Che-430 – Lab Project

Life story of Copper Nanocubes

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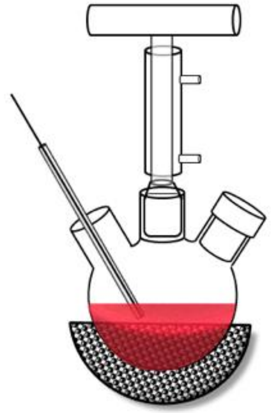
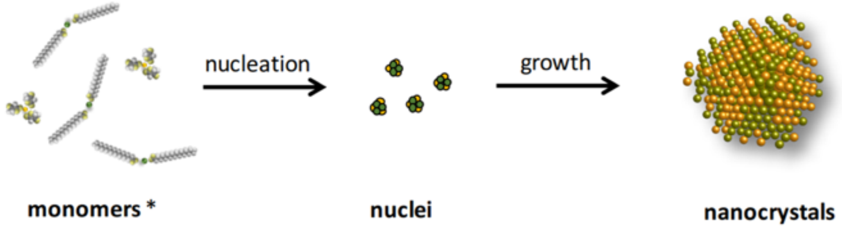
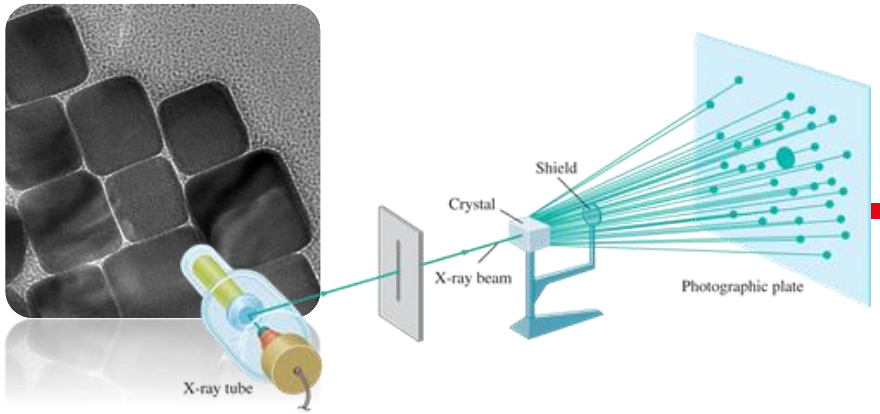
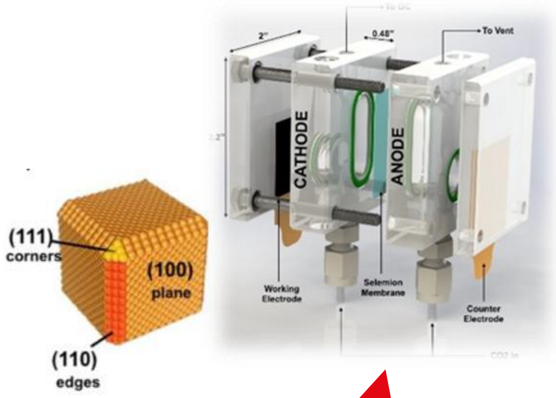
Fall 2025









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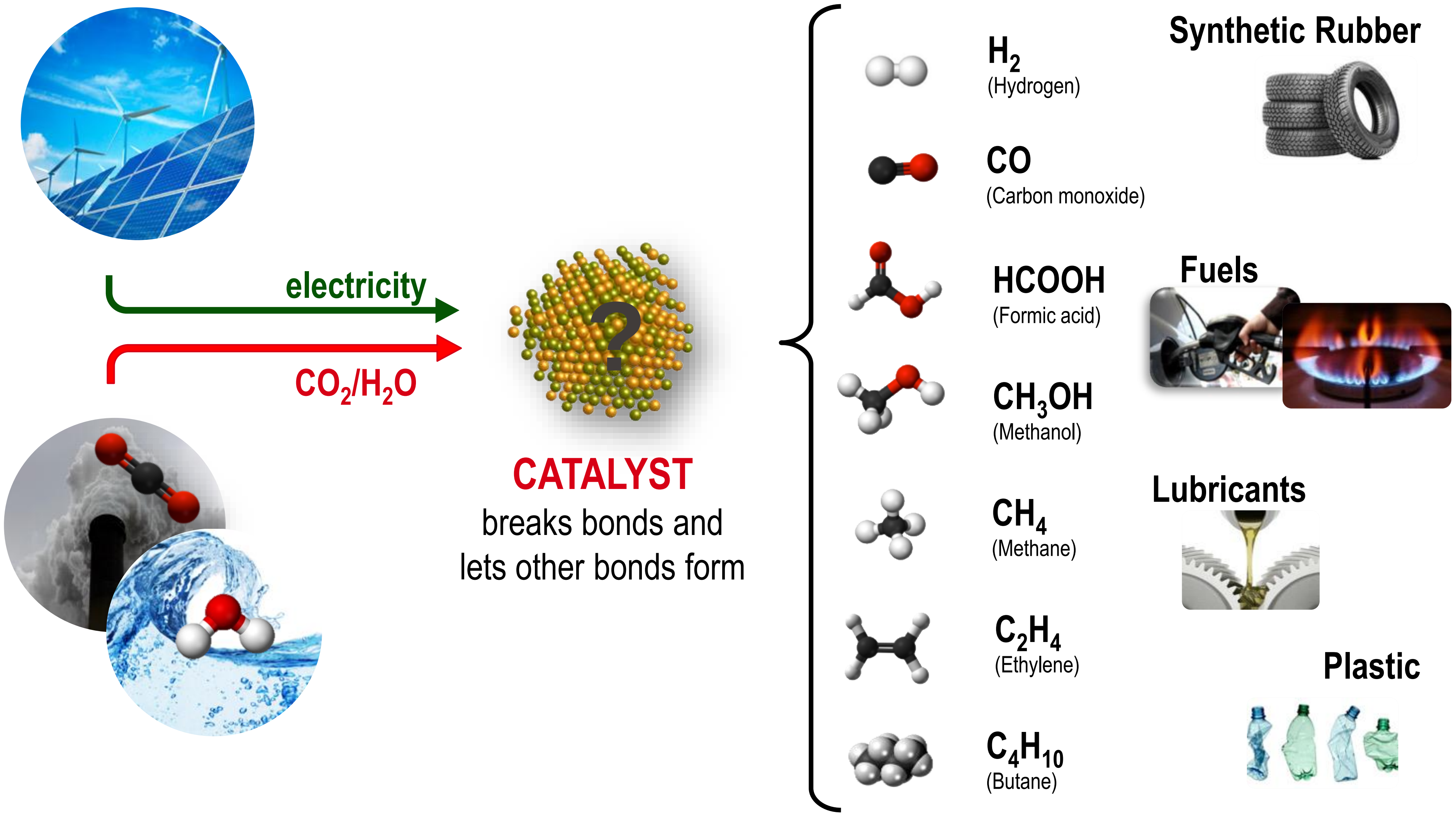
INTRODUCTION

Electrochemical CO_2 Reduction (eCO_2R)



electricity

CO_2/H_2O

CATALYST

breaks bonds and lets other bonds form

H_2 (Hydrogen)

CO (Carbon monoxide)

$HCOOH$ (Formic acid)

CH_3OH (Methanol)

CH_4 (Methane)

C_2H_4 (Ethylene)

C_4H_{10} (Butane)

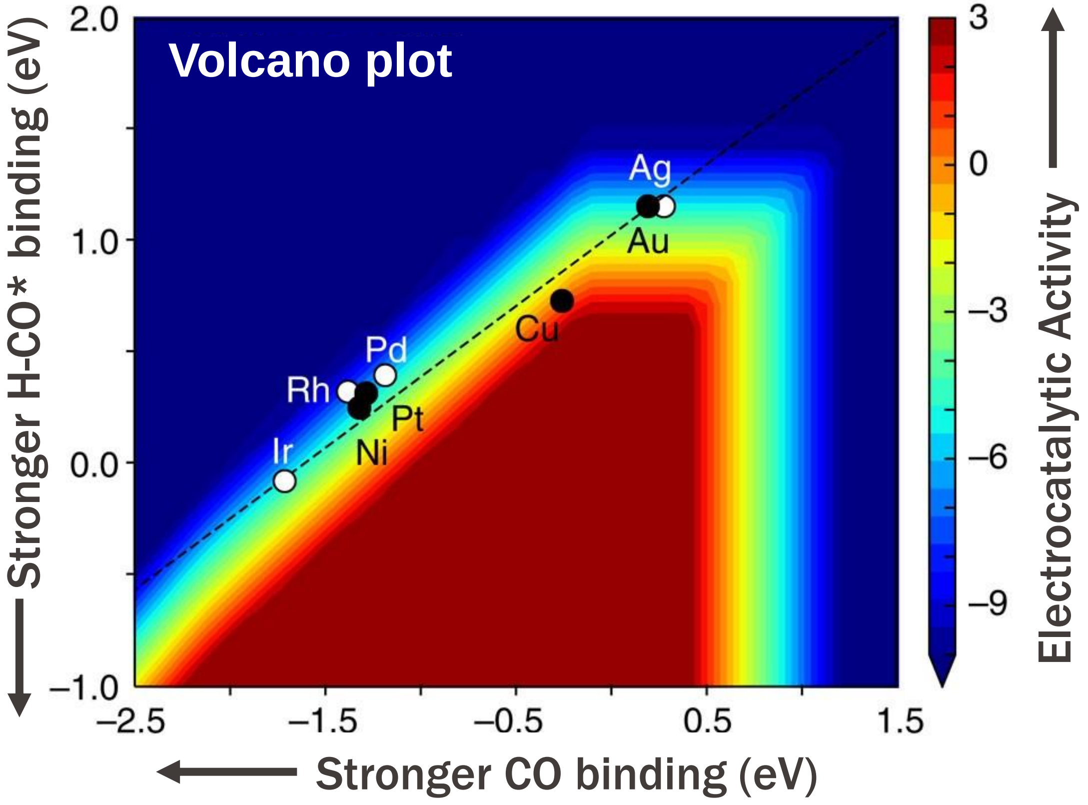
Synthetic Rubber

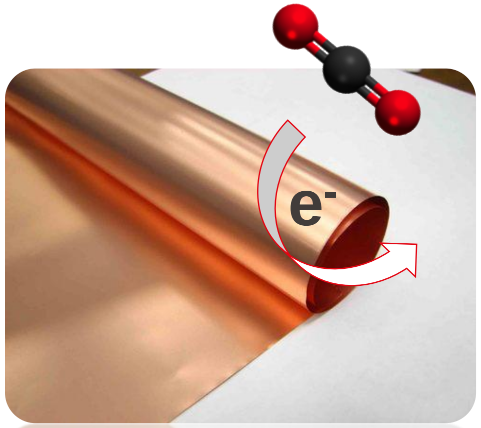
Fuels

Lubricants

Plastic

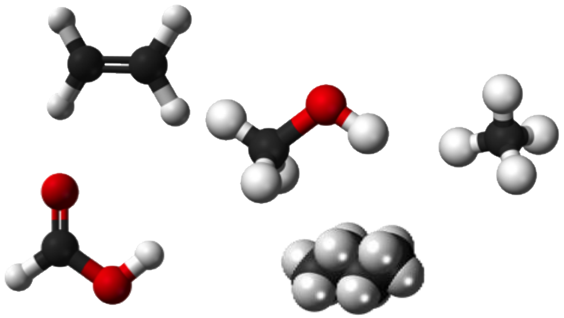
Copper is unique for CO2 reduction





Polycrystalline
Copper

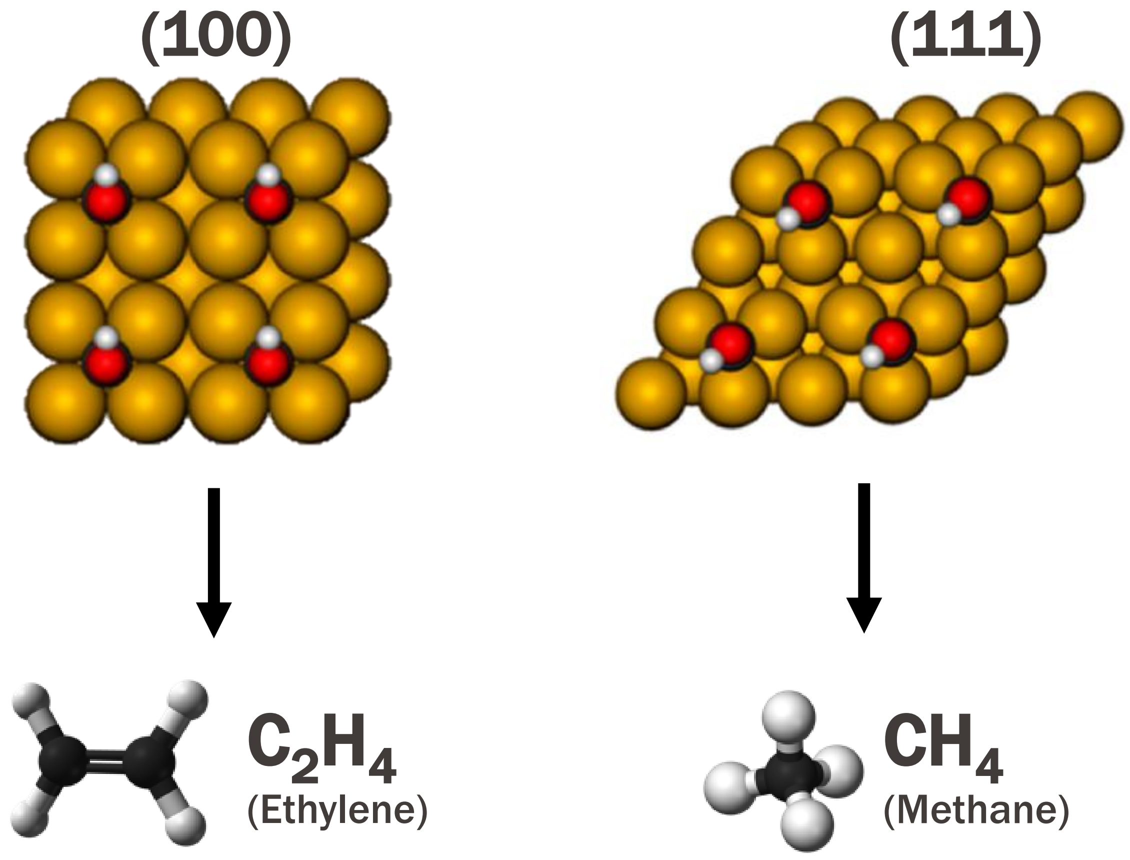
16 different products!



