Methods of Study of Nanosized Systems

Lecture-presentation on “Basics of Nanochemistry and Nanotechnology”

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Objectives of lecture –presentation:

Study of different methods of nanosystems investigations

Plan of lecture –presentation:

Lecture 5

1. Method of Electron Microscopy

2. Sonde Microscopy

3. Diffraction Methods

The basic methods of nanoparticles' sizes and some properties in gaseous phase determination:

- ionization by photons and electrons with analysis of obtained mass-spectra in quadruple or time-running mass-spectrometer;

- atomizing of neutral clusters and their selection according to mass;

- electron X-ray microscopy over screens (information about form and sizes of particles).

Methods of study of particles on the surface:

- X-ray and scanning electron microscopy (information about sizes/forms of particles, their distribution and topology);
- diffraction of electrons (information about size, phase – solid/liquid, structure and length of bonds);
- scanning tunnel microscopy (particle size, its form and inner structure determination);
- gas adsorption (information about surface area);
- photoelectron spectroscopy (electron structure determination);
- electric conductivity (information about zone of conductivity, percolation and topology).

Methods of study of particles in volume:

- X-ray and scanning electron microscopy, electric conductivity, as well as electron diffraction provide as with data on particles in volume, i.e. information similar to that obtained for particles on the surface.
- Sizes and inner structure of particles can be determined by means of roentgenography.
- Extended fine structure and adsorption of X-rays provide as with information about particles’ sizes, while methods of electron paramagnetic resonance (EPR) and nuclear magnetic resonance gives us data on electron structure.

1. Method of Electron Microscopy

Microscopy is the main method for determination nanoparticles’ sizes. They use electron microscopy, and different types of sonde microscopes.

Electron microscopy is divided to two main directions:

- X-ray electron microscopy (XEM);
- Raster scanning electron microscopy (SEM).

1. Method of Electron Microscopy

X-ray electron microscopy. Object in form of thin film is X-rayed by accelerated electrons with energy of 50-200 keV in vacuum. Electrons deflected to small angles by atoms of object and passed through the object reach the system of magnetic lenses which form magnified 10^6 times image of inner structure of object on the screen and the film.

Usually they study films with 0.01 mkm thickness. Modern ultra-microscopes possess to study films with thickness of 10-100 nm. It is possible to obtain diffraction images which give information about crystal structure of objects by means of X-ray microscopes.

1. Method of Electron Microscopy

Scanning electron microscopy.

This method is used mostly for study of surface particles. Electron rays are compressed by magnetic lenses in thin (1-10 mm) sonde which moves over the object from one point to another that is scans it.

1. Method of Electron Microscopy

Several types of rays occur when electrons interact with the object:

- Secondary and reflected electrons,
- Passed electrons,
- Roentgen brake rays,
- Light.

