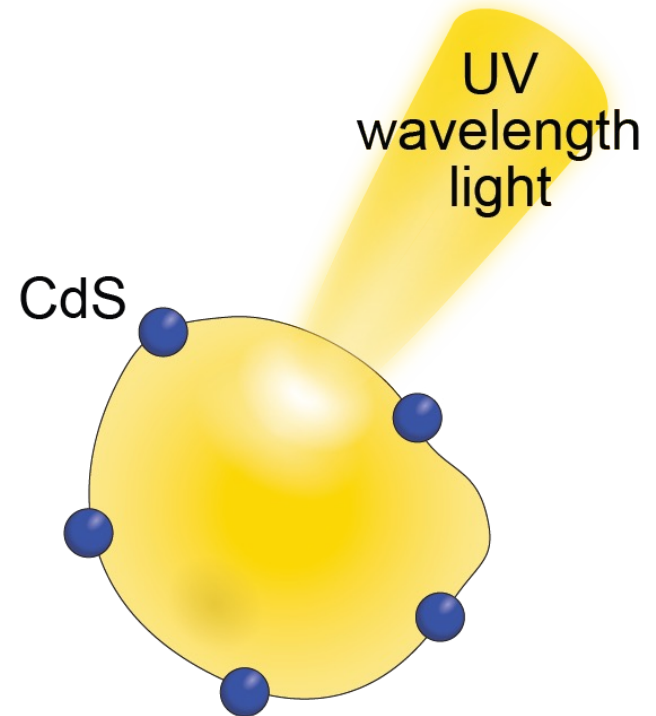
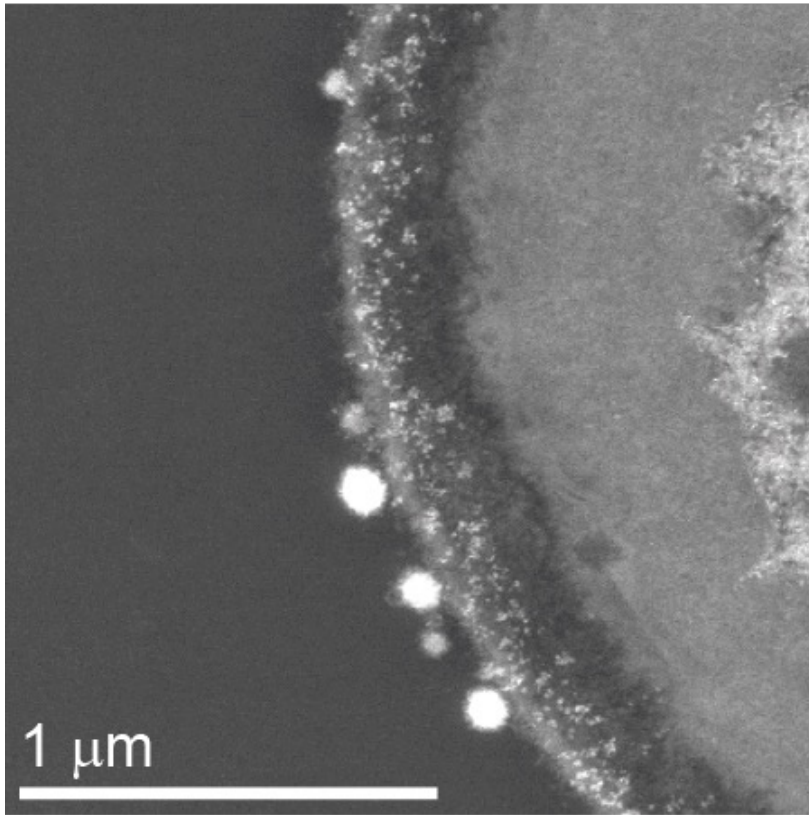
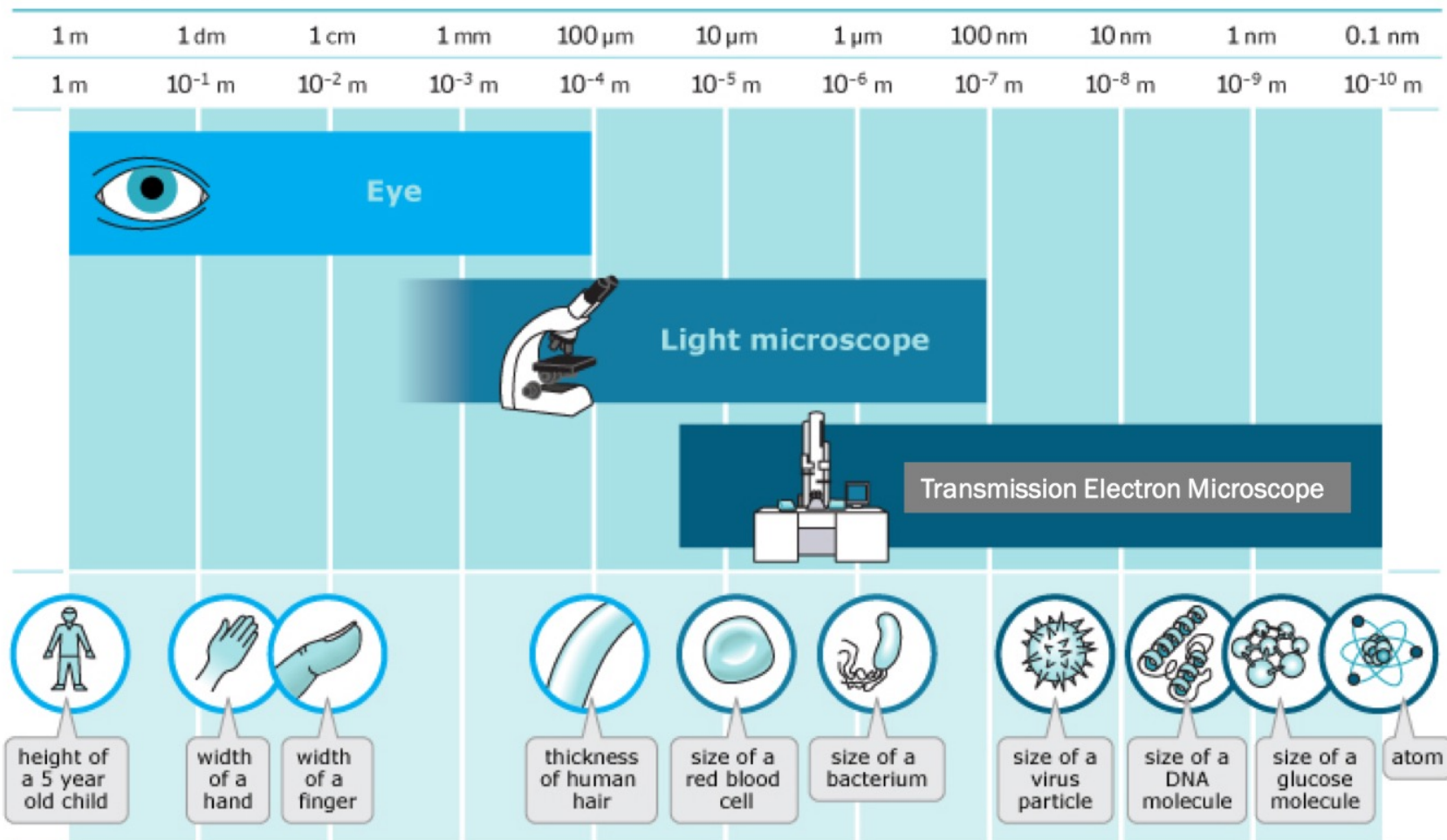


