# KARPAGAM ACADEMY OF HIGHER EDUCATION

**(Deemed University Established Under Section 3 of UGC Act 1956)**

**COIMBATORE-21**

## DEPARTMENT OF CHEMISTRY

## M.Sc CHEMISTRY

**Semester– III**

**16CHP304 NANOCHEMISTRY 4H 4C**

---

**Instruction Hours/week:L: 4 T:0 P:0 Marks: Internal:40 External: 60 Total:100**

### Scope

Nano chemistry frames much of our understanding of the natural world and continues to bring new technologies that are useful to every aspect of human life. Nano chemistry is an exciting and challenging course, which helps us to understand the various aspects of compounds used in our day to day life. Nano chemistry interfaces with a myriad of other disciplines and fields. It is fundamental to understand other areas of chemistry, biology and medicine. Due to highly prized nature of Natural product chemistry and its diverse topics, it lays the foundation for extremely productive and exciting career in variety of disciplines as pharmaceutical, agrochemical, mineralogy, molecular biology, biotechnology, nanotechnology, polymer technology, teaching research, scientific publication and so on. The importance of this subject would not diminish over time, so it will remain a promising career path. This course presents the basic principles of nano products and nano particles.

### Programme Outcome

- To understand the various aspects of compounds used in our day to day life in nanoscale range
- To understand the basic principles of nano products and nano particles
- To understand the advantages and disadvantages of Nano materials

### Programme Learning Outcome

- The students know the various aspects of compounds used in our day to day life in nanoscale range
- They undersold the basic principles of nano products and nano particles
- The students understood the natural world and continues to bring new technologies

**Methodology**

Blackboard teaching, Powerpoint presentation and group discussion.

**UNIT I:** Introduction: History scope and perspectives of nano-chemistry

**UNIT II:** Synthesis and stabilization of nanoparticles, chemical reduction; reactions in micelles, emulsions, and dendrimers; photochemical and radiation chemical reduction; cryochemical synthesis: Physical methods, particles of various shapes and films.

**UNIT III:** Experimental techniques: Electron microscopy: Transmission electron microscopy: probe

Microscopy: Probe microscopy: diffraction techniques X-ray diffraction, neutron diffraction: Miscellaneous

Techniques, comparison of spectral techniques used for elemental analysis

**UNIT IV:** Size effects in nanochemistry: Models of reactions of metal atoms in matrices; properties;

Kinetic peculiarities of chemical processes on the surface of nanoparticles; Thermodynamic features of nanoparticles.

**UNIT V:** Applications of nanoparticle in various fundamental research, industries, medical field and environmental issue; toxicity, biosafety and ethical issue in application of nanoparticle

**SUGGESTED READINGS:**

**Text Books:**

1. Er.Rakesh Rathi, Nano Technology, Technology Revolution of 21st Century, 2009, S.Chand & Company, RamNagar, New Delhi.
2: B.Viswanathan, 2013, Nano materials, Narosa publishing house, New Delhi.
3: T.Pradeep, Nano The essentials, 2003, Tata Mcgraw Hill Education private Ltd. New Delhi.

**Reference Books:**

**e- book**

1. Br’echignac, C., Houdy., & Lahmani, M. (2007). *Nanomaterials and Nanochemistry*. New York: Springer Berlin Heidelberg.

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**(Deemed University Established Under Section 3 of UGC Act 1956)**

**COIMBATORE-21**

## DEPARTMENT OF CHEMISTRY

## M.Sc CHEMISTRY

## LECTURE PLAN

| | | |
|---|---|---|
| Name of the Staff | : | **Dr. M. MAKESWARI** |
| Department | : | **Chemistry** |
| Subject | : | **Nano Chemistry** |
| Subject Code | : | **16CHP304** |
| Class | : | **II M.Sc-Chemistry** |
| Year and Semester | : | **II / III** |
| Total Hours | **:** | **60 Hours** |

## UNIT-I

**HOURS REQUIRED -10**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|---|---|---|---|
| 1 | 1 | Introduction of Nano Chemistry | **T1:** 1-10 |
| 2 | 1 | Definition of Nano Chemistry | **T1:** 10-15 |
| 3 | 1 | History of nano-chemistry | **T1:** 16 |
| 4 | 1 | Early uses of History of nano-chemistry | **T1:** 16 |
| 5 | 1 | scope of nano-chemistry | **T1:** 29 |
| 6 | 1 | scope of nano-chemistry in various fields | **T1:** 29 |
| 7 | 1 | perspectives of nano-chemistry | **T1:** 80 |
| 8 | 1 | perspectives of nano-chemistry – Experimental advances | **T1:** 80 |
| 9 | 1 | Revision and Discussion of possible questions | |
| 10 | 1 | Revision and Discussion of possible questions | |

**Support Materials:**

**Text Book**

1. Er.Rakesh Rathi, Nano Technology, Technology Revolution of 21st Century, 2009, S.Chand

& Company, RamNagar, New Delhi.

**e-Book**

1. Br’echignac, C., Houdy., & Lahmani, M. (2007). *Nanomaterials and Nanochemistry*. New York: Springer Berlin Heidelberg. (e-Book).

## UNIT-II

**HOURS REQUIRED -13**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|---|---|---|---|
| 1 | 1 | Synthesis of nanoparticles- Reduction methods | **T2:** 1.3, **W1** |
| 2 | 1 | Synthesis of nanoparticles-Physical methods | **T2:** 1.4-1.5, **W1** |
| 3 | 1 | Stabilization of nanoparticles | **T2:** 2, **W1** |
| 4 | 1 | Chemical reduction | **T2:** 1.3-1.4, **W1** |
| 5 | 1 | Reactions in micelles, | **T2:** 1.5, **W1** |
| 6 | 1 | Emulsions and dendrimers; | **T2:** 3.6, **W1** |
| 7 | 1 | Emulsions and dendrimers; | **T2:** 3.7, **W1** |
| 8 | 1 | photochemical and radiation chemical reduction; | **T2:** 3.8, **W1** |
| 9 | 1 | cryochemical synthesis | **T2:** 3.9, **W1** |
| 10 | 1 | Physical methods | **T2:** 3.9, **W1** |
| 11 | 1 | Particles of various shapes and films. | **T2:** 1.8, **W1** |
| 12 | 1 | Revision and Discussion of important questions | |
| 13 | 1 | Revision and Discussion of important questions | |

**Support Materials:**

**Text Book**

**T2:** B.Viswanathan, 2013, Nano materials, Narosa publishing house, New Delhi.

**Website:**

**W1:** https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4326978/

**e-Book**

1. Br’echignac, C., Houdy., & Lahmani, M. (2007). *Nanomaterials and Nanochemistry*. New York: Springer Berlin Heidelberg. (e-Book)

## UNIT-III

**HOURS REQUIRED - 13**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|---|---|---|---|
| 1 | 1 | Experimental techniques: | **T3:** 20 |
| 2 | 1 | Electron microscopy: Principle and Instrumentation | **T3:** 20 |
| 3 | 1 | Electron microscopy: Advantages and Applications | **T3:** 21 |
| 4 | 1 | Transmission electron microscopy: Principle and Instrumentation | **T3:** 34 |
| 5 | 1 | Transmission electron microscopy: | **T3:** 35 |
| 6 | 1 | Probe Microscopy: | **T3:** 43 |
| 7 | 1 | Diffraction techniques -X-ray diffraction, | **T3:** 75 |
| 8 | 1 | neutron diffraction: | **T3:** 76 |
|  | 1 | Miscellaneous Techniques, | **T3:** 77 |
| 9 | 1 | Comparison of Miscellaneous Techniques, | **T3:** 78 |
| 10 | 1 | spectral techniques used for elemental analysis | W1 |
| 11 | 1 | comparison of spectral techniques used for elemental analysis | W1 |
| 12 | 1 | Revision and Discussion of important questions |  |
| 13 | 1 | Revision and Discussion of important questions |  |

**Support Materials:**

**<u>Text Book</u>**

**T3:** T.Pradeep**,** Nano The essentials, 2003, Tata Mcgraw Hill Education private Ltd. New Delhi.

**W1:** https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4326978/

**e-Book**

1. Br’echignac, C., Houdy., & Lahmani, M. (2007). *Nanomaterials and Nanochemistry*. New York: Springer Berlin Heidelberg. (e-Book)

## UNIT-IV

**HOURS REQUIRED -13**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|---|---|---|---|
| 1 | 1 | Size effects in nanochemistry: Introduction | **T2:** 1.3, 2-2.1 |
| 2 | 1 | Size effects in nanochemistry: | **T2:** 1.3, 2-2.3 |
| 3 | 1 | Models of reactions of metal atoms in matrices; | **T2:** 2.3 |
| 4 | 1 | Models of reactions of metal atoms in matrices; | **T2:** 2.7 |
| 5 | 1 | Mechanical Properties | **T2:** 2.8 |
| 6 | 1 | Properties - Magnetic | **T2:** 2.9 |
| 7 | 1 | Kinetic peculiarities of chemical processes | **T2:** 3.1 |
| 8 | 1 | Kinetic peculiarities of chemical processes on the surface of nanoparticles | **T2:** 3.4 |
| 9 | 1 | Kinetic features of nanoparticles. | **T2:** 3.5 |
| 10 | 1 | Thermodynamic features of nanoparticles-Introduction | **T2:** 3.6 |
| 11 | 1 | Thermodynamic features of nanoparticles. | **T2:** 3.7-3.8 |
| 12 | 1 | Revision and Discussion of important questions | |
| 13 | 1 | Revision and Discussion of important questions | |

**Support Materials:**

**Text Book**

**T2:** B.Viswanathan, 2013, Nano materials, Narosa publishing house, New Delhi.

**e-Book**

1. Br’echignac, C., Houdy., & Lahmani, M. (2007). *Nanomaterials and Nanochemistry*. New York: Springer Berlin Heidelberg. (e-Book)

## UNIT-V

**HOURS REQUIRED - 11**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|---|---|---|---|
| 1 | 1 | Applications of nanoparticle in various fundamental research | **T1:** 112, **W2** |
| 2 | 1 | Applications of nanoparticle in industries | **T1:** 114, **W2** |
| 3 | 1 | Applications of nanoparticle in medical | **T1:** 122, **W2** |
| 4 | 1 | Applications of nanoparticle in environmental issue | **T1:** 124, **W2** |
| 5 | 1 | Toxicity- Human | **T1:** 125, **W2** |
| 6 | 1 | Toxicity-Environment | **T1:** 125, **W2** |
| 7 | 1 | Biosafety and ethical issue in application of nanoparticle | **T1:** 126, **W2** |
| 8 | 1 | Revision and Discussion of important questions | |
| 9 | 1 | ESE- Question paper Discussion | |
| 10 | 1 | ESE- Question paper Discussion | |
| 11 | 1 | ESE- Question paper Discussion | |

**Support Materials:**

**<u>Text Book</u>**

**T1:** Er.Rakesh Rathi, Nano Technology, Technology Revolution of 21st Century, 2009, S.Chand & Company, RamNagar, New Delhi.

**Web Site**

**W2 :** https://en.wikipedia.org/wiki/Applications_of_nanotechnology

**e-Book**

1. Br'echignac, C., Houdy., & Lahmani, M. (2007). *Nanomaterials and Nanochemistry*. New York: Springer Berlin Heidelberg. (e-Book)

# LECTURE NOTES

## UNIT-I

## SYLLABUS

Introduction: History scope and perspectives of nano-chemistry

### Introduction to Nano Chemistry

Nanochemistry is the combination of chemistry and nanoscience. Nanochemistry is a branch of **nanoscience**, deals with the chemical applications of **nanomaterials** in **nanotechnology**. Nanochemistry involves the study of the synthesis and characterisation of materials of nanoscale size.

Nanochemistry is associated with synthesis of building blocks which are dependent on size, surface, shape and defect properties. Nanochemistry is being used in chemical, materials and physical, science as well as engineering, biological and medical applications. Nanochemistry and other nanoscience fields have the same core concepts but the usages of those concepts are different.

The nano prefix was given to nanochemistry when scientists observed the odd changes on materials when they were in nano meter scale size. Several chemical modification on nanometer scaled structures, approves effects of being size dependent.

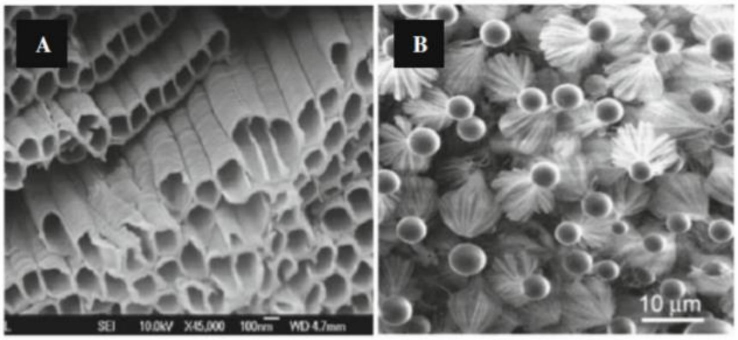
Nanochemistry can be characterized by concepts of size, shape, self-assembly, defects and bio-nano; So the synthesis of any new nano-construct is associated with all these concepts. Nano-construct synthesis is dependent on how the surface, size and shape will lead to self-assembly of the building blocks into the functional structures; they probably have functional defects and might be useful for electronic, photonic, medical or bioanalytical problems.

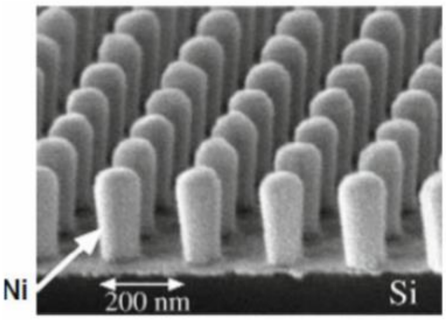
Silica, Gold, Polydimethylsiloxane, Cadmium Selenide, Iron Oxide and Carbon are materials that show the transformative power of nanochemistry. Nanochemistry can make the most effective contrast agent of MRI out of iron oxide (rust) which has the ability of detecting cancers and even killing them at their initial stages . Silica (glass) can be used to bend or stop light in its tracks.Developing countries also use silicone to make the circuits for the fluids to attain developed world’s pathogen detection abilities. Carbon has been used in different shapes and forms and it will become a better choice for electronic materials.

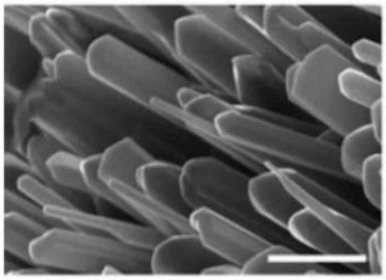
Overall nanochemistry is not related to the atomic structure of compounds rather its about different ways of transformation of materials into solutions for problems . Chemistry mainly deals withdegrees of freedom of atoms in the periodic table however nanochemistry brought other degrees of freedom that controls material’s behaviors.

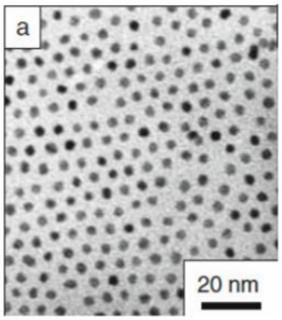
Nanochemical methods can be used to create carbon nanomaterials such as carbon nanotubes (CNT), graphene and fullerenes which have gained attention in recent years due to their remarkable mechanical and electrical properties.

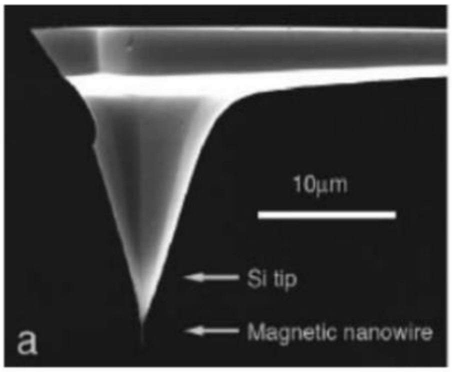
## Nano Structures











**Nanochemistry** is a relatively new branch of chemistry concerned with the unique properties associated with assemblies of atoms or molecules of nanoscale (~1-100 nm), so the size of nanoparticles lies somewhere between individual atoms or molecules (the 'building blocks') and larger assemblies of bulk material which we are more familiar with.

There are physical and chemical techniques in manipulating atoms to form molecules and nanoscale assemblies.

Physical techniques allow atoms to be manipulated and positioned to specific requirements for a prescribed use.

Traditional chemical techniques arrange atoms in molecules using well characterised chemical reactions.

Nanochemistry is the science of tools, technologies, and methodologies for novel chemical synthesis e.g. employing synthetic chemistry to make nanoscale building blocks of desired (prescribed) shape, size, composition and surface structure and possibly the potential to control the actual self-assembly of these building blocks to various desirable size.

At this extremely small scale level, quantum effects can be significant, fascinating and potentially scientifically very rewarding innovative ways of carrying out chemical reactions are possible.

The small size of nanoparticles gives these particles 'unusual' structural and optical properties with applications in catalysis, electrooptical devices etc.

As well as the huge numbers of man-made nanoparticles structures being synthesised, there are naturally occurring nanoparticle assemblies e.g. phospholipid vesicles, polypeptide micelle of the iron storage protein, ferritin.

Nanoparticles are VERY tiny aggregations of atoms BUT bigger than most molecules.

There is no strict dividing line between nanoparticles and 'ordinary bulk' particles of a material such as baking powder or grains of sand, BUT particle size matters! ...

... BECAUSE nanoparticles can display properties significantly different from the bulk material and these properties can be exploited for many different uses. If you compare the size of nanoparticles to that of conventional industrially produced materials you find they have novel uses such as sunscreens and many present future applications e.g.

Nanoparticles have a high surface to volume ratio which has a dramatic effect on their properties compared to non-nanoscale more bulky forms of the same material.

Pieces of gold are, fairly obviously, gold-coloured, but gold nanoparticles are deep red or even black when mixed with water. use?

Titanium dioxide is a white solid used in house paint where plainly it reflects visible light. However, titanium dioxide nanoparticles are so small that they do not reflect visible light, so they cannot be seen and are used in sunblock creams because they block harmful ultraviolet light from the Sun without appearing white on the skin (as in $TiO_2$ in paint).

Silver foil shows virtually no reaction with dilute hydrochloric acid but nanoparticles of silver rapidly react with hydrochloric acid because of the very large surface are to volume ration (think of limestone lumps and very fine powder illustrates this effect at the much larger non-nanoparticle level.

***Uses of nanoparticles***

some are described in more detail on other pages, see index at the end and links here too.

New applications for nanoparticle materials are an important area of research.

- ✓ Nanoparticles have many applications in medicine for controlled drug delivery - example of nanomedicine.
- ✓ Nanotechnology is being applied to the production of synthetic skin and **implant surgery**.
- ✓ Nanomaterials that conduct electricity are being used in electronics as minute conductors to produce circuits for microchips.
- ✓ Materials in cosmetics, deodorants and **sun creams** may be of nanoparticle size.
- ✓ Nanoscale materials are being developed as new catalysts for fuel cells.
- ✓ Nanoparticle substances are incorporated in fabrics to **prevent the growth of bacteria**.

Nanotubes (more details of specific examples on other pages), one of the most widespread studied and used nanomaterials, consist of tiny cylinders of **carbon** (and other materials like **boron nitride**), no wider than a strand of DNA with a wide range of properties of great use to materials scientists. Nanotubes can be stronger than steel with only $^{1}/_{6}$th the weight. Some nanotubes are excellent insulators, semiconductors or conduct electricity as well as copper!

Incredibly, there are lots of varieties of nanotubes, even for the same element or compound, differing in size and atomic arrangement, which can have very different properties! Therefore a wide range of nanomaterials are being developed for an even wider range of applications and technological uses. See **carbon** and **boron nitride** to illustrate this point.

- ✓ The large surface to volume ratio will allow the development of new industrial catalysts.

Nanomaterials can be used to make sensors that detect specific molecules.

- ✓ These detectors will find applications in detecting and monitoring pollutants in water.

Nanotubes can be fabricated into strong and light materials, sometimes as composites with other non-nanomaterials.

- ✓ Such materials can used in such diverse applications as aircraft construction (fuselage, wings etc.) and sports equipment.

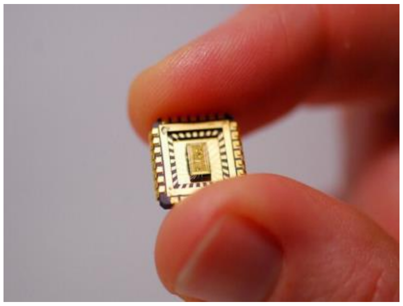
The increased reactivity and small size of nanoparticles compared to larger ones are two important factors which frequently crop up when studying the function of nanomaterials.

- ✓ Nanoparticles have a high surface are to volume ratio, this increases their rate of chemical reaction (greater reactivity) and this also enhances their catalytic effect.
- ✓ Nanomaterials can even be used for such mundane-unexciting applications as in self-cleaning ovens and self-cleaning windows!, but not mundane to domestic work in the Nanoparticles are already being used in deodorants, sun blockers (sun tan creams).
- ✓ The work on nanochemistry can include colloid chemistry.

**Aim and Scope**

- Advances in nanostructured materials such as nano-MOFs, CNTs, meso-porous silica and nano-zeolites
- Applications of nanomaterials in catalysis and in energy conversion/storage
- Developments in nano-sensors and nano-biosensors
- Utilization of nanomaterials for water treatment
- Modeling and Simulation of nanostructures
- Synthesis and characterization of organic, inorganic or hybrid nanomaterials by top-down, bottom-up or biological approaches

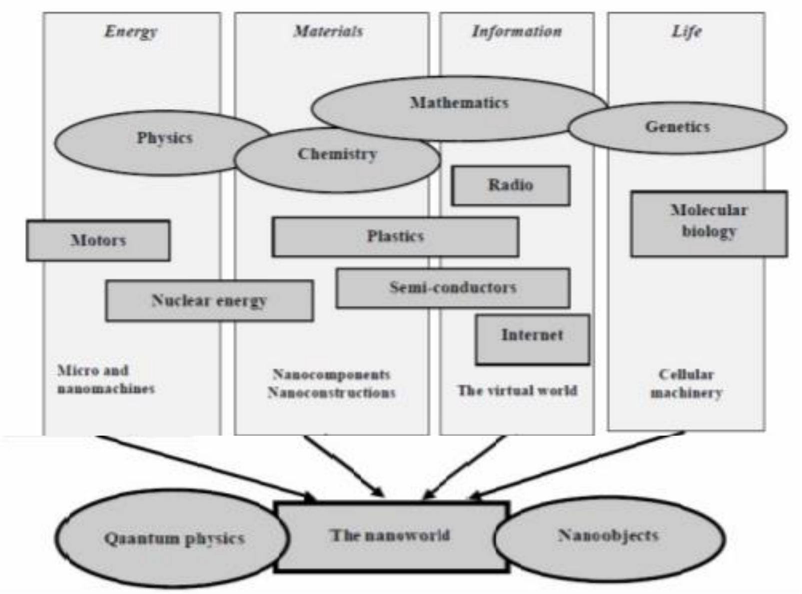
## Scope of Nanotechnology



## Nanoscience and nanotechnology

**Nanoscience** deals with the scientific study of objects with sizes in the 1 – 100 nm range in at least one dimension. Nanoscience is interesting in part of course because it by definition is new. But a more profound and important reason is that it deals with objects which are only slightly larger than an atom. This means that the properties of the objects can be influenced by direct manifestations of quantum mechanics.

**Nanotechnology** deals with using objects in the same size range to develop products with possible practical application. It is usually based on nanoscience insights. It is also possible that nanoscale objects do behave just like as expected from (semi)classical physics, but the downgrading in size opens up possible new applications.



## Scope of Nanotechnology:

### India:

India is still in the development stage for Nanotechnology and it will take quite a few years for this field to become established in India. Research labs and institutions such as IISc, TIFR, NCBS, IITs etc are performing excellent research in India. However, when compared with countries such as UK, Germany and USA, output of high quality research pales significantly. This is due to several reasons such as lack of integration between different departments for R&D in Nanotechnology. Students interested in the research aspect of Nanotechnology can join any one of the prestigious institutions listed below. On the other hand, students interested in working in the Nanotechnology industry have limited options.

### Abroad:

Nanotechnology is doing very well abroad in nations such as USA, UK, Singapore, Germany, China etc in terms of R&D. There has been significant development towards the usage of Nanotechnology in cosmetics, food and textiles. Nanomedicine is still in the R&D stage and widespread growth is yet to be expected and intensive research is being conducted in breakneck speed. For scope of this field abroad, please read Professor Mukhopadhyay's interview here.

**Universities that offer MTech & PhD in Nanotechnology in India:** Many universities in India offer Nanotechnology and related courses for MTech and PhD studies and some of them are as follows

- ✓ NIT, Calicut (MTech in Nanotechnology)
- ✓ JMI, New Delhi (MTech in Nanotechnology)
- ✓ IIT, Roorkee (MTech and PhD in Nanotechnology)
- ✓ DTU (MTech in Nanoscience and Nanotechnology)
- ✓ IISc (MTech and PhD in Nanoscience and Engineering)
- ✓ NIT, Bhopal (MTech in Nanotechnology)
- ✓ NIT, Kurukshetra (MTech in Nanotechnology)
- ✓ MANIT, Bhopal (MTech in Nanotechnology)
- ✓ IIT, Patna (MTech in Nanotechnology)

### MS & PhD abroad:

Numerous universities in the US offer programs in Nanotechnology at the undergraduate and graduate level. Some of these Nanotechnology programs are offered as specializations/concentrations in chemical engineering and electrical engineering programs. UK is another great option for students interested in pursuing higher studies in Nanotechnology.

Apart from being offered as a specialization/concentration along with other majors, there are many universities that offer stand alone courses in Nanotechnology such as an MSc in Nanotechnology and Nanoelectronics.

Germany is also home to many specialized nanotechnology programs at the undergraduate and graduate (MSc and PhD) level.

Singapore’s NUS offers a PhD program in their Nanoscience and Nanotechnology institute. NUS’s electrical and chemical engineering department also offers nanotechnology related specializations at the masters and PhD level. NTU offers Nanotechnology related specializations in the department of chemical and bioengineering.

Canada is also home to numerous programs related to Nanotechnology. Some of these programs are specialized while some of them are offered as concentrations in the department of electrical, chemical and bioengineering.

In Australia, Flinders, La Trobe University and University of Melbourne offer specialized programs in Nanotechnology. Most other universities have nanotechnology as a specialization/concentration coupled with major engineering courses.

**Companies, Universities and Research Institutions in India for Nanotechnology:** Following is a list of reputed institutions and research centers in India for Nanoscience and Nanotechnology with high quality publications in world renowned journals for Nanotechnology.

- ✓ Centre for Research in Nanotechnology & Science (CRNTS), IIT Bombay
- ✓ Centre of Nanotechnology, IIT Roorkee
- ✓ Bhabha Atomic Research Center, Mumbai
- ✓ Institute of Nano Science and Technology (INST), Punjab
- ✓ IBM Semiconductor Research and Development, Bangalore
- ✓ Centre for Nanotechnology, IIT Guwahati
- ✓ Centre for Nanotechnology and Nanoscience, Jamia Millia Islamia
- ✓ Centre for Nanoscience and Nanotechnology, Bharathidasan University, Tiruchirappalli

Apart from the above mentioned institutes, Nanotechnology research is also conducted in the Physics, Chemistry, Materials Sciences and Biological Sciences departments of famed institutions such as NCBS, IISc, TIFR, JNCASR, IITs and NITs, IISERs, BITS Pilani, BARC, University of Hyderabad, CSIR etc.

## History of Nanotechnology

The history of nanotechnology traces the development of the concepts and experimental work falling under the broad category of nanotechnology. Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time. The emergence of nanotechnology in the 1980s was caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985, with the elucidation and popularization of a conceptual framework for the goals of nanotechnology beginning with the 1986 publication of the book Engines of Creation. The field was subject to growing public awareness and controversy in the early 2000s, with prominent debates about both its potential implications as well as the feasibility of the applications envisioned by advocates of molecular nanotechnology, and with governments moving to promote and fund research into nanotechnology. The early 2000s also saw the beginnings of commercial applications of nanotechnology, although these were limited to bulk applications of nanomaterials rather than the transformative applications envisioned by the field.

## Early uses of nanomaterials

The earliest evidence of the use and applications of nanotechnology can be traced back to carbon nanotubes, cementite nanowires found in the microstructure of wootz steel manufactured in ancient India from the time period of 600 BC and exported globally.

Although nanoparticles are associated with modern science, they were used by artisans as far back as the ninth century in Mesopotamia for creating a glittering effect on the surface of pots.

In modern times, pottery from the Middle Ages and Renaissance often retains a distinct gold- or copper-colored metallic glitter. This luster is caused by a metallic film that was applied to the transparent surface of a glazing, which contains silver and copper nanoparticles dispersed homogeneously in the glassy matrix of the ceramic glaze. These nanoparticles are created by the artisans by adding copper and silver salts and oxides together with vinegar, ochre, and clay on the surface of previously-glazed pottery. The technique originated in the Muslim world. As Muslims were not allowed to use gold in artistic representations, they sought a way to create a similar effect without using real gold. The solution they found was using luster.

## Conceptual orginis

### Richard Feynman

The American physicist Richard Feynman lectured, "There's Plenty of Room at the Bottom," at an American Physical Society meeting at Caltech on December 29, 1959, which is often held to have provided inspiration for the field of nanotechnology. Feynman had described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Van der Waals attraction would become more important.

Richard Feynman gave a 1959 talk which many years later inspired the conceptual foundations of nanotechnology.

After Feynman's death, scholars studying the historical development of nanotechnology have concluded that his actual role in catalyzing nanotechnology research was limited, based on recollections from many of the people active in the nascent field in the 1980s and 1990s. Chris Toumey, a cultural anthropologist at the University of South Carolina, found that the published versions of Feynman's talk had a negligible influence in the twenty years after it was first published, as measured by citations in the scientific literature, and not much more influence in the decade after the Scanning Tunneling Microscope was invented in 1981. Subsequently, interest in “Plenty of Room” in the scientific literature greatly increased in the early 1990s. This is probably because the term “nanotechnology” gained serious attention just before that time, following its use by K. Eric Drexler in his 1986 book, *Engines of Creation: The Coming Era of Nanotechnology*, which took the Feynman concept of a billion tiny factories and added the idea that they could make more copies of themselves via computer control instead of control by a human operator; and in a cover article headlined "Nanotechnology", published later that year in a mass-circulation science-oriented magazine, *OMNI*. Toumey's analysis also includes comments from distinguished scientists in nanotechnology who say that “Plenty of Room” did not influence their early work, and in fact most of them had not read it until a later date.

These and other developments hint that the retroactive rediscovery of Feynman's “Plenty of Room” gave nanotechnology a packaged history that provided an early date of December 1959, plus a connection to the charisma and genius of Richard Feynman. Feynman's stature as a Nobel laureate and as an iconic figure in 20th century science surely helped advocates of nanotechnology and provided a valuable intellectual link to the past.

**Norio Taniguchi**

The Japanese scientist called Norio Taniguchi of Tokyo University of Science was first to use the term "nano-technology" in a 1974 conference, to describe semiconductor processes such as thin film deposition and ion beam milling exhibiting characteristic control on the order of a nanometer. His definition was, "'Nano-technology' mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule." However, the term was not used again until 1981 when Eric Drexler, who was unaware of Taniguchi's prior use of the term, published his first paper on nanotechnology in 1981.

**K. Eric Drexler**

K. Eric Drexler developed and popularized the concept of nanotechnology and founded the field of molecular nanotechnology.

In the 1980s the idea of nanotechnology as a deterministic, rather than stochastic, handling of individual atoms and molecules was conceptually explored in depth by K. Eric Drexler, who promoted the technological significance of nano-scale phenomena and devices through speeches and two influential books.

In 1980, Drexler encountered Feynman's provocative 1959 talk "There's Plenty of Room at the Bottom" while preparing his initial scientific paper on the subject, “Molecular Engineering: An approach to the development of general capabilities for molecular manipulation,” published in the *Proceedings of the National Academy of Sciences* in 1981. The term "nanotechnology" (which paralleled Taniguchi's "nano-technology") was independently applied by Drexler in his 1986 book *Engines of Creation: The Coming Era of Nanotechnology*, which proposed the idea of a nanoscale "assembler" which would be able to build a copy of itself and of other items of arbitrary complexity. He also first published the term "grey goo" to describe what might happen if a hypothetical self-replicating machine, capable of independent operation, were constructed and released. Drexler's vision of nanotechnology is often called "Molecular Nanotechnology" (MNT) or "molecular manufacturing."

His 1991 Ph.D. work at the MIT Media Lab was the first doctoral degree on the topic of molecular nanotechnology and (after some editing) his thesis, "Molecular Machinery and Manufacturing with Applications to Computation," was published as *Nanosystems: Molecular Machinery, Manufacturing, and Computation,* which received the Association of American Publishers award for Best Computer Science Book of 1992. Drexler founded the Foresight Institutein 1986 with the mission of "Preparing for nanotechnology.” Drexler is no longer a member of the Foresight Institute.

## Experimental advances

Nanotechnology and nanoscience got a boost in the early 1980s with two major developments: the birth of cluster science and the invention of the scanning tunneling microscope (STM). These developments led to the discovery of fullerenes in 1985 and the structural assignment of carbon nanotubes a few years later.

## Invention of scanning probe microscopy

Gerd Binnig (left) and Heinrich Rohrer (right) won the 1986 Nobel Prize in Physics for their 1981 invention of the scanning tunneling microscope.

The scanning tunneling microscope, an instrument for imaging surfaces at the atomic level, was developed in 1981 by Gerd Binnig andHeinrich Rohrer at IBM Zurich Research

Laboratory, for which they were awarded the Nobel Prize in Physics in 1986. Binnig,Calvin Quate and Christoph Gerber invented the first atomic force microscope in 1986. The first commercially available atomic force microscope was introduced in 1989.

IBM researcher Don Eigler was the first to manipulate atoms using a scanning tunneling microscope in 1989. He used 35 Xenon atoms to spell out the IBM logo. He shared the 2010 Kavli Prize in Nanoscience for this work.

## Advances in interface and colloid science

Interface and colloid science had existed for nearly a century before they became associated with nanotechnology. The first observations and size measurements of nanoparticles had been made during the first decade of the 20th century by Richard Adolf Zsigmondy, winner of the 1925 Nobel Prize in Chemistry, who made a detailed study of gold sols and other nanomaterials with sizes down to 10 nm using an ultramicroscope which was capable of visualizing particles much smaller than the light wavelength .Zsigmondy was also the first to use the term "nanometer" explicitly for characterizing particle size. In the 1920s, Irving Langmuir, winner of the 1932 Nobel Prize in Chemistry, and Katharine B. Blodgett introduced the concept of a monolayer, a layer of material one molecule thick. In the early 1950s, Derjaguin and Abrikosova conducted the first measurement of surface forces.

In 1974 the process of atomic layer deposition for depositing uniform thin films one atomic layer at a time was developed and patented by Tuomo Suntola and co-workers in Finland.

In another development, the synthesis and properties of semiconductor nanocrystals were studied. This led to a fast increasing number of semiconductor nanoparticles of quantum dots.

## Discovery of fullerenes

Harry Kroto (left) won the 1996 Nobel Prize in Chemistry along with Richard Smalley (pictured below) and Robert Curl for their 1985 discovery of buckminsterfullerene, while Sumio Iijima (right) won the inaugural 2008 Kavli Prize in Nanoscience for his 1991 discovery of carbon nanotubes.

Fullerenes were discovered in 1985 by Harry Kroto, Richard Smalley, and Robert Curl, who together won the 1996 Nobel Prize in Chemistry. Smalley's research in physical chemistry investigated formation of inorganic and semiconductor clusters using pulsed molecular beams and time of flight mass spectrometry. As a consequence of this expertise, Curl introduced him to Kroto in order to investigate a question about the constituents of astronomical dust. These are carbon rich grains expelled by old stars such as R Corona Borealis. The result of this collaboration was the discovery of $C_{60}$ and the fullerenes as the third allotropic form of carbon.

Subsequent discoveries included theendohedral fullerenes, and the larger family of fullerenes the following year.

The discovery of carbon nanotubes is largely attributed to Sumio Iijima of NEC in 1991, although carbon nanotubes have been produced and observed under a variety of conditions prior to 1991. Iijima's discovery of multi-walled carbon nanotubes in the insoluble material of arc-burned graphite rods in 1991 and Mintmire, Dunlap, and White's independent prediction that if single-walled carbon nanotubes could be made, then they would exhibit remarkable conducting properties helped create the initial buzz that is now associated with carbon nanotubes. Nanotube research accelerated greatly following the independent discoveries by Bethune at IBM and Iijima at NEC of*single-walled* carbon nanotubes and methods to specifically produce them by adding transition-metal catalysts to the carbon in an arc discharge.

In the early 1990s Huffman and Kraetschmer, of the University of Arizona, discovered how to synthesize and purify large quantities of fullerenes. This opened the door to their characterization and functionalization by hundreds of investigators in government and industrial laboratories. Shortly after, rubidium doped $C_{60}$ was found to be a mid temperature (Tc = 32 K) superconductor. At a meeting of the Materials Research Society in 1992, Dr. T. Ebbesen (NEC) described to a spellbound audience his discovery and characterization of carbon nanotubes. This event sent those in attendance and others downwind of his presentation into their laboratories to reproduce and push those discoveries forward. Using the same or similar tools as those used by Huffman and Kratschmer, hundreds of researchers further developed the field of nanotube-based nanotechnology.

## Government support

Mihail Roco of the National Science Foundation formally proposed theNational Nanotechnology Initiative to theWhite House, and was a key architect in its initial development.

