Décharges dans les liquides : quels réels apports à la synthèse de nanomatériaux ?

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GDR EMILI - Journées 25-28 octobre 2021 – Ecole Polytechnique

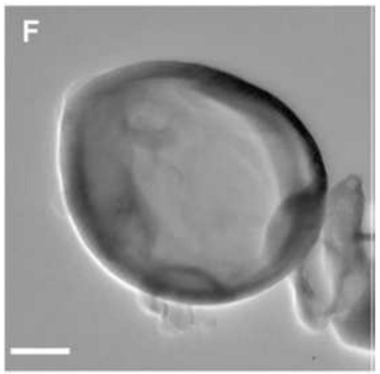
(GDR2098, Etude des Milieux Ionisés : Plasmas froids créés par décharge et laser)

1. INTRODUCTION

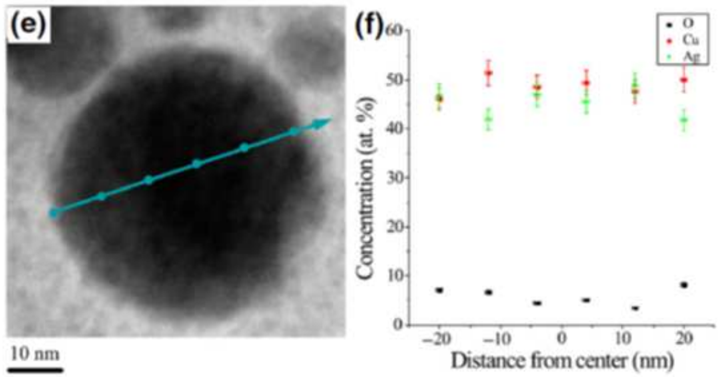
How to compete with chemists?

Synthesizing « complex » nanoparticles is still a challenge:

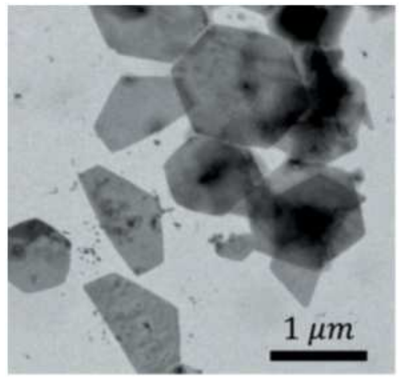
- *e.g.* nanoparticles made of MOFs, HEA, quasicrystals, Perovskite, etc.
- *e.g.* alloys of non-miscible elements, like Fe-Au, Cu-Ag, etc.
- *e.g.* non-spherical nano-objects



Mingabudinova *et al.*
(2019) *Nanoscale* **11**, 10155



Tarasenka *et al.*
(2020) *Phys. Rev. Appl.* **13**, 014021



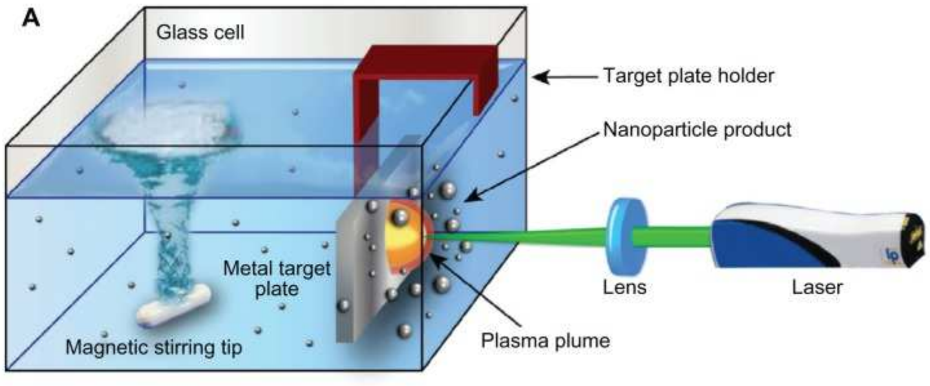
Kabbara *et al.*
(2019) *J. Appl. Cryst.* **52**, 304

1. INTRODUCTION

Discharges in liquids are a promising way because:

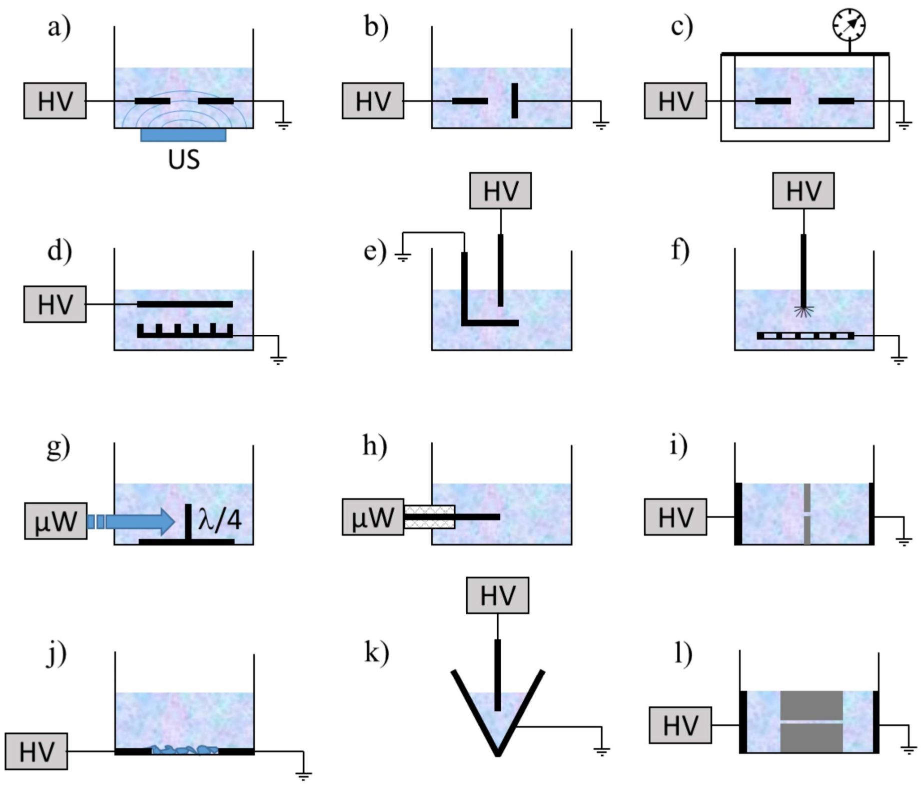
- processes are safe
- they are easy to run and upscale
- they bring huge gradients into play

They can also be created by laser.



Zamiri *et al*. 2014 in "*Bioengineering Nanomaterials*", Ed. Tiwari & Tiwari, CRC press pp 269-290

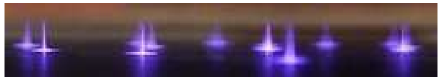
Examples of processes based on discharges created in liquids



INSTITUT JEAN LAMOUR

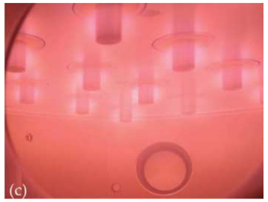
1. INTRODUCTION

Ne ~ 10^{13}-10^{14} cm^{-3} DBD



Ne ~ 10^{10}-10^{11} cm^{-3}

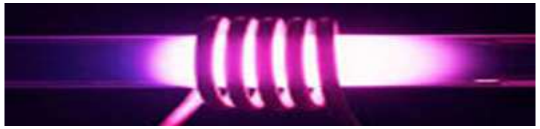
ECR



Latrasse et al., J. Microw. Pow. Elect. Energ. 51 (2017) 237

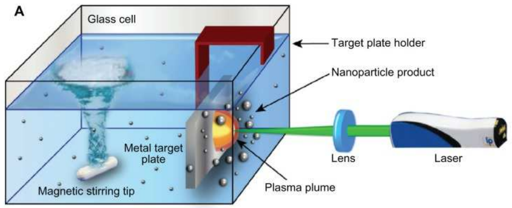
Ne ~ 10^{11}-10^{12} cm^{-3}

HF discharge



Ne ~ 10^{16}-10^{18} cm^{-3}

LAL



Zamiri *et al*. 2014 in "*Bioengineering Nanomaterials*", Ed. Tiwari & Tiwari, CRC press pp 269-290

10^0 10^1 10^2 10^3 10^4 10^5 10^6 10^7 10^8 Pa

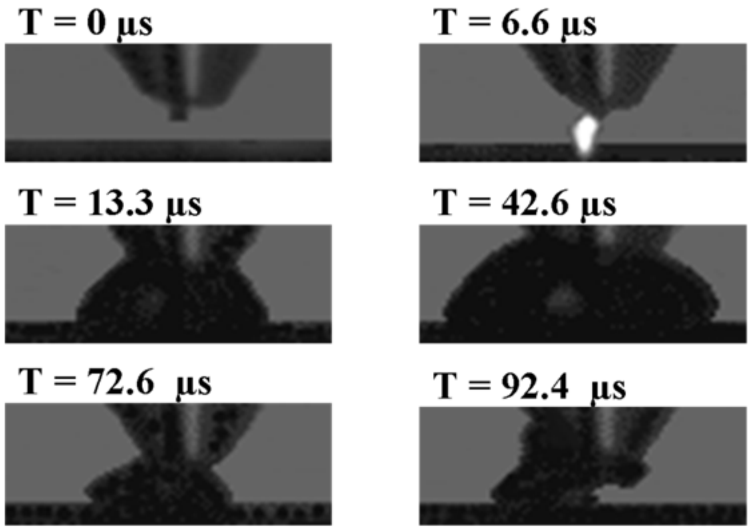
10^{-2} 10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5 10^6 mbar