# Yeast Nanoparticles Clean- up

Is seeing believing? 20.109

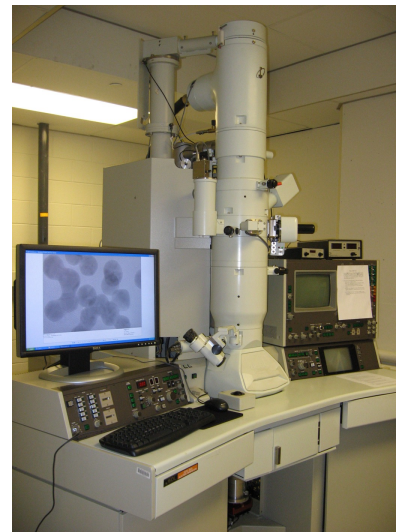


# Resolving Power of Microscopes

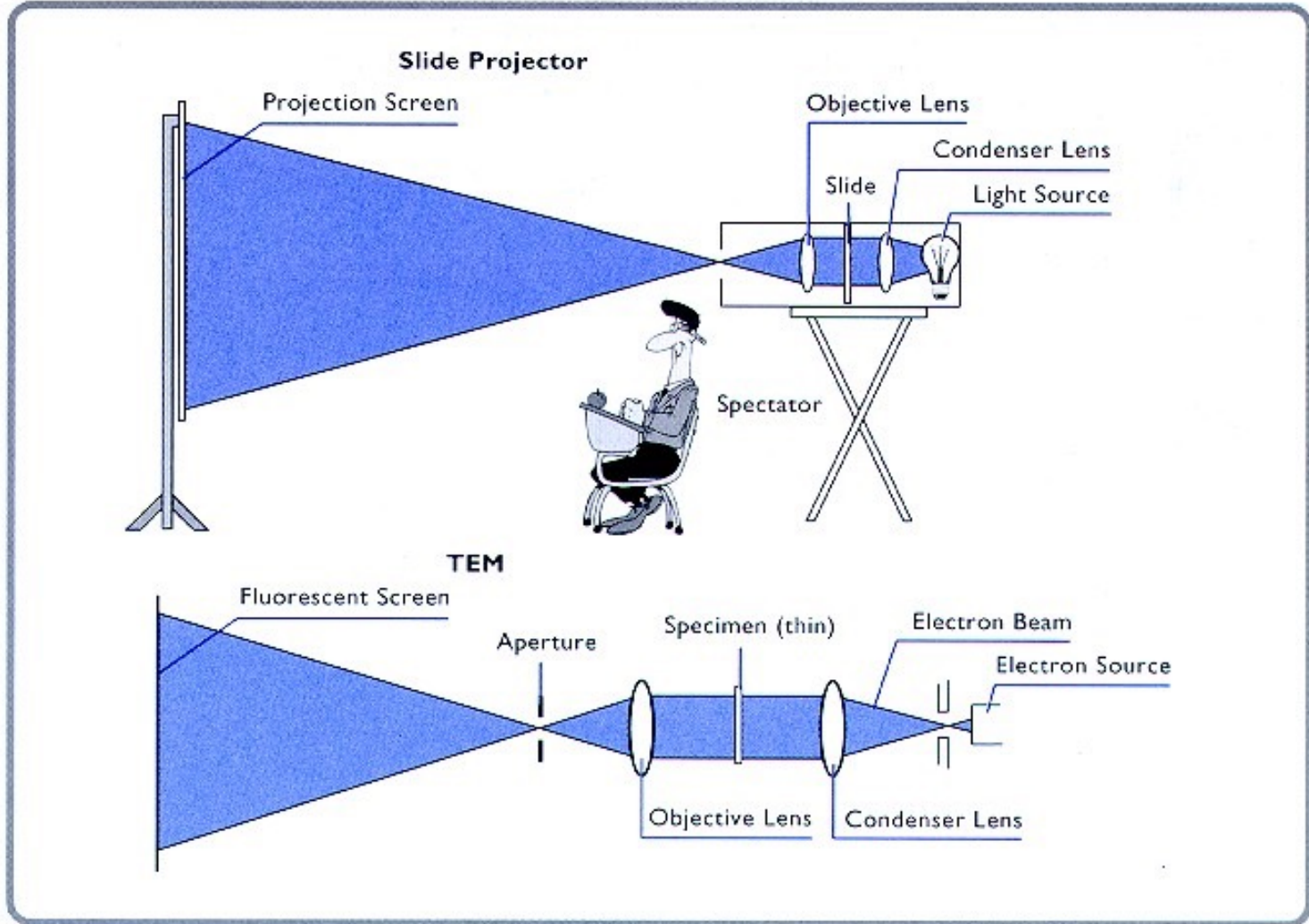


# What's TEM

- An electron-optical microscope that uses electromagnetic lenses to focus and direct an electron beam.
- Bright field imaging is from electrons interacting with electron dense materials to cast a shadow on a screen or camera.
- High voltages between 10KV and 1MV. The higher the voltage is, the shorter the wavelength of electrons, giving the better resolution. **200KV.** ultimate point-to-point resolution of 0.19 nm

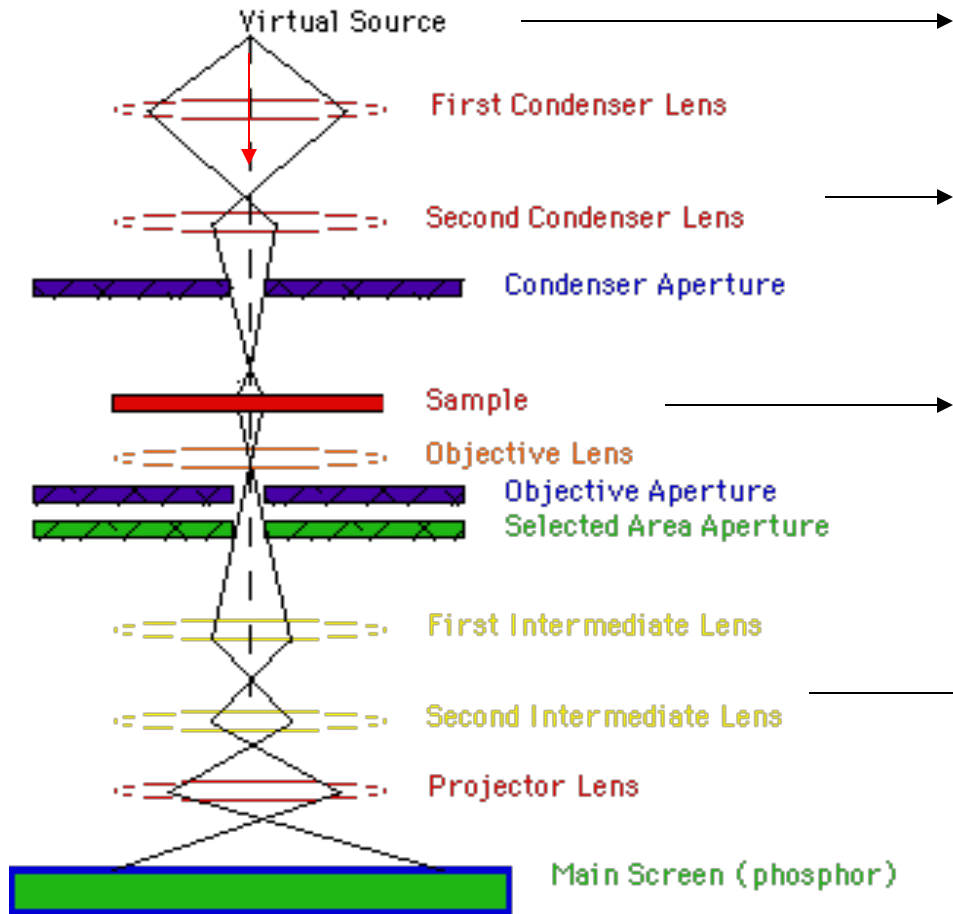






# What's TEM

## Electron beam path



Source is a beam of high velocity electrons

Lanthanum hexaboride cathode or tungsten

Electron beam focused by condenser lens onto specimen

If a sample is thin enough, electron beam can pass through it

Transmission/scattering beam is focused by objective lens/intermediate/projection lens. Final image/electron diffraction pattern forms on a screen for viewing

# Why We Need TEM

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The main use of the TEM is to examine the microstructure structure, composition, and properties of specimens in ways that cannot be examined using other equipment or techniques.

## **Morphology (Bright Field Image, Dark Field , HRTEM)**

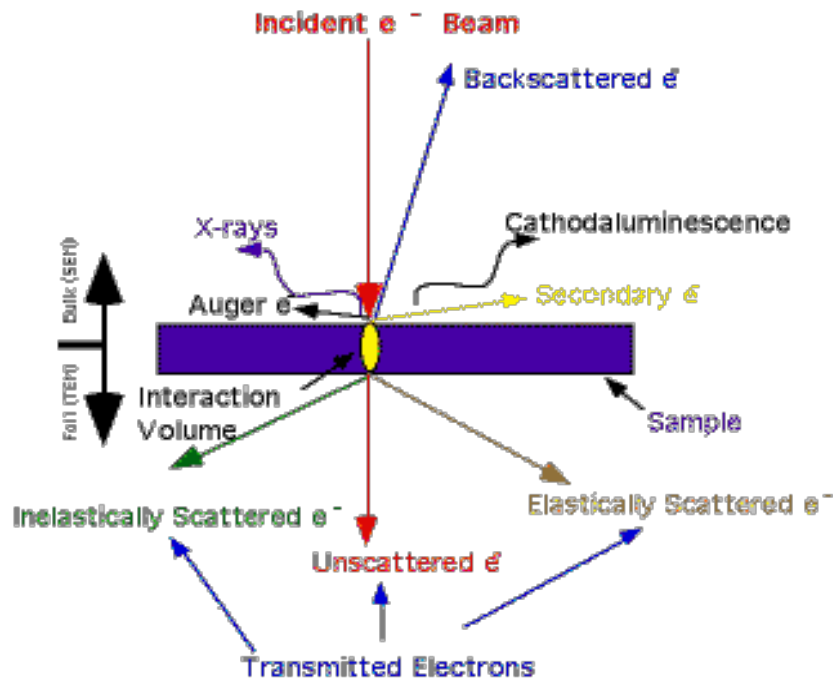
- The size, shape, morphology, and distribution of the particles as well as their relationship to each other on the scale of atomic diameters.
- Contrast comes from electrons interacting with electron dense atoms in the sample, the scattered electrons cause a shadow to be cast on the camera or screen.
- Crystalline samples scatter more electrons than noncrystalline samples, so **amorphous samples have less contrast** than crystalline samples

# Why We Need TEM

- **Crystallographic Information (Electron Diffraction, HRTEM)**
  - For crystalline samples, crystal structure, degree of ordering, and detection of atomic-scale defects in areas a few nanometers in diameter can be determined
- **Compositional Information (Energy dispersive spectroscopy (EDX), Electron energy loss spectroscopy (EELS))** The elements and compounds the sample is composed of and their relative ratios, in areas a few nanometers in diameter

# What's TEM

Different equipment in TEM is then used to collect scattered electrons produced by the specimen-electron interaction, giving different types of information

