FUNDAMENTALS OF MATERIALS CHEMISTRY

CHAPTER 1: **INTRODUCTION TO MATERIALS CHEMISTRY**

1.1. Introduction

Life in the 21st century is increasingly reliant on an almost limitless array of modern materials. As consumers, it is simple to take for granted the nanoscopic, micro, and macro building pieces that are the foundation of every object ever manufactured. We have become spoilt by technological advancements that make our lives easier, such as digital cell phones, laptop computers, microwave ovens, and more convenient ways of public transit. We, on the other hand, rarely stop to consider and evaluate the materials that go into the construction of these modern technical marvels (Heilbron 2003; Klabunde & Richards, 2009; Wright & Sommerdijk, 2018).

Material may be described as any solid-state element or technology that has the potential to be employed to meet a present or future societal requirement. Shelter, for example, can be provided by simple building materials like coatings, wood, nails, and other such items. Other, more subtle materials, like nanodevices, may not have yet been extensively demonstrated for specific uses, but they will be critical for the demands of our society in the foreseeable future. It is important to note that while the above description contains solid nanostructural building blocks that may be assembled to form bigger materials, it does not include complex liquid chemicals like fossil oil, which may be more appropriately regarded as a precursor for materials (Brush, 1988; Shirota, 2000; Von Schomberg, 2010).

Figure 1.1 depicts a general explanation of the many sorts of materials, which is further explained in the text. Although this demonstrates significant boundaries between several groups, there is sometimes uncertainty over the appropriate classification for a given item. For instance, a thin film is described as having a film thickness of < 1 micron; but, if the film thickness decreases to fewer than 100 nanometers, the components may be more correctly characterized as belonging to the nanometer scale (Brock, 1993; Pasch & Schrepp, 2003). Similarly, liquid crystals are best defined as having characteristics that are midway between those of the amorphous and those of the crystalline phases, while hybrid compound materials contain both organic and inorganic components (Suslick & Price, 1999; Tatko & Waters, 2004).

When taken as a whole, materials chemistry is concerned with figuring out how to comprehend the links that exist among the arrangement of the molecules, ions, or atoms that make up a material and the whole bulk physical/structural characteristics of that material. Common fields such as surface chemistry, solid-state, and polymer would all be included under the purview of materials chemistry because of this categorization. Examining the structures and characteristics of present materials, synthesizing and characterizing new materials, as well as employing advanced computational tools to anticipate the properties and structures of materials that have not yet been created are all part of this large field of research (Liu et al., 2005; Duer, 2008; Fahlman, 2018).