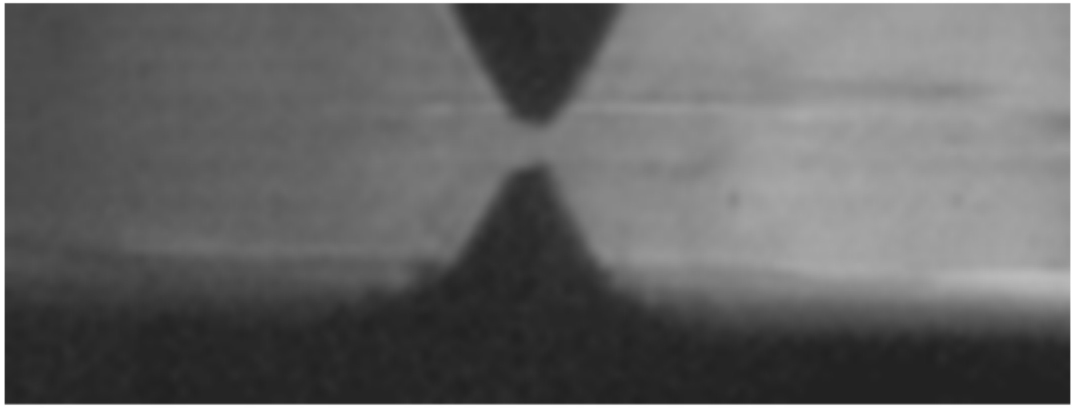
Pressure

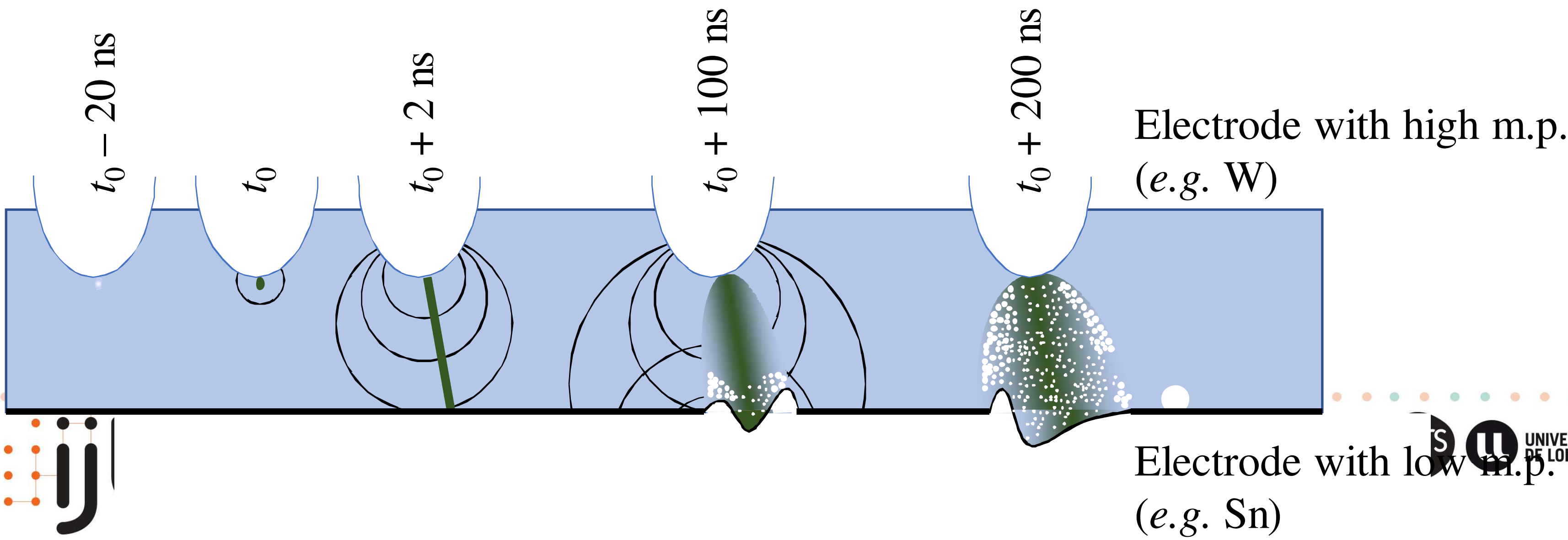
1 torr = 0.75 mbar

1. INTRODUCTION

Discharge in dielectric liquids: A small explosion (Tens of GW in hundreds of µm3)

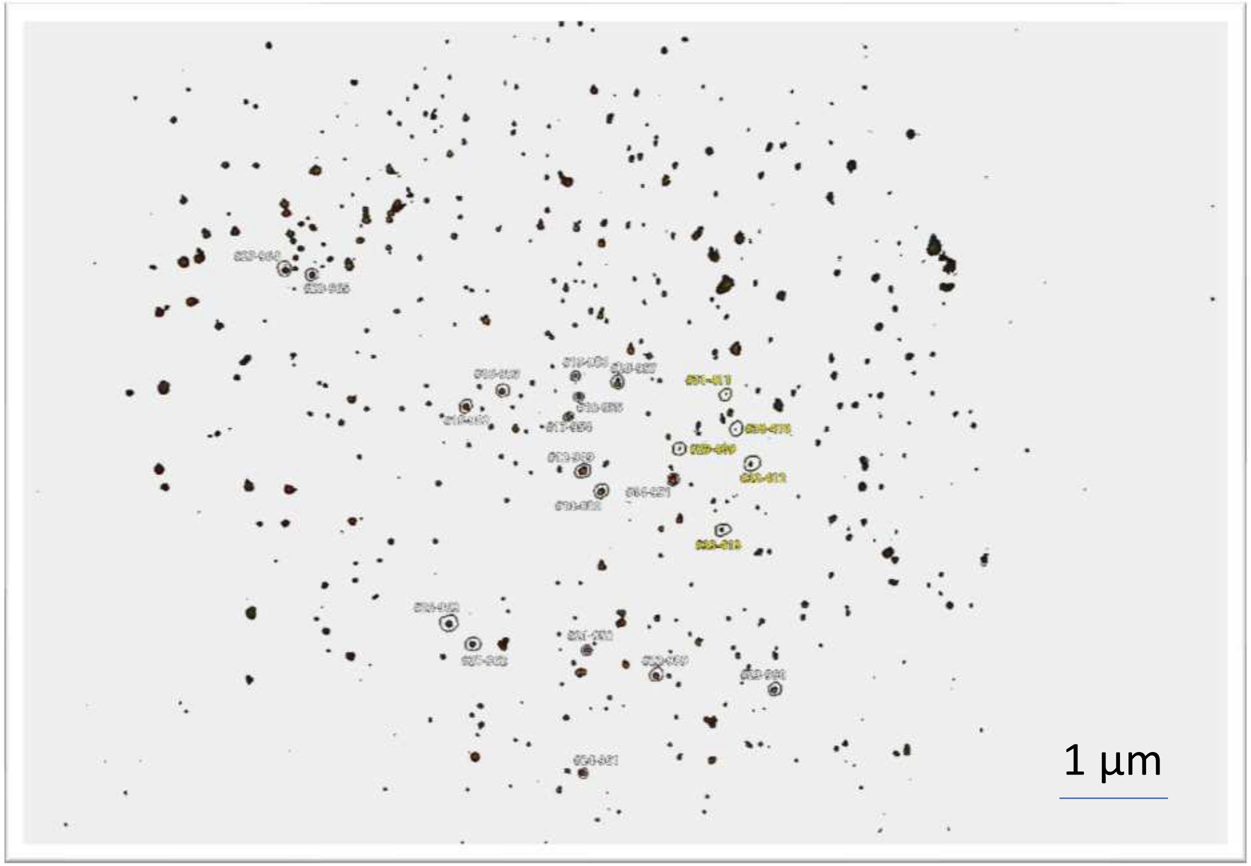






1. INTRODUCTION

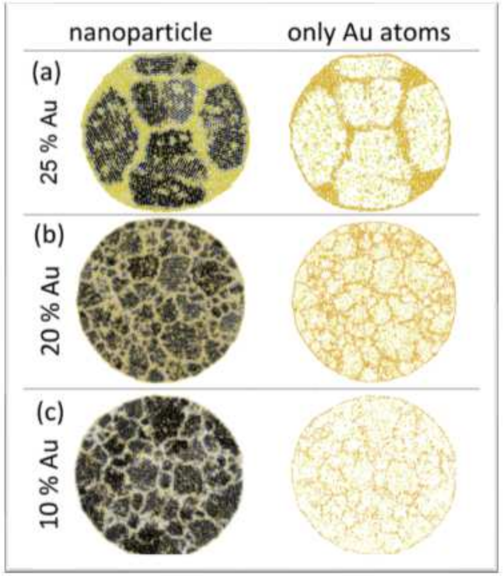
Dark field images of NPs. The marks denote spectra acquisition