Copper has the right binding energy BUT lack of selectivity!

- Norskov et al., *J. Phys. Chem. Lett.* (**2013**) ; Kuhl et al., *Energy Environ. Chem.* (**2012**)

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

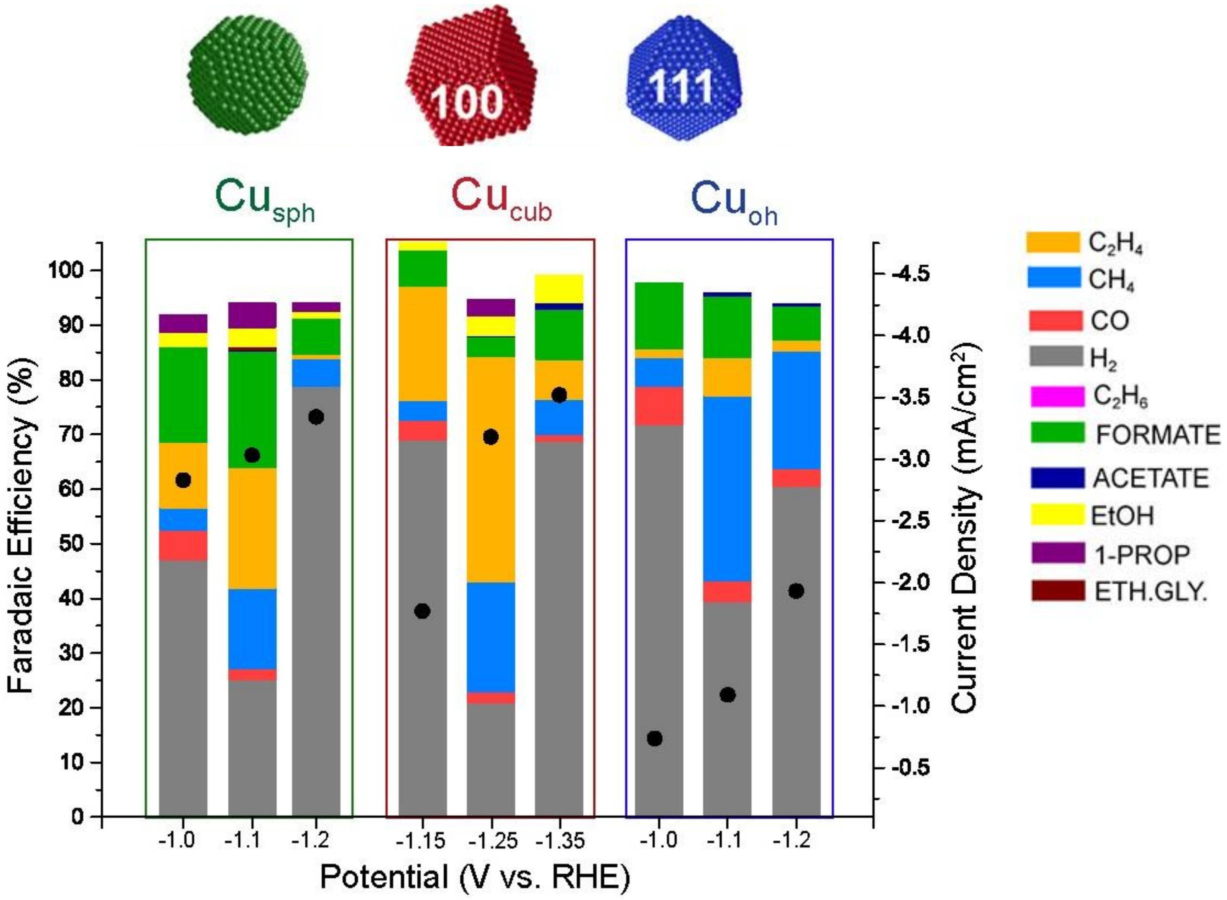


(100)

(111)

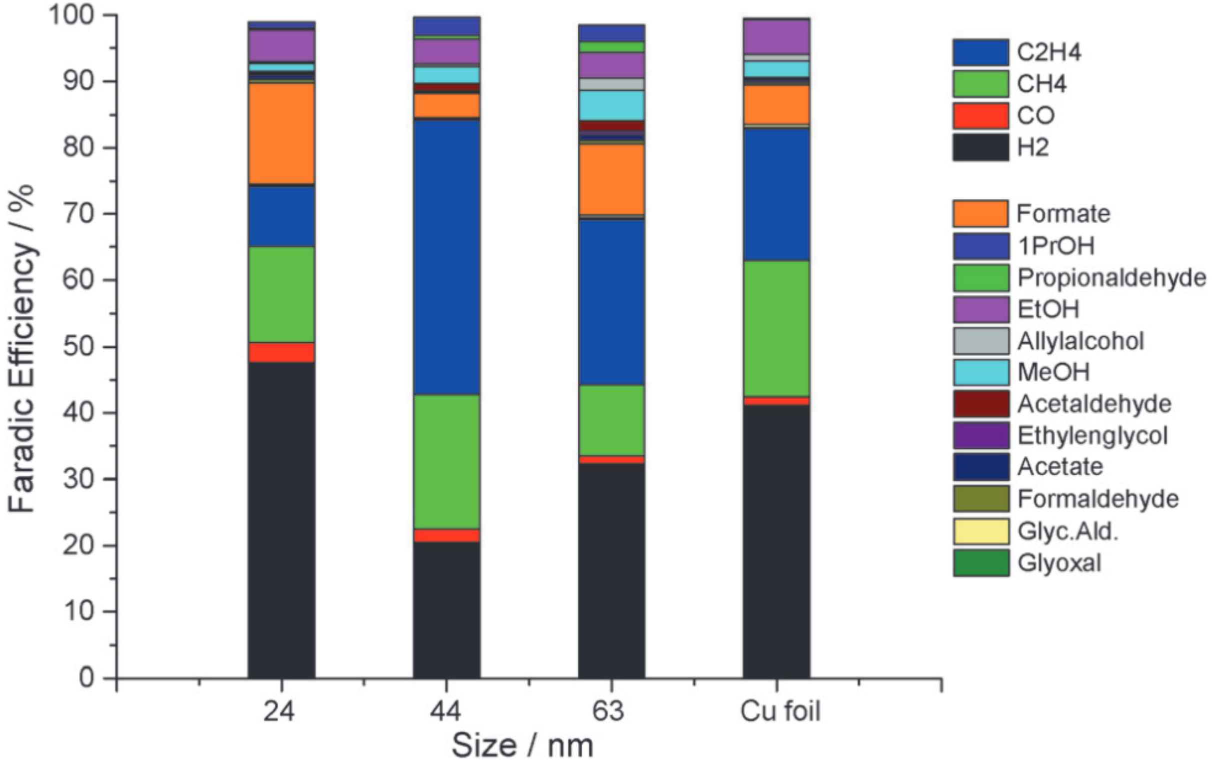
C_2H_4
(Ethylene)

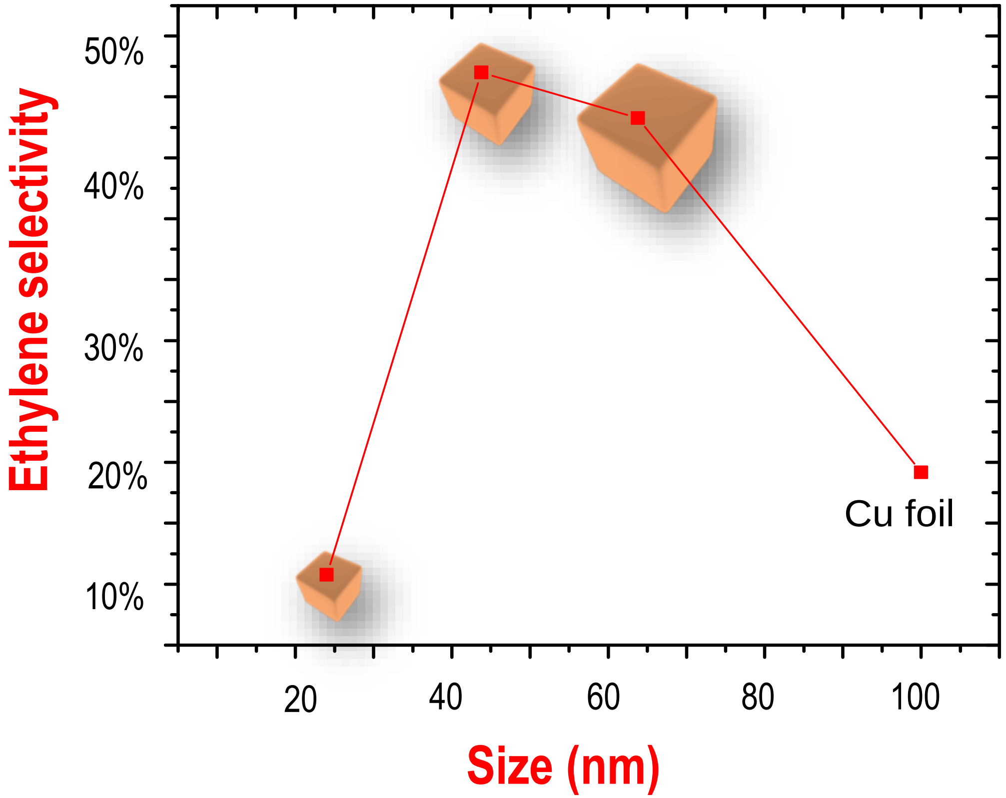
CH_4
(Methane)



- Hori et al. *J. Mol. Catal. A: Chem.* (**2003**) ; De Gregorio et al., *ACS Catal.* (**2020**)

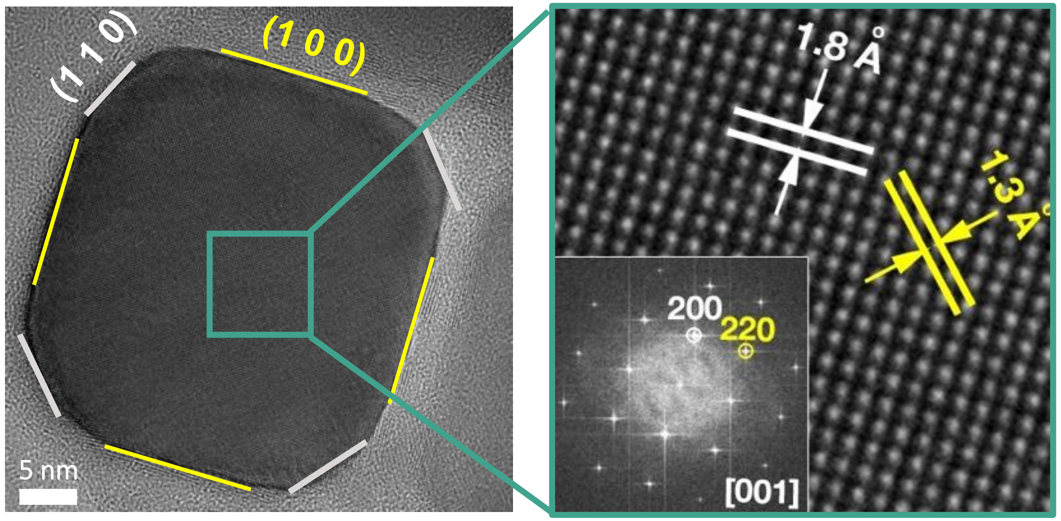
44nm cubes show the highest selectivity towards ethylene!