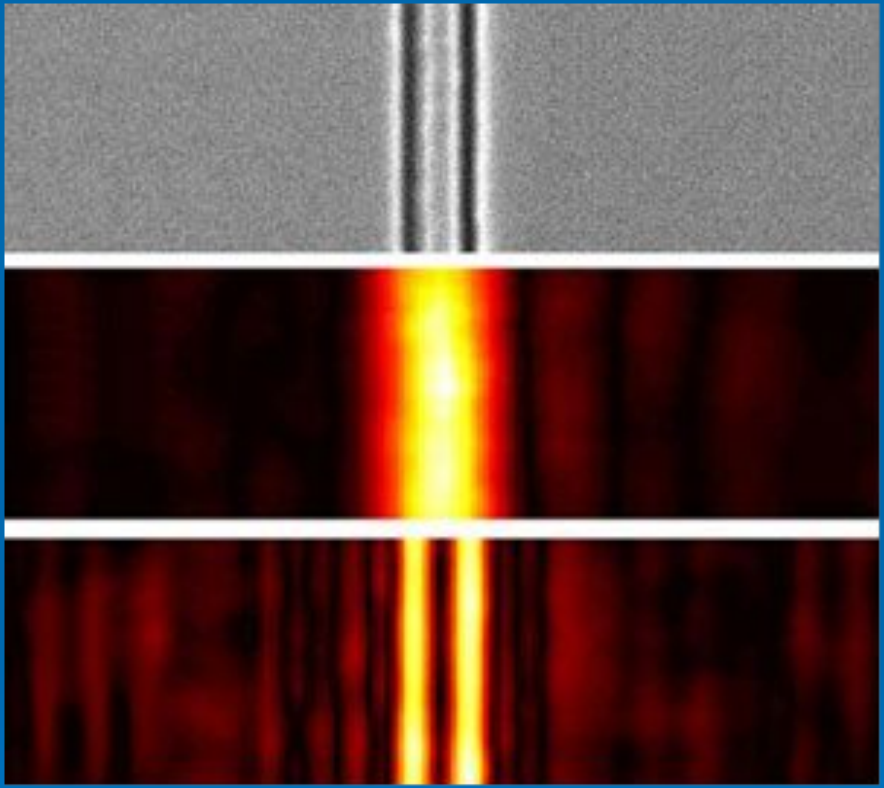
1. Method of Electron Microscopy

The main value of this method – is that it is highly informative.

Disadvantage - great duration of the process.

They use this method for particles with sizes more than 5 nm.

1. Method of Electron Microscopy



Top: Scanning electron micrograph of a line-pair testing object with 50nm linewidth and 70nm gap.

Middle: Diffraction-limited image taken with a conventional optical microscope.

Bottom: The far-field superlens image resolves the line-pair object

2. Sonde Microscopy

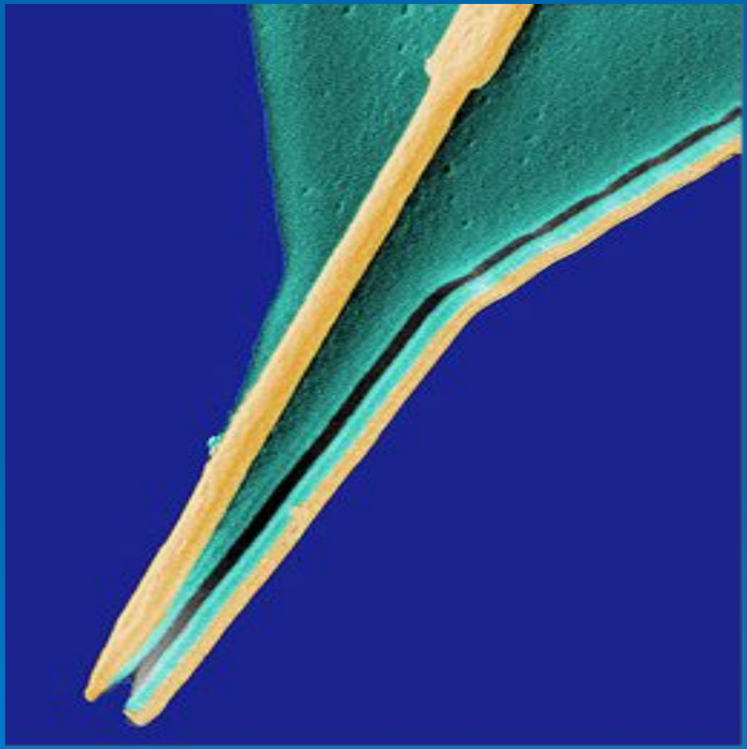
In 1981 Binnig and Rorer created scanning tunnel microscope (STM) and in 1986 they were awarded Nobel Price for it.

Microscope possesses to study surfaces with nanometer and sub nanometer spatial resolution.

The method of gaining information about the properties of studied surface is general for all scanning tunnel microscopes.

