

国外化学经典教材系列（影印版）

1

材料化学

Materials Chemistry
(2nd Edition)

Bradley D. Fahlman

原著第2版



科学出版社

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Materials Chemistry

by Bradley D. Fahlman

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Preface

Most colleges and universities now have courses and degree programs related to materials science. *Materials Chemistry* addresses inorganic, organic, and nano-based materials from a structure vs. property treatment, providing a suitable breadth and depth coverage of the rapidly evolving materials field in a concise format. The material contained herein is most appropriate for junior/senior undergraduate students, as well as first-year graduate students in chemistry, physics, and engineering fields. In addition, this textbook has also been shown to be extremely useful for researchers in industry as an initial source to learn about materials/techniques. A comprehensive list of references is provided for each chapter, which is essential for more detailed topical research.

It is a daunting task for a textbook to remain contemporary, especially when attempting to cover evolving fields such as advanced polymeric materials and nanotechnology, as well as applications related to energy storage, biomedicine, and microelectronics, among others. Accordingly, I began working on updates for *Materials Chemistry* while the first edition was still in production! The 2nd edition continues to offer innovative coverage and practical perspective throughout. After providing a historical perspective for the field of materials in the first chapter, the following additions/changes have been adopted in this greatly expanded edition:

The solid-state chemistry chapter uses color illustrations of crystalline unit cells and digital photos of models to clarify their structures. This edition features more archetypical unit cells and includes fundamental principles of X-ray crystallography and band theory. In addition, the ample amorphous-solids section has been expanded to include more details regarding zeolite syntheses, as well as ceramics classifications and their biomaterial applications. Sections on sol-gel techniques and cementitious materials also remain, which are largely left out of most solid-state textbooks.

The metals chapter has been re-organized for clarity, and continues to treat the full spectrum of powder metallurgical methods, complex phase behaviors of the

Fe-C system and steels, and topics such as magnetism, corrosion inhibition, hydrogen storage, and shape-memory phenomena. The mining/processing of metals has also been expanded to include photographs of various processes occurring in an actual steel-making plant. The structure/properties of other metallic classes, such as the coinage metals and other alloys, has also been expanded in this edition.

The semiconductor chapter addresses the evolution of modern transistors, as well as IC fabrication and photovoltaics. Building on the fundamentals presented earlier, more details regarding the band structure of semiconductors is now included, as well as discussions of GaAs vs. Si for microelectronics applications, and surface reconstruction nomenclature. The emerging field of ‘soft lithographic’ patterning is now included in this chapter, and thin film deposition methodologies are also greatly expanded to now include more fundamental aspects of chemical vapor deposition (CVD) and atomic layer deposition (ALD). The current trends in applications such as LEDs/OLEDs, thermoelectric devices, and photovoltaics (including emerging technologies such as dye-sensitized solar cells) are also provided in this chapter.

The polymeric/‘soft’ materials chapter represents the largest expansion for the 2nd edition. This chapter describes all polymeric classes including dendritic polymers, as well as important additives such as plasticizers and flame-retardants, and emerging applications such as molecular magnets and self-repairing polymers. This edition now features ‘click chemistry’ polymerization, silicones, conductive polymers and biomaterials applications such as biodegradable polymers, biomedical devices, drug delivery, and contact lenses.

The nanomaterials chapter is also carefully surveyed, focusing on nomenclature, synthetic techniques, and applications taken from the latest scientific literature. The 2nd edition has been significantly updated to now include nanotoxicity, vapor-phase growth of 0-D nanostructures, and more details regarding synthetic techniques and mechanisms for solution-phase growth of various nanomaterials. Graphene, recognized by the 2010 Nobel Prize in Physics, is now also included in this edition.

The last chapter is of paramount importance for the materials community – characterization. From electron microscopy to surface quantitative analysis techniques, and everything in between, this chapter provides a thorough description of modern techniques used to characterize materials. A flowchart is provided at the end of the chapter that will assist the materials scientist in choosing the most suitable technique(s) to characterize a particular material. In addition to comprehensive updates throughout the chapter, a new technique known as atom-probe tomography (APT) has been included in this edition.

