
INTRODUCTION

The prefix *nano* in the word *nanotechnology* means a billionth (1×10^{-9}). Nanotechnology deals with various structures of matter having dimensions of the order of a billionth of a meter. While the word *nanotechnology* is relatively new, the existence of functional devices and structures of nanometer dimensions is not new, and in fact such structures have existed on Earth as long as life itself. The abalone, a mollusk, constructs very strong shells having iridescent inner surfaces by organizing calcium carbonate into strong nanostructured bricks held together by a glue made of a carbohydrate–protein mix. Cracks initiated on the outside are unable to move through the shell because of the nanostructured bricks. The shells represent a natural demonstration that a structure fabricated from nanoparticles can be much stronger. We will discuss how and why nanostructuring leads to stronger materials in Chapter 6.

It is not clear when humans first began to take advantage of nanosized materials. It is known that in the fourth-century A.D. Roman glassmakers were fabricating glasses containing nanosized metals. An artifact from this period called the Lycurgus cup resides in the British Museum in London. The cup, which depicts the death of King Lycurgus, is made from soda lime glass containing silver and gold nanoparticles. The color of the cup changes from green to a deep red when a light source is placed inside it. The great varieties of beautiful colors of the windows of medieval cathedrals are due to the presence of metal nanoparticles in the glass.

The potential importance of clusters was recognized by the Irish-born chemist Robert Boyle in his *Sceptical Chymist* published in 1661. In it Boyle criticizes Aristotle's belief that matter is composed of four elements: earth, fire, water, and air. Instead, he suggests that tiny particles of matter combine in various ways to form what he calls *corpuscles*. He refers to "minute masses or clusters that were not easily dissipable into such particles that composed them."

Photography is an advanced and mature technology, developed in the eighteenth and nineteenth centuries, which depends on production of silver nanoparticles sensitive to light. Photographic film is an emulsion, a thin layer of gelatin containing silver halides, such as silver bromide, and a base of transparent cellulose acetate. The light decomposes the silver halides, producing nanoparticles of silver, which are the pixels of the image. In the late eighteenth century the British scientists Thomas Wedgewood and Sir Humprey Davy were able to produce images using silver nitrate and chloride, but their images were not permanent. A number of French and British researchers worked on the problem in the nineteenth century. Such names as Daguerre, Niepce, Talbot, Archer, and Kennet were involved. Interestingly James Clark Maxwell, whose major contributions were to electromagnetic theory, produced the first color photograph in 1861. Around 1883 the American inventor George Eastman, who would later found the Kodak Corporation, produced a film consisting of a long paper strip coated with an emulsion containing silver halides. He later developed this into a flexible film that could be rolled, which made photography accessible to many. So technology based on nanosized materials is really not that new.

In 1857 Michael Faraday published a paper in the *Philosophical Transactions of the Royal Society*, which attempted to explain how metal particles affect the color of church windows. Gustav Mie was the first to provide an explanation of the dependence of the color of the glasses on metal size and kind. His paper was published in the German Journal *Annalen der Physik* (Leipzig) in 1908.

Richard Feynman was awarded the Nobel Prize in physics in 1965 for his contributions to quantum electrodynamics, a subject far removed from nanotechnology. Feynman was also a very gifted and flamboyant teacher and lecturer on science, and is regarded as one of the great theoretical physicists of his time. He had a wide range of interests beyond science from playing bongo drums to attempting to interpret Mayan hieroglyphics. The range of his interests and wit can be appreciated by reading his lighthearted autobiographical book *Surely You're Joking, Mr. Feynman*. In 1960 he presented a visionary and prophetic lecture at a meeting of the American Physical Society, entitled "There is Plenty of Room at the Bottom," where he speculated on the possibility and potential of nanosized materials. He envisioned etching lines a few atoms wide with beams of electrons, effectively predicting the existence of electron-beam lithography, which is used today to make silicon chips. He proposed manipulating individual atoms to make new small structures having very different properties. Indeed, this has now been accomplished using a scanning tunneling microscope, discussed in Chapter 3. He envisioned building circuits on the scale of nanometers that can be used as elements in more powerful computers. Like many of present-day nanotechnology researchers,

he recognized the existence of nanostructures in biological systems. Many of Feynman's speculations have become reality. However, his thinking did not resonate with scientists at the time. Perhaps because of his reputation for wit, the reaction of many in the audience could best be described by the title of his later book *Surely You're Joking, Mr. Feynman*. Of course, the lecture is now legendary among present-day nanotechnology researchers, but as one scientist has commented, "it was so visionary that it did not connect with people until the technology caught up with it."

