Microscopy Methods in Nanochemistry

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• “In the next decade, morphology effect of materials and so nanomaterials play very important role on them applications.
• I think morphology effect of materials and nanomaterials would be important enough role that science influence and domination will nanotechnology.
• When we say “Nanoparticle”, “Nanowires”, “Nanostars”, Nanoplates”, “Nanotubes”, Nanoflowers”, “Nnaobelts” and/or other morphology of Nanomaterials, we should certitude this word indicate the Notability of Microscopy methods to analysis of Nanomaterials at bulk materials.
• Therefore, morphology analysis and its role in nanomaterials and bulk materials are possible only through microscopic techniques and this is shows very important role for chemical reactions and mechanisms designers or reactions engineering’s that is possible only according by microscopy methods”.

1. Abstract

Two parameters are very important in nanotechnology. One of them size and other is morphology. In recent years morphology effect at nanoparticles characters play important role. The microscopy methods is an invaluable tool for the characterization of nanostructured materials, providing a range of different imaging modes and size with the ability to provide information on morphology, elemental composition and electronic structure at the ultimate sensitivity, that of a single atom.

Keywords Nanochemistry, Microscopy, Analysis, Nanoparticles,

2. Introduction

Imagine how much control over resultant properties you would have if you were able to deposit and maneuver individual atoms into predefined arrangements, en route toward a new material. This is fast becoming a reality, and is the realization of the ultimate in “bottom-up” materials design. Thus far, one is able to easily fabricate materials comprised of a small number of atoms, with features on the nanometer scale (10⁻⁹ m) one-billionth of a meter. To put this into perspective, think of a material with dimensions approximately 8,000 times smaller than the diameter of a human hair follicle! As we will see, it is now even possible to push individual atoms around a surface using specialized techniques.

We are at the crossroads of unprecedented applications that will only be possible using nanoscale building blocks. More effective devices will be constructed to remove pollutants from the environment and detect/deactivate chemical warfare agents. Integrated circuitry with the capabilities of current workstations will be the size of a grain of sand and will be able to operate for decades with the equivalent of a single wristwatch battery. Robotic spacecraft’s that weigh only a few pounds will be sent out to explore the solar system, and widespread space travel will be possible for the masses. Oh, yes “one that is near to us all” inexpensive alternative energy sources will power our vehicles, rather than depending on dwindling oil reserves and the daily fluctuations of (soaring) gas prices!

2.1 What is Nanotechnology?:

Although there is much current excitement about nanomaterials, there is really nothing new about nanoscience. In fact, the earliest civilizations used nanoscale materials for a variety of applications. For example, the Mayans used magnesium aluminum silicate clay called palygorskite, which contained nanosized channels that were filled with water. The Mesopotamian civilizations used colored glass for decorative applications that contained embedded metallic nanoparticles. Physics Nobel Laureate Richard Feynman gave the first lecture regarding the applications for nanoscale materials. His talk, entitled “There’s Plenty of Room at the Bottom,” was delivered on 29 December 1959 at the annual American Physical Society meeting on the campus of Caltech. Feynman pointed out those designing materials atom-by-atom is a real possibility, as it would not violate any physical laws. He also predicted such sci-fi accomplishments as writing 24 volumes of the Encyclopaedia Britannia on the head of a pin, and even more amazingly, the complete reproduction of every book ever produced to fit within a small handheld pamphlet of less than 40 pages! “But he not talk about morphology effect properties in application of this atoms assembling, because in 1959 microscopy methods were not developed” To put these prophetic statements into context, at the time he delivered this speech,
Physical and chemical methods were developed: ball millings, a flame by vapor phase reaction and condensation, in the study of their physical properties and the use of nanomaterials in various technologies is their production. Quantities in a state than can be manipulated and that behave as pure macromolecular substances. The essential first step is a mixture of several compounds and its structure is unknown. The surfactant is used as a polymer and plays an important role in formation of nanorods. One of the challenges is to produce anisotropic nanocrystals. Colloidal solutions can be used as a nano-reactor whose shape partially plays a role in the shape of the nanomaterial produced (see below). In the last two years, a large number of groups have succeeded in making nanorods. Various nanomaterials such as silver, gold, platinum, copper and semiconductors were produced. In most cases, a surfactant, usually cetyltriethylammonium bromide or its derivatives, is added to the preparation solution. However, the colloidal solution is a mixture of several compounds and its structure is unknown. The surfactant is used as a polymer and plays an important role in formation of nanorods. The aspect ratio (length to width ratio) markedly depends on the amount of surfactant, but the key factor in favoring the nanocrystal growth in a given direction is not known. Self-assembled nanocrystals are now high enough to provide images of individual atoms, and are often fitted with detectors that are capable of determining the chemical composition and/or oxidation state of the surface atoms.

During the last decade, due to the emergence of a new generation of high technology materials, the number of groups involved in nanomaterials has increased exponentially. Nanomaterials are implicated in several domains such as chemistry, electronics, high density magnetic recording media, sensors and biotechnology. This is, in part, due to their novel material properties, that differ from both the isolated atoms and the bulk phase. An ultimate challenge in materials research is now the creation of perfect nanometer-scale crystallites (in size and shape) identically replicated in unlimited quantities in a state than can be manipulated and that behave as pure macromolecular substances. The essential first step in the study of their physical properties and the use of nanomaterials in various technologies is their production. Physical and chemical methods were developed: ball millings, a flame by vapor phase reaction and condensation, chemical reduction and co-precipitation have been employed to control the particle size (up to 10 nm) and morphology. More recently, new preparation methods have been developed such as sonochemical reactions, gel-sol, microwave plasma and low energy cluster beam deposition. In 1988, we developed a method based on reverse micelles (water in oil droplets) for preparing nanocrystals. In 1995, we were able to control size and shape of nanocrystals by using colloidal solutions as templates. Using these methods we fabricated various types of nanomaterials: metals semiconductors (CdS, CdTe etc...) and alloys (Fe-Cu, CdMnS, CdZnS). Normal micelles make it possible to produce ferrite magnetic fluids. Some of the techniques described above enable preparing amorphous nanoparticles whereas others favor formation of highly crystallized nanoobects. One of the challenges is to produce anisotropic nanocrystals. Colloidal solutions can be used as a nano-reactor whose shape partially plays a role in the shape of the nanomaterial produced (see below). In the last two years, a large number of groups have succeeded in making nanorods. Various nanomaterials such as silver, gold, platinum, copper and semiconductors were produced. In most cases, a surfactant, usually cetyltrimethylammonium bromide or its derivatives, is added to the preparation solution. However, the colloidal solution is a mixture of several compounds and its structure is unknown. The surfactant is used as a polymer and plays an important role in formation of nanorods. The aspect ratio (length to width ratio) markedly depends on the amount of surfactant, but the key factor in favoring the nanocrystal growth in a given direction is not known. Self-assembled nanocrystals are now high enough to provide images of individual atoms, and are often fitted with detectors that are capable of determining the chemical composition and/or oxidation state of the surface atoms.