This edition continues to build on the promotion of student engagement through effective student–instructor interactions. At the end of each chapter, a section entitled “Important Materials Applications” is provided, along with open-ended

questions and detailed references/bibliography. Appendices are also provided which contain an updated/expanded timeline of major materials developments and the complete Feynman speech “There’s Plenty of Room at the Bottom”. An expanded collection of materials-related laboratory modules is also included, which now includes the fabrication of porous silicon films, silicon nanowires, and links to experiments related to ferrofluids, metallurgical phase transitions, and the heat treatment of glasses.

My wife Diyonnn continues to be a source of inspiration and support for my pedagogical and research projects. Thank you for your love, support, and heartfelt professional advise. I am also grateful to my parents Frank and Pearl for their continuing support and Godly wisdom, to whom I attribute all of my many blessings and successes. To say that my recent sabbatical at the Universidad de Costa Rica was life-changing is an under-statement. Muchas gracias a Profesores Arturo Ramirez Porras, Daniel Azofeifa Alvarado, Leslie Pineda, y Mavis Montero por su hospitalidad y amistad. Our ‘adoptive Costa Rican family’ (Giancarlo and Marisol DeFranco, Grace Pastrana, Keylin Wu, Marcela Pastrana, and Luce Pastrana) and close friends (Marian Zerpa and Jose Morales) will never be forgotten – thanks for your continuing friendship and love.

I am also very appreciative for the input provided by students and instructors who have either adopted or considered the adoption of the first edition. I continue to offer thanks to every reader of this book, and solicit your comments to my email fahlmanb@gmail.com. Please let me know what you think of this edition; I will continue to incorporate your suggestions to strengthen future editions.

Bradley D. Fahlman, Ph.D.
Mount Pleasant, Michigan
December 2010

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CHAPTER 1

WHAT IS MATERIALS CHEMISTRY?

Life in the twenty-first century is ever dependent on an unlimited variety of advanced materials. In our consumptive world, it is easy to take for granted the macro-, micro-, and nanoscopic building blocks that comprise any item ever produced. We are spoiled by the technology that adds convenience to our lives, such as microwave ovens, laptop computers, digital cell phones, and improved modes of transportation. However, we rarely take time to think about and appreciate the materials that constitute these modern engineering feats.

The term *material* may be broadly defined as any solid-state component or device that may be used to address a current or future societal need. For instance, simple building materials such as nails, wood, coatings, *etc.* address our need of shelter. Other more intangible materials such as nanodevices may not yet be widely proven for particular applications, but will be essential for the future needs of our civilization. Although the above definition includes solid nanostructural building blocks that assemble to form larger materials, it excludes complex liquid compounds such as crude oil, which may be more properly considered a *precursor* for materials.

A general description of the various types of materials is illustrated in Figure 1.1. Although this indicates sharp distinctions between various classes, there is often ambiguity regarding the proper taxonomy for a specific material. For example, a *thin film* is defined as having a film thickness of less than 1 μm ; however, if the thickness drops to below 100 nm, the dimensions may be more accurately classified within the nanoscale regime.^[1] Likewise, liquid crystals are best described as having properties intermediate between amorphous and crystalline phases, and *hybrid composite* materials involve both inorganic and organic components.

The broadly defined discipline of *materials chemistry* is focused on understanding the relationships between the arrangement of atoms, ions, or molecules comprising a material, and its overall bulk structural/physical properties. By this designation, common disciplines such as polymer, solid-state, and surface chemistry would all be placed within the scope of materials chemistry. This broad field consists of studying the structures/properties of existing materials, synthesizing and characterizing new materials, and using advanced computational techniques to predict structures and properties of materials that have not yet been realized.

