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Frank K. Ko and Yuqin Wan
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1 Introduction

1.1 How big is a nanometer?

By definition, a nanometer, abbreviated as nm, is a unit for length that measures one billionth of a meter. (1 nm $= 10^{-3}$ µm $= 10^{-6}$ mm $= 10^{-7}$ cm $= 10^{-9}$ m.) Our hair is visible to the naked eye. Using an optical microscope we can measure the diameter of our hair, which is in the range of 20–50 microns (µm) or 20 000–50 000 nm. Blood cells are not visible to the naked eye, but they can be seen under the microscope, revealing a diameter of about 10 microns or 10 000 nm. The diameter of hydrogen atoms is 0.1 nm. In other words 10 hydrogen atoms can be placed side-by-side in 1 nm. Figure 1.1 provides an excellent illustration of the relative scales in nature. The discovery of nanomaterials ushered us to a new era of materials. We have progressed from the microworld to the nanoworld.

1.2 What is nanotechnology?

According to the National Science Foundation in the United States nanotechnology is defined as [1]:

> Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1–100 nanometer range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size. The novel and differentiating properties and functions are developed at a critical length scale of matter typically under 100 nm. Nanotechnology research and development includes manipulation under control of the nanoscale structures and their integration into larger material components, systems and architectures. Within these larger scale assemblies, the control and construction of their structures and components remains at the nanometer scale. In some particular cases, the critical length scale for novel properties and phenomena may be under 1 nm (e.g., manipulation of atoms at ~0.1 nm) or be larger than 100 nm. (e.g., nanoparticle reinforced polymers have the unique feature at ~ 200–300 nm as a function of the local bridges or bonds between the nanoparticles and the polymer).

Accordingly nanotechnology is the scientific field that is concerned with the study of the phenomena and functions of matters within the dimensional range of 0.1–100 nm. It is the study of the motion and changes of atoms, molecules, and of other forms of

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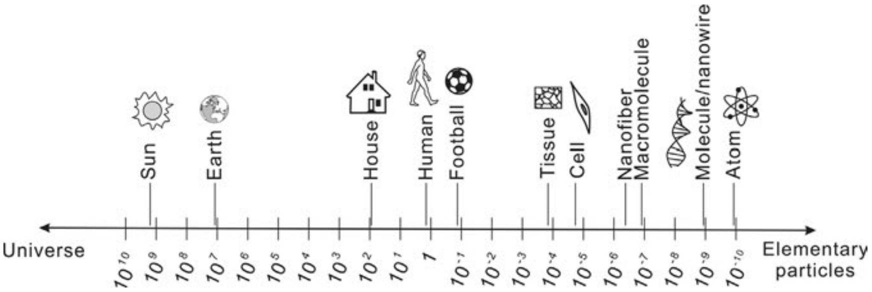

Fig. 1.1 Illustration of relative scale in nature. (The linear distance is indicated on this logarithmic scale in meters.)

matter. Nanotechnology, building upon the foundation of nanoscience, is concerned with the manufacturing of new materials, new devices and the development of research methodology and techniques for new technology.

Nanotechnology can also be referred to as the technology for the formation of nanomaterials and nanodevices, including the formation of nanostructural units according to a specific methodology to form macroscopic treatment (processing) of nanomaterials such as dispersion, forming technology as in the case of the formation of nanofibers and their composites.

Nanotechnology can be organized into three levels. The first level is molecular (atomic) nanotechnology wherein the molecules (atoms) are spatially organized in the nanospace in a repetitive manner. This in turn will create internally ordered nanostructures. Self-assembly and mineralization in biological materials are examples of molecular nanotechnology. The technology for controlling the morphology and uniformity of nanostructures is called the second level of nanotechnology. For example, in colloids and gels we do not concern ourselves with the order of arrangement of the molecule itself at the nanoscale. They form only morphologies of nanostructure of certain regularity. The third level of nanotechnology is concerned with the technology of the formation of nanosacle structures but is unable to control the degree of order of the molecules and atoms in the nanostructures. At the third level of nanotechnology the morphology and uniformity of the nanostructure are also uncontrolled [2].

