Nanoparticles Metrology and Beyond

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Outline presentation

- Np metrology definitions
- Np characterization methods
- Case study: SiC np
- Case study: Gold NP
- Case study: Porous semiconductors
Np Metrology Definitions

- Need for NP standardization
- NP terminology
- NP characterization techniques
International Organization for Standardization

In the post-war era of the late 1940s, global leaders of government and industry formed a central body to “facilitate the international coordination and unification of industrial standards.” Twenty-six member nations came together in 1947 to form the International Organization for Standardization (ISO).

ISO and its national member bodies – including the American National Standards Institute (ANSI) –

In June 2005, ISO formed a new Technical Committee to help focus the world’s attention on standards that would support the growth of nano-related industries. The scope of that committee, ISO/TC 229 – Nanotechnologies, includes standardization in the areas of terminology and nomenclature; measurement and instrumentation; material specifications; and health, safety and the environment.
TC 229 Nanotechnologies

Scope: Standardization in the field of nanotechnologies that includes either or both of the following:

1. Understanding and control of matter and processes at the nanoscale, typically, but not exclusively, below 100 nanometres in one or more dimensions where the onset of size-dependent phenomena usually enables novel applications,

2. Utilizing the properties of nanoscale materials that differ from the properties of individual atoms, molecules, and bulk matter, to create improved materials, devices, and systems that exploit these new properties. Specific tasks include developing standards for: terminology and nomenclature; metrology and instrumentation, including specifications for reference materials; test methodologies; modelling and simulations; and science-based health, safety, and environmental practices.
Need for NP Standardization

Why do we need Standard terminology?

The use of standard definitions helps to ensure better understanding during discussion between parties, particularly in new emerging technologies.

Why do we need standard analysis methodology?

The use of standard analysis methods, including sample preparation, helps to ensure better reproducibility between laboratories.
Need for NP Standardization

Why do we need Standard reports?

The use of standard report specifications helps to ensure better understanding of characterization results between parties.

Why do we need certified reference materials?

The use of certified reference materials helps to ensure that the analysis methods and instrumentation are providing expected results, improving confidence in the results produced for analyzed samples.
NP Terminology

From ISO/TS 27687: 2008 from ISO/TC229

**Particle** – minute piece of matter with defined physical boundaries

**Nanoscale** – size range from approximately 1 nm to 100 nm

**Nano-object** – Material with one, two or three external dimensions in the nanoscale
NP Terminology

**Aggregate** - particles strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components.
NP Terminology

**Agglomerates** - collection of weakly bound particles or aggregates or mixtures of the two where the resulting external surface are similar to the sum of the surface areas of the individual components.
NP Terminology

Nanoparticles: a nano-object with all the three dimension in the nanoscale range
NP Terminology

Nanoplate: nano-object with one external dimension in the nanoscale range, and the other two dimensions significantly larger.
NP Terminology

Nanofiber: Nano-object with the two dimensions in the nanoscale range and the third dimension significantly larger
NP Terminology

**Nanotube** – hollow nanofiber

**Nanorod** - solid nanofiber

**Nanowire** - electrical conducting or semiconducting nanofiber

**Quantum dot** – Crystalline nanoparticles that exhibit size-dependent properties due to quantum confinement effects on the electronic states.
Particle Characteristic
NP Characterization methods

