MRSEC Education and Outreach

Carbon Nanotubes Activity Guide

Quick Reference Activity Guide

Activity Materials

chicken wire models of different nanotube types
description pages for counting schemes
solid models for graphite and diamond structures

Starting Points

Have you learned about the elements in school? Elements are types of atoms. They make up all of the things around us. One element that is commonly found in everyday objects (including humans!) is carbon. We're going to talk about the different structures carbon can make when one carbon atom bonds to another.

Can you name some forms of carbon? Hints: Some people wear rings made from it, and most of you probably use another form to write everyday in class. Diamond is one form of carbon; the graphite used in pencils is another.

Hold up the solid models of diamond and graphite, and explain that each plastic sphere represents an atom. Ask the students to make some observations about these two structures. Then, focus their responses with the following question: How are the two structures different? Diamond has connections (bonds) occurring in all three dimensions, which makes the structure very rigid. That's why diamond is the hardest natural material known and why diamond can cut glass. On the other hand, graphite has connections in only two dimensions that form sheets of carbon, called graphene sheets. These graphene sheets stack one on top of another in layers which easily slip off the pencil onto the paper when we write. Even though these materials are made of the exact same element – carbon – the atoms can arrange in such a way to make one of the hardest materials *and* one of the softest.

Now, imagine taking one graphene sheet and rolling it up into a cylinder – this is a new form of carbon called a nanotube. If you rolled that same graphene sheet into a ball (so it looks like a nano-sized soccer ball), you get a fourth form of carbon called a fullerene or buckyball.

Demonstration Procedures

Use starting points to introduce the four forms of carbon to be discussed - diamond, graphite, fullerenes, carbon nanotubes.

Compare the sheet of chicken wire to the solid model of graphite. The sheets have the same hexagonal pattern. Explain that we will pretend that there is a carbon atom at each intersection on the sheet.

Use the sheet to demonstrate how a carbon nanotube can be formed by bending the sheet so that the opposite edges touch. Note that if you roll it up in different ways then you get different patterns along the cross section of the tube. Show the three pre-rolled nanotube models.

Explain that scientists have found that these different types of carbon nanotubes have slightly different structures which change their properties. Because of this scientists have developed a scheme to classify nanotubes - armchair, zigzag, chiral. Show the three models and ask the students to look for the different patterns they make.

Describe how to count around the circumference of the nanotube to determine what type (zig-zag, chiral, or armchair) it is. (detailed information on how to count the chirality of the tube can be found in the 'Background and Supporting Information' section) The zig-zag model is the easiest one to count and the best one to start with. Hold the model up and have the students count along with you. Next, show the counting on an armchair model, followed by the chiral model.

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Fact Sheet

Carbon has atomic number of 6 and an atomic weight of 12.

There are three basic methods by which carbon nanotubes are made. Scientists can make modifications to each technique to suit their specific research purpose.

1. **Electric arc discharge**. A current is passed between two graphite rods, one acting as an anode and one as a cathode, forming a hot, bright arc of electricity that vaporizes carbon from the anode and generates a plasma of carbon. The carbon recondenses on the cathode to form nanotubes. This method produces mostly multi-walled nanotubes (i.e. single-walled nanotubes stacked one inside another), but can produce single-walled nanotubes with the addition of certain metal nanoparticles on either the anode or the cathode.
2. **Chemical Vapor Deposition (CVD)**. Metal catalyst particles (usually iron, nickel or cobalt) are placed on a surface, such as a silicon wafer, and heated to high temperatures in the presence of hydrocarbon gas. The high temperature and the catalyst particles break the hydrogen and carbon atoms in the gas apart. The catalyst particle acts like a "seed" and anchors the nanotube to the surface as it grows out from the catalyst, growing longer and longer as more carbon atoms are released from the gas. This method produces both multi-walled and single-walled nanotubes depending on the temperature.
3. **Laser Ablation**. A high power laser is used to vaporize carbon from a graphite target at high temperature. The resulting "soot" is collected by a water cooled collector. This method forms single-walled nanotubes.