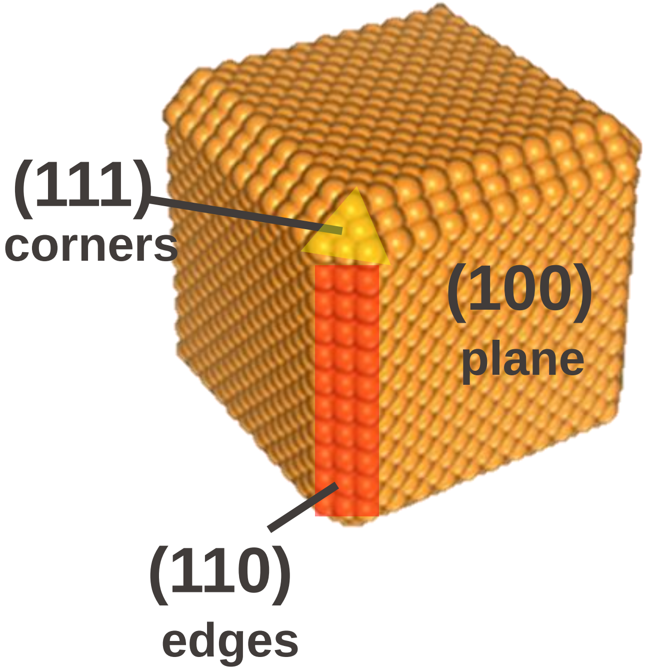




- A. Loiudice et al., *ACIE* (**2016**)

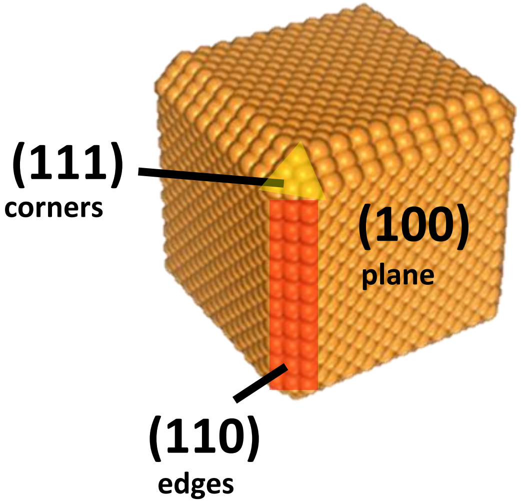
Learning about the crystal structure of the cubes

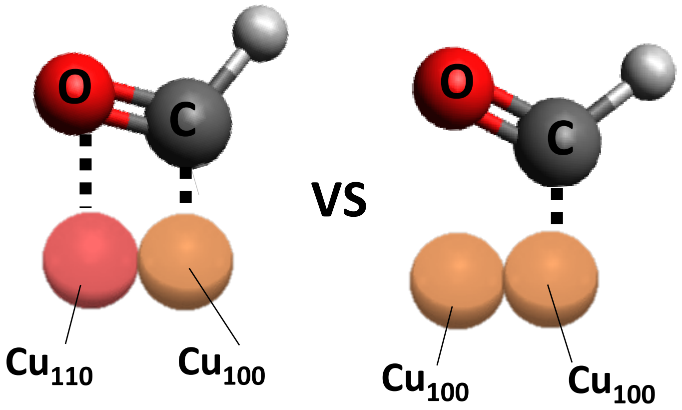




- J. Huang et al., *Nat. Comm.* (**2018**)

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 ($Cu_{edges}/Cu_{planes}=0.025$)

Lab days organization

~ 40 nm
copper cubes

Day 1
Colloidal Synthesis

Day 2
Characterization

Transmission electron microscopy (TEM)

X-ray diffraction (XRD)

Inductively coupled plasma - optical emission spectrometry (ICP-OES)

Dropcasting the electrodes
Electrochemistry experiment

Day 2
CO2RR tests

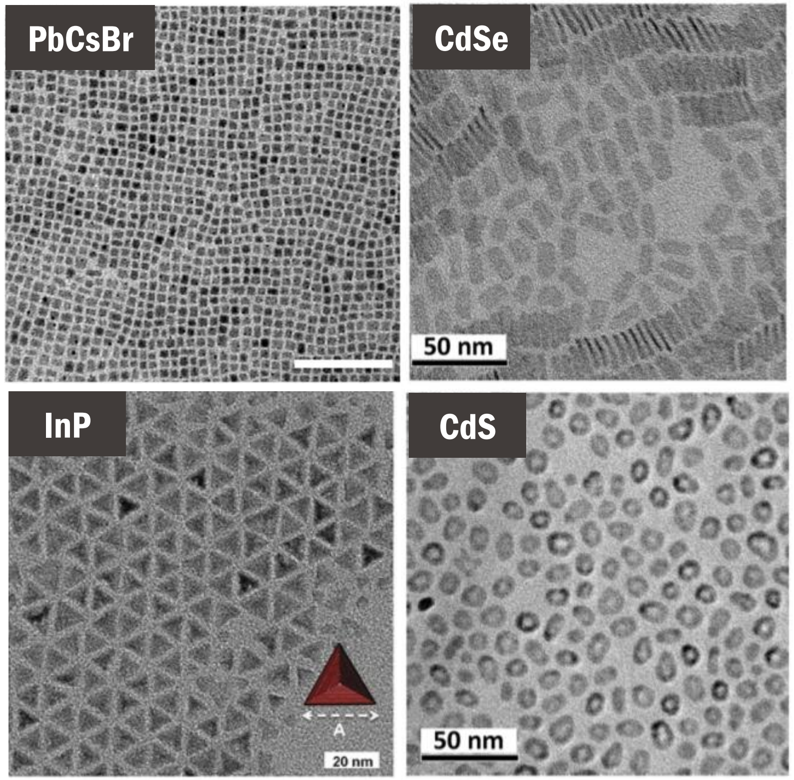
COLLOIDAL SYNTHESIS

Recap on Colloidal Synthesis

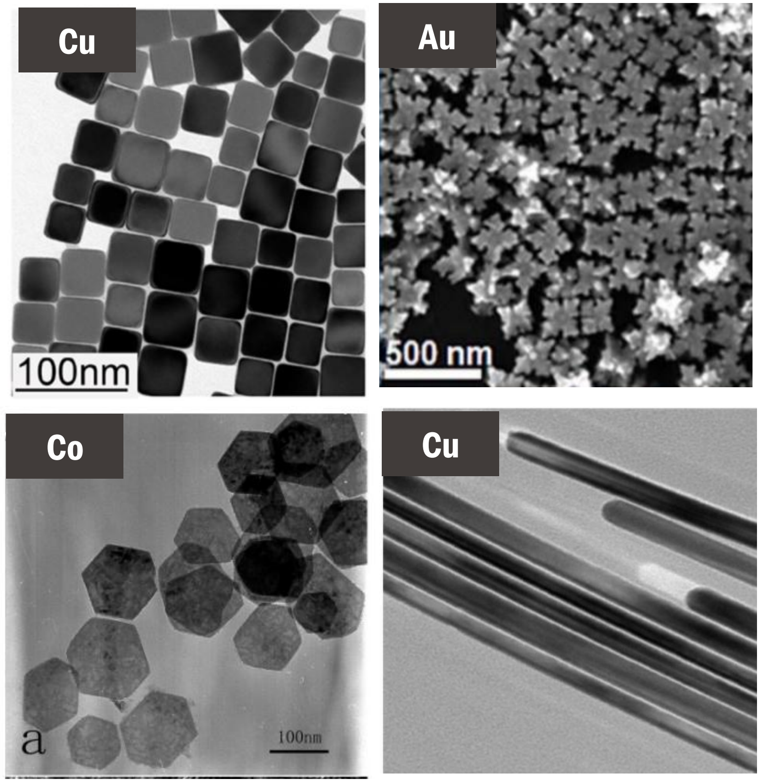
What: Wet chemistry approach in organic solvent and (often) carried out under inert atmosphere in presence of organic surfactants where decomposition of precursors lead to monomers and then to NCs

Why:

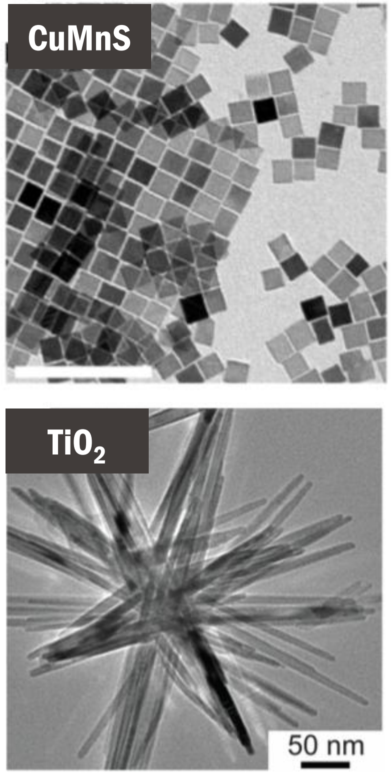
Semiconductors - QDs



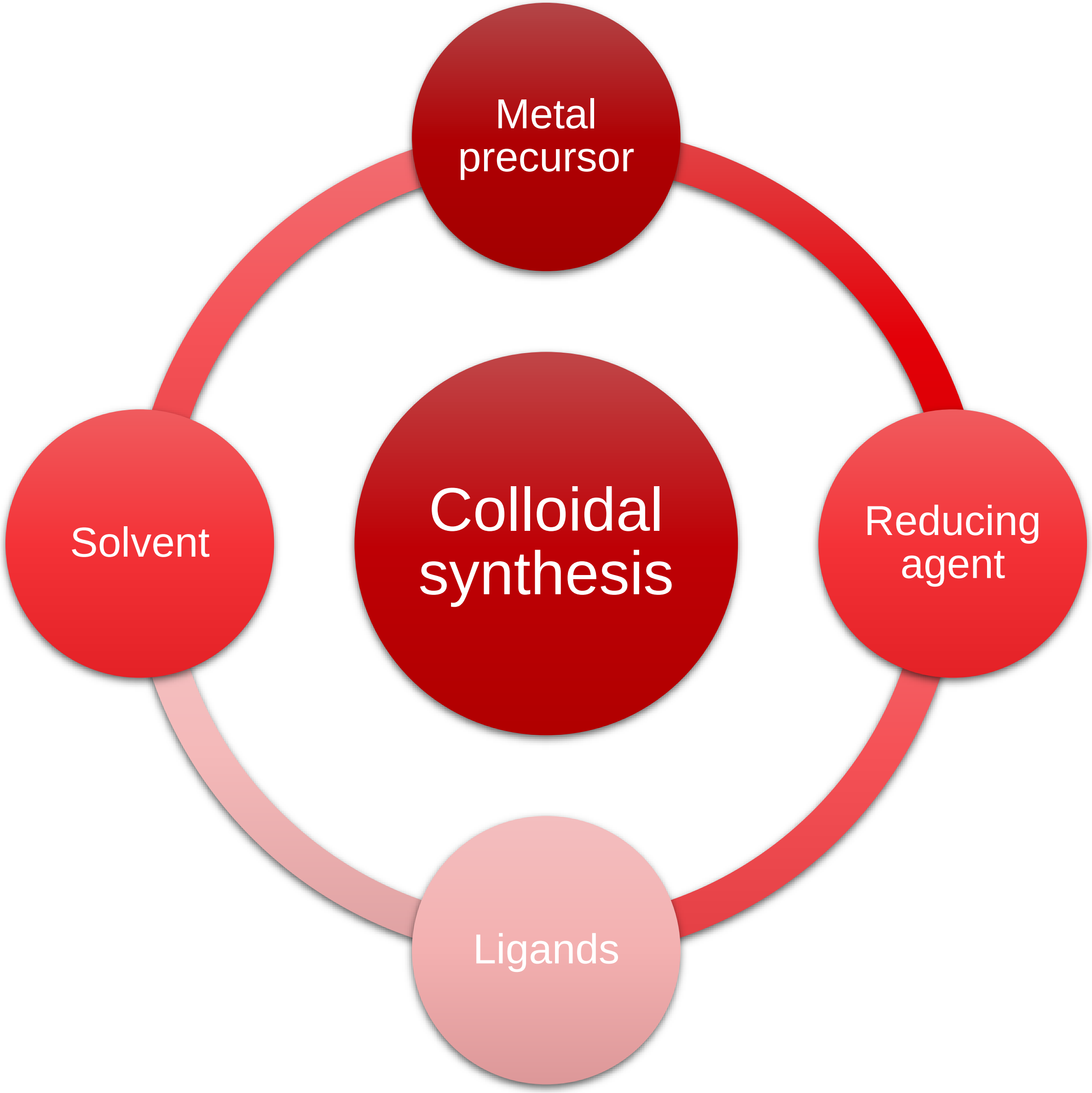
Metal Nanocrystals



Metal-Oxide



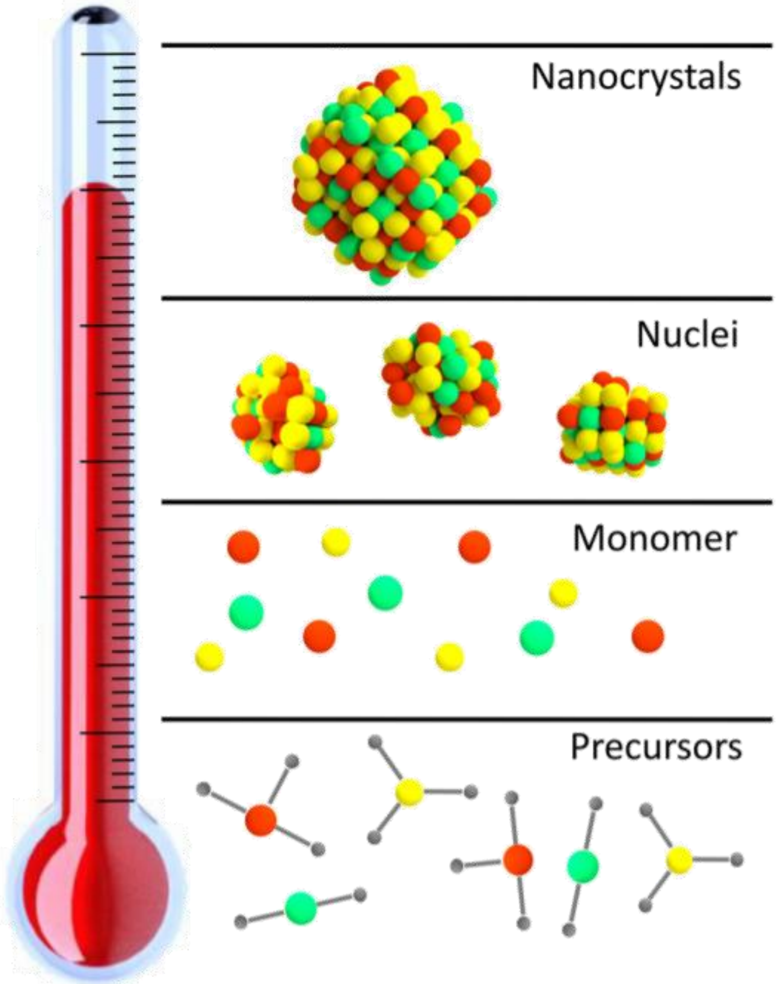
Rule of thumb in colloidal chemistry

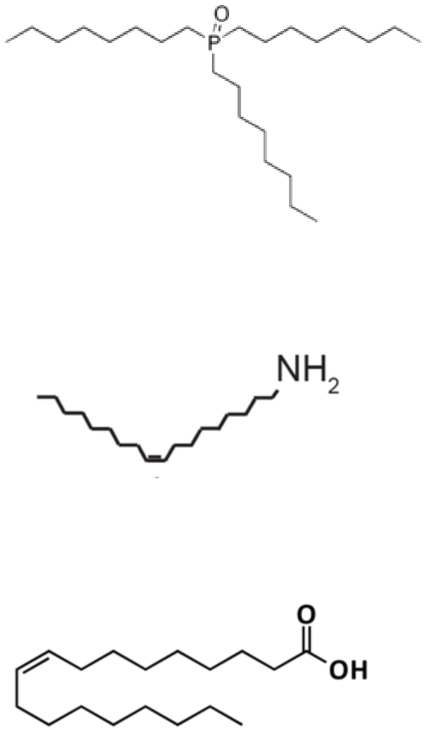


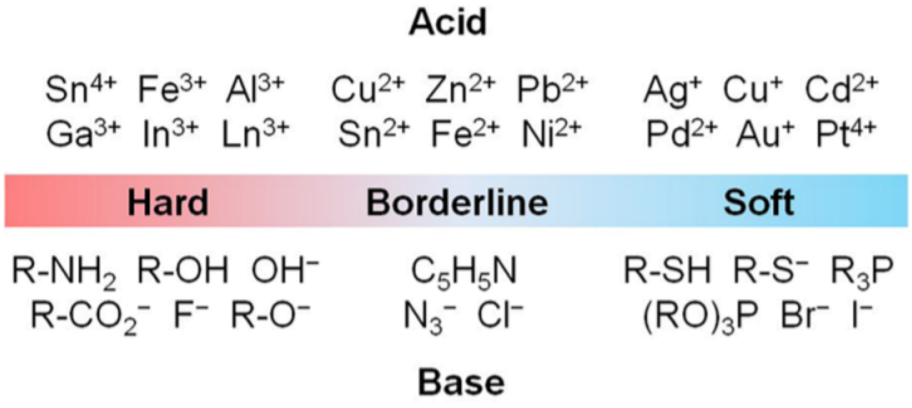
Some chemicals can
play more than one role!