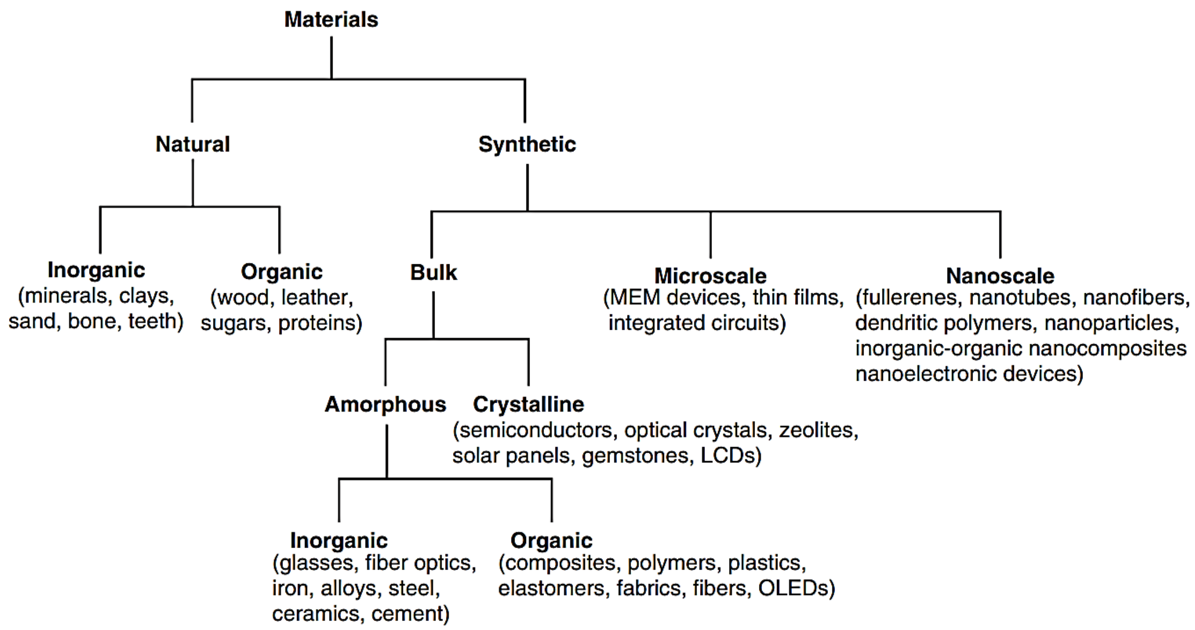

Figure 1.1. Schema of classification for the numerous sorts of building materials.

Source: https://www.researchgate.net/figure/1-Classification-Scheme-for-the-Various-Composite-Types_fig1_321977658

1.2. History of Materials Chemistry

Even though the education of materials chemistry is a comparatively new addition to equally graduate and undergraduate courses, it has always been an essential part of the field of chemistry. AppendixA has an intriguing chronology of the evolution of materials from primitive times to the current day. To the best of most historians' knowledge, Neolithic man (10,000–300 B.C.) was the first person to recognize that specific materials like clay, wood, and limestone were very easily shaped into materials that could be employed as weaponry, tools, and utensils (Weimerskirch, 1989; Mann, 2001). Copper was employed for a wide range of ornamental, protective, and functional purposes as far back as the Chalcolithic Age (4,000–1,500 B.C.) when it would be employed for a wide range of protective, functional, and ornamental purposes. This evolution was the first to recognize the basic properties of metals, like thermal and malleability conductivity, and to apply these properties to their construction. Chalcolithic man, on the other hand, was the first to put top-down materials into practice combination, as they established methods to remove copper from oxide ores like malachite, which they then used in a wide range of applications (Shirota, 2000; Nair et al., 2014).

A chance discovery led to the discovery that doping copper with other compounds drastically altered the physical properties of the material during the Bronze Age (1,400 B.C. –0 B.C.), during which time metal alloys were first used. Arsenic-doped copper has been discovered in artifacts from the Middle East that date back to 3,000 B.C. This is because of the widespread accessibility of domeykite and lautite ores, which are both rich in arsenic and copper and can be found in abundance. However, because of the arsenic-related deaths, these alloys were immediately swapped with tin–copper alloys, which were generally employed because they had a lower brittleness, lower melting point, and higher hardness than their arsenic-based predecessors (Wilkes, 2002; Davis, 2014).

The Iron Age (1,000 B.C. –1,950 A.D.) was the era in which the first applications for iron-based materials were discovered. Because the earth's crust includes meaningfully more iron than copper (Table 1.1), it is not surprising that bronze was eventually phased out of use in the production of building materials and other products. Iron silicate, also called wrought iron, was discovered unintentionally as a by-product of copper processing and was used as a building material (Hu et al., 2014; Kitchen et al., 2014).

Table 1.1The Natural Presence of Elements in the Crust of the Earth.

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

Because when compared to bronze, this substance was softer., it was not widely employed till the Hittites discovered steel about 1,400 B.C. The spread of steel technology to other regions of the world was most expected a result of the Hittites' war-related departure from the Middle East about 1,200 B.C. The Chinese improved on present iron-making technologies by developing ways for creating iron alloys that allowed iron to be molded into desired forms. Several more empirical advancements were carried out in different regions of the world during this time; nevertheless, scientists did not begin to grasp why these various processes were beneficial until the 18th and 19th centuries A.D (Hill, 1998; Hofmann & Hagey, 2014).