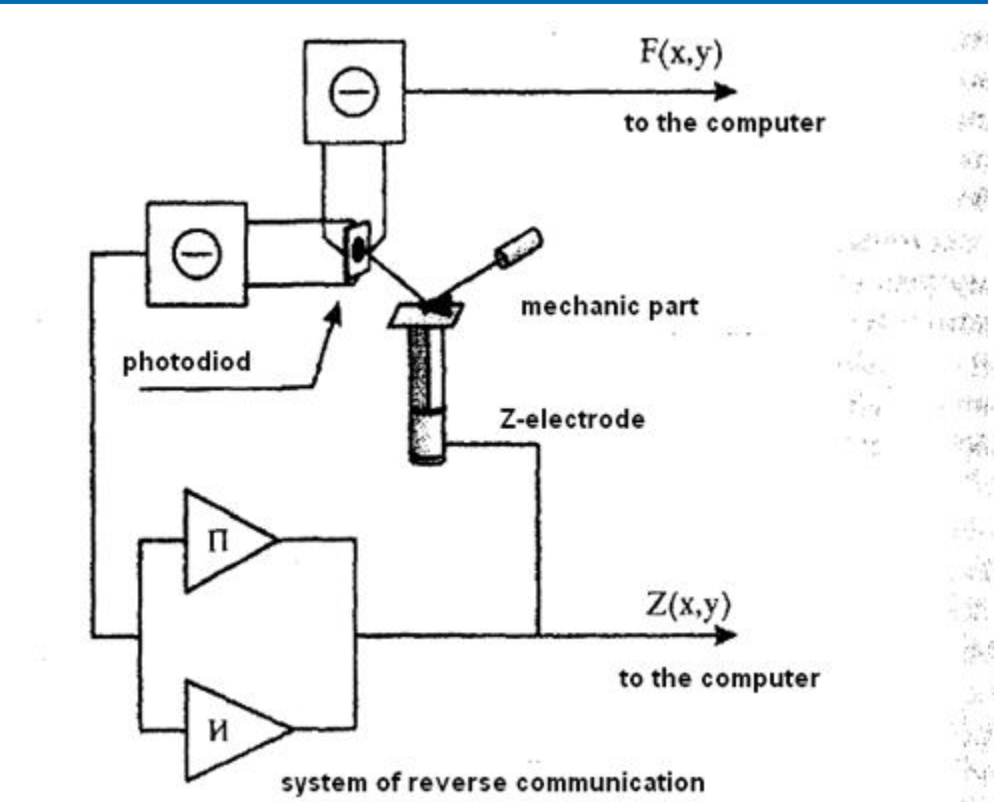
2. Sonde Microscopy

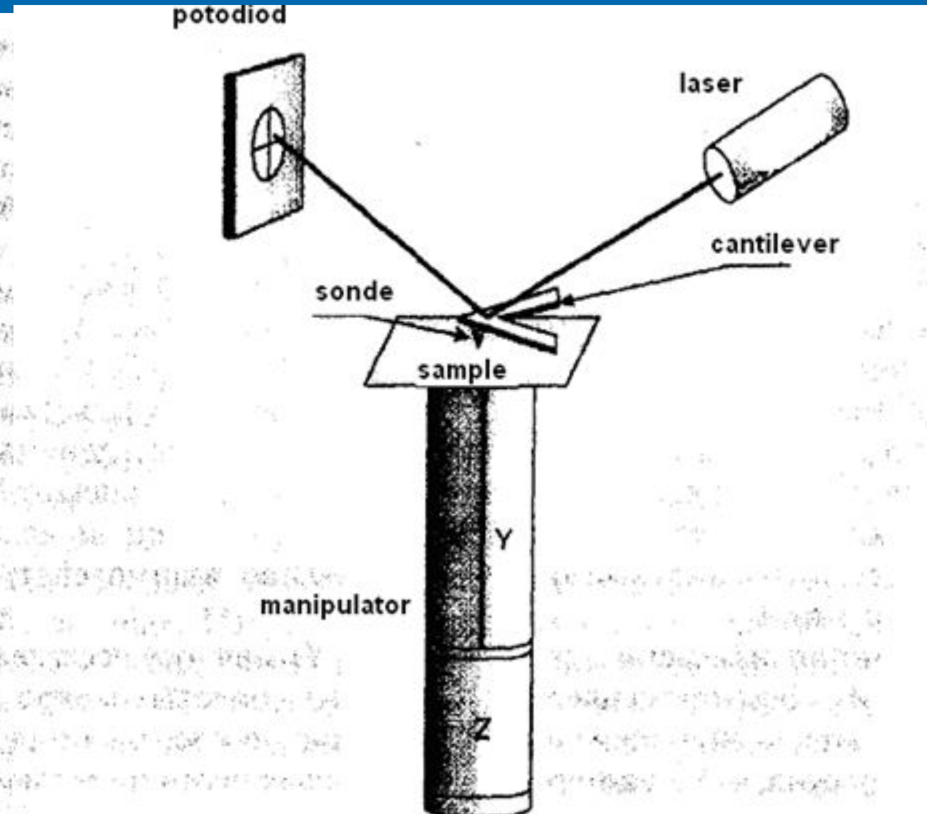
Scanning electron microscopy (SEM) can provide particle size, morphological and chemical composition information on collected single nanoparticles in a vacuum environment.