1.3 Historical development of nanotechnology

Although the use of nanomaterials can arguably be traced back to over 1000 years ago when the smoke from a candle was used in China as ink, the first scientific discussion of nanotechnology is widely attributed to the 1959 Nobel Prize winning physicist Richard Feynman in his well known “There’s Plenty of Room at the Bottom” lecture at the California Institute of Technology (Caltech). In this lecture he boldly challenged his audience in his now famous statement.

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People tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction. Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?

It is of interest to note that, 40 years after the Feynman lecture, coincidentally in the year 2000, US President Clinton announced the Notational Nanotechnology Initiative (NNI) that kicked-off the global gold rush in nanotechnology. Over a period of 10 years, developed countries have invested over $22.134 billion in nanotechnology research with more than a third ($8.918 billion) of that amount spent in the USA alone [3].

Notwithstanding the foresight of Professor Feynman, the development of nanotechnology as a revolutionary/game-changing technology is the results of three ingredients: (1) the availability of tools to see and manipulate matter at the nanoscale; (2) astute observations and recognition of nanoscale matters and nanoeffects; and (3) sustained financial support from government and industry.

More than a decade after the Feynman lecture, in 1974 Norio Taniguchi, University of Tokyo, coined the word nanotechnology when he made the distinction between engineering of micrometer scale microtechnology and a new submicrometer level which he dubbed 'nanotechnology' [3].

In 1981, IBM's scanning tunneling microscope (STM) was developed at the IBM Zurich Research Laboratory. STM and its offspring, including the atomic force microscope, provided researchers around the world with the basic tools they needed to explore and manipulate materials at the atomic scale [3].

The atomic force microscope was invented by ZRL researchers Gerd Binnig and Christoph Gerber, together with Professor Calvin Quate of Stanford University. Their invention earned them the Nobel Prize and expanded the scope of nanotechnology research to nonconducting materials [3].

In 1989, IBM Fellow Don Eigler was the first to controllably manipulate individual atoms on a surface, using STM to spell out 'I-B-M' by positioning 35 xenon atoms and, in the process, perhaps creating the world's smallest logo [3].

Armed with the new tools, several discoveries of fullerenes were made and they have added considerable excitements to the rapidly growing field of nanotechnology. For example, although there are conflicting opinions, Sumio Iijima from Japan is largely credited for the discovery of fullerene-related carbon nanotubes in 1991 [3, 4]. The tubes contained at least two layers, often many more, and ranged in outer diameter from about 3 nm to 30 nm. They were invariably closed at both ends. In 1996, Smalley shared the Nobel Prize in Chemistry with his Rice University colleague Robert Curl and the British chemist Harold Kroto for their discovery of the buckyballs in 1985. A good example of the application of nanoeffects is the nanoshells invented in 1998 by Naomi Halas at Rice University. The nanoshells are a new class of multi-layered nanoscale