There were other visionaries. Ralph Landauer, a theoretical physicist working for IBM in 1957, had ideas on nanoscale electronics and realized the importance that quantum-mechanical effects would play in such devices.

Although Feynman presented his visionary lecture in 1960, there was experimental activity in the 1950s and 1960s on small metal particles. It was not called *nanotechnology* at that time, and there was not much of it. Uhlir reported the first observation of porous silicon in 1956, but it was not until 1990 when room-temperature fluorescence was observed in this material that interest grew. The properties of porous silicon are discussed in Chapter 6. Other work in this era involved making alkali metal nanoparticles by vaporizing sodium or potassium metal and then condensing them on cooler materials called *substrates*. Magnetic fluids called *ferrofluids* were developed in the 1960s. They consist of nanosized magnetic particles dispersed in liquids. The particles were made by ballmilling in the presence of a surface-active agent (surfactant) and liquid carrier. They have a number of interesting properties and applications, which are discussed in Chapter 7. Another area of activity in the 1960s involved electron paramagnetic resonance (EPR) of conduction electrons in metal particles of nanodimensions referred to as *colloids* in those days. The particles were produced by thermal decomposition and irradiation of solids having positive metal ions, and negative molecular ions such as sodium and potassium azide. In fact, decomposing these kinds of solids by heat is one way to make nanometal particles, and we discuss this subject in Chapter 4. Structural features of metal nanoparticles such as the existence of magic numbers were revealed in the 1970s using mass spectroscopic studies of sodium metal beams. Herman and co-workers measured the ionization potential of sodium clusters in 1978 and observed that it depended on the size of the cluster, which led to the development of the jellium model of clusters discussed in Chapter 4.

Groups at Bell Laboratories and IBM fabricated the first two-dimensional quantum wells in the early 1970s. They were made by thin-film (epitaxial) growth techniques that build a semiconductor layer one atom at a time. The work was the beginning of the development of the zero-dimensional quantum dot, which is now one of the more mature nanotechnologies with commercial applications. The quantum dot and its applications are discussed in Chapter 9.

However, it was not until the 1980s with the emergence of appropriate methods of fabrication of nanostructures that a notable increase in research activity occurred, and a number of significant developments resulted. In 1981, a method was developed to make metal clusters using a high-powered focused laser to vaporize metals into a hot plasma. This is discussed in Chapter 4. A gust of helium cools the vapor, condensing the metal atoms into clusters of various sizes. In 1985, this

method was used to synthesize the fullerene (C_{60}). In 1982, two Russian scientists, Ekimov and Omushchenko, reported the first observation of quantum confinement, which is discussed in Chapter 9. The scanning tunneling microscope was developed during this decade by G. K. Binnig and H. Rohrer of the IBM Research Laboratory in Zürich, and they were awarded the Nobel Prize in 1986 for this. The invention of the scanning tunneling microscope (STM) and the atomic force microscope (AFM), which are described in Chapter 3, provided new important tools for viewing, characterizing, and atomic manipulation of nanostructures. In 1987, B. J. van Wees and H. van Houten of the Netherlands observed steps in the current–voltage curves of small point contacts. Similar steps were observed by D. Wharam and M. Pepper of Cambridge University. This represented the first observation of the quantization of conductance. At the same time T. A. Fulton and G. J. Dolan of Bell Laboratories made a single-electron transistor and observed the Coulomb blockade, which is explained in Chapter 9. This period was marked by development of methods of fabrication such as electron-beam lithography, which are capable of producing 10-nm structures. Also in this decade layered alternating metal magnetic and nonmagnetic materials, which displayed the fascinating property of giant magnetoresistance, were fabricated. The layers were a nanometer thick, and the materials have an important application in magnetic storage devices in computers. This subject is discussed in Chapter 7.