Figure 1.2 depicts the primary materials science development activities, together with the approximate year each topic was initially explored. The creation of better ceramics and glasses, which were first discovered by the ancient civilizations, is still of ongoing interest in each of these disciplines. While architectural and structural materials like asphalt ceramics glassware have remained relatively unchanged since their conception, the world of electronics has moved rapidly. Several novel designs for sophisticated material design are undoubtedly still to be discovered, as scientists strive to replicate the fundamental structural order present in live animals and plants, which can be seen when looking at their tiny regimes (Shanahan et al., 2011).

Existing materials become outdated when civilization moves on to newer technology, or their ideas are adapted to novel uses. A good instance of this is gramophones, which were widely used in the primary to mid-1900s. Nevertheless, due to the favored tape format, there was a steep reduction in record usage once Marvin Camras invented magnetic tape in 1947. The introduction of small disc technology in 1982 put the last nail in the casket of records, which are now just available at vintage stores and service department sales. The barbs that were once required to perform records are no longer commercially viable, but they have inspired another use at the micro-and nanoscale level: atomic force microscopy, often known as scanning probe microscopy (Ali & Armstrong, 2008).

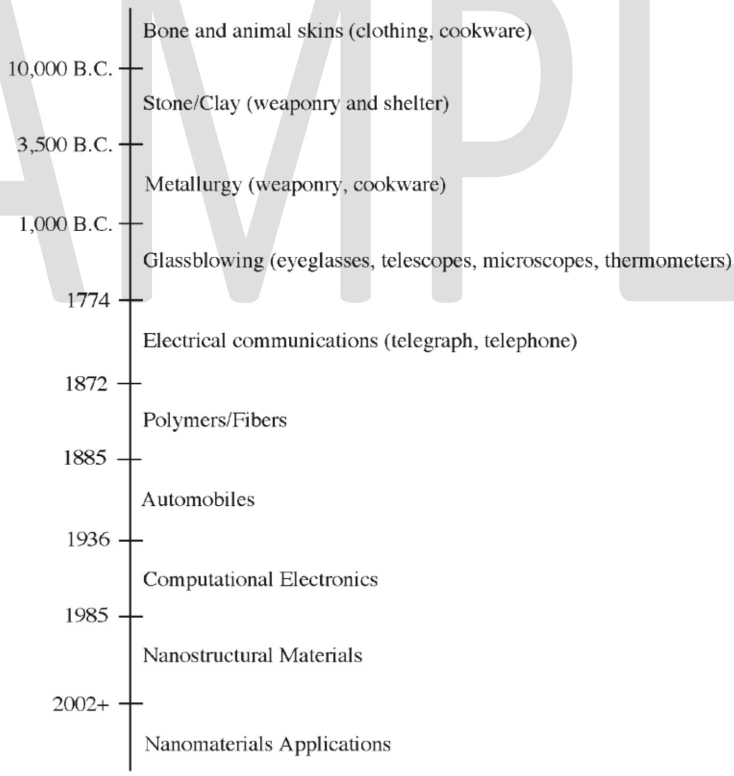

Figure 1.2. Schedule of significant development endeavors in the field of materials science and engineering.

Source: https://www.degruyter.com/document/doi/10.1515/ci.2009.31.3.4/html

This materials characterization technology creates pictures of the surface topology of a sample using a tip like a record needle used in phonographs – even includes the regulated positioning of individual atoms (Figure 1.3)! As a result, even if society's requirements and aspirations are continually altering, the obsolete materials that are being phased out may, however, be useful in the development of new materials and technologies.

Without a grasp of the link between material structure and characteristics, the early world of materials discovery was based primarily on empirical findings. Each civilization had distinct demands that were met by adapting any materials were available at the time. Even though this adequately handled whatever social concerns were there at the time, like a trial-and-error approach to materials layout caused in sluggish progress (Düren et al., 2004).