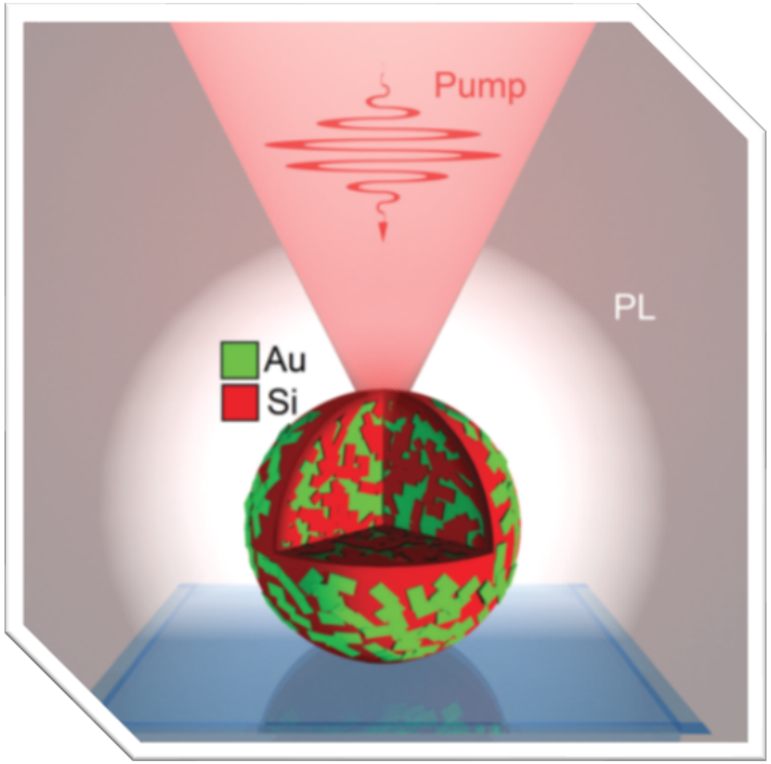


Metalab, ITMO universty, Russia

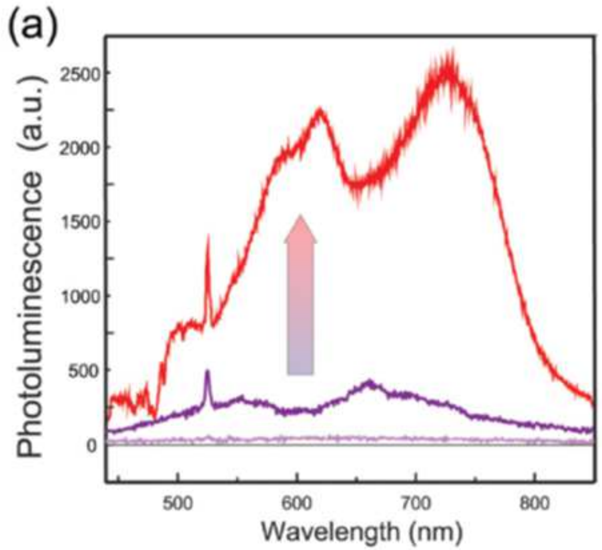
1. INTRODUCTION

These new kinds of nanoparticles have unexpected optical properties





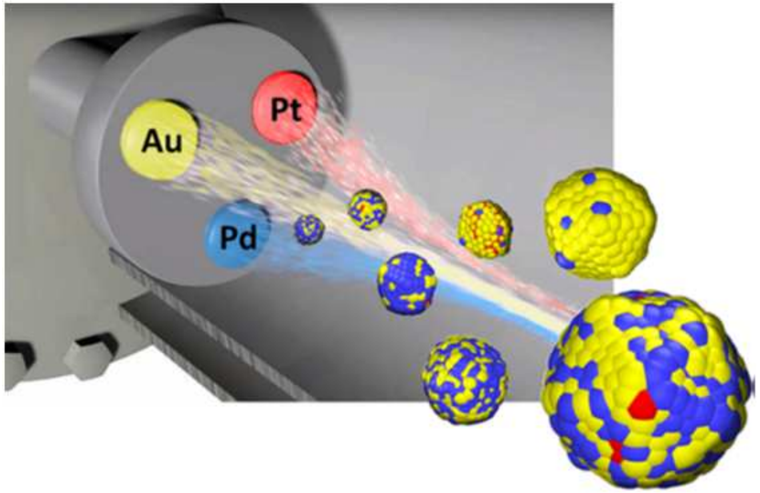
Photoluminescence of 150 nm Si/Au (red line), 150 nm Si (light pink), and 300 nm (dark pink) nanoparticles.



Larin *et al.* (2020) *Nanoscale* **12**, 1013

1. INTRODUCTION

New recent works aiming at alloying 3 (or more) different metallic elements



Mattei et al., Chem. Mater. 2019, 31, 2151

Ternary FeCoNi alloy nanoparticles embedded in N-doped carbon nanotubes for efficient oxygen evolution reaction electrocatalysis.

Li *et al*. (2020) *Electrochimica Acta* **339**, 135886.

Enhancing Thermocatalytic Activities via Up-shift of the d-Band Center of Exsolved Co-Ni-Fe Ternary Alloy Nanoparticles for Dry Reforming of Methane.

Joo *et al*. (2021) *Angewandte Chemie*.

Electrodeposition of ternary CuNiPt alloy nanoparticles on graphenized pencil lead electrodeas a new electrocatalyst for electro-oxidation of ethanol.

Imanzadeh & Habibi (2020) *Solid State Sciences* **105**, 106239.

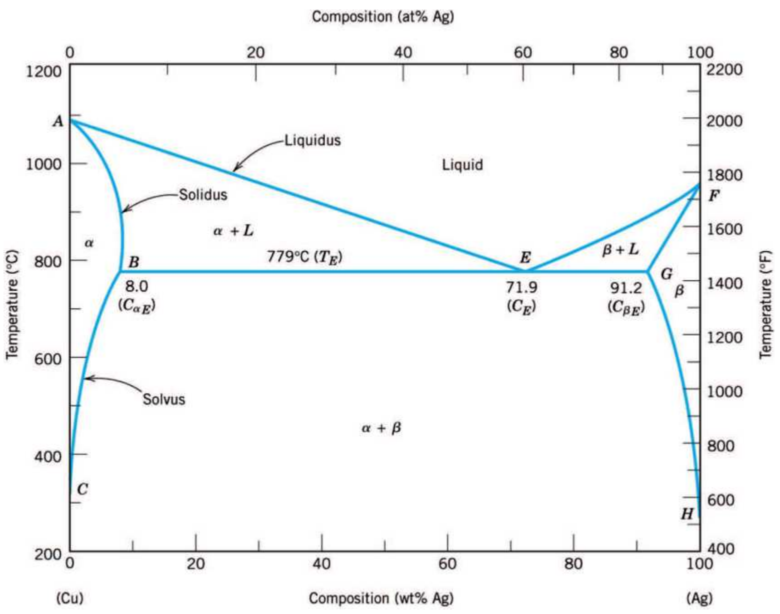
Anchoring ternary CoNiSn alloys nanoparticles on hollow architectured SnO2 for exceptional lithium storage performance.

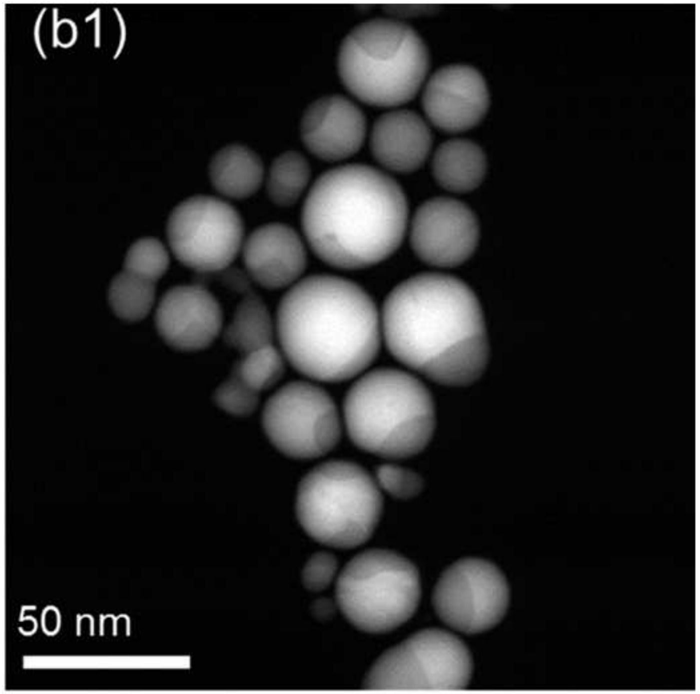
Su *et al*. (2020). *Journal of Power Sources* **450**, 227626.