Shape-Controlled Synthesis - Simple Chemistry Meets Complex Physics

How:



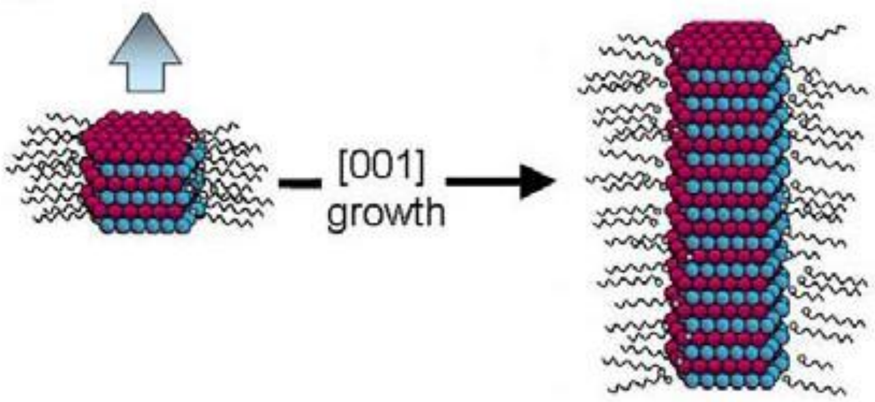




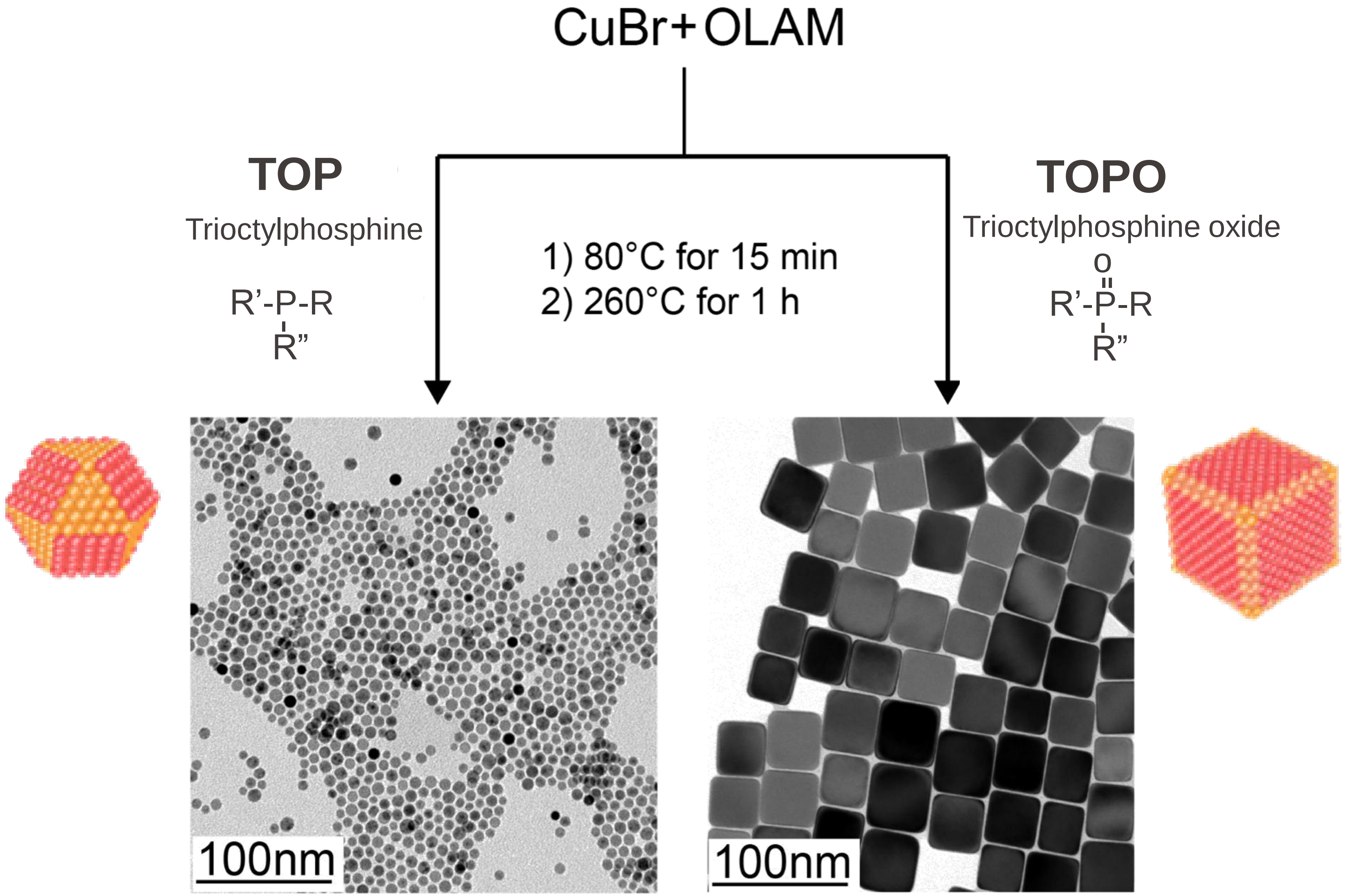
Acid

Hard	Borderline	Soft
Sn^{4+} Fe^{3+} Al^{3+} Ga^{3+} In^{3+} Ln^{3+}	Cu^{2+} Zn^{2+} Pb^{2+} Sn^{2+} Fe^{2+} Ni^{2+}	Ag^{+} Cu^{+} Cd^{2+} Pd^{2+} Au^{+} Pt^{4+}
$R\text{-}NH_2$ $R\text{-}OH$ OH^- $R\text{-}CO_2^-$ F^- $R\text{-}O^-$	C_5H_5N N_3^- Cl^-	$R\text{-}SH$ $R\text{-}S^-$ R_3P $(RO)_3P$ Br^- I^-

Base



Shape selectivity with Cu Nanocrystals – Key role of the ligands



CuBr+OLAM

TOP

Trioctylphosphine

$$R'\text{-}\underset{\displaystyle R''}{\underset{|}{P}}\text{-}R$$

1) 80°C for 15 min

2) 260°C for 1 h

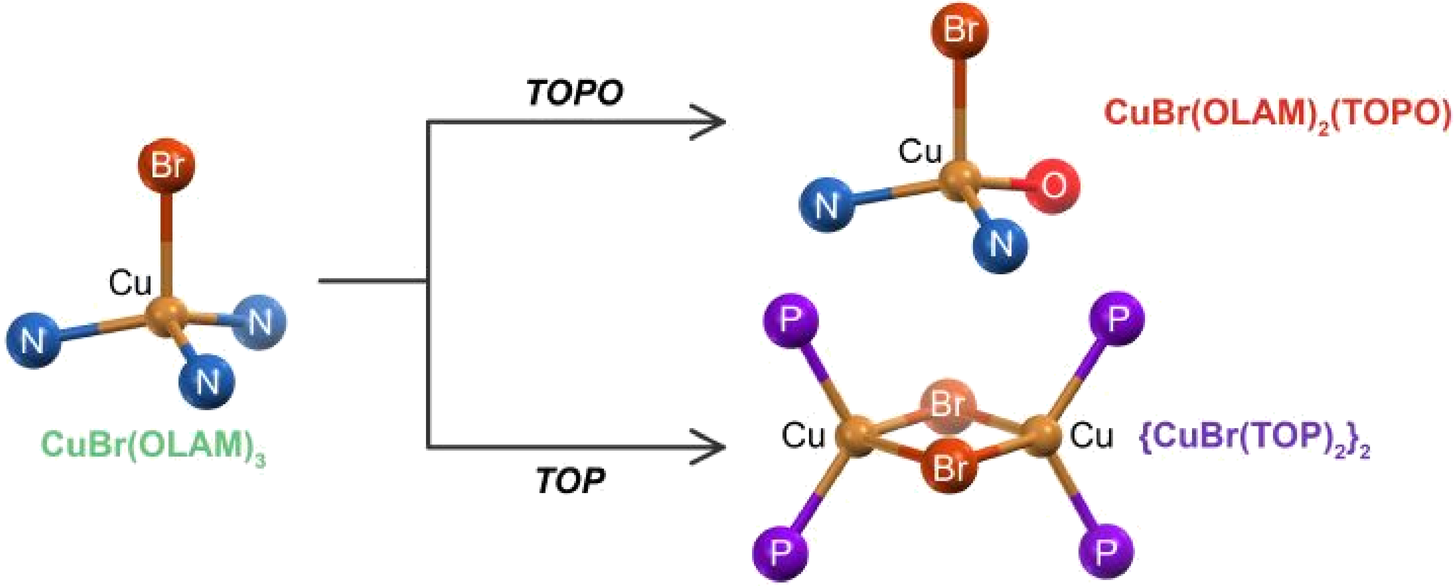
TOPO

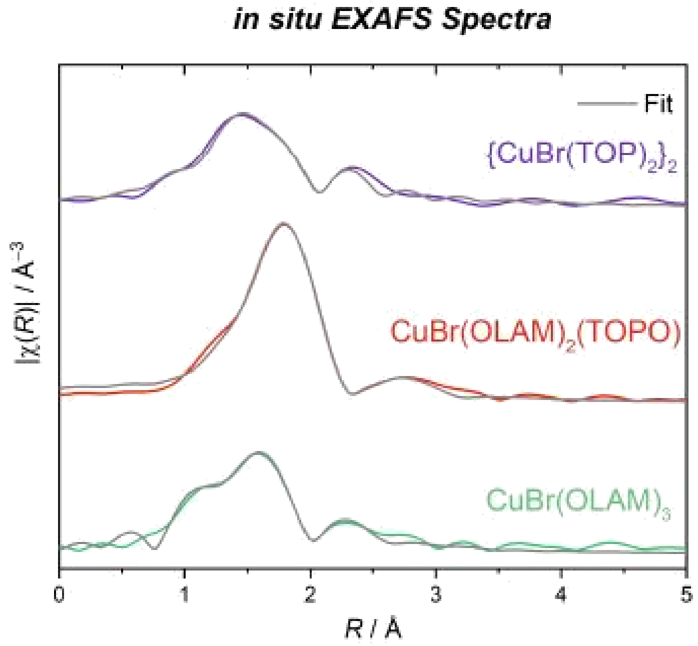
Trioctylphosphine oxide

$$R'\text{-}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R''}{\underset{|}{P}}}}\text{-}R$$

Identification of monomers

Plateau at 80°C



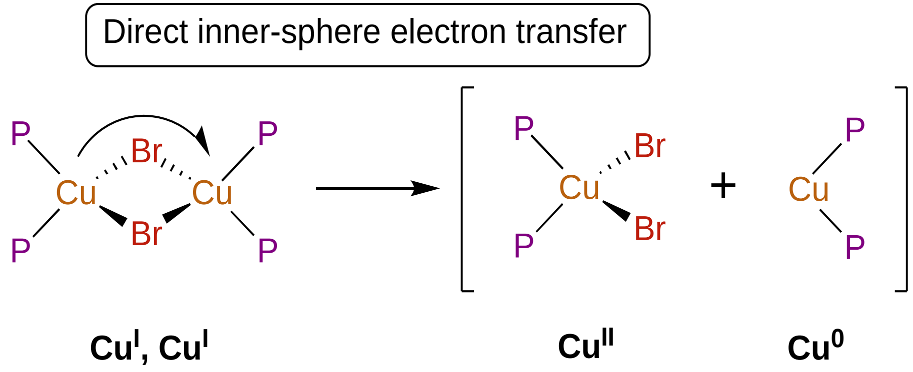


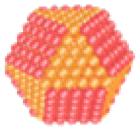
TOPO and TOP both act as complexing agents, forming complexes of different properties that then act as intermediates for the monomers