Microscopy: Spatially resolved interaction of sample with electrons, light, particles/molecules (SEM, TEM, …)
Fractionating methods; Fraction (acc. To mobility) detection
Static scattering techniques (SLS, SAXS, SANS)
Dynamic scattering techniques (DLS, DXS)
Other spectroscopies methods (light, acoustic, Electric field)
Integral/concentration measurement (BET, Turbidity, CPC,..)
Techniques for characterizing the interfacial properties (E-Kinetic, E-Acoustic, non linear optic)
<table>
<thead>
<tr>
<th>Technique</th>
<th>Measures</th>
<th>Sample</th>
<th>Sensitivity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission Electron Microscopy (TEM)</td>
<td>particle size and characterization</td>
<td>&lt; 1μg has to be prepared as a thin film and be stable under an electron beam and a high vacuum</td>
<td>down to 1nm</td>
<td>additions to TEM can provide more information e.g. Scanning Transmission Electron Microscopy (STEM), High-Resolution TEM (HRTEM) or in-situ measurements as Environmental TEM</td>
</tr>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>particle size and characterization</td>
<td>sample must be conductive or sputter coated, easier to prepare than TEM sample</td>
<td>down to 1nm</td>
<td>can be used in-situ as Environmental SEM</td>
</tr>
<tr>
<td>Atomic Force Microscopy (AFM)</td>
<td>particle size and characterization</td>
<td>samples must adhere to a substrate and be rigid and dispersed on the substrate. The appropriate substrate must be chosen. Air or liquid samples.</td>
<td>1nm - 8μm</td>
<td>a form of Scanning Probe Microscopy (SPM). Requires less time and cost than SEM and TEM.</td>
</tr>
<tr>
<td>Photon Correlation Spectroscopy (PCS)</td>
<td>average particle size and size distribution</td>
<td>sample must be a very dilute suspension</td>
<td>1nm - 10μm</td>
<td>based on Dynamic Light Scattering, an extension of the technique is Photon Cross Correlation Spectroscopy (PCCS) for high concentration opaque suspensions giving particle size and stability of nanoparticles</td>
</tr>
<tr>
<td>Nanoparticle Surface Area Monitor (NSAM)</td>
<td>human lung-deposited surface area of nanoparticles</td>
<td>aerosol, concentrations 0 to 10,000μm²/cm³, temp 10 - 35°C</td>
<td>down to 10nm</td>
<td>similar to an Electrical Aerosol Detector (EAD).</td>
</tr>
<tr>
<td>Condensation Particle Counter (CPC)</td>
<td>number concentrations of particles</td>
<td>aerosol, concentrations 0 to 100,000 particles/cm³, can be in a flow, higher temps to 200°C possible</td>
<td>2.5 to &gt;3,000nm</td>
<td>can be used for a flow, hand held models available</td>
</tr>
<tr>
<td>Differential Mobility Analyzer</td>
<td>particle size distribution</td>
<td>aerosol</td>
<td>down to 3nm</td>
<td>can be combined with other techniques to create Tandem DMA or DMPS</td>
</tr>
<tr>
<td>Scanning Mobility Particle Sizer (SMPS)</td>
<td>particle size distribution</td>
<td>aerosol, can be a concentrated sample of 1,000,000 - 2,400,000 particles/cm³</td>
<td>3 – 1,000nm</td>
<td>uses an electrostatic classifier and a CPC, can also add DMA</td>
</tr>
<tr>
<td>Nanoparticle Tracking Analysis (NTA)</td>
<td>particle size and size distribution</td>
<td>500μl suspension, temp 5 - 50°C, wide range of solvents can be used</td>
<td>10 – 1,000nm</td>
<td>use with DLS or PCS</td>
</tr>
<tr>
<td>X-Ray Diffraction (XRD)</td>
<td>average particle size for a bulk sample</td>
<td>larger crystalline samples (&gt;1mg) required</td>
<td>down to 1nm</td>
<td>can identify individual crystals</td>
</tr>
<tr>
<td>Aerosol Time of Flight Mass Spectroscopy</td>
<td>particle size and composition</td>
<td>aerosol</td>
<td>100 – 3,000nm</td>
<td>the efficiency of this method is less for smaller particles.</td>
</tr>
<tr>
<td>Aerosol Particle Mass Analyzer (APM)</td>
<td>particle mass</td>
<td>aerosol sample with particle density approx 1g/cm³</td>
<td>equivalent to 30 - 580nm</td>
<td>gives only mass information and is not dependent on particle size or shape</td>
</tr>
</tbody>
</table>
NP Characterization methods

Different techniques will suit different types of sample. For example some techniques require the sample to be as an aerosol and others will use a suspension or liquid sample. There may be a sample protocol to be followed for collection of the sample for analysis by a certain technique.
Microscopy Methods

Transmission Electron Microscopy (TEM) uses an electron beam to interact with a sample to form an image on a photographic plate or specialist camera. The sample must therefore be able to withstand the electron beam and also the high vacuum chamber that the sample is put into. The sample preparation can be difficult as a thin sample on a support grid must be prepared. The process can also be time consuming and this, along with the cost, are the main criticisms of TEM. High-Resolution TEM (HRTEM) looks at the interference of the electron beam by the sample rather than the absorbance of the beam as with ordinary TEM. This gives a higher resolution which is beneficial when studying nanoscale samples. However it does require understanding of the sample to allow interpretation of the results, as the phase-contrast resulting information can be difficult to interpret. This can therefore restrict the use of HRTEM. Environmental TEM allows TEM to be carried out in-situ by using the relevant gaseous atmosphere as opposed to the vacuum used for TEM.
Microscopy Methods