Intriguingly, the chemistry was seen as a religion until the 19th century, as it was developed from alchemical foundations that centered on a mystical desire to make meaning of the cosmos.

The experimenters were on the lookout for the keys to immortality, a "philosopher's stone" that could turn base matter into the higher matter, techniques to manufacture gold, and magical cures for ailments. Despite their great intentions, their endeavors remained unfulfilled due to a lack of a determined level theory to guide their work (Politzer et al., 2007).

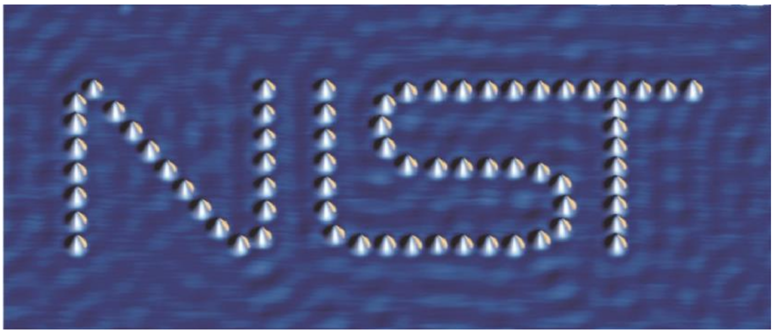

Figure 1.3. Using the manipulation of Co atoms on a Cu(111) surface, we were able to create a 40-nm wide logo for the NIST. Similar to how ripples appear in a pond when stones are put in, the ripples in the background are caused by electrons in the fluid-like layer at the copper surface jumping off cobalt atoms, creating the shapes seen there.

Source: https://link.springer.com/book/10.1007%2F978-94-024-1255-0

Aside from that, their qualitative characterization was limited to their trial-and-error methods, and it was incredibly difficult to regulate the reaction circumstances, making it almost impossible to reproduce the precise operation several times.

Thus, just a handful of new compounds were discovered between 1,000 B.C. and 1,700 A.D., all of which turned out to be elements like mercury, iron, and copper in later years. This organization led to the advancement of several modern chemistry experimentation techniques, but the true development of new material design can only be achieved via prescience, which depends on an intense study of local relationships among the properties and structure of a material. According to the evidence shown in this article, even with this expertise, many essential materials discoveries have been achieved by chance — because of an unanticipated event occurring through the meticulously planned synthesis of a distinct chemical!

1.3. Factors in the Design of New Materials

The present social demand and resource availability drive the creation of novel materials. The acceptance of material, on the other hand, is mostly determined by its cost, as seen by variations in the chemical components of currencies across time. Instead of the high quantities of metals such as copper, nickel, gold, and silver seen in early coins, today's coinage includes worthless ferrous alloys (Oermann et al., 2000). When a new technology or material is developed, it nearly usually comes with a high cost to adopt it. Consider the price of plasma televisions and computers when they were first introduced — tens of thousands of dollars!

The costs of a device's components determine its market price. In the late 1940s, just after the creation of germanium-based transistors, the price of a single transistor was around $8–10. Nevertheless, when germanium was replaced by silicon and manufacturing processes enhanced, the cost of these materials plummeted below one-millionth of a cent! This has resulted in extraordinary increases in computing efficiency without a corresponding rise in total cost (Yaghi et al., 2003; Ok, 2016).

There are two ways to material synthesis: "top-down" and "bottom-up"; Figure 1.4 shows examples of materials created using both methods. Unlike the transformation of complicated natural products into desired materials, which is mostly done from the top-down, synthetic materials are mostly made from the bottom up. This method is the simplest to grasp, and it is even used by youngsters who put together individual LEGOTM building bricks to create more sophisticated structures. Indeed, the relatively new area of nanotechnology has fundamentally altered our understanding of bottom-up procedures, moving away from the traditional technique of molding/combining large precursor materials and toward the self-assembly of individual molecules and atoms. The capacity to change the material design at the atomic level will provide researchers unparalleled control over the qualities that arise. This will open the door to a plethora of potential uses, including speedier electronic gadgets, more effective medicine delivery agents, and "green" energy options like fuel-cell and hydrogen-based technology (Arakaki et al., 2003; Nappi, 2017).