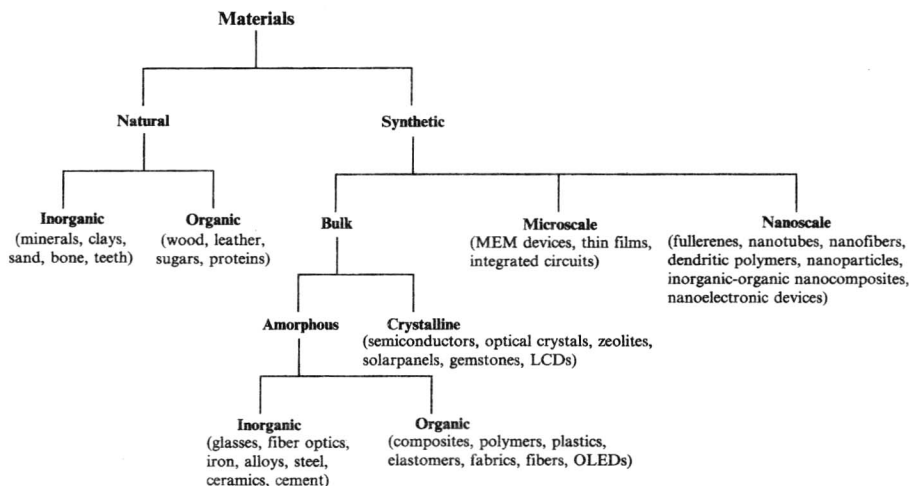


Figure 1.1. Classification scheme for the various types of materials.

1.1. HISTORICAL PERSPECTIVES

Although the study of materials chemistry is a relatively new entry in both undergraduate and graduate curricula, it has always been an important part of chemistry. An interesting timeline of materials developments from Prehistoric times to the present may be found in Appendix A. By most accounts, Neolithic man (10,000–300 B.C.) was the first to realize that certain materials such as limestone, wood, shells, and clay were most easily shaped into materials used as utensils, tools, and weaponry. Applications for metallic materials date back to the Chalcolithic Age (4,000–1,500 B.C.), where copper was used for a variety of ornamental, functional, and protective applications. This civilization was the first to realize fundamental properties of metals, such as malleability and thermal conductivity. More importantly, Chalcolithic man was the first to practice *top-down* materials synthesis (see later), as they developed techniques to extract copper from oxide ores such as malachite, for subsequent use in various applications.

Metal alloys were first used in the Bronze Age (1,400–0 B.C.), where serendipity led to the discovery that doping copper with other compounds drastically altered the physical properties of the material. Artifacts from the Middle East dating back to 3,000 B.C. are found to consist of arsenic-doped copper, due to the wide availability of lautite and domeykite ores, which are rich in both arsenic and copper. However, due to arsenic-related casualties, these alloys were quickly replaced with tin–copper alloys (bronze) that were widely used due to a lower melting point, higher hardness, and lower brittleness relative to their arsenic forerunner.

The Iron Age (1,000 B.C.–1,950 A.D.) first brought about applications for iron-based materials. Since the earth's crust contains significantly more iron than copper

Table 1.1. Natural Abundance of Elements in the Earth's Crust^a

Oxygen	46.1%
Silicon	28.2%
Aluminum	8.2%
Iron	5.6%
Calcium	4.2%
Sodium	2.4%
Magnesium	2.3%
Potassium	2.1%
Titanium	0.57%
Hydrogen	0.14%
Copper	0.005%
Total	99.8%

^aData taken from Reference^[2].

(Table 1.1), it is not surprising that bronze was eventually abandoned for materials applications. An iron silicate material, known today as *wrought iron*, was accidentally discovered as a by-product from copper processing. However, this material was softer than bronze, so it was not used extensively until the discovery of steel by the Hittites in 1,400 B.C. The incorporation of this steel technology throughout other parts of the world was likely an artifact of the war-related emigration of the Hittites from the Middle East in 1,200 B.C. The Chinese built upon the existing iron-making technology, by introducing methods to create iron alloys that enabled the molding of iron into desired shapes (*i.e.*, cast iron production). Many other empirical developments were practiced in this time period through other parts of the world; however, it must be stated that it was only in the eighteenth and nineteenth century A.D. that scientists began to understand why these diverse procedures were effective.

