INTRODUCTION TO NANOSCIENCE AND NANOTECHNOLOGY

Chris Binns

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PREFACE

This book has been a long time in the making. I was taken aback recently when I looked at the original proposal and found that it was written in Spring 2005. At the time there did not appear to be any books that covered the entire field of nanotechnology in a holistic manner written for the layman. To me, one of the most exciting aspects of Nanoscience and Nanotechnology is that they transcend the barriers between the mainstream scientific disciplines of Physics, Chemistry, Biology and Engineering. Thus they provide new insights into the nature of matter and dazzling possibilities for new technology. So full of enthusiasm I put hand to keyboard and embarked on my project to fill this gap, with an original intention to finish in 18 months. Of course the entire sweep of the topic, including, as it does, all the mainstream sciences, is incredibly broad and the intention was to cover it with a relatively light touch to give the reader the ‘feel’ of what is exciting about the subject. Nanotechnology has a way of sucking you in however and there were so many things that I just couldn’t resist including that the touch soon began to get heavier. At some stage in this process of increasing depth I decided to go a stage further and increase the academic level by including ‘Advanced Reading Boxes’ and some worked problems. This was so that the book could be used as an introductory text for University courses on Nanotechnology, which are becoming increasingly common. Indeed much of the material has been foisted on our own undergraduates at the University of Leicester where we run such a course. The book is still written so that the subject material is covered if one never ventures into these boxes but they provide additional depth for the serious student.

So, four and a half years later, here we are with a longer and more detailed book than I originally intended but in which, I hope, the original intention of giving the reader a holistic feel of the subject has not been lost. There are now many excellent books on Nanotechnology available at a range of different academic levels but I believe that this one still has the widest scope. Despite that, there are still holes, for example, the important areas of Nanomechanics and Nanofluidics, which I hope to fill in future editions. Whatever your use for the book I hope you enjoy it and get from it the excitement that is fundamental to the topic.

Chris Binns
December 2009

ACKNOWLEDGMENTS

I don't think it is possible for a person, at least, a person with a family, to write a book without a good deal of support. In my case I have had massive support from my wife, Angela who has also been a constant source of inspiration and indeed practical help by proof-reading the book. I dedicate this book to her.

I thank my extended family accrued from two marriages, that is, Callum, Rory, Connor, Edward, Tamsyn and Sophie for bringing inspiration and joy to my life as well as the inevitable problems. I would also like to thank my first wife Nerissa for supporting me in my early career and shouldering a large part of the burden of looking after our children.

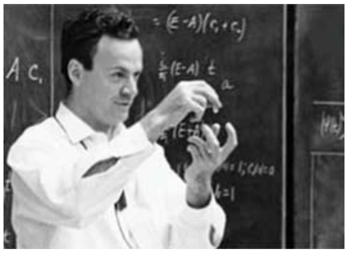
Finally I would like to thank my parents who with meager resources supported me in pursuit of higher education despite their feeling that I should get a proper job.

NANOTECHNOLOGY TIME LINE

1931 Ernst Ruska and Max Knoll build the first Transmission Electron Microscope (TEM) [1]. See chapter 4, section 4.4.6

1959 Lecture by Richard Feynman entitled "There is plenty of room at the bottom, an invitation to enter a new field of physics" [2]. In it he said:

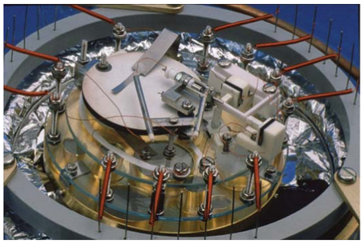
> "*. . . I am not afraid to consider the final question as to whether, ultimately-in the great future-we can arrange the atoms the way we want; the very atoms, all the way down! What would happen if we could arrange the atoms one by one the way we want them. . . .*" See chapter 4 section 4.4.2



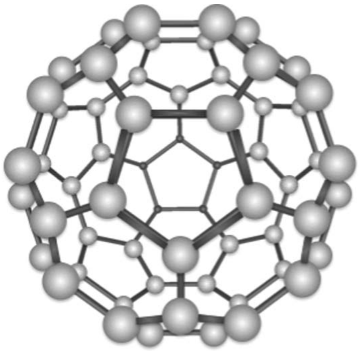
1968 Development of Molecular Beam Epitaxy (MBE) by Arthur and Cho that enables materials to be grown an atomic layer at a time.

