Our Nanotechnology Future

Atlantis Advances in Nanotechnology, Material Science and Energy Technologies

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The aim of “Atlantis Advances in Nanotechnology, Material Science and Energy Technologies” is to publish high quality manuscripts giving an up-to-date and clear view on topical scientific contents in nanotechnology, material sciences and energy technologies.

These three fields evolve rapidly and their understanding is essential with regard to contemporary science and as well as in the context of everyday life. Nanotechnology is a fast growing science and a technological field with applications in numerous areas such as materials, health, electronics, information processing, defence and security, catalysis, sensors, food, cosmetics and many more. The results of material sciences are the basis for any object around us, they are omnipresent in human life. Mastering materials and processes is therefore crucial. In particular, research on microscopic understanding is essential to develop models predicting the properties of new materials and structures. The final goal is to be able to predict macroscopic properties of materials from their microscopic properties. Finally, energy technologies enfold a complex area where each technological advance has to be weighed against economical, environmental, political and sociological constraints. Energy is closely linked to economic development and, more generally speaking, to everyday life.

As nanotechnology, materials science and energy technologies are closely interconnected, this series offers the reader both, highly specialized monographs as well as easy-to-grab overviews. Each publication focuses on one of the fields. At the same time, it is highly relevant to explore their interconnections and to include interdisciplinary approaches.

All book proposals submitted to this series are being reviewed by key experts before publication and each book focuses on a certain field putting it into perspective with its implications at the economic and societal level.

Our Nanotechnology Future

Christian Ngô and Joseph B.Natowitz

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Introduction

Nanotechnology is pervasive in contemporary life. With applications in food, electronics, medicine, cosmetics, catalysis, construction, defense etc. Many of natural materials around us have a nanostructure that determines their behavior. Nanoscience and nanotechnology generally deal with objects that have one or more dimensions in the range of 1-100 nm. This range is arbitrarily fixed by convention and sometimes must be expanded. Modern nanoscience and nanotechnology really started about three decades ago when it was demonstrated that it is possible to observe and manipulate nano-objects. Before that, most manufactured nanomaterials were films or coatings with thicknesses in the range of 1-100 nm.

Nano-objects can be built from elementary components (atoms or molecules), or by breaking down or carving bulk materials using different methods. The first approach is usually called "bottom-up" while the second one is termed as "top-down". Nanocharacterization techniques play a major role in these processes because they can be used to monitor the properties of these objects in a size range spanning the region between the microscopic world that encompass atoms, small molecules and nuclei- where the physics is governed by quantum phenomena - and the macroscopic world that can be described by classical theories such as classical mechanics. A good understanding of phenomena at the nanoscale, affords us the ability to boost the properties of manmade materials by tailoring nanomaterials for specific purposes. The properties manifested at the nanoscale level can be harnessed to provide remarkable new materials and capabilities.

Although the rate of development of nanotechnology today is smaller than was foreseen a decade ago, it increases regularly in an irreversible way. This short book is intended to give the reader a flavor of this expanding domain and its applications The book is divided in two parts. Part 1 presents the fundamental tenets of nanoscience and nanotechnology. Part 2 discusses current and future applications that have, or will have, a major influence on our lives.

Because a sharp rise in the use of nanotechnology in commercial products is expected in the future, the question of the possible risk that nanoparticles pose to human health is an important issue. Although humans have always been faced with the presence of natural nanoparticles, the manufacturing and use of engineered nanoparticles should be carefully investigated as far as the risk to living species is concerned. The risk must be carefully balanced against the advantages that can be obtained through nanoparticle usage.

Part 1 Nanotechnology basics

I. Nanoscience and nanotechnology

The size domain of nanoscience and nanotechnology

Nanoscience is the study of the performance of ultra-small autonomous structures. The nanoscience domain is typically viewed as having dimensions ranging between 1 nm and 100 nm. One nanometer (1 nm) is one billionth of a meter and one millionth of a millimeter. It is a very small distance. in fact, it is a length comparable to the size of individual atoms. One gold atom has a diameter of ≈ 0.144 nm. Seven gold atoms placed in a line and touching would extend for about 1 nm. For comparison, the cross sectional diameter of a strand of a human DNA molecule is about 2.5 nm, the diameter of a blood cell is about 7,000 nm and the diameter of a human hair is in the range of 80,000 to 100,000 nm.

