

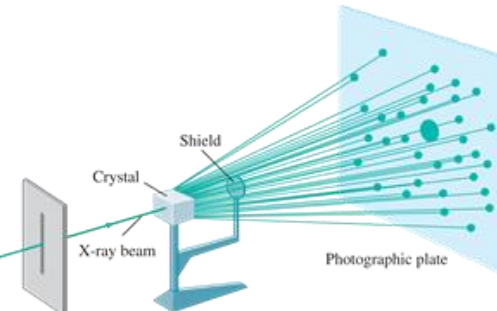
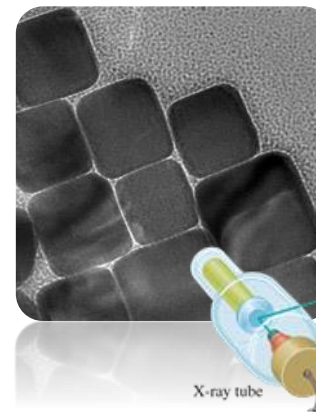
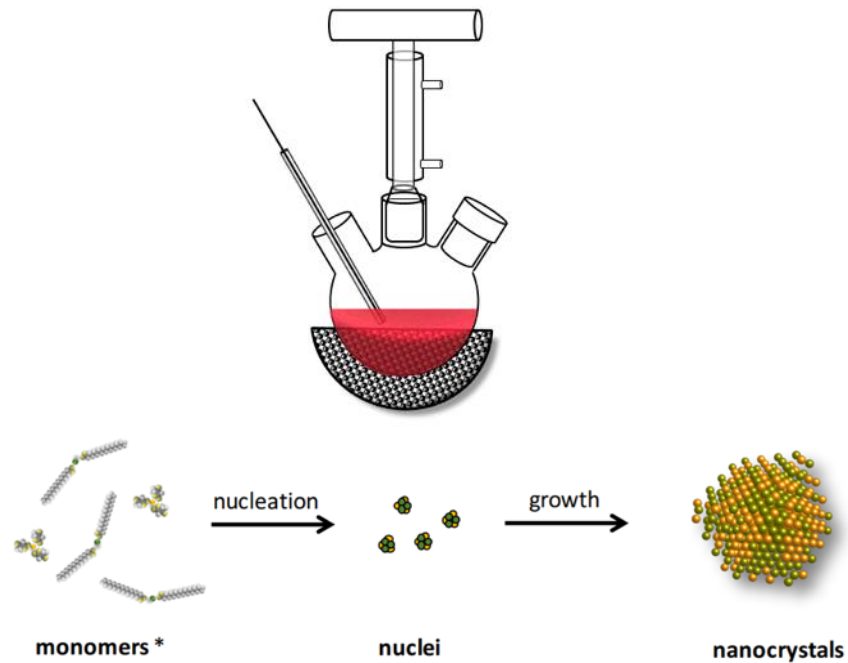
Che-430 – Lab Project

A story in the Life of the Copper Nanocubes

Prof. Raffaella Buonsanti

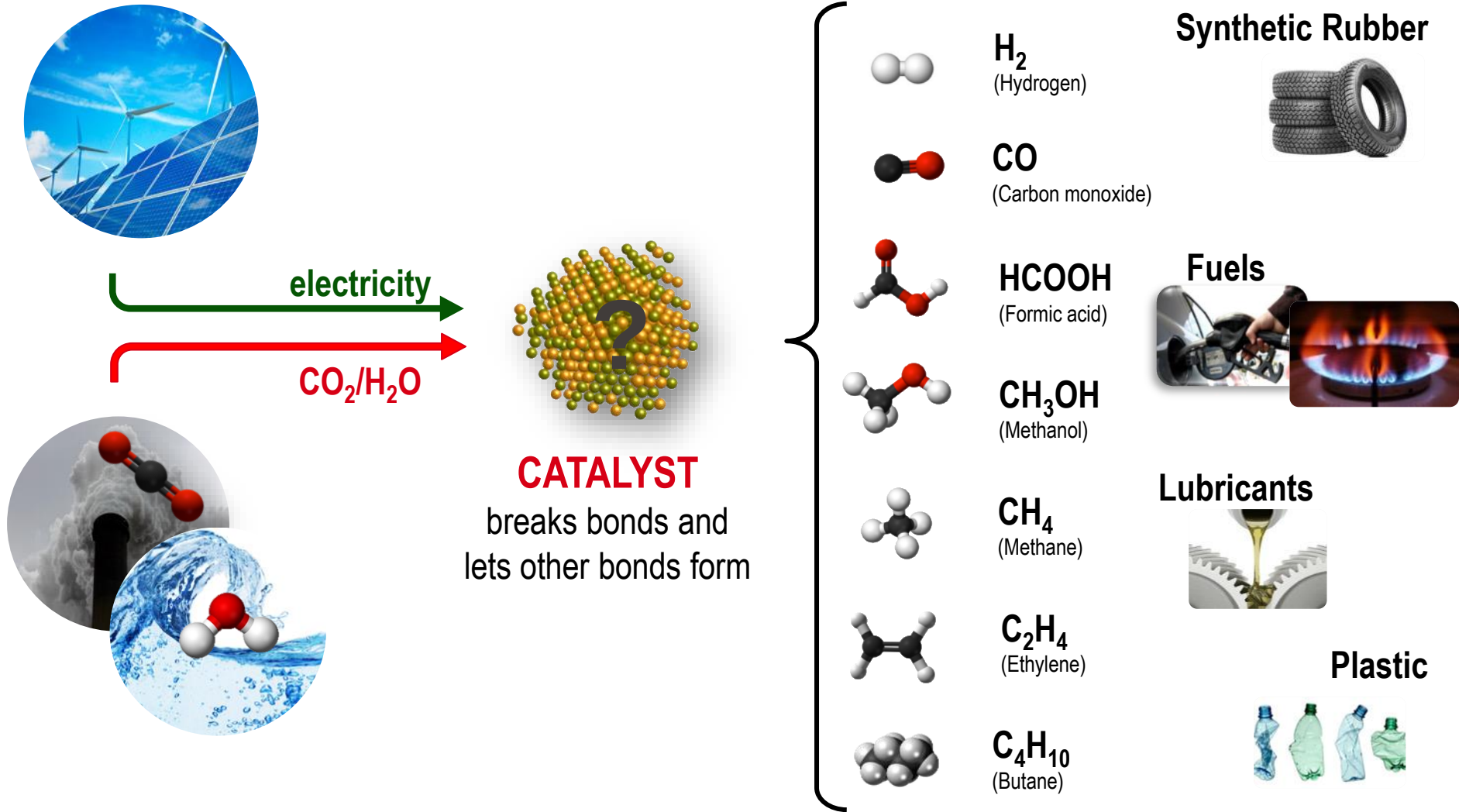
Coline Boulanger, Jennifer Calderon Mora, Moritz Tritschler, Seyedmohamadjavad Chabok

Fall 2024

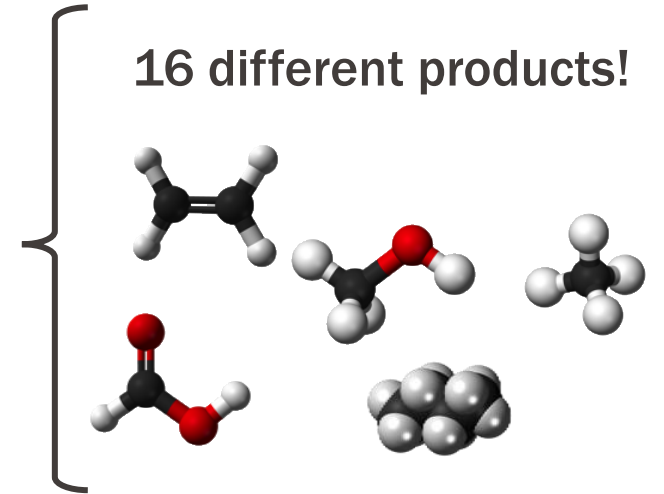
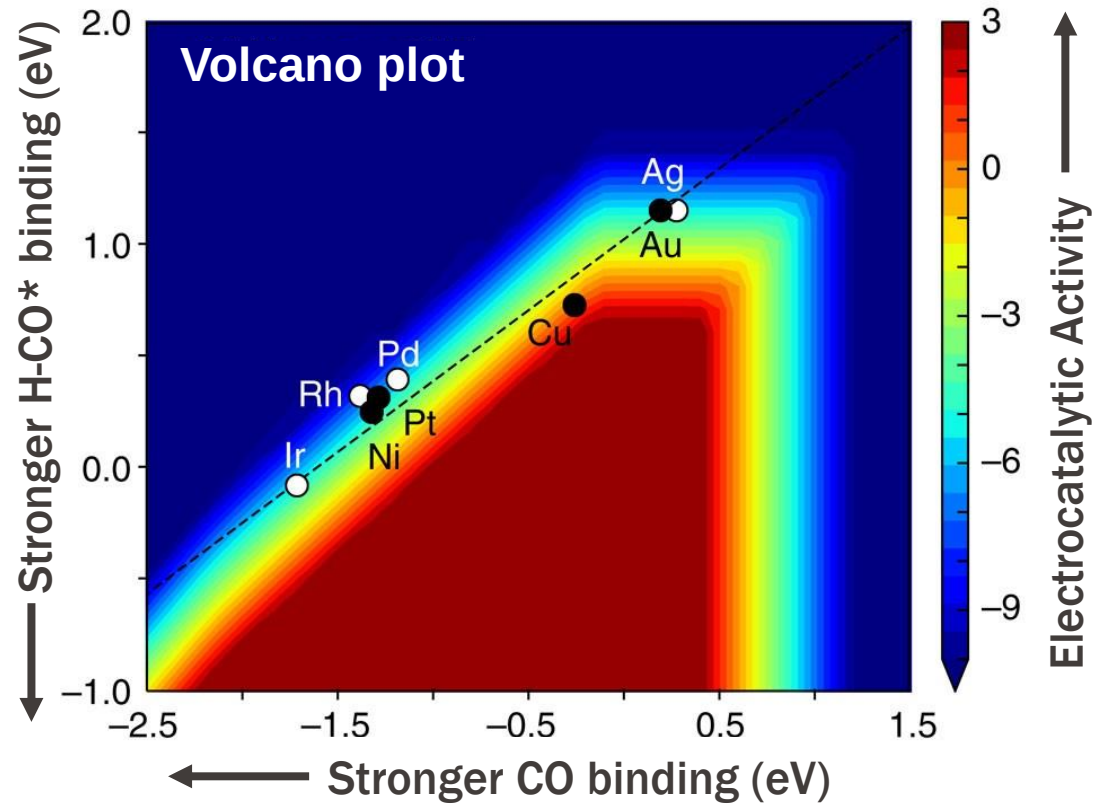


INTRODUCTION

Electrochemical CO₂ Reduction (eCO₂R)

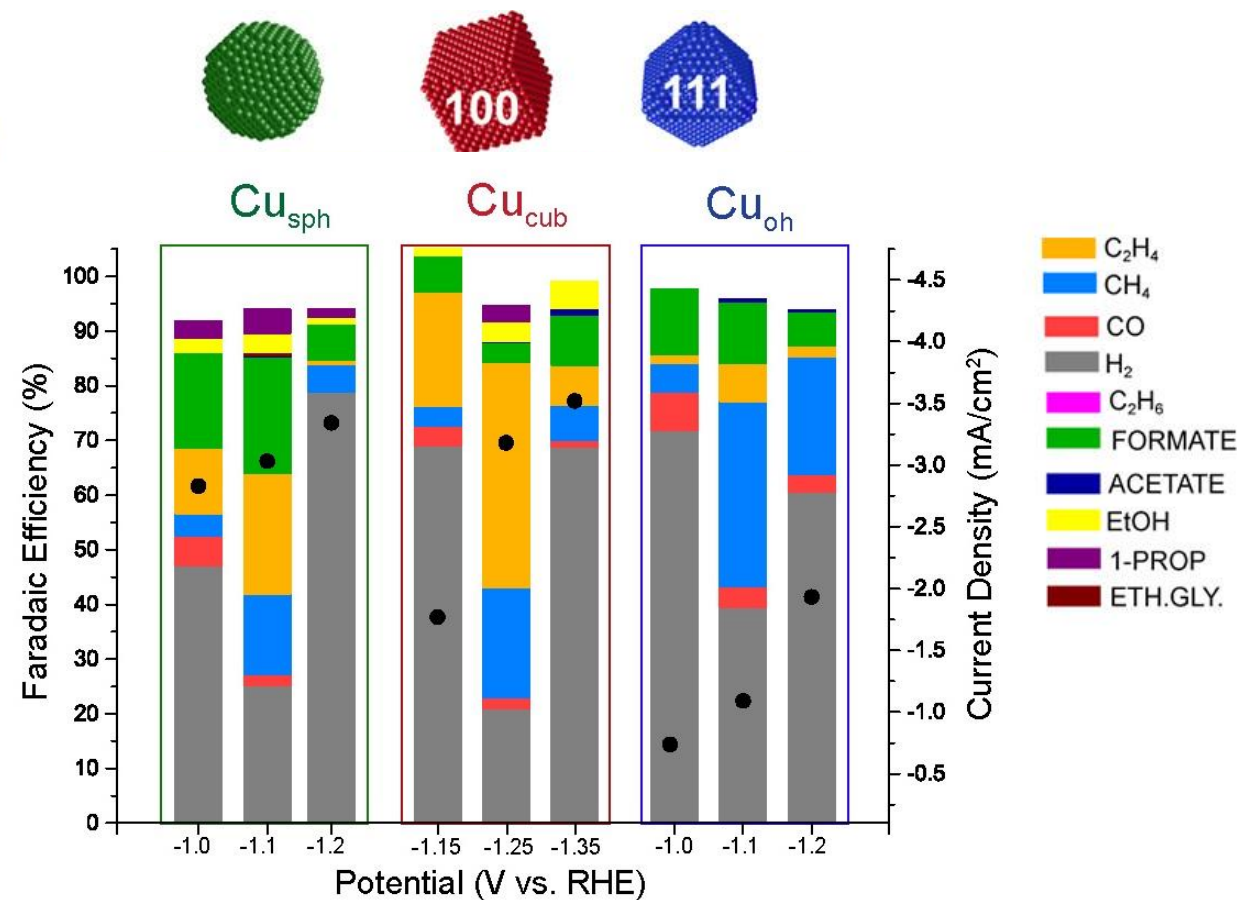
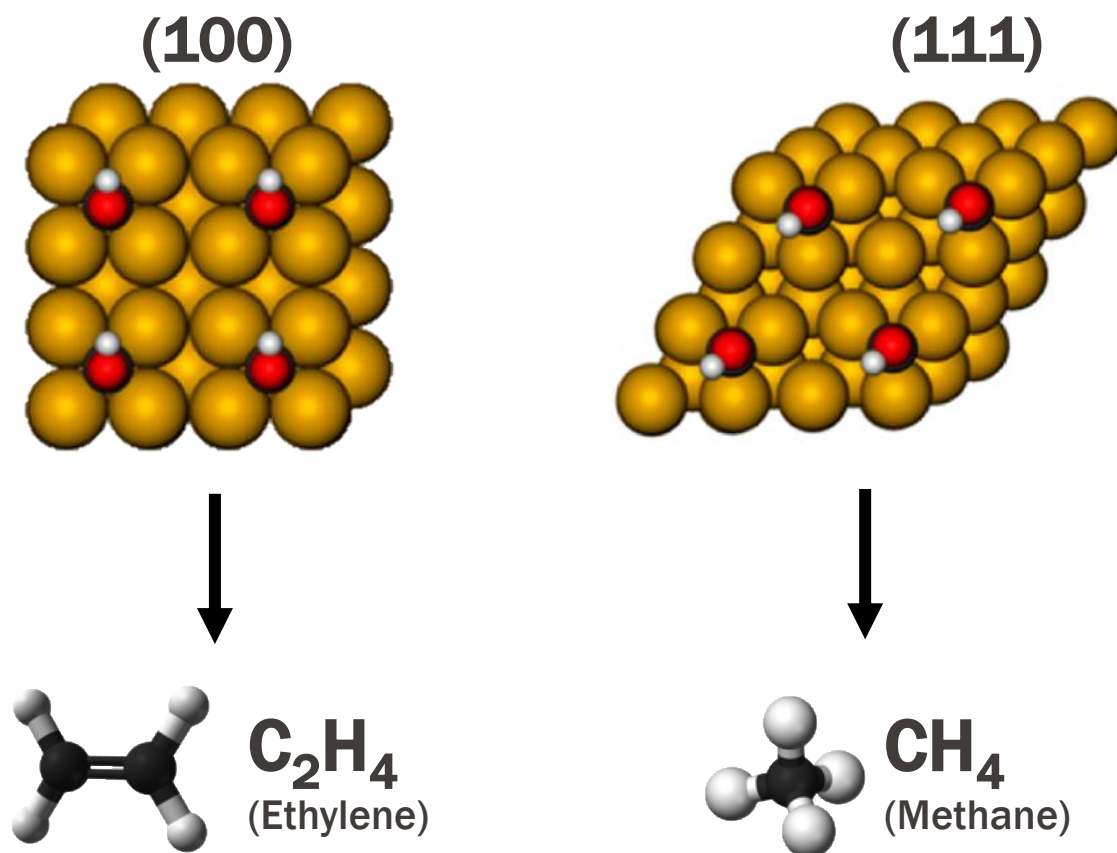