1974 N. Taniguchi generally credited for using the word 'Nanotechnology' for the first time [3].

1981 Development of Scanning Tunneling Microscope (STM) by Rohrer and Binnig enables atomic resolution images of surfaces [4]. See chapter 4, section 4.4.1.



1985 Discovery of C_{60} and other fullerenes by Harry Kroto, Richard Smalley and Robert Curl, Jr. [5]. See chapter 3, section 3.2.

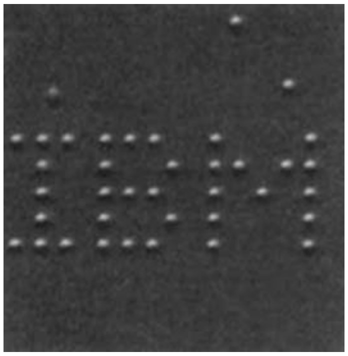


1985 Tom Newman wrote the first page of Charles Dickens' novel *A tale of two cities* with a reduction factor of 25 000 using Electron Beam Lithography (EBL) [6] thus winning a prize of $1,000 offered by Richard Feynman after his 1959 speech. See chapter 4, section 4.2.1.

1986 Development of Atomic Force Microscope (AFM) by Binnig and co-workers [7]. See chapter 4, section 4.4.4.

1987 Development of Magnetic Force Microscope (MFM) by Martin and Wickramasinghe [8]. See chapter 4, section 4.4.4.

1990 D. M. Eigler and E. K. Schweizer use an STM to demonstrate atomic-scale positioning of individual Xe atoms on a Ni surface at low temperature (4K) to write "IBM" [9]. This is the first step towards the realization of the Feynman dream set out in the highlighted statement statement from his lecture above. See chapter 4, section 4.4.2.

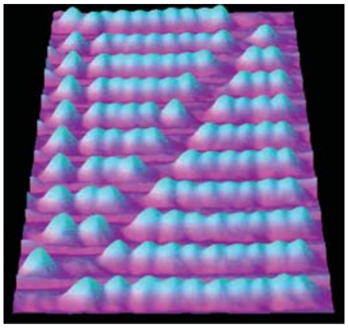


1991 Sumio Iijima discovers carbon nanotubes [10]. See chapter 3, section 3.8

1993 Iijima and Ichihashi grow single-wall carbon nanotubes [11]. See chapter 3, section 3.8.

1995 Takahashi and co-workers demonstrate single-electron transistor operating at room temperature [12]. See chapter 5, section 5.3

1996 Cuberes, Schlittler and Gimzewski demonstrate room temperature positioning of individual C_{60} fullerenes with an STM to produce the "C_{60} abacus" [13]. See chapter 4, section 4.4.2.



1997 Steve Lamoreaux measures the Casimir force at sub-micron distances [14]. See chapter 8, section 8.2

1998 Umar Mohideen and Anushree Roy use AFM used to measure the Casimir force at distance scales down to 90 nm [15]. See chapter 8, section 8.2

2001 Postma and co-workers, demonstrate single-electron transistor operation in a carbon nanotube [16]. See chapter 5, section 5.4.

2002 Regression of tumour in mouse achieved using magnetic nanoparticle hyperthermia achieved by Brusentsov and co-workers [17]. See chapter 6, section 6.2.2.

2007 Johanssen and co-workers conduct first human clinical trials of magnetic nanoparticle hyperthermia treatment of cancer [18]. See chapter 6, section 6.2.2.