Although the concept of photonic crystals was theoretically formulated in the late 1980s, the first three-dimensional periodic photonic crystal possessing a complete bandgap was fabricated by Yablonovitch in 1991. Photonic crystals are discussed in Chapter 6. In the 1990s, Iijima made carbon nanotubes, and superconductivity and ferromagnetism were found in C_{60} structures. Efforts also began to make molecular switches and measure the electrical conductivity of molecules. A field-effect transistor based on carbon nanotubes was demonstrated. All of these subjects are discussed in this book. The study of self-assembly of molecules on metal surfaces intensified. *Self-assembly* refers to the spontaneous bonding of molecules to metal surfaces, forming an organized array of molecules on the surface. Self-assembly of thiol and disulfide compounds on gold has been most widely studied, and the work is presented in Chapter 10.

In 1996, a number of government agencies led by the National Science Foundation commissioned a study to assess the current worldwide status of trends, research, and development in nanoscience and nanotechnology. The detailed recommendations led to a commitment by the government to provide major funding and establish a national nanotechnology initiative. Figure 1.1 shows the growth of U.S. government funding for nanotechnology and the projected increase due to the national nanotechnology initiative. Two general findings emerged from the study.

The first observation was that materials have been and can be nanostructured for new properties and novel performance. The underlying basis for this, which we discuss in more detail in later chapters, is that every property of a material has a characteristic or critical length associated with it. For example, the resistance of a material that results from the conduction electrons being scattered out of the direction of flow by collisions with vibrating atoms and impurities, can be

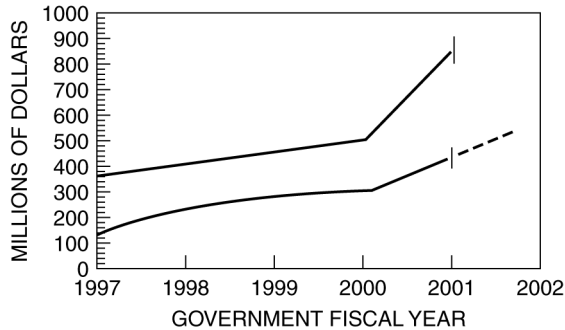


Figure 1.1. Funding for nanotechnology research by year. The top tracing indicates spending by foreign governments; bottom, U.S. government spending. The dashed line represents proposed spending for 2002. (From U.S. Senate Briefing on nanotechnology, May 24, 2001 and National Science Foundation.)

characterized by a length called the *scattering length*. This length is the average distance an electron travels before being deflected. The fundamental physics and chemistry changes when the dimensions of a solid become comparable to one or more of these characteristic lengths, many of which are in the nanometer range. One of the most important examples of this is what happens when the size of a semiconducting material is in the order of the wavelength of the electrons or holes that carry current. As we discuss in Chapter 9, the electronic structure of the system completely changes. This is the basis of the quantum dot, which is a relatively mature application of nanotechnology resulting in the quantum-dot laser presently used to read compact disks (CDs). However, as we shall see in Chapter 9, the electron structure is strongly influenced by the number of dimensions that are nanosized.

If only one length of a three-dimensional nanostructure is of a nanodimension, the structure is known as a *quantum well*, and the electronic structure is quite different from the arrangement where two sides are of nanometer length, constituting what is referred to as a *quantum wire*. A quantum dot has all three dimensions in the nanorange. Chapter 9 discusses in detail the effect of dimension on the electronic properties of nanostructures. The changes in electronic properties with size result in major changes in the optical properties of nanosized materials, which is discussed in Chapter 8, along with the effects of reduced size on the vibrational properties of materials.

