ChemMatters

DEMYSTIFYING EVERYDAY CHEMISTRY

OCTOBER 2009

The Origin of the Chemical Elements ... Exploding Stars, p.6

national chemistry week

Chemistry—It's Elemental

Celebrating the elements in honor of the 140th anniversary of the Periodic Table of Elements.

QUESTION FROM THE CLASSROOM

By Bob Becker

Q My chemistry teacher told our class that all colored gases are poisonous. He said that gases are generally invisible, so if you can see the gas, it surely is bad for you. But what about steam? That's a gas you can see but it is just made up of water in the gaseous state, so it can't be poisonous—right?

A You are right that water in the gaseous state is not poisonous. And your chemistry teacher is also right that all colored gases are poisonous: Any gas that you can see is dangerous and should be avoided. Here's the catch: What you are calling "steam" is not really water in the gaseous state.

SHUTTERSTOCK

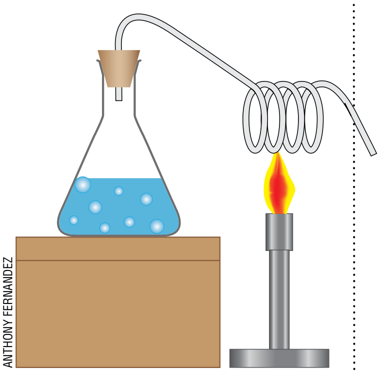
Pure gaseous water only exists next to the spout of the kettle. Elsewhere, it is mixed with liquid droplets to make the visible steam.

Let's say you put some liquid water in a kettle on the stove. Within a few minutes, the water inside reaches 100 °C, and it begins boiling. You then start to see what you think is gaseous water billowing out of the spout. Actually, pure gaseous water is present only in the gap between the spout of the kettle and the beginning of the billowy cloud. (Some gaseous water is also present in between the visible steam particles, but at much lower pressures and mixed with air.) This gap is shown in the picture below.

This gas only lasts a few milliseconds, because as soon as this hot invisible gas hits the cool air in the room, it quickly condenses into little tiny droplets of liquid water, which is what you are seeing. The droplets, in the form of mist, are suspended momentarily in the air, but they do not represent gaseous water.

Many chemistry textbooks contain the same misconception. So, I do the following demonstration, as illustrated below. I boil some water in a large Erlenmeyer flask on a hot plate. The flask is fitted with a one-holed rubber stopper that has a 50- to 60-centimeter long copper tube protruding from it. This tubing is bent to the side and wrapped into a coil.

Once the water starts boiling, and what looks like steam starts pouring out of the end of the tube, I light a burner and place



ANTHONY FERNANDEZ

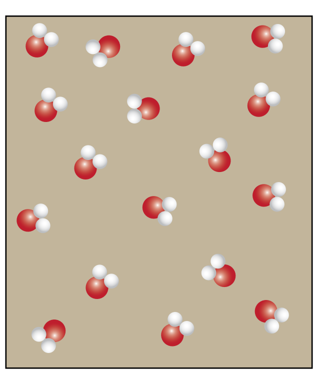
Erlenmeyer flask on a hot plate.

it beneath the copper coil. This takes the 100 °C gas passing through the copper tube and heats it up to well above 200 °C. At that temperature, it takes much longer for the gas to cool to temperatures at which it would condense to droplets of liquid water.

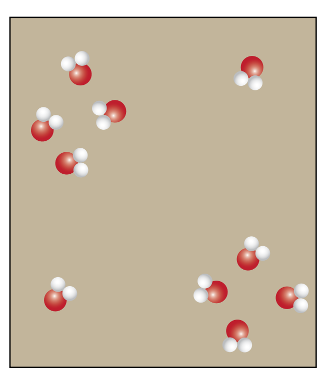
After about 15 seconds of heating, the billowy cloud simply disappears and all they see is—nothing. In fact, it looks as though there is nothing at all coming out of the end of the tube. I point out to them that they can see the water still boiling vigorously in the flask, and all that gaseous water has to be coming out of the tube, because there is nowhere else for it to go.

I hold a digital thermometer in the invisible stream of gas, and the thermometer quickly rises to 200 °C—its upper limit. I also hold a piece of white paper in the hot stream, and after a few seconds, it starts to scorch. Although the paper does not quite catch on fire, a wooden match held in the hot stream quickly ignites.