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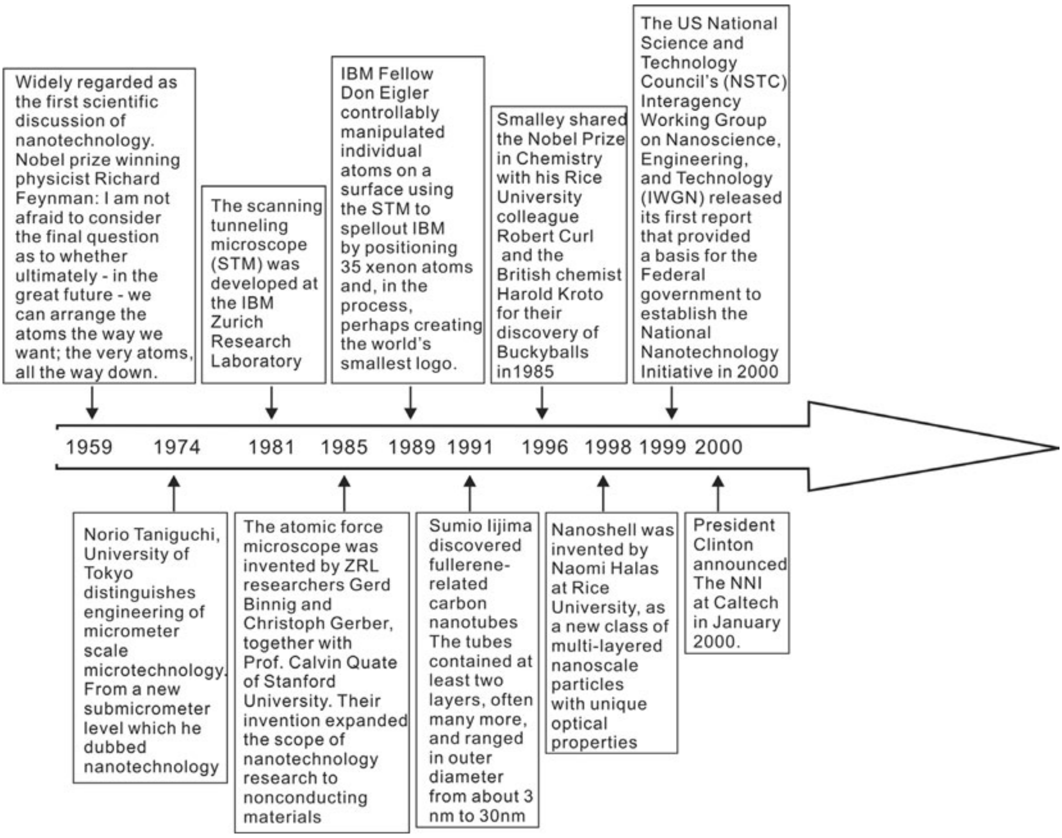

Fig. 1.2 Nanotechnology historical timeline (adapted from Ref. [5] with modifications).

particles with unique optical properties controlled by the thickness and composition of their constituent layers. By varying the relative size of the glass core and the gold shell layer, researchers can ‘tune’ nanoshells to respond to different wavelengths of light. For biomedical applications, nanoshells can be designed and fabricated to absorb near-infrared light. Near-infrared light, a region of the spectrum just beyond the visible range, is optimal for medical imaging and treatment because it passes harmlessly through soft tissue.

With the seed planted by Feynman, the tools invented by researchers in IBM, and the innovative discoveries by scientists from Japan, Rice University and elsewhere in the 1980s and 1990s, created the necessary but insufficient conditions for the coming of the nanotechnology age until the establishment of the National Nanotechnology Initiative thanks largely to dedicated effort of dedicated governmental scientific officers such as Dr. Roco [3]. The 1999 IWGN workshop report prepared by the National Science and Technology Council Committee on Technology Interagency Working Group on Nanoscience, Engineering and Technology (IWGN) forms the basis for the NNI announced by President Clinton in 2000. Figure 1.2 shows the nanotechnology historical timeline.

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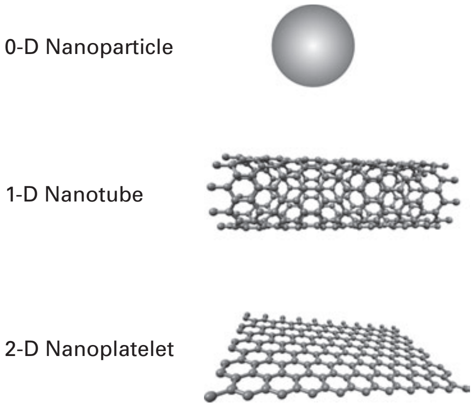

Fig. 1.3 Dimensional classification of nanomaterials.