Scanning Electron Microscopy also uses a high energy electron beam but the beam is scanned over the surface and the back scattering of the electrons is looked at. The sample must again be under a vacuum and for SEM it must be electrically conductive at the surface. This can be achieved by sputter coating a non-conductive sample. This requirement can be restrictive and again this technique can be time consuming and expensive. Environmental SEM is available where samples can be looked at again in a low pressure gas environment as opposed to a vacuum.

Scanning Transmission Electron Microscopy combines the ideas of looking at the surface of the sample and into the sample with an electron beam.
Microscopy Methods

Atomic Force Microscopy is a form of Scanning Probe Microscopy. It uses a mechanical probe to feel the surface of a sample. A cantilever with a nanoscale probe is moved over the surface of a sample and the forces between the probe tip and the sample measured from the deflection of the cantilever. The deflection moves a laser spot that reflects into an arrangement of photodiodes. This can offer a 3D visualisation. Air samples or liquid dispersions can be looked at and AFM is less costly and time consuming than TEM or SEM. However the sample must adhere to a substrate and be rigid and dispersed on it. The roughness of the substrate must be less than the size of the nanoparticles being measured.
X-Ray Diffraction (XRD)

XRD can be used to look at single crystal or polycrystalline materials. A beam of x-rays is sent into the sample and the way the beam is scattered by the atoms in the path of the x-ray is studied. The scattered x-rays constructively interfere with each other. This interference can be looked at using Bragg’s Law to determine various characteristics of the crystal or polycrystalline material. Measurements are made in Angströms, 1 Angström = 0.1nm. The use of XRD is often compared to the microscopy techniques. XRD avoids issues of representative samples and determining crystals as opposed to particles as discussed above. However XRD can be time consuming and requires a large volume of sample.
Photon Correlation Spectroscopy (PCS)

PCS measures the scattering pattern produced when light is shown through a sample. It combines this with calculations of the diffusion caused by Brownian Motion in the sample in a relationship described in the Stokes-Einstein equation. This will give the radius of a particle and therefore an estimation of the average particle size and distribution of particles through the sample. The sample must be a liquid, solution or suspension. It must also be very dilute or the scattering of light can be unclear. The technique is sensitive to impurities and the viscosity of the sample must be known. The range of particle sizes that can be measured has been quoted between 1nm - 10µm.

Concentration: Multiple scattering - Particle particle interaction

Stability of samples: Coagulation, Hydrophilic Hydrophobic sample surfaces, Zeta potential

Dust in the sample
Dynamic light scattering

Is a technique used to determine size distribution profile of small particle in suspension

When the light hits the particles the light is elastic scattered in all directions (Rayleight Scattering)
Dynamic light scattering

If the light source is monochromatic and coherent the scattering intensity is time dependent. The effect is due to the fact that the nanoparticles are undergoing Brownian motion. The scattered light interfere costructively or destructively therefore the intensity fluctuation brings the information of time scale motion of the particles in solutions. In the same condition of temperature and fluid viscosity small particle move faster generating fast scattering intensity variation while bigger particle move slower creating a slow variation of scattered light intensity. The velocity of the Brownian motion is defined by a property known as the translational diffusion coeffient D.
Dynamic light scattering

The experiment’s theory is based essentially on two assumptions. The first condition is that the particles are in Brownian motion (also called ‘random walk’); in this situation we know the probability density function, given by the formula:

\[ P(r,t) = (4\pi D t)^{-1/2} \exp(-r^2/4D t) \]

where \( D \) is the diffusion constant. The second assumption is that the beads used in the experiment, are spherical particles with a diameter small compared to the molecular dimensions. If it is so, then it is possible to apply the Stoke-Einstein relation and hence have a formula that easily gives the diffusion constant:

\[ D = \frac{k_B T}{6 \pi \eta a} \]

where \( a \) is the radius of the beads, \( k_B \) is the Boltzmann constant, \( T \) is the temperature in Kelvin degrees and \( \eta \) is the viscosity of the solvent. Since from the light scattering is possible to obtain information about the position of the particles, thought the formulas above is easy to get the radius of the beads.
Dynamic light scattering

The diameter that is measured in the DLS is a value that measures how fast the particle diffuse within the fluid. This is hydrodynamic diameter. This diameter will depend not only on the size of the particle core, but also on any surface structure as well as the concentration and type of ions in the medium.