## National Nanotechnology Initiative

The National Nanotechnology Initiative is a United States federal nanotechnology research and development program. “The NNI serves as the central point of communication, cooperation, and collaboration for all Federal agencies engaged in nanotechnology research, bringing together the expertise needed to advance this broad and complex field." Its goals are to advance a world-class nanotechnology research and development (R&D) program, foster the transfer of new technologies into products for commercial and public benefit, develop and sustain educational resources, a skilled workforce, and the supporting infrastructure and tools to advance nanotechnology, and support responsible development of nanotechnology. The initiative was spearheaded by Mihail Roco, who formally proposed the National Nanotechnology Initiative to the Office of Science and Technology Policy during the

Clinton administration in 1999, and was a key architect in its development. He is currently the Senior Advisor for Nanotechnology at the National Science Foundation, as well as the founding chair of theNational Science and Technology Council subcommittee on Nanoscale Science, Engineering and Technology.

President Bill Clinton advocated nanotechnology development. In a 21 January 2000 speech at the California Institute of Technology, Clinton said, "Some of our research goals may take twenty or more years to achieve, but that is precisely why there is an important role for the federal government." Feynman's stature and concept of atomically precise fabrication played a role in securing funding for nanotechnology research, as mentioned in President Clinton's speech:

My budget supports a major new National Nanotechnology Initiative, worth $500 million. Caltech is no stranger to the idea of nanotechnology the ability to manipulate matter at the atomic and molecular level. Over 40 years ago, Caltech's own Richard Feynman asked, "What would happen if we could arrange the atoms one by one the way we want them?"

President George W. Bush further increased funding for nanotechnology. On December 3, 2003 Bush signed into law the 21st Century Nanotechnology Research and Development Act, which authorizes expenditures for five of the participating agencies totaling US$3.63 billion over four years. The NNI budget supplement for Fiscal Year 2009 provides $1.5 billion to the NNI, reflecting steady growth in the nanotechnology investment.

## Growing public awareness and controversy

### "Why the future doesn't need us"

"Why the future doesn't need us" is an article written by Bill Joy, then Chief Scientist at Sun Microsystems, in the April 2000 issue of *Wired* magazine. In the article, he argues that "Our most powerful 21st-century technologies — robotics, genetic engineering, and nanotech — are threatening to make humans an endangered species." Joy argues that developing technologies provide a much greater danger to humanity than any technology before it has ever presented. In particular, he focuses on genetics, nanotechnology and robotics. He argues that 20th-century technologies of destruction, such as the nuclear bomb, were limited to large governments, due to the complexity and cost of such devices, as well as the difficulty in acquiring the required materials. He also voices concern about increasing computer power. His worry is that computers will eventually become more intelligent than we are, leading to such dystopian scenarios as robot rebellion. He notably quotes the Unabomber on this topic. After the publication of the article, Bill Joy suggested assessing technologies to gauge their implicit dangers, as well as having scientists refuse to work on technologies that have the potential to cause harm.

In the AAAS Science and Technology Policy Yearbook 2001 article titled *A Response to Bill Joy and the Doom-and-Gloom Technofuturists*, Bill Joy was criticized for having technological tunnel vision on his prediction, by failing to consider social factors.[42] In Ray Kurzweil's *The Singularity Is Near*, he questioned the regulation of potentially dangerous technology, asking "Should we tell the millions of people afflicted with cancer and other devastating conditions that we are canceling the development of all bioengineered treatments because there is a risk that these same technologies may someday be used for malevolent purposes?".

### ***Prey***

*Prey* is a 2002 novel by Michael Crichton which features an artificial swarm of nanorobots which develop intelligence and threaten their human inventors. The novel generated concern within the nanotechnology community that the novel could negatively affect public perception of nanotechnology by creating fear of a similar scenario in real life.

### **Drexler–Smalley debate**

Richard Smalley, a codiscoverer of the fullerenes, was involved in a public debate with Eric Drexler about the feasibility of molecular assemblers.

Richard Smalley, best known for co-discovering the soccer ball-shaped “buckyball” molecule and a leading advocate of nanotechnology and its many applications, was an outspoken critic of the idea of molecular assemblers, as advocated by Eric Drexler. In 2001 he introduced scientific objections to them attacking the notion of universal assemblers in a 2001 *Scientific American* article, leading to a rebuttal later that year from Drexler and colleagues, and eventually to an exchange of open letters in 2003.

Smalley criticized Drexler's work on nanotechnology as naive, arguing that chemistry is extremely complicated, reactions are hard to control, and that a universal assembler is science fiction. Smalley believed that such assemblers were not physically possible and introduced scientific objections to them. His two principal technical objections, which he had termed the “fat fingers problem" and the "sticky fingers problem”, argued against the feasibility of molecular assemblers being able to precisely select and place individual atoms. He also believed that Drexler’s speculations about apocalyptic dangers of molecular assemblers threaten the public support for development of nanotechnology.

Smalley first argued that "fat fingers" made MNT impossible. He later argued that nanomachines would have to resemble chemical enzymes more than Drexler's assemblers and could only work in water. He believed these would exclude the possibility of "molecular assemblers" that worked by precision picking and placing of individual atoms. Also, Smalley argued that nearly all of modern chemistry involves reactions that take place in a solvent (usually water), because the small molecules of a solvent contribute many things, such as lowering binding energies for transition states. Since nearly all known chemistry requires a solvent, Smalley felt that Drexler's proposal to use a high vacuum environment was not feasible.

Smalley also believed that Drexler's speculations about apocalyptic dangers of self-replicating machines that have been equated with "molecular assemblers" would threaten the public support for development of nanotechnology. To address the debate between Drexler and Smalley regarding molecular assemblers *Chemical & Engineering News* published a point-counterpoint consisting of an exchange of letters that addressed the issues.

Drexler and coworkers responded to these two issues in a 2001 publication. Drexler and colleagues noted that Drexler never proposed universal assemblers able to make absolutely anything, but instead proposed more limited assemblers able to make a very wide variety of things. They challenged the relevance of Smalley's arguments to the more specific proposals advanced in *Nanosystems*. Drexler maintained that both were straw man arguments, and in the case of enzymes, Prof. Klibanov wrote in 1994, "...using an enzyme in organic solvents eliminates several obstacles..." Drexler also addresses this in Nanosystems by showing mathematically that well designed catalysts can provide the effects of a solvent and can fundamentally be made even more efficient than a solvent/enzyme reaction could ever be. Drexler had difficulty in getting Smalley to respond, but in December 2003, *Chemical & Engineering News* carried a 4-part debate.

Ray Kurzweil spends four pages in his book 'The Singularity Is Near' to showing that Richard Smalley's arguments are not valid, and disputing them point by point. Kurzweil ends by stating that Drexler's visions are very practicable and even happening already.

## Royal Society report on the implications of nanotechnology

The Royal Society and Royal Academy of Engineering's 2004 report on the implications of nanoscience and nanotechnologies was inspired by Prince Charles' concerns about nanotechnology, including molecular manufacturing. However, the report spent almost no time on molecular manufacturing. In fact, the word "Drexler" appears only once in the body of the report (in passing), and "molecular manufacturing" or "molecular nanotechnology" not at all. The report covers various risks of nanoscale technologies, such as nanoparticle toxicology. It also provides a useful overview of several nanoscale fields. The report contains an annex (appendix) on grey goo, which cites a weaker variation of Richard Smalley's contested argument against molecular manufacturing. It concludes that there is no evidence that autonomous, self replicating nanomachines will be developed in the foreseeable future, and suggests that regulators should be more concerned with issues of nanoparticle toxicology.

### Initial Commercial applications

The early 2000s saw the beginnings of the use of nanotechnology in commercial products, although most applications are limited to the bulk use of passive nanomaterials. Examples include titanium dioxide and zinc oxide nanoparticles in sunscreen, cosmetics and some food products; silver nanoparticles in food packaging, clothing, disinfectants and household appliances such as Silver Nano;carbon nanotubes for stain-resistant textiles; and cerium oxide as a fuel catalyst. ]As of March 10, 2011, the Project on Emerging Nanotechnologies estimated that over 1300 manufacturer-identified nanotech products are publicly available, with new ones hitting the market at a pace of 3–4 per week.

The National Science Foundation funded researcher David Berube to study the field of nanotechnology. His findings are published in the monograph Nano-Hype: The Truth Behind the Nanotechnology Buzz. This study concludes that much of what is sold as “nanotechnology” is in fact a recasting of straightforward materials science, which is leading to a “nanotech industry built solely on selling nanotubes, nanowires, and the like” which will “end up with a few suppliers selling low margin products in huge volumes." Further applications which require actual manipulation or arrangement of nanoscale components await further research. Though technologies branded with the term 'nano' are sometimes little related to and fall far short of the most ambitious and transformative technological goals of the sort in molecular manufacturing proposals, the term still connotes such ideas. According to Berube, there may be a danger that a "nano bubble" will form, or is forming already, from the use of the term by scientists and entrepreneurs to garner funding, regardless of interest in the transformative possibilities of more ambitious and far-sighted work.

### Perspectives of nano chemistry

**cross the span** of my 40-plus-year career, I was fortunate to be involved in the birth and growth of a futuristic field of science that my colleagues and I came to call nanochemistry. The central tenet of nanochemistry is the synthesis of nanoscale materials from the bottom up, literally atom-by-atom. That’s in contrast to sculpting nanostructured materials with a top-down engineering-physics fabrication approach.

Today, nanoscale solids and materials filled with nanoscale voids enable a cornucopia of electronic, optical, magnetic, mechanical, and thermal applications. These advances have benefited from what I call the “nano advantage”—the unique properties exhibited by nanoscale materials that are not displayed by molecules or bulk materials of the same chemical composition.

Chemistry and nanotechnology are now forever united through nanochemistry. And despite the successes in advanced materials and biomedical technologies society has witnessed, it feels like we are only just getting started. What we have achieved so far with nanochemistry is a foundation for developing a new round of futuristic technologies that will allow us to tackle and wisely manage our interrelated energy, food, health, climate, and environmental needs to live in asustainable world.

## Extending Nanochemistry's Reach

In the midst of creating new materials in the lab, the University of Toronto's Geoffrey Ozin thought attaining the full potential of nanochemistry would not be complete without public engagement. Ozin's outreach efforts now include writing "MaterialsViews," a series of opinion pieces for the Wiley-VCH family of materials journals (www.materialsviews.com/category/opinion). The goal of the series, with 50 articles published to date, is to inform and inspire students, researchers, and the general public on "chemistry-related hot-button issues affecting everyone's common future." And in collaboration with artist Todd Siler, Ozin created ArtNano Innovations, a project to "inform the public of the visual beauty of the nanoworld" through multimedia artwork (www.artnanoinnovations.com).

My adventure in nanochemistry began in 1969 as a new assistant professor at the University of Toronto. Those early days were full of monumental scientific and technological breakthroughs that included*Sputnik* and Apollo 11, DNA, Teflon, the microchip, optical fibers, and lasers. I was inspired by the famous 1959 lecture "There's Plenty of Room at the Bottom" by California Institute of Technology physicist Richard P. Feynman and the idea of being able to carry out atom-by-atom self-assembly.

The big question, unanswered at the time, was how to use chemistry to prepare and stabilize nanoscale forms of well-known materials, with dimensions in the quantum regime of around 1 nm to 100 nm, and study their size-tunable behavior with an eye toward real-world applications.

Working initially under cryogenic conditions to slow reactions down, and using various in situ analytical techniques, I witnessed naked metal atoms forming nanoclusters. It occurred to me that because these nanomaterials were metastable compared with bulk materials they would have to be protected in some way. One approach was to perform the chemistry within the nanometer-sized voids of a solid material such as zeolites—a strategy coined host-guest chemistry.

Aspects of the work remained frustrating, however. For instance, there was a narrow focus on using zeolites in catalysis, gas separation, and ion exchange. I saw their potential in other areas, such as data storage, batteries and fuel cells, photocatalysis, chemical sensing, and drug delivery. Subsequent discoveries of metal-organic frameworks, covalent-organic frameworks, porous aromatic frameworks, hydrogen-bonded organic frameworks, and porous polymers—today's leading contenders for gas separation and storage technologies—have enriched the field of nanoporous materials and brought those applications to life.

Another frustration with zeolite hosts is that their 1-nm maximum pore size imposes limits on their imbibed guests, which restricted our ability to work in the 1-nm to 1,000-nm regime. The discovery of mesoporous silica in the early 1990s with pore sizes up to 100 nm gave us a little elbow room. Later on, larger pore sizes up to 1,000 nm became accessible in silica and polymer opals, leading to breakthroughs in developing photonic crystals of wide-ranging compositions that spawned applications in optical telecommunications and tunable photonic color devices.

The new ability to synthesize materials with structural features that traversed all nanometer length scales set the scene for a "panomaterials" revolution. It became possible to produce nanomaterials from organic and inorganic components over all scales, composed of assemblies of 3-D frameworks, 2-D layers, 1-D wires, and 0-D dots, perfect in size and shape down to the last atom. The potential was breathtaking.

[+]Enlarge

Geoffrey A. Ozin is Distinguished University Professor at the University of Toronto and is considered the "father of nanochemistry."

Credit: Courtesy of Geoffrey Ozin

There's now a rich opportunity to take the nanochemistry knowledge we have cultivated and apply it to today's pressing problems. One example is developing new materials that enable global energy technologies to capture $CO_2$ and convert it to fuels that will help replace fossil resources and ameliorate climate change.

Here, a prescient quote from a 1971 *Life* magazine interview with architect and inventor Richard Buckminster Fuller is worth recalling: "Pollution is nothing but resources we're not harvesting. We allow them to disperse because we've been ignorant of their value. But if we got onto a planning basis, the government could trap pollutants in the stacks and spillages and get back more money than this would cost out of the stockpiled chemistries they'd be collecting."

The nanochemistry needed to achieve that vision will require new adventurous cross-disciplinary torchbearers to seek out and discover innovative materials solutions. Learning how to exploit the "nano advantage" to enable advances with a high likelihood of widespread use by society is a monumental idea just as alive today as it was for me in 1969.

Beyond carbon capture and utilization and safer and more secure renewable energy, a few other "holy grails" come to mind as being ripe for nanochemistry solutions: next-generation information technology; improved health care in the developing world; safety from terrorism; water purification and desalination; pollution prevention and reduction; better nutrition and crop protection; and autonomous nanomachines for medical diagnosis, intracellular drug delivery, and surgery. Let's see what we can do.

# POSSIBLE QUESTIONS

## UNIT-I

### PART- A (Each carry one mark)

1. Who first used the term nanotechnology and when?
**(a) Richard Feynman, 1959** **(b)** Norio Taniguchi, 1974
(c) Eric Drexler, 1986 (d) Sumio Iijima, 1991
2. Who prepared and explained nanotubes for the first time?
**(a) SumioTijima** (b) Richard Smalley (c) Eric Drexler (d) Richard Feynmann
3. Nano particles of which atom are used to control collateral damage due to explosion?
(a)Copper (b) **Aluminium** **(c)** Carbon (d) Lead
4. The term "nano-technology" was first used by?
**(a)Norio Taniguchi** (b) Eric Drexler (c) Minsky (d) Richard feynman
5. Who first used the term nanotechnology and when?
**(a)Richard Feynman, 1959** (b) Norio Taniguchi, 1974
(c)Eric Drexler, 1986 (d) Sumio Iijima, 1991
6. Who coined the word Nanotechnology?
**(a)Eric Drexler** (b) Michael Faraday (c) Granqvist and Buhrman (d) Buhrman
7. The term "nano-technology" was first used by?
**(a)Norio Taniguchi** (b) Eric Drexler (c) Minsky (d) Richard feynman
8. A nanometer is a?
(a) Millionth of a meter (b) Trillionth of a meter
**(c) Billionth of a meter** (d)Millimeter
9. What is grey goo?
**(a) A hypothetical substance composed of out-of-control self-replicating nanobots that consumes all living matter on Earth**
(b) The feeder material used to grow grey nanoparticles in the laboratory
(c) Toxic byproduct resulting from the synthesis of carbon nanotubes
(d) Waste product from the production of nanoglue made from the membranes on the feet of the Madagascan Grey Gecko
10. Nanoscience can be studied with the help of?
**(a)Quantum mechanics** (b)Newtonian mechanics
(c) Macro-dynamics (d) Geophysics
11. The size of nanoparticles is between?
(a) 100 to 1000 nm (b) 0.1 to 10 nm **(c) 1 to 100 nm** (d) 0.01 to 1 nm
12. How much is 1 micron in meter?
(a)$10^{-5}$ meter (b) $10^{-4}$ meter **(c) $10^{-6}$ meter** (d) $10^{-8}$ meter
13. Carbon atoms make ____ type of bond with other carbon atoms.
**(a)covalent** (b)ionic (c)metallic (d)hydrogen
14. Fullerene or bucky ball is made up of ____ carbon atoms.
(a)100 (b)20 (c)75 **(d)60**
15.The thermal conductivity of a standard SWNT along its length is ____ watt/(m.K)

**(a)3500** (b)385 (c)35000 (d)35

16. "There is plenty of room at the bottom." This was stated by _____.
   (a) Eric Drexler **(b) Richard Feynmann**
   (c) Harold Croto (d) Richard Small

17. Nanoscience can be studied with the help of...
   **(a) quantum mechanics** (b) Newtonian mechanics
   (c) macro-dynamics (d) geophysics

18. Egyptians were using ____ to prepare make-up for eyes.
   (a)Nano Copper (b) Nano aluminium (c) Nano steel **(d) Nano lead**

19. Greeks and Romans had used nanoparticles in the manufacture of...
   (a)cosmetics for eyes (b) medicines
   (c) metal articles **(d) hair-dye**

20. The sword of Tipu Sultan was made of...
   (a)Nano lead (b) Nano aluminium **(c) Damascus steel** (d) Pure steel

## PART- B (Each carry six mark)

1. Discuss about the introduction of nanochemistry.
2.Briefly explain the perspectives of nano chemistry.
3.Explain the history of nanochemistry.
5. What is nanochemistry? Briefly explain the perspectives of nano chemistry.
6. Explain the aim and scope of nano Chemistry.
7. What is nano technology? Discuss about the introduction of nanochemistry.
8. Explain the aim and scope of nano Chemistry.
9. Briefly explain the origins of nanochemistry.

## PART- C (Each carry Ten mark)

1. What are nano Particles?What are the applications of nano particles and write some disadvantages of using nanoparticles on human?
2. What is nano chemistry?Briefly explain the perspectives of nano chemistry.
3. Define nanochemistry. Expalain the introduction of nanochemistry.

# KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

## DEPARTMENT OF CHEMISTRY

## M.Sc CHEMISTRY

| | | |
|---|---|---|
| Name of the Staff | : | Dr. M. MAKESWARI |
| Department | : | Chemistry |
| Subject | : | Nano Chemistry |
| Subject Code | : | 16CHP304 |
| Class | : | II M.Sc-Chemistry |
| Year and Semester | : | II / III |

## UNIT-III

### UNIT II –OBJECTIVE QUESTIONS FOR ONLINE EXAMINATION (Each carry one mark)

| S. No | Questions | Option 1 | Option 2 | Option 3 | Option 4 | Answer |
|---|---|---|---|---|---|---|
| 1 | The diameter of hydrogen atom is... | 1 | 10 | 0.1 | 0.01 | **0.1** |
| 2 | Carbon atoms make ____ type of bond with other carbon atoms. | covalent | ionic | metallic | hydrogen | **covalent** |
| 3 | Fullerene or bucky ball is made up of ____ carbon atoms. | 100 | 20 | 75 | 60 | **60** |
| 4 | The thermal conductivity of a standard SWNT along its length is ____ | 3500 | 385 | 35000 | 35 | **3500** |

| | | | | | | |
|---|---|---|---|---|---|---|
| | watt/(m.K) | | | | | |
| 5 | "There is plenty of room at the bottom." This was stated by _____. | Eric Drexler | Richard Feynmann | Harold Croto | Richard Small | **Richard Feynmann** |
| 6 | 1 m = _____ nm. | $10^{-9}$ | $10^{-8}$ | $10^{9}$ | $10^{8}$ | **$10^{9}$** |
| 7 | Who coined the word 'nanotechnology'? | Eric Drexler | Richard Feynmann | SumioTijima | Richard Smalley | **Eric Drexler** |
| 8 | According to the definition by CRN, nanotechnology is... | mechanical engineering | atomic engineering | Newtonian mechanics | micro-electronics | **atomic engineering** |
| 9 | Nanoscience can be studied with the help of... | quantum mechanics | Newtonian mechanics | macro-dynamics | geophysics | **quantum mechanics** |
| 10 | Egyptians were using ____ to prepare make-up for eyes. | Nano aluminium | Nano copper | Nano steel | Nano lead | **Nano lead** |
| 11 | Greeks and Romans had used nanoparticles in the manufacture of... | cosmetics for eyes | medicines | metal articles | hair-dye | **hair-dye** |
| 12 | The sword of Tipu Sultan was made of... | Nano lead | Nano aluminium | Damascus steel | Pure | **Damascus steel** |
| 13 | iro_____ contains nanoparticles prepared by using biologically processed metal ores. | Homeopathic medicines | Modern antibiotics | Ayurvedic 'Bhasmas' | Modern cosmetics | **Ayurvedic 'Bhasmas'** |
| 14 | Who was the first scientist to describe that substances having nanodimensions possess altogether different and unique properties? | Richard Feynmann | Eric Drexler | Archimedes | Michael Faraday | **Michael Faraday** |
| 15 | It is a general-purpose technology. | It is a general-purpose technology | It can be called Green technology. | Newtonian mechanics can describe it | It involves rearrangement of atoms. | **Newtonian mechanics can describe it** |
| 16 | The diameter of human hair is ____ nm. | **50,000** | 75,000 | 90000 | 100000 | **50,000** |
| 17 | The diameter of human hair is ____ m. | $5 \times 10^{-8}$ | $5 \times 10^{-7}$ | $5 \times 10^{-6}$ | $5 \times 10^{-5}$ | **$5 \times 10^{-5}$** |
| 18 | The cut-off limit of human eye is ____ nm. | 2000 | 5000 | 10000 | 50000 | **10000** |
| 19 | The size of E.Coli bacteria is ____ nm. | 2000 | 5000 | 50 | 90 | **2000** |
| 20 | The size of RBC is ____ nm. | 50 | 90 | 2000 | 5000 | **5000** |
| 21 | The thickness of a transistor is ____ nm. | 50 | 90 | 2000 | 5000 | **90** |
| 22 | Who first used the term nanotechnology and when? | **Richard Feynman, 1959** | Norio Taniguchi, 1974 | Eric Drexler, 1986 | SumioIijima, 1991 | **Richard Feynman, 1959** |

| | | | | | | |
|---|---|---|---|---|---|---|
| 23 | What is the size of a nanoshell? | 100 nm | 1 nm | 10 nm | 1000 nm | **100 nm** |
| 24 | The size of a virus is ____ nm. | 2 | 20 | 50 | 2000 | **50** |
| 25 | The diameter of a bucky ball is ____ nm. | 1000 | 100 | 10 | 1 | **1** |
| 26 | The width of a typical DNA molecule is ____ nm. | 1 | 2 | 5 | 10 | **2** |
| 27 | 1 micrometer (micron) = ______ m. | $10^{-9}$ | $10^{-8}$ | $10^{-7}$ | $10^{-6}$ | **$10^{-6}$** |
| 28 | 1 micrometer (micron) = ______ nm. | 1000 | 100 | 10 | 0.01 | **1000** |
| 29 | What does 'F' stand for in AFM? | Fine | Front | Force | Flux | **Force** |
| 30 | Which ratio decides the efficiency of nanosubstances? | Weight/volume | Surface area/volume | Volume/weight | Pressure/volume | **Surface area/volume** |
| 31 | The surface area to volume ratio of a sphere with radius 1 cm is R1 and that of a sphere with radius 5 cm is R2. Then R1 = ____ R2. | 3 | 1/3 | 5 | 1/5 | **5** |
| 32 | The surface area to volume ratio of a cube with side 1 unit is R1 and that of a cube with side 10 units is R2. Then R2 = ____ R1. | 1/10 | 10 | 1/100 | 100 | **1/10** |
| 33 | The two important properties of nanosubstances are... | pressure and friction | sticking and friction | sticking and temperature | temperature and friction | **sticking and friction** |
| 34 | With the help of _____, Robert F. Curl and others discovered fullerene | electron microscope | magnetic resonance | condensation technique | mass spectrograph | **mass spectrograph** |
| 35 | In the structure of fullerene each carbon atom forms covalent bonds with ____ other carbon atoms. | One | Two | Three | Four | **Three** |
| 36 | Who had invented the famous 'Geodesic' dome structure? | Eric Drexler | Buckminster Fuller | Richard Smalley | Faraday | **Buckminster Fuller** |
| 37 | The largest cluster of carbon atoms in Bucky balls known till today consists of ____ carbon atoms. | 60 | 75 | 180 | 540 | **540** |
| 38 | The smallest cluster of carbon atoms in Bucky balls known till today consists of ____ carbon atoms. | 75 | 60 | 20 | 15 | **20** |
| 39 | The tensile strength of an MWNT is ____ Pa. | 63 x $10^{6}$ | 63 x $10^{7}$ | 63 x $10^{8}$ | 63 x $10^{9}$ | **63 x $10^{9}$** |
| 40 | The compressive strength of a nanotube | is less than | is greater than | is equal to | may be greater than | **is less than** |

| | | | | | | |
|---|---|---|---|---|---|---|
| | _____ its tensile strength. | | | | | |
| 41 | The hardness of a standard SWNT is ____ Pa. | 63 x $10^6$ | 25 x $10^6$ | 25 x $10^9$ | 25 x $10^{-9}$ | **25 x $10^9$** |
| 42 | The bulk modulus of a standard SWNT is ____ that of diamond. | less than | greater than | equal to | less than or equal to | **greater than** |
| 43 | How much current can be passed through 1 $cm^2$ cross-section of a metal nanotube? | $10^{-9}$ A | $10^9$ A | 1000 A | 0.001 A | **109 A** |
| 44 | The electrical conductivity of a nanotube is ____ times that of copper. | 10 | 100 | 1000 | 1/100 | **1000** |
| 45 | An MWNT possesses electrical superconductivity up to temperature of... | 12 K | 12°C | 100 K | 100° | **12 K** |
| 46 | At room temperature, the thermal conductivity of a copper wire is ____ watt/(m.K). | 3500 | 350 | 385 | 38.5 | **385** |
| 47 | In radial direction, the thermal conductivity of a nanotube is ____ watt/(m.K). | 3500 | 385 | 350 | 0 | **0** |
| 48 | The thermal stability of a nanotube is seen up to ____ K in vacuum. | 10 | 1000 | 2200 | 3100 | **3100** |
| 49 | The thermal conductivity of an SWNT along length is ____ watt/(m.K). | 35 | 350 | 385 | 3500 | **3500** |
| 50 | The size of a quantum dot is ____ nm. | 5 | 10 | 50 | 100 | **5** |
| 51 | The capacity of a normal human eye to see the smallest object is ____ µm. | 10000 | 1000 | 100 | 10 | **10** |
| 52 | The wavelength of visible light is ____ nm. | 40-70 | 400-700 | 4000-7000 | 40000-70000 | **400-700** |
| 53 | 10 nm = _____ m | $10^{-8}$ | $10^{-7}$ | $10^{-9}$ | $10^{-10}$ | **$10^{-8}$** |
| 54 | The size of nanoparticles is between _____ nm. | 100 to 1000 | 0.1 to 10 | 1 to 100 | 0.01 to 1 | **1 to 100** |
| 55 | The diameter of hydrogen atom is... | 1 | 10 | 0.1 | 0.01 | **0.1** |
| 56 | Which of the following statement/s is are true? | Volume to surface area ratio is very large for nanomaterials. | The cut-off limit of human eye is $10^{-5}$ m. | Hardness of a SWNT is about 63 x 109 Pa. | Carbon nanotubes are cylindrical fullerenes. | **Carbon nanotubes are cylindrical fullerenes.** |

| | | | | | | |
|---|---|---|---|---|---|---|
| 57 | The suffix '-ene' in the name of fullerene shows the presence of _____ in the molecule. | one triple bond | one double bond | two single bonds | two triple bonds | **two single bonds** |
| 58 | Who prepared and explained nanotubes for the first time? | SumioTijima | Richard Smalley | Eric Drexler | Richard Feynmann | **SumioTijima** |
| 59 | Nano particles of which atom are used to control collateral damage due to explosion? | Copper | **Aluminium** | Carbon | Lead | **Aluminium** |
| 60 | Nanoparticles of which substance were found on the surface of the sword of Tipu Sultan? | Gold | Lead | Carbon | Silicon | **Carbon** |
| 61 | The thermal stability of a nanotube is seen up to ____ K in air. | 100 | 1000 | 2000 | 3100 | **1000** |
| 62 | The width of a carbon nanotube is ____ nm. | 1 | 1.3 | 2.5 | 1 | **1.3** |
| 63 | Richard Feynman is often credited with predicting the potential of nanotechnology. What was the title of his famous speech given on December 29, 1959? | There is a tiny room at the bottom | Things get nanoscopic at the bottom | Bottom? What bottom? | There is plenty of room at the bottom | **There is plenty of room at the bottom** |
| 64 | What is grey goo? | A hypothetical substance composed of out-of-control self-replicating nanobots that consumes all living matter on Earth | The feeder material used to grow grey nanoparticles in the laboratory | Toxic byproduct resulting from the synthesis of carbon nanotubes | Waste product from the production of nanoglue made from the membranes on the feet of the Madagascan Grey Gecko | **A hypothetical substance composed of out-of-control self-replicating nanobots that consumes all living matter on Earth** |
| 65 | The term "nano-technology" was first used by? | Norio Taniguchi | Eric Drexler | Minsky | Richard feynman | **Norio Taniguchi** |
| 66 | A nanometer is a? | Millionth of a meter | Trillionth of a meter | Billionth of a meter | Millimeter | **Billionth of a meter** |

# LECTURE NOTES
# UNIT II
# SYLLABUS

Synthesis and stabilization of nanoparticles, chemical reduction; reactions in micelles, emulsions, and dendrimers; photochemical and radiation chemical reduction; cryochemical synthesis: Physical methods, particles of various shapes and films.

## Nanoparticle synthesis

**Nanoparticle synthesis** refers to methods for creating **nanoparticles**. **Nanoparticles** can be derived from larger molecules, or synthesized by 'bottom-up' methods that, for example, nucleate and grow particles from fine molecular distributions in liquid or vapour phase. There are several methods for creating **nanoparticles**, including gas condensation, attrition, chemical precipitation, pyrolysis and hydrothermal **synthesis**

.

Generally, metal **nanoparticles** can be prepared and stabilized by chemical, physical and biological **methods**; the chemical approach, such as chemical reduction, electrochemical **techniques**, photochemical reduction and pyrolysis and physical**methods**, such as Arc-discharge and physical vapor condensation (pvc) is used.

Free **nanoparticles are formed** through either the breaking down of larger particles or by controlled assembly processes. Natural phenomena and many human industrial and domestic activities, such as cooking, manufacturing or road and air transport release **nanoparticles** into the atmosphere.

## Chemical methods

## Synthesis of silver nano particles using Chemical reduction method

Metallic nanoparticles can be synthesized through many methods ¨ The two most popular methods for synthesizing silver nanoparticles (Ag NP) via chemical reduction are:

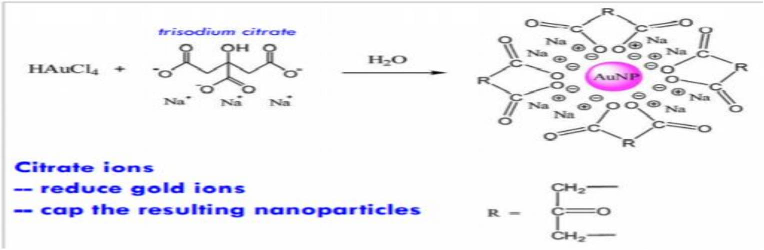
The most common approach for synthesis of silver NPs is chemical reduction by organic and inorganic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride ($NaBH_4$), elemental hydrogen, polyol process, Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol)-block copolymers are used for reduction of silver ions ($Ag^+$) in aqueous or non-aqueous solutions.

These reducing agents reduce $Ag^+$ and lead to the formation of metallic silver ($Ag^0$), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloidal silver particles. It is important to use protective agents to stabilize dispersive NPs during the course of metal nanoparticle preparation, and protect the NPs that can be absorbed on or bind onto nanoparticle surfaces, avoiding their agglomeration. The presence of surfactants comprising functionalities (*e.g.*, thiols, amines, acids, and alcohols) for interactions with particle surfaces can stabilize particle growth, and protect particles from sedimentation, agglomeration, or losing their surface properties.

## Stabilisation of silver nanoparticles

Polymeric compounds such as poly (vinyl alcohol), poly (vinylpyrrolidone), poly (ethylene glycol), poly (methacrylic acid), and polymethylmethacrylate have been reported to be the effective protective agents to stabilize NPs.

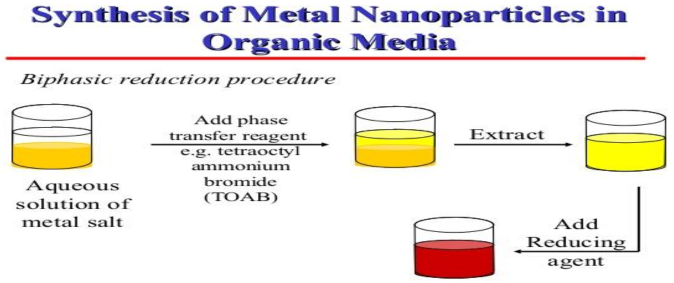
In one study, Oliveira and coworkers prepared dodecanethiol-capped silver NPs, according to Brust procedure based on a phase transfer of an $Au^{3+}$ complex from aqueous to organic phase in a two-phase liquid-liquid system, which was followed by a reduction with sodium borohydride in the presence of dodecanethiol as stabilizing agent, binding onto the NPs surfaces, avoiding their aggregation and making them soluble in certain solvents. They reported that small changes in synthetic factors lead to dramatic modifications in nanoparticle structure, average size, size distribution width, stability and self-assembly patterns.



## Synthesis of Ag Nano particles in various shapes

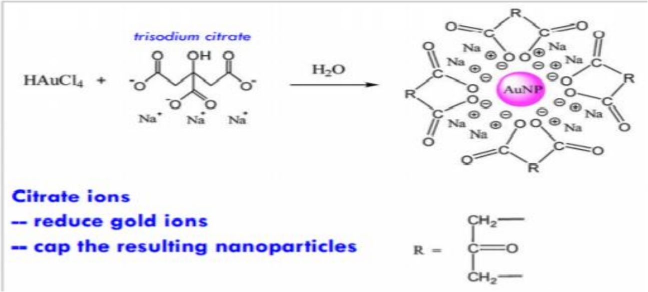
Kim and colleagues reported synthesis of spherical silver NPs with a controllable size and high monodispersity using the polyol process and a modified precursor injection technique. In the precursor injection method, the injection rate and reaction temperature were important factors for producing uniform-sized silver NPs with a reduced size.

Silver NPs with a size of 17 ± 2 nm were obtained at an injection rate of 2.5 ml/s and a reaction temperature of 100 °C. The injection of the precursor solution into a hot solution is an effective means to induce rapid nucleation in a short period of time, ensuring the fabrication of silver NPs with a smaller size and a narrower size distribution.



Zhang and coworkers used a hyper branched poly (methylene bisacrylamide aminoethyl piperazine) with terminal dimethylamine groups (HPAMAM-$N(CH_3)_2$) to produce colloids of silver. The amide moieties, piperazine rings, tertiary amine groups and the hyper-branched structure in HPAMAM-$N(CH_3)_2$ are important to its effective stabilizing and reducing abilities. Chen and colleagues have shown the formation of monodispersed silver NPs using simple oleylamine-liquid paraffin system. It was reported that the formation process of these NPs could be divided into three stages: growth, incubation and Oatwald ripening stages. The higher boiling point of 300 °C of paraffin affords a broader range of reaction temperature and makes it possible to effectively control the size of silver NPs by varying the heating temperature alone without changing the solvent. Moreover, the size of the colloidal silver NPs could be regulated not only by changing the heating temperature, or the ripening time, but also by adjusting the ratio of oleylamine to the silver precursor.

Silver NPs can be prepared at room temperature, by simple mixing of the corresponding metal ions with reduced polyoxometalates which serves as reducing and stabilizing agents. Polyoxometalates are soluble in water and have the capability of undergoing stepwise, multielectron redox reactions without disturbing their structure. It was demonstrated that silver NPs were produced by illuminating a deaerated solution of polyoxometalate/S/$Ag^+$. Furthermore, green chemistry-type one-step synthesis and stabilization of silver nanostructures with $Mo^V$–$Mo^{VI}$ mixed-valence polyoxometalates in water at room temperature has been reported .



## Microemulsion techniques

Uniform and size controllable silver NPs can be synthesized using microemulsion techniques. The NPs preparation in two-phase aqueous organic systems is based on the initial spatial separation of reactants (metal precursor and reducing agent) in two immiscible phases. The interface between the two liquids and the intensity of inter-phase transport between two phases, which is mediated by a quaternary alkyl-ammonium salt, affect the rate of interactions between metal precursors and reducing agents. Metal clusters formed at the interface are stabilized, due to their surface being coated with stabilizer molecules occurring in the non-polar aqueous medium, and transferred to the organic medium by the inter-phase transporter. One of the major disadvantages is the use of highly deleterious organic solvents.

Thus large amounts of surfactant and organic solvent must be separated and removed from the final product. For instance, Zhang and coworkers used dodecane as oily phase (a low deleterious and even nontoxic solvent), but there was no need to separate the prepared silver solution from the reaction mixture. On the other hand, colloidal NPs prepared in nonaqueous media for conductive inks are well-dispersed in a low vapor pressure organic solvent, to readily wet the surface of polymeric substrate without any aggregation. The advantages can also be found in the applications of metal NPs as catalysts to catalyze most organic reactions, which have been conducted in non-polar solvents. It is very important to transfer metal NPs to different physicochemical environments in practical applications.

## UV-initiated photoreduction

A simple and effective method, UV-initiated photoreduction, has been reported for synthesis of silver NPs in the presence of citrate, polyvinylpyrrolidone, poly (acrylic acid), and collagen. For instance, Huang and Yang produced silver NPs via photoreduction of silver nitrate in layered inorganic laponite clay suspensions which served as stabilizing agent for prevention of NPs aggregation. The properties of produced NPs were studied as a function of UV irradiation time. Bimodal size distribution and relatively large silver NPs were obtained when irradiated under UV for 3 h. Further irradiation disintegrated the silver NPs into smaller sizes with a single distribution mode until a relatively stable size and size distribution was obtained. Silver NPs (nanosphere, nanowire, and dendrite) have been prepared by UV irradiation photoreduction technique at room temperature using poly (vinylalcohol) (as protecting and stabilizing agent). Concentration of both poly (vinylalcohol) and silver nitrate played significant role in the growth of the nanorods and dendrites.

Sonoelectrochemistry technique utilizes the ultrasonic power primarily to manipulate the material mechanically. Pulsed sonoelectro-chemical synthetic method involves alternating sonic and electric pulses, and electrolyte composition plays a crucial role in shape formation. It was reported that silver nanospheres could be prepared by sono-electrochemical reduction using a complexing agent, nitrilotriacetate to avoid aggregation.

## Photoinduced reduction

Silver NPs can be synthesized by using a variety of photoinduced or photocatalytic reduction methods. Photochemical synthesis is a clean process which has high spatial resolution, convenience of use, and great versatility. Moreover, photochemical synthesis enables one to fabricate the NPs in various mediums including cells, emulsion, polymer films, surfactant micelles, glasses, etc. Nano-sized silver particles with an average size of 8 nm were prepared by photoinduced reduction using poly (styrene sulfonate)/poly (allylamine hydrochloride) polyelectrolyte capsules as microreactors. Moreover, it was demonstrated that photoinduced method could be used for converting silver nanospheres into triangular silver nanocrystals (nanoprisms) with desired edge lengths in 30-120 nm range. Particle growth process was controlled using dual-beam illumination of NPs. Citrate and poly (styrene sulfonate) were used as stabilizing agents. In another study, silver NPs were prepared through a very fast reduction of $Ag^+$ by α-aminoalkyl radicals generated from hydrogen abstraction toward an aliphatic amine by the excited triplet state of 2-substituted thioxanthone series ($TX\text{-}O\text{-}CH_2\text{-}COO^-$ and $TX\text{-}S\text{-}CH_2\text{-}COO^-$). Quantum yield of this prior reaction was tuned by substituent effect on thioxanthones, and led to a kinetic control of conversion of silver ion ($Ag^+$) to silver metal ($Ag^0$).

The direct photo-reduction process of $AgNO_3$ in the presence of sodium citrate (NaCit) was carried out with different light sources (UV, white, blue, cyan, green and orange) at room temperature. Sato-Berrú and coworkers have shown that this light-modification process results in a colloid with distinctive optical properties which can be related to the size and shape of the particles. Moreover, Ghosh and colleagues reported a simple and reproducible UV photo-activation method for the preparation of stable silver NPs in aqueous Triton X-100 (TX-100). The TX-100 molecules act as reducing agent and also as NPs stabilizer through template/capping action.

Furthermore, surfactant solution helps to carry out the process of NPs growth in the diffusion controlled way by decreasing the diffusion or mass transfer co-efficient of the system. It also helps to improve the NPs size distributions by increasing the surface tension at the solvent-NPs interface. Huang and coworkers reported the synthesis of silver NPs in an alkaline aqueous solution of $AgNO_3$/carboxymethylated chitosan (CMCTS) using UV light irradiation.

CMCTS, a water-soluble and biocompatible chitosan derivative, served simultaneously as a reducing agent for silver cation and a stabilizing agent for the silver NPs. The diameter range of produced silver NPs was 2–8 nm, and they can be dispersed stably in the alkaline CMCTS solution for more than 6 months.

## Electrochemical synthetic method

Electrochemical synthetic method can be used to synthesize silver NPs. It is possible to control particle size by adjusting electrolysis parameters and to improve homogeneity of silver NPs by changing the composition of electrolytic solutions. Polyphenylpyrrole coated silver nanospheroids (3-20 nm) were synthesized by electrochemical reduction at the liquid/liquid interface. This nano-compound was prepared by transferring the silver metal ion from aqueous phase to organic phase, where it reacted with pyrrole monomer. In another study, monodisperse silver nanospheroids (1-18 nm) were synthesized by electrochemical reduction inside or outside zeolite crystals according to silver exchange degree of compact zeolite film modified electrodes. Furthermore, spherical silver NPs (10-20 nm) with narrow size distributions were conveniently synthesized in aqueous solution by an electrochemical method.

Poly N-vinylpyrrolidone was chosen as the stabilizer for the silver clusters in this study. Poly N-vinylpyrrolidone protects NPs from agglomeration, significantly reduces silver deposition rate, and promotes silver nucleation and silver particle formation rate. Application of rotating platinum cathode effectively solves the technological difficulty of rapidly transferring metallic NPs from cathode vicinity to bulk solution, avoiding the occurrence of flocculates in vicinity of cathode, and ensures monodispersity of particles. Addition of sodium dodecyl benzene sulfonate to the electrolyte improved particle size and particle size distribution of silver NPs.

## Synthesis of silver NPs

### Physical methods

Evaporation-condensation and laser ablation are the most important physical approaches. The absence of solvent contamination in the prepared thin films and the uniformity of NPs distribution are the advantages of physical synthesis methods in comparison with chemical processes. Physical synthesis of silver NPs using a tube furnace at atmospheric pressure has some disadvantages, for example, tube furnace occupies a large space, consumes a great amount of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability. Moreover, a typical tube furnace requires power consumption of more than several kilowatts and a preheating time of several tens of minutes to reach a stable operating temperature. It was demonstrated that silver NPs could be synthesized via a small ceramic heater with a local heating area. The small ceramic heater was used to evaporate source materials. The evaporated vapor can cool at a suitable rapid rate, because the temperature gradient in the vicinity of the heater surface is very steep in comparison with that of a tube furnace.

This makes possible the formation of small NPs in high concentration. The particle generation is very stable, because the temperature of the heater surface does not fluctuate with time. This physical method can be useful as a nanoparticle generator for long-term experiments for inhalation toxicity studies, and as a calibration device for nanoparticle measurement equipment. The results showed that the geometric mean diameter, the geometric standard deviation and the total number concentration of NPs increase with heater surface temperature. Spherical NPs without agglomeration were observed, even at high concentration with high heater surface temperature. The geometric mean diameter and the geometric standard deviation of silver NPs were in the range of 6.2-21.5 nm and 1.23-1.88 nm, respectively.

Silver NPs could be synthesized by laser ablation of metallic bulk materials in solution. The ablation efficiency and the characteristics of produced nano-silver particles depend upon many parameters, including the wavelength of the laser impinging the metallic target, the duration of the laser pulses (in the femto-, pico- and nanosecond regime), the laser fluence, the ablation time duration and the effective liquid medium, with or without the presence of surfactants.

One important advantage of laser ablation technique compared to other methods for production of metal colloids is the absence of chemical reagents in solutions. Therefore, pure and uncontaminated metal colloids for further applications can be prepared by this technique. Silver nanospheroids (20-50 nm) were prepared by laser ablation in water with femtosecond laser pulses at 800 nm. The formation efficiency and the size of colloidal particles were compared with those of colloidal particles prepared by nanosecond laser pulses. As a result, the formation efficiency for femtosecond pulses was significantly lower than that for nanosecond pulses. The size of colloids prepared by femtosecond pulses were less dispersed than that of colloids prepared by nanosecond pulses. Furthermore, it was found that the ablation efficiency for femtosecond ablation in water was lower than that in air, while in the case of nanosecond pulses, the ablation efficiency was similar in both water and air.

Tien and coworkers used the arc discharge method to fabricate silver NPs suspension in deionized water with no added surfactants. In this synthesis, silver wires (Gredmann, 99.99%, 1 mm in diameter) were submerged in deionized water and used as electrodes. With a silver rod consumption rate of 100 mg/min, yielding metallic silver NPs of 10 nm in size, and ionic silver obtained at concentrations of approximately 11 ppm and 19 ppm, respectively. Siegel and colleagues demonstrated the synthesis of silver NPs by direct metal sputtering into the liquid medium. The method, combining physical deposition of metal into propane-1,2,3-triol (glycerol), provides an interesting alternative to time-consuming, wet-based chemical synthesis techniques. Silver NPs possess round shape with average diameter of about 3.5 nm with standard deviation 2.4 nm. It was observed that the NPs size distribution and uniform particle dispersion remains unchanged for diluted aqueous solutions up to glycerol-to-water ratio 1:20.

## Irradiation methods

Silver NPs can be synthesized by using a variety of irradiation methods. Laser irradiation of an aqueous solution of silver salt and surfactant can produce silver NPs with a well defined shape and size distribution. Furthermore, laser was used in a photo-sensitization synthetic method of making silver NPs using benzophenone. At short irradiation times, low laser powers produced silver NPs of about 20 nm, while an increased irradiation power produced NPs of about 5 nm. Laser and mercury lamp can be used as light sources for production of silver NPs. In visible light irradiation studies, photo-sensitized growth of silver NPs using thiophene (sensitizing dye) and silver nanoparticle formation by illumination of $Ag(NH_3)^+$ in ethanol has been done.

**Microwave-assisted synthesis**

Microwave-assisted synthesis is a promising method for synthesis of silver NPs. Microwave heating is better than a conventional oil bath when it comes to consistently yielding nanostructures with smaller sizes, narrower size distributions, and a higher degree of crystallization. Microwave heating has shorter reaction times, reduced energy consumption, and better product yields which prevents the agglomeration of the particles formed. Moreover, other than the elimination of the oil bath, microwave-assisted synthesis, in conjunction with benign reaction media, can also drastically reduce chemical wastes and reaction times in several organic syntheses and chemical transformations.

It was reported that silver NPs could be synthesized by microwave-assisted synthesis method employing carboxymethyl cellulose sodium as reducing and stabilizing agent. The size was depended on concentration of sodium carboxymethyl cellulose and silver nitrate. The produced NPs were uniform and stable, and were stable at room temperature for 2 months without any visible changes. Production of silver NPs in the presence of Pt seeds, polyvinyl pyrrolidine and ethylene glycol was also reported.

Furthermore, starch has been employed as a template and reducing agent for synthesis of silver NPs with an average size of 12 nm, using microwave-assisted synthetic method. Starch functions as a template, preventing the aggregation of produced silver NPs. Microwaves in combination with polyol process were applied for synthesis of silver nanospheroids using ethylene glycol and poly N-vinylpyrrolidone as reducing and stabilizing agents, respectively. In a typical polyol process inorganic salt is reduced by the polyol (*e.g.*, ethylene glycol which serves as both solvent and reducing agent) at a high temperature. Yin and coworkers reported that large-scale and size-controlled silver NPs could be rapidly synthesized under microwave irradiation from an aqueous solution of silver nitrate and trisodium citrate in the presence of formaldehyde as a reducing agent. Size and size distribution of produced silver NPs are strongly dependent on the states of silver cations in the initial reaction solution. Silver NPs with different shapes can be synthesized by microwave irradiation of a silver nitrate-ethylene-glycol-$H_2[PtCl_6]$-poly(vinylpyrrolidone) solution within 3 min. Moreover, the use of microwave irradiation to produce monodispersed silver NPs using basic amino acids (as reducing agents) and soluble starch (protecting agent) has been reported. Radiolysis of silver ions in ethylene glycol, in order to synthesize silver NPs, was also reported. Moreover, silver NPs supported on silica aero-gel were produced using gamma radiolysis. The produced silver clusters were stable in 2-9 pH range and started agglomeration at pH>9. Oligochitosan as a stabilizer can be used in preparation of silver NPs by gamma radiation. It was reported that stable silver NPs (5-15 nm) were synthesized in a 1.8-9.0 pH range by this method. Silver NPs (4-5 nm) were also synthesized by $\gamma$-ray irradiation of acetic water solutions containing silver nitrate and chitosan.

Silver nanospheroids (1-4 nm) have been produced by $\gamma$-ray irradiation of silver solution in optically transparent inorganic mesoporous silica. Reduction of silver ions within the matrix is brought about by hydrated electrons and hydroalkyl radicals generated during radiolysis of 2-propanol solution. The produced NPs within the silica matrix were stable in the presence of oxygen for at least several months. Moreover, silver NPs have been produced by irradiating a solution, prepared by mixing silver nitrate and poly-vinyl-alcohol, with 6-MeV electrons. Pulse radiolysis technique has been applied to study reactions of inorganic and organic species in silver nanoparticle synthesis, to understand the factors controlling the shape and size of the NPs synthesized by a common reduction method using citrate ions (as reducing and stabilizing agents), and to demonstrate the role of phenol derivatives in formation of silver NPs by the reduction of silver ions with dihydroxy benzene. Dihydroxy benzene could be used to reduce silver ions to synthesize stable silver NPs (with an average size of 30 nm) in air-saturated aqueous solutions.

Silver, gold, platinum, and gold-palladium nanostructures have been prepared using microwave-assisted synthetic approach. Morphologies and sizes of NPs can be controlled by altering some experimental parameters such as the concentration of metallic precursors, surfactant polymers, solvents, and temperature. Moreover, monodisperse silver NPs can be synthesized in large quantities using microwave-assisted chemistry method in an aqueous system. In this method, amino acids act as reducing agents and soluble starch acts as a protecting agent.

Not only silver, but silver doped lanthanum chromites can also be synthesized with microwave energy. Microwave energy and thermal reduction can be coupled to synthesize silver NPs that can be deposited on oxidized carbon paper electrodes. The silver NPs that are synthesized through this method maintain a uniform size between particles and are well-dispersed over the carbon paper substrate. The microwave-assisted synthesis of silver NPs is made possible by depositing the silver catalysts on carbon paper electrodes. This method can potentially be used in alkaline fuel cells because the synthesis occurs quickly, there is high activity, and the process is very simple.

Nanosized calcium deficient hydroxy-apatites can be used to generate nanosized calcium deficient hydroxyapatite with a silver substitution in three different concentrations by microwave-assisted synthesis. This study showed that controlling the parameters of the microwave process could influence the size of the crystals produced. It was shown that the microwave power had more of an impact on the size of the particles than the length of time of the treatment. The ensuing powder product could be used in the field of medicine and biomedical engineering to make grafts and coating metal implants in addition to work against bacterial infections without the use of antibiotics. This method can reduce medicinal costs and time of hospitalization.

Polymer based silver composites were produced using microwave energy on the basis of interfacial polymerization. A water/chloroform interface was used under microwave irradiation with no oxidizing agent. The produced silver NPs (about 20 nm in size) were spherical and well-dispersed. Silver nitrate provided silver ions for the thermal polymerization of pyrrole. The ions were converted to silver/polypyyrole nano-composites. Transmission electron microscopy (TEM) images proved that the particles were about 5−10 nm in size. The silver/polypyyrole had a thick film, which could sense ammonia, hydrogen sulfide, and carbon dioxide at 100, 250, and 350°C, respectively.

Microwave radiation and ethylene glycol can be used to synthesize silver powders from silver nitrate at temperatures of 100-200°C. It was reported that when polyvinyl pyrrolidone was used in the mixture of silver nitrate, the NPs ranged from 62 to 78 nm in diameter. Moreover, Fe-Ag bimetallic NPs could be synthesized by using microwave heating and an oil-soluble silver salt. The produced silver NPs were characterized through freeze-etching replication TEM which revealed the nanoparticle diameter and distribution. The produced silver NPs (30 nm) were spherical in shape.

Hydrolysis of alkoxysilanes along with the silver salt, in the presence of microwave irradiation, can produce silver/$SiO_2$ composite sols, which displayed antimicrobial properties. Meng and coworkers discussed the utilization of various water-based synthesis routes toward the shape-controlled synthesis of silver NPs and microstructures. Several one-pot methods employing commercial microwave ovens, inexpensive/low power ultrasound cleaners, or two-electrode electro-chemistry were described. Synthesis of silver nanostructures with various shapes in solution and their doping on unmodified silica and on/inside carbon spheres were investigated.

Microwave-assisted synthesis was used to prepare different kinds of nanosilver colloids. Silver nitrate was mixed with sodium citrate and then split into five groups. Each group was heated for varying durations of time at different temperatures. It was determined that the nanosilver colloids had a negatively charged surface when heated for a long period of time and a positively charged surface when heated for a short period of time. Moreover, silica-alumina can be used to synthesize silver NPs with precursors like $Ag_2O$ or $AgNO_3$. The particles were as small as 3 nm in diameter or as big as 50 nm. They were not oxidized, and the particles were well spread out. In another study, nanosilver/polyvinylpyrrolidone composite materials were synthesized using the microwave approach. The produced NPs ranged from 15-25 nm and were evenly spread out in the polyvinylpyrrolidone matrix.

Polymers and polysaccharides

Silver NPs were prepared using water as an environmentally friendly solvent and polysaccharides as capping/reducing agents. For instance, synthesis of starch-silver NPs was carried out with starch (capping agent) and β-D-glucose (reducing agent) in a gently heated system.

The binding interactions between starch and produced silver NPs were weak and could be reversible at higher temperatures, allowing separation of the synthesized NPs. In dual polysaccharide function, silver NPs were synthesized by reduction of silver ions inside of nanoscopic starch templates. The extensive network of hydrogen bands in templates provided surface passivation or protection against nanoparticle aggregation. Green synthesis of silver NPs using negatively charged heparin (reducing/stabilizing agent and nucleation controller) was also reported by heating a solution of silver nitrate and heparin to 70 °C for about 8 h. TEM micrographs demonstrated an increase in particle size of silver NPs with increased concentrations of silver nitrate (substrate) and heparin. Moreover, changes in heparin concentration varied the morphology and size of silver NPs. The synthesized silver NPs were highly stable, and showed no signs of aggregation after two months. In another study, stable silver NPs (10-34 nm) were synthesized by autoclaving a solution of silver nitrate (substrate) and starch (capping/reducing agent) at 15 psi and 121 °C for 5 min. These NPs were stable in solution for three months at about 25 °C. Smaller silver NPs ($\leq$ 10 nm) were synthesized by mixing two solutions of silver nitrate containing starch (capping agent), and NaOH solutions containing glucose (reducing agent) in a spinning disk reactor with a reaction time of less than 10 min.

## Bio-based methods

A number of reports prevailed in the literatures indicate that synthesis of nanoparticles by chemical approaches are eco-unfriendly and expensive. Thus, there is a growing need to develop environmentally and economically friendly processes, which do not use toxic chemicals in the synthesis protocols. This has conducted researchers to look at the organisms. The potential of organisms in nanoparticle synthesis ranges from simple prokaryotic bacterial cells to eukaryotic fungi and plants. Some examples of nanoparticle production include using bacteria for gold, silver, cadmium, zinc, magnetite, and iron NPs; yeasts for silver, lead and cadmium NPs; fungi for gold, silver and cadmium NPs; algae for silver and gold NPs; plants for silver, gold, palladium, zinc oxide, platinum, and magnetite NPs.

Bio-based protocols could be used for synthesis of highly stable and well-characterized NPs when critical aspects, such as types of organisms, inheritable and genetical properties of organisms, optimal conditions for cell growth and enzyme activity, optimal reaction conditions, and selection of the biocatalyst state have been considered. Sizes and morphologies of the NPs can be controlled by altering some critical conditions, including substrate concentration, pH, light, temperature, buffer strength, electron donor (*e.g.*, glucose or fructose), biomass and substrate concentration, mixing speed, and exposure time. In the following section, we discussed the synthesis of NPs using microorganisms and biological systems.

## Stabilization of nano particles

Stabilization of metal nanoparticles Dealing with phenomena associated with surfaces, it is useful to specify the term “clean surface”. Atomically clean metal surfaces can be made and maintained only under ultra high vacuum, but do not exist in a chemical flask. As soon as the surface gets into contact with matter, it adsorbs it (as this process generally results in a decrease of the total energy of the interface), even when this material is an inert gas or an alkane. The adsorption mode (physi- or chemisorption) determines how strong the interaction is. Generally, we call adsorption to be Gads is higher than ~ 30-40 kJ/mol. This implies that theΔstrong, when the adsorption energy probability that the sorbate desorbs from the surface at room temperature is very small (RT = a, the time passed between adsorption of a sorbateτ2.48 kJ/mol at 298 K). The residence time molecule and subsequent desorption from the surface, is an exponential function 0τa = τ .e 0 isτGads and the reverse of the temperature T, where ΔGads/RT of the adsorption energy Δ the characteristic time of surface atom vibrations (typically 10-12 1/s). The residence time quickly decreases with increasing temperature. At a given temperature, the residence time can be decreased, when the system (sorbate on surface) is exposed to an external influence, such as an external electric field, e.g., induced by the presence of polar solvent molecules (vide supra). In further, we call a surface to be clean, when no molecules are strongly adsorbed, while it may be covered with weakly interacting molecules (molecules of dissolved gas, alkanes, etc.).

Nanoparticles have a particular tendency to lower their very high surface energy, which is the origin of their thermodynamic instability. Bare nanoparticles tend to stabilise themselves either by sorption of molecules from the surroundings or by lowering the surface area www.intechopen.com Concepts for the Stabilization of Metal Nanoparticles in Ionic Liquids 237 through coagulation and agglomeration. In order to avoid the later, nanoparticles have to be (kinetically stabilized. The three conceptions of electrostatic, steric, and their combination electrosteric repulsive forces are generally discussed in literature and are summarized below. The concept of stabilising nanoparticles in viscous media, where the diffusion constants are low, will be introduced new.

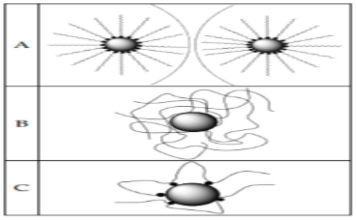
## Electrostatic stabilization

The origin of electrostatic stabilization is the repulsive electrostatic force, which nanoparticles experience, when they are surrounded by a double layer of electric charges. The Derjaguin, Landau, Verwey and Overbeek (DLVO) theory considers initially charged colloidal particles whereby the electric charges are uniformly distributed over their surface. The total energy potential VT of the interaction between two particles is then described as the sum of attractive (van der Waals) contributions and repulsive forces (due to a double layer of counter ions). The height of the overall potential barrier VT determines, whether the particles are stable (the kinetic energy Ek of particle motion is less than VT) or not (Ek > VT). The average kinetic energy is defined through the quadratic mean velocity or temperature of the system according to formula (1).

$$E_k = \frac{m < V^2 >}{2} = \frac{3}{2}kT$$

**Steric stabilization**

Another stabilization mechanism is based on the steric repulsion between molecules or ions adsorbed on neighbouring particles. Size and chemical nature of these molecules determine the degree of stabilization. Due to geometric constraints around nanoparticles, large, bulky molecules provide a particularly effective stabilization and an elongated or conical geometry is advantageous to keep the approaching nanoparticles apart (Table 3 A).



Schematic illustration of steric stabilization: A – Elongated or conical molecules adsorbed via anchoring centres (small black dot) hinder nanoparticles from close contact. B – Long polymer threads encapsulate a nanoparticle. C – Chelate effect, when the stabilizer is adsorbed via more than one anchoring centre (small black dots).

Applications of Ionic Liquids in Science and Technology When the length of the stabilizer is significantly longer than the characteristic size of the nanoparticles, a sphere can be formed encapsulating the nanoparticle. Because of that, high molecular weight polymers are often employed as stabilizers for nanoparticles. Another important requirement is that the stabilizer has to be adsorbed strongly enough on the surface of the nanoparticles to provide long residence time and to prevent its spontaneous desorption. When a stabilizer provides more than one adsorption centre, the chelating effect can increase the probability that the stabilizer remains adsorbed. Frequently, chemisorption is the driving force for strong binding between adsorbate and metal surface. Metals with more valence orbitals than valence electrons have an “electrondeficient” surface. Thus, molecules readily “donating” electron density (i.e. with chemical groups associated with free electron lone pair, such as divalent sulphur, trivalent phosphorus and trivalent nitrogen moieties or molecules with π-electrons, e.g., aromatic systems) often adsorb very strongly on metal surfaces (although the opposite examples are also known.

## POSSIBLE QUESTIONS

## UNIT-II

### PART- A (Each carry one mark)

1. Which of the following particle sizes are considered as nanoparticles?
(a) Less than 100 μm diameter (b) 1 to 100 μm
**(c) 1 to 100 nm** **(**d) <200nm

2. The size of the nano particles was determined by
**(a) X-Ray method** (b) AFM (c)UV (d)IR

3. Nano thermodynamics deals with systems of finite particles, or so called
**(a)Nano composites** (b) Nanowires (c)nanophases (d) Nanorods

4. Density of the nanoparticles are measured byusing
(a) SEM (b) TEM **(c) Pycnometer** (d) XRD

5. Nano thermodynamics deals with systems of finite particles, or so called
(a)Nano composites (b) Nanowires (c) nanophases (d) Nanorods

6. What is the diameter of the hydrogen atom?
(a) 1 nm (b) 0.001 nm **(c) 0.1 nm** (d) 0.01 nm

7. Pycnometer is used to measure the ------ of the nanoparticles
(a) Enthalphy (b) Entropy **(c) Density** (d) Diameter

8. TEM refers to a photomicrograph taken by a
(a) Scanning tunneling microscope (b) Scanning electron microscope
(c) Atomic force microscope **(d) Transmission electron microscopy**

9. Which one of the following is a typical example of ‘top down’ method of synthesis of nanomaterials?
**(a)Mechanical attrition** (b) Physical attrition
(c)Nano attrition (d) Chemical attrition

10. Which milling is typically achieved using high energy shaker, planetary ball and tumbler mills?
(a)Physical **(b)Mechanical** (c) Electrical (d)Thermal

11. Nanoparticles are produced by the shear action during?
(a) Powdering (b)Shaking **(c)Grinding** (d)Mixing

12. Nanotechnology, in other words, is
(a)Carbon engineering **(b)Atomic engineering**
(c)Small technology (d)Microphysics

13. Iro_____ contains nanoparticles prepared by using biologically processed metal ores.
(a)Homeopathic medicines (b) Modern antibiotics
**(c)Ayurvedic 'Bhasmas'** (d) Modern cosmetics

14. Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for which structure?
(a)Aromatic (b) Platy (c) Linear **(d) Photonic band gap**

15. Colloidal suspension is known as?
(a) Gel (b) Gel and sol **(c) Sol** (d) Electrical

16. In sol-gel process the starting material is processed to form a dispersible oxide and forms a sol in contact with ?
(a)Water (b) Dilute acid **(c) Water or dilute acid** (d) Acid or alkali

## PART- B (Each Carry six mark)

1. How will you synthesis the nanoparticles using chemical reduction and photochemical reduction method.
2.What are nano particles? Discuss the physical methods for the synthesis of nanoparticles.

3.How will you synthesis the nanoparticles using variusreduction methods.
4.Discuss the physical methods for the synthesis of nanoparticles.
5.Write notes on the synthesis of nanoparticles of various shapes and films.
6.Discuss the physical methods for the synthesis of nanoparticles.
7.Write notes on (i)Micelles (ii)Emulsions (iii)Dentrimers
8.Explain the synthesis of nanoparticles using chemical and radiation chemical reduction methods.

## PART- C (Each carry Ten mark)

1. What are nano Particles?What are the applications of nano particles and write some disadvantages of using nanoparticles on human?
2.What are nano particles? Discuss the physical methods for the synthesis of nanoparticles.
3. Explain the impact of nanoparticles on human and environment.

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**(Deemed University Established Under Section 3 of UGC Act 1956)**

**COIMBATORE-21**

## DEPARTMENT OF CHEMISTRY

## M.Sc CHEMISTRY

Name of the Staff : **Dr. M. MAKESWARI**

Department : **Chemistry**

Subject : **Nano Chemistry**

Subject Code : **16CHP304**

Class : **II M.Sc-Chemistry**

Year and Semester : **II / III**

## UNIT II

## OBJECTIVE QUESTIONS FOR ONLINE EXAMINATION (Each carry one mark)

| **S. No** | **Questions** | **Option 1** | **Option 2** | **Option 3** | **Option 4** | **Answer** |
|---|---|---|---|---|---|---|
| **1** | Which One of the following is first scientific report of synthesized colloidal gold particles. | Granqvist | Buhrman | Michael Faraday | Flemming | Michael Faraday |
| **2** | Popular inert- gas evaporation technique was published by ? | Granqvist | Buhrman | Granqvist and Buhrman | Michael Faraday | Granqvist and Buhrman |

| | | | | | | |
|---|---|---|---|---|---|---|
| **3** | Nanophase silicon, which differs from normal silicon in which properties? | Electronic | Physical | Mechanical | Physical and electronic | physical and electronic |
| **4** | The beautiful tone of the which colour is obtained only when both these nanoparticles and the superlattice are present | Red | Blue | Yellow | Orange | Blue |
| **5** | Which one of the following is a typical example of ‘top down’ method of synthesis of nanomaterials? | Mechanical attrition | Physical attrition | Nano attrition | Chemical attrition | Mechanical attrition |
| **6** | Which milling is typically achieved using high energy shaker, planetary ball and tumbler mills? | Physical | Mechanical | Electrical | Thermal | Mechanical |
| **7** | Nanoparticles are produced by the shear action during ? | Powdering | Shaking | Grinding | Mixing | Grinding |
| **8** | Nanotechnology, in other words, is | Carbon engineering | Atomic engineering | Small technology | Microphysics | Atomic engineering |
| **9** | If the mechanical milling imparts sufficient energy to the constituent powders which is formed? | Heterogeneous alloy | Homogeneous alloy | Low density alloy | High density alloy | Homogeneous alloy |
| **10** | Based on the energy of the milling process and which properties of the constituents the alloy can be rendered amorphous by this processing? | Electrical | Chemical | Thermodynamic | Mechanical | Thermodynamic |
| **11** | Where single crystals are etched in an aqueous solution for producing nanomaterials it is? | Bottom up method | Up down method | Down method | Top down method | Top down method |
| **12** | Which one of the following is consisting of sol-gel method, precipitation. | Bottom up method | Up down method | Down method | Top down method | Bottom up method |
| **13** | Where materials containing the desired precursors are mixed in a controlled fashion to form which solution? | Acid | Base | Colloidal | Water | Colloidal |
| **14** | In sol-gel process the starting material is processed to form a dispersible oxide and forms a sol in contact with ? | Water | Dilute acid | Water or dilute acid | Acid or alkali | Water or dilute acid |
| **15** | Calcination of the gel produces ? | Calcium | Carbon | Sulphur-di-oxide | Oxide | Oxide |

| | | | | | | |
|---|---|---|---|---|---|---|
| **16** | In sol-gel process removal of the liquid from the sol yields the gel, and the sol/gel transition controls the ? | Process | Particle size and shape | Partical size | Partical shape | Particle size and shape |
| **17** | Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as ? | M(OR)z | MOH | $SiO_2$ | $Si(OEt)_4$ | $Si(OEt)_4$ |
| **18** | MOR + $H_2O$ → MOH + ROH it is? | Hydrolysis | Condensation | Deposition | Decomposition | Hydrolysis |
| **19** | Gelation resulting from the formation of an oxide- or alcohol- bridged network by which reaction? | Polycondensation | Substitution | Addition | Decomposition | Polycondensation |
| **20** | The aging process of gels can exceed about? | 6 days | 5 days | 7 days | 8 days | 7 days |
| **21** | Ostwald ripening is also referred to as ? | Polycondensation | Coarsening | Sol-gel | Decomposition | Coarsening |
| **22** | Drying of gel is a complicated process due to fundamental changes in the structure of? | Sol | Product size | Gel | Product shape | Gel |
| **23** | Monolith is termed as? | Xerogel | Gel | Sol | Syneresis | Xerogel |
| **24** | If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an? | Xerogel | Gel | Sol | Aerogel | Aerogel |
| **25** | Dehydration, during which surface-bound M-OH groups are removed, there by stabilizing the gel against? | Decomposition | Rehydration | Dehydration | Condensation | Rehydration |
| **26** | In this process a laser beam is used as the primary excitation source of ablation for generating clusters directly from a solid sample in a wide variety of applications? | Microwave Plasma Processing | Sputtered Plasma Processing | CVD processing | Laser ablation | Laser ablation |
| **27** | Colloidal suspension is known as? | Gel | Gel and sol | Sol | Electrical | Sol |
| **28** | In heterogeneous CVD, the solid is formed on the substrate surface, which catalyses the reaction and a dense film is formed? | Dense film | Light films | Particulate films | Thin films | Dense film |
| **29** | Which one is occurs only when the vapour is supersaturated and in these | Evaporation | Vapourisation | Dense film | Condensation | Evaporation |

| | | | | | | |
|---|---|---|---|---|---|---|
| | processes homogeneous nucleation in the gas phase is utilised to form particles? | | | | | |
| **30** | Which one of the following is vaporised using thermal evaporation sources such as crucibles, electron beam evaporation devices? | Zinc oxide | Metal oxide | Suboxide | Hydroxide | Suboxide |
| **31** | Which one of the method is specifically suitable for the preparation of ultrapure and non-agglomerated nanoparticles of metal? | Microwave Plasma Processing | Sputtered Plasma Processing | CVD processing | CVC Processing | Sputtered Plasma Processing |
| **32** | This technique is similar to the previously discussed CVC method but employs plasma instead of high temperature for decomposition of the metal organic precursors? | Microwave Plasma Processing | Sputtered Plasma Processing | CVD processing | CVC Processing | Microwave Plasma Processing |
| **33** | In homogeneous CVD, particles form in the gas phase and diffuse towards a cold surface due to thermophoretic forces, and can either be scrapped of from the cold surface to give nano-powders, or deposited onto a substrate is called? | Dense films | Thin films | Particulate films | Thin and particulate films | Particulate films |
| **34** | Au/NPs are prepared by raman spectroscopy by using inositol hexakisphosphate to reduce---- | $HAuCl_4$ | $NaAuCl_4$ | $KAuCl_4$ | $CaAuCl_4$ | $HAuCl_4$ |
| **35** | Which is used in the preparation of Au/Nps by thermal citrate reduction method | Trisodium citrate | Tri potassium citrate | Sodium citrate | Tripotassium phosphate | Trisodium citrate |
| **36** | Au/Nps are prepared by the reduction of | $HAuCl_4$ | $NaAuCl_4$ | $KAuCl_4$ | $CaAuCl_4$ | $HAuCl_4$ |
| **37** | In the preparation of Au nanoparticles which is used as the stabiliser | Sodium citrate | Peptide-polyvinyl hydrides | Peptide-Biphenyl hydrides | Sodium borohydride | Peptide-Biphenyl hydrides |
| **38** | The dentrimer /Au Nps can be prepared by using | Sodium citrate | Trisodium citrate | Sodium borohydride | Tri potassium citrate | Sodium borohydride |

| | | | | | | |
|---|---|---|---|---|---|---|
| **39** | In physical processes, metal nanoparticles are generally synthesiszed by | Evaporation-condessation | reduction | Oxidation | Biological method | Evaporation-condessation |
| **40** | The laser ablation method is used for the preparation nano particles as | Emulsion | Dentrimers | Colloids | Gel | Colloids |
| **41** | Colloidal nano particles are prepared by which method | Chemical reduction | Laser ablation | Photochemical reduction | Biological method | Laser ablation |
| **42** | The advantage of laser ablation method is | Nano particles are synthesized in presence of Sunlight | Nano particles are synthesized in absence of chemical reagents | Nano particles are synthesized in absence of chemical reagents | Nano particles are synthesized in presence of UV light | Nano particles are synthesized in absence of chemical reagents |
| **43** | The microemulsion method used to prepare the | Uniform and size controllable nanoparticles | Macrosize nanoparticles | Microsize nanoparticles | Colloidal nanoparticles | Uniform and size controllable nanoparticles |
| **44** | Uniform and size controllable nanoparticles are prepared by which method | Chemical method | Physical method | Micro emulsion method | Biological method | Micro emulsion method |
| **45** | How much is 1 micron in meter ? | $10^{-5}$meter | $10^{-4}$ meter | $10^{-6}$ meter | $10^{-8}$ meter | $10^{-6}$ meter |
| **46** | What is the diameter of the hydrogen atom? | 1 nm | 0.001 nm | 0.1 nm | 0.01 nm | 0.1 nm |
| **47** | What is the diameter of human hair? | 75000 nm | 65000 nm | 85000 nm | 5000 nm | 75000 nm |
| **48** | What is the size of a nanoshell? | 100 nm | 1 nm | 10 nm | 1000 nm | 100 nm |
| **49** | cubic silver nanoparticles are prepared by the reduction of | silver nitrate using ethylene glycol in the presence of poly(vinyl pyrrolidone) (PVP). | silver nitrate using ethylene in the presence of poly(vinyl pyrrolidone) (PVP). | silver nitrate using glycol inthepresence of poly(vinyl pyrrolidone) (PVP). | silver nitrate using Methanol inthe presence of poly(vinyl pyrrolidone) (PVP). | silver nitrate using ethylene glycol in the presence of poly(vinyl pyrrolidone) (PVP). |
| **50** | In polyol process, Which act as both solvent andreducing agent. | alcohol containing hydroxyl groups such as ethanol and pentanediol | alcohol containing hydroxyl groups suchas methonalandpentanediol | alcohol containing hydroxyl groups suchas ethylene glycol and pentanediol | alcohol containing hydroxyl groups suchas glycol and pentanediol | alcohol containing hydroxyl groups such as ethylene glycol and |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | pentanediol |
| **51** | Generally nanorods can be made by | Physical method | Thermal method | Chemical method | Biological method | Thermal method |
| **52** | Generally nanorods can be made by | Physical method | Thermal method | Chemical method | Biological method | Thermal method |
| **53** | Generally nanorods can be made by | Physical method | Photochemical method | Chemical method | Biological method | Photochemical method |
| **54** | flower-shapedmicrostructuredsilver naoparticles can be synthesized by | Wet –chemical method | Physical method | Photochemical method | Chemical method | Wet –chemical method |
| **55** | Wet-chemical method is used to synthesis silver nanoparticles as | Nanowires | nanorods | Flower-shaped particles | nanocubes | Flower-shaped particles |
| **56** | Nanotubes are also known as | Rolled up carbon lattices | Nanosheets | Nanorods | Nano particles | Rolled up carbon lattices |
| **57** | The two important properties of nanosubstances are? | Pressure and friction | Sticking and friction | Sticking and temperature | Temperature and friction | Sticking and Friction |
| **58** | What is the general name for the class of structures made of rolled up carbon lattices? | Nanotubes | Nanosheets | Nanorods | Nano particals | Nanotubes |
| **59** | Which one of the following is the manipulation of matter on atomic, molecular, and supramolecular scale? | Molecular chemistry | Nano tribology | Nanotechnology | Nano biology | Nanotechnology |
| **60** | Xerogel is also known as | Monolith | Sol | Aerosol | Gel | Monolith |

# LECTURE NOTES

## UNIT-III

## SYLLABUS

Experimental techniques: Electron microscopy: Transmission electron microscopy: probe Microscopy: Probe microscopy: diffraction techniques X-ray diffraction, neutron diffraction: Miscellaneous Techniques, comparison of spectral techniques used for elemental analysis

## Experimental techniques

### Electron microscope

The electron microscope is a type of microscope that uses a beam of electrons to create an image of the specimen. It is capable of much higher magnifications and has a greater resolving power than a light microscope, allowing it to see much smaller objects in finer detail.

They are large, expensive pieces of equipment, generally standing alone in a small, specially designed room and requiring trained personnel to operate them.

### The history of EM

By the middle of the 19th century, microscopists had accepted that it was simply not possible to resolve structures of less than half a micrometre with a light microscope because of the Abbe’s formula, but the development of the cathode ray tube was literally about to change the way they looked at things; by using electrons instead of light! Hertz (1857-94) suggested that cathode rays were a form of wave motion and Weichert, in 1899, found that these rays could be concentrated into a small spot by the use of an axial magnetic field produced by a long solenoid. But it was not until 1926 that Busch showed theoretically that a short solenoid converges a beam of electrons in the same way that glass can converge the light of the sun, that a direct comparison was made between light and electron beams. Busch should probably therefore be known as the father of electron optics.

The faster the electrons travel, the shorter their wavelength. The resolving power of a microscope is directly related to the wavelength of the irradiation used to form an image. Reducing wavelength increases resolution. Therefore, the resolution of the microscope is increased if the accelerating voltage of the electron beam is increased. The accelerating voltage of the beam is quoted in kilovolts (kV). It is now possible to purchase a 1,000kV electron microscope, though this is not commonly found.

Although modern electron microscopes can magnify objects up to about two million times, they are still based upon Ruska's prototype and the correlation between wavelength and resolution. The electron microscope is an integral part of many laboratories such as The John Innes Centre. Researchers can use it to examine biological materials (such as microorganisms and cells), a variety of large molecules, medical biopsy samples, metals and crystalline structures, and the characteristics of various surfaces. Nowadays, electron microscopes have many other uses outside research. They can be used as part of a production line, such as in the fabrication of silicon chips, or within forensics laboratories for looking at samples such as gunshot residues. In the arena of fault diagnosis and quality control, they can be used to look for stress lines in engine parts or simply to check the ratio of air to solids in ice cream!

## ELECTRON MICROSCOPE

If you've ever used an ordinary microscope, you'll know the basic idea is simple. There's a light at the bottom that shines upward through a thin slice of the specimen. You look through an eyepiece and a powerful lens to see a considerably magnified image of the specimen (typically 10–200 times bigger). So there are essentially four important parts to an ordinary microscope:

1. The source of light.
2. The specimen.
3. The lenses that makes the specimen seem bigger.
4. The magnified image of the specimen that you see.

In an electron microscope, these four things are slightly different.

1. The light source is replaced by a beam of very fast moving electrons.
2. The specimen usually has to be specially prepared and held inside a vacuum chamber from which the air has been pumped out (because electrons do not travel very far in air).
3. The lenses are replaced by a series of coil-shaped electromagnets through which the electron beam travels. In an ordinary microscope, the glass lenses bend (or refract) the light beams passing through them to produce magnification. In an electron microscope, the coils bend the electron beams the same way.
4. The image is formed as a photograph (called an **electron micrograph**) or as an image on a TV screen.

That's the basic, general idea of an electron microscope. But there are actually quite a few different types of electron microscopes and they all work in different ways. The three most familiar types are called transmission electron microscopes (TEMs), scanning electron microscopes (SEMs), and scanning tunneling microscopes (STMs).

### *Transmission electron microscopes (TEMs)*

A TEM has a lot in common with an ordinary optical microscope. You have to prepare a thin slice of the specimen quite carefully (it's a fairly laborious process) and sit it in a vacuum chamber in the middle of the machine. When you've done that, you fire an electron beam down through the specimen from a giant electron gun at the top. The gun uses electromagnetic coils and high voltages (typically from 50,000 to several million volts) to accelerate the electrons to very high speeds. Thanks to our old friend wave-particle duality, electrons (which we normally think of as particles) can behave like waves (just as waves of light can behave like particles). The faster they travel, the smaller the waves they form and the more detailed the images they show up. Having reached top speed, the electrons zoom through the specimen and out the other side, where more coils focus them to form an image on screen (for immediate viewing) or on a photographic plate (for making a permanent record of the image). TEMs are the most powerful electron microscopes: we can use them to see things just 1 nanometer in size, so they effectively magnify by a million times or more.

## Scanning electron microscope

**scanning electron microscope** scans a beam of electrons *over* a specimen to produce a magnified image of an object. That's completely different from a TEM, where the beam of electrons goes right through the specimen.

1. Electrons are fired into the machine.
2. The main part of the machine (where the object is scanned) is contained within a sealed vacuum chamber because precise electron beams can't travel effectively through air.
3. A positively charged electrode (anode) attracts the electrons and accelerates them into an energetic beam.
4. An electromagnetic coil brings the electron beam to a very precise focus, much like a lens.
5. Another coil, lower down, steers the electron beam from side to side.
6. The beam systematically scans across the object being viewed.
7. Electrons from the beam hit the surface of the object and bounce off it.
8. A detector registers these scattered electrons and turns them into a picture.
9. A hugely magnified image of the object is displayed on a TV screen.

## *Scanning tunneling microscopes (STMs)*

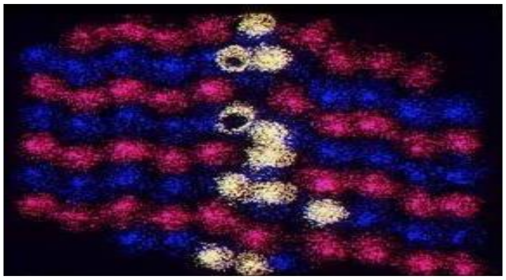


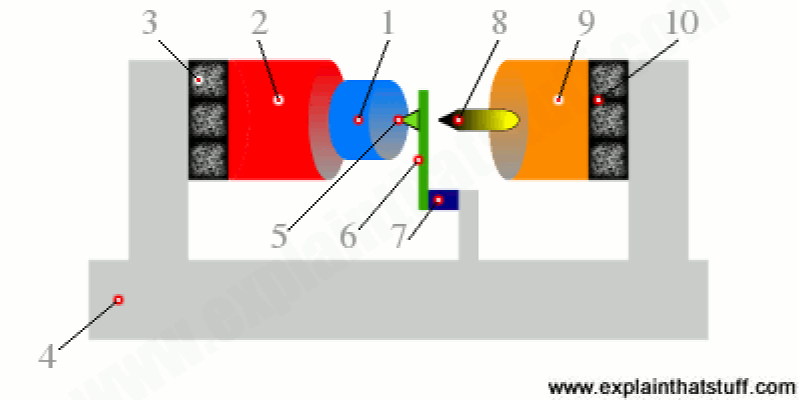
Photo: An STM image of the atoms on the surface of a solar cell.

Among the newest electron microscopes, STMs were invented by Gerd Binnig and Heinrich Rohrer in 1981. Unlike TEMs, which produce images of the insides of materials, and SEMs, which show up 3D surfaces, STMs are designed to make detailed images of the atoms or molecules on the surface of something like a crystal. They work differently to TEMs and SEMs too: they have an extremely sharp metallic probe that scans back and forth across the surface of the specimen. As it does so, electrons try to wriggle out of the specimen and jump across the gap, into the probe, by an unusual phenomenon called "tunneling". The closer the probe is to the surface, the easier it is for electrons to tunnel into it, the more electrons escape, and the greater the tunneling current. The microscope constantly moves the probe up or down by tiny amounts to keep the tunneling current constant. By recording how much the probe has to move, it effectively measures the peaks and troughs of the specimen's surface. A computer turns this information into a map of the specimen that shows up its detailed atomic structure. One big drawback of ordinary electron microscopes is that they produce amazing detail using high-energy beams of electrons, which tend to damage the objects they're imaging. STMs avoid this problem by using much lower energies.

### *Atomic force microscopes (AFMs)*

If you think STMs are amazing, AFMs (atomic force microscopes), also invented by Gerd Binnig, are even better! One of the big drawbacks of STMs is that they rely on electrical currents (flows of electrons) passing through materials, so they can only make images of conductors. AFMs don't suffer from this problem because, although they use still tuneling, they don't rely on a current flowing between the specimen and a proble, so we can use them to make atomic-scale images of materials such as plastics, which don't conduct electricity.

An AFM is a microscope with a little arm called a cantilever with a tip on the end that scans across the surface of a specimen. As the tip sweeps across the surface, the force between the atoms from which it's made and the atoms on the surface constantly changes, causing the cantilever to bend by minute amounts. The amount by which the cantilever bends is detected by bouncing a laser beam off its surface. By measuring how far the laser beam travels, we can measure how much the cantilever bends and the forces acting on it from moment to moment, and that information can be used to figure out and plot the contours of the surface. Other versions of AFMs (like the one illustrated here) make an image by measuring a current that "tunnels" between the scanning tip and a tunneling probe mounted just behind it. AFMs can make images of things at the atomic level and they can also be used to manipulate individual atoms and molecules—one of the key ideas in nanotechnology.



Artwork: How Gerd Binnig's original AFM worked—greatly simplified. The specimen to be scanned (1) is mounted on a drive mechanism (2) that can move it in three dimensions. To prevent unwanted vibrations, that mechanism is fixed to a rubber cushion (3) mounted on a firm aluminum base (4), which is further cushioned by multiple layers of aluminum plates and rubber pads (not shown). To create an image, the specimen is slowly moved around the sharp, fixed imaging point (5), which is mounted on a spring cantilever made of thin gold foil (6), attached to a piezoelectric crystal (7), and fixed to the same aluminum base. At the other end of the apparatus, a tunneling probe (8) is moved very close (to within about 0.3nm) of the spring cantilever by a second drive mechanism (9), isolated by another rubber cushion (10). As the sample (1) moves around the imaging point (5), the current that tunnels between the spring cantilever (6) and the tunneling tip (8) is constantly measured. These measurements are converted into data that can be used to draw a detailed surface map of the specimen. Atomic force microscope and method for imaging surfaces with atomic resolution.

### Disadvantages of TEM

Electron microscopes are very expensive to buy and maintain. They are dynamic rather than static in their operation: requiring extremely stable high voltage supplies, extremely stable currents to each electromagnetic coil/lens, continuously-pumped high/ultra-high vacuum systems and a cooling water supply circulation through the lenses and pumps. As they are very sensitive to vibration and external magnetic fields, microscopes aimed at achieving high resolutions must be housed in buildings with special services.

A significant amount of training is required in order to operate an electron microscope successfully and electron microscopy is considered a specialised skill.

The samples have to be viewed in a vacuum, as the molecules that make up air would scatter the electrons. This means that the samples need to be specially prepared by sometimes lengthy and difficult techniques to withstand the environment inside an electron microscope. Recent advances have allowed some hydrated samples to be imaged using an environmental scanning electron microscope, but the applications for this type of imaging are still limited.

## Transmission Electron Microscopy

### Operating principle of a Transmission Electron Microscope

**Transmission electron microscopy** (**TEM**, also sometimes **conventional transmission electron microscopy** or **CTEM**) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a charge-coupled device.

Transmission electron microscopes are capable of imaging at a significantly higher resolution than light microscopes, owing to the smaller de Broglie wavelength of electrons. This enables the instrument to capture fine detail—even as small as a single column of atoms, which is thousands of times smaller than a resolvable object seen in a light microscope. Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences. TEMs find application in cancer research, virology, and materials science as well as pollution, nanotechnology and semiconductor research.

At lower magnifications TEM image contrast is due to differential absorption of electrons by the material due to differences in composition or thickness of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

The first TEM was demonstrated by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolution greater than that of light in 1933 and the first commercial TEM in 1939. In 1986, Ruska was awarded the Nobel Prize in physics for the development of transmission electron microscopy.

A **Transmission Electron Microscope** (TEM) utilizes energetic electrons to provide morphologic, compositional and crystallographic information on samples.

At a maximum potential magnification of 1 nanometer, TEMs are the most powerful microscopes. TEMs produce high-resolution, two-dimensional images, allowing for a wide range of educational, science and industry applications.

Ernst Ruska developed the first electron microscope, a TEM, with the assistance of Max Knolls in 1931. After significant improvements to the quality of magnification, Ruska joined the Sieman’s Company in the late 1930s as an electrical engineer, where he assisted in the manufacturing of his TEM.

**TEMs consist of the following components:**

- An electron source
- Thermionic Gun
- Electron beam
- Electromagnetic lenses
- Vacuum chamber
- 2 Condensers
- Sample stage
- Phosphor or fluorescent screen
- Computer

A Transmission Electron Microscope functions under the same basic principles as an optical microscope.

In a TEM, electrons replace photons, electromagnetic lenses replace glass lenses and images are viewed on a screen rather than through an eyepiece.

## TEM Imaging

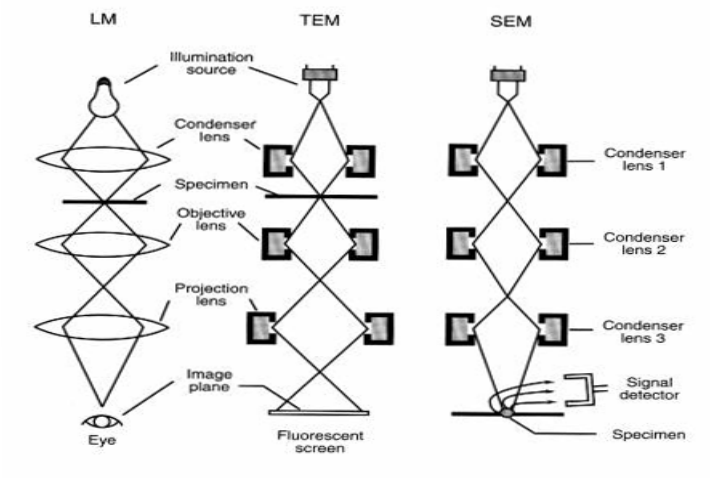
**A Transmission** Electron Microscope produces a high-resolution, black and white image from the interaction that takes place between prepared samples and energetic electrons in the vacuum chamber.

- ✓ Air needs to be pumped out of the vacuum chamber, creating a space where electrons are able to move.
- ✓ The electrons then pass through multiple electromagnetic lenses. These solenoids are tubes with coil wrapped around them.
- ✓ The beam passes through the solenoids, down the column, makes contact with the screen where the electrons are converted to light and form an image.
- ✓ The image can be manipulated by adjusting the voltage of the gun to accelerate or decrease the speed of electrons as well as changing the electromagnetic wavelength via the solenoids.
- ✓ The coils focus images onto a screen or photographic plate.
- ✓ During transmission, the speed of electrons directly correlates to electron wavelength; the faster electrons move, the shorter wavelength and the greater the quality and detail of the image.
- ✓ The lighter areas of the image represent the places where a greater number of electrons were able to pass through the sample and the darker areas reflect the dense areas of the object.
- ✓ These differences provide information on the structure, texture, shape and size of the sample.
- ✓ To obtain a TEM analysis, samples need to have certain properties. They need to be sliced thin enough for electrons to pass through, a property known as electron transparency.
- ✓ Samples need to be able to withstand the vacuum chamber and often require special preparation before viewing.
- ✓ Types of preparation include dehydration, sputter coating of non-conductive materials, cryofixation, sectioning and staining.

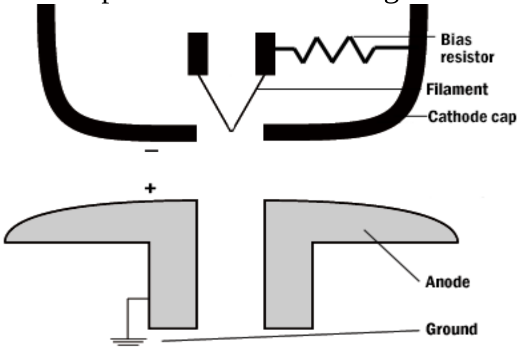
The transmission electron microscope (TEM) operates on many of the same optical principles as the light microscope. The TEM has the added advantage of greater resolution. This increased resolution allows us to study ultrastucture of organelles, viruses and macromolecules. Specially prepared materials samples may also be viewed in the TEM. The light microscope and TEM are commonly used in conjunction with each other to complement a research project.

Since electrons are very small and easily deflected by hydrocarbons or gas molecules, it is necessary to use the electron beam in a vacuum environment. A series of pumps are used to accomplish an adequate vacuum for this purpose. Rotary Pumps are the first in the series. They are also called the "roughing pumps" as they are used to initially lower the pressure within the column through which the electron must travel to 10 -3 mm of Hg range. Diffusion Pumps may achieve higher vacuums (in the 10-5 mm Hg range) but must be backed by the rotary pump. The diffusion pump also maintains pressure. In addition a Turbo, Ion, or Cryo Pumps backed by the preceding pumps may be used when an even greater vacuum is required.

The organization of the transmission electron microscope (TEM) is similar to that of the light microscope.



The illumination source (or electron gun) in a thermo-ionic emission TEM works much like a light bulb. A filament (cathode) is the source of electrons. It is usually a hairpin-shaped tungsten wire. An accelerating voltage (fixed amount of negative high voltage) is applied to the surrounding cathode cap. A small emission current is then applied to the filament to achieve the release of electrons. The point at which the gun achieves good thermal emission as well as an acceptable filament life is called the saturation point. The cathode cap ( also called Wehnelt cylinder) must be slightly more negative than the filament. A resister is located in the gun assembly and is controlled by a knob marked "bias". It creates the difference in negative voltage between the filament and the cathode cap. This allows the electrons to collect inside the cap, forming an electron "cloud" . An Anode located below the gun assembly, is electrically at ground, creating a positive attraction for the negatively charged electrons, which overcome the negative repulsion of the cathode cap and accelerate through the small hole in the anode.



Glass lenses of course, would impede electrons, therefore electron microscope (EM) lenses are electromagnetic converging lenses. A tightly wound wrapping of copper wire makes up the magnetic field that is the essence of the lens. Surrounding these coils is a shroud made of a metal that will not hold a magnetic charge when the lens is shut off. The electron moves through the center hole in this solenoid. The electron path is further constricted by a brass lining inside this space known as the pole piece. The pole piece has a small gap within it at which point the beam is most influenced by the electromagnetic current. This is appropriately referred to as the pole piece gap.

The condenser lenses in the TEM serve much the same function as that of the condenser in the light microscope. They gather the electrons of the first crossover image and focus them onto the specimen to illuminate only the area being examined. A condenser aperture is used to reduce spherical aberration. The Objective lens is used primarily to focus and initially magnify the image. The specimen stage is inserted into the objective lens for imaging purposes. A cold finger or anticontaminator also sits near the objective lens. It consists of a thin copper rod at liquid nitrogen temperatures, so that contaminants are attracted to it. The cold finger reservoir must be must be filled with liquid nitrogen before the microscope is used. Contaminants sometimes cause a phenomenon known as drift. Drift is the apparent "movement" of the specimen across the screen. It is caused by poor contact between the grid and the specimen holder causing a buildup of heat and static charges. An objective aperture is used to enhance specimen contrast. Intermediate lenses magnify the image coming from the objective lens. Finally, projector lenses further magnify the image coming from the intermediate lens and projects it on to the phosphorescent screen.

To optimize imaging in the TEM a beam alignment should be performed prior to use. A tool for this alignment is a holey grid. A holey grid is a TEM grid support coated with a thin plastic film and a stabilizing carbon layer. It is manufactured to contain small round holes useful in alignment of the TEM. The holes in the grid create Fresnel fringes when the electron beam diffracts around the edges as the electrons come together at overfocus. The edge of the hole appears to have bands or fringes.

The final image is viewed by projection onto a phosphorescent screen which gives off photons when irradiated by the electron beam. A film camera is located beneath the phosphorescent screen. The screen is raised in order to expose a special photographic film with a thicker emulsion layer than light film. An alternative to photographic film is digital capture with a computer digitizing and archiving (CCD) camera.

The operator is responsible for adjusting variable bias, recognition of aberrations, image drift, photography, specimen contrast, resolution, even illumination, and filling the anticontaminators with liquid nitrogen before using the TEM.

Instrument maintenance that requires staff or company repair are filament saturation, filament exchange, aperture cleaning or replacement, specimen holder cleaning, vacuum pump maintenance, and viewing screen.

The theoretical resolution described by Abbe for the light microscope can be modified and applied to the TEM by using DeBroglie's formula. DeBroglie stated that the wavelength of an electron beam is a function of the accelerating voltage used. By increasing the accelerating voltage, a shorter wavelength is obtained. The shorter wavelength is applied to Abbe's equation and the increased resolution can be calculated. Typical accelerating voltages for a biological TEM range up to 125,000 Volts.

**Abbe's equation:** $r = 0.612 \times l$

sin a r = resolution

l = wavelength (nm)

a = angle of incoming beam

Resolution is defined as the distance at which two points or objects can be distinguished. Therefore as r approaches zero we say that the resolution is increased.

**DeBroglie's formula:**

l = h/mv

h = Plank's constant

(6.626 x 10 –23 ergs/ sec)

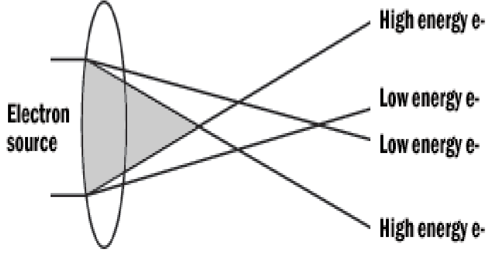
m = mass of the electron

v = electron velocity

DeBroglie's formula states that if the accelerating voltage is increased, electron velocity will increase as will resolution.

As in the light microscope several factors detract from this number. Spherical aberration is also present in the TEM as electrons passing through the periphery of the lens are refracted more than those passing along the axis. All the electrons will therefore not reach a common focal point. To reduce spherical aberration, an aperture is used to eliminate some of the periphery electrons.

One would not normally expect chromatic aberration to be a problem in an electron microscope, but, electromagnetic radiation of different energies converge at different focal planes. This is essentially the same problem as the chromatic aberration observed in the light microscope. To correct for chromatic aberration, increase accelerating voltage, improve the vacuum and/or use a thinner specimen.



An astigmation occurs when a lens field is not symmetrical in strength, but weaker in one plane than another. Astigmation can be caused by imperfect polepiece boring, non-homogenous blending of polepiece materials, or by dirt on the polepieces, apertures, and/or specimen holders. A stigmator can be used to apply a correcting field of the appropriate strength in the proper direction to counteract the asymmetry. Stigmators are located in the objective and condenser lenses.

Although diffraction can be useful, diffraction of electron waves around the aperture openings can interfere with the initial wave front. The results are an unclear or out-of-focused image. It is important to create a balance between reduction of spherical aberration and diffraction by selecting an appropriate sized aperture.

Image fomation in the electron microscope is achieved by electron scattering. The interaction between the primary electron beam and sample results in a change of energy and/or trajectory without altering its kinetic energy. Backscattered electrons are an example of elastic scattering. Inelastic scattering occurs when an electron transfers some kinetic energy of the atoms of the sample. Examples of inelastic scattering are secondary electrons, auger electrons, and transmitted electrons.

**Definitions**

**Accelerating voltage**-The fixed amount of high voltage applied to the cathode cap of the transmission electron microscope.

**Anode**-Located below the gun assembly, the anode is at ground with a small aperture for electrons to move through. This aperture serves as the first lens encountered by the electron.

**Astigmation**-An aberration caused by uneven electrical fields surrounding a lens.

**Cathode**-The filament or source of the primary electron beam. Cathode Cap-(also called Wehnelt cylinder) surrounds the gun assembly. The high voltage is applied here.

**Cold finger**-A long copper rod extending along the inside of the electron column. When its reservoir is kept filled with liquid nitrogen, the rod attracts contaminants that might otherwise degrade the chamber's vacuum.

**Condenser aperture**-A small laser-bored hole in a flat strip of molybdenum placed near the condenser lens that helps to limit spherical aberration.

**Condenser lens**-The first electromagnetic lens that the electron beam encounters. Focuses the electrons onto the specimen.

**Chromatic aberration**-Electromagnetic radiation of different energies converging at different focal planes.

**Crossover**-The point at which the electrons converge. The smallest visual beam image on the phosphorous screen.

**DeBroglie's formula**-The wavelength of an electron is a function of the accelerating voltage used.

**Diffusion pump**-The second pump in series in the evacuation of the TEM column.

**Drift**-The apparent "movement" of a specimen across the field of view.

**Elastic scattering**-Electron scattering where little kinetic energy is lost, but the trajectory of the electron is substantially changed.

**Electron scattering**-The displacement of an electron beam by a sample, causing formation of an image.

**Emission current**-A small amount of heat added to the electron source in order to release electrons through the column.

**Fresnel fringe**-A diffraction pattern formed around a small hole when the beam is over-focused onto it.

**Holey grid**-A thin support film manufactured to have holes so that it may be used to align a TEM.

**Inelastic scattering**-Scattering of electrons in which the electron loses kinetic energy, but changes trajectory only minimally.

**Intermediate lens**-Help the objective lenses to magnify the specimen.

**Objective aperture**-A small laser-bored hole in a flat strip of molybdenum placed near the objective lens. Adjustment of this aperture strip can aid in adjustment of contrast of the image.

**Objective lens**-The main magnifying lens.

**Phosphorescent screen**-The screen at the bottom of the electron column, where the specimen is viewed.

**Pole piece**-A brass fitting inside an electromagnetic lens to assist in narrowing the primary electron beam.

**Projector lens**-The final lens in a TEM. Used to assist in magnifying the image and to project the magnified image onto the phosphorus screen.

**Rotary pump**-Also called the roughing pump. The first pump in the vacuum pump series.

**Saturation Point**-The point at which good electron emission from the gun is achieved without shortening the filament life appreciably.

**Shroud**-The soft iron casing surrounding the electromagnetic lenses of the TEM. Solenoid-An electromagnetic lens fashioned by copper windings with a direct current running through it.

**Specimen stage**-The platform on which a specimen sits while being imaged.

**Spherical aberration**-Electrons passing through the periphery of a lens are refracted more than those passing through the center of a lens. The electrons, therefore do not reach a common focal point. Improved with the addition of an aperture.

**TEM aplplications**

- ✓ A Transmission Electron Microscope is ideal for a number of different fields such as life sciences, nanotechnology, medical, biological and material research, forensic analysis, gemology and metallurgy as well as industry and education.
- ✓ TEMs provide topographical, morphological, compositional and crystalline information.
- ✓ The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture.
- ✓ This information is useful in the study of crystals and metals, but also has industrial applications.
- ✓ TEMs can be used in semiconductor analysis and production and the manufacturing of computer and silicon chips.
- ✓ Technology companies use TEMs to identify flaws, fractures and damages to micro-sized objects; this data can help fix problems and/or help to make a more durable, efficient product.
- ✓ Colleges and universities can utilize TEMs for research and studies.
- ✓ Although electron microscopes require specialized training, students can assist professors and learn TEM techniques.

**Advantages**

A Transmission Electron Microscope is an impressive instrument with a number of advantages such as:

- TEMs offer the most powerful magnification, potentially over one million times or more
- TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields
- TEMs provide information on element and compound structure
- Images are high-quality and detailed
- TEMs are able to yield information of surface features, shape, size and structure
- They are easy to operate with proper training

**Disadvantages**

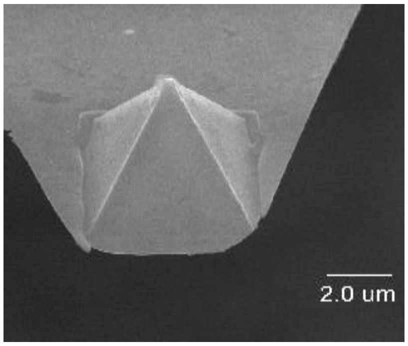
- Some cons of electron microscopes include:
- TEMs are large and very expensive
- Laborious sample preparation
- Potential artifacts from sample preparation
- Operation and analysis requires special training
- Samples are limited to those that are electron transparent, able to tolerate the vacuum chamber and small enough to fit in the chamber
- TEMs require special housing and maintenance
- Images are black and white

Electron microscopes are sensitive to vibration and electromagnetic fields and must be housed in an area that isolates them from possible exposure.

A Transmission Electron Microscope requires constant upkeep including maintaining voltage, currents to the electromagnetic coils and cooling water.

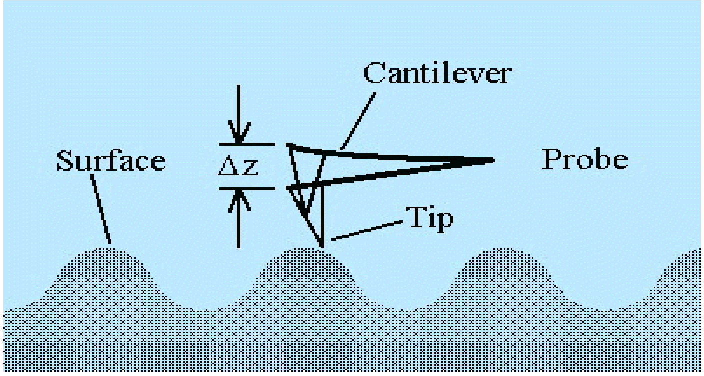
## Probe microscopy

### Introduction



Above: A probe used for atomic force microscopy.

Below: How a probe tip scans over a sample (not to scale).



Scanning probe microscopy covers several related technologies for imaging and measuring surfaces on a fine scale, down to the level of molecules and groups of atoms.

At the other end of the scale, a scan may cover a distance of over 100 micrometers in the x and y directions and 4 micrometers in the z direction. This is an enormous range. It can truly be said that the development of this technology is a major achievement, for it is having profound effects on many areas of science and engineering.

SPM technologies share the concept of scanning an extremely sharp tip (3-50 nm radius of curvature) across the object surface. The tip is mounted on a flexible cantilever, allowing the tip to follow the surface profile (see Figure).

When the tip moves in proximity to the investigated object, forces of interaction between the tip and the surface influence the movement of the cantilever. These movements are detected by selective sensors. Various interactions can be studied depending on the mechanics of the probe

## Probe Techniques

The three most common scanning probe techniques are:

**Atomic Force Microscopy** (AFM) measures the **interaction force** between the tip and surface. The tip may be dragged across the surface, or may vibrate as it moves. The interaction force will depend on the nature of the sample, the probe tip and the distance between them.

**<u>Scanning Tunneling Microscopy</u>** (STM) measures a **weak electrical current** flowing between tip and sample as they are held a very distance apart.

**<u>Near-Field Scanning Optical Microscopy</u>** (NSOM) scans a very **small light source** very close to the sample. Detection of this light energy forms the image. NSOM can provide resolution below that of the conventional light microscope.

There are numerous variations on these techniques. AFM may operate in several <u>modes</u> which differ according to the force between the tip and surface:

| **Mode of Operation** | **Force of Interaction** |
|---|---|
| contact mode | strong (repulsive) - constant force or constant distance |
| non-contact mode | weak (attractive) - vibrating probe |
| intermittent contact mode | strong (repulsive) - vibrating probe |
| lateral force mode | frictional forces exert a torque on the scanning cantilever |
| magnetic force | the magnetic field of the surface is imaged |
| thermal scanning | the distribution of thermal conductivity is imaged |

In contact mode, the tip is usually maintained at a constant force by moving the cantilever up and down as it scans. In non-contact mode or intermittent contact mode (tapping mode$^{TM}$) the tip is driven up and down by an oscillator. Especially soft materials may be imaged by a magnetically-driven cantilever (MAC Mode$^{TM}$). In non-contact mode, the bottom-most point of each probe cycle is in the *attractive* region of the force-distance curve. In intermittent contact mode the bottom-most point is in the *repulsive* region. Variations in the measured oscillation amplitude and phase in relation to the driver frequency are indicators of the surface-probe interaction.

To image *frictional force*, the probe is dragged along the surface, resulting in a torque on the cantilever. To image the magnetic field of the surface, a magnetically-susceptible probe is used. In other variations, the electric charge distribution on the surface or the surface capacitance is imaged. For thermal scanning microscopy (TSM) the thermal conductivity of the surface with is probed with a resistive tip that acts as a tiny resistance thermometer.

In addition to these modes, many instruments are also designed to plot the phase difference between the measured modes, for example frictional force versus contact profile. This plot is called **phase mode**.

Several types of probes with different tips are used in scanning probe microscopy. Tip selection depends on the mode of operation and on the type of sample.

## Applications

These techniques have the ability to operate on a scale from microns down to nanometers and can image clusters of individual atoms and molecules. STM relies on the electrical conductivity of the sample, so at least some features on the sample surface must be electrically conductive to some degree. AFM is used for studies of non-conductors and is the technique more commonly used for studies of macromolecules and biological specimens. AFM has been used for measurements on a wide variety of sample types, including:

| **Inorganic and Synthetic Materials** | |
|---|---|
| **Surfaces** | **Nanostructures** |
| Natural surface topography | Buckyballs and Nanotubes |
| Surface Chemistry | Surfaces of Polymers |
| Silicon wafers | Diffraction gratings |
| Data storage media | Integrated circuits |
| Ceramics | |
| **Biological Materials** | |
| **Polymers and Polymer Matrix** | **Biological Structures** |
| Natural resins and gums | Bacterial flagellae |
| Muscle proteins | Amyloid-beta |
| DNA | Chromosomes |
| Plant cell walls | Cell and membrane surfaces |

## Scanning probe microscopy (SPM)

**Scanning probe microscopy** (**SPM**) is a branch of microscopy that forms images of surfaces using a physical probe that scans the specimen. SPM was founded in 1981, with the invention of the scanning tunneling microscope, an instrument for imaging surfaces at the atomic level. The first successful scanning tunneling microscope experiment was done by Binnig and Rohrer. The key to their success was using a feedback loop to regulate gap distance between the sample and the probe.

Many scanning probe microscopes can image several interactions simultaneously. The manner of using these interactions to obtain an image is generally called a mode.

The resolution varies somewhat from technique to technique, but some probe techniques reach a rather impressive atomic resolution.[*citation needed*] This is due largely because piezoelectric actuators can execute motions with a precision and accuracy at the atomic level or better on electronic command. This family of techniques can be called "piezoelectric techniques". The other common denominator is that the data are typically obtained as a two-dimensional grid of data points, visualized in false color as a computer image.
Image forming

To form images, scanning probe microscopes raster scan the tip over the surface. At discrete points in the raster scan a value is recorded (which value depends on the type of SPM and the mode of operation, see below). These recorded values are displayed as a heat map to produce the final STM images, usually using a black and white or an orange color scale.

### Constant interaction mode

In constant interaction mode (often referred to as "in feedback"), a feedback loop is used to physically move the probe closer to or further from the surface (in the *z* axis) under study to maintain a constant interaction. This interaction depends on the type of SPM, for scanning tunneling microscopy the interaction is the tunnel current, for contact mode AFM or MFM it is the cantilever deflection, etc. The type of feedback loop used is usually a PI-loop, which is a PID-loop where the differential gain has been set to zero (as it amplifies noise). The *z* position of the tip (scanning plane is the *xy*-plane) is recorded periodically and displayed as a heat map. This is normally referred to as a topography image.

In this mode a second image, known as the ″error signal" or "error image" is also taken, which is a heat map of the interaction which was fed back on. Under perfect operation this image would be a blank at a constant value which was set on the feedback loop. Under real operation the image shows noise and often some indication of the surface structure. The user can use this image to edit the feedback gains to minimise features in the error signal.

If the gains are set incorrectly, many imaging artifacts are possible. If gains are too low features can appear smeared. If the gains are too high the feedback can become unstable and oscillate, producing striped features in the images which are not physical.

### Constant height mode

In constant height mode the probe is not moved in the *z*-axis during the raster scan. Instead the value of the interaction under study is recorded (i.e. the tunnel current for STM, or the cantilever oscillation amplitude for amplitude modulated non-contact AFM). This recorded information is displayed as a heat map, and is usually referred to as a constant height image.

Constant height imaging is much more difficult than constant interaction imaging as the probe is much more likely to crash into the sample surface. Usually before performing constant height imaging one must image in constant interaction mode to check the surface has no large contaminants in the imaging region, to measure and correct for the sample tilt, and (especially for slow scans) to measure and correct for thermal drift of the sample. Piezoelectric creep can also be a problem, so the microscope often needs time to settle after large movements before constant height imaging can be performed.

Constant height imaging can be advantageous for eliminating the possibility of feedback artifacts.

### *Probe tips*

The nature of an SPM probe depends entirely on the type of SPM being used. The combination of tip shape and topography of the sample make up a SPM image.[29][*citation needed*] However, certain characteristics are common to all, or at least most, SPMs.[*citation needed*]

Most importantly the probe must have a very sharp apex.[*citation needed*] The apex of the probe defines the resolution of the microscope, the sharper the probe the better the resolution. For atomic resolution imaging the probe must be terminated by a single atom.[*citation needed*]

For many cantilever based SPMs (e.g. AFM and MFM), the entire cantilever and integrated probe are fabricated by acid [etching],[30] usually from silicon nitride. Conducting probes, needed for STM and SCM among others, are usually constructed from platinum/iridium wire for ambient operations, or tungsten for UHV operation. Other materials such as gold are sometimes used either for sample specific reasons or if the SPM is to be combined with other experiments such as TERS. Platinum/iridium (and other ambient) probes are normally cut using sharp wire cutters, the optimal method is to cut most of the way through the wire and then pull to snap the last of the wire, increasing the likelihood of a single atom termination. Tungsten wires are usually electrochemically etched, following this the oxide layer normally needs to be removed once the tip is in UHV conditions.

It is not uncommon for SPM probes (both purchased and "home-made") to not image with the desired resolution. This could be a tip which is too blunt or the probe may have more than one peak, resulting in a doubled or ghost image. For some probes, *in situ* modification of the tip apex is possible, this is usually done by either crashing the tip into the surface or by applying a large electric field. The latter is achieved by applying a bias voltage (of order 10V) between the tip and the sample, as this distance is usually 1-3 Angstroms, a very large field is generated.

### *Advantages*

The resolution of the microscopes is not limited by diffraction, only by the size of the probe-sample interaction volume (i.e., point spread function), which can be as small as a few picometres. Hence the ability to measure small local differences in object height (like that of 135 picometre steps on <100> silicon) is unparalleled. Laterally the probe-sample interaction extends only across the tip atom or atoms involved in the interaction.

The interaction can be used to modify the sample to create small structures (Scanning probe lithography).

Unlike electron microscope methods, specimens do not require a partial vacuum but can be observed in air at standard temperature and pressure or while submerged in a liquid reaction vessel.

### *Disadvantages*

*The detailed shape of the scanning tip is sometimes difficult to determine. Its effect on the resulting data is particularly noticeable if the specimen varies greatly in height over lateral distances of 10 nm or less.*

The scanning techniques are generally slower in acquiring images, due to the scanning process. As a result, efforts are being made to greatly improve the scanning rate. Like all scanning techniques, the embedding of spatial information into a time sequence opens the door to uncertainties in metrology, say of lateral spacings and angles, which arise due to time-domain effects like specimen drift, feedback loop oscillation, and mechanical vibration.

The maximum image size is generally smaller.

Scanning probe microscopy is often not useful for examining buried solid-solid or liquid-liquid interfaces.

### *Visualization and analysis software*

In all instances and contrary to optical microscopes, rendering software is necessary to produce images. Such software is produced and embedded by instrument manufacturers but also available as an accessory from specialized work groups or companies. The main packages used are freeware: Gwyddion, WSxM (developed by Nanotec) and commercial: SPIP (developed by Image Metrology), FemtoScan Online (developed by Advanced Technologies Center), MountainsMap SPM (developed by Digital Surf), TopoStitch (developed by Image Metrology).

## Diffraction

**Diffraction** refers to various phenomena that occur when a wave encounters an obstacle or a slit. It is defined as the bending of light around the corners of an obstacle or aperture into the region of geometrical shadow of the obstacle. In classical physics, the diffraction phenomenon is described as the interference of waves according to the Huygens–Fresnel principle. These characteristic behaviors are exhibited when a wave encounters an obstacle or a slit that is comparable in size to its wavelength. Similar effects occur when a light wave travels through a medium with a varying refractive index, or when a sound wave travels through a medium with varying acoustic impedance. Diffraction occurs with all waves, including sound waves, water waves, and electromagnetic waves such as visible light, X-rays and radio waves.

Since physical objects have wave-like properties (at the atomic level), diffraction also occurs with matter and can be studied according to the principles of quantum mechanics. Italian scientist Francesco Maria Grimaldi coined the word "diffraction" and was the first to record accurate observations of the phenomenon in 1660.

While diffraction occurs whenever propagating waves encounter such changes, its effects are generally most pronounced for waves whose wavelength is roughly comparable to the dimensions of the diffracting object or slit. If the obstructing object provides multiple, closely spaced openings, a complex pattern of varying intensity can result. This is due to the addition, or interference, of different parts of a wave that travel to the observer by different paths, where different path lengths result in different phases (see diffraction grating and wave superposition). The formalism of diffraction can also describe the way in which waves of finite extent propagate in free space. For example, the expanding profile of a laser beam, the beam shape of a radar antenna and the field of view of an ultrasonic transducer can all be analyzed using diffraction equations.

## Diffraction techniques

### X-ray Powder Diffraction

(XRD) X-ray powder **diffraction** (XRD) is a rapid analytical **technique** primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

### Fundamental Principles of X-ray Powder Diffraction (XRD)

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

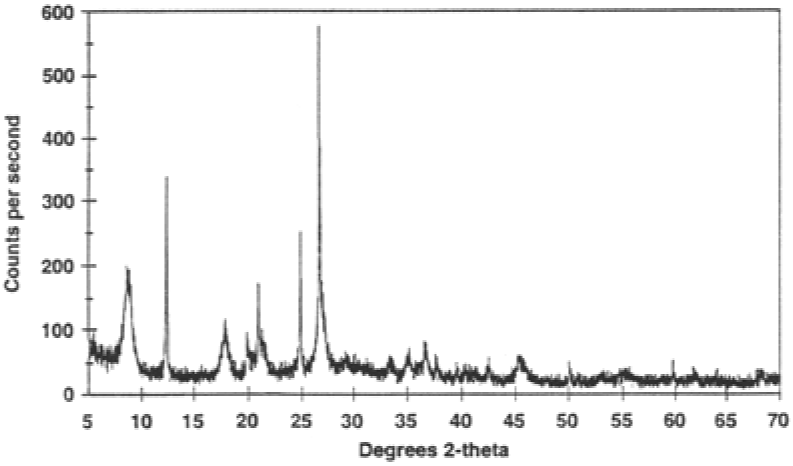
X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of $2\theta$angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

### *X-ray Powder Diffraction (XRD) Instrumentation -*

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector.

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being $K_{\alpha}$ and $K_{\beta}$. $K_{\alpha}$ consists, in part, of $K_{\alpha1}$ and $K_{\alpha2}$. $K_{\alpha1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha1}$and $K_{\alpha2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with $CuK_{\alpha}$ radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.



X-ray powder diffractogram. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this patter can be used to 'fingerprint' the mineral. Details

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

***Applications***

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

**Other applications include:**

- characterization of crystalline materials
- identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- determination of unit cell dimensions
- measurement of sample purity

With specialized techniques, XRD can be used to:

- determine crystal structures using Rietveld refinement
- determine of modal amounts of minerals (quantitative analysis)
- characterize thin films samples by:
    - determining lattice mismatch between film and substrate and to inferring stress and strain
    - determining dislocation density and quality of the film by rocking curve measurements
    - measuring superlattices in multilayered epitaxial structures
    - determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements
- make textural measurements, such as the orientation of grains, in a polycrystalline sample

***Strengths and Limitations of X-ray Powder Diffraction (XRD)?***

**Strengths**

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward

**Limitations**

- Homogeneous and single phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacings, *hkl*s)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur and worsens for high angle 'reflections'

### *Applications of X-ray diffraction*

X-ray diffraction has a wide and various applications on the chemical, biochemical, physical, material and mineralogical sciences. Laue`s said that 'has extended the power of on serving minute structure ten thousand times beyond that of the optical microscope. X-ray diffraction produced a microscope with atomic resolution which shows the atoms and their electron distribution. X-ray diffraction, electron diffraction, and neutron diffraction give information about the structure of matter, crystalline and non-crystalline, at the atomic and molecular level. In addition, they are attached to the properties of all materials, inorganic, organic or biological. Due to the diffraction importance and variety of application of diffraction by crystals, a large number of Nobel Prizes were presented to studies involving X-ray.

### X-ray method for investigation of drugs

X-ray diffraction was used for the identification of antibiotic drugs such as: eight β-lactam (ampicillin sodium, penicillin G procaine, cefalexin, ampicillin trihydrate, benzathine penicillin, benzylpenicillin sodium, cefotaxime sodium, Ceftriaxone sodium), three tetracycline (doxycycline hydrochloride, oxytetracycline dehydrate, tetracycline hydrochloride) and two macrolide (azithromycin, erythromycin estolate) antibiotic drugs. Each of these drugs has a unique XRD pattern that makes their identification possible.

### X-ray method for investigation of textile fibers and polymers

Forensic examination of any trace evidence is based upon Locard's exchange principle. This states that *every contact leaves a trace*. In practice, even though a transfer of material has taken place, it may be impossible to detect, because the amount transferred is very small. Textile fibers are a mixture of crystalline and amorphous substances. Therefore the measurement of the degree of crystalline gives useful data in the characterization of fibers using X-ray diffractometry. It has been reported that X-ray diffraction was used to identify of a "crystalline" deposit which was found on a chair. The deposit was found to be amorphous, but the diffraction pattern present matched that of polymethylmethacrylate. Pyrolysismass spectrometry later identified the deposit as polymethylcyanoacrylaon of Boin crystal parameters.

### X-ray method for investigation of bones

Hiller investigated the effects of heating and burning on bone mineral using X-ray diffraction (XRD) techniques. The bone samples were heated in temperature of 500, 700, and 900 C° for 15 and 45 min. The results show bone crystals began to change during the first 15 min of heating at 500 C0 and above. At higher temperatures, thickness and shape of crystals of bones appear stabilized, but when the samples were heated at lower temperature or for shorter period, XRD traces showed extreme changes in crystal parameters.

## Neutron diffraction

**Neutron diffraction** or **elastic neutron scattering** is the application of neutron scattering to the determination of the atomic and/or magnetic structure of a material. A sample to be examined is placed in a beam of thermal or coldneutrons to obtain a diffraction pattern that provides information of the structure of the material. The technique is similar to X-ray diffraction but due to their different scattering properties, neutrons and X-rays provide complementary information: X-Rays are suited for superficial analysis, strong x-rays from synchrotron radiation are suited for shallow depths or thin specimens, while neutrons having high penetration depth are suited for bulk samples.

### *Instrumental and sample requirements*

The technique requires a source of neutrons. Neutrons are usually produced in a nuclear reactor or spallation source. At a research reactor, other components are needed, including a crystal monochromators as well as filters to select the desired neutron wavelength. Some parts of the setup may also be movable. At a spallation source, the time of flight technique is used to sort the energies of the incident neutrons (higher energy neutrons are faster), so no monochromator is needed, but rather a series of aperture elements synchronized to filter neutron pulses with the desired wavelength.

The technique is most commonly performed as powder diffraction, which only requires a polycrystalline powder. Single crystal work is also possible, but the crystals must be much larger than those that are used in single-crystal X-ray crystallography. It is common to use crystals that are about 1 $mm^3$.

Summarizing, the main disadvantage to neutron diffraction is the requirement for a nuclear reactor. For single crystal work, the technique requires relatively large crystals, which are usually challenging to grow. The advantages to the technique are many - sensitivity to light atoms, ability to distinguish isotopes, absence of radiation damage,[2] as well as a penetration depth of several cm.

### *Nuclear scattering*

Like all quantumparticles, neutrons can exhibit wave phenomena typically associated with light or sound. Diffraction is one of these phenomena; it occurs when waves encounter obstacles whose size is comparable with the wavelength. If the wavelength of a quantum particle is short enough, atoms or their nuclei can serve as diffraction obstacles. When a beam of neutrons emanating from a reactor is slowed down and selected properly by their speed, their wavelength lies near one angstrom (0.1 nanometer), the typical separation between atoms in a solid material. Such a beam can then be used to perform a diffraction experiment. Impinging on a crystalline sample it will scatter under a limited number of well-defined angles according to the same Bragg's law that describes X-ray diffraction.

Neutrons and X-rays interact with matter differently. X-rays interact primarily with the electron cloud surrounding each atom. The contribution to the diffracted x-ray intensity is therefore larger for atoms with larger atomic number (Z). On the other hand, neutrons interact directly with the *nucleus* of the atom, and the contribution to the diffracted intensity depends on each isotope; for example, regular hydrogen and deuterium contribute differently. It is also often the case that light (low Z) atoms contribute strongly to the diffracted intensity even in the presence of large Z atoms. The scattering length varies from isotope to isotope rather than linearly with the atomic number. An element like vanadium is a strong scatterer of X-rays, but its nuclei hardly scatter neutrons, which is why it is often used as a container material. Non-magnetic neutron diffraction is directly sensitive to the positions of the nuclei of the atoms.

Unlike X-rays, neutrons scatter mostly from the nuclei of the atoms, which are tiny. Furthermore, there is no need for an atomic form factor to describe the shape of the electron cloud of the atom and the scattering power of an atom does not fall off with the scattering angle as it does for X-rays. Diffractograms therefore can show strong well defined diffraction peaks even at high angles, particularly if the experiment is done at low temperatures. Many neutron sources are equipped with liquid helium cooling systems that allow data collection at temperatures down to 4.2 K. The superb high angle (i.e. high *resolution*) information means that the atomic positions in the structure can be determined with high precision. On the other hand, Fourier maps (and to a lesser extent difference Fourier maps) derived from neutron data suffer from series termination errors, sometimes so much that the results are meaningless.

### *Magnetic scattering*

Although neutrons are uncharged, they carry a spin, and therefore interact with magnetic moments, including those arising from the electron cloud around an atom. Neutron diffraction can therefore reveal the microscopic magnetic structure of a material.[3]

Magnetic scattering does require an atomic form factor as it is caused by the much larger electron cloud around the tiny nucleus. The intensity of the magnetic contribution to the diffraction peaks will therefore decrease towards higher angles.

### *Uses*

Neutron diffraction can be used to determine the static structure factor of gases, liquids or amorphous solids. Most experiments, however, aim at the structure of crystalline solids, making neutron diffraction an important tool of crystallography.

Neutron diffraction is closely related to X-ray powder diffraction.[4] In fact the single crystal version of the technique is less commonly used because currently available neutron sources require relatively large samples and large single crystals are hard or impossible to come by for most materials. Future developments, however, may well change this picture. Because the data is typically a 1D powder diffractogram they are usually processed using Rietveld refinement. In fact the latter found its origin in neutron diffraction (at Petten in the Netherlands) and was later extended for use in X-ray diffraction.

One practical application of elastic neutron scattering/diffraction is that the lattice constant of metals and other crystalline materials can be very accurately measured. Together with an accurately aligned micropositioner a map of the lattice constant through the metal can be derived. This can easily be converted to the stress field experienced by the material.[1] This has been used to analyse stresses in aerospace and automotive components to give just two examples. The high penetration depth permits measuring residual stresses in bulk components as crankshafts, pistons, rails, gears. This technique has led to the development of dedicated stress diffractometers, such as the ENGIN-X instrument at the ISIS neutron source.

Neutron diffraction can also be employed to give insight into the 3D structure any material that diffracts.

Hydrogen, null-scattering and contrast variation

Neutron diffraction can be used to establish the structure of low atomic number materials like proteins and surfactants much more easily with lower flux than at a synchrotron radiation source. This is because some low atomic number materials have a higher cross section for neutron interaction than higher atomic weight materials.

One major advantage of neutron diffraction over X-ray diffraction is that the latter is rather insensitive to the presence of hydrogen (H) in a structure, whereas the nuclei $^1$H and $^2$H (i.e. Deuterium, D) are strong scatterers for neutrons. The greater scattering power of protons and deuterons means that the position of hydrogen in a crystal and its thermal motions can be determined with greater precision by neutron diffraction. The structures of metal hydride complexes, e.g., $Mg_2FeH_6$ have been assessed by neutron diffraction.[7]

The neutron scattering lengths $b_H$ = -3.7406(11) fm[8] and $b_D$ = 6.671(4) fm,[8] for H and D respectively, have opposite sign, which allows the technique to distinguish them. In fact there is a particular isotope ratio for which the contribution of the element would cancel, this is called null-scattering.

It is undesirable to work with the relatively high concentration of H in a sample. The scattering intensity by H-nuclei has a large inelastic component, which creates a large continuous background that is more or less independent of scattering angle. The elastic pattern typically consists of sharp Bragg reflections if the sample is crystalline. They tend to drown in the inelastic background. This is even more serious when the technique is used for the study of liquid structure. Nevertheless, by preparing samples with different isotope ratios it is possible to vary the scattering contrast enough to highlight one element in an otherwise complicated structure. The variation of other elements is possible but usually rather expensive. Hydrogen is inexpensive and particularly interesting because it plays an exceptionally large role in biochemical structures and is difficult to study structurally in other ways.

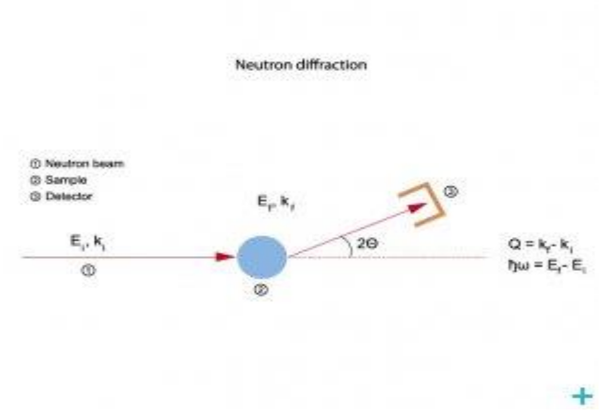
## Neutron difraction

**Neutron diffraction**. **Neutron diffraction** experiments determine the atomic and/or magnetic structure of a material. This **technique** can be applied to study crystalline solids, gasses, liquids or amorphous materials.

**Neutron diffraction** or **elastic neutron scattering** is the application of neutron scattering to the determination of the atomic and/or magnetic structure of a material: A sample to be examined is placed in a beam of thermal, hot or cold neutrons to obtain a diffraction pattern that provides information of the structure of the material.

The technique is similar to X-ray diffraction but due to the different scattering properties of neutrons versus x-rays, complementary information can be obtained. In particular, neutron diffraction is advantageous for the localisation of light atoms and the determination of magnetic ordering.

### *Neutron diffraction principle*



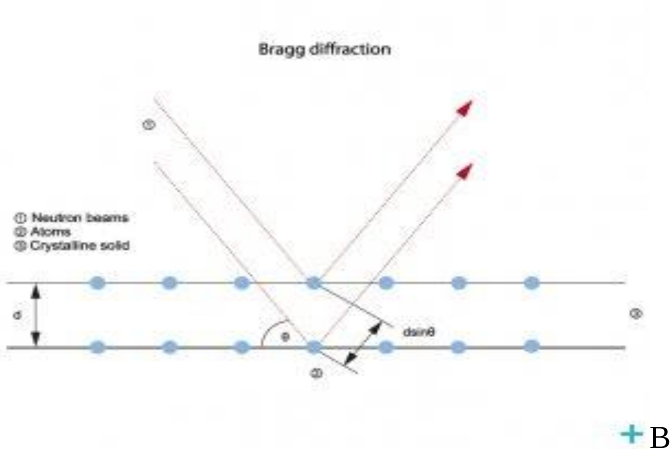
### Neutron diffraction

Neutron diffraction has some unique characteristics when compared to other types of radiation. This makes it very useful for the study of the atomic structure of liquids, amorphous materials and crystalline materials.

Diffraction can see the ordered part of systems, which means, for ordered systems (crystals), their average structure but also deviations from this perfect order; for disordered systems, the ordered portions existing amid this disorder.

Diffraction methods can be divided into two interactions, **nuclear diffraction**: diffraction due to the interaction between neutrons and atomic nuclei, and **magnetic diffraction**: diffraction due to the interaction between the magnetic moments of neutrons and magnetic moments of atoms.

### *Bragg equation*



Bragg diffraction

The measurement principle of neutron diffraction is based on the Bragg Equation. Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings are incident upon a crystalline sample, are scattered in a specular fashion by the atoms in the system, and undergo constructive interference in accordance to Bragg's law.

For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d. Where the scattered waves interfere constructively, they remain in phase since the path length of each wave is equal to an integer multiple of the wavelength. The path difference between two waves undergoing constructive interference is given by $2d\sin\theta$, where $\theta$ is the scattering angle.

This leads to **Bragg's law**, which describes the condition for constructive interference from successive crystallographic planes of the crystalline lattice:

$$2d\cdot\sin(\theta)=n\lambda$$

Where n is an integer determined by the order given, and $\lambda$ is the wavelength.

***Diffraction methods and their applications:***

Powder diffraction:

- Refinement of crystallographic or magnetic structure on polycrystalline materials
- Phase transformations and reaction pathways as a function of external parameters (temperature, magnetic or electric field, mechanical strain or pressure)

Single-crystal diffraction :

- Refinement of crystallographic or magnetic structure on polycrystalline materials
- Structure solution on complex systems or proteins

Strain/ texture analysis:

- Analysis of residual strain on engineering materials
- Analysis of texture on engineering materials (Can be found at BER II , NPL.)

Diffuse scattering:

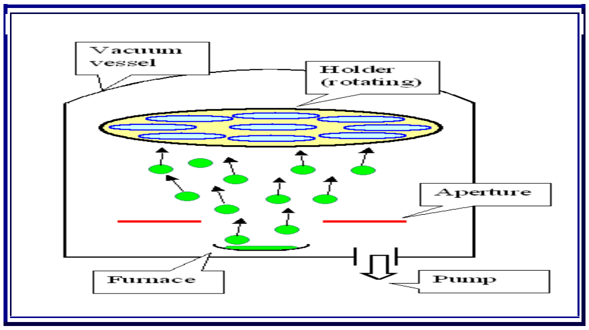
- Investigation of non-crystalline structures: liquids, amorphous materials
- Disorder and short-range in crystals

## Miscellaneous techniques

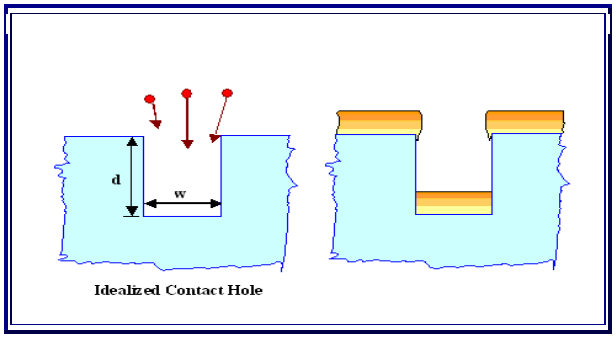
### Miscellaneous Techniques and Comparison

### Evaporation

- By now you may have wondered why the time-honored and widely used technique of evaporation has not been mentioned in context with **Si** technology.
  - The answer is simple: *It is practically not used*. This is in contrast to other technologies, notably optics, where evaporation techniques played a major role.
  - In consequence, this paragraph shall be kept extremely short. It mainly serves to teach you that there are more deposition techniques than meets the eye (while looking at a chip).
- What is the evaporation technique? If your eye glasses or your windshield ever fogged, you have seen it: Vapor condenses on a cold substrate.



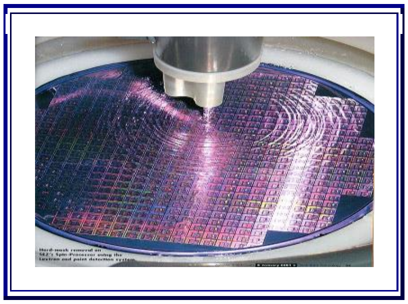
  - What works with water vapor also works with all other vapors, especially metal vapor.
  - All you have to do is to create the vapor of your choice, always inside a vacuum vessel kept at a good vacuum. The (usually) metal atoms will leave the crucible or "boat" with an kinetic energy of a few **eV** and sooner or later will condense on the (cooled) substrate (and everywhere else if you don't take special precautions).
  - Your substrate holder tends to be big, so you can accommodate several wafers at once (Opening up and loading vacuum vessels takes expensive time!)
- The technique is relatively simple (even taking into account that the heating nowadays is routinely done with high power electron beams hitting the material to be evaporated), but has major problems with respect to **IC** production:
  - The atoms are coming from a "point source", i.e. their incidence on the substrate is nearly perpendicular. Our typical contact hole filling problem thus looks like this:



Idealized Contact Hole

  - In other words: Forget it!
  - It is also clear that it is very difficult to outright impossible to produce layers with arbitrary composition, e.g. **Al** with **0,3% Si** and **0,5% Cu**. You would need three independently operated furnaces to produce the right mix.
- All things considered, sputtering is usually better and evaporation is rarely used nowadays for microelectronics.

**Spin-on Techniques**



- **Spin-on techniques**, a special variant of so-called *sol-gel techniques*, start with a liquid (and usually rather viscous) source material, that is "painted" on the substrate and subsequently solidified to the material you want.
  - The "*painting*" is not done with a brush (although this would be possible), but by spinning the wafer with some specified **rpm** value (typically **5000 rpm**) and dripping some of the liquid on the center of the wafer. Centrifugal forces will distribute the liquid evenly on the wafer and a thin layer (typically around **0,5 µm**) is formed.
  - Solidification may occur as with regular paint: the solvent simply evaporates with time. This process might be accelerated by some heating. Alternatively, some chemical reaction might be induced in air, again helped along by some "baking" as it is called.
- As a result you obtain a thin layer that is rather smooth - nooks and crannies of the substrate are now planarized to some extent. The film thickness can be precisely controlled by the angular velocity of the spin process (as a function of the temperature dependent viscosity of the liquid).
  - Spin-on coating is the technique of choice for producing the light-sensitive **photo resist** necessary for lithography. The liquid resist rather resembles some viscous paint, and the process works very well. It is illustrated on the right.
  - Most other materials do not have suitable liquid precursors, the spin-on technique thus can not be used.
- A noteworthy exception, however, is **spin-on glass**, a form of **SiO$_2$**mentioned before.

  - The liquid consists basically of Silicon-tetra-acetate (**$Si(CH_2COOH)_4$**) (and some secret additions) dissolved in a solvent. It will solidify to an electronically not-so-good **$SiO_2$** layer around **200 °C**.
  - Using spin-on glass is about the only way to fill the interstices between the **Al** lines with a dielectric at low temperatures. The technique thus has been developed to an art, but is rather problematic. The layers tend to crack (due to shrinkage during solidifications), do not adhere very well, and may interact detrimentally with subsequent layers.
- A noteworthy example of a material that can be "spun on", but nevertheless did not make it so far are **Polyimides**, i.e. polymers that can "take" relatively high temperatures
  - They look like they could be great materials for the intermetal dielectric - low □$_r$, easy deposition, some planarizing intrinsic to spin-on, etc. They are great materials - but still not in use. If you want to find out why, and how new materials are developed in the real world out there, use this link.

### Other Methods

- Deposition techniques for thin layers is a rapidly evolving field; new methods are introduced all the time. In the following a couple of other techniques are listed with a few remarks
- **Molecular Beam Epitaxy** (***MBE***). Not unlike evaporation, except that only a few atoms (or molecules) are released from a tricky source (an "effusion cell") at a time.
  - **MBE** needs ultra-high vacuum conditions - i.e. it is very expensive and not used in **Si-IC** manufacture. **MBE** can be used to deposit single layers of atoms or molecules, and it is relatively easy to produce multi layer structures in the **1 nm** region. An example of a **Si-Ge** multilayer structure is shown in the link
  - **MBE** is the method of choice for producing complicated epitaxial layer systems with different materials as needed, e.g., in advanced optoelectronics or for superconducting devices. An example of what you can produce with **MBE** is shown in the link
- **Laser Ablation**. Not unlike sputtering, except that the atoms of the target are released by hitting it with an intense Laser beam instead of **Ar** ions extracted from a Plasma.
  - Used for "sputtering" ceramics or other non conducting materials which cannot be easily sputtered in the conventional way.
- **Bonding techniques**. If you bring two ultraflat**Si** wafers into intimate contact without any particles in between, they will just stick together. With a bit of annealing, they fuse completely and become bonded.
  - Glass blowers have done it in a crude way all the time. And of course, in air you do not bond **Si** to **Si**, but **$SiO_2$** to **$SiO_2$**. One way to use this for applications is to produce a defined **$SiO_2$** layer first, bond the oxidized wafer to a **Si** wafer, then polish off almost all of the **Si** except for a layer about **1 µm** thick
  - Now you have a regular wafer coated with a thin oxide and a perfect single crystalline **Si** layer - a so-called "**silicon on insulator**" (***SOI***) structure. The **Si** industry in principle would love **SOI** wafers - all you have to do to become rich immediately, is to make the process cheap. But that will not be easy. You may want to check why **SOI** is a hot topic, and how a major company is using wafer bonding plus some more neat tricks, including mystifying electrochemistry, to make **SOI** affordable.
  - Bonding techniques are rather new; it remains to be seen if they will conquer a niche in

the layer deposition market.

- **Galvanic techniques**, i.e. electrochemical deposition of mostly metals. Galvanizing materials is an old technique (think of chromium plated metal, anodized aluminium, etc.) normally used for relatively thick layers.
  - It is a "dirty" process, hard to control, and still counted among the black arts in materials science. No self-respecting **Si** process engineer would even dream of using galvanic techniques - except that with the advent of **Cu** metallization he was not given a choice.
  - Using **Cu** instead of **Al** for chip metallization was unavoidable for chips hitting the market around **1998** and later - the resistivity of the **Al** was too high.
  - As it turned out, established techniques are no good for **Cu** deposition - galvanic deposition is the method of choice. **Cu** metallization calls for techniques completely different from Al metallization - the catchword is "damascene technology". The link takes you there - you may also enjoy this module from the *"Defects" Hyperscript* because it contains some other interesting stuff in the context of (old) materials science.
- And not to forget: Galvanic techniques are also used in the packaging of chips

### Comparison of Various Layer Deposition processes

- *First*, lets look at **edge coverage**, i.e. the dependence on layer thickness on the topography of the substrate. This is best compared by looking at the ability to fill a small contact hole with the layer to be deposited.

- *Second*, lets look at what you can deposit.
  - **CVD** methods are limited to materials with suitable gaseous precursors. While it is not impossible to deposit mixtures of materials (as done, e.g. with doped poly **Si** or flow glass), it will not generally work for arbitrary compositions.
  - Sputter methods in practice are limited to conducting materials - metals, semiconductors, and the like. Arbitrary mixtures can be deposited; all you have to do is make a suitable target. The target does not even have to be homogeneous; you may simply assemble it by arranging pie-shaped wedges of the necessary materials in the required composition into a "cake" target.
  - Evaporation needs materials that can be melted and vaporized. Many compounds would decompose, and some materials simply do not melt (try it with **C**, e.g.). If you start with a mixture, you get some kind of distillation - you are only going to deposit the material with the highest vapor pressure. Mixtures thus are difficult and can only be produced by co-evaporation from different sources.

## POSSIBLE QUESTIONS

## UNIT-III

## PART- A (Each carry one mark)

1. Who argued that mechano synthesis is impossible due to the difficulties in mechanically manipulating individual molecules?
(a)Richard Feynman (b) Eric Drexler
(c)Norio Taniguchi **(d) Richard Smalley**

2. Which one is a type of felectron microscopethat produces images of a sample by scanning it with a focused beam of electrons?
(a) Scanning tunneling microscope **(b)scanning electron microscope**
(c) transmission electron microscope (d)scanning probe microscope

3. Which type of microscope has useful magnification limit of about 1,000X ?
(a)scanning electron microscope **(b) light microscope**
(c)scanning probe microscope (d) transmission electron microscope

4. Scanning electron microscope can achieve resolution better than?
**(a)1 nanometer** (b)2 nanometer (c)3 nanometer (d)<1 nanometer

5. Which type of microscope uses electrons to provide a three-dimensional view of the surface of the object?
(a) Scanning tunneling microscope **(b) Scanning electron microscope**
(c) Atomic force microscope (d) Transmission electron microscopy

6. TEM" refers to a photomicrograph taken by a
(a) Scanning tunneling microscope (b) Scanning electron microscope
(c) Atomic force microscope **(d) Transmission electron microscopy**

7. Transmission electron microscopy is best for high magnification viewing of
**(a) internal structure of fixed cells.** (b)internal structure of live, motile cells.
(c) surface structure of fixed cells. (d) surface membranes of live, motile cells.

8. The first commercial Transmission electron microscopy in?
(a) 1937 (b) 1938 (c) 1936 **(d) 1939**

9. Molecule manufacturing is sometimes called?
(a)Nano biology (b) Molecular chemistry
(b)Molecular nanotribology **(d) Molecular Nanotechnology**

10. Which type of microscope uses electrons to provide a three-dimensional view of the surface of the object?
**(a) Scanning electron microscope** (b)Light microscope
(c) Transmission electron microscope (d) Scanning probe microscope

11. When the term "nanotechnology" was independently coined and popularized by?
(a) Richard Feynman **(b) Eric Drexler**
(c) Norio Taniguchi (d) Micheal farady

12. Who argued that mechano synthesis is impossible due to the difficulties in mechanically manipulating individual molecules?
(a)Richard Feynman (b) Eric Drexler
(c) Norio Taniguchi **(d) Richard Smalley**

13. In sol-gel process removal of the liquid from the sol yields the gel, and the sol/gel transition

controls the ------
(a) Process **(b) Particle size and shape** (c) Partical size (d) Partical shape

14. In scanning electron microscope the most common mode of detection is by secondary electrons emitted by atoms excited by the ?
(a) electron detector **(b) electron beam** (c) recorder (d) amblifier

15. Which of the following is an instrument for imaging surfaces at the atomic level
**(a) scanning tunneling microscope** (b) scanning electron microscope
(c) Transmission electron microscopy (d) scanning probe microscope

16. Which one of the microscopy is capable of imaging at a significantly higher resolution than light microscopy?
(a)Scanning tunneling microscope (b) Scanning electron microscope
**(c)Transmission electron microscopy** (d) Atomic force microscope

17. Which one of the method is specifically suitable for the preparation of ultrapure and non-Agglomerated nanoparticles of metal?
**(a) Microwave Plasma Processing** (b) Sputtered Plasma Processing
(c) CVD processing (d) CVC Processing

18.Inventors of scanning tunneling microscope is?
(a)Richard Feynman and Norio Taniguchi (b) Richard Smalley and Eric Drexler
**(c)Gerd Binnig and Heinrich Rohrer** (d) Norio Taniguchi and Eric Drexler

19. The scanning tunneling microscope is based on the concept of ?
(a)scattering (b)transmission **(c) Guantum tunneling** (d) absorption

20. Transmission electron microscopy is best for high magnification viewing of
**(a)Internal structure of fixed cells.** (b) internal structure of live, motile cells.
(c) surface structure of fixed cells. (d) surface membranes of live, motile cells.

## PART- B (Each Carry six mark)

1.Explain briefly about the Instrumentation and working principle of Transmission electron microscope.

2. Explain briefly about working principle of electron probe microscopy and its applications.

3. Write short notes on Transmission electron microscope.

4.Explain the Instrumentation and working principle of X-Ray diffraction techniques.

5. Discuss the working principle of electron probe microscopy and its applications.

6.Write notes on Neutron diffraction technique.

7. Explain briefly about the Instrumentation and working principle of TEM.

## PART- C (Ten mark)

1. What are nano Particles? Explain briefly about the Instrumentation and working principle of TEM.

2. Explain the Instrumentation and working principle of X-Ray diffraction techniques.

3. Explain the advantages and disadvantages of using nanoparticles in various fields.

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**(Deemed University Established Under Section 3 of UGC Act 1956)**

**COIMBATORE-21**

## DEPARTMENT OF CHEMISTRY

## M.Sc CHEMISTRY

| | | |
|---|---|---|
| Name of the Staff | : | Dr. M. MAKESWARI |
| Department | : | Chemistry |
| Subject | : | Nano Chemistry |
| Subject Code | : | 16CHP304 |
| Class | : | II M.Sc-Chemistry |
| Year and Semester | : | II / III |

## UNIT-III

### UNIT II –OBJECTIVE QUESTIONS FOR ONLINE EXAMINATION (Each carry one mark)

| S. No | Questions | Option 1 | Option 2 | Option 3 | Option 4 | Answer |
|---|---|---|---|---|---|---|
| 1 | The full form of STM is… | Scanning Tunneling Microscope | Scientific Technical Microscope | Systematic Technical Microscope | Super Tensile Microscope | **Scanning Tunneling Microscope** |
| 2 | What does ‘F’ stand for in AFM? | Fine | Front | Force | Flux | **Force** |
| 3 | A high-powered microscope that produces an image from scattered secondary electrons is the | Immune fluorescence microscope | Bright-field light microscope | transmission electron microscope | scanning electron microscope | scanning electron microscope |

| | | | | | | |
|---|---|---|---|---|---|---|
| **4** | Nanotechnology refers to the projected ability to construct items? | Bottom down | Bottom up and down | Bottom up | Bottom up or down | Bottom up |
| **5** | Molecule manufacturing is sometimes called? | Nano biology | Molecular chemistry | Molecular nanotribology | Molecular Nanotechnology | Molecular Nanotechnology |
| **6** | Which type of microscope uses electrons to provide a three-dimensional view of the surface of the object? | Scanning electron microscope | Light microscope | Transmission electron microscope | Scanning probe microscope | Scanning electron microscope |
| **7** | Who argued that mechano synthesis is impossible due to the difficulties in mechanically manipulating individual molecules? | Richard Feynman | Eric Drexler | Norio Taniguchi | Richard Smalley | Richard Smalley |
| **8** | Which oneis a type of electron microscopethat produces images of a sample by scanning it with a focused beam of electrons? | Scanning tunneling microscope | scanning electron microscope | transmission electron microscope | scanning probe microscope | scanning electron microscope |
| **9** | Which type of microscope has useful magnification limit of about 1,000X ? | scanning electron microscope | light microscope | scanning probe microscope | transmission electron microscope | light microscope |
| **10** | Scanning electron microscope can achieve resolution better than ? | 1 nanometer | 2 nanometer | 3 nanometer | <1 nanometer | 1 nanometer |
| **11** | In scanning electron microscope the most common mode of detection is by secondary electrons emitted by atoms excited by the ? | electron detector | electron beam | recorder | amblifier | electron beam |
| **12** | Which of the following is an instrument for imaging surfaces at the atomic level | scanning tunneling microscope | scanning electron microscope | Transmission electron microscopy | scanning probe microscope | scanning tunneling microscope |
| **13** | The scanning tunneling microscope can be used not only in ultra-high vacuum but also in? | air | acid | solid | air and solid | air |
| **14** | The scanning tunneling microscope can be used not only in ultra-high vacuum but also in air, water, and various other liquid or gas ambient, and at temperatures ranging from________? | 1 Kelvin | >1 Kelvin | 5 Kelvin | zero Kelvin | 1 Kelvin |

| | | | | | | |
|---|---|---|---|---|---|---|
| **15** | Inventors of scanning tunneling microscope is? | Richard Feynman and Norio Taniguchi | Richard Smalley and Eric Drexler | Gerd Binnig and Heinrich Rohrer | Norio Taniguchi and Eric Drexler | Gerd Binnig and Heinrich Rohrer |
| **16** | The scanning tunneling microscope is based on the concept of? | scattering | transmission | Guantum tunneling | absorption | Guantum tunneling |
| **17** | All of the following are aspects of scanning electron microscopy EXCEPT? | Whole specimens can be observed | secondary electrons are used to visualize the specimen | specimens must be placed into a vacuum | scanning electron micrographs typically appear two-dimensional | scanning electron micrographs typically appear two-dimensional |
| **18** | Scanning electron microscopy is most often used to reveal ? | surface structures | internal structures | both surface and internal structures simultaneously | either surface or internal structures, but not simultaneously | surface structures |
| **19** | Which one of the following is capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons? | Scanning tunneling microscope | scanning electron microscope | Transmission electron microscopy | atomic force microscope | Transmission electron microscopy |
| **20** | Scanning electron microscopy (SEM) is best used to study? | Surface morphology | surface structures | internal structures | small internal cell structures | surface morphology |
| **21** | The first Transmission electron microscopy was built by Max knoll and Ernst Ruska in ? | 1932 | 1930 | 1931 | 1933 | 1931 |
| **22** | The first commercial Transmission electron microscopy in ? | 1937 | 1938 | 1936 | 1939 | 1939 |
| **23** | The first Transmission electron microscopy was built by? | Max knoll and Ernst Ruska | Richard Feynman and Norio Taniguchi | Richard Smalley and Eric Drexler | Gerd Binnig and Heinrich Rohrer | Max knoll and Ernst Ruska |
| **24** | Who shown that the friction force scan images are found to be more similar to the 3D plot of slope of the roughness scan? | Bhushan | Richard Feynman | Norio Taniguchi | Richard Smalley | Bhushan |
| **25** | The adhesive force, F = ? | BC x t | CB x k | BC x p | BC x k | BC x k |
| **26** | Scratching and wear, a single crystal diamond tip is used in? | Individual mode | Contact mode | Non individual mode | Individual and contact mode | Contact mode |
| **27** | Nano-indentation is important measurement in? | Nano biology | Nano technology | Nano triology | Nano tribology | Nano tribology |

| | | | | | | |
|---|---|---|---|---|---|---|
| **28** | Where the projected area of indent is the area of the indent projected on to a plane? | Parallel to the tip | Bottom to the tip | Perpendicular to the tip | Side to the tip | Perpendicular to the tip |
| **29** | The AFM relies on a scanning technique to produce ? | Two- dimensional images | Four-dimensional images | Three-dimensional images | Dimensional images | Three-dimensional images |
| **30** | The AFM relies on a scanning technique to produce three-dimensional images of sample surfaces of ? | Resolution | Low resolution | High resolution | Medium resolution | High resolution |
| **31** | AFM can be used measure the ? | Ultra-small forces | Small forces | Ultra high forces | High forces | Ultra-small forces |
| **32** | In atomic force microscope the force sensor is a contact type with a tip mounted on a cantilever and a sensor to detect the deflection of the lever at the ? | Top | Side | Tip | Bottom | Tip |
| **33** | John pethica and co=workers have made useful contributions to the study of ? | Nano indentation | Nano technology | Nano triology | Nano tribology | Nano indentation |
| **34** | This having a digitally calculated feedback system which can perform force spectroscopy on a sample in order to map out the local stiffness of the sample in addition to providing the topography of the sample? | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Atomic force microscope |
| **35** | Which one of the following is consists of a three-dimensional piezoelectric scanner, scanning either the sample or a force sensor? | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Atomic force microscope |
| **36** | A microscope consists of a three-dimensional piezoelectric scanner, scanning either the sample or a force sensor? | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Atomic force microscope |
| **37** | Which one of the microscopy is capable of imaging at a significantly higher resolution than light | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Transmission electron microscopy |

| | | | | | | |
|---|---|---|---|---|---|---|
| | microscopy? | | | | | |
| **38** | Which one of the microscope analysis the small de Broglie wave length of the electrons? | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Transmission electron microscopy |
| **39** | Surface morphology can be best studied using | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Scanning electron microscope |
| **40** | Surface structures can be best studied using | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Scanning electron microscope |
| **41** | Three-dimensional images can be best studied using | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Atomic force microscope |
| **42** | A high-powered microscope that produces an image from scattered secondary electrons is the | Immunofluorescence microscope | Bright-field light microscope | Aransmission electron microscope | Scanning electron microscope | Scanning electron microscope |
| **43** | A microscope in which an image is formed by passing an electron beam through a specimen and focusing the scattered electrons with magnetic lenses is called a | Scanning tunneling microscope | Scanning electron microscope | Transmission electron microscopy | Atomic force microscope | Transmission electron microscopy |
| **44** | Transmission electron microscopy is best for high magnification viewing of | Internal structure of field cells | Internal structure of motile cell | Surface structure of field cells | Surface structure of motile cell | Internal structure of field cells |
| **45** | The scanning electron microscope has a magnification that ranges from | 1x to 100x | 100x to 10,000x | 10x to 100,000x | 10x to 10,000x | 10x to 100,000x |
| **46** | Which one is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons? | Scanning tunneling microscope | scanning electron microscope | transmission electron microscope | scanning probe microscope | **scanning electron microscope** |
| **47** | The first Transmission electron microscopy was built by Max knoll and Ernst Ruska in ? | 1932 | 1930 | 1931 | 1933 | **1931** |
| **48** | The first commercial Transmission electron microscopy in ? | 1937 | 1938 | 1936 | 1939 | **1939** |
| **49** | Which type of microscope uses electrons to provide a three-dimensional view of the surface of the object? | Scanning tunneling microscope | Scanning electron microscope | Atomic force microscope | Transmission electron microscopy | **Scanning electron microscope** |
| **50** | TEM" refers to a | Scanning tunneling | Scanning electron | Atomic force | Transmission | **Transmission** |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | microscope | microscope | microscope | electron microscopy | **electron microscopy** |
| **51** | Transmission electron microscopy is best for high magnification viewing of | Internal structure of fixed cells. | Internal structure of live, motile cells. | Surface structure of fixed cells. | Surface membranes of live, motile cells. | **Internal structure of fixed cells.** |
| **52** | Which of the following statements about Transmission Electron Microscopy is not true. | **The specimen must be stained with osmium or other heavy metal.** | The specimens are placed in a high vacuum for viewing. | The beam is focused by electromagnetic lenses. | The specimens must be sliced very thin, 20-100 nm in thickness. | **The specimen must be stained with osmium or other heavy metal.** |
| **53** | Nano composite materials can be analysed by | Neutron diffraction | X-Ray diffraction | Scanning tunneling microscope | Scanning electron microscope | Neutron diffraction |
| **54** | Neutron diffraction is used to analyse | Nano composite materials | Crystals | Organic compounds | Inorganic compounds | Nano composite materials |
| **55** | Light element materials are analysed using | Neutron diffraction | X-Ray diffraction | Scanning tunneling microscope | Scanning electron microscope | Neutron diffraction |
| **56** | Neutron diffraction is used to analyse | Light element materials | Crystals | Organic compounds | Inorganic compounds | Light element materials |
| **57** | The first neutron diffraction experiments were carried out in | 1945 | 1954 | 1935 | 1964 | **1945** |
| **58** | The first neutron diffraction experiments were carried out in 1945 by the scientist | Norio Taniguchi | Ernest O. Wollan | Eric Drexler | Gerd Binnig | Ernest O. Wollan |

# LECTURE NOTES

## UNIT-V

## SYLLABUS

Applications of nanoparticle in various fundamental research, industries, medical field and environmental issue; toxicity, biosafety and ethical issue in application of nanoparticle

### Introduction of nanoparticles

Nanoparticles are particles between 1 and 100 nanometers in size. In nanotechnology, a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties. Particles are further classified according to diameter. Ultrafine particles are the same as nanoparticles and between 1 and 100 nanometers in size, fine particles are sized between 100 and 2,500 nanometers, and coarse particles cover a range between 2,500 and 10,000 nanometers. Scientific research on nanoparticles is intense as they have many potential applications in medicine, physics, optics, and electronics. The U.S. National Nanotechnology Initiative offers government funding focused on nanoparticle research.

### Nanoclusters

Nanoclusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution. Nanopowders are agglomerates of ultrafine particles, nanoparticles, or nanoclusters. Nanometer-sized single crystals, or single-domain ultrafine particles, are often referred to as nanocrystals.

### Uniformity

The chemical processing and synthesis of high-performance technological components for the private, industrial, and military sectors requires the use of high-purity ceramics (oxide ceramics, such as aluminium oxide or copper(II) oxide), polymers, glass-ceramics, and composite materials, as metal carbides (SiC), nitrides (Aluminum nitrides, Silicon nitride), metals (Al, Cu), non-metals (graphite, carbon nanotubes) and layered (Al + Aluminium carbonate, Cu + C). In condensed bodies formed from fine powders, the irregular particle sizes and shapes in a typical powder often lead to non-uniform packing morphologies that result in packing density variations in the powder compact.

Uncontrolled agglomeration of powders due to attractive van der Waals forces can also give rise to microstructural heterogeneity. Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed, and thus highly dependent upon the distribution of porosity. Such stresses have been associated with a plastic-to-brittle transition in consolidated bodies, and can yield to crack propagation in the unfired body if not relieved.

In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role in the sintering process by growing and thus limiting end-point densities. Differential stresses arising from inhomogeneous densification have also been shown to result in the propagation of internal cracks, thus becoming the strength-controlling flaws.

Inert gas evaporation and inert gas deposition are free many of these defects due to the distillation (cf. purification) nature of the process and having enough time to form single crystal particles, however even their non-aggreated deposits have lognormal size distribution, which is typical with nanoparticles. The reason why modern gas evaporation techniques can produce a relatively narrow size distribution is that aggregation can be avoided. However, even in this case, random residence times in the growth zone, due to the combination of drift and diffusion, result in a size distribution appearing lognormal.

It would, therefore, appear desirable to process a material in such a way that it is physically uniform with regard to the distribution of components and porosity, rather than using particle size distributions that will maximize the green density. The containment of a uniformly dispersed assembly of strongly interacting particles in suspension requires total control over interparticle forces. Monodisperse nanoparticles and colloids provide this potential.

Monodisperse powders of colloidal silica, for example, may therefore be stabilized sufficiently to ensure a high degree of order in the colloidal crystal or polycrystalline colloidal solid that results from aggregation. The degree of order appears to be limited by the time and space allowed for longer-range correlations to be established. Such defective polycrystalline colloidal structures would appear to be the basic elements of submicrometer colloidal materials science and, therefore, provide the first step in developing a more rigorous understanding of the mechanisms involved in microstructural evolution in high performance materials and components.

## Properties of nano particles

Nanoparticles are of great scientific interest as they are, in effect, a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of the surface in relation to the percentage of the volume of a material becomes significant. For bulk materials larger than one micrometer (or micron), the percentage of the surface is insignificant in relation to the volume in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.

Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects.

For example, gold nanoparticles appear deep-red to black in solution. Nanoparticles of yellow gold and grey silicon are red in color. Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C);. Absorption of solar radiation is much higher in materials composed of nanoparticles than it is in thin films of continuous sheets of material. In both solar PV and solar thermal applications, controlling the size, shape, and material of the particles, it is possible to control solar absorption.

Other size-dependent property changes include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. What would appear ironic is that the changes in physical properties are not always desirable. Ferromagnetic materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage.

Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid.

The high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. In theory, this does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters. Moreover, nanoparticles have been found to impart some extra properties to various day to day products. For example, the presence of titanium dioxide nanoparticles imparts what we call the self-cleaning effect, and, the size being nano-range, the particles cannot be observed. Zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions, is completely photostable and toxic.

Clay nanoparticles when incorporated into polymer matrices increase reinforcement, leading to stronger plastics, verifiable by a higher glass transition temperature and other mechanical property tests. These nanoparticles are hard, and impart their properties to the polymer (plastic). Nanoparticles have also been attached to textile fibers in order to create smart and functional clothing.

Metal, dielectric, and semiconductor nanoparticles have been formed, as well as hybrid structures (e.g., core–shell nanoparticles). Nanoparticles made of semiconducting material may also be labeled quantum dots if they are small enough (typically sub 10 nm) that quantization of electronic energy levels occurs. Such nanoscale particles are used in biomedical applications as drug carriers or imaging agents.

Semiconductor nanoparticle (quantum dot) of lead sulfide with complete passivation by oleic acid, oleyl amine and hydroxyl ligands (size ~5nm)

Semi-solid and soft nanoparticles have been manufactured. A prototype nanoparticle of semi-solid nature is the liposome. Various types of liposome nanoparticles are currently used clinically as delivery systems for anticancer drugs and vaccines.

Nanoparticles with one half hydrophilic and the other half hydrophobic are termed Janus particles and are particularly effective for stabilizing emulsions. They can self-assemble at water/oil interfaces and act as solid surfactants.

Hydrogel nanoparticles made of N-isopropylacrylamide hydrogel core shell can be dyed with affinity baits, internally. These affinity baits allow the nanoparticles to isolate and remove undesirable proteins while enhancing the target analytes.

## Applications of Nano particles

If one thinks about possible applications of nanoparticles, then the first thought is usually that it has to be sophisticated; some type of high-tech product. Therefore it might be surprising that large scale applications of nanoparticles entered our daily lives decades ago, and they are not particularly spectacular. A prominent example along these lines is carbon black. It is an amorphous powder, consisting of nanoparticles in the size range of typically 20–50 nm. Its annual industrial production amounts to an unbelievable 10 million metric tons, worldwide. Over 90% of carbon black is used for the reinforcement of rubber, mainly car tires. It is produced by the incomplete combustion of heavy aromatic oil or natural gas.

A completely different application of nanoparticles is in food products. Amorphous silica nanoparticles are used as anti-caking agent to maintain the flow properties in powder products (*e.g.*, instant soups) and to thicken pastes The conventional form of amorphous silica is known as food additive E551. Like in the case of many other nanopowders, it is controversially debated, whether E551 is a nanomaterial or not, because during the production process the nanosized primary particles agglomerate to larger structures. From a characterization point of view, it is often very difficult to distinguish primary particles from aggregates or agglomerates.

Another major application of nanoparticles is in cosmetics, especially in sunscreens. Sunscreens contain titanium dioxide and zinc oxide nanoparticles, because they are colorless and reflect/scatter ultraviolet light more efficiently than larger particles. The small size of nanoparticles provides the benefit of making them transparent, which results in better consumer acceptance and thus improves the protection of human skin against UV-induced damage.

Amazingly, taking advantage of optical effects to improve the appearance of materials is still a major application of nanoparticles, just as in ancient times. A prominent example is automotive coatings, which consist of several layers. The two topmost layers are the colored base coat and the clear coat which protects the paint from the environment. Mercedes-Benz brought nanoparticle-based clearcoat into series production for both metallic and non-metallic paint finishes by the end of 2003. The coating fulfills a practical and an esthetical role. On the one hand it increases the scratch resistance, and on the other hand it visibly enhances the gloss Liquid magnets, so-called ferrofluids, represents another example of nanoparticles at work.

In addition to these mass applications, selected nanoparticles have found their way into more sophisticated, high-tech products. However, the timeline from the discovery in the laboratory to a commercial product is typically very long. For example, from the first report on the use of titanium dioxide nanoparticles in a dye-sensitized solar cell. it took more than 20 years to develop a commercially available product. In summer 2012 the hardware manufacturer Logitech brought an external iPad keyboard on the market, which is powered by any light, representing the first major commercial use of dye-sensitized solar cells.

## Applications of nano particles in Medicine

One highly researched application of nanochemistry is medicine. A simple skin-care product using the technology of nanochemistry is sunscreen. Sunscreen contains nanoparticles of zinc oxide and titanium dioxide. These nano chemicals protect the skin against harmful UV light by absorbing or reflecting the light and prevent the skin from retaining full damage by photoexcitation of electrons in the nanoparticle. Effectively, the excitation of the particle blocks skin cells from DNA damage.

## Drug Delivery

Emerging methods of drug delivery involving nanotechnological methods can be advantageous by improving increased bodily response, specific targeting, and efficient, non-toxic metabolism. Many nanotechnological methods and materials can be functionalized for drug delivery. Ideal materials employ a controlled-activation nanomaterial to carry a drug cargo into the body. Mesoporous silica nanoparticles (MSN) have been increasing in research popularity due to its large surface area and flexibility for various individual modifications while demonstrating high resolution performance under imaging techniques. Activation methods greatly vary across nanoscale drug delivery molecules, but the most commonly used activation method uses specific wavelengths of light to release the cargo. Nanovalve-controlled cargo release uses low intensity light and plasmonic heating to release the cargo in a variation of MSN containing gold molecules. ]The two-photon activated photo-transducer (2-NPT) uses near IR wavelengths of light to induce breaking of a disulfide bond to release the cargo. Recently, nanodiamonds have demonstrated potential in drug delivery due to non-toxicity, spontaneous absorption through the skin, and ability to enter the blood-brain barrier.

## Tissue Engineering

Because cells are very sensitive to nanotopographical features, optimization of surfaces in tissue engineering has pushed the frontiers towards implantation. Under the appropriate conditions, a carefully crafted 3-dimensional scaffold is used to direct cell seeds towards artificial organ growth. The 3-D scaffold incorporates various nanoscale factors that control the environment for optimal and appropriate functionality. The scaffold is an analog of the in vivo extracellular matrix in vitro, allowing for successful artificial organ growth by providing the necessary, complex biological factors in vitro. Additional advantages include the possibility of cell expression manipulation, adhesion, and drug delivery.

### Wounds

For abrasions and wounds, nanochemistry has demonstrated applications in improving the healing process. Electrospinning is a polymerization method used biologically in tissue engineering, but can be functionalized for wound dressing as well as drug delivery. This produces nanofibers which encourage cell proliferation, antibacterial properties, and controlled environment. These properties have been created in macroscale; however, nanoscale versions may show improved efficiency due to nanotopographical features. Targeted interfaces between nanofibers and wounds have higher surface area interactions and are advantageously in vivo.

There is evidence certain nanoparticles of silver are useful to inhibit some viruses and bacteria.

New developments in nanochemistry provide a variety of nanostructure materials with significant properties that are highly controlable. Some of the application of these nanostructure materials include SAMs and lithography, use of nanowires in sensors, and nanoenzymes.

### Electrics

### Nanowire Compositions

Scientist also devised a large number of nanowire compositions with controlled length, diameter, doping, and surface structure by using vapor and solution phase strategies. These oriented single crystals are being used in semiconductor nanowire devices such as diodes, transistors, logic circuits, lasers and sensors. Since nanowires have one dimensional structure meaning large surface to volume ratio, the diffusion resistance decreases. In addition, their efficiency in electron transport which is due to the quantum confinement effect, make their electrical properties be influenced by minor perturbation.Therefore, use of these nanowires in nanosensor elements increases the sensitivity in electrode response. As mentioned above, one dimensionality and chemical flexibility of the semiconductor nanowires make them applicable in nanolasers. Peidong Yang and his co-workers have done some research on room-temperature ultraviolet nanowire nanolasers in which the significant properties of these nanolasers have been mentioned. They have concluded that using short wavelength nanolasers have applications in different fields such as optical computing, information storage, and microanalysis.

### Catalysis

### Nanoenzymes

Nanostructure materials mainly used in nanoparticle-based enzymes have drawn attraction due to the specific properties they show. Very small size of these nanoenzymes (1-100 nm) have provided them unique optical, magnetic, electronic, and catalytic properties. Moreover, the control of surface functionality of nano particles and predictable nanostructure of these small sized enzymes have made them to create a complex structure on their surface which in turn meet the needs of specific applications.

### Areas where nanotechnology is used

Today, a life without nanotechnology is hard to imagine. Nanotechnologies – to be more specific: nanomaterials – are already used in numerous products and industrial applications. Our Nanotechnology Products and Applications database already provides an overview of how nanomaterials and nanostructuring applications are used today in industrial and commercial appplications across industries (please note: This is NOT a consumer products database that you can find elsewhere; so no antibacterial socks, bathroom cleaners, face creams, or pet products here...).

Our section "Ten things you should know about nanotechnology" provides you with an excellent first overview of what nanotechnologies are, what they are used for, and what some of the key issues are. If you want to get a more in-depth view of nanotechnology in important industry areas, then this section is for you.

Here is a brief overview of some current applications of nanomaterials. Most of them represent evolutionary developments of existing technologies: for example, the reduction in size of electronics devices.

### Nanocomposites

An important use of nanoparticles and nanotubes is in composites, materials that combine one or more separate components and which are designed to exhibit overall the best properties of each component. This multi-functionality applies not only to mechanical properties, but extends to optical, electrical and magnetic ones. Currently, carbon fibres and bundles of multi-walled CNTs are used in polymers to control or enhance conductivity, with applications such as antistatic packaging. The use of individual CNTs in composites is a potential long-term application. A particular type of nanocomposite is where nanoparticles act as fillers in a matrix; for example, carbon black used as a filler to reinforce car tyres. However, particles of carbon black can range from tens to hundreds of nanometres in size, so not all carbon black falls within our definition of nanoparticles.

### Nanoclays

Clays containing naturally occurring nanoparticles have long been important as construction materials and are undergoing continuous improvement. Clay particle based composites – containing plastics and nano-sized flakes of clay – are also finding applications such as use in car bumpers.

### Nanocoatings and nanostructured surfaces

Coatings with thickness controlled at the nano- or atomic scale have been in routine production for some time, for example in molecular beam epitaxy or metal oxide chemical vapor depositionfor optoelectonic devices, or in catalytically active and chemically functionalized surfaces. Recently developed applications include the self-cleaning window, which is coated in highly activated titanium dioxide, engineered to be highly hydrophobic (water repellent) and antibacterial, and coatings based on nanoparticulate oxides that catalytically destroy chemical agents. Wear and scratch-resistant hard coatings are significantly improved by nanoscale intermediate layers (or multilayers) between the hard outer layer and the substrate material. The intermediate layers give good bonding and graded matching of elastic and thermal properties, thus improving adhesion. A range of enhanced textiles, such as breathable, waterproof and stainresistant fabrics, have been enabled by the improved control of porosity at the nanoscale and surface roughness in a variety of polymers and inorganics.

### Tougher and Harder Cutting Tools

Cutting tools made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide, are more wear and erosion-resistant, and last longer than their conventional (large-grained) counterparts. They are finding applications in the drills used to bore holes in circuit boards.

### Nanopaints

Incorporating nanoparticles in paints could improve their performance, for example by making them lighter and giving them different properties. Thinner paint coatings (‘lightweighting’), used for example on aircraft, would reduce their weight, which could be beneficial to the environment. However, the whole life cycle of the aircraft needs to be considered before overall benefits can be claimed. It may also be possible to substantially reduce solvent content of paints, with resulting environmental benefits. New types of foulingresistant marine paint could be developed and are urgently needed as alternatives to tributyl tin (TBT), now that the ecological impacts of TBT have been recognised. Anti-fouling surface treatment is also valuable in process applications such as heat exchange, where it could lead to energy savings. If they can be produced at sufficiently low cost, fouling-resistant coatings could be used in routine duties such as piping for domestic and industrial water systems. It remains speculation whether very effective anti-fouling coatings could reduce the use of biocides, including chlorine. Other novel, and more long-term, applications for nanoparticles might lie in paints that change colour in response to change in temperature or chemical environment, or paints that have reduced infra-red absorptivity and so reduce heat loss.

Concerns about the health and environmental impacts of nanoparticles may require the need for the durability and abrasion behaviour of nano-engineered paints and coatings to be addressed, so that abrasion products take the form of coarse or microscopic agglomerates rather than individual nanoparticles.

### Nanolubricants

Nanospheres of inorganic materials could be used as lubricants, in essence by acting as nanosized ‘ball bearings’. The controlled shape is claimed to make them more durable than conventional solid lubricants and wear additives. Whether the increased financial and resource cost of producing them is offset by the longer service life of lubricants and parts remains to be investigated. It is also claimed that these nanoparticles reduce friction between metal surfaces, particularly at high normal loads. If so, they should find their first applications in high-performance engines and drivers; this could include the energy sector as well as transport. There is a further claim that this type of lubricant is effective even if the metal surfaces are not highly smooth. Again, the benefits of reduced cost and resource input for machining must be compared against production of nanolubricants. In all these applications, the particles would be dispersed in a conventional liquid lubricant; design of the lubricant system must therefore include measures to contain and manage waste.

In the following, we are taking a closer look at how nanotechnologies already are impacting many industrial areas. An excellent staring point is this chart that lists an impressive array of applications of nanoparticles:

## Safety

Nanoparticles present possible dangers, both medically and environmentally. Most of these are due to the high surface to volume ratio, which can make the particles very reactive or catalytic. They are also able to pass through cell membranes in organisms, and their interactions with biological systems are relatively unknown. However, it is unlikely the particles would enter the cell nucleus, Golgi complex, endoplasmic reticulum or other internal cellular components due to the particle size and intercellular agglomeration. A recent study looking at the effects of ZnO nanoparticles on human immune cells has found varying levels of susceptibility to cytotoxicity. There are concerns that pharmaceutical companies, seeking regulatory approval for nano-reformulations of existing medicines, are relying on safety data produced during clinical studies of the earlier, pre-reformulation version of the medicine. This could result in regulatory bodies, such as the FDA, missing new side effects that are specific to the nano-reformulation.

Whether cosmetics and sunscreens containing nanomaterials pose health risks remains largely unknown at this stage. However considerable research has demonstrated that zinc nanoparticles are not absorbed into the bloodstream in vivo.

Concern has also been raised over the health effects of respirable nanoparticles from certain combustion processes. As of 2013 the U.S. Environmental Protection Agency was investigating the safety of the following nanoparticles:

## Carbon Nanotubes:

Carbon materials have a wide range of uses, ranging from composites for use in vehicles and sports equipment to integrated circuits for electronic components. The interactions between nanomaterials such as carbon nanotubes and natural organic matter strongly influence both their aggregation and deposition, which strongly affects their transport, transformation, and exposure in aquatic environments. In past research, carbon nanotubes exhibited some toxicological impacts that will be evaluated in various environmental settings in current EPA chemical safety research. EPA research will provide data, models, test methods, and best practices to discover the acute health effects of carbon nanotubes and identify methods to predict them.

**Cerium oxide:** Nanoscale cerium oxide is used in electronics, biomedical supplies, energy, and fuel additives. Many applications of engineered cerium oxide nanoparticles naturally disperse themselves into the environment, which increases the risk of exposure. There is ongoing exposure to new diesel emissions using fuel additives containing CeO2 nanoparticles, and the environmental and public health impacts of this new technology are unknown. EPA's chemical safety research is assessing the environmental, ecological, and health implications of nanotechnology-enabled diesel fuel additives.

**Titanium dioxide:** Nano titanium dioxide is currently used in many products. Depending on the type of particle, it may be found in sunscreens, cosmetics, and paints and coatings. It is also being investigated for use in removing contaminants from drinking water.

**Nano Silver:** Nano silver is being incorporated into textiles, clothing, food packaging, and other materials to eliminate bacteria. EPA and the U.S. Consumer Product Safety Commission are studying certain products to see whether they transfer nano-size silver particles in real-world scenarios. EPA is researching this topic to better understand how much nano-silver children come in contact with in their environments.

**Iron:** While nano-scale iron is being investigated for many uses, including "smart fluids" for uses such as optics polishing and as a better-absorbed iron nutrient supplement, one of its more prominent current uses is to remove contamination from groundwater. This use, supported by EPA research, is being piloted at a number of sites across the country.

## Laser applications

The use of nanoparticles in laser dye-doped poly(methyl methacrylate) (PMMA) laser gain media was demonstrated in 2003 and it has been shown to improve conversion efficiencies and to decrease laser beam divergence.[80] Researchers attribute the reduction in beam divergence to improved dn/dT characteristics of the organic-inorganic dye-doped nanocomposite. The optimum composition reported by these researchers is 30% w/w of $SiO_2$ (~ 12 nm) in dye-doped PMMA.

The presence of nanomaterials (materials that contain nanoparticles) is not in itself a threat. It is only certain aspects that can make them risky, in particular their mobility and their increased reactivity. Only if certain properties of certain nanoparticles were harmful to living beings or the environment would we be faced with a genuine hazard. In this case it can be called nanopollution.

In addressing the health and environmental impact of nanomaterials we need to differentiate between two types of nanostructures: (1) Nanocomposites, nanostructured surfaces and nanocomponents (electronic, optical, sensors etc.), where nanoscale particles are incorporated into a substance, material or device (“fixed” nano-particles); and (2) “free” nanoparticles, where at some stage in production or use individual nanoparticles of a substance are present. These free nanoparticles could be nanoscale species of elements, or simple compounds, but also complex compounds where for instance a nanoparticle of a particular element is coated with another substance (“coated” nanoparticle or “core-shell” nanoparticle). There seems to be consensus that, although one should be aware of materials containing fixed nanoparticles, the immediate concern is with free nanoparticles.

Nanoparticles are very different from their everyday counterparts, so their adverse effects cannot be derived from the known toxicity of the macro-sized material. This poses significant issues for addressing the health and environmental impact of free nanoparticles.

To complicate things further, in talking about nanoparticles it is important that a powder or liquid containing nanoparticles almost never be monodisperse, but contain instead a range of particle sizes. This complicates the experimental analysis as larger nanoparticles might have different properties from smaller ones. Also, nanoparticles show a tendency to aggregate, and such aggregates often behave differently from individual nanoparticles.

## Health impact

The health impacts of nanotechnology are the possible effects that the use of nanotechnological materials and devices will have on human health. As nanotechnology is an emerging field, there is great debate regarding to what extent nanotechnology will benefit or pose risks for human health. Nanotechnology's health impacts can be split into two aspects: the potential for nanotechnological innovations to have medical applications to cure disease, and the potential health hazards posed by exposure to nanomaterials.

## Medical applications

Nanomedicine is the medical application of nanotechnology.[4] The approaches to nanomedicine range from the medical use of nanomaterials, to nanoelectronic biosensors, and even possible future applications of molecular nanotechnology. Nanomedicine seeks to deliver a valuable set of research tools and clinically helpful devices in the near future. The National Nanotechnology Initiative expects new commercial applications in the pharmaceutical industry that may include advanced drug delivery systems, new therapies, and in vivo imaging. Neuro-electronic interfaces and other nanoelectronics-based sensors are another active goal of research. Further down the line, the speculative field of molecular nanotechnology believes that cell repair machines could revolutionize medicine and the medical field.

Nanomedicine research is directly funded, with the US National Institutes of Health in 2005 funding a five-year plan to set up four nanomedicine centers. In April 2006, the journal Nature Materials estimated that 130 nanotech-based drugs and delivery systems were being developed worldwide. Nanomedicine is a large industry, with nanomedicine sales reaching $6.8 billion in 2004. With over 200 companies and 38 products worldwide, a minimum of $3.8 billion in nanotechnology R&D is being invested every year[ As the nanomedicine industry continues to grow, it is expected to have a significant impact on the economy.

## Health hazards

Nanotoxicology is the field which studies potential health risks of nanomaterials. The extremely small size of nanomaterials means that they are much more readily taken up by the human body than larger sized particles. How these nanoparticles behave inside the organism is one of the significant issues that needs to be resolved. The behavior of nanoparticles is a function of their size, shape and surface reactivity with the surrounding tissue. Apart from what happens if non-degradable or slowly degradable nanoparticles accumulate in organs, another concern is their potential interaction with biological processes inside the body: because of their large surface, nanoparticles on exposure to tissue and fluids will immediately adsorb onto their surface some of the macromolecules they encounter. The large number of variables influencing toxicity means that it is difficult to generalise about health risks associated with exposure to nanomaterials – each new nanomaterial must be assessed individually and all material properties must be taken into account. Health and environmental issues combine in the workplace of companies engaged in producing or using nanomaterials and in the laboratories engaged in nanoscience and nanotechnology research. It is safe to say that current workplace exposure standards for dusts cannot be applied directly to nanoparticle dusts.

The extremely small size of nanomaterials also means that they are much more readily taken up by the human body than larger sized particles. How these nanoparticles behave inside the body is one of the issues that needs to be resolved. The behavior of nanoparticles is a function of their size, shape and surface reactivity with the surrounding tissue. They could cause overload on phagocytes, cells that ingest and destroy foreign matter, thereby triggering stress reactions that lead to inflammation and weaken the body’s defense against other pathogens. Apart from what happens if non-degradable or slowly degradable nanoparticles accumulate in organs, another concern is their potential interaction with biological processes inside the body: because of their large surface, nanoparticles on exposure to tissue and fluids will immediately adsorb onto their surface some of the macromolecules they encounter. This may, for instance, affect the regulatory mechanisms of enzymes and other proteins.

The National Institute for Occupational Safety and Health has conducted initial research on how nanoparticles interact with the body’s systems and how workers might be exposed to nano-sized particles in the manufacturing or industrial use of nanomaterials. NIOSH currently offers interim guidelines for working with nanomaterials consistent with the best scientific knowledge. At The National Personal Protective Technology Laboratory of NIOSH, studies investigating the filter penetration of nanoparticles on NIOSH-certified and EU marked respirators, as well as non-certified dust masks have been conducted. These studies found that the most penetrating particle size range was between 30 and 100 nanometers, and leak size was the largest factor in the number of nanoparticles found inside the respirators of the test dummies.

Other properties of nanomaterials that influence toxicity include: chemical composition, shape, surface structure, surface charge, aggregation and solubility,[14] and the presence or absence of functional groups of other chemicals. The large number of variables influencing toxicity means that it is difficult to generalise about health risks associated with exposure to nanomaterials – each new nanomaterial must be assessed individually and all material properties must be taken into account.

## Environmental impact

The environmental impact of nanotechnology is the possible effects that the use of nanotechnological materials and devices will have on the environment. As nanotechnology is an emerging field, there is debate regarding to what extent industrial and commercial use of nanomaterials will affect organisms and ecosystems.

Nanotechnology's environmental impact can be split into two aspects: the potential for nanotechnological innovations to help improve the environment, and the possibly novel type of pollution that nanotechnological materials might cause if released into the environment.

## Environmental applications

Green nanotechnology refers to the use of nanotechnology to enhance the environmental sustainability of processes producing negative externalities. It also refers to the use of the products of nanotechnology to enhance sustainability. It includes making green nano-products and using nano-products in support of sustainability. Green nanotechnology has been described as the development of clean technologies, "to minimize potential environmental and human health risks associated with the manufacture and use of nanotechnology products, and to encourage replacement of existing products with new nano-products that are more environmentally friendly throughout their lifecycle.

Green nanotechnology has two goals: producing nanomaterials and products without harming the environment or human health, and producing nano-products that provide solutions to environmental problems. It uses existing principles of green chemistry and green engineering to make nanomaterials and nano-products without toxic ingredients, at low temperatures using less energy and renewable inputs wherever possible, and using lifecycle thinking in all design and engineering stages.

## Pollution

Nanopollution is a generic name for all waste generated by nanodevices or during the nanomaterials manufacturing process. Nanowaste is mainly the group of particles that are released into the environment, or the particles that are thrown away when still on their products.

## Social imopact

Beyond the toxicity risks to human health and the environment which are associated with first-generation nanomaterials, nanotechnology has broader societal impact and poses broader social challenges. Social scientists have suggested that nanotechnology's social issues should be understood and assessed not simply as "downstream" risks or impacts. Rather, the challenges should be factored into "upstream" research and decision-making in order to ensure technology development that meets social objectives.

Many social scientists and organizations in civil society suggest that technology assessment and governance should also involve public participation. Over 800 nano-related patents were granted in 2003, with numbers increasing to nearly 19,000 internationally by 2012. Corporations are already taking out broad-ranging patents on nanoscale discoveries and inventions. For example, two corporations, NEC and IBM, hold the basic patents on carbon nanotubes, one of the current cornerstones of nanotechnology. Carbon nanotubes have a wide range of uses, and look set to become crucial to several industries from electronics and computers, to strengthened materials to drug delivery and diagnostics. Carbon nanotubes are poised to become a major traded commodity with the potential to replace major conventional raw materials.

Nanotechnologies may provide new solutions for the millions of people in developing countries who lack access to basic services, such as safe water, reliable energy, health care, and education. The 2004 UN Task Force on Science, Technology and Innovation noted that some of the advantages of nanotechnology include production using little labor, land, or maintenance, high productivity, low cost, and modest requirements for materials and energy. However, concerns are frequently raised that the claimed benefits of nanotechnology will not be evenly distributed, and that any benefits (including technical and/or economic) associated with nanotechnology will only reach affluent nations.

Longer-term concerns center on the impact that new technologies will have for society at large, and whether these could possibly lead to either a post-scarcity economy, or alternatively exacerbate the wealth gap between developed and developing nations. The effects of nanotechnology on the society as a whole, on human health and the environment, on trade, on security, on food systems and even on the definition of "human", have not been characterized or politicized.

## Regulations

Significant debate exists relating to the question of whether nanotechnology or nanotechnology-based products merit special government regulation. This debate is related to the circumstances in which it is necessary and appropriate to assess new substances prior to their release into the market, community and environment.

Regulatory bodies such as the United States Environmental Protection Agency and the Food and Drug Administration in the U.S. or the Health & Consumer Protection Directorate of the European Commission have started dealing with the potential risks posed by nanoparticles. So far, neither engineered nanoparticles nor the products and materials that contain them are subject to any special regulation regarding production, handling or labelling. The Material Safety Data Sheet that must be issued for some materials often does not differentiate between bulk and nanoscale size of the material in question and even when it does these MSDS are advisory only.

Limited nanotechnology labeling and regulation may exacerbate potential human and environmental health and safety issues associated with nanotechnology. It has been argued that the development of comprehensive regulation of nanotechnology will be vital to ensure that the potential risks associated with the research and commercial application of nanotechnology do not overshadow its potential benefits. Regulation may also be required to meet community expectations about responsible development of nanotechnology, as well as ensuring that public interests are included in shaping the development of nanotechnology.

In "The Consumer Product Safety Commission and Nanotechnology," E. Marla Felcher suggests that the Consumer Product Safety Commission, which is charged with protecting the public against unreasonable risks of injury or death associated with consumer products, is ill-equipped to oversee the safety of complex, high-tech products made using nanotechnology.

## Nanotechnology and the environment - Hazard potentials and risks

### Potential environmental processes that can influence the behavior and the properties of nanomaterials

*Dissolution*: A solid nanomaterial dissolves in a solvent, yielding a chemical solution. Precipitation/Sedimentation: Nanomaterials are separated from a suspension or solution.*Speciation*: Formation of chemical variants (species) of a nanomaterial that are in a reaction equilibrium with one another.*Binding to biotic or abiotic particles*: Nanomaterialien interact with other living or non-living materials in the environment, for example in the form of adhesion or sorption.*Transformation*: A nanomaterial undergoes a biological or chemical transformation.*Agglomeration/Disagglomeration*: Nanomaterials combine into larger units or are separated again.*Mineralization*: Transformation of a carbon-containing nanomaterial into an inorganic state through biotic and abiotic decomposition.*Diffusion*: Transport of a nanomaterial from a zone of high concentration into one with a lower concentration through random (Brownian) molecular movement.*Deposition*: Deposition of a nanomaterial, for example from the air into the water.*Resuspension*: Renewed distribution of an insoluble nanomaterial in a liquid or a gas (for example from a surface into gas or from sediment into water) after it was previously separated through precipitation.

## Environmental toxicity

Nanoparticles have been naturally present in the environment since the origin of earth, for example as the result of combustion processes (forest fires), in volcanic ash, in most natural waters, or as dust in the air due to weathering and erosion.Organisms produce various substances in nanoform (for example proteins, DNA) in their cells or are themselves only several nanometers large, such as viruses. During their evolution, all living organism have adapted to an environment that contains nanoparticles, some of which can also be toxic (e.g. volcanic ash). This adaptation is a function of exposure, dose and the speed with which habitats change13.These natural nanoparticles in the environment are now accompanied by those that have been released unintentionally due to human activities such as household heating, industry, slash-and-burn clearance, transport and, most recently, through the industrial application of various, extremely polymorphic synthetic nanoparticles in unknown amounts. This additional burden on humans and the environment has taken place over a very short period (from an evolutionary standpoint). To what degree can organisms deal with such artificial nanoparticles without suffering damage?Most data on acute toxicity as well as on sublethal effects are available for freshwater organisms (e.g. water fleas, fishes). More studies on marine and terrestrial invertebrates are also necessary to determine potential toxicities, as are further studies on amphibians, reptiles, birds or plants, bacteria and in particular microorganisms. To date, no ecotoxicological studies are available that could explain in detail the mechanisms of uptake, distribution, metabolization and excretion of nanoparticles13.In an overview of the relevant scientific literature compiled in 2010, only 12 studies were identified that can actually be classified as ecological studies (i.e. that more or less consider the complexity of natural ecosystem). These few studies on the effects of ENPs on ecological communities failed to detect significant increases in mortality rates or changes in their compositions1.The following paragraphs briefly summarize the results of ecotoxicological studies on selected nanomaterials

## Carbon nanotubes (CNTs)

The ecotoxicity of CNTs has been treated in only a few studies, and in some cases the results are highly contradictory. While some studies were unable to determine any negative effects on test organisms, others clearly did, for example in the case of fishes and amphibian larvae. The reason for this is the great variability of CNTs: they differ considerably in length, structure, surface charge, surface chemistry, agglomeration behavior and purity (see also14; 15). Moreover, investigating the toxicity of CNTs for aquatic organisms is very difficult because CNTs are very poorly soluble in water, have different sizes and diameters, and form complex aggregates5.CNTs are often surface functionalized so that their fine distribution in water remains very stable and they do not sediment to the bottom. Such surface changes, however, promote the tendency of CNTs to accumulate heavy metals, which can influence their transport in water bodies or even in biological systems.

### *Nano-TiO2*

Titanium dioxide nanoparticles are among the most frequently investigated nanomaterials. A range of standardized tests are already available for fishes, crustaceans and algae. Nano-TiO2 has a photocatalytic effect, i.e. under UV radiation, reactive oxygen species (ROS) develop that can damage the cell membrane of microorganisms.Studies have been conducted to simulate the conditions in natural running waters at the laboratory scale (so-called aquatic microcosms). They show that TiO2 nanoparticles and low concentrations of larger, naturally developed agglomerates can both significantly damage the cell membranes of microorganisms.Microorganisms are very sensitive to nano-TiO2 – the precise effect on ecosystem function, however, remains unknown17. Preliminary results show that aquatic organisms such as small crustaceans (which play an important role as zooplankton in aquatic food chains) are not damaged by the photocatalytic effect of nano-TiO2. Nonetheless, the nanoparticles can attach themselves to the chitinous exoskeleton of the animals and hinder molting, which is necessary for growth in juveniles. This can kill such animals. This effect was determined atconcentrations of 0.24 mg/liter of water; nano-TiO2 proved to be twice as toxic as the larger form18.*Nanosilver*Silver ions from silver compounds or those that develop from nanosilver particles through contact with water are highly toxic to microorganisms such as bacteria, fungi and algae (see also 19). Soil microorganisms can be affected when, for example, sewage sludge contaminated with nanosilver is spread on fields. Nanosilver particles show negative effects on fishes and crustaceans already at low concentrations; in mammals, this material is toxic only at very high concentrations.Few studies on plants are available, but a more recent paper shows an impact of nanosilver particles on the growth of grass seedlings due to cell damage20. A plausible primary entry pathway of nanosilver is via water because nanosilver can be washed out of special textiles or is an ingredient in cosmetics and cleaning agents. Nanosilver in waste water has therefore been identified by an international group of researchers from different scientific disciplines as one of 15 areas of concern that can threaten biological diversity22.

### Exposure

Whether ENPs pose a risk to the environment depends not only on the toxicity of the respective material but also on exposure, i.e. on the amount released into the environment.Unfortunately, no quantitative data are available for even a single nanomaterial. This is because there is no obligatory registration of nanomaterials, and companies are very reticent about divulging production volumes23. Only very few studies have dealt with the environmental exposure to nanomaterials.

These are based on rough estimates of production volumes and releases as well as on model calculations, which do not allow comprehensive risk assessments.Thus, a recently published study23 estimates the annual production volume of nano-TiO2 in the USA at 7800 to 38,000 t, followed by CNTs at 55 to 1101 t and nano-ceroxide at 35 to 700 t. The production volume of nanosilver is estimated to be 2.8 to 20 t per year. Knowledge about production volumes alone is insufficient to estimate potential environmental risk: the actually released amounts must be known.To date, the assumption has been that nanomaterials that are tightly embedded in a matrix pose no or only minimal environmental risk. This holds true for example for CNTs that are incorporated into plastics or for nano-TiO2 in permanent photocatalytic coatings.

Nonetheless, only very few studies have examined the release of ENPs from consumer products. Nanosilver, both in the form of particles as well as ions, can be released when such treated textiles are washed; the release rate depends strongly on the type of production process24. TiO2-particles can also be washed out of facade paints and enter the environment8.For Europe, the USA and Switzerland, the concentrations of five nanomaterials expected in the environment ("Predicted Environmental Concentrations", PEC) were estimated based on model calculations. The highest concentration in all environmental compartments was found for nano-TiO2, followed by nano-zinc oxide.

These values were compared with concentrations of the studied nanomaterials for which no negative environmental effects are expected ("Predicted No-Effects-Concentration", PNEC).The results revealed a potential risk for aquatic organisms through nano-TiO2, nanosilver and nano-zinc oxide in wastewater of sewage treatment plants. The PEC of CNTs and fullerenes was classified as so low that no environmental risk is currently to be expected25.The most likely entry pathways of nanomaterials into the environment are sewage water and wastes. Wastes that contain nanomaterials can arise either during the production of the raw materials, the manufacture of products with nanomaterials, as well as at the end of the products' lifecycles. The current legal framework contains no specific regulations for treating wastes containing nanomaterials26. A release of ENPs into the environment from wastes is possible, although virtually no studies have been conducted on this aspect. The assumption is that ENPs are efficiently removed by filters during waste incineration27.

LEDs contain nano-scale coatings of the semiconductor materials arsenic, gallium, phosphorus and their compounds. They therefore belong to the waste category requiring special treatment or monitoring. In particular the semiconductor material gallium arsenide is problematic because, in the absence of atmospheric oxygen and water, a very thin layer can develop on the surface of the material. This is highly toxic and could create environmental damage in a normal landfill28.Nanosilver can enter wastewater via various pathways, for example when washing special textiles, through cosmetics or cleaning agents. About 90% of the nanosilver is apparently removed from waste water in sewage treatment plants and is then contained in the sewage sludge29. If this is spread on fields as fertilizer, this nanomaterial enters the environment, whereby damage to soil microorganisms cannot be excluded. An additional open question is the recyclability of products that contain nanomaterials. Plastic bottles made of polyethylene terephthalate (PET) can be recycled as long as they do not contain coloring agents or additives.

Coatings of nanocomposite materials, which reduce gas permeability or provide light protection, create recycling problems.

Little is known about the fate and behavior of synthetic nanomaterials in the environment, and suitable methods to detect them in complex environmental media are only in the development stage. Model calculations on exposure alone are insufficient for comprehensive risk assessments. This calls for developing methods to monitor nanomaterials in the environment.Ecotoxicological investigations show a certain hazard potential of some nanomaterials. Even though scientific uncertainties still exist, the precautionary principle should be applied in the sense of preventive risk minimization. Environmental inputs should be avoided to the extent possible. Ecotoxicological research should increasingly focus on the environmental relevance of the materials and consider the complexity of natural systems.Longterm studies would be necessary to determine delayed impacts of environmental exposure to ENPs and to help determine potential adaptive mechanisms. More studies on bioaccumulation in the food chain are also necessary, as are studies on the interaction of ENPs with other pollutants in the environment. Under certain conditions, ENPs might change the transport and effects of such pollutants.

## POSSIBLE QUESTIONS

## UNIT-V

### PART- A (Each carry one mark)

1. The adhesive force, F =?
(a)BC x t (b)CB x k (c)BC x p **(d)BC x k**
2. Scratching and wear, a single crystal diamond tip is used in?
(a)Individual mode **(b) Contact mode**
(c) Non individual mode (d) Individual and contact mode
3. Nano-indentation is important measurement in?
(a)Nano biology (b) Nano technology
(c) Nano triology **(d) Nano tribology**
4. The way Nanomaterials do not enter the human body?
(a) Inhalation (b) Ingestion
**(c) Transportation** (d) Skin absorption
5. Toxicity of nanomaterials is not primarily dependent on
a) Surface chemistry **b) Particle size and shape**
c) Thermal conductivity d) Surface area
6. Which of following practice does not prevent inhalation?
a) Aeration of the laboratory **b) Fume hood**
c) Biosafety cabinets d) Respirator masks

7.Among the following which is used for controlled release drug delivery

**(a)Dendrimers** (b) Buky balls (c) Emulsions (d) Nanowires

8. Polyethylene glycol (PEG) nano particles carrying payload of antibiotics at its core were used to target

(a) **bacterial infection** (b)Fungal infection

(c) Cancer treatment (d) Brain cancer

9. The way Nanomaterials do not enter the human body?

(a) Inhalation (b) Ingestion

**(c) Transportation** (d) Skin absorption

10. Toxicity of nanomaterials is not primarily dependent on

a) Surface chemistry **b) Particle size and shape**

c) Thermal conductivity d) Surface area

11. Which type of Nano shells having the diameter of 120 nm, were used to kill cancer tumors in mice

**(a)coated with gold** (b)coated with silver

(c)Coated with cobalt (d)coated with lead

17. Polyethylene glycol (PEG) nano particles carrying payload of antibiotics at its core were used to target

(a) **bacterial infection** (b)Fungal infection

(c) Cancer treatment (d) Brain cancer

18. The way Nanomaterials do not enter the human body?

(a) Inhalation (b) Ingestion

**(c) Transportation** (d) Skin absorption

19. Toxicity of nanomaterials is not primarily dependent on

a) Surface chemistry **b) Particle size and shape**

c) Thermal conductivity d) Surface area

20. Which type of Nano shells having the diameter of 120 nm, were used to kill cancer tumors in mice

**(a)coated with gold** (b)coated with silver

(c)Coated with cobalt (d)coated with lead

17. Which are useful for disease protein biomarker detection

(a) Nano tubes (b) Nano crystals **(c) Nanowires** (d) Nanorods

18. Which has**,** less than 10 nm in size are useful for controlled release drug delivery, and as image contrast agents.

(a) Nano tubes (b) Nano crystals (c) Nanowires**(d) Dentrimers**

19. Which is used in finding the application in tumor-specific imaging, deep tissue thermal ablation

**(a)Nano shells** (b) Nano carbons (c) Nano tubes (d) Nanorods

20. The way Nanomaterials do not enter the human body?

(a) Inhalation (b) Ingestion

**(c) Transportation** (d) Skin absorption

## PART- B (Each Carry six mark)

1.Write the applications of nanoparticles in various fundamental research.
2. Explain the applications of nanoparticles in industries.
3.How will you explain the applications of nanoparticles in medical field?
4.Explain the applications of nanoparticles in biosafety.
5. Write notes on the applications of nanoparticles in medical field?
6.Write notes on the toxicity of nanoparticles on human and environment.

## PART- C (Ten mark)

1. What are nano Particles?What are the applications of nano particles and write some disadvantages of using nanoparticles on human?
2. Explain the advantages and disadvantages of using nanoparticles in various fields.
3. What are nano particles?Write notes on the applications of Nano particles in medicinal field.
4. Explain the toxicity of nanoparticles on human and environment.
5. How will you explain the applications of nanoparticles in medical field?

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**(Deemed University Established Under Section 3 of UGC Act 1956)**

**COIMBATORE-21**

## DEPARTMENT OF CHEMISTRY

## M.Sc CHEMISTRY

Name of the Staff : **Dr. M. MAKESWARI**

Department : **Chemistry**

Subject : **Nano Chemistry**

Subject Code : **16CHP304**

Class : **II M.Sc-Chemistry**

Year and Semester : **II / III**

## UNIT-V

## OBJECTIVE QUESTIONS FOR ONLINE EXAMINATION (Each carry one mark)

| S. No | Questions | Option 1 | Option 2 | Option 3 | Option 4 | Answer |
|---|---|---|---|---|---|---|
| **1** | Nanocoatings and nanocomposites are finding uses in? | Bicycles | Automobiles | Bicycles and automobiles | Tooth brushes | Bicycles and automobiles |
| **2** | Nanostructured semiconductors are used as window layers in ? | Cells | Walls | Solar cells | Thermal | Solar cells |
| **3** | Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the ? | Automobile industry | Electronic industry | Spinning industry | Cosmetic industry | Electronic industry |
| **4** | Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in which applications? | Industrial | Electrical | Catalytic | Mechanical | Catalytic |
| **5** | Which finds application for rechargeable batteries for cars or consumer goods? | $CO_2$ | $MnO_2$ | $SO_2$ | C | $MnO_2$ |
| **6** | Among the following which is used in rechargeable batteries for cars or consumer goods? | $CO_2$ | $MnO_2$ | $SO_2$ | C | $MnO_2$ |
| **7** | Among the following which one is a gas sensors? | $CO_2$ | $MnO_2$ | $SO_2$ | C | $CO_2$ |
| **8** | Nano particles of which atom are used to control collateral damage due to explosion? | Copper | Aluminium | Carbon | Lead | Aluminium |
| **9** | Among the following which is used as anti-bacterial agent | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |
| **10** | Among the following which is used as anti-bacterial agent in the health industry | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |
| **11** | Among the following which is used in textile coatings | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |
| **12** | Among the following which is used food storage | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |

| | | | | | | |
|---|---|---|---|---|---|---|
| **13** | Conventional optical spectroscopy requires …………..of many particles, i.e. nanoparticle based nano composites | macroscopic samples | microscopic samples | Nano sized samples | small amount of samples | macroscopic samples |
| **14** | The way Nanomaterials do not enter the human body? | Inhalation | Ingestion | **Transportation** | Skin absorption | **Transportation** |
| **15** | Toxicity of nanomaterials is not primarily dependent on | Surface chemistry | **Particle size and shape** | Thermal conductivity | Surface area | **Particle size and shape** |
| **16** | Among the following which is used for controlled release drug delivery | **Dendrimers** | Buky balls | Emulsions | Nanowires | **Dendrimers** |
| **17** | Which of following practice does not prevent inhalation? | Aeration of the laboratory | **Fume hood** | Biosafety cabinets | Respirator masks | **Fume hood** |
| **18** | Among the following which is used in the detection of DNA mutation | **Carbon nano tubes** | Dentrimers | Nanoshells | Nanowires | **Carbon nano tubes** |
| **19** | Polyethylene glycol (PEG) nano particles carrying payload of antibiotics at its core were used to target | **bacterial infection** | Fungal infection | Cancer treatment | Brain cancer | **bacterial infection** |
| **20** | Which type of Nano shells having the diameter of 120 nm, were used to kill cancer tumorsin mice | **coated with gold** | coated with silver | Coated with cobalt | coated with lead | **coated with gold** |
| **21** | Scratching and wear, a single crystal diamond tip is used in? | Individual mode | **Contact mode** | Non individual mode | Individual and contact mode | **Contact mode** |
| **22** | Nano-indentation is important measurement in? | Nano biology | Nano technology | Nano triology | **Nano tribology** | **Nano tribology** |
| **23** | Which finds application for rechargeable batteries for cars or consumer goods? | $CO_2$ | **$MnO_2$** | $SO_2$ | C | **$MnO_2$** |
| **24** | Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in which applications? | Industrial | Electrical | **Catalytic** | Mechanical | **Catalytic** |
| **25** | Cold welding properties combined | Automobile industry | **Electronic** | Spinning industry | Cosmetic | **Electronic** |

| | | | | | | |
|---|---|---|---|---|---|---|
| | with the ductility make them suitable for metal-metal bonding especially in the? | | **industry** | | industry | **industry** |
| **26** | Very small particles have special atomic structures with discrete electronic states, which giverise to special properties in addition to which behavior? | **Super-paramagnetism** | Super-magnetism | Super-speciality | Electrical behaviour | **Super-paramagnetism** |
| **27** | Which is used in the medical treatment of cancer | Ag/Nps | Co /Nps | Au /Nps | Pt /Nps | Au /Nps |
| **28** | Gold nanoparticles are used in the treatment of | Cancer | Skin treatment | **Lungs** | Brain tumor | Cancer |
| **29** | As antibacterial agents , which is used in the disinfecting medical devices | Ag/Nps | Co /Nps | Au /Nps | Pt /Nps | Ag /Nps |
| **30** | Among the following which is in home appliances for water treatment | Ag/Nps | Co /Nps | Au /Nps | Pt /Nps | Ag /Nps |
| **31** | Silver nano particles are used as an antibacterial agents in the home appliances for------ | Water treatment | Electrical Devices | Electronic devices | For walls | Water treatment |
| **32** | Which is used in textile industry to use in textile fabrics | Ag/Nps | Co /Nps | Au /Nps | Pt /Nps | Ag /Nps |
| **33** | Ag/Nps are used in textile industries in | dyeing | Yarning | Finishing | Fabrics | Fabrics |
| **34** | The high anti-bacterial activity of the cotton fibres are due to the presence of | Silver nano particles | Gold nanoparticles | Cobalt nano particles | Iron nano particles | Silver nano particles |
| **35** | Due to heir electrochemical properties siver nanoparticles are used in | dyeing | Nanoscale sensors | Water treatment | Electrical Devices | Nanoscale sensors |
| **36** | Which property of silver nanoparticles enhances used in the | Electrochemical properties | Conductivity | Density | Size | Electrochemical properties |

| | | | | | | |
|---|---|---|---|---|---|---|
| | nanoscale sensors | | | | | |
| **37** | The optical property of a metallic silver nanoparticle depend on its | Size | Surface area | Surface plasmon resonance | High volume | Surface plasmon resonance |
| **38** | Nano clusters composed of | 2-6 silver atoms | 2-5 silver atoms | 2-8 silver atoms | 2-10 silver atoms | 2-8 silver atoms |
| **39** | Nanocoatings and nanocomposites are finding uses in? | Bicycles | Automobiles | Bicycles and automobiles | Tooth brushes | Bicycles and automobiles |
| **40** | Nanostructured semiconductors are used as window layers in ? | Cells | Walls | Solar cells | Thermal | Solar cells |
| **41** | Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the ? | Automobile industry | Electronic industry | Spinning industry | Cosmetic industry | Electronic industry |
| **42** | Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in which applications? | Industrial | Electrical | Catalytic | Mechanical | Catalytic |
| **43** | Which finds application for rechargeable batteries for cars or consumer goods? | $CO_2$ | $MnO_2$ | $SO_2$ | C | $MnO_2$ |
| **44** | Among the following which is used in rechargeable batteries for cars or consumer goods? | $CO_2$ | $MnO_2$ | $SO_2$ | C | $MnO_2$ |
| **45** | Among the following which one is a gas sensors? | $CO_2$ | $MnO_2$ | $SO_2$ | C | $CO_2$ |
| **46** | Nano particles of which atom are used to control collateral damage due to explosion? | Copper | Aluminium | Carbon | Lead | Aluminium |
| **47** | Among the following which is used as anti-bacterial agent | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |
| **48** | Among the following which is used as anti-bacterial agent in the health industry | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |
| **49** | Among the following which is used in textile coatings | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |

| | | | | | | |
|---|---|---|---|---|---|---|
| **50** | Among the following which is used food storage | Ag nano particle | Au nano particle | Cu nano particle | Al nano particle | Ag nano particle |
| **51** | Conventional optical spectroscopy requires …………..of many particles, i.e. nanoparticle based nano composites | macroscopic samples | microscopic samples | Nano sized samples | small amount of samples | macroscopic samples |
| **52** | The way Nanomaterials do not enter the human body? | Inhalation | Ingestion | **Transportation** | Skin absorption | **Transportation** |
| **53** | Toxicity of nanomaterials is not primarily dependent on | Surface chemistry | **Particle size and shape** | Thermal conductivity | Surface area | **Particle size and shape** |
| **54** | Among the following which is used for controlled release drug delivery | **Dendrimers** | Buky balls | Emulsions | Nanowires | **Dendrimers** |
| **55** | Which of following practice does not prevent inhalation? | Aeration of the laboratory | **Fume hood** | Biosafety cabinets | Respirator masks | **Fume hood** |
| **56** | Among the following which is used in the detection of DNA mutation | **Carbon nano tubes** | Dentrimers | Nanoshells | Nanowires | **Carbon nano tubes** |
| **57** | Polyethylene glycol (PEG) nano particles carrying payload of antibiotics at its core were used to target | **bacterial infection** | Fungal infection | Cancer treatment | Brain cancer | **bacterial infection** |
| **58** | Which type of Nano shells having the diameter of 120 nm, were used to kill cancer tumorsin mice | **coated with gold** | coated with silver | Coated with cobalt | coated with lead | **coated with gold** |

[16CHP304] Reg. No....................

# KARPAGAM UNIVERSITY,
(Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

## PG DEGREE EXAMINATION, JULY 2017
(For the candidates admitted from 2016 onwards)

DEPARTMENT OF CHEMISTRY
ODD SEMESTER

*II M.Sc., CHEMISTRY*

INTERNAL EXAM-I
NANO CHEMISTRY

**Time: 2 hours** **Maximum: 50 marks**
**Date :**

### PART- A (20 x 1=20 Marks)

**Answer All the Questions**

1. Who first used the term nanotechnology and when?
(a)Richard Feynman, 1959 (b) Norio Taniguchi, 1974
(c)Eric Drexler, 1986 (d) Sumio Iijima, 1991

2. Richard Feynman is often credited with predicting the potential of nanotechnology. What was the title of his famous speech given on December 29, 1959?
(a) There is a tiny room at the bottom (b) Things get nanoscopic at the bottom
(c) Bottom? What bottom? (d) There is plenty of room at the bottom

3. What is grey goo?
(a) A hypothetical substance composed of out-of-control self-replicating nanobots that consumes all living matter on Earth
(b) The feeder material used to grow grey nanoparticles in the laboratory
(c) Toxic byproduct resulting from the synthesis of carbon nanotubes
(d) Waste product from the production of nanoglue made from the membranes on the feet of the Madagascan Grey Gecko

4. Who coined the word Nanotechnology?
(a)Eric Drexler (b) Michael Faraday (c) Granqvist and Buhrman (d) Buhrman

5. The term "nano-technology" was first used by"
(a)Norio Taniguchi (b) Eric Drexler (c) Minsky (d) Richard feynman

6. A nanometer is a?
(a) Millionth of a meter (b) Trillionth of a meter
(c) Billionth of a meter (d )Millimeter

7. Nanoscience can be studied with the help of ?
(a)Quantum mechanics (b)Newtonian mechanics
(c) Macro-dynamics (d) Geophysics

8. The size of nanoparticles is between ?
(a) 100 to 1000 nm (b) 0.1 to 10 nm (c) 1 to 100 nm (d) 0.01 to 1 nm

9. How much is 1 micron in meter ?
(a)10-5 meter (b) 10-4 meter (c) 10-6 meter (d) 10-8 meter

10. What is the diameter of the hydrogen atom?
(a) 1 nm (b) 0.001 nm (c) 0.1 nm (d) 0.01 nm

11. What is the diameter of human hair?
(a) 75000 nm (b) 65000 nm (c) 85000 nm (d) 5000 nm

12. What is the size of a nanoshell?
(a) 100 nm (b) 1 nm (c) 10 nm (d )1000 nm

13. Which one is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons?
(a) scanning tunneling microscope (b) scanning electron microscope
(c) transmission electron microscope (d) scanning probe microscope

14. The first Transmission electron microscopy was built by Max knoll and Ernst Ruska in ?
(a) 1932 (b) 1930 (c) 1931 (d)1933

15. The first commercial Transmission electron microscopy in ?
(a) 1937 (b) 1938 (c) 1936 (d) 1939

16. The first Transmission electron microscopy was built by?
(a) Max knoll and Ernst Ruska (b) Richard Feynman and Norio Taniguchi
(c) Richard Smalley and Eric Drexler (d) Gerd Binnig and Heinrich Rohrer

[16CHP304]　　　　Reg. No.....................

# KARPAGAM UNIVERSITY,
(Under Section 3 of UGC Act 1956)
COIMBATORE-641 021
PG DEGREE EXAMINATION, 2017
(For the candidates admitted from 2016 onwards)

## DEPARTMENT OF CHEMISTRY
ODD SEMESTER

*II M.Sc., CHEMISTRY*

## INTERNAL EXAM-II
NANO CHEMISTRY

**Time: 2 hours**　　　　**Maximum: 50 marks**
**Date :**

### PART- A (20 x 1=20 Marks)

**Answer All the Questions**

1. Thin films of TiC are:
   (a) Used for wear-resistant coatings　　(b) Used as Semiconductor
   (c) Used in solar cells　　(d) Used as Phosphorescent

2. To be classed as "nanoscale", an object must have one dimension that is of the order of
   (a) $10^{-9}$m　　(b) $10^{-12}$m　　(c) $10^{-7}$ m　　(d) $10^{-15}$ m

3. A graphene sheet differs from the framework of a fullerene because:
   (a)the graphene sheet consists of $C_n$ rings in which $n = 5$ and 6, but in a fullerene $n = 5$
   (b) the graphene sheet consists of $C_n$ rings in which $n = 6$, but in some fullerenes $n = 5$
   (c) the graphene sheet consists of $C_n$ rings in which $n = 6$, but in fullerenes $n = 5$ and 6
   (d) the graphene sheet consists of $C_n$ rings in which $n = 5$ or 6, but in most fullerenes $n = 6$

4. Nanotubes usually form in bundles. Which is the best description of such a bundle?
   (a)The tubes are connected together by covalent C-C bonds
   (b) The tubes are randomly organized, with the axes of the tubes lying in random directions
   (c) The tubes are aligned, axes parallel, with van der Waals forces operating between adjacent tubes
   (d) The bundles are of discrete sizes, and dipole-dipole forces hold the tubes together

5. In Which way the Nanomaterials do not enter the human body?
   (a) Inhalation　　(b) Ingestion
   (c) Transportation　　(d) Skin absorption

---

No of copies - 114

6. Toxicity of nanomaterials is not primarily dependent on
   a) Surface chemistry　　b) Particle size and shape
   c) Thermal conductivity　　d) Surface area

7. Which of following practice does not prevent inhalation?
   a) Aeration of the laboratory　　b) Fume hood
   c) Biosafety cabinets　　d) Respirator masks

8. Among the following which is used for controlled release drug delivery
   (a)Dendrimers　　(b) Buky balls　　(c) Emulsions　　(d) Nanowires

9. What is the general name for the class of structures made of rolled up carbon lattices?
   (a) Nanotubes　　(b) Nano sheets　　(c) Nano rods　　(d) Nano particles

10. Which ratio decides the efficiency of nano substances?
    (a) Weight/volume　　(b) Surface area/volume
    (c)Volume/weight　　(d) Pressure/volume

11. Among the following which is used in the detection of DNA mutation
    (a) Carbon nano tubes　　(b) Dentrimers　　(c) Nanoshells　　(d) Nanowires

12. Polyethylene glycol (PEG) nano particles carrying payload of antibiotics at its core were used to target
    (a) bacterial infection　　(b)Fungal infection
    (c) Cancer treatment　　(d) Brain cancer

13. Which type of Nano shells having the diameter of 120 nm, also used to kill cancer tumors in mice
    (a) Coated with gold　　(b)coated with silver
    (c)Coated with cobalt　　(d)coated with lead

14. Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in which applications?
    (a)Industrial　　(b) Electrical　　(c) Catalytic　　(d) Mechanical

15. Which finds application for rechargeable batteries for cars or consumer goods?
    (a)$CO_2$　　( b) $MnO_2$　　(c) $SO_2$　　(d) C

16. Scratching and wear, a single crystal diamond tip is used in?
    (a)Individual mode　　(b) Contact mode
    (c) Non individual mode　　(d) Individual and contact mode

17. The size of RBC is ____ nm.
    (a)50　　(b) 90　　(c) 2000　　(d) 5000

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**(Deemed University Established Under Section 3 of UGC Act 1956)**

**COIMBATORE-21**

## DEPARTMENT OF CHEMISTRY

## ODD SEMESTER

## *II M.Sc., CHEMISTRY*

## INTERNAL EXAM-I - NANO CHEMISTRY

## ANSWER KEY

## PART- A (10 x 2=20 Marks)

**Answer All the Questions**

1. (a)Richard Feynman, 1959
2. (d) There is plenty of room at the bottom
3. (a) A hypothetical substance composed of out-of-control self-replicating nanobots that consumes all living matter on Earth
4. (a)Eric Drexler
5. (a)Norio Taniguchi
6. (c) Billionth of a meter
7. (a)Quantum mechanics
8. (c) 1 to 100 nm
9. (c) 10-6 meter
10. (c) 0.1 nm
11. (a) 75000 nm
12. (a) 100 nm
13. (b) scanning electron microscope
14. (c) 1931
15. (d) 1939
16. (a) Max knoll and Ernst Ruska
17. (b) Scanning electron microscope
18. (d) Transmission electron microscopy
19. (a) internal structure of fixed cells.
20. (a) The specimen must be stained with osmium or other heavy metal.

## PART- B (3 x 2 = 6 Marks)

**Answer All the Questions**

21. Molecular nanotechnology (MNT) is a technology based on the ability to build structures to complex, atomic specifications by means of mechanosynthesis. This is distinct from nanoscale materials

22. Principles of Transmission Electron Microscopy. Illumination - Source is a beam of high velocity electrons accelerated under vacuum, focused by condenser lens (electromagnetic bending of electron beam) onto specimen. ... Emergent electronbeam is focused by objective lens.

23. Nanoparticle synthesis refers to methods for creating nanoparticles. Nanoparticles can be derived from larger molecules, or synthesized by 'bottom-up' methods that, for example, nucleate and grow particles from fine molecular distributions in liquid or vapour phase. There are several methods for creating nanoparticles, including gas condensation, attrition, chemical precipitation, pyrolysis and hydrothermal synthesis.

## PART- C (3 x 8 = 24 Marks)

**Answer All the Questions**

24. (a) Nanochemistry is the combination of chemistry and nanoscience. Nanochemistry is a branch of **nanoscience**, deals with the chemical applications of **nanomaterials** in **nanotechnology**. Nanochemistry involves the study of the synthesis and characterisation of materials of nanoscale size.

Nanochemistry is associated with synthesis of building blocks which are dependent on size, surface, shape and defect properties. Nanochemistry is being used in chemical, materials and physical, science as well as engineering, biological and medical applications. Nanochemistry and other nanoscience fields have the same core concepts but the usages of those concepts are different.

The nano prefix was given to nanochemistry when scientists observed the odd changes on materials when they were in nano meter scale size. Several chemical modification on nanometer scaled structures, approves effects of being size dependent.

Nanochemistry can be characterized by concepts of size, shape, self-assembly, defects and bio-nano; So the synthesis of any new nano-construct is associated with all these concepts. Nano-construct synthesis is dependent on how the surface, size and shape will lead to self-assembly of the building blocks into the functional structures; they probably have functional defects and might be useful for electronic, photonic, medical or bioanalytical problems.

Silica, Gold, Polydimethylsiloxane, Cadmium Selenide, Iron Oxide and Carbon are materials that show the transformative power of nanochemistry. Nanochemistry can make the most effective contrast agent of MRI out of iron oxide (rust) which has the ability of detecting cancers and even killing them at their initial stages . Silica (glass) can be used to bend or stop light in its tracks.Developing countries also use silicone to make the circuits for the fluids to attain developed world's pathogen detection abilities. Carbon has been used in different shapes and forms and it will become a better choice for electronic materials.

Overall nanochemistry is not related to the atomic structure of compounds rather its about different ways of transformation of materials into solutions for problems . Chemistry mainly deals withdegrees of freedom of atoms in the periodic table however nanochemistry brought other degrees of freedom that controls material's behaviors.

Nanochemical methods can be used to create carbon nanomaterials such as carbon nanotubes (CNT), graphene and fullerenes which have gained attention in recent years due to their remarkable mechanical and electrical properties.

Nanoparticles have a high surface to volume ratio which has a dramatic effect on their properties compared to non-nanoscale more bulky forms of the same material.

Pieces of gold are, fairly obviously, gold-coloured, but gold nanoparticles are deep red or even black when mixed with water. use?

Titanium dioxide is a white solid used in house paint where plainly it reflects visible light. However, titanium dioxide nanoparticles are so small that they do not reflect visible light, so they cannot be seen and are used in sunblock creams because they block harmful ultraviolet light from the Sun without appearing white on the skin (as in $TiO_2$ in paint).

Silver foil shows virtually no reaction with dilute hydrochloric acid but nanoparticles of silver rapidly react with hydrochloric acid because of the very large surface are to volume ration (think of limestone lumps and very fine powder illustrates this effect at the much larger non-nanoparticle level.

**(OR)**

(b) ***Uses of nanoparticles***

some are described in more detail on other pages, see index at the end and links here too. New applications for nanoparticle materials are an important area of research.

- ✓ Nanoparticles have many applications in medicine for controlled drug delivery - example of nanomedicine.
- ✓ Nanotechnology is being applied to the production of synthetic skin and **implant surgery**.
- ✓ Nanomaterials that conduct electricity are being used in electronics as minute conductors to produce circuits for microchips.
- ✓ Materials in cosmetics, deodorants and **sun creams** may be of nanoparticle size.
- ✓ Nanoscale materials are being developed as new catalysts for fuel cells.

- ✓ Nanoparticle substances are incorporated in fabrics to **prevent the growth of bacteria**.

Nanotubes (more details of specific examples on other pages), one of the most widespread studied and used nanomaterials, consist of tiny cylinders of **carbon** (and other materials like **boron nitride**), no wider than a strand of DNA with a wide range of properties of great use to materials scientists. Nanotubes can be stronger than steel with only $^{1}/_{6}$th the weight. Some nanotubes are excellent insulators, semiconductors or conduct electricity as well as copper!

Incredibly, there are lots of varieties of nanotubes, even for the same element or compound, differing in size and atomic arrangement, which can have very different properties! Therefore a wide range of nanomaterials are being developed for an even wider range of applications and technological uses. See **carbon** and **boron nitride** to illustrate this point.

- ✓ The large surface to volume ratio will allow the development of new industrial catalysts.

Nanomaterials can be used to make sensors that detect specific molecules.

- ✓ These detectors will find applications in detecting and monitoring pollutants in water.

Nanotubes can be fabricated into strong and light materials, sometimes as composites with other non-nanomaterials.

- ✓ Such materials can used in such diverse applications as aircraft construction (fuselage, wings etc.) and sports equipment.

The increased reactivity and small size of nanoparticles compared to larger ones are two important factors which frequently crop up when studying the function of nanomaterials.

- ✓ Nanoparticles have a high surface are to volume ratio, this increases their rate of chemical reaction (greater reactivity) and this also enhances their catalytic effect.
- ✓ Nanomaterials can even be used for such mundane-unexciting applications as in self-cleaning ovens and self-cleaning windows!, but not mundane to domestic work in the Nanoparticles are already being used in deodorants, sun blockers (sun tan creams).
- ✓ The work on nanochemistry can include colloid chemistry.

### 25. (a) **Synthesis of silver nano particles using Chemical reduction method**

Metallic nanoparticles can be synthesized through many methods ¨ The two most popular methods for synthesizing silver nanoparticles (Ag NP) via chemical reduction are:

The most common approach for synthesis of silver NPs is chemical reduction by organic and inorganic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride ($NaBH_4$), elemental hydrogen, polyol process, Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol)-block copolymers are used for reduction of silver ions ($Ag^+$) in aqueous or non-aqueous solutions.

These reducing agents reduce $Ag^+$ and lead to the formation of metallic silver ($Ag^0$), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloidal silver particles. It is important to use protective agents to stabilize dispersive NPs during the course of metal nanoparticle preparation, and protect the NPs that can be absorbed on or bind onto nanoparticle surfaces, avoiding their agglomeration. The presence of surfactants comprising functionalities (*e.g.*, thiols, amines, acids, and alcohols) for interactions with particle surfaces can stabilize particle growth, and protect particles from sedimentation, agglomeration, or losing their surface properties.

### Photoinduced reduction

Silver NPs can be synthesized by using a variety of photoinduced or photocatalytic reduction methods. Photochemical synthesis is a clean process which has high spatial resolution, convenience of use, and great versatility. Moreover, photochemical synthesis enables one to fabricate the NPs in various mediums including cells, emulsion, polymer films, surfactant micelles, glasses, etc. Nano-sized silver particles with an average size of 8 nm were prepared by photoinduced reduction using poly (styrene sulfonate)/poly (allylamine hydrochloride) polyelectrolyte capsules as microreactors. Moreover, it was demonstrated that photoinduced method could be used for converting silver nanospheres into triangular silver nanocrystals (nanoprisms) with desired edge lengths in 30-120 nm range. Particle growth process was controlled using dual-beam illumination of NPs. Citrate and poly (styrene sulfonate) were used as stabilizing agents. In another study, silver NPs were prepared through a very fast reduction of $Ag^+$ by α-aminoalkyl radicals generated from hydrogen abstraction toward an aliphatic amine by the excited triplet state of 2-substituted thioxanthone series ($TX\text{-}O\text{-}CH_2\text{-}COO^-$ and $TX\text{-}S\text{-}CH_2\text{-}COO^-$). Quantum yield of this prior reaction was tuned by substituent effect on thioxanthones, and led to a kinetic control of conversion of silver ion ($Ag^+$) to silver metal ($Ag^0$).

The direct photo-reduction process of $AgNO_3$ in the presence of sodium citrate (NaCit) was carried out with different light sources (UV, white, blue, cyan, green and orange) at room temperature. Sato-Berrú and coworkers have shown that this light-modification process results in a colloid with distinctive optical properties which can be related to the size and shape of the particles. Moreover, Ghosh and colleagues reported a simple and reproducible UV photo-activation method for the preparation of stable silver NPs in aqueous Triton X-100 (TX-100). The TX-100 molecules act as reducing agent and also as NPs stabilizer through template/capping action.

**(OR)**

(b) **Nanoparticles** are particles between 1 and 100 nanometres (nm) in size with a surrounding interfacial layer. The interfacial layer is an integral part of nanoscale matter, fundamentally affecting all of its properties. The interfacial layer typically consists of ions, inorganic and organic molecules. Organic molecules coating inorganic nanoparticles are known as stabilizers, capping and surface ligands, or passivating agents. In nanotechnology, a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties.

### Synthesis of silver NPs

### Physical methods

Evaporation-condensation and laser ablation are the most important physical approaches. The absence of solvent contamination in the prepared thin films and the uniformity of NPs distribution are the advantages of physical synthesis methods in comparison with chemical processes. Physical synthesis of silver NPs using a tube furnace at atmospheric pressure has some disadvantages, for example, tube furnace occupies a large space, consumes a great amount of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability. Moreover, a typical tube furnace requires power consumption of more than several kilowatts and a preheating time of several tens of minutes to reach a stable operating temperature. It was demonstrated that silver NPs could be synthesized via a small ceramic heater with a local heating area. The small ceramic heater was used to evaporate source materials. The evaporated vapor can cool at a suitable rapid rate, because the temperature gradient in the vicinity of the heater surface is very steep in comparison with that of a tube furnace.

This makes possible the formation of small NPs in high concentration. The particle generation is very stable, because the temperature of the heater surface does not fluctuate with time. This physical method can be useful as a nanoparticle generator for long-term experiments for inhalation toxicity studies, and as a calibration device for nanoparticle measurement equipment. The results showed that the geometric mean diameter, the geometric standard deviation and the total number concentration of NPs increase with heater surface temperature. Spherical NPs without agglomeration were observed, even at high concentration with high heater surface temperature. The geometric mean diameter and the geometric standard deviation of silver NPs were in the range of 6.2-21.5 nm and 1.23-1.88 nm, respectively.

Silver NPs could be synthesized by laser ablation of metallic bulk materials in solution. The ablation efficiency and the characteristics of produced nano-silver particles depend upon many parameters, including the wavelength of the laser impinging the metallic target, the duration of the laser pulses (in the femto-, pico- and nanosecond regime), the laser fluence, the ablation time duration and the effective liquid medium, with or without the presence of surfactants.

One important advantage of laser ablation technique compared to other methods for production of metal colloids is the absence of chemical reagents in solutions. Therefore, pure and uncontaminated metal colloids for further applications can be prepared by this technique. Silver nanospheroids (20-50 nm) were prepared by laser ablation in water with femtosecond laser pulses at 800 nm. The formation efficiency and the size of colloidal particles were compared with those of colloidal particles prepared by nanosecond laser pulses. As a result, the formation efficiency for femtosecond pulses was significantly lower than that for nanosecond pulses. The size of colloids prepared by femtosecond pulses were less dispersed than that of colloids prepared by nanosecond pulses. Furthermore, it was found that the ablation efficiency for femtosecond ablation in water was lower than that in air, while in the case of nanosecond pulses, the ablation efficiency was similar in both water and air.

Tien and coworkers used the arc discharge method to fabricate silver NPs suspension in deionized water with no added surfactants. In this synthesis, silver wires (Gredmann, 99.99%, 1 mm in diameter) were submerged in deionized water and used as electrodes. With a silver rod consumption rate of 100 mg/min, yielding metallic silver NPs of 10 nm in size, and ionic silver obtained at concentrations of approximately 11 ppm and 19 ppm, respectively. Siegel and colleagues demonstrated the synthesis of silver NPs by direct metal sputtering into the liquid medium. The method, combining physical deposition of metal into propane-1,2,3-triol (glycerol), provides an interesting alternative to time-consuming, wet-based chemical synthesis techniques. Silver NPs possess round shape with average diameter of about 3.5 nm with standard deviation 2.4 nm. It was observed that the NPs size distribution and uniform particle dispersion remains unchanged for diluted aqueous solutions up to glycerol-to-water ratio 1:20.

## Irradiation methods

Silver NPs can be synthesized by using a variety of irradiation methods. Laser irradiation of an aqueous solution of silver salt and surfactant can produce silver NPs with a well defined shape and size distribution. Furthermore, laser was used in a photo-sensitization synthetic method of making silver NPs using benzophenone. At short irradiation times, low laser powers produced silver NPs of about 20 nm, while an increased irradiation power produced NPs of about 5 nm. Laser and mercury lamp can be used as light sources for production of silver NPs. In visible light irradiation studies, photo-sensitized growth of silver NPs using thiophene (sensitizing dye) and silver nanoparticle formation by illumination of $Ag(NH_3)^+$ in ethanol has been done.

26. (a)

## Operating principle of a Transmission Electron Microscope

Transmission electron microscopy (TEM, also sometimes conventional transmission electron microscopy or CTEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a charge-coupled device.

**TEMs consist of the following components:**

- An electron source
- Thermionic Gun
- Electron beam
- Electromagnetic lenses
- Vacuum chamber
- 2 Condensers
- Sample stage
- Phosphor or fluorescent screen
- Computer

A Transmission Electron Microscope functions under the same basic principles as an optical microscope.

In a TEM, electrons replace photons, electromagnetic lenses replace glass lenses and images are viewed on a screen rather than through an eyepiece.

## TEM Imaging

**A Transmission** Electron Microscope produces a high-resolution, black and white image from the interaction that takes place between prepared samples and energetic electrons in the vacuum chamber.

- ✓ Air needs to be pumped out of the vacuum chamber, creating a space where electrons are able to move.
- ✓ The electrons then pass through multiple electromagnetic lenses. These solenoids are tubes with coil wrapped around them.
- ✓ The beam passes through the solenoids, down the column, makes contact with the screen where the electrons are converted to light and form an image.
- ✓ The image can be manipulated by adjusting the voltage of the gun to accelerate or decrease the speed of electrons as well as changing the electromagnetic wavelength via the solenoids.
- ✓ The coils focus images onto a screen or photographic plate.
- ✓ During transmission, the speed of electrons directly correlates to electron wavelength; the faster electrons move, the shorter wavelength and the greater the quality and detail of the image.
- ✓ The lighter areas of the image represent the places where a greater number of electrons were able to pass through the sample and the darker areas reflect the dense areas of the object.
- ✓ These differences provide information on the structure, texture, shape and size of the sample.
- ✓ To obtain a TEM analysis, samples need to have certain properties. They need to be sliced thin enough for electrons to pass through, a property known as electron transparency.
- ✓ Samples need to be able to withstand the vacuum chamber and often require special preparation before viewing.
- ✓ Types of preparation include dehydration, sputter coating of non-conductive materials, cryofixation, sectioning and staining.

The transmission electron microscope (TEM) operates on many of the same optical principles as the light microscope. The TEM has the added advantage of greater resolution. This increased resolution allows us to study ultrastucture of organelles, viruses and macromolecules. Specially prepared materials samples may also be viewed in the TEM. The light microscope and TEM are commonly used in conjunction with each other to complement a research project.

Since electrons are very small and easily deflected by hydrocarbons or gas molecules, it is necessary to use the electron beam in a vacuum environment. A series of pumps are used to accomplish an adequate vacuum for this purpose. Rotary Pumps are the first in the series. They are also called the "roughing pumps" as they are used to initially lower the pressure within the column through which the electron must travel to 10 -3 mm of Hg range. Diffusion Pumps may achieve higher vacuums (in the 10-5 mm Hg range) but must be backed by the rotary pump. The diffusion pump also maintains pressure. In addition a Turbo, Ion, or Cryo Pumps backed by the preceding pumps may be used when an even greater vacuum is required.

The organization of the transmission electron microscope (TEM) is similar to that of the light microscope.

## TEM aplplications

- ✓ A Transmission Electron Microscope is ideal for a number of different fields such as life sciences, nanotechnology, medical, biological and material research, forensic analysis, gemology and metallurgy as well as industry and education.
- ✓ TEMs provide topographical, morphological, compositional and crystalline information.
- ✓ The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture.
- ✓ This information is useful in the study of crystals and metals, but also has industrial applications.
- ✓ TEMs can be used in semiconductor analysis and production and the manufacturing of computer and silicon chips.
- ✓ Technology companies use TEMs to identify flaws, fractures and damages to micro-sized objects; this data can help fix problems and/or help to make a more durable, efficient product.
- ✓ Colleges and universities can utilize TEMs for research and studies.
- ✓ Although electron microscopes require specialized training, students can assist professors and learn TEM techniques.

**Advantages**

A Transmission Electron Microscope is an impressive instrument with a number of advantages such as:

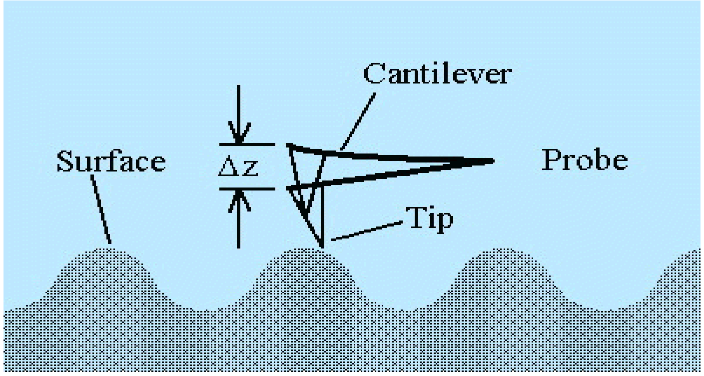
- TEMs offer the most powerful magnification, potentially over one million times or more
- TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields
- TEMs provide information on element and compound structure
- Images are high-quality and detailed
- TEMs are able to yield information of surface features, shape, size and structure
- They are easy to operate with proper training

**Disadvantages**

- Some cons of electron microscopes include:
- TEMs are large and very expensive
- Laborious sample preparation
- Potential artifacts from sample preparation
- Operation and analysis requires special training
- Samples are limited to those that are electron transparent, able to tolerate the vacuum chamber and small enough to fit in the chamber
- TEMs require special housing and maintenance
- Images are black and white

**(OR)**

(b) **Probe microscopy**



Scanning probe microscopy covers several related technologies for imaging and measuring surfaces on a fine scale, down to the level of molecules and groups of atoms.

At the other end of the scale, a scan may cover a distance of over 100 micrometers in the x and y directions and 4 micrometers in the z direction. This is an enormous range. It can truly be said that the development of this technology is a major achievement, for it is having profound effects on many areas of science and engineering.

SPM technologies share the concept of scanning an extremely sharp tip (3-50 nm radius of curvature) across the object surface. The tip is mounted on a flexible cantilever, allowing the tip to follow the surface profile (see Figure).

When the tip moves in proximity to the investigated object, forces of interaction between the tip and the surface influence the movement of the cantilever. These movements are detected by selective sensors. Various interactions can be studied depending on the mechanics of the probe

## Probe Techniques

The three most common scanning probe techniques are:

**Atomic Force Microscopy** (AFM) measures the **interaction force** between the tip and surface. The tip may be dragged across the surface, or may vibrate as it moves. The interaction force will depend on the nature of the sample, the probe tip and the distance between them.

**Scanning Tunneling Microscopy** (STM) measures a **weak electrical current** flowing between tip and sample as they are held a very distance apart.

**Near-Field Scanning Optical Microscopy** (NSOM) scans a very **small light source** very close to the sample. Detection of this light energy forms the image. NSOM can provide resolution below that of the conventional light microscope.

There are numerous variations on these techniques. AFM may operate in several modes which differ according to the force between the tip and surface:

| **Mode of Operation** | **Force of Interaction** |
|---|---|
| contact mode | strong (repulsive) - constant force or constant distance |
| non-contact mode | weak (attractive) - vibrating probe |

| | |
|---|---|
| intermittent contact mode | strong (repulsive) - vibrating probe |
| lateral force mode | frictional forces exert a torque on the scanning cantilever |
| magnetic force | the magnetic field of the surface is imaged |
| thermal scanning | the distribution of thermal conductivity is imaged |

In contact mode, the tip is usually maintained at a constant force by moving the cantilever up and down as it scans. In non-contact mode or intermittent contact mode (tapping mode$^{TM}$) the tip is driven up and down by an oscillator. Especially soft materials may be imaged by a magnetically-driven cantilever (MAC Mode$^{TM}$). In non-contact mode, the bottom-most point of each probe cycle is in the *attractive* region of the force-distance curve. In intermittent contact mode the bottom-most point is in the *repulsive* region. Variations in the measured oscillation amplitude and phase in relation to the driver frequency are indicators of the surface-probe interaction.

To image *frictional force*, the probe is dragged along the surface, resulting in a torque on the cantilever. To image the magnetic field of the surface, a magnetically-susceptible probe is used. In other variations, the electric charge distribution on the surface or the surface capacitance is imaged. For thermal scanning microscopy (TSM) the thermal conductivity of the surface with is probed with a resistive tip that acts as a tiny resistance thermometer.

In addition to these modes, many instruments are also designed to plot the phase difference between the measured modes, for example frictional force versus contact profile. This plot is called **phase mode**.

Several types of probes with different tips are used in scanning probe microscopy. Tip selection depends on the mode of operation and on the type of sample.

**Applications**

These techniques have the ability to operate on a scale from microns down to nanometers and can image clusters of individual atoms and molecules. STM relies on the electrical conductivity of the sample, so at least some features on the sample surface must be electrically conductive to some degree. AFM is used for studies of non-conductors and is the technique more commonly used for studies of macromolecules and biological specimens.

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**(Deemed University Established Under Section 3 of UGC Act 1956)**

**COIMBATORE-21**

## DEPARTMENT OF CHEMISTRY

***II M.Sc., CHEMISTRY***

## INTERNAL EXAM-II-NANO CHEMISTRY

## ANSWER KEY

## PART- A (20 x 1=20 Marks)

**Answers**

1.( b) used as Semiconductor
2. (b) $10^{-12}$m
3. (c) the graphene sheet consists of $C_n$ rings in which $n = 6$, but in fullerenes $n = 5$ and 6
4. (d) The bundles are of discrete sizes, and dipole-dipole forces hold the tubes together
5. (c) Transportation
6. (b) Particle size and shape
7. (b) Fume hood
8. (a)Dendrimers
9. (c) Nano rods
10. (b) Surface area/volume
11. (a) Carbon nano tubes
12. (a)bacterial infection
13. (a) Coated with gold
14. (c) Catalytic
15. (b) $MnO_2$
16. (b) Contact mode
17. (d) 5000
18. (b) 90
19. (a) bacterial infection
20. (c) 10000

## PART- B (3 x 2=6 Marks)

## Answer All the Questions

21. Diffraction methods and their applications:

<u>Powder diffraction</u>:

- Refinement of crystallographic or magnetic structure on polycrystalline materials

- Phase transformations and reaction pathways as a function of external parameters (temperature, magnetic or electric field, mechanical strain or pressure)

Single-crystal diffraction :

- Refinement of crystallographic or magnetic structure on polycrystalline materials
- Structure solution on complex systems or proteins

Strain/ texture analysis:

- Analysis of residual strain on engineering materials
- Analysis of texture on engineering materials

22. How will you classify nanotechnology on the basis of their size?

**Classification of nano structures materials**

Nano particle;

1. Nano cluster
2. Nano rod
3. Nano tube and
4. Nanowires

23.

Monometallic, bimetallic and semiconductor **nanoparticles** have been synthesized using this method.

The primary **use** for DEN's is as a catalyst due to their extremely high surface area to volume ratio.

Advantages that DENs have over other**nanoparticles** is that they are monodisperse and easy to make.

## PART- C (3 x 8 =24 Marks)

## Answer All the Questions

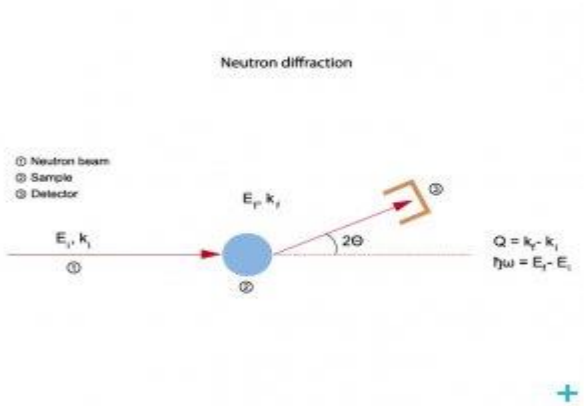
24. (a)

**Neutron diffraction**. **Neutron diffraction** experiments determine the atomic and/or magnetic structure of a material. This **technique** can be applied to study crystalline solids, gasses, liquids or amorphous materials.

**Neutron diffraction** or **elastic neutron scattering** is the application of neutron scattering to the determination of the atomic and/or magnetic structure of a material: A sample to be examined is placed in a beam of thermal, hot or cold neutrons to obtain a diffraction pattern that provides information of the structure of the material.

The technique is similar to X-ray diffraction but due to the different scattering properties of neutrons versus x-rays, complementary information can be obtained. In particular, neutron diffraction is advantageous for the localisation of light atoms and the determination of magnetic ordering.

### *Neutron diffraction principle*



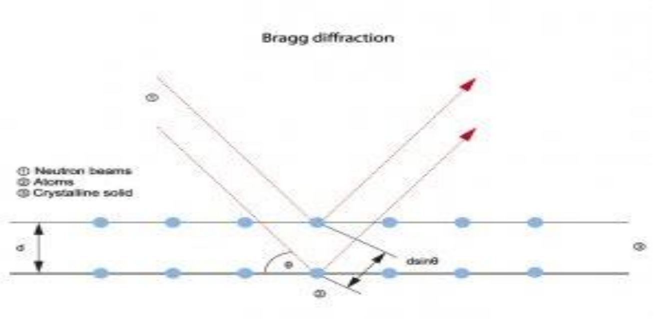
## **Neutron diffraction**

Neutron diffraction has some unique characteristics when compared to other types of radiation. This makes it very useful for the study of the atomic structure of liquids, amorphous materials and crystalline materials.

Diffraction can see the ordered part of systems, which means, for ordered systems (crystals), their average structure but also deviations from this perfect order; for disordered systems, the ordered portions existing amid this disorder.

Diffraction methods can be divided into two interactions, **nuclear diffraction**: diffraction due to the interaction between neutrons and atomic nuclei, and **magnetic diffraction**: diffraction due to the interaction between the magnetic moments of neutrons and magnetic moments of atoms.

### *Bragg equation*



Bragg diffraction

The measurement principle of neutron diffraction is based on the Bragg Equation. Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings are incident upon a crystalline sample, are scattered in a specular fashion by the atoms in the system, and undergo constructive interference in accordance to Bragg's law.

For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d. Where the scattered waves interfere constructively, they remain in phase since the path length of each wave is equal to an integer multiple of the wavelength. The path difference between two waves undergoing constructive interference is given by 2dsinθ, where θ is the scattering angle.

This leads to **Bragg's law**, which describes the condition for constructive interference from successive crystallographic planes of the crystalline lattice:

$$2d\cdot\sin(\theta)=n\lambda$$

Where n is an integer determined by the order given, and λ is the wavelength.

***Diffraction methods and their applications:***

Powder diffraction:

- Refinement of crystallographic or magnetic structure on polycrystalline materials
- Phase transformations and reaction pathways as a function of external parameters (temperature, magnetic or electric field, mechanical strain or pressure)

Single-crystal diffraction :

- Refinement of crystallographic or magnetic structure on polycrystalline materials
- Structure solution on complex systems or proteins

Strain/ texture analysis:

- Analysis of residual strain on engineering materials
- Analysis of texture on engineering materials

**(OR)**

(b) How will you explain the thermodynamic features of nanoparticles?

**Distinction between molecules, nano-particles and bulk materials – illustration with examples.**

1. **Reduced Melting Point --** Nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably **reduced lattice constants (spacing between atoms is reduced)**, **due to a huge fraction of surface atoms** in the total amount of atoms.
2. **Ultra Hard --** Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk

form. The enhancement in mechanical strength is simply **due to the reduced probability of defects**.

3. **Optical properties** of nanomaterials can be significantly different from bulk crystals. --- **Semiconductor Blue Shift** in adsorption and emission **due to an increased band gap.**

*Quantum Size Effects, Particle in a box.* --- **Metallic Nanoparticles Color Changes** in spectra **due to Surface Plasmons Resonances** *Lorentz Oscillator odel.*

4. **Electrical conductivity decreases** with a reduced dimension **due to increased surface scattering**.

   **Electrical conductivity increases** due to the **better ordering** and **ballistic transport.**

5. **Magnetic properties** of nanostructured materials are distinctly different from that of bulk materials. **Ferromagnetism disappears** and transfers to **superparamagnetism** in the nanometer scale **due to the huge surface energy**.
6. **Self-purification** is an intrinsic thermodynamic property of nanostructures and nanomaterials **due to enhanced diffusion of impurities/defects/dislocations** to the nearby surface.

**Increased perfection enhances chemical stability.**

Two primary factors cause nanomaterials to behave significantly differently than bulk materials:

*surface effects* (causing smooth properties scaling due to the fraction of atoms at the surface) and *quantum effects* (showing discontinuous behavior due to quantum confinement effects in materials with delocalized electrons). These factors affect the chemical reactivity of materials, as well as their mechanical, optical, electric, and magnetic properties. The fraction of the atoms at the surface in nanoparticles is increased compared to microparticles or bulk. Compared to microparticles, nanoparticles have a very large surface area and high particle number per unit mass. For illustration, one carbon microparticle with a diameter of 60 µm has a mass of 0.3 µg and a surface area of 0.01 $mm^2$. The same mass of carbon in nanoparticulate form, with each particle having a diameter of 60 nm, has a surface area of 11.3 $mm^2$ and consists of 1 billion nanoparticles. For example, the melting temperature of 3 nm gold nanoparticles is more than 300 degrees lower than the melting temperature of bulk gold. An example of a class of materials that clearly exploits quantum effects is quantum dots - synthesized nanostructures with sizes as small as a few nanometers. The electronic behavior of quantum dots is similar to that of individual atoms or small molecules, and quantum dots are regarded as akin to artificial atoms Nano materials have superior properties than bulk materials.

| Bulk (eg. Gold) | Nano (eg. Gold) |
|---|---|

| | |
|---|---|
| 1. Lustrous–Shiny surface when polished.<br>2. Malleable–Can be hammered, bent or rolled®any desired shape.<br>3. Ductile–Can be drawn out into wires<br>4. Yellow colour when in a mass<br>5. Heat & electricity conductor<br>6. High densities<br>7. High melting point (1080°C)<br>8. Tough with high tensile strength<br>9. Inert-unaffected by air and most reagents | 1. Vary in appearance depending on size & shape of cluster.<br>2. Are never gold in colour!.<br>3. Are found in a range of colours.<br>4. Are very good catalysts.<br>5. Are not ―metals‖ but are semiconductors.<br>6. Melts at relatively low temperature (~940° C).<br>7. Size & Shape of the nanoparticles determines the color.<br>8. For example; Gold particles in glass:<br>25 nm — Red reflected<br>50 nm — Green reflected (Unexpected visible properties & they are small enough to scatter visible light rather than absorb) |

25. (a)

### Nano-rod, nano-tube(CNT) and nano-wire (CNT).

### Classification of nano structures materials

Nano particle;

1. Nano cluster
2. Nano rod
3. Nano tube
4. anowires

### Nanoclusters

Nanoclusters constitute an intermediate state of matter between molecules and solids. Nanocluster sizes range from sub-nanometer to about 10 nanometres in diameter and are of technological interest in numerous areas of applied science (e.g. materials science, catalysis and opto-electronics). Often one differentiates between:

(i) nanoclusters consisting of up to a couple of hundred atoms, and

(ii) larger aggregates containing $10^3$ or more atoms which are more often called nanoparticles.

The properties of nanoparticles gradually approach those of bulk materials or extended surfaces, i.e. are scalable with size. Nanoclusters, however, have properties and structures which are very sensitive to their composition and size (i.e. ―every atom counts‖) which can lead to new and interesting properties not realised in the corresponding bulk material.

### <u>Cluster model</u>

### Nanorods

Nanorods are one morphology of nanoscale objects. Each of their dimensions range from 1–100 nm. They may be synthesized from metals or semiconducting materials. Standard aspect ratios (length divided by width) are 3-5. Nanorods are produced by direct chemical synthesis. Combinations of ligands act as shape control agents and bond to different facets of the nanorod with different strengths. This allows different faces of the nanorod to grow at different rates, producing an elongated object.

One potential application of nanorods is in display technologies, because the reflectivity of the rods can be changed by changing their orientation with an applied electric field. Another application is for micro-electromechanical systems (MEMS). Nanorods, along with other noble metal nanoparticles, also function as the agnostic agents. Nanorods absorb in the near IR, and generate heat when excited with IR light. This property has led to the use of nanorods as cancer therapeutics. Nanorods can be conjugated with tumor targeting motifs and ingested. When a patient is exposed to IR light (which passes through body tissue), nanorods selectively taken-up by tumor cells are locally heated, destroying only the cancerous tissue while leaving healthy cells intact.

**Nanorod**

### Nano tube (Carbon nanotubes (CNT))

A carbon nanotube (CNT) is a miniature cylindrical carbon structure that has hexagonal graphite molecules attached at the edges.

Nanotubes look like a powder or black soot, but they're actually rolled-up sheets of graphene that form hollow strands with walls that are only one atom thick. Nanotubes, which are sometimes called bulky tubes, were developed from the Fullerene, a structure that is similar to the geodesic domes.

Nanotubes, which are grown in a laboratory, are strong and exhibit many thermal and electrical properties that are desirable to chip makers. Carbon nanotubes have the potential to be used as semiconductors, for example, potentially replacing silicon in a wide variety of computing devices.

Nanotubes can be characterized by their number of concentric cylinders, cylinder radius and cylinder length. Some nanotubes have a property called chirality, an expression of longitudinal twisting. Multiple nanotubes can be assembled into microscopic mechanical systems called nanomachines.

**Corbon nanotube**

### Nanowires

A nanowire is a nanostructure, with the diameter of the order of a nanometer ($10^{-9}$ meters). It can also be defined as the ratio of the length to width being greater than 1000. Alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of 7 nanometers or less and an unconstrained length. At these scales, quantum mechanical effects are important — which coined the term "quantum wires". Many different types of nanowires exist, including metallic (e.g., Ni, Pt, Au), semiconducting (e.g., Si, InP, GaN, etc.), and insulating (e.g., $SiO_2$, $TiO_2$). Molecular nanowires are composed of repeating molecular units either organic (e.g. DNA) or inorganic (e.g. Mo6S9-xIx).

**Nanowire**

## Synthesis: of nano-materials: precipitation, thermolysis, hydrothermal and solvothermal methods.

### Synthesis of nanomaterials

Top-down and bottom-up are two approaches for the manufacture of products. These terms were first applied to the field of nanotechnology by the Foresight Institute in 1989 in order to distinguish between molecular manufacturing (to mass-produce large atomically precise objects) and conventional manufacturing (which can mass-produce large objects that are not atomically precise). Bottom-up approaches seek to have smaller (usually molecular) components built up into more complex assemblies, while top-down approaches seek to create nanoscale devices by using larger, externally controlled ones to direct their assembly.

**(OR)**

(b)

### Size dependent properties nanomaterials

Nanoparticles are of great scientific interest as they are, in effect, a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.

Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects.

For example gold nanoparticles appear deep-red to black in solution. Nanoparticles of yellow gold and grey silicon are red in color. Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C)

Other size-dependent property changes: The high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. In theory, this does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters. Moreover, nanoparticles have been found to impart some extra properties to various day to day products. For example, the presence of titanium dioxide nanoparticles imparts what we call the self-cleaning effect, and, the size being nano-range, the particles cannot be observed. Zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions, and is completely photostable.

### Nano-rod, nano-tube(CNT) and nano-wire (CNT).

### Classification of nano structures materials

Nano particle; 1. Nano cluster 2. Nano rod 3. Nano tube and 4. Nanowires

***Mechanical properties:*** The mechanical properties of carbon nanotubes in the radial (transverse) direction. Carbon nanotubes are one of the strongest materials in nature. Carbon nanotubes (CNTs) are long hollow cylinders of graphene. Although graphene sheets have 2D symmetry, carbon nanotubes by geometry have different properties in axial and radial directions. It has been shown that CNTs are very strong in the axial direction. Young's modulus on the order of 270 - 950 GPa and tensile strength of 11 - 63 GPa were obtained. On the other hand, there was evidence that in the radial direction they are rather soft. The first transmission electron microscope observation of radial elasticity suggested that even the van der Waals forces can deform two adjacent nanotubes. Later, nanoindentations with atomic force microscope were performed by several groups to quantitatively measure radial elasticity of multiwalled carbon nanotubes and tapping/contact mode atomic force microscopy was also performed on single-walled carbon nanotubes.

- ***Catalytic Properties:*** Functionalized metal nanoparticles are more stable in solution compared to non-functionalized metal nanoparticles. In liquid solutions, the metal nanoparticles are close enough together to be affected by van der Waals force. If there isn’t anything to oppose these forces, then the nanoparticles will aggregate, which will lead to a decrease in catalytic activity by lowering the surface area. For organometallic functionalized nanoparticles, ligands are coordinated to the metal center to prevent aggregation. Using different ligands alters the properties and sizes of the nanoparticle catalysts. Nanoparticles can also be functionalized with polymers or oligomers to sterically stabilize the nanoparticles by providing a protective layer that prevents the nanoparticles from interacting with each other. Alloys of two metals, called bimetallic nanoparticles, are used to create synergistic effects on catalysis between the two metals.
- ***Magnetic Properties:*** In magnetic nanoparticles, the energy of magnetic anisotropy may be that small that the vector of magnetization fluctuates thermally; this is called superparamagnetism. Such a material is free of remanence, and coercitivity. Touching superparamagnetic particles are loosing this special property by interaction, except the particles are kept at distance. Combining particles with high energy of anisotropy with superparamagnetic ones leads to a new class of permanent magnetic materials.
- ***Optical Properties:*** Distributions of non-agglomerated nanoparticles in a polymer are used to tune the index of refraction. Additionally, such a process may produce materials with non-linear optical properties. Gold or CdSe nanoparticles in glass lead to red or orange coloration. Semi-conducting nanoparticles and some oxide-polymer nanocomposites exhibit fluorescence showing blue shift with decreasing particle size.

26. (a) **Applications of nanomaterial**

Since nanomaterials possess unique, beneficial chemical, physical, and mechanical properties, they can be used for a wide variety of applications. These applications include, but are not limited to, the following:

- *Next-Generation Computer Chips:* The microelectronics industry has been emphasising miniaturisation, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size.
- *Kinetic Energy (KE) Penetrators with Enhanced Lethality:* The Department of Defense (DoD) is currently using depleted-uranium (DU) projectiles (penetrators) for its lethality against hardened targets and enemy armoured vehicles.
- *Better Insulation Materials:* Nanocrystalline materials synthesised by the sol-gel technique result in foam like structures called "aerogels." These aerogels are porous and extremely lightweight; yet, they can loads equivalent to 100 times their weight. Aerogels are composed of three-dimensional, continuous networks of particles with air (or any other fluid, such as a gas) trapped at their interstices. Since they are porous and air is trapped at the interstices, aerogels are currently being used for insulation in offices, homes, etc.
- *Phosphors for High-Definition TV:* The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors.
- *Low-Cost Flat-Panel Displays:* Flat-panel displays represent a huge market in the laptop (portable) computers industry. However, Japan is leading this market, primarily because of its research and development efforts on the materials for such displays.
- *Tougher and Harder Cutting Tools:* Cutting tools made of nanocrystalline materials, such as tungsten carbide, tantalum carbide, and titanium carbide, are much harder, much more wear-resistant, erosion-resistant, and last longer than their conventional (large-grained) counterparts.
- *Elimination of Pollutants:* Nanocrystalline materials possess extremely large grain boundaries relative to their grain size. Hence, nanomaterials are very active in terms of their of chemical, physical, and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.
- *High Energy Density Batteries:* Conventional and rechargeable batteries are used in almost all applications that require electric power. These applications include automobiles, laptop computers, electric vehicles, next-generation electric vehicles (NGEV) to reduce environmental pollution, personal stereos, cellular phones, cordless phones, toys, and watches. The energy density (storage capacity) of these batteries is quite low requiring frequent recharging. The life of conventional and rechargeable batteries is also low. Nanocrystalline materials synthesised by sol-gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than their conventional counterparts.
- *High-Sensitivity Sensors:* Sensors employ their sensitivity to the changes in various

parameters they are designed to measure. The measured parameters include electrical resistivity, chemical activity, magnetic permeability, thermal conductivity, and capacitance.

- *Automobiles with Greater Fuel Efficiency:* Currently, automobile engines waste considerable amounts of gasoline, thereby contributing to environmental pollution by not completely combusting the fuel. A conventional spark plug is not designed to burn the gasoline completely and efficiently. This problem is compounded by defective, or worn-out, spark plug electrodes.
- *Aerospace Components with Enhanced Performance Characteristics:* Due to the risks involved in flying, aircraft manufacturers strive to make the aerospace components stronger, tougher, and last longer. One of the key properties required of the aircraft components is the fatigue strength, which decreases with the component's age.

**(OR)**

(b)

**Health hazards**

Nanotoxicology is the field which studies potential health risks of nanomaterials. The extremely small size of nanomaterials means that they are much more readily taken up by the human body than larger sized particles. How these nanoparticles behave inside the organism is one of the significant issues that needs to be resolved. The behavior of nanoparticles is a function of their size, shape and surface reactivity with the surrounding tissue. Apart from what happens if non-degradable or slowly degradable nanoparticles accumulate in organs, another concern is their potential interaction with biological processes inside the body: because of their large surface, nanoparticles on exposure to tissue and fluids will immediately adsorb onto their surface some of the macromolecules they encounter. The large number of variables influencing toxicity means that it is difficult to generalise about health risks associated with exposure to nanomaterials – each new nanomaterial must be assessed individually and all material properties must be taken into account. Health and environmental issues combine in the workplace of companies engaged in producing or using nanomaterials and in the laboratories engaged in nanoscience and nanotechnology research. It is safe to say that current workplace exposure standards for dusts cannot be applied directly to nanoparticle dusts.

The extremely small size of nanomaterials also means that they are much more readily taken up by the human body than larger sized particles. How these nanoparticles behave inside the body is one of the issues that needs to be resolved. The behavior of nanoparticles is a function of their size, shape and surface reactivity with the surrounding tissue. They could cause overload on phagocytes, cells that ingest and destroy foreign matter, thereby triggering stress reactions that lead to inflammation and weaken the body's defense against other pathogens. Apart from what happens if non-degradable or slowly degradable nanoparticles accumulate in organs, another concern is their potential interaction with biological processes inside the body: because of their large surface, nanoparticles on exposure to tissue and fluids will immediately adsorb onto their surface some of the macromolecules they encounter. This may, for instance, affect the regulatory mechanisms of enzymes and other proteins.

The National Institute for Occupational Safety and Health has conducted initial research on how nanoparticles interact with the body's systems and how workers might be exposed to nano-sized particles in the manufacturing or industrial use of nanomaterials. NIOSH currently offers interim guidelines for working with nanomaterials consistent with the best scientific knowledge. At The National Personal Protective Technology Laboratory of NIOSH, studies investigating the filter penetration of nanoparticles on NIOSH-certified and EU marked respirators, as well as non-certified dust masks have been conducted. These studies found that the most penetrating particle size range was between 30 and 100 nanometers, and leak size was the largest factor in the number of nanoparticles found inside the respirators of the test dummies.

Other properties of nanomaterials that influence toxicity include: chemical composition, shape, surface structure, surface charge, aggregation and solubility,[14] and the presence or absence of functional groups of other chemicals. The large number of variables influencing toxicity means that it is difficult to generalise about health risks associated with exposure to nanomaterials – each new nanomaterial must be assessed individually and all material properties must be taken into account.

## Environmental impact

The environmental impact of nanotechnology is the possible effects that the use of nanotechnological materials and devices will have on the environment. As nanotechnology is an emerging field, there is debate regarding to what extent industrial and commercial use of nanomaterials will affect organisms and ecosystems.

Nanotechnology's environmental impact can be split into two aspects: the potential for nanotechnological innovations to help improve the environment, and the possibly novel type of pollution that nanotechnological materials might cause if released into the environment.