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Nanotechnology and Environmental Nanotechnology

1.1 Nanoscale

Nano is derived from the Greek word *νᾶνος* (meaning "dwarf") and is often used as a prefix to denote "one-billionth," or a factor of 10^{-9}. For example, one nanometer (*nm*) is one-billionth of a meter (*m*) and one nanogram (*ng*) is one-billionth of a gram (*g*). In the International System of Units (SI), the base unit for length is the meter (*m*).

We are familiar with commonly used SI length units such as meter (*m*), decimeter (*dm, 10^{-1} m*), centimeter (*cm, 10^{-2} m*), and millimeter (*mm, 10^{-3} m*), which are mainly used to describe the macroworld (Figure 1.1). In contrast, for the microworld, however, SI units such as micrometer (*μm, 10^{-6} m*), *nm*, and picometer (*pm, 10^{-12} m*) are rarely used in our daily life (Figure 1.1).

In chemistry, a commonly used length unit to describe atoms and molecules is angstrom (*Å*), which is 10^{-10} *m* or 0.1 *nm*. For example, the diameter of a hydrogen atom is about 1 *Å* or 0.1 *nm*. This tells us that one nanometer is roughly the length of ten connected hydrogen atoms in a row, which can help us understand just how small the nanoscale is.

Table 1.1 gives examples of the dimensions of some commonly known objects in both the macro- and microworld. Most things in the macroworld such as the Golden Gate Bridge and ants are visible and tangible, allowing us to observe them and "feel" their existence. The finest objects visible to the naked eye are often larger than 50 μm, even for those with the best eyesight. Therefore, the dimension scale of the macroworld is typically larger than **10 *μm*** (Figure 1.1).

On the other hand, the dimension scale of the microworld is less than **10 *μm***. In the microworld, therefore, things are often smaller than the resolution of human eyes. That is why we do not "see" the living organisms in the microworld such as *Escherichia coli* (*E. coli*) bacterium, which is about 2 μm long and about 0.25 μm in diameter (Table 1.1). Nowadays, we know that microorganisms are everywhere on the Earth and account for a large percentage of its biodiversity. Before the

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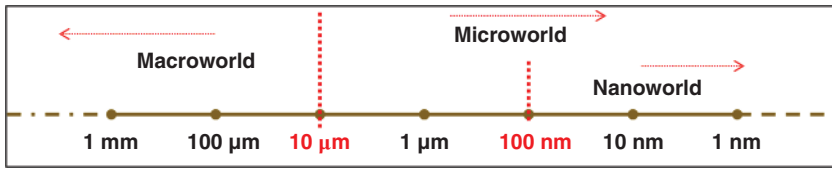

Figure 1.1 Dimension scales of macro-, micro-, and nanoworld.

Table 1.1 Examples of the dimensions in macro- and microworld.

Macroscale		Microscale	
Golden Gate Bridge	**2.74 *km***	**Blood cell**	**6.2–8.2 *µm***
Empire State Building	443 *m*	*E. coli*	~2 *µm*
Alligator	3–4.6 *m*	Coronavirus	80–120 *nm*
Ant	0.75–52 *mm*	Glucose molecule	~1 *nm*
Paper thickness	~0.1 mm	Water molecule	0.275 nm

invention of the microscope, it was hard to imagine that there are living organisms at the microscale. In some Buddhist texts and tales, Buddha once told his students and followers that there are eighty-four thousand (means "many" in Buddhism) beings in a drop of water, which might be one of the earliest perceptions of the microworld. With the invention of tools such as microscopes, people have made great progress in exploring and understanding the microworld. Antonie Van Leeuwenhoek, a Dutch businessman and scientist, designed a single-lensed microscope and was the first to observe bacteria in 1676 (Robertson, 2015). He also determined their size and thus is considered to be the father of microbiology.

Later developments in visualization and other detection technologies further expand the capacity to explore the microworld at an even smaller scale, the nanoworld (the dimension scale is less than **100 *nm***). For example, modern microscopes such as the atomic force microscope (AFM) can detect and reveal objects at atom levels, exposing phenomena at the **nanoscale** (1–100 nm). The US National Nanotechnology Initiative (NNI) defines **nanotechnology** as "*a science, engineering, and technology conducted at the nanoscale (1 to 100 nm), where unique phenomena enable novel applications in a wide range of fields, from chemistry, physics and biology, to medicine, engineering and electronics*" (https://www.nano.gov). This definition has also been extended to include nanomaterials that have at least one dimension smaller than 100 nm. In practice, the boundary of 100 nm could be relaxed (to several hundred nm) as long as the properties of the materials are inherently size dependent.