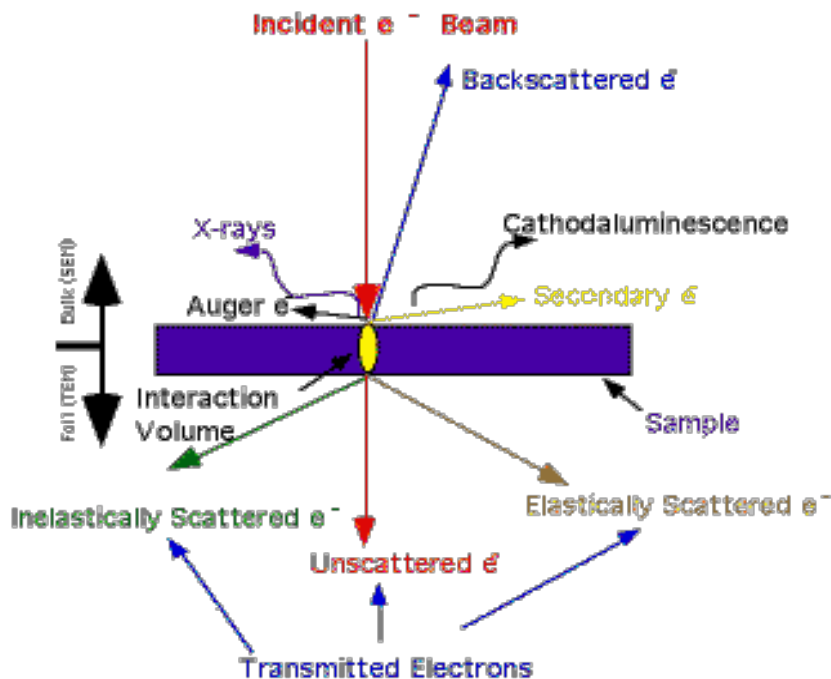


} Compositional Information

} Morphology &  
Crystallographic Information



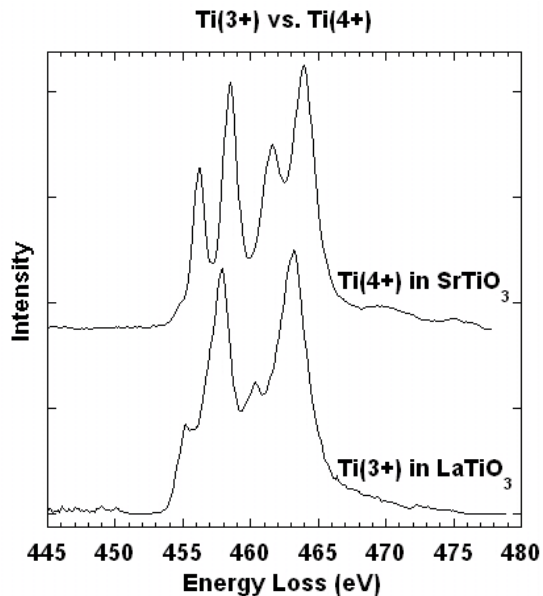
# Elemental mapping and information



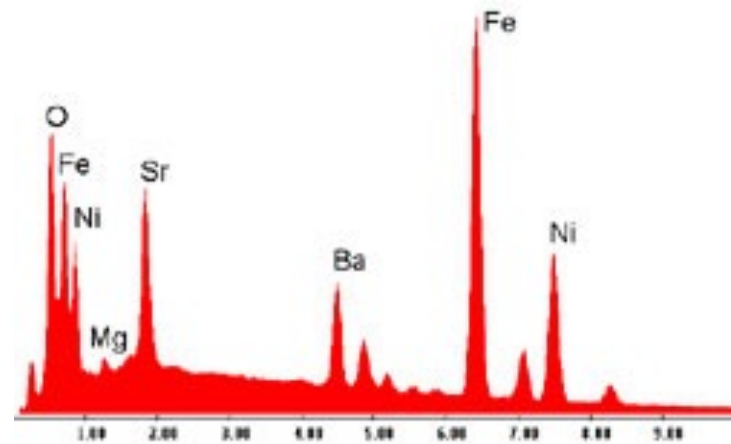
- Elemental mapping can be done by two methods, STEM and EELS
- STEM involves rastering an electron beam through a sample and determining the elemental composition of each spot by either X-ray analysis or EELS (element specific)

# Elemental Analysis

- The  $e^-$  beam has the energy to remove core electrons
- This causes for a measurable loss of energy in the electron beam (EELS)
- And also for the emission of X-rays (EDX)
- Both techniques are element specific and can be combined to show images that isolate where each element is present in the sample

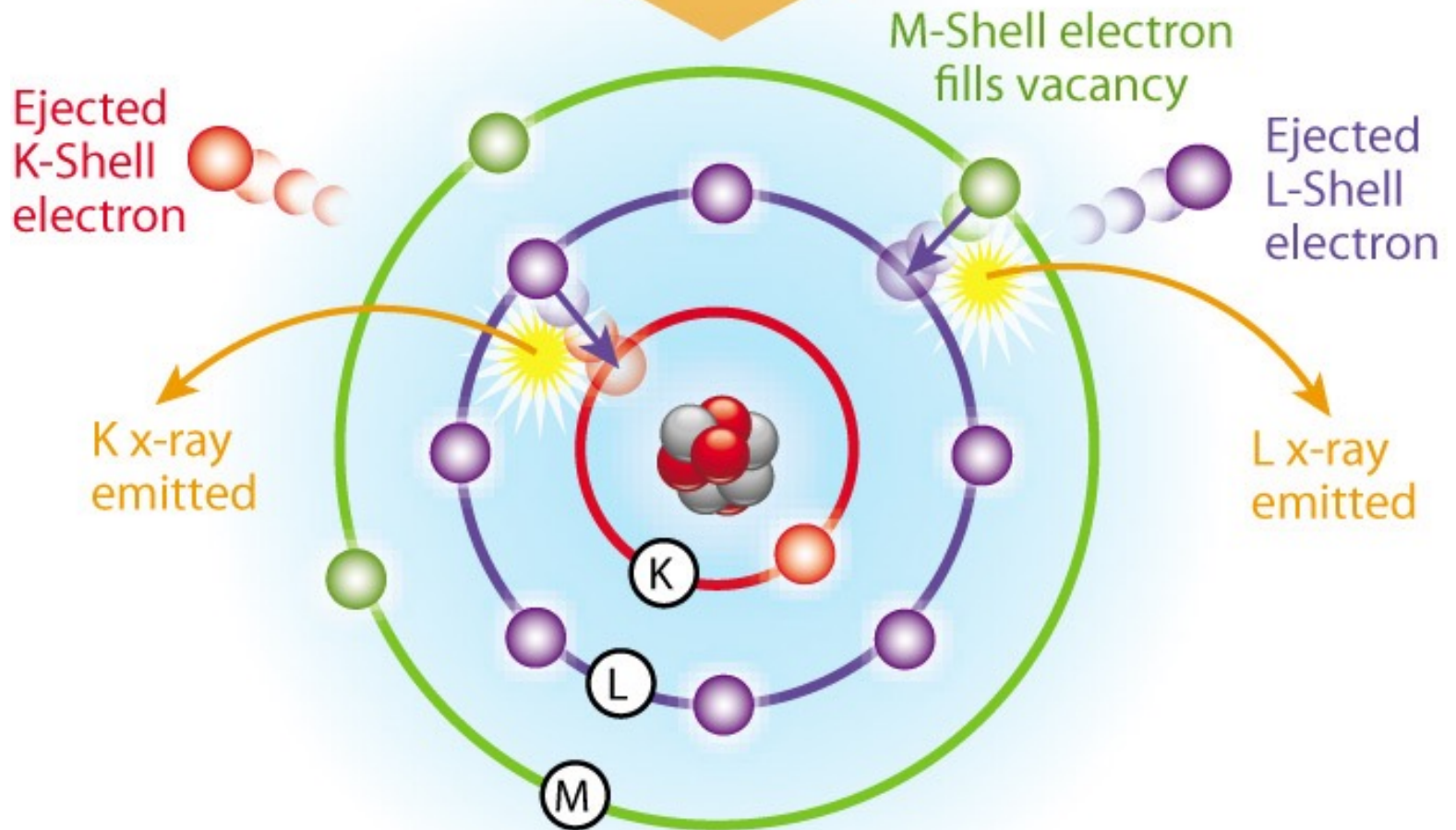


EELS of Titanium particles shows a difference between  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$



EDX of  $\text{BaSrO}_x$  shows all the elements present in the sample

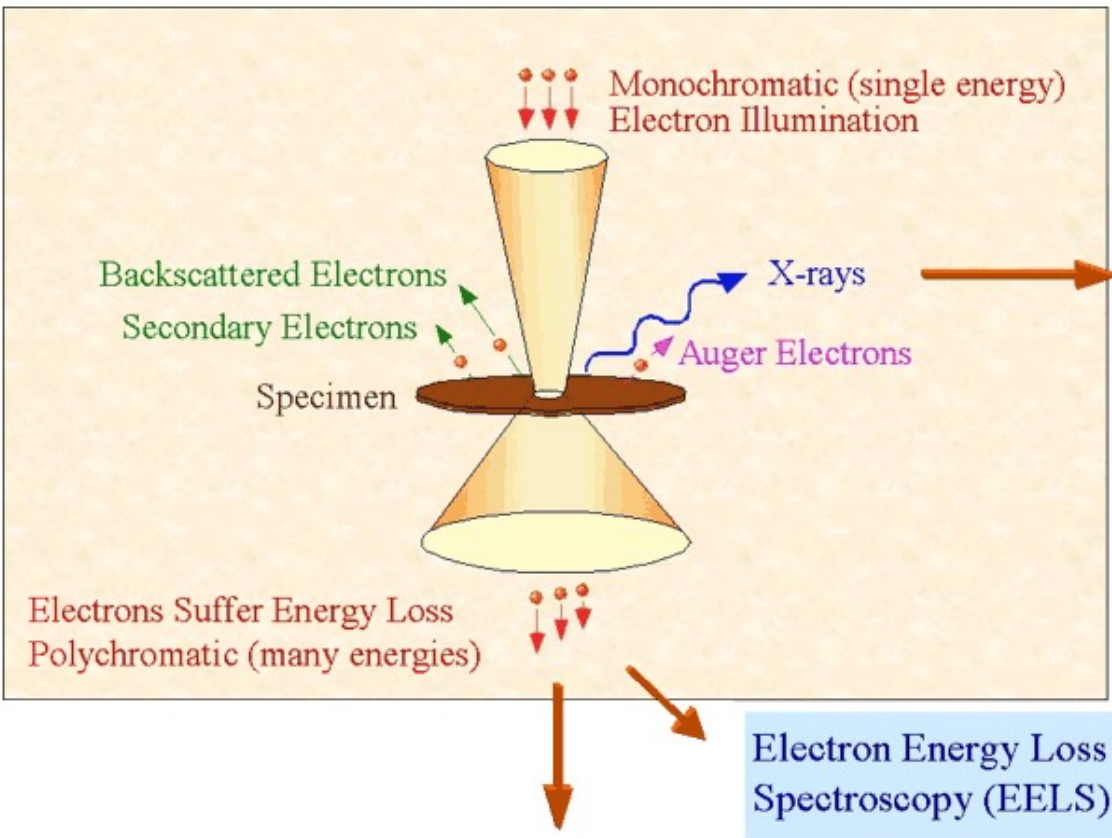
Incident Radiation from  
Primary X-ray Source



## Energy Dispersive X-ray Spectroscopy (EDXS)

Different elements emit different characteristic X-rays when excited by an electron beam.