Synthesis challenges. One of the current challenges in CNT research is developing a synthesis technique for growing SWNTs of an exact type (e.g. zig-zag) with an exact orientation (e.g. perpendicular to a surface).

The structures of the nanotubes can be correlated with their physical properties such as:

- **Mechanical properties (tensile strength)** Based on small-scale experiments and theoretical calculations, a one-inch thick rope of CNTs is predicted to be 100 times stronger than steel and 1/6 the weight of steel.
- **Thermal conductivity properties** CNTs conduct heat very well. A nanotube's thermal conductivity is predicted to be ten times higher than silver. Unlike metals (which conduct heat by moving electrons), CNTs conduct by wiggling the covalent bonds between the carbon atoms themselves.
- **Electrical conductivity properties** One of the main things that distinguish nanotubes from other nanomaterials is their electrical properties. Unlike any other known material, nanotubes can have semiconducting properties (some zig-zag, chiral) *AND* metallic properties (armchair, some zigzag).

Carbon nanotubes are currently being used for a number of significant applications (see Background for more details):

- **AFM probe tips.**
- **Flat panel display screens.**
- **Microelectromechanical (MEMS) devices.**
- **Hydrogen storage.**
- **Actuators/Artificial muscles.**
- **Chemical sensors.**
- **Nanoscale electronics/nanocomputing.**
- **Nanothermometers.**

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Background an Supporting Information

Background

By middle school, kids have learned about the elements and they have been introduced to the concept of the atom. When starting this activity it will be important to remind them of what they know – atoms are the building block of everything around them, elements are different kinds of atoms – and build on this knowledge to teach them something new. The carbon nanotube activity is a great way to build on their understanding of atoms and the elements, and teach them something new about nanotechnology. To do this you might also need to help them understand how small nano is and why it is exciting for scientists and engineers to create materials and devices at the nanoscale. (Refer to the "How Small is Nano?" Activity Guide.)

Carbon is one of the most abundant elements on our planet. Many students will know that it makes up a major percentage of the elements in our body and is included in the air as well as many other materials around us. This is important to acknowledge, but in this activity we are just focussing on structures made up of only carbon and no other elements.

Most students will be familiar with diamond and graphite and may even know that these materials are made up of carbon. Diamond is the hardest substance found in nature (a diamond ring can scratch glass easily), but graphite is one of the softest (pencils use graphite to make a black mark and graphite is also often used as a lubricant to allow two surfaces to slide freely). With a little help and encouragement, students will be able to identify graphite and diamonds (pencils and engagement rings). Give them the opportunity to brainstorm the different properties associated with each material. Both are made up only of carbon atoms, but these atoms are arranged very differently (diamond = tetragonal; graphite = hexagonal sheet, each atom bonded to three others). The differences between these two types of carbon arise at the nanoscale – when the structure of carbon atoms have different arrangements. Nature gave us these two types of carbon, but scientists have been able to create other forms of carbon - fullerenes and nanotubes. Our goal in this activity is introduce the structures and properties of the four types of carbon. Be sure to allow the students to see and play with the structures of each form of carbon.

Given the dramatic difference between diamond and graphite, we expect fullerenes and nanotubes to have very different properties as well. Scientists can look at these other two forms of carbon – using special microscopes that can see at the nanoscale - to learn more about how the carbon atoms are arranged within them. (Remember: the key to the material's property lies in how the atoms are arranged!) Originally these forms of carbon were made by zapping graphite with a high energy laser until most of the graphite was gone. In the soot that was left over, scientists found fullerenes and nanotubes. Since that first discovery, scientists and engineers have devised more efficient ways to make carbon nanotubes; in fact, nanotube synthesis has become a major area of nanoscience research.