At the nanoscale, it is possible to manipulate matter and create "new" materials by changing individual atoms and molecules, which may lead to dramatic changes in the physical, chemical, biological, and optical properties of the materials. Unlike their larger counterparts (in bulk form), nanoparticles can exhibit unique properties in reactivity, conductivity, strength, flexibility, or reflectivity. Nanoparticles, particularly engineered nanoparticles (ENPs), thus have attracted increasing research attention in various fields including water research, which is also the focus of this book.

1.2 Nanotechnology: A Short History

The history of man-made nanomaterials and nanostructures can be traced back to more than one thousand years ago (Bayda et al., 2020). Even without understanding or being aware of the concept of nanotechnology, skilled craftsmen in ancient times were able to use their empirical experience to manipulate and create nanomaterials and nanostructures. In the 4^{th} century, the Romans had already developed technologies to use nanosized/colloidal gold and silver particles to control the color of glass. Those technologies further developed and applied in the stained-glass windows in European cathedrals in the 6^{th}–15^{th} centuries and in glowing ceramics in the Islamic world in the 9^{th}–17^{th} centuries. Modern nanotechnology, however, only has a relatively short history. In fact, the term "nanotechnology" was first introduced by a Japanese scientist Norio Taniguchi in 1974 during a conference of Japan Society of Precision Engineering. When describing nanoscale semiconductor processes, Taniguchi pointed out: "'*Nanotechnology' mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule*." (Taniguchi, 1974).

It is widely accepted in the scientific communities that the concept of nanotechnology was first formally outlined by Richard Phillips Feynman, an American theoretical physicist and Nobel Prize winner. At an American Physical Society meeting in 1959, Prof. Feynman gave a famous lecture "*There's Plenty of Room at the Bottom*" (Feynman, 1960). Many would like to set this as the beginning of modern nanotechnology.

In the lecture, Prof. Feynman pointed out that: "*The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom*." This provides the theoretical support for the "bottom-up" approach, which is now widely used in the fabrication of nanomaterials. Nowadays, nanomaterials or nanostructures can be produced by way of either a top-down approach (i.e., reducing the size of a bulk material to nanoparticles) or a bottom-up approach (i.e., nanoparticles are built atom by atom or molecule by molecule) (Figure 1.2). At the end of his talk, Prof. Feynman also posed two challenges with a prize of

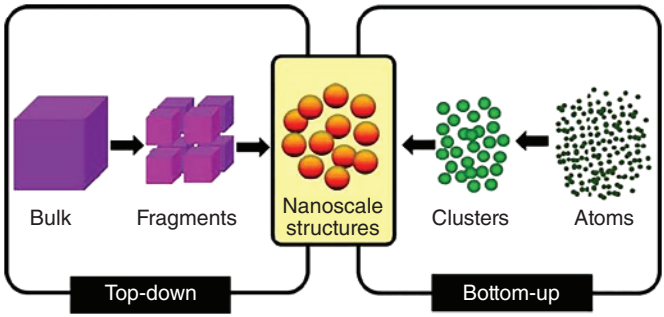

Figure 1.2 "Top-down" and "bottom-up" approaches in nanotechnology. Source: Rawat (2015)/IOP Publishing/CC BY 3.0.

1000 dollars each to promote the development of nanotechnology. The first one was on a tiny motor and the second one was on fitting the entire encyclopedia on the head of a pin. The two changes were achieved in 1960 and 1985, respectively. In addition to Prof. Feynman, others have also made great contributions to the conceptualization of nanotechnology. As mentioned previously, Prof. Norio Taniguchi coined the term "nanotechnology" (Taniguchi, 1974). As the founder of molecular nanotechnology (Drexler, 1981), Dr. K. Eric Drexler, an American engineer, further developed and popularized the concept of nanotechnology.

The breakthroughs in supramolecular chemistry in the 1960s–1980s also contributed greatly to the further development of nanotechnology, particularly with respect to the synthesis of nanomaterials (Toma and Araki, 2009). Unlike traditional chemical that centers on individual atoms or molecules, supramolecular chemistry deals with organized entities of molecules, which are conceptually similar to nanomaterials. Some of the important concepts of supramolecular chemistry, such as molecular self-assembly and noncovalent interactions, are also crucial to the nanofabrication processes (Figure 1.3). In fact, most of the bottom-up syntheses of nanomaterials in nanotechnology are based on supramolecular chemistry (Schubert et al., 2003). In other words, supramolecular chemistry provides a powerful tool for researchers and scientists to develop novel nanomaterials from concept to reality.