Copper is unique for CO₂ reduction

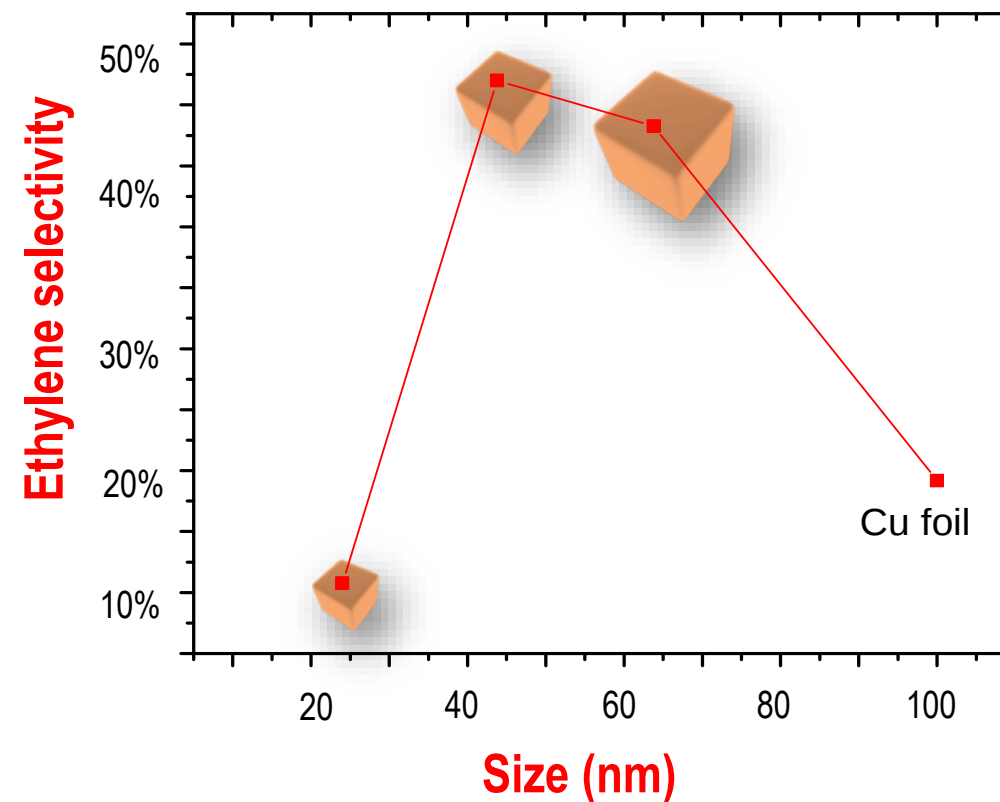
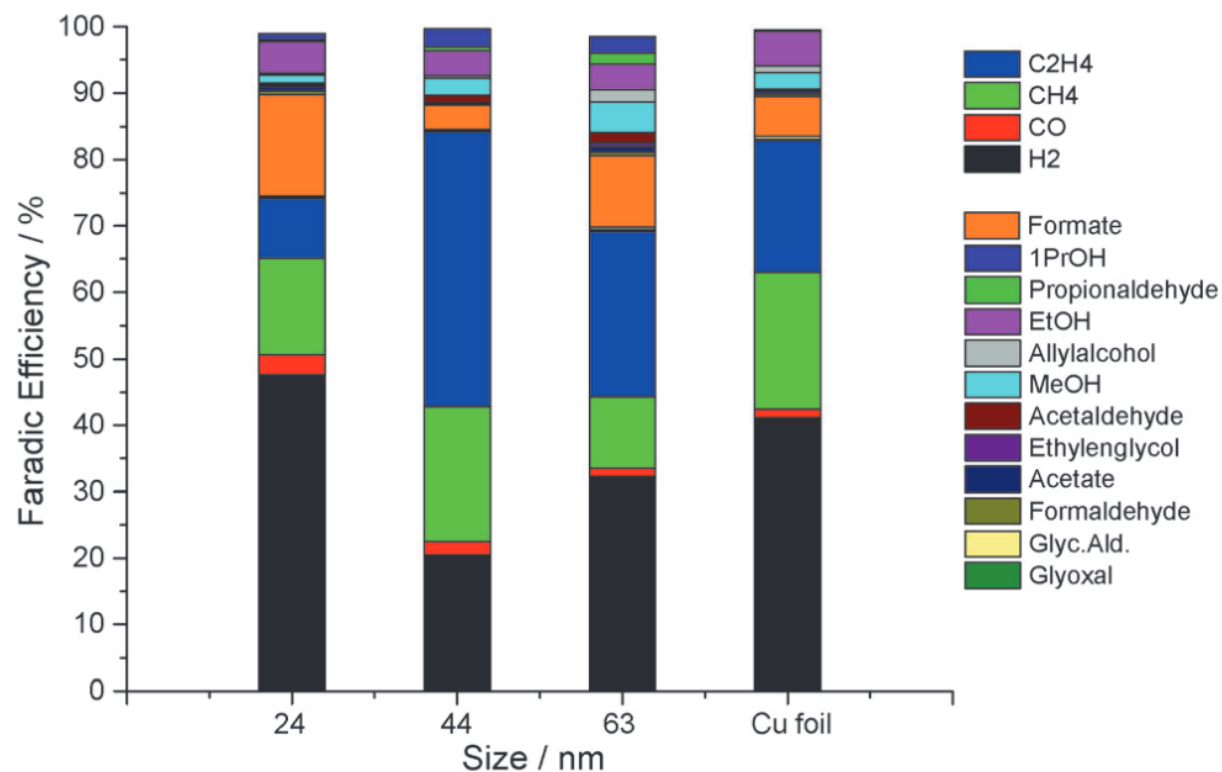


Copper has the right binding energy BUT lack of selectivity!

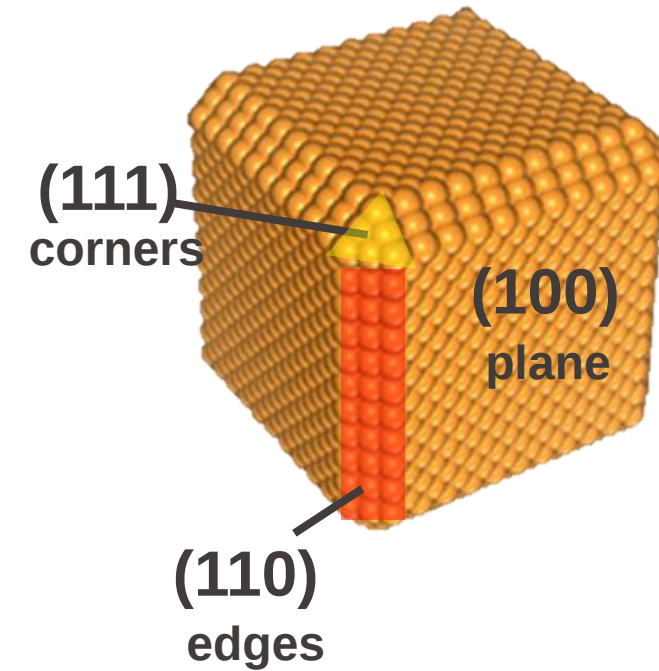
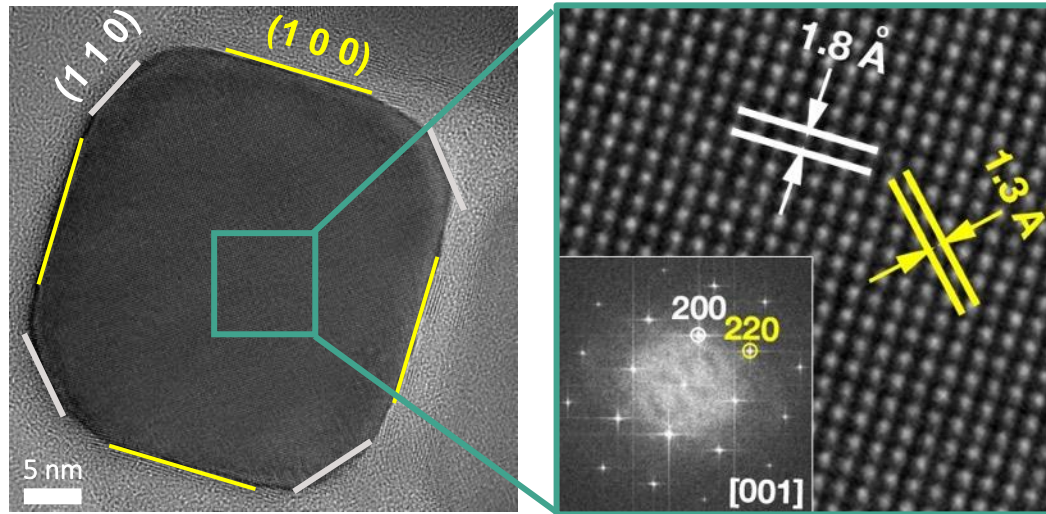
EPFL Going down to the nanoscale with well define size and shape to improve selectivity



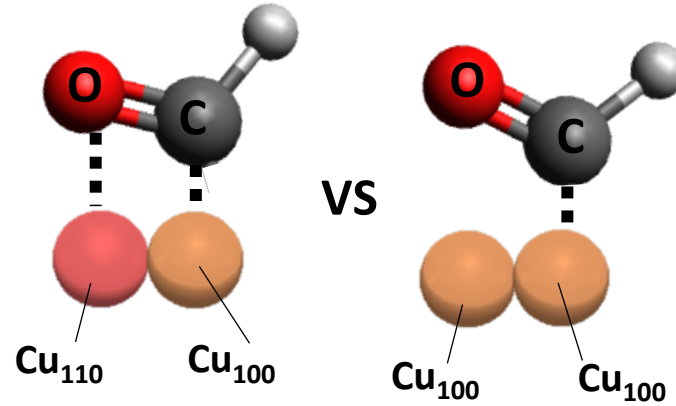
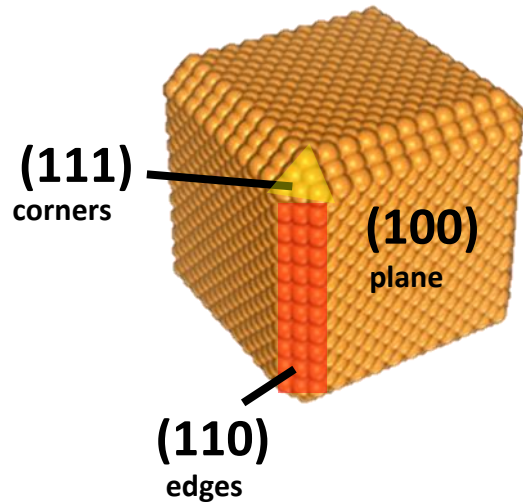
44nm cubes show the highest selectivity towards ethylene!