The students should be introduced to fullerenes, which are soccer ball-shaped molecules that consist of 60 carbon atoms. This unusual shape can be found in many different places such as sports (soccer balls and new golf balls), architecture, and art (examples of each will be shown). These molecules were named after an architect, Buckminster Fuller, who was responsible for the design of the first geodomes. A geodome that many kids will be able to recognize is "Spaceship Earth" at Epcot Center (Disney World). Fullerenes consist of hexagons and pentagons that form a spherical shape. Fullerenes have also been proposed as possible HIV inhibitors as well as potential constituents in interstellar space. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley, Robert Curl and Harold Kroto for the discovery of fullerenes. These molecules are relatively new to the field of chemistry as they were first discovered in 1985, but their structure has been seen through history.

Carbon nanotubes, the most recent discovery of a form of carbon, should also be introduced. These molecules are shaped like a tube (imagine a sheet of graphite, or "graphene sheet", rolled into a tube) and were first discovered by Sumio Iijima in 1991, six years after fullerenes. Ironically, nanotubes were discovered by accident. Iijima was trying to make fullerenes when he noticed long, needle-like structures in addition to the round buckyballs he was expecting. There are three different types of carbon nanotubes, determined by how the carbon sheet is wrapped into a tube. Over the course of this activity, students will be introduced to the three types of nanotubes, armchair, zig-zag, and chiral [e.g. zig-zag (n, 0); armchair (n, n); and chiral (n, m)]. Nanotubes can also be described as single-walled (SWNT – like a single graphene sheet, rolled up) or multi-walled (MWNT – like a bunch of SWNT stacked one inside of another).

Carbon nanotubes and fullerenes are good examples of how, like many things in nature, subtle differences in the structure of something can change the behavior that it exhibits.

How are carbon nanotubes made?

One method used to grow CNTs is Electric Arc Discharge. Two graphite rods, one acting as an anode and one as a cathode, are placed close together in an inert environment of He gas. A current is passed between the two rods forming a hot, bright arc of electricity that vaporizes carbon from the anode and generates a plasma of carbon and helium. The carbon from the plasma recondenses on the cathode to form mostly MWNT. Adding metal catalyst particles to either the anode or the cathode produces SWNT.

In 1996, Richard Smalley reported another way to synthesize nanotubes, called Laser Ablation. Instead of an electric arc, a laser is used to form a carbon vapor from a heated (1200C) graphite rod. An inert carrier gas (Helium or Argon) carries the carbon vapor from the 1200C graphite rod to a water-cooled "cold-finger" where the carbon vapor recondenses to form SWNTs.

The third method of growing CNTs is Chemical Vapor Deposition (CVD). Metal catalyst particles (usually iron, nickel or cobalt) are placed on a surface, such as a silicon wafer, and heated to high temperatures in the presence of hydrocarbon gas. The high temperature and the catalyst particles break the hydrogen and carbon atoms in the gas apart. There is still debate over what exactly happens with the metal catalyst particle and the carbon atoms, but the catalyst acts like a "seed" and the nanotube grows out from it, growing longer and longer as more carbon atoms are released from the gas. This method produces both multi-walled and single-walled nanotubes depending on the temperature.

One of the current challenges in CNT research is developing a technique for growing SWNTs of an exact type with an exact orientation. Scientists are also growing very long ropes and bundles of SWNTs in order to make woven nanotube threads, which could ultimately be used to make nanotube fabric!

How can you tell what type of nanotube it is?

Scientists determine the *chirality* of a tube, or how the graphene sheet is rolled up, by counting the number of carbon atoms along the circumference of the tube. However, because graphite is a lattice, there are only 2 allowed counting directions, $\mathbf{a_1}$ and $\mathbf{a_2}$. Starting from an arbitrary carbon atom, the $\mathbf{a_1}$ and $\mathbf{a_2}$ directions point towards the closest equivalent carbon atoms in the lattice. (Figure 1) The chirality is determined by how many times you have to move in the $\mathbf{a_1}$ direction (n) and how many times you have to move in the $\mathbf{a_2}$ direction (m) in order to return to your starting point. Chirality is notated as (n, m) where n and m are called the *chiral numbers*. Zig-zag tubes are (n, 0), armchair tubes are (n, n) and chiral tubes are (n, m).