Figure 1. Scanning Tunneling Microscope (STM) image of the placement of individual Xe atoms on a Ni(110) surface no surprise, by researchers at IBM. Reproduced with permission from Eigler, D. M.; Schweizer, E. K. Nature 1990, 344, 524. Copyright 1990 Macmillan Publishers Ltd.
nanocrystals have attracted increasing interest over the last five years. The level of research activity is growing seemingly exponentially, fueled in part by the observation of physical properties that are unique to the nanoscale domain. The first two- and three-dimensional superlattices were observed with and CdSe nanocrystals. Since then, a large number of groups have succeeded in preparing various self-organized lattices of silver, gold, cobalt, and cobalt oxide. With the exception of CdSe and cobalt nanocrystals, most superlattice structures have been formed from nanocrystals whose surfaces are passivated with alkanethiols. When nanocrystals are characterized by a low size distribution, they tend to self-organize in compact hexagonal networks. Conversely, if the distribution is too large they are randomly dispersed on a substrate. This is obtained when a drop of solution containing the nanocrystal is deposited on the substrate lying on a paper. Conversely, when the substrate is fixed with anti-capillary tweezers, rings made of nanocrystals, and surrounded by bare substrate, are formed. This is observed with silver, gold, CdS and ferrite nanocrystals. These phenomena were attributed to either wetting or magnetic properties. In fact, they are due to Marangoni instabilities. Under other deposition conditions, large "wires" composed of silver nanoparticles have been observed, in which the degree of self-organization varies with the length of the alkyl chains coating the particles. Interestingly, it has been recently demonstrated that the physical properties of silver, cobalt and ferrites nanocrystals organized in 2D and/or 3D superlattices differ from those of isolated nanoparticles. These changes in the physical properties are due to the short distances between the nanocrystals. Such collective properties are attributed to dipole-dipole interactions. Furthermore, the electron transport properties drastically change with the nanocrystal organization. [12-16]

On the other hand, Nanomaterials represent the logical next step in applications of electron microscopy: why simply image when one can image and manipulate in real time simultaneously with no loss of resolution? The incorporation of robotic manipulators in scanning electron microscopes (SEM) began as a way to characterize the mechanical properties of novel nanostructures. However, the applications for nanomaterials have expanded to include electrical characterization of nanostructures, as well as contact level integrated circuit (IC) probing, and the manipulation of virus nanoblocks. The term nanomaterials can be loosely defined as any kind of electromechanical device used for controlled placement of an end effector with better than 100 nm resolutions. The restriction on the resolution of the tool arises from the industry standard length scale definition of nanotechnology: structures with one or more dimensions at sub-100 nm. Obviously, the positioning resolution of the nanomaterials must conform to the length scales of the materials to be characterized and manipulated. Constructing a nanomaterial’s requires conforming to several other restrictions that will be discussed later. Before the introduction of nanomaterials, scientists were forced to resort to arduous and time-consuming techniques in order to characterize nanostructures. For example, to measure the electrical properties of a nanotube, one had to deposit nanotubes onto a surface, locate an isolated nanotube using atomic force or SEM, deposit metal contacts with lithographical techniques, and finally perform the electrical characterization using microprobes. Although this technique has produced excellent data, the overhead in equipment and personnel is prohibitive. The nanomaterials operated inside an SEM allows the scientist to locate a nanostructure using SEM imaging, connect electrodes or other end effectors to it using the manipulator, and perform mechanical and/or electrical measurements all in a single experiment. Essentially, an SEM with nanomaterials is a direct analog of an optical light microscope with a microprober station. The SEM can image nanometer-scale structures in real time, and the vacuum pressures allow measurements to be made in a clean, dry environment. Additional advantages over previous techniques come from the ability to make dynamic measurements on nanostructures, such as measuring the electrical response of some carbon nanostructures to a mechanical deformation. Performing similar experiments using AFM resulted in strained contacts, which obviously affect the outcome of the experiment.

Nanomaterials are also compatible with focused ion beam (FIB) systems. FIB systems are used for milling sections out of semiconductor devices for failure analysis (FA). Materials and structures can be extracted with high precision using nanomaterials for transmission electron microscopy (TEM) characterization. However, they can also be used to deposit metal to modify probe tips and create electrodes on surfaces. FIB systems coupled with nanomaterials form the tool of choice for nanotechnology applications in physical characterization of nanostructures and nanomaterials. Nanomaterials have also been adapted for use in transmission electron microscopes. Nanostructures can be analyzed and even altered with the added functionality of manipulation systems in situ to the TEM. TEM manipulation of multilayered nanotubes yielded some of the first insights into the engineering of nanoelectromechanical systems (NEMS).

Hence, nanotechnology can be defined as the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new properties and functions. Nanotechnology can be described as the precision-creation and precision-manipulation of atomic-scale matter; hence, it is also referred to as precision molecular engineering. [17-25]

3. What is the Microscopy Methods?

The development of microscopy and human interest in it needs a remark about its history. Probably no other scientific techniques have contributed so much to scientific development in biology, medicine, and material science, as the different microscopy techniques. Even if they might seem totally different in construction and performance, the different microscopy techniques have one thing in common they magnify our ability to “see” small features that we
otherwise would not be able to see with our naked eyes. To this, some microscopic techniques can also contribute other information, such as spectroscopic data and crystallographic properties of material. In this book, one of the latest developed microscopy techniques, scanning force microscopy, is described. Only less than a decade after its invention, it is hard to evaluate the scientific importance of this technique, as it is still undergoing rapid progress. Refinement of microscopy techniques has always been interplay between scientists’ urging for better visualization possibilities and scientific engineers. Scanning force microscopy development is no exception. In the following, a short description about the different microscopy techniques and a brief historical review of microscopy will be presented.

3.1 Optical Microscopy:
The first optical microscope that consisted of more than one lens, a so-called compound microscope, was most likely built in Italy around 1590 by Giambattista della Porta and in Holland around 1595 by the eyeglass maker Hans Jensen. The true scientific developer of the optical microscope (as well as the telescope) around 1610 was Galilei Galileo, who, in turn, called it “a Dutch invention” and Johannes Kepler, who further developed the technique shortly after that time. The problems of chromatic and spherical aberration were disc overed early, and in 1637, Rene Descartes explained how to avoid spherical aberration by using hyperbolic lenses, which were impossible to manufacture in that time, and in 1671, Isaac Newton explained the reason for chromatic aberration. The technique to assemble convex and concave lenses in order to reduce chromatic aberration was invented by Chester Moor Hall in 1733 and was commercialized by John Dollond 25 years later. Today, modern optical microscopes have been optimized to near perfection, so the fundamental physical laws set the limits of the resolution in these microscopes. The diffraction limit for maximal resolution is set by the wavelength of the light to be around 100 nm in extreme UV light but is normally not better than 250 nm (in immersion oil). Frits Zemike was awarded the Nobel Prize in Physics in 1953, “for his demonstration of the phase-contrast method, especially for his invention of the phase-contrast microscope.”

3.2 Electron Microscopy:
The first electron microscope was built in 1931. As electrons are particles that can be accelerated, focused, and detected, these particles have given a shorter “wavelength” than visible light and illuminate the specimen, giving higher resolutions than in the optical microscope. The transmission electron microscope (TEM) is conceptually similar to the transmission optical microscope, in the arrangement of specimen, “light source,” and image plane, with the difference being that here, electrons instead of light are used, and electrostatic and magnetic lenses replace glass lenses. The detection here is done with a fluorescent screen. Another important type of electron microscope is the scanning electron microscope (SEM), which can almost be seen as a link between the TEM and the SPM. Here, the electron beam is focused onto a small spot and scanned in parallel linear scans (raster) over the surface of the specimen, and the electrons that are going back out from the surface are detected simultaneously with an electron detector. The principles of the SEM technique were first explained in 1938. Today, the resolution of the SEM is set by the quality of the lenses, which also involves the diffraction limit, as the opening angle must be kept small, and the interaction process, when electrons hit the specimen. Ernst Ruska was awarded the Nobel Prize in Physics in 1986 “for his fundamental work in electron optics.” Until two decades ago, the electron microscope method and some other similarly sensitive methods provided some of this information about the interfaces, although there were always some limitations inherent in all of these techniques, which needed improvements. However, these days, due to relentless technical advance, electron crystallography is capable of producing images at resolutions close to those attained by x-ray crystallography or multidimensional NMR. A little more than a decade ago, a new procedure for molecular microscopy was invented, and that will be delineated herein. The basic method was merely, in principle, to be able to move a sharp tip over a solid surface with a sensor with molecular scale sensitivity in the longitudinal and height directions. The idea to measure the surface topography using a sharp conducting tip was already described in 1972. This gave almost a new dimension [in the nanometer (nm = 10⁻⁹ m = 0.1 Å) range] to surface chemical research, which was much needed at this stage. All of these procedures can be performed at ambient temperature and pressure, unlike with electron microscopy. All of the images (digital) thus obtained are presented three-dimensionally, and in some SPMs, one can even manipulate molecules. The characteristics of the nanosensor have been found to be of a variety of kinds. In fact, due to these developments, the last decade has experienced a new aspect of science, so-called nanotechnology. Originally, two types of microscopes were invented: the scanning tunneling microscope (STM) and later, the atomic force microscope (AFM). The areas of applications of SPMs are vast and expanding rapidly, as will be described in this book extensively. These developments clearly indicate how the SPMs are contributing to the scientific developments, where the main aim is to be able to see at a molecular level (in three dimensions) and to be able to manipulate.