Figure 1.2 presents the major developmental efforts related to materials science, showing the approximate year that each area was first investigated. Each of these areas is still of current interest, including the design of improved ceramics and glasses, originally discovered by the earliest civilizations. Although building and structural materials such as ceramics, glasses, and asphalt have not dramatically changed since their invention, the world of electronics has undergone rapid changes. Many new architectures for advanced material design are surely yet undiscovered, as scientists are now attempting to mimic the profound structural order existing in living creatures and plant life, which is evident as one delves into their microscopic regimes.

As society moves onto newer technologies, existing materials become obsolete, or their concepts are converted to new applications. A prime example of this is related to phonographs that were commonplace in the early to mid-1900s. However, with the invention of magnetic tape by Marvin Camras in 1947, there was a sharp drop in record usage due to the preferred tape format. The invention of compact disk technology in 1982 has driven the last nail in the coffin of records, which may now only be found in antique shops and garage sales. The needles that were essential to play records no longer have marketability for this application, but have inspired another application at the micro- and nanoscale regime: *atomic force microscopy*, more generally referred to as *scanning probe microscopy* (SPM, see Chapter 7).

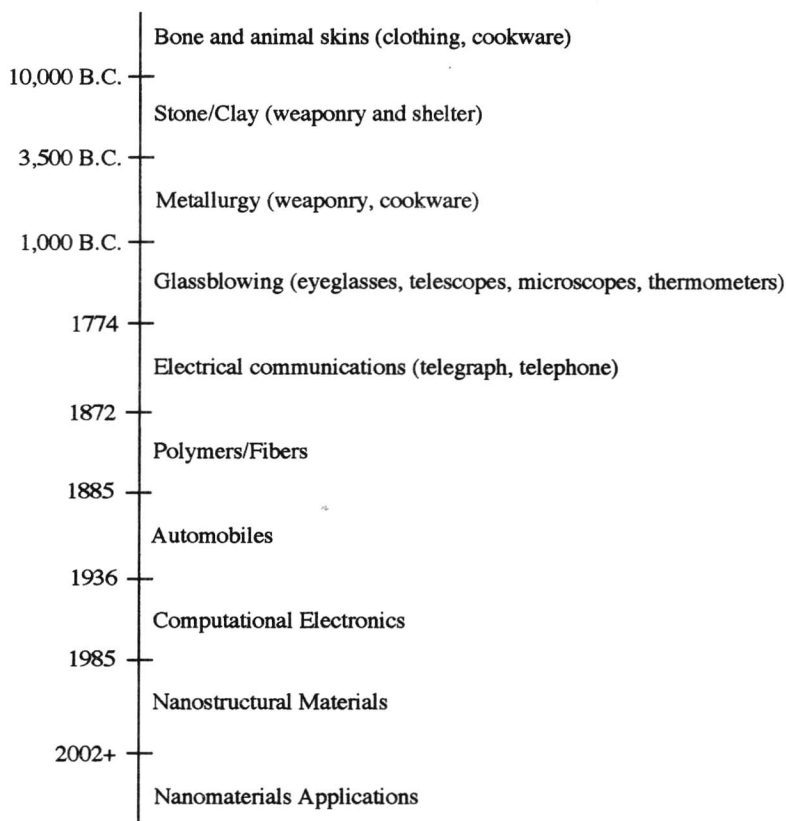


Figure 1.2. Timeline of major developmental efforts related to materials science.

This materials characterization technique uses a tip, analogous to the record needle that was once used in phonographs, to create images of the surface topology of a sample – even including the controlled placement of individual atoms (Figure 1.3)! Hence, even though the needs and desires of society are constantly changing, the antiquated materials that are being replaced may still be of benefit toward the design of new materials and technology.

The early world of materials discovery consisted solely of empirical observations, without an understanding of the relationship between material structure and properties. Each civilization had specific needs (*e.g.*, materials for shelter, clothing, warfare), and adapted whatever materials were available at the time to address these desires. Although this suitably addressed whatever issues were of societal concern at the time, such a trial-and-error manner of materials design resulted in slow growth.