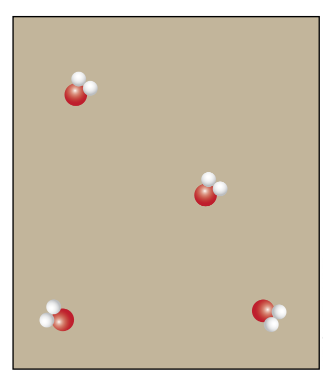
This experiment is perhaps most impressive, and I always enjoy pointing out to my students that they just witnessed a fire started by water!



Liquid Water



Steam



Gaseous Water

ANTHONY FERNANDEZ

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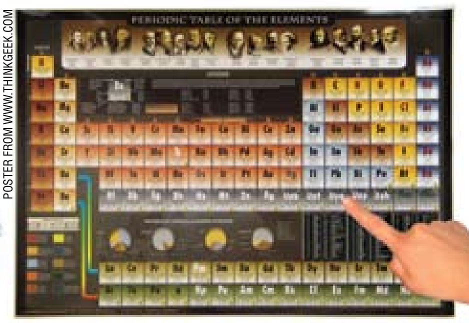

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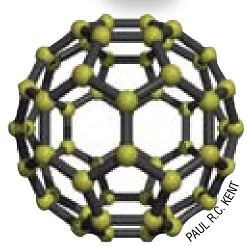

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COVER PHOTOGRAPHY COURTESY OF THE EUROPEAN SPACE AGENCY AND JUSTYN R. MAUND (UNIVERSITY OF CAMBRIDGE). In this artist's view the red supergiant supernova progenitor star (left) is exploding following the transfer of about 10 solar masses of hydrogen gas to the blue companion star (right).

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Where Do Chemical Elements Come From?

By Carolyn Ruth

In 1054, Chinese astronomers recorded what they called a "guest star" in the constellation of Taurus, the Bull. This star had never been seen before, and it became brighter than any star in the sky. In the American Southwest, a culture rich in astronomical tradition called the Anasazi also witnessed this brilliant new star. Easily visible in broad daylight, the observers could read by it at night. Today, we know the Chinese and Anasazi were witnessing a huge star explosion, called a supernova.

NASA,ESA, HEIC, AND THE HUBBLE HERITAGE TEAM (STScI/AURA)

What these observers did not know is that during the explosion, the star not only emitted huge amounts of light—more light than a billion suns—but also released chemicals in space. Inside the star were most of the first 26 elements in the periodic table, from simple elements, such as helium and carbon, to more complex ones, such as manganese and iron; and the giant explosion sprayed them in space. During the explosion, other elements were created as well, and after the explosion, the chemicals in space combined with each other to form ions and molecules.

These elements travel in space and ultimately end up in planets like Earth, being part of everything we see around us and ourselves. The carbon in our cells, the oxygen in the air, the silicon in rocks, and just about every element, were all forged inside ancient stars before being strewn across the universe when the stars exploded.

During the past century, scientists have been studying how chemical elements form in stars and in outer space. Like genealogists—experts who study the origins of people and families—these scientists can track down where most chemical elements came from and how they descended from each other. And, similar to forming a family tree, studying the links between the chemical elements has brought—and keeps bringing—many surprises and interesting discoveries.

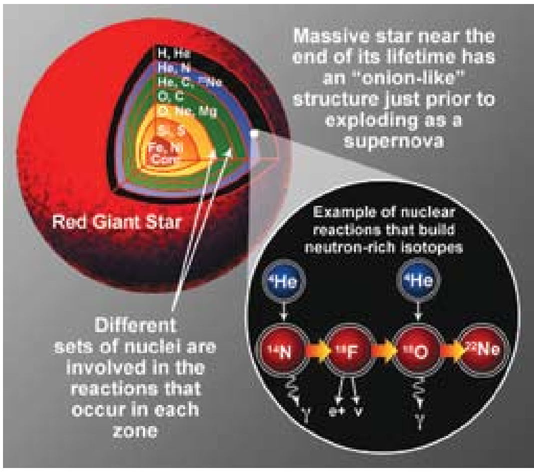
Stellar ovens

A young star is composed primarily of hydrogen, the simplest chemical element. This hydrogen ultimately leads to all known elements. First, the two constituents of each hydrogen atom—its proton and electron—are separated. The high pressure inside the star can literally squeeze together two protons, and sometimes, a proton will capture an electron to become a neutron.

