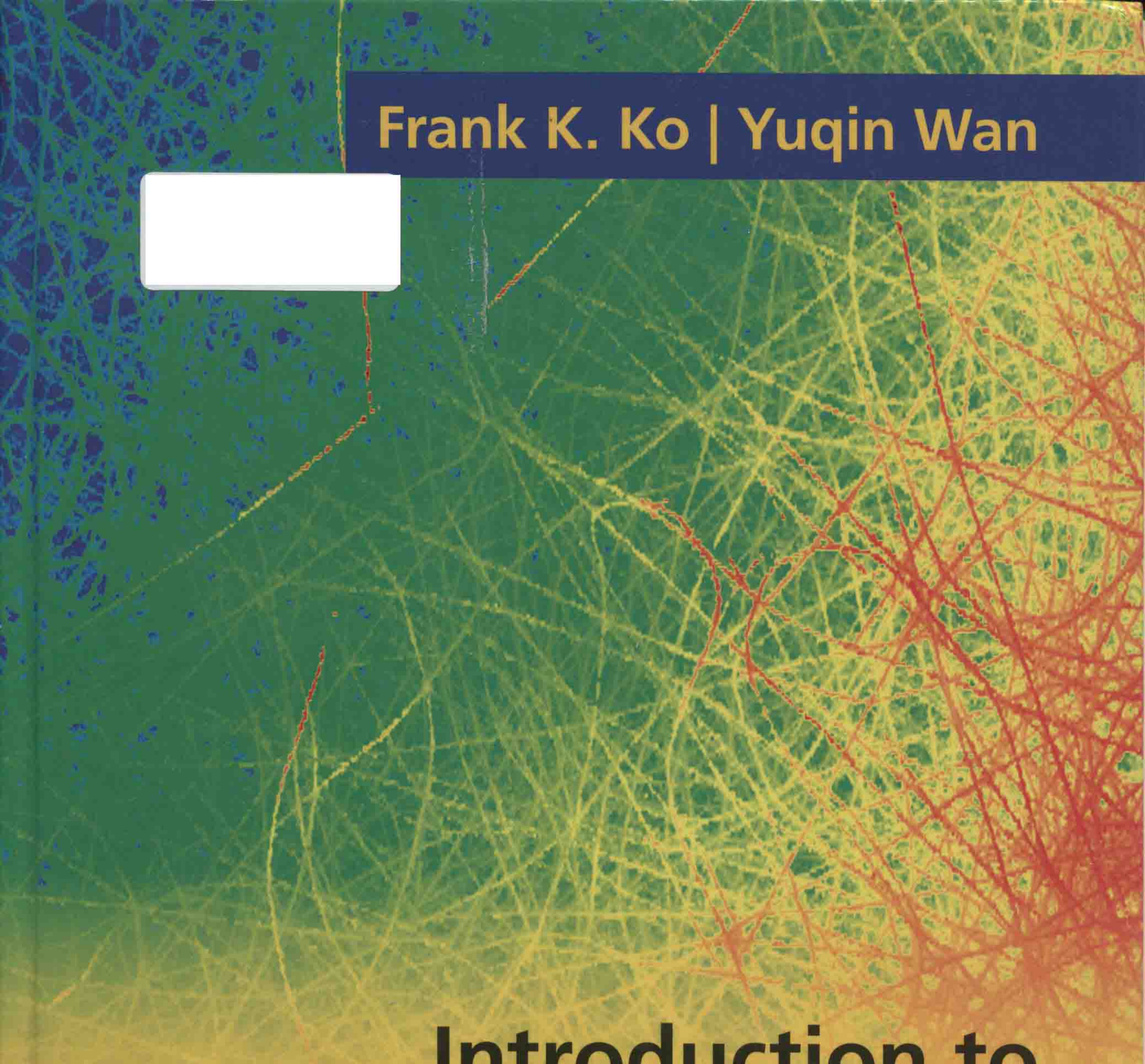
Frank K. Ko | Yuqin Wan



Introduction to Nanofiber Materials

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FRANK K. KO

and

YUQIN WAN

University of British Columbia, Vancouver

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Introduction to Nanofiber Materials

Presenting the latest coverage of the fundamentals and applications of nanofibrous materials and their structures for graduate students and researchers, this book bridges the communication gap between fiber technologists and materials scientists and engineers. Featuring intensive coverage of electroactive, bioactive, and structural nanofibers, it provides a comprehensive collection of processing conditions for electrospinning and includes recent advances in nanoparticle-/nanotube-based nanofibers. The book also covers mechanical properties of fibers and fibrous assemblies, as well as characterization methods.

