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NANOTECHNOLOGY 1

FUNDAMENTALS OF NANOTECHNOLOGY

UNINANO
Universal Nanotechnology Skills Creation And
Motivation Development

Proje no: 2016-1-TR01-KA2030034520

EDITORS

Prof Dr. Mustafa ERSÖZ
Dr. Arzum IŞITAN
Meltem BALABAN

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Denizli 2018

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PREFACE

Nanotechnology, which is the fundamental technology of the industrial revolution of 21st century, is the science of controlling matter at atomic and molecular levels. At its simplest meaning and depending on scientific determinations and experiences, as a consequence of its contribution to environment, energy, materials strength and proper consumption, the share of nanotechnology in preserving the world's livability is very clear.

Today, the high value-added technology is vital for business lines that require intense competition such as military, medical, automotive, textile applications. In recent years, nanotechnological investigations have brought a significant progress in especially materials science and many new products or process taking place in our lives..

In general, nanotechnology education is conducted in post-graduate level and the number of nanotechnology education programs within master's and doctoral programs increase constantly in many Universities. However, nanotechnology education is very limited at undergraduate level in many natural sciences and engineering programmes.

The books aimed at natural sciences and engineering undergaraduate students as well as young students provide a complete review of all relevant aspects from the nanotechnology and applications perspectives. The books provide practice-based knowledge at undergraduate level through creating awareness of this subject area and also support visual and e-learning in degree schemes that relate to nanotechnology materials.

The Book 1 is devoted to provide a theoretical description of the basic principles and fundamental properties of nanotechnology.

The Book 2 is devoted to presenting the characterisation techniques, microscopy, spectroscopy and application of nanotechnology for environmental, health and safety issues.

We would like to thank very much to all researchers and authors who contributed to this two parts. We are deeply grateful to Erasmus+ Programme for funding the Universal Nanotechnology Skills Creation and Motivation Development" KA203- Strategic Partnerships Project; 2016-1-TR01-KA203-034520 " and the publication of these books.

Prof. Dr. Mustafa Ersoz, Editor

UNINANO PROJECT

You are reading Nanotechnology 1 book which is the one of the outputs of “Universal Nanotechnology Skills Creation and Motivation Development / UNINANO” Project as numbered 2016-1-TR01-KA203-034520 supported by Turkish National Agency under Erasmus+ Key Action 2 Strategic Partnership in the field of Higher Education (KA203).

In UNINANO Project, Pamukkale University as coordinator and beneficiary institution, Selçuk University and Afyon Kocatepe University from Turkey, Bruno Kessler Foundation and Cosvitec from Italy, Cluj-Napoca University from Romania, and CCS from Greece have taken part.

To increase awareness of nanotechnology which is one of Turkey's 2023 strategic goals has been the main objective of UNINANO Project. In line with this main objective, written and visual educational materials have been prepared, and aimed to contribute to the advancement of nanotechnology knowledge by students and instructors using these materials. For this purpose, two course books have been prepared in both printed and electronic versions, in both Turkish and English:

- *Nanotechnology 1: Fundamentals of Nanotechnology*
- *Nanotechnology 2: Characterization and Applications*

The electronic versions of the books are available on the www.pau.edu.tr/uninano project website. Additionally, the answers of the questions at the end of the book, also located on the web page can be accessed from e-learning materials.

With the happiness of completing our project;

We would like to thank to the Presidency of Turkey's National Agency for support of our project.

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Dr. Arzum Işıtan
Project Coordinator

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SECTION 1

INTRODUCTION
TO
NANOTECHNOLOGY

1.1 MACRO, MICRO, NANO

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INTRODUCTION

In the broadest sense, the term "technology" is defined as "application information covering the construction methods, tools, instrument and equipment used in an industry, and their ways of use" [1].It can also be defined as all of the equipment, all the information pertaining to these devices, developed by humankind in order to facilitate life, speed up production, change existing structures and conduct research.

This definition is expressed as nanotechnology if it is applied to a dimension that is defined as one billionth of meter. How did this adventure that can change from meter to millimeter, millimeter to micrometers, micrometers to nanometers had started?

1 m ↔ 10^3 mm ↔ 10^6 µm ↔ 10^9 nm

Keywords: Macro, Micro, Nano

Abbrevisions: Meter (m), Milimeter (mm), Nanometer (nm)

1.1.1 Production Methods in Development of Technology and the Importance of Material

The adventure had started with the discovery of fire. With the discovery of fire, the most basic requirement for mine melting, casting and shaping was obtained in addition to fundamental needs. Wood, stone and metal processing has become increasingly easier. Although some casting methods have never changed for about 6000 years, today scientists and engineers are constantly working on developing new production techniques and new materials for faster, more economical and more convenient production.

From past to present, technology has always been used as a combination of both artist elegance and engineering skills. These have all been achieved with the same way as the queen's embroidered necklaces or royal crowns. However, as it is well known, wars and weapons developed for those have a major role in the development of technology. Light and sharp swords, light armors and large cannonballs have changed the fate of both nations and of technology.

The needs that increase with population have advanced technology further from water-powered mills to flour factories, single-floor stone houses to skyscrapers, from winding wheels to textile factory, carts to automobiles, boats to transatlantic liners, stone bridges to suspended bridges that connect continents. Because not only these structures, but also the tools and machinery necessary to realize these structures were developed. By bringing together different materials, composite materials that are completely different than the ones that formed them have been produced. Or the existing materials have been improved with new production and thermal techniques. Materials were processed at macro, micro and nano levels, and as a result of all these developments, while telegraph was an effective communication at the beginning of the century, telephones and mobile phones have revolutionized communication. The transition from radio to television, computer to tablet, air-land-railway transportation to interplanetary space vehicles has become even faster.

At first, humankind met the needs from natural materials like stone, ceramics and wood and built their structures with these; however, with the discovery of bronze production, humankind paved a new and fast path.

Discovery of steel and its functionality had formed the foundation of industrial revolution. The discovery of today's light metals such as aluminum and titanium, is very new in comparison to others and it is being used only for two centuries. These metals were followed by the discovery of polymers. Although composites are being used as building materials since ancient times, they have become popular technological materials for the past 50-60 years.

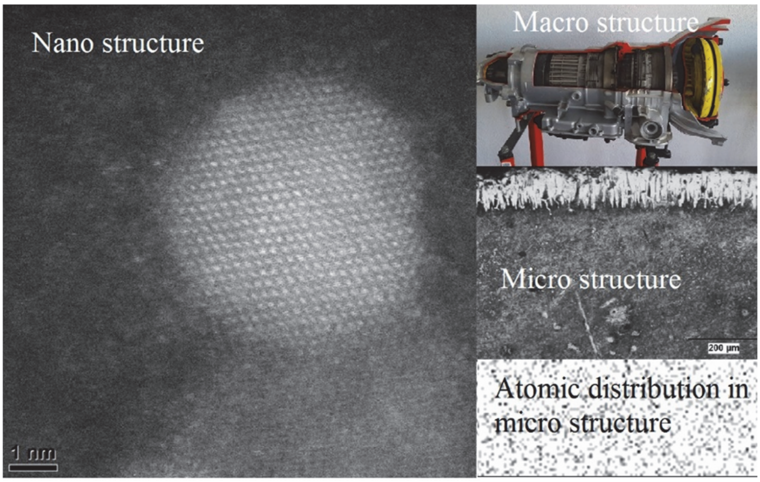
Different properties can be obtained for the same material with different production methods, and the properties of the materials can be changed through thermal processes applied after production. The properties are characterized by color and brightness in terms of macro scale, while in micro scale, the particles affect all mechanical, physical and chemical properties and in the nano scale they represent atomic dimensions.

As a result of the collaborations of engineering technologies with the fundamental physics, chemistry and biology sciences, it became possible to analyze characteristics of organic and inorganic materials more thoroughly, they were better understood and developed faster. The development of production and analysis technologies has led to tremendous progress in many areas from medical applications to the furniture sector.

1.1.2. Importance of Size in Material Characterization

Nano materials/nano objects are materials that have one or more nano-sized external dimensions [2,3].The nano scale is the last step of the material before the atom. If all three dimensions of the material are less than 100 nm, such materials are called nanoparticles, quantum dots, nanoshells, nanorings and nanocapsules; if only two dimensions are less than 100 nm, they are called nanotube, nanowire and fiber; if only one dimension is less than 100 nm, it is called thin film, layer and coating [4].

Optical, mechanical, electrical and color properties of the same material in macro/micro and nano size may be different or even the opposite of other scales [4].Some properties that do not occur in macro size may appear in nano size. The main reason for this is the increased surface area/volume ratio with decreased material size and the non-continuous dimensions in nano-scale compared to macro dimensions [5,6,7].As the surface area/volume ratio increases, materials with low molecular weight can be formed [6,7].



- Human hair: 10^{-4} m, Red blood cell: 10^{-6} m, DNA: 10^{-8} m, Carbon nanotube: 3.10^{-9} m, Sİ atom: 10^{-10} m
- Human nail grows 1 mm per second.

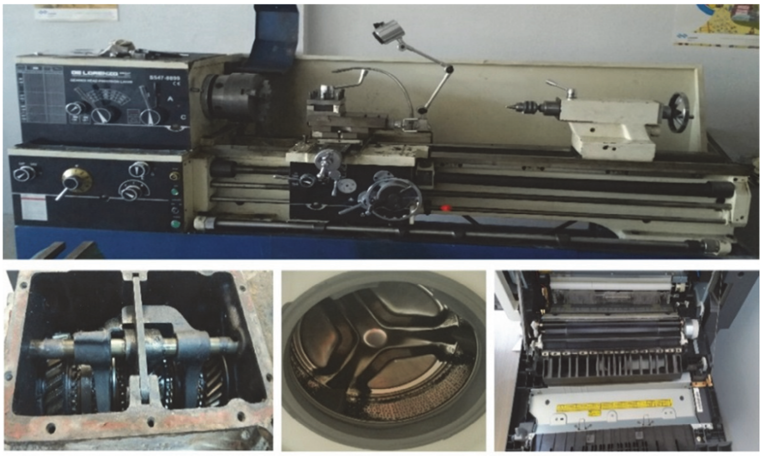
1.1.3 Macro Structures

Macro structures are defined as visually observable and easily measurable systems. Standards have been developed to determine the physical and chemical properties of parts or equipment with macro size. If the materials are structural load-carrying elements, the mechanical properties that define the behavior of the material under the load become very important. The priorities according to the material selection and characterization can be listed as follows:

a) Durability
b) Wear resistance
c) Corrosion resistance
d) High/low temperature resistance
e) Ability to be shaped
f) Compatibility with assembly techniques
g) Appearance/brightness
h) Biocompatibility

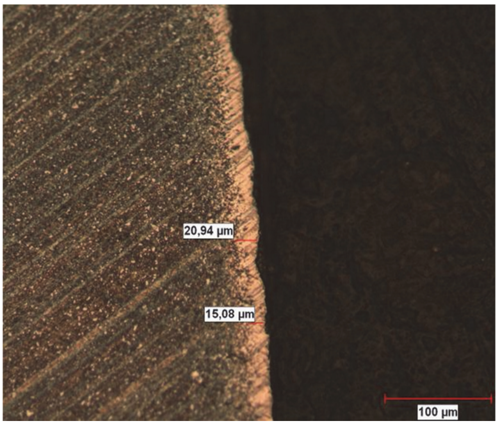
The properties expected from the parts of a machine tool are different than the properties desired for a photocopy machine or a washing machine. The properties of the glass used in the windows differ from the glass of a fish glass. Although both are ceramic, the properties expected from porcelain plates in our homes are different than a flower pot and all these properties are expressed in macro sense.

The reason for the use of platinum and titanium instead of stainless steel, which was initially used as prosthetic material, is due to their higher biocompatibility.



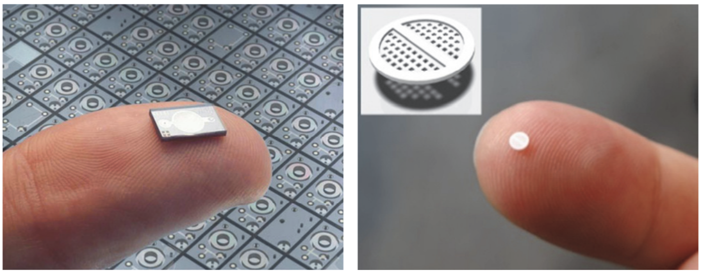
1.1.4 Micro Structures

Micro structures are systems that can’t be seen by eye, and can only be characterized with microscope. The size and shape of the particles forming the micro-sized metallic materials and the type and thickness of the coatings on the material are very influential on the mechanical properties. However, macro and micro properties of the same material are basically the same.



In addition to the advantages of micro sizes in material technology, miniature systems are being developed to obtain desired properties in macro scales. These systems are being developed to obtain desired properties in macro scales. These systems are called microelectromechanical systems (MEMS)/micro systems technology (MST)/micromachines [9,10].These are miniature embedded systems that contain one or more pieces of micro machine or structure.

Micro components make a system smaller, faster, more reliable, cheaper and let them have more complex functions. In the most general sense, MEMS microstructures are systems that are consisted of microsensors, microactuators and microelectronic components onto a silicon chip [9]. Microsensors detect changes in the system environment by measuring mechanical, thermal, magnetic, chemical or electromagnetic information or phenomena [9].



https://www.hysitron.com/applications/semiconductor-electronics/mems

http://internetofthingsagenda.techtarget.com/definition/micro-electromechanical-systems-MEMS

Google 17/05/2017

Sensor is a device that measures information and provides an electrical output signal in response to the measured parameter. They can conduct mechanical, thermal, chemical, magnetic and electrical measurements. A transducer is a device that converts a signal or energy into another form. The actuator is a device that converts the received electrical signal into a process.

The most prominent feature of MEMS technology is the miniature dimensions. Although MEMS technology is in miniature dimensions, it allows us to get the desired tasks and targeted efficiencies at macroscopic levels also in miniature dimensions [8].MEMS or micro technology is a rapidly evolving technology and has a great potential to reshape the life standards of the future. By using this technology [8,9]

- it is possible to reduce microsystem size by integrating micro-electronic circuits or mechanical structures on the same integrated structure,

- one-piece integration and production of devices with very low cost.

The most advantageous potential material for MEMS is silicon because of its physical and commercial properties. Microprocessing is especially specially developed for the production of basic microelectromechanical devices such as miniature sensors and actuators. Micro processing of silicon is the most mature form of micro-processing technologies and allows for the production of MEMS that have sub-millimeter size [10]. Silicon micro-processing is forming a microscopic mechanical part from a silicon substrate or a silicon bottom layer.

Uses of MEMS technology [8]

- biomedical sensors, miniature biochemical analytical instruments, pacemakers, catheters, drug delivery systems,
- motor and drive control, automotive safety/brake/suspension systems,
- fiber optic components,
- low power and high density mass data storage systems,
- control of wireless electronic, aerodynamic and hydrodynamic systems,
- integrated fluid systems for miniature propulsion and combustion control,
- early detection systems against biological and chemical threats,
- electromechanical signal processing for small and low voltage fluctuations.
- night vision systems

Micro-optoelectromechanical systems (MOEMS) are also a subset of the MST and they form specialized technology fields by using miniature optical, electronic and mechanical combinations with MEMS [8].

1.1.5 Nano Structures

Nano structures are atomic or nano-scaled systems and they are obtained by using one or more mechanical, physical, chemical and thermal processes. For example, two fluids that have droplet sizes of 0.1-1.0 µm form a thermodynamically instable emulsion by completely dispersing within each other, and they get separated in time due to gravity; however, emulsion that have droplet sizes smaller than 100 nm form microemulsion that are thermodynamically stable, time-independent, not affected by processes such as agitation and they have transparent appearance, and they allow for water-oil combination. In addition to nanoparticle synthesis, this method is used for paint, textile coating, cosmetics and pharmaceutical areas.

Nanostructures obtained by very different production methods are used in many different areas such as drug delivery, self-cleaning fabrics, flexible and highly durable materials, and nano-sized machine production.

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1.2 The HISTORY of NANOTECHNOLOGY

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INTRODUCTION

Stainless fabrics, unscratchable surfaces, color changing paints, anti-aging cosmetic products and more... Nanotechnology, which has been described as the comprehension, control and modification of functional materials at 1-100 nanometer briefly, takes attention with nanotechnology products and which we are frequently encountered on advertising panels and televisions, is regarded as a new technology revolution. In this chapter, the historical development of nanotechnology, which is included in our lives today quickly, will be discussed.

1.2.1 Historical Development of Nanotechnology

In fact, the use of nanotechnological products, which has an older history than expected, dates back to ancient history. When we examine the histor-ical development in this regard, the Lycurgus Cup is considered as one of the greatest successes of the glass industry of antiquity used by the Ro-mans in the 4th century. The most important feature of this Cup which is still exhibited in the British Museum and is at an age of 1600 is the color change. The secret of the Cup which is green when it is illuminated in the front and is red when it is illuminated from back has been uncovered in 1990.

The Lycurgus Cup at the British Museum; illuminated in front (left) and back (right)
(This image is published on https://twitter.com/britishmuseum/status/829336475548471296 and retrieved from Google Images.)

Research has shown that the cup contains soda-lime glass and that there is 1% gold and silver and 0.5% manganese in this glass. The researchers then assumed that the unusual color change and spreading effect of glass was provided by colloidal gold. With the advances on research techniques in later years, scientists discovered that gold and silver particles were found on the cup's glass using electron microscopes and radiographs, ranging from 50 to 100 nanometers in size, one thousand times thinner than a hair and one thousand times smaller than common salt.(Tolochko, 2009). In his work on plasmon published in the 2007 Scientific American, H.A. Atwater described these color changes by plasmon stimulation of metal nanoparti-cles. This color-changing cup made by glass masters in the ancient Roman period using nanoparticles is one of the first examples of nanotechnology.

Rose window on the north facade of Notre Dame Cathedral

(This image is published on https://www.alamy.com/stock-photo/north-rose-window-notre-dame-cathedral.html and retrieved from Google Images.)

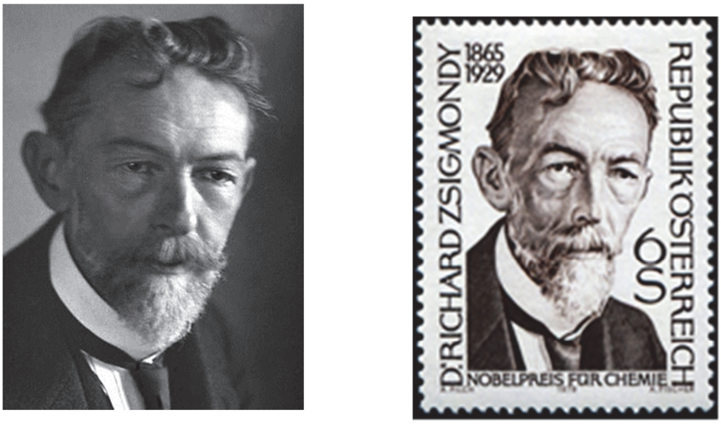
Another example of the nanotechnology known in the history is the stained glass window which was frequently used in the European cathedrals be-tween the 6th and 15th centuries and which lasted until today. These win-dows have dazzling colors thanks to nanoparticles of gold chloride and other metal oxides and chlorides. It was revealed that between 9th and 17th centuries, the living, shiny and bright ceramic glazes used in the world of Islam and later in Europe contained silver, copper or other metallic nano-particles (Tolochko, 2009).

Carbon nanotubes and cementite nanowires have also been used in the construction of the Damascus swords, which are known for their sharp-ness, flexibility and durability in the 13th and 18th centuries (Reibold, Pau-fler, Levin, Kochmann, Pätzke and Meyer, 2006; Tolochko, 2009).

Damascus Sword Known for its sharpness, flexibility and durability

(This image is published on Google images and retrieved from Google Images at 17/05/2017.)

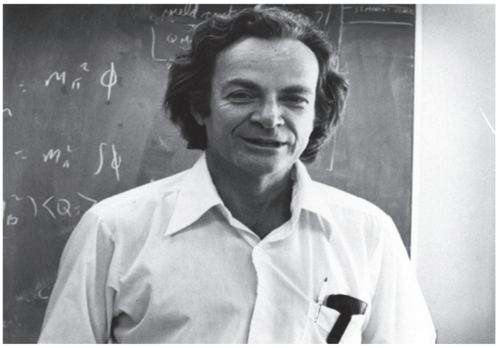
When the history of science is examined, it is seen that the use of nano-particles with sizes ranging from 1 to 100 nm, which is the core of nano-technology used in glass coloring since ancient times, has been a research topic only since the middle of the 19th century. In fact, Michael Faraday (1857) took the greatest step in the development of nanotechnology with his systematic studies of the properties of metal colloids, especially gold colloids. Faraday has prepared aqueous colloidal blends containing less than 100 nm of gold nanoparticles and has determined that these blends have exceptional optical and electrical properties. Faraday has compared the optical and electrical properties of gold-colloidal mixtures to those of very fine gold leaves and found that they have different properties. This difference is related to the granular structure of the colloidal gold (Baalousha, How, Valsami-Jones and Lead, 2014). It was not possible to determine and control the size distribution of the gold particles during the nineteenth century when this remarkable invention was made. Richard Zsigmondy, who received the Nobel Prize in Chemistry for the first time in 1925, measured the dimensions of nanoparticles such as gold colloids and used the nanoparticles concept for the first time (Baalousha et al., 2014; Hulla, Sahu and Hayes, 2015).



Richard A. Zsigmondy, the first person to use the nanometer concept

(This image is published on https://www.stampcommunity.org/topic.asp?TOPIC_ID=6541&whichpage=7 and retrieved from Google Images.)

Richard Feynman is accepted as the idea father of modern nanotechnolo-gy. Richard Feynman, who has been awarded the Nobel Prize in physics in 1965, said in his speech "There is plenty of room at the bottom" at the meeting of the American Physical Society in Caltech on December 29, 1959 as an idea without the use of nanotechnology word that it is possible that atomic and molecular sizes could be manufactured by developing special measurement and production methods in nanoscale. In his speech, Feynman said that in small dimensions, laws like gravity would decline and weaker micro-level forces like Van der Waals would become more important.



Richard Feynman, the mastermind of nanotechnology

(This image is published on https://www.atomicheritage.org/profile/richard-feynman and retrieved from Google Images.)

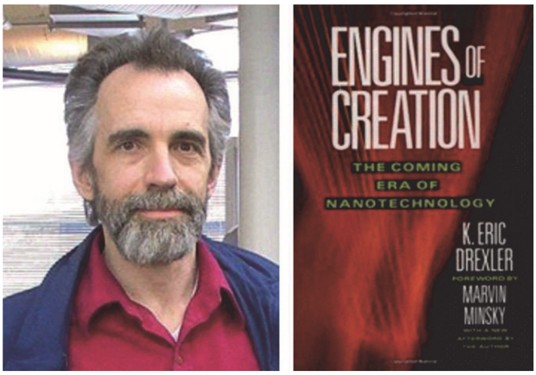
Feynman believes that adolescents will be a driving force in the scientific development, and in this important speech, he has announced two prob-lems to researchers and promised to give $ 1,000 a prize when the problem has been solved. One of the problems was the construction of a nanomo-tor. The problem was solved immediately in 1960 with the construction of a cube-shaped engine with an edge length of 1/64 inch (0.3 mm). The sec-ond problem was that all Encyclopedia Britannica had to be reduced in size to write on top of a nail. This problem was solved in 1985 by Tom Newman, a graduate of Stanford University. He wrote the first page of Charles Dickens' "The Story of Two Cities" with electron beams on the top of the nail and received the second $ 1,000 prize. Today, the "Feynman Award" is given by the Foresight Institute to science enthusiasts who have made advances in the name of nanotechnology in memory of Feynman (Keiper, 2003).

Approximately 15 years after Feynman's speech, the nanotechnology term was first used by Norio Taniguchi in 1974. Using the focused ion beam technique, atomic layer deposition and other methods, Taniguchi used the term nanotechnology (nano-technology) to describe the processes of forming semiconductor structures with nanometric precision. Nanotechnology has been characterized by processes of processing, separation, joining, and deformation of materials by a major atom or mole-cule (Keiper, 2003; Hulla, Sahu and Hayes, 2015).

Norio Taniguchi used the term nanotechnology for the first time

(This image is published on http://www.nanotechnologyresearchfoundation.org/nanohistory.html and retrieved from Google Images.)

Another important person in the history of nanotechnology is Eric Drexler,who has the first doctoral degree in molecular nanotechnology from the Massachusetts Institute of Technology (MIT). He became famous and was known with his books titled "Engines of Creation: The Coming Era of the Nanotechnology" and "Nanosystems: Molecular,Machinery,Manufacturing and Computation" published in 1986.



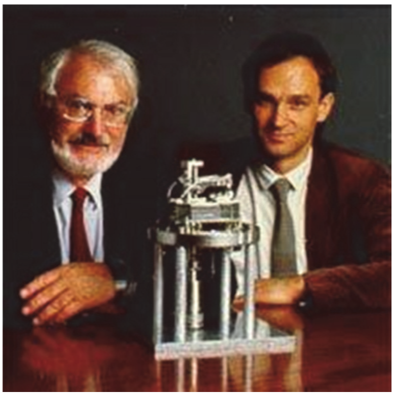
Eric Drexler, the first person in the world had a doctorate in molecular nanotechnology

(This image is published on http://www.thenanoage.com and retrieved from Google Images.)

In his books, Drexler noted that nanorobots could exist, using biological systems to make devices at the molecular level, and tried to reveal the effects of this technology. In addition, he established the Foresight Insti-tute, a California-based, non-profit organization that tries to educate socie-ty about both the potential benefits and risks of nanotechnology. In addi-tion, "Engines of Creation: The Coming Era of the Nanotechnology" is the first nanotechnology book published (Keiper, 2003).

An important breakthrough in the development of nanotechnology is the scanning tunneling microscope (STM) invented by Gerd Binnig and Hein-rich Rohrer in 1981 in IBM's Zurich research lab.

STM is a powerful microscope that does not require special light, special lens, or electron source for radiation, high resolving power that shows the three-dimensional structure of the surface of objects small enough to be imaged by conventional microscopes or powerful electron microscopes. It is widely used in both industrial and basic research to obtain atomic scale metal surface images. Binnig and Rohrer were awarded the Nobel Prize for Physics in 1986 for this invention (Filippino and Sutherland, 2013). In 1986 Gerd Binnig, Calvin Quate and Christoph Gerber developed the first atomic force microscope (AFM).



Gerd Binning and Heinrich Rohrer invent the Scanning Tunneling Microscope

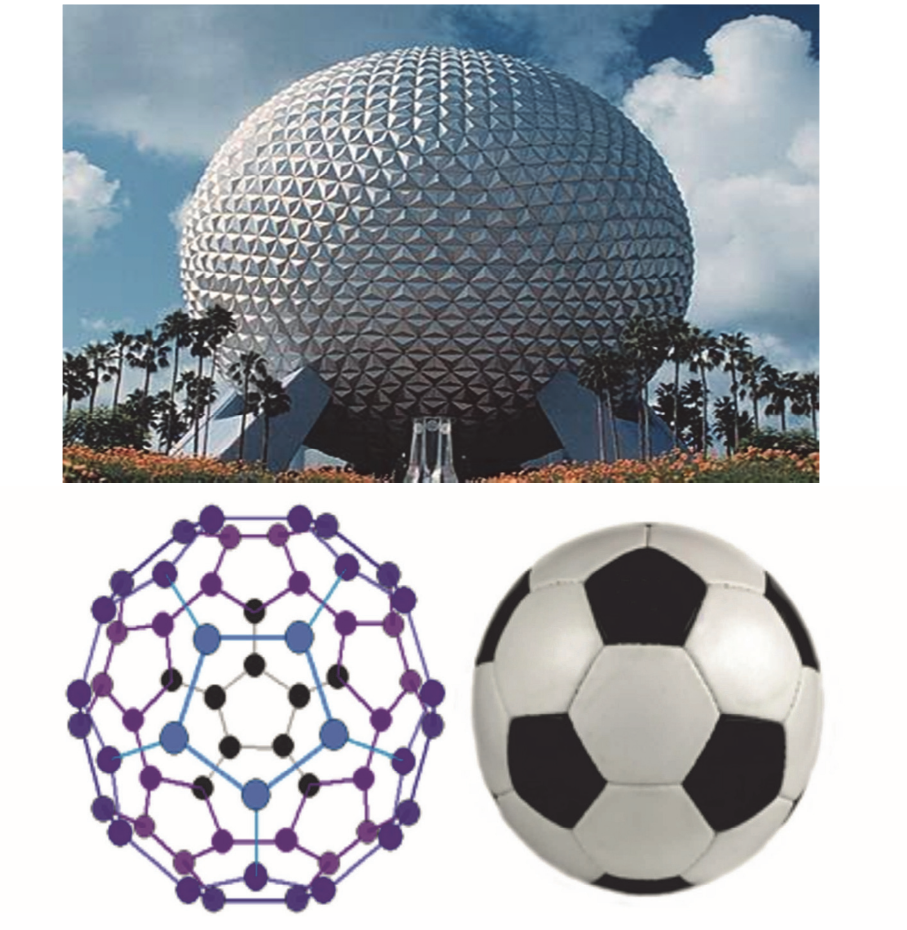
(This image is published on http://www.nobelprize.org and retrieved from Google Images.)

The first commercial AFM was put on the market in 1989. Today, AFM is one of the most advanced tools in nanoscale imaging, measurement and material processing and is used to solve processing and material problems in a wide variety of technologies that affect the tele-communications, biological, chemical, automotive, aerospace and energy industries. The AFM not only resembles surface imaging at atomic resolu-tion but also measures infinitesimal forces at the nano-newton scale (Flippino and Sutherland, 2013).

Gerd Binnig, Calvin Quate and Christoph Gerber, invented Atomic Force Microscope

(This image is published on http://www.kavliprize.org and retrieved from Google Images.)

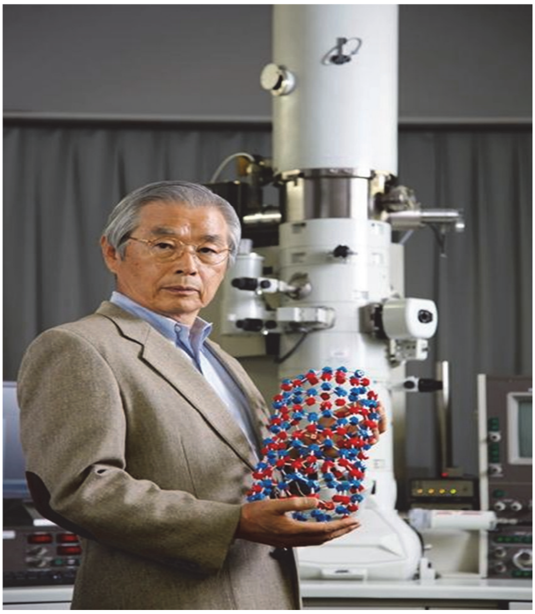
In 1985, Richard E. Smalley, Harold W. Kroto and Robert F. Curl discovered a new form of hard carbon element after diamond and graphite, consisting of 60 carbon atoms (C60). In fact, the first article on C60 was published by Eiji Osawa at Toyohashi University in 1970. In Osawa's article, he suggested that carbon may have a cage structure like ball. However, the publication is not recognized worldwide because it is Japanese. On the other hand, the studies published by Smalley, Kroto and Curl in Nature magazine in 1985 received great interest in the scientific world and won the 1996 Nobel Prize for Chemistry (Erkoç, 2012).



The similarity of the C60 molecule with the football and the Geodetic Dome

(a- This image is published on http://www.gcsescience.com/a38-buckminsterfullerene.htm and retrieved from Google Images. b- This image is published on http://thenanoage.com/buckminsterfullerene.htm and retrieved from Google Images.)

As a famous architect, Buckminster Fuller is very similar to the geodetic dome design, carbon molecules consisting of this new form of carbon element, which is composed of sixty carbon atoms, are called "Buckminsterfullerene". Also known as "Buckyballs", which resemble footballs, these structures are stronger than steel, lighter in weight, and have an electrical and heat-permeable structure at a nanometer scale especially in drug delivery and nanotechnology applications (Flippino and Sutherland, 2013). Following this discovery, in 1991, the Japanese NEC company announced that its researchers Sumio Iijiman found carbon nanotubes. Carbon nanotubes have a stretched shape of the C60 molecule and have similarly important properties; 100 times stronger than steel, and the weight is about 6 times the weight of steel (Baalousha, How, Valsami-Jones and Lead, 2014). Carbon nanotubes are used extensively in transistors and fuel cells, on large TV screens, and in ultra-sensitive sensors due to their unique electrical properties and extraordinarily thin nanoscale dimensions (Erkoç, 2012).



Sumio Iijima, the first person to find carbon nanotubes

(This image is published on http:// www.meijo-u.ac.jp/english/news/detail.html?id=xhFEUY and retrieved from Google Images)

At the beginning of the 21st century, very important advances were made in the use of nanotechnology in fields such as medicine, biotechnology, computer technology, aviation, energy use, space studies, materials and manufacturing.

In 1999, the National Nanotechnology Initiative, the first official govern-ment program to promote the speed of nanotechnology research, devel-opment and commercialization, was launched in the United States. In 2001, nanotechnology studies included the European Union Framework Programme as a priority area. Japan is one of the countries that invest in nanotechnology in Asian countries. Japan is the second country in the world to support the largest number of R & D studies in the field of nano-technology after the United States. Among Asian countries, China and Korea stand out among the countries that follow Japan. While most of the work carried out in China are concentrating on semiconductor manufactur-ing techniques and nano-technology based electronic devices, Korea con-ducts research on microelectronic applications and microelectromechanical systems (MEMS) (Roco, 2011). Turkey, who wants to participate in the nanotechnology revolution started in the middle of the 20th century by providing support to sectors especially such as paint-coating, technical textile, chemical materials, automotive, construction sector, materials and polymer composite, has increased its investment in researches made in this area (Körözlü, 2016). In the future, as nanotechnology will play a major role in the discovery of new components and in the development of exist-ing technologies, it is inevitable that the indispensable place of this tech-nology loft will remain for many years.

Summary

Nanoparticles, which are the foundation stone of these products, started to be investigated only in the middle of the 19th century, though today's products of nanotechnology based on the past are very common. The greatest step in the development of nanotechnology was made by Michael Faraday in 1857, preparing aqueous colloidal blends containing small gold nanoparticles and examining the optical and electrical properties of these blends. The size of the nanoparticles was first measured by Richard Zsig-mondy in 1925 and the nanometer concept was used for the first time. Richard Feynman (1959), who said that it would be possible to manufac-ture atomic and molecular sizes by developing special measurement and production methods at the nanoscale, and that there could be many new discoveries on this scale is considered as the mastermind of the nanotechnology. The first scientist to use the term nanotechnology was Norio Taniguchi (1974). Taniguchi has stated that nanotechnology consists of processes of processing, separation, joining and deformation of materials by a major atom or a molecule. Eric Drexler is another important name that made nanotechnology popular.

Drexler has tried to educate society on the potential benefits and risks of nanotechnology with publications. One of the important inventions that helped nanotechnology evolve is the Scanning Tunneling Microscope, invented by Gerd Binnig and Heinrich Rohrer (1981); And the other is the atomic force microscope developed by Gerd Binnig, Calvin Quate and Christoph Gerber (1986). A new form of a carbon atom which is made of 60 carbon atoms (C60), 1 nanometer in size, and is stronger than steel, lighter in plastic and lighter in electricity and heat-permeable, was discov-ered in 1985 by Richard E. Smalley, Harold W. Kroto and Robert F. Curl.

C60 is mainly used for drug release and nanotechnology applications. Carbon nanotubes with similarly important properties with a stretched shape of the C60 molecule were discovered in 1991 by Sumio Iijima.

Carbon nanotubes are often used in ultra-sensitive sensors in transistors and fuel cells, large TV screens, due to their electrical properties and their fine structure. These rapid developments recorded in nanotechnology will enable the future to emerge lighter materials with lower error levels and unmatched durability, and these lightweight materials will bring revolution-ary innovations for many of the existing industrial processes.

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1.3 DEVELOPMENT of NANOTECHNOLOGY

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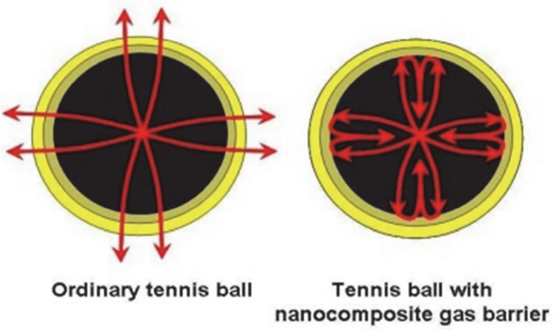
INTRODUCTION

Nanotechnology, the key technology of the 21st century, presents us with the latest applications for diagnosing and treating diseases, monitoring and protecting the environment, generating and storing energy, improving crop production and food quality, and building complex structures. In this section, latest developments and application fields of nanotechnology, which has become an important part of our life, will be explained.

1.3.1 Nanotechnology in Material and Production

Today, more durable, longer-lasting, cheaper, lighter and smaller devices with higher quality can be developed with the use of nanotechnology. These developed products stand out with their less material and energy requirement, cheaper expenses and easy shipping, more functionality and ease of use (Ramsden, 2011; Lines, 2008).

Nanoparticles, with their sizes between 1-100 nm and the significant improvements they provide in the functionality of metal, ceramic, polymeric or composite systems, form the basis of not only nano-sized materials but also nanotechnology as well. Nanomaterials are now being used for the development of many products that we use in our daily life. Skiing materials made of waterproof nanofibers and tennis balls produced by using clay based polymer nanocomposites are two of the best examples of such products. These products, developed with nanotechnology, are relatively more durable, longer-lasting and lighter.

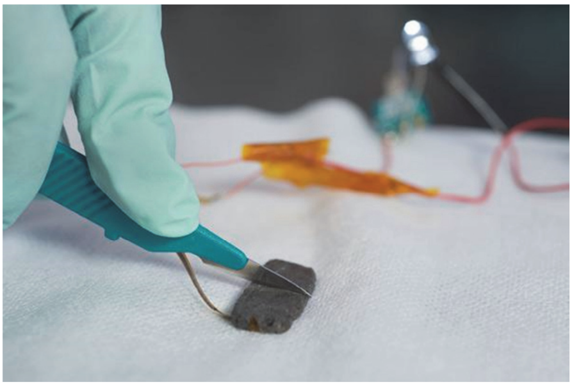


Structure of tennis balls produced with nanotechnology.

(This image is published on http://nano--tech.blogspot.com.tr/p/leisure.html and retrieved from Google Images.).

Increased surface area and quantum effects are two of the most important properties that differentiate nanoparticle-enhanced materials from other materials. For a particle of 30 nm, the atom ratio on the surface is 5%, whereas, this ratio goes as high as 20% for a size of 10 nm. Therefore, nanoparticles have higher surface/volume ratio than large particles. This situation makes nanoparticles more sensitive than large particles in terms of reactivity, resistance, rigidity and electrical properties. In addition, as the size of the materials decreases in nanoscale, their quantum effects can impact and change the optical, electrical and magnetic properties of the material.

As these properties of nanoparticles are revealed, significant developments have emerged about using nanoparticles in production and materials. Nanoparticles are especially being widely used for coating, surfaces and functional structures. Self-cleaning surfaces and glasses are the best examples. These materials, coated using titanium dioxide with high activation, have non-water retentive and antibacterial properties. The synthetic material produced using polymer composites, which are sensitive to touch, and enhanced with nickel nanoparticles, which can rapidly and repeatedly recover themselves at the room temperature, is another example. After this synthetic material is cut, it can restore itself back to its original form within about 30 minutes by slightly combining the cut pieces together. Such advancements are expected to lead to the development of self-repairing smart prostheses (Servick, 2012).



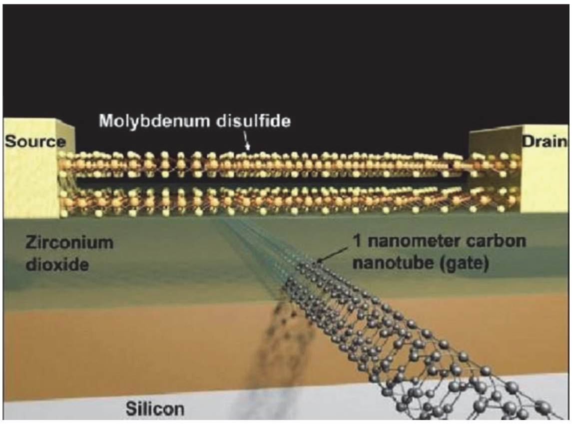
Self-assembly synthetic material produced with nanotechnology.
(This image is published on http://news.stanford.edu/news/2012/november/healing-plastic-skin-111112.html and retrieved from Google Images.)

Clothes that have properties such as waterproof, self-cleaning, protection against sunlight or anti-static can be manufactured by coating the fabrics with nanoparticles. In addition, clothes are protected against bacteria since the nanoparticles are being used in ventilation filters or washing machines.

1.3.2 Nanotechnology in Electronics and Information Technologies

Nanotechnology, which aims to produce high-performance and economic materials and devices, had and still have great contributions to the advancements in the fields of electronics and information technologies. Faster, smaller and more portable systems that can manage and store larger and more information are developed with the use of nanotechnology. The best example of this is the basic switches, or transistors, that activate all modern computers that have an important role in the development of computer technology. Transistors are electrical circuits components that regulates a voltage or current source and another voltage or current source. Transistors form the basis of all electronic devices that we use every single day, such as computers, smart phones and televisions.

At the beginning of the century, a typical transistor size was between 130 nm and 250 nm, however, in 2016, a research team working at Lawrence Berkeley National Laboratory had managed to make 1 nanometer transistor by using “carbon nanotubes" and "molybdenum disulfide (MoS_2).This is the smallest transistor ever produced (Desai et al., 2016).



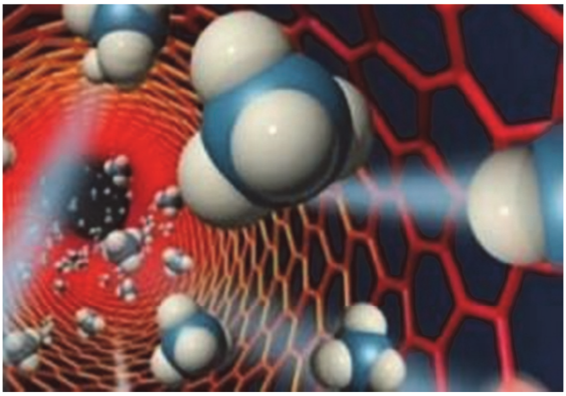
The smallest transistor in the world is produced by using carbon nanotubes and molybdenum disulfide, which are alternatives to silicon.
(This image is published on http://www.techtimes.com/articles/181282/20161007/worlds-smallest-transistor-built-using-carbon-nanotubes-and-engine-lubricant.htm and retrieved from Google Images.)

The electrical properties of carbon nanotubes, which have a thickness of a millionth of a millimeter and became popular in recent years, can be very different and advantageous compared to semiconductors such as silicon.IBM, the largest information technologies company in the world, is aware of the potential of this material and defined carbon nanotubes as the "foundation of the future beyond silicon". Instead of millions of electrons, information can be processed with the movement of a single electron in nano-sized transistors. As a result, it is possible to achieve significant energy-saving. In addition, since it is very small, billions of transistors can be fit into an area of one centimeter square. Therefore, computers can operate faster and efficiency can be further increased. In short, smaller, faster and better transistors mean whole memory of the computers can be stored inside a single tiny chip. With the production of nano-scaled electrical circuit components, computers manufactured with nanotechnology are expected to be smaller, faster, have greater capacity with less energy consumption than those produced by using today's technology.

1.3.3 Nanotechnology in Medical Applications

Nano-scaled materials and nano electronic biosensors are used to diagnose, monitor, follow-up and prevent the diseases in nanomedicine, which is the application of nanotechnology in medicine. Today, many diseases from diabetes, cancer to Parkinson and Alzheimer's are threatening human life and accurate diagnosis is of crucial importance in order to provide the correct treatment. Nanosensors and nanoparticles produced with nanotechnology play an important role in the correct diagnosis and timely treatment.

Drug delivery is one of the most important applications of nanotechnology in medicine and many studies are being conducted on these applications. By injecting the drugs that are loaded with nanoparticles, it is possible to detect diseased cells, such as cancer cells, via these nanoparticles. Nanoparticles deliver the drugs they carry to the diseased cells and they help the body to destroy these cells without harming healthy cells. The best example of this application is the Chemotherapy drugs that are loaded into nanoparticles for the cancer treatment.



Drug delivery is one of the most important fields of nanotechnology in medicine. (This image is published on http://www.inovatifkimyadergisi.com/tag/nano-ilaclar and retrieved from Google Images.)

Another important implementation of nanotechnology in medicine is the use of quantum dots for the diagnosis and treatment of tumors in the human body. Although this is still a developing technique, it is a promising approach for the cancer treatment.

Cancer diagnosis can be performed by detecting the location of cancerous tissues by using iron oxide nanoparticles, which have magnetic properties. First, special antibodies marked with iron oxide nanoparticles that are developed against the tumor being sought for are injected to the body. If the sought tumor cannot be found in the body, marked antibodies attach to the antigens on the tumor surface. Tumors can be detected with the MRI device using the magnetic signals emitted from the iron oxide particles present in the antibodies that are gathered in the cancerous tissue. Even a very small tumor tissue in the body can be detected (Nikalje, 2015).

In addition, the nano-vaccine field is rapidly developing with the recent emergence of new nanotechnology tools and more information on polymeric drug delivery. Nano-vaccines, developed by a group of scientists, are consisted of synthetic polymer nanoparticles that contain tumor proteins recognizable by the immune system, and they help people to fight cancer (Luo et. Al., 2017).

Nanoparticle vaccinations that will be used for the treatment of many diseases in the future (This image is published on https://id-ea.org/researchers-explore-new-class-of-synthetic-vaccines/ and retrieved from Google Images.)

Another application is Buckyballs fullerene, a nanomaterial that is used for the reduction of inflammation during allergic reactions and for the involvement of free radicals that occur during these reactions. In addition, nanoshells are used to destroy cancer cells that are heated with infrared rays without damaging the healthy cells. The use of aluminosilicate nanoparticles with water absorption properties in trauma patients is very useful. Because of these properties, aluminosilicate nanoparticles cause faster clotting and reduce bleeding. Nanotechnology can also be used to kill microorganisms. The wound can be purged from microbes with silver nanoparticles. Some nanoparticles are used to treat infections. Nitric oxide gas inserted wound creams can be given as an example. When these creams applied on the wound, these nanoparticles release the nitric oxide gas they carry and destroy the bacteria (Adnan, 2010).

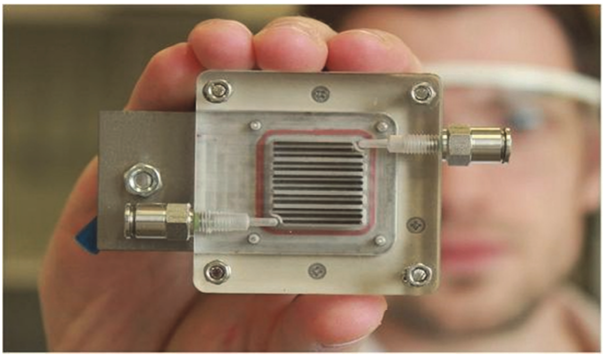
1.3.4 Energy, Environment and Nanotechnology

In addition to efficient energy use, storage and generation, nanotechnology is also being used to detect and clean the environmental pollutants. Nanotechnology has different applications from providing clean potable water, increasing air quality, developing new energy resources and removing hazardous and toxic substances away from our environments and nanotechnology will definitely help to create a sustainable environment.