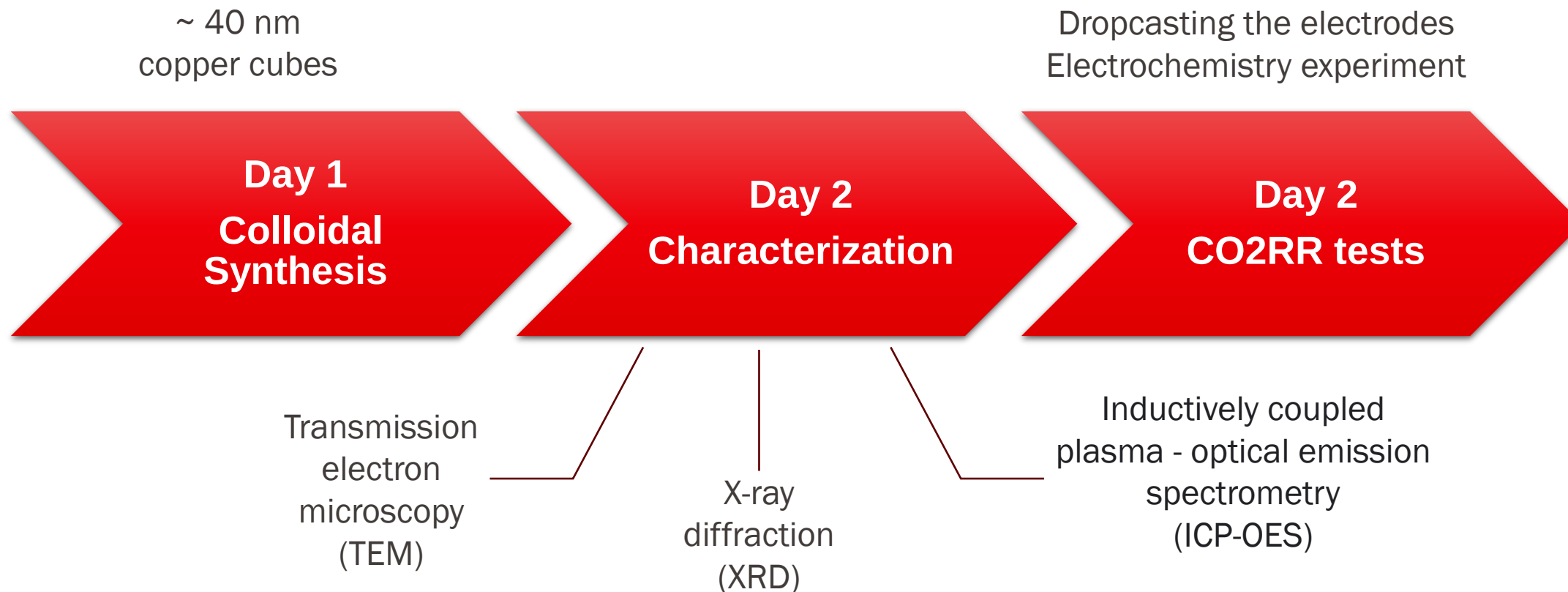
Learning about the crystal structure of the cubes



Edge- and plane-atoms behave as different catalytic sites



Copper atoms along the edges or on the planes behave as different catalytic sites. The 44 nm cubes give the optimal ratio between edge and plane sites ($\text{Cu}_{\text{edges}}/\text{Cu}_{\text{planes}}=0.025$)

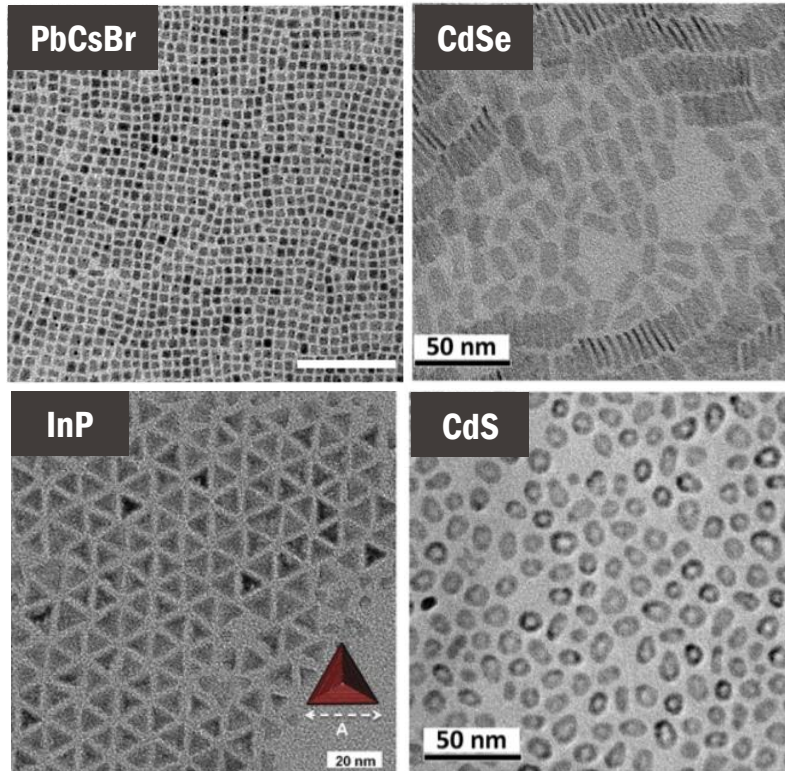


COLLOIDAL SYNTHESIS

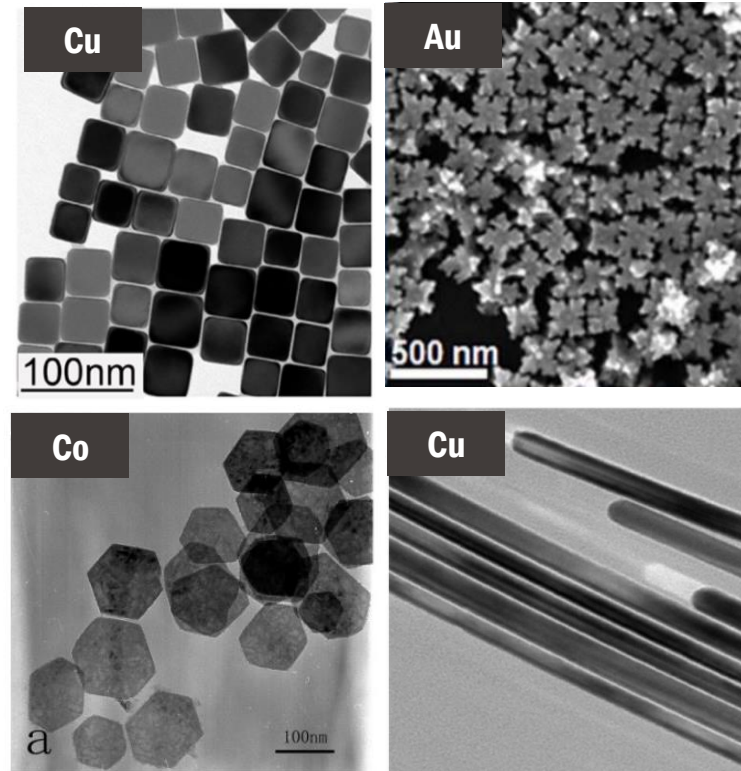
What: Wet chemistry approach in organic solvent and (often) carried out under inert atmosphere in presence of organic surfactants where decomposition of precursors lead to monomers and then to NCs

Why:

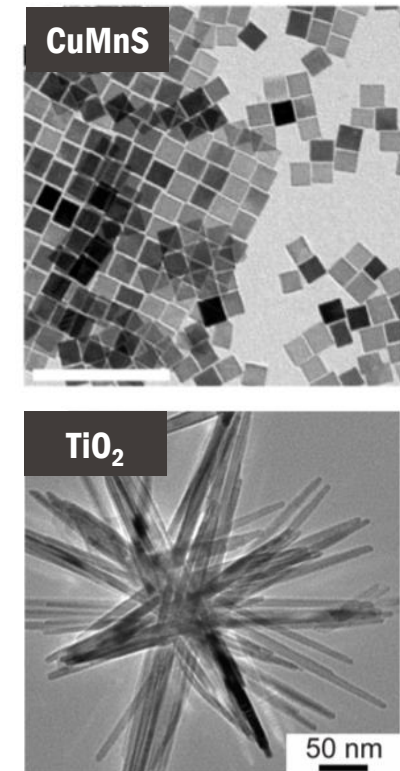
Semiconductors - QDs

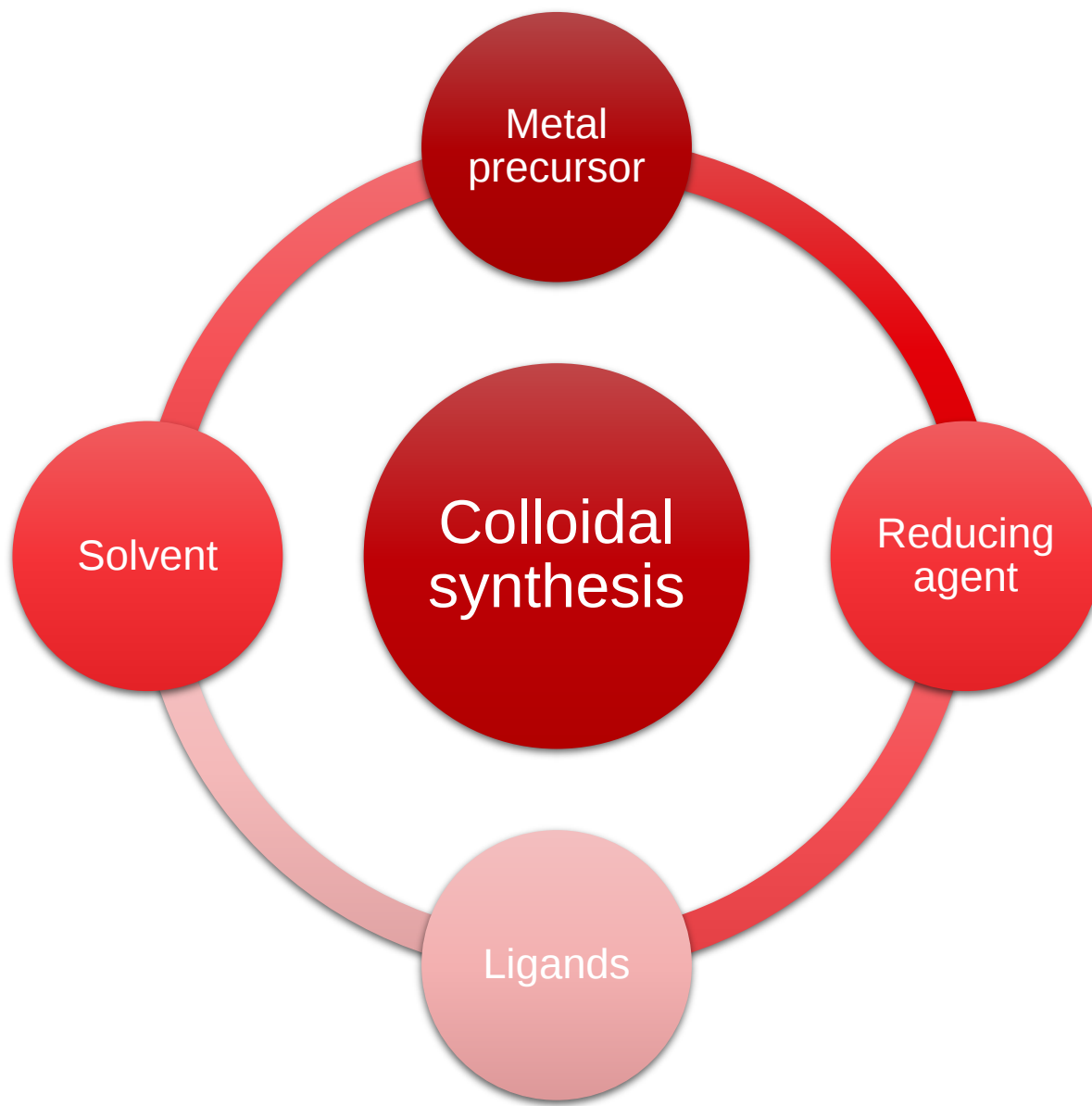


Metal Nanocrystals



Metal-Oxide

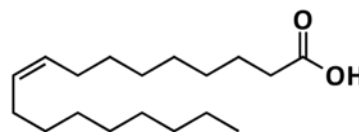
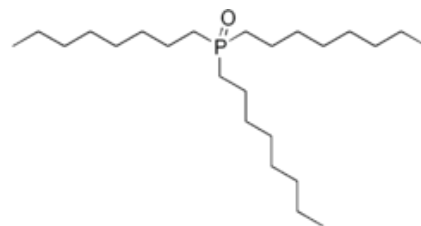
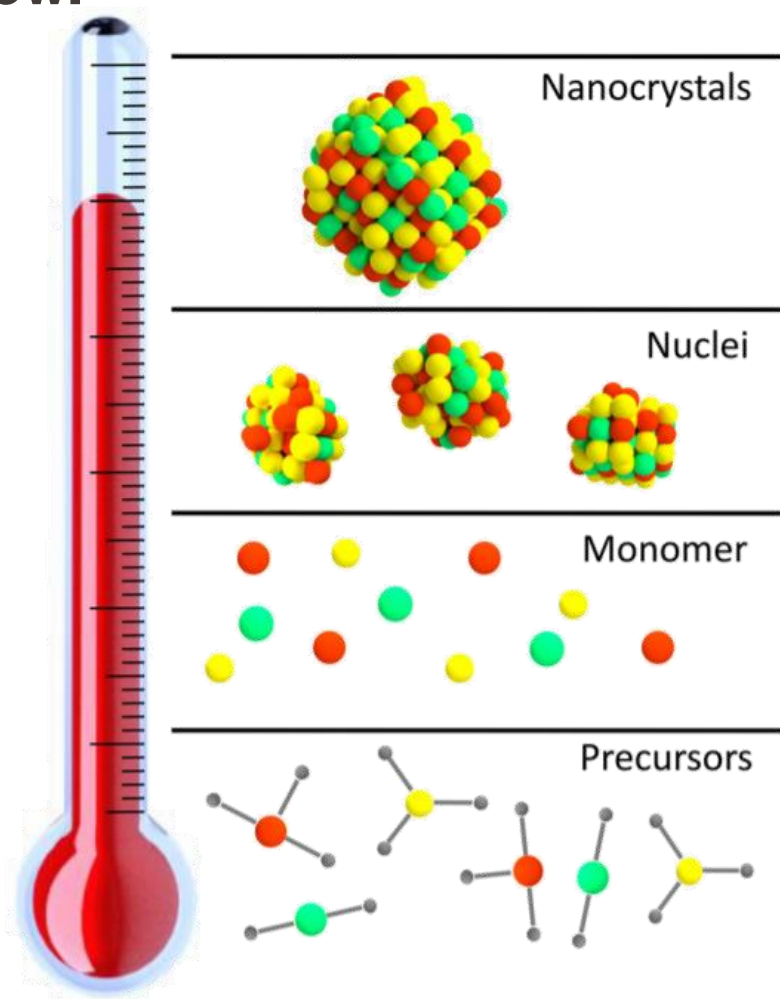