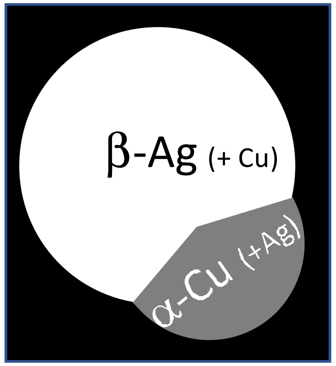
2. Alloying non-miscible elements: Cu-Ag system

Basic concepts

Non-miscible elements tend to segregate



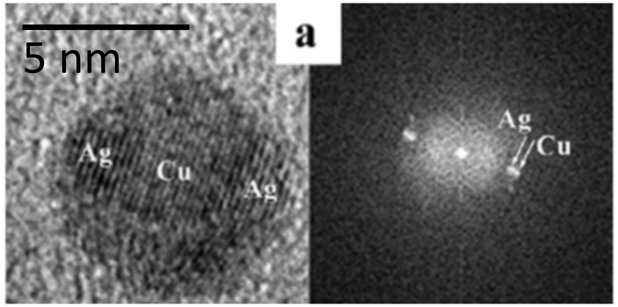


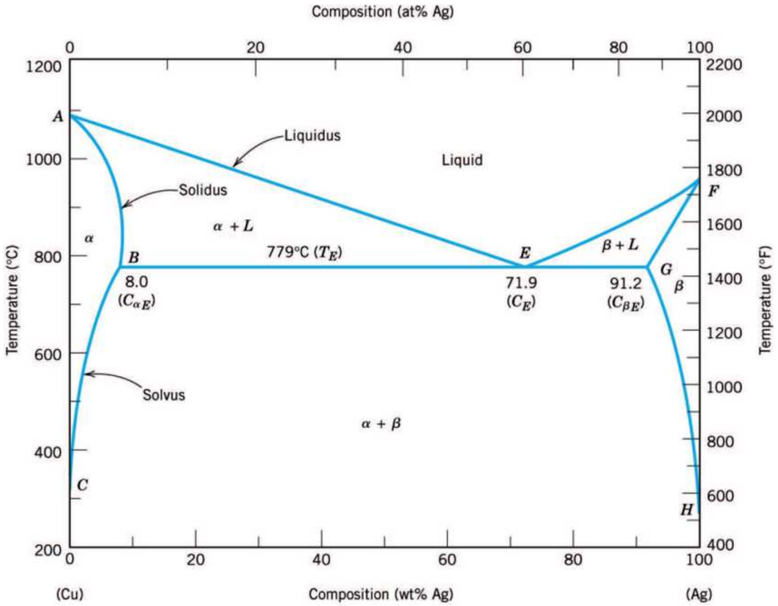


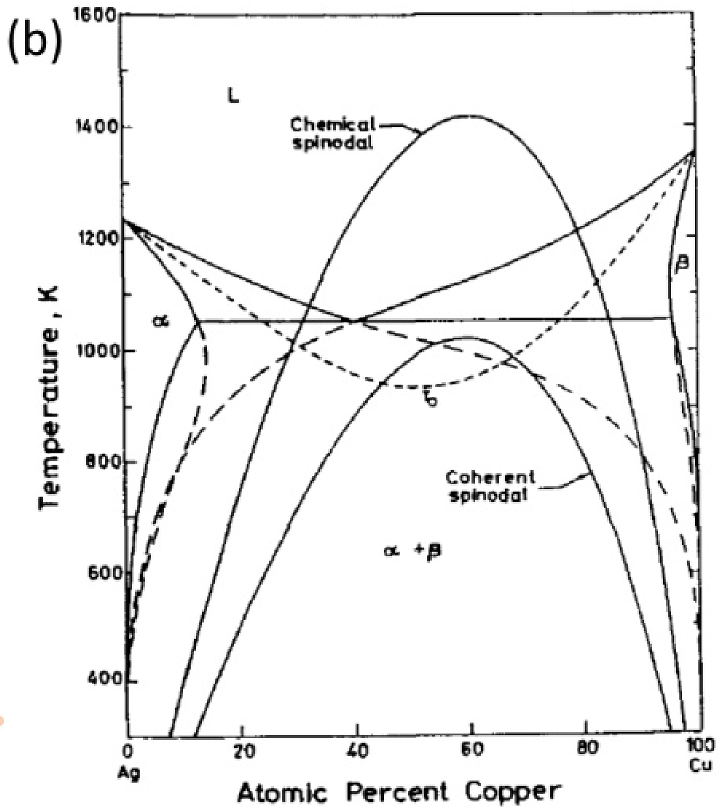
2. Alloying non-miscible elements: Cu-Ag system

Basic concepts

Surface vs volume

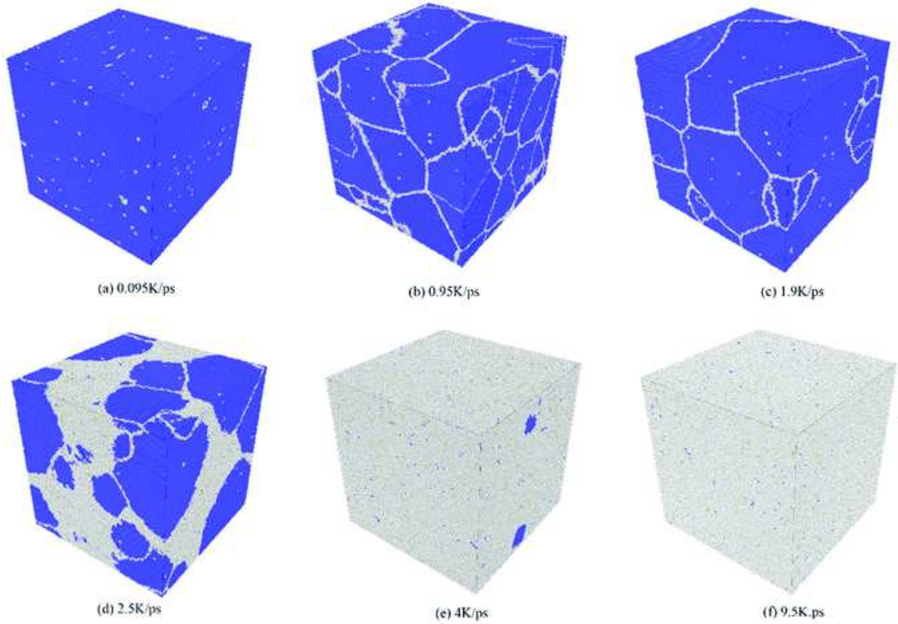






2. Alloying non-miscible elements: Cu-Ag system

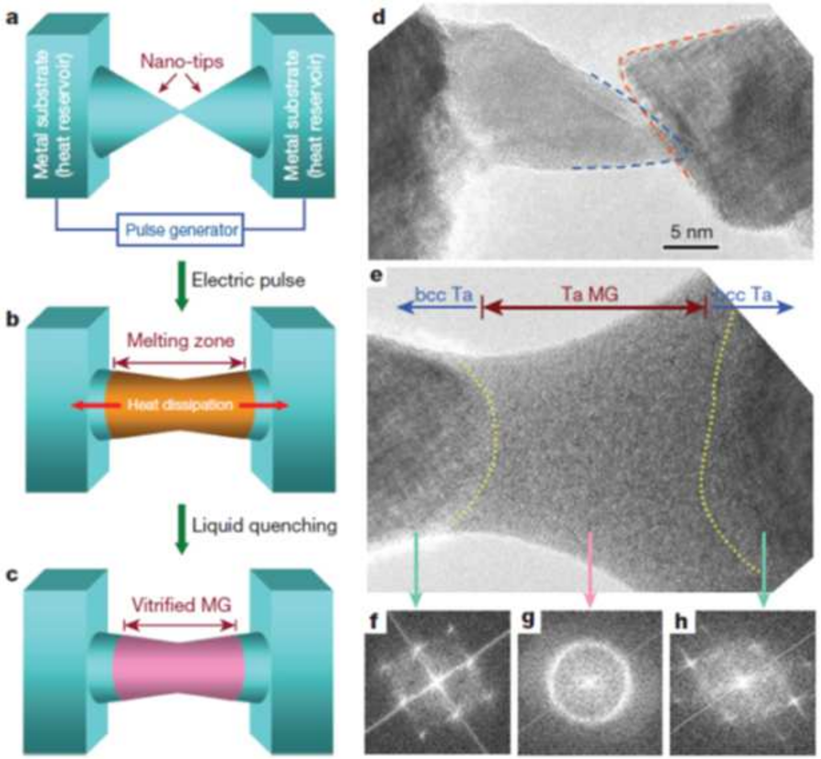
Basic concepts



Snapshots of the simulated solidification structures under different cooling rates of: (a) 0.095 K ps^{-1}, (b) 0.95 K ps^{-1}, (c) 1.9 K ps^{-1}, (d) 2.5 K ps^{-1}, (e) 4 K ps^{-1}, and (f) 9 K ps^{-1}. The blue, red, green, yellow, and grey balls denote bcc, fcc, hcp, ICO, and the other configurations (unknown coordination structures, such as amorphous liquid and solid, grain boundary, and so on), respectively. (box side length: 35 nm)