M. Strach*, V.Mantella*, J. R. Pankhurst,* R. Buonsanti et. al. *J. Am. Chem. Soc*. (2019)

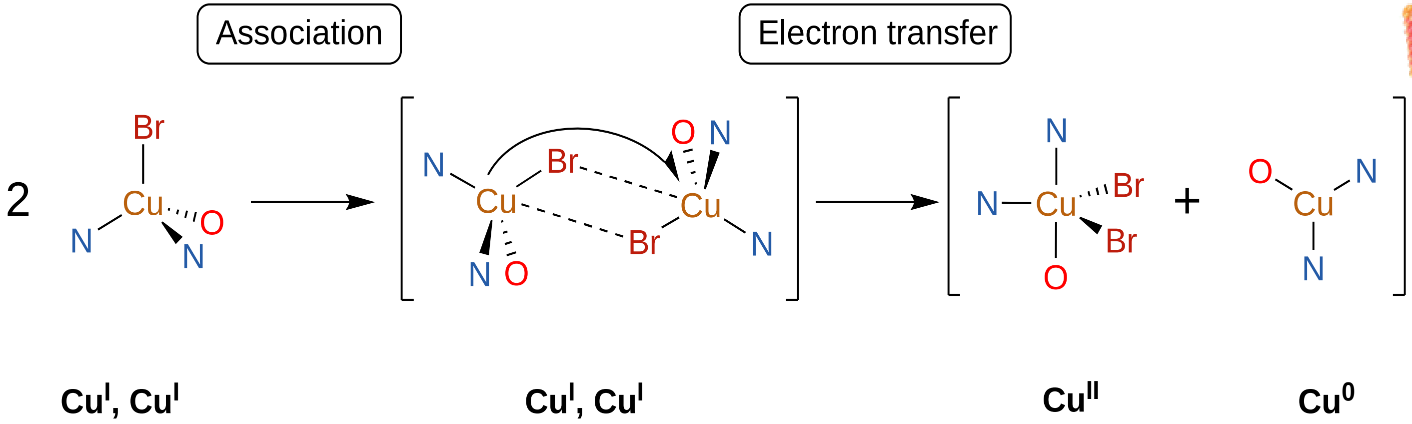
The chemical nature of the Cu(I)-complexes explains the different disproportionation kinetics

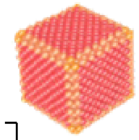
TOP synthesis





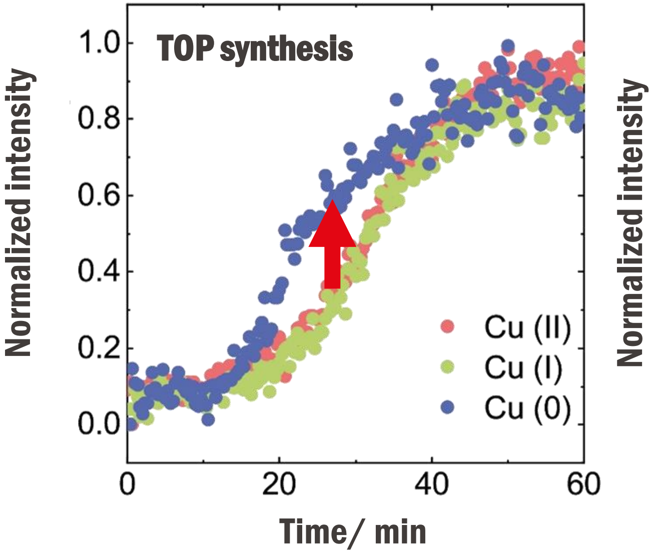
TOPO synthesis





- M. Strach*, V.Mantella*, J. R. Pankhurst,* R. Buonsanti et. al. *J. Am. Chem. Soc*. (2019)

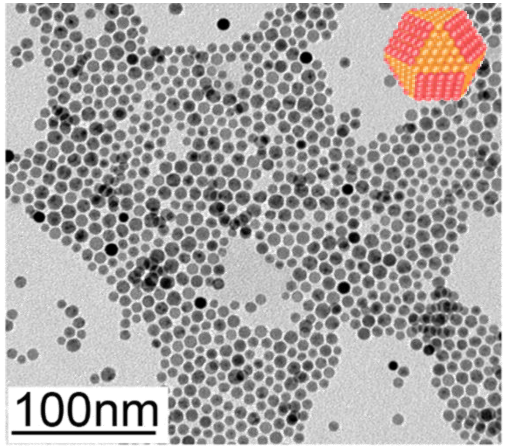
The monomer flux is key to differentiate between thermodynamic and kinetic products…

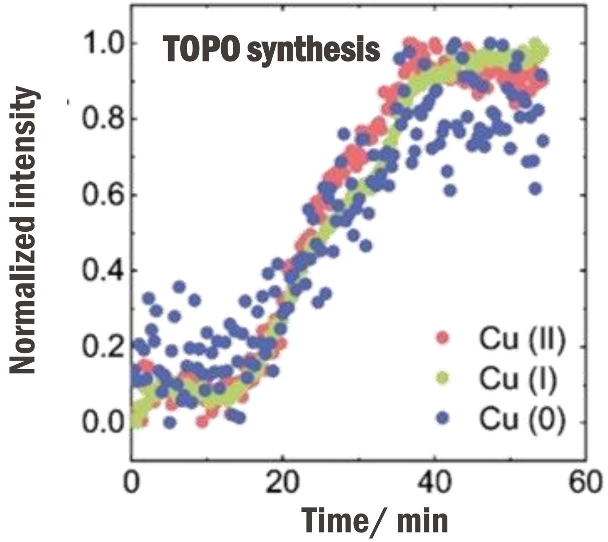


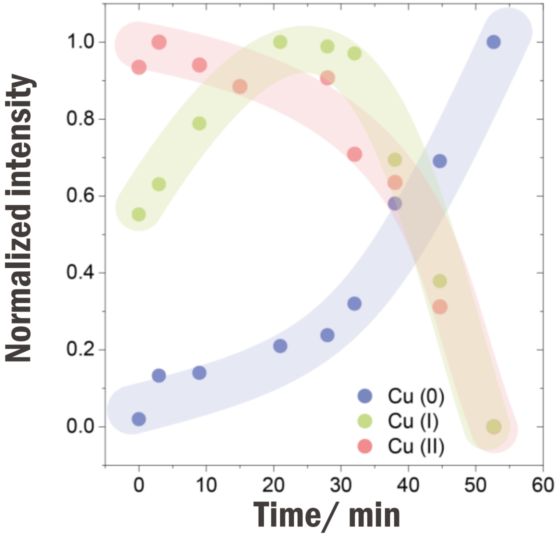
Cu(0)=monomers

Gradual monomer release

Thermodynamic regime

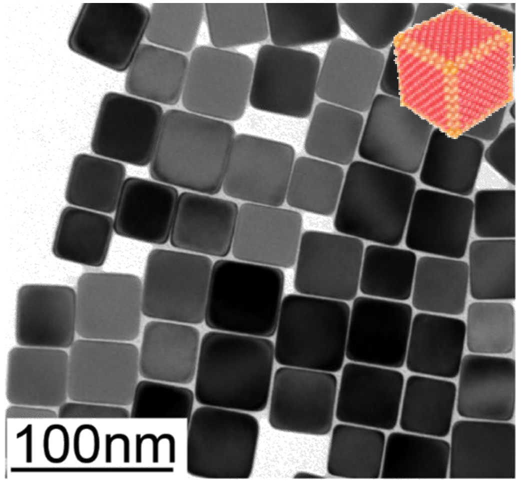






Fast monomer release

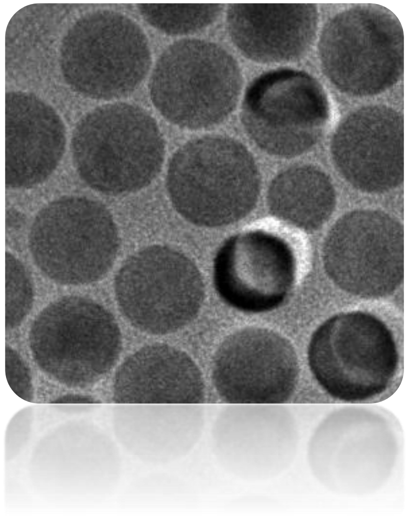
Kinetic regime



Conclusions

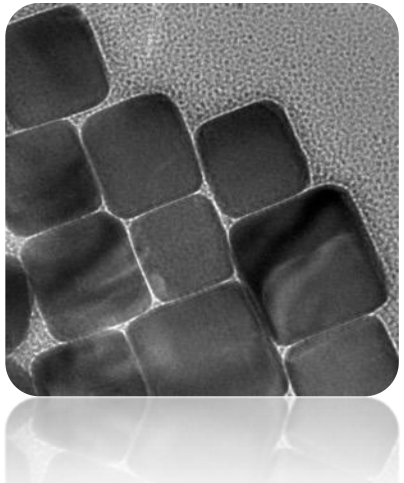
- ❖ Nanocube or Nanosphere synthesis by monomer flux control.
- ❖ The added ligand, TOP or TOPO, complex with the precursor forming complexes with different properties
- ❖ TOP complexing results in a dimeric complex for which disproportionation happens easily and gradually

  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)

Why XRD and TEM ?

Information we can gain from:

X-Ray Diffraction (XRD)

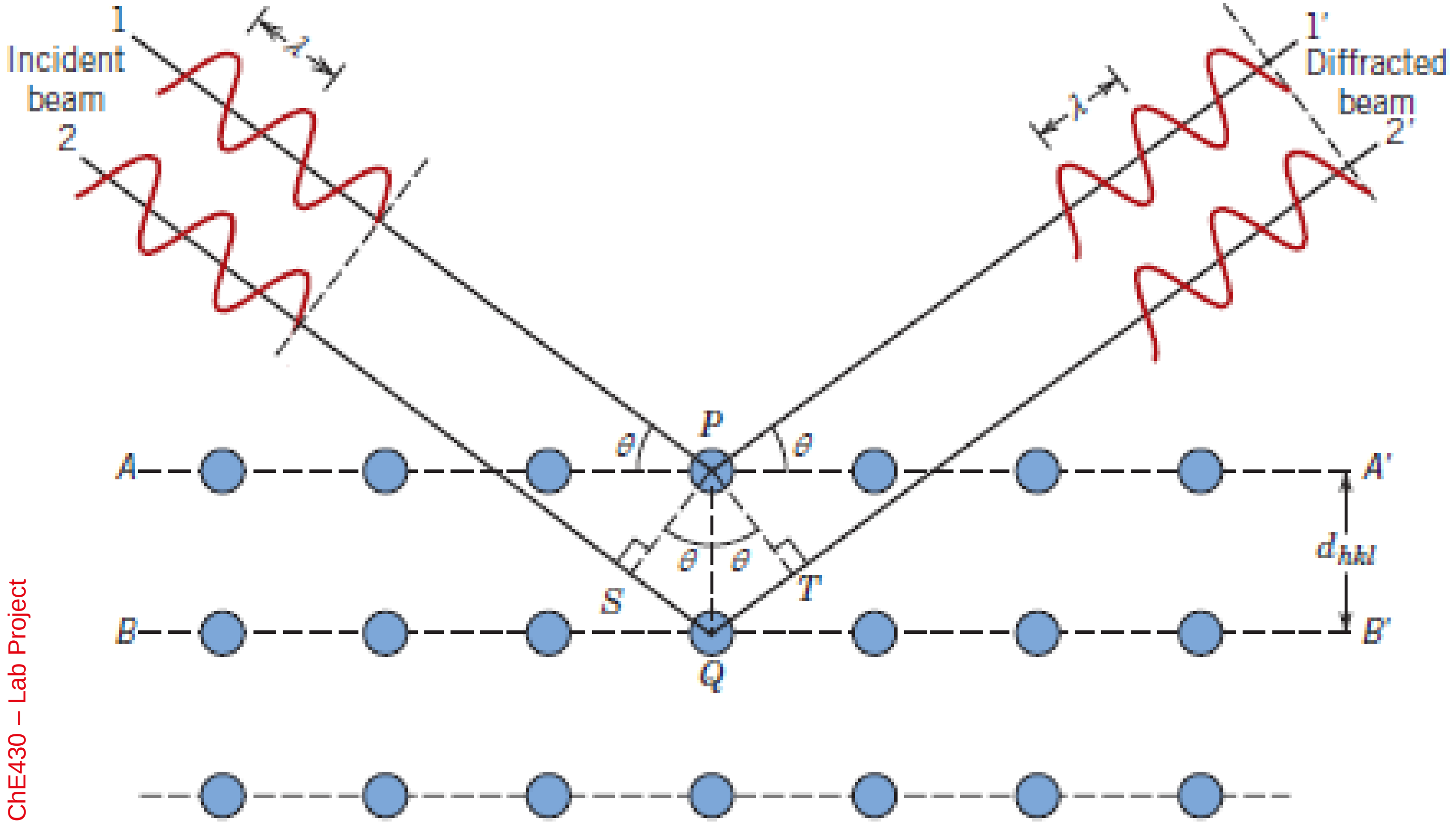
- **Crystal structure**
- **Lattice parameters**
- **Phase composition**

Transmission Electron Microscopy (TEM)

- **Shape**
- **Size**
- **Distribution**

A diffraction pattern results from constructive interference of the scattered waves

Diffraction of X-Rays by planes of atoms



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

$$n\lambda = d\sin\theta + d\sin\theta \; = 2d\sin\boldsymbol{\theta}$$

$$\boxed{n\lambda = d\sin\theta}$$

Bragg's law

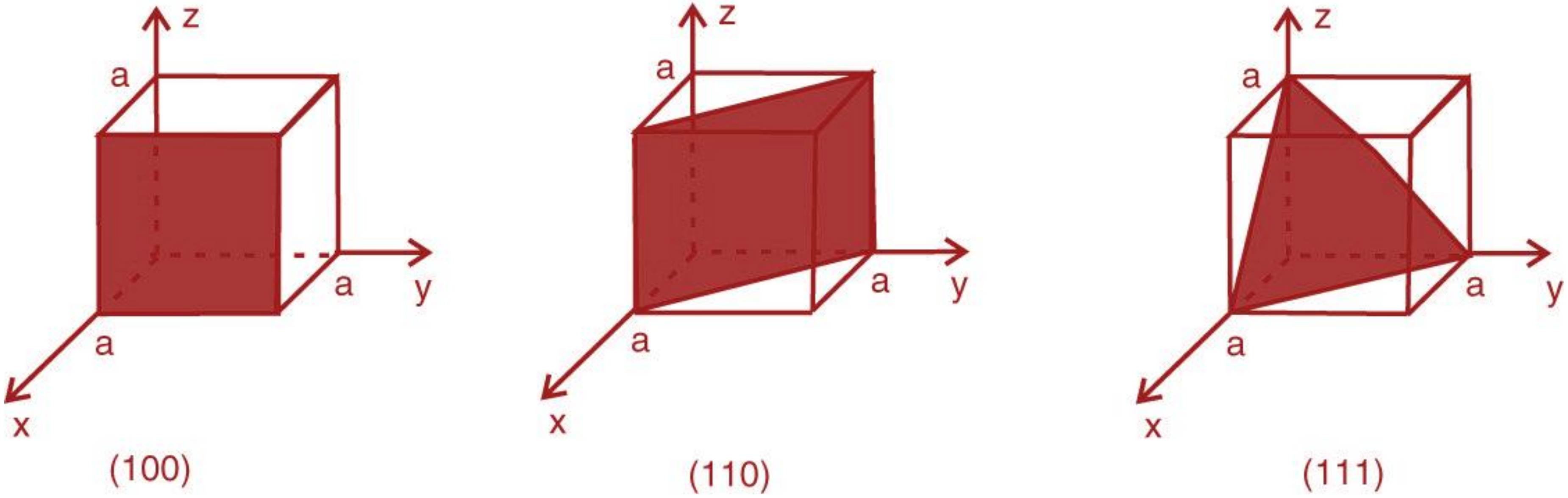
Constructive interference condition

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***.