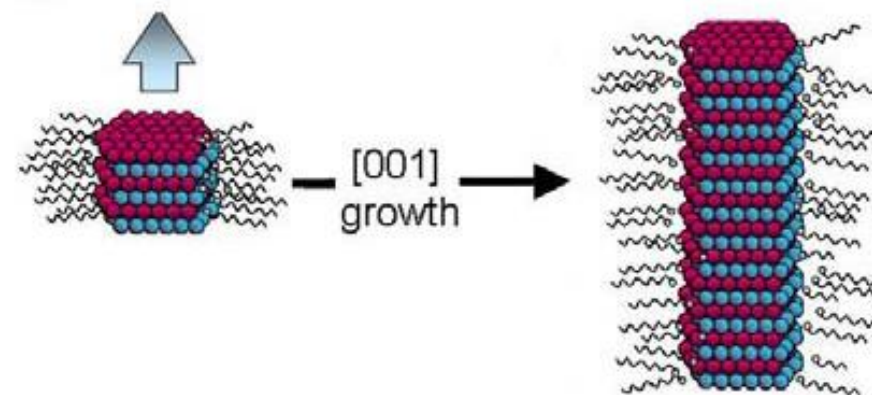
Some chemicals can
play more than one role!

Shape-Controlled Synthesis - Simple Chemistry Meets Complex Physics

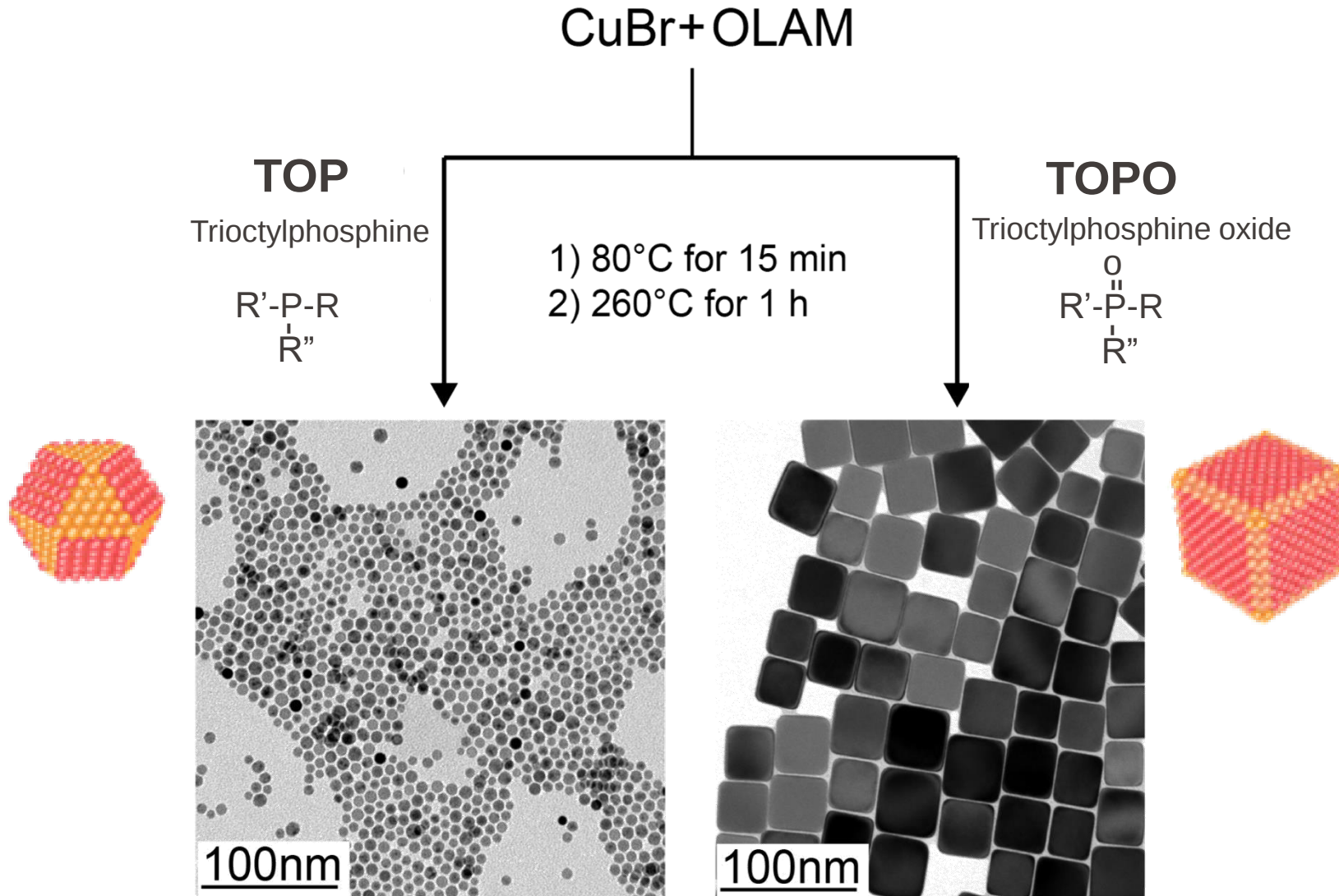
How:



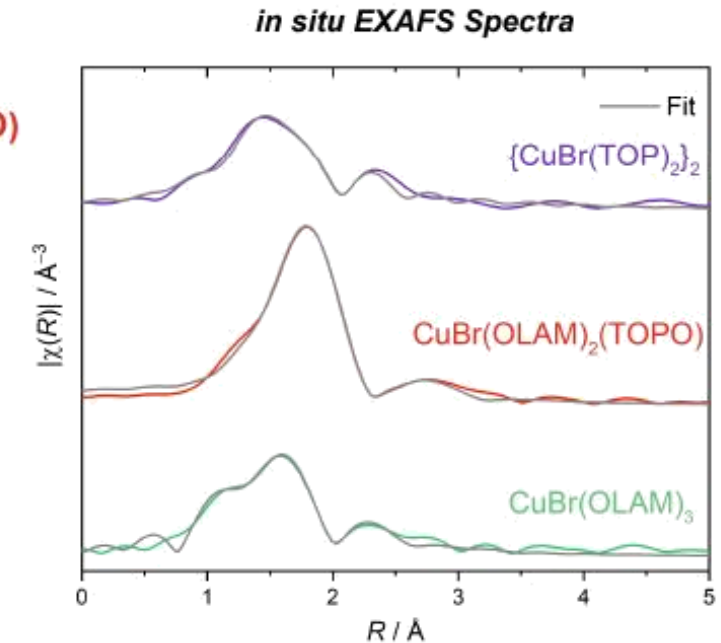
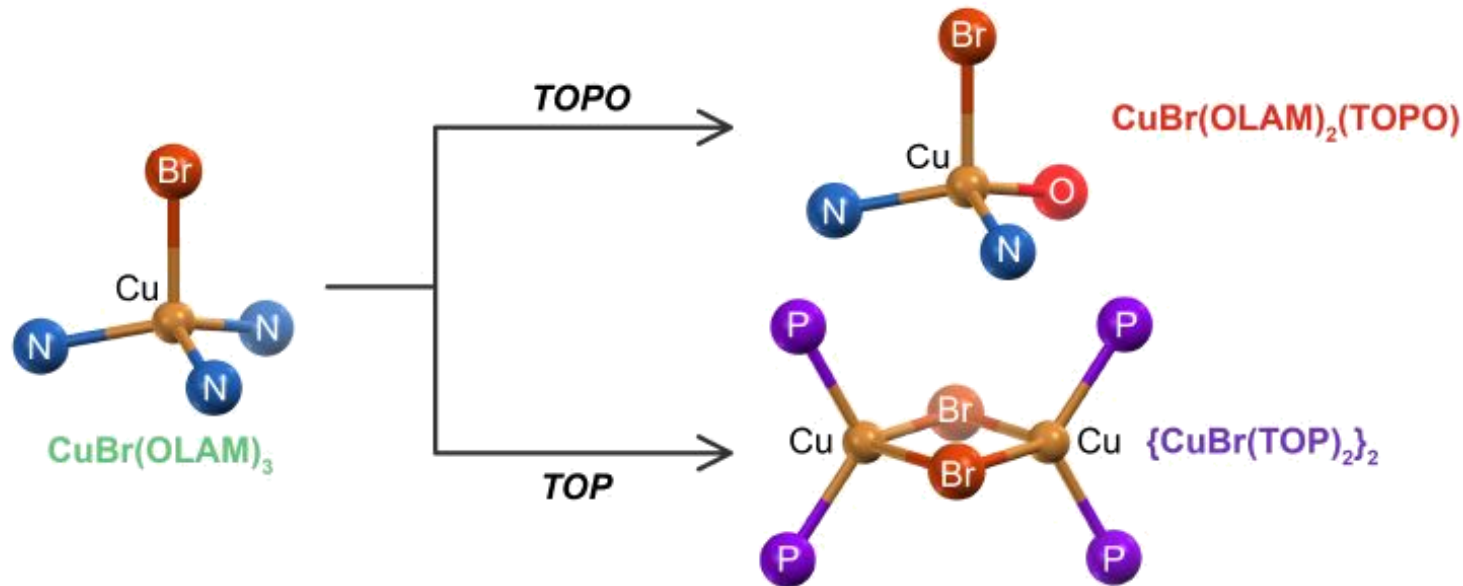
Acid								
Sn ⁴⁺	Fe ³⁺	Al ³⁺	Cu ²⁺	Zn ²⁺	Pb ²⁺	Ag ⁺	Cu ⁺	Cd ²⁺
Ga ³⁺	In ³⁺	Ln ³⁺	Sn ²⁺	Fe ²⁺	Ni ²⁺	Pd ²⁺	Au ⁺	Pt ⁴⁺
Hard			Borderline			Soft		
R-NH ₂	R-OH	OH ⁻	C ₅ H ₅ N			R-SH	R-S ⁻	R ₃ P
R-CO ₂ ⁻	F ⁻	R-O ⁻	N ₃ ⁻	Cl ⁻		(RO) ₃ P	Br ⁻	I ⁻
Base								



Shape selectivity with Cu Nanocrystals – Key role of the ligands



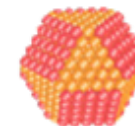
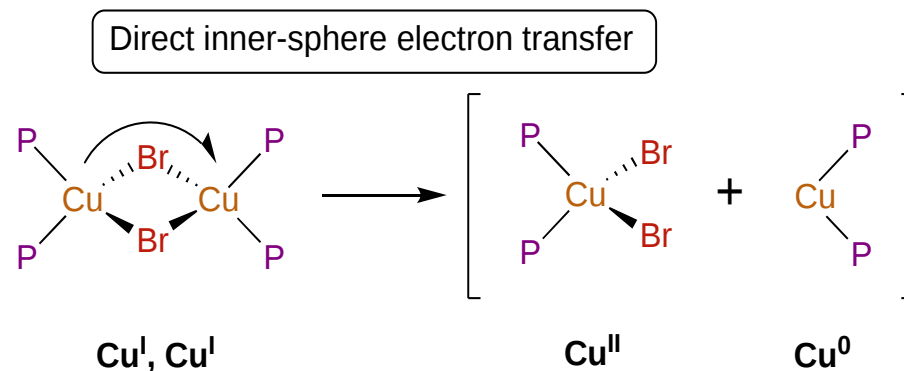
Plateau at 80°C



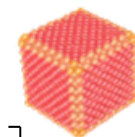
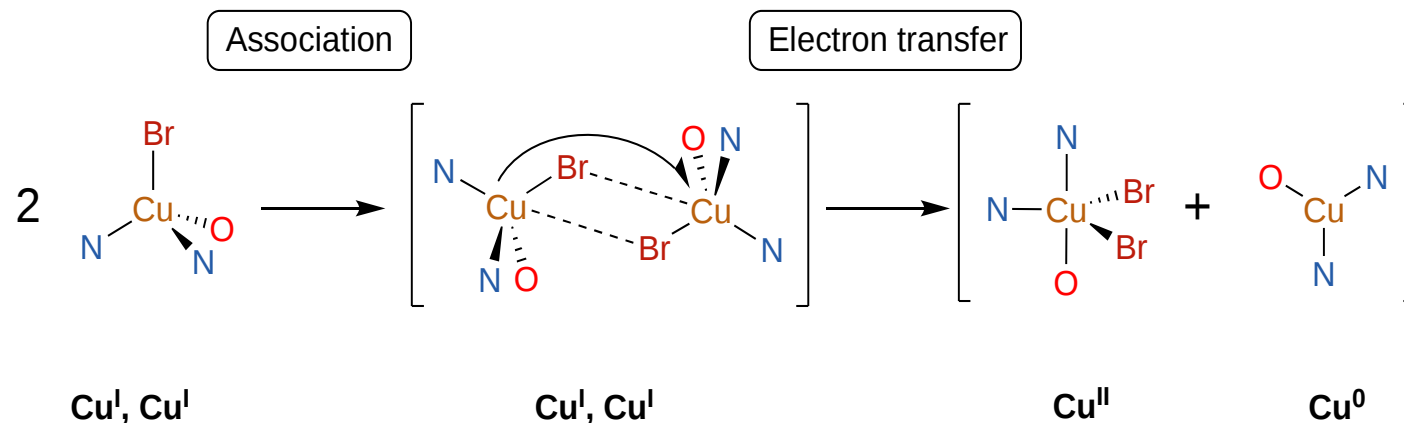
TOPO and TOP both act as complexing agents, forming complexes of different properties that then act as intermediates for the monomers