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INTRODUCTION

Research in nanotechnology is a growth industry, with worldwide government-funded research spending running at over four billion dollars per year and growing at an annual rate of about 20% [1]. Industry is also willing to spend vast sums on investigating nanotechnology, with, for example, major cosmetics companies announcing big increases in their annual Research and Development budgets for the field. It is clear that nanotechnology is expected to have a significant impact on our lives, so what is it and what does it do? These simple direct questions, unfortunately, do not have simple direct answers, and it very much depends on who you ask. There are thousands of researchers in nanotechnology in the world, and one suspects that one would get thousands of different responses. A definition that would probably offend the smallest number of researchers is that nanotechnology is the study and the manipulation of matter at length scales of the order of a few nanometers (100 atoms or so) to produce useful materials and devices.

This still leaves a lot of room for maneuver. A nanotechnologist working on suspensions of particles might tell you that it is achieving better control of tiny particles a few nanometers across (nanoparticles) so that face creams can penetrate the epidermis (outer skin layer). A scientist working at the so-called “life sciences interface” would say that it is finding ways of attaching antibodies to magnetic nanoparticles to develop revolutionary cancer treatments. A researcher working on “molecular electronics” will tell you that it is creating self-ordered assemblies of nanoparticles to produce electronic circuits in which the active components are a thousand times smaller than a single transistor on a Pentium IV chip. Some nanotechnologists (a small minority) would tell you that it is finding ways to build tiny robots whose components are the size of molecules (nanobots).

We will talk in detail about size scales in Chapter 1; but for the moment consider Fig. 0.1, which shows, schematically, the size scale of interest in nanotechnology (the nanoworld). For reasons that will become clear in Chapter 1, the upper edge of the nanoworld is set at about 100 nm. Even though this is hundreds of times smaller than the tiniest mote you can see with your eyes and is smaller than anything that can be resolved by the most powerful optical microscope, a chunk of matter this size or bigger can be considered to be a “chip off the old block”—that is, a very tiny piece of ordinary material. If we were to assemble

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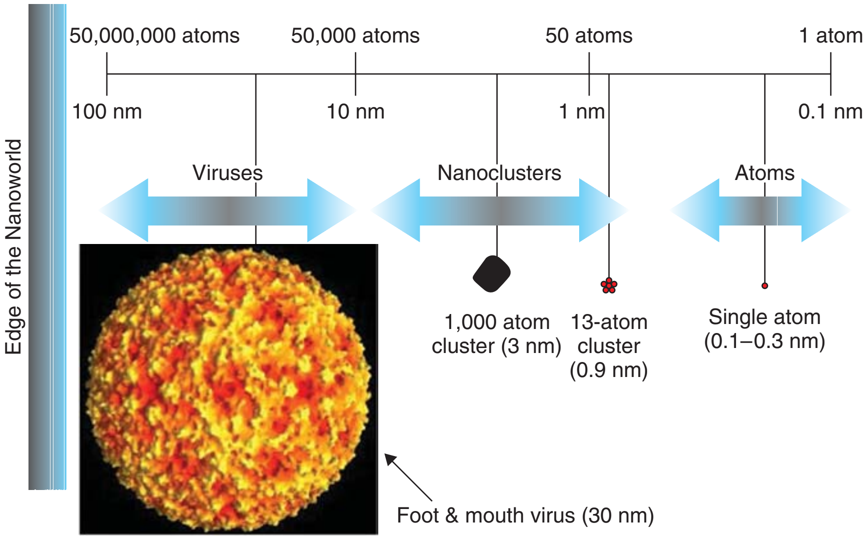


Fig. 0.1 The nanoworld. The size range of interest in nanotechnology and some representative objects.

pieces of copper or iron this big into a large chunk, the resulting block would behave exactly as we would expect for the bulk material. Thus nanotechnology does not consider pieces of matter larger than about 100 nm to be useful building blocks.

As shown in Fig. 0.1, viruses are small enough to be inhabitants of the nanoworld whereas bacteria are much larger, being typically over 10 μm (10,000 nm) in size, though they are packed with "machinery" that falls into the size range of the nanoworld (see Chapter 6, Section 6.1.3). Going down in size, the figure shows typical sizes of metal particles, containing ~1000 atoms that can be used to produce advanced materials. The properties of these (per atom) deviate significantly from the bulk material, and so assembling these into macroscopic chunks produces materials with novel behavior.