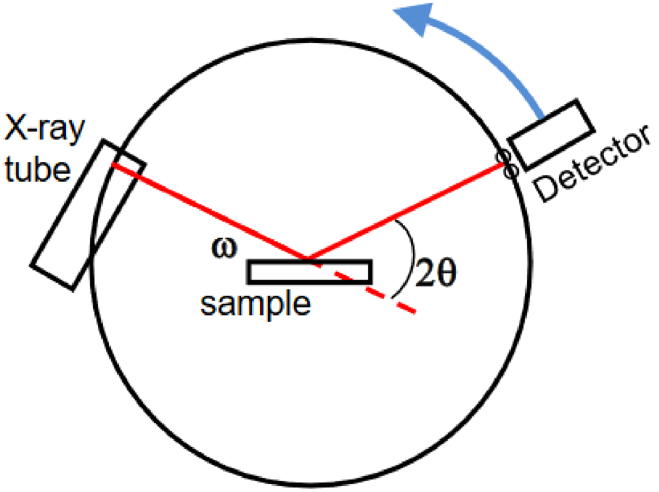
Crystallographic planes are specified by three **Miller indices** as (*hkl*).



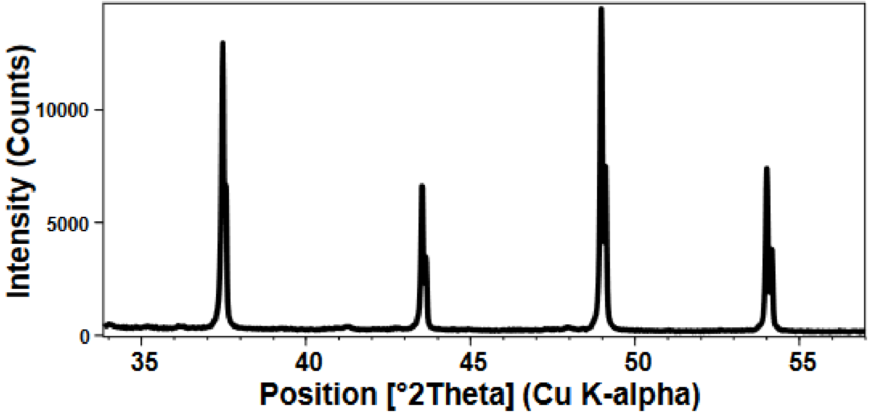
Interplanar spacing d_{hkl} - the magnitude of the distance between two adjacent and parallel planes of atoms

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

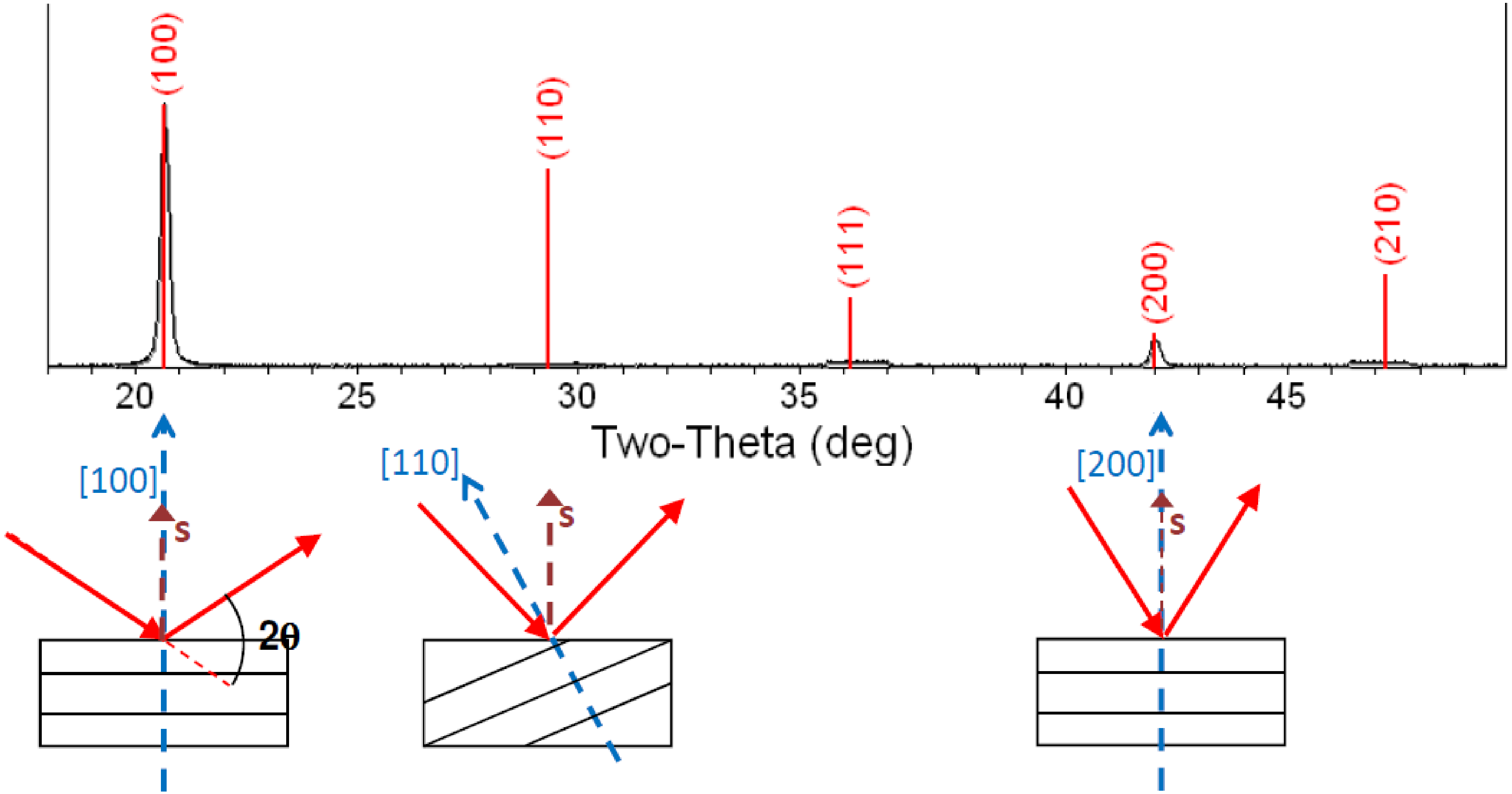


Diffraction pattern



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

XRD pattern of a single crystal (preferred orientation)



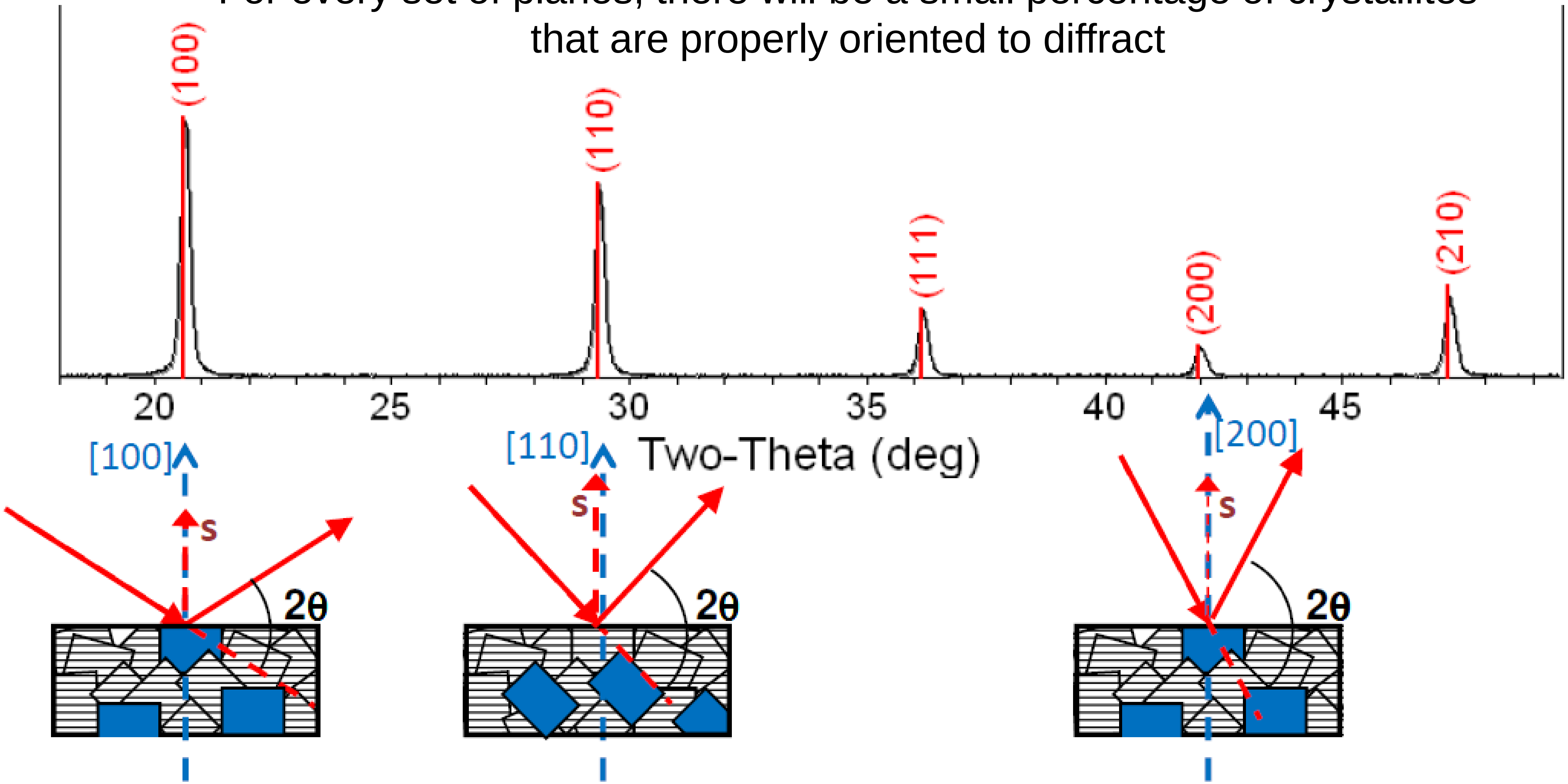
2θ = 20.6°
Plane **(100)**

The plane **(110)** should
give diffraction
at 2θ = 29.3° but
it is not properly aligned

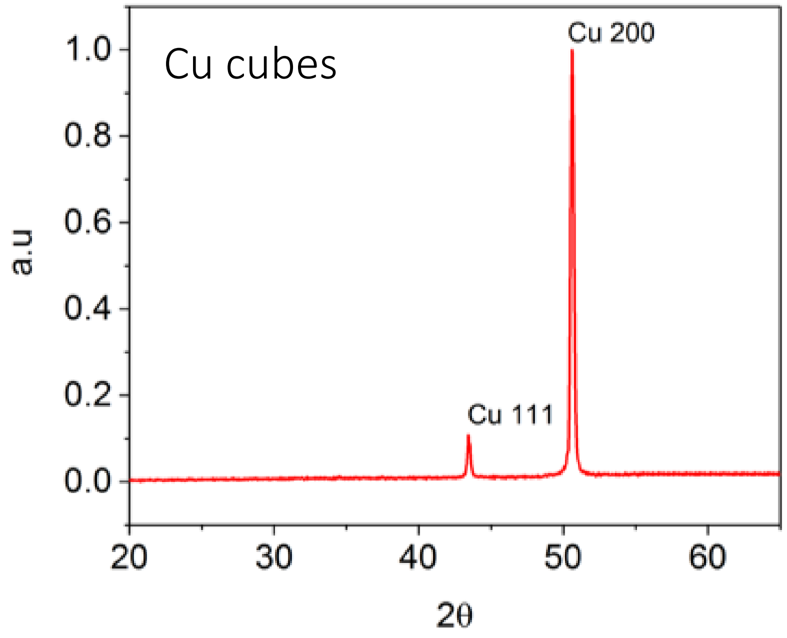
2θ = 41.2°
Plane **(200)**

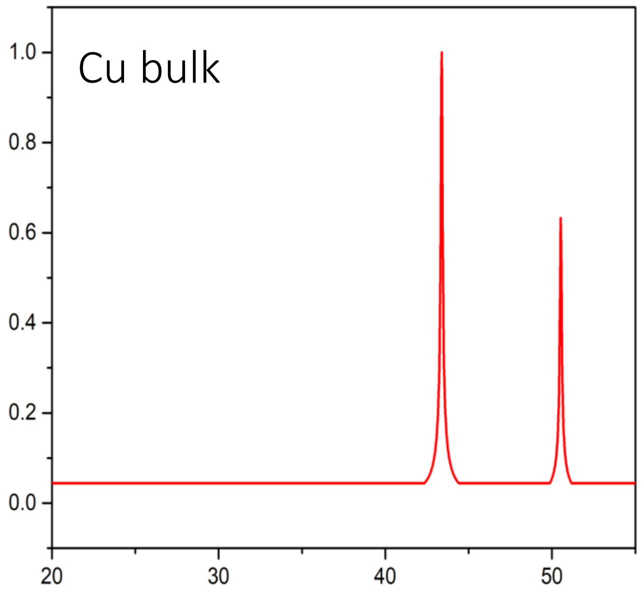
XRD pattern of a polycrystalline sample (random orientation)