Nanotechnological applications will be effective in the creation of a sustainable environment.

(This image is published on http://nanoday.com/single/1013/benefits-of-nanotechnology-applications-in-different-fields and retrieved from Google Images.)

Today, natural resources are running out at a high rate due to ever-increasing energy-fuel consumption. As a result, the search for alternative energy sources has increased in recent years and developed countries have allocated important financial support for the research, especially on alternative energy sources. The most important ones are the studies on Hydrogen energy. One of these studies is about a generator powered by light and cleans the air while generating hydrogen fuel. With the nanoparticles present in the catalyst of the device, hydrogen fuel is produced as the dirty air is cleaned (Verbruggen et al., 2017).



A light-powered generator that generates hydrogen fuel and cleans the air.
(http://www.inovacaotecnologica.com.br/noticias/noticia.php?artigo=ar-poluido-usado-produzir-combustivel-limpo&id=010115170515#.WbEYzNSLQsY and retrieved from Google Images.)

It is possible to store this produced hydrogen gas as fuel and hydrogen buses are the best example of this. However, in order to spread the use of this energy, first it is necessary to store hydrogen in high density and in a safe way. However, storing high density hydrogen is a difficult and expensive task. Today, scientists showed that hydrogen can be stored at very high capacities in carbon nanotubes and molecules that are functionalized by transition elements (Pt, Pd, Ti, V etc).Hydrogen-powered automobiles can become more common with this discovery and this will lead to environmentally friendly fuel consumption. This way, solution can be found for clean air and alternative energy need.

Another important development in energy industry occurred in the studies for battery life. Scientists used highly conductive nanowires, which are thousands time thinner than human hair, in the batteries to increase the battery life. These wires create a large surface area, therefore, provide a larger storage capacity; this way, more electrons can be transferred. However, studies showed that these wires are very fragile and cannot be re-charged many times. A group of researchers coated nanowires inside a manganese dioxide and plexiglass-gel electrode compound to eliminate this problem. The safety and durability of this mixture are revealed through testing over more than 200.000 cycles. As a result of tests, batteries didn't lose capacity and used nanowires didn't break down (Thai, Chandran, Dutta, Li and Penner, 2016).This study is expected to prolong the life of commercial batteries significantly. With such developments, smart phones, computers, cars and other battery-powered vehicles may not need their batteries replaced.

Quality of potable water can be increased by using nanoparticles.

(This image is published on https://www.cnbc.com/2015/11/12/light-work-getting-clean-water-with-nanotech.html and retrieved from Google Images.)

Applications in water treatment processes are another important implementation of nanotechnology. Nanomaterials such as nanomembranes, carbon nanotubes, nanoclays and aluminum fibers are being used for water treatment applications. These materials are cheap, portable and easily cleanable systems. Nanofilters can clean the precipitates, chemical wastes, charged particles, bacteria and other pathogens such as virus from the water. In addition, they can also clean toxic trace elements like arsenic and viscous liquid contamination such as oil (OECD, 2004).

1.3.5 Textile and Nanotechnology

Today, integrating different properties in nanometer dimensions to the materials used in textile industry leads to very important developments and it is expected to continue. The most common application of nanotechnology is anti-stain and anti-wrinkle products and products that are resistant to liquid spills. Scientists have developed titanium dioxide nanolayer particles that react with sunlight to destroy dirt and other organic materials, and they have allowed the fabric to stay clean by coating this layer with cotton. Nanoparticles like clay, metal oxide, carbon black, and graphite nanofibers and carbon nanotubes are being used to improve the physical properties of textile products such as increasing their mechanical resistance and enhancing their conductivity and antistatic behavior. The most commonly used materials for nano-scaled filling materials are carbon nanofibers and carbon black nanoparticles with high chemical resistance and electrical conductivity. Carbon nanofibers increase the tensile strength of composite fibers and carbon black nanoparticles increase abrasion resistance and durability. In addition, composite fibers reinforced with clay nanoparticles that have electrical, thermal, chemical resistance and ultraviolet blocking properties exhibit flame retardant, anti-ultraviolet and abrasion resistance properties (OECD, 2004).

In recent years, one of the important developments in the textile industry is self-cleaning fabrics. A group of scientists found that when a textile product coated with copper and silver-based nanoparticles, it became self-cleaning as a result of being exposed to sunlight or any other form of light (Anderson et al., 2016).

Thin, flexible and light filaments that can generate and store electricity from the sun and can be used as textiles.

(This image is published on http://www.nanowerk.com/nanotechnology-news/newsid=45064.php and retrieved from Google Images.)

Another important development in textile is the thin, flexible and light filaments of copper strips that can be woven as textile and can generate and store electricity from sunlight. These filaments, developed through nanotechnology, have solar cells on one side and energy storing plates on the other side. In the future, our mobile phones will be able to be recharged with the clothes made from fabrics woven with these filaments. Maybe we will get to monitor our heart beat, body temperature and blood sugar regularly with our clothes (Li et al., 2016).

Uniforms produced with nanotechnology will provide convenience for soldiers.
(This image is published on http://www.fibre2fashion.com/industry-article/3046/military-uniform?page=6 and retrieved from Google Images.)

These developments in the textile sector have provided positive contributions to the defense industry and will continue to do so. In addition to superior protection capabilities of intelligent uniforms and intelligent materials being developed by nanotechnology, the fact that they have much more durability, longevity, lightweight and resistance than conventional materials will increase their use in military. In the future, the uniforms will gain new dimensions with flexible and washable nanosensors integrated into the fabrics, such as generating energy, sensing the body temperature and warning the soldier to allow the necessary intervention to be performed, and detecting chemical and biological agents. In addition, widespread use of all-seasons, durable, light and long-lasting clothes, boots etc., will also contribute to the country's economy in financial terms (Bayındır, 2017).

1.3.6 Food Industry and Nanotechnology

Nanotechnology applications in food industry are fairly new. The capability to use nanotechnology is expected to allow food companies to design and manufacture cheaper, safer, and more durable and more nutritious products. It is also projected that food companies will use less water and chemicals in the preparation and production of these foods. A food company has placed nanosensors that warn the user in food packaging. When the food inside the package is contaminated or started to degenerate, the nanosensor changes color and this warns the consumer. In addition, scientists have developed a portable nanosensor that detects pathogens and toxins found in food. This way it will be possible to control the food during farm, slaughterhouse, transport or packaging processes, and this will increase the food safety.

Packages produced with nanotechnology will reduce food waste.

(This image is published on http://m.meatpoultry.com/articles/news_home/Business/2017/06/Nanotechnology_offers_benefits.aspx?ID={4D25222A-B878-4896-8BD4-79828A445D81 and retrieved from Google Images.)

Some food companies have produced plastics containing clay-based nanoparticles. These nanoparticles in the plastics prevent oxygen, carbon dioxide, and damp, and this allows food and meat to remain fresh (Mongillo, 2007).In addition, scientists have developed clay nanotubes that will protect people from food poisoning by inhibiting rotting and bacterial growth. Normally the permeability of the packages allows water vapor and oxygen circulation, causing ethylene accumulation around the food, and this accelerates the degradation and decay of food. Polyethylene films with hollow clay nanotubes are the most common plastic compounds. It is shown that the nanotubes contained in these polyethylene films inhibit the formation of ethylene gas around the food by preventing water vapor and oxygen intake, and it is determined that foods are protected for a longer period (Lavars, 2017).

There are nanotechnology applications on functional foods that can respond to the needs of the body.

(This image is published on https://www.linkedin.com/pulse/nanotechnology-food-satisha-naraharimurthy and retrieved from Google Images.)

In addition to these applications, nanotechnology also has effective applications on the development of nutritious and functional foods that can respond to the needs of the body and effectively deliver nutrients to the body. Scientists are currently trying to produce on-demand foods that are stand still in the body and get activated when needed and have nanocapsules embedded in it. Another development in the food processing is nanoparticles that increase the absorption of nutrients (Mongillo, 2007).In the food industry, new nanotechnology applications are emerging every day.

Summary

The applications of nanotechnology, the most important technological development of the 21st century, start from science fields such as chemistry, physics and biology and extend to different fields from from health, engineering, food and electronic applications. Nanotechnology is an emerging technology and applications are increasing day by day. Materials at the nano scale are lighter, more durable and programmable materials, and they require less material use in manufacturing and less energy consumption at the production stage. One of the best examples of this application is the production of nano-scale electrical circuit components. The circuit components in the nanometer range are produced with less energy consumption, and the computers in which these circuit components are used will be smaller, faster and with greater capacity. Nanotechnology applications will also contribute to the sustainable environment. Hydrogen-powered automobiles will consume less fuel and will cause less environment pollution, thus lead to eco-friendly fuel consumption. In addition clean water can also be obtained by using nanoparticles that can clean up such as water sediments, chemical wastes, charged particles, bacteria and other pathogens like viruses. It will also be possible to prevent food waste through packaging produced by nanotechnology. Another important application of nanotechnology is stain-resistant, non-shrinking, liquid spill resistant and self-cleaning fabrics. Today, nanotechnology is frequently used in medicine. Nanoscale materials and nanoelectronic biosensors are used for a variety of purposes such as diagnosing, monitoring, treating and preventing diseases. Every day, a new application of nanotechnology that makes life easier emerges and the number of such applications will continue to increase.

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1.4 NANOMETROLOGY

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INTRODUCTION

Metrology is defined as "the science of measurement, embracing both experimental and theoretical determinations at any level of uncertainty in any field of science and technology" by the International Bureau of Weights and Measures (BIPM).1

Nanometrology is a part of metrology and it deals with measurements at the nanoscale. ISO (International Organization for Standardization) definition of the term nanoscale2 is:
"Size range from approximately 1 nm to 100 nm", nm(nanometer) being the unit of length at nanoscale.

Nanotechnology operates at nanoscale. At nanoscale, size is important due to both miniaturization of technology and changing properties of materials. For example, at nanoscale metals become harder, ceramics become softer, chemical resistance increases, weight is reduced, new electrical and biological properties occur. Laws of physics change at nanoscale, too.

Nanometrology is actually the "science" of nanoscale level measurement, taking into account the definition of metrology above. It relies on both experimental and theoretical studies concerned with nanoscale domain measurement. Studying matter at the level of atoms and molecules, which are structures sized as billionths of a meter (nanometers) or less, requires nanometrology.

Table 1.4.1 shows SI base quantities and their respective units of measurement.

Keywords: *Metrology, Nanometrology, Nano Scale, BIPM (Bureau International des Poids et Mesures)*

Table 1.4.1 SI base quantities and respective units of measurement

Base Quantity	**Name and Symbol of SI Unit of Measurement**
Length	Meter(m)
Mass	Kilogram(kg)
Time, Duration	Second(s)
Electric current	Ampere(A)
Thermodynamic Temperature	Kelvin(K)
Amount of substance	Mole(mol)
Luminious Intensity	Candela(cd)

SI prefixes, referring to powers of 10, are shown in Table 1.4.2.

Table 1.4.2 SI prefixes expressed in powers of 10

Factor	**Name**	**Symbol**	**Factor**	**Name**	**Symbol**
10^1	deka	Da	10-1	deci	d
10^2	hekto	H	10-2	centi	c
10^3	kilo	K	10-3	milli	m
10^6	mega	M	10-6	micro	µ
10^9	giga	G	10-9	nano	n
10^{12}	tera	T	10-12	pico	p
10^{15}	peta	P	10-15	femto	f
10^{18}	exa	E	10-18	atto	a
10^{21}	zetta	Z	10-21	zepto	z
10^{24}	yotta	Y	10-24	yocto	y

1.4.1 The Nanometer (nm)

The nano prefix comes from a Greek word nanos, and it means dwarf. As stated in other parts of this book, the nanometer(nm), the unit of length at nanoscale, is equivalent to 10^{-9} meters(m). The prefix "nano" means one-billionth, or 10^{-9} in the International System of Units (abbreviated SI from French: Le Système International d'Unités). Since the prefix "nano" means one-billionth, one nanometer is one-billionth of a meter.

3 atoms which are lined up are approximately 1 nm long. A single human hair is about 80,000 nanometer (nm) wide, a red blood cell is approximately 7,000 nm wide, a DNA molecule 2-2.5 nm or a water molecule is 0.24 nm. The diameter of an atom is 0.1-0.5 nm. The wavelength range of visible light is 400-700 nm. The single-layer(one-atom) thickness of graphene is 0.345 nm. The hydrogen atom is about 0.1 nm. A virus may be about 100 nm.

Figure 1.4.1 shows some natural and manmade things' dimension measurements in nanometers and the relative scaling of the micro-sized and the nano-sized matters:

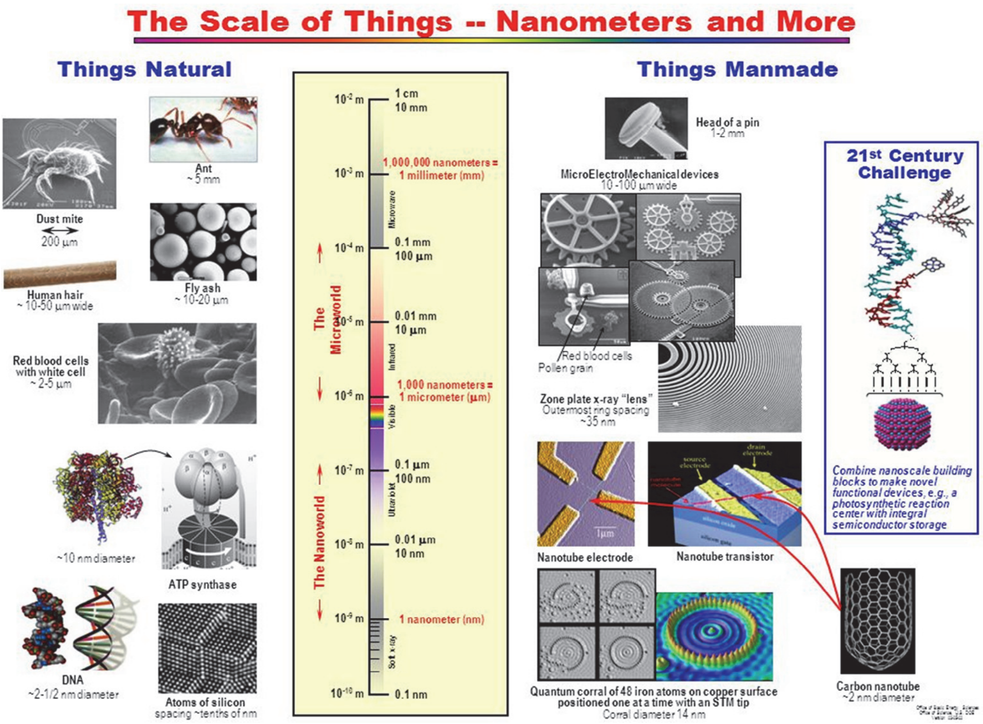

Figure 1.4.1 The Scale of Things - Nanometers and More.

(Source: Office of Science, U.S. Department of Energy)

1.4.2 The Nanogram (ng)

The nanogram is the unit of mass at nanoscale. It is equivalent to 10^{-9} grams(g). The number of atoms in 1 ng of an element can be calculated by:

$$\left(\frac{6{,}022x10^{23}}{Molar\ Mass}\right)x10^{-9}$$

6,022x10^{23} in the above formula is Avogadro's number*. Table 4.3 shows the number of atoms in 1 ng of some well-known elements· Avogadro sayısıdır. Tablo 1.4.3'te bazı elementlerin 1 ng'ındaki atom sayısı gösterilmiştir.

Table1.4.3 Number of atoms in 1 ng of some elements

Element	**Molar Mass (gr/mol)**	**No. of atoms in 1 ng**
Hydrogen	1,0079	597.479.908.721.103,00
Helium	4,0026	150.452.206.066.057,00
Carbon	12,0107	50.138.626.391.467,60
Oxygen	15,9994	37.638.911.459.179,70
Calcium	40,0780	15.025.699.885.223,80
Iron	55,8500	10.782.452.999.104,70
Copper	63,5460	9.476.599.628.615,49
Silver	107,8700	5.582.645.777.324,56
Gold	196,9700	3.057.318.373.356,35
Lead	207,1900	2.906.510.931.994,79
Mercury	200,5900	3.002.143.676.155,34

As can be seen from the table above, even a very small quantity like 1 ng of an element has trillions of atoms in it.

Some of the instruments used for nanoscale measurement are listed below:

- Scanning Electron Microscopes(SEM),
- Transmission Electron Microscopes(TEM),
- Field Ion Microscopes(FIM),
- Scanning Tunneling Microscopes(STM),
- Atomic Force Microscopes(AFM).

All of the above instruments are used for seeing at nanoscale, so that nanometric measurements can be accomplished.

1.4.3 Current Nanoscale Measurement Studies

Measurements on Thin Films

A thin film is a layer of material. Its thickness ranges from fractions of a nanometer (monolayer) to several micrometers. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications. The characterisation of these films and coatings is an important branch of nanometrology, with a large variety of measurement problems and tasks. Sample applications of thin films are:

- semiconductors and dielectrics,
- optical components,
- wear resistant coatings, and
- solar cells.

Typical nanoscale measurement requirements regarding thin films are listed below:

- Thickness and density of the thin film,
- Morphology of the thin film outer surface,
- The thickness, roughness and density of the individual sublayers for multilayer films,
- Chemical compositions of the individual layers,
- Uniformity of the individual layers,
- Surface quality and material of the substrate,
- Functional properties of the film (e.g., adhesion strength, hardness, friction coefficient, wear resistance).

A universal technique for thickness measurements at the nanoscale does not exist. Every measurement task requires a dedicated analysis to identify and select the most appropriate measurement method adjusted to the specific problem.

Measurements on Structured Surfaces

Samples with structured surface features are classified as being at nanoscale if the smallest feature size, the critical dimension, is less than 100 nm. Such structures are nowadays part of many industrial devices and applications including:

- Semiconductors and integrated circuits,
- Micro-electro-mechanical systems,

- Biomedical devices, and
- Optical devices.

Typical parameters to be measured within this field are height, width, angle, pitch (of periodic structures) and diameter (of e.g., particles).

The measurement quantities dealt with in this section are dimensional. The sizes of the structures or features define the physical behaviour of the whole system – even the material properties may change, if the structures are smaller than a certain limit.

Measurements on Engineered Nanoparticles

Nanoparticles are ultra-small particles that have one dimension less than or equal to 100 nanometers. The properties of many conventional materials change when formed from nanoparticles. This is typically because nanoparticles have a greater surface area per weight than larger particles which causes them to be more reactive to some other molecules.

Nanoparticles engineered for shape, size, and surface properties possess special functionalities including catalytic behavior, improved strength, enhanced thermal and electrical conductivity, and controlled release of host molecules. These advanced properties make engineered nanoparticles usable in applications in biomedicine, nanoenergetic materials, and functional nanocomposites.

Nanoparticle-sizing is an important area of study in nanometrology. It's necessary to measure how big the particles are. Counting the number of particles in a specific substrate and through the use of an Equivalent Diameter (the diameter of a perfectly spherical particle which would create the same fluctuation of scattered light intensity, sedimentation time responses, etc.), and finding average sizing values is a typical measurement approach of metrology for engineered nanoparticles.

Measurements on Nanobiotechnology

At nanoscale, proteins take the specific shapes necessary to conduct their functions. It is also the scale that holds the width of DNA molecules and viruses, and the thickness of the membrane forming the wall of cells. Nanotechnology and biotechnology are closely related, in consequence of these facts. Some applications of nanobiotechnology are

- magnetic nanoparticles used to destroy cancer cells,
- surface modification and coatings at the nanoscale to tailor biological responses to materials used in e.g., implants
- pharmaceuticals where the nanoscale structure and chemical composition are tailored for efficient delivery of the drug to its target
- better food packaging and storage materials, prolonging the shelf life of fresh food.

The metrology field is focused on physical measurements (e.g., mass, time, length). A particular issue is the measurements in biology and medicine that are dealing with amount of substance. An example is the amount of nanoparticles binded to Magnetic biosensors for in-vitro diagnostics. Another example is the surface roughness on the nanometre scale which plays an important role for the tribological aspects (friction, lubrication and wear) of medical implants. Nanobiotechnology deals with coatings and thin films, structured surfaces, and particles, and therefore dimensional analysis methods mentioned in the previous sections are relevant for nanobiotechnology, too.

Natıonal Metrology Instıtutes

Member institutions of European Association of Metrology Institutes-EURAMET) are listed in the Table 1.4.4.

Table 1.4.4 Member metrology institutions of EURAMET

Country	**Organization**
Germany	Physikalisch-Technische Bundesanstalt (PTB)
United States	National Institute of Standards and Technology (NIST)
Albania	General Directorate of Metrology (DPM)
Australia	National Measurement Institute(NMIA)
Austria	Bundesamt für Eich- und Vermessungswesen (BEV)
Belgium	Quality and Safety Department, Ministry of Economic Affairs (SMD)
Bosnia Herzegovina	Institute of Metrology of Bosnia and Herzegovina

	(IMBIH)
Bulgaria	Bulgarian Institute for Metrology (BIM)
Croatia	Croatian Metrology Institute (HMI)
Czechoslovakia	Czech Metrology Institute/Ceský metrologický institut (CMI)
China	National Institute of Metrology of the People’s Republic of China (NIM)
Denmark	Danish Fundamental Metrology Ltd (DFM)
Estonia	Central Office of Metrology (AS METROSERT)
Finland	Mittatekniikan Keskus, Centre for Metrology and Accreditation (MIKES)
France	Laboratoire National de Métrologie et d'Essais (LNE)
India	Indian Institute of Legal Metrology
Netherlands	VSL Dutch Metrology Institute (VSL)
United Kingdom	National Physical Laboratory (NPL)
Spain	Centro Español de Metrología (CEM)
Sweden	RISE Research Institutes of Sweden AB (RISE)
Switzerland	Federal Institute of Metrology (METAS)
Ireland	NSAI National Metrology Laboratory (NSAI NML)
Italy	National Institute of Metrological Research (INRIM)
Japan	National Metrology Institute of Japan(NMIJ)
Montenegro	Bureau of Metrology (BMM)
Letonia	Latvian Metrology Bureau (LATMB)
Lithuania	Centre for Physical Sciences and Technology: Metrology Department (FTMC)
Luxemburg	Bureau luxembourgeois de métrologie (ILNAS)
Hungary	Government Office of the Capital City Budapest (BKFH)
Malta	Malta Competition and Consumer Affairs Authority - Standards and Metrology Institute (MCCAA-SMI)
Macedonia	Bureau of Metrology, Ministry of Economy (BOM)

Egypt	National Institute of Standards (NIS) of Egypt
Norway	Norwegian Metrology Service, Justervesenet (JV)
Poland	Central Office of Measures (GUM)
Portugal	Instituto Português da Qualidade (IPQ)
Romania	National Institute of Metrology (INM)
Serbia	Directorate of Measures and Precious Metals (DMDM)
Slovakia	Slovak Institute of Metrology/Slovenský Metrologický Ústav (SMU)
Slovenia	Metrology Institute of the Republic of Slovenia (MIRS)
Taiwan	National Measurement Laboratory(NMI)
Turkey	National Metrology Institute/TÜBITAK Ulusal Metroloji Enstitüsü (UME)

1.4.4 Difficulties Encountered in Nanometrology

Error margin of nanoscale dimensional metrology must be below 1nm. Most frequently encountered difficulties in nanoscale measurements, currently, are:

- Calibration of sensors whose resolution is under 1nm (which are used, for example, in measurements of electron and ray beams),
- Contamination that is frequently encountered in characterisation/grading laboratories,
- Measurement of large amounts of nanomaterials such as carbon nanotubes,
- Sample preparation for nanoscale imaging devices (for which high-vacuum environment must be provided).

1.4.5 Improvement Areas for Nanometrology

Some of the current improvement areas for nanometrology are given in the following paragraphs. Difficulties in the below-mentioned improvement areas can be overcome by primarily understanding and studying well the happenings that occur at the nanoscale:

- Development/calibration of methods for measurement at nanoscale,
- Development/improvement of new instruments for measurement at nanoscale,
- Establishment/sustainability of an infrastructure guaranteeing reliable nanoscale measurement results of nanomaterials and nanoproducts (This challenge is heavily dependent on the appropriate theoretical, experi-

mental, and applicable establishment of the first two challenges mentioned above. In order to realize this challenge, global co-operation of nanotechnology research and development (R&D) studies and works should be motivated, followed through, and sustainably consolidated.),
- Establishment of new reference materials and standards,
- Determination/Measurement of new unique nanoscale characteristics,
- Studies on portability/transferability of micro-scale technologies to nanoscale,
- Studies related to uncertainties in nanoscale dimensional metrology.

Conclusion

Nanometrology is a part of metrology and it deals with measurements at the nanoscale. Nanoscale is “Size range from approximately 1 nm to 100 nm”, nm(nanometer) being the unit of length at nanoscale. Properties of nanomaterials change at nanoscale. For example, at nanoscale metals become harder, ceramics become softer, chemical resistance increases, weight is reduced, and new and unique electrical and biological properties occur. Nanometrology is required for studying matter at the level of atoms and molecules, which are structures sized as billionths of a meter (nanometers) or less. Nano scaling studies began approximately 20 years ago. Nanoscale measurements must be correct, sensitive, and reliable, in order to achieve sound process control in nano-production.

Nanometrology is extensively used in medical products, pharmaceuticals, electronics, automotive, and forestry sectors. Its usage areas will broaden, covering unexpected sectors, too, as long as further sectors’ studies are conducted at nanoscale.

Don’t forget:

“It is not possible to produce an object that cannot be measured.”

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1.5 IMPACT of NANOTECHNOLOGY

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INTRODUCTION

Nanotechnologies represent engineering on a very small scale. They can be applied in many areas, such as: health and medicine, information and communication technology and energy and the environment. Nanotechnologies are currently considered "emerging technologies" that can revolutionize a large number of application domains. Nanotechnologies can have some revolutionary implications for our society in terms of applications or tools that can be accomplished. Nanotechnology is impacting businesses and will offer new and improved products and processes and will allow companies to innovate and enter with new generation products on a new global market.

1.5.1 The impact of nanotechnology

As a preamble to the nanotechnology impact the diagram below (Figure 1.5.1) illustrating the complexity domain of nanotechnology, technologies and areas of application.

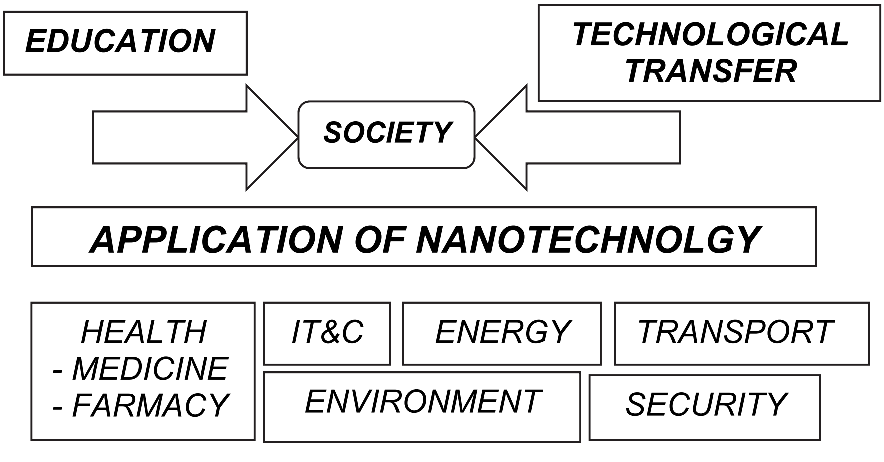


Figure 1.5.1. Nanotechnology impact

Nano Impact aims to play an important role in disseminating knowledge about nanomaterials in human and environmental systems. It focuses on four main areas:

Human nanotoxicology – including the interactions between nanomaterials and biological systems (nano-bio interactions) at the cellular and organism level, mechanisms of disease development and in vitro and in vivo toxicity screening strategies

Nano-eco toxicology – nano-bio interactions and effects on organism and ecosystem health

Exposure – release of nanomaterials throughout the life cycles of products and applications, the fate and behavior of nanomaterials in a variety of settings and the development and application of analytical methods to quantify and characterize the nanomaterials in environmental and biological media

Risk and life cycle assessment – human and environmental risk assessment, and development of life cycle assessment methods and use of life cycle perspectives.

The risk posed by nanomaterials is poorly understood because of a lack of detailed data, the novelty of the area and the potential novel behaviors of nanomaterials. But they are important emerging contaminants, so to protect health and ensure the long-term sustainability of the technology, these risks need to be understood, quantified and reduced.

Nanotechnology becamme a daily ineed in the future with positive impact in our life. The impact of nanotechnolgy can be identify in different fields from our life and economical sectors. The benefits and applications are presented in Table
1.5.1.

Table 1.5.1. Nanotechnology Applications

	Applications and Uses	**Benefits**
Advanced Manufacturing	faster electronics, new material development	cntrolled manufacturing processes, economical and high output with low cost.
Aerospace	nanocomposites, advanced sensors, faster electronics for data processing	CO_2 reduction, lighter materials, move to less fuel consumption cost savings, improved functionality of materials, minimising risk, flexibility and new systems
Agriculture	nanoparticles for removing contamination, moisture sensors, detection of pathogens	higher crop yields, reduction in the use of pesticides and improved water management
Automotive	lubricant / hydraulic additives, nanoparticles in catalytic converters, fuel cells, hydrogen storage	CO_2 reduction, lighter materials, move to less fuel consumption
Chemical Industries	fuel cells, nanoparticles as catalysts	reduction of waste and CO_2 reduction
Construction	thermal insulation, Energy storage devices	lower energy needs, CO_2 reduction
Cosmetics	clear sunscreens, beauty care products, cosmeceuticals, nutraceuticals	UV protection, enhanced delivery of medicated skin products
Creative Industries	changing effects, advanced display systems	bioinspired product development
Electronics	advanced display technologies with conductive nanomaterials, quantum computing, data	providing faster, smaller and enhanced hand held devices

	storage, printable and flexible electronics, magnetic nanoparticles for data storage	
Environment	Air and water filtration, waste and water treatment, hazourdous materials disposal, in-building Environmental systems, remediation	CO_2 reduction and clean-up
Food and drink packing	improved barrier properties and heat-resistance, anti-microbial and anti-fungal packaging, smart sensing, biodegradable packaging	tracking, quality monitoring and anti-counterfeiting, provides enhanced information on product and is environmentally friendlly
Healthcare	Nanoparticulate drug delivery, Nanosilver dressings, Fluorescent biological labels	better patient care and understanding of biological processes
Low Carbon Technologies	energy storage devices	environmentally friendly with the goal to reduce CO_2 production
Materials	anti-fouling coatings, nanotube polymers, printed electronics	sronger and lightweight materials, functionalised materials
Safety	PPE equipment, stronger materials	employee monitoring, advancing imaging, better testing, new characterisation methods

Textiles	stain-resistant fabrics, self cleaning and anti-bacterial coatings, protection and detection, healthcare, new wearable textiles incorporating solar cells, sensors and self cleaning properties	hospital garments, emergency clothing and PPE, fashion on demand

Source: Adaptation after http://workshop-nano.wikispaces.com/Nano

1.5.2 How can nanotechnologies change our lives in the future?

Nanotechnologies have played an important role in producing smaller, more efficient and multifunctional devices.

In the future, our lives could change through many technological innovations such as:

- Introducing medications that can be activated and controlled from the outside of the human body into the circulatory system;
- They could collect data and send them to the physician to modify treatment (teranostics);
- Nano-sized devices for transporting drugs and targeting cancer cells;
- Tattoos on the skin to monitor salt levels and other metabolites and to alert athletes or diabetics;
- Footwear or clothing with sensors to collect data during training;
- Integrated energy collector systems (in textiles, footwear, etc.) to collect solar and mechanical energy to charge electronic devices;
- Flexible and transparent solar panels integrated into windows, ceramic tiles, etc., with high efficiency conversion of solar energy;
- Surfaces and textiles to remove nitrogen oxides and other smog gases from the urban atmosphere.
- Smart food packaging with sensors to detect the way it is used to transport the product, for detection of contamination, which are:
  - fitted with tracking system;
  - communication to warn;
  - manufacturer and trader.

1.5.3 The economic and social impact of nanotechnology

Nanotechnology has a large number and variety of applications in many different sectors. Potentially, nanotechnology could lead to a more efficient and sustainable use of resources and maybe have a beneficial impact for the vast majority of people around the world.

However, as all the technologies that exist, it could have a negative impact on society in what concerns aspects of:

1. confidentiality;
2. division of society;
3. communication risks.

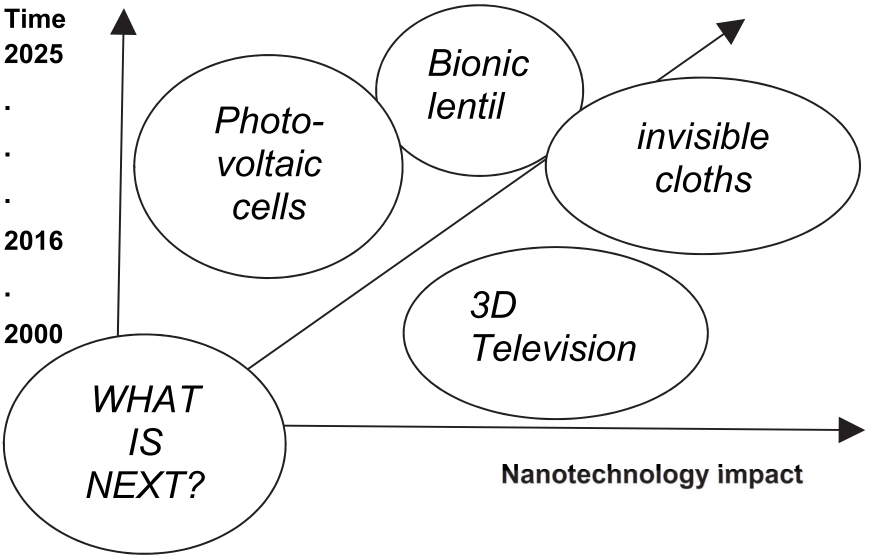
Confidentiality: The potential for abuse is present and the limits of the type of information that can be captured must be clearly defined by society, through the legislative system.

Divide society: As with previous technologies such as IT, nanotechnology could has the effect of widening the gap between the rich and the poor, or more precisely the developed world in developing. Many of the precious metals and minerals that new nano materials are going to replace, and thus reduce dependence on non-renewable, are exploited in developing countries. Loss of these incomes, without a strategy of replacing them, will have a negative impact on the economy and development of these countries. To respond to these potential effects, strategies in nanotechnology must be approached differently in different countries, depending on the needs of those countries.

Communication: Accepting new advances in nanotechnology and, in particular, its effects on the scale broad, it can only be achieved through communication and dialogue between scientists, industry, governments and society in general. This has often been ignored and led to misinformation and misunderstanding on the risks and benefits associated with new advances. The need for communication was recognized by governments, research and industry funding agencies and these institutions have now initiatives to actively exploit the dialogue with scientists and citizens interested through.

1.5.4 Nanotechnology Future today

The 21st century It is also called manufacturing technology. It is a multidisciplinary field that combines the great scientific achievements in physics, chemistry, biology, mathematics and materials science in the construction of atoms and nanoscale molecules of materials with artificial intelligence. Nanotechnology is a collective term for technological developments at nanoscale. The nanometric structures are not only very small, reaching even to the atomic scale, but they possess some totally unique and unexpected properties, compared to the same substance taken at the macroscopic level.



Nano impact evolution between 2011-2015:

- Nanomaterials to replace current materials, for example polymers;
- Nanoparticle-based target drugs become a standard tool (for therapeutic purposes, increasing performance);
- Intelligent probes (which illuminate when they reach their target) are basically used for in-vivo diagnostics;
- Nano tools (such as optical tweezers) are used inside cells while retaining cell integrity and activity;

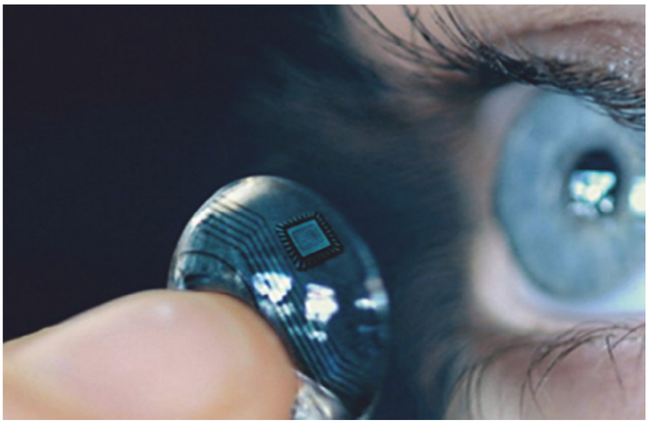
- Nanoprobes are widely used for different applications in diverse sectors, including households;
- Integrated DNA-based circuits for the purpose of specific diagnostics in the current practice of hospitals;
- Biochips in vitro tests replace animal tests for different applications (eg in pharmacy, cosmetics);
- Biosensors for single molecule detection based on nano devices are commercially available;
- Auto assembly is widely implemented as a technique for developing materials and devices;
- Chips based on bimolecular as active elements are manufactured on a commercial scale;
- Nanoelectronic chips are manufactured on a commercial scale using DNA or peptides.

Nano impact evolution between 2016-2020:

- The fundamental processes of the cell cycle are widely known;
- Human organs can be developed in vitro due to nano bio technological advances;
- Bio molecular engines are used in nano and Microsystems;
- The general public uses biochips for personal purposes;
- Artificial systems have self-reputation skills.

Nano impact evolution between 2020-2025:

Nano machines for therapy and diagnosis inside the body are commonly used; the researchers are trying to improve their vision. It's not about correcting vision defects, but about a lens that you can see. For example, you are in an unknown city and need to get to a destination quickly. In this case, the contact lens will turn on, and over the landscape you see as a rule will show all kinds of indicators that will allow you to focus. The difference between a regular contact lens and a contact lens with display is that the latter have electrical connections and LED array.



Inteligent lens

(This is a featured Picture on Google images,https://gadgetreport.ro/gadget/tehnologie-sf-devine-realitate-cum-arata-lentilele-de-contact-inteligente-video/)

1.5.6 Nano impact today

a) Nanotubes

The most difficult problem faced by scientists when they proposed building a space elevator was linked to the material that would be most appropriate to meet such a high demand. A Japanese researcher discovered in 1991 a novel combination of carbon, which he called the 'tube nano' and which proved to be breathtaking. The space elevator will be designed to send space to the satellites. Ultimately, it would make it a tourist attraction, offering the curious to travel in space.

Space elevator

(This is a featured Picture on Google images)

b) Nokia Morph The Phone To Be Transformed

Thanks to nanotechnology, which tends to generate seemingly magical functionality in common devices, Nokia has succeeded in bringing together in a fascinating device a series of technologies that will be available for mobile equipment over the next decade. Baptized Morph, the prototype created by Nokia can change its shape in a variety of ways, from bracelet to regular phone or office desk. It is transparent, has a surface capable of cleaning itself and the assembly can detect and even use power sources nearby. Exposed at the Modern Art Museum in New York, Morph is a concept that aims to demonstrate the extreme flexibility of mobile devices that our near future holds for us.

Nokia Morph

(Picture taken from Google http://www.dreambloggers.com/5068/nokia-morph-nano-technology-phone-future-of-mobile-phones-features-specs/)

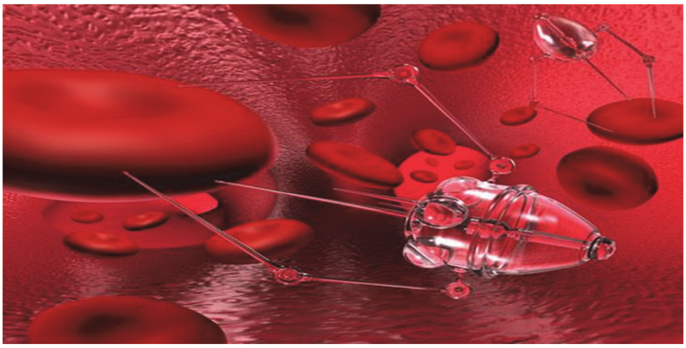
c) Nano Robots Doctors in 30 Years

How would we be able to swallow a tiny doctor who could travel through blood to any sick cell of his body?

The nanodoctor would be good at all: to provide medication, to remove tumors, to analyze and to "put the shoulder" on the reconstruction of accidentally destroyed tissues. Today are very little effective due to precautions. When we make an antibiotic for killing bacteria, we must make sure that it does not kill our body's cells.

A nanorobot, able to administer poison only to the bacteria we are targeting, would greatly simplify things. Diseases can be diagnosed before the person feels the first inconvenience, which would further simplify their treatment. Human organs that suffer wear damage such as liver, kidneys and brain may be helped to recover damaged cells.

Nano robots will be able to place cells exactly at the "disaster" site and then, after they multiply - turning into a tissue identical to the one to be replaced, the robots will stop the process to avoid the appearance of tumors. So complex we will have in only 30 years.



Nano robots

(This is a featured Picture on Google images http://www.groupin.pk/blog/nanotechnology-a-daily-need-in-the-future/)

d) Nano Spaces

The lotus plant is immune to maculation (smear, dirt), there is no dirty lotus. It is an intelligent light-spreading plant that has a high energy efficiency. Every dripping drip drives dust and dirt after it. The concept were used as a start-up on auto products. The development of nano -spaces which it can be applied in the nanotechnological facilities for cars, car service, show-rooms, industrial and production halls and underground parking.

Lotus effect

(Picture taken from Google https://biomimeticdesign.wordpress.com/2008/08/27/lotus-effect-efecto-lotus/)

THE FUTURE IS NANO!

The term “nanotechnology” has been evolved around couple of years. Nanotechnology is actually the technology of building electronic circuits and devices of size smaller than 100 nanometers. It is shortened to word “Nanotech”. Almost every industry is using that advanced technology as they produce a large quantity of products at a very cheap price. It has opened a new dimension for companies and entrepreneurs. It is impacting businesses and keeps on introducing new, cheap and improved products and processes. Nanotechnology gives a full chance to companies to innovate and enter new market.

Nanotechnology will affect every aspect of our lives, from the medicines we use, to the food we consume and the energy supplies we require, the cars we drive, the buildings we live in, and the clothes we wear. Nanotechnology will helps us in achieving a better and safer life

If these short-term uses of nanotechnology seem impressive, the long-term capabilities are tedious. NASA's Advanced Concept Institute (ICA) has been specifically designed to promote visionary research into space technologies that will take between 10 and 40 years to be frustrated like:

- the use of a large number of molecular microscopic machines to produce any object by assembling it with an atom;

-have 100 times the tensile strength of steel, but only one-eighth of weight; -they are 40 times stronger than graphite fibers;

-have a higher conductivity than copper;

-can be both conductors and semiconductors, depending on atomization;

-there are excellent thermal conductors.

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SECTION 2

PRODUCTION

2.1 EMULSION

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INTRODUCTION

Emulsion methods is one of the liquid-phase nanoparticle preparation techniques. An emulsion is the complete mixture of two liquids. Ordinary emulsions are instable in terms thermodynamics and the droplets that have average sizes of 0.1 - 1.0 microns grow with the gravitational effect and two phases separate from each other again. Emulsions have a blurry appearance. However, microemulsions are defined as thermodynamically stable emulsions. Their properties are time-independent and they are not affected by production steps such as agitation process. Their average drop sizes are smaller than 100 nm. Microemulsions, contrary to emulsions, appear transparent as they don't refract the light due to their extremely small droplet sizes despite the fact that they contain high amounts of water and oil. Their superior properties enabled microemulsion method to be used widely in nanoparticle production.

2.1.1 Microemulsion

There is a wide variety of methods in nanoparticle synthesis. Microemulsion is one of the liquid-phase synthesis methods. The emulsion, which is the basis of the method, is consisted of oil (nonpolar phase) and water (polar phase). These two phases are immiscible and they separate back into two phases when they are mixed with an external force. In order these two phases to mix, an energy that can enable water-oil mixture is required instead of water-water and oil-oil interaction. Intermediate surface tension occurs in the presence of two phases. Approximately 3.0-5.0 x 10^{-2} N force per unit length (m) is required to remove the intermediate surface tension between water and oil surfaces (Bourrel and Schechter, 1988). Surfactants consisted of organic molecules that have hydrophilic head and lipophilic tail (Figure 2.1.1) are used to overcome this force. Hydrophilic part of surfactant is consisted of non-ionic or ionic groups. These groups are bonded to the hydrophobic long-chain hydrocarbons with covalent bonding.

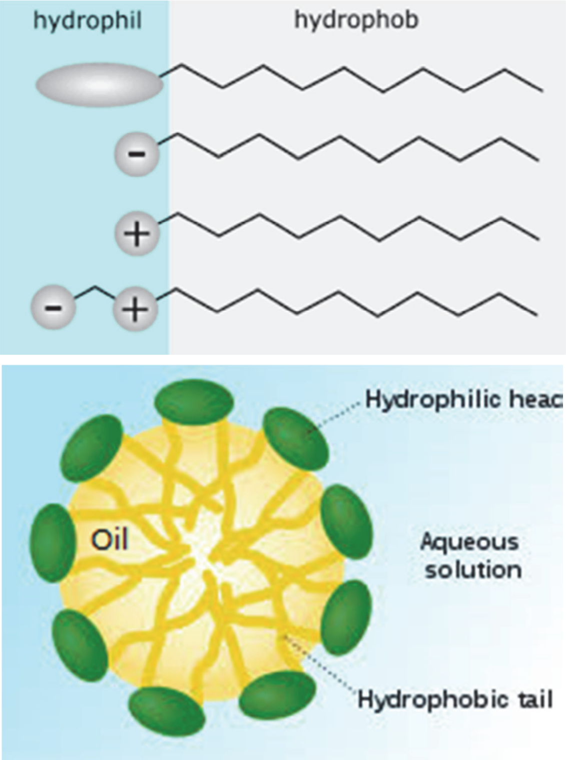

Figure 2.1.1. Surfactants

(The image is published on https://en.wikipedia.org/wiki/Surfactant and retrieved from Google Images.)
Yüzey aktif maddeler

There are four types of surfactants; anionic (eg; dioctyl sodium sulfosuccinate (DOSS), commercial name PENTEX® 99), cationic (eg; cetyl trimethyl amonium bromide, CATB), non-ionic (eg; sorbitan alkyl esters, commercial name Span®) and dual groups with both anion and cation group (eg; amonium sulfobetaine). Therefore, emulsions are consisted of at least three components; oil, water and surfactant.

In the presence of enough surfactants in the medium, surfactant decreases the intermediate surface tension between water and oil molecule and creates an intermediate surface between water and oil (Gelbart and Benshau, 1996). If a very small amount of suitable surfactant is added into water-oil medium and agitated, a liquid medium called continuous phase, in which emulsion is formed, where droplets of one phase is dispersed in the other phase that has a surface covered with surfactant (Figure 2.1.2). These emulsions have blurry appearances and droplets inside are approximately 0.1-1.0 micron in size.