SEM of a scanning gate probe.

2. Sonde Microscopy





General scheme of sonde microscope work

Mechanic part of atomic-force microscope

3. Diffraction Methods

These methods include diffraction of X-rays and neutrons and are less general than electron microscopy methods. At the same time analysis of diffraction reflexes caused by atomic structures of single particles is suitable for very small particles.

Roentgenography.
X-rays are an efficient tool for ensuring product quality, optimizing manufacturing processes and researching new materials.

3. Diffraction Methods

Neutrons diffraction.

Neutron is the particle which due to its properties is appropriate to be used for study of different materials.

In nuclear reactors there are formed thermal neutrons with maximal energy 0,06 eV.

De Broil wave with λ ~ 1 Ǻ close to the distances between atoms corresponds to these neutrons. Method of structural neutronography is based on this fact.

Plan of lecture –presentation:

Lecture 6

1. Mass-Spectrometry
2. Photoelectron Spectroscopy

1.Mass-Spectrometry

- **Mass spectrometry** (**MS**) is an analytical technique that produces spectra (singular *spectrum*) of the masses of the atoms or molecules comprising a sample of material.

- The spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to elucidate the chemical structures of molecules, such as peptides and other chemical compounds. Mass spectrometry works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios.

1.Mass-Spectrometry

- Mass spectrometry works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios.

- A sample (solid, liquid, or gas) is ionized. The ions are separated according to their mass-to-charge ratio. The ions are detected by a mechanism capable of detecting charged particles.

- Signal processing results are displayed as spectra of the relative abundance of ions as a function of the mass-to-charge ratio.

Steps of mass-spectrometry:

1. Ionisation - Gaseous atoms of a particular element are bombarded with electrons fired from an electron gun. These electron particles will give the gaseous atoms of the specific element a charge.

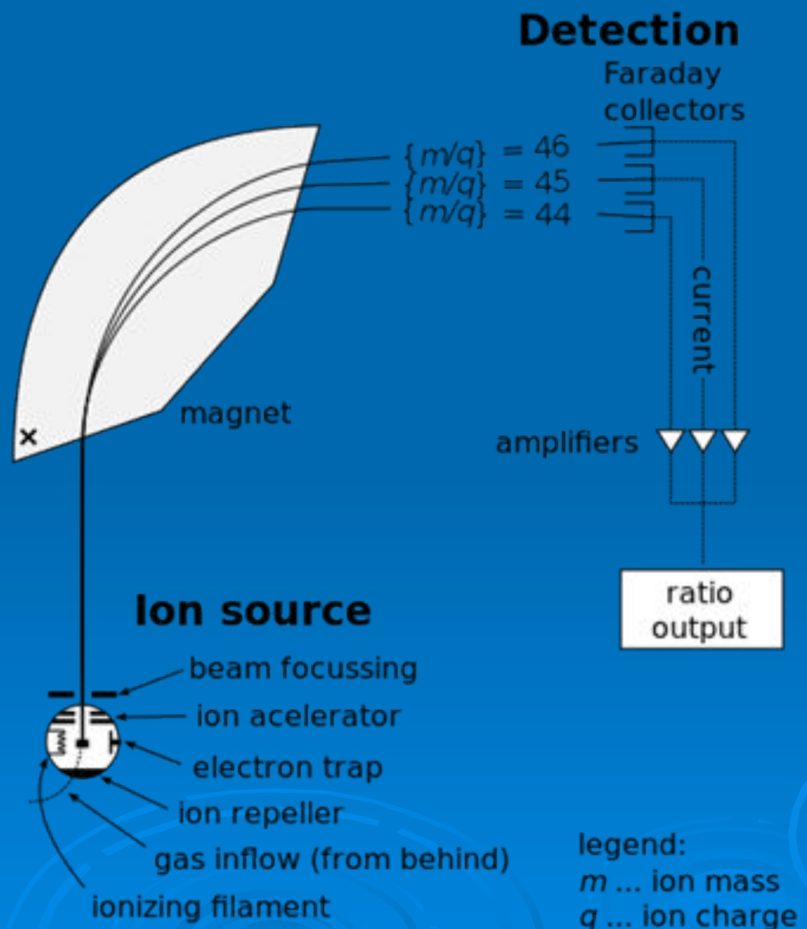
2. Acceleration - The atoms, now charged (ions) and because these ions are charged they can be accelerated by an electric field.