If we could shrink all distances of our macroscopic world by one billion, one meter would become 1 nm. In this case the distance between the earth and the moon (≈ 360,000 km) would become 36 cm and the distance between the earth and the sun (≈ 150,000,000 km) would become 150 m.

In figure 1 we list some common units of length ranging from one meter to one femtometer, 10^{-15} meter. The nuclei of atoms have diameters in the range of 1 to 20 femtometers.

The conventional delineation of 1 nm to 100 nm for the nanoscience domain is useful, but should not be considered as a rigorous definition. Structures with larger dimensions can, in some cases, manifest phenomena belonging to this domain. It is important to investigate the different phenomena taking place on this size scale because they are often size dependent and different from those observed in our macroscopic world. Understanding and learning to model, simulate and manipulate nanoscale matter is a necessary step toward providing a firm underpinning for nanotechnology. *Nanotechnology* deals with the practical techniques of design, manufacturing and applications of nanostructured materials and devices. Nanotechnology has applications in many fields, including health, food, materials science, manufacturing, energy and chemical processes, among others. Nanotechnology is rapidly becoming more and more important in improving the materials and objects we routinely use in our daily lives.

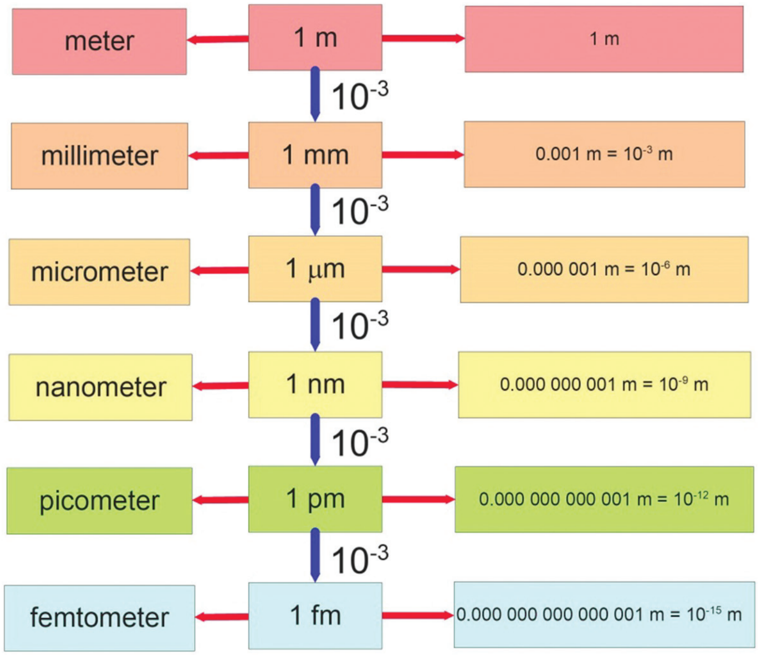

Figure 1. Length units descending from 1 meter to 1 femtometer. Each unit represented is separated from the adjacent units by a factor 1,000.

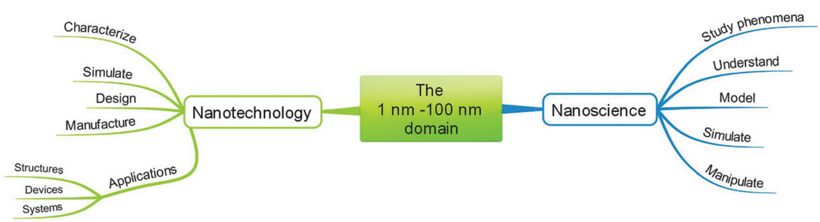

Figure 2. Some keywords of nanoscience ad nanotechnology.

Figure 2 provides a schematic view of the components constituting nanoscience and nanotechnology.

Nanomaterials need not be man-made. A number of natural nanostructured material exist. These occur in animals, in plants and in minerals. Examples include structures on the eye of a moth which increase the moth's ability to see in the dark, surface structures on the leaves of a lotus plant which make them water repellent and nano-structured clays which are often employed as additives to modify material properties.

Figure 3. The Lycurgus cup exhibited at the British museum. It was manufactured by the Romans around the 4th century AD. The color varies. This dichroic property comes from the presence of nanoparticles, which were produced during the manufacturing of the glass.