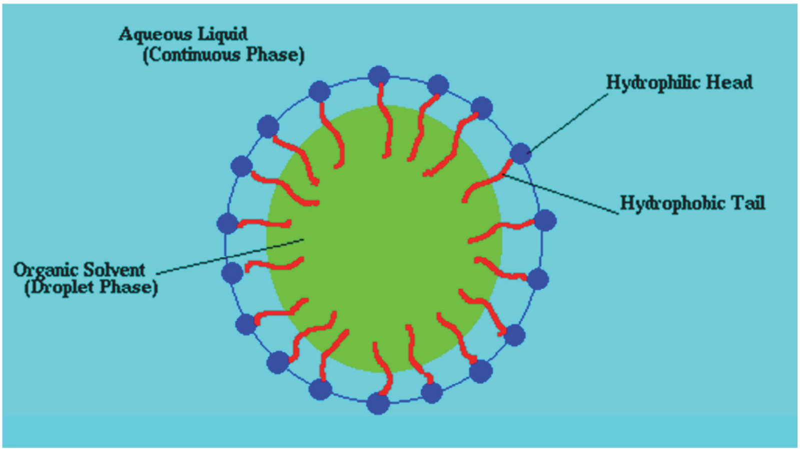

Figure 2.1.2. Emulsion formation

(This image is published onhttp://www.physics.emory.edu/faculty/weeks//lab/emulsion/ and retrieved from Google Images.)

The most important part of emulsion formation process is to decide which phase will be the continuous phase. The surfactant to be selected will be of great importance for this purpose. If the surfactant is hydrophilic, it will be emulsified inside continuous water phase with oil droplets. In the contrary case when lipophilic surfactant is used, water droplets will be formed in continuous oil phase (Bancroft, 1913).

Although emulsions are kinetically stable, they cannot remain stable thermodynamically for a long time. As the surfactant dissolves in a phase, droplets come together again. Thus, medium returns to separate water and oil phase (Gelbert and BenShau, 1996). If a surfactant that has a balanced hydrophilic and lipophilic properties is used at the right concentration, a different oil and water system is produced. This new system is called microemulsions (Figure 2.1.3) and they have different properties than emulsions. Droplet sizes of microemulsions vary between 5 nm and 50 nm. They are stable in terms of kinetics and thermodynamics, and they have low viscosity. Microemulsions are homogeneous macroscopically and heterogeneous microscopically and different structures such as lamel, cylinder and sponge-like are observed. In addition, intermediate surface tension is much lower than 10-6 mN/m.

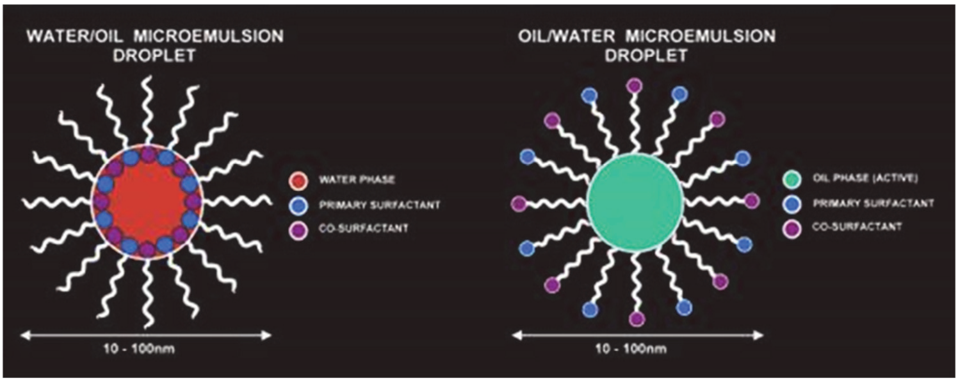

Figure 2.1.3. Microemulsion drops

(This image is published on http://www.enviroquestgpt.co.uk/content/micro-emulsion.html and retrieved from Google Images.) Mikroemülsiyon damlaları

2.1.2 Microemulsion Types

Systematic examination and understanding of phase behaviors of emulsions or mircoemulsion like liquid crystal phases and their related systems carry great importance. Winsor (1948) had recommended a classification diagram for liquid formulations that contain oil, water and surfactants. Systems have four different types based on equilibrium phase (Figure 2.1.4) (Hloucha, 2015; Paroor, 2012). In Winsor I type oil/water (O/W) microemulsion, the inner phase consisted of oil droplets that are covered by surfactants are dispersed inside continuous water phase. As the surfactant dissolves in the water phase, water phase is rich in terms of surfactant and oil phase is poor in surfactants. In Winsor II type, water/oil (W/O) microemulsion is consisted of water droplets dispersed in continuous oil phase, which is known as inverse-micelle. Oil phase is rich in surfactant, however, water phase is poor. In Winsor III microemulsions, there is excess water phase at the bottom, excess oil phase at top and there is surfactant dissolved in two continuous phases in the intermediate region that is in balanced between these two phases. This is the microemulsion type that contains three different phases; oil/water (O/W), water/oil (W/O) and water+oil+surfactant (W+O+S). In Winsor IV type microemulsion, it appears like a single phase containing water+oil+surfactant since the phase borders are not clear in macroscopic level.

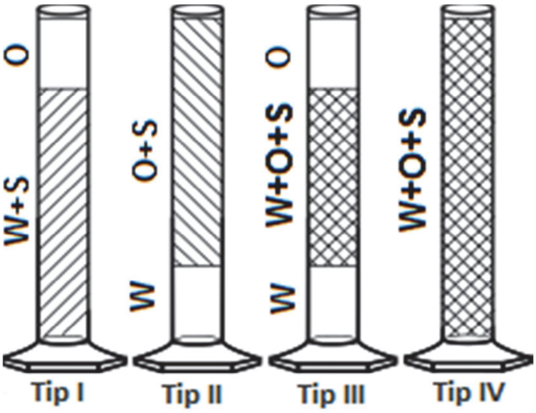

Figure 2.1.4. Winsor type microemulsion Type I: O/(W+S), Type II: W/(O+S), Type III: O/(W+O+S)/W, Type IV: W+O+S
(This image is published on https//fr.wikipedia.org/wiki/Type_Winsor and retrieved from Google Images.)

Fish diagram is used to determine the type of microemulsion (Figure 2.1.5). In this graphic, total surfactant concentration is on the x-axis, and settings parameter (such as temperature, surfactant mixture or salt concentration) is on the y-axis and Winsor type systems are attained over the graphic.

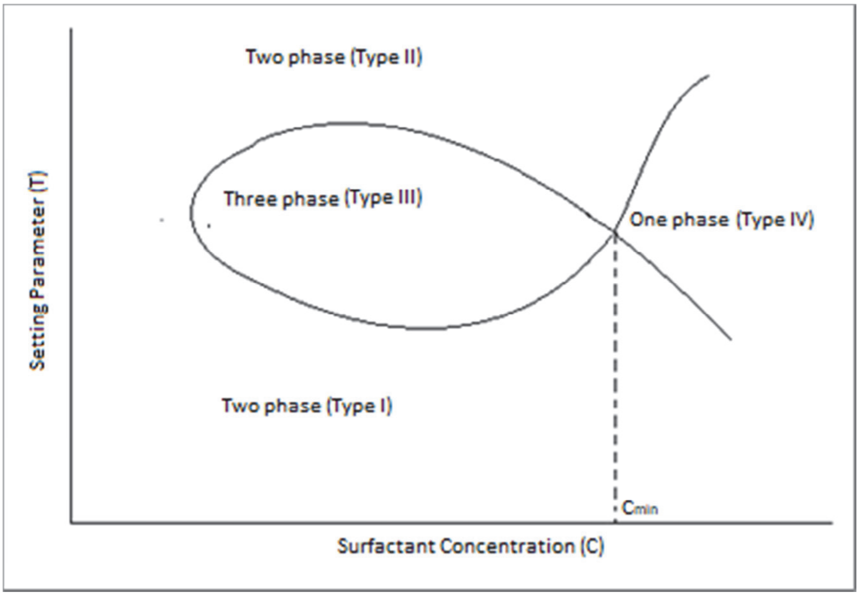

Figure 2.1.5. Fish phase diagram used for microemulsions

In case of high total surfactant concentrations and narrow setting parameter values, Winsor IV type single phase emulsions are formed. This region is called tail region. In conditions lower than the lowest surfactant concentration, Winsor type I, II and III emulsions are obtain that has 2 and 3 phases.

Generally, microemulsions are consisted of lipophilic phase, hydrophilic phase, surfactant and second surfactant (Zielińska-Jurek, 2012). In order for microemulsions to have low intermediate surface tension and good solubility, they must be well-formulized. For a good formulation, parameters of oil/surfactant and surfactant/second surfactant ratio, surfactant, second surfactant, aqeous and oil phase concentration and nature, pH, temperature and polarity hydrophilicity/lipophilicity must be determined (Malik, 2012). In addition to these factors, suitability of surfactant and second surfactant is very important for the microemulsion wanted to be obtained. Triple phase diagrams are used to study the phase behaviors of microemulsions that contain water, oil and surfactant at constant pressure and temperature (Figure 2.1.6) (Malik, 2012; Paroor, 2012). Each corner of the phase diagram corresponds to the 100% concentration of its component. When four components are used, one corner on the pseudo-triple phase shows a double mixture of surfactant+second surfactant.

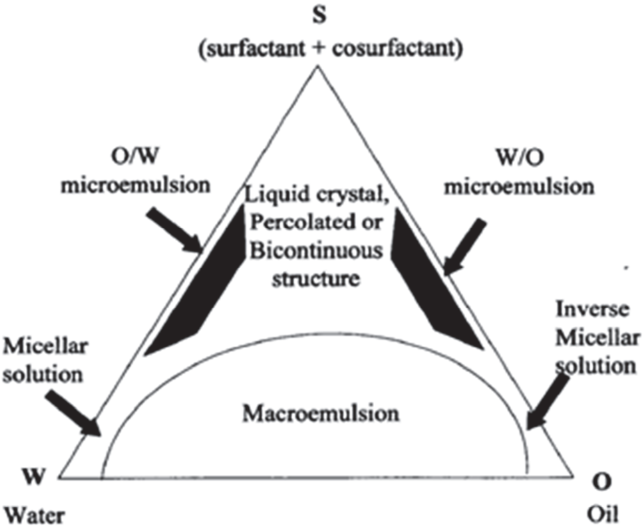

Figure 2.1.6. Microemulsion three-phase diagram

(This image is published on http://www.pharmatutor.org/articles/formulation-characterization-of-microemulsion-based-gel-antifungal-drug?page=2 and retrieved from Google Images.)

Generally, water/oil (W/O) microemulsions are preferred for the attainment of nanoparticles. Water emulsion in oil (W/O) is obtained by the dispersion of water inside a hydrocarbon-based continuous phase. In this region, surfactant produces clusters known as inverse micelle (Malik, 2012). Central nuclei of these inverse micelles start to separate with the addition of polar or ionic component. This way, organic or inorganic materials disperse regularly inside the oil. These systems are dynamic. Micelles frequently collide in random Brownian motion. Collisions enable micelle contents to be exchanged and mix the inorganic reagents inside them. This exchange process forms the basis of nanoparticle synthesis that allows different reagents dissolved in different micelle solutions to react after agitation. Micelles that provide suitable conditions for controlled nucleation and growth can be defined as nanoreactors. After the growth step, surfactant prevents nanoparticles from clustering (Lopez-Quintela, 2003).

Only a limited number of organic nanoparticles can be prepared by using oil microemulsions dispersed in continuous water phase, which is also called microemulsion polymerization (Lopez-Quintela, 2003; Malik, 2012; Hloucha, 2015). This technique could not be further developed due to the difficulties in separation of phases. Polymeric nanoparticles can be obtained with the use of polymerization reactions in O/W emulsions that enable the dispersion of hydrophobic nanoparticles with sizes of 10-40 nm inside water. Rapid polymerization is one of the most important advantages of this method.

Summary

Microemulsions are emulsions that are formed by spontaneous mixture of two liquid phases under certain conditions. Although they are homogeneous in macro scale, they are heterogeneous in micro scale. Tension between phases is quite low. Since the formed droplets are smaller that visible wave length, these microemulsions appear transparent. They are stable in terms of kinetics and thermodynamics. A wide variety of nanomaterials can be prepared by using solely microemulsion method or in conjunction with other methods. Microemulsions are a unique class of colloidal systems with their high degree of inter-phase dispersion, very small sized droplets and ability to control the chemical reaction. In addition to nanoparticle synthesis, microemulsion method is also used for recovery of oil, fuel additive, paint, textile coating, cosmetics and pharmaceutical areas.

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2.2 PRECIPITATION

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INTRODUCTION

Superior magnetic, optical, conductivity and durability properties of nanomaterials allow them to be used in many industrial areas. Industry's interest in these material also led to a diversity in production methods. There are two main approaches in nanomaterial synthesis; one of them is production by starting from atom or molecule (bottom-top), another one is breaking large particles into smaller structures (top-bottom). In general, production methods of nanomaterials can be classified in three: solid phase methods, liquid phase methods and gas phase methods. Coprecipitation method is widely used in the industry as one of the liquid phase methods.

2.2.1 Chemical Precipitation

The most critical point of precipitation method is to synthesize the nanomaterial in situ and to study in the same liquid medium. This prevents physical changes and the aggregation of small crystals. Synthesis contains the reaction in the compound substance dissolved in the solution. Additive substance is added into the main solution before the precipitation reaction. Surfactant is used to preserve the separation between the formed particles. The resulting nanocrystal is separated via centrifuge, washed and dried with vacuum (Rajput, 2015).

Chemical precipitation is one of the most suitable liquid phase synthesis methods. Because the starting materials can be mixed in atomic level and they can synthesize metal-oxide and ceramic nanoparticles that have complete composition through chemical precipitation method. Figure 2.2.1 shows the basic steps of chemical precipitation.

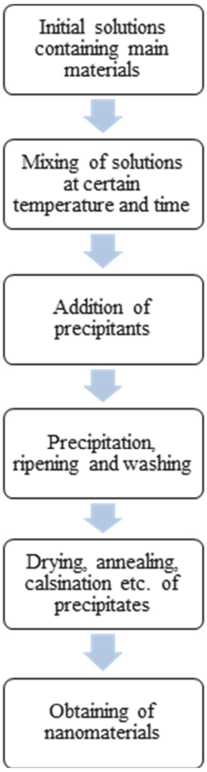

Figure 2.2.1. Flowchart of chemical precipitation process (Nuraje and Su, 2013; Cox, 2014; Zhong et al 2012)

First, main solutions consisted of starting materials such as metal oxides (eg. Li_2O_3), metal salts (eg. $FeCl_2$, $AgNO_3$) and organimetallic compounds (eg. $Fe(Ac)_2$) or hydrates of these (eg. $FeCl_2•6H_2O$), are prepared by dissolving these starting materials in a suitable solution (Zhong et al 2012). Widely used solutions are deionized water, ethanol, methanol and acidic solutions. Then, prepared solutions are directly mixed or one solution is added onto other one drop by drop. Although high reaction temperature is not needed, hours of vigorous agitation is required in order for starting materials to react. For many nanomaterials, this synthesis process is conducted in room temperature or a little bit higher temperatures. Precipitation of the dissolved substance from the solution can occur due to the low solubility. Two precipitation processes take place in chemical precipitation synthesis. In the first process, reaction products precipitate after the reaction is completed as shown in the below reaction because they have lower solubility in the solution;

$MgCl_2\ (aq) + 2\ AgNO_3\ (aq) \rightarrow 2\ AgCl\ (s)\downarrow + Mg(NO_3)_2\ (aq)$

In the second process, when the reaction products dissolve in the main solution, a precipitator (insoluble) is added into the solution to precipitate the reaction products (Zhong et al 2012). Precipitator mixes with the main solution, however, it does not dissolve the reaction products which cause the precipitation of the reaction products in the main solution-precipitator mixture. Second process is a form of coprecipitation, and since the solubility here is depended on pH, precipitation is sensitive towards pH (Zhong et al 2012). Certain pH level forces the reaction products into precipitation. Generally, metal salts require basic or weak acidic environments (Macingova and Luptakova, 2012). The popular precipitation agents used, such as NH_4OH, NaOH and Na_2CO_3, for the precipitation are basic materials. There are no strict rules about the addition time of precipitators into the system, however, precipitator is recommended to be added drop by drop in oder for the convenient control of the pH level. Before the separation of the precipitates, conditioning (maturing) period with waiting time from several hours to several days is required to obtain cleaner and bulk particles. Precipitates like metal hydroxides and metal complexes are often separated from the solution by centrifuge or filtering methods. Precipitates are subject to washout process several times by using deionized water, pure alcohol or other solvers in order to attain highly pure nanomaterials and to remove impurities. Precursor compound powders are obtained after drying for a sufficient amount of time at temperatures higher than 100°C or by freeze drying. Nanoparticle powders with desired crystal structures are obtained by applying thermal processing methods, such as tempering, sintering and calcination, to precursor compound powders for several hours at high temperatures (Macingova and Luptakova, 2012; Lateef and Nazi, 2016).

A chemical precipitation method is consisted of three main stages; chemical reaction, nucleation and crystal growth. Chemical precipitation kinetic is generally not a controlled process in terms of solid-phase nucleation and growth. Therefore, solid materials attained through chemical precipitation have larger particle size distribution and uncontrolled particle morphology due to agglomeration. In order to obtain nanoparticles with narrow particle size distribution, some certain conditions, such as supersaturation, homogeneous concentration distribution across the whole reactor and single growth time for all particles, are required (Macingova and Luptakova, 2012; Lateef and Nazi, 2016).

Another solution method widely used in the synthesis of multicomponent oxide ceramics is the "coprecipitation" that produces two or more simultaneous undissolved precipitates (Lateef and Nazi, 2016). Precursors used in this method are generally inorganic salts such as nitrate, chloride and sulphate. A homogeneous solution is created by dissolving these precursor compounds in water or another suitable solver medium. These salts are separated from the solution in the forms of hydroxides, aqueous oxides or oxalates with the use of pH tracking or vaporization process. Crystal growth and agglomeration processes are affected by parameters like salt concentration, temperature, true pH and pH change rate. After the precipitation process, solid mass is collected, washed and dried slowly by heating the solver medium up to boiling point. Washout and drying procedures applied for coprecipitated hydroxides affect the agglomeration degree in the final powder. Generally, calcination step is required to the convert hydroxide into crystal oxides. In majority of double, triple and quadruple systems, a crystallization step, which would be performed via calcination or hydrothermal procedure in high pressure autoclaves, may be required. Homogeneity of constituent distribution, relatively low reaction temperature, weak agglomerated particles, regular particle size and low costs are some of the most important advantages of the precipitation method. However, coprecipitation reactions are highly sensitive against environmental conditions. In addition, these reactions are not suitable for the systems that have amphoteric properties (Lateef and Nazi, 2016).

Summary

To summarize, chemical precipitation is consisted of two steps; chemical synthesis inside a liquid and solid state thermal processing. While first step determines the chemical composition and pre-crystal structures of the nanomaterials, second step affects the final crusyal structures and phase morphologies. Chemical composition is the most fundamental property that affects the performance and structure of nanomaterials. Therefore, mixing the starting material with a constant molar ratio during the synthesis process is the most important step. Generally, precipitated precursor powders are poorly arranged and have poor crystallinity. In addition, they exhibit large sizes and particle size distribution. Many chemical reactions, including dehydration, that take place during the thermal processing contribute to the regulation of properties such as crystallinity, crystal size, size distribution and phase transformation.

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2.3 SONICATION

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INTRODUCTION

Nanomaterials are inevitable parts of human life. New technologies and methods are constantly being developed for the synthesis of these materials. In addition to the conventional chemical reactions, emerging new methods can also be used to control particle sizes and particle size distribution of the nanomaterials used for energy conversions and biological applications. Ultrasonic synthesis, one of the synthesis method of nanomaterials, is an emerging technology that has an important potential for the production of large scale functional materials.

2.3.1 Sonication

Most of the living creatures use sound waves to communicate. Sound pass through an elastic medium as longitudinal waves in a series of compression and rarefaction cycles (Figure 2.3.1). This stimulates the medium, such as liquid, to cause replacement parallel to the direction of the wave (Ashokkumar, 2016). Frequency and acoustic amplitude are the most important properties that characterize the pressure wave (sound wave).

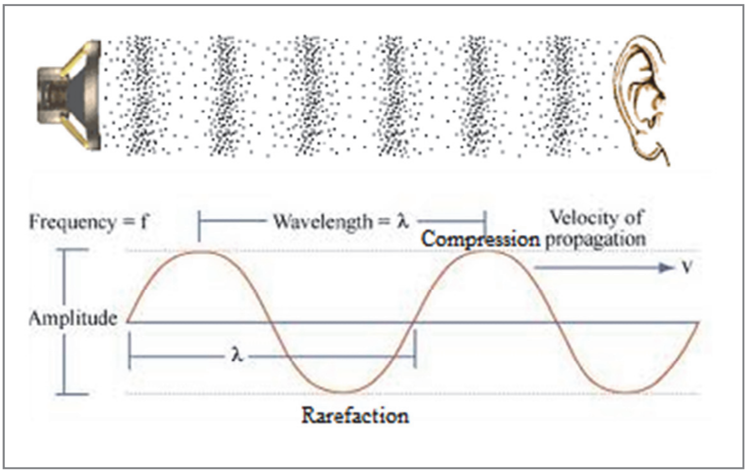

Figure 2.3.1. Sound wave

(http://www.mediacollege.com/audio/01/sound-waves.html ,
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Sound waves can be classified in different frequency ranges depending on their form and purpose. Frequencies lower than 20 Hertz (Hz) are called subsonic waves. Human ear cannot hear this sound. Sometimes infra-sound (subsonic) waves can be felt as shock waves like during earthquakes. 20 Hz-20 kHz is the hearing range of human ear. Frequencies higher than 20 kHz are called ultrasound. Based on the applied frequency, ultrasound use can be classified in two (Kuijpers, 2004);

- Low intensity, high frequency ultrasound (2-500 MHz, 0,1-0,5 W/cm^2)
- High intensity, low frequency power ultrasound (20-900 kHz, <10 W/cm^2)

First ultrasound type is used for medical diagnosis. This type of ultrasound is not used for reactions. On the contrary, power ultrasound uses its energy to form cavitations that contain bubble formation, growth and fluctuation (Kuijpers, 2004).

Generally, mechanical vibrations produced by sound waves are used in many applications such as quality control of food and other material, medical diagnosis, cleaning of small and large equipment, extraction and emulsification in pharmaceutical field (Ashokkumar, 2016).

Interaction of sound waves with water leads to some events. Especially as the ultrasound passes through a liquid medium, it strongly interacts with small gas bubbles present in the liquid. The interaction between gas bubbles and ultrasound leads to a phenomenon known as acoustic cavitation (Suslick, 1999).

In comparison to conventional energy sources, ultrasonic effect allows highly extraordinary reaction conditions otherwise not achievable by other methods, such as extremely high temperature and pressure in liquids. When liquids are exposed to ultrasound, compressed acoustic waves with changing amplitudes create bubbles and these bubbles vibrate. These bubbles are formed in the "negative" pressure period of rarefaction phase of the sound wave (Figure 2.3.2). Vibrating bubbles can effectively accumulate ultrasonic energy by growing up to a certain size. Under correct conditions, this bubble grows and then collapses. The intense energy accumulated inside the bubble (with heating and cooling ratio >1010 K/s) is then rapidly released with the collapse. Exploding collapse of the bubbles can cause extreme temperatures (5000 K) and pressures (1000 bar). These hot spots can lead to irreversible changes (Bang and Suslick, 2010).

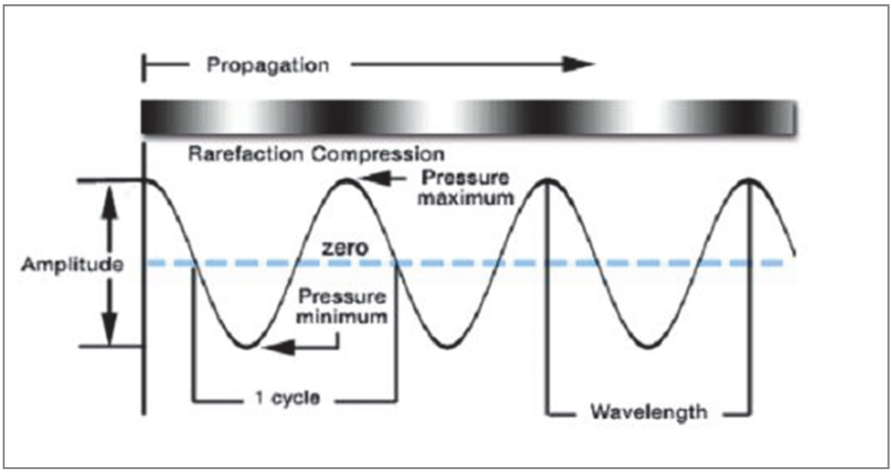

Figure 2.3.2. Representation of sound wave phases

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2.3.2 Bubble Formation Mechanism

Ultrasound waves in a liquid cause molecules to vibrate around their present locations. The distance between molecules reduced during the positive pressure cycle, and increases during the negative pressure cycle. In the presence of high enough intensity, the critical distance between the molecules is exceeded during the negative pressure period and a cavity forms (Kuijpers, 2004; Ashokkumar, 2016). Due to the presence of dissolved gases and nuclei such as solid foreign bodies, these cavities are formed under significantly lower sound pressure than expected (Kuijpers, 2004). After the formation of a cavity, a critical sound pressure must be exceeded for the exploding growth of this bubble. This exploding growth is monitored by implosive collapse (Figure 2.3.3). The bubble content is adiabatically heated during this collape; this leads to local short-lived hot spots inside the liquid. Depending on certain conditions, pressure and temperature inside the bubble can increase up to 200 bar and 5000 K, respectively (Leong, 2011; Kuijpers, 2004).

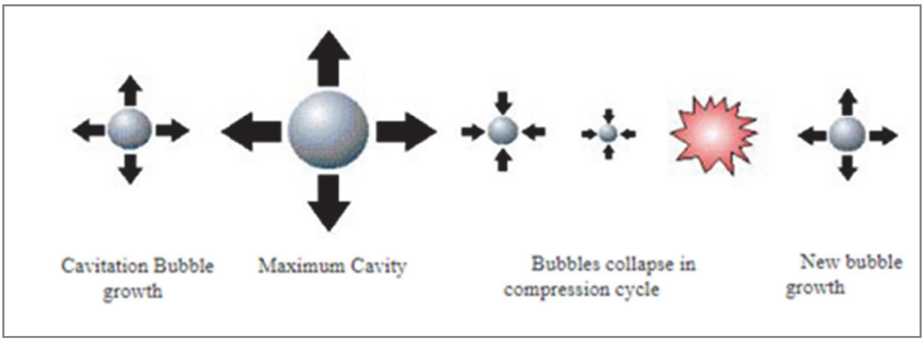

Figure 2.3.3. Formation and collapse of bubble

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Resulting high temperature and pressure levels cause a series of chemical reactions in and around the bubble. Extreme conditions convert acoustic energy into luminous energy which has a very short emission life (Figure 2.3.4). This interesting physics phenomenon, known as sonoluminescence, was first observed in 1930s (Bang and Suslick, 2010).

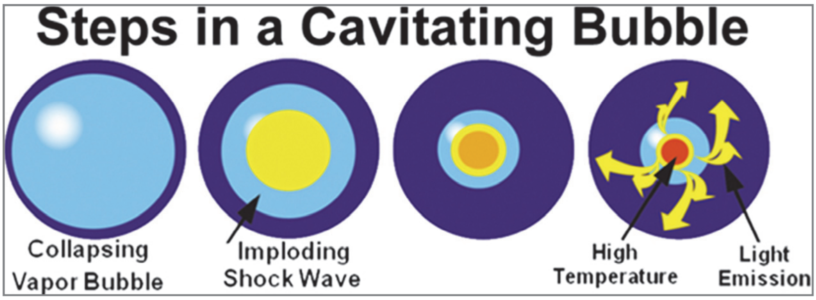

Figure 2.3.4. Conversion of acoustic energy into light energy

(This image is published on http://www.ecowaterchc.com/solution/cavitation-basics/ and retrieved from Google Images.)

Free radicals are formed with the sonolysis of water as a result of ultrasonic irradiation of the aqueous liquids. Primary sonolysis products in water are H* ve OH* radicals. These radicals either come back together to return their original forms or combine to produce H_2 ve H_2O_2. They may produce HO_2* radical by reacting with O_2. These strong oxidizing and reducing substances are used for various sonochemical reactions in aqueous solutions (Leong, 2011).

2.3.3 Synthesis Mechanism of Nanoparticles

The fundamental mechanism in the production of metal or metal compounds is the heat released from the cavitation bubbles. In order to produce metal and metal oxides, volatile metal complexes are used in organic solutions and metal salts in aqueous solution. These two methodologies have completely different mechanisms for the production of functional nanoparticles. Some researchers used volatile coordination compounds that contain zerovalent metal atoms to produce metal nanoparticles (Leong, 2011; Ashokkumar, 2016). Cavitation bubbles expand during the rarefaction cycle of the sound wave and volatile compounds vaporize inside the bubble. $Fe(CO)_5$ dissolved in octanol used for Fe nanoparticle production diffuses into the bubble and degrades during the collapse of the bubbles due to the high temperature conditions that lead to the formation of Fe nanoparticles. Produced material has amorphous structure and they exhibit high catalytic activity in comparison to its commercial counterparts (Leong, 2011).

While metal nanoparticle formation takes place in the hot regions of the cavitation bubbles in organic solutions, they are produced either in bubble/solution intermediate phase or in the bulk solution in aqueous solutions. Produced H atoms may act as reducing agents. When dissolved metal ion containing aqueous solution is exposed to sound waves, H atoms produced inside the bubbles are diffused into the bulk and react with metal ions to produce metal atoms that can agglomerate for metal nanoparticle production (Ashokkumar, 2016).

Ultrasonic synthesis of polymer nanoparticles has numerous advantages over conventional polymerization process (Kuijpers, 2004; Ashokkumar, 2016). Increased rate, particle size control, polymerization without initiator and single molecule weight distribution are some of the most important advantages. Mechanism of ultrasonic polymerization process includes both physical and chemical forces produced during acoustic cavitation (Figure 2.3.5). Initially generated shear forces and hairline forces on the interface help the production of nanometer-sized monomeric emulsion drops in aqueous phase. Primary and secondary radicals produced in the cavitation bubbles are diffused into the monomer drops that initiate the polymerization, thus, each monomer droplet is converted into a polymer particle. Surfactants added to the medium are used to make monomer drops stable. Reaction mechanism of ultrasonic polymerization is discovered by Bradley and Grieser (Bradley and Grieser, 2002).

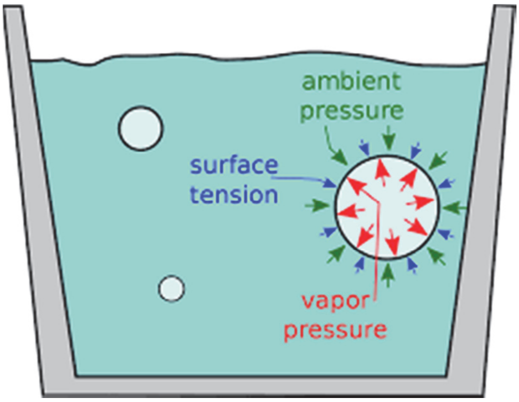

Figure 2.3.5. Physical forces that bubbles are exposed to

(This image is published on https://upload.wikimedia.org/wikipedia/commons/thumb/5/59/Superheating.svg/1280px-Superheating.svg.png and retrieved from Google Images.)

SUMMARY

Chemical outcomes of acoustic cavitation is very extensive, Bubble collapse in the liquids creates unique high-energy conditions to trigger chemical reactions in otherwise cold liquids. Benefits of sonochemistry are researched and a wide variety of important applications with exciting potentials are developed for the synthesis of extraordinary inorganic and biomedical materials. Development of effective drugs for the disease treatment by using ultrasound is a commonly used area with health benefits. Another emerging area is the use of ultrasound to provide new food substances and studies are especially focused on the production of new dairy products.

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2.4 ECO-FRIENDLY SYNTHESIS (GREEN CHEMISTRY)

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INTRODUCTION

Investments on nanotechnological research and applications are growing everyday, thus, increases the concentration of nanostructures in the nature as a result. Although we have very limited information about the impacts and risks of nanostructures on the environment and human health, they are already incorporated into the compounds of various commercial products [Andreotti et al., 2015]. Nanomaterials change the properties of any material with their characteristics that make them appealing, such as surface chemistry, surface area, size, shape and functionalization. Therefore, in recent years, scientists are working on different methods for the synthesis of nanoparticles. However, since the chemicals used in conventional synthesis methods are known to have adverse effects on lively life, Green Chemistry method is preferred for the synthesis of nanoparticles. This way, nanoparticles can be intracellularly or extracellularly synthesized from extracts and metal ions that are acquired from yeast, fungal bacterias or plants, which have extensive application fields.

2.4.1 Historical Overview

The process had started in mid 20th century by establishing environmental protection rules, environmental regulations and environmental awareness rules and became official with the formation of Environmental Protection Agency (EPA) in 1970. Scientists, who are concerned with the future, shifted from pollution elimination to pollution prevention with these initiatives and the office of "Pollution Prevention and Toxic Substances" was formed in 1988 within EPA. Initiatives of EPA continued with their contribution to "Green Chemistry: Theory and

Application" authored by Paul Anastas and John C. Warner in 1998. In 2001 and 2005, Knowles, Noyori, Sharpless, and Chauvin Grubbs, Schrock received Nobel Prize, respectively. These Nobel Prizes reinforced the importance of researches in "Green Chemistry" field and helped scientists to raise a higher awareness that the future of chemistry must be more "green".

2.4.2 Principles of "Green" Synthesis

12 principles of Green Chemistry, as mentioned in "Green Chemistry: Theory and Application" book by Anastas and Warner, can be listed as follows [Anastas and Warner, 1998].

- **Waste prevention:** It is better to prevent waste than to treat or clean up waste after it has been created.
- **Atom economy:** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- **Less hazardous chemical synthes:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- **Designing safer chemicals:** Chemical products should be designed to affect their desired function while minimizing their toxicity.
- **Safer solvents and auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- **Design for energy efficiency:** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- **Use of renewable raw materials:** A raw material should be renewable rather than depleting whenever technically and economically practicable.
- **Reduce derivatives:** Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- **Design for degradation:** Chemical products should be designed so that

at the end of their function they break down into innocuous degradation products and do not persist in the environment.

- **Real-time analysis for pollution prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- **Inherently safer chemistry for accident prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

2.4.3 Methods

Synthesis of nanoparticles can be achieved through many physical and chemical methods (electrochemical reduction etc.) [Bar et al., 2009]. Despite being successfully synthesized by different methods, environmental friendly, inexpensive, biocompatible methods are being studied in recent years due to the high cost of the methods, and environmental and biological risks of the hazardous chemicals used. Nanoparticles prepared by eco-friendly synthesis and other biological methods are simple in application, they are economic, compatible with biomedical and pharmacological applications and convenient for commercial production [Flippo et al., 2010].

Nanoparticles can be synthesized by using living organisms or chemicals such as plant extracts, microbes, fungi, yeast, algae, virus etc. [Bar et al., 2009, Kasthuri et al., 2009, Philip et al., 2010, Dubey et al., 2010].

In order for a synthesis method or a material to be environmentally friendly, it needs to have a safe, single reaction step, not produce any waste, use renewable raw materials, have acceptable environmental hazard, 100% efficient and the resulting nanoparticle must be easily separated from the reaction medium.

2.4.4 Application Examples

Below listed success examples of environmentally friendly studies show how green chemistry affects a wide range of fields from pharmacology to household goods and offers a way to a better world. In addition to the examples, during the transition of environmentally friendly studies from research to practical stage, 2005 Nobel Prize in Chemistry was rewarded to the discovery of a catalytic chemical process called metathesis that has a wide applicability in chemistry industry. The process has the potential of using significantly less energy and reduces the greenhouse gas emissions for many important processes. In addition, this is a system that is stable under normal temperatures and pressures can be used with environmentally friendly solvents and produces less hazardous waste. In 2012, Presidential Green Chemistry Challenge Award was given to a study on a catalyst technology to break down natural oils and recombine the fragments into novel, high-performance green chemicals. This study was translated into practice with the production of special chemicals for many areas of use such as high concentration cold water detergents that provide better cleaning with reduced energy costs.

Computer Chips

Many chemicals, large amount of water and energy are needed for the manufacturing of computer chips. In a previously conducted study, the ratio of chemical and fossil fuels required to manufacture one computer chip was found to be 630:1. It means that in order to manufacture one chip, it is necessary to use source materials 630 times as much of the chip's weight. To compare, this ratio is 2:1 for an automobile. Feather-based printed circuit boards, which can work twice as fast as conventional circuit boards, are produced by using light and mechanical and thermal stress resistant fibers made out of protein and keratin found in feathers. Although this technology is still being used for commercial purposes, conducted studies led to the discovery of other use areas for feathers as source material, including biofuel.

Medicine

In the pharmaceuticals industry, new methods to develop drugs with fewer side effects and to use processes that produce less toxic wastes are being sought.

A safe, highly efficient active pharmaceutical ingredient that produces less waste is developed by enzymatic methods with environmentally friendly biocatalysts for use in Type 2 diabetes. Although high amounts of hazardous reagents and toxic waste are involved in the formation of multistage conventional prescription for the treatment of high cholesterol, with the green synthesis that uses synthetic enzyme and low-cost raw materials, wastes and hazardous substances are reduced and low-cost drugs that meet consumer needs are offered.

Biodegradable Plastics

Instead of using petroleum-derived plastics for water bottles and yoghurt containers, environmentally friendly production is enabled with the use of microorganisms that transforms corn starch into a resin that is as strong as plastics. Studies to obtain biodegradable raw materials from bio-waste are ongoing.

Starch-based and calcium carbonate augmented biodegradable market bags that are burst and tear-resistant, waterproof, printable and flexible can be manufactured. Using these bags, which can be completely decomposed in water, CO_2 and biomass, in industrial compost system instead of commercial plastic bags will significantly reduce household waste very soon.

Paint

When oil-based alkyd paints are dried, they cause large amounts of volatile compound to evaporate and lead to more environmental impact, however, new paints using soy oil and sugar mixture instead of fuel-fossil-derived paint resin are discovered and they reduce the hazardous volatile substance levels by 50%. Water-based acrylic alkyd paints with low levels of volatile compounds can be produced from recyclable soda bottle plastics (PET), acrylics and soy oil.

Results

EPA and ACS (American Chemistry Society) play an important role in supporting the research and education on pollution prevention and reduction of toxic substances conducted by Green Chemistry Institute for the past thirty years. Governments and scientific institutions around world have stated that application of green chemistry and engineering will not only lead to a cleaner and more sustainable world, but they will also do good in terms of positive social and economic impacts. Since 1996, the United Nations has been annually awarding the Presidential Green Chemistry Challenge Award to reward and celebrate the significant achievements in Green Chemistry. Success of green chemistry for a better world is proved by its wide range of applications from medical products to household goods.

Summary

- Since green chemistry has a low cost most of the time, pollution prevention is cheaper than pollution reduction.
- If a valuable use can be found, waste is not a waste. However, it is more favorable to find a better process to eliminate the waste.
- Chemical accidents caused by human errors will be frequently encountered. If the chemicals used are nontoxic, severity of the accidents will be significantly reduced.
- A green and sustainable society cannot be built overnight: The journey is long and uncertain.
- In an ideal chemistry factory, the waste free product is targeted. The better a real factory uses its waste, the closer it is to its ideal, the greater is the gain.
- Green chemistry can guide chemists in the design of both effective and safe products.
- Green chemistry is part of a multidisciplinary approach directed at building a sustainable society.
- Technological advancements should not come at the cost of health and prosperity of future generations.
- Green chemistry may remove the necessity of choosing between technology and sustainability.
- Governments and scientific communities around the world agree that green chemistry and engineering applications will not only lead to a cleaner and more sustainable world, but they will also do good in terms of positive social and economic impacts. These advantages encourage businesses and governments to support the development of sustainable products and processes.

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2.5. SOL - GEL METHOD

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INTRODUCTION

Sol - Gel process is one of the liquid-phase synthesis methods, which is a bottom-up approach, used in nanomaterial production. What makes liquid-phase important is that it creates the most suitable medium to let materials affect each other by coming together at a certain ratio. [21 and article]. Sol-Gel method, as with other liquid-phase methods, is about forming a solid gel in a liquid phase from a suspension consisted of solid metal salts by utilizing the effects of catalyst agent and medium. "SOL" repre-sents a suspension consisted of liquid and solid particles, while "GEL" represents the solid state of this suspension.

Sol-Gel method is a economic and low-temperature method for small scale production of nanomaterials; it is easier than other nanomaterial production methods and it can be performed under laboratory environments (at room temperature). Conversion of attained gel into glass was first used in 1970s. The method gained immediate interest as it allowed for nanomaterial pro-duction with low energy consumption. This interest kept growing in 1980s and used in glass manufacturing by a German company.

Abundant variety of nanomaterials that can be produced by Sol-Gel meth-od, size differences, purity rates and homogenous distributions made this method an inevitable technique of technological and scientific studies. [5,8,9, article]. It is most widely used for ceramic production.

Generally, the Sol-Gel process is based on hydrolysis and subsequent condensation (the process where two molecules combine together by removing a small molecule, like a water molecule, they have inside) of metal oxide pre-initiators, such as nitrate, sulphate etc., with or without catalysts, inside ethanol or water based acidic or basic solution.

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[1] ***Condensation:*** *The process where two molecules combine together by removing a small molecule, like a water molecule, they have inside*

Alkoxides present inside a water - alcohol solution are removed from the medium through hydrolysis by pre-initiators (acidic or basic). Metal oxide bonds are formed from the metal that remains in the structure after hydrol-ysis and they create a mesh-like structure by growing to make the whole volume consisted of Metal + Oxide + Metal, and then gel is formed. At-tained gel is left for aging and porous gel (xerogel) or nanomaterial pro-duction by burning with high-temperature processing is performed.

In the past, this method was used only for small amounts of nanomaterial production, however, today this method is well-established in the industry and became a standard procedure.

Keywords: Nanomaterial production method, sol-gel

2.5.1 Sol - Gel Method Production Stages

- ✓ Hydrolysis of pre-initiators
- ✓ Condensation
- ✓ Gelling
- ✓ Aging
- ✓ Drying
- ✓ High-temperature processing

The most important feature of this method is that it allow ceramic material production at 8 oC–room temperature.

Figure 2.5.1. Hydrolysis and condensation mechanisms

Alkoxide groups inside the alcohol-water solution are gradually removed by hydrolysis in the presence of acidic or basic catalyst and replace the hydroxyl groups that will form the metal + oxygen + metal bonds.

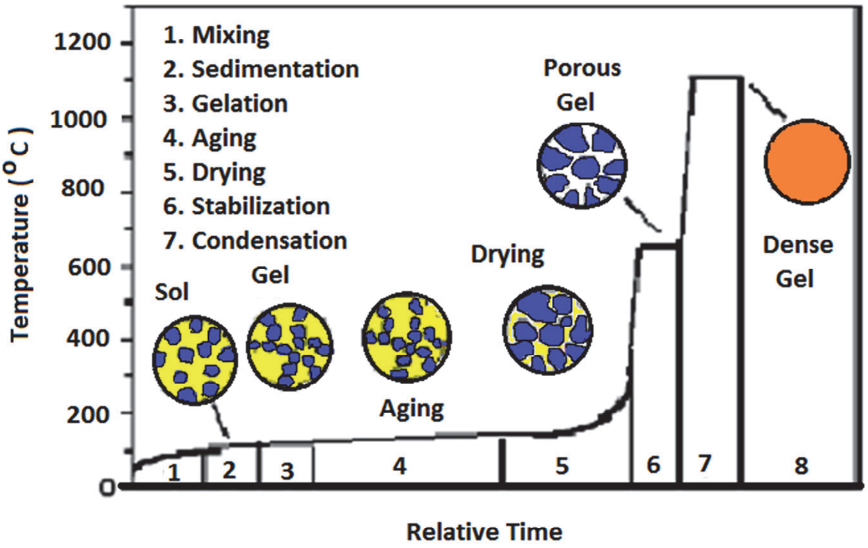

Figure 2.5.2. Schematic representation of Sol - Gel Method

(https://www.ttu.ee/public/m/.../Lecture12_Synthesis2.pdf)

Sol-gel process has a particular importance since all chemical reactions and all starting and resulting materials can be controlled.

Products with different characteristic properties can be obtained under similar experiment conditions. The reason is each step of Sol - Gel pro-cess causes different effects on final product to be produced. Therefore, product-specific process steps are required for the desired final product with utmost attention in all steps.

2.5.2 Sol-Gel Material Components

Sol-gel process involves the transition of the sol compound from a liquid “sol” phase to solid “gel” phase. Inorganic sol and gels are directly pro-duced with synthesis from chemical reagents that are generally dissolved in a liquid medium. The reagent that contains a metal (M) cation in an inor-ganic sol or gel is called pre-initiators. The chemical transformation of this structure is significantly complex.

Conversion of sol into gel also involves very complex reactions on a mo-lecular level. These reactions enable controlled distribution of dense col-loidal particles inside the sol or allows agglomeration of these in the gel to be controlled.

The components used in Sol-Gel process can be classified as follows;

Pre-initiators

All soluble pre-initiator can be used in sol-gel process. These can be defined under two main groups: Metal salts and alkoxides

a) Metal Salts

The general formula of metal salts is MmXn. Here, M metal, X an anionic group, and m and n stoichiometric constants. $AlCl_3$ can be given as an example for metal salts.

b) Metal Alkoxides

Alkoxides are expressed in M(OR)n general formula. Aluminum ethoxide (Al(OC2H5)3) can be given as an metal alkoxide example.

Metal alkoxides actively participate in reactions. These compounds are highly reactive in the presence of humidity, heat or light.

Table 2.5.1. Alkoxides

Alcohol R(OH)	**Alkoxide**
Methanol (CH_3OH)	Methoxide
Ethanol (C_2H_5OH)	Ethoxide
1 – Propanol (n – propanol) (C_3H_7OH)	1 – Propoxide (n – Propoxide
2 – Propanol (iso – propanol) (C_3H_7OH)	2 – Propoxide (iso – propoxide)
1 – Butanol (n- butanol) (C_4H_9OH)	1 – Buthoxide (n – buthoxide)
2 – Butanol (C_4H_9OH)	2 – Buthoxide (sec – buthoxide)
2- Methyll propanol (iso –propanol) (C_4H_9OH)	2 – methyl propoxide (iso - propoxide)

2 – Methyll – prop –2– ol (tertio – butanol) ($C_4H_9(OH)$)	Tertio buthoxide

Solvents

As metal salt and alkoxide pre-initiators used in the method vary depend-ing on the type of the nanomaterial to be produced, solvent must be se-lected according to the pre-initiator type. Pre-initiators must go into reac-tion inside the solvent used. Therefore, if metal salts are used as pre-initiators, solvent must be water, and if metal alkoxides are used, solvent must be alcohol [4, 6, 11, 14].

Catalysts

Catalysts used in Sol-Gel method are studied under to main categories. These acidic catalysts and basic catalysts. Generally used catalysts are given in Figure 2.5.3.

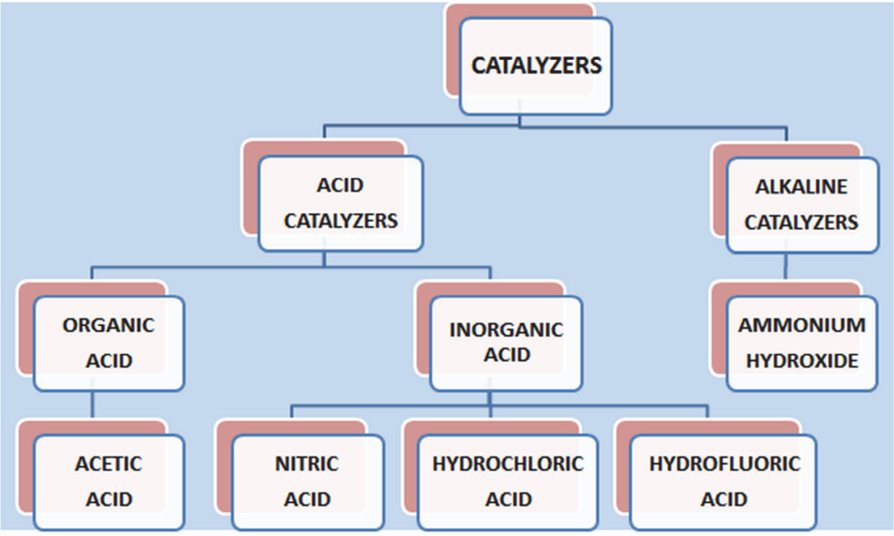

Figure 2.5.3. Catalyst types

2.5.3 3. Structures Created in Sol-Gel Method

Sol-Gel method uses more suitable conditions for nanomaterial pro-duction in comparison to other methods. Therefore, Sol-Gel method is used to produce different products with various physical properties like fibers, films, monoliths and particles.