2. Alloying non-miscible elements: Cu-Ag system

Basic concepts



Quenching rate:
~10^{14} K s^{-1}

Freezing a liquid melt and stop all atom movements

Zhong *et al.* (2014) *Nature* **512** , 177

2. Alloying non-miscible elements: Cu-Ag system

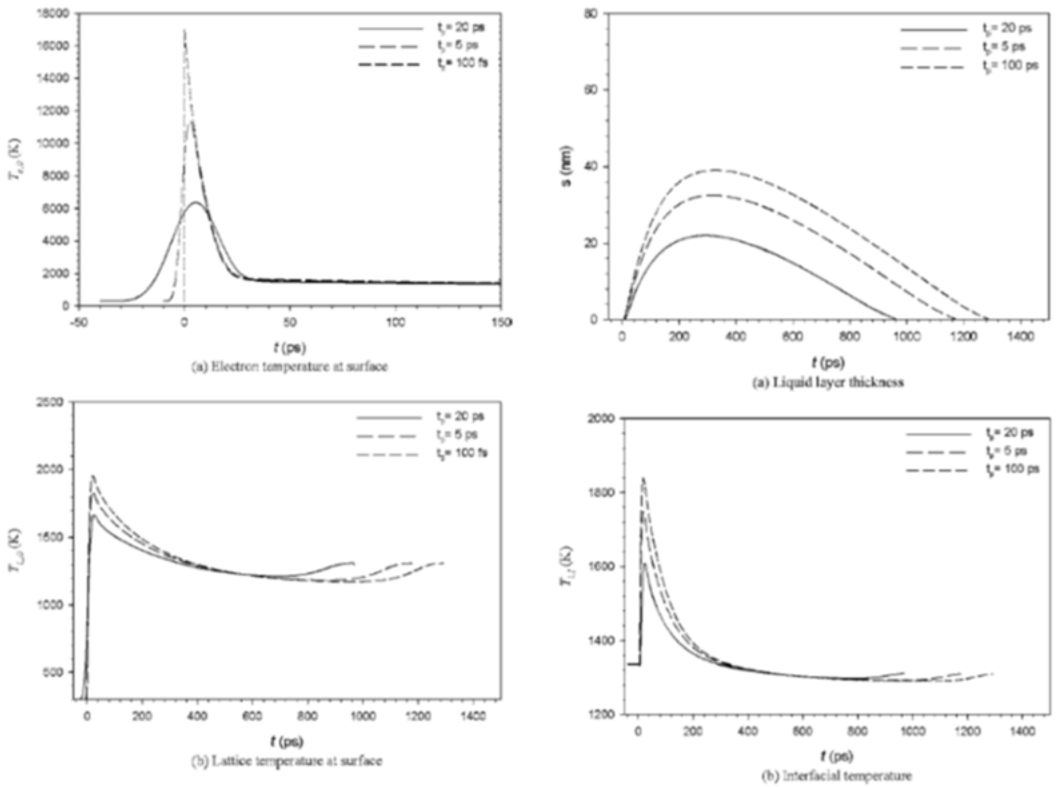
Basic concepts

Ultra-fast heating by fs –laser…

HR:

1953 K / 100 fs = 2x10^{16} K s^{-1}

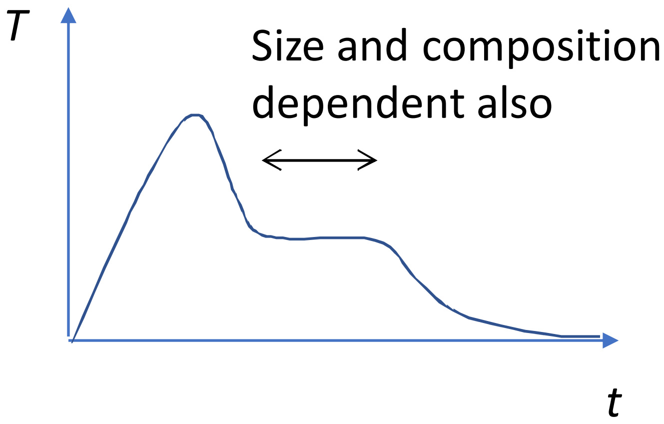
1666 K / 20 ps = 8x10^{13} K s^{-1}



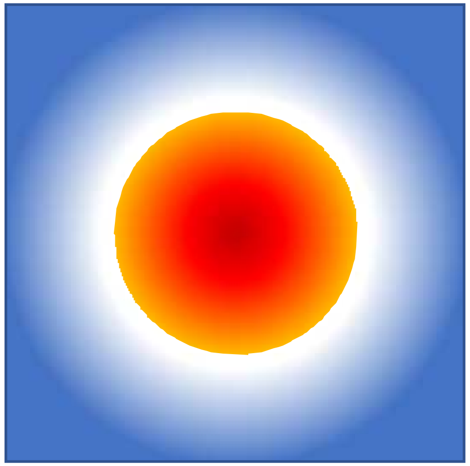
Zhang & Chen (2008) *J. Appl. Phys.* **104**, 054910

2. Alloying non-miscible elements: Cu-Ag system

Basic concepts



… but cooling is hindered by latent heat extraction



$$\left.\frac{dq}{dt}\right|_{cc} = hS_p\left(T_p - T_{boil}^{liq}\right)$$

$$\left.\frac{dq}{dt}\right|_{rad} = \sigma S_p T_p^4$$

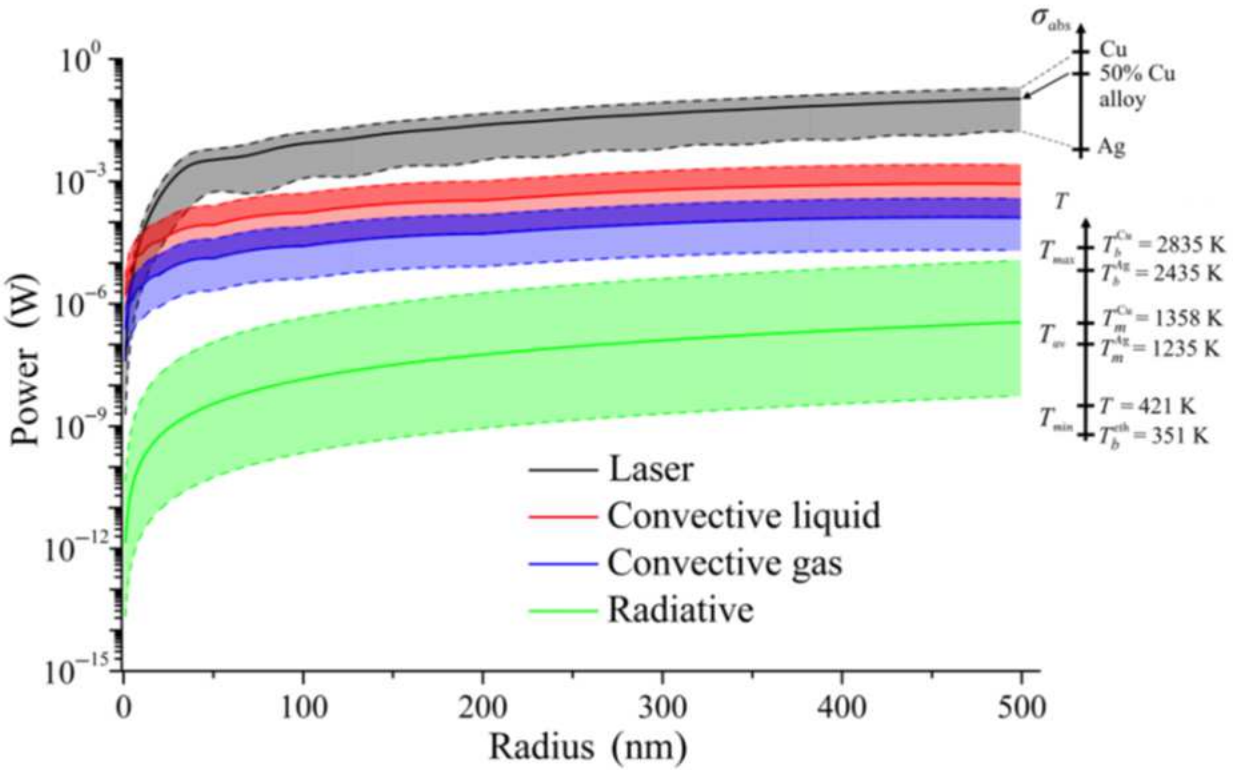
Zhang & Chen (2008) *J. Appl. Phys.* **104**, 054910

CR: < 10^9 K s^{-1}
for nanoparticles smaller than 5 nm
with interface velocity = 1 cm s^{-1}

CR: < 10^{12} K s^{-1}
for nanoparticles smaller than 50 nm
with interface velocity = 1 cm s^{-1}