1.4 Classification of nanomaterials

The materials produced in nanotechnology can be classified according to dimension, chemical composition, materials properties, material applications and manufacturing technology. From the view of dimension, nanomaterials are classified as zero-dimensional (0-D), one-dimensional (1-D) and two-dimensional (2-D) materials, as shown in Fig. 1.3. A 0-D nanomaterial has three directions of nanosymmetry. Quantum dots and nanoparticles are examples of 0-D nanomaterials. 1-D nanomaterials such as nanowires and nanotubes have two directions of nanosymmetry or have dimensions less than 100 nm. Examples of 2-D materials are nanoclays and graphene sheets wherein the through thickness direction is less than 100 nm.

Based on chemical composition we have nanometals, nanoceramics, nanopolymers, nanoglasses and nanocrystals. Regarding material properties we have nanomagnetic materials, nonlinear nanophotonic materials, superconducting nanomaterials, thermoelectric nanomaterials, semiconducting nanomaterials, etc. One can also classify nanomaterials based on their applications; these include nanoelectronic materials, optoelectronic materials, energy storage nanomaterials, nanosensor materials, nanomedicines, etc.

1.5 Nanofiber technology

Although promising, most nanotechnology research is limited to dozens to a few hundred particles or molecules [6, 7]. In order to realize massive assembly techniques, large-scale devices and commercializable products need to be developed. Another challenge for nanotechnology is the lack of effective and efficient ways for fabricating macroscale structures. To be utilized in this macroworld, nanomaterials need to be converted to micromaterials and macromaterials. Nanofiber technology is a technique involving the synthesis, processing, manufacturing and application of fibers with nanoscale dimension. As a technique of fabrication of continuous 1-D nanomaterials, nanofiber technology is a

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promising technique that can massively assemble 1-D and 2-D nanomaterials, realize large-scale production of nanomaterials involved products and prepare continuous 1-D fibrous elements that facilitate the fabrication of microscale and macroscale structures.

Fibers are solid-state linear nanomaterials characterized by flexibility and an aspect ratio greater than 1000:1. Nanofibers are defined as fibers with a diameter equal to or less than 100 nm. But in general, all the fibers with a diameter below 1 μm (1000 nm) are recognized as nanofibers. Materials in fiber form are of great practical and fundamental importance. The combination of high specific surface area, flexibility and superior directional strength makes fibers a preferred material form for many applications varying from clothing to reinforcements for aerospace structures. Fibrous materials in the nanometer scale are the fundamental building blocks of living systems. For instance, DNA molecules are double helix strands with a diameter of 1.5 nm, cytoskeleton filaments have a diameter around 30 nm, and even sensory cells such as hair cells and rod cells of the eyes are structures with extracellular matrices or a multifunctional structural backbone for tissues and organs formed with nanofibers.

Analogous to nature's design, nanofibers of electronic polymers and their composites can provide fundamental building blocks for the construction of devices and structures that perform unique functions that serve the needs of mankind. Other areas impacted by nanofiber technology include drug delivery systems and scaffolds for tissue engineering, wires, capacitors, transistors and diodes for information technology, systems for energy transport, conversion and storage, such as batteries and fuel cells, and structural composites for aerospace structures.

Considering the potential opportunities provided by nanofibers, there is an increasing interest in nanofiber manufacturing technology. Amongst the technologies, including the template method [8], vapor grown [9], phase separation [10] and electrospinning [9, 11–27], electrospinning has attracted the most recent interest. Using the electrospinning process, Reneker and co-workers [11] demonstrated the ability to fabricate organic nanofibers with diameters as small as 3 nm. These molecular bundles, self-assembled by electrospinning, have only six or seven molecules across the diameter of the fiber! Half of the 40 or so parallel molecules in the fiber are on the surface. Collaborative research in MacDiarmid and Ko's laboratory [12, 15] demonstrated that blends of nonconductive polymers with conductive polyaniline polymers and nanofibers of pure conductive polymers can be electrospun. Additionally, *in situ* methods can be used to deposit films of 25 nm thickness of other conducting polymers, such as polypyrrole or polyaniline, on preformed insulating nanofibers. Carbon nanotubes, nanoplatelets and ceramic nanoparticles can easily be embedded in nanofibers by being dispersed in polymer solutions and consequent electrospinning of the solutions [28].