The chemical nature of the Cu(I)-complexes explains the different disproportionation kinetics

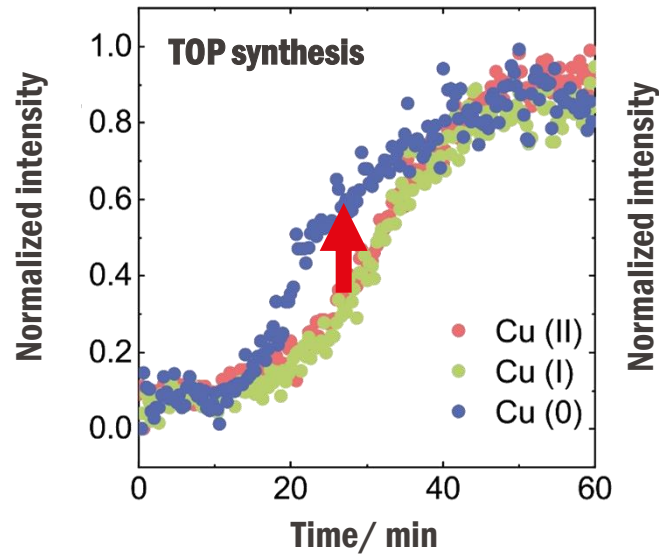
TOP synthesis



TOPO synthesis



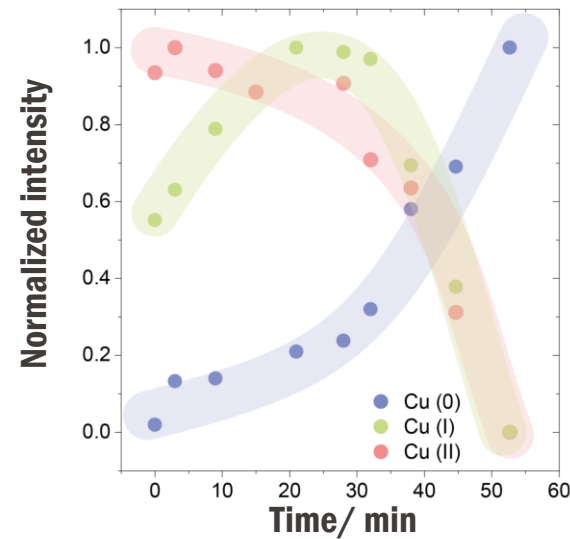
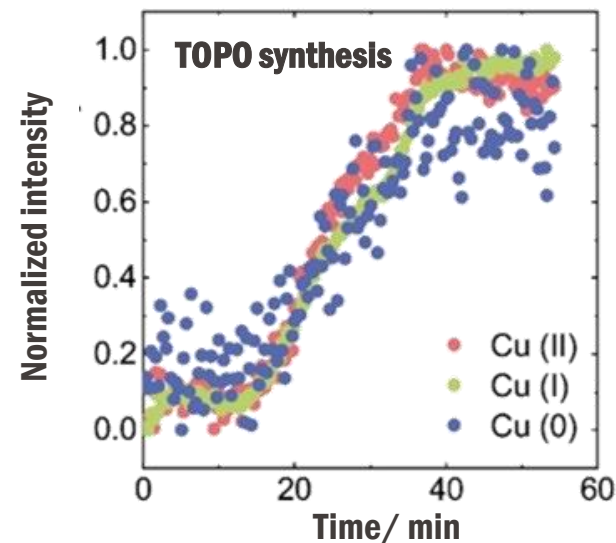
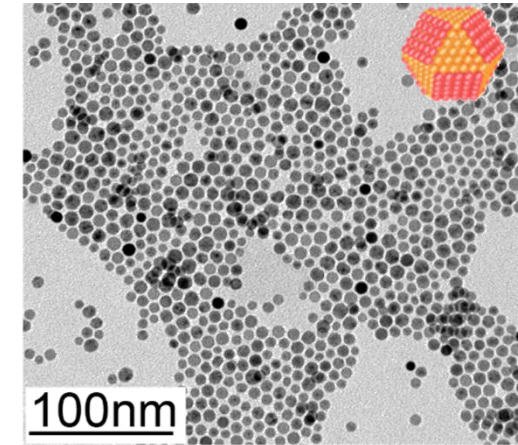
The monomer flux is key to differentiate between thermodynamic and kinetic products...



Cu(0)=monomers

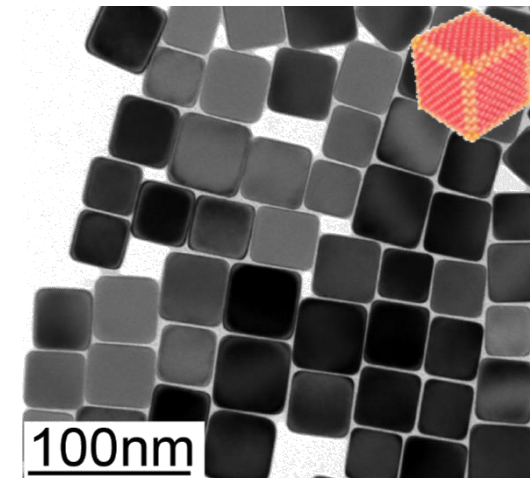
Gradual monomer release

Thermodynamic regime

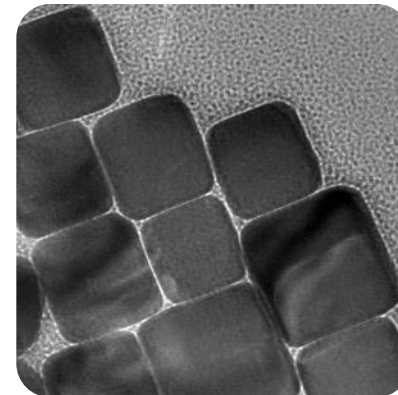
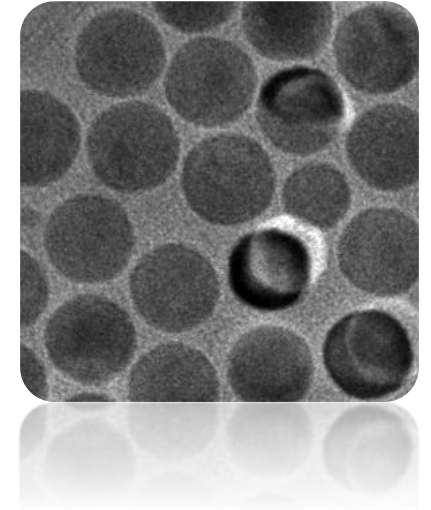


Fast monomer release

Kinetic regime



- ❖ Nanocube or Nanosphere synthesis by monomer flux control.
- ❖ The added ligand, TOP or TOPO, complex with the precursor forming complexes with different properties
- ❖ TOP complexing results in a dimeric complex for which disproportionation happens easily and gradually
constant monomer flux, thermodynamic regime → spherical shape
- ❖ TOPO complexing results in a monometallic complex for which fast disproportionation happens at higher T and suddenly
fast monomer flux, kinetic regime → cubic shape

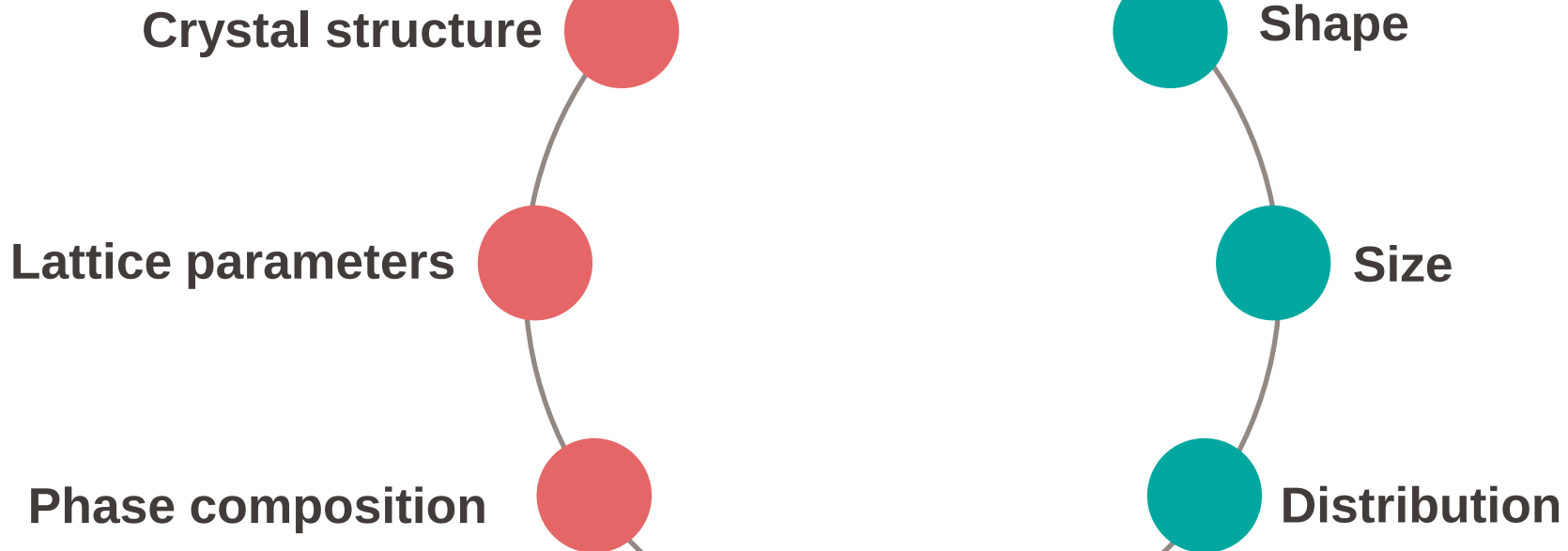


CHARACTERIZATION (TEM & XRD)

Information we can gain from:

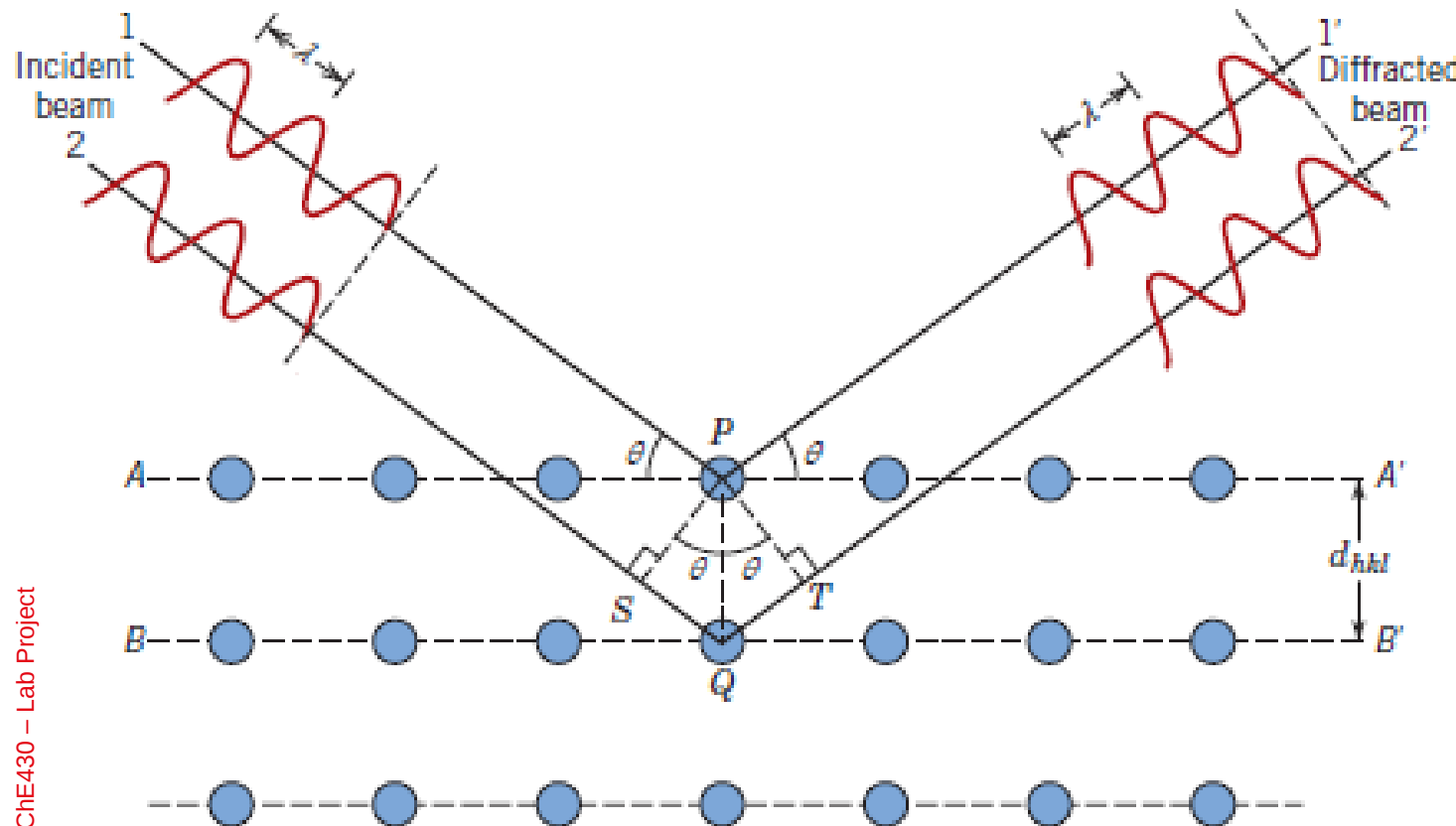
X-Ray Diffraction (XRD)

**Transmission Electron
Microscopy (TEM)**



A diffraction pattern results from constructive interference of the scattered waves