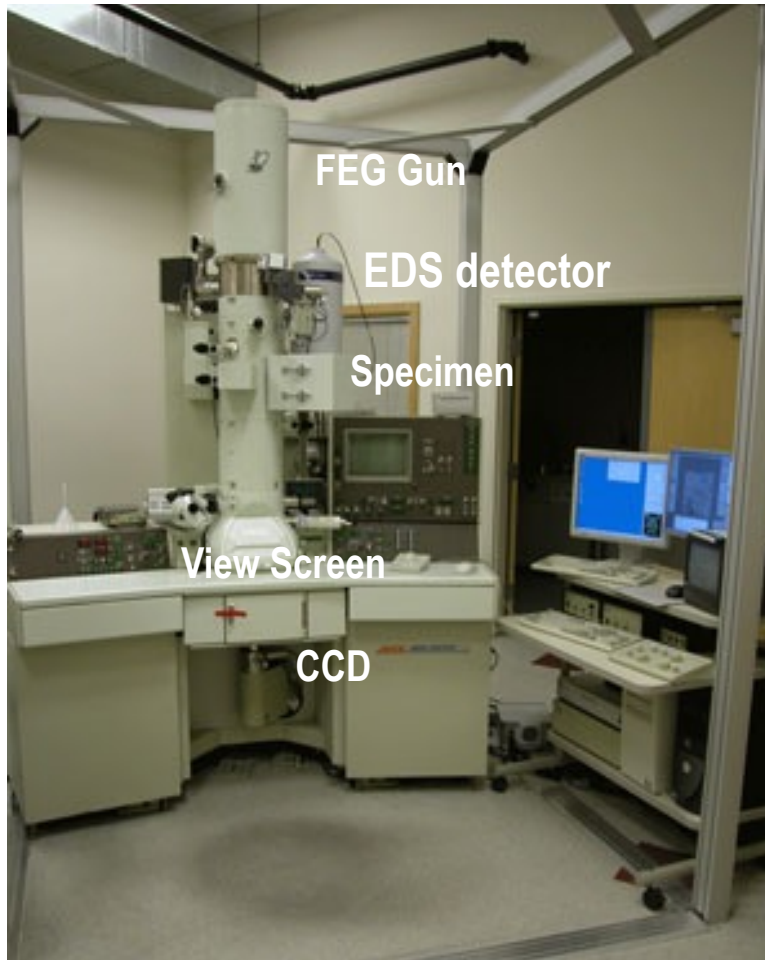
These X-rays can be used to **identify the elements present, quantify their relative or absolute concentration, and map their distribution.**



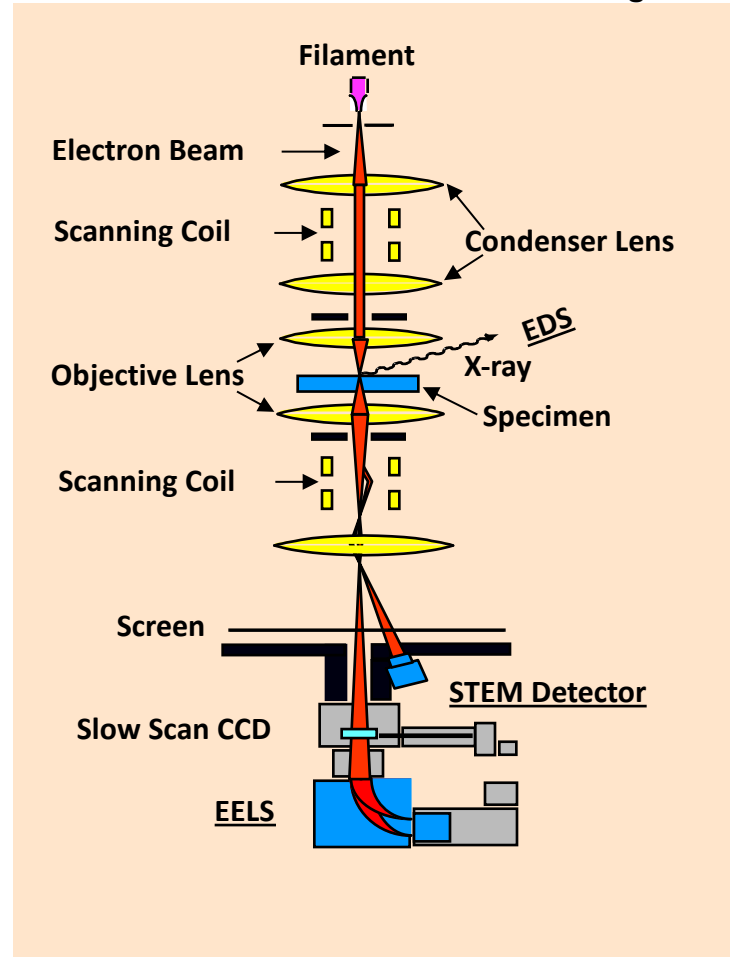
Different elements cause incident electrons to lose different amounts of energy. EELS can be used to identify the elements present, quantify their relative or absolute concentration.

# JEOL 2010 Field Emission Gun(FEG) TEM

## 2010FEG TEM Photo



## 2010FEG TEM Schematic Diagram



## 2010FEG TEM Characteristics

1. **Point Resolution** : less than 0.2nm
2. **Brightness** : 2-order higher brightness than with the LaB6 electron gun,(JEOL 2010 TEM)  
3-order higher with tungsten thermionic gun(JEOL 200CX TEM)
3. **Nanoanalysis** : Atomic arrangement, Grain Size, Crystal Orientation, Defects,  
Chemical analysis - elements, composition



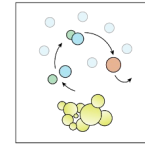
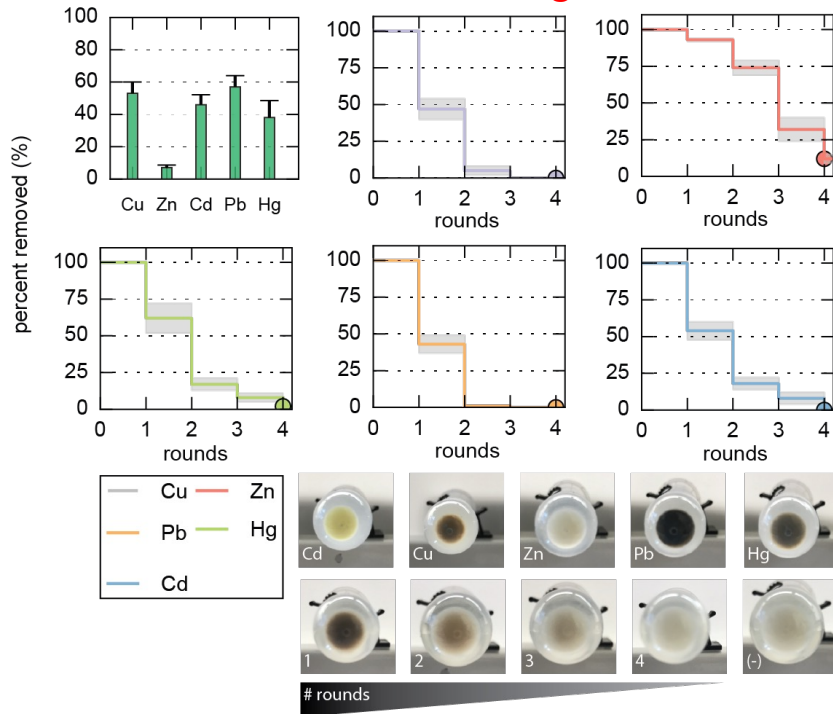
## Alberta Canada Oil Sands



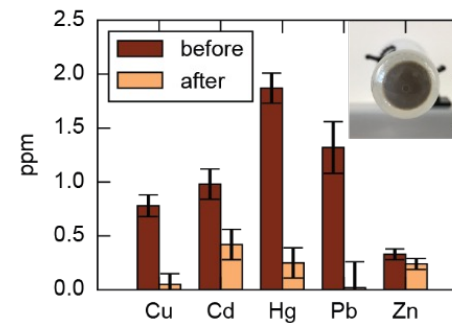
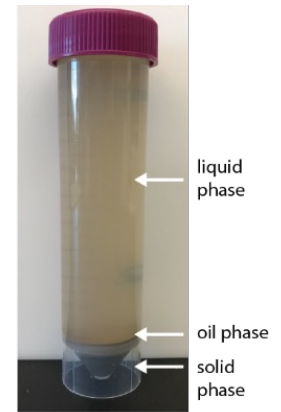


# Bio-precipitation of heavy metals

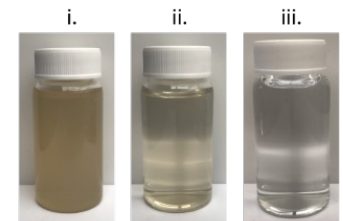
Metabolic engineering for heavy metal precipitation, *we can clean to EPA standards for Cu, Pb, Hg, Cd, Zn*



Real world example:  
Canadian Athabasca Oil Sands

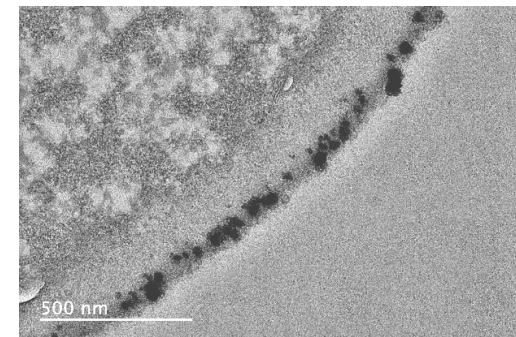
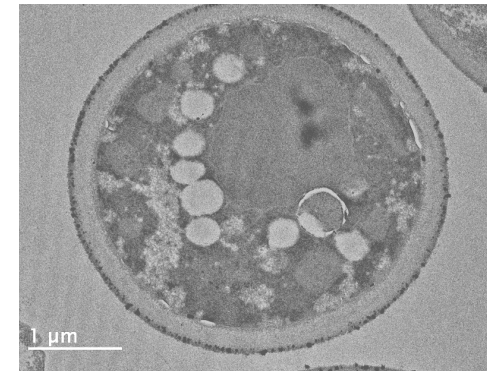
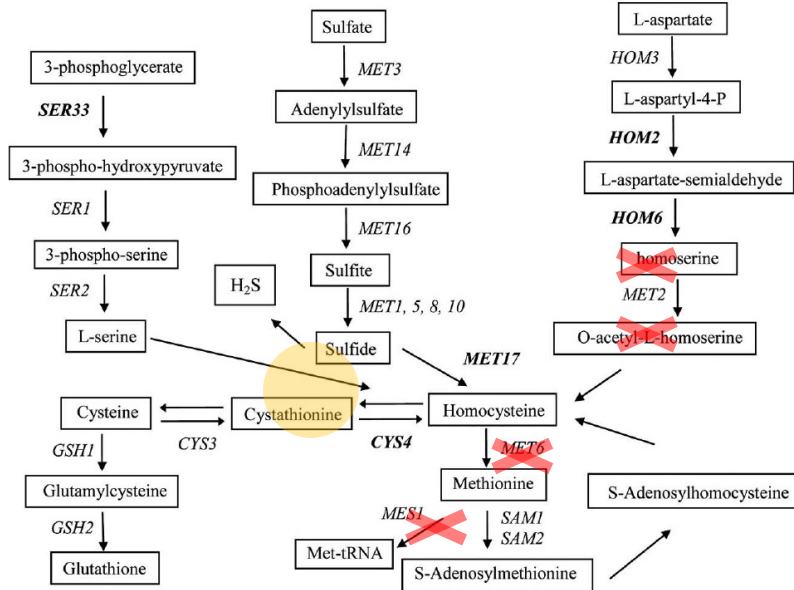