3. Deflection - The charged ions of the particular element, now being accelerated through the deflector, will now be deflected by a magnetic or electric field.

4. Detection - By the charged ions being deflected, they will hit a detection material-either electric or photographic.

Schematics of a simple mass spectrometer with sector type mass analyzer.

This one is for the measurement of carbon dioxide isotope ratios IRMS) as in the carbon-13urea breath test



2. Photoelectron Spectroscopy

This method is based on the measurement of spectrum energies of electrons which flow out during photoelectron emission.

They analyze emission of electrons by solid objects under the action of photons.

According to Einstein sum of bond energy of flowing out electron and its kinetic energy is equal to the energy of falling photon.

2. Photoelectron Spectroscopy

They determine energies of interactions of electrons and their energy levels in studied substance according to their spectrum.

This method possesses to study the distribution of electrons in conductivity zone and to analyze the substance’s composition and chemical bond type.

Comparative analysis of spectrum methods

Method	Detection limits (solid)		Sample
	Relative %	g	
Atomic-emission spectrum analysis	$10^{-7} - 10^{-4}$	$10^{-9} - 10^{-7}$	10 - 100 mg
Atomic-absorption analysis	$10^{-6} - 10^{-3}$	$10^{-13} - 10^{-11}$	0.1 - 1 mg
Atomic fluorescence analysis	$10^{-8} - 10^{-6}$	$10^{-11} - 10^{-9}$	1 – 5 mg
Roentgen fluorescence analysis	$10^{-5} - 10^{-4}$	$10^{-7} - 10^{-6}$	0.1 mg
Spectrophotometry	$10^{-4} - 10^{-3}$	$10^{-11} - 10^{-8}$	0.2 – 10 mg
Laser mass-spectrography	$10^{-6} - 10^{-3}$	$10^{-12} - 10^{-11}$	5 – 100 mg

Check Yourself

1. What is the most significant for study of chemical interactions?
2. What are the basic methods of nanoparticles’ sizes and some properties in gaseous phase determination?
3. What methods of study provide as with data on particles in volume?
4. What information gives us extended fine structure and adsorption of X-rays?
5. What information gives us methods of electron paramagnetic resonance (EPR) and nuclear magnetic resonance?
6. What is the main method for determination nanoparticles’ sizes?
7. What are main directions of electron microscopy?
8. Describe method of X-ray electron microscopy.
9. Describe method of scanning electron microscopy.
10. Which types of rays occur when electrons interact with the object?
11. What is the main value of scanning electron microscopy?
12. What is the major advantage of single-molecule techniques?

Check Yourself

13. What restricts the resolution of conventional lenses?
14. Describe the method suggested by Zhang's group.
15. How does scanning tunnel microscope (STM) and work?
16. What information gives us scanning electron microscopy (SEM)?
17. How does sonde microscope work?
18. List diffraction methods of study.
19. What is the principle of diffraction methods?
20. Describe method of roentgenography.
21. What are the steps of obtaining results by means of diffractometer?

Check Yourself

22. Which are the main requirements for crystals to be studied by roentgenography method?
23. Describe the method of neutrons diffraction.
24. Describe the method of mass-spectrometry.
25. What measurements are held in method of photoelectron spectroscopy?
26. Compare different spectrum methods.
27. What are the main difficulties of several methods of analysis use at the same time to study nanoparticles?

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