Diffraction of X-Rays by planes of atoms



$$n\lambda = \overline{SQ} + \overline{QT}$$

$$n\lambda = d \sin \theta + d \sin \theta = 2d \sin \theta$$



$$n\lambda = d \sin \theta$$

Bragg's law

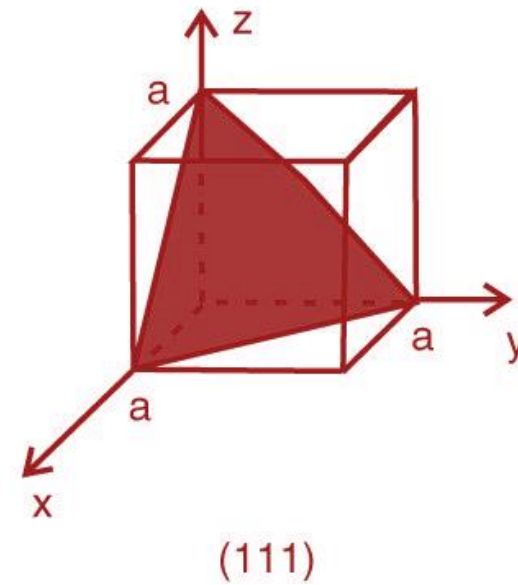
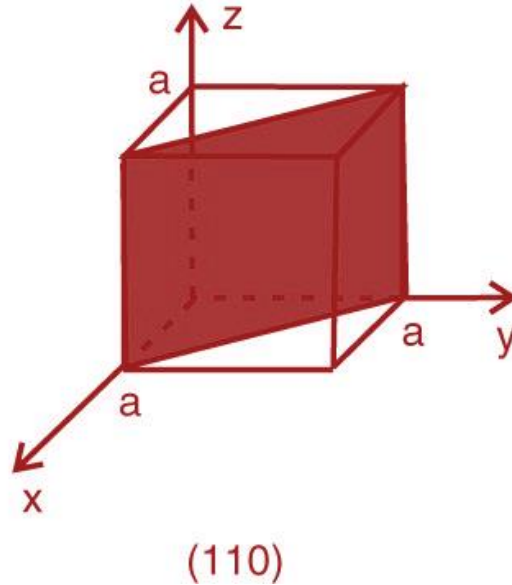
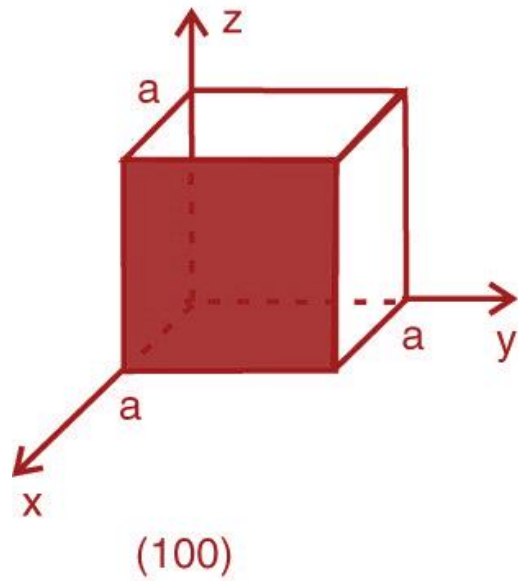
**Constructive interference
condition**

Crystallographic planes. Miller indices.

Crystallographic planes - set of parallel and equally spaced planes that may be supposed to pass through the centers of atoms in crystals.

Miller indices (hkl) are determined from the reciprocals of axial intercepts x , y , z .

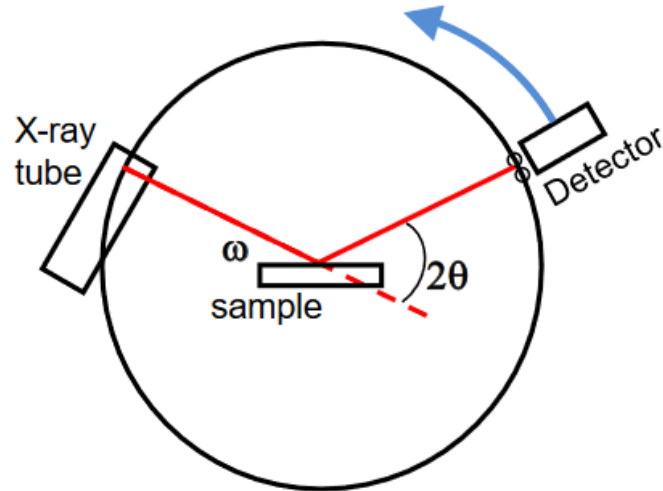
Crystallographic planes are specified by three **Miller indices** as (hkl) .



Interplanar spacing d_{hkl} - the magnitude of the distance between two adjacent and parallel planes of atoms

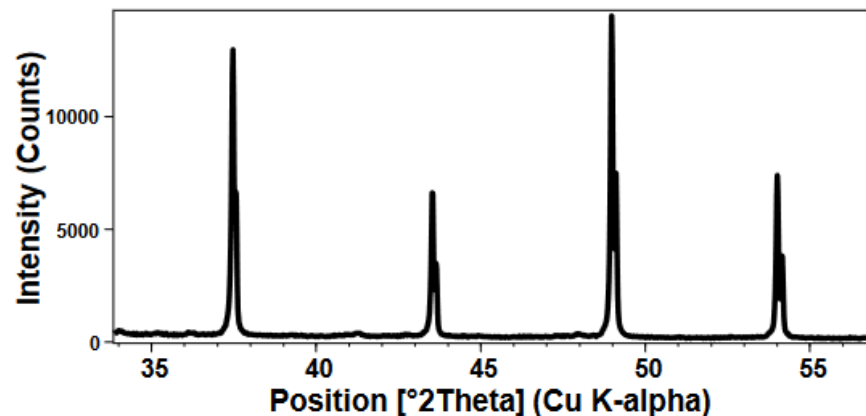
An X-ray powder diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample

Schematic diagram of an x-ray diffractometer

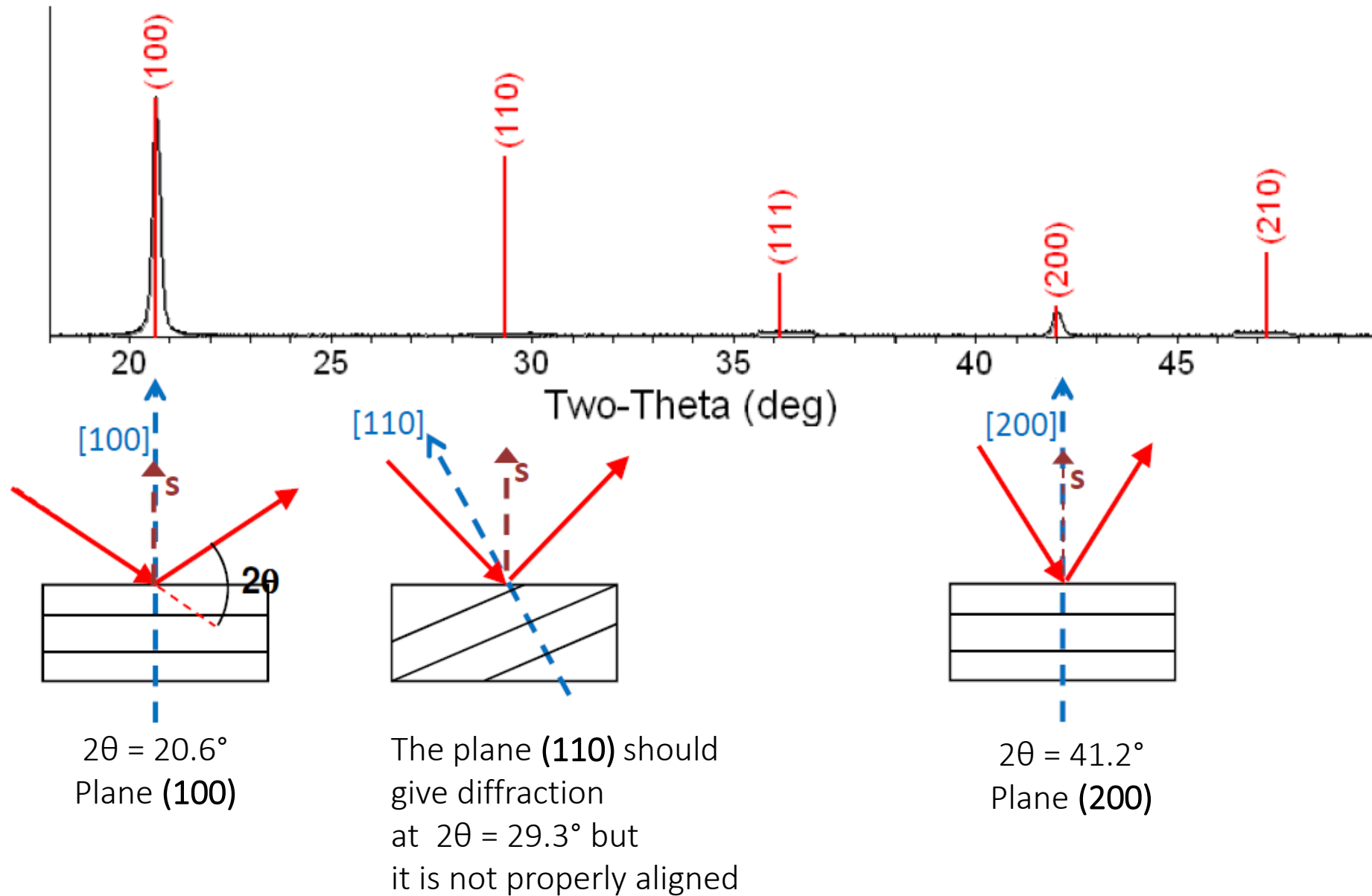


- The detector moves in a circle around the sample
- The detector position is recorded as the angle 2θ
- The detector records the number of X-rays observed at each angle 2θ

Diffraction pattern

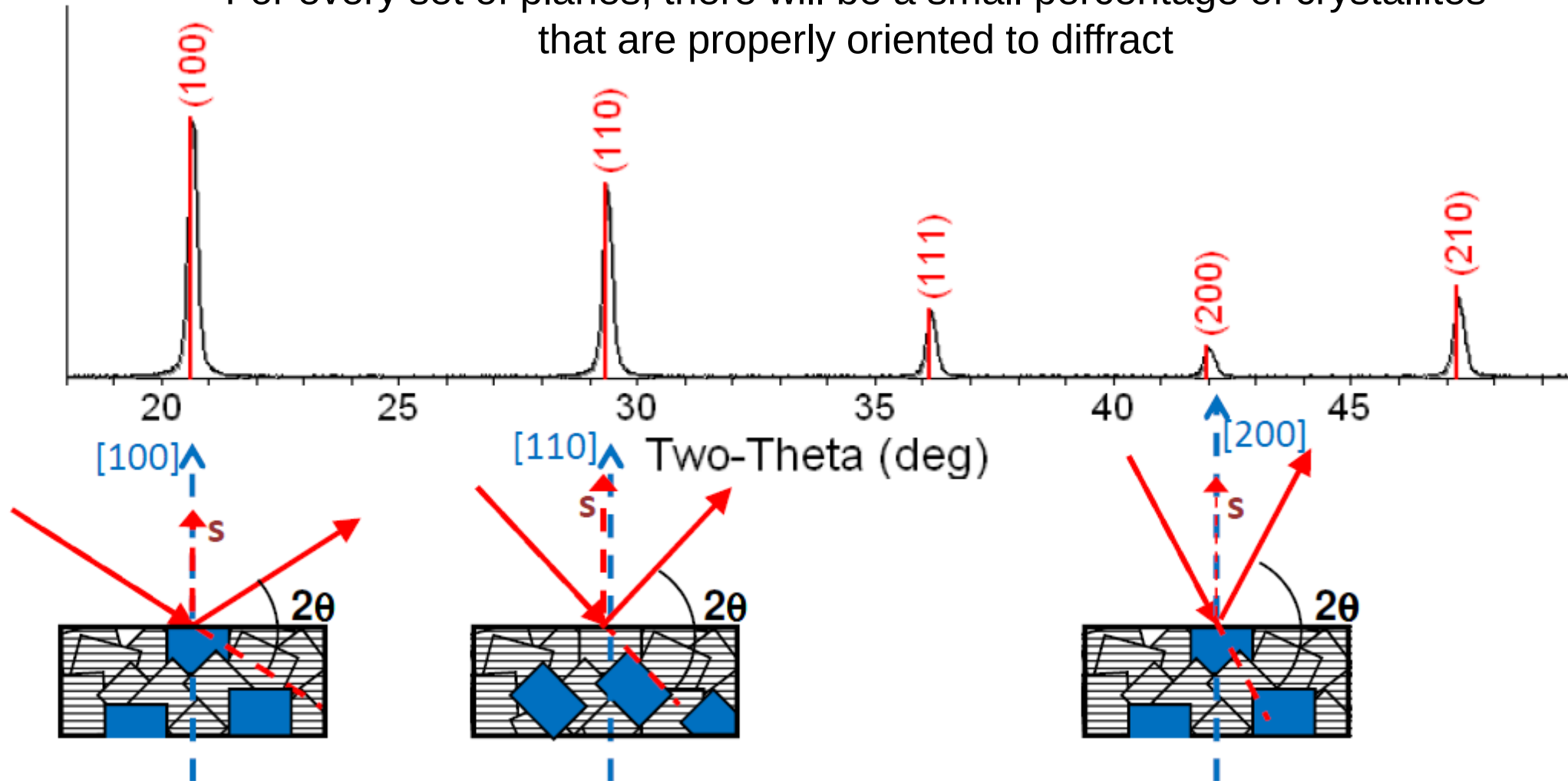


XRD pattern of a single crystal (preferred orientation)