When two protons and two neutrons band together, they form the nucleus of helium, which is the second element in the periodic table. Then, when two nuclei of helium fuse with each other, they form the nucleus of another element, beryllium. In turn, the fusion of beryllium with helium produces a carbon nucleus; the fusion of carbon and helium nuclei leads to an oxygen nucleus, and so on. This way, through successive fusion reactions, the nuclei of most elements lighter than iron can be formed (Fig. 1). Scientists call this process nucleosynthesis (for "synthesis of nuclei").

In stars, these fusion reactions cannot form elements heavier than iron. Up until the formation of iron nuclei, these reactions release energy, keeping the star alive. But nuclear reactions that form elements heavier than iron do not release energy; instead, they consume energy. If such reactions happened, they would basically use the star's energy, which would cause it to collapse.

Not all stars form iron, though. Some stars explode before creating that many ele-



LAWRENCE LIVERMORE NATIONAL LABORATORY

Figure 1. The chemical composition of a star before it explodes into a supernova.

ments. In stars less massive than the sun, the reaction converting hydrogen into helium is the only one that takes place. In stars more massive than the sun but less massive than about eight solar masses, further reactions that convert helium to carbon and oxygen take place in successive stages before such stars explode. Only in very massive stars (that are more massive than eight solar masses), the chain reaction continues to produce elements up to iron.

A star is a balancing act between two huge forces. On the one hand, there is the crushing force of the star's own gravity trying to squeeze the stellar material into the smallest and tightest ball possible. On the other hand, there is tremendous heat and pressure from the nuclear reactions at the star's center trying to push all of that material outward.

The iron nucleus is the most stable nucleus in nature, and it resists fusing into any heavier nuclei. When the central core of a very massive star becomes pure iron nuclei, the core can no longer support the crushing force of gravity resulting from all of the matter above the core, and the core collapses under its own weight.

NASA/CXC/ASU/J. HESTER ET AL.

Combined X-ray and optical images of the Crab Nebula.

The collapse of the core happens so fast that it makes enormous shock waves that blow the outer part of the star into space—a supernova. It is during the few seconds of the collapse that the very special conditions of pressure and temperature exist in the supernova that allow for the formation of elements heavier than iron. The newly created elements are ejected into the interstellar dust and gas surrounding the star.

"The amount of elements released through a supernova is truly phenomenal," says Stan Woosley, professor of astronomy and astrophysics at the University of California at Santa Cruz. "For example, SN1987A, a supernova seen in 1987, ejected 25,000 Earth masses of iron alone."

How stars make elements heavier than iron

Elements that are heavier than iron can be assembled within stars through the capture of neutrons—a mechanism called the "s" process. The process starts when an iron nucleus captures neutrons, thus creating new nuclei. These nuclei can be either stable, that is, they do not change, or radioactive, meaning that they transform, or decay, into another element after a certain amount of time, which can be as short as a fraction of a second and as long as a few million years.

Also, the newly formed nuclei can be different versions of a given element. These different versions of an element are called isotopes. They all contain the same number of protons in their nucleus but have different numbers of neutrons. Some isotopes are radioactive, while others are stable and never change.

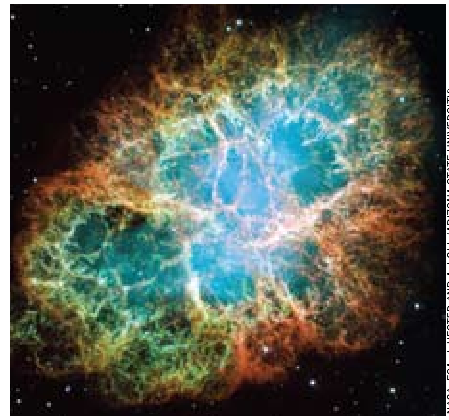
For example, nickel can appear in the form of 23 different isotopes. They all have 28 protons, but each isotope contains between 20 and 50 neutrons. Of these 23 isotopes, only five are stable, while the others are radioactive.

If a nucleus produced through the "s" process is stable, it may capture another neutron. If it is radioactive, it transforms into another nucleus. This other nucleus can, in turn, absorb another neutron, leading to a heavier nucleus.