Production by Sol-Gel method continues to gain importance day by day in various fields, such as catalysts, sensors used in chemistry, membranes, fibers, optical sensors, development of new materials for chemical devices, ceramic production, and nuclear and electron-ics industries.

2.5.4 Coating with Sol – Gel Method

Dip Coating

In this process, material to be coated is dipped into the solution and pulled back at a specified speed under controlled atmosphere and controlled temperature. A thin film forms on the surface of the material to be coated. The thickness of this film changes depending on the maximum pulling speed, viscosity of the liquid and the content of the solid onside the liq-uid.

The next step is the condensation of the solvent and tempering after gel-ling in order to obtain oxide coating.

Angle-based Dip Coating

In this method, thickness of the coating depends on the angle between the bottom layer and the liquid surface; therefore, different layer thicknesses can be achieved on the top and bottom sides of the bottom layer.

Spin Coating Process

This method is used to perform thin coating on flat surfaces. The ma-terial to be converted into coating is dissolved or dispersed with a solvent. Dispersed coating material is accumulated on the bottom layer and then spinned until a smooth layer is obtained.

Flow Coating Process

In this method, liquid coating material is poured onto the material to be coated. Coating thickness depends on the inclination angle of the bottom layer, viscosity and solvent vaporization rate. Advantage of the method is that it provides easy coating for non-planar large surfaces.

2.5.5.Advantages of the Sol-Gel Method

- ✓ Sol-Gel method allows materials to form oxide compounds and enables the production of organic or inorganic materials.
- ✓ Except for the condensation step, it allows material production at low temperatures and prevents thermal degradation of the material.
- ✓ Highly pure materials can be produced.
- ✓ High-porosity materials and nanocrystals can be produced.
- ✓ Since each step can be controlled during the material production, particle size, amount of pores, surface roughness of the material to be produced can be controlled
- ✓ As liquid starting materials are used, it provides shape variety in ceramıc material casting without melting the materials and allows the production of thin film and fibers.
- ✓ This method is widely used in optical part manufacturing since the materials produced with this method have high optical quality.

2.5.6. Disadvantages of The Sol-Gel Method

- ✓ Pre-initiator materials are generally expensive and sensitive against humidity. This situation causes errors in special applications like large scale optical coatings.
- ✓ Method takes a lot of time due to its multi-stage structure.
- ✓ Aging and drying processes must be conducted very carefully and meticulously. Desired properties cannot be obtained because of the dimensional changes and strain fractures during aging and drying stages.
- ✓ Method does not allow for large scale production.

Summary

Sol-Gel method is the most widely used liquid phase method. The method is low cost and it allows nanomaterial production in laboratory conditions with a simple setting. However, costs increase for large scale productions due to the multiple stages involved. It allows for production of nanomaterials that have different shapes and sizes. Nanomaterials with more homogeneous structures can be produced in comparison to other methods. Shape and size of the produced material can be changed by meticulous control of the process steps. In addition, even surfaces of complex shapes can be coated with Sol-Gel method.

Sol-Gel method is an important and widely used technique for nanomaterial production.

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2.6 PHYSICAL VAPOR DEPOSITION METHOD (PVD)

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INTRODUCTION

Today, nanoparticles can be produced by using many different meth-ods. Production methods of nanoparticles can be examined under two main topics. These are wet chemical synthesis and synthesis un-der gas phase environment. These methods have various advantages and disadvantages over each other. Nanoparticles to be produced in gas phase environment are either particles that are obtained by form-ing gas phase from a solid-form material in a vacuum environment or thin film coatings. One of the most common techniques for synthesis in gas phase environment is the physical vapor deposition (PVD) method.

PVD is a common method used in industry for thin production and coating in high vacuum environments. This method is being used since 1800s and now, in parallel with the development of nanotech-nology, it is used to produce nano-scaled materials and perform coat-ings with nanometric thicknesses. PVD is a thin film coating tech-nique that is commonly used in medicine, automotive industry, metal processing industry and other industries. Physical vapor deposition method is defined as the accumulation of physically vaporized or ejected particles on a substrate. These techniques have many types and most common ones are sputter and vaporization methods. Nano-particles to be produced using this method are obtained through sub-limation on a substrate or as powder in a gas phase environment. The most important feature of this method is that it enables controlled acquisition of particles in a vacuum environment without requiring different solution mediums necessary for chemical reactions. This way, particle crystallization, size and shape can be easily controlled. Parameters that regulate the properties of the particles are pressure, gas flow and thermal heat values of the production environment.

2.6.1 Sputter Technique

Sputter technique is based on the physical accumulation of atoms, which are ejected from a target material by positive ions, on a sub-strate. In order to produce a material with this method, the environ-ment called vacuum chamber, where the reaction will take place, is vacuumed by using a vacuum pump. Then, a controlled inert that gas does not react is used inside the vacuum chamber. This gas is general-ly Argon (Ar). Ar atoms are ionized by colliding them with electrons that are accelerated under a high electrical field. Ar atoms, which are now + ions, move towards cathode inside the electrical field and they eject atoms from the target material, which is placed in front of the cathode, by hitting the said material. The process is concluded by the deposition of these atoms, which gain kinetic energy as a result of this collision, on the substrate that is placed in front of the anode (Figure 2.6.1). Depending on the target material that is wanted to be grown, two different sputter processes can be performed, namely, DC and RF voltage. DC sputter is used if the target material is a conducter and RF sputter technique is used when the desired materi-al will be produced out of conductor and semi-conductor targets.

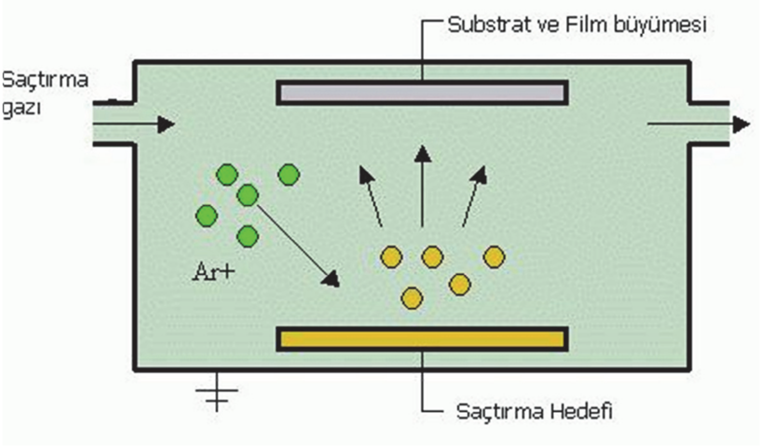

Figure 2.6.1. Schematic view of sputter system

(https://en.wikipedia.org/wiki/Sputter_deposition)

In magnetron sputter technique, magnetic field is used to confine electrons that are close to the target in order to control the amount of atoms wanted to be grown and to eject atoms from a specific region of the target material (Figure 2.6.2). This way, Ar atoms ionized in these areas can eject atoms from the target material.

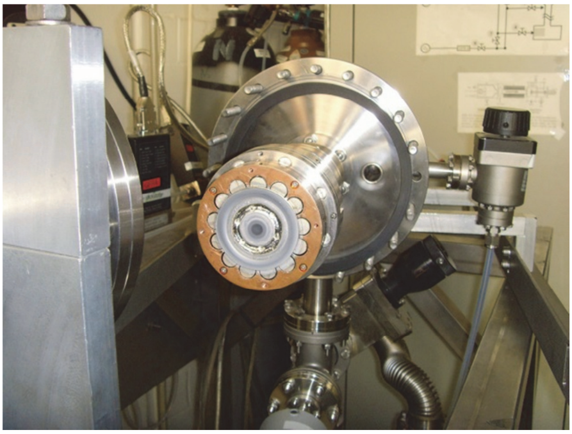

Figure 2.6.2. Target and magnets of a magnetron sputter system

Schematic view of a magnetron sputter system used to grow nanopar-ticles is shown in Figure 2.6.3.

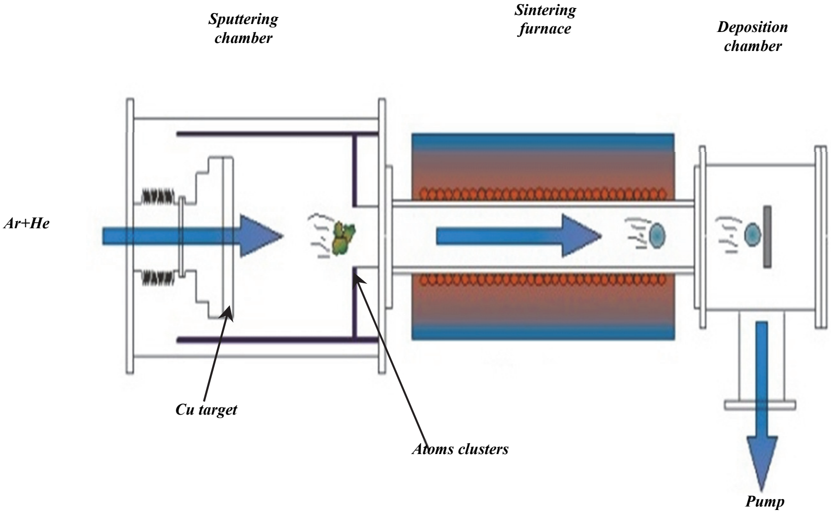

Figure 2.6.3. Schematic view of magnetron sputter system used to produce nanoparticles

High resolution transmission electron microscopy (HRTEM) images of nanoparticles with different types and properties obtained by this method are shown in Figure 2.6.4.

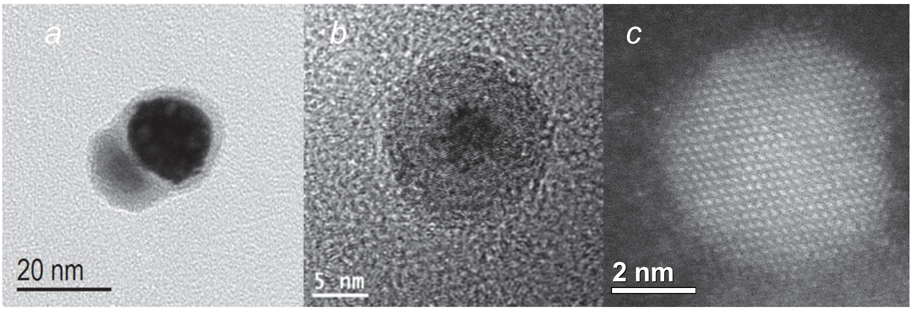

Figure 2.6.4. HRTEM images of a) Fe-Bi dumbbell-like, b)Fe-Mg core-shell, c) Cu nanoparticles produced by magnetron sputter method

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2.7 CHEMICAL VAPOR DEPOSITION METHOD (CVD)

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INTRODUCTION

Chemical Vapor Deposition Method (CVD) is a material production procedure that is being used for many years in material science. In general, this method allows obtaining a gas-phase material in solid form. This method is used for surface coating of materials, which are generally named as thin film.

This method is based on the deposition of the material consisted of gases on determined suitable substrate surfaces by going through chemical reaction with a carrier gas under temperature and in mediums such as plasma. Although this method is used to produce thin films on a material, it is also being used to obtain high-purity bulk materials, powder materials, and, recently, nanomaterials. Nanometric material production can be conducted by controlling the necessary parameters in the system like gas flow rate, deposition duration, pressure and temperature. Especially in recent years, CVD has become one of the most important production techniques used to obtain carbon allotropes of artificial diamond, graphene and carbon nanotubes. Wide variety of different materials can be produced by CVD method.

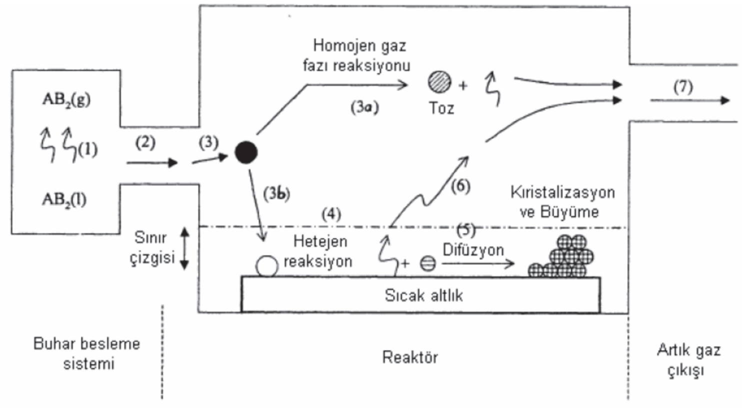

Figure 2.7.1. Chemical vapor deposition method

(Karslioglu, R., (2007), Production of SnO2 Coatings by Chemical Vapor Deposition Method, Master Thesis, Sakarya University, Institute of Science)

In CVD method, material or materials to be produced are put into the system in gas form and are deposited on a substrate surface, which is a specified heated catalyzer, as a chemical vapor. Chemical reaction occurs on hot surface or close to it. Formed vapor creates a film layer on the substrate surface it is deposited. Unwanted reaction products, that are produced as a result of the reaction, are removed from the system as vapor. Steps of a basic CVD production methods are as follows;

- A mixture of reactant gases, carrier gases and inert gases is sent into the vacuum chambers, where the reaction will take place, in certain ratios and flow rates,
- Gases that will react move on the substrates used as catalyzer,
- Reactants are absorbed from the substrate surface,
- Surface and reactants go into chemical reaction and a thin film is formed on the surface.
- Inert products are removed from the vacuum chamber.

CVD method has many advantages. Produced thin films have a very homogeneous distribution in terms of thickness and matter quantity. Another advantage over other methods is the fact that many different materials can be produced by this method. Produced materials can be obtained in significantly pure forms. Deposition rate is very high in CVD method. Therefore, it doesn't require high vacuum values.

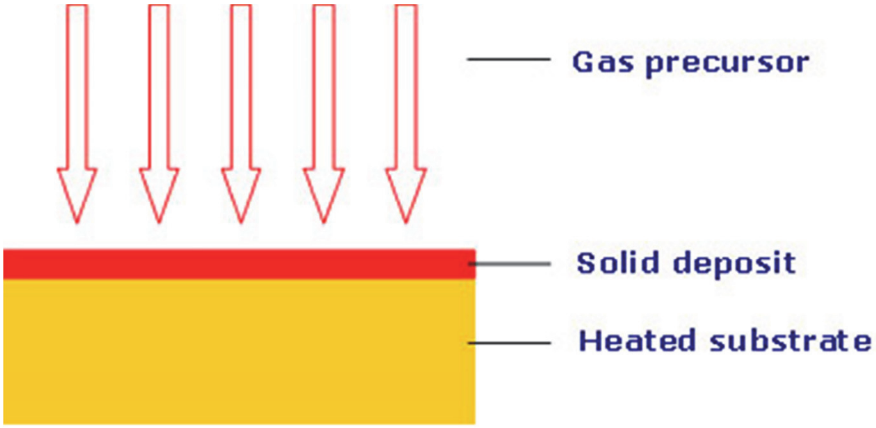

Figure 2.7.2 Chemical Vapor Deposition Method

There are different types of CVD methods that enable the production of materials required for various application fields. These methods include hot wall reactors, cold wall reactors, atmospheric pressure CVD, and low pressure CVD.

- Hot Wall CVD: In the system, the reactor walls, where the reaction takes place, are also heated during the heating of the substrates.
- Cold Wall CVD: This method is based on keeping the reactor walls, where the reaction occurs, cold. IR-lamps are used inside the reactor for the heating system.
- Atmospheric Pressure CVD (APCVD): Reaction occurs under atmospheric pressure. Production method is significantly easy and rapid. Production temperature is cold. Contamination is high.
- Low Pressure CVD (LPCVD): Reaction takes place under medium pressure (30-250 Pa) and high temperature. High quality and purity products are obtained. This method requires high temperature and production rate is slow.

Generally, temperature requirement for CVD production is between 200 and 1600 oC. In addition, there are other CVD techniques like Plasma CVD, Laser CVD, Hot Filament CVD.

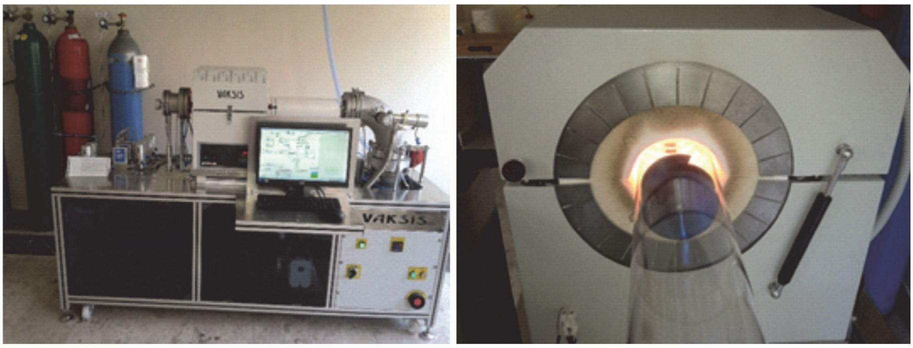

Figure 2.7.3 Graphene production on Cu with Thermal CVD system

Materials wanted to be produced must be in gas form under room temperature and this condition can be given as one of the disadvantages of the method. This makes it difficult to produce many elements. In addition, most of the gases used in CVD method are toxic and flammable. They are required to be disposed of without damaging the nature and the environment. Therefore, an additional filtering system is required. And some gases may be expensive.

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2.8 LITOGRAPHY

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INTRODUCTION

Most of the top-down miniaturization methods starts with litography, which is used to transfer the copies of a master mould onto the surface of solid material like a silicon chip plate. The word litography is derived from “Lithos - stone + graphein - to write” and called as “stone print” in the literature. In this chapter, different forms of litography will be discussed in detail and their differences from most of the miniaturization processes will be put forward.

2.8.1 Historical Development

Although many attempts had been made to copy using various resins under day light, Nicéphore Niépce had managed to copy a worn down print onto an oil paper placed on a glass plate that is coated with tar (asphalt) dissolved in lavendar oil (French, 1822). After 2-3 hours under sun light, it was observed that unshaded regions on the tar were more soluble and became more rigid than shaded regions that can be washed with a mixture of turpentine and lavendar oil. Niépce's recommended mixture corresponds to a negative-type photoresist. Five years later, in 1827, a Parisian engraver Lamaitre managed to make a worn down copy of a engraving piece of Cardinal d’Arnboise by using a strong acid on a layer developed by Niépce. Latest copy represents the first mould transferred by photolithography and chemical milling [Pfeiffer, 2010].

Actually, the word litography (means stone [lithos] and to write [graphein] in Greek language) defines a process that was discovered by Aloys Senefelder in 1796. Senefelder found that when a stone (Bavarian limestone) is suitably inked and processed with chemicals, an engraved image can be transferred onto paper. The chemical processing of the stone pulls the ink to the area with image and water to the area without image; therefore, these areas become lipophilic (hydrophobic) and lipophobic (hydrophilic), respectively.

Niépce process became one of the most important studies in early development of photography. In recent years, the photomasking performed subsequent toafter chemical processing has opened the way for photolithography that is used for integrated circuit production and miniaturization sciences. Not only until the Second World War, method was further developed even 100 years after Niépce and Lemaitre and first applications of printed circuit board had emerged. Connections are made by soldering electronic parts on to a mould of "wires" produced by photoradiation of copper folio layer that is plaalced layer-by-layer on a plastic plate. Starting from 1961, new methods are invented for transferring many number of transistors onto a thin silicon slice by using photoetching process. Today photolithograpy, x-ray lithography and charged particle lithography all achieved sub-micron printing.

Lithography (or shaping) includes shapes of various components of integrated circuit (IC), their sizes and a series of process steps to determine the location. Current development in IC design is possible by shaping the small areas on the chip plate by utilizing reduced chip sizes (miniaturization) and increased density of transistors. Therefore, majority of IC design success is achieved by lithography [Chou, 1996].

For lithography process, first a printed copy of the mould must be produced. This called reticule or mask. The process is completed by transferring the design on the mask onto the chip plate [Piner et al, 1999]. Transfer can take place with a 1:1 ratio (i.e. without any reduction in the size), however, generally the size is reduced, thus, mould is transferred to a small area on the chip plate. This is achieved by using lenses that are suitable for mould reduction. Lithography has two stages, and each of them has several steps:

1. In the first stage, mould is transferred to a photoresist layer on a chip plate. Photoresist is mildly sensitive material and its properties change when exposed to light with a certain wavelength. This process is called developing. The mould formed in this step is temporary and it can be easily removed. This is particularly important if the mould is not fully aligned with the chip plate or another mould on the chip plate.

2. Mould is transferred from photoresist to chip mould. Exposed chip plate surfaces or layers accumulated on top of that can be etched (removal of material).

Dopant materials are added to the partitions of chip plate along the mould. This is the final stage, and the removal of the formed moulds without damaging the chip moulds underneath is a difficult process.

After mould is formed on the photoresist and chip plate surface is exposed (developing process), exposed chip plate surface is etched. It is possible to accumulate material on the exposed surface [Parikh, 2008].

Photolithography is the most widely used lithography method. In the IC industry, mould transfer from masks to thin films almost started with photolithography. Correct recording and a series of exposure of successful moulds result in complex, multi-layered ICs. This two-dimensional process has a limited tolerance for non-planar topography; this also introduces a major limitation for non-IC miniaturized systems that exhibit extreme topographies. Photolithography developed very rapidly and maintained a constant advanceement with its ability to resolve even the tiniest properties. This ongoing improvement prevented the adaptation of alternative high-resolution lithography techniques, such as x-ray litography, for IC industry.

2.8.2 Photoresists

The use of photoresists in chip plate production had started in 1950s. This technology was adapted from photography industry. There are general purpose resists and resists that are specific for special applications. These are generally adjusted to a certain wavelength. Components of a photoresist are as follows:

1. Polymer - a light-sensitive polymer with properties that change when exposed to light. The desired characteristic is generally a resolution that changes in a certain solvent.
2. Solvent - solvent is used to thin the resist, thus, it can be applied onto chip plate with spinning process. Solvent is generally removed by heating up to 100°C, a method known as soft roasting process.
3. Sensitizers - they are used to control the chemical reaction during exposure.
4. Additives - Various chemicals added to achieve certain processes like painting.

Photoresists general initiate the reaction with ultraviolet (UV) or visible light, therefore they are called optical resists. In addition, there are special resists for other radiation types like x-ray and e-beam.

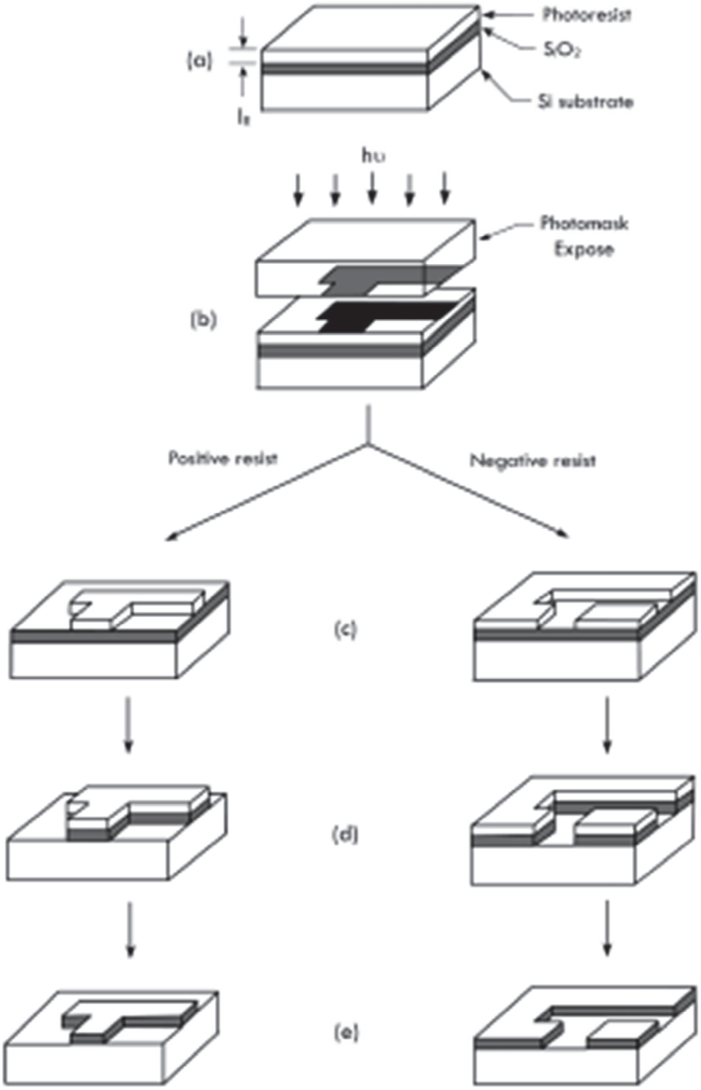

Figure 2.8.1. Schematic view of positive and negative resists

Generally, photoresists are classified in two groups:

1. Positive resists - These become more soluble when they are exposed to UV rays.
2. Negative resists - These become less soluble when they are exposed to UV rays.

Differences between these two types are shown on Figure 1. Photoresists directly transfers the mould from mask to the chip plate, therefore, mask protects the resist lower than itself against exposure to UV rays. Remaining part of the resist, the exposed part, becomes more soluble and can be easily removed [Ivanisevic, 2001]. On the other hand, negative resists transfer the negative of the mask mould onto the chip plate. This is a process similar to the negative process of photography. For negative resists, the part protected by the mask is more soluble because it is not exposed to UV ray and radiation makes the remaining part of the resist more rigid [Kim, 2008].

2.8.3 Nanolithography

Nanolithography is a branch of nanotechnology and it is related to the studies and applications of nanoproduction of nanometer-sized structures, and it is the nanocoating of at least one horizontal dimension between the sizes of an atom and 100 nm. Although it means small writing on stone, recently it is also used, in terms of nanotechnology, for nanoproduction of groundbreaking semi-conductor integrated circuits, nanoelectromechanical systems (NEMS) [Ruizab and Chen Christopher, 2007] or other applications that are related to other various scientific branches in nanoresearch [Venugopal and Kim, 2013].

There are many lithography techniques where micro/nano coating is possible [Stevenson J. T. M. ve Gundlach, 2014]. These are;

- Photolithography: This is a conventional and classic technique and called optical or UV lithography. A photolithography system is typically consisted of a light source, a mask and an optical projection system. This technique uses the exposure of photoresist to ultraviolet light in order to obtain desired mould. Photolithography can produce integrated circuits and other internal computer parts. At the same time, it can also be used to produce organic memory devices for the production of microcircuits (NEMs, MEMs) and array structure.

- X-ray Lithography: This method is an extension of photolithography. The only difference is that this method uses x-rays instead of UV for as light source. In this method, a mask is required since direct writing or moulding is not possible. X-ray lithography is used for building block integrated micro fluid structures. This technique hasve application fields in the production of miniaturized devices such as genetic and microchips, microelectrophoresis devices. In addition, it is used for the production of flaming diffractive optical elements with the help of x-ray mask.

- Electron Beam Litography: This method is used for production of nano-scale moulds. This technique uses an accelerated electron beam to focus on an electron-sensitive resist in order to expose the material. This electron beam is scanned over a resist, which has a several nanometers of layer-by-layer structure, to produce desired consecutive moulds. The process involves the steps of preparation of a resist like a polymethylmethacrylate (PMMA) by using spin method, removal of any solvent and rigidification of a film as mentioned in photolithography. Desired mould with high-resolution up to 10 nm in size by exposing the selected area to high energy of the electron beam. Scanning electron microscope (SEM) can be turned into electron beam lithography machine and used. Its application fields include telecommunication, sensors, optical photobiology and phototherapy sciences. 1D and 2D photonic crystals and silicon-insulated photonic wires can be obtained with this method.

Alternative Nanolithographic Techniques:

◦ Micro-contact printing: This is a soft printing method. It allows for creating moulds as self assembled monolayers of ink on masters such as polydimethylsiloxane (PDMS) sealing. It can be easily removed from the substrate during production due to the low melting point of PDMS, a prepolymer. This technique is used in fields like cell, DNA and protein shaping, microQRCode and MEMs, cell biology, miniature mechanization and surface chemistry.

◦ Nano-stamp lithography: This is a process similar to soft lithography. In this method, desired methods can be obtained by using a mold to process the photoresist by dilating it. The nano-stamp lithography is based on the modification of thin polymer film; mechanical sealing deformation is achieved through a thermo-mechanic or UV curing process by using a template containing nanomoulds (a mould or seal). Low cost LED devices, polarizers, plasmonic devices and photonic crystals can be produced in high efficiency with this technique. In addition, this technology is also effective in the production of electronic devices such as MOS-FE, O-TFT and single-electron memory. It has key applications in formatting of magnetic medium for optical storage (EBR) and hard disc drives.

Conclusion

In this chapter, where different types of nanodevice production are explained and differences between different lithography techniques are given, it can be seen that nanolithography has a wide range of application fields. It is highlighted that lithography techniques are effectively preferred especially for the production of different types of sensors and other devices that contain nano-scaled components. In conclusion, it is clear that nanolithography technology will be very helpful for the structuring of nanoscience and technology of future.

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SECTION 3

NANOMATERIALS

3.1 NATURAL NANOPARTICLES

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INTRODUCTION

Nanotechnology is a branch of science that deals with materials that have sizes of one billionth of a meter and works with materials that can be controlled at atomic/molecular scale. A nanoparticle generally covers a size range of 1 to 100 nm and is the most fundamental component in the production of nanostructures. In addition, they are larger that a simple molecule or atom that is regulated by the rules of quantum mechanics, but significantly smaller than the objects that are mentioned within the Newtonian law of motion. As particles get smaller, they manifest different properties. For example, metallic nanoparticles have physical and chemical properties desired in various industrial applications and are different from bulk metals, such as low melting point, high surface Area, specific optical properties and mechanical force. It can be seen in historical artworks that especially the optical properties of nanoparticles have been known for a long time and widely used in paintings and sculptures. Whereas a 20 nm gold nanoparticle has the characteristic wine red, silver has yellowish gray, platinum and palladium have black colors (Figure 3.1.1). Natural nanoparticles can be formed by one or more processes in the atmosphere, hydrosphere, lithosphere and biosphere that cover the earth. Extraterrestrial processes that form the cosmic dusts are also part of these processes. In this section, general information of natural nanoparticles will be given.

3.1.1 Natural Nanoparticles

Nanoparticles can be formed by chemical, photochemical, mechanical, thermal and biological ways separately or with the combination of several natural processes in the atmosphere, hydrosphere, lithosphere and biosphere that cover the Earth. Extraterrestrial processes that form the cosmic dusts are also part of these processes. The major natural sources of nanoparticles in the atmosphere are volcanic eruptions, desert surfaces, and dusts emitted from cosmic sources in the solar system. Particulate matters, which can also be created by crashing of a meteor passing through the atmosphere or the accumulation of cosmic dusts, are carried up in the sky to different distances by volcanic eruptions, storms or air currents formed by strong winds. Hurricanes carry large amounts of water from the ocean surfaces to the atmosphere. Evaporation allows water, salt and algae to release their spore contents, and other unicellular organisms. Due to these complex events, which occur simultaneously most of the time, the atmosphere is constantly filled with nanoparticles that cause various reactions that affect biosphere at various altitudes and distances. At the same time, natural nanoparticles (NNP) can be spontaneously created as a result of human-induced mining, waste water production and other wastes created by industrial processes and during other activities. A recent estimation conducted for NNP formation suggests that several thousand teragrams (1 Tg = 1012 g) of NNP is created via only biochemical processes (Sharma et al., 2015, Hochella et al. 2015).

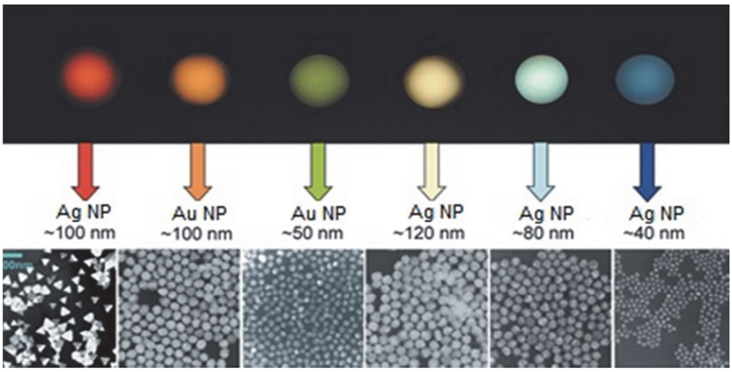

Figure 3.1.1. Colors of silver (Ag) and gold (Au) nanoparticles with different shapes and sizes
(http://sciencegeist.net/the-shape-of-things/ sayfasında yayınlanan bu fotoğraf Google görsellerinden alınmıştır.)

Gold and silver has been used as the foundational component of jewelry, metal coins and color-leaded windows of cathedrals for centuries. Today, they also became the focal points of nanomaterials and the gold-silver nano pair, which are artificially attained as engineering materials, has numerous applications. Silver nanoparticles are one of the most studied types due to their exclusive detection, catalytic, optical and antimicrobial properties and being sensitive sensors for the detection of various biomolecules and monitoring of biological conversions (Batley et al. 2013, Sharma et al. 2014, Sharma et al. 2015). Similarly, gold nanoparticles are being used for the diagnosis and treatment of cancer, chemical and biological imaging, catalysis and sensors (Saha et al. 2012). The constant increase in the use of these gold and silver nanoparticles that are produced as engineering materials, their release to the environment, and their potential impact on ecological system due to release have caused concerns, however, toxic properties of naturally formed nanoparticles have drawn relatively less interest.

3.1.2 Natural Nanoparticles in the Atmosphere

There are 3 fundamental sources for the natural nanoparticles in the atmosphere. These are volcanic eruptions, desert and cosmic dusts.

1) Volcanic Eruptions

The ash released by volcanic eruptions has a complex structure consisted of liquid/solid particles that are carried upwards by the hot gas flow and can reach temperatures above 1400°C (Strambeanu et al. 2015, Juravle 2012). After the eruption of the volcano, ash spreads to the atmosphere, gas temperature drops and gas composition changes (Figure 3.1.2). Chemical reactions or electrostatic interaction forces cause particles to accumulate in bulks. Content of volcanic gas emissions change depending on kinetic conditions such as thermodynamic conditions, pressure, temperature, reaction rate and the natural structure of the magma.

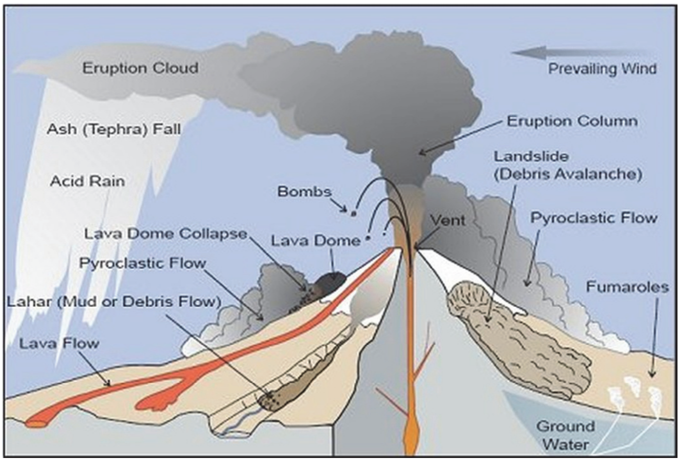

Figure 3.1.2. Volcanic explosion

(The image is published on https://www.slideshare.net/PandeyAman/hw-homework-science-amanpptx-mmmm and retrieved from Google Images.)

Basaltic magma is rich in terms of magnesium and iron, and poor in silica. In addition, it has a reduced gas concentration containing mainly carbon dioxide and sulfur dioxide and low viscosity. Generally, hydrogen sulfur (H_2S) and hydrogen chloride (HCl) are dominant in the gas emissions (Strambeanu et al. 2015, Symond et al. 1994, 1988, Cadle et al. 1980, Chin et al., 1993). Hydrogen chloride is highly soluble in water. The water vapor in the upper layers of the atmosphere condensates above the ash particles and causes acid rains. These gases are quickly moved away from the atmosphere with the acid rains occurring during the eruptions. Hydrosulphuric acid oxidized by ozone in the troposphere also has the same effect. The concentration of hydrobromic acid is relatively low (Strambeanu et al. 2015, McElroy et al. 1992, Bureau et al. 2000). In addition to hydrosulphuric acid oxidization, hydrobromic acid also has significant contribution to the reduction of both ozone and diatomic oxygen concentrations. Volcanoes are thought to be the source of the hydrofluoric acid in the atmosphere. Therefore, there is very limited knowledge about its concentration in the atmosphere. In some cases where the hydrofluoric acid emissions are too high, it has been reported that these emissions significantly pollute the plant cover and cause animals and people to die. As with other halogen acids, hydrofluoric acid also spreads around the volcano through acid rains. Therefore, excessive fluoride ions can cause animal deaths in large areas even a long time after the eruption. If the concentration goes above 250 ppm, it may cause plant intoxication, thus, harming the plant cover (Strambeanu et al. 2015, Textor et al. 2003). Chemical composition of the ash can be easily detected from the emissions of dormant volcanoes. Dry fumaroles do not contain water, therefore they exceed critical temperature of the water (374°C). It contains nitrogen gas (N_2), carbon monoxide gas (CO), hydrogen gas (H_2), methane gas (CH_4) and sodium chloride vapor (NaCl), potassium chloride (KCl) and copper (II) oxide (CuO). Fumaroles produce halite (NaCl), sylvine (KCl) and tenorite (CuO) by accumulation on the edges of the crater and during eruption or on the surfaces thrown in the form of ash. Acid fumaroles contain hydrogen sulfur (H_2S), sulfur dioxide (SO_2), carbon dioxide (CO_2) and water vapor. Their critical temperature is close to that of water. If acidity is not too high, acid fumaroles contain iron (II)/(III) chlorides ($FeCl_2$, $FeCl_3$), copper (I)/(II) chlorides (CuCl, $CuCl_2$) or iron oxides in the form of magnetite (Fe_2O_3). In the presence of sulfur (especially in underwater fumaroles), iron exists in the forms of marcasite (white iron pyrite) and pyrite (FeS, FeS_2). Alkali fumaroles are produced from the reaction of ammonium chloride (NH_4Cl), ammonia hydroxide (NH_4OH) and water vapor in the presence of ammonia (NH_3). Ammonia chloride takes the form of micrometer or submicrometer particles. Temperatures of these fumaroles are 100-400°C. Eruptions are natural volcanic vapor ventilations where hot water vapor and sulphur gases are dominant. Fumaroles release sulfurous acid (H_2SO_3) and more stable sulfuric acid (H_2SO_4) gases in the presence of sulfur, hydrogen sulfur (H_2S)/sulfur dioxide (SO_2) and water vapor. Sulfurous arsenic, caused by the condensation of the vapor, is defined as the solid of orpiment (As_2S_3), iron and copper pyrites, iron sulfate ($FeSO_4$) natural sulfur substances (Juravle, 2012).

2) Deserts

Other important sources of nanoparticles that are flown by air flows and dust storms and carried to the atmosphere are the large deserts. Long range migration of metal powders and human-induced pollutants over the continents has become the focal point of recent studies. These studies revealed that approximately 50% of the aerosols in the troposphere are desert-originated minerals. Chemical composition of very thin desert sand dust changes depending on the air currents and anthroogenic activities (Strambeanu et al. 2015, Shi et al. 2005).

Analyses showed that the composition of the particulate substance, formed during the dust storm between China and South Korea (Figure 3.1.3), contained high concentrations of silicon, aluminum, calcium and iron. In addition, heavy metals (Hg and Cd) and poly(nuclear) aromatic hydrocarbons (PAH), which are generally produced by coal combustion, are also detected in the stratosphere, however, their sources are not known (Strambeanu et al. 2015, Xiaodan 2007, Chun et al. 2008).

Analyses conducted around Xian city, which is located close to the huge atmospheric dust transfer from the Gobi desert, and the Hua mountain revealed the presence of sulphide, nitrate and ammonium ions originating from anthropogenic activities in addition to high concentrations of carbon and organic nitrogen concentration, which are thought to be originating from microbiological activities in the atmosphere. These particles carried by the wind have sizes between 80 nm and 1000 nm.

In recent years, the types and behavior of Saharan aerosols have been extensively studied in the Sahel region, in some parts of the Atlantic Ocean and in Southern Europe. The contribution of Sahara to the particulate matter (PM10) is determined through the gravimetric analysis of Al, Si, Fe, Ti, non-sea originating Ca, Na and K oxides (Strambeanu et al. 2015, Wang et al. 2012).

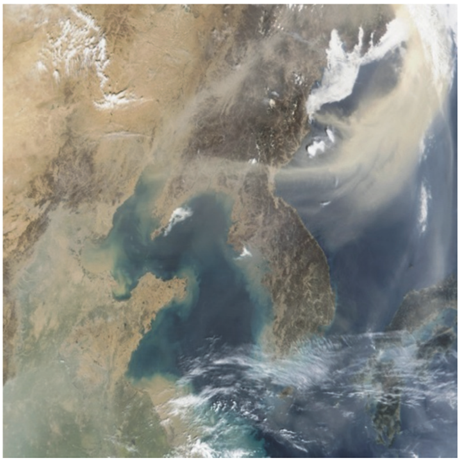

Figure 3.1.3. Desert storm between Cape Verde Islands and Senegal

(The image is published on http://www.gmes-atmosphere.eu/news/dust_senegal/ and retrieved from Google Images.)

An estimation about the ionic balance of the atmosphere suggests that the reactions containing anthropogenic acids and micro crystal particles may play an important role in the sedimentation of nanoparticle systems, and that they may affect the intake of these by the cellular structures of living organisms (Strambeanu et al. 2015, Wang et al. 2012).

The results of other studies conducted during the fine particle transportation between the Cape Verde Islands (Strambeanu et al. 2015, Wang et al. 2012) and Sal Island (Figure 3.1.3) close to Senegal coasts caused by Harmattan (Figure 3.1.4) suggests (Strambeanu et al. 2015, Taylor 2002) that dust particle currents in the main cloud are localized based on their masses. Estimations based on Al_2O_3 concentration revealed that air opacity and O_3 concentrations are decreased above 4.500 m. Same studies (Strambeanu et al. 2015, Marconi et al. 2013, Goudie et al. 2001) detected nanoparticle compounds that are created as a result of the reaction between anthropogenic aerosols, especially ammonium sulphate (NH_4HSO_4), and their components. Samples collected at high altitudes are associated with air masses traveling from North Africa deserts and coming from Europe. As the nitrate concentration is not increased, this hypothesis is more plausible than the hypothesis based on the large impact of local biomass combustion emissions. At high altitudes, the old contamination layers from fossil fuel combustions, possibly of North American origin, were encountered.

Harmattan is the name of the dust-laden, dry wind that blows from the shores of Western Africa coasts.

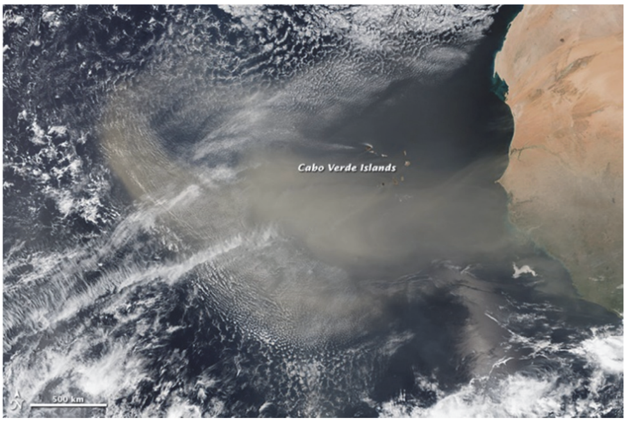

Figure 3.1.4. Desert storm between Cape Verde Islands and Senegal
http://www.gmes-atmosphere.eu/news/dust_senegal/ sayfasında yayınlanan bu fotoğraf Google görsellerinden alınmıştır.)

Geochemical indications of the dust particles, arising from the above mentioned findings, are consistent with the previous results obtained from the area. According to these results, Si, Fe and Ti concentrations have not changed consistently with the composition of the soil. However, concentrations of other elements, such as Ca and S, have increased due to the industrial operations conducted in the African deserts in the last decade (Strambeanu et al. 2015, Formenti 2003).

3) Cosmic Dusts

Total annual transportation of cosmic dusts (Figure 3.1.5) on the Earth is approximately 40.000 tonnes. Majority of the cosmic dusts are originated from the interplanetary dust cloud surrounding the Sun, star masses between Mars and Jupiter or comets (Strambeanu et al. 2015, Zook 2001). Regardless of their sizes, cosmic objects pass through the space on very high speeds, sometimes even exceeding 150.000 km/hour. As they get closer to the Earth, they slow down due to the friction in the atmosphere and this causes meteors to burn and characteristically flare. Speeds of smaller particles also decrease due to the friction in the atmoshpere, however, they reach the surface of the Earth without burning (Strambeanu et al. 2015, Zook 2001).

Composition and size of interplanetary dusts are measured by using the satellites in the space and infrared detection applications. Old and new studies revealed that cosmic dust is consisted of micro particles, nano particles and their accumulation. These dusts have irregular shapes and their porosity changes based on whether the structure is spongy or compact. Their compositions, sizes and physicochemical properties depend on their original source.

Figure 3.1.5. Kozmik Toz Bulutu

(https://www.nasa.gov/image-feature/goddard/2016/hubble-peers-into-the-storm sayfasında yayınlanan bu fotoğraf Google görsellerinden alınmıştır.)

Interstellar dust clouds contain carbon monoxide, silicon carbide, amorphous calcium silicate, water ice and poly(nuclear) aromatic hydrocarbons (PAH) or other basic organic structure, whereas interstellar medium contains carbon and silicon particles. On the other hand, comet dusts have different composition than that of those originating from asteroid disruption. Comet dusts have similar compositions to interstellar clouds, but the dusts originating from asteroid disruption have large amounts of silicon and iron (Strambeanu et al. 2015, Love et al. 1992, Humphreys et al. 1972, Donald et al. 1999). In the comet dust samples collected during recent space studies (Strambeanu et al. 2015, Donald et al. 2011) presence and ratios of different elements such as hydrogen, oxygen, carbon and nitrogen were discovered. Relations between these elements provide information about the distance between the Sun and where the comets are formed, and the types of existing comets (e.g. ones closer to the Sun have higher temperatures).

In addition, it was also revealed that cosmic dust contained organic matter complexes in the form of aromatic-aliphatic mixtures, which can be spontaneously created in the universe. Computational chemistry studies on complex organic molecules that form the basis of life have lead to the theory that these types of molecules might be created by the nanoparticles orbiting around the Sun before the Earth was formed (Strambeanu et al. 2015, Starkey 2013). Other studies (Strambeanu et al. 2015, Gudipati et al. 2012) revealed that poly(nuclear) aromatic hydrocarbons (PAH) are converted into amino acids and nucleotides via hydrogenation, hydroxylation or partial oxidation under conditions similar to the medium of stars. According to the recent estimations, it has been claimed that more than 20% of the carbon compounds are based on PAH, that they were formed a little after the Big Bang and that they have played a role in the formation of new stars and outer planets by spreading into the universe.