Nanotechnology in the past

The first human created nanostructures were not understood to be such. For example the "Lycurgus cup", presently in the British Museum in London, is a glass cup manufactured in Rome around the fourth century A.D., representing a scene from mythology, it was made from dichroic glass, glass which undergoes color changes in different lighting conditions. Illuminated from the outside, the cup looks green. Illuminated from the inside the cup appears ruby red except for the figure of the king which takes on a purplish hue (figure 3).

The dichroism of the glass is due to nanosized particles (up to 100 nm) embedded in the glass. These nanoparticles are of silver and gold. There is also a small amount of copper nanoparticles. The absorption and the scattering of light by these nanoparticles determines the color which is observed. When this cup was made, nothing was known about nanotechnology, but the manufacturer succeeded in creating this unique object.

Nanoparticles are also present in other objects produced in the Middle Ages. In the 1850s the British physicist and chemist Michael Faraday proposed that the observed color variations in stained glass windows could be attributed to variations in size of the clusters of metal atoms embedded in them. Some Chinese porcelains produced in the same time period contain 20-60 nm nanosized gold particles.

Intellectual foundations of nanotechnology

On December 1959, Richard Feynmann (Nobel Prize in Physics, 1965) gave a visionary lecture entitled “There’s plenty of room at the bottom”. In that lecture he stated his belief that it should be possible to manipulate atoms on an atomic scale and arrange them in desired patterns using nanoscale machines. At the end of his talk, he challenged his listeners to accomplish two tasks. The first was to build an electric motor smaller than 0.4 mm on a side. The second was to scale letters small enough to be able to write the entire Encyclopedia Britannica on the head of a pin. This requires being able to write a standard printed page on a surface 25,000 times smaller than that page. To do so each letter must have a size of about 9 nm. He offered $1,000 prizes to the first people able to solve either of these challenges.

The first task was achieved in November 1960 by William McLellan, who manufactured a motor weighing 2500 μg and having 13 parts which could function at 2000 rpm. Feynman was a bit disappointed because it was constructed with conventional tools and did not employ any new technology. The second challenge was met in 1985 by Tom Newman, a Stanford graduate student, who used an electron beam to inscribe the first page of Charles Dickens’ *“A Tale of Two Cities”* on the head of the pin. Because most of the area of the head of the pin remained empty, he later actually had a hard time finding the written text on the pin.

Today Feynman’s lecture is generally considered as the starting point of the nanotechnology story. The word “nanotechnology” itself was first introduced in 1979 by Norio Taniguchi, a Japanese scientist, to describe the control of semiconductor processes on the nanometer scale.

Can we see atoms?

Around 450 BC, Leucippus and Democritus, two Greek philosophers, suggested that matter was made of very small particles, invisible to a naked eye. A convincing verification of this concept came in 1805, thanks to the work of English chemist John Dalton. The macroscopic matter we see around us is indeed composed of individual units we call atoms. Atoms are the smallest units of a chemical element which retain the characteristics of that element. While we have known for over two centuries that matter is made up of atoms, our understanding of the nature and structure of atoms has evolved greatly during that period.

"Seeing is believing." is a credo firmly ingrained in the human psyche. However there are many objects which the unaided human eye is not capable of seeing. Atoms are in this realm. We must rely on instruments much more sensitive than our eyes to detect or see individual atoms. In figure 4, we show examples of objects of different sizes and indicate the different length scales, each separated by a factor 1,000, associated with these objects. For example, we can easily see people with our eyes. Small insects may have a size of a few millimeters or centimeters and a magnifying glass may be needed to observe them better. Red blood cells with a size on the order of 7-8 μm can be observed with an optical microscope. Silicon wires of an integrated circuit, such as shown at the far right in figure 4, have widths of several nanometers and can be observed with electron microscopes or scanning tunneling microscopes.

Electron microscopes are instruments that employ accelerated electrons to observe small objects. The physical laws governing the propagation of these electrons lead to size resolutions ~ 100,000 times better than those achievable with visible light. With this higher the electron microscope can "see" extremely small objects. Figure 5 illustrates the kinds of images obtainable using different electron microscopy techniques.

The spatial resolution of a scanning electron microscope can be about 1 nm to 20 nm depending on the instrument. The transmission electron microscope has a better spatial resolution and can reach 0.05 nm.