2. Alloying non-miscible elements: Cu-Ag system

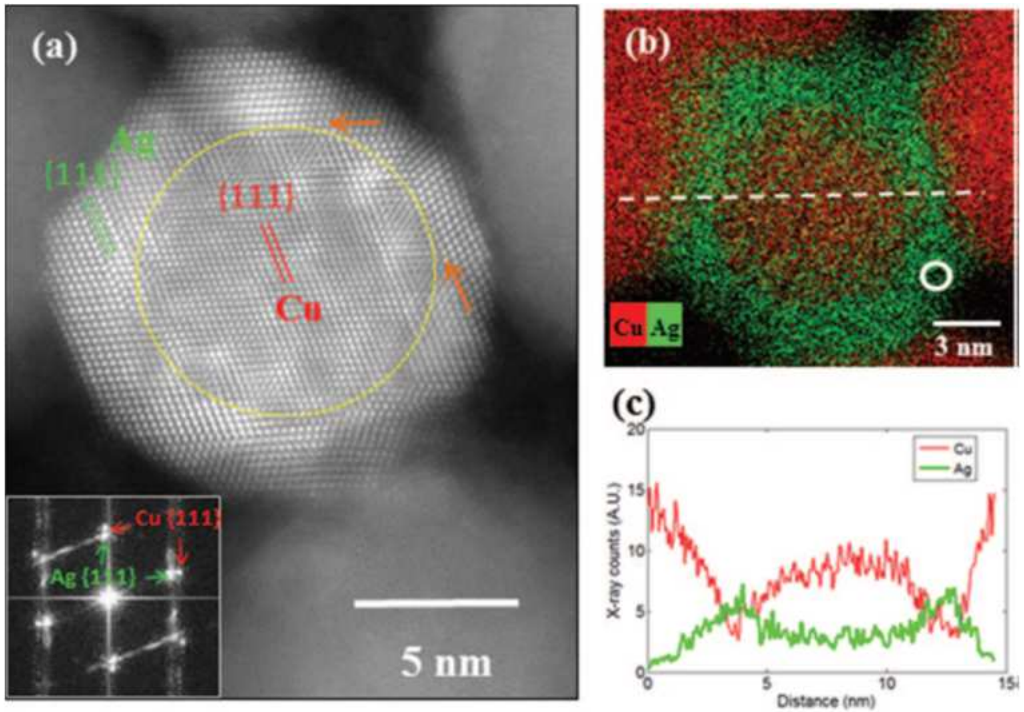
Basic concepts



Tarasenka *et al.* (2020) Phys. Rev. A **13**, 014021

3. Cu-Ag system

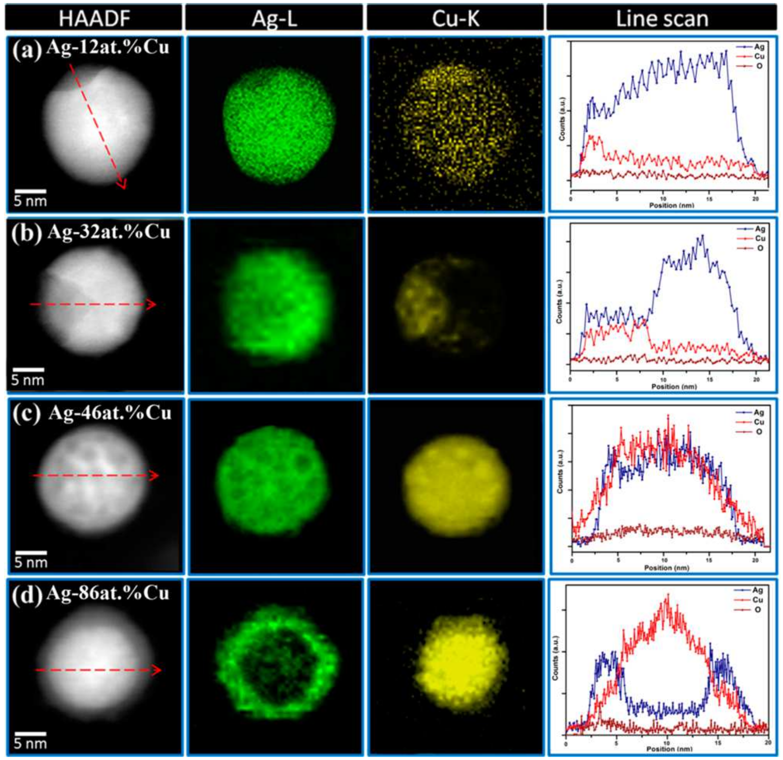
If the cooling rate is slow, thermodynamics predicts surface segregation of silver that has a lower surface energy (1210 mJ m^{-2}) than copper (2130 mJ m^{-2}).



Lu *et al.* (2014) *APL Materials* **2**, 022107

3. Cu-Ag system

Phase distribution in small nanoparticles (~20 nm in diameter) is composition-dependent



(a–d) Compositional variation in nanoparticles corresponding to target composition Ag–X atom Cu (X = 20, 40, 60, 80), respectively.

Malviya and Chattopadhyay (2014) *J. Phys. Chem. C* **118**, 13228

3. Cu-Ag system

How to accelerate quenching? Increase Particle-(Wall or larger particle) interactions

Mardanian *et al.* (2013) *Eur. Phys. J. D* **67**, 208

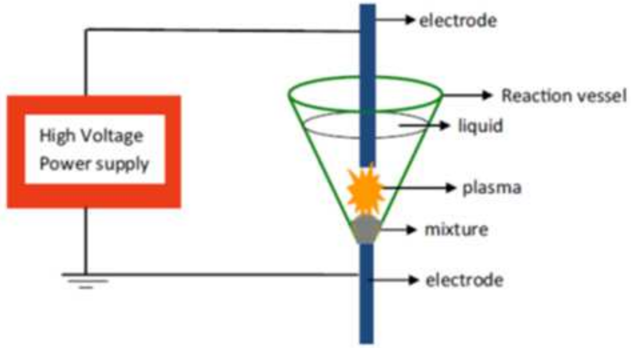
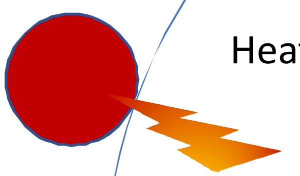


Fig. 1. Schematic diagram of the set-up for CIS nanoparticles synthesis by pulsed spark discharge in liquid.