1.6 Unique properties of nanofibers

By reducing fiber diameters down to the nanoscale, an enormous increase in specific surface area to the level of 1000 m^2/g is possible. The reduction in dimension and increase in surface area greatly affect the chemical, biological reactivity and

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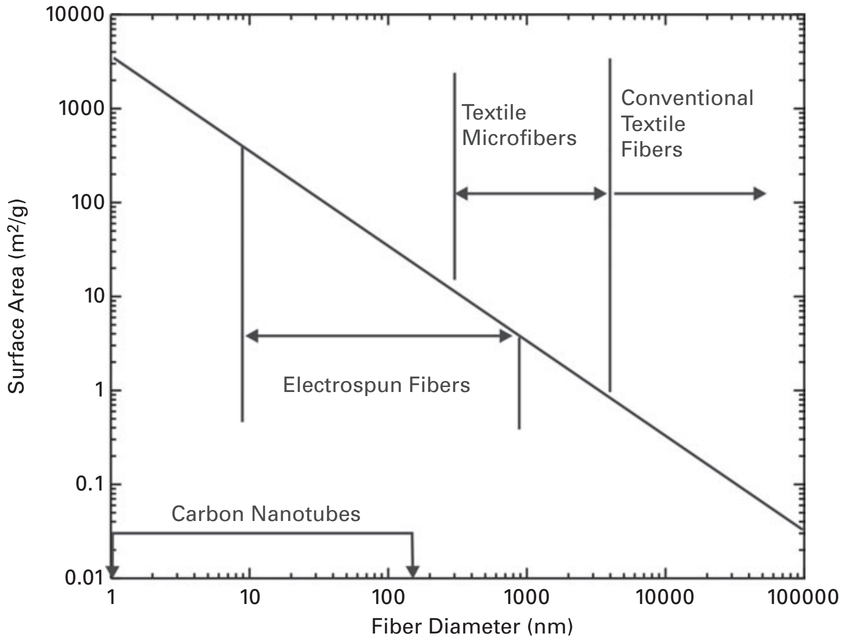

Fig. 1.4 Relation of surface area to fiber diameter [30].

electroactivity of polymeric fibers. By reducing the fiber diameter from 10 μm to 10 nm, a million times increase in flexibility is expected. Recognizing the potential nanoeffect that will be created when fibers are reduced to the nanoscale, there has been an explosive growth in research efforts around the world [29]. Specifically, the role of fiber size has been recognized in the significant increase in surface area, bio-reactivity, electronic properties and mechanical properties.

1.6.1 Effect of fiber size on surface area

For fibers having diameters from 5 nm to 500 nm, the surface area per unit mass is around 10 000 to 1 000 000 square meters per kilogram, as shown in Fig. 1.4. In nanofibers that are 3 nm in diameter, and which contain about 40 molecules; about half of the molecules are on the surface. As seen in Fig. 1.4, the high surface area of nanofibers provides a remarkable capacity for the attachment or release of functional groups, absorbed molecules, ions, catalytic moieties and nanometer-scale particles of many kinds. One of most significant characteristics of nanofibers is the enormous availability of surface area per unit mass.

1.6.2 Effect of fiber size on bioactivity

Considering the importance of surfaces for cell adhesion and migration, experiments were carried out in the Ko Laboatory (the Fibrous Materials Laboratory at Drexel University) using osteoblasts isolated from neonatal rat calvarias and grown to