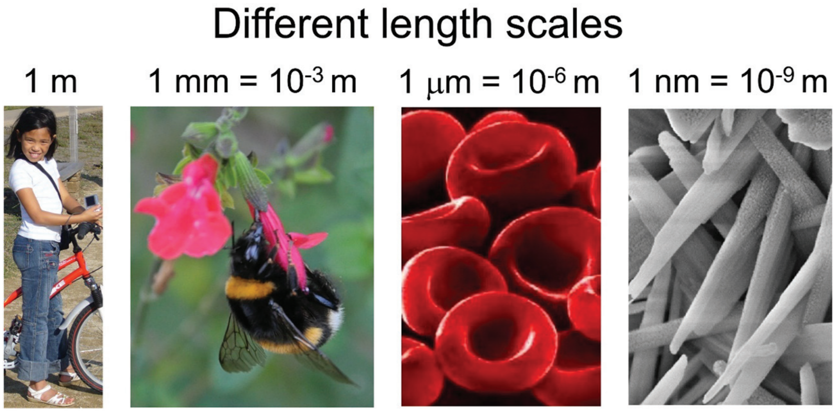

Figure 4. Examples of objects of different sizes.

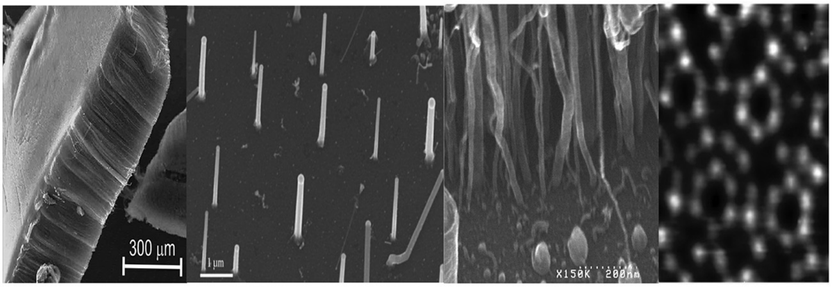

Figure 5. Images showing objects of various sizes taken using different microscopic techniques. From left to right – a carbon nanotube monolayer forest as seen by a standard electron microscope, a scanning electron microscope image showing silicon nanowires synthesized by vapor-liquid-solid techniques with diameters in the range 30-100 nm, a scanning electron microscope image of carbon nanotubes grown on a silicon substrate in a reactor at the CEA, an STM image of a silicon crystal with the surface oriented along the (111) plane. In the latter case, the bright dots correspond to individual Si-atoms at the surface. All these images are courtesy of CEA/LETI (France).

The scanning tunneling microscope

An important breakthrough in the observation of the constituents of matter was made in 1981 when Gerd Binnig and Heinrich Rohrer, researchers at IBM-Zurich in Switzerland, invented the *Scanning Tunneling Microscope* (STM). With this device, it became possible to see (after computer processing) individual atoms on an electron microscope screen and, furthermore, to manipulate and arrange these individual atoms. In 1986 these two scientists received the Nobel Prize in Physics for this achievement.

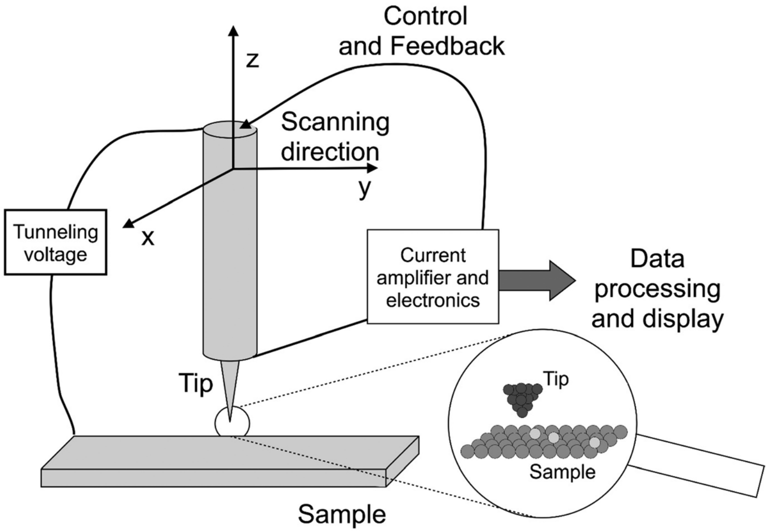

Figure 6. Schematic diagram of a scanning tunneling microscope.