Finally, the lower edge of the nanoworld is defined by the size of single atoms, whose diameters vary from 0.1 nm (hydrogen atom) to about 0.4 nm (uranium atom). We cannot build materials or devices with building blocks smaller than atoms, and so these represent the smallest structures that can be used in nanotechnology.

There are so many aspects to nanotechnology that one of the difficulties in writing about it is finding ways to organize the text into a coherent structure. This book will largely follow a classification scheme introduced by Richard Jones in his book *Soft Machines Nanotechnology and Life* [2] that helps to categorise nanotechnology into a logical framework. He defines three categories in order of increasing sophistication—that is, *incremental, evolutionary*, and *radical* nanotechnology. These are described in detail below.

0.1 INCREMENTAL NANOTECHNOLOGY

All substances, even solid chunks of metal, have a grain structure, and controlling this grain structure allows one to produce higher performance materials. This could mean stronger metals, magnetic films with a very high magnetization, suspensions of nanoparticles with tailored properties, and so on. Actually, some aspects of incremental nanotechnology can be considered to date back to the ancients. For example, the invention of Indian ink, probably in China around 2700 B.C., relies on producing carbon nanoparticles in water. Also medieval potters in Europe knew how to produce a lustre on pots by coating them with copper and silver nanoparticles [3], a process that can be traced back to 9th century A.D. Mesopotamia. Figure 0.2 shows an electron microscope image of the glaze of a 16th-century Italian pot, whose luster derives from the coating by 5-nm-diameter copper particles.

Most modern nanotechnologists would be proud of the size control of the particles in this picture. Whereas these days a process that involved nanoparticles such as this would be proudly claimed to be nanotechnology and thus open the door

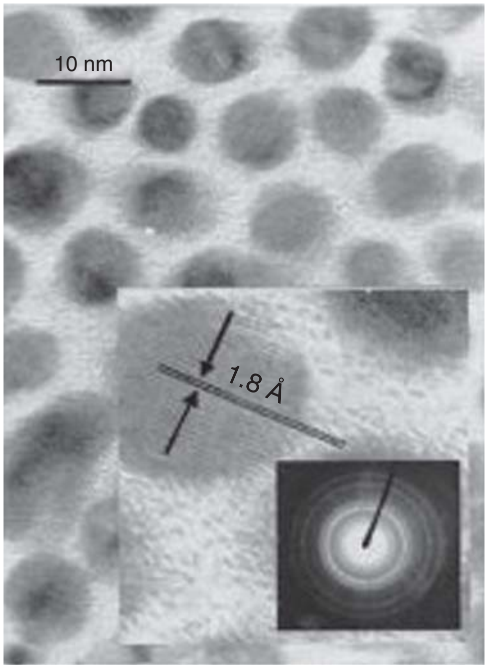


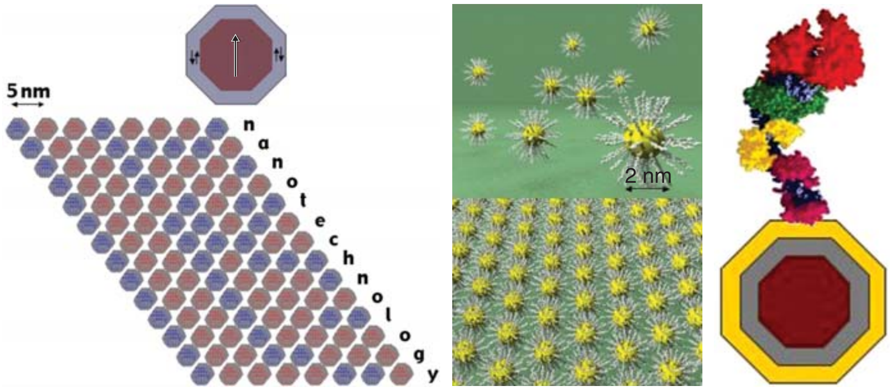
Fig. 0.2 **Ancient Incremental Nanotechnology.** Copper nanocrystals on a 10th century pot of about 10 nm diameter used to produce a surface luster. The inset shows an increased magnification image of a single 7 nm diameter particle with atomic planes visible revealing its crystallinity. Reproduced with the permission of Elsevier Science from I. Borgia et al. [3].