For example, nickel-64, which contains 28 protons and 36 neutrons, can absorb a neutron, leading to nickel-65, which contains 28 protons and 37 neutrons:

Ni-64 (28 protons, 36 neutrons) + neutron →
Ni-65 (28 protons, 37 neutrons)

Nickel-65 is radioactive. It exists for only 2 and a-half hours, and then transforms into copper-65—the next element in the periodic table, which contains 29 protons and 36 neutrons. This is a process called beta decay, in which a neutron transforms into a proton and an electron:



NASA, ESA, J. HESTER AND A. LOLL (ARIZONA STATE UNIVERSITY)

The Crab Nebula is a six-light-year-wide expanding remnant of a star's supernova explosion.

Ni-65 (28 protons, 37 neutrons) →
electron + Cu-65 (29 protons, 36 neutrons)

Copper-65 is stable, so nothing happens after that.

This neutron capture mechanism, called the "s" process, is extremely slow. Hundreds or thousands of years might elapse between neutron strikes. But another process, called the "r" process, which stands for "rapid," allows for the rapid capture of neutrons. Unlike the "s" process, which occurs inside a star before it explodes, the "r" process happens only during the explosion of a star.

Exploding and cooking elements at the same time

When a star explodes into a supernova, it produces a huge amount of light and releases an extremely high number of neutrons (on the order of 10 thousand billion billion neutrons per square inch per second). These neutrons are then rapidly captured by the various nuclei that are also released by the exploding star, producing new nuclei through the "r" process.

In this process, even though many neutrons are available, only a limited number can be added to a given nucleus; otherwise, a nucleus becomes radioactive and breaks up. Neutrons in a nucleus are thought to occupy shells—similar to successive shells on a hard candy. When a nucleus gets "saturated" with neutrons, that is, when its shells are filled up, it undergoes a beta decay process to become the nucleus of the next element on the periodic table. This new nucleus, in turn, absorbs as many neutrons

Finding Chemicals Inside Stars

To determine which chemical elements are formed inside stars, scientists use a technique known as visible spectroscopy. It is based on a device, called a spectroscope, which spreads visible light into its component colors by passing it through a prism or grating.

These colors are called an emission spectrum, and their position and intensity differ according to the chemical element that emits the light. For example, the hydrogen's emission spectrum consists of four lines: purple, blue, green, and red, located at positions that correspond to their wavelengths. The emission spectrum of helium consists of six lines that are purple, cyan, green, yellow, orange, and red. In other words, atoms and molecules produce their own "fingerprint" or "signature" when the light they emit is spread in a spectroscope.

Astronomers also measure how much light is present at each spectral line. The overall strength or weakness of all the lines of an element depends on the number of atoms of that element. The percentage composition of the atoms in a stellar body can also be determined. For example, by looking at the light emitted by the sun, scientists have been able to determine the relative number of atoms from specific elements and infer their percentage by mass.

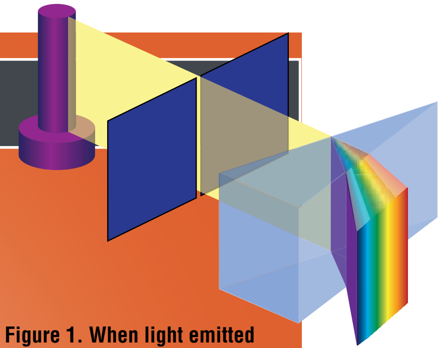


Figure 1. When light emitted by hydrogen is spread through a spectroscope, it reveals a characteristic emission spectrum specific only to hydrogen.

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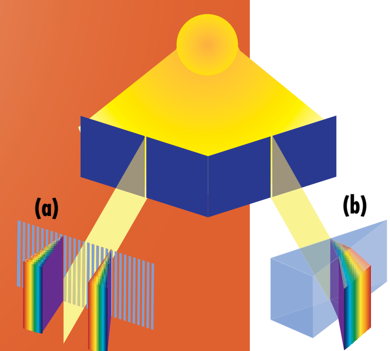

Figure 2. Sketch of a spectroscope and how it forms a spectrum. The light emitted by a source from space goes through a narrow slit to form a beam of light, which is then spread into its components by a grating (a) or a prism (b), resulting in the light's spectrum.

as it can hold, and then decays when it is "saturated" with neutrons, and the cycle starts again. When an element formed through the "r" process becomes really heavy (total number of protons and neutrons close to 270), it spontaneously breaks apart through a process called nuclear fission.

"The neutrons add very rapidly at a temperature of a few billion degrees, going from iron to uranium in less than 1 second," Woosley says.