Interestingly, until the nineteenth century, the practice of chemistry was viewed as a religion, being derived from alchemical roots that focused on a spiritual quest to make sense of the universe.^[3] The alchemists searched for a number of intriguing

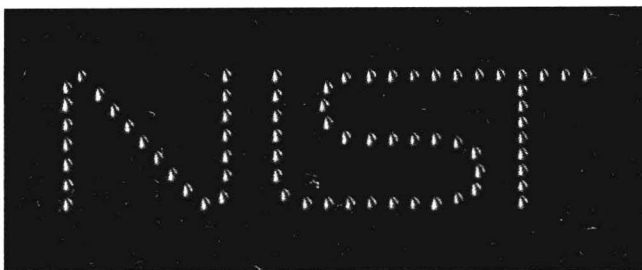


Figure 1.3. A 40-nm wide logo for NIST (National Institute of Standards and Technology), made by the manipulation of Co atoms on a Cu(111) surface. The ripples in the background are due to electrons in the fluid-like layer at the copper surface, bouncing off the cobalt atoms – much like the patterns produced when pebbles are dropped in a pond. Image provided courtesy of J. A. Stroscio and R. J. Celotta (NIST, Gaithersburg, MD).

discoveries including the keys to immortality, a “philosopher’s stone” to transform base matter into higher matter, methods to synthesize gold (or transform any other metal into gold), and magic potions to cure diseases. However noble these pursuits were, they remained unaccomplished due to the lack of an underlying chemical theory to guide their experimentation. In addition, their trial-and-error methodology involved only qualitative characterization, and it was extremely difficult to control the reaction conditions, making it virtually impossible to repeat the exact procedure a number of times.

As a result, from 1,000 B.C. to 1,700 A.D., only a few new substances were discovered which later turned out to be elements such as copper, iron, and mercury. Although this foundation resulted in the development of many experimental techniques of modern chemistry, it is not hard to see that true progress toward new material design may only be accomplished through foresight, based on an intimate understanding of specific relationships between the structure and property of a material. However, as you will see throughout this text, even with such knowledge, many important materials discoveries have been made by accident – the result of an unplanned occurrence during a carefully designed synthesis of an unrelated compound!

1.2. CONSIDERATIONS IN THE DESIGN OF NEW MATERIALS

The development of new materials is governed by the current societal need and availability of resources. However, the adoption of a material depends primarily on its cost, which is even observed by changes in the chemical makeup of currencies through the years. Coins currently comprise worthless ferrous alloys rather than high concentrations of metals such as gold, silver, copper, and nickel that comprised early coins. When a new technology or material is introduced, there is almost always a high price associated with its adoption. For example, consider the cost of computers and plasma televisions when they first became available – worth tens of thousands of dollars!

The market price of a device is governed by the costs of its subunits. Shortly after the invention of germanium-based transistors in the late 1940s, the price of an individual transistor was approximately US \$8–10. However, as germanium was substituted with silicon, and fabrication techniques were improved, the price of these materials has exponentially decreased to its current price of one-millionth of a penny! This has allowed for an unprecedented growth in computational expediency, without a concomitant increase in overall price.

There are two rationales for the synthesis of materials – “top-down” and “bottom-up”; Figure 1.4 illustrates examples of materials synthesized from both approaches. Whereas the transformation of complex natural products into desirable materials occurs primarily via a top-down approach (*e.g.*, gemstones from naturally occurring mineral deposits, etching features on silicon wafers for chip production), the majority of synthetic materials are produced using the bottom-up approach. This latter technique is the easiest to visualize, and is even practiced by children who assemble individual LEGO™ building blocks into more complex architectures. Indeed, the relatively new field of nanotechnology has drastically changed the conception of bottom-up processes, from the historical approach of combining/molding bulk precursor compounds, to the self-assembly of individual atoms and molecules. This capability of being able to manipulate the design of materials from the atomic level will provide an unprecedented control over resultant properties. This will open up possibilities for an unlimited number of future applications, including faster electronic devices, efficient drug-delivery agents, and “green” energy alternatives such as hydrogen-based and fuel cell technologies.