to research funding, spin-off companies, and so on, the ancients were developing processes that did something invisible to the materials but nevertheless allowed them to achieve certain results. In this sense, a lot of incremental nanotechnology can sometimes be considered to be a re-branding of other, more traditional lines of research such as materials science and chemistry. The nanotechnology title is still useful, however, since nanotechnology is, by its nature, multidisciplinary and it encourages cross-disciplinary communication between researchers.

The aspect of incremental nanotechnology that has really changed in the modern world is the development of instruments (see Chapter 4) that can probe at the nanoscale and image the particles within materials or devices. Researchers can actually observe what is happening to the particles or grains in response to changes in processing. This not only makes development of new processes more efficient but also leads to the discovery of completely new structures that were not known to exist and hence new applications. Nature is full of surprises when one studies sufficiently small pieces of matter, as will become clear throughout this book.

0.2 EVOLUTIONARY NANOTECHNOLOGY

Whereas *incremental nanotechnology* is the business of assembling vast numbers of very tiny particles to produce novel substances, *evolutionary nanotechnology* attempts to build nanoparticles that *individually* perform some kind of useful function. They may need to be assembled in vast numbers to form a macroscopic array in order to produce a device, but a functionality is built into each one. Such nanoparticles are necessarily more complex than those used in incremental nanotechnology. A simple example is a magnetic nanoparticle that is used to store a single bit of information by defining the direction of its magnetization. If one wants to do this using nanoparticles with diameters smaller than about 6 nm at ambient temperature, simple elemental nanoparticles made, for example, of pure Fe will not work because thermal vibrations will instantly change their direction of magnetization. To produce a particle that doesn't lose its "memory" without cooling to very low temperatures, each one has to be made with more than one material and formed either as a uniform alloy or as a core-shell particle (see Fig. 0.3a)—that is, a kind of nanoscale chocolate peanut with a core consisting of one material surrounded by a shell of a different substance. As stated above, these have to be assembled in vast numbers into some sort of ordered array (the big unsolved problem with this technology) to produce a useful device, but each particle has within it the capacity to store a data bit. If and when this technology succeeds, it would represent a storage density about 1000 times greater than existing hard disks on computers. For example, the bottom image in Fig. 0.3a shows an array of core-shell nanoparticles used to store the word "nanotechnology" in ASCII code. The storage density represented would allow about two million books or a large library to be written in an area the size of a postage stamp.



(a) (b) (c)

Fig. 0.3 Functionalized nanoparticles. (a) A "core-shell" magnetic nanoparticles consisting of a ferromagnetic metal core (e.g. iron or cobalt) surrounded by an antiferromagnetic shell, e.g. cobalt-oxide or manganese) that is specialized to record a single bit of information encoded by the direction of the core magnetization (see Chapter 5, Section 5.1). The lower picture shows an array storing the word 'nanotechnology' in ASCII format with blue representing down magnetization or '0' and red representing up magnetization or '1'. Writing at this density would enable the storage of about two million books (a large University library) on an area the size of a postage stamp. (b) Gold nanoparticles with attached thiol molecules. Each nanoparticle can behave as a transistor and the thiols can bond onto other thiol-coated gold nanoparticles via electrically resistive or capacitive links to build circuits with a component density 1000 times greater than existing devices (see Chapter 5, Section 5.3). Reproduced with the permission of Dr. Mark Everard from [4]. (c) A core-shell magnetic nanoparticle (as in (a)) with a second shell of gold that makes it easy to attach biological molecules such as proteins or antibodies, or drugs. The magnetic core of the particle can be utilized to steer the attached molecule to specific areas of the body by external fields for targeted drug delivery. Alternatively, the attached biological molecule could be used to target specific cells (e.g. tumor cells) that could then be heated and killed by a weak external radio-frequency magnetic field that is harmless to healthy tissue (see Chapter 6, Section 6.2.2).