Factor that influence the Radius:

Ionic strength of medium can affect the particle diffusion speed by changing the thickness of the electric double layer called Debye length ($k^{-1}$). Thus a low conductivity medium will produce an extended double layer of ions around the particle, reducing the diffusion speed and resulting in a larger, apparent hydrodynamic diameter. Conversely, higher conductivity media will suppress the electrical double layer and the measured hydrodynamic diameter.
Factor that influence the Radius:

**Surface Structure**
Any change to the surface of a particle that affects the diffusion speed will correspondingly change the apparent size of the particle.

**Non-Spherical Particles**
All particle-sizing techniques have an inherent problem in describing the size of non-spherical particles. The sphere is the only object whose size can be unambiguously described by a single figure. The hydrodynamic diameter of a non-spherical particle is the diameter of a sphere that has the same translational diffusion speed as the particle.

The performance of a DLS instrument is normally verified by measurement of a suitable polystyrene latex standard. If the standard needs to be diluted prior to measurement, then dilution in an appropriate medium is important. The International Standard on DLS (ISO13321 Part 8 1996) says that dilution of any polystyrene standard should be made in 10mM NaCl. This concentration of salt will suppress the electrical double layer and ensure that the hydrodynamic diameter reported will be the same as the hydrodynamic diameter on the certificate or the expected diameter.
Nanoparticle Tracking Analysis (NTA)

This technique provides information of particle size, size distribution and a real time view of the nanoparticles in the sample. The sample must be a suspension for which a wide range of solvents can be used. It is placed on an optically opaque background and a laser light used so that the nanoparticles can be directly visualised through an optical microscope. A digital camera is also used to record the observed particles. Software can then produce a frequency size distribution graph.
Zeta Potential

The majority of particles or nanoparticles dispersed in water have a surface charge, caused by phenomena of ionization or absorption of charged species. The charged particles are surrounded by several layers ion in solution, whose composition is different from that of the bulk. When they move in solution (Brownian movement, for example) the particles move together to a double layer ion. The Zeta potential is the potential at the level of this double layer, also called sliding plane (slipping plane).

![Diagram of Zeta Potential](image-url)
Zeta Potential

The liquid layer surrounding the particle exists as two parts; an inner region, called the Stern layer, where the ions are strongly bound and an outer, diffuse, region where they are less firmly attached. Within the diffuse layer there is a notional boundary inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane.

If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency to flocculate.
Electrokinetic effects

**Electrophoresis:** The movement of a charged particle relative to the liquid it is suspended in under the influence of an applied electric field.

**Electroosmosis:** The movement of a liquid relative to a stationary charged surface under the influence of an electric field.

**Streaming potential:** The electric field generated when a liquid is forced to flow past a stationary charged surface.

**Sedimentation potential:** The electric field generated when charged particles move relative to a stationary liquid.

The velocity of a particle in a unit electric field is referred to as its electrophoretic mobility. Zeta potential is related to the electrophoretic mobility by the Henry equation:

\[
UE = \frac{\varepsilon_r \varepsilon_0 \zeta f(\kappa a)}{\eta}
\]

where \(UE\) = electrophoretic mobility, \(\zeta\) = zeta potential, \(\varepsilon\) = permittivity, \(\eta\) = viscosity and \(f(\kappa a)\) = Henry’s function.
Is there an optimum size?