Studies conducted on the properties of nanoparticles provide very valuable information about the formation of planetary systems, source of organic matters and water that produce the spontaneously growing systems that form the life, and their roles.

3.1.3 Natural Nanoparticles in the Hydrosphere

Nanoparticles that are carried by natural water can be found everywhere. Very small sizes ranging from 1 to 100 nanometers ensure that they are both highly mobile and chemically reactive. Colloids and nanoparticles can be present in numerous compositions and in different forms around us. Majority of colloids are formed from biological degradation, low molecular weighted degradation products (humic material) and from minerals produced during the chemical abrasion of rocks, especially the oxides of iron (Fe), manganese (Mn) and aluminum (Al), and oxyhydroxides and aluminosilicates.

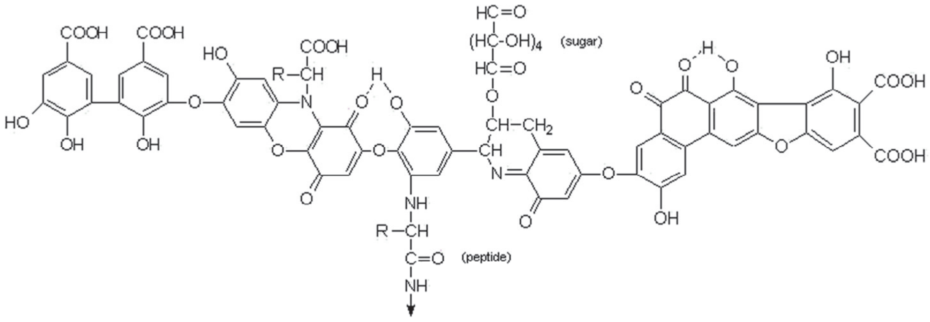

Figure 3.1.6. Rough formula of humic substance

(The image is published on http://karnet.up.wroc.pl/~weber/kwasy2.htm and retrieved from Google Images.)

The most studied sub class of natural organic matters is the humic substances (HS). HS (Figure 3.1.6) can come together as irregular materials in a small portion of nano size range (<5 nm) and as potentially larger structures (especially mineral colloids) outside the nano range (Hartland et al. 2013, Tipping 2001).

Other natural organic substances found in natural waters include peptides, proteins, peptidoglycans, polysaccharides and similar biomolecules. Polysaccharides have fibrillary or cage-like configurations, however, proteins are generally globular and they degrade less than HS because of their differences. On the other hand, HS generally reduce aggregation through charge and/or steric stabilization, and such compounds have an effect to increase the sizes of nanoparticles and colloids (Figure 3.1.7) via coagulation (Hartland et al. 2013, Buffle and Leppard 1995). In all environmental systems, metal oxides, especially iron and manganese, are important nano-scaled phases that are capable of binding trace elements.

Nanoparticles and colloids typically have a negative electrostatic surface charge in the neutral pH (~ pH 7) of natural waters. Thus, despite their original surface potentials, almost all inorganic colloids in the natural waters have a negative surface charge due to the HS surface coatings (Hartland et al. 2013, Tipping and Higgins 1982). Similar charges between the particle surface, for example, negative and negative charges, allow nanoparticles and colloids to remain in a dispersed stable state in the water and form a suspension since similar charges repel each other, whereas, surface charge differences of all particles, for example positive and negative charges, balance the opposite ions by forming a double layer around the particle (Figure 3.1.8).

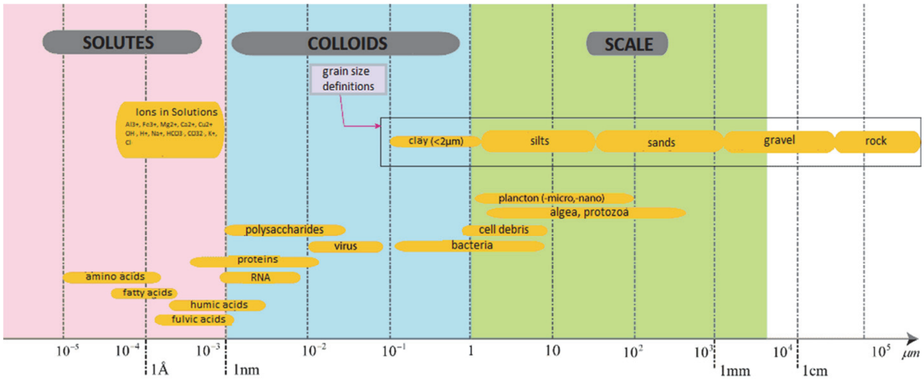

Figure 3.1.7. Grain size distribution of natural particles

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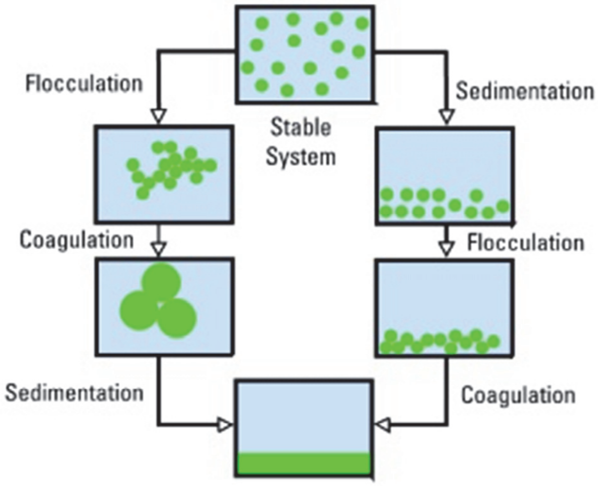

Figure 3.1.8. The stability of the colloidal system

(The image is published on http://www.silver-colloids.com/Tutorials/Intro/pcs7.html and retrieved from Google Images.)

In general, the mobility of nanoparticles in surface waters is limited only by their colloidal stability. Similarly, nanoparticles can move smoothly in broken aquifers. However, nanoparticles and colloid mobility is more limited since nanoparticles are more likely to collide with soil particles in underground surface porous media (e.g. Alluvial underground water aquifers). The number of collisions of soil particle (Hartland et al. 2013, Tufenkji and Elimelech 2004, Nelson and Ginn 2005) is determined by various events such as Brownian motion, shearing, precipitation, inertia and hydrodynamic forces. Smaller particles move with a largely random Brownian motion, this is especially true for nanoparticles. Various retention mechanisms such as filtering, maximum holding time capacity of the surface and charge heterogeneity on the soil surface can also be important for the motion of nanoparticles and colloids in the porous medium.

3.1.4 Mechanisms for the formation of natural nanoparticles (NNPs)

All potential paths leading the classification and formation of NNPs are complex and extensive. NNP formation occurs in all areas surrounding the world, chemical elements/species and wide range of mechanisms, processes and conditions.

Mentioned syntheses can take place with bottom-up approach starting from molecular/ionic species, such as iron hydride NNP formation from microbiological activities or halogenure and aqueous sulphide NNP formation from the evaporation of sea spray. Syntheses can take place with a top-down approach starting from larger particles, such as nano-sized mineral particles produced via wind erosion on the deserts or the formation of carbon nanoparticles through the combustion of biomass (Sharma et al., 2015, Hochella et al. 2015, Wu et al. 2012, Konishi et al. 2012).

Nano-sized objects in the world are formed in all areas involving troposphere, hydrosphere that covers oceans, lakes, rivers, underground waters, lithosphere that covers soil, rocks, magma etc., and the biosphere where all organisms live including microorganisms and humans (Sharma et al., 2015, Hochella et al. 2015).

Basic processes that lead only to the formation of inorganic NNP (Figure 3.1.9);

- may only involve nucleation and growth of various inorganic phases in the atmosphere, hydrosphere and even in the lithosphere as a result of inorganic reactions or with the contribution of organic substances. Reactions in surface waters and hydrothermal flues that contribute to the production of NNP can take place with thermal, non-thermal and photochemical processes. Typical Fe(II) formation in geochemical environment can ease the formation of iron hydride nanoparticles that can be made stable via silicon ions (Sharma et al., 2015, Konishi et al. 2012). Other nanoparticles containing Mn, Cr, Cu, Ba and Pb can be formed in cold carbon dioxide leakages.

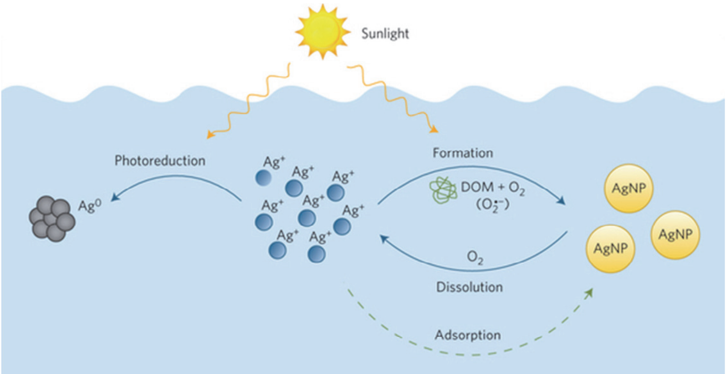

Figure 3.1.9. An example for the formation of Ag NNP

(The image is published on http://www.nature.com/nnano/journal/v11/n8/full/nnano.2016.93.html?WT.feed_name=subjects_nanotoxicology and retrieved from Google Images.)

Some of the mechanical processes affecting the NNP formation are mechanical grinding of Earth's crusts during earthquake, wind erosions in unforested and non-planted soils and desert winds. In addition, mainly biomass combustion in equatorial region of the world can be the best example for thermal processes.

Organisms, especially microorganisms, produce natural NP in the world. Biological processes (or biomineralization) in the world can create several inorganic nanomaterials like calcium phosphate, calcium carbonate, Fe and Si based nanominerals. Two processes are well understood and defined. One is the biologically induced mineralization (BIM), and the other one is biologically regulated mineralization (BRM). In BIM process, aside from solid substrate attaching to the bacteria or its the relation with bacteria cell, no other function specially controlled by microorganisms take place in the formation of nanoparticles. However, nucleation and growth of the particles are controlled by microogranisms from start to finish in the BRM process and nanominerals are generally created on the cells under certain conditions. Therefore, mineral particles produced based on the BRM process are well-defined crystals with narrow particle size distribution. Nanoparticles that are produced via this process have various functions for microorganisms. For example, well-known magnetotactic bacteria (Figure 3.1.10) use magnetic nanoparticles to find direction (Sharma et al., 2015, Schuler and Frankel 1999).

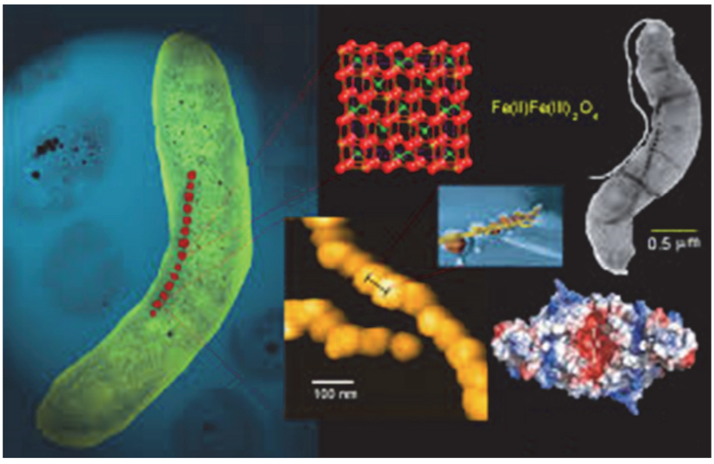

Figure 3.1.10. Magnetotactic bacteria

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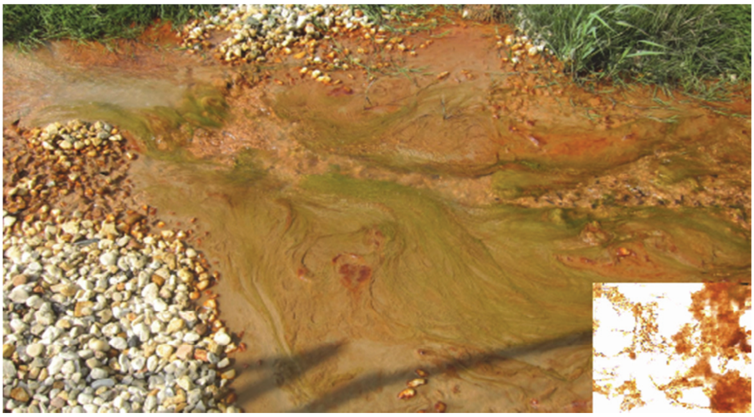

Figure 3.1.11. Red coloring of the waters as a result of iron production by bacteria (BIM process).

(The images are published on http://cfb.unh.edu/phycokey/Choices/Tribophyceae/TRIBONEMA/Tribonema_key.html,https://bacteria.ee/ and retrieved from Google Images.)

Alternatively, as exemplified in the production of Mn and Fe oxide nanocrystals (typical BIM process), NNPs are produced via reduction reactions in microbial medium that are indirectly related to metabolic processes. Best examples are bacterial formation of ferric oxyhydroxide that is detected in sedimentation, underground waters and soil, and the production of ferrihydrite by iron oxidizing bacteria (Leptothrix, Gallionella) (Figure 3.1.11).

Nanoparticles can be formed naturally in aerosols, waters, soil, deep sea hydrothermal vents, natural ores and microbial systems (Sharma et al., 2015, Hochella et al. 2015). NNPs are formed by wind erosion at solid-gas phase threshold, by the evaporation of sea spray at liquid-gas phase threshold, and by the abrasion of rocks at the solid-liquid phase threshold. NNPs have a wide range in terms of chemical composition and element diversity;

- metal oxides/hydroxides (for example; iron oxides/hydroxides, goethite, lepidochrosite, akaganeite, manganese oxides/hydroxides etc.)
- metals and alloys (for example; metal nanoparticles)
- carbon allotropes and other non-metals
- silicates (for examples; aqueous aluminum silicate, fiber clay minerals such as sepiolit etc.)

- sulfides (for example; pyrites containing Cu and Zn (FeS_2) etc.)
- sulfates, halogens and carbonates

Metal and noble metal nanoparticles have a particular importance among this chemical group due to their impacts on the nature (Sharma et al., 2015, Kolar et al. 2014, Quigg et al. 2013).

It is also known that metal salts react with plant extracts, sugars, vitamins and a wide range of antioxidants, and that the interaction of metal ions with natural organic substances (NOS) and reactive oxygen species (ROS) has a crucial importance on the formation of natural metal nanoparticles present in the nature (Sharma et al., 2015, Adegboyega et al. 2014, Yücel 2011, Hou et al. 2013, Yin et al. 2012, Yin et al. 2014). NOS are complex matrices consisted of humic substances (HS), which form the basic elements of underground waters, surface water and rivers, precipitations and soils, and compositions such as protein and polysaccharides. HS phenolic groups include conjugated double bonds and aromatic carbons. Their definite structure is not completely known due to its high complexity. Its estimated structure is shown in Figure 1. HS can be sub-groups of humic acids (HA), fulvic acids (FA) and humin. Normally, HA are consisted of components that have high molecular weight and not soluble in low pH. Contrary to this, FA are consisted of components with low molecular weight that are soluble in a wide range of pH. Humin is insoluble in any pH. ROS generally contains $^1O_2$, $O_2^{-\bullet}$, H_2O_2 and $^\bullet OH$ which are produced in natural surface waters via Fenton or Fenton-like reactions and photochemical ways (Sharma et al., 2015, Adegboyega et al. 2014, Yin et al. 2012, Yin et al. 2014).

Inorganic sulfur (H_2S and HS-) is the most important part of global biogeochemical sulfur cycle under anaerobic conditions, which includes mud purification systems, continental soils, precipitations, mine water, hydrothermal vents (Figure 3.1.12). Metals and sulfurs in the oceans can spread from the high-temperature ventilations and they can react with each other to be used as the source of metal-carrying sulfur nanoparticles. Metals and their sulfide nanoparticles can remain in colloidal form as suspended. A series of metal sulfide nanoparticles (Ag_2S, CuS, CdS and ZnS) are found in sulfide environment (Sharma et al., 2015, Levard et al. 2012, Mullaugh and Luther III 2011, Schaffie and Hosseini 2014, Ma et al. 2014). Natural formation of noble metal sulfides affects the speciation, motion and bioavailability of many important metals. For example, sulfur inside the metal sulfides resist against oxidation due to the strong complexation with the metal and this limits the bioavailability of the metal (Sharma et al., 2015, Thalmann et al. 2014).

Although there are many studies about the natural formation of inorganic nanoparticles, it is still difficult to explain the formation mechanisms. There are very limited number of detailed mechanical studies on chemical, photochemical, mechanical, thermal and biological processes that form natural nanoparticles. In nature, more than one reaction pathway can contribute to the formation of natural nanoparticles.

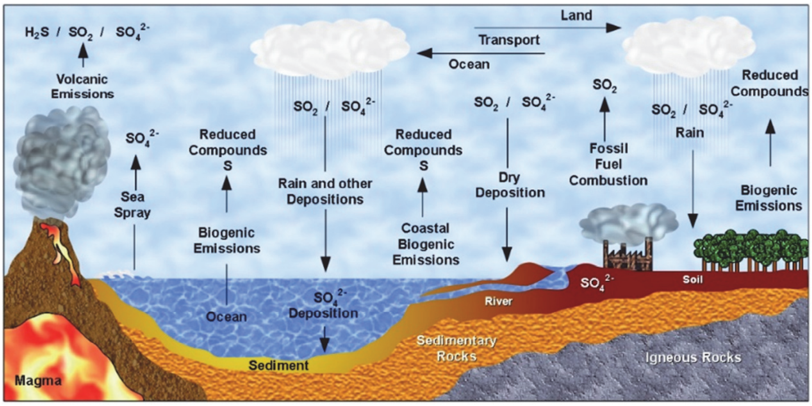

Figure 3.1.12. Sulfur cycle

(The image is published on https://commons.wikimedia.org/wiki/File:Sulfur_Cycle_(Ciclo_do_Enxofre).png and retrieved from Google Images.)

In recent years, some progress has been observed for the explanation of formation mechanisms of noble metal nanoparticles in various systems. The interaction of precursor noble metal ions with natural organic substances under thermal and irradiance conditions of oxygenated water is mostly responsible for the formation of noble metal nanoparticles (gold and silver nanoparticles). The formation of noble metal nanoparticles varies by source species, such as sediments, aquatic and solid, and from fulvic acid to humic acid. It has been suggested that alcohol, aldehyde and phenol parts of humic acid can trigger photoreduction and produce noble metal nanoparticles. However, due to the opposing views on the formation of noble metal nanoparticles under sunlight, more advanced mechanical details required more detailed examination for completely understanding the reduction process under sunlight in the presence of natural organic substance. We need more information to explain the roles of reactive oxygen species and temporary organic substances on noble metal formation mechanism from special complexes under natural conditions. In addition to the properties of dissolved organic substance, valence status of reduction species present in solution mixture also plays an important in the formation of noble metal nanoparticles. How iron species (Fe(II)/Fe(III)) increase the formation of noble metal nanoparticles under thermal conditions and how do sunlights take place in formation mechanisms require more advanced examinations. In situ demonstration of particle formation is still a problem.

According to the published results, noble metal nanoparticles, such as silver and gold nanoparticles, formed via the reduction of ionic salts are produced by humic and fulvic acids under thermal and irradiation conditions and are stable for long periods of time in aquatic environment. Naturally occurring noble metal nanoparticles with this high stability are highly likely to be migrated to the distances far away from their original locations. However, the pH, ionic strength and chemistry of solid and aqueous phases affect the conversion, dissolution, agglomeration and hence mobility of natural nanoparticles.

As a result, the natural organic functional groups that surround naturally occurring noble metal nanoparticles can significantly affect their toxicity. There is very limited information about how these nanoparticles interact with organisms in the water. These nanoparticles may exhibit varying toxicity depending on the formation of reactive oxygen species and the functional properties of the organic substances. Future studies to assess the mechanisms underlying the toxicity of naturally occurring nanoparticles are of great importance.

Natural nanoparticles have a great importance on global biogeochemical cycles, weather conditions, metal binding and transport, bioavailability and ecotoxicity in the earth's system. In addition, the effect of nanoparticles on the bioavailability of nutrients and toxic elements has been a factor in the evolution and development of high organisms, potentially buffering the environmental systems against change (Tipping 2001). Therefore, it is interesting that produced nanoparticles became a focus of attention since they are present in much lower amounts than their natural counterparts. This is because the produced nanoparticles differ from those found in nature and is made from specific structures and chemicals that organisms can not have the proper defense mechanisms for.

Summary

Nanoparticles are substances having the sizes of one billionth of a meter. The discovery and use of nanoparticles have a long history. The first used nanoparticles were the nanoparticles produced by the nature in different ways. The developments in technology have enabled us to see them and allowed diversity in their production. There are many natural processes that enable the natural formation of nanoparticles. Lots of processes have been suggested, especially when it is examined in terms of atmospheric, aquatic and terrestrial formation sources. Since nanoparticles can be present in every edge of life that covers the world, they can also be formed through the solar events. The recent and rapid developments in the science have led nanoparticles to take an important place in the explanation of the theories about how the universe and the life in our world had taken shape immediately after the Big Bang. There is still no clear and detailed explanation for the formation of naturally occurring nanoparticles, but it is known that noble metals and humics play an active role in such formation. However, there is very limited information on the toxicity of NNP, and there are many studies on the toxic effects and different applications of nanoparticles produced for engineering purposes.

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3.2 METAL and ALLOY NANOPARTICLES

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INTRODUCTION

Metal and alloy nanoparticles are nano-scale particles with size of 1-100 nm. These particles are agglomerates of atoms and they can be synthesized from the same atom as well as two or more different atoms [Baletto and Ferrando, 2005]. These nanoparticles draw great attention in recent years since their optical, electrical and catalytic properties can be adjusted depending on the quantum sizes. Optical, electrical and catalytic properties of alloy nanoparticles can be ad-justed simply by changing the composition of the alloy. In the syn-thesis of metal and alloy nanoparticles, it is possible to produce alloy nanoparticles below 10 nm in size and they can exhibit diverse size-dependent variations [Raveendran et al., 2006]. Surface structures, compositions and decomposition properties of nano-alloys determine their reactive and catalytic behaviors. Therefore, bimetallic nano-alloy can manifest synergistic properties and can have significantly different structures and properties than the metal clusters with the same size [Ferrando et al., 2008]. Unlike the metals, synergistic ef-fects enables the improvement of certain properties of the alloy after it is formed, therefore, metal alloys has found wide applications fields in ecology, electronics, materials and machinery [Ruban et al., 1999].

3.2.1 Production Methods in Development of Technology and the Importance of Material

Nanotechnology covers the design, production and functional use of nanomaterials and production of metal nanoparticles (NP) is one of the most important steps for new materials in nanotechnology. Metal NPs can be produced in a wide chemical range and morphology. The reason for NPs to stand out can be listed as quantum size effects, size dependency of electrical structure, unique characteristics of surface atom and high sur-face/volume ratio [Liveri, 2006]. They take part in the preparation of many technological and pharmacological products, catalysts, special technolog-ical materials for optical applications, superconductors, abrasion-resistant additives, surface active agents and drug carriers. Today, NPs having dif-ferent morphologies such as core-shell, additive, sandwich, hollow, spheri-cal, rod-like and other geometric features with desired properties can be prepared from metal, metal alloy, ceramic, polymer-based or combinations of these.

In the preparation of nano-structured materials, physical approach includ-ing thermal and heat treatment, diffusion, electrolysis, chemical approach including core formation, reduction and electrochemical processes or bio-logical approach including microorganisms and plants are accepted in general. In addition, different systems such as chemical vapor condensa-tion, hydrogen reduction, and noble gas condensation, production from microheterogeneous systems, flame synthesis, mechanical abrasion and ultrasonic spray pyrolysis methods are used for the production of metallic and oxide-based NPs [Liveri, 2006].

Synthesized NP initially starts to form a core for which the shape, size and composition can be adjusted, then the nano-sized shell of the second metal is agglomerated on top it; this process step is critical and the core/shell nanosystem is heated up to very high temperatures in order for the metals to diffuse into each other.

Nanomaterials are of great importance due to their unique properties relat-ed to their high surface-volume ratio, and they have a wide range of appli-cations including catalysts, drug industry, optical materials, sensors, ener-gy storage-transmission [Haverkamp and Marshall, 2009]. Functions and areas of use of these materials vary depending on the size and composi-tion of the NPs. Silver (Ag) NPs can be used in household tools, platinum (Pt) NPs in industrial and biomedical applications and gold (Au) NPs can be used in sensor studies.

Depending on the filling of the electronic shells of the alkali metal bulks formed by the agglomeration of small atomic masses such as Cu and Ag, the sizes will be enlarged and certain nuclei will become partially stable like the jellium model. Bulks of some main group metals (Al, Ca and Sr) and transition metals generally have large sizes in polyhedral bulks with con-centric geometric shells and the competition between the bonding and surface energy effects is what provides the stable shape of a bulk [Fer-rando et al., 2008].

Nano alloys can be synthesized in variety of ways including gas phase, solution and various mediums supported by a lower layer or a matrix (Figure 3.2.1) [Schmid, 2011].

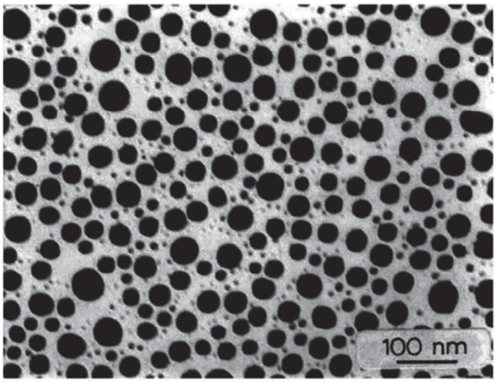

Figure 3.2.1. Transmission electron microscope (TEM) image of Bi-Pb alloy NPs formed through in situ agglomeration

(Copyright 2004 American Physical Society) [Jesser et al., 2004].

3.2.2 Biosynthesis of Metal NPs

Reduction of metal ions with sodium reducing agents is the most widely used method in the synthesis of metal NP. Sodium borohydride and sodi-um citrate as well as glucose, fructose and sucrose sugars are used as reducing agents in the synthesis of metal NPs [Panigrahi et al., 2004]. In addition to health, environmental and economic concerns, it is difficult to keep the particle size and morphology within a certain range with produc-tion using conventional chemical methods. The production of metal NPs by biological methods has attracted interest in recent years as an alterna-tive to conventional chemical methods. Not using toxic agents in the syn-thesis of NP, the ability to carry out the synthesis at ambient temperature and pressure are among the advantages of the biological method [Raveendran et al., 2003]. Biomineralization of NPs in protein holes is one of the biological methods for NP production. This method allows controlling the particle size and morphology [Sau and Rogach, 2010]. Bacteria, fungi, lichens and algae are used in biogenic NP synthesis. These biologi-cal creatures secrete large amounts of extracellular and intracellular pro-teins, and these proteins function as a template for the reduction of metal cations to metallic form [Mandal et al., 2006]. The fundamental criteria in microorganism selection are whether the microorganisms have the reduc-tase enzyme. In other words, microorganisms that are capable of releasing reductase enzyme are used in metal NP synthesis. From bacteria species; Bacillus subtilis, Bacillus Licheniformis, Bacillus mycoides, Bacillus methylotrophicus, Bacillus cereus, Streptococcus thermophilus, Escherichia coli, Lactobacillus acidophilus and Enterococcus sp., from fungi; Aspergil-lus sp., Fusarium sp., Penicillium sp., Trichoderma sp., Verticillium sp. ve Trichothecium sp. and from yeasts; Saccharomyces cerevisiae, Saccharo-myces boulardii, Yarrowia lipolytica, Candida sp., Rhodotorula sp. and Pich-ia pastoris) are used in metal NP synthesis [Vaseghi et al., 2017]. Recently, various plant extracts are also being frequently used in metal NP synthesis in addition to the microorganisms [Nadagouda and Varma, 2008; Iravani, 2011].

3.2.3 Metals used in NP synthesis

Metals such as gold, silver, copper, zirconium, cadmium, magnesium, aluminum, iron, titanium, platinum, paladium and metal oxides such as TiO2, ZnO, NiO, MnO2, Cr2O3, Cu2O, Fe3O4, ZrO2, In2O are utilized in NP pro-duction and being used in various applications [Iravani, 2011; Ng et al., 2013].

3.2.4 Uses of Metal NPs

The properties of metal NPs depend on their size and shape. Many metal NPs produced in different size, shape and morphology are widely used in chemical and biosensor manufacturing studies, catalyst synthesis, elec-tronic device component preparation, imaging systems, medical and envi-ronmental applications. Some examples of NPs areas of use can be sum-marized as follows:

Gold NPs are biocompatible and have found widespread use in medical practice for their affinity in -SH groups. Colloidal gold NPs are used as a cancer-targeted drug delivery device [Paciotti et al., 2004] and in cancer diagnosis [El-Sayed et al., 2005].

Silver NPs have been used in healthcare industry, food storage ap-plications and textile products because of its anti-bacterial proper-ties [El-Nour et al., 2010]. Silver NPs immobilized in hydrogel exhib-ited anti-bacterial effect against E. coli [Mohan et al., 2007]. In an-other study, silver NPs were used as antibacterial agents in the sur-face coating of plastic catheters [Roe et al., 2008]. In addition, silver NPs are also widely used in electronics [Alshehri et al., 2012].

Similar with the silver, antimicrobial, antifungal and antiviral proper-ties of copper are also known for centuries. In recent studies, cop-per NPs are frequently being used as alternatives to silver NPs due to their low costs [Ingle et al., 2014].

Zirconium coated graphite electrodes are used to make peroxide bi-osensor [Liu et al., 2004]. Zinc oxide NPs are attractive semiconduc-tors for their photoluminescence properties. They are used in ultra-violet laser devices and biomedical marking because of these prop-erties [Xiong et al., 2009].

Metal and alloy NPs also represent one of the most innovative tech-nologies for ecological use. For example, nano-scale (1-100 nm) Fe and Pd-Fe particles are used for the treatment of waste water [Wang and Zhang, 1997]. In addition, Pd-Au NPs are also used for improv-ing the underground waters containing trichloroethene and other chlor-based compounds [Nutt et al., 2005].

3.2.5 Alloy NPs

Researchers who want to specify the exact structure and properties of nanomaterials in nanoscale are shifted from single-atom systems to bi-metallic or multi-metallic systems. The ability to adjust the physical and chemical properties of nanomaterials by altering the composition of the compounds in metal alloy systems is one of the main reasons why nano-alloys draw that much interest. The composi-tion, distinction degree and surface structure of nano-alloys deter-mine the chemical reactivity and catalytic activity of nanomaterials. The interesting thing is alloy NPs may exhibit properties different from the pure particles of the metals that form them. Sometimes synergistic effect is observed in catalytic systems where nanoalloys are used.

3.2.6 Arrangement of metal atoms in alloy NPs

Different arrangements are observed as the metal atoms form alloys in the nano scale. These are;

i. Core-shell configuration (AcoreBshell) is the most common configuration and the metal core composing the shell completely surrounds the metal,

ii. Layered-derived NPs (“Janus” double-sided particles); two different atoms forming the particle compose a different side of the nanomaterial,

iii. Mixed configuration; is the most general alloy configuration and atoms may be partially ordered or randomly mixed [Ferrando et al., 2008].

3.2.7 Uses of Alloy NPs

Like metal NPs, the physical and chemical properties of alloy NPs depend on their size and morphology. In bimetallic or multi-metallic alloy systems, the properties of the nanomaterials also depend on the chemical composi-tion of the materials and the arrangement of the atoms. This way, it is pos-sible to synthesize nanoparticles with very different properties by manipu-lating the elemental composition of the nano-alloy, conditions of the syn-thesis process and the array configuration of the atoms. This versatility of nano-alloys has opened up the way for use in a variety of areas such as biological identification, drug release, biosensors and catalytic systems [Rosi and Mirkin, 2005].

The reciprocal effect of neighboring metal atoms in catalyst systems can lead to synergistic effects, and in general, nano-alloy systems can exhibit better catalytic activity than monoatomic systems [Ferrando et al., 2008; Zaheer et al., 2011]. In a catalyst study conducted with nano-alloys, silver-rich AgPd nanoaluminum was used in the reduction of oxygen in an alka-line environment [Slanac et al., 2012]. In another study, NiCoB nano-alloy catalyst was used in the hydrogenation of p-chloronitrobenzene [Shen and Chen, 2007].

There is increasing interest in the use of nano-alloys in biosensor studies in recent years. Ni–Cu/TiO_2 electrodes are used as glucose sensors [Li et al., 2013]. Pt:Co nano-alloy is used for the voltammetric detection of B9 vita-min in food samples [Jamali et al., 2014].

Conclusion

Metal NPs and nano-alloys are very important among nanomaterials. As their properties can be controlled, many metal particles can be prepared in nano scale and used in different applications. Biological synthesis of met-al NPs, in addition to conventional chemical and physical methods, might be an indicator that this field will further expand.

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3.3 NATURAL POLIMERIC NANOPARTICLES

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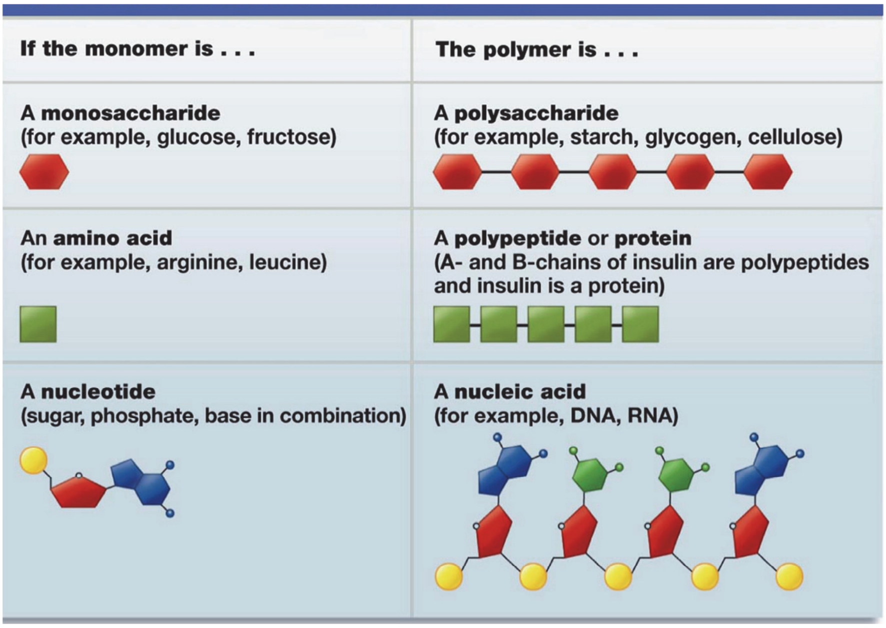
INTRODUCTION

Polymers are comprised of chemical structures called monomers and they have many molecules, therefore they are also called macromolecules and they form a class of synthetic or natural matters. Living organisms have many polymers including cellulose, proteins and nucleic acids. Synthetically produced materials like cement, glass, paper and plastic are known to be polymers consisted of minerals such as graphite, quartz and feldspar. Some natural polymers are consisted of a single monomer. As with copolymer, many natural and synthetic polymers can be formed by combination of two or more monomers. Some natural polymers are presented in Table 3.3.1. DNA, RNA, protein and polysaccharides are among the most well-known natural polymers. Natural polymers of polysaccharides and proteins are widely used in nanotechnological studies.

Table 3.3.1. Some natural polymers



If the monomer is . . .	The polymer is . . .
A **monosaccharide** (for example, glucose, fructose)	A **polysaccharide** (for example, starch, glycogen, cellulose)
An **amino acid** (for example, arginine, leucine)	A **polypeptide** or **protein** (A- and B-chains of insulin are polypeptides and insulin is a protein)
A **nucleotide** (sugar, phosphate, base in combination)	A **nucleic acid** (for example, DNA, RNA)

This image is published on https://www.studyblue.com/notes/hh/examples-monomers/24537649871212579 and retrieved from Google Images.)

3.3.1 Natural Polymers

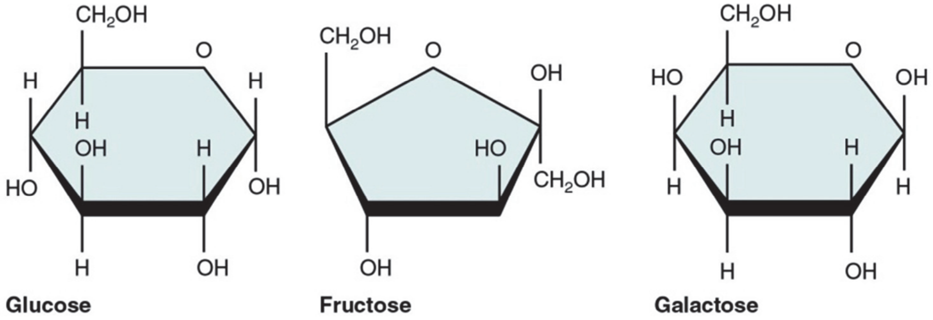
Various natural polymers are used for the preparation of nanoparticles, especially to minimize the side effects that may occur during tissue engineering and drug delivery studies. Polysaccharides and proteins are among the most studied polymer class.

3.3.2 Polysaccharides

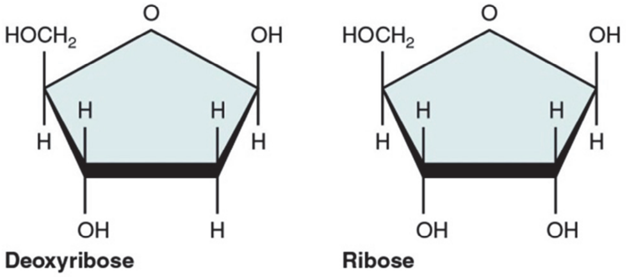
Polysaccharides are complex carbohydrates made up of monosaccharide (Figure 3.3.1) monomer units and they are present in the nature in a wide scale from microbiological creatures to animals and plants. They are mostly used in drug delivery studies since they are biodegradable. Polysaccharides are biocompatible for humans and therefore they are not toxic. They attach to the target tissues due to their reactive functional groups and they bond to the epithelial cells with non-covalent bonds. In addition, they have the specific receptor recognition ability. Since they provide neutral coating with low surface energy, they enable non-specific protein adsorption. They have many hydroxyl groups that enable special ligands to join the structure. Dextrine, chitosan and alginate are examples of polysaccharides (Martínez et al. 2012, Reddy et al. 2015, Yang et al. 2015).

3.3.3 Chitosan

Chitosan is a natural polymer obtained by removing an acetyl from chitin, which is attained from testaceans such as lobster, shrimp and crab (Figure 3.3.2). Chitin is the second most abundant polymer in the nature after cellulose (Martínez et al. 2012, Reddy et al. 2015). Therefore, chitosan is an abundant and relatively cheap product. Chitin is a non-toxic and eco-friendly polysaccharide and it is a good biocatalyst. Although chitin is insoluble in many solvents, chitosan is soluble in all solvents with pH lower than 6.5 such as formic acid, acetic acid, sitric acid and tartaric acid. Chitosan provides the convenience of working under moderate conditions for manufacturers and users, and the ability to produce with desired porosity and polymer length and to control its mechanical/biological properties. In addition, the presence of suitable chemical side groups to bond with other molecules extends its use in tissue engineering. Chitosan is also being used for many studies about wound dressing and drug delivery systems. The most important disadvantage of chitosan in tissue engineering applications is the low tolerance and inconsistent behaviors of its polymeric structure. Chitosan's ability to easily be bonded with the other molecules and cells is its most important advantage and turns its disadvantage into positive. With this property, chitosan mixture with synthetic polymers like polyvinyl alcohol and polyethylene glycol or its mixture with natural polymers such as collagen can be produced. These mixtures are promising studies conducted to improve the poor properties of chitosan (Martínez et al. 2012, Hudson and Margaritis 2014, Reddy et al. 2015, Yang et al. 2015).



(a) Hexoses



(b) Pentoses

Figure 3.3.1. Monosaccharide examples

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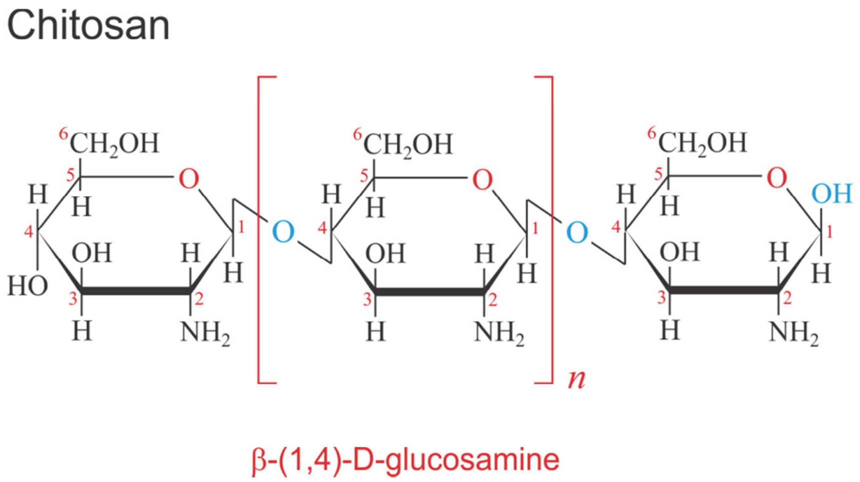

Figure 3.3.2. Structure of chitosan

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3.3.4 Dextran

Dextran (Figure 3.3.3) is a branched and complex polysaccharide consisted of chains with various lengths and many glucose molecules. These types of polysaccharides are comprised of simple sugar glucose monomer and are stored as energy sources in yeast and bacteria. In addition to being a natural product, dextran is also being used in many areas for its superior humidification properties, clinical safety and excellent biocompatibility (Martínez et al. 2012, Reddy et al. 2015). They are widely used in food industry applications as thickener, emulsion former and stabilizer. They are easily soluble in water, methyl sulphoxide, ethylene glycol and glycerol. In spite of that, some of the dextran fractions are only soluble under strong heating effect. The most important characteristic of dextran is that it is a polysaccharide. Therefore, it has a wide application field (Martínez et al. 2012, Reddy et al. 2015, Yang et al. 2015).

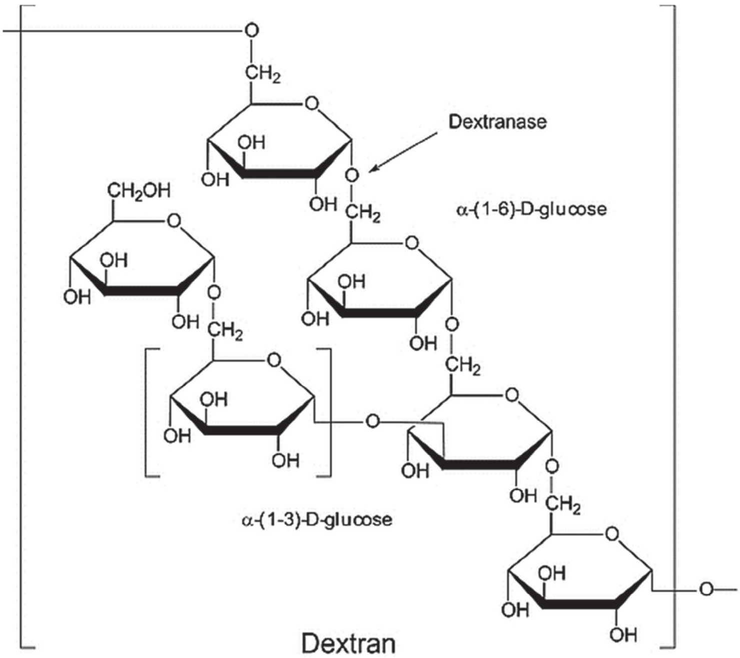


Figure 3.3.3. Structure of calcium alginate

(This image is published on https://en.wikipedia.org/wiki/Calcium_alginate and retrieved from Google Images.)Dekstranın yapısı

3.3.5 Alginate

Alginate is a polysaccharide produced from brown algae. It is also a copolymer that is naturally formed from glucuronic and mannuronic acid. Alginate is widely used in wound dressing, food products and pharmaceutical applications with its characteristics that are similar to chitosan, such as low toxicity, low inflammation, biodegradability, controllable porosity and ability to form bonds with biologically active molecules (Martínez et al. 2012, Reddy et al. 2015, Yang et al. 2015). Simple aqueous gel formation of sodium alginate under the presence of cations with 2 valence electrons such as calcium (Ca^{2+}) (Figure 3.3.4) makes it preferable for drug delivery applications. Drug entrapment capacity that is as high as 70-90% can be achieved in such applications. Since they can be attained in sizes smaller than 100 nm, they are aimed to be used in gene delivery studies as well. Alginate is obtained in bead and solid gel forms under mild processing conditions for uses that allow cell entrapment. Entrapment of cells inside alginate particles increases the survival and growth likelihood of the cells; therefore, alginate is being investigated to be used in tissue engineering studies. In order to improve the low mechanical resistance and poor cell bonding properties of alginate, it is being used by mixing with natural polymers such as agarose, chitosan (Martínez et al. 2012, Hudson D. and Margaritis A. 2014, Reddy et al. 2015, Yang et al. 2015).

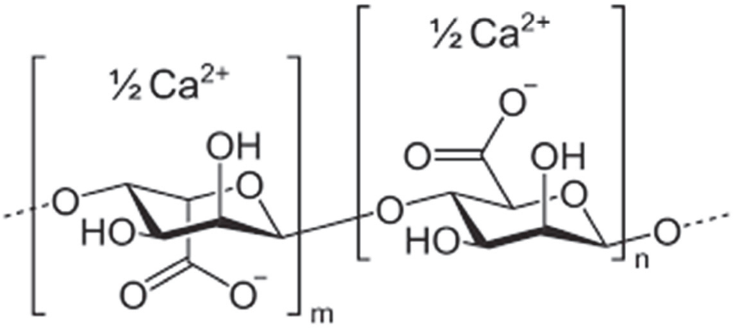


Figure 3.3.4. Structure of calcium alginate

(This image is published on https://en.wikipedia.org/wiki/Calcium_alginate and retrieved from Google Images.)Kalsiyum aljinat yapısı

3.3.6 Proteins

Proteins are consisted of many amino acid units that are connected with peptide bonds (Figure 3.3.5). Proteins are vital units in humans, animals and plants. Certain proteins have drawn attention as biodegradable polymers. Due to low production efficiency and high production costs, very few can be produced on an industrial scale. Soybean, corn and wheat proteins are obtained from plants, casein, collagen, gelatin and keratin proteins are obtained from animals in terms of protein sources. Many proteins are made up of straight polymers made from approximately 20 different amino acid sequences. The side chains of the standard amino acid have different chemical structures and properties. Proteins can be classified as fibrous, spherical and film in terms of shape and solubility. The fibrous proteins have a relatively simple and regular flat structure. Since the polypeptide chain is tightly folded in spherical proteins, hydrophilic groups are located on the outside to interact with solvents and hydrophobic groups are on the inside. Therefore, spherical proteins are highly soluble in aqueous environments. Film proteins interact with different membrane systems of the cells. Hydrophobic segments of film proteins are arranged in an outward manner to enable interaction with the membrane systems. Therefore, they are very slightly soluble in aqueous environments (Lohcharoenkal et al. 2014, Reddy et al. 2015).