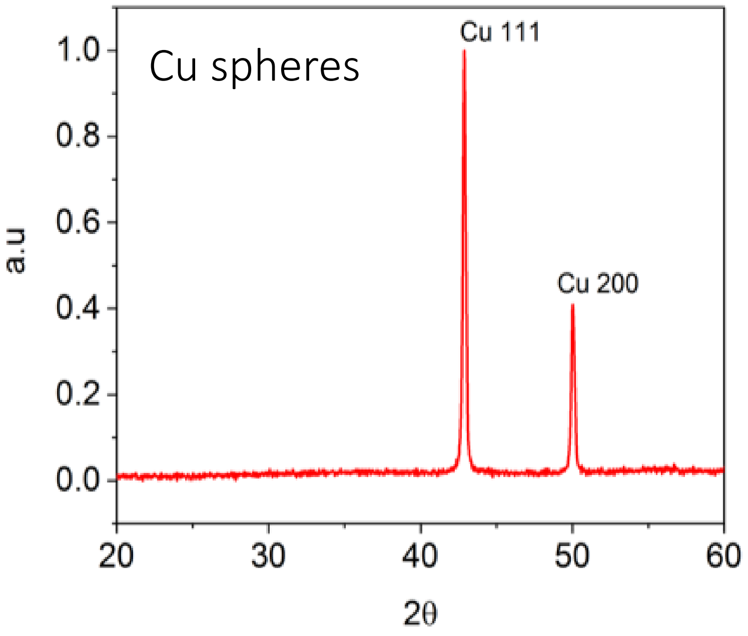
For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract



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







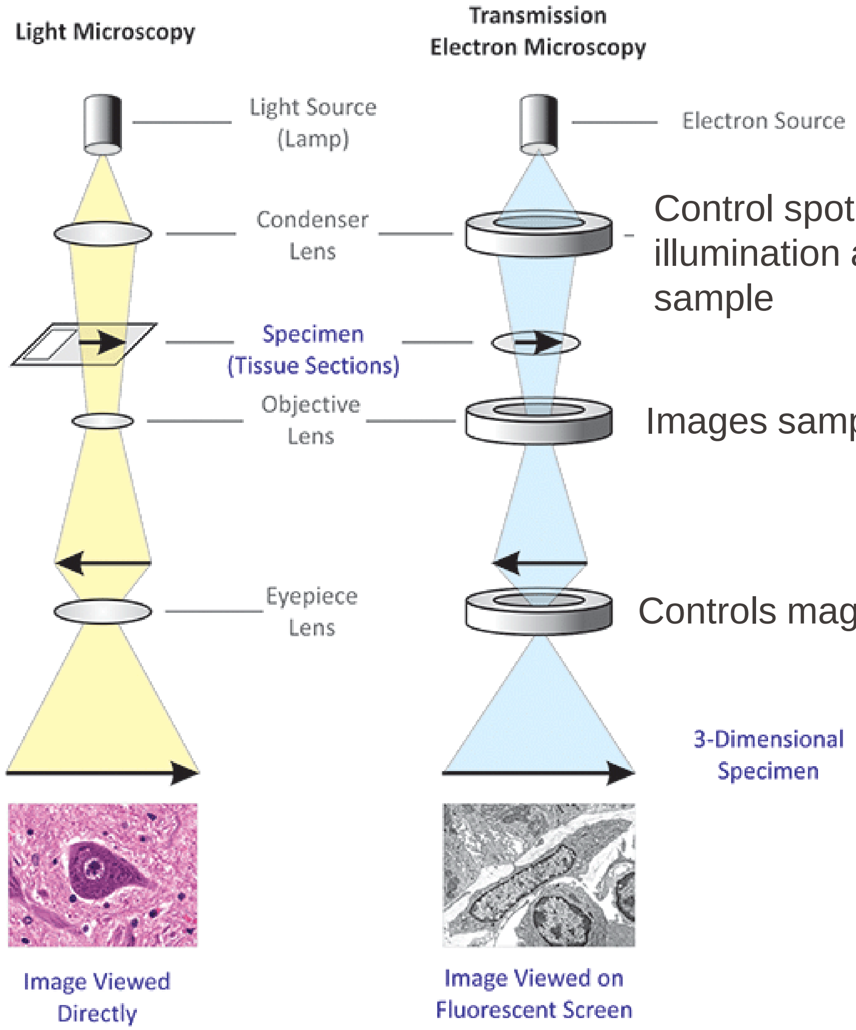
Width → Crystallite size

Intensity →
- Preferred orientation
- Structure factor

↓

Scattering by an atom= f [Z, θ, λ]

TEM: powerful technique to visualize nanometer features



Control spot size and illumination area on the sample

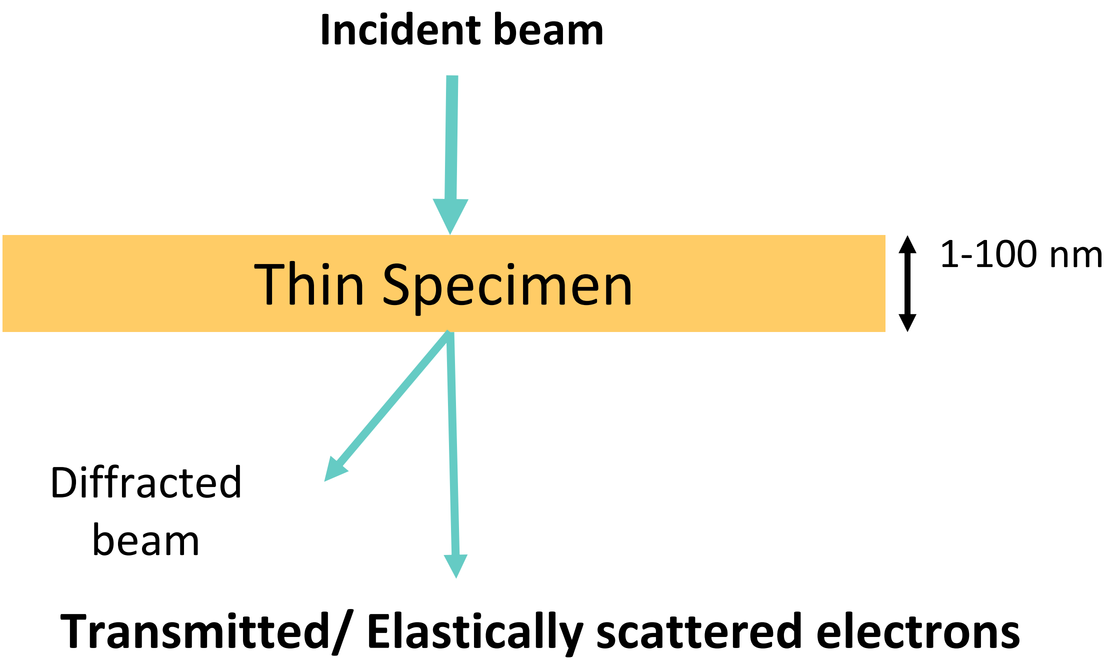
Images sample

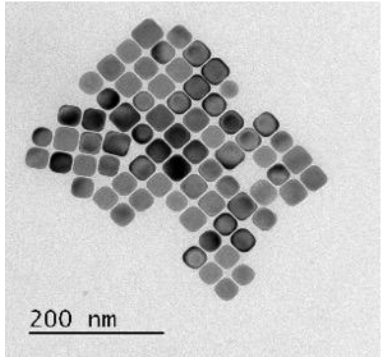
Controls magnification

Theoretical resolution

0.2 µm

0.015 nm





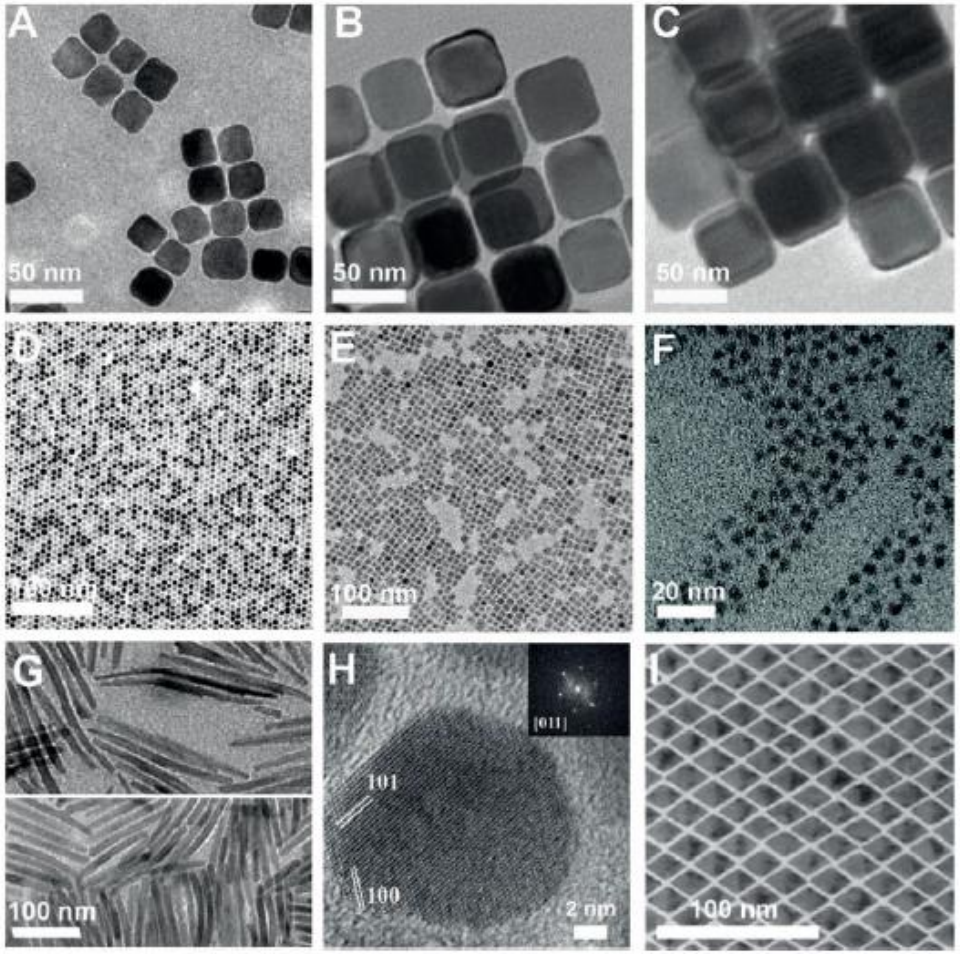
What gives different contrast in TEM images?

Thickness

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

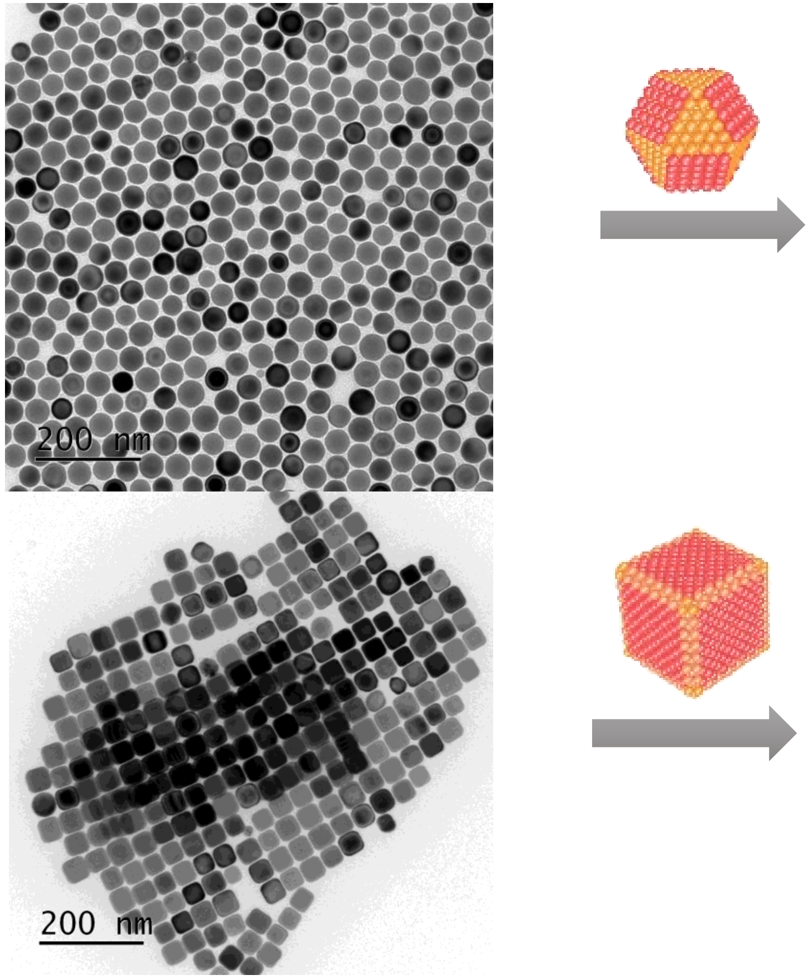
Different atomic numbers (Z)