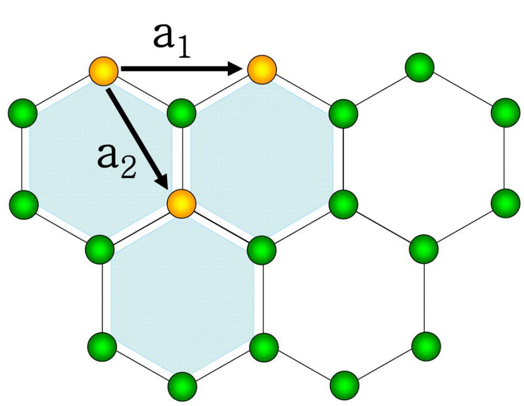


Figure 1. The counting directions (a_1 and a_2) point from an arbitrary "origin" atom towards the closest equivalent carbon atoms in the graphene lattice.

For example, to count a (5,0) zig-zag nanotube, choose an arbitrary carbon atom as your starting point (red star, Figure 2). Move to the closest carbon atom in the $\mathbf{a}_1$ direction. This is count one. Move again in the $\mathbf{a}_1$ direction: two. Continue counting along the $\mathbf{a}_1$ direction until you reach your starting point. It should take you five counts in the $\mathbf{a}_1$ direction to return to the starting point.

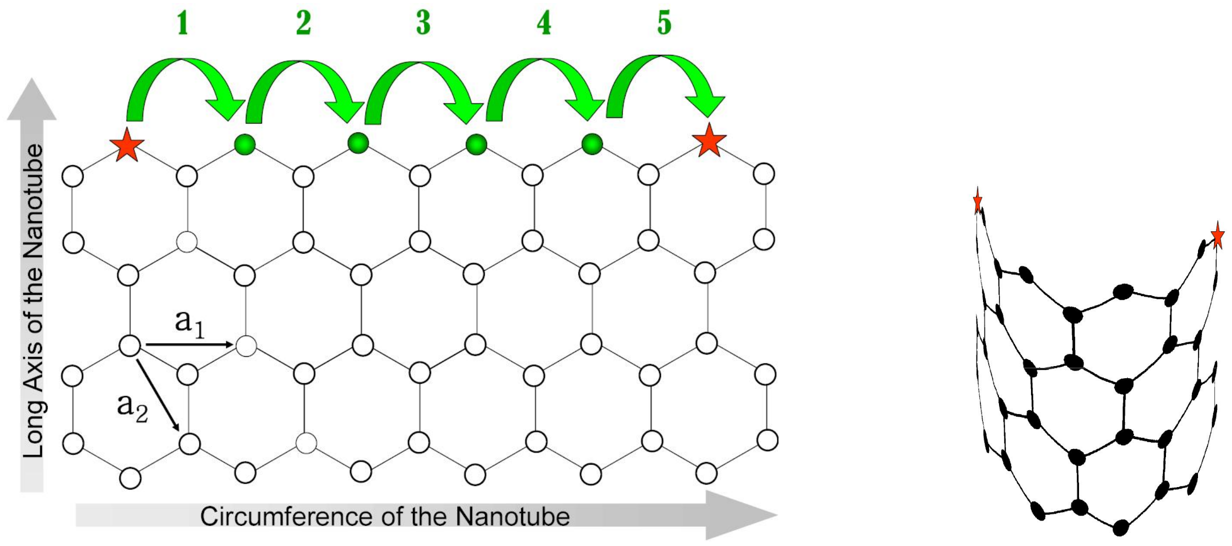


Figure 2. Counting a (5,0) zig-zag nanotube. The red stars represent the same carbon atom; the stars would overlap if you were to "roll" the graphene sheet into a tube.