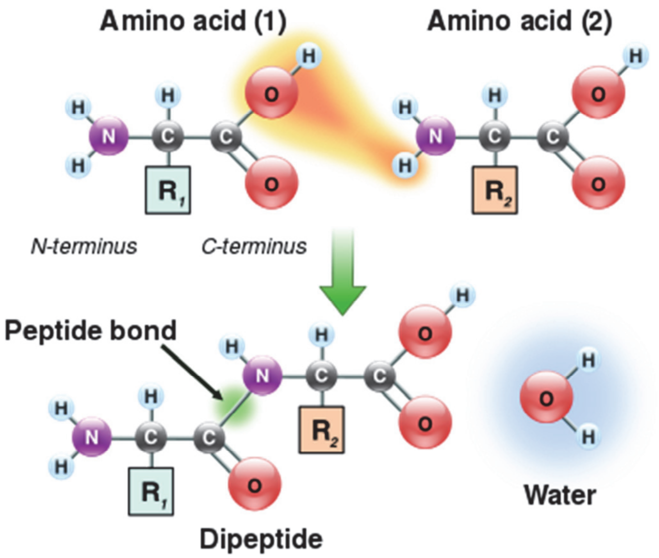


Figure 3.3.5. Peptide bonds that form the proteins

(This image is published on https://en.wikipedia.org/wiki/Amino_acid and retrieved from Google Images.)

3.3.7 Collagen

Collagen (Figure 3.3.6) is a protein that is widely found in mammals and it provides strength to the tissues. A typical collagen molecule is consisted of three intertwined protein chains that form helical structures. These molecules undergo polymerization to produce collagen fibers with different length, thickness and mesh patterns. It is considered that there are at least 15 different collagens in terms of their different structures, functions, locations and other properties. The most dominant form used in biomaterial applications is the string shaped Type I collagen, which can be found almost anywhere in the body and includes bones and skins. Collagen can be absorbed by the body and it is not toxic; it just has a slight immune response. In addition, they are excellent in terms of biological interaction and bonding with the cells. Collagen can be converted into various shapes such as porous rubber, gels and layers, and they can be cross bonded with chemicals to change the degradation speed or to enhance the structure. Collagen has many different biomedical applications from surgery, cosmetics, bioprosthesis implants and to create artificial organs in tissue engineering. In addition, collagen may manifest alterations such as unsuitable mechanical properties or structural reduction (contraction) mainly due to from cell behaviors. Since cells easily interact with collagen, cells push the collagen fibers and re-organize them.

If the collagen is not supported with another material or not chemically bonded, the structure loses its backbone. In such cases, collagen can be easily bonded with other biological/artificial materials to have them change their path when the cells grow or to improve their mechanical properties. Therefore, the studies conducted to bond the collagen as a signaling molecule to the various proteins or growth factors to adapt cell behavior to special applications are very exciting (Lohcharoenkal et al. 2014, Reddy et al. 2015).

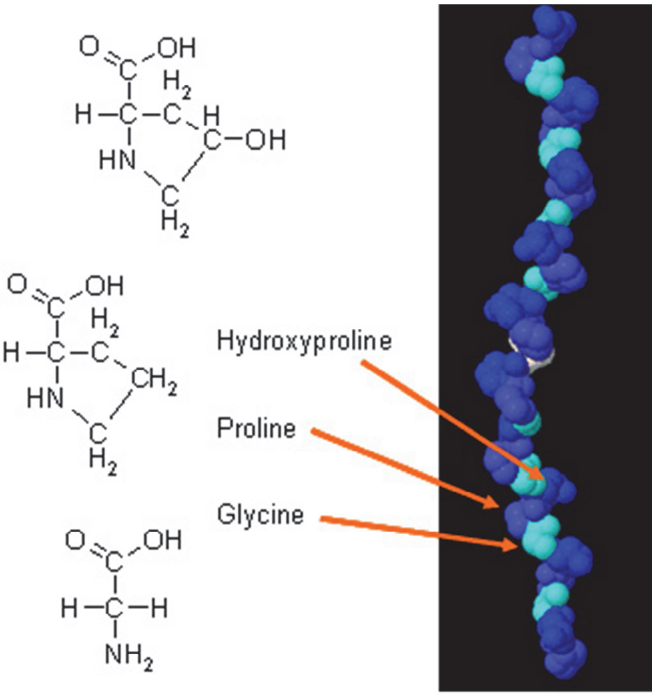


Figure 3.3.6. Structure of collagen

(This image is published on http://proteopedia.org/wiki/index.php/Collagen#Structure_of_a_Segment and retrieved from Google Images.)Kollajen yapısı

3.3.8 Gelatin

Gelatin (Figure 3.3.7) is one of the protein materials used in the production of nanoparticles. Gelatin is obtained from the controlled hydrolysis of collagen, which is found as the fundamental material of the skin, bones and connective tissue. Gelatin is a transparent, odorless, tasteless, non-toxic, biodegradable and pale yellow biological material that can be cross linked and chemically modified, and can be commercially produced in the forms of powder, granule and plate. Gelatin contains cationic and anionic hydrophilic groups within its structure. Mechanical and thermal properties vary depending on the cross bonding degree of these cationic and anionic groups. Gelatin is soluble inside hot water, glycerol and acetic acid, however, it is sometimes insoluble in less polar organic solvents like acetone. This natural polymer is being used in food, pharmaceutical and health industries for many years due to its excellent biocompatibility, easy processing and low costs (Lohcharoenkal et al. 2014, Hudson and Margaritis 2014, Reddy et al. 2015).

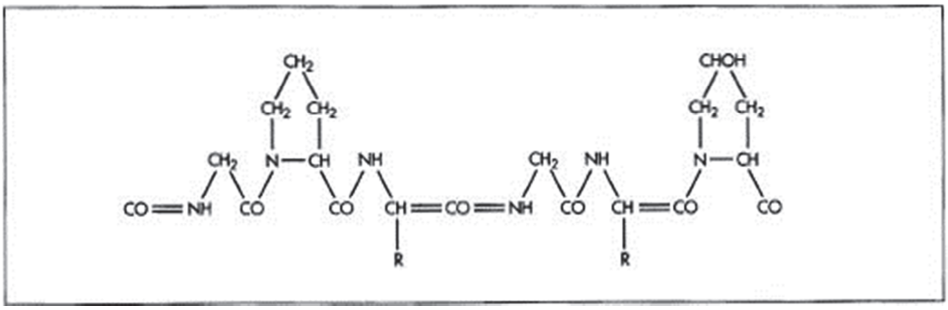


Figure 3.3.7. Structure of gelatin

(This image is published on http://www.madehow.com/Volume-5/Gelatin.html and retrieved from Google Images.)

3.3.9 Albumin

Albumin is another natural polymer that is widely used to prepare nanocapsules and nanospheres. Albumin (Figure 3.3.8) is widely preferred for nanoparticle production for its availability in pure form, biodegradability, non-toxicity and its properties that have no impact on immune system. Albumin is an important plasma protein (bovine serum albumin, BSA and human serum albumin, HSA). Albumin nanoparticles are also biodegradable and it is easy to prepare them in desired sizes. Due to the reagent groups like thiol, amino and carboxylic groups it carries on its surface, its surface can be more conveniently modified and bonded with ligand (Lohcharoenkal et al. 2014, Hudson and Margaritis 2014, Reddy et al. 2015).

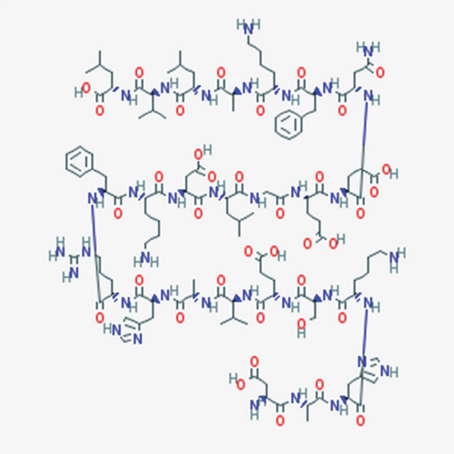


Figure 3.3.8. Structure of gelatin

(This image is published on http://www.madehow.com/Volume-5/Gelatin.html and retrieved from Google Images.)

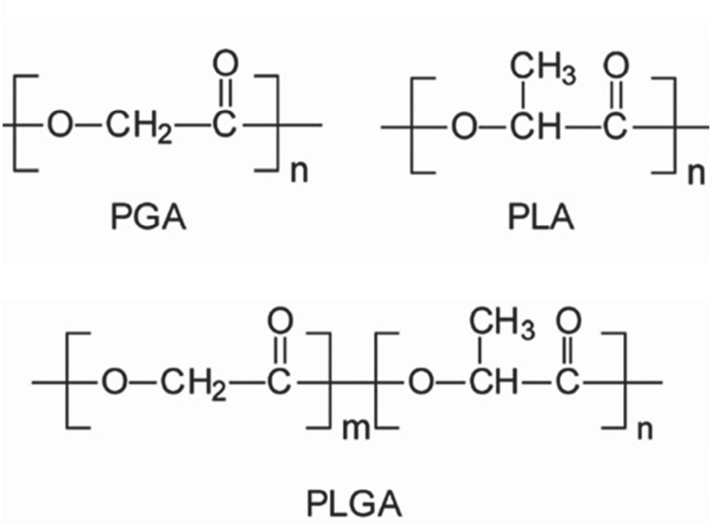
3.3.10 Synthetic Polymers

In comparison with natural polymers, synthetic polymers have similar chemical properties, and therefore they are very appealing due to the reproducibility of synthesized nanoparticles. Polyamides, polyesters, polyortoesters, moly(amino acids) are among the synthetic polymer class.

3.3.11 Lactide and Glycolide Copolymers

These are the most popular biodegradable polymers that are used in drug delivery. They are aliphatic polyester copolymers based on lactide and glycolic acids. Poly(P;L-lactide-co-glycolide) (PLGA) (Figure 3.3.9) is known as a biocompatible polymer produced from the natural products of lactic and glycolic acid. PLGA is used for the production of implants and inseams. PLGA is widely used in nanomedicine field. The most important reason of this is the fact that PLGA is transformed into biologically degradable lactic acid and glycolic acid monomers through hydrolysis in the body. These monomers are metabolized in the body via the Krebs cycle and they are disposed of as carbon dioxide and water. Degredation of PLGA nanoparticles depends on chemical composition, porosity, hydrophilic/hydrophobic characteristics, morphology (crystalline/amorphous), molecular weight and molecular weight distribution. Lactide polymer (PLA) is more hydrophobic than glycolide polymer (PGA) due to the methyl group it contains. The duration these linear (straight) polyesters stay in the body can be increased by mixing them with more hydrophobic comonomers such as polycaprolactone (Makadia and Siegel 2011, Mirakabad et al. 2014, Reddy et al. 2015).

Figure 3.3.9. Chemical structure of poly lactic-co-glycolic acid



(This image was published on http://www.drug-dev.com/Main/Back-Issues/PLGAPEG-Block-Copolymers-for-Drug-Formulations-406.aspx and retrieved from Google Images.)

3.3.12 Poli(ε-Caprolactons)

Despite being hydrophobic and having high crystallinity, poly(ε-Caprolactone) (Figure 3.3.10) is a water permeable polyester type polymer. During its biodegradation, poly(ε-Caprolactone) undergoes bulk erosion that is initiated with random chain scission at the first stage and results in a reduction in the molecular weight of the polymer. In the subsequent second stage, these segments with low molecular weight are exposed to phagocytosis or dissolution in the body fluid. Poly(ε-Caprolactone) breaks down at a significantly low rate than PLA, PGA and PLGA; therefore, poly(ε-Caprolactone) is less appealing for general tissue regeneration applications. However, it is more attractive for long-term applications such as implants and drug delivery systems (Azimi et al. 2014, BaoLin and Ma 2014,
Reddy et al. 2015, Mohan et al. 2016).

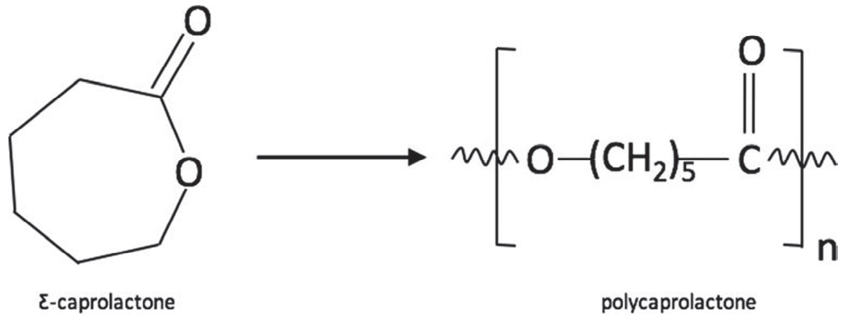


Figure 3.3.10. Structure of polycaprolactone

(This image is published on https://www.intechopen.com/books/periodontitis-a-useful-reference/polycaprolactone-based-biomaterials-for-guided-tissue-regeneration-membrane and retrieved from Google Images.)

3.3.13 Polyanhydride

Hydrophobic and crystalline polyanhydride (Figure 3.3.11) are being used in drug delivery applications. When drugs are embedded in such polymers, they can be better protected because before polymer is worn away, almost no water gets inside. The degradation in the body starts with surface erosion, i.e. hydrolysis. Monomeric anhydrite bonds on the surface are highly reactive against water and they undergo hydrolysis to form dicarboxylic acid. At low pH values, oligomeric products formed on the matrix surface have low solubility; this prevents the nucleus (core) from degradation. They are started to be used in tissue studies for this characteristics (Vroman and Tighzert 2009, BaoLin and Ma 2014, Reddy et al. 2015).).

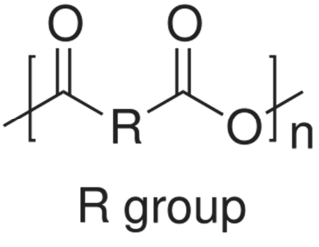


Figure 3.3.11. Structure of polyanhydride

(This image is published on https://en.wikipedia.org/wiki/Polyanhydrides and retrieved from Google Images.)

3.3.14 Dendrimers

Polymer chemistry and technology is generally focused on linear (straight) polymers, which traditionally have wide field of application. Linear macromolecules only occasionally contain smaller or longer branches. In recent years, multi-branched macromolecules are found to have different properties than conventional polymers. They were first disovered by Donald Tomalia and his friends in the early 1980s. These hyperbranched molecules are called dendrimers. The term is derived from the Greek word 'dendron' which means a tree. Although they were named differently before, 'dendrimer' is the most commonly used term (Klajnert and Bryszewska 2001, Abbasi et al. 2014).

Dendrimers are nano-sized, well-defined, homogeneous and monodisperse structures that are consisted of tree-like branches. These hyperbranched molecules contain symmetrically branched units that are formed around a linear polymer nucleus or a small molecule. Dendrimer is just a designed architectural pattern, it is not a compound. As a function of the increased generations (Figure 12), they change in terms of size, shape and flexibility. Their physicochemical or biological properties are modified through the outermost functionalized groups. Therefore dendrimers have properties that make them very special for very special applications. These well-defined materials are the best class of nano-scaled delivery devices of macromolecules with their advantages. These dendritic macromolecules tend to increase their diameter in a linear way and they gain more spherical shapes with increasing dendrimer generation. Therefore, they are remarkable for use in cancer treatment and diagnostic imaging applications (Klajnert and Bryszewska 2001, Abbasi et al. 2014).

Structure of dendrimer molecules start with a central atom or a group of atoms labelled as core. From this central structure, branches of other atoms called dendrons grow outwards from the core molecule via various chemical reactions. The core molecule reacts with monomer molecules containing one reactive and two dormant groups giving the first generation dendrimer. Then the new periphery of the molecule is activated for reactions with more monomers. Each new generation is numbered to define the dendrimer (G1, G2, G3, etc.) (Figure 3.3.12). Every dendrimer with different number manifests different properties. Dendrimers can be prepared in a controlled way and this enables the formation of almost monodisperse, spherical macromolecules which cannot be achieved with most linear polymers that have many peripheral groups (Klajnert and Bryszewska 2001, Abbasi et al. 2014).

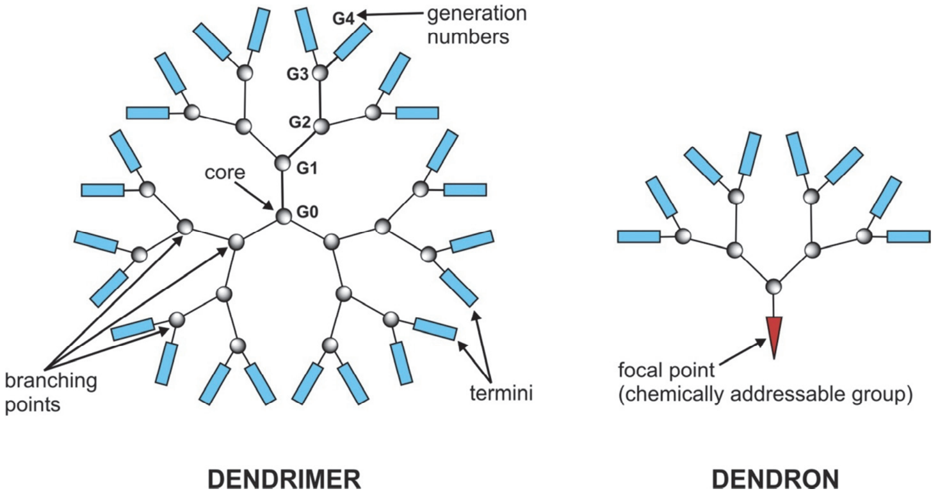


Figure 3.3.12. . Structure of dendrimer and dendron

(This image is published on https://en.wikipedia.org/wiki/Dendrimer and retrieved from Google Images.

Dendrimers are a new class of polymers. Their chemistry is one of the most attractive and rapidly growing areas of modern chemistry. Dendrimer chemistry has its own terminology and abbreviations, like in other research areas. In addition, a short structural nomenclature is applied to describe the different chemical events that occur on the surface of the dendrimer (Klajnert and Bryszewska 2001, Abbasi et al. 2014).

Summary

Natural polymeric nanoparticles can be classified as sugars and proteins based on the frequency of use. Chitosan, gelatin and albumin are among the most common natural polymers. In order to overcome the disadvantages of each of them, new studies are being conducted by preparing two or more compositions. In addition, synthetically synthesized polymeric nanoparticles provide new promises in application. Among these, the most common ones are; poly (lactic acid-co-glycolic acid), poly (ε-caprolactone). With their monodisperse distribution and controllable dimensions, the dendrimers are the new class of macromolecules, and they stand out in many applications with their superior properties.

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3.4 CERAMIC NANOPARTICLES

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INTRODUCTION

Materials with nanocrystal structures posses very important changes in their physical, chemical and mechanical properties with their reduced sizes. Development of advanced engineering materials became possible through the combination of these unique and exceptional mechanical, electrical and thermal properties of these materials with various matrices (polymers, ceramics and metals). Nanostructured ceramic materials gained great importance in the past twenty years with their high durability properties at both normal and high temperatures, chemical resistance, high mechanical strength and rigidity. These materials are especially suitable for sintering and reactions with different oxides. These nanoscaled materials attracted the interest of many studies in various fields from material sciences to biotechnology and genetics.

In recent years, use of ceramic materials, which are being used in many applications for their unique properties when mixed with metal and polymers, has significantly increased. The most advantageous properties of ceramic materials are rigidity, stiffness, abrasive toughness and low density. Ceramics belong to a material class defined as “inorganic, ametalic solids”. They have the wide range functions of all known materials. In recent years, exceptional potentials of functional ceramics, which are based on unique dielectric, ferroelectric, piezoelectric, pyroelectric, ferromagnetic, magnetoresistan, ionic, electronic, superconductive, electrooptical and gas sensor properties, are being developed. Similar scientific developments took their place in structural ceramics. Thermal, chemical and mechanical stability of many oxide and non-oxide compounds have established the foundation for improvement processes of micro-structured design and error control. Therefore, this resulted in unique developments about the reliability in mechanical performance and reliability of components and devices. In addition, exceptional combinations of thermal, insulating and mechanical properties formed the basis of incredible applications in the production of microelectronics and power semi-conductors. Therefore, ceramic materials became the building blocks of advanced technologies such as energy conversion, storage and supply, information technologies, transportation systems, medical technology and manufacturing technologies. In addition to these trends, today's environmental regulations, recycling of the materials and awareness will affect the use of these materials and lead to cheaper production processes. Needs for future ceramic researches can be divided into four main group in line with the technological trends:

(1) to research the materials and material properties in order to extend the scope of the field and to meet the needs of future applications,
(2) to research information about economical and ecological production processes for materials, compounds and devices,
(3) to provide miniaturization and integration
(4) to create complementary or superseding models and numeric simulations for current areas of experimental studies, thus, not just only directing the research towards identified questions, but also to reduce practical operation and duration through product development.

Nanocrystal ceramic materials have been the focal point of researches for the past 20 years for their significantly improved mechanical properties when particle sizes are decreased to nanometer scale. However, although there are various technologies for manufacturing nano sized ceramic powders, attainment of true nanocrystal ceramics (average particle size <100 nm) is very hard due to the difficulties encountered during the sintering of particle growth. Particle growth takes place compact or at surface contamination due to use of conventional methods of powder consolidation, high temperatures and long sintering duration. Therefore, particle growth must be minimized by controlling consolidation parameters, sintering temperature and careful regulation of time. It is also difficult to evaluate mechanical properties of nanocrystal ceramic materials because there are very few published data about true nano-sized particles. Nanoceramic powder constitute a major part of all nanostructured materials. Indeed, it can be said these materials are the one third of all new nano-structured materials.

Nanoceramics are commercially available as dry powder or liquid dispersion. The most important commercially available nanoceramic materials are basic oxides, silica (SiO_2), titanium (TiO_2), alumina (Al_2O_3), iron oxide (Fe_3O_4, Fe_2O_3), zinc oxide (ZnO), cerium dioxide (CeO_2) and zirconium (ZrO_2). Silica and iron oxide nanoparticles have more than half a century of commercial history. On the other hand, nanocrystal titania, zinc oxide, cerium dioxide, indium tin oxide (ITO) and other oxides are new in the market.

Nanostructured materials are known as middle-sized objects between microscopic and molecular structures. With various advantages and disadvantages, metal oxides, metal nanoparticles, metal complexes, polymers, carbon nanotubes and recently graphene are among the nanomaterials used for the design of gas sensors. Ceramic nanomaterials offer ideal options for manufacturing of high-performance gas sensor thanks to the exceptional combination of their physical and chemical properties. Ceramic nanomaterials increase sensitivity, selectivity and stability, and reduce process temperature and response time for gas sensors. Therefore, performance of gas sensors can be improved by using ceramic nanomaterials with their morphology, content, size and physicochemical properties.

Ceramics in nano phase draw special attention because they gain a more ductile characteristic than coarse-grained ceramics at higher temperatures.

3.4.1 Conventional Sintering Method

Ceramic materials with dense nanostructures are general obtained by using pressure supported pressing methods of nano powders such as hot pressing, hot isostatic pressing, sinter forging and traditional sintering methods [(Mayo, 1997; Groza, 1999; Veljovic et al, 2007].). In conventional sintdering methods, high sintering temperatures and long sintering durations for assembling ceramic powders generally result in particle growth, ceramic degradation and deterioration of mechanical properties of ceramic (Gua et al, 2004; Tang et al, 2009). Hot pressing of some ceramic materials allows condensation at lower temperatures than traditional sintering (Halouani et al, 1994; Veljovic et al, 2009). Improved compression kinetics and limitation of particle growth are the advantages of hot pressing technique. On the other hand, limited geometry of the final product and high cost of required equipment are among the disadvantages of this method.

3.4.2 Advanced Sintering Method

Assembly of nanocrystal powders is a difficult problem that needs to be solved. The weird thing about sintering of nanocrystal powders is the competition between compression and microstructure growth processes, which take place in parallel. In order to assembly a material at a density close to its theoretical value and with smallest possible particle size, various techniques are developed that accelerate the first process and decelerate the second one. Fast heating, high pressure, shrinking accelerator and particle growth inhibitor agents are the most widely known agents for such purpose. Non traditional sintering and compression techniques are recommended to overcome the particle growth problem. Advanced sintering has a great potential in ceramic processing field. These are; use of agents that prevent particle growth in a solid solution or form separate second phase, compression at high pressure, arc-plasma sintering and related techniques, shock compression, high frequency induction heating and magnetic pulse compression [Allen et al, 1996; Kim and Khalil, 2006; Godlinski et al, 2002; Krell et al, 2003; Jiang et al, 2007].

3.4.3 Usage areas of nano sized ceramic materials

Nano structured ceramic materials have good thermal resistance at both high and low temperatures, good chemical resistance and good mechanical resistance and rigidity. They are especially suitable for sintering and reaction with other oxides. These nano-scaled materials have attracted the interest of many studies in various fields from material sciences to biotechnology and genetics.

In recent years, there is an ever-increasing interest towards nano structured ceramics that are synthesized in sized sizes smaller than 100 nm. This interest has grown larger with various applications in the industry; sensors, batteries, capacitors, corrosion-resistant coating, thermal barrier coatings, solid electrolytes for fuel cells, catalysts, cosmetic products, health, automotive, bioengineering, optoelectronics, computer and electronic devices [Veljovic et al, 2007].

Nanomaterials in luminescence field also gained importance because these materials exhibit advanced optical, electronic and structural properties. Many new physical and chemical production methods are developed in the past twenty years. Nanoparticles and nanorods of some ceramic materials are produced. Recent studies revealed that optical, luminescence and other properties can be modified by shape and size, integration of impurities in different locations and with the presence or absence of certain flaws [Godlinski et al, 2002].

Right now, ceramic materials are being rapidly developed for biomedical applications. Hydroxyapatite (HA), zirconia (ZrO_2), silica (SiO_2), titanium oxide

(TiO_2), and alumina (Al_2O_3), which are among nano sized ceramics, can be produced with new synthetic methods to improve their physicochemical properties.

Controlled drug release in biomedicine became the most widely area of use for ceramic nanoparticles. In this application, where dose and size are of crucial importance, high stability, high loading capacity, easy inclusion in hydrophobic and hydrophiliphlic systems and different administration routes (oral or respiratory) are the other properties.

Conclusion

Although there are various techniques used to obtain nano sized ceramic powders, attainment of correct nanocrystal ceramic (average particle size <100 nm) is a major problem due to the difficulties in controlling the particle growth during sintering. Instead of conventional methods that result in unwanted ceramic sizes due to high temperature and long sintering durations, new advanced sintering methods are recommended that can minimize particle growth by controlling assembly parameters, temperature and duration.

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3.5 MAGNETIC NANOPARTICLES

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INTRODUCTION

The concept of magnetism, in its basic form, can be understood by looking at a mag-net that pulls metal needles at a certain distance towards itself. The question is why those metal needles are pulled with a greater force as they get closer to the magnet? We can mention a force field that is invisible but felt by the matter. The pulling or push-ing field created by the magnet is called the magnetic field.

Figure 3.5.1. Magnetism

Here, another question comes to mind: why does the magnet create such a powerful pull field around itself and how do the metal needles detect it? The answer is hidden in the atoms that form the magnet and the needles. As we all know, each matter is formed by atoms. According to the classical view, atoms are made of a nucleus con-sisted of protons and neutrons, and electrons that orbit around this nucleus. Although all matters are formed by atoms, the difference beetween the number of these sub-atomic particles creates different types of atoms. And matters with different physical and chemical properties are obtained when different types of atoms come together. In the most basic level, moving charges create magnetic fields. Electrons moving around the nucleus have an orbital angular momentum, which is defined as magnetic moment that depends on the movement direction. The addition of angular momentum called spin, which depends on the intrinsic properties of the particles, and the orbital anguar momentum forms the net magnetic moment of that particle.

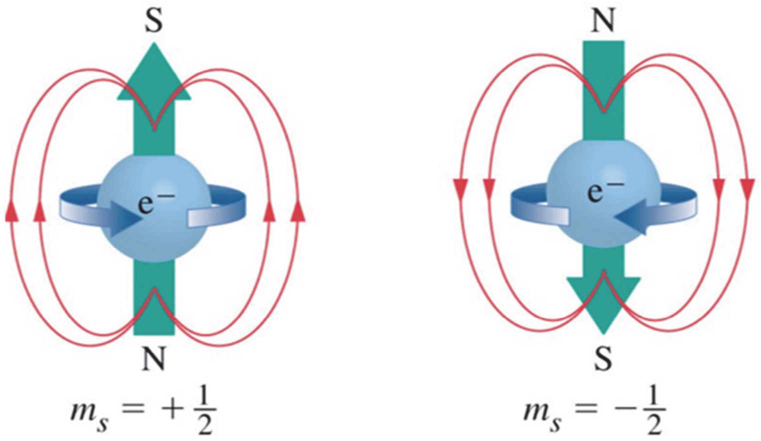

Figure 3.5.2. Electron spin momentum

Similarly, protons inside the nucleus have magnetic moment since they are also charged particles. Unpaired electrons inside a matter that is formed by the bonding of atoms or ions cause the matter to exhibit magnetic properties and they react against an externally applied magnetic field.

Magnetic Properties of Matter

Materials have three different categories based on their magnetic properties. These are:

- Dia magnetic materials
- Paramagnetic materials and
- Ferromagnetic materials.

Diamagnetic Materials

These materials do not have unpaired electrons, all of them are paired. They re-act in the opposite direction to the applied magnetic field. Their susceptibility values, a measure of magnetic properties of materials, are small and negative. Materials such as copper, silver, gold and bismuth have diamagnetic properties. Superconductors, materials that exhibit zero resistance under certain tempera-tures, are also diamagnetic materials.

Paramagnetic Materials

Paramagnetic materials react to the magnetic field in the same direction but their reaction is weak. Their susceptibility values are small and positive. Materials such as aluminum and platinum have paramagnetic properties. There is no magnetic field inside the paramagnetic matters and the directions of magnetic moments are random. Therefore, the total magnetisation is zero. If a field is ap-plied, they direct towards the field. When the magnetic field is removed, they align randomly again and the total magnetisation becomes zero. Nuclear Mag-netic Resonance (NMR) system used in medicine utilizes the paramagnetism inside the body to perform imaging.

Ferromagnetic Mateials

These materials have high susceptibility and react to the applied magnetic field in the same direction. Even when they are placed in-side a weak magnetic field, they align parallel to the field and create a very strong magnetisation, therefore they are frequently used in applications. These strong magnetisation properties are due to the magnetic moments aligned in the same direction with each other as groups inside the regions called domain within their inner structures.

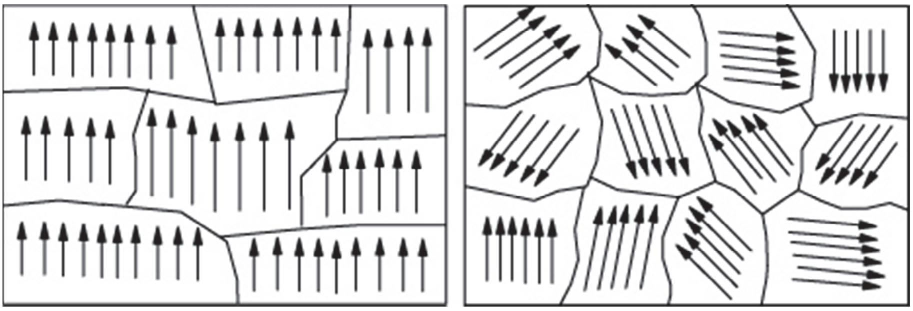

Figure 3.5.3. Magnetic areas

(http://iopscience.iop.org/article/10.1088/0022-3727/42/3/032006)

Susceptibility values of ferromagnetic materials vary between 50 and 10000. Many transition metals like iron, cobalt, nickel, and some rare earth elements and their alloys have ferromagnetic properties.

Similar to ferromagnetics, there are materials that have magnetic arrangements inside. These materials are classified as ferromagnetic materials due to the magnetic arrangements they have. These materials are Ferromagnetic,

Antifer-romagnetic, Helimagnetic and Superparamagnetic materials. Especially the su-perparamagnetic materials are interesting types with nanometric-sized materials.

Superparamagnetic Materials

Superparamagnetic materials act as single-domain materials due to their sizes. Therefore, each nanoparticle is like a single domain. When an external magnetic field is applied, they align parallel to the field, and when the field is removed, they go back to random alignment and the total magnetisation becomes zero. Therefore, due to these properties, superparamagnetic particles do not exhibit hysteresis, which is observed in ferromagnetics. Although they have high saturation magnetisation values, their permanent magnetisation and coercivity values are zero. Such materials are used in many application fields from medicine to electronics. These include medical imaging, hyperthermia, drug delivery and registration systems. Magnetic hyperthermia treatment is the destruction of cancerous tumor tissues with heat by using magnetic nanoparticles. In this treatment method, the magnetic nanoparticles delivered into the cancerous tissue are oscillated by applying an external AC field. Particles are heated as a result of this oscillation.

Tumor cells, which are extremely sensitive against heat, degrade and die when they reach approximately 42 oC. This way, cancerous tissues can be destroyed without damaging the normal tissues.

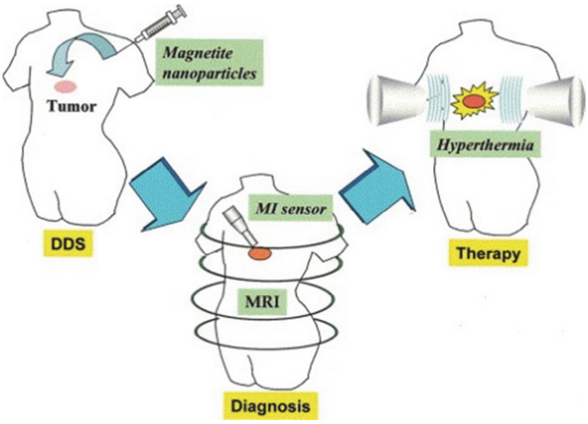

Figure 3.5.4. Hypotermia

(http://trialx.com/curetalk/2012/11/19/cancer-treatment-multifunctional-magnetic-nanoparticles-for-molecular-imaging-and-hyperthermia/)

In the drug delivery applications, drug attached to a nanoparticles is injected to the body and carried to the desired location via the magnetic particles by applying magnetic field to the target region.

References

1) http://iopscience.iop.org/article/10.1088/0022-3727/42/3/032006)

2) (http://trialx.com/curetalk/2012/11/19/cancer-treatment-multifunctional-magnetic-nanoparticles-for-molecular-imaging-and-hyperthermia/)

3.6 CONDUCTOR AND SEMICONDUCTOR NANOMATERIALS

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INTRODUCTION

Everything that has mass, volume and inertia property is made of atoms, and atoms are consisted of a positive nucleus (proton and neutron) and negatively loaded particles (electron) moving around the nucleus in different orbitals. Movement of the electrons create what is known as electrical current, measured in ampere, which is the number of electrons passing on a conductor per unit of time. Electron movement is not the same for every material; therefore, materials are classified as conductors, semiconductors and insulators depending on the movement of the electrons. However, in recent years, a new category known as superconductors is added to the group. Reason for this classification is the differences between band gaps in solid matters.

Solid-state matters have two different bands; conduction and valence bands, and there is a band gap between them. Conduction band represent the energy levels where free electrons participate in conduction, valence band represents the energy levels filled with valence electrons of the atoms of the solid and the band gap between these two represents the forbidden energy levels for the electrons (Figure 3.6.1.). In order to understand whether a material is a conductor, semiconductor or an insulator, the distance between the valence band and conduction band must be examined. To define a material as a conductor, band gap between the two bands must be small.

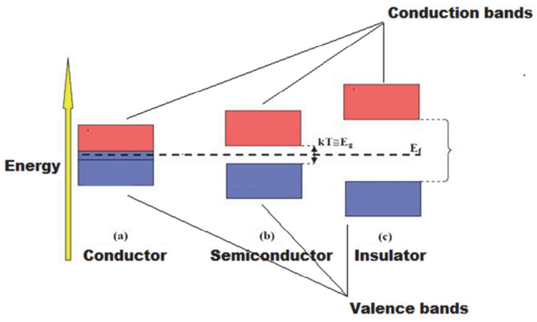

Figure 3.6.1. Conductors, semiconductors and insulators based on their band gaps
(This image is published on goo.gl/txgT3s and retrieved from Google Images.)

3.6.1 Conductors

Objects where electrical or thermal energy can flow are called conductors. Ability of an object to conduct heat is called thermal conductivity, and the ability to conduct electricity is called electrical conductivity.

Heat conduction in thermal conductivity is possible in three different forms; conduction, convection and radiation. During conduction, heat is conducted to the different parts of an object through molecular interaction and mechanical energy changes. In convection, heat is transfered via mass transfer, and in radiation, it is transfered via wave transfer. Each object transfers heat to some degree, however, heat transfered from a unit section of an object per unit of time is referred as heat transfer coefficient and greater this value, better conductor an object.

In electrical conductivity, electrons take part. The most important factor determining the conductivity of a matter is the number of valence electrons in the last orbital of the atoms, known as the valence orbital (Figure 3.6.2.). Valence electrons have a weaker bonding to the atom nucleus than the electrons that are on the inner orbitals. However, since properties like charge, nucleus diameter, total number of protons and electrons differentiate the matters, they affect how strongly the nucleus pulls the electrons. To generalize, matters having more than 4 valence electrons are insulators, and matters with less than 4 valence electrons are conductors.

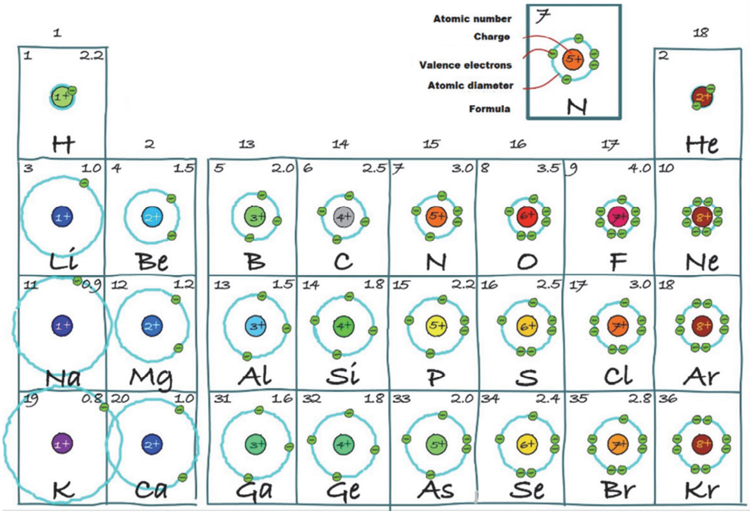

Figure 3.6.2. A sample for valence electrons from the periodic table

(This image is published on goo.gl/KXJdTC and retrieved from Google Images.)

Resistance of some conductor matters like gold, silver and copper decreases with the decreased temperature of the matter. But resistance never falls to zero even when the temperature is close to the absolute zero, which is the lowest possible temperature, due to impurity and structural irregularities of a metal. However, in 1911, physicist Heike Kamerlingh Onnes discovered the phenomenon of superconductivity, a quantum mechanical phenomenon where the electrical resistance of a matter is exactly zero below a certain "critical" temperature. Electrical current can continue inside a superconductor material without having power supply from a source. Generally, liquid nitrogen is used to cool superconductor materials to this critical temperature where they present the superconducting state. Materials with critical temperature lower than the boiling point of nitrogen (77 Kelvin) are called low-temperature superconductors; ones with higher critical temperature are called high-temperature superconductors.

Superconducting materials posses important properties; zero electrical resistance against direct current (d.c.), very high current carrying capacity and very low signal dispersion compared to normal conductors, signal carrying capacity at speeds close to the speed of light, very low resistance even at high frequencies and electrical current conduction without resistance/dissipationless. Therefore, they have a significant importance in carrying and storing the electrical current, construction of powerful magnets, generators, manufacturing of sensitive electrical devices, communication technologies and defense industry.

3.6.2 Semiconductors

Semiconductors are classified between conductors and insulators, and they are the crystalline or amorphous solids in the 3rd and 5th groups of the periodic table. Silicon and germanium are the most well known and most widely used semiconductors in applications. Their valence electron number is 4, which allows them to both receive and give electrons at the same time. They are insulators in their normal states, however, they are exposed to external impacts such as heat, light and magnetic effect or activated by some special materials to impart semiconductor properties, but this conductivity is temporary and is lost when the external effect is re-moved. Semiconductors are studied in two groups, n- and p-type semiconductors, depending on their free electrons or free holes, respectively. Bonding between arsenic and silicon can be explained as an example of an n-type semiconductor. Arsenic atoms have 5, silicon atoms have 4 electrons in their valence orbitals. As a result of the covalent bonding between these two atoms, 1 electron of arsenic atom becomes free and separates. This is called n-type semiconductor due to the presence of a free electron that is not bonded to an atom and it can be said that conductivity is increased. This situation can be explained as the doping of silicon to increase the number of holes in the conduction band of a pure silicon atom. For this purpose, phosphorus, bismuth and antimony, which have 5 electrons in valence orbital, can be used instead of arsenic (Figure 3.6.3).

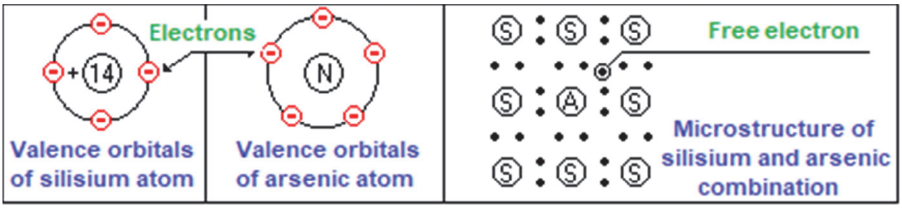

Figure 3.6.3. Formation of an n-type semiconductor material
(This image is published on goo.gl/pfrGbj and retrieved from Google Images.)

Boron element present in certain proportions in pure silicon may be given as an example for p-type semiconductors. There are 3 electrons in the valence orbital of the boron atom and 4 electrons in the silicon atom. When 3 valence electrons of boron atom and 3 valence electrons of silicon atom form a covalent bond, 1 electron of silicon atom remains without bonding, thus, creates a lack of electron or in other words, holes. Since the holes have positive charge, they are called p-type semiconductors. Aluminum and gallium can be used as well instead of boron (Figure 3.6.4.).

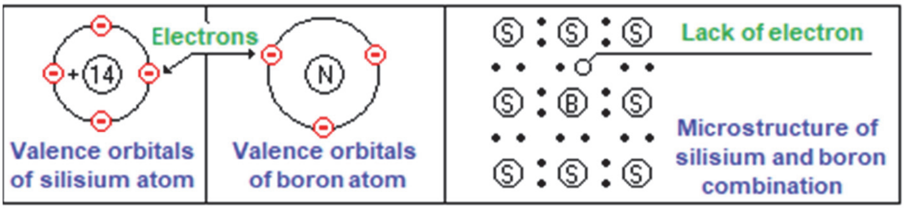

Figure 3.6.4. Formation of a p-type semiconductor material
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3.6.3 Insulators

Electrical insulation is the lack of electrical conductivity in the materials for which the electric charge can not freely flow. A charge, which is a condition for conductivity, flows only when electrons can move freely. If this is not the case, the matter is an insulator. However, perfect isolation is not possible. Insulator materials have the largest band gaps among the ones shown in Figure 3.6.1. They are used to support electrical conductors in electric materials and to disconnect them without allowing current flow, to wrap electrical cables or other materi-als, to connect distribution and transmission lines in electrical poles and transmission towers.

3.6.4 Conductor and semiconductor nanostructures

The most known examples of conductor nanostructures are conducting polymers that have polymeric chain with high π conjugation or the ones transformed from insulators via electrochemical doping (Shi et al., 2015). With their conjugated π-electron backbones, they have electrical properties including high electrical conductivity, high affinity and low ionization potential, as well as optical properties such as low-energy optical transmittance (Vidal et al., 2003). In addition, their conjugated structures provide these polymers with strong UV-Vis adsorption.

Neutral conjugated systems with low conductivity between 10^{-10} and 10^{-5} S/cm can be turned into semiconducting or conducting polymers with conductivity values between 1 and 10^{4} S/cm (MacDiarmid, 2001). This is called doping. Backbone of the conducting polymer contains positive (p-doping) or negative (n-doping) charge carriers, therefore, opposite ions are either captured or released to provide charge balance to the polymer (Figure 3.6.5.).

Conventional conducting polymers are polyaniline, polypyrrole and polythiophene. Conducting polymer nano-composites, which became an active field in studies and applications of composite materials, are consisted of conductive nanofilled materials such as metal nanoparticle, carbon nanotube and graphene, and polymer ma-trix. Because of their ease of process, low densities, adjustable electrical properties, oxidation resistance and flexibility, conducting polymer nanocomposites are used in versatile electrical applications such as antistatic protection, electromagnetic interference protection, energy storage electrode, sensors, flexible electronics and thermoelectric devices (Thomson and Frechet, 2008; Li et al., 2009; Tang et al., 2017).

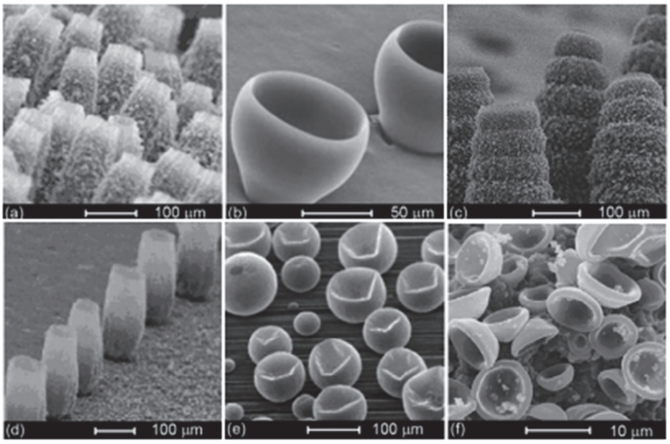
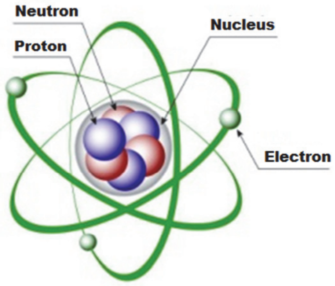


Figure 3.6.5. Images of polypyrrole nanospheres, which are synthesized as doped with different materials or electrochemically, obtained by scanning electron microscope (Bajpai et al., 2004; Gao et al., 2006; Li et al., 2009; Qu et al., 2003; Qu et al., 2004; Qu and Shi, 2004; Yuan et al., 2004)

Conducting polymers can be chemically or electrochemically synthesized. In chemical synthesis, powder nano-materials that can be easily scaled are obtained. However, in electrochemical synthesis, electropolymerization reactions occur at the surface of the electrode, and the nanostructures of the conducting polymers accumulate as a film on the electrode surface. And in some cases, the nanostructures grow with the electric field to form oriented structures. The electrochemical polymerization rate can be easily controlled by the current density or potential, and by the systems for which the product amount is integrated into the system. The morphology and properties of nanomaterials can be changed by the conditions during the electrochemical polymerization. Therefore; electrochemical polymerization method is a single step and effective technique for preparing conductive nanomaterials with desired properties (Li et al., 2009; Teng et al., 2017).

NOTES



Structure of an atom
(This image is published on goo.gl/NsjCu1 and retrieved from Google Images.)

✓ Conduction can be in the form of thermal or electrical energy.

✓ Electron is a charge carrier.

✓ The unit for electrical charge is Coulomb and it is represented as “C”.

✓ Flow speed of the electrical charge is called electrical current and its unit is Ampere.

✓ There are two types of charge; positive and negative, and opposite charges attract each other, whereas like charger repel each other.