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

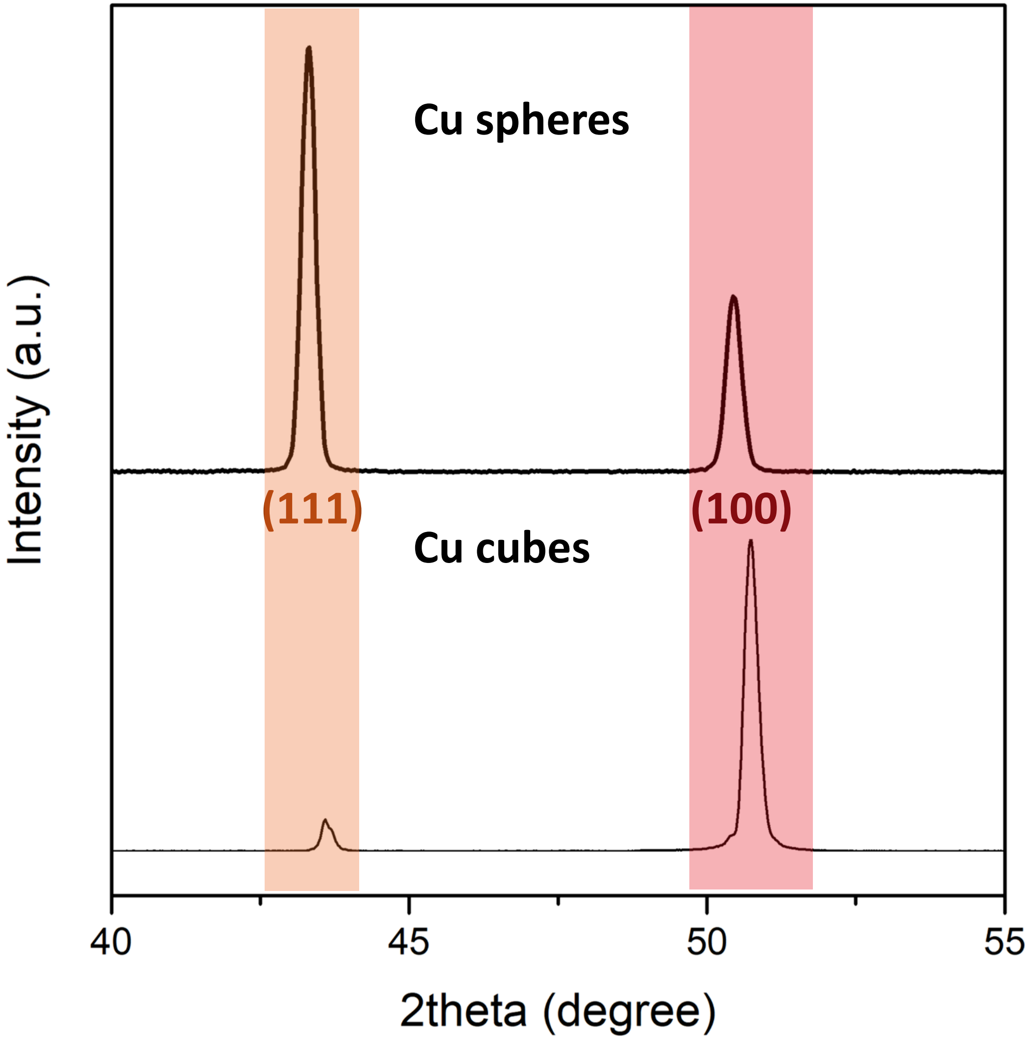


XRD and TEM are the main techniques to characterize the colloidal nanocrystals

Transmission Electron Microscopy (TEM)

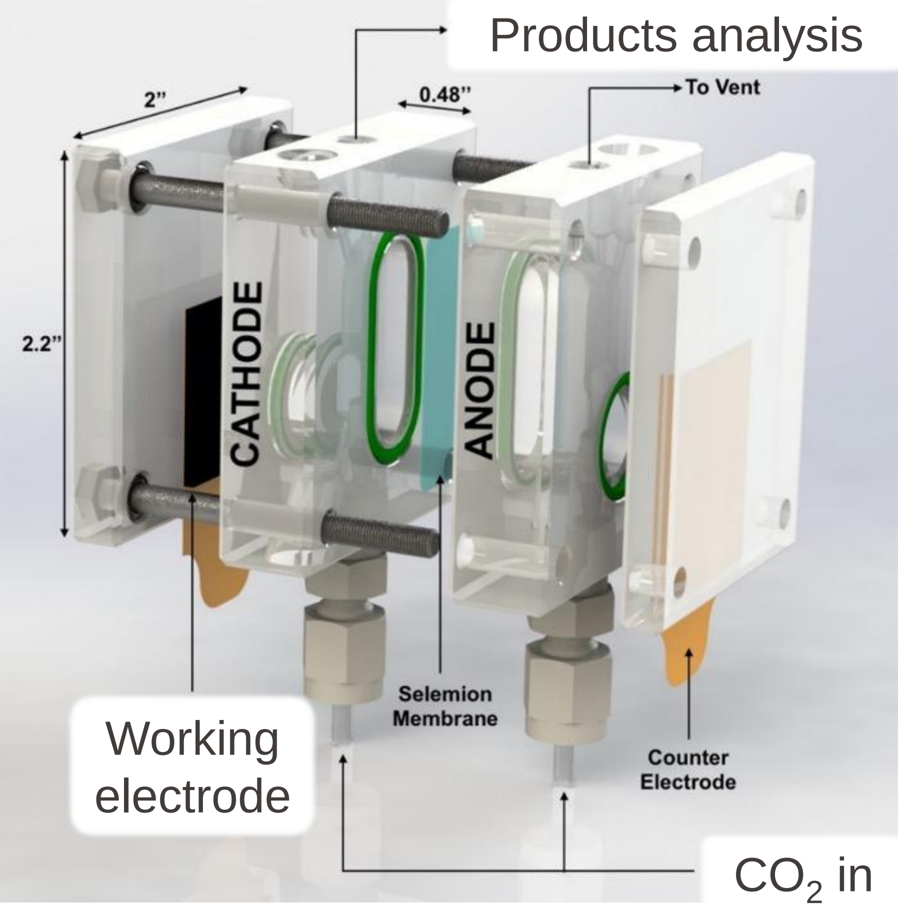


X-Ray Diffraction (XRD)



ELECTROCHEMICAL CO_2 REDUCTION

"Regular" testing is done in liquid H-type cell

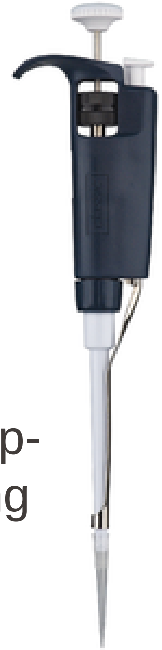


Liquid-fed reactor

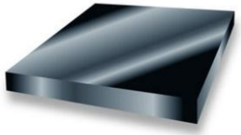
- Continuous flow (CO_2) electrochemical cell
- 0.1 M $KHCO_3$ aqueous electrolyte
- -1.1 to -1.4 V vs. RHE (reversible hydrogen electrode)
- Products analysis: gas chromatography and high-performance liquid chromatography

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

1. Desired quantity of nanocubes solution

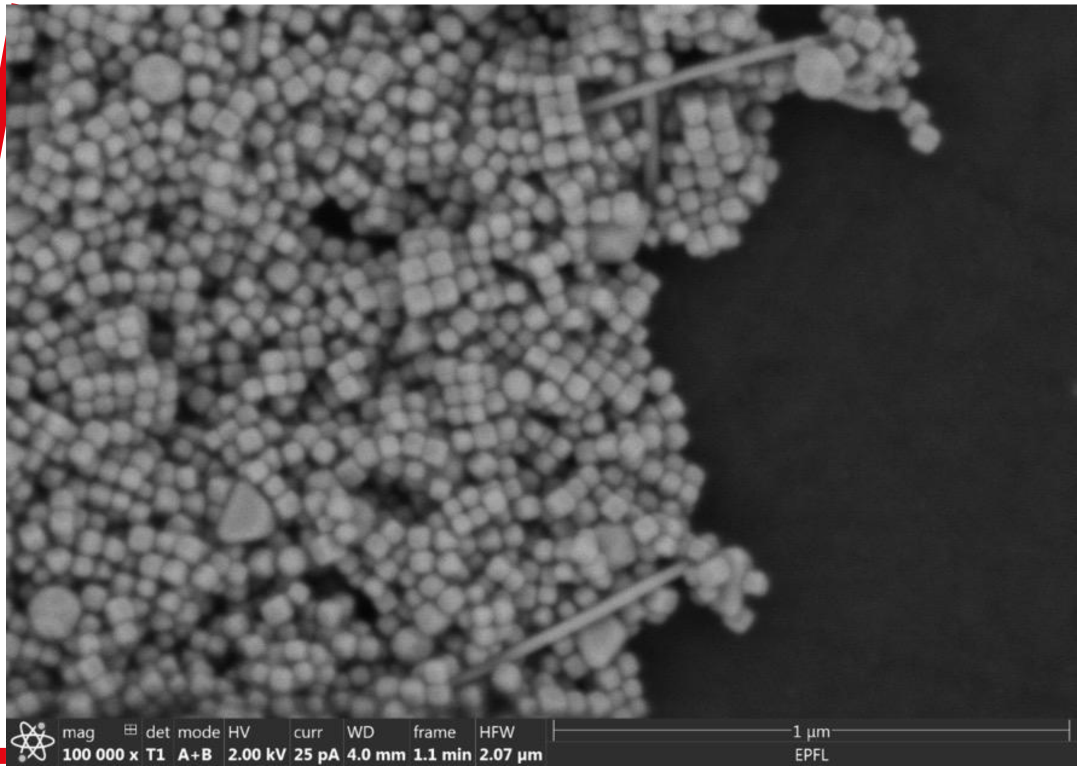


2. Drop-casting



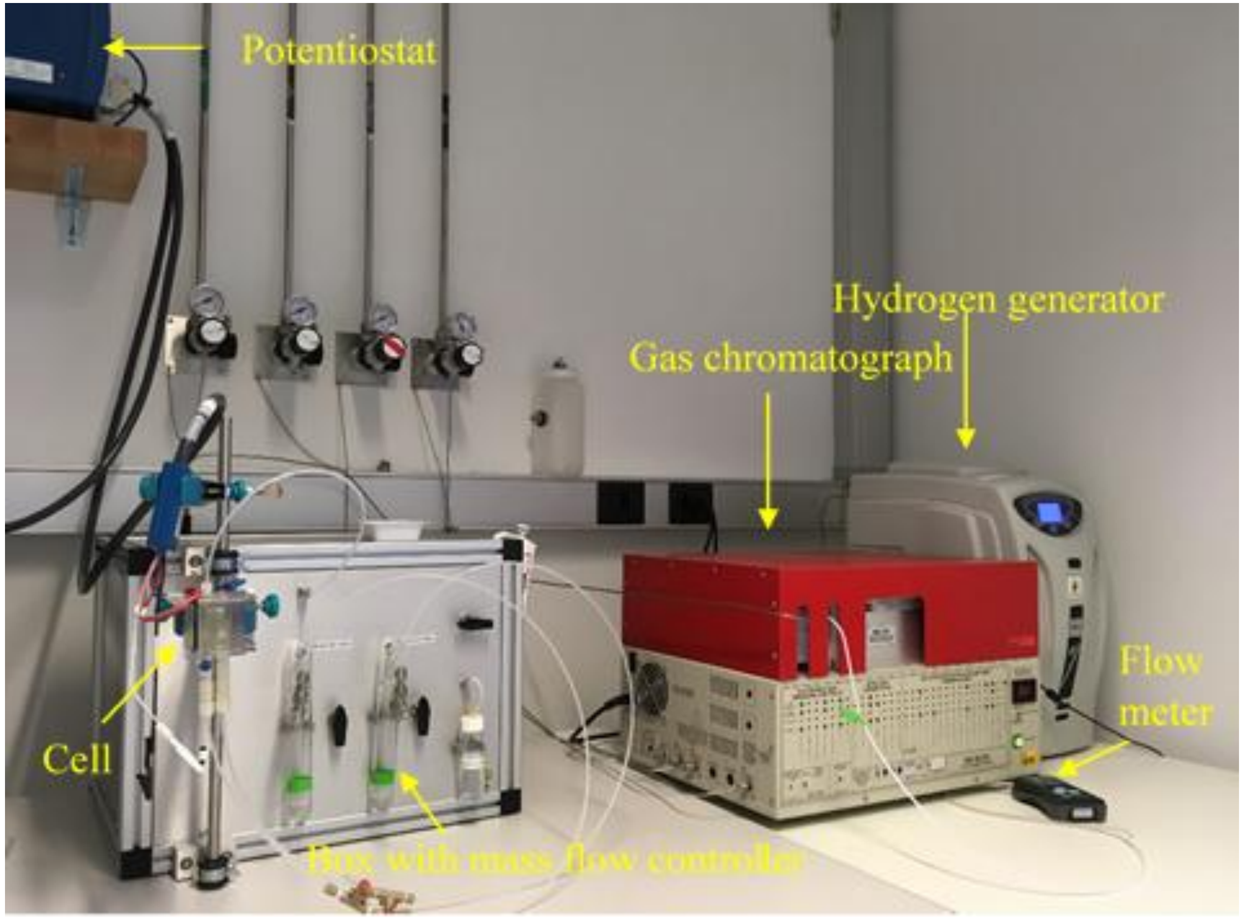
Solvent evaporation

3. Prepared working electrode



Microscope (SEM) image of the working electrode

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



Gas line

- CO_2 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!