An example of a more sophisticated "functionalized" nanoparticle, shown in Fig. 0.3b, is a gold nanoparticle about 2 nm across with attached molecules called *thiols*. If wires could be attached to this nanoparticle, it could be made to act like a transistor by a process called Coulomb blockade (see Chapter 5, Section 5.3). It turns out that the thiols, of which there are many types, can act as wires if they come together in the right way. A slight change in the bonding produces a change in the resistance of the link or makes it capacitive (insulating). In other words, an entire circuit network consisting of transistors, capacitors, and resistors can be produced by placing an array of thiol-coated nanoparticles in the correct positions. This, of course, is the unsolved problem but is a tantalizing one because the density of components in such an array means that about 1000 nanoparticle transistors could be placed in the space occupied by a single silicon-based transistor on a Pentium IV chip.

No one can fail to be impressed by the huge increases in performance and density of components/memory elements in devices made by the electronics and magnetic recording industries in the last few decades. The above two examples illustrate, however, that there is still a long way to go, nicely reinforcing a lecture on nanotechnology given by the visionary Nobel laureate Richard Feynman and entitled *There's Plenty of Room at the Bottom*. The amazing thing about this lecture was that it was given in 1959.

Continuing the trend toward complexity of individual nanoparticles, Fig. 0.3c shows a combination of the types in Figs. 0.3a and 0.3b consisting of a magnetic core-shell particle, with controlled properties, coated with a second shell of gold that facilitates its attachment to complex biological molecules—for example, drugs, proteins, or antibodies. The magnetic core of the particle can be utilized to steer the attached molecule to specific areas of the body by external fields for targeted drug delivery. Alternatively, the attached biological molecule could be used to target specific cells (e.g., tumor cells) that could then be heated and killed by a weak external radio-frequency field that is harmless to healthy tissue (see Chapter 6, Section 6.2.2).

As a rough guide to where we are with evolutionary nanotechnology, the functional nanoparticles shown in Fig. 0.3 can be routinely manufactured, but their use in technologies such as those described above awaits the solution to enormously difficult technological problems such as controlling their self-assembly into arrays.

0.3 RADICAL NANOTECHNOLOGY

Finally, the most far-reaching version of nanotechnology, described as *radical nanotechnology* by Richard Jones, is the construction of machines whose mechanical components are the size of molecules. The field has bifurcated into two distinct branches, that of (a) *molecular manufacturing* in which macroscopic structures and devices are built by assembling their constituent atoms, and (b) nanorobots or *nanobots*, which are invisibly small mobile machines. Molecular manufacturing was originally proposed by the Nobel laureate Richard Feynman in his famous lecture in 1959 and was subsequently advocated with much enthusiasm by Eric Drexler [5]. In 1990 the IBM research laboratories in Zurich demonstrated that they could move and position individual atoms using a scanning tunneling microscope (STM—see Chapter 4, Section 4.4.2), lending support to the idea that molecular manufacturing may, at least in principle, be possible. The problems and the emergence of some enabling technologies for molecular manufacturing are presented in Chapter 7.

Nanobots have generated a good deal of controversy, especially ones that can play atomic Lego and build anything out of atoms lying around. If this were possible, then one could, in principle, build a nanobot that moved around exploring the surface it occupied. If it were equipped with an assembler that could assemble atoms and molecules, it could make a copy of itself by rooting around and finding the atoms it needed to reproduce. Obviously, this kind of activity would need on-board intelligence, and this could be provided by either a mechanical computer, again with molecular-sized components, or something more akin to a the molecular electronic-type circuit shown in Fig. 0.3b. Since each nanobot could make multiple copies of itself, the population could increase exponentially and would quickly produce a sufficiently vast army to build macroscopic objects. Drexler himself pointed out the doomsday scenario where the nanobots multiply out of control like a virus and eventually exist in such vast numbers that they could rearrange the atoms of the planet to produce a kind of "gray goo." Unfortunately, this scenario has tended to hijack discussions on radical nanotechnology; and since the two branches of radical nanotechnology have been melded together in the public debate, there is a general feeling that all radical nanotechnology is dangerous. The reality is that exponentially self-replicating machines are not required for molecular manufacturing [6] and nanobots do not need to be built with assemblers to self-replicate in order to perform useful functions.