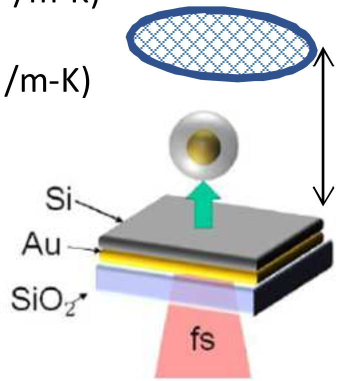


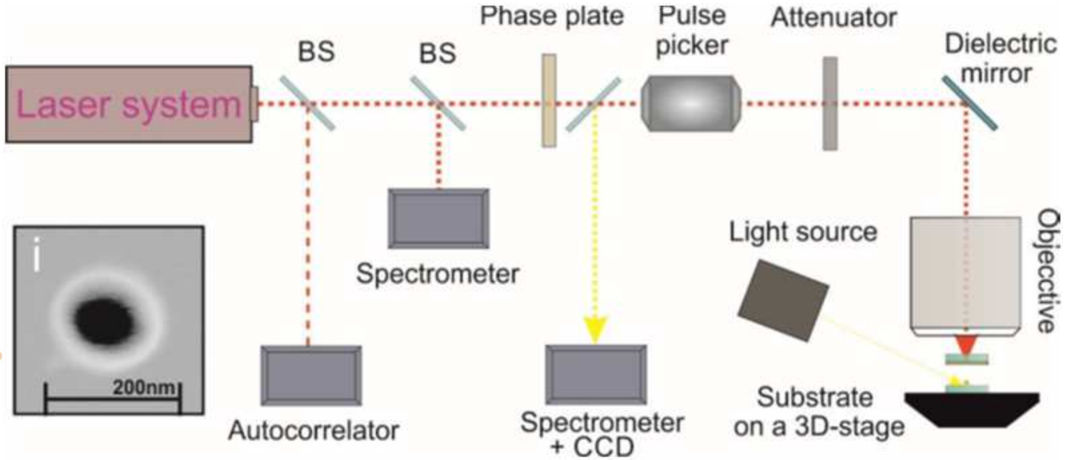
Heat transfer coefficient x ~10

New reactor design

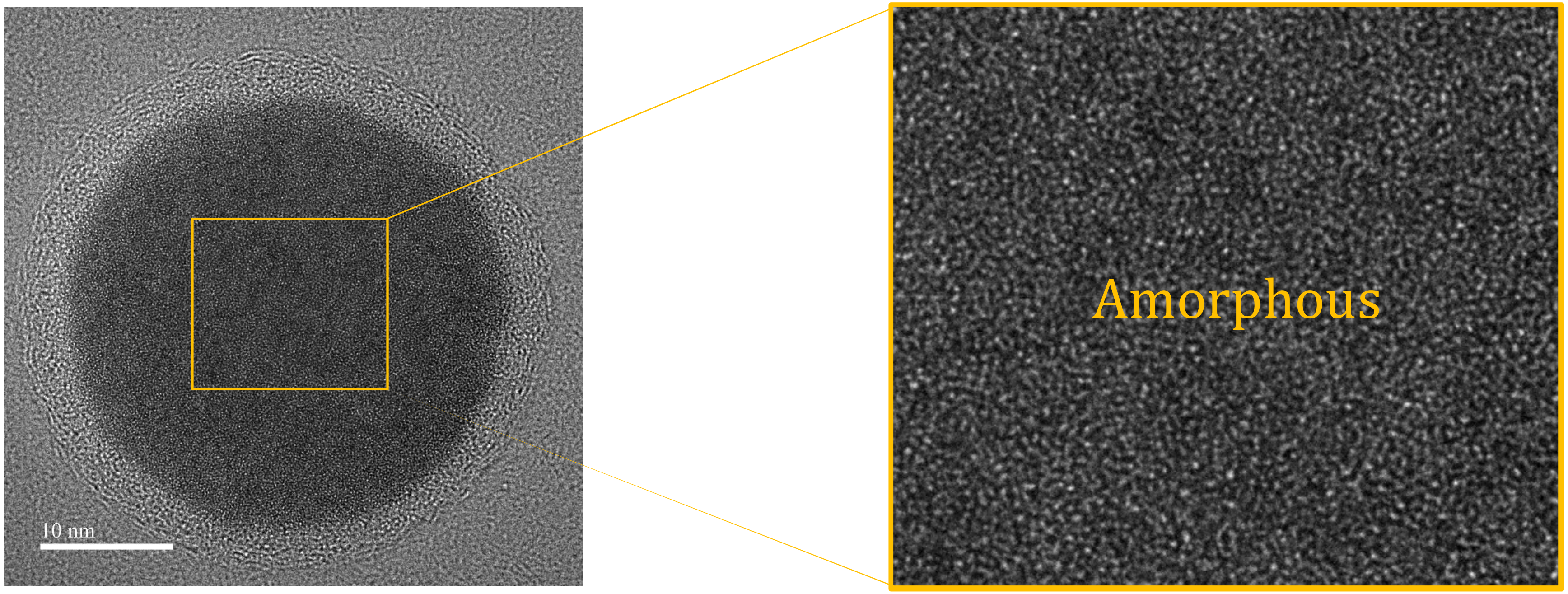
Zograf *et al.* (2016) *J. Phys. C* **741**, 012119

BN (751 W /m-K)
vs
Si (148 W /m-K)

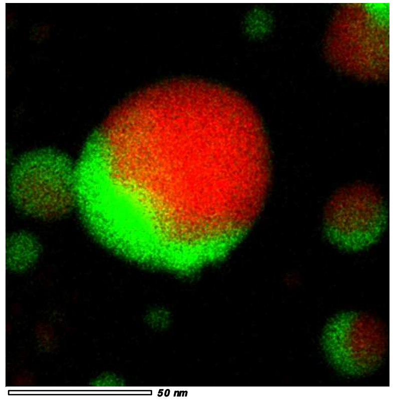


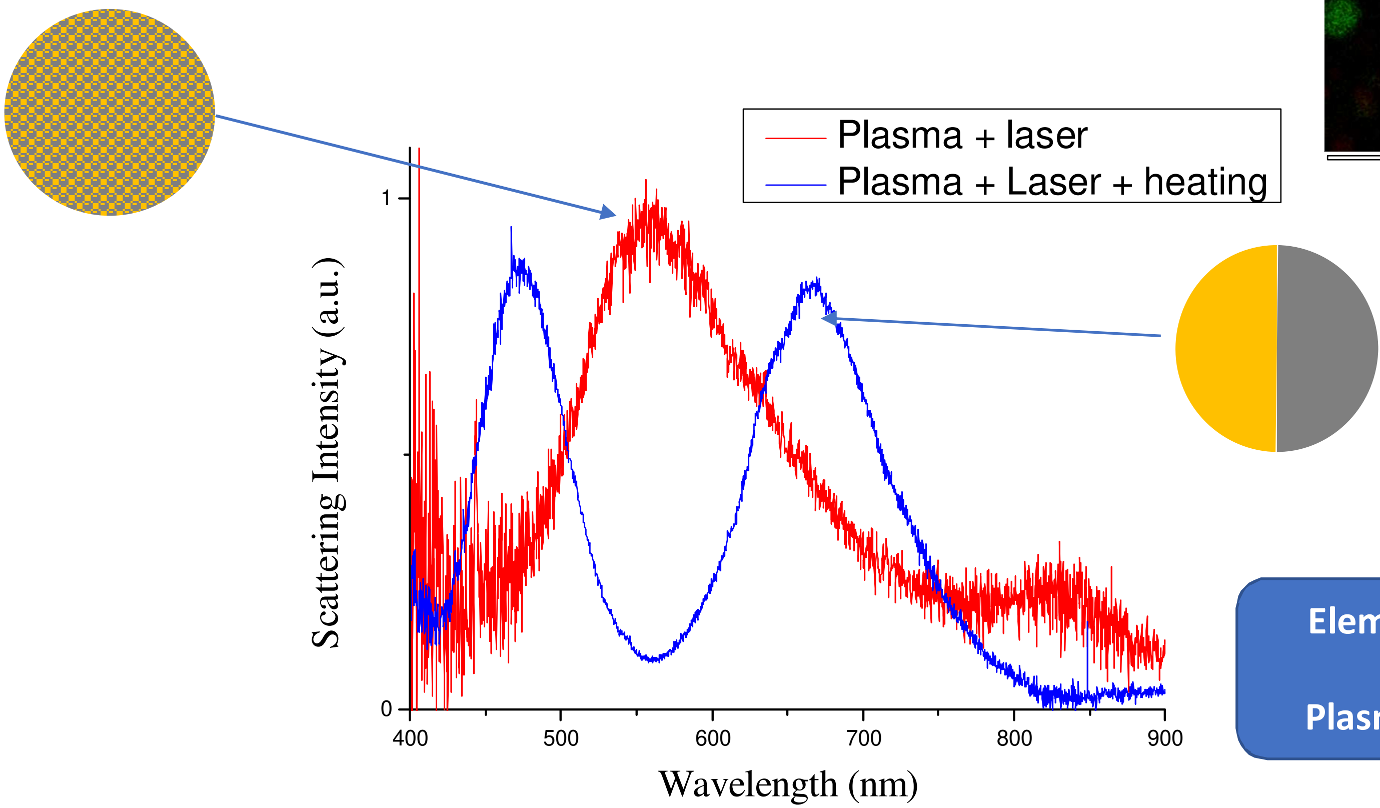


3. Cu-Ag system



Cu-Ag metastability: a simple example





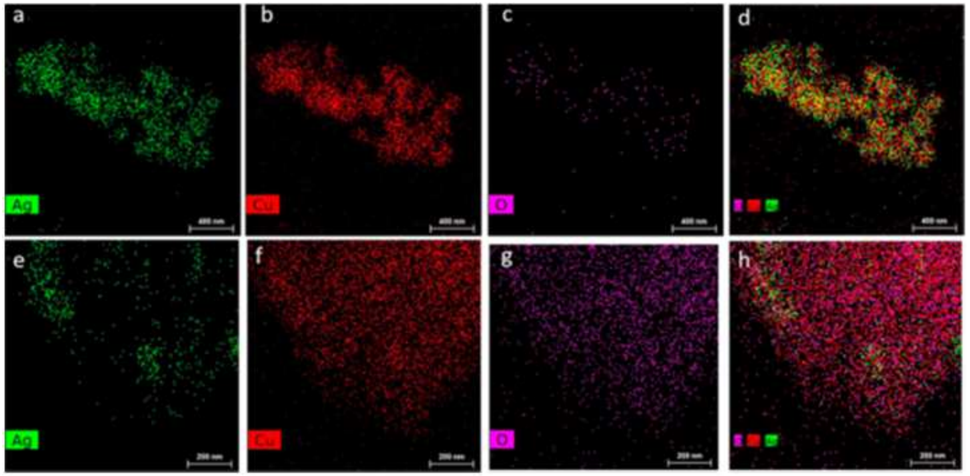
Element splitting
=
Plasmon splitting

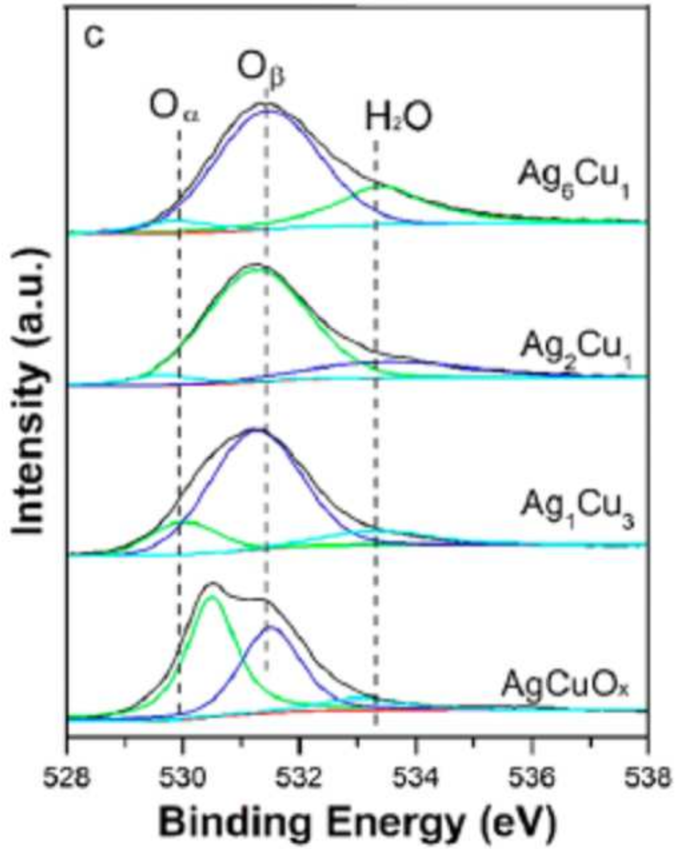
3. Cu-Ag system

Oxidation

Copper is oxidized if sufficiently concentrated

lattice oxygen at ~530.0 eV (O_α)
chemisorbed surface oxygen at ~531.5 eV (O_β)
adsorbed water (H_2O) at ~533.0 eV.



