other researchers have studied similar electron movements on flat gold surfaces because that is a simple system, making it easier to test theories. However, I found that the electron movements were very different on the carbon surface than on gold. This was important because some researchers had expected that the electron movements on other systems would be the same as those on gold.

My first binding method was a good way to test our theories about attaching molecules to carbon nanofibers, but the result wasn't very stable. A stable attachment is essential for this catalytic system, so I adapted a new method for binding molecules to the nanofiber surface.

The binding method I adapted to the nanofiber surface is known as "click" chemistry and has been widely used in other branches of chemistry. This method was inspired by the way that amino acids bind to form proteins, particularly the way they take two very reactive, unstable molecules and join them to make an extremely stable linkage. I adapted this reaction to the nanofiber surface by immobilizing one reactant on the surface and then exposing the surface to a solution of the second reactant. The method is much faster than the UV light method, taking only five hours to complete.

I again used ferrocene as a probe of electronic activity and showed that the new attachment was also effective at electron transfer. The new attachment was extremely stable, capable of cycling between the electronic states of ferrocene at least 1500 times, while the UV method could only cycle ~200 times. That test indicated that the attachment method would have similar stability when used with catalysts

Catalysts attached to carbon nanofibers

I then figured out how to attach catalysts to the nanofiber surface. I was able to attach three of them, a CO_2 reduction catalyst that could help convert excess CO_2 to useful products, a water oxidation catalyst that would be an essential part of a fuel cell system, and a catalyst used in industrial processes that is particularly toxic. The future work on this project will focus on how well the catalysts convert reactants to products while attached to the surface.