Frank K. Ko is the Canada Research Chair Professor Tier 1 in Advanced Fibrous Materials and Director of the Advanced Fibrous Materials Laboratory, University of British Columbia.

Yuqin Wan is Research Associate in the Advanced Fibrous Materials Laboratory, Advanced Materials and Process Engineering Laboratory, University of British Columbia, Canada, and Associate Professor in the School of Textiles and Clothing, Jiangnan University, China.

Foreword

Professor Frank Ko is a recognized expert on the production, braiding and weaving of textile fibers, with strong interests in polymer science. He and I worked together in the mid 1990s, in a cooperative research effort supported by the US Army, on new polymer fibers, including nanofibers. Our complementary experience and knowledge were synergistic.

Early information about nanofibers made by electrospinning was sequestered in the research departments of a few filter manufacturers, and in the notebooks and memories of engineers from the former Soviet Union, who designed and manufactured gas masks. Since the 1930 patents of A. Formhals, little research on nanofibers was published except for a paper by P. K. Baumgarten in 1971 and papers by R. St. J. Manley in 1981, until my publications that began in 1995, with graduate student Jayesh Doshi.

Other polymer scientists soon began to develop their interests in electrospinning and nanofibers. The number of publications on nanofibers grew exponentially. By 2003, a paper on this subject, with mathematical models of co-author Alexander Yarin, was credited as "the frequently cited paper in a fast moving front of materials science," a part of materials science previously left almost entirely to scientists in industrial textile fiber laboratories. Activity in the form of research and nanofiber manufacturing in the filtration industry, development of other useful products, and the establishment of startup companies, has ramified into a multitude of industries and now extends throughout the world.

Professor Ko presents fundamental knowledge that will enable students and other readers to create and use polymer, ceramic, carbon and metal nanofibers for a wide spectrum of purposes.

It is clear that the information in this book will be useful to researchers learning or working in the following areas.

Filtration industry, a complex industry of rapidly growing scientific sophistication.
Bioanalytical extracellular matrix material.
Drug delivery in clinical medicine.
Scaffolding for growth of implantable organs.
Components of electronic devices.
Selective transport of ions.
Solar sails and other "gossamer" structures manufactured and used in interplanetary space.

Support of molecules and other tiny structures for examination in high resolution transmission electron microscopes.

For molecular scale observation of changes in molecular substances produce by energetic electrons (a great advance in radiation chemistry).

Development of smart textiles containing wearable computers and sensors.

The list of the things that are already being done with nanofibers in laboratories throughout the world is much longer, with fascinating possibilities yet to be articulated. This book provides a portal to the future, set in a context of polymers, fibers, textiles and materials science.

Darrell H. Reneker
The University of Akron

Preface

Polymeric materials in nanofiber form are of fundamental and practical importance.

Nanofibrous materials are the fundamental building blocks of living systems, from the 1.5 nm double helix strand of DNA molecules to the nanoscale fibres of sensory cells forming the extracellular matrices for tissues and organs. Considering the abundant evidence of nature's material design using nanofibers, it is reasonable to expect that the availability of nanoscale fibers having adjustable electronic, biological and mechanical properties will create the enabling technology for clean energy, clean environment, health care, microelectronics and nanoscience research. Inspired by these fibrous material designs in nature, coupled with the rapid development of research tools for nanotechnology fueled by substantial funding from Government programs such as the Multidisciplinary University Research Initiative (MURI) and by the National Science Foundation (NSF), a conducive environment was created in the 1990s for great strides in the new field of nanofiber technology. Specifically, in a MURI program sponsored by the Army Research Office (ARO), under the leadership of Professor Darrell Reneker, a versatile method was rediscovered for the formation of nanofibers by the electrospinning process. The MURI program has triggered unprecedented growth in nanofiber technology. I was fortunate to be involved in the ARO MURI program and enjoyed stimulating collaborations with Professor Reneker in the electrospinning of nanofiber yarns and the spinning of electrically conductive polymer into nanofibers with the late Nobel laureate Professor Alan MacDiarmid.