Elements created this way include transuranium elements—elements whose number of protons is higher than that of uranium—such as curium-250, californium-252, californium-254, and fermium-257.

Our stellar origins

When a supernova spews its newly made elements into space, the elements become part of an enormous cloud of gas and dust, called an interstellar cloud. The gas is made of 90% hydrogen, 9% helium, and 1% heavier atoms. The dust contains silicates (compounds made of silicon), carbon, iron, water ice, methane (CH_4), ammonia (NH_3), and some organic molecules, such as formaldehyde (H_2CO).

NASA

Supernova remnant ejected from the explosion of a massive star that occurred some 3,000 years ago.

Such clouds are found so often between stars in our galaxy that astronomers think that all stars and planets have formed from them. Except for hydrogen, which appeared when the universe formed through the Big Bang explosion, all of the elements on Earth have been cooked for billions of years in stars and then released in the universe through supernova explosions. The nitrogen in our DNA, the calcium in our teeth, the iron in our blood, and the carbon in our apple pies were all made in the interiors of stars. The gold in jewels, tungsten in light bulbs, and silver in cookware were all produced during stellar explosions. We ourselves are made of "star stuff."

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Carolyn Ruth is an adjunct professor of chemistry at Mercyhurst College, Erie, Pa. Her most recent *ChemMatters* article, "Letting Off Steam," appeared in the April 2009 issue.

NANOTECHNOLOGY'S BIG IMPACT

By Nadia Halim

BACKGROUND GRAPHIC: ISTOCK

Imagine a doctor injecting a patient with tiny devices that can rove the body in search of cancer cells or disease-causing bacteria. Such devices would deliver medicine targeted specifically to a diseased organ or to the bacteria.

Though still years away scientists are trying to make such a scenario possible through nanotechnology, a hot research area in which scientists use atoms and molecules to build materials that can be used in many areas, such as health care, clean energy sources, and shrinking electronics.

These "nanomaterials" measure between 1 and 100 nanometers. Derived from "nanos"—the Greek word for "a small person"—a nanometer is 1 billionth of a meter. In comparison, a strand of hair is roughly 100,000 nanometers wide.

One of the main appeals of nanomaterials is that they have different properties than everyday materials. For example, they do not melt at the same temperature as everyday materials and do not conduct electricity like everyday materials.

These different properties are due to an increase in the surface area of nanomaterials and to their unusual shapes—such as tubes and hollow balls—which can affect how durable they are, how they conduct electricity and heat, and how they absorb light.

Nanotubes and Nanowires

An essential part of the nanotechnology toolkit is a tiny cylinder, called a nanotube, which has attracted widespread attention since the early 1990s. A nanotube is basically a sheet of pure, carbon graphite rolled into a cylinder. Nanotubes are usually a few nanometers in diameter and between 1 and 100 micrometers—1 thousandth of a millimeter—in length.

In an individual graphite layer, called graphene, carbon atoms form a series of six-sided hexagons next to one another. So, when a graphene sheet is rolled up to form a tube, the tube's wall is made of carbon hexagons (Fig. 1). The hexagons can be parallel to the axis of the tube (Figs. 1a and 1c) or form a helix that winds along the tube (Fig. 1b).

A nanotube's diameter and how the hexagons are arranged on the wall affect the way nanotubes conduct electricity, making them useful for making electronic components much smaller than those currently used. Also, these tiny tubes are lighter and stronger than steel so they could make good body armor. Research from Alan Windle, a professor of materials science at the University of Cambridge, United Kingdom, suggests that carbon nanotubes in the shape of long, yarn-like fibers could outperform even the strongest bullet-proof materials on the market.

Solid rods of silicon or other materials that are only a few nanometers wide are called nanowires. A nanowire's length is much longer than its width and it behaves like a wire in which electrons can move, thus conducting an electric current.

Nanowires have shown potential applications in solar cells, which harvest the sun's energy and turn it into electricity more efficiently than present solar cells. Also, researchers have used nanowires to build sensors that can detect disease-triggering molecules in the body or harmful chemicals in the air.