Before---middle--after



# Engineering H<sub>2</sub>S Production Mechanism

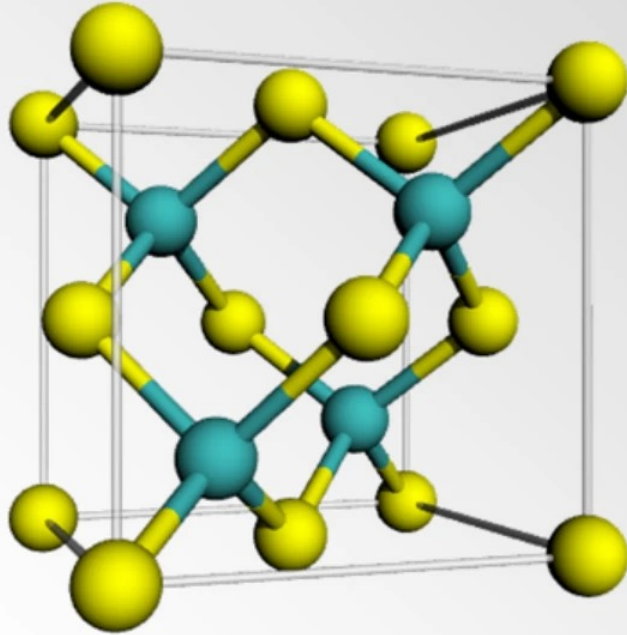
## Engineering H<sub>2</sub>S strains



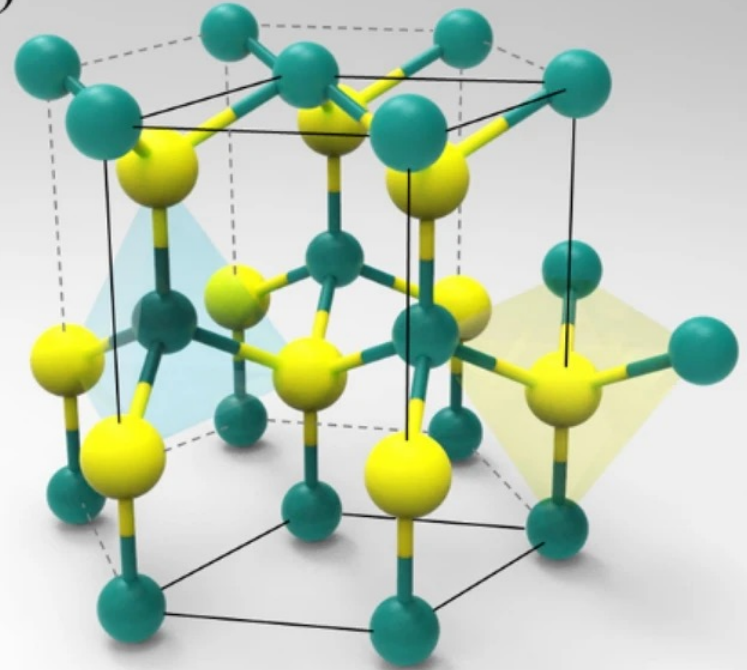
Shalmalee Pandit

# Crystal lattices

(a)



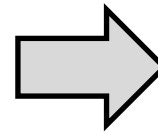
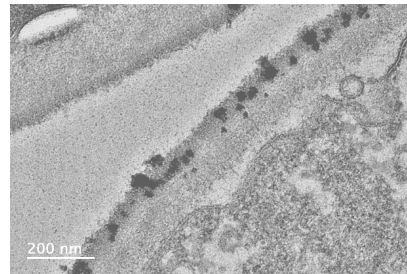
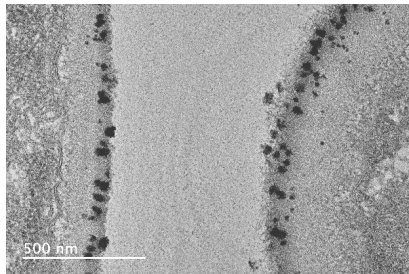
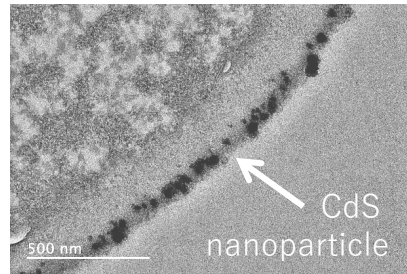
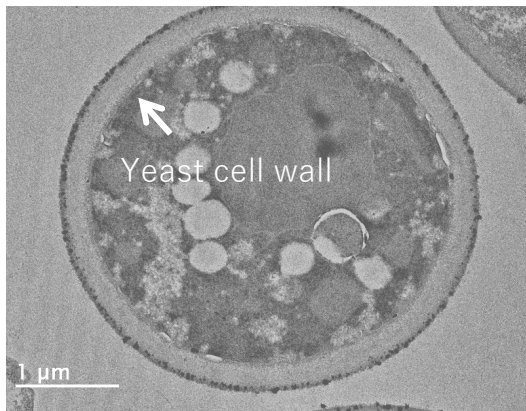
(b)



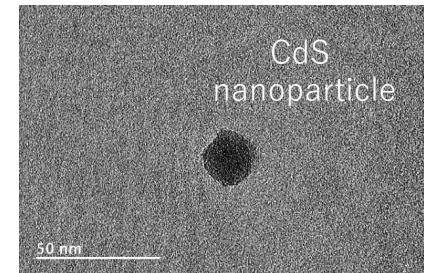
(a) cubic zinc blende and (b) hexagonal wurtzite structures

# Taking a closer look: quantum dot synthesized

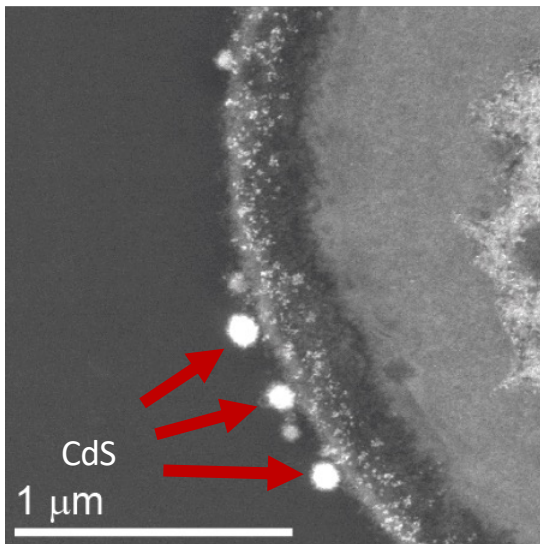
CdS precipitation



Purified CdS from yeast



# Localization of nanoparticles in yeast cell wall

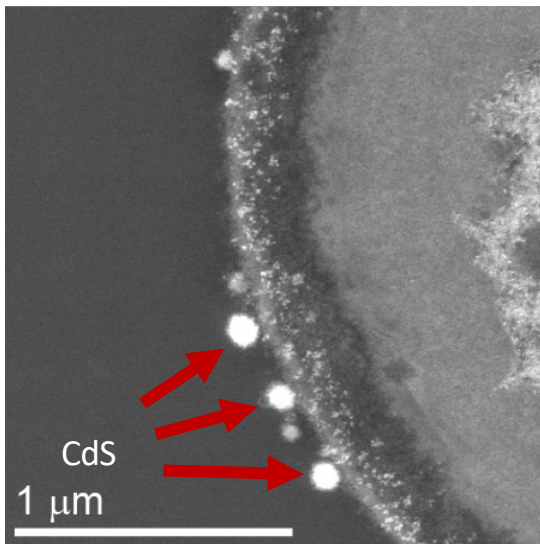


TEM image of  $\Delta$ Met17 displaying CdS nanoparticles on the cell surface

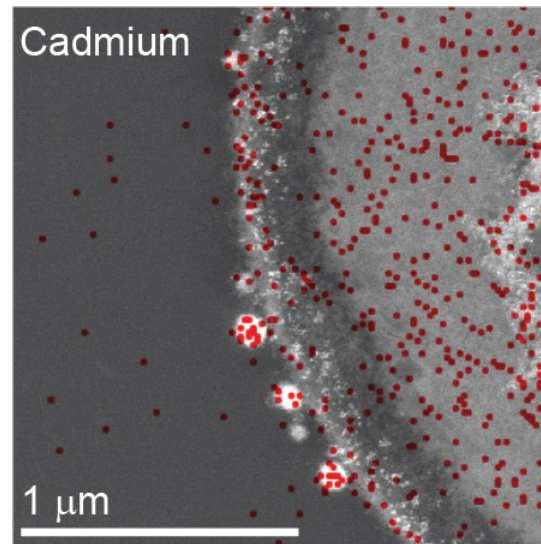
Transmission electron microscopy: like an atomic scale x-ray: electrons pass through the sample to form an image



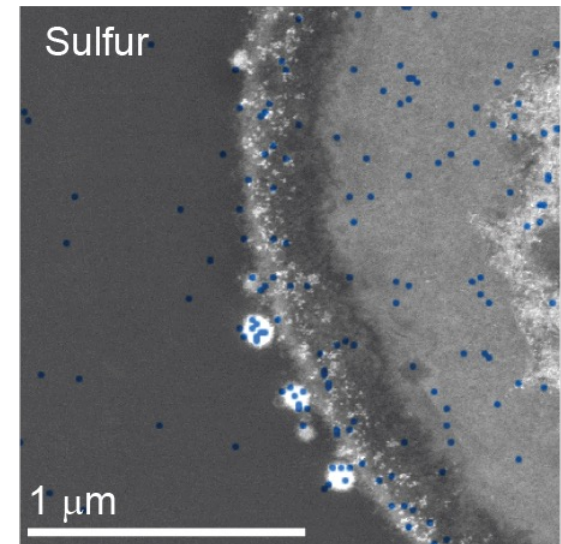
# Localization of nanoparticles in yeast cell wall



TEM image of  $\Delta$ Met17 displaying CdS nanoparticles on the cell surface



Elemental analysis of cadmium.