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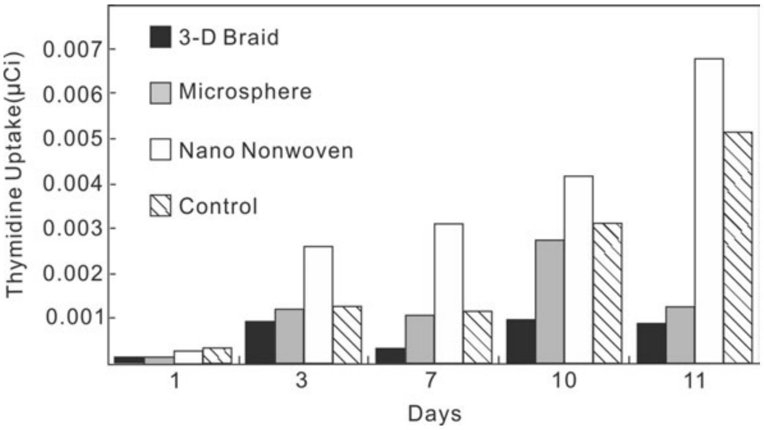

Fig. 1.5 Fibroblast cell proliferation as indicated by the thymidine uptake of cells as a function of time showing that a polylactic–glycolic acid nanofiber scaffold is most favorable for cell growth [30].

confluence in Ham's F-12 medium (GIBCO), supplemented with 12% Sigma foetal bovine on PLAGA sintered spheres, 3-D braided filament bundles and nanofibrils [14]. Four matrices were fabricated for the cell culture experiments. These matrices include (1) 150 300 μm PLAGA sintered spheres, (2) unidirectional bundles of 20 mm filaments, (3) 3-D braided structure consisting of 20 bundles of 20 μm filaments and (4) nonwoven matrices consisting of nanofibrils. The most prolific cell growth was observed for the nanofibrils scaffold as shown in the thymidine–time relationship illustrated in Fig. 1.5. This can be attributed to the greater available surface for cell adhesion as a result of the small fiber diameter which facilitates cell attachment.

1.6.3 Effect of fiber size on electroactivity

The size of the conductive fiber has an important effect on system response time to electronic stimuli and the current carrying capability of the fiber over metal contacts. In a doping–de-doping experiment, Norris *et al.* [15] found that polyaniline/PEO submicron fibrils had a response time an order of magnitude faster than that of bulk polyaniline/PEO. There are three types of contact to a nanopolymeric wire: ohmic, rectifying and tunneling. Each is modified due to nanoeffects. There exist critical diameters for wires below which metal contact produces much higher barrier heights, thus showing much better rectification properties. According to Nabet [31], by reducing the size of a wire we can expect to simultaneously achieve better rectification properties as well as better transport in a nanowire. In a preliminary study [32], as shown in Fig. 1.6, it was demonstrated, using submicron PEDT conductive fiber mat, that a significant increase in conductivity was observed as the fiber diameter decreases. This could be attributed to intrinsic fiber conductivity effects or to the geometric surface and packing density effect, or both, as a result of the reduction in fiber diameter.

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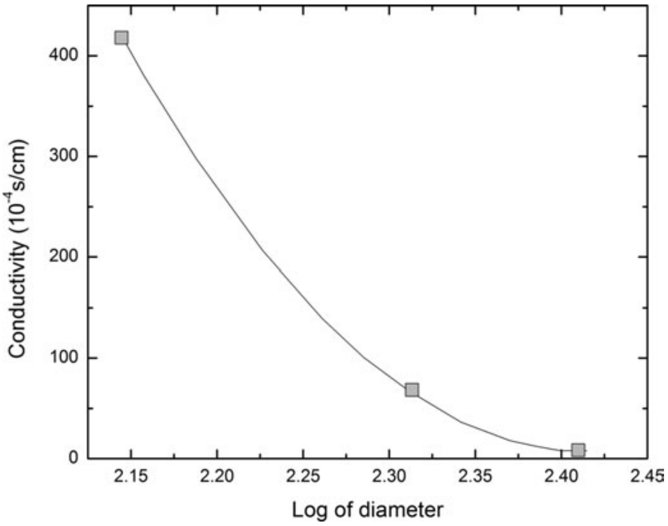

Fig. 1.6 Effect of fiber diameter on electrical conductivity of PEDT nanofibers [30].