Benefiting from the experience gained in nanofiber technology from the MURI program, this book is an outgrowth of course notes designed by me for students enrolled in an NSF funded Research-Curriculum Development in Tissue Engineering (CRCD) Program led by Professor Cato Laurencin at Drexel University. The course was organized into ten lectures plus three laboratory sessions for students of diverse academic backgrounds including materials engineering, chemical engineering, mechanical engineering and biomedical engineering. Most of the students had no background in fibrous materials.

Building on the CRCD lecture notes, this book is organized into ten chapters. Chapter 1 provides an introduction to nanomaterials in general and nanofibers in specific. Chapter 2 presents an overview of polymer science with an emphasis on fiber forming polymers. Chapter 3 deals with nanofiber technology with a specific focus on electrospinning. Chapter 4 concerns process modeling of the electrospinning process and mechanistic modeling of nanofibrous assemblies that include yarn mechanics and mechanics of nonwoven structures. In Chapter 5 we describe the various methods for the characterization of nanofiber materials. Chapters 6, 7 and 8 are devoted to functional nanofibers with Chapter 6 focusing on bioactive nanofibers, Chapter 7 focusing on electroactive nanofibers, and Chapter 8 focusing on structural composite nanofibers. In Chapter 9, various applications of nanofibers are presented and finally, in Chapter 10, the book concludes with an overview of the trend in nanofiber technology.

For various reasons the writing of the book was put on hold for a period of time until I moved to the University of British Columbia in Canada where I had the good fortune of having Dr. Lynn Yuqin Wan join the book project. With the dedicated participation of Lynn the book project was revived. As the book is based on the lecture notes delivered over the past decade, it draws heavily from the research results generated by my students, postdoctoral fellows and collaborators. I would like to thank them, in rough chronological order: Ali Ashraf, Manal Shaker, Ian Norris, Hoa Lam, Nic Titchenol, Haihu Ye, Afaf El-Aufy Jason Lyons, Jonathan Ayutsede, Milind Gahndi, Heejae Yang, Yoshihiro Yamashita, Sachiko Sukigara, Jie Xiong, Nasir M. Uddin, Takako Inoue, Chunhong Wang, Yuan Li, Jiashen Li, Lin Li Masoumeh Bayat, Wuyi Zhou, Nicole Lee, Justin Richie, Ian Dallmeyer, Phoebe Y. Li, Victor Leung, LiTing Lin and Ryan Huizing. Special thanks go to Professor Darrell Reneker for his generous sharing of the knowledge on electrospinning and to the late Professor Alan MacDiarmid who enthusiastically shared his knowledge in conductive polymers and helped to establish the area of electroactive nanofibers.

It must be noted that the research work of my group would not be possible without the sustained support of various funding agencies including the ARO, ONR, AFOSR, NSF, NASA, the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canada Foundation of Innovation (CFI). I would like to pay special tribute to the late Hidefumi Kato of Kato-tech who took my advice to build one of the earliest commercial Nanofiber Electrospinning Units (NEUs) and funded an extensive literature collection project in my laboratory that we utilize extensively in this book.

Finally I want to thank the editorial staff of Cambridge University Press, Production Editor Vania Cunha and Sarah Marsh (nee Matthews) Editor, Engineering, who patiently shepherded us through the completion of this book. Last but not the least I want to thank my daughter Jana Ko who patiently proofread the earlier version of the manuscript.

Frank K. Ko

Contents

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

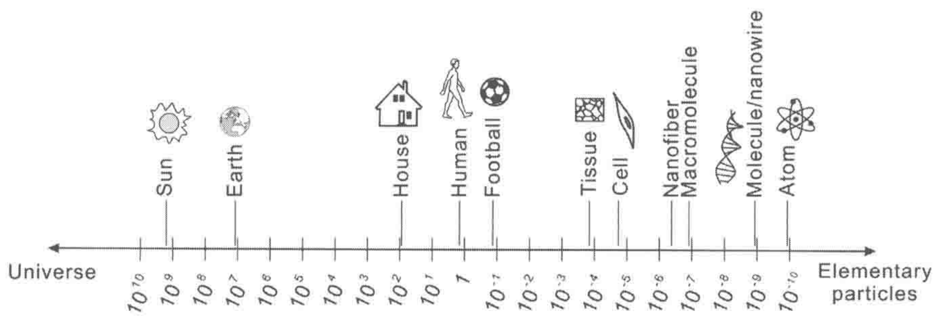

Fig. 1.1 Illustration of relative scale in nature. (The linear distance is indicated on this logarithmic scale in meters.)

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.