Self-autonomic/repairing healing structural materials, which were recently discovered, are an instance of the next generation of "smart materials." These materials are meant to experience rapid physical modification with no or little human involvement, like how our bodies are built to repair themselves. Imagine a future where building cracks heal on their own and car bodywork is restored to showroom condition immediately after an accident. These materials might be used to reduce faulty components on an assembly line over the next few decades, and they could even be used in structures that are now difficult to repair, like implanted medical devices or integrated circuits. The uses will only be restricted by our imaginations as we understand more about how to construct materials with certain qualities from basic molecular/atomic subunits (King, 1995; Fuad et al., 2017).

1.4. Design of New Materials through A "Critical Thinking" Method

While critical thinking is necessary for logical problem solving, this way of reasoning is not taught in most bachelor and post-baccalaureate curriculum. Regrettably, the curriculum emphasizes memorizing and preparation for standardized tests. Furthermore, with television, movies, and the Internet has such a huge impact on today's society, the concept of evoking an intentional flow diagram of thinking is not universally relevant (Muhlisin et al., 2016; Rusmansyah et al., 2019).

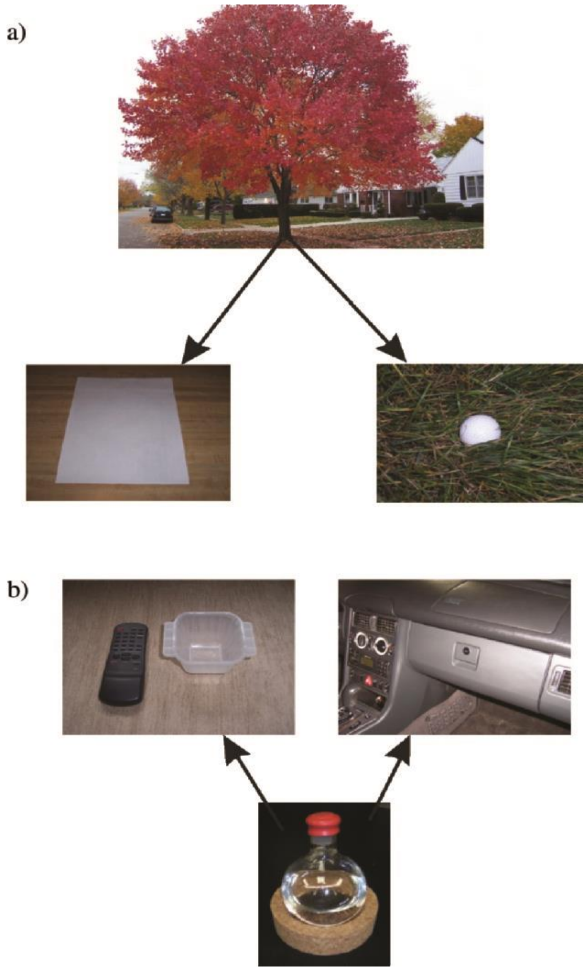

Figure 1.4. Illustrations for the "top-down" and "bottom-up" approach to materials synthesis.

Source: https://text.123docz.net/document/4814644-materials-chemistry.htm

<u>Note:</u>

The topdown approach is frequently employed in the transformation of naturally occurring goods into useable building materials. A few examples of the types of representations described above also include the conversion of wood into paper goods and specific types of golf ball coverings. (b) The bottom-up approach to materials synthesis is the most widely used method.