✓ Voltage and current in a system encounters with forces that can be defined as difficulties affecting the passage of the electrons on the system. These forces are called resistance. Resistance can also be defined as the ratio of voltage to the current.

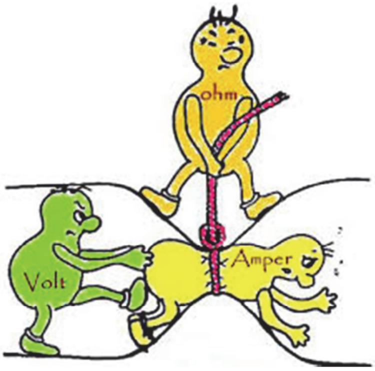
✓ Resistivity is defined as the ratio of electrical field strength to the current density. Conductance is the inverse of resistivity.

✓ Metals can be classified as good and bad conductors.

✓ Metals with valence electrons, such as gold, silver and copper, are classified as good conductors.

✓ Although copper is less conductive than gold and silver, and cannot be obtained in a completely pure form, it is more commonly preferred because of its low cost and abundance.

✓ Gold and silver are the best two conductors but they cannot be preferred due to their costs.



Current-potential and resistance relation
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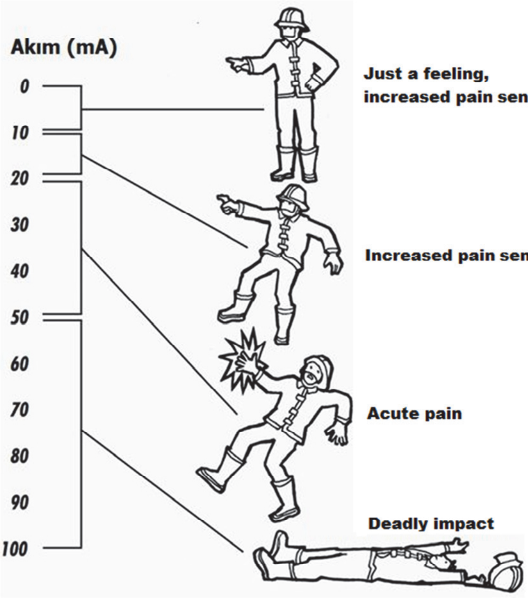

Effects of electric shock
(This image is published on goo.gl/PB538a and retrieved from Google Images.=

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3.7 QUANTUM DOTS

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INTRODUCTION

Quantum dots (QDs) are semiconductor particles with the size of a few nanometers. Quantum dots have unique luminescence and electrical properties such as wide and continuous absorption spectrum, narrow emission spectrum and high light stability. Crystal diameters of quantum dots are generally 1-10 nm and their optical and electrical properties change depending on their sizes [Jamieson, 2007]. As the crystal diameter of the quantum dots increase, the florescence emission shifts to the red region. This shift to red region occurs due to the narrowing of the band gap between valence and conduction bands. However, this narrowing of the band gap continues until a certain magnitude of the crystal size and then remains unchanged depending on the particle size. This is a consequence of quantum confinement effect, which is the behavior of electrons inside a particle due to spatial limitations [Murray, 2000]. As it can be seen in Figure 1, quantum dot structures with different sizes have different radiation colors due to the quantum confinement effect.

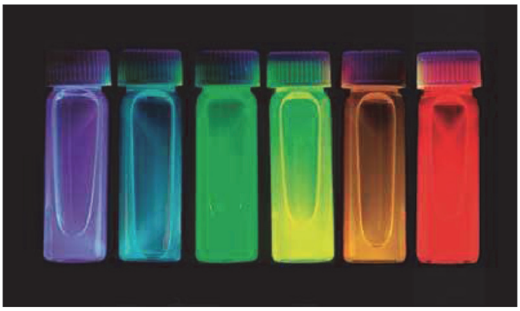

Figure 3.7.1. Appearance of CdSe quantum dots having sizes between 2 nm and 8 nm under UV lamp (quantum confinement effect) [Dabbousi, 1997].

Another factor that affects the optical properties of quantum dot structures is the surface characteristics. Surface regions originating from the vacancies on the surfaces of quantum dot structures cause the formation of new electronic energy levels at the band gaps of this semiconductor structure. Abundance of trap regions on the surfaces of quantum dot structures causes decreased efficiency, decreased florescence quantum efficiency, narrow florescence interval and florescence blinking during recombination in the applications containing quantum dots. Photocatalytic activity can be increased by coating with a surface active agent and synthesis in core/shell structure or alloy structures in order to improve the surface properties of quantum dot structures [Kershaw, 2013].

Since the sizes of the quantum dots can be adjusted experimentally, synthesis of application-specific quantum dots is possible. With their unique optical and electrical properties, quantum dots can be used in many application fields like chemical sensors [Chen, 2002; Frasco, 2009], biosensors [Grigsby ,2012] bioimaging [Lim, 2015; Huang, 2012], photocatalysis and electrocatalysis [Zhang, 2016; Li, 2010; Yang, 2011; Tang, 2014], photovoltaic devices [Schaller, 2004] and light emitting diodes [Frecker, 2016].

3.7.1 Synthesis of Quantum Dot Structures

Quantum dots can be synthesized through various methods [Bera, 2010]. Generally, methods used for the synthesis of quantum dots are classified in two approaches; top-down and bottom-up. These two methods are briefly explained below.

Top-down synthesis method: Top-down synthesis method of quantum dot structures involves techniques such as electron beam litography, X-ray litography, ion implantation, beam epitaxy [Bera, 2010; Valizadeh, 2012]. The purpose of top-down synthesis approach is to obtain quantum dot structures by thinning the bulk semiconductor [Bera, 2010].

Bottom-up synthesis method: Bottom-up synthesis of quantum dot structures contains spontaneous agglomeration techniques and can be classified in two as wet chemical and gas phase methods [Valizadeh, 2012].

Wet chemical method involves careful control of the parameters for one dispersion or a dispersion mixture, and common precipitation methods. Precipitation process includes both nucleation and the limited growth of nanoparticles. Generally, wet chemical methods are classified as microemulsion, sol-gel, hot dissolution [Bang, 2006; Spanhel, 1991; Qu, 2002; Murray, 1993; Qu, 2011] competitive reaction chemistry, sound waves or microwave [Li, 2005] and electrochemistry.

Gas phase method is initiated with atom by atom growth in layers in order to obtain quantum dot structures [Valizadeh, 2012] and finally, spontaneous agglomeration of quantum dots is realized on the substrate without patterning [Xin, 1996; Leonardi, 1998; Kurtz, 2000; Swihart, 2003].Gas phase methods are generally classified as molecular beam epitaxy, injection, liquid metal ion sources or agglomeration of gas monomers [Bera, 2010].

3.7.2 Application Fields of Quantum Dot Structures

Chemical sensors

In the field where quantum dots are used as chemical sensors, there are different applications such as pH determination, ion sensors and detection of organic substances. Damping of the luminescence properties of quantum dots and their sensor properties are studied in these fields. In the ion sensors, surface active agent on the quantum dots forms a complex with metal ions and causes florescence damping [Chen, 2002]. In the organic substance assays, quantum dots form a complex with the organic substances present in the medium and causes florescence damping [Fasco, 2009].

Biosensors

Quantum dots that are used as biosensors are generally utilized in the determination of different biological materials such as nucleic acids, proteins and enzymes.Here, material determination is performed through florescence resonance energy transfer [Grigsby , 2012].Florescence intensity drops due to the electron transfer.

Bioimaging

Quantum dot structures are widely used in bioimaging applications for their high florescence emission properties. In this field, generally non-toxic and eco-friendly carbon quantum dots are being used [Lim, 2015]. Bioimaging is performed by florescence microscope and confocal microscope, which are optical microscopes. In addition, quantum dots in the field of nanomedicine are being used for both imaging and photodynamic therapy applications [Huang, 2012].

Photocatalysis

In recent years, photocatalytic studies using quantum dot structures have gained great importance as an alternative to organic syntheses. In comparison with organic dyes, quantum dots are widely used as photocatalytic in environmental treatment, water splitting and synthetic chemistry due to their low cost, low toxicity, easy functionalization, high biocompatibility, adjustable florescence emissions, high light resistance and chemically inert structures [Zhang, 2016].In addition to being used as photocatalysts, quantum dots are also used to sensitize photocatalysts that cannot be excited in the UV region, such as TiO2 [Li, 2010].

Electrocatalysis

Quantum dot structures can be used as electrocatalysts in applications that posses technological importance such as fuel cells and clean fuel production in clean energy generation. For example, quantum dot structures have been used as photocatalysts in oxygen reduction reaction and oxygen generation reaction, and showed a catalytic effect that is very similar to the noble metal of Pt [Yang, 2011; Tang, 2014].

Photovoltaic devices

Properties of quantum dots such as their adjustable absorption spectrum and high absorption coefficients have made them attractive for use in photovoltaic systems [Schaller, 2004].Quantum dots can increase the efficiency and reduce the cost of today’s typical silicon photovoltaic cells.

Light emitting diodes

As quantum dots emit natural monochromatic light, they can be more effective than light sources with color filters. Quantum dots are very suitable for imaging systems for their specific emission spectrums. As quantum dot imaging systems make bright emission in visible regions, they have sharper image quality than florescence imaging systems [Frecker, 2016].

Summary

- Quantum dots are semiconductor particles that are several nanometers in size.
- Optical and electrical properties of the quantum dots change depending on their sizes.
- Quantum dot structures with different sizes have different radiation colors due to the quantum confinement effect.
- Another factor that affects the optical properties of quantum dot structures is the surface characteristics.
- Synthesis of quantum dots can be achieved by two methods that are called top-down and bottom-up.
- Quantum dot structures can be used in different applications such as sensors, imaging, photocatalysis, photovoltaic devices and LEDs.

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3.8 CORE SHELL

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INTRODUCTION

Analysis and quantification of toxic pollutants in the ecological and biological samples have gained significant importance due to the ever-increasing pollution as a result of meeting the needs of increas-ing population of the world. In addition, energy need of the world is increasing every day and this led the science communities to look for alternative energy sources. In this context, studies to perform analysis with cheap techniques and methods, and produce renewa-ble energy sources using cheap electronic materials are becoming more and more prevalent in the science world. This energy need is expected to be met at least partially through obtaining nanocrystals with florescence properties and using these crystals to make optical (light emitting diodes) and electrical (solar cells) devices by taking advantage of their improvable optical properties, in addition to their applications in quantification of biological and chemical materials. These materials, which stand out with their very small particle sizes and florescence properties, can be prepared in types called core, core-shell and alloy.

3.8.1 Preparation and Importance of Core Shell Structure

In recent years, nanomaterials are drawing great attention with their interest-ing properties and their benefits in many fields such as nanocatalysis, nanoelectronics and medicine. Nanoparticles containing noble metals func-tion as active catalytic compounds and these materials can be synthesized in different compositions and structures having different patterns, shapes and sizes. This type of controlled attainability, potentially leads to the de-velopment of new technologies for application fields that involve environ-mentally-conscious and economically practicable processes [Gawande et al., 2015].

Conventionally, composite nanomaterials are consisted of an inner core and an outer layer called shell, therefore they are called core-shell struc-tures. Materials that generally have dual structures and are formed by the combination of metals and anionic types (chalcogen elements) are called core structures. Core structures can be obtained in forms such as CdTe, CdSe, CdS, PbS, PbTe, PbSe; Ni/Pd, Pd/Co and Ag nanoparticles can be obtained in shapes like Ag/Ni, Ag/Co. Interior of such materials features the same properties everywhere [Li et al., 2009; Xing et al., 2008; Yu et al., 2009, Son et al., 2004, Wang et al., 2012, Wang et al., 2010, Guo et al., 2011]. Nanomaterials with core structure are coated with shell structures to make them more durable against external factors (Figure 3.8.1) [Baslak, 2014].

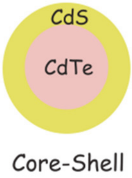

Figure 3.8.1: A nanomaterial with core/shell structure [Baslak, 2014].

Since crystal surface can break down easily, outside of the core nanocrys-tal is coated with another crystal shell structure, which has a higher band gap, during synthesis in order to protect the core structure. Thereby, nano-crystal surface defect is removed and various optical and electrical proper-ties of the crystal is improved [Baslak, 2014]. In addition, it is possible to attain structures known as core-shell-shell, which are multi-layered struc-tures defined as onionlike, by using different synthesis methods. Core-shell nanostructures can be classified as to involve different types such as inorganic/inorganic, inorganic/organic, organic/inorganic and organ-ic/organic, depending on the compositions and arrangements of the two compounds in the materials [Amouri et al., 2012; Park et al., 2013]. Both core and shell structures can also be consisted of triple structures in addi-tion to double ones [Pons et al., 2009].

Nanomaterials with core-shell structure can be classified as organic and inorganic. Organic ones are carbon-based materials (mostly polymers), whereas inorganic ones are the materials containing metal, metalloid and metal salt. Syntheses of organic materials are mostly based on polymeri-zation techniques for the preparation of organic core, shell or both. Fun-damental strategy of polymerization technique is to add several units of suitable monomeric substrates with important functionalities and to form 3-dimensional structures. Inorganic can be classified under two main groups as silica- and metal-based. Silica-based ones are synthesized using the sol-gel method. Metallic nanomaterials are synthesized through the reduc-tion of corresponding metal salt via trans-metalizing that uses external reducing agents ($NaBH_4$, hydrazine etc.) or intrinsic redox properties of metallic initiators. Reaction medium, temperature and the type of reducing agent affect the reaction and changing of these parameters also changes the particle growth, size, shape, and therefore the chemical, physical, opti-cal and biological properties.

The properties of the obtained materials must be firstly determined in order to use them in various applications. Performance and properties of the nanomaterials depend on their sizes, morphologies and structural compo-sitions. Combination of inner material and outer shell in the core-shell struc-tures and the distribution of various functional groups on the material have a significant impact on the variety of the applications. Therefore, character-ization studies are not just important in terms of learning the structural and physical properties of the core-shell nanomaterials, but also important to provide a deep insight to the mechanisms involved in many applications utilizing these nanosystems. To do this, chemical and physical properties of these materials, such as size and shape of the particles, surface proper-ties, nature of the surface coating and the presence of foreign additives, must be clarified. There are many methods to clarify and characterize the structures of the materials. To give brief information on these techniques;

Images obtained from SEM - scanning electron microscope, TEM - transmission electron microscope and HRTEM - high resolution transmission electron microscope devices are used to determine the morphology, size and homogeneity of nanomaterials. However, since the signal collection on SEM is achieved through the collection of secondary electrons reflected from the surface, this instrument provides only the surface images of a material. Therefore, it is difficult to differentiate the core from the shell using the SEM analysis. However, different fingerprint regions of core and shell can be clearly observed from an image of a single nanomaterial seg-ment using the HRTEM technique (Figure 3.8.2).

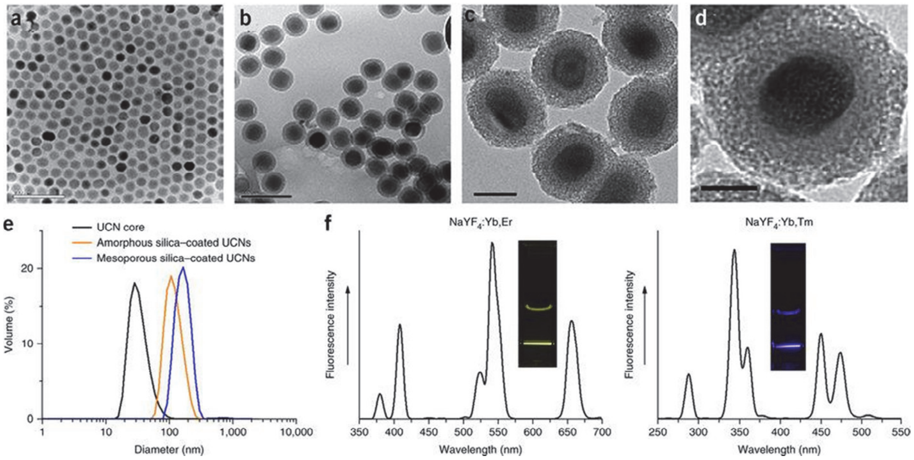

Figure 3.8.2: a) UCN core structure, b) amorphous silica coated UCNs, TEM images of mesoporous silica coated UCNs c) in 50 nm and d) in 25 nm [Gnanasam-mandhan et al. 2016].

X-Ray Diffraction (XRD) device is widely preferred to examine the phases and microstructures within the crystal structure of various materials, includ-ing the core-shell nanomaterials. XRD device is especially important in-strument that can shed light to the presence of core-shell structures and it even enables the simultaneous detection of separate phases of the core and shell. In addition, it is possible to determine the distribution of materi-als inside a specified region by using the energy distribution spectrometer (EDS) integrated into the TEM device. Another important technique, espe-cially for elemental mapping and sometimes depth profiling of the com-pound, is the Electron Energy Loss Spectroscopy (EELS), which is con-sidered as a complementary technique to EDS. Various spectroscopic techniques are also developed for direct or indirect characterization of optical properties of core-shell nanomaterials due to their absorption, emission and plasmonic properties. UV-Vis spectroscopy is one of the spectroscopic techniques that can absorb especially the UV-Vis region of electromagnetic radiation. Infrared spectroscopy can be used to identify the organic core/shell nanostructures and the organic molecules inside them. Raman spectroscopy is also very important in terms of surface properties of core-shell structures. Brunauer-Emmett-Teller (BET) method is used for the determination of specific surface area of porous core-shell nanomaterials [Gawande et al., 2015].

These nanomaterials are developed as a very important class of materials with such unique, useful and practicable properties and they have a wide variety of application fields. For examples these materials are widely used in areas such as bio-nanotechnology [Rosenthal et al., 2011], advanced optical devices [Nann et al., 2011], special magnetic devices [Muckel et al,. 2017], electronic optical devices (Anikeeva et al., 2008), biological imaging systems [Jin et al., 2011], energy storage materials, genetic engineering and stem cells [Jamieson et al., 2007], fuel cells [Robel et al., 2006], dye-sensitized solar cells [Tian et al., 2013] and very important catalytic pro-cesses [Iyer et al., 2014]. The ones with flores-cence properties are used to make light emitting diodes (LED), semiconductor ones with absorption ability are used for solar cells, catalyzing reactions due to their catalytic activities, and for making sensor probes by using their optical and electri-cal properties.

Conclusion

These nanomaterials are developed as a very important class of materials with such useful and practicable properties arising from their core-shell structures and they have a wide variety of application fields.

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3.9 CARBON-BASED NANOMATERIALS

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INTRODUCTION

Carbon atom has 6 electrons and belongs to the group IV of the periodic table together with silicon, germanium, tin, lead and flerovium elements. However, in contrast with other groups in the periodic table, these 6 elements are significantly different than each other chemically and the most distinct element of this group, the carbon atom, is the lightest (12.011 g/mol) and the least metallic element of the group.

The first two electrons in the $1s^2\ 2s^2\ 2p^2$ electron distribution of neutral carbon atom has no impact on binding and the energy difference between other electrons is large, therefore, carbon atom has 4 valence electrons ready for bonding and this enables carbon to form different structures. Carbon atom generally forms covalent bonds instead of ionic bonds since it has a small atomic number, thus, valence electrons that are closest to the nucleus are very strongly held.

Materials formed with carbon atoms manifest different physical and chemical properties due to the sp, sp^2 ve sp^3 bonding geometry, which is caused by the combination of electrons that are involved in the bonding of carbon atoms between themselves. In the bonding formed with sp hybridization, for which the acetylene can be given as an example, carbon atoms form a linear geometry with each other and each atom has two bonds. In the bonding formed with sp^2 hybridization, for which the graphite plates can be given as an example, carbon atoms form a triangular geometry with each other and each atom has three bonds. And in the bonding formed with sp^3 hybridization, for example diamond crystal, carbon atom has four bonds. Each different geometric shape of bondings means different materials. Carbon atom is a special element in the periodic table since it is the only element that can form bondings with sp, sp^2 and sp^3 hybridization.

The most abundant carbon compounds found in the nature are carbonate minerals, such as carbon dioxide, calcite, coal and marble, and hydrocarbons, which are the building blocks of coal, petroleum and natural gas. In addition, diamond and graphite are other natural forms with their different crystal forms. In the transparent diamond, among natural materials, which is rigid and robust, has scratching and abrasive properties, has no electrical conductivity but a good thermal conductor, each carbon bonds with four different carbon atoms to form a three-dimensional solid structure.

On the other hand, graphite, which is known with its softness due to the weak bonding between its layers, a good electrical conductor with a poor thermal conductivity, has carbon atoms bonded on a two-dimensional plane where they form wide, flat plates that are piled up on each other. These flat plates can slide on top of each other, which makes graphite a suitable dry lubricant to reduce or prevent the moving parts in the machines from abrasion due to friction. The reason why graphite leaves a trace on paper is that these thin plates are separated from the graphite by friction and remain on paper, for which the pencil tips hardened by adding clay into the graphite can be given as an example. In addition to diamond and graphite, carbon also has natural allotropes such as hexagonal diamond, and unnatural artificial allotropes like glassy carbon, fullerene, carbon nanotube, linear acetylenic carbon (Figure 3.9.1.). Alltropes of carbon, which do not have any distinct, unique structure or form, are called amorphous carbon. Coal is an amorphous carbon type.

With its unique properties, the carbon element has an undeniable importance within the context of nanotechnology, which was pioneered by renowned physicist Richard Feynman in 1974 and has made great contributions since then with its theory and applications. There are interesting structures consisted of only carbon atoms in nanometer scale that can be classified as balls, tubes, rods and rings. How a cluster structure that can be represented with Cn in this classification is formed depends on the “n” value. If the atomic number is an odd number, cluster structure is formed as a one-dimensional like a chain, if atomic number is an even number, than the cluster becomes two-dimensional like a ring. However, n=2 is exempt from this generalization.

Carbon nanostructures have many theoretical study and applications in fundamental sciences like physics, chemistry and biology, as well as in engineering fields and health applications with their robustness, different electrical and mechanical properties (Ahmadi et al., 2017; Chen et al., 2017; Dasgupta et al., 2017; Kumar et al., 2017).

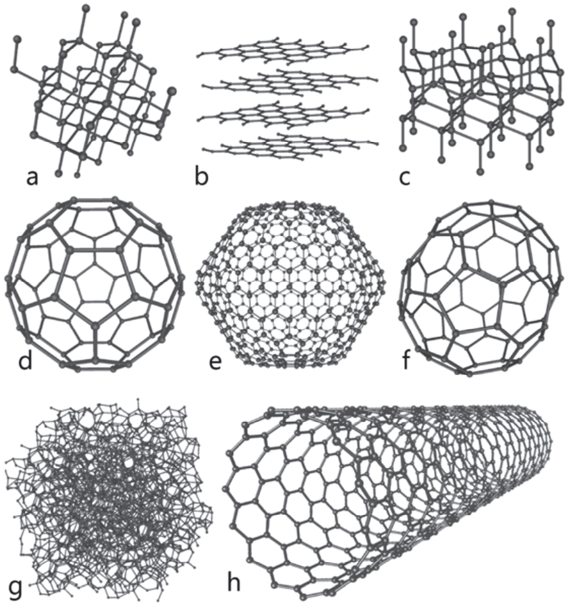

Figure 3.9.1. Some carbon allotropes: a) diamond; b) graphite; c) hexagonal diamond; d-f) fullerenes (C60, C540, C70); g) amorphous carbon; h) carbon nanotube

(This image was published in page goo.gl/CEzPJv and retrieved from Google Images.)

3.9.1 Carbon nanoballs

Harold W. Kroto, Robert F. Curl ve Richard E. Smalley won the 1996 Nobel Prize in Chemistry with their discovery of a new carbon allotrope where atoms are arranged in closed shells back in 1985. They determined that this new form had an icosahedral structure and named it as Buckminster-fulleren after the architect Buckminster Fuller, who designed geodetic domes in 1960s.

Carbon nanoballs can have many different sizes from twenty atoms to thousands of atoms. The smallest one has 20 atoms consisted of 12 regular pentagons (Figure 3.9.2.). The most widely known carbon nanoball is C_{60}, which is called fullerene and formed with 60 carbon atoms that are bonded together with sp^2 hybridization. C_{60} is a spherical structure and consisted of 12 pentagonal and 20 hexagonal sides with its dodecahedral symmetry (icosahedral symmetry). Another structure that can be classified as carbon nanoballs is C_8 (cubane) which consisted of 8 carbon atoms with less than 20 atoms. Although this structure does not have a ball shape, it is classified in this group due to its cage structure.

Generally, nanoballs with icosahedral symmetry are single-walled with different sizes, but they can also be in dimer groups or structures similar to interwoven onion layers.

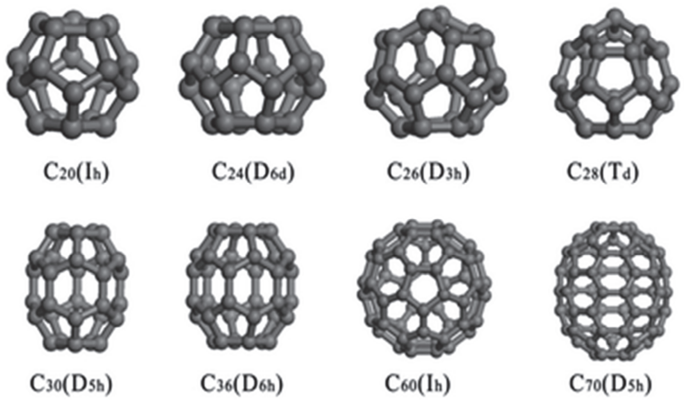

Figure 3.9.2. Some fullerene examples (Guo et al, 2013)

Carbon nanoballs can be found in pure form, but they can also be doped by placing different atoms into the balls without disrupting their geometric structure. Doping of carbon nanoballs causes changes in their electrical, mechanical and optical properties (Tayfun et al., 2015; Kausar, 2017; Noh et al., 2017; Youn et al., 2017).

3.9.2 Carbon nanotubes

Carbon nanotubes were first discovered experimentally by Iijima in 1991 and they are an allotrope of carbon element with the largest length: diameter ratio of 28x106:1 that no other material can possess. The tubes, obtained from graphite by evaporation method, are structures formed by curving the graphite plate into the cylinder (Figure 3.9.3.).

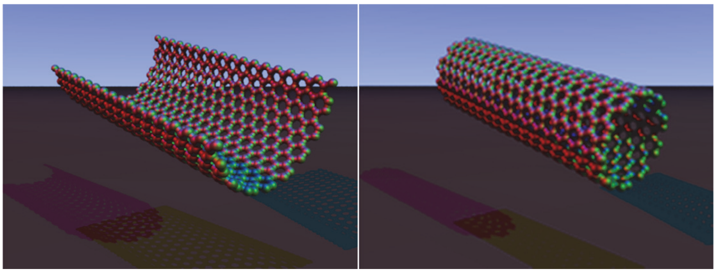

Figure 3.9.3 a) graphene, b) single layered carbon nanotube

(This image is published on goo.gl/m79Rvx and retrieved from Google Images.)

In orderly carbon nanotube structures, atoms are bonded together with sp2 hybridization as in graphite plates. Atoms form only hexagonal geometry and each atom has just three neighbors. Carbon tubes can be very fragile in macroscopic sizes or very flexible and robust in nanometer dimensions. An undamaged carbon nanotube is robust enough to withstand a load of 300 million times its own weight and has a larger mass:area ratio than normal materials, therefore, it is the most robust material known. Today, there is no other material with this level of robustness.

These structures, which can have different diameter and sizes, can be found as single layered (single walled-SWCNT) or multi layered (multi walled-MWCNT).

Depending on the curling direction of the graphite plate, tubes can have zigzag and armchair structures, and bent nanotubes can be formed by bending one of these structures. Tubes manifest different mechanical and electrical properties depending on their directions (Figure 3.9.4.). For example, armchair structure has metallic properties, whereas zigzag structure has semiconductor properties. For zigzag structure to have metallic properties, number of rings around the tube must be multiples of 3.

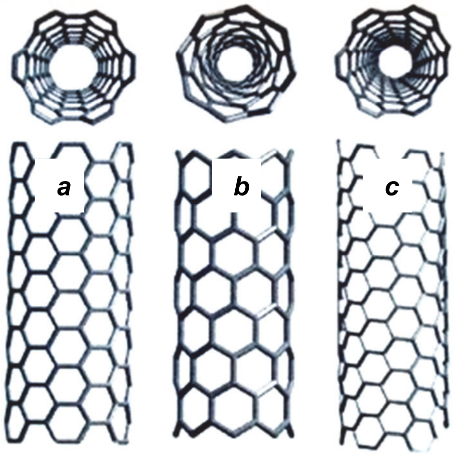

Figure 3.9.4. a) Armchair, b) Zigzag and c) Bent carbon nanotubes
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Depending on whether the carbon is in a solid or gas state, carbon nanotubes can be obtained through methods like arc discharge, laser abrasion, chemical vapor precipitation and electrolysis, and can be purified by processes like oxidization, acid application, thermal treatment and filtering. Carbon nanotubes are mostly used in electronics and energy fields.

3.9.3 Carbon nanorods

Carbon nanorods are less flexible than carbon nanotubes and they are consisted of interwoven and walled carbon nanotubes. The distance between the walls of these interwoven tubes is longer than the distance between two carbon atoms. In case the distance between the walls become shorter than that of between two carbon atoms, carbon atoms in the different interwoven walls bond with each other through sp3 hybridization. Carbon nanorods are formed as a result of the bonding between the walls of carbon nanotube. Mechanical and electrical properties of nanorods change depending on the nanotubes that take part in the bonding.

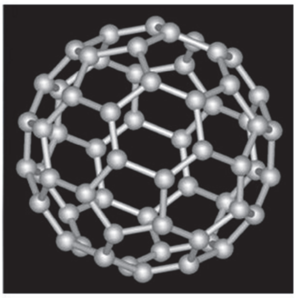
3.9.4 Carbon nanorings

Nanotubes can be turned into rings with 0.7 micron diameter that are consisted of single walled nanotubes or helical structures. Nanotubes used to form rings have very small diameters of 1.4 nm. Very different ring models can be obtained by using structures having different inner and outer diameters, and rings have different properties depending on the properties of the structures used. However, this is just a corporate taught for now.

NOTES:

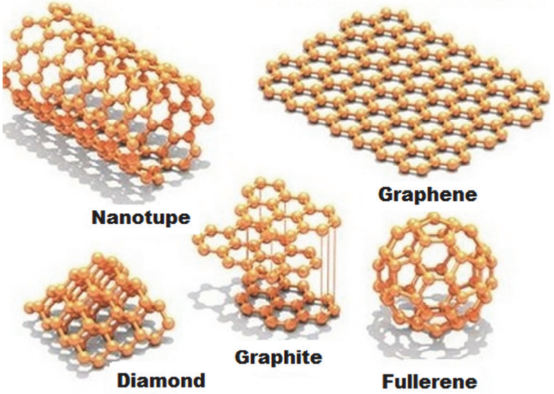
- ✓ Carbon has different stable structures from three-dimensional (3D) semiconductor diamond structure and two-dimensional (2D) semi-metallic graphite in macro scale to one-dimensional conductor and semiconductor nanotubes and zero-dimensional (0D) nano-balls in nano scale.
- ✓ Since 1D and 0D structures are in nano scale, these systems called nanotubes and nanoballs, which form the basis of carbon nanostructures.

Years of 1996 and 2010 Nano Carbon Nobel Prize



C60-Fullerene
1996 Nobel Prize in Chemistry

Graphene
2010 Nobel Prize in Physics



Only reason for the difference between these structures is the different arrays of carbon atoms!!!

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3.10 GRAPHENE

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INTRODUCTION

Graphene is carbon allotrope with superior properties and is consisted of a single layer of carbon atoms arranged in an hexagonal lattice and it is the first two-dimensional material to be obtained in the world. Graphene was discovered by Russian scientists Andre Geim and Kostas Novoselov from Manchester University in 2004 and they won the Nobel Prize in 2010 as graphene is the first two-dimensional material ever to be produced. It became the focus of science world since 2010 and it is being studied as the main material in many research. Graphene earned its ever-increasing reputation with its superior electrical and thermal conductivity and mechanical properties.

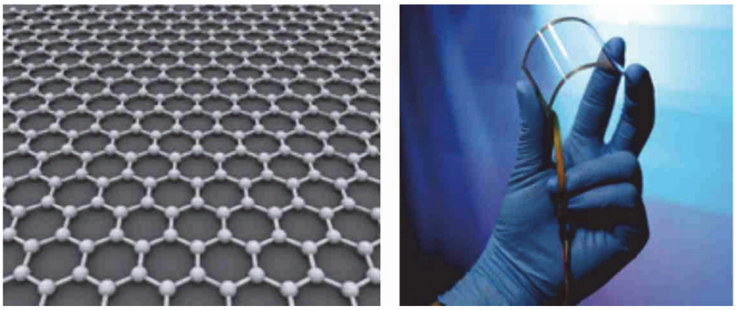

Figure 3.10..1. Graphene
(http://tr.wikipedia.org/index.php?q=aHR0cHM6Ly90ci53aWtpcGVkaWEub3JnL3dpa2kvR3JhZmVu)
(http://www.techandfacts.com/what-is-graphene/)

In fact, graphene is the fundamental structure of graphite, the raw material of lead pencil which we use every day. Graphite is the name of the structure that is formed when multiple graphene layers are combined together on top of each other. Therefore, when we examine our lead pencil under microscope, we can easily its layered structure. The reason why our lead pencil breaks when we write is this layered structure. Now, we may think about another question. Why is our lead pencil, which is made of graphene that is even stronger than strongest material diamond, can be broken under very small pressures. We should remember that in fact, diamond is another carbon allotrope that is formed by the three-dimensional crystallization of carbon atoms, which also form the graphene. The answer is the way that carbon atoms come together. We call this the crystal structure of carbon atoms. The forms, in which the carbon atoms come together with different shapes, are called the allotropes of carbon. Different allotropes of carbon are shown in Figure 3.10.2.

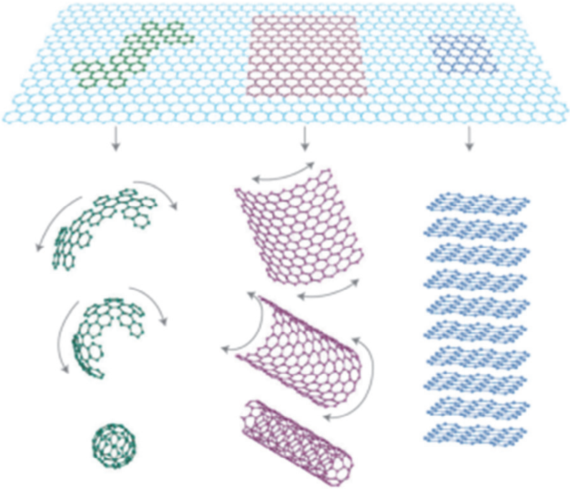

Figure 3.10.2. 2D graphene, which is the building block of all other graphitic materials (Geim and Novoselov 2007)

The study that helped Andre Geim and Kostas Novoselov to discover graphene in 2004 is actually based on an experiment that everyone can try at their homes. Despite the long-standing prediction of theoretical physicists that a 2-dimensional material cannot remain stable, these scientists made their discovery by using a piece of sellotape and some graphite. They put some graphite powder on the tape, sticked the tape together and then pulled it back again; this way, layers inside the graphite were separated and they transferred these separated layers onto a silicon substrate. They showed the presence of graphene through the examinations that had conducted under microscope. This method is called mechanical exfoliation method (Fig. 3.10.3).

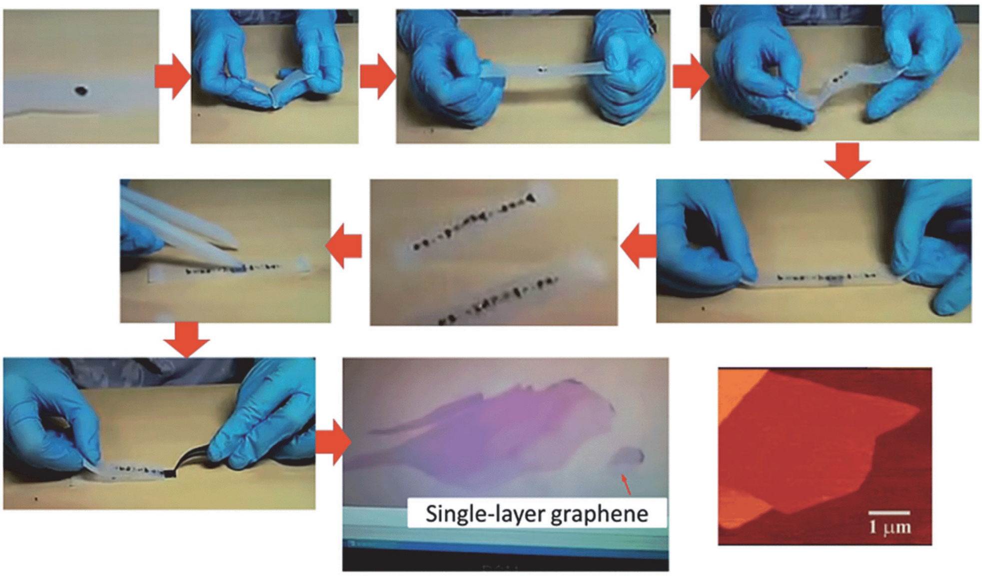

Figure 3.10..3. Mechanical exfoliation method

http://pubs.rsc.org/en/content/articlehtml/2015/ta/c5ta00252d)

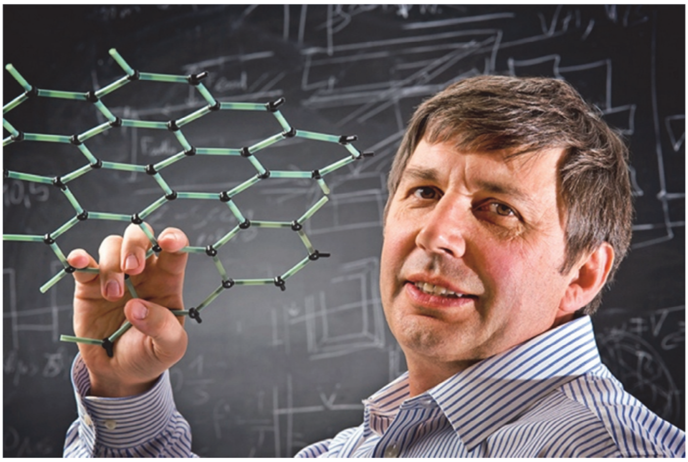

Figure 3.10.4. Andre Geim

(http://www.nature.com/news/andre-geim-graphene-s-buzz-has-spread-1.17861)

Folding mobile phones, tablets and screens are produced, flexible and elastic energy related and electrical applications become possible with the discovery of graphene. Today, studies are rapidly ongoing for the wide use of graphene in many areas such as energy, electronics, biosensor, implant, medicine, food and environment.

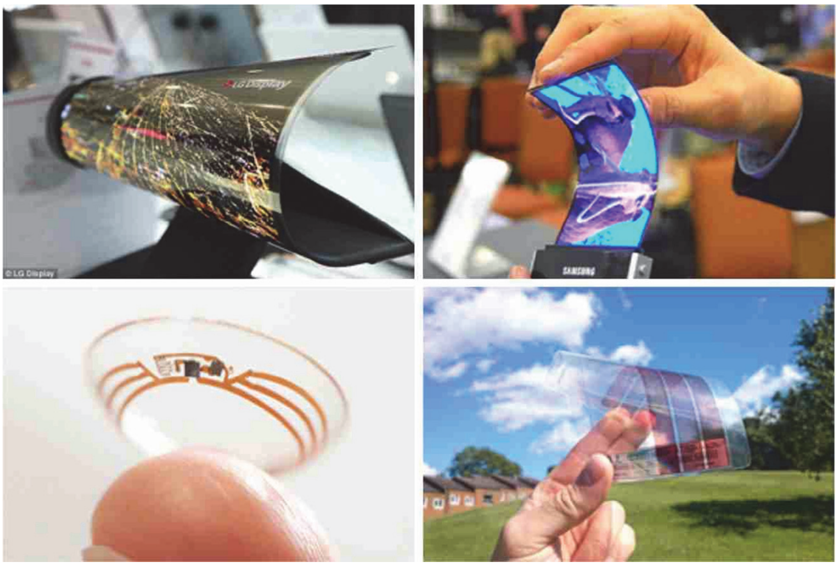

Figure 3.10.5**.** Different graphene applications

Properties of Graphene:

Mechanical Properties:

Graphene is an extremely rigid, durable and highly elastic material. The young modulus of graphene, which is a concept used to understand mechanical properties of materials, is approximatel y1 TPa and its fracture resistance is 130 GPa. These superior mechanical properties is a result of the ways that carbon atoms of the graphene come together. Due to the hexagonal shape of carbon atoms, C-C bonds have 120o degrees of angle and this enables them to bend under pressure and constraint. Graphene is the thinnest material ever to be produced to date and it is 200 times more durable than steel used in structures thanks to this bonding structure.

Thermal Properties:

Graphene has the highest thermal conductivity of all materials. Thermal conductivity of graphene is 6000 W/m K. Therefore, it rapidly conducts temperature.

Optical Properties:

Graphene absorbs 2.3% of the light, and it has 97.7% transparency. Therefore, it is a potential material that can be used for conductive screen applications necessary for mobile phones and tablets. The reason for this high transparency is the single-layered structure of graphene. Experiments conducted on the number of layers of graphene, structures with more than 10 layers were shown to lose transparency.

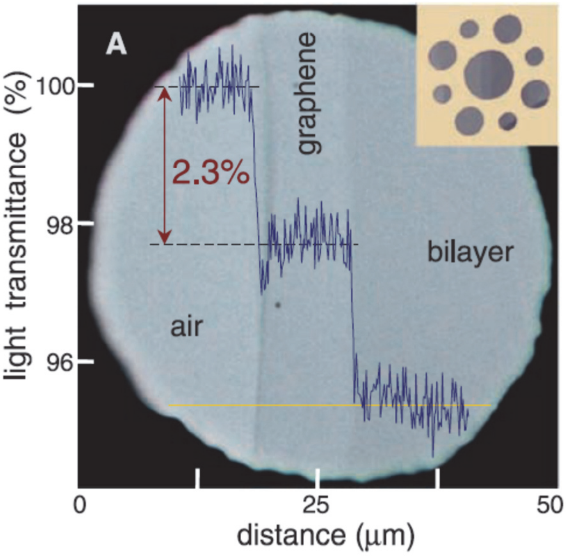

Figure 3.10.6. Graphenin optic mikroskop görüntüsü (Fine Structure Constant Defines Visual Transparency of Graphene R. R. Nair,1 P. Blake,1 A. N. Grigorenko,1 K. S. Novoselov,1 T. J. Booth,1 T. Stauber,2 N. M. R. Peres,2 A. K. Geim1* Science 320 (5881), 1308)

Electrical Properties:

Graphene is a semimetal that exhibits semi-conductors properties with zero forbidden energy interval. Valance and conductivity bands of graphene meet at Dirac point, so, graphene is a semi-conductor material with zero forbidden energy interval. Therefore, graphene has very good electrical conductivity. Carrier mobility of graphene is approximately 200000 cm2.V-1.s-1. This value is even higher than that of gold and copper, which are known to be very good conductors.

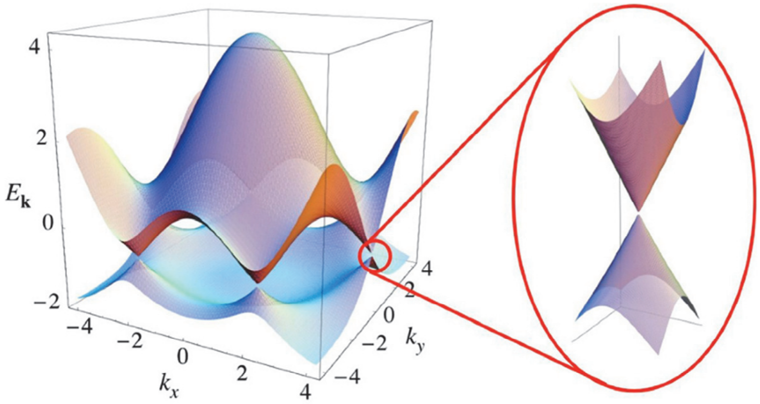

Figure3.10.1.7. Optic microscop image of graphene (Fine Structure Constant Defines Visual Transparency of Graphene R. R. Nair,1 P. Blake,1 A. N. Grigorenko,1 K. S. Novoselov,1 T. J. Booth,1 T. Stauber,2 N. M. R. Peres,2 A. K. Geim1* Science 320 (5881), 1308)

Production Methods:

After its discovery, many production methods are developed to obtain high quality single-layered graphene that has large surface area. Today, researches are ongoing to obtain better quality and cheaper graphene via different methods. Production methods have many advantages and disadvantages compared to each other. For graphene production, there are two methods parallel to the nanomaterial production techniques; bottom-up methods and top-down methods. Bottom-up method is the attainment of structures by constructing atoms, the building blocks of the matter, one by one. Obtaining nano structures with this method contains extremely complex and difficult processes. Top-down methods involve the reduction of bulk materials into nano sizes by mechanical, physical and chemical dissolution. These methods include simpler and cheaper processes than the bottom-up method. The mechanical exfoliation, the method that enabled the discovery of graphene, is an example for top-down production methods.

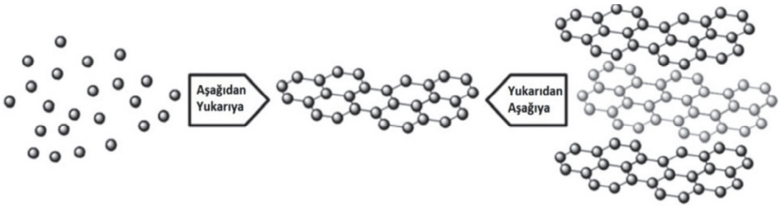

Figure 3.10.8. Production schematics of graphene based on bottom-up and top-down processes (Edwards, R. S. and Coleman, K. S., “Graphene synthesis: relationship to applications”, Nanoscale, 5 (1), 38-51, (2013)).

To give examples, top-down methods: Mechanical exfoliation, reduction of graphite oxide, arc discharge method, divergence of carbon nanotubes, chemical exfoliation methods. Bottom-methods are: Epitaxial growth on SiC, chemical vapor deposition (CVD) etc. Among these, CVD methods is the successful one in attaintment of quality graphene with large surface area.

Post-production graphene presence and structure can easily be determined via Raman spectroscopy, optical microscopy, electron microscopy, atomic force microscopy methods.