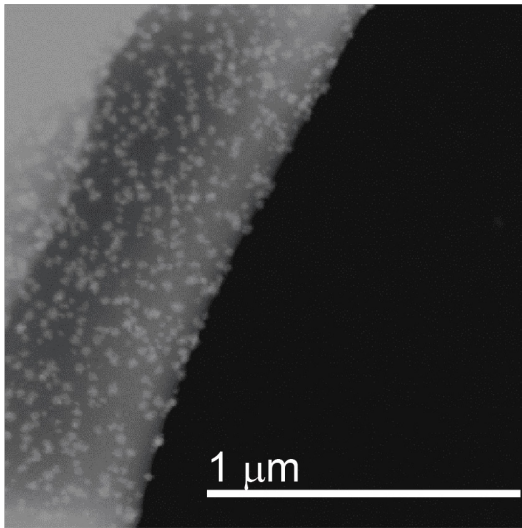


Elemental analysis of sulfur.

Transmission electron microscopy: like an atomic scale x-ray: electrons pass through the sample to form an image



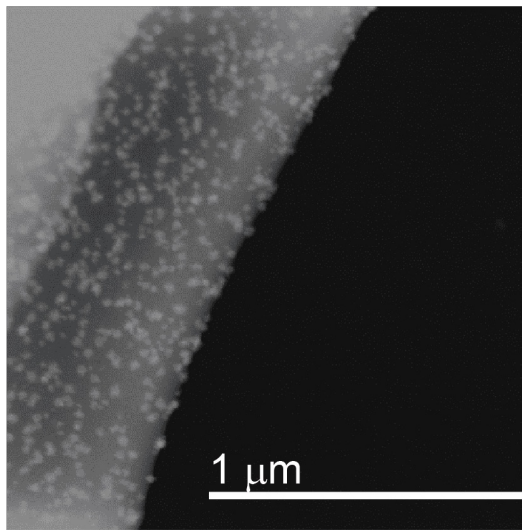
# Localization of nanoparticles in yeast cell wall



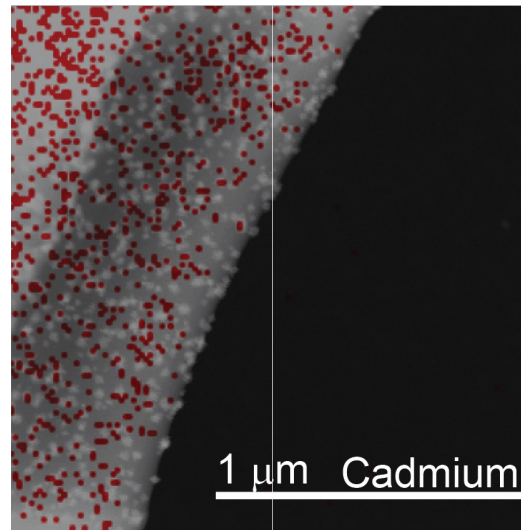
TEM image of unsliced  $\Delta$ Met17 displaying CdS nanoparticles on the cell surface

Transmission electron microscopy: like an atomic scale x-ray: electrons pass through the sample to form an image

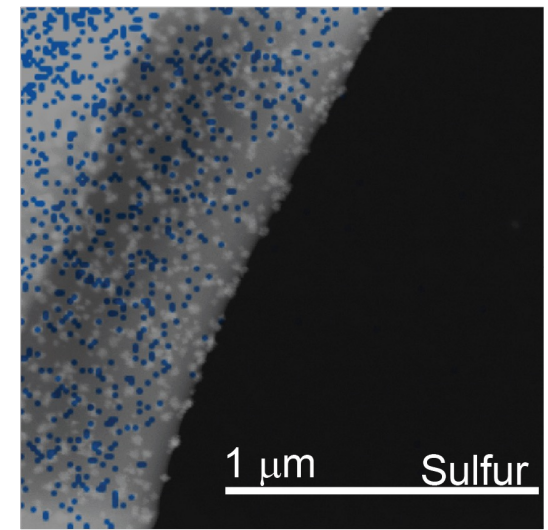
# Localization of nanoparticles in yeast cell wall



TEM image of unsliced  $\Delta$ Met17 displaying CdS nanoparticles on the cell surface



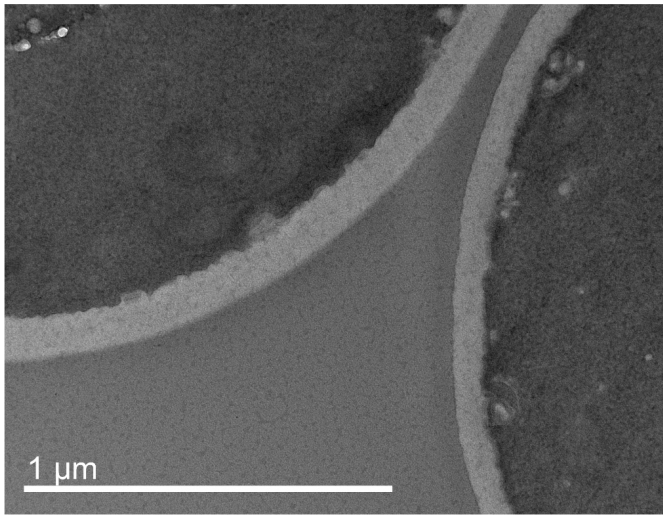
Elemental analysis of **cadmium**.



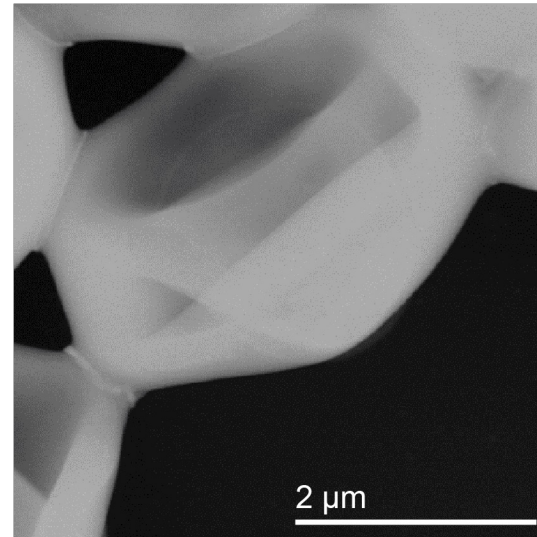
Elemental analysis of **sulfur**.

Transmission electron microscopy: like an atomic scale x-ray: electrons pass through the sample to form an image