The principle of the STM is shown in figure 6. A conducting tip is brought to a very small distance (a distance below 1 nm) from the surface of the sample being scanned. Materials used for the tip can be tungsten, a platinum-iridium alloy and even gold. The sample can be a conductor or a semi-conductor. The important interaction is between the outermost atom on the tip and an atom on the surface of the sample. When the tip and the surface are very close to each other, electrons can *tunnel* from the sample to the tip or vice versa depending upon the sign of the voltage difference between the tip and the sample. This exchange of electrons is not a classical phenomenon, but a quantum mechanical phenomenon. Quantum phenomena are discussed further in Chapter 2. The tunneling current which is measured depends on the tip position, on the applied voltage, and on the local density of electronic states of the sample. The tunneling current varies exponentially with the distance separating the tip from the surface. A 10 % decrease in this distance (≈ 1 nm) typically increases the current by an order of magnitude and vice versa. The range of distance separating the tip from the surface of the sample typically varies from 0.4-0.7 nm. A lateral resolution of about 0.1 nm and a depth resolution of 0.01 nm can be obtained with the STM.

A STM can operate in a wide range of temperatures from near zero Kelvin (≈-273°C) up to a few hundred degrees Celsius. The position of the tip with respect to the surface has to be perfectly controlled mechanically. This is done using piezoelectric mechanisms.

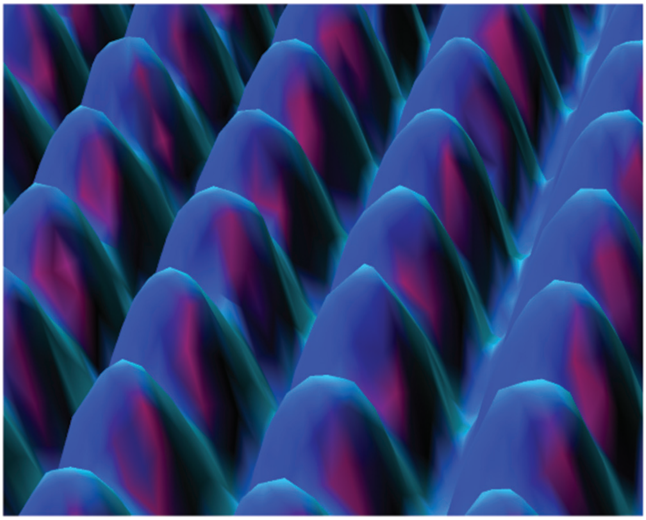

Figure 7. STM image of the surface of a nickel crystal. Image originally created by IBM Corporation.

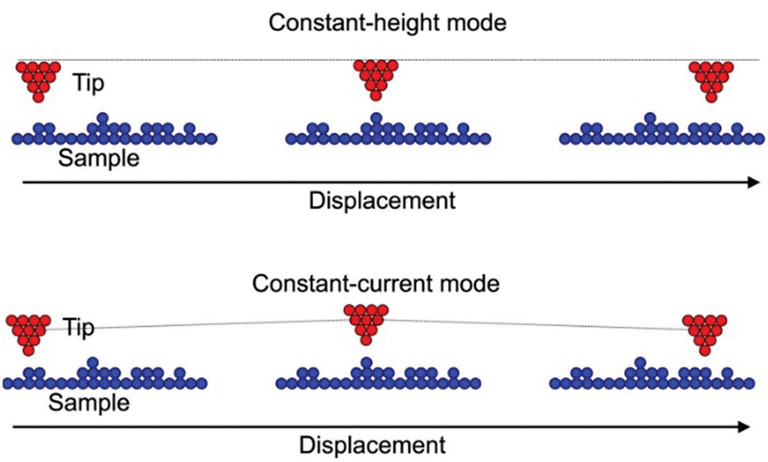

Figure 8. Schematic illustration of the two operating modes of the STM.

The measurement of the local density of the electron quantum states allows the imaging of the spatially-resolved electron density of the sample. Computer processing of that information produces an image of surface atoms on a screen. An example of such an image is that in figure 7 showing the regular arrangement of the nickel atoms on the surface of a nickel crystal.