To count an armchair or chiral tube, it is necessary to move along both the $\mathbf{a}_1$ and a_2 directions. If you were to count only along the $\mathbf{a}_1$ direction, you would never be able to return to your starting point; it is necessary to count along the $\mathbf{a}_1$ direction, then turn and count along the $\mathbf{a}_2$ direction in order to return to the starting point. For example, to count a (3, 3) armchair tube, choose an arbitrary carbon atom as your starting point (red star, Figure 3). Move to the closest carbon atom in the $\mathbf{a}_1$ direction. Move a total of 3 times in the $\mathbf{a}_1$ direction. You will notice that if you continue in the $\mathbf{a}_1$ direction, you will not return to your starting point. From the same carbon atom you just reached, turn and move 3 times in the $\mathbf{a}_2$ direction. You should have returned to your starting point. Chiral and armchair nanotubes can both be counted in this manner.

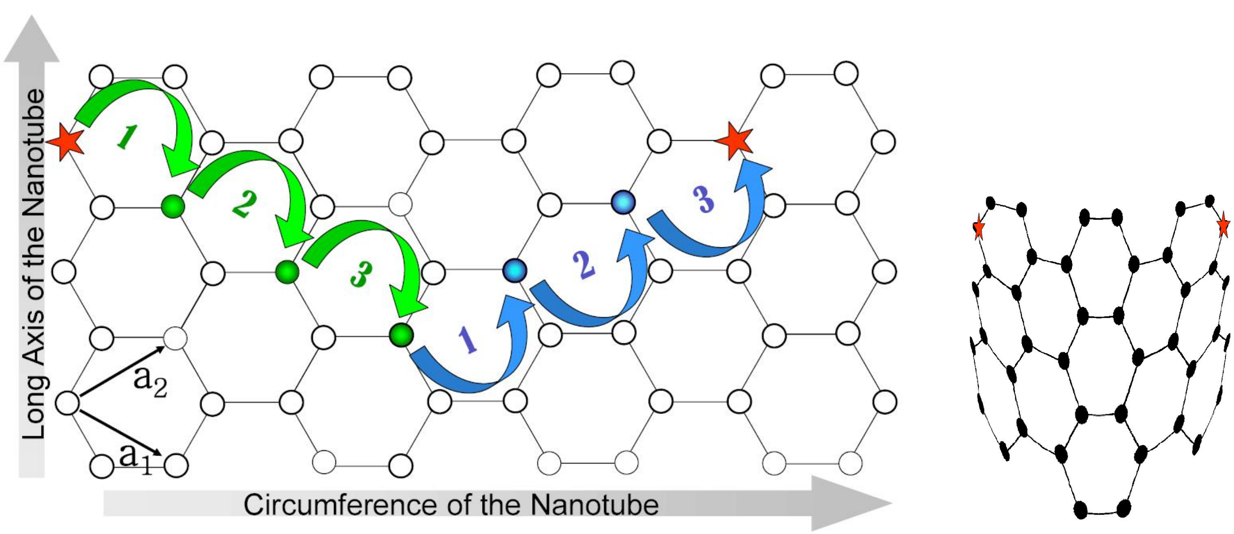


Figure 3. Counting a (3,3) armchair nanotube. The red stars represent the same carbon atom; the stars would overlap if you were to "roll" the graphene sheet into a tube.

Applications of Carbon Nanotubes

Carbon nanotubes are currently being used for a number of significant applications:

- **AFM probe tips.** Single-walled carbon nanotubes have been attached to the tip of an AFM probe to make the tip “sharper”. This allows much higher resolution imaging of the surface under investigation; a single atom has been imaged on a surface using nanotube-enhanced AFM probes. Also, the flexibility of the nanotube prevents damage to the sample surface and the probe tip if the probe tip happens to “crash” into the surface.
- **Flat panel display screens.** When a nanotube is put into an electric field, it will emit electrons from the end of the nanotube like a small cannon. If those electrons are allowed to bombard a phosphor screen then an image can be created. Several companies (Samsung, in particular) are researching how to use this technology to replace the bulky electron guns of conventional TV sets with these significantly smaller carbon nanotube electron guns. In the spring of 2005, Motorola announced a new “NanoEmissive Display” (NED) technology that could make more energy-efficient and cost-effective ultra-flat (<1” thick) display screens a reality. Learn more about how conventional televisions work at www.howstuffworks.com. Learn more about a flat panel display prototype: Wang, Q.H., Yan, M., and Chang. *Appl. Phys. Lett.* **78**, 1294 (2001).
- **Nanocomposite materials.** Dr. Morinobu Endo at Shinshu University mixed nylon with carbon *fibers* (100-200 nm diameter threads made in a similar manner to nanotubes) creating a nanocomposite material that could be injected into the world’s smallest gear mold (as of 2004). The carbon fibers have excellent thermal conductivity properties that cause the nanocomposite material to cool more slowly and evenly allowing for better molding characteristics of the nanocomposite. The “improved” properties of the nanocomposite allow it more time to fill the tiny micron-sized mold than nylon would by itself. The tiny gears currently are being made in collaboration with Seiko and Showa Denko KK (SDK) for use in watches. (see www.sdk.co.jp/contents_e/news/news02/02-02-06.htm)
- **Hydrogen storage.** As we move into a new century, there is a global focus on a cleaner environment and developing renewable energy sources. To that end, a great deal of research is being devoted to hydrogen fuel cells. When oxygen and hydrogen react in a fuel cell, electricity is produced and water is formed as a byproduct. If industry wants to make a hydrogen-oxygen fuel cell, scientists and engineers must find a safe way to store hydrogen gas needed for the fuel cell. Carbon nanotubes may be a viable option. Carbon nanotubes are able to store hydrogen and could provide the safe, efficient, and cost-effective means to achieve this goal. Hydrogen atoms bond to the carbon atoms of the nanotube, and can be later released with slight changes in temperature and pressure. While nanotube-based hydrogen fuel cells are promising, there are no viable products on the market yet. (for information on how nanotubes store hydrogen, see Dillon, A.C. et al. *Science.* **286**, 1127 (1999).)
- **Actuators/Artificial muscles.** An actuator is a device that can induce motion. In the case of a carbon nanotube actuator, electrical energy is converted to mechanical energy causing the nanotubes to move. Two small pieces of “buckypaper,” paper made from carbon nanotubes, are put on either side of a piece of double-sided tape and attached to either a positive or a negative electrode. When current is applied and electrons are pumped into one piece of buckypaper and the nanotubes on that side expand causing the tape to curl in one direction. This has been called an artificial muscle, and it can produce 50 to 100 times the force of a human muscle the same size. Applications include: robotics, prosthetics. Learn more about carbon nanotube actuators: Baughman, R.H. et al. *Science.* **284**, 1340 (1999).
- **Chemical sensors.** Semiconducting carbon nanotubes display a large change in conductance (i.e. ability to store charge) in the presence of certain gases (e.g., NO_2 and NH_3). Researchers have been able to use nanotubes as sensors by exposing it to gas and measuring the change in conductance. When compared to conventional sensors, carbon nanotubes provide the advantages of a smaller size, an increased sensitivity, and a faster response. In March 2005, researchers at the Naval Research Laboratory were able to detect minute amounts of sarin gas in under 4 seconds using a prototype nanotube gas sensor (previous sensors took over a minute to detect the same amount!). In the future, nanotube sensors could be used for security and environmental applications. For more information, see Snow et al. *Science*, Vol 307, 1942 and Wei, Q.-H. et al. *Science.* 287, 622 (2000).
- **Nanoscale electronics.** Scientists have exploited the mechanical and electrical properties of carbon nanotubes to produce molecular electronic devices. One of the most significant applications is nanotube transistors. Transistors are devices that can act like an on/off switch or an amplifier for current and are used in nearly every piece of electronic equipment in use today. Scientists have been able to use semiconducting nanotubes as compact, more efficient alternatives to conventional transistors. For more information about nanotube transistors, see the IBM

Nanoscience Group page http://www.research.ibm.com/nanoscience/. For information on how transistors work, visit the IEEE Virtual Museum http://www.ieee-virtual-museum.org/collection/tech.php?taid=&id=2345729&lid=1

Additional Demonstrations and Experiments

Several accompanying demonstrations can be used to supplement the basic carbon nanotube demonstration discussed above.

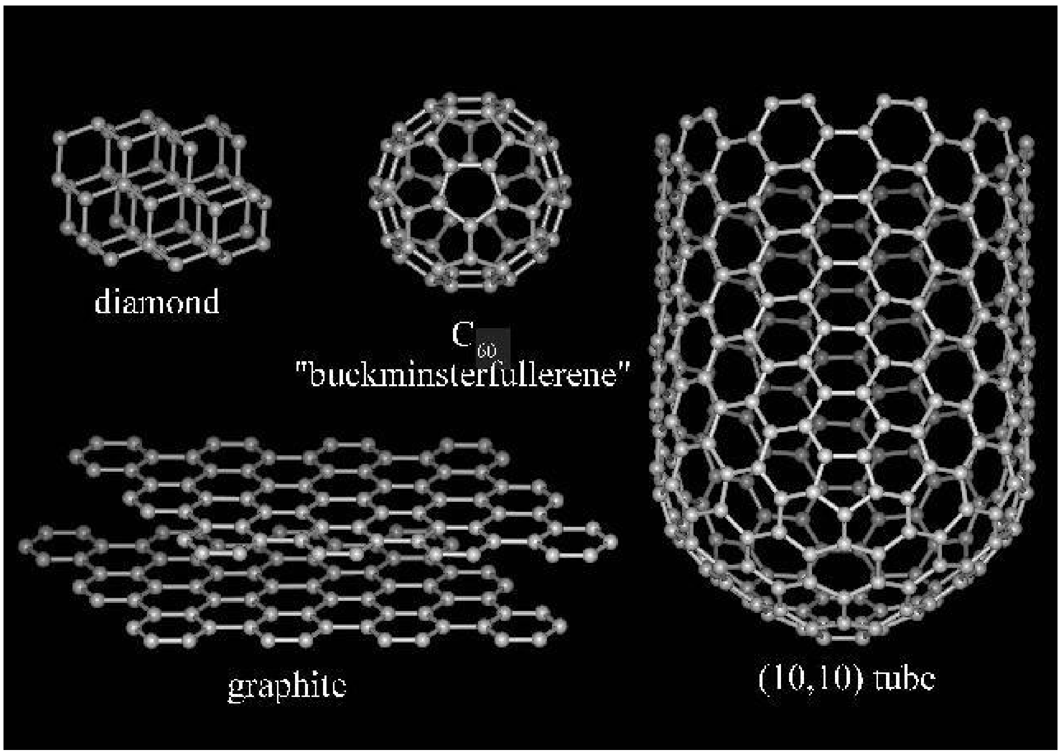
In some outreach venues a giant five foot tall carbon nanotube model is used. After learning how to classify and count carbon nanotubes, students can be asked to try out their new skills on the giant model. If they are successful in classifying the giant model (or close) the students can spin the prize wheel and take away a give-away item.

When discussing the different properties of the different forms of carbon, the thermal conductivity of diamond (diamond tip scribes held against ice) and electrical conductivity of graphite can be demonstrated.