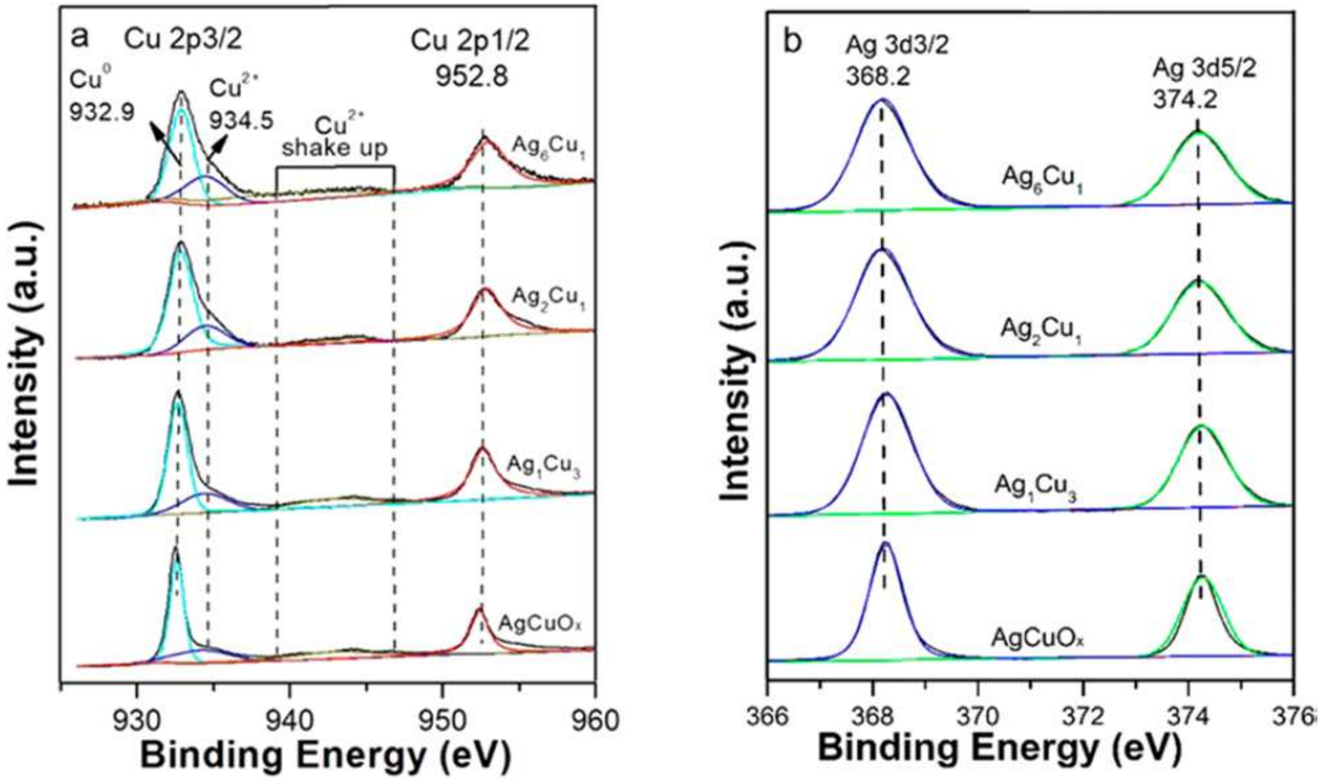


Zhou *et al*. (2019) *ACS Appl. Mater. Interfaces* **11**, 46875

3. Cu-Ag system

Oxidation

Copper is oxidized if sufficiently concentrated

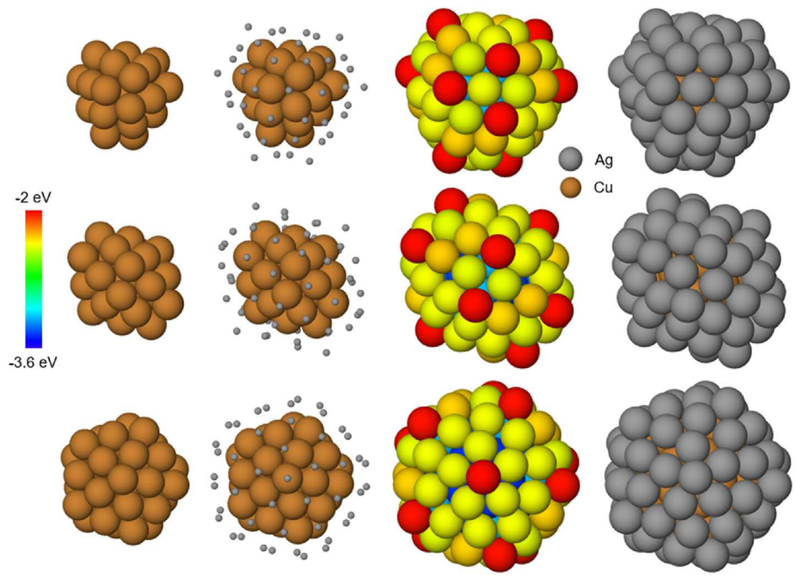


Zhou *et al*. (2019) *ACS Appl. Mater. Interfaces* **11**, 46875

3. Cu-Ag system

Chemical ordering

Chemical ordering leads to atomic segregation and Cu core–Ag shell structures



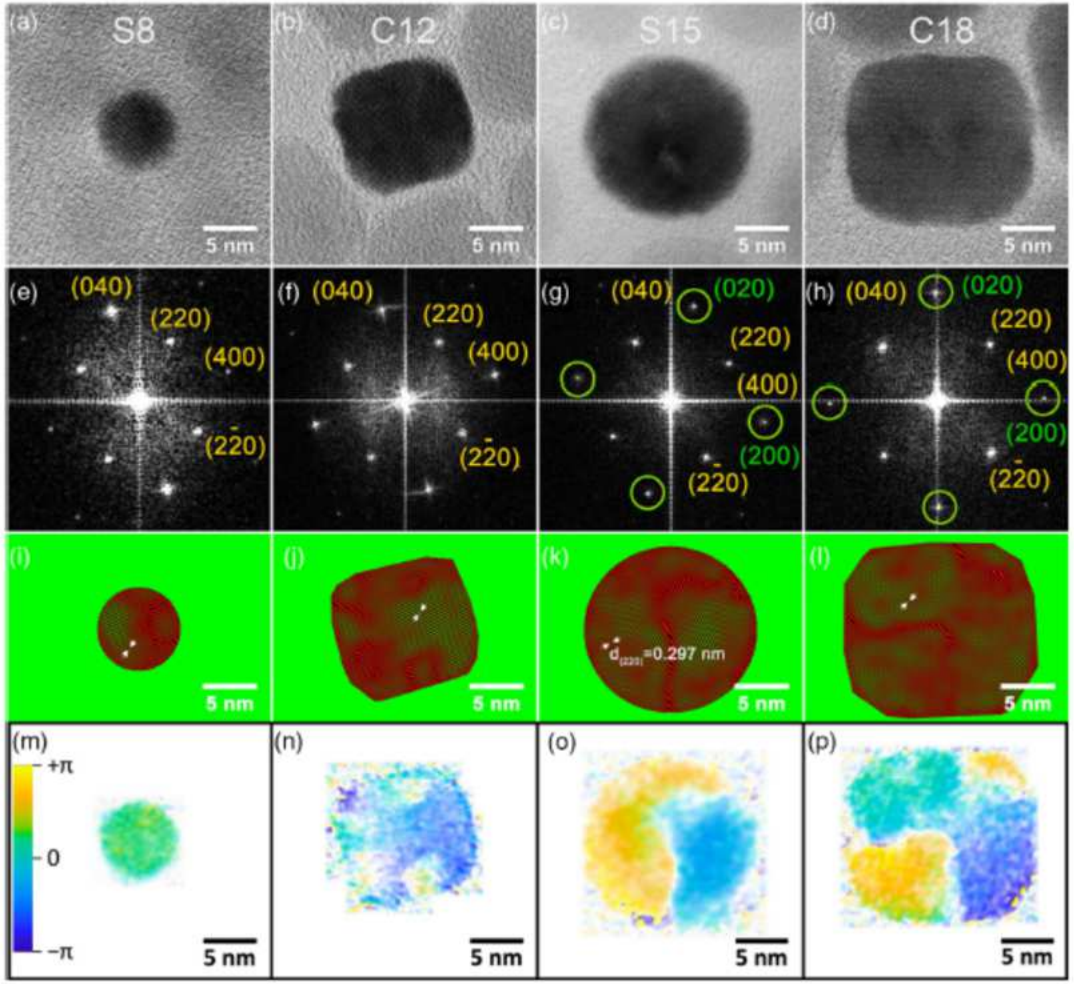
Arrangement of the Ag shells (columns 2 to 4) in the lowest sized nanoalloys $Ag_{52}Cu_{28}$ (first