The second general observation of the U.S. government study was a recognition of the broad range of disciplines that are contributing to developments in the field. Work in nanotechnology can be found in university departments of physics, chemistry, and environmental science, as well as electrical, mechanical, and chemical engineering. The interdisciplinary nature of the field makes it somewhat difficult for researchers in one field to understand and draw on developments in another area. As Feynman correctly pointed out, biological systems have been making nanometer functional devices since the beginning of life, and there is much to learn from

biology about how to build nanostructured devices. How, then, can a solid-state physicist who is involved in building nanostructures but who does not know the difference between an amino acid and a protein learn from biological systems? It is this issue that motivated the writing of the present book. The book attempts to present important selected topics in nanotechnology in various disciplines in such a way that workers in one field can understand developments in other fields. In order to accomplish this, it is necessary to include in each chapter some introductory material. Thus, the chapter on the effect of nanostructuring on ferromagnetism (Chapter 7) starts with a brief introduction to the theory and properties of ferromagnets. As we have mentioned above, the driving force behind nanotechnology is the recognition that nanostructured materials can have chemistry and physics different from those of bulk materials, and a major objective of this book is to explain these differences and the reasons for them. In order to do that, one has to understand the basic chemistry and physics of the bulk solid state. Thus, Chapter 2 provides an introduction to the theory of bulk solids. Chapter 3 is devoted to describing the various experimental methods used to characterize nanostructures. Many of the experimental methods described such as the scanning tunneling microscope have been developed quite recently, as was mentioned above, and without their existence, the field of nanotechnology would not have made the progress it has. The remaining chapters deal with selected topics in nanotechnology. The field of nanotechnology is simply too vast, too interdisciplinary, and too rapidly changing to cover exhaustively. We have therefore selected a number of topics to present. The criteria for selection of subjects is the maturity of the field, the degree of understanding of the phenomena, and existing and potential applications. Thus most of the chapters describe examples of existing applications and potential new ones. The applications potential of nanostructured materials is certainly a cause of the intense interest in the subject, and there are many applications already in the commercial world. Giant magnetoresistivity of nanostructured materials has been introduced into commercial use, and some examples are given in Chapter 7. The effect of nanostructuring to increase the storage capacity of magnetic tape devices is an active area of research, which we will examine in some detail in Chapter 7. Another area of intense activity is the use of nanotechnology to make smaller switches, which are the basic elements of computers. The potential use of carbon nanotubes as the basic elements of computer switches is described in Chapter 5. In Chapter 13 we discuss how nanosized molecular switching devices are subjects of research activity. Another area of potential application is the role of nanostructuring and its effect on the mechanical properties of materials. In Chapter 6, we discuss how consolidated materials made of nanosized grains can have significantly different mechanical properties such as enhanced yield strength. Also discussed in most of the chapters are methods of fabrication of the various nanostructure types under discussion. Development of large-scale inexpensive methods of fabrication is a major challenge for nanoscience if it is to have an impact on technology. As we discuss in Chapter 5, single-walled carbon nanotubes have enormous application potential ranging from gas sensors to switching elements in fast computers. However, methods of manufacturing large quantities of the tubes will have to be

developed before they will have an impact on technology. Michael Roukes, who is working on development of nanoelectromechanical devices, has pointed out some other challenges in the September 2001 issue of *Scientific American*. One major challenge deals with communication between the nanoworld and the macroworld. For example, the resonant vibrational frequency of a rigid beam increases as the size of the beam decreases. In the nanoregime the frequencies can be as high 10^{10} Hertz, and the amplitudes of vibration in the picometer (10^{-12}) to femtometer (10^{-15}) range. The sensor must be able to detect these small displacements and high frequencies. Optical deflection schemes, such as those used in scanning tunneling microscopy discussed in Chapter 3, may not work because of the diffraction limit, which becomes a problem when the wavelength of the light is in the order of the size of the object from which the light is to be reflected. Another obstacle to be overcome is the effect of surface on nanostructures. A silicon beam 10 nm wide and 100 nm long has almost 10% of its atoms at or near the surface. The surface atoms will affect the mechanical behavior (strength, flexibility, etc.) of the beam, albeit in a way that is not yet understood.