# Images of wild-type yeast treated with $\text{Cd}^{2+}$ display no formation of CdS nanoparticles



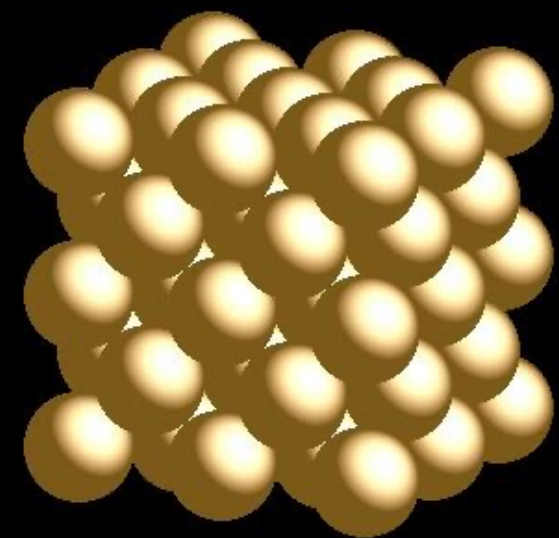
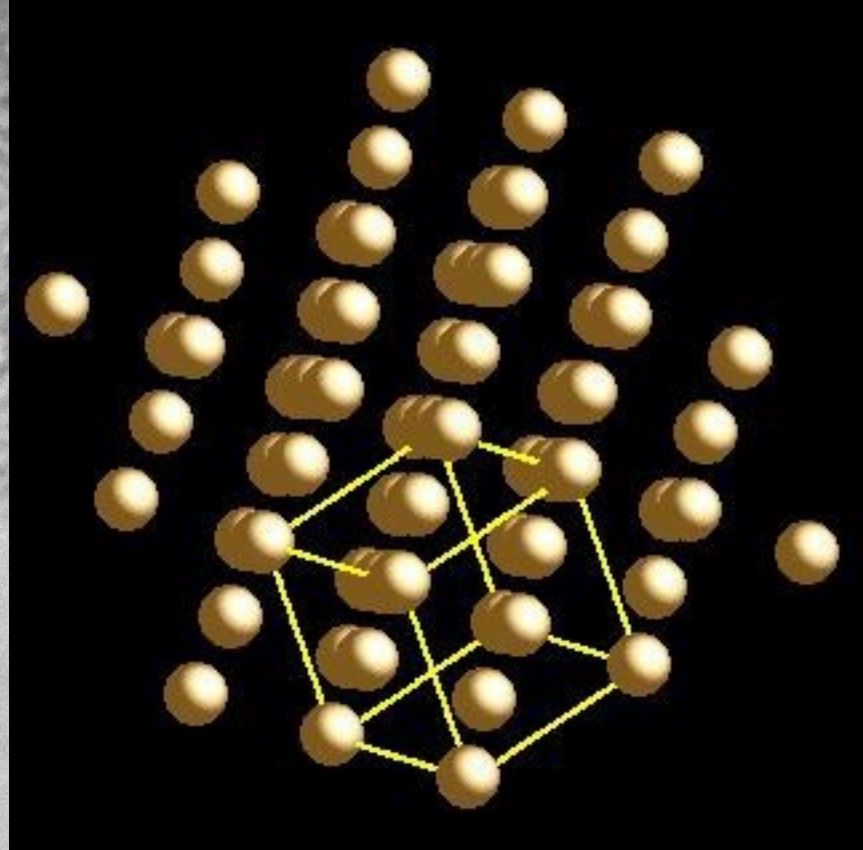
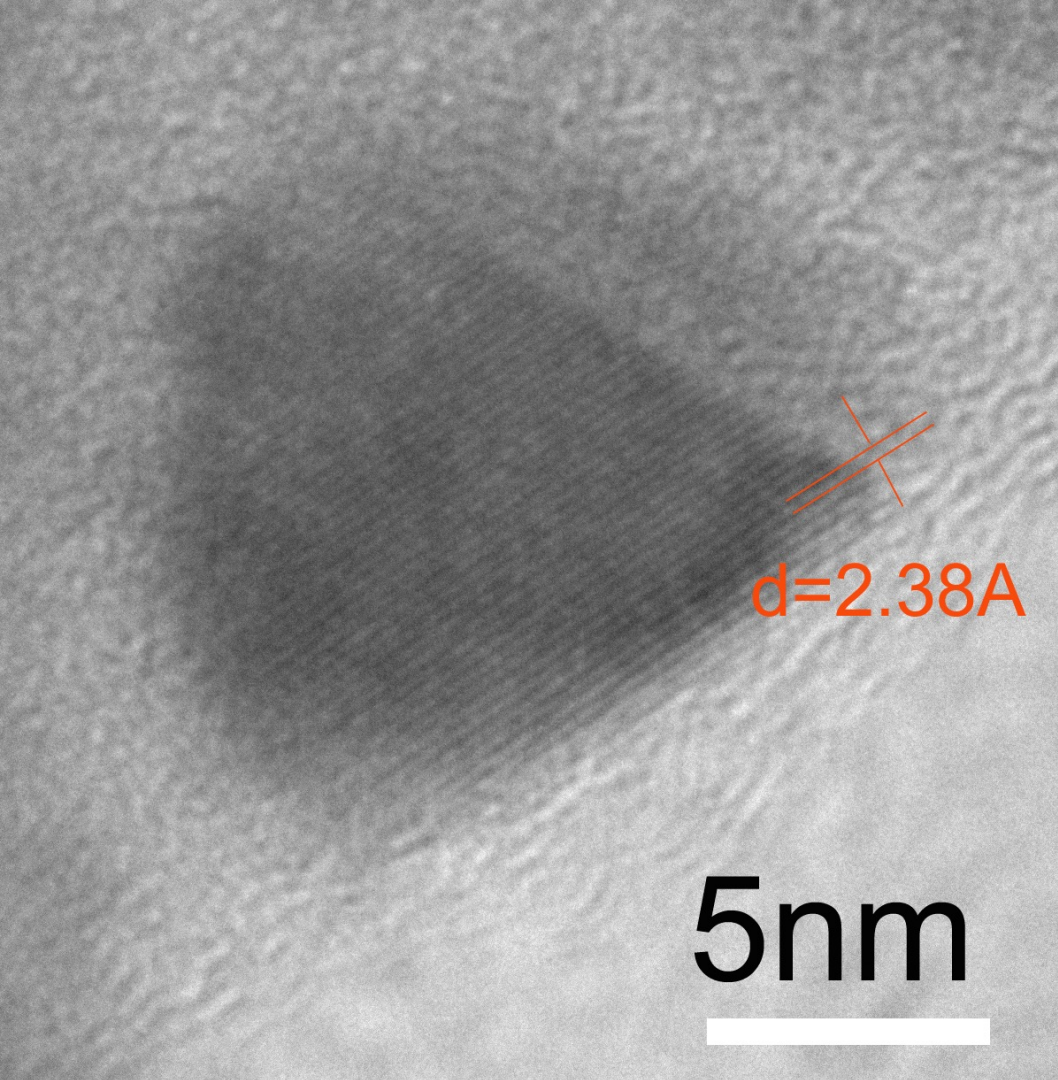
TEM image of a sliced W303 $\alpha$  sample treated with  $\text{Cd}^{2+}$



TEM image of an unsliced W303 $\alpha$  sample treated with  $\text{Cd}^{2+}$

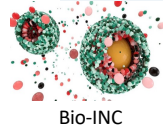
Transmission electron microscopy: like an atomic scale x-ray: electrons pass through the sample to form an image





lattice distance is about 2.38Å, very close to the gold (111) plane's distance 2.36Å

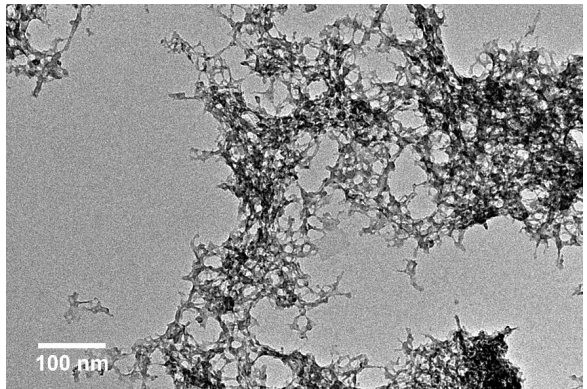




Bio-INC

# Month 2 Milestone : Demonstrate the ability to use a bioengineering approach to change the identity of specific REE incorporated within the structure of a biosynthesized inorganic nanoparticle for $\geq 2$ different REEs. **Biological synthesis of sodium rare-earth fluorides nanoparticles; Bio- $\text{NaREEF}_4$ ( $\text{NaYF}_4:\text{Yb,Er}$ )**

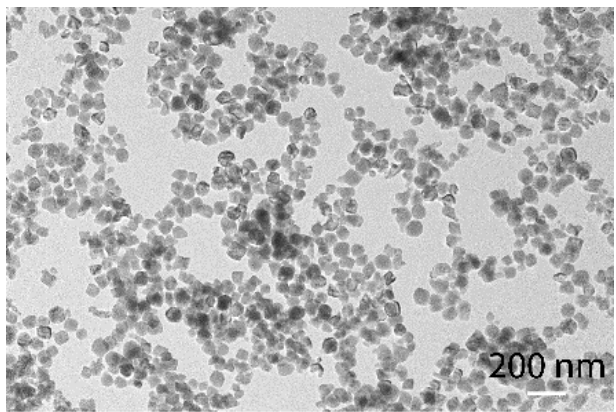
(a) **Aqueous solution synthesis Bio-REE hydroxide precursors**



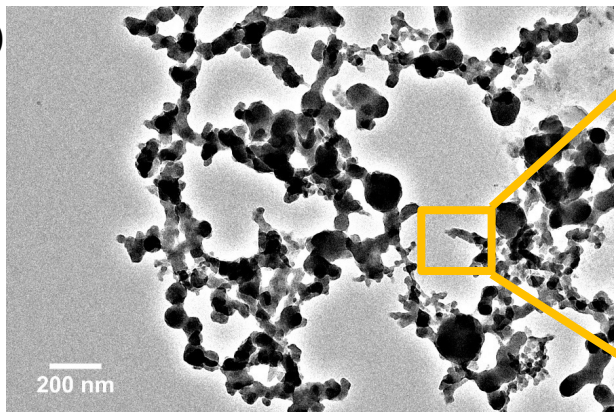
add sodium trifluoroacetate, Heat in organic solvents

M13 phage template aqueous solution synthesized of Bio-YYbEr(OH)<sub>x</sub> as the precursors for synthesis of NaYF<sub>4</sub>:Yb, Er NPs. Initially [Y]:[Yb]:[Er] = 78: 20:2, using REE nitrite or chloride salts as the starting materials.

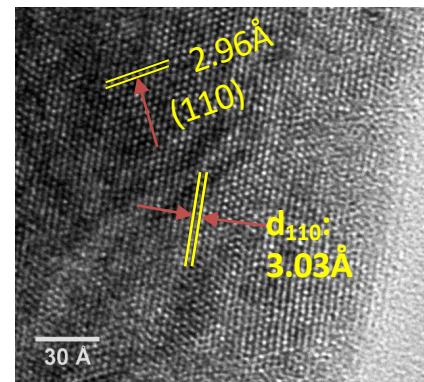
(b)



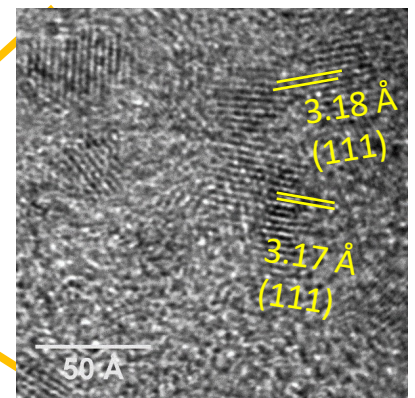
(c)



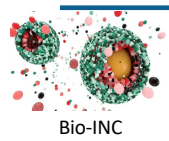
(d)