Because nanomaterials are in the tiny nanoworld, it is critical to have an instrument that can observe and characterize these materials, like the optical microscopes in the microworld. In the 1980s, the inventions of the scanning tunneling microscope (STM) and then the AFM helped researchers and scientists "see" and experience the materials and phenomena in the nanoworld at the atomic level (Toumey, 2012). Drs. Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory were awarded the Nobel Prize in Physics for the invention of the STM in 1986 (Binnig and Rohrer, 1986). Both STM and AFM use atomic tips to closely scan the surface of an object to provide the atomic-scale

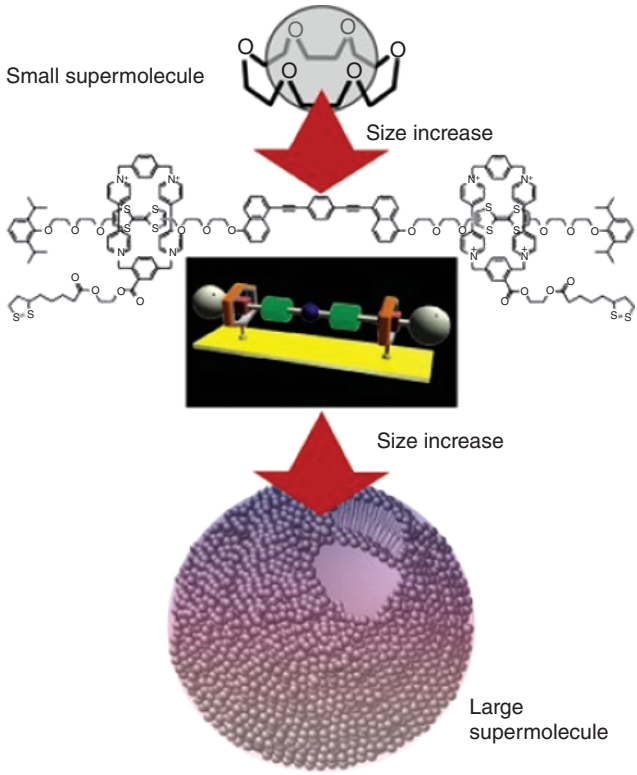

Figure 1.3 Self-assembly of supramolecular complexes. Source: Ariga (2016)/with permission of Elsevier.

visualization (Figure 1.4). Details about STM and AFM are discussed in Chapter 8. These powerful visualization tools can provide insights into the synthesis, characterization, and applications of nanomaterials and thus have promoted the further development of nanotechnology.

It seems that all the essential components were ready for the booming of nanotechnology. Great minds have pointed out the directions; supramolecular chemistry has enabled the synthesis and production, and STM and AFM have allowed the visualization and characterization. The boom of nanotechnology is a pile of dry wood that only needs a match to ignite the fire. The discovery of the buckminsterfullerene (C60, buckyball, Figure 1.5) by Drs. Harry Kroto, Richard Smalley, and Robert Curl in 1985 is the match because of the unique and promising properties of carbon nanomaterials (Kroto et al., 1985). The three professors received the Nobel Prize in Chemistry for this discovery in 1996. The discovery of carbon nanotubes (CNTs, Figure 1.5) further fueled the boom in nanotechnology. Although CNTs have been reported previously, Dr. Sumio Iijima of NEC in Japan

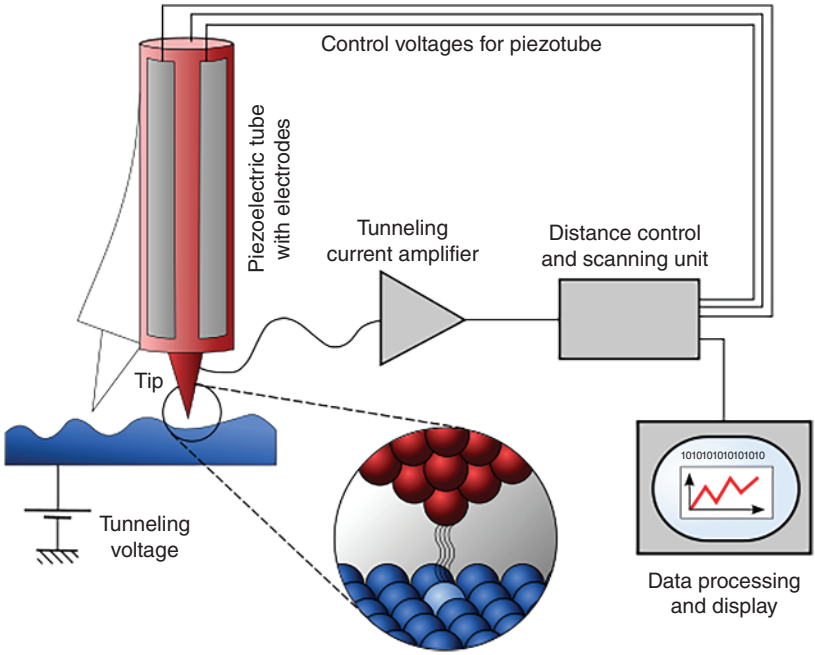

Figure 1.4 Schematic description of STM. Source: Michael Schmid/Wikimedia Commons/CC BY-SA 2.0.