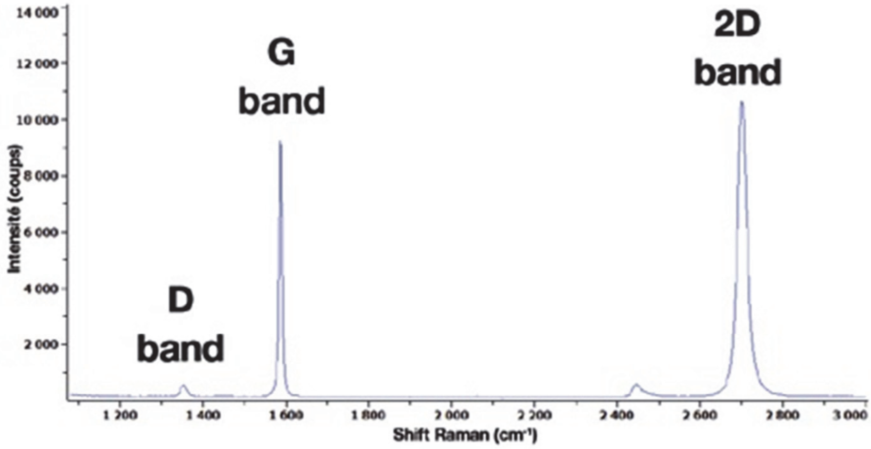

Figure 3.10.9. Raman spectroscopy of graphene (https://www.azom.com/article.aspx?ArticleID=10130)

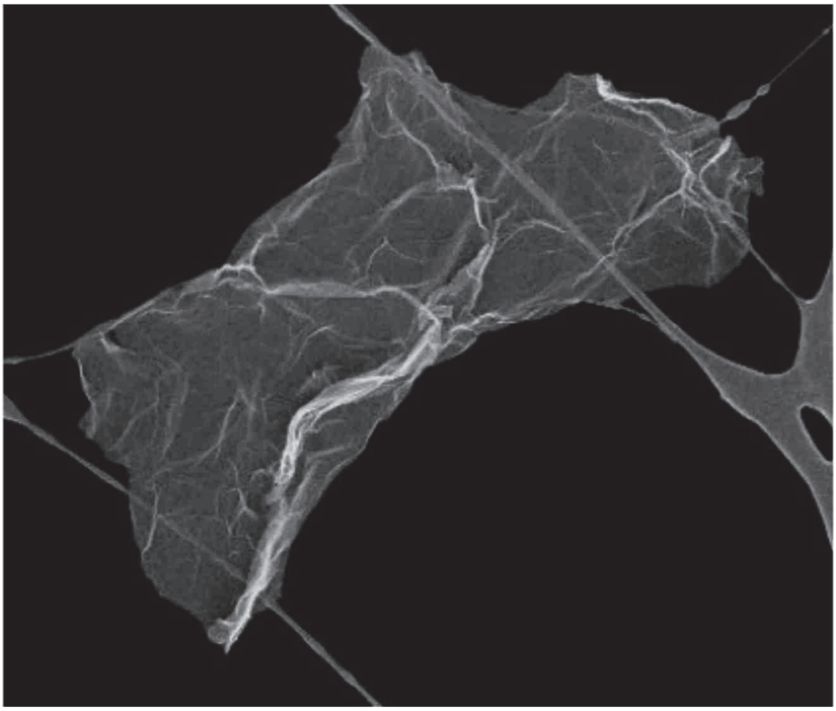

Figure 3.10.10. Image of graphene under electron microscope (http://www.megantech.pl/en/top/graphene/graphene-oxide/powders-flakes/single-layer-graphene-oxide/)

3.11 THIN FILMS

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INTRODUCTION

Coating glass and ceramic materials with pure metals in the past centuries has increased the interest towards thin films in 1940s and 1950s, and this trend continues to grow in recent years. Thin films are materials that are thinner than 1 m□. These materials form an atomic or molecular thin layer, on a surface that supports the formation of the film by using different production methods. This thin film significantly improves the mechanical, electrical and optical properties of the new materials and tools. Large number of particles forming the thin films shows a gradual transition from solid structure to molecular structure [2]. These are present in all kinds of devices that we use in our daily lives. Different properties of the thin films are used for desired purposes.

Thin films are used in many applications: on surfaces with reflection ability by using their optical properties, on memory disks of electronic circuits by using their magnetic properties, on circuit components of superconductor/semiconductor devices by using their electrical properties, coating of insulation surfaces, for anti-corrosion purposes by using their superior chemical properties. In recent years, use of thin films in nanomaterial industry is rapidly increasing for their cost-effective application [5].

Keywords:Thin Films

3.11.1 ThİnFİlms

Thin films were first used for decorative purposes on leaded glasses and ceramics. After these processes, they were used to obtain silver films on glass surfaces by using silver salts. Their first scientific attainment was achieved in 1838 by using electrolysis method. Later on, thin films were produced through chemical reaction by Bunsen in 1852, through vaporization in noble gas by Faraday, and via Joule heating method by Kundt and Nahrwold [6].

Types of thin films can be classified as follows depending on the type of material used:

- ✓ Superconductor films
- ✓ Semiconductor films
- ✓ Transparent conductor films
- ✓ Organic films
- ✓ Semiconductor alloy films with amorphous structures
- ✓ Ferroelectric films
- ✓ Inorganic polymeric films
- ✓ Pyroelectric films

3.11.2 Thin Films Production Teqniques

Thin film production methods include all nanomaterial production methods. However, properties of thin films can be very different from each other depending on their production method. The method to be used for thin film production must be determined based on the type and size of the surface to be coated with thin film, coating temperature, coating material of of the surface to be coated, cost and the intended purpose of the thin film. Thin film production methods are listed in Figure 3.11.1.

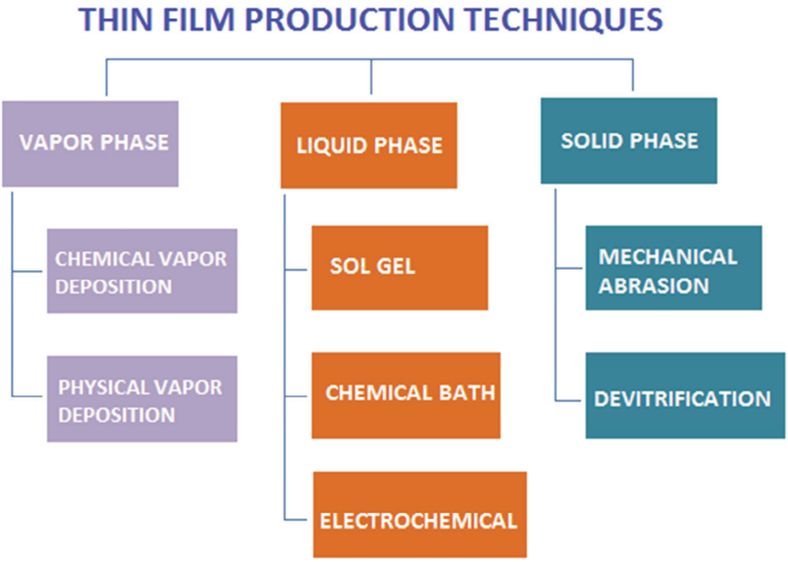

Figure 3.11.1. Thin film production techniques

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3.12 NANOPARTICLE SHAPES

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INTRODUCTION

Nanomaterials have different shapes than bulk materials and this makes them unique for use in common applications such as biomedicine, catalysis, fuel cells, solar cells and magnetic data storage. There are two fundamental approaches to the synthesis of nanomaterials; “bottom-up” and “top-down”. Nanomaterials with different size and structure can be obtained through the application of different methods of synthesis. Shapes can be classified as 0D (isotropic structure), 1D, 2D and 3D (anisotropic structure) in terms of nanomaterial sizes. Solid and mesoporous/hollow morphologies of size-based nanoparticles are shown in Figure 3.12.1.

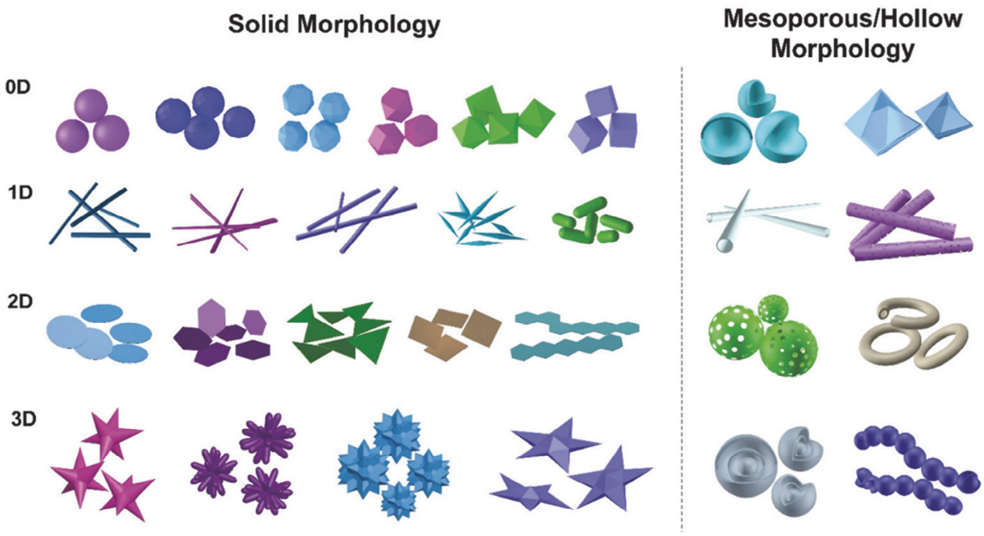

Figure 3.12.1. Typical morphologies of solid and mesoporous/hollow nanoparticles with 0D, 1D and 2D shapes and other 3D complex structures [Wu, 2016

Primary shapes of 0D nanoparticles include spherical, pseudo-spherical, dodecahedral, tetrahedral, octahedral, cubic and their corresponding hollow morphologies.1D shapes can be classified as nanotubes, nanoneedles, nanorods or nanowires, nanoshuttles, nanocapsules and their hollow structures [Zhang, 2014; Lu, 2015]. Circular disks, hexagonal / triangular / tetragonal plates or layers, belts, mesoporous hollow nanospheres, hollow rings etc. are known as 2D shape class [Li, 2012].3D morphologies of nanoparticles are complex and include nanothorns, nanoflowers, nanostar, polyhedral nanoframes, poly hollow shell, hollow bundle and similar nanoparticles [Lv, 2015; Lin, 2012; Wu, 2016].

In addition, examples of 0D, 1D, 2D and 3D shape classifications of nanoparticles are given in Figure 3.12.2 [Tan, 2011]. In each row, from left to right, particles become geometrically higher-level structures in terms of aspect ratio, edge and face number or dendrite number. Last particle of each row represents a hollow structure. Sixth row includes various complex nanoparticles, seventh row includes various hollow polygonal and polyhedral nanoparticles.

A great deal of effort has been put to control the shape of nanoparticles [Ho, 2011; Radi, 2010]. Generally, shape formation of nanoparticles is thermodynamically or kinetically controlled as dispersion. Production of thermodynamically controlled shapes of nanoparticles is achieved through chemical potential driving based on the temperature and supersaturation of the reaction dispersion.

On the other hand, kinetically controlled morphologies with different sizes can be obtained by changing the reaction conditions depending on the nucleation theory. Growth of nucleus in kinetically controlled processes contributes to the formation of nanoparticles with anisotropic shapes [Nyugen, 2013]. Therefore, synergistic effect of thermodynamic and kinetic factors plays critic roles in the determination of final shape of nanoparticles [Zhang, 2013]. Factors affecting the shape of the nanoparticles are briefly explained below.

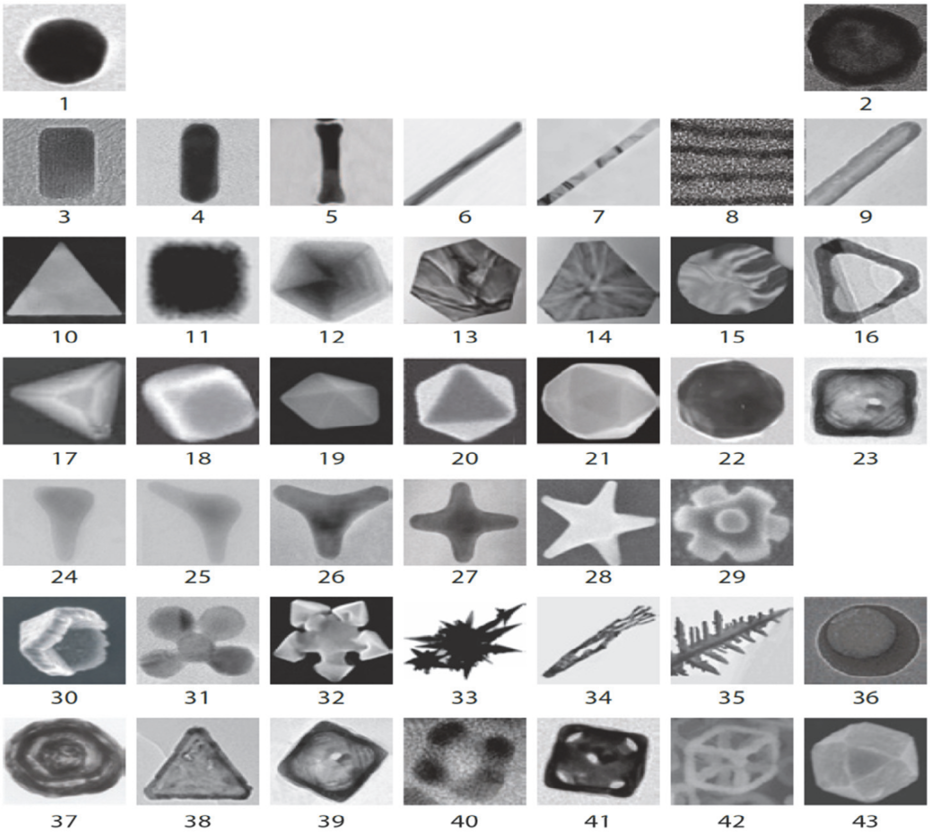

Figure 3.12.2. Classification of nanoparticles based on geometric parameters (1- nanosphere, 2- hollow nanosphere, 3- nanobar, 4- nanorod, 5- nanobone, 6- nanobeam, 7- nanobelt, 8- nanowire, 9- hollow nanorod, 10- triangle, 11- square, 12- pentagon, 13- hexagon, 14- truncated triangle, 15- disk, 16- nanoring, 17- tetrahedron, 18- cube, 19- decahedron, 20- octahedron, 21- icosahedron, 22- rhombicuboctahedron, 23- hollow nanocage, 24- monopod, 25- bipod, 26- tripod, 27- tetrapod, 28- star-shaped, 29- octapod, 30- nanopyramid, 31- nanoclover, 32- nanosnowflake, 33- nanothorn, 34- nanotree, 35- dendtrite, 36- nanocrescent, 37- nanoshell (ring), 38- porous triangle, 39- nanoshell (cubic), 40- truncated octahedron, 41- nanocage, 42- nanoskeleton, 43- nanobox) [Tan, 2011].

3.12.1 Factors affecting the shape control of nanoparticles

Supersaturation

Nanoparticle synthesis processes include reaction dispersion, precursor monomers, reducing agents, solvents, stabilizers and other additives. Supersaturation means the initial monomer concentration or the monomer ratios in the presence of multiple monomers. According to classical nucleation and growth theory, supersaturation plays a direct and significant role in the determination of nucleation and growth ration [Chang, 2014; Do, 2011]. Therefore, supersaturation is one of the important factors that affect the shape of nanoparticles.

Concentration of Precursor Monomer and Additives

Supersaturation is directly and significantly dependent factors such as on precursor concentration, reducing agent concentration [Ho, 2011] or ratio [Wang, 2014]. As it can be seen on Figure 3, shape of the nanoparticles, formed by increased ascorbic acid concentration, which is used as a reducing agent.

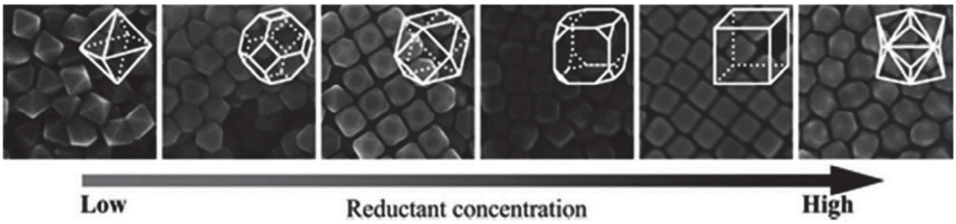

Figure 3.12. 3 SEM images showing the change in the shape of Au nanoparticles induced by reducing agent concentration [Eguchi, 2012].

pH effect

Changing the pH by adding acid or base (H^+, OH^- or NH_3) may change the states of chemical types in the dispersion and cause coordination bonds with ions inside the precursor monomer dispersion to form a complex. Therefore, pH is an important factor in the control of the nanoparticle shapes (Figure 3.12.4).

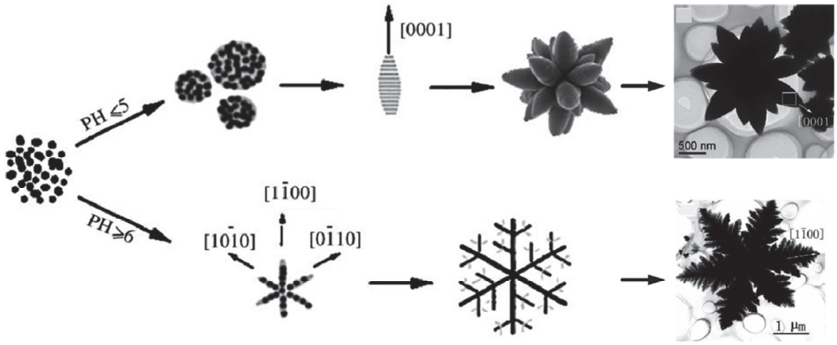

Figure 3.12.4. TEM images of α-Fe_20_3 with different shapes due to the changes in pH [Jia, 2006]

Solvent

Solvents with different functional groups like ionic liquids provide coordination with precursor monomer. This is significantly advantageous for thermodynamically- or kinetically-controlled nanoparticle synthesis due to increased supersaturation [Wagle, 2004; Niederberger, 2006; Kobayashi, 2012]. In addition, different solvent mixtures and solvent compounds enable the control of nanoparticle shape [Han, 2009; Liu, 2012].

Temperature

Temperature is the thermodynamic parameter of the reaction dispersion. Increased reaction temperature in the synthesis of nanoparticles also increases the supersaturation and the reduction rate of the precursor agent in the dispersion. Temperature increase leads to faster thermodynamically-controlled nucleation and growth, therefore reducing the duration of the reaction [Guy-Lopez, 2008].

Surfactants and additives

Most nanoparticles tend to agglomerate as large particles with irregular and unwanted shapes due to their high free energy at nanoscale. Surfactants and additives reduce the surface energies of the nanoparticles and are considered as most suitable tools to achieve the desired shapes. Beside this, the stable layers formed on the surface of nanoparticles by surfactants and additives, protects the dispersed particles against agglomeration [Xing, 2014; Wang, 2010].

Summary

- There are two fundamental approaches to the synthesis of nanomaterials; “bottom-up” and “top-down”.
- Shapes can be classified as 0D (isotropic structure), 1D, 2D and 3D (anisotropic structure) in terms of nanomaterial sizes.
- Shape formation of nanoparticles is thermodynamically or kinetically controlled as dispersion.
- Factors affecting the shape control of nanoparticles can be listed as supersaturation, concentration of precursor monomer and additives, pH effect, solvent, temperature, surfactants and additives.

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3.13 SURFACE MODIFICATION of NANOMATERIALS

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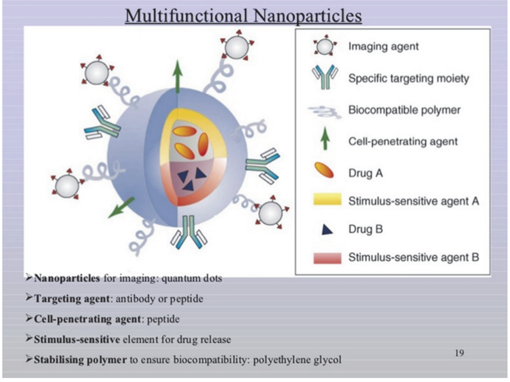
INTRODUCTION

Nanoparticles aggregate very easily due to their high surface energy and large surface area. On the other hand, NP has poor affinity for materials with relatively poor surface energy. When these two types of materials are mixed, a phase separation occurs since these materials are not compatible inside each other. If a solution to prevent agglomeration of nanoparticles in the material is found, nanoparticles can be used for different and good applications in special material, and therefore material performance in mechanical, optical, thermal and other aspects can be significantly improved. Therefore, the effort to maintain the nano size of the NP in the material is one of the purposes of surface modification process in nanotechnology field. NP surface modification is the most important part of surface engineering.

3.13.1 Surface Modification of Nanoparticles

Surface engineering is a design consisted of a system surface, and substrate materials integrated onto this surface. Surface engineering is a system engineering that involves the use of various surface technologies that allows the required modification to the surface of material, which is absent from the material itself but needed to have the necessary performance (Figure 3.13.1).

Nano-surface engineering is an advanced technology derived from the combination of conventional surface technologies and modern physical and chemical methods. This technology covers a wide material range from metallic and non-metallic to ceramic and composite etc. and deals with all areas of these materials, including their intermediate surfaces. Surface coating, surface thin film and surface modification come to mind in nano-surface engineering. Manufacturing technology moved from submicron level to nanometer and even to atomic or molecular level when the development of nanotechnology was combined with the design and manufacturing of microelectromechanical systems. Since nanoparticles are presented with different characteristics than macro materials in terms of power, electrical, sound, light, thermal and magnetic properties, it is understood that modification of surface characteristics and use of conventional surface processing and design methods are no longer applicable. Nanotechnological surfaces are particularly important for conventional materials and caused nano-surface engineering to be formed. Nano-surface engineering is an engineering field that equips the material with nanotechnological surface through the use of special processes. Nanostructure process is the series of processes applied to modify the surface, to add a new property or to enhance it. Depending on the surface characteristics needed to be achieved, nano-surface engineering has a comprehensive application field including high technology fields such as aviation, MARITIME, computer technologies, electronics, and in other important aspects of human life from transportation to oil, chemistry, construction, irrigation and machinery industries.



Multifunctional Nanoparticles

- **Nanoparticles** for imaging: quantum dots
- **Targeting agent**: antibody or peptide
- **Cell-penetrating agent**: peptide
- **Stimulus-sensitive** element for drug release
- **Stabilising polymer** to ensure biocompatibility: polyethylene glycol

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Figure 3.13.1. Nanoparticle sample with surface modification

(This image is published on https://www.slideshare.net/Reset_co/surface-modification-of-nanoparticles-for-biomedical-applications and retrieved from Google Images.)

Inorganic materials (e.g. Al_2O_3, SiO_2, ZnO etc.), organic materials (alkaly amines, fatty acids like oleic acid and stearic acid, sodium laurat, sodium dodesil benzene sulphonate etc.) and polymers (polyethylene glycole, polyvinyl alcohol, polyoxypropylene etc.) can be used as surface regulators in nanomaterials.

3.13.2 Surface Modification Mechanism of Nanoparticles

This is the reaction performed between the surface and surface regulator to increase the intermediate surface compatibility of nanoparticles and to improve their solubility through the concept of surface modification of nanoparticles. Thus, nanoparticles can easily disperse in organic compounds or water. Molecular structure of a surface regulator must have the properties of the substrate group which can easily react with the surface of nanoparticles. This special group can be obtained from the design of the molecular structure of the surface regulator. Modification can be divided into coating modification and synthesis modification based on the reaction between the surface regulator and nanoparticles.

Coating application is the improvement process performed for preventing or reducing the agglomeration of nanoparticles by coating the surface of nanoparticles with organic or inorganic compounds (Figure 3.13.2). Coated materials provide a steric hindrance effect, which makes it significantly more difficult for particles to aggregate, in order to enable the modification to be successful. Coating mechanism may occur as adsorption, fixation, simple chemical reaction or aggregation of the coating on the surface.

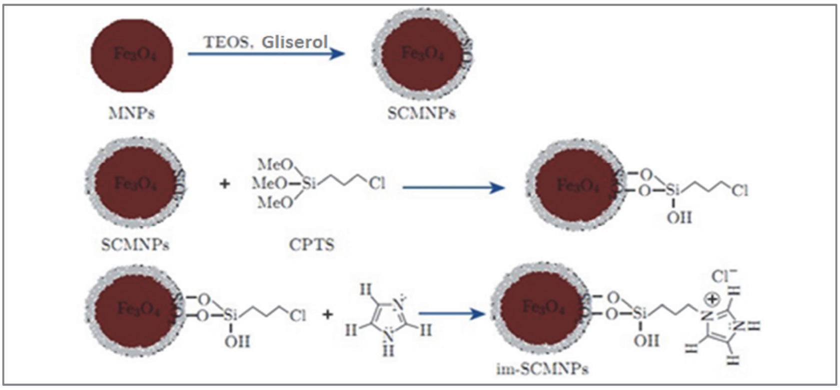

Figure 3.13.2. Schematic representation of surface modification reactions of magnetic nanoparticles using imidazol

(This image is published on http://nmstr.org/2015/08/05/preparing-modified-silica-coated-magnetite-nanoparticles-by-co-precipitation-method-and-the-application-in-removal-of-iodine-from-water-samples/ and retrieved from Google Images.)

Synthesis mechanism corresponds to the chemical coupling reaction that occurs on the surface of the nanoparticles. In addition to coordination bonds, hydrogen bonds or Van der Waals forces, ionic or covalent bonding between two compounds may also occur. Surface of nanoparticles are highly compatible with the organic materials in the process that is conducted with the help of synthesis agents. Synthesis agent molecules must have two groups: Groups that can chemically react with the surface of inorganic nanoparticles, or organic functional groups that can compatible with organic substrates, e.g. dioxin acetate titanate, vinyl trietoxysilane etc. Synthesis modification process has many options in terms of synthesis agents and easier that the other method. Therefore, this method is more widely used in nanocomposite materials.

Three methods, mechanical dispersion, ultrasonic dispersion and high-energy processing, are used in the modification of nanoparticles.

In the application where mechanical force is used, generally the mechanical effects formed through external shear force or impact force are utilized (Figure 3.13.3). The surface of the nanoparticle under this effect undergoes chemical changes to react with its chemical environment. Either branching occurs from organic chain compounds on the surface or a protective layer forms on the surface in order to catalyze the dispersion of the nanoparticles.

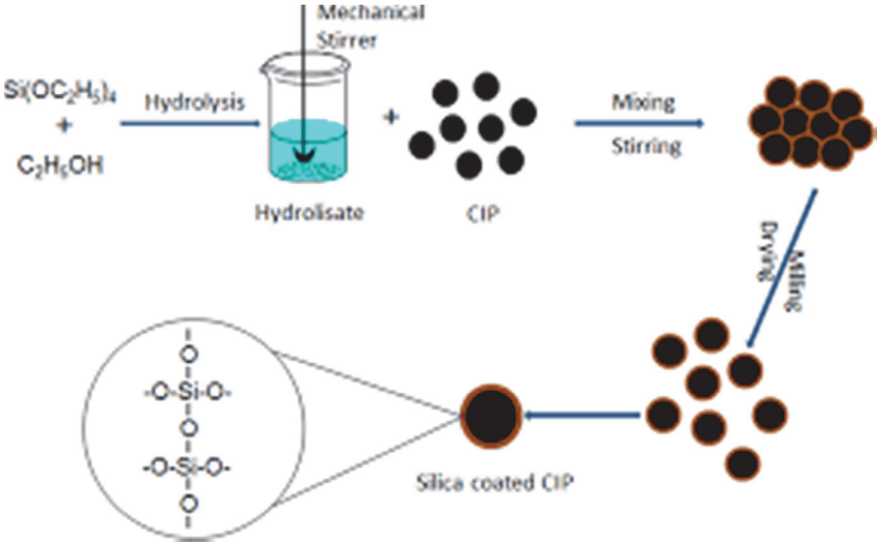

Figure 3.13.3. Mechanical surface modification of carbonyl iron powder

(This image is published on http://iopscience.iop.org/article/10.1088/0964-1726/25/11/115005 and retrieved from Google Images.)

It is widely used in chemistry due to its important effects such as ultrasound, dispersion of particulate structures, polymer degradation, and synthesis of compounds (Figure 3.13.4).

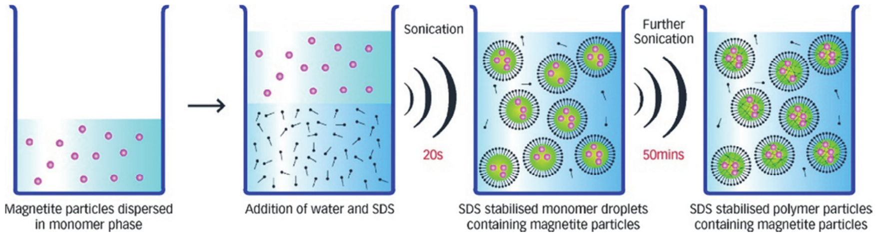

Figure 3.13.4. Ultrasonic surface modification of iron oxide nanoparticles

(This image is published on http://iopscience.iop.org/article/10.1088/1468-6996/16/2/023501 and retrieved from Google Images.)

High-energy approach includes the use of plasma radiation, electrical discharge, infrared and ultraviolet for the modification of nanoparticle surface (Figure 3.13.5).

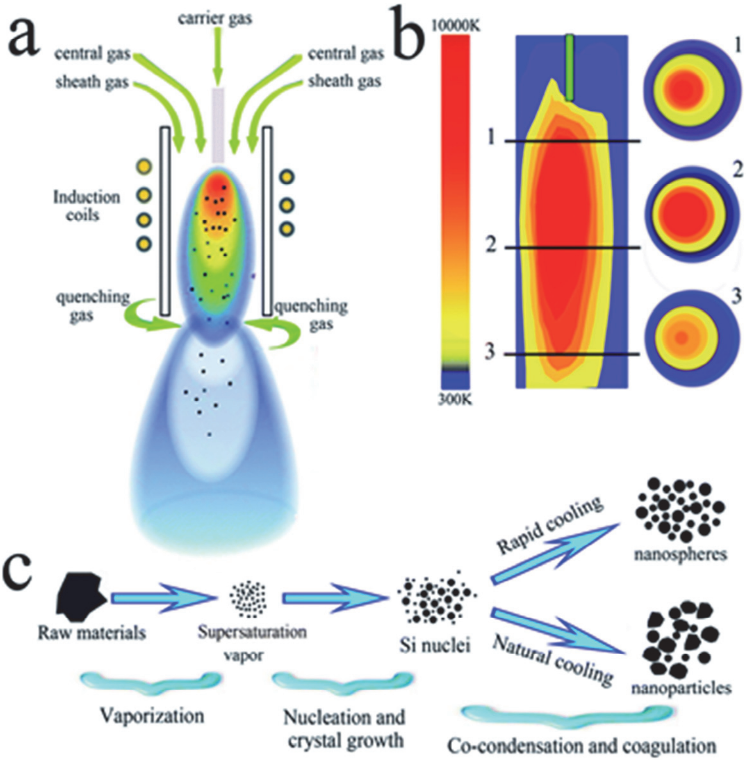

Figure 3.13.5. Nanoparticle synthesis using high energy

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Summary

Nanoparticles aggregate very easily due to their high surface energy and large surface area. Since agglomeration of nanoparticles disrupts their nano-sizes, it prevents NPs from being used in many important fields. If agglomeration of NPs can be hindered, these important applications can be possible. NPs can be prevented from agglomeration via surface modification methods. Therefore, surface engineering emerged. Through various studies, this engineering field investigates methods that will allow NPs to maintain their nano-scale sizes in applications. Three different methods have been put forward for this purpose. Nanoparticles can be maintained at nano sizes by applying surface modification via mechanical force, ultrasonic impact or high-energy sources.

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QUESTIONS

QUESTION 1) If the material has ……………………….., these materials are called nanoparticles, quantum dots, nanoshell, nanoring and micro capsule.

a) Three dimensions smaller than 100 nm
b) Two dimensions smaller than 100 nm
c) One dimension smaller than 100 nm
d) Three dimensions smaller than 100 µm

QUESTION 2) If the material has ……………………….., these materials are called nanotube, nanowire and fiber.

a) Three dimensions smaller than 100 nm
b) Two dimensions smaller than 100 nm
c) One dimension smaller than 100 nm
d) Three dimensions smaller than 100 µm

QUESTION 3) If the material has ……………………….., these are called thin film, layer and coating.

a)Three dimensions smaller than 100 nm
b) Two dimensions smaller than 100 nm
c) One dimension smaller than 100 nm
d)Three dimensions smaller than 100 µm

QUESTION 4) As the ……………… Increases, materials with low molecular weight can be created.

a) Volume/surface area ratio
b) Temperature
c) Temperature and time
d) Surface area/volüme

QUESTION 5) Microelectromechanical systems (MEMS) are the integration of microsensors, microactuators and microelectronic components ……………………………….

a) in an emulsion
b) with ultrasound waves
c) on a silicon chip
d) none of the above

QUESTION 6) Which of the following is a Nanotechnology product?

a) Lycurgus Cup

b) Stained-glass Windows in Churches

c) Damascus Swords

d) all of the above

QUESTION 7) Who used the term nanotechnology first and when this term was used?

a) Richard Feynman, 1959

b) Norio Taniguchi, 1974

c) Eric Drexler, 1986

d) Sumio Lijima, 1991

QUESTION 8) "What is Buckyball?

a) a Carbon molecule (C60)

b) Mercedes-Benz's modern car design (C111)

c) Plastic explosive nanoparticles

d) Gold nanoparticles

QUESTION 9) What is the title of the famous talk of Richard Feynman, who was accept-ed as the mastermind of modern nanotechnology on 29 December 1959?

a) Nanoscopic Things happen at the bottom

b) There is plenty of room at the bottom

c) There is plenty of discover at the bottom

d) There is a small room at the bottom

QUESTION 10) In which country was the scanning tunnel microscope (SEM) capable of displaying the nanoscale?

a) Germany

b) United States

c) Switzerland

d) Japan

QUESTION 11) Which of the following is an example for nanotechnology use today?

a) Stain-proof fabrics
b) Scratch-proof surfaces
c) Color changing dyes
d) All of the above

QUESTION 12) How does nanotechnology work?

a) Production by controlling nano-scaled structures.
b) Production by processing the metal containing mineral ores.
c) Production by controlling polymers.
d) Production by changing the chemical structures, energy contents or physical states of the materials.

QUESTION 13) Which of the following is not an expected benefit of nanotechnology for environment?

a) Efficient use, storage and generation of energy
b) Detection of environmental pollutants
c) Developing molecular-level chemicals to protect plants against insects
d) Creating a sustainable environment

QUESTION 14) Which of the following is a nanotechnology application developed for foods?

a) Batteries with nanowires
b) Drugs embedded into nanoparticles
c) Clay nanotubes preventing rotting and bacteria growth
d) Nano-scale fertilizer

QUESTION 15) Which of the following is not an application of nanotechnology in medicine?

a) Drugs loaded onto nanoparticles
b) Tumor detection with iron oxide nanoparticles
c) Destroying the cancer cells with nanoshells
d) All of the above

QUESTION 16) Which of the below cannot be said for nanometrology?

- a) It is necessary to conduct studies at atomic and molecular level.
- b) It is used for measuring structures which are sized as billionth of a meter or less.
- c) It is used for measuring structures which are sized as 10-12 and less.
- d) It is the science of measurement.

QUESTION 17) What is the scale of measurement that nanotechnology deals with?

- a) 1-100 nm
- b) 1-10 nm
- c) 1-100 µm
- d) 1-10 µm

QUESTION 18) At nanoscale:

- a) Metals become harder.
- b) Chemical resistance increases.
- c) Ceramics become softer.
- d) All of the above are correct.

QUESTION 19) Which formula is used for calculating the number of atoms in 1 ng of an element whose molar mass is 40,08?

- a) $\left(\frac{6{,}022x10^{23}}{40{,}08}\right)x10^{-9}$
- b) $\left(\frac{40{,}08}{6{,}022x10^{23}}\right)x10^{-9}$
- c) $6{,}022x10^{23}$
- d) $\left(\frac{40{,}08}{6{,}022x10^{23}}\right)$

QUESTION 20) Which of the below is not a nanoscale measurement requirement?

- a) Thickness and density of thin film
- b) Height at structured surface
- c) Diameter of engineered nanoparticles
- d) Microelectronic measurements

QUESTION 21) The technologies that exist, it could have a negative impact on society in what concerns aspects of:

a) confidentiality;
b) division of society;
c) communication;
d) risks.

QUESTION 22) Nano Impact aims to play an important role in disseminating knowledge about nanomaterials in human and environmental systems. It focuses on four main areas:

a) Human nanotoxicology
b) Nano-eco toxicology
c) Exposure
d) Risk and life cycle assessment

QUESTION 23) Choose the correct answer

☐ *True* ☐ *False*

Nano Impact aims to play an important role in disseminating knowledge about nanomaterials in human and environmental systems.

QUESTION 24) Identify somenew concepts for future nanotechnology impact products

a) Nano spaces
b) Nano robot
c) Nano elevator
d) Nano morph

QUESTION 25) Mention some application of nanotechnology.

QUESTION 26) What systems can you prepare by using microemulsion method? Choose one of these systems, explain your reason and which parameters you should pay attention as you prepare the system.

QUESTION 27) Is there a chance for us to encounter precipitation method in daily incidents? Discuss.

QUESTION 28) Which nanoparticles can be produced by using precipitation method? Research.

QUESTION 29) What are the nanoparticles systems where you can use ultrasonic energy? For what purpose would you use, explain.

QUESTION 30) Green chemistry aims to......
a) design chemical products and processes that will increase the profitability.
b) design safer chemical products and processes that will reduce or cease the use and production of hazardous substances.
c) design more efficiently working chemical products and processes.
d) use non-renewable energy.
e) None of the above

QUESTION 31) Dr. Paul Anastas and Dr. John Warner authored the 12 principles of “Green Chemistry” to reduce or cease the use and production of hazardous substances.

a) True
b) False

QUESTION 32) Which of the following is one of 12 principles of Green Chemistry?
a) Designing commercially applicable products
b) Using only new solvents
c) Using catalysts instead of stoichiometric reagents
d) Re-using the wastes
e) None of the above

QUESTION 33) Green chemistry is more expensive than conventional chemistry.
a) True
b) False

QUESTION 34) Which of the following can be an example of green chemistry?

a) Recycled carpet
b) A product prepared on world day
c) A sublimation reaction
d) Bioplastics
e) None of the above

QUESTION 35) Which of the following is not one of the primary benefits of SOL-GEL method?

a) High-purity product attainment
b) Product attainment at low temperature
c) Product attainment at high temperature
d) High homogeneity

QUESTION 36) Which of the following is not related to condensation process?

a) Removal of the water inside the structure
b) Obtaining large molecules from smaller molecules inside the structure
c) Removal of the alcohol inside the structure
d) Removal of the oxide inside the structure

QUESTION 37) Which of the following is the correct order of SOL-GEL process?

a) Drying + gelling + hydrolysis of pre-initiators + high temperature processing + aging + condensation
b) Hydrolysis of pre-initiators + condensation + gelling + aging + drying + high temperature processing
c) Condensation + hydrolysis of pre-initiators + gelling + aging + drying + high-temperature processing
d) Gelling + aging + hydrolysis of pre-initiators + drying + high-temperature processing + condensation

QUESTION 38) Which of the following is not a coating process conducted with SOL-GEL method?

a) Angle-based dip coating
b) Dip coating process
c) Spin coating process
d) Coating with electrolysis method

QUESTION 39) Which of the following is not an advantage of SOL-GEL method?

a) Process is easy.
b) Process can be conducted under laboratory conditions
c) Process does not take place at high temperatures
d) Process does not allow the production of different types of nanomaterials

QUESTION 40) Which of the following is not a lithography technique?

a) Electron beam
b) Spin
c) Nano-stamp
d) Micro-contact printing
e) Photolithography

QUESTION 41) .... is an image and it is formed by creating a pattern on the stone, inking it and printing the inked stone onto a paper.

a) Quantum dot
b) Nanophotonic crystal
c) Lithography
d) Microfabrication
e) Etching

QUESTION 42) Which of the following is (are) correct?

(I) Positive resists - These become more soluble when they are exposed to UV rays.

(II) Negative resists - These become less soluble when they are exposed to UV rays.

(III) Photoresists general initiate the reaction with ultraviolet (UV) or visible light, therefore they are called optical resists.

a) Only I
b) Only II
c) I and II
d) Only III
e) II and III

QUESTION 43) Which of the following is not a component of photoresist?

a) Catalyst
b) Polymer
c) Sensitizer
d) Solvent
e) Additives like paint

QUESTION 44) Which of the following is not an area of use of lithography?

a) integrated circuits
b) internal computer components
c) production of microcircuits (NEMs, MEMs)
d) organic memory devices
e) scanning electron microscope (SEM)

QUESTION 45) Which of the following is not a reason that causes the formation of nanoparticles?

a) Volcanic eruption
b) Biomineralization
c) Comets
d) Desert dusts
e) Agglomeration of humic substance

QUESTION 46) Which of the following is not an example of organic natural nanoparticles?

a) Humic acid
b) Fulvic acid
c) CdS
d) Peptides
e) Proteins

QUESTION 47) Which is the most striking difference of produced nanoparticles from NNPs?

a) Ability to produce at desired ratios
b) Production using chemicals
c) Ability to release to the nature
d) Unknown toxic effects
e) Being used in many applications

QUESTION 48) Which of the following does not have the morphological structure of nanoparticles synthesized today?

a) Core-shell
b) Sandwich
c) Doped
d) Hollow
e) 4D structure

QUESTION 49) Which of the following exhibits different morphological nanoparticle shapes?

a) Metal alloy
b) Ceramic
c) Polymer-based
d) Metal composite
e) Plant-based

QUESTION 50) With which of the following mediums can nano alloys be prepared?

I. Gas phase
II. Precipitate phase
III. By supporting with a matrix

a) Only I
b) Only II
c) I and II
d) I, II and III
e) None of the above

QUESTION 51) Which of the following is not a method used for the synthesis of metal nanoparticle?

a) Bacteria species
b) Fungi
c) Yeasts
d) Plant extracts
e) Waste water

QUESTION 52) Which of the following is an area of use for nanoparticles?

a) Milk industry
b) Fruit juice
c) Drug delivery
d) Bread making
e) Salt production

QUESTION 53) In which applications would you prefer to use natural and synthetic polymeric nanoparticles and dendrimers. Explain with reasons.

QUESTION 54) If you want to produce a nanomaterial related to your professional field, which material do you choose? Explain why. What are the disadvantages of using the material you choose? To get rid of these disadvantages, what materials and what method do you consider to improve the surface of your material? Please explain.

QUESTION 55) What is electrical puncture?

QUESTION 56) What is the Meissner effect?

QUESTION 57) What is the working principle of solar cells?

QUESTION 58) What can you say about the resistances of two conductors with the same length but different diameters, assuming all other conditions are the same except their diameters?

QUESTION 59) What can you say about the resistances of two conductors, assuming that only the lengths of two conductors are different and they are the same in all other conditions?

QUESTION 60) Which of the following is not a quantum dot property?

a) They have wide and continuous absorption spectrum
b) They have narrow emission spectrum
c) They have high light stability
d) They have quite good luminescence and electrical properties
e) Quantum dots have sizes in micrometer scale

QUESTION 61) Which of the following explains why quantum dot structures with different sizes radiate in different colors?

a) Quantum confinement effect
b) Surface properties
c) Use of different surface active agents in the synthesis of quantum dot structures
d) Quantum dots having different crystal
e) Quantum dots being synthesized in core/shell structure

QUESTION 62) Which of the following quantum dot structure synthesis methods cannot be used as top-down synthesis method?

a) Electron beam litography
b) X-ray litography
c) Sol-Gel method
d) Molecular beam epitaxy
e) Ion implantation

QUESTION 63) Which of the following is not a reason why quantum dot structures are being used in photocatalysis applications?

a) Low cost
b) Low toxicity
c) Adjustable florescence emissions
d) Having sizes in nanometer scale
e) Chemically inert structure

QUESTION 64) Which of the following is referred to as "florescence quantum efficiency"?

a) The ratio of the number of absorbed photons to the number of emissions
b) The ratio of the number of emissions to the number of absorbed photons
c) Difference between the number of emissions and the number of absorbed photons
d) The number of absorbed photons
e) The number of emissions

QUESTION 65) Which of the following does not have the morphological structure of nanoparticles synthesized today?

a) Core-shell
b) Sandwich
c) Doped
d) Hollow
e) 4D structure

QUESTION 66) Which of the following exhibits different morphological nanoparticle shapes?

a) Metal alloy
b) Ceramic
c) Polymer-based
d) Metal composite
e) Plant-based

QUESTION 67) With which of the following mediums can nano alloys be prepared?

I. Gas phase
II. Precipitate phase
III. By supporting with a matrix
a) Only I
b) Only II
c) I and II
d) I, II and III
e) None of the above

QUESTION 68) Which of the following is not a method used for the synthesis of metal nanoparticle?

a) Bacteria species
b) Fungi
c) Yeasts
d) Plant extracts
e) Waste water

QUESTION 69) Which of the following is an area of use for nanoparticles?

a) Milk industry
b) Fruit juice
c) Drug delivery
d) Bread making
e) Salt production

QUESTION 70) Discuss the importance of different hybridization of carbon atom.

QUESTION 71) Which company owns the most patents in the world on studies at nano-scale studies? Explain the nan-otechnology-based design in the logo of the related company.

QUESTION 72) Which country makes the most nanotube production in the world? Mention the related country's nano-technology-based productions for daily life.

QUESTION 73) What is Bucky ball?

QUESTION 74) Which of the following does not belong to the shape classification of nanomaterials in terms of their sizes?

a) Isotropic structure
b) 1D structure
c) 2D structure
d) Anisotropic structure
e) 4D structure

QUESTION 75) Which of the following is not a 1D shape of nanoparticles?

a) Spherical structure
b) Nanorods
c) Circular disks
d) Nanostar
e) Nanoflower

QUESTION 76) Which of the following parameters contribute to the kinetically-controlled shape formation of nanoparticles?

a) Temperature
b) Concentration
c) Chemical Potential
d) Nucleation theory
e) pH effect

QUESTION 77) Which of the following is not a factor that affects the shapes of nanoparticles?

a) Supersaturation
b) Concentration
c) Light
d) Solvent effect
e) pH effect

QUESTION 78) Which factor that affects the shape control of nanoparticles is used for reducing the surface energies of nanoparticles?

a) Surfactants and additives
b) Temperature
c) Precursor monomer concentration
d) Supersaturation
e) pH effect

QUESTION 79) Which of the following is not a nanoceramic material?

a) SiO_2
b)TiO_2)
c)$Ca(OH)_2$
d) Al_2O_3
e) ZrO_2

QUESTION 80) Which of the following can be applied to nanoceramics to obtain the smallest possible particle size?

a) fast heating
b) high pressure,
c) addition of shrinking accelerator agents
d) addition of particle growth inhibitor agents
e) instant cooling

QUESTION 81) Which of the following can be given as an advanced sintering technique for synthesis of desired nanoceramics?

a) electron beam litography
b) high pressure compression
c) arc-plasma sintering
d) shock compression,
e) high frequency induction heating

QUESTION 82) List at least 3 application fields where nanoceramics are used.

QUESTION 83) Which of the following(s) is a disadvantage of traditional sintering method?

(I) frequent particle growth
(II) deterioration of ceramic,
(III) worsening of mechanical properties of ceramic

a) I and II
b) I, II, III
c) Only I
d) Only III
e) II and III

QUESTION 84) Which of the following is not a superior property of thin film?

a) Optical properties
b) Chemical properties
c) Electrical properties
d) Physical properties

QUESTION 85) Which of the following is not within the size range of thin films?

a) Materials smaller than 1 mμ
b) Materials larger than 5 mμ
c) Materials larger than 1 mμ
d) Materials smaller than 10 mμ

QUESTION 86) Which of the following is a thin film production method?

a) Physical abrasion method
b) Chemical abrasion method
c) Sol – Gel method
d) Chemical liquid deposition method

QUESTION 87) Which of the following is a type of thin film?

a) Double conductor films
b) Mega conductor films
c) Superinsulator films
d) Superconductor films

QUESTION 88) Which of the following is one of the advantages of thin film production method?

a) Process is easy.
b) Allows for the use of any kind of production method.
c) Coating thickness depends on the production method.
d) Poor optical properties.

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