As shown in figure 8, a STM can be operated in two different modes,: the constant-height mode and the constant-current mode. In the constant-height mode, the tip remains at a fixed height and scans the sample while remaining in a horizontal plane. This mode can quickly scan the sample, but requires a smooth sample surface. In the constant-current mode a feedback loop is used to adjust the distance between the tip and the surface of the sample in order to keep the tunneling current constant. This mode is slower than the preceding one, but is able to scan irregular surfaces.

The atomic force microscope

One of the shortcomings of the STM is that it can only study conductive or semi-conductive surfaces. In 1986, Gerd Binnig, Christoph Gerber and Calvin Quate invented the *Atomic Force Microscope* (AFM) which can be used on insulating surfaces also. The principle, shown in figure 9, is to use a tip attached to a cantilever (flexible arm). When this tip is moved over the surface of the sample the atomic forces attract or repel the tip as the tip moves along. The motion of the tip induces a motion of the cantilever. A laser beam directed at the cantilever is reflected and the angle of reflection of this beam is measured (see figure 9). From this information, it is possible to build an image of the surface as the tip moves.

There are some basic differences between an AFM and a STM. With an AFM the tip makes a gentle direct contact with the scanned surface while the tip of a STM does not make direct contact and just measures the tunnel current existing between the tip and the surface. The AFM resolution turns out to be better than the STM resolution.

An AFM is well suited for nanotechnology studies because it gives better surface measurements than a STM and can be operated in a wider variety of environments. It can be used with conductors, semiconductors and insulators.

An AFM can be operated in several modes. In the *dynamic mode*, the cantilever vibrates around a given frequency and the tip oscillates with an amplitude of a few nanometers close to the surface of the sample. The long range forces, such as Van der Waals forces, affect the frequency of oscillation and a feedback loop is used to keep the frequency of oscillation constant by changing the distance separating the tip from the surface of the sample. In this way a topological mapping of the surface can be made. In the *intermittent* or *tapping mode*, the oscillations of the cantilever are much larger and there is an intermittent contact between the tip and the surface. This technique is particularly suitable when a thin layer of liquid

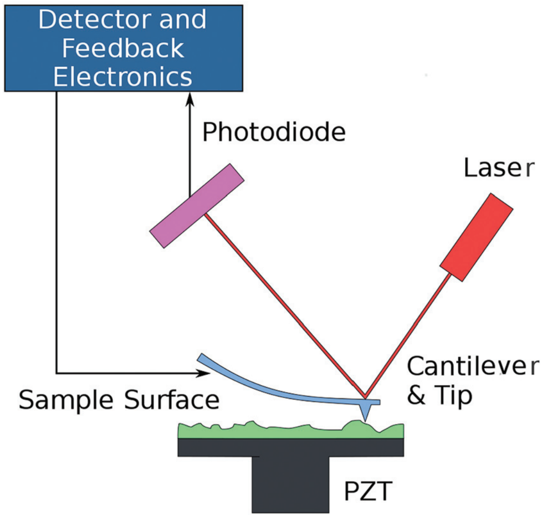

Figure 9. Schematic of an atomic force microscope with optical detection of the deflection of the microcantilever. Image from Wikimedia Commons (http://commons.wikimedia.org). Author Grzegorz Wielgoszewski.

has developed on the surface of the sample because of the environmental conditions. It is the method most often employed in AFM measurements. In the *contact mode*, the tip touches the surface. The electrons of the atoms repel it and the cantilever is deflected.

Manipulating atoms

Using a STM it is possible not only to see atoms but also to move individual atoms from one point on the surface to another. In 1989, Don Eigler, an IBM researcher, using a STM, picked up and moved an individual atom for the first time. He moved a xenon atom back and forth 3 times in order to check reproducibility. *In his lab notebook Eigler wrote "Did it," "Did it" and "Did it again! 3 in a row".* After this crucial breakthrough, in November 1989, Eigler succeeded in arranging 35 atoms of xenon on the surface of a nickel crystal to write the word "IBM" (figure 10). Eigler claimed that once the atom-moving process was under control, the biggest challenge was "remembering how to spell IBM".