The manufacturing of plastics and vinyl, which can be found in everyday home items and automobile interiors, is represented in the illustration above. Polymerization processes, which begin with basic monomeric chemicals and progress through a variety of stages, may be used in any professional path. These abilities are also extremely transferable to the creation of novel materials, which is the subject of this manual. Figure 1.5 is an instance of a critical thinking flow diagram that might be used in the project of a novel material, as shown in the text (Budi & Sunarno, 2018; Tang et al., 2020).

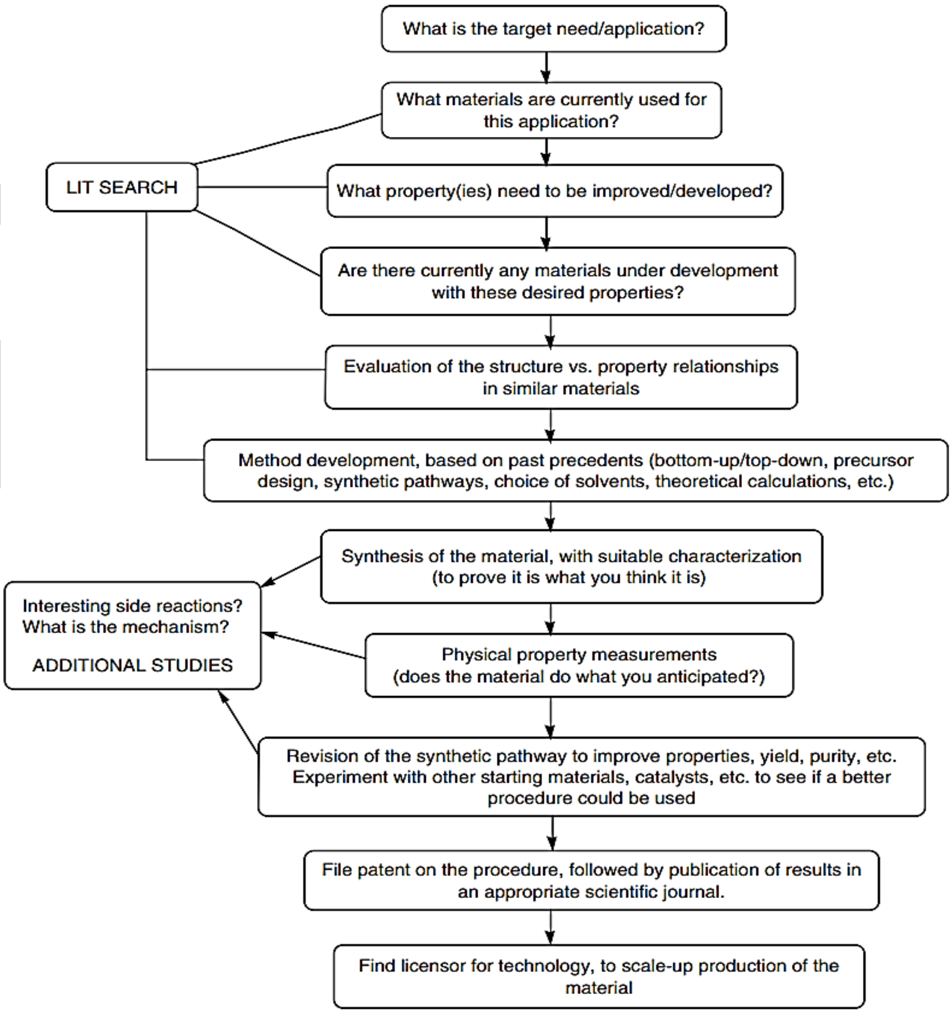

Figure 1.5. For the design of a novel material, here is an example of a critical thinking strategy.

Source: https://www.wiley.com/en-us/Introduction+to+Materials+Chemistry%2C+2nd+Edition-p-9781119347255

While there are several alternatives for such progress, the subsequent are critical components of each new improvement (Astleitner, 2002; Bağ & Gürsoy, 2021):

(i) Create a clear definition of the societal demand and the sort of substance that is being pursued. In other words, establish the desired qualities of the novel material before proceeding.