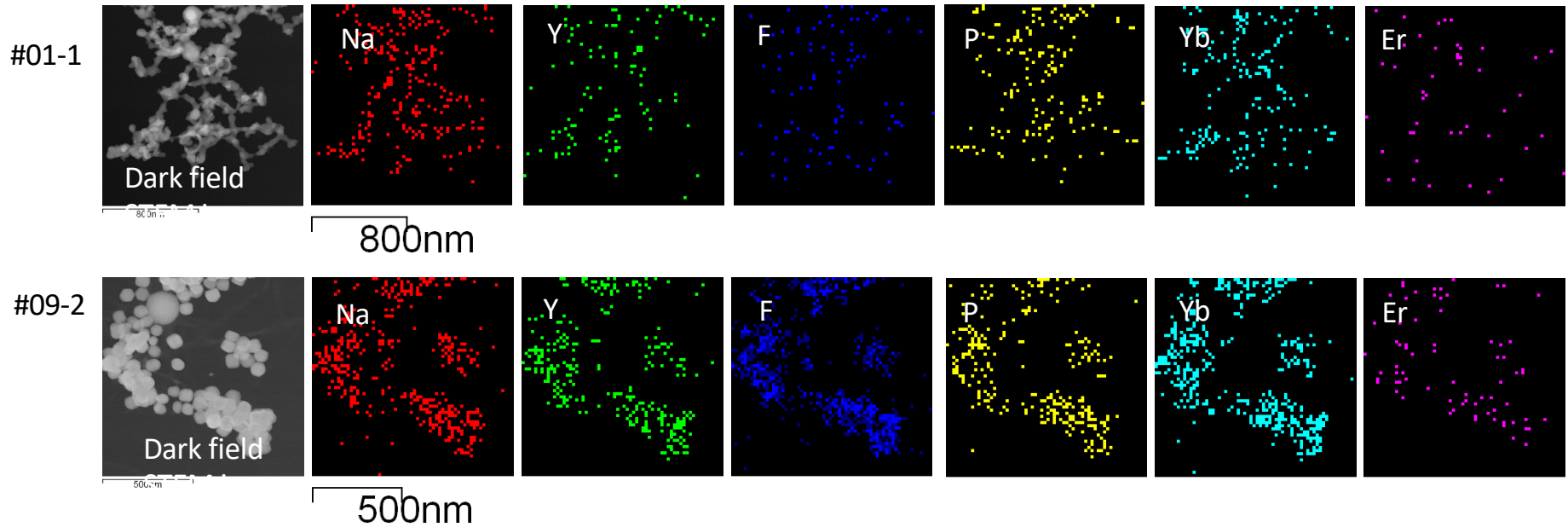
(e)



# Biological synthesis of sodium rare-earth fluorides nanoparticles;



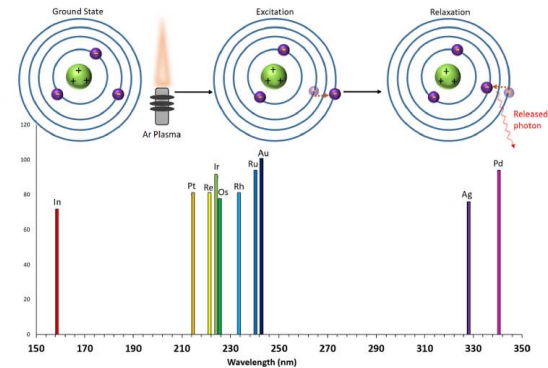
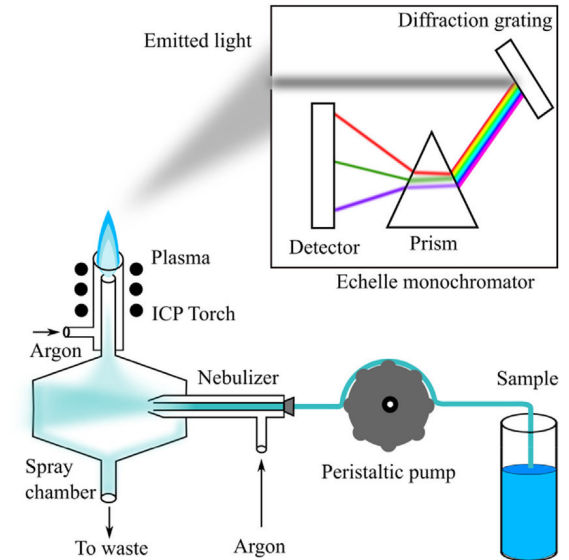
STEM-EDX elemental mapping of Bio- $\text{NaYF}_4:\text{Yb,Er}$  samples showing all the elements of Na, Y, F, Yb, Er are overcoat on the biotemplates (P from DNA).





# ICP (Inductively Coupled Plasma) Spectroscopy

- ❖ ICP is an analytical technique used to measure and identify elements within a sample matrix based on the ionization of the elements within the sample.
- Inductively coupled plasma mass spectrometry (ICP-MS)  
This technique uses an argon plasma to convert a sample into ions. The ions are then measured using a mass spectrometer. ICP-MS can measure elements at trace levels in biological fluids.
- Inductively coupled plasma - optical emission spectrometry (ICP-OES)  
This technique uses plasma and an optical spectrometer to determine the composition of elements in samples. ICP-OES has been commercially available since 1974
- ❖ ICP analysis requires the use of liquified sample solutions, so solid samples and biological samples must be digested prior to analysis. Once the sample is liquid, the ICP uses argon (Ar) carrier gas to aerosolize the sample sending only the smallest droplets through the chamber and into the argon plasma torch.
- ❖ The Ar plasma causes the sample to desolvate and ionize.

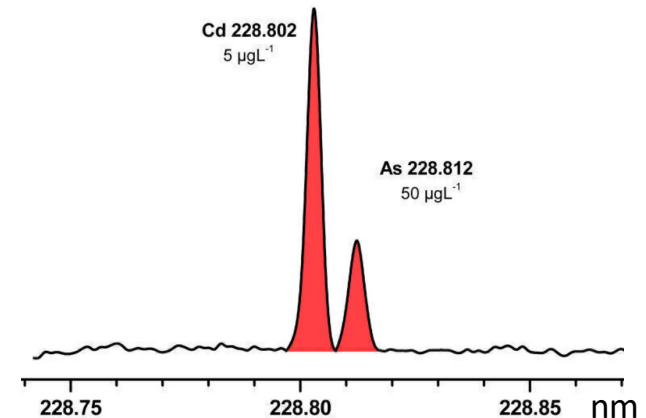


## *Sample preparation - how to deliver samples for ICP test*

- Samples should be delivered in 12 – 15 ml tubes (at least 5ml solution).
- Samples should be acidified (preferably with 1-5 % HNO<sub>3</sub> in order to keep metals in solution)
- Solid material should be destructed, preferably with nitric acid only (concentration HNO<sub>3</sub> below 10%, ideally 1%), or if necessary with HNO<sub>3</sub>/H<sub>2</sub>O. This step can be performed as a closed destruction in a microwave-oven.
- HCl can cause precipitates and the sulfur in sulfuric acid interferes in the analysis.
- The torches present at the GI are not resistant to HF.
- For the ICP samples should not contain any organic solvents.
- Indicate as far as possible what concentration level may be expected in the samples

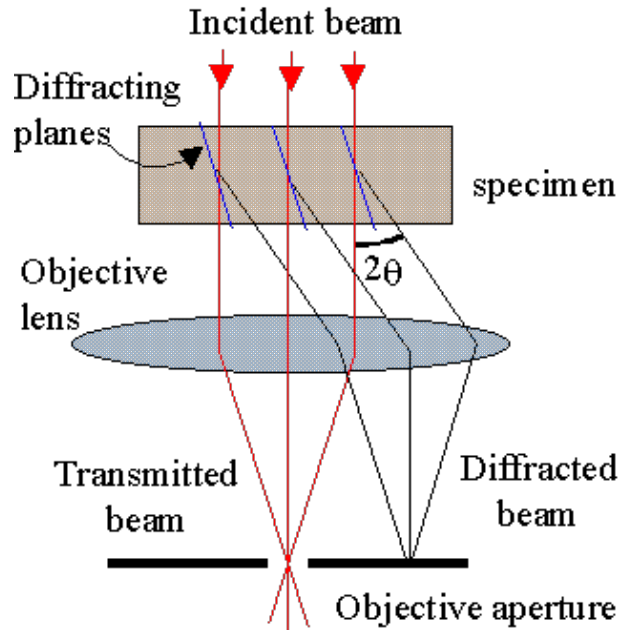


AGILENT 5100 ICP-OES SPECTROMETER

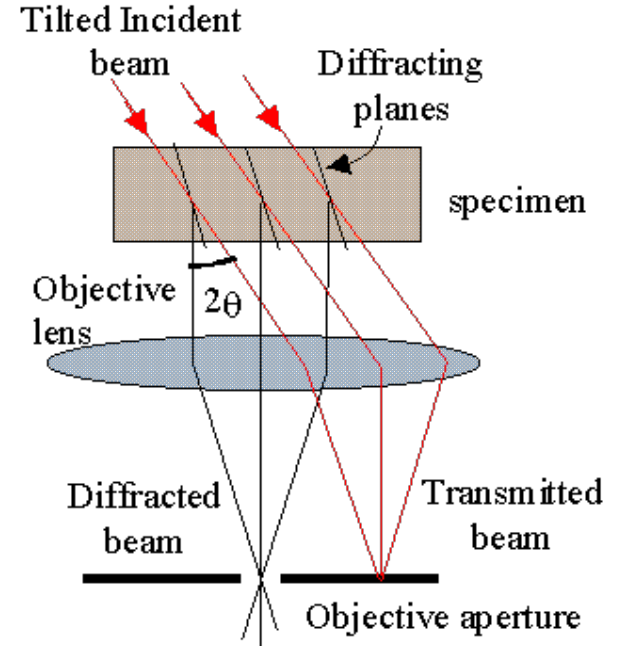
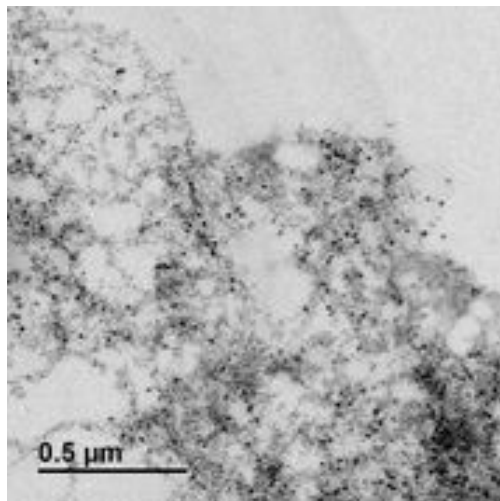


High-Resolution ICP-OES spectrum of Cd and As

# Dark Field



Bright Field Imaging



On-axis Dark Field