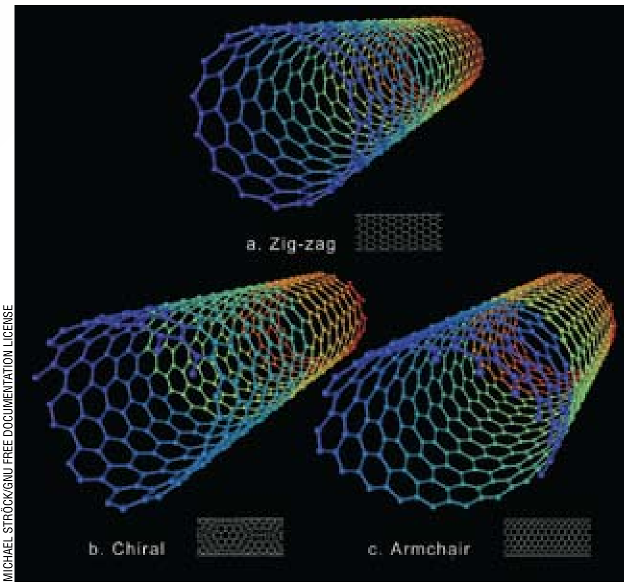

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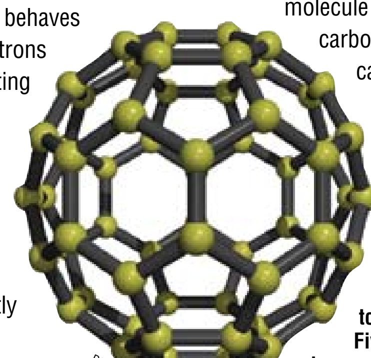
Figure 1. Structures of different types of carbon nanotubes: (a and c) Hexagons parallel to the axis of the tube; and (b) hexagons forming a helix that winds along the tube.

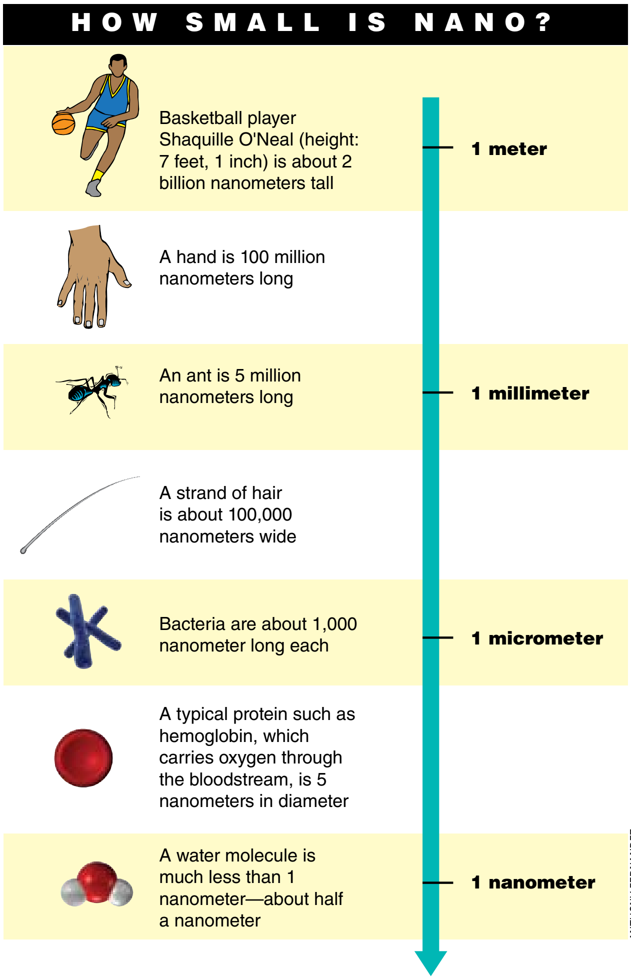
Nanoballs

Another important structure used extensively in nanotechnology is called a fullerene or "buckyball." This hollow soccer ball-shaped molecule is made of 60 carbon atoms, each carbon atom bonded to three adjacent carbon atoms (Fig. 2). The sphere is about 1 nanometer in diameter. Other existing buckyballs contain either 70 or 80 carbon atoms.



PAUL R.C. KENT, OAK RIDGE NATIONAL LAB

Figure 2. Structure of a buckyball. The buckyball has 60 carbon atoms, each carbon atom bonded to three adjacent carbon atoms. Five-sided pentagons and six-sided hexagons are arranged on the surface.