(ii) Conduct a thorough review of the literature to establish which items are currently in use in the field. This must be completed for the new product to be competitive in the consumer and industrial markets. This ensures that wide research efforts are not unexploited by reinventing the wheel when rather previously exists and patent literature.

(iii) It should be highlighted that every practice in critical thinking will improve outcomes in more questions than were expected at the start of the practice. According to the flowchart beyond, one will seek intriguing reactions/products and get underway to think about the process of action of the process when looking for interesting products/reactions. It is necessary to have a "first-principle" knowledge of the procedure to boost yields of the material and scale up the process for industrial applications.

(iv) Following the protection of new equipment through the filing of patents, publishing in scientific publications is essential to encourage ongoing research and the development of new and advanced materials. Top scientific journals like Science, Nature, The Journal of the American Chemical Society, The Nano Letters, Advanced Materials, Chemistry of Materials, and Small publish articles every week on the most recent advancements in the most active areas of science. Nature, Science, The Journal of the Advanced Materials, The Chemistry of Materials, American Chemical Society, Small, and Nano Letters are just a few examples of the journals that publish articles every week on the most recent improvements in the most active areas of science. There has been an exponential growth in the number of articles on materials-related topics in recent years. As information continues to accumulate, it encourages greater advancement in the fields of characterization, synthesis, and modeling of materials. Nevertheless, this is only likely to occur when active researchers communicate their findings with their international peers.

One of the primary goals of Materials Chemistry is to give students a broad understanding of the numerous types of materials available, with an emphasis on synthetic techniques and correlations between a material's structure and its overall attributes. A section named "Important Materials Applications" will be included in each chapter, and it will discuss an intriguing present or future application connected to a certain kind of material. Solar cells, depleted uranium, fuel cells, "self-healing" polymers, and molecular machines are some of the topics covered in these subsections (Zhou et al., 2012; Vong & Kaewurai, 2017).

The following major classes of materials will be examined (Chen & Hwang, 2020):

- Superconductors

- Metals
- Semiconductors
- Ceramics and glasses
- Magnetic materials
- *Soft* materials, like composites and polymers
- Nanostructural materials
- Thin films

It will be necessary to thoroughly detail the molecular and atomic structures of all these materials in order to fully comprehend their different qualities. We will not be capable of growing our culture with new, better materials, which will further enhance our way of life unless we have a thorough understanding of these linkages in place.

Any discipline of chemistry that requires substantial characterization procedures must employ them. Using nuclear magnetic resonance (NMR) or spectroscopic methods, for example, one can determine whether the proper chemical has been created following an organic synthesis. A similar situation exists in the field of materials chemistry, where characterization methods must be utilized to validate the identification of a material, as well as to discover why a particular material has stopped, to influence the creation of new technologies. This work will provide examples of characterization procedures, which will serve as illustrations of the complex approaches that are utilized to examine the structures and characteristics of contemporary materials. As a result of the extensive coverage of common techniques in other workbooks, this book will concentrate on the methods that are commonly employed by modern materials chemists, like U.V.–visible absorption spectroscopy, atomic absorption/emission spectroscopy, nuclear magnetic resonance (NMR), mass spectrometry, and infrared spectrometry, among others:

- Surface/nanoscale analysis– PES (Photoelectron spectroscopy)
  - SEM (Scanning electron microscopy)
  - AES (Auger electron spectroscopy)
  - EDS/EDX (Energy-dispersive spectroscopy)
  - TEM (Transmission electron microscopy)
  - XAFS (X-ray absorption fine structure)
  - SIMS (Secondary ion mass spectrometry)
  - SPM (Scanning probe microscopy)
  - EELS (Electron energy-loss spectroscopy)
- Bulk characterization
  - TGA (Thermogravimetric analysis)
  - X-ray diffraction

- GPC (Gel-permeation chromatography)
- SAXS (Small-angle X-ray scattering)
- DSC (Differential scanning calorimetry)