The taste of both peanut butter and chocolate is affected by the size of their respective ingredients.
Extremely fine amorphous silica is added to tomato ketchup to control its flow.
Pharmaceutical tablets dissolve in our systems at rates determined in part by particle size and exposed surface area.
Pigment size controls the saturation and brilliance of paints.
The setting time of concrete, dental fillings, and broken-bone casts proceeds in accordance with particle size and surface area exposure.
Some materials, gums in particular, do not dissolve in water but absorb water to form viscous colloidal sols.
The particle size of the powder determines the type of dispersion.
Larger particles form a discontinuous mucilage and fine powders yield homogeneous dispersions.
NP applications

- Cosmetics and personal care products (~60%)
- Paints & coatings (~10%)
- Catalysts & lubricants (~10%)
- Security printing
- Textiles & sports
- Medical & healthcare
- Food and nutritional supplements
- Food packaging
- Agrochemicals
- Veterinary medicines
- Water decontamination
- Construction materials
- Electrical & electronics
- Fuel cells & batteries
- Paper manufacturing
- Weapons & explosives

Over 800 consumer products already available*
Titanium dioxide NP

Rutile and Anatase - Tetragonal
Titanium dioxide is a common additive in many food, personal care, and other consumer products used by people. It is important to quantify the amount of titanium in common food products, derives estimates of human exposure to dietary (nano-) TiO₂, and discusses the impact of the nanoscale fraction of TiO₂ entering the environment. The foods with the highest content of TiO₂ included candies, sweets, and chewing gums. Among personal care products, toothpastes and select sunscreens contained 1% to >10% titanium by weight. While some other crèmes contained titanium, despite being colored white, most shampoos, deodorants, and shaving creams contained the lowest levels of titanium (<0.01 μg/mg). For several high-consumption pharmaceuticals, the titanium content ranged from below the instrument detection limit (0.0001 μg Ti/mg) to a high of 0.014 μg Ti/mg.
Amount of Ti in some food products
Cancer Research

Titanium Dioxide Nanoparticles Induce DNA Damage and Genetic Instability *In vivo* in Mice

Benedicte Trouiller¹, Ramune Reliene¹,³, Aya Westbrook¹,⁴, Parrisa Solaimani¹,⁴, and Robert H. Schiestl¹,²,⁵

Do we need to determine the safe limit of these NP?
NP Safety

![Diagram showing the process of NP safety testing and characterization.](image-url)
Case Study 1

UV Emission from 6H Silicon Carbide Quantum Dots
Aims

- Obtain PL from Indirect Band Gap Material Like Silicon.
- Obtain UV Emission from Nanocrystals by means Quantum Confinement.
- 6H SiC is very Stable Material and could be used in Harsh Environment.
- The SiC it is a Biocompatible Material.
Nanostructured Semiconductors

Nanostructured semiconductors are interesting because of quantum effects.

The band structure can be modified by quantum confinement.
Nanostructured Semiconductors

Dimension? Energy? Wavelength?

\[ \Delta E_g = \frac{\hbar^2}{8\mu R^2} - \frac{1.78e^2}{\varepsilon R} + \text{smaller term} \]
Porous Silicon Carbide Fabrication

Basic Reaction of Porous Silicon Carbide Formation

\[
\text{SiC} + \text{H}_2\text{O} + 6\text{F}^- + 6\text{H}^+ = \text{SiF}_6^{2-} + \text{CO} + 2\text{H}^+ \\
\text{SiC} + 2\text{H}_2\text{O} + 6\text{F}^- + 8\text{H}^+ = \text{SiF}_6^{2-} + \text{CO}_2 + 4\text{H}^+
\]
The particles have a spherical shape with a large dimension distribution from 1 nm up to 10 nm in diameter.

The distance between the plane 1020 is 2.5 Å and 1100 is 1.5 Å, it is consistent with the hexagonal structure of 6H.
PL from SiC in Different Solvent

SiC nanoparticles suspension under excitation with 360 nm light
Effective Mass Approximation

**Effective Mass**

\[ \mu = \frac{m_e m_h}{m_e + m_h} \]

\[ R \approx 1.3 \text{nm} \quad E_g \approx 3.5 \text{ eV} \]

Bohr Radius 6H SiC = 1.3nm

Energy of first excited state

Kinetic energy

Screened Coulomb interaction

Polarization term
## Case Study 2

### Noble Metal Nanoparticles

- High chemical stability
- Low toxicity
- New chemical-physical properties at the nanoscale

### Applications

<table>
<thead>
<tr>
<th>Applications</th>
<th>Au</th>
<th>Ag</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic ink for ink-jet printing tech.</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Antibacterial additive</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Catalysts</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Thermal nanofluids</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Bioimaging and cancer therapy</td>
<td>X</td>
<td></td>
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<tr>
<td>Optical device</td>
<td>X</td>
<td>X</td>
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</tr>
</tbody>
</table>
Gold as bulk material

Favorable Properties:

- High electrical conductivity
- Reflectivity
- Malleability
- Resistance to corrosion and oxidation
Gold as nanomaterial

New Optical Properties:

- Light Absorption: Different colors based on different sizes
- Localized Surface Plasmon Resonance (LSPR)
- Enhancement of the local electromagnetic field of the incoming light (e.g., Surface Enhanced Raman Scattering)

Hunag et al., Nanomedicine (2007), 2(5) 681-693
Gold Nanoparticles History

Stained Glasses

The First Nanotechnologists

Ancient stained-glass makers knew that by sputtering tiny amounts of gold and silver in the glass, they could produce the red and yellow tints in stained-glass windows. Similarly, today's scientists and engineers have found that it takes only small amounts of a nanoparticle, precisely placed, to change a material's physical properties.

Gold particles in glass
- Size: 25 nm
- Shape: sphere
- Color: reflected:

Silver particles in glass
- Size: 100 nm
- Shape: sphere
- Color: reflected:

Had medieval artists been able to control the size and shape of the nanoparticles, they would have been able to use the two metals to produce other colors. Examples:

- Size: 40 nm
- Shape: sphere
- Color: reflected:

- Size: 100 nm
- Shape: prism
- Color: reflected:

Chinese Ruby color pottery using gold particles.

Source: Dr. Chad A. Mirkin, Institute of Nanotechnology, Northwestern University
Gold Nanoparticles History

1850s

Preparation of pure colloidal gold using phosphorus to reduce gold chloride. *He recognized that the colour was due to the small size of colloids.*

1900s
Using Maxwell's electromagnetic theory applied to spherical Gold particles, Gustav Mie provided a theoretical treatment of plasmon resonance absorption of Gold colloids. *When a gold nanoparticle is irradiated with light, strong absorption and/or scattering will occur at specific resonant wavelengths, which depend greatly on the morphology and dielectric environment of the gold nanoparticle.*
Gold Nanoparticles History

Turkevich Method (1951), Discuss. Faraday. Soc. 11, 55-75

\[ \text{Au}^{3+} \xrightarrow{\text{Reduction at 100 °C}} \text{Citrate} \xrightarrow{} \text{Au NP} \]


Different sizes of colloidal gold particles

Citrate as reducing and stabilizing agent
Gold Nanoparticles History


\[ \text{Au}^{3+} \rightarrow \text{Au(I)-thiol} \rightarrow \text{Au NP} \]

Reduction at room \( T \)

Toluene or Hexane

\[ \text{HAuCl}_4 \rightarrow \text{NaBH}_4/\text{TOAB} \rightarrow \text{Au NP} \]
Plasmons can be described in the classical picture as an oscillation of free electron density with respect to the fixed positive ions in a metal.

Plasmons play a large role in the optical properties of metals. Light of frequency below the plasma frequency is reflected, because the electrons in the metal screen the electric field of the light. Light of frequency above the plasma frequency is transmitted, because the electrons cannot respond fast enough to screen it.

Some metals, such as copper and gold, have electronic interband transitions in the visible range, whereby specific light energies (colors) are absorbed, yielding their distinct color

Surface plasmons are those plasmons that are confined to surfaces and that interact strongly with light resulting in a polariton.
Raman spectroscopy probes bonds in molecules and provides characteristic chemical information about compounds.

Raman spectroscopy provides:
- fingerprint spectra (molecular identity)
- information about 3d structural changes (orientation, conformation)
- information about intermolecular interactions
- dynamics

Advantages of Raman spectroscopy:
- non-destructive, non-invasive
- works in-situ and in-vitro for biological samples
- works under a wide range of conditions: (temperature, pressure)
Raman spectroscopy is closely related to infrared absorption spectroscopy

- Provides fingerprint spectra (molecular identity, sample composition)
- Complementary to IR
- Sensitive to molecular conformation, environment
- Laser-based (easy to focus beam); diffraction-limited spatial resolution
- Useful for biological applications
  - non-destructive
  - analytes do not photobleach
  - provides contrast without specific labeling
Fluorescence is limited by the need to label and photobleaching. > **Raman spectroscopy** provides molecular information

Raman: inelastic light scattering

\[ E_i = h\nu_i \]

\[ E_s = h\nu_s \]

\[ \Delta E = E_i - E_s \]

**Raman spectrum of a single bacterial spore**

### Raman spectroscopy provides
- Fingerprint spectra (molecular identity)
- Information about 3d structural changes (orientation, conformation)
- Information about intermolecular interactions
- Dynamics
In 1977, an interesting finding was reported, starting the “age of surface enhanced Raman spectroscopy”

- Flat surfaces give Raman enhancements in the range of $10^3 - 10^6$
- Jeanmaire and Van Duyne, *J. Electroanal. Chem.*, 84, 1 (1977)
Needs in SERS

Surface-enhanced Raman spectroscopy required:

- specific metals (e.g. Au, Ag, Cu, Pt, ...)
- surfaces with roughness on the nanometer scale
- it is wavelength-specific
- no enhancements observed for water, methanol, etc - most solvents...
- certain molecules provided much higher Raman intensities (mostly molecules with carbon double-bonds)
Plasmon Resonant Particles (PRP) lead to novel probes for biological applications...

What cause the increase of the Raman signal:

Chemical enhancement through the formation of a charge-transfer complex


Chemical enhancement has been estimated to contribute a factor of up to $10^2$ to the SERS enhancement
What cause the increase of the Raman signal:

The incident electric field causes collective oscillations in the conduction electrons in the metal sphere. These oscillations, called surface plasmons, result in an induced electric field that decays exponentially from the surface of the sphere.

Calculations have shown that the electromagnetic enhancement of the SERS signal can be as large as $10^{11}$-$10^{12}$.
Biological Applications of SERS

- Spectroscopy of Single Hemoglobin Molecules

- Glucose Detection

- Cancer Gene Detection

- Pathogen Detection

- Optical Tags using SERS

- Detection Platforms for Biological Toxins

- Intracellular SERS Detection
More recently, SERS has seen a new spark of interest in the research community because of an exciting new discovery:

Aggregated colloids have been shown to produce Raman enhancements of $10^{14} - 10^{15}$ making single molecule detection possible

- Nie, S. et al., *Science*, 275, 1102 (1997)
AuNPs Synthesis
AuNPs Optical Properties

Localized Surface Plasmon Resonance

Interaction of an electromagnetic radiation with a metal nanoparticle. A dipole is induced, which oscillates in phase with the electric field of the incoming light. Transversal and longitudinal oscillations of electrons occur in a metal nanorod.

AuNPs Surface Chemistry

AuNPs Applications

P.M. Tiwary et al. Nanomaterials (2011), 1, 31-63
Chemical and Biological Sensing

Sensing Strategies

- Colorimetric sensing
- Fluorescence-based sensing
- Electrical and Electrochemical
- AuNP-based SPR Sensors
- Surface Enhanced Raman Scattering (SERS)-based Sensing

Chemical and Biological Sensing

Colorimetric sensing

Heavy Metal Ions Detection

Glucose Detection


Chemical and Biological Sensing

- Fluorescence based sensors

**DNA Detection**

**Bacteria Detection**

Chemical and Biological Sensing

Electrical and Electrochemical Sensors

Fabrication of GOx electrode by the reconstitution of GOx on a FAD-functionalized AuNP:
(a) The adsorption of AuNP-reconstituted of apo-GOx to a dithiol monolayer assembled on a gold electrode
(b) the adsorption of FAD-AuNPs to a dithiol-modified gold electrode followed by the reconstitution of apo-GOx onto functional AuNPs.

Y. Xiao et al. Science (2003), 299, 1877
Chemical and Biological Sensing

**AuNP-based SPR Sensors**

The general principle behind LSPR-based sensors is the wavelength shift in the LSPR spectrum arising from local dielectric changes caused by analyte adsorption.

AuNPs have been used to enhance the signals of the propagating SPR spectroscopic signals to increase sensor sensitivity.

The signal amplification was explained by the electronic coupling interaction of the propagating surface plasmons with localized surface plasmons of AuNPs and depends on various factors such as size, shape, and the distance from the metal generating SPR.

Chemical and Biological Sensing

Surface Enhanced Raman Scattering (SERS)

Raman Effect

Enhancement factor $10^{10}$ to $10^{11}$

Almost Single Molecule Detection

Case Study: Melamine

Food Adulteration

- Boost Protein Content in milk (rich of N)
- Kidney failures in children in China

AuNPs-based Melamine Sensing

ø 40 nm AuNPs synthesis

AuNPs Synthesis:
- 0.01% HAuCl$_4$ in water
- 0.01% Trisodium Citrate
- Reduction at 100°C
AuNPs-based Melamine Sensing

Colorimetric sensing

Advantages
- High Sensitivity
- Rapid Test
- Low Cost

Drawbacks
- False Positive Response (Eg. Adenine, ATP etc.)
- Short Dynamic range (saturation above 2.5 ppm)
AuNPs-based Melamine Sensing

Raman Spectroscopy

SERS EFFECT

Raman Spectrum of solid Melamine

Melamine (MEL)

AuNPs

Ring breathing mode at 676 cm$^{-1}$

Melamine
AuNPs-based Melamine Sensing

- SERS in solution
SERS Substrate Fabrication

Functionalization Scheme

Protocol:
- Cleaning with Acqua Regia (HCl:HNO₃, 3:1)
  - Removing metal residues that induce AuNPs precipitation
- Cleaning with Piranha solution (H₂SO₄:H₂O₂, 3:1)
  - Removing organic materials and forming SiOH groups on the surface
- Silanization with APTMS (3-Aminopropyltrimethoxysilane)
  - Positively charged amino groups able to bind negatively charged AuNPs

AuNPs-based Melamine Sensing

- SERS substrate
- AuNPs
- Microscope Glass
- Graph showing Raman Shift vs. Intensity with plots for SERS substrate + Melamine and Glass substrate + Melamine.
AuNPs distribution on Glass

- Electrostatic immobilization of AuNPs on the substrate
- Objective: AuNPs monolayer – C
- Inter particles distance close enough to have SERS effect

AuNPs distribution on Glass

30 minutes

2 hours

1 day

3 days
Porosity

Porosity Surface area and porosity as a function of particle size or surface area and porosity independent of particle size are other physical characteristics that play an important role in particle technology. The effectiveness of odor removers depends on the active surface area of the adsorbent in them. The tightness of the weave of a cloth raincoat, and therefore its porosity, is adjusted to retard water penetration but permit air and vapour passage for comfort. Adsorbent towels and tissues, on the other hand, are made to have pores that readily wick up liquids. The tips of felt-tip pens have a still different requirement: their pore structure must hold a viscous ink but release it when compressed.
Porous Semiconductors

Why porous materials?

High specific surface
High reactivity
Biocompatibility
Compatible with microelectronics
Why Porous Silicon?

✓ Easy to obtain:

Anodization in HF (a few minutes)

Si wafer

PS sample

✓ Large specific surface (\(\sim 200 \text{ m}^2/\text{cm}^3\)):
it is a “nano-sponge”

Same surface area as a medium sized football pitch.
Butterflies = lepidoptera = “wings with scales”

Several structural levels
- wing (macroscopic) =>
- scales (50 x 100 µm) =>
- ridges & cross ribs (micron size) =>

NANOSTRUCTURE (< 100 nm)

(Vukusic, 1999)
The large family of insects known as Buprestidae possesses many vividly colored members. *Chrysochroa vittata*, shown here, is special in that its body displays a metallic green finish, which turns blue under large incidences. The ventral part hidden of the abdomen is red under normal incidence, but shifts to green under large angles. Spectral filtering of visible light by the cuticle of metallic woodboring beetles and microfabrication of a matching bioinspired material...
Algae Discovered to Use Photonic Crystals Against UV Radiation

Tiny calcite crystals surrounding certain algae achieve the same effect as chemical sunscreens, reflecting ultraviolet radiation while allowing longer wavelengths through for photosynthesis.

Physical Sunscreen. The alga Calyptrolithophora papillifera is encased in a shell of calcite crystals with a two-layer structure (visible on oblique face). Calculations show that this protective covering reflects ultraviolet light.

Photonic crystals

PCs are present in nature

Artificial materials

Bragg law: \( n\lambda = 2d \sin \Theta \)
Photonic crystals

Porous silicon microcavity

DBR # 1

~ 5.25 µm

DBR # 2

Si p⁺ type

High PL

Low PL
That’s a wonderful world

Thank to

Andrea Mario Giovannozzi Ph.D
Annalisa Nastro PhD
Dario Imbraguglio Ms
Barbara Massessi Ms