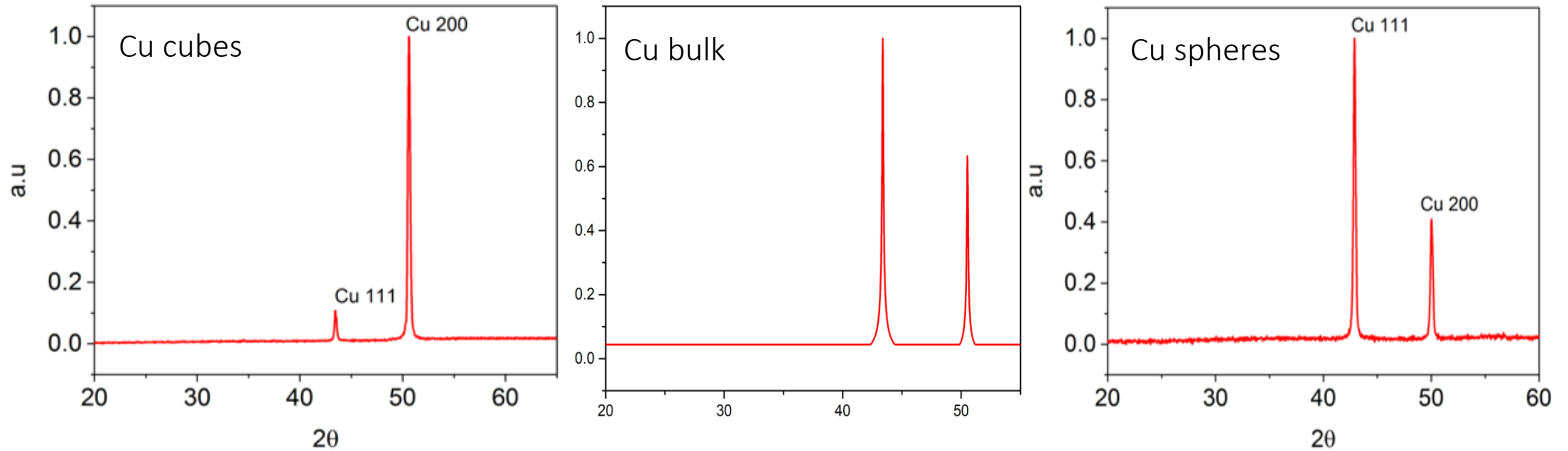


XRD pattern of a polycrystalline sample (random orientation)

For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract



XRD peaks: intensity and width contain important information on the crystal structure



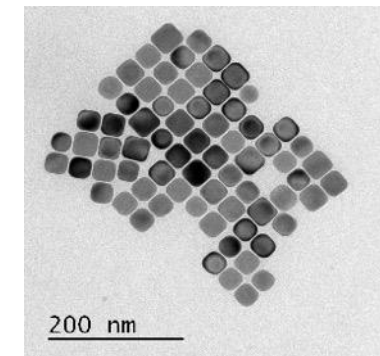
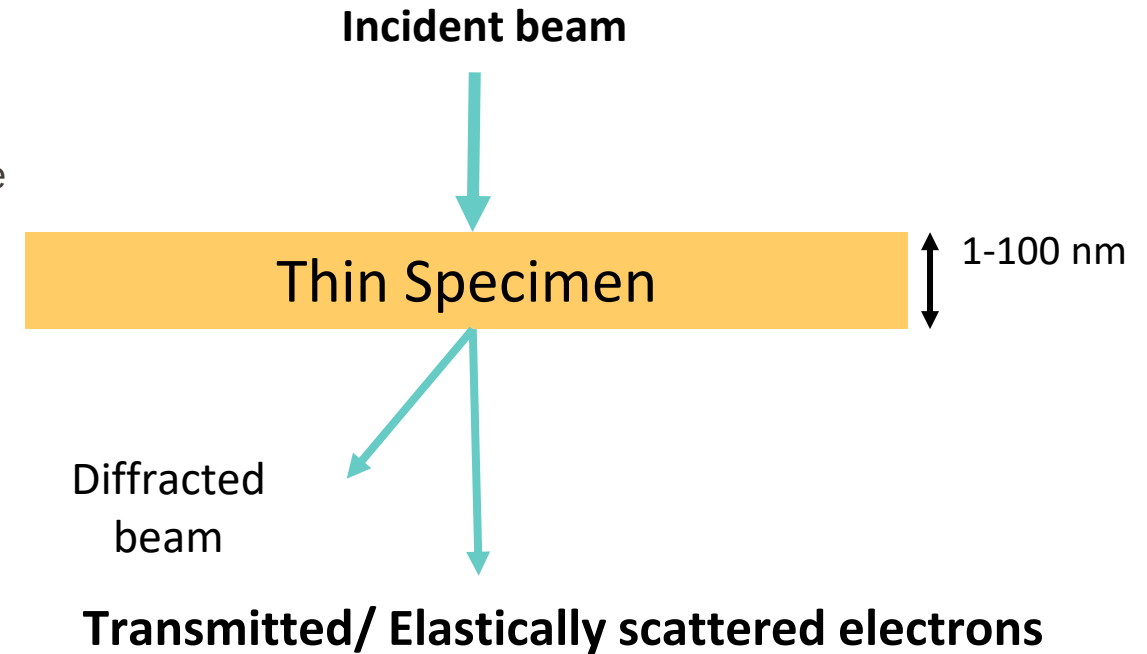
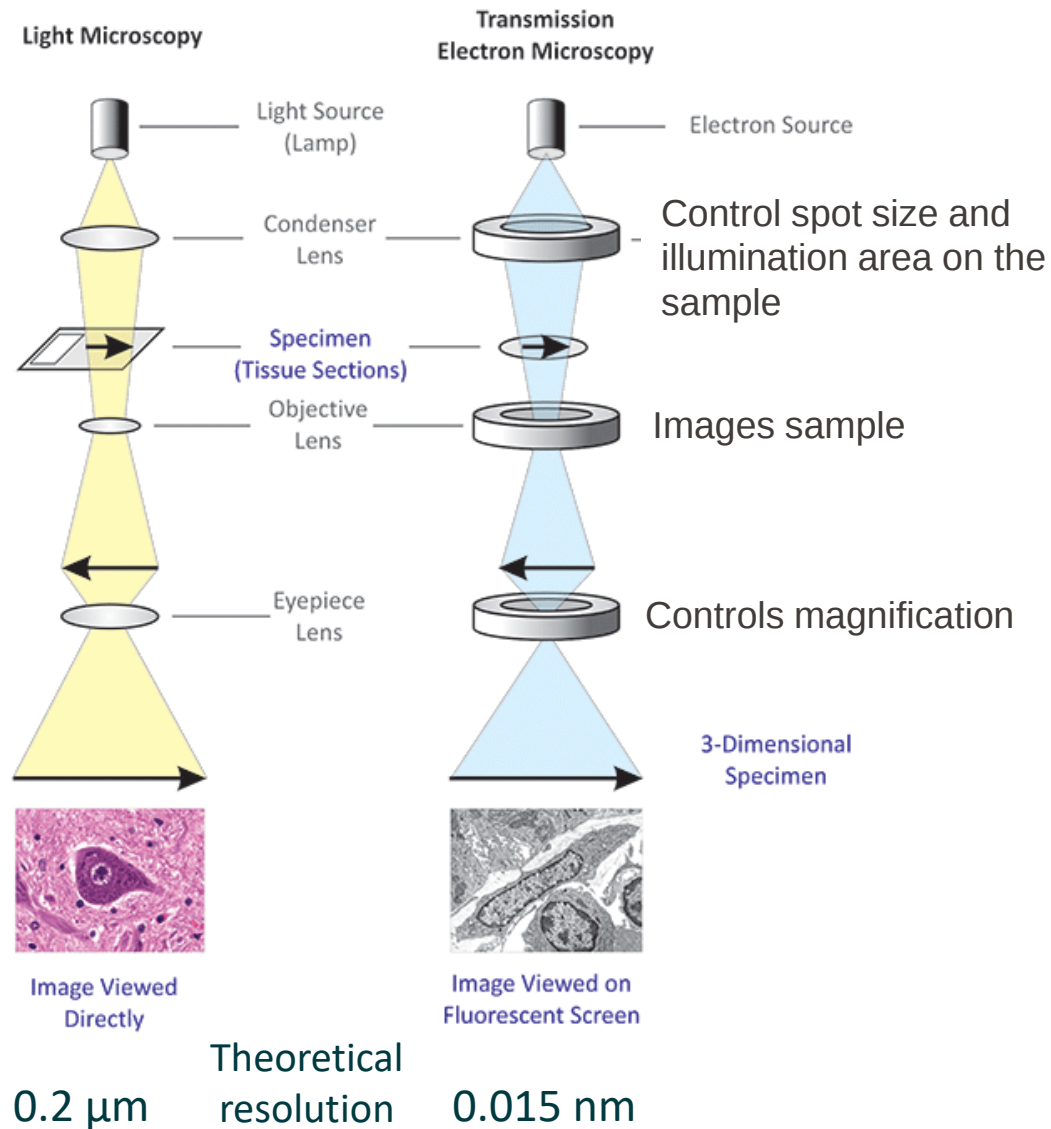
Width $\longrightarrow$ Crystallite size

Intensity $\longrightarrow$

- Preferred orientation
- Structure factor

$\downarrow$
Scattering by an atom = $f [Z, \theta, \lambda]$

TEM: powerful technique to visualize nanometer features



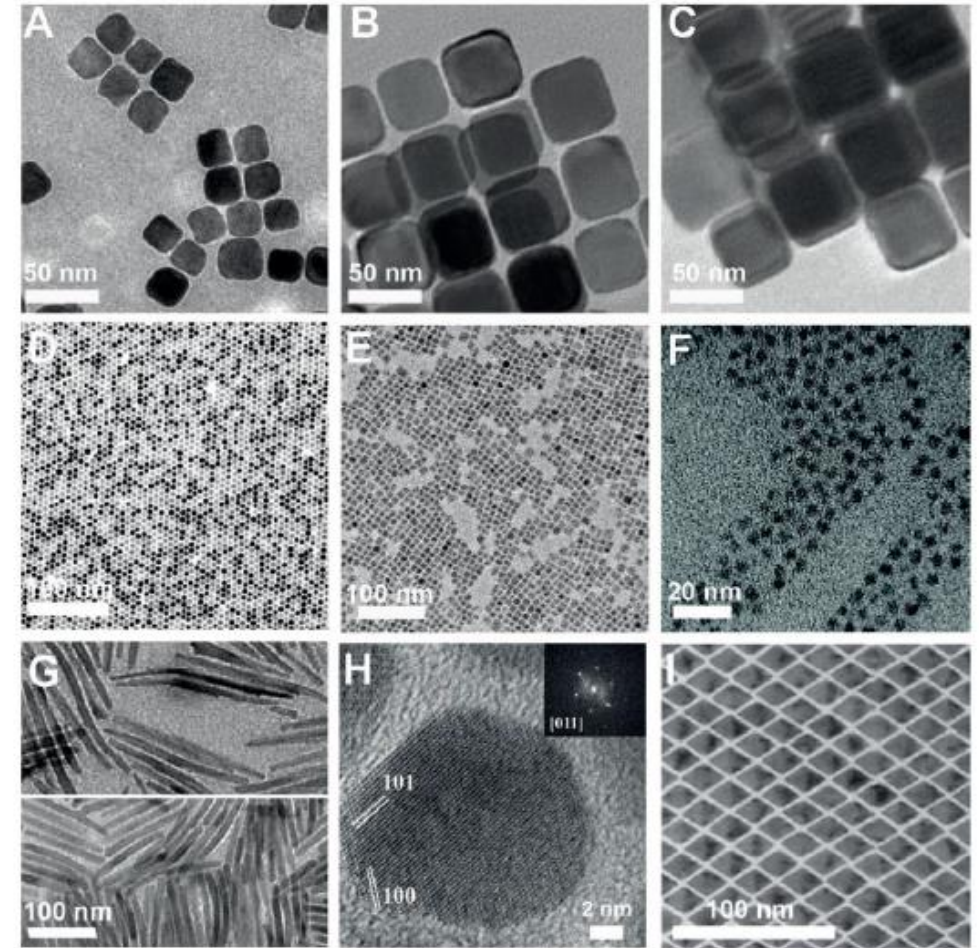
What gives different contrast in TEM images?

Thickness

Thicker regions will scatter more electrons than thinner regions of the same average Z.

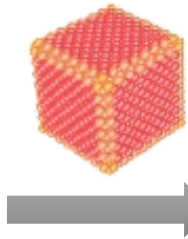
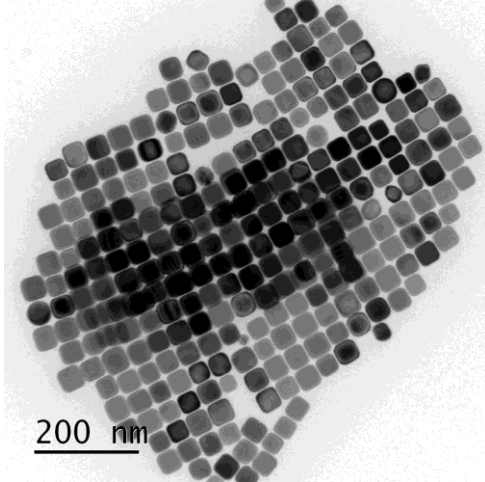
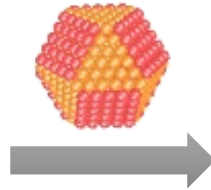
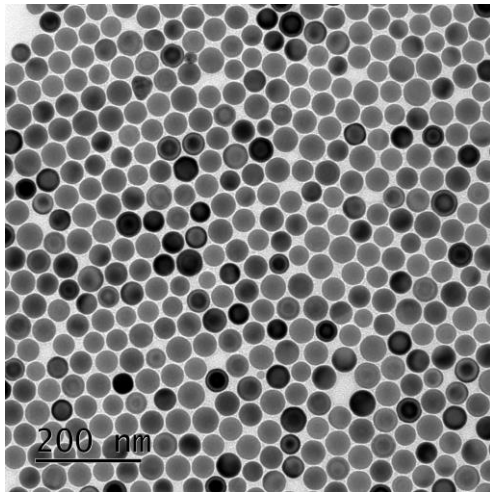
Different atomic numbers (Z)

High-Z (i.e., high-mass) regions of a specimen scatter more electrons than low-Z regions of the same thickness