ANTHONY FERNANDEZ

Several academic laboratories and companies are developing modified buckyballs for therapeutic uses. Luna Innovations, a company based in Roanoke, Va., that develops products for the health care, telecommunications, energy, and defense markets, is testing buckyball-based therapeutics to block inflammation, swelling, and pain associated with medical conditions, such as allergies, arthritis, and wound healing.

This technology is based upon the buckyballs' unique ability to trap harmful free radicals, which increase inflammation and can damage or kill cells. Free radicals are molecules that have an uneven number of electrons. Some free radicals form as part of an immune response targeting viruses and bacteria. Environmental factors such as pollution, radiation, cigarette smoke, and herbicides may create free radicals, too.

The unpaired electron makes free radicals highly reactive. To become stable, free radicals seek to pair that lone electron by taking an electron from another molecule. When this molecule loses its electron, it becomes a free radical itself. This chain reaction ultimately damages the cell when the body cannot cope with too many free radicals.

Luna Innovations has shown that buckyballs can neutralize a dangerous free radical when its unpaired electron is transferred to the buckyball forming a bond. When tested in human-cell culture experiments and mice, Luna Innovations found the buckyballs blocked allergic response.

Nano-drug delivery

Scientists are turning to nanotechnology to solve other health care issues. For instance, the standard pill that is swallowed does not efficiently get a drug to the right place and in the right amount. It releases a drug quickly, but its concentration rapidly decreases in the body. So, patients need to take medication often.

Tejal Desai, of the University of California at San Francisco, is developing a better way to deliver medicines to the body. Her group has designed a microchip with nanometer-sized channels that will be able to steadily release a drug over time.

By using pores as small as 7 nanometers in diameter, the scientists observed constant release for tiny molecules of glucose. The steady release of the glucose molecules over time is a result of the tiny size of the nanochannels, which limits how fast the molecule can be released.

Then there are other obstacles to overcome in drug delivery. A good oral drug delivery vehicle has to survive extreme acidity and digestive enzymes as well as mechanical agitation in the stomach, and transfer the drug across a mucous layer, which is meant to keep out foreign invaders, such as pathogens.

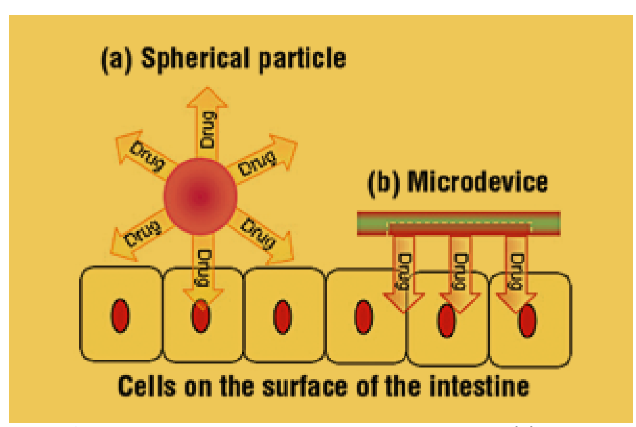
"If you can prolong the residence time of a drug or a drug carrier at the site of interest, and if you can improve the contact between the drug-delivery device and your absorbing surface, you can increase the amount of drug available to the body," Desai says. To accomplish this, she and her team have created a flat delivery device which is able to dock on the intestinal wall and release drug through it (Fig. 3). This way, most of the drug goes to the targeted area.

Buckyballs have high potential for drug delivery. This approach involves attaching drug molecules to the carbon atoms on the surface of the buckyball. Other chemical groups are added to make the molecules water soluble. This allows the medicine-loaded buckyball to be absorbed by the bloodstream when swallowed or injected. The buckyball can then release the drug upon reaching a chemical trigger, such as a change in pH or a particular chemical substance, such as those released by cancer cells.

Future challenges

Though the potential for nanotechnology is great, there are still many hurdles to overcome before nanomaterials and nanomachines become part of everyday life. One important challenge is creating better manufacturing methods. Creating large quantities of nanoscale materials is still time-consuming and expensive.

"It's like trying to make things out of Lego blocks with boxing gloves on your



TEJAL DESAI, UNIVERSITY OF CALIFORNIA AT SAN FRANCISCO

Figure 3. Drugs can be delivered through the intestine by (a) a traditional spherical particle, which releases drug in all directions, but not all the drug makes it into the intestinal cells. Alternatively, (b) a microdevice, such as the one devised by Tejal Desai and colleagues, delivers all the drug directly to the intestinal cells.

hands," says Ralph Merkle, senior research fellow at the Institute for Molecular Manufacturing, Palo Alto, Calif.

The next step will be to take the gloves off and develop methods of snapping atoms together. New technologies will have to be developed to safely and reliably do so, and standards and measurements will need to be created to ensure the quality of the resulting nanomaterials.

Along with the promise to improve the quality of life, nanotechnology still holds many unknowns. While the basic research is conducted by scientists and engineers, several programs are looking at the possible societal and ethical impacts of nanotechnology. Others are testing the safety of exposing our environment and our bodies to nanomaterials.

For instance, mice and fruit flies have been exposed to carbon nanotubes with mixed results. In one study, mice were injected with water-soluble carbon nanotubes. Kostas Kostarelos, a professor of pharmacy at the University of London's School of Pharmacy, and colleagues found that the nanotubes were harmlessly excreted intact in urine. Other studies have found that inhaled nanotubes can accumulate in the lungs and cause inflammation.

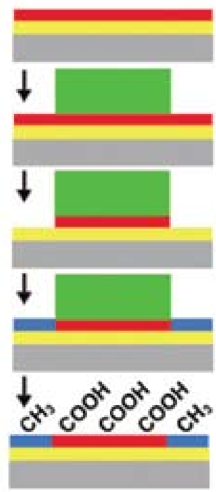
Since the data is limited and many more studies are necessary to help determine the real risks of nanomaterials, the U.S. Congress has stepped into the field. Earlier this year, the U.S. House of Representatives passed a bill that requires federal agencies participating in the National Nanotechnology Initiative—a program established in 2001 to coordinate nanotechnology research among various federal agencies—to develop a plan for environmental and safety research. A similar bill is expected in the U. S. Senate soon. While the safety debate continues, scientists will forge ahead in their search for nanotechnology solutions to life's challenges.

HOW TO BUILD NANOMATERIALS

There are basically two ways to build nanomaterials. Researchers can modify a starting material much like an artist shapes a sculpture from a slab of marble, adding to it and taking material away from it. With this method, called the "top-down" approach, a material is altered by mechanical or chemical means.

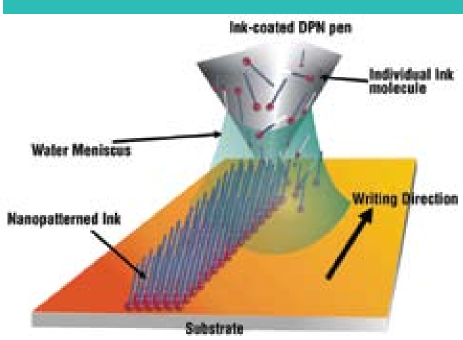
An electron beam or light are usually used to create these incredibly small structures. The techniques are called electron beam lithography and photolithography, respectively. In electron beam lithography, a focused beam of electrons forms the circuit patterns needed for depositing material on or removing material from a surface. In contrast, photolithography uses light for the same purpose.

Photolithography is limited in the size of the patterns it creates by the wavelength of visible light, which range between 400 nanometers and 700 nanometers. Narrower features can be made by using ultraviolet light with shorter wavelengths, between 380 nanometers and 10 nanometers, which is more expensive. In contrast, electron beam lithography produces patterns in the order of 20 nanometers but takes longer and is expensive.



An example of a "top-down" technique to make nanomaterials called photolithography.

PAUL S. WEISS AND MARK HORN, PENNSYLVANIA STATE UNIVERSITY



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An example of a "bottom-up" technique to make nanomaterials called dip-pen nanolithography (DPN).

Alternatively, the "bottom-up" approach starts with individual molecules or atoms and brings them together to form a product in which every atom is in a designated location. Often molecules are designed and created so that they can spontaneously self-assemble when a chemical or physical trigger is applied. An example of this in nature is the formation of a double strand of DNA, the genetic material in every cell.

Weak interactions play an important role in bottom-up manufacturing. These bonds can be made and broken much more easily than the covalent bonds that bind most atoms in molecules.

Although bottom-up processes are less developed and understood, they hold great promise for the future, because they lead to a wider variety of structures. In practice, both top-down and bottom-up methods are useful and being actively pursued, but the ultimate goal of building products with atomic precision will require a bottom-up approach. Some scientists foresee a day when nanomachines will be programmed to replicate themselves, or to work synergistically to build larger machines.

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