1.6.4 Effect of fiber size on strength

Materials in fiber form are unique in that they are stronger than bulk materials. As the fiber diameter decreases, it has been well established in glass fiber science that the strength of the fiber increases exponentially due to the reduction of the probability of including flaws, as shown in Fig. 1.7a. As the diameter of matter gets even smaller, as in the case of nanotubes, the strain energy per atom increases exponentially, contributing to the enormous strength of over 30 GPa for carbon nanotube, as showm in Fig. 1.7b.

Although the effect of fiber diameter on the performance and processibility of fibrous structures has long been recognized, the practical generation of fibers down to the nanometer scale was not realized until the rediscovery and popularization of the electrospinning technology by Professor Darrell Reneker almost a decade ago [16]. The ability to create nanoscale fibers from a broad range of polymeric materials in a relatively simple manner using the electrospinning process coupled with the rapid growth of nanotechnology in recent years have greatly accelerated the growth of nanofiber technology. Although there are several alternative methods for generating fibers in a nanometer scale, none matches the popularity of the electrospinning technology due largely to the great simplicity of the electrospinning process. In this book we will focus on the electrospinning technology. The relative importance of the various processing parameters in solution electrospinning is discussed. The structure and properties of the fibers produced by the electrospinning process are then examined with particular attention paid to the mechanical and chemical properties. There is a gradual recognition that the deceptively simple process of electrospinning requires a deeper scientific understanding and engineering development in order to capitalize on the benefits promised by the attainment of the nanoscale and to translate the technology from a laboratory curiosity to a robust manufacturing process. To illustrate the method

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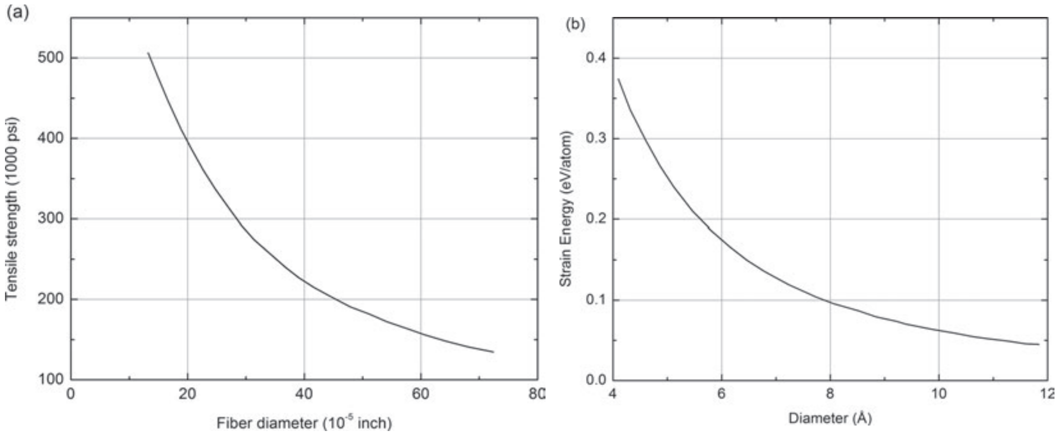

Fig. 1.7 (a) Dependence of glass fiber strength on fiber diameter [33], and (b) strain energy as a function of nanotube diameter (adapted from Ref. [34]).

for connecting properties of materials in the nanoscale to macrostructures, the approach of multi-scale modeling and a concept for the translation of carbon nanotubes to composite fibrous assemblies is presented.

Nanotechnology is anticipated to have a tremendous impact on a broad range of industries including the textile industry as is evident in the stain-resistant clothing and precision filter media. The rapid growth of nanofiber technology in recent years can be attributed to the rediscovery of the 70-year-old electrostatic spinning technology or the electrospinning technology [8]. This technique has been used to produce high-performance filters [9, 10], wearable electronics [11] and for scaffolds in tissue engineering that utilize the high surface area unique to these fibers.

Accordingly, it is the objective of this book to introduce the basic elements of nanofiber technology. Through the electrospinning process, we will examine the parameters that affect the diameter of electrospun fibers. Examples of applications of electrospun fibers will be presented to illustrate the opportunities and challenges of nanofibers.

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