The recent discovery of self-repairing/autonomic healing structural materials is an example of the next generation of “smart materials.” Analogous to the way our bodies are created to heal themselves, these materials are designed to undergo spontaneous physical change, with little or no human intervention. Imagine a world where cracks in buildings repair themselves, or automobile bodies actually appear in showroom condition shortly following an accident. Within the next few decades, these materials could be applied to eliminate defective parts on an assembly line, and could even find use in structures that are at present impractical or impossible to repair, such as integrated circuits or implanted medical devices. This is the exciting world that lies ahead of us – as we learn more about how to reproducibly design materials with specific properties from simple atomic/molecular subunits, the applications will only be limited by our imaginations!

1.3. DESIGN OF NEW MATERIALS THROUGH A “CRITICAL THINKING” APPROACH

Although it is essential to use critical thinking to logically solve problems, this method of reasoning is not being taught in most baccalaureate and postbaccalaureate curricula. Unfortunately, the curricular pattern is focused on memorization and standardized-exam preparation. Further, with such a strong influence of television,

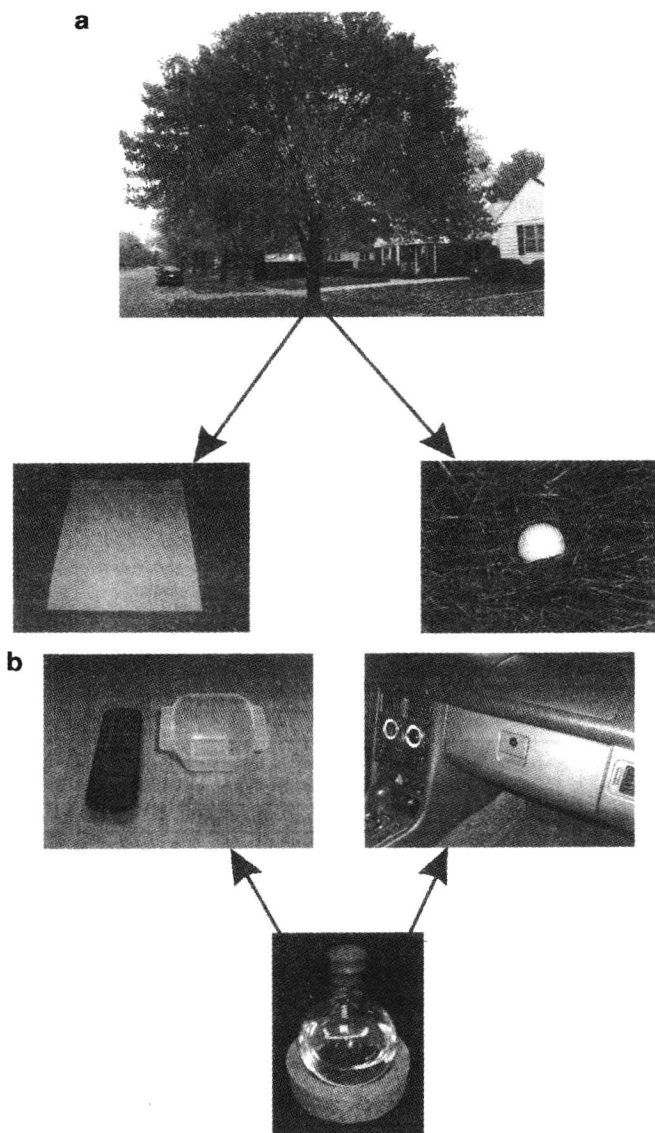


Figure 1.4. Illustrations for the “top-down” and “bottom-up” approach to materials synthesis. (a) The top-down route is often used to transform naturally occurring products into useful materials. Representations shown above include the conversion of wood into paper products, as well as certain golf ball covers.^[4] (b) The bottom-up route of materials synthesis is most prevalent. The representation shown above is the fabrication of plastics and vinyl found in common household products and automotive interiors, through polymerization processes starting from simple monomeric compounds (see Chapter 5).