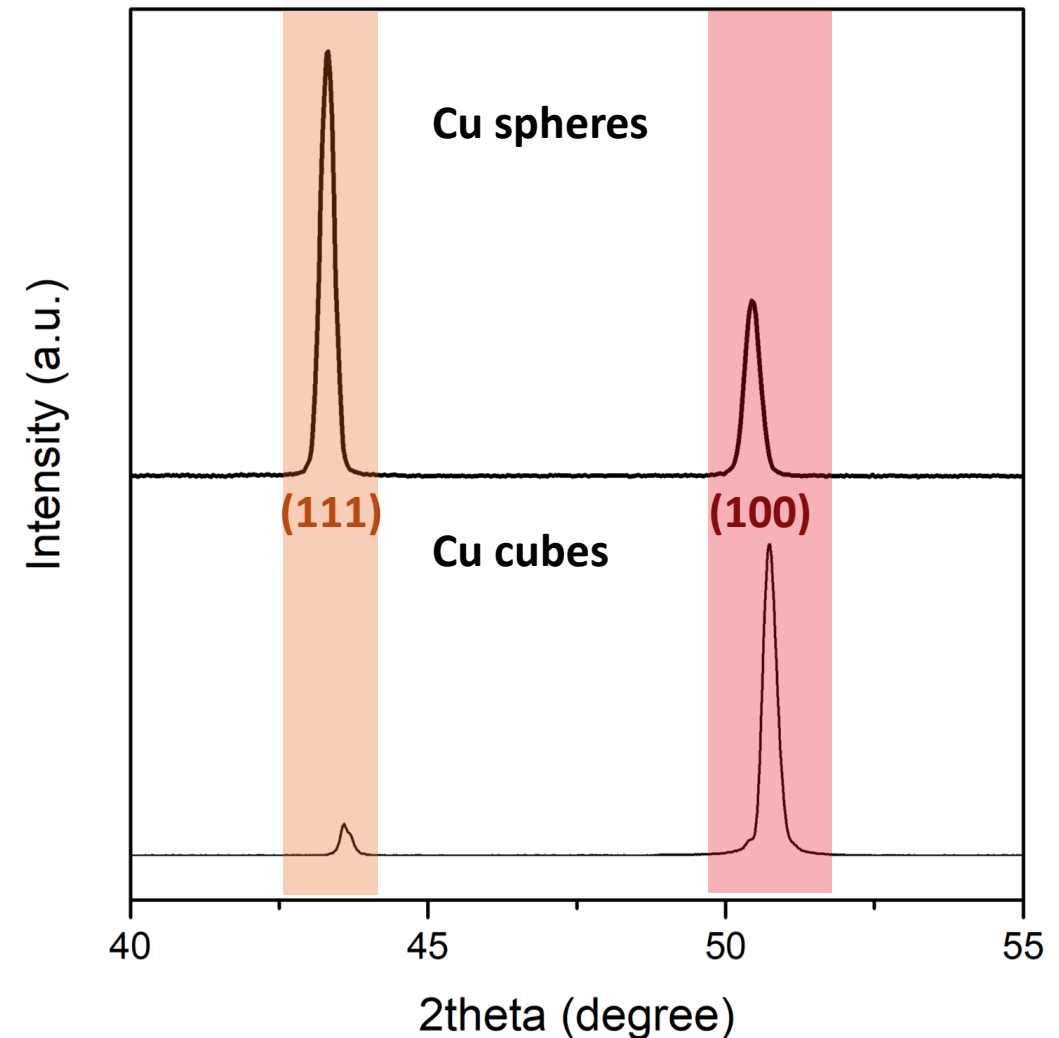


XRD and TEM are the main techniques to characterize the colloidal nanocrystals

Transmission Electron Microscopy (TEM)

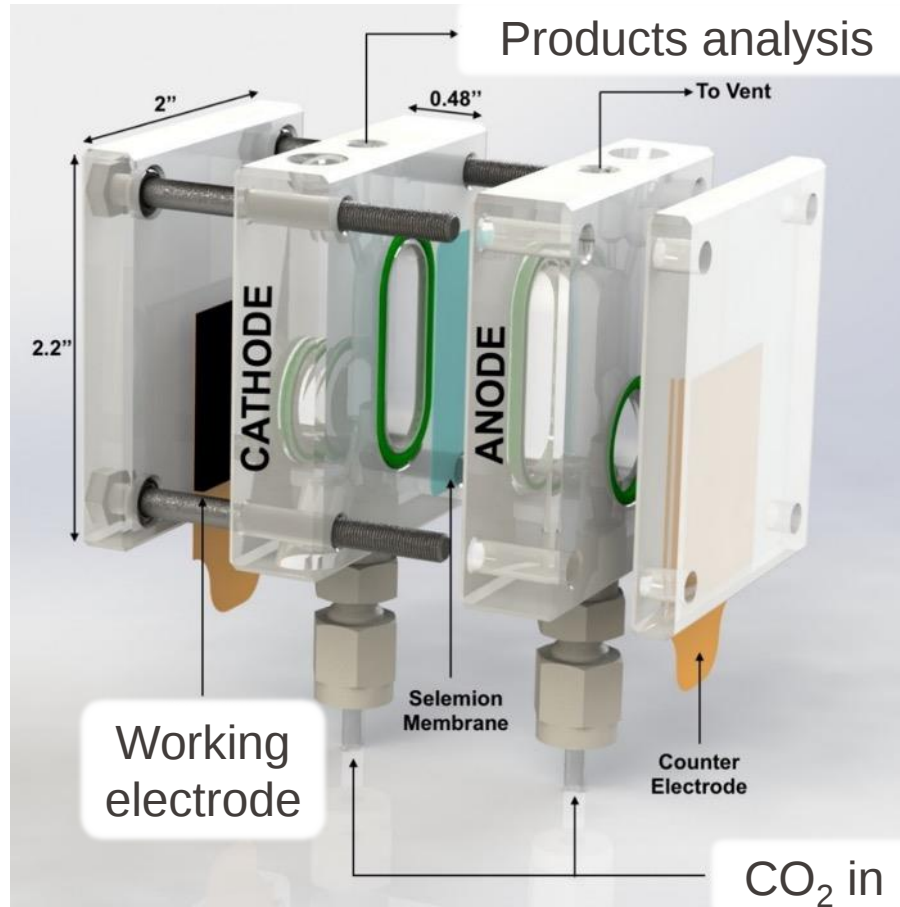


X-Ray Diffraction (XRD)



ELECTROCHEMICAL CO₂ REDUCTION

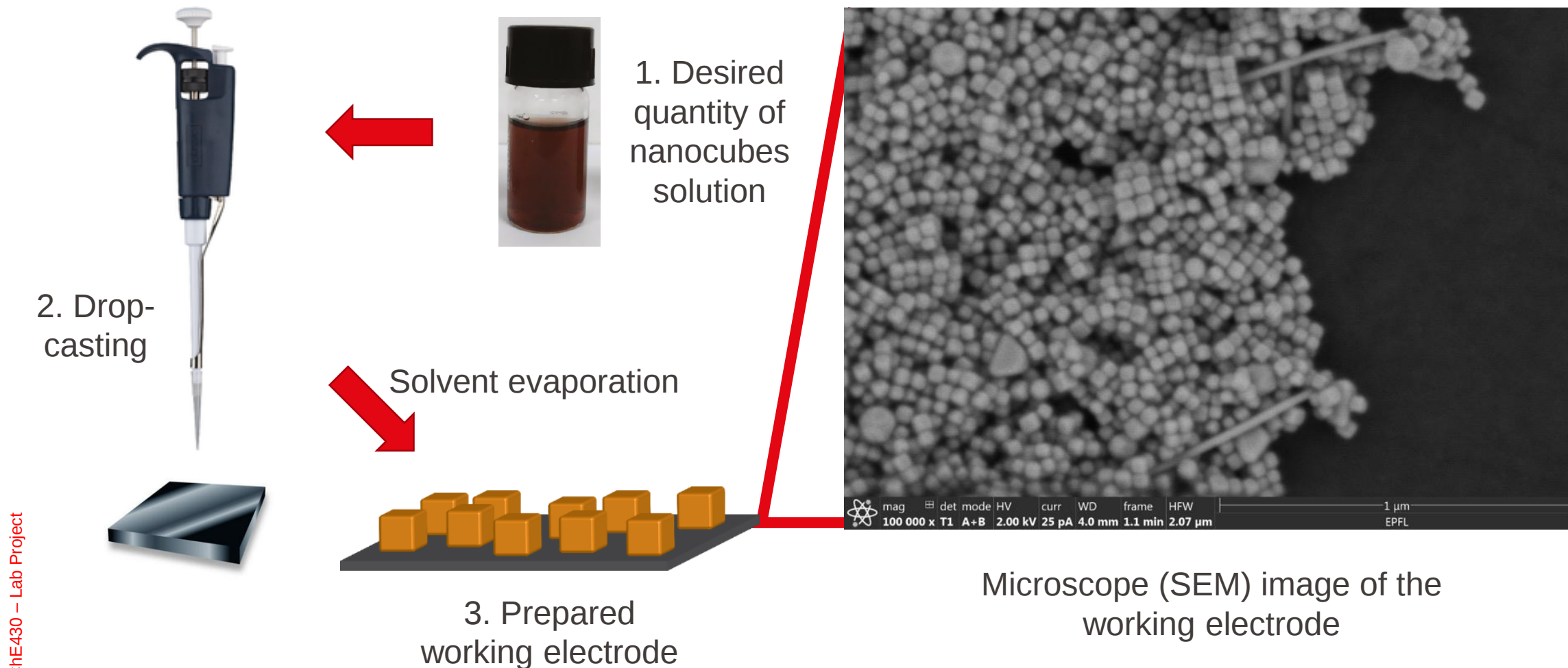
“Regular” testing is done in liquid H-type cell



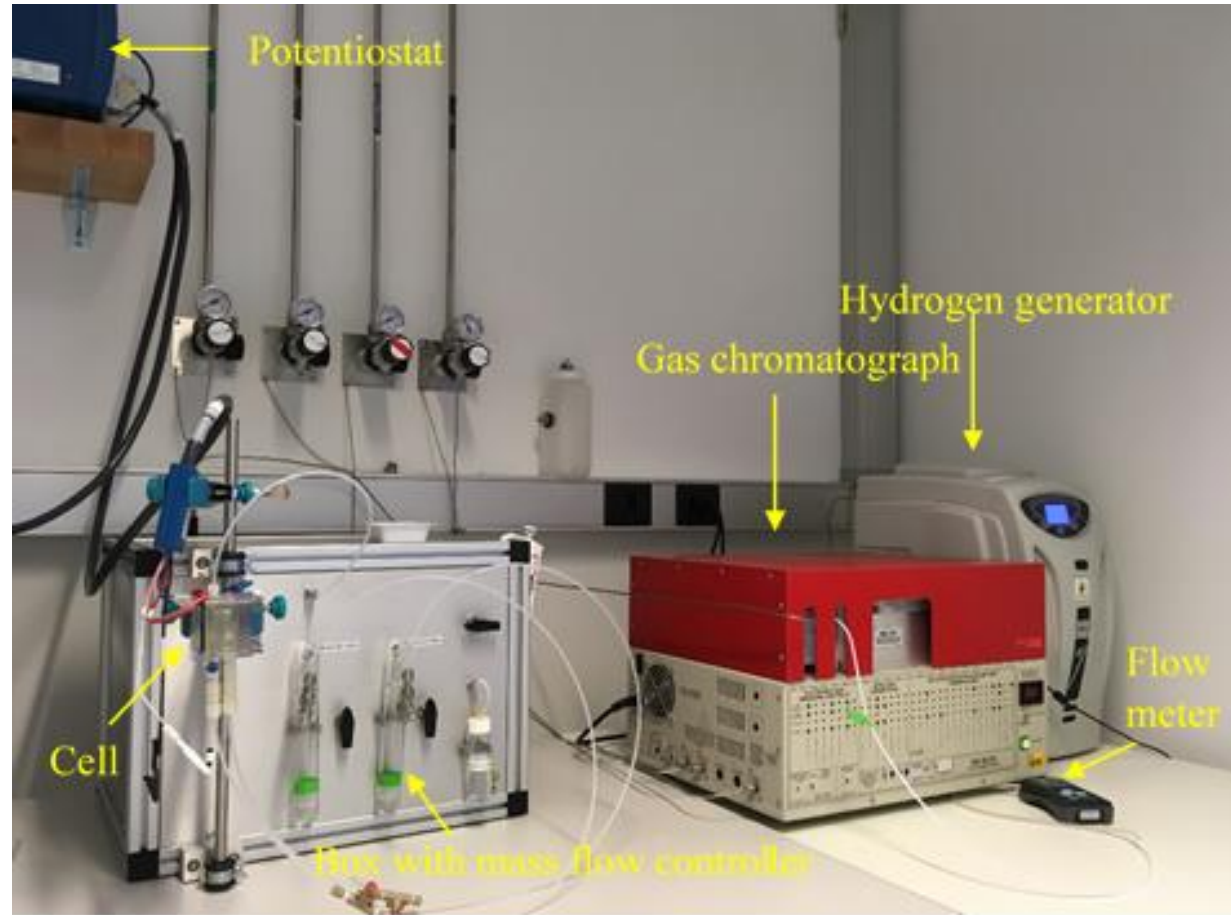
Liquid-fed reactor

- Continuous flow (CO₂) electrochemical cell
- 0.1 M KHCO₃ aqueous electrolyte
- -1.1 to -1.4 V vs. RHE (reversible hydrogen electrode)
- Products analysis: gas chromatography and high-performance liquid chromatography

Cu nanocubes are deposited on flat glassy carbon to make a working electrode



The setup is composed of the gas supply, cell and product analysis parts together with potentiostat



Gas line

- CO₂ is supplied from the bottle and fed through the cell
- Obtained gas mixture is sent to the chromatograph for products analysis

Gas chromatograph

- Flame ionization detector (FID) to detect hydrocarbons and CO
- Thermal conductivity detector (TCD) to detect hydrogen

Faradaic efficiency is calculated as fraction of charge consumed to form given product

$$FE_{product}(\%) = \frac{Q_{product}}{Q_{total}} = \frac{N_{product} * n_{product} * F}{i_{total} * t_{sampling}}$$

$N_{product}$ = Moles of detected product

$n_{product}$ = number of electrons required for reaction

F = Faraday's constant (96485 C/mol)

i_{total} = Average total current during sampling time

$t_{sampling}$ = sampling time

Thanks for attention!