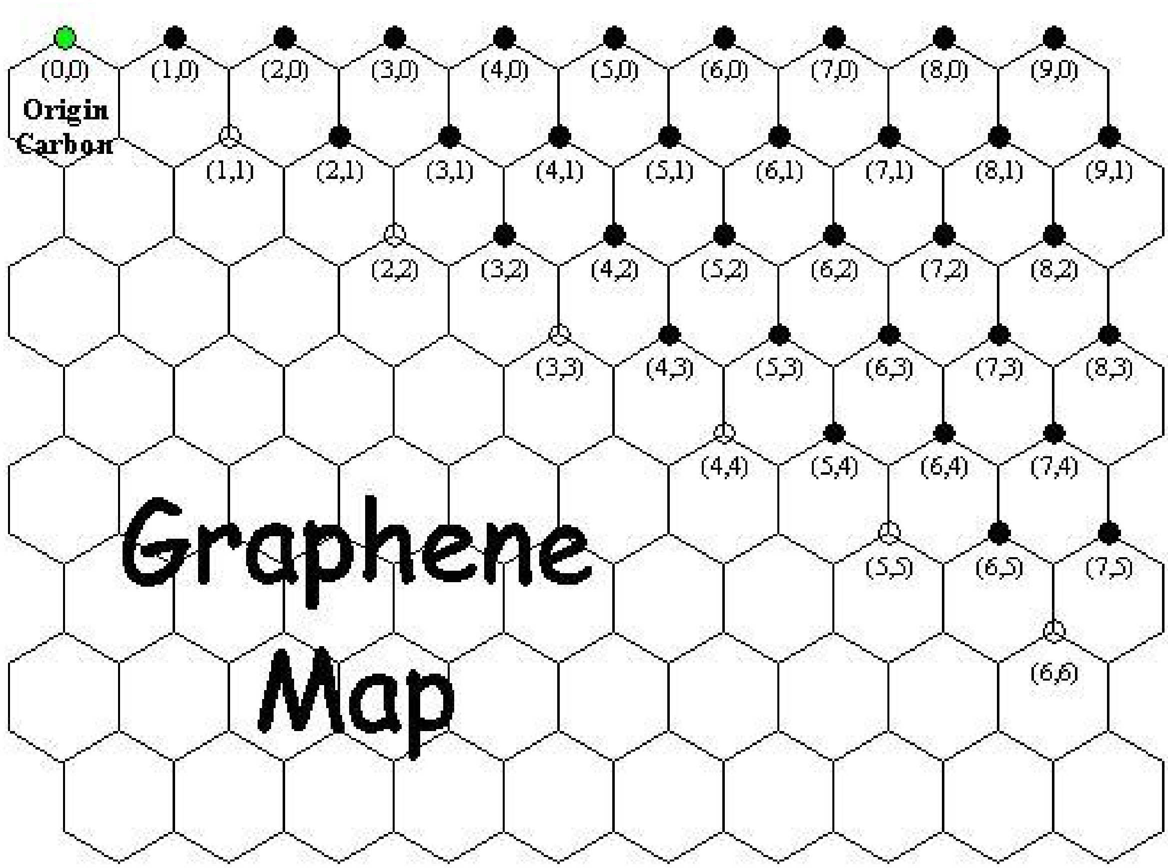
When discussing the form of fullerenes, the students can be given the opportunity to put together a paper model of a fullerene (either C_{60} or C_{70}).

When discussing the superconducting properties of fullerenes, the effect can be demonstrated with the demonstration that places a magnet "magically floating" above a superconducting plate.

In addition to the chicken wire models, pencils with the three basic types of nanotubes printed on them may also be available. Each student can be given a pencil (Each pencil will have the design of one of the types of nanotubes) and will have to figure out which type of nanotube they are holding.



Four forms of carbon slide created by Prof. Richard Smalley of Rice University.


Graphene Map
(0,0)
Origin Carbon
(1,0) (2,0) (3,0) (4,0) (5,0) (6,0) (7,0) (8,0) (9,0)
(1,1) (2,1) (3,1) (4,1) (5,1) (6,1) (7,1) (8,1) (9,1)
(2,2) (3,2) (4,2) (5,2) (6,2) (7,2) (8,2)
(3,3) (4,3) (5,3) (6,3) (7,3) (8,3)
(4,4) (5,4) (6,4) (7,4)
(5,5) (6,5) (7,5)
(6,6)