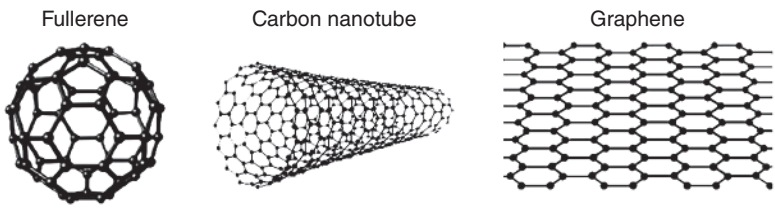

Figure 1.5 Schematics of buckminsterfullerene, single-walled carbon nanotube, and graphene. Source: Hong et al. (2015)/with permission of American Chemical Society.

is often cited as the inventor of CNT. His 1991 Nature paper, "*Helical microtubules of graphitic carbon*" (Iijima, 1991), generated unprecedented interest in carbon nanomaterials and thus has attracted much research and public interest in nanotechnology. Using a mechanical exfoliation process called the scotch tape technique, Drs. Andre Geim and Kostya Novoselov at the University of Manchester extracted single-layer graphene (Figure 1.5) from bulk graphite in 2004 (Novoselov et al., 2004). For their pioneering research on graphene, Drs. Geim and Novoselov were awarded the Nobel Prize in Physics in 2010. Although research on graphene can be traced back to the beginning of the last century (Kohlschütter

and Haenni, 1919), the emergence of graphene and its derivatives (e.g., graphene oxide) in the 2000s has fueled intense research in nanotechnology.

1.3 Nanotechnology in Water Research

Based on the NNI definition, nanotechnology deals with matter with at least one dimension sized from 1 to 100 nm, at which the matter may demonstrate special properties. This novel technology has attracted much interest from both the scientific community and the public because of its promising applications in improving quality of life. It is widely accepted that nanotechnology could create new materials and products to advance a variety of fields including medicine, energy, defense, electronics, and consumer products. In fact, engineered nanomaterials such as nanosized metal, metal oxides, and carbonaceous materials are already used in various industries and consumer products in our daily lives (Figure 1.6). For example, silver, titanium dioxide, and zinc oxide nanoparticles, as well as CNTs, are used in personal care products because of their unique properties including color, transparency, solubility, chemical reactivity, and biological activity (Gupta and Xie, 2018; Iavicoli et al., 2018).

As one of the most promising technologies, nanotechnology has shown advantages in many industrial sectors such as electronics, health, agriculture and food, energy, and environment (Figure 1.7). In the semiconductor industry, engineered nanomaterials and nanofabrication play a crucial role in controlling the size and efficiency of electronic devices. Nanotechnology also has strong impacts on the development of biomedical field by creating new medicines, devices, and methods for more effective and precise, faster, and safer cures. Engineered nanomaterials such as nanosized silver and copper have been widely used in agriculture and food industry for a long time because of their antimicrobial activities (Chen, 2018). Nanotechnology is also the backbone of the recent development of clean and renewable energy and has many potential applications in the energy sector to improve efficiency and sustainability of energy sources, conversion, distribution, storage, and usage. All these developments obviously would greatly benefit the environment. As a double-edged sword, however, nanotechnology may also introduce unintended negative impacts. There are increased public concerns over the emission, exposure, and toxicity of engineered nanomaterials. Nevertheless, the great promise held by nanotechnology to the environment makes it especially attractive to environmental scientists and engineers. Several books have been published on environmental applications and impacts of nanotechnology.

Nanotechnology in Water Research: Understanding Pollution Control, Water Quality, and Hydrologic Pathways is also a book on environmental nanotechnology; however, it mainly focuses on nanotechnology in water research.