There is a scientific debate about whether this technology is feasible, even in the long term, or indeed desirable, but the discussion has moved on from generalities to a consideration of the detailed processes required for molecular manufacturing (see Chapter 7 and the references therein). A frequently proposed argument in favor of radical nanotechnology is that it already exists in all living things. Biological cells are filled with what may be regarded as nanomachines and molecular assemblers. Biology, however, is very different to the nanoscale process-engineering path envisaged by radical nanotechnologists, as explained in *Soft Machines Nanotechnology and Life* [2]. It is fair to say that both the feasibility and timescale of Radical Nanotechnology divides the community. The point is that while incremental nanotechnology exists and evolutionary nanotechnology is close ($\sim$10 years), radical nanotechnology, if feasible, is probably decades away. Whatever the twists and turns of the debate, once we get away from the argument over nanobots, there is no doubt that the ability to produce nanomachines and achieve safe nonexponential molecular manufacturing will reap enormous benefits.

It is possible that the solution to some of the more difficult technological problems involved with radical nanotechnology may arise from a better fundamental understanding of the true nature of empty space. The quantum description of our universe predicts new types of force at very short distance scales (nanometers) arising directly out of the properties of vacuum. Although we can only detect these forces with very sensitive instruments (the tools of nanotechnology in fact—see Chapters 4 and 8), to a nanoscale machine whose components are within nanometers of each other, these forces will be as natural a part of their environment as gravity is to us. Research on these forces and how to utilize them in nanotechnology is already being undertaken by several research groups worldwide. This may be the missing link between biology and radical nanotechnology—that is, natural systems, whose inner workings happen on the same scale as nanomachines have evolved over billions of years and must have utilized all available forces including the exotic ones.

0.4 BOTTOM-UP/TOP-DOWN NANOTECHNOLOGY

Finally in this introduction it is worth mentioning another way of categorizing nanotechnology, that is, *bottom-up* and *top-down* approaches. Everything discussed so far has been part of a bottom-up approach in which the building block (nanoparticle, molecular machine component, etc.) is identified and produced naturally and then assembled to produce the material or device required. In the top-down approach, you start with a block of some material and machine a device or structure out of it. This is akin to conventional engineering using lathes and millers to machine a shape out of a solid block. The modern tools of nanotechnology, however, are able to machine structures with sizes of a few nanometers, so the size of components made with a top-down approach is not much different from the building blocks of the bottom-up approach. The flexibility of top-down tools—in particular, focused ion beam systems (FIBs)—is further enhanced by their ability to deposit material to produce nanoscale features as well as to remove it. This is beautifully illustrated in Fig. 0.4, which shows an example of a "wineglass" with a cup diameter 20 times smaller than the width of a human hair produced by depositing carbon. Although this is a rather big structure on the scale of nanometers, the smallest feature size that can be produced by a modern FIB is less than 100 nm.

The two approaches (top-down and bottom-up) are complementary, and some of the most exciting research arises out of combining them. For example, if one wants to measure the electrical or magnetic properties of an individual nanoparticle, the fantastic precision of a modern top-down tool enables the production of electrodes that can attach to it. In general terms, the bottom-up/top-down categorization can be applied separately to each of the incremental, evolutionary, and radical nanotechnology categories.