Atoms moved and positioned on the surface of a crystal are often called *adatoms*[1]. The move can be done manually or with the aid of a computer. An autonomous atom assembler has been recently developed by researchers from the US Center for Nanoscale Science and Technology. It provides

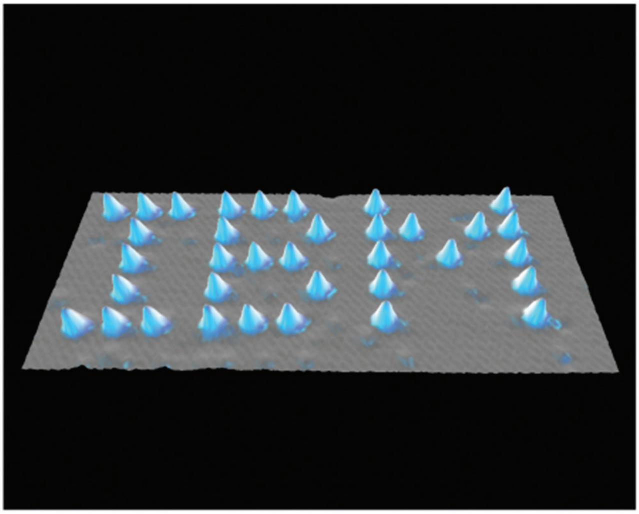

Figure 10. Atoms of xenon arranged on a nickel crystal surface to spell IBM. Courtesy of IBM company (www.almaden.ibm.com).

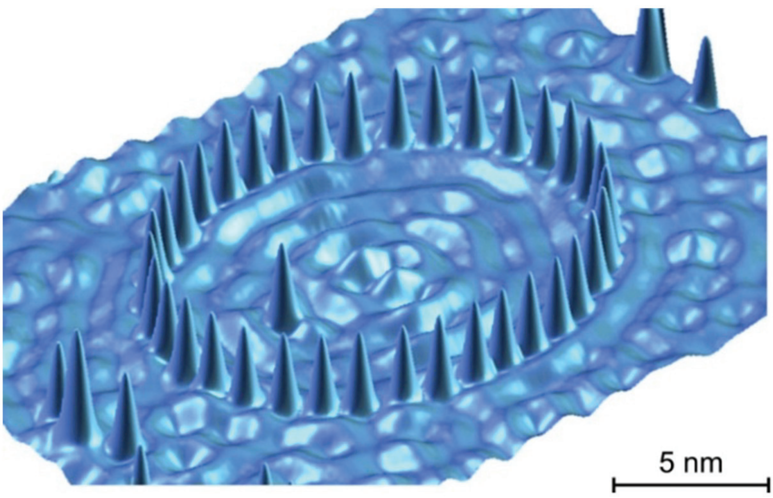

Figure 11. Image of an elliptical quantum corral built using the autonomous atom assembler; Co atoms were deposited at sub-monolayer coverage on a Cu(111) at 7K in ultra high vacuum and subsequent STM measurements were performed at a 4.3 K sample temperature. J.A. Stroscio, R.J. Celotta, S.R. Blankenship and F.M. Hess, http://www.nist.gov/cnst/epg/atom_manipulation_stm.cfm. Image from Wikimedia Commons (http://commons.wikimedia.org).

the ability to assemble a desired nanostructure from atoms initially randomly distributed on the surface of a crystal. The autonomous atom assembler is a dedicated instrument based upon an STM with upgraded hardware and software components. Figure 11 shows the result of the manipulation of cobalt adatoms on a copper surface to form a closed quantum structure (quantum corral) in which electrons can be trapped. The geometry of this structure defines new energy levels in this region of the surface. Such a structure, made to measure, may have important applications in the future.

Summary

It is now possible to routinely see and move atoms. This represents an important technological breakthrough and opens a wide number of science and technological applications. The main issue is to be able to work at the nanoscale at a pace suffiency large to quickly obtain objects useful in the macroscopic word and a competitive cost.

The ability to see details in the nanosized range is necessary and essential for all developments of nanotechnology because it allows to control nanotechnology research developments and manufacturing processes. The possibility to see details, at the scale of the nanometer or better, allows a rational development of nanomaterials by giving the possibility to understand the mechanisms involved rather than developing materials using trial and error methods as it was done in the past.

An adatom is an additional atom lying on the surface of a crystal. This word comes from the contraction of the expression “adsorbed atom”. An adatom can be viewed as the opposite of a surface vacancy in which an atom has disappeared.