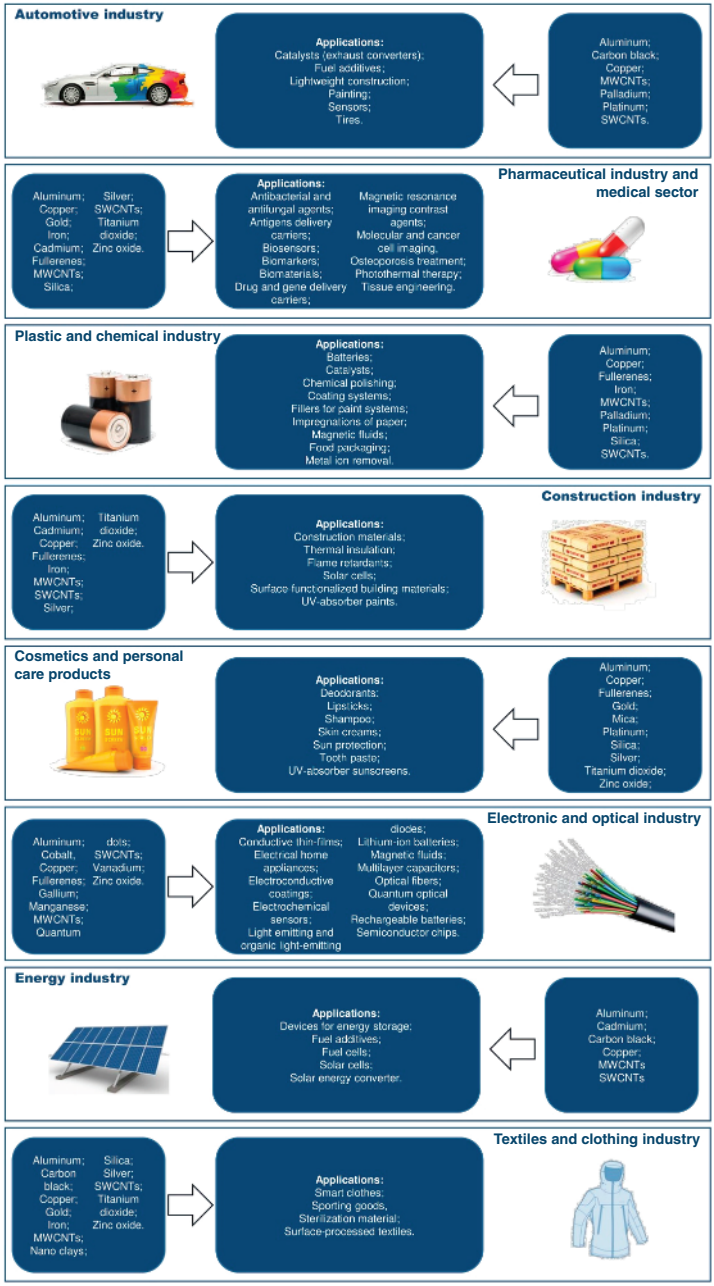

Figure 1.6 Examples of nanomaterials in daily life. Source: Iavicoli et al. (2018)/MDPI/CC BY 4.0.

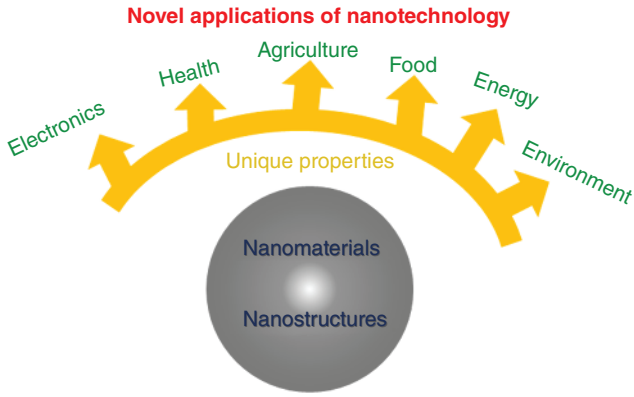

Figure 1.7 Novel applications of nanotechnology.

The goal of this book is to provide an overview as well as examples for students, researchers, and environmental professionals on the applications and implications of nanotechnology in water research. After introducing the basic knowledge and potential benefits of engineered nanomaterials in Chapter 2, four applications of nanotechnology in water research including water quality monitoring (nanosensors, Chapter 3), groundwater remediation (Chapter 4), membrane filtration (Chapter 5), and adsorption (Chapter 6) are presented. The rest of the book is more focused on the implications of engineered nanomaterials in water research. Chapter 7 introduces the basic characterization techniques of nanoparticles in water, while Chapters 8 and 9 focus on the stability and removal of nanoparticles from water, respectively. The last two chapters (10 and 11) are on the fate and transport of nanoparticles in surface and subsurface flow.

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