The above is an attempt at a lightning tour of nanotechnology with generic descriptions and without addressing details. The rest of the book looks in detail at these and other aspects of nanotechnology. Chapter 1 aims to instill a feeling of how small the nanometer length scale is in comparison to macroscopic objects and why it is special. It discusses the basic conception of the discrete nature of matter starting from the original philosophical ideas of Leucippus and Democritus of ancient Greece to the modern view of atomic structure. It also describes why the properties of pieces of matter with a size in the nanometer range (nanoparticles) deviate significantly from the bulk material and how these special properties may be used to produce high-performance materials and devices. In Chapter 2 the discussion is broadened to include naturally occurring nanoparticles, both in the Earth's atmosphere and in space. Chapter 3 is dedicated to nanoparticles composed of carbon, and the justification for devoting a chapter to a single element is the rich variety of nanostructures produced by carbon and

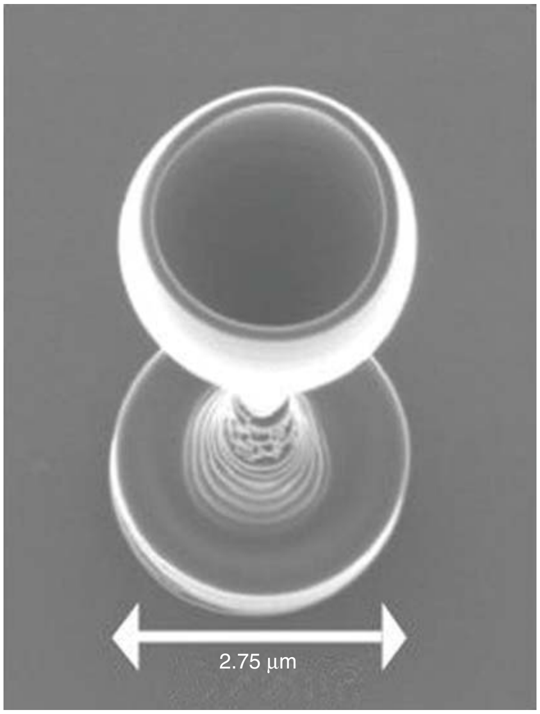


Fig. 0.4 The smallest wineglass in the world (authorized by *Guinness World Records*). Wine glass whose cup diameter is 20 times smaller than the width of a human hair produced by deposition of carbon using a focused ion beam (FIB) machine. The structure arose from a Joint development by SII NanoTechnology, NEC, and the University of Hyogo, Japan. Although this is a rather big structure on the scale of nanometers, the smallest feature size that can be produced by a modern FIB is less than 100 nanometers (see Chapter 4, Section 4.2.2).

their importance in the rest of nanotechnology. Chapter 4 presents the tools of nanotechnology that can build, image, and manipulate nanostructures to build materials and devices using a bottom-up approach. It also describes top-down manufacturing methods that are capable of shaping nanostructures and perhaps one of the most exciting aspects of the field—that is, combining bottom-up and top-down approaches so that *individual* nanostructures can be probed. Chapter 5 is about artificially produced nanostructures that have a built-in functionality. Examples presented include magnetic nanoparticles that can store a data bit, nanoparticles that can function as transistors and quantum dots, which behave as “artificial atoms” with novel optical and electronic properties. Chapter 6 shows how combining advances in the production of nanoparticles and in biotechnology makes it possible to produce biologically active nanoparticles that can interact with specific cells in the body. These can then be used as nanoscale-amplifiers in biological images or they can be used to destroy their attached cells under the application of external stimulation, such as microwave or infrared radiation leading to powerful new treatments for cancer. Chapter 7 presents radical nanotechnology and discusses the potential for building autonomous machines with nanoscale components. Chapter 8 discusses how the tools of nanotechnology can be exploited to study the basic nature of vacuum itself via the Casimir effect. This is a strange "force from nothing" that arises from the zero-point energy density of empty space. These experiments may one day uncover a deeper level to our universe that underlies the observable universe consisting of all particles and all normal energy that we can sense or detect with instruments. The Casimir force may also be an important phenomenon for the practical implementation of nanomachines as a method to transmit force without contact.

The three-tier classification scheme divides among the chapters as follows. Chapters 1 and 3 deal with incremental nanotechnology, Chapters 5 and 6 deal with evolutionary nanotechnology, and Chapter 7 deals with radical nanotechnology. Where appropriate, a separate bottom-up/top-down categorization is introduced. Chapter 2 deals with naturally occurring nanoparticles, Chapter 4 deals with the tools of nanotechnology, and Chapter 8 deals with the Casmir force, so these stand outside the broad classification scheme.

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