4. Results and Discussions:
Nanotechnology is the application of nanoscience to control processes on the nanometer scale that is, between 1 to 100 nm or call better 2 to 50 nm. The field is also known as molecular engineering or molecular nanotechnology (MNT). MNT deals with the control of the structure of matter based on atom-by-atom and/or molecule-by-molecule.
engineering; also, it deals with the products and processes of molecular manufacturing. The term engineered nanoparticles describes particles that do not occur naturally; humans have been putting together different materials throughout time, and now with nanotechnology they are doing so at the nanoscale. As it might be inferred, nanotechnology is highly interdisciplinary as a field, and it requires knowledge drawn from a variety of scientific and engineering arenas: Designing at the nanoscale is working in a world where physics, chemistry, electrical engineering, mechanical engineering, and even biology become unified into an integrated field.

“Building blocks” for nanomaterials include carbon-based components and organics, semiconductors, metals, and metal oxides; nanomaterials are the infrastructure, or building blocks, for nanotechnology. The term nanotechnology was introduced by Nori Taniguchi in 1974 at the Tokyo International Conference on Production Engineering. He used the word to describe ultrafine machining: the processing of a material to nanoscale precision. This work was focused on studying the mechanisms of machining hard and brittle materials such as quartz crystals, silicon, and alumina ceramics by ultrasonic machining. Years earlier, in a lecture at the annual meeting of the American Physical Society in 1959 (There’s Plenty of Room at the Bottom) American Physicist and Nobel Laureate Richard Feynman argued (although he did not coin or use the word nanotechnology) that the scanning electron microscope could be improved in resolution and stability, so that one would be able to “see” atoms. Feynman proceeded to predict the ability to arrange atoms the way a researcher would want them, within the bounds of chemical stability, in order to build tiny structures that in turn would lead to molecular or atomic synthesis of materials. Based on Feynman’s idea, K. E. Drexler advanced the idea of “molecular nanotechnology” in 1986 in the book Engines of Creation, where he postulated the concept of using nanoscale molecular structures to act in a machinelike manner to guide and activate the synthesis of larger molecules. Drexler proposed the use of a large number (billions) of robotic-like machines called “assemblers” (or nanobots) that would form the basis of a molecular manufacturing technology capable of building literally anything atom by atom and molecule by molecule. At this time, an engineering discipline has already grown out of the pure and applied science; however, nanoscience still remains somewhat of a maturing field. Nanotechnology can be identified precisely with the concept of “molecular manufacturing” (molecular nanotechnology) introduced above or with a broader definition that also includes laterally related sub-disciplines. The nanoscale is where physical and biological systems approach a comparable dimensional scale. A basic “difference” between systems biology and nanotechnology is the goal of the science: systems biology aims to uncover the fundamental operation of the cell in an effort to predict the exact response to specific stimuli and genetic variations (has scientific discovery focus); nanotechnology, on the other hand, does not attempt to be so precise but is chiefly concerned with useful design. Figure 2. depicts the current evolution of various disciplines toward a nanoscale focus. [21-28]

![Figure 2](image-url)

**Figure 2.** Evolution of various disciplines toward nanoscale focus.

### Table 1. Putting nano in context.

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Factor</th>
<th>Symbol</th>
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<tbody>
<tr>
<td>Desi</td>
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<tr>
<td>Centi</td>
<td>10^-2</td>
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<td>Mili</td>
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<td>Micro</td>
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<tr>
<td>Nano</td>
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<tr>
<td>Pico</td>
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<td>Femto</td>
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A nanometer is about the width of four silicon atoms (with a radius of 0.13 nm) or two hydrogen atoms (radius of 0.21 nm); also see Figure 3. Figure 4. and Figure 5. depicts an actual nanostructure. For comparison purposes, the core of a single-mode fiber is 10,000 nm in diameter, and a 10 nm nanowire is 1000 times smaller than (the core of) a fiber. The nanoscale exists at a boundary between the “classical world” and the “quantum mechanical world”; therefore,
realization of nanotechnology promises to afford revolutionary new capabilities. In this context, the following quote is noteworthy:

![Figure 3](image1.png)

**Figure 3.** Diagram of size for natural and synthesis materials.

The nanoparticles are ultrafine particles in the size of nanometer order. “Nano” is a prefix denoting the minus 9th power of ten, namely one billionth. Here it means nanometer (nm) applied for the length. One nm is extremely small length corresponding to one billionth of 1 m, one millionth of 1 mm, or one thousandth of 1 μm. The definition of nanoparticles differs depending upon the materials, fields and applications concerned. In the narrower sense, they are regarded as the particles smaller than 10 to 20 nm, where the physical properties of solid materials themselves would drastically change. On the other hand, the particles in the three digit range of nanometer from 1 nm to 1 μm could be called as nanoparticles. In many cases, the particles from 1 to 100 nm are generally called as nanoparticles, but here they will be regarded as the particles smaller than those called conventionally “submicron particles”, and concretely less than the wavelength of visible light (its lower limit is about 400 nm) as a measure, which need to be treated differently from the submicron particles.

4.1 Features of nanoparticles: “Activation of particle surface”

All the solid particles consist of the atoms or the molecules. As they are micronized, they tend to be affected by the behavior of atoms or the molecules themselves and to show different properties from those of the bulk solid of the same material. It is attributable to the change of the bonding state of the atoms or the molecules constructing the particles. For example, as shown in Figure 6, if a cube with a side length of 1 cm is divided into a cube of 1 μm, the particle number increases to $10^{12}$ and being divided into the one of 10 nm, then it amounts to $10^{18}$, where the fraction of the atoms or the molecules located at the surface on the particles plays a great role, since they are more active than those inside the solid particles because of the free hand, which leads to easy bonding with the contacting materials and causes various changes in particle properties. The diameter of the smallest hydrogen atom is 0.074 nm, and that of the relatively large lead atom (atomic number is 82) is 0.35 nm. From these sizes, it is estimated that the particle with a size of 2 nm consists of only several tens to thousands atoms. When the particle is constructed by larger molecules, the number decreases furthermore. It is indicated that the fraction of surface atoms of a 20 μm cubic particle is only 0.006%, but it increases to 0.6% for a 200 nm particle and then it is estimated almost half of the atoms are situated at the surface of a 2 nm particle.
4.2 Increase of surface area:

On the other hand, as the micronization of solid particles, the specific surface area increases generally in reversal proportion to the particle size. In the above-mentioned case, when the particle of 1 cm is micronized to 1 μm and 10 nm, the specific surface area becomes ten thousand times and million times, respectively. As the increase in the specific surface area directly influences such properties like the solution and reaction rates of the particles, it is one of major reasons for the unique properties of the nanoparticles different from the bulk material together with the change in the surface properties of the particles itself. [29-32]

4.3 Evaluation of size of nanoparticles:

In order to elucidate the change in properties and characteristics of nanoparticles with the particle size, it is essential first of all to measure the size of the nanoparticles accurately. The most basic method to measure the size of nanoparticles is the size analysis from the picture image using the transmission electron microscope, which could also give the particle size distribution. For this analysis, preparation of the well-dispersed particles on the sample mount is the key issue. The grain size of the particles can be obtained from peak width at half height in the X-ray diffraction analysis and it is regarded as an average primary particle size of particles. Meanwhile, the laser diffraction and scattering method, which is popular for the size analysis of micron-sized particles, would hardly measure the particle size of individual nanoparticles but that of the agglomerated particles. The photon correlation method often used for the particle analysis in the nanosized range might not give accurate results in many cases, when the particle size distribution is wide. Then the BET (Brunauer-Emmett-Teller) specific surface measurement based on the gas adsorption is often applied as a simple method to evaluate the size of nanosized primary particles. By this method, it is possible to estimate the particle size from the specific surface area under the assumption of spherical particle shape. This equivalent particle size based on the specific surface area is useful for the evaluation of nanoparticle size, though it may differ from the particle size observed by the electron microscope depending upon the surface state and the inner structure of the particles. [33-37]

4.4 Wet Technologies for the Formation of Organic Nanostructures:

Chemical methods of material processing were known for years, existing in parallel with physical and other methods of film deposition. Recent advances in electron microscopy and scanning nanoprobe microscopy (STM, AFM) have revealed that some of the materials produced by the chemical methods have distinctive nanocrystalline structure. Furthermore, due to the achievements of colloid chemistry in the last 20 years, a large variety of colloid nanoparticles have become available for film deposition. This has stimulated great interest in further development of chemical methods as cost-effective alternatives to such physical methods as: thermal evaporation; magnetron sputtering; chemical and physical vapor deposition (CVD, PVD); and molecular beam epitaxy (MBE).

4.5 Formation of Colloid Nanoparticles:

The most advanced chemical method for nano-structured materials processing is the deposition of colloid inorganic particles. Recent achievements in colloid chemistry have made a large variety of colloid compounds commercially available. The list of colloid nanoparticles with uniform (low-dispersed) dimensions in the range from 3 to 50 nm includes the noble metals (e.g., Au, Ag, Pt, Pd, and Cu), semiconductors (e.g., Si, Ge, III-V and II-VI, and metal oxides), insulators (e.g., mica, silica, different ceramic materials, polymers), and magnetic materials (e.g., Fe₂O₃, Ni, Co, and Fe). The growth of colloid particles is usually stabilized during synthesis by adding surfactants to the reagents. Therefore, the stable nanoparticles produced are coated with a thin shell of functionalized hydrocarbons, or some other compounds. Typical examples of the chemistry of formation of colloid nanoparticles are shown below. Gold stable colloids can be prepared by the reduction of AuCl₄ with sodium borohydride in the presence of alkane-thiols. Other colloids, such as Ag, CdS, CdSe, and ZnS, can be prepared in a similar way. In Pnanocrystals can be synthesized by the
following reaction, with temperatures ranging from 150 °C to 280 °C in the presence of either primary amines, tri-\(n\)-octylphosphine (TOP), or tri-\(n\)-octylphosphine oxide (TOPO) as stabilizing agents, preventing further InP aggregation.

\[
\text{InCl}_3 + [(\text{CH}_3)_3\text{Si}]_3\text{P} \rightarrow \text{InP} + 3(\text{CH}_3)_3\text{SiCl}
\]

The particles appear to be mono-dispersed, with a mean cluster size varying from 2 to 6 nm depending on the stabilizer used. The particles show strong resonance luminescence after etching in HF. Cobalt mono-dispersed nanocrystals can be produced by rapid pyrolysis of the organic precursor Co(CO)\(_8\) in an inert Ar-atmosphere, and in the presence of organic surfactants, such as oleic-acid and trioctylphosphonic acid at high temperatures. The particles appear to have ideal spherical, cubical, or rod-like shapes, with sizes in the range from 3 to 17 nm depending on surfactant concentration. The Co nanoparticles demonstrate superparamagnetic ferromagnetic transition. CdTe nanoparticle colloids can be prepared by the reaction of Na\(_2\)Te with CdI\(_2\) in methanol at –78 °C.

The diameter of CdTe colloid particles is in the range from 2.2 to 2.5 nm. An alternative method for the formation of stabilized colloid particles is to utilize self-assembled membranes, such as micelles, microemulsions, liposomes, and vesicles. Typical dimensions are from 3 to 6 nm for reverse micelles in aqueous solutions, from 5 to 100 nm for emulsions, and from 100 to 800 nm for vesicles. Liposomes are similar to vesicles, but they have bilayer membranes made of phospholipids. Such membranes may act as the reaction cage during the formation of nanoparticles, and may prevent their further aggregation. The idea of the formation of nanoparticles inside micelles is to trap respective cations there. This can be done by sonification of the mixture of required salts and surfactants. Since the permeability of the membrane for anions is about 100 times higher than for cations, the formation of nanoparticles takes place within micelles, with a constant supply of anions from outside. The process of the formation of CdSe clusters within a reverse micelle is shown schematically in Figure 7. [38-40]

![Figure 7](image)

**Figure 7.** Schematic diagram of the formation of CdSe nanoparticles within a reverse micelle.

A number of different colloids, such as CdSe, Ag\(_2\)O, Fe\(_2\)O\(_3\), Al\(_2\)O\(_3\), and cobalt ferrite, were prepared using the above methods.

### 4.6 Self-Assembly of Colloid Nanoparticles:

The deposition of colloid nanoparticles onto solid substrates can be accomplished by different methods, such as simple casting, electrostatic deposition, Langmuir-Blodgett, or spin coating techniques. However, the simplest method of nanoparticles deposition, which gives some remarkable results, is the so-called self-assembly or chemical self-assembly method. This method, which was first introduced by Netzer and Sagiv [41], is based upon strong covalent bonding of the adsorbed objects (i.e., monomer or polymer molecules and nanoparticles) to the substrate via special functional groups. It is known, for example, that the compounds containing thiol (SH) or amine (NH\(_2\)) groups have strong affinity to gold. The silane group (SiH\(_3\)) with silicon is another pair having very strong affinity. Such features can be exploited for the film deposition of nanoparticles (modified, for example, with SH groups) onto the surface of bare gold, or vice versa, gold clusters onto the surface modified with thiol groups, as shown schematically in Figure 8.

![Figure 8](image)

**Figure 8.** Two examples of the self-assembly of (a) alkylthiol modified nanoparticles onto bare gold and (b) pure Au particles onto alkylthiol modified surface.
The first work on the self-assembly of gold colloid particles capped with alkanethiols was done by Brust and coworkers. This routine has been adopted by other scientists for the deposition of self-assembled monolayers of different colloid nanoparticles (e.g., Ag, CdS, CdSe, and ZnS), which were prepared using mercapto-alcohols, mercaptocarboxylic acids, and thiophenols as capping agents. Self-assembled nanoparticles usually show well-ordered lateral structures, proved by numerous observations with SEM, STM, and AFM.

Two-dimensional ordering in self-assembled nanoparticle monolayers can be substantially improved by thermal annealing at temperatures ranging from 100 °C to 200 °C, depending on the material used. The use of bi-functional HS-(CH$_2$)$_{10}$-COOH bridging molecules, which combines both the affinity of thiol groups to gold and carboxylic group to titania, can provide more flexibility in the self-assembly. Both self-assembly routes were exploited for deposition of TiO$_2$ nanoparticles onto the gold surface. In the first one, unmodified TiO$_2$ nanoparticles were self-assembled onto the gold surface, coated with a monolayer of HS-(CH$_2$)$_{10}$-COOH; while in the second one, TiO$_2$ nanoparticles stabilized with HS-(CH$_2$)$_{10}$-COOH were self-assembled onto the bare gold surface. For some time, chemical self-assembly was limited to the formation of organized monolayers. The use of bi-functional bridge molecules overcomes this relative disadvantage. For example, multi-layers of Au colloid particles can be deposited using di-thiol spacing layers. A similar routine was applied for the fabrication of Au/CdS super lattices.

4.7 Morphology and Crystallography of Nanostructured Materials Prepared by Chemical Routes:

The structural study of materials was always of a high priority, because the physical properties of materials depend very much on their structure. There are several levels of structural study, which start with the investigation of the morphology of the material surfaces, closely related to their in-plane ordering. Many nano-structured materials prepared with the help of layer-by-layer deposition techniques, such as LB or electrostatic self-assembly, have a distinctive periodicity in the direction normal to the surface, which determines their main electrical and optical properties. This is why the study of the layer-by-layer structure of such materials is of crucial importance.

The materials consisting of colloid nanoparticles have a tendency to form two dimensional structures according to the close packing order. This trend can stimulate the formation of multilayered quasi-3D structures of closely packed nanoparticles. The final stage of structural study is the crystallography of individual nanoparticles, clusters, and grains of materials. This is a very interesting and important subject, since the crystallography of nanoclusters, which consist of several hundred to several thousand atoms, is very often different from that of their respective bulk materials.

The planar order of nanostructures deposited by chemical routes has become an important issue, because of the competition with solid-state nanotechnology capable of the fabrication of fine two-dimensional structures. The main concern is with the layers of nanoparticles produced by chemical self-assembly, because methods of electrostatic self-assembly and LB is not capable of producing two-dimensional ordered arrays of nanoparticles. The features of the lateral arrangement of particles, which are buried under layers of either closely packed amphiphilic compounds or polymers, are usually smeared and difficult to observe. In the case of relatively thick (quasi-3D) films, produced by electrodeposition and sol-gel techniques, the morphology study usually reveals polycrystallites. Therefore, the quality of these materials can be assessed by the size of the crystallites and by the presence of preferential orientation, which may cause anisotropy of the electrical and optical properties of materials. [42-46]

4.8 Methods of Morphology Study:

Electron microscopy is one of the traditional and well-established methods in surface science. SEM operates in a vacuum, with a high energy electron beam (typically from 5 to 20 keV) focused into a spot of several tens of nanometers in diameter (or fractions of nanometers in modern high-resolution instruments). Because of the very short wavelength of the electrons used (e.g., electrons with an energy of 104 eV have a wavelength $\lambda_e$ equal to 0.12 nm), the resolution of SEM is limited by the beam diameter and image distortions, (e.g., astigmatism) introduced by the focusing system. A complex electromagnetic system provides both the formation of the electron beam and its scanning over the sample surface (see Figure. 9.).
The electrons that are reflected (backscattered) from the surface, or the emitted secondary electrons, are collected with a sensitive detector to provide imaging of the studied surfaces. SEM can be used to study samples of different nature and shape, practically without any limitations. Ideally, the samples for SEM study should be conductive to avoid electrical charging the sample with an electron beam, which is a side effect causing image distortion. Therefore, the samples of insulating materials for SEM study are recommended to coat (decorate) with thin metal film. This reproduces the surface profile. Another possible characteristic of SEM lies in the film damage caused by high energy electrons, which is particularly important for organic film study. The interpretation of SEM images of composite samples may not always be straightforward. This is especially true for secondary electron images, which represent a combination of both the surface and the work function profiles. TEM produces images by a high energy focused electron beam penetrating through the material, so that materials for TEM study are meant to be thin films. Sample preparation for TEM study is therefore a very important experimental stage, and usually requires deposition of a studied material onto fine metal meshes or hollow carbon substrates. Resolution of TEM is higher than of SEM, and reaches angstrom level in the best instruments. Since the electrons’ energy in TEM is normally higher than in SEM, this increases the danger of samples being damaged by high energy electrons, which is particularly important in studying thin organic films. We cannot imagine the morphology study of materials without scanning nanoprobe techniques, such as STM, AFM, and many other techniques derived from them. Examples include magnetic force microscopy (MFM), electrochemical force microscopy (ECFM), linear force microscopy (LFM), surface potential microscopy (SPM), and scanning near-field optical microscopy (SNOM). The AFM method, developed soon after STM, was more universal and applicable to all kinds of surfaces. The basic idea of AFM is slightly different from STM, and is illustrated in Figure. 10(a).

Although the main unit is the same [X, Y, Z piezo-ceramic positioner (1)], the principle of registration of vertical movement of the tip (3), which is usually made by CVD of Si₃N₄ on a flexible cantilever (2), is optical. The laser beam reflected from the cantilever is registered with the position sensitive photo-detector (5). This construction is universal, and is adopted by the majority of scanning nanoprobe instruments. Many nanoprobe scanning techniques (e.g., MFM, ECFM, and LFM) derived from AFM deploy modified tips to measure magnetic, electrostatic, or specific biointeraction.

Figure.9. The Scheme of SEM: (1) Electron Gun, (2) Electromagnetic beam focusing system, (3) Electromagnetic X, Y scanner and (4) Specimen.

Figure.10. (a) The scheme of AFM: The X, Y and Z piezo-ceramic positioned (1), The cantilever (2), The tip (3), The laser (4), The position-Sensitive photodetector (5) and The studied surface (6). (b) The atomic force diagram. Set points for the contact modes are indicated with dotted lines.
forces. The measurements of the ac current between the vibrating conducting (metallized) AFM tip and the surface allow the measurement of the surface potential ($\phi$), according to the following formula:

$$I = \frac{dQ}{dt} = \phi \frac{dC}{dt}$$

Where $C$ is the tip capacitance. This is a realization of a Kelvin probe, with a lateral resolution in nanometer range called surface potential microscopy (SPM). SNOM is a unique method that allows the overcoming of the diffraction limit in optical microscopy. It stands apart from the rest of the nanoprobe techniques, because it exploits the registration of the light scattered in the gap between the nanotip and the studied surface on the distances much smaller than the wavelength of the light under study. The lateral resolution of SNOM is usually on an order of 10 less than that of AFM.

AFM can operate in three different modes-contact mode, noncontact mode, and tapping mode. Figure 10(b) shows the dependence of the interaction force on the distance between the tip and the sample surface. At larger distances from the surface, the attraction force is dominating, while the repulsion force starts to dominate at smaller distances (in the range of a few angstroms). In the contact mode, the tip is brought into close contact with the sample surface, so that the force between the tip and the sample becomes repulsive. The deflection of the cantilever caused by this force is registered with a photodetector. The signal is compared to the predefined value of deflection (force), and the dc feedback system generates a certain voltage applied to the Z-part of the piezo-ceramic to keep the value of deflection (force) constant. This dc voltage measures the surface roughness.

The vertical resolution of the AFM contact mode is in the range of 10–2 nm, while the lateral resolution could reach the values less than 1 nm, depending mostly on the tip radius. The disadvantage of the contact mode is that it could damage both the sample and the tip. The tip could leave scratches in the surface of soft materials, and the tip could be broken on hard rough surfaces. Consequently, the scan speed should be kept very low (usually less than 1 Hz), depending on the studied surface. If the set-point is chosen in a range from 5 to 10 nm away from the surface, the tip will be attracted to the surface, and thus cause the cantilever to bend towards it. The surface profile can be recorded by maintaining the same value of the cantilever deflection, by using a feedback system. This is called the noncontact mode. Since the attraction force is much weaker than the repulsion force, the cantilever is vibrated in order to deploy more sensitive ac registration techniques. The resolution of the noncontact AFM is much lower in comparison to the registration of the contact mode; however, the scanning is much faster, making this method suitable for studying large and rough surfaces of various natures. [47-52]

The tapping mode combines the advantages of both previous approaches. The cantilever is set to oscillate at frequencies in the range from 100 to 500 kHz, with an amplitude of approximately 20 nm, so that the tip is just touching (i.e., tapping) the surface. The amplitude of these oscillations depends on the distance from the surface, and thus provides a measure of the surface roughness. At the same time, recording the phase of oscillations may give the information on the visco-elastic properties of the material. For example, inclusion of materials with different mechanical properties will cause a contrast in phase images. The resolution of tapping mode AFM is almost the same as that of contact mode, but it is faster and much less damaging than noncontact AFM.

The majority of scanning nanoprobe techniques can be deployed in ultrahigh vacuum as well as in air and liquids, which make these methods universal for studying a large range of objects atomically clean surfaces, various nanostructure surfaces, and real surfaces of materials using both chemical and biological processes.

4.9 Methods of Crystallography Study:

Diffraction is one of the most powerful methods of the structural study of materials, which may involve X-ray, electrons or neutrons. Disregarding the type of irradiation used the same Bragg diffraction conditions can be applied to find positions of minimum and maximum intensity in the pattern. A zero phase shift between two or more waves, reflected from the regular pattern of the studied sample, gives the maximal intensity, while the waves in opposite phase will cancel each other and yield minimal intensity. For example, in the case of light reflection from a layered structure with spacing ($d$) between the reflecting planes, the Bragg conditions for diffraction maxima can be obtained by subtracting the path-lengths $abc$ and $ad$, as shown in Figure 11.

![Figure 11. The calculation of a pass length difference in diffraction experiments.](image)
$2d \sin \theta = n \lambda$

Where $\lambda$ is the wavelength and $\theta$ is the angle of incidence. Generally speaking, the diffraction pattern reflects the distribution in reciprocal space of either the electron density in electron diffraction or atomic density in neutron diffraction. Therefore, the profile of electron or atomic density can be extracted from the respective diffraction patterns.

Diffraction pattern can be registered as a whole two-dimensional image on the luminescent screen (in case of electron diffraction), or by scanning the angle of incidence of the beam and recording its intensity on reflection (in X-ray and neutron diffraction). In the latter method, often referred to as $\theta$-2$\theta$ configuration, the rotation of the sample on an angle $\theta$ is linked with the rotation of the detector on 2$\theta$, and very often the experimental data was presented in the intensity versus 2$\theta$. The interpretation of diffraction patterns obtained from two-dimensional and quasi-3D systems includes calculating the characteristic distances in different crystallographic directions using Bragg’s formula, and comparing the obtained values to the database of the parameters of known crystallographic lattices. The parameters of elementary unit cells for particular crystallographic lattices can be also found. [53-58]

4.10 The Layer-by-Layer Structure of Thin Films:

We now discuss films produced by LB or layer-by-layer electrostatic deposition techniques. These are usually studied using the method of small angle X-ray diffraction (SAXD), with the X-ray beam hitting the sample at grazing angles ranging from 1° to 5°. LB films, having a highly periodical layer-by-layer structure, are exemplary objects for such study. A typical SAXD pattern registered for multilayered LB films of fatty acids (i.e., stearic acid Cd salt) is shown in Figure. 12(a).

The seven diffraction fringes observed (only five of which are shown) demonstrate the high periodicity of the film in normal direction. This is not a unique occurrence, since observations of 10 to 12 diffraction fringes were reported in similar systems.

The interplane distance ($d$) can be easily evaluated from the position of each diffraction maximum. For the above system, the value of 5.03 nm was evaluated, which corresponds closely to a double chain-length of stearic acid. It is interesting to observe dramatic changes in the diffraction pattern of the same film after exposure to H$_2$S gas. All Bragg peaks disappear, indicating a randomized structure caused by the formation of CdS clusters within LB film. The LB films of some other compounds may not have such a high level of periodicity. For example, LB films of calixarene Cd salt show only one broad Bragg diffraction maximum [see Figure. 12(b)], which yields a value of $d = 2.47$ nm as an interlayer distance. At the same time, there are several small maxima observed at the angles below the first Bragg peak. They are called interference fringes (or Kiessig fringes), and represent the interference of electromagnetic waves reflected both from the top film surface and from the bottom film/substrate interface. A total film thickness ($D$) can therefore be calculated from the position of the Kiessig fringes:

$n \lambda = 2 D \sin \theta_n$, \hspace{1cm} n = 1, 2, 3, ...$

Figure. 12. SAXD Patterns (a) For LB Films (5 Bilayers) of Cd Stearate and (b) For Calix[8]-Resorcinarene Both Before (Curve 1) and After (Curve 2) Exposure to H2S Gas.

For this particular object [see Figure. 12(b)], calculations yield $D = 13.2$ nm, which is very close to the thickness of 10 layers or 5 bilayers ($5d = 5 \times 2.47 = 12.35$ nm) of calixarene LB film. The formation of CdS clusters within LB film of calixarene Cd salt has little effect on SAXD pattern [see Figure. 12(b)], because the film is not well-ordered in the first place.

Electrostatically self-assembled films produced by consecutive deposition of polycations and polyanions onto electrically charged substrates are supposed to have periodic structure in the normal direction. However, this suggestion is not confirmed by X-ray and neutron diffraction. The SAXD pattern of one of the classical example of polyelectrolyte films (i.e., PVSA/PAH film) shows no Bragg peaks, but only Kiessig interference fringes [see Figure. 13(a)].
It is somehow expected, considering the quite flexible polymer structure and interpenetration of polycation and polyanion chains. As a matter of fact, the absence of Bragg diffraction may not be only attributed to a poor layer-by-layer ordering, but also to the lack of contrast in either electron or atomic density. Both polymers (PAA and PAH) consist mostly of carbon, and thus do not show significant difference in electron density (in X-ray diffraction experiments), nor in atomic nuclear density (in neutron scattering experiments).

As one can see from Figure 13(a), the number of Kiessig fringes increases with the increase of in number of PVS/PAH layers deposited. From the slope of the dependence of the film thickness compared to the number of PVS/PAH layers deposited [see Figure. 13(b)], the thickness of the PVS/PAH repeating unit was found to be 1.34 \pm 0.03 \text{ nm}.

4.11 Morphology and Crystallography of Chemically Self-Assembled Nanoparticles:
In contrast to the previous deposition techniques (i.e., LB and electrostatic self-assembly), nanoparticles, which are chemically self-assembled onto the solid substrates, tend to form regular two-dimensional structures, especially after annealing at moderate temperatures. The type of two-dimensional structure, which usually follows the trend of close packing arrangement, depends on the particles’ shapes. For example, a simple hexagonal pattern is formed by spherical nanoparticles. A classic example of such structures is gold colloid particles chemically self-assembled onto the surface of gold via thiol groups. The observation of such structures is possible with scanning nanoprobe microscopy, such as STM and AFM, as well as with TEM and high resolution SEM. [59-60]

4.12 Elemental and Chemical Composition of Organic/Inorganic Nanostructures:

4.12.1 Experimental Methods of Composition Study:
All traditional methods of elemental and chemical composition study, such as XPS, Auger spectroscopy, Raman spectroscopy, Furrier Transformed Infrared Spectroscopy (FTIR) and some other novel spectroscopy were adopted for nanostructural materials. Electron spectroscopy is based upon two schemes of interaction of either high-energy electrons or X-rays with electrons on core atomic levels (see Figure. 14).
In the first case [Figure. 14(a)], an incident high energy electron beam may cause secondary electron emission from one of the core levels. The vacancy is immediately filled with an electron from the higher level, and results in both the emission of an electromagnetic wave in the X-ray spectral region (1), and the energy transfer to another electron and its subsequent emission (2). The second event is called the Auger process. Both processes are exploited for the elemental analysis of the material. The spectrum of emitted X-rays provides a crude elemental analysis called energy dispersion X-ray (EDX) analysis. This technique goes along with standard SEM, and requires an additional X-ray detector. The accuracy of this method is not great, but it is sufficient to get a general idea of the material’s elemental composition and stoichiometry. Another advantage of this technique, combined with electron beam scanning, is the possibility of mapping the material by plotting two-dimensional images formed by different elements. Similar information can be obtained with Auger electron spectroscopy (AES).

The method of XPS, which is based on the registration of electron spectra emitted from core atomic levels as a result of X-ray irradiation, gives more accurate information on the material’s composition. The resolution of the spectra of secondary electrons emitted from the atomic levels is in the range of fractions of electron volts, which is enough to distinguish between different chemical forms of the same elements. Another excellent technique for chemical analysis is infrared spectroscopy (IR), which is based upon the registration of characteristic spectra of molecular vibrations in the materials. Such spectra can be measured with conventional IR, FTIR spectroscopy, or Raman spectroscopy. The latter is based on the registration of vibration spectra excited by a powerful laser in the visible spectral range. Raman spectral shift between the main excitation line and coupled vibration frequencies is the characteristic parameter for the recognition of molecular vibrations. An extensive database exists for vibration frequencies of different elements in different materials, which allows researchers to find chemical composition fairly easily.

4.13 Stabilization of Colloidal Metal Particles in Liquids:

Before beginning a description of synthetic methods, a general and crucial aspect of colloid chemistry should be considered, and that is the means by which the metal particles are stabilized in the dispersing medium, since small metal particles are unstable with respect to agglomeration to the bulk. At short inter-particle distances, two particles would be attracted to each other by van-der-Waals forces and in the absence of repulsive forces to counteract this attraction an unprotected sol would coagulate. This counteraction can be achieved by two methods, electrostatic stabilization and steric stabilization. In classical gold sols, for example, prepared by the reduction of aqueous \([\text{AuCl}_4]^-\) by sodium citrate, the colloidal gold particles are surrounded by an electrical double layer formed by adsorbed citrate and chloride ions and cations which are attracted to them. This results in a Coulombic repulsion between particles. The weak minimum in potential energy at moderate interparticle distance defines a stable arrangement of colloidal particles which is easily disrupted by medium effects and, at normal temperatures, by the thermal motion of the particles.

Thus, if the electric potential associated with the double layer is sufficiently high, electrostatic repulsion will prevent particle agglomeration, but an electrostatically stabilized sol can be coagulated if the ionic strength of the dispersing medium is increased sufficiently. If the surface charge is reduced by the displacement of adsorbed anions by a more strongly binding neutral adsorbate, the colloidal particles can now collide and agglomerate under the influence of the van-der-Waals attractive forces. This phenomenon is nicely demonstrated by the addition of pyridine to a gold sol of the type mentioned above, as shown in Figure. 15.

![Figure. 15. Attractive van der Waals forces are outweighed by repulsive electrostatic forces between adsorbed ions and associated counter-ions at moderate interparticle separation. Electrostatic stabilization of metal colloid particles.](image)
Even in organic media, in which electrostatic effects might not normally be considered to be important, the development of charge has been demonstrated on inorganic surfaces, including metals, in contact with organic phases such as solvents and polymers. For example, the acquisition of charge by gold particles in organic liquids has been demonstrated, and the sign and magnitude of the charge has been found to vary as a function of the donor properties of the liquid. Thus, even for colloidal metals in suspension in relatively non-polar liquids, the possibility cannot be excluded that electrostatic stabilization contributes to the stability of the sol.

A second means by which colloidal particles can be prevented from aggregating is by the adsorption of molecules such as polymers, surfactants or ligands at the surface of the particles, thus providing a protective layer. Polymers are widely used, and it is obvious that the protectant, in order to function effectively, must not only coordinate to the particle surface, but must also be adequately solvated by the dispersing fluid - such polymers are termed amphiphilic. The choice of polymer is determined by consideration of the solubility of the metal colloid precursor. The solvent of choice and the ability of the polymer to stabilize the reduced metal particles in the colloidal state. Natural polymers such as gelatin and agar were often used before the advent of synthetic polymer chemistry, and related stabilizers such as cellulose acetate, cellulose nitrate, and cyclodextrins have been used more recently. Thiele proposed the Protective Value as a measure of the ability of a polymer to stabilize colloidal metal. It was defined, similarly to the older Gold Number of Zsigmondy, as the weight of the polymer which would stabilize 1 g of a standard red gold sol containing 50 mg/L gold against the coagulating effect of 1% sodium chloride solution. Several other studies have been performed on the relative ability of polymers to act as steric stabilizers, and, despite the fact that these quite subjective studies focus on very specific (and quite different) sol systems, it seems that, of the synthetic polymers considered, vinyl polymers with polar side groups such as poly(vinylpyrrrolidone) (PVP) and poly(vinyl alcohol) are especially useful in this respect. The use of copolymers introduces another degree of variability to colloidal stabilization. As the co-monomer ratio can be varied. For example, the use of vinyl-pyrrolidone-vinyl-alcohol copolymers is reported for the preparation of platinum and silver hydrosols. The silver sols were stable only in the presence of the copolymer, and the size of the silver particles decreased with an increase in vinyl-pyrrolidone content of the copolymer. Electrostatic and steric stabilization are in a sense combined in the use of long chain alkyl-ammonium cations and surfactants, either in single-phase sols or in reverse micelle synthesis of colloidal metals. A new class of metal colloids has recently been established in which the surface of the particle is covered by relatively small ligand molecules such as sulfonatedtriphenylphosphine or alkane-thiols.

At the end of the 20th century, we found a big surge in the development of important techniques available for science (nanoscience) and technology [self-assembly structures (vesicles); biomolecules; biosensors; surface and colloid chemistry; nanotechnology]. In fact, these developments indicated that there was no end to this trend, as regards the vast expansion in the sensitivity and level of information; therefore, in this chapter, we would like to explain some of these exciting new developments to the reader. Typical of all humans, seeing believes, so the microscope attracted much interest for many decades. All of these inventions, of course, were basically initiated on the principles laid out by the telescope (as invented by Galileo) and the light optical microscope (as invented by Hooke).

Over the years, the magnification and the resolution of microscopes improved. However, for the man to understand the nature, the main aim of mankind has been to be able to see atoms or molecules. This goal has been achieved, and the subject as described here will explain the latest developments which were invented only approximately 15 years ago. The ultimate aim of scientists has always been to be able to see molecules while active. In order to achieve this goal, the microscope should be able to operate under ambient conditions. Further, all kinds of molecular interactions between a solid and its environment (gas or liquid or solid), initially, can take place only through the surface molecules of the interface. It is obvious that when a solid or liquid interacts with another phase, knowledge of the molecular structures at these interfaces is of interest. The term “surface” is generally used in the context of gas-liquid or gas-solid phase boundaries, while the term “interface” is used for liquid-liquid or liquid-solid phases. Furthermore, many fundamental properties of surfaces are characterized by morphology scales of the order of 1 to 20 nm [1 nm = 10^-9m = 10 Å (Å = Angstrom = 10^-10 cm)].

Depending on the sensitivity and experimental conditions, the methods of molecular microscopy are many and varied. The applications of these microscopes is also varied and extensive. For example, information about crystal structures and three-dimensional configurations of macromolecules has been obtained. The most popular application of microscopy is the study of molecules at surfaces. Generally, the study of surfaces is dependent on understanding not only the reactivity of the surface but also the underlying structures that determine reactivity. Understanding the effects of different morphologies may lead to a process for enhancement of a given morphology and, hence, to improved reaction selectivity and product yields. Atoms or molecules at the surface of a solid have fewer neighbors as compared with atoms in the bulk phase, which is analogous to the liquid surface; therefore, surface atoms are characterized by an unsaturated, bond-forming capability and, accordingly, are quite reactive. Until a decade ago, electron microscopy and some other similarly sensitive methods provided some information about the interfaces. Although, there were always limitations inherent in all of these techniques, which prompted needed improvements. A decade ago, the best electron microscope images of globular proteins were virtually little more than shapeless blobs. However, these days, due to relentless technical advances, electron crystallography is capable of producing images at resolutions close to those attained by x-ray crystallography or multidimensional nuclear magnetic resonance (NMR) imaging. In order to improve
upon some of the limitations of the electron microscope, newer methods were needed. A decade ago, a new procedure for molecular microscopy was invented and will be delineated herein. The new scanning probe microscopes not only provide new kinds of information than that known from x-ray diffraction, for example, but also open a new area of research (for example, nanoscience and nanotechnology). The basic method of these scanning probe microscopes (SPMs) was essentially to be able to move a tip over the substrate surface with a sensor (probe) with molecular sensitivity (nm) in the longitudinal and height directions. This may be compared with the act of sensing with a finger over a surface, or more akin to the old-fashioned record player with a metallic needle (a probe for converting mechanical vibrations to musical sound) on a vinyl record. The sensor movement was controlled under a highly sensitive feedback system, which when coupled to a variety of signals, could provide atomic surface details. This gave almost a new dimension “in the nanometer (nm = 10^-9 m = 10 Å) range” to surface chemical research, which was much needed at this stage. Due to these developments, the last decade has experienced a new aspect of science, the so-called nanotechnology. Originally, two types of microscopes were invented: scanning tunneling microscopes (STM) and atomic force microscopes (AFM). The AFM later developed into a large variety of so-called scanning force microscopes. Additionally, other types of microscopes are being developed, such as the friction force microscope (FFM), etc. AFM thus provides much more useful information than the two-dimensional images of a surface produced using an SEM. AFM can be used for thin films, polymer coatings, and single-crystal substrates. The aim of this book is to describe all of these developments extensively. This approach is one of a kind in the current literature. The scanning tunneling microscope was invented by Binnig and Rohrer in 1982 (for which they were awarded the Nobel Prize in 1986). Later, the atomic force microscope was developed based on the principles of the STM but with resolving surface structures for nonconducting and conducting materials. The advent of these scanning microscopes revolutionized this field. In recent years, other modifications of original STM and AFM have been designed, which are also described herein. STM and AFM proved to be powerful tools for obtaining information on the packing order of molecular adsorption on a surface. Data obtained from STM images can be useful in providing information on the relative importance of molecule-molecule and molecule-substrate interactions, as well as the types of forces responsible for the packing order at the surface. This is useful in such applications as epitaxial growth of thin films, chromatography, lubrication, and microelectronics fabrication, each of which involves interactions between molecules on a surface and can be investigated by using these procedures. The complementary properties of STM and AFM make it attractive to apply these methods to organic surfaces and interfaces.

5. Morphology study of Nanoparticles:

5.1 Morphology effect in design of Chemical reactions:

In this part we augment about some nanoparticles that synthesized and analysed in our laboratory at different morphology. In Figure. 16. We see the SEM images of compound [Pb(µ-bpp)(µBr)2]n=PBB. This indicates that the compounds average size of the particles is 40 nm, which is in agreement with that observed by scanning electron microscopy (SEM). The morphology of compound PBB prepared by the hydrothermal (Figure. 16(a) and sonochemical methods (Figure. 16(b)) is the same and they are composed of particles with sizes of about 40 nm.

Figure. 16 (a) SEM image of nanoparticles of PBB as produced by hydrothermal and (b) SEM image of nanoparticles of PBB as produced by ultrasound.

Figure. 17(a and b) show the SEM images of the PbBr2 and PbO nanoparticles obtained from calcination of compound [Pb(µ-bpp)(µBr)2]n=PBB under argon and air atmosphere, respectively. The morphology of the nanoparticles of PbBr2 and PbO is very similar to that of compound [Pb(µ-bpp)(µBr)2]n=PBB (see Figure. 17(a) and 17(b)). This point may be due to the direct removal of the bpp ligand without changing of morphology under the calcinations in argon and air.
On the other hand, another reaction designed in my laboratory by formula \([\text{Pb}(\mu-\text{bdabpm})(\mu-\text{Br})_2]_n\) [bdabpm=1,4-Benzenediamine, N,N'-bis(3-pyridinylmethylene)]\(^{(ncp)}\) for preparation another morphology of PbBr\(_2\) and PbO nanoparticles. The morphology of the compound \((ncp)\) prepared sonochemical method (Figure. 18.) is the same and they are composed of particles with sizes of about 40 nm.

Figure. 18. SEM image of \((ncp)\) nanopowders, produced by sonochemistry method (a) and TEM image of \((ncp)\) nanopowders, produced by sonochemistry method (b).

Figure. 19 (a, b, c and d) shows the SEM and TEM images of the PbBr\(_2\) and PbO nanopowders obtained from calcinations of the compound \((ncp)\) under argon and air atmosphere, respectively. The morphology of the nanoparticles of PbBr\(_2\) and PbO is very similar to that of the compound \((ncp)\) (see Figure. 18(a) and 18(b)). This point may be due to the direct removal of the bdabpm ligand without changing of morphology under the calcinations in argon and air.

Figure. 19. SEM photograph of PbBr\(_2\) nanopowders produced by calcination of compound \((ncp)\) under argon atmosphere (a) and TEM photograph of PbBr\(_2\) nanopowders produced by calcination of compound \((ncp)\) under argon atmosphere (b) and SEM photograph of PbO nanopowders produced by calcination of compound \((ncp)\) in air atmosphere (c) and TEM photograph of PbO nanopowders produced by calcination of compound \((ncp)\) in air atmosphere (d).
This indicates that the study and help of microscopy methods very interesting and important for us to designing and engineering the some other materials to prepare the one case of materials for different morphologies.

For survey another compounds, we prepared [Pb(2-pyc)(NCS)]_n and [Pb(3-pyc)(NCS)]_n for morphology analysis. The average size of the particles was found to be around 55 nm, which is in agreement with the value obtained from the SEM images (Figure. 20(a and b)).

Figure. 20. (a) SEM photograph of [Pb(2-pyc)(NCS)]_n (1) nano-particles and (b) SEM photograph of [Pb(3-pyc)(NCS)]_n (2) nanorods.

Figure. 21(a and b) show SEM images of PbS nanorods, produced by calcinations of compound [Pb(2-pyc)(NCS)]_n and very interesting nanoplate, produced by calcinations of compound [Pb(3-pyc)(µ-NCS)]_n. The morphology and size of the particles are different in the two samples obtained by two different compounds.

Figure. 21. (a) SEM photograph of PbS nanorods (produced by calcination of compound [Pb(2-pyc)(NCS)]_n) and (b) SEM photograph of PbS nanoplate (produced by calcination of compound [Pb(3-pyc)(µ-NCS)]_n).

So, we synthesized other compounds for supplementary analysis, the average size of the [Pb(DPAcO)₂]_n and [Pb(MPAcO)₂]_n particles was found to be around 85 nm, which is in agreement with the value obtained from the SEM images (Figure. 22(a and b)).

Figure. 22. (a) SEM photographs of [Pb(DPAcO)₂]_n (1) nanobelts and (b) SEM photographs of [Pb(MPAcO)₂]_n (2) nano particles.
Figure. 23(a and b). show SEM images of PbO nanopowders, produced by calcinations of compounds [Pb(DPAcO)2]n and [Pb(MPAcO)2]n. The morphology and size of the particles are different in the two samples obtained by two different compounds.

Figure. 23. (a) SEM photographs of PbO nano-powders (produced by calcinations of nanostructured compound [Pb(DPAcO)2]n and (b) SEM photographs of PbO nano-powders (produced by calcinations of nanostructured compound [Pb(MPAcO)2]n).

This results indicate that the morphology of nanoparticles play very important role in synthetic mechanism of chemical reactions. [61-75].

6. Conclusion:

- In the next decade, morphology effect of materials and so nanomaterials play very important role on them applications.
- I think morphology effect of materials and nanomaterials would be important enough role that science influence and domination will nanotechnology.
- When we say “Nanoparticle”, “Nanowires”, “Nanostars”, Nanoplates”, “Nanotubes”, “Nanoflowers”, “Nnaobelts” and/or other morphology of Nanomaterials, we should certitude this word indicate the Notability of Microscopy methods to analysis of Nanomaterials at bulk materials.
- Therefore, morphology analysis and its role in nanomaterials and bulk materials are possible only through microscopic techniques and this is shows very important role for chemical reactions and mechanisms designers or reactions engineering’s that is possible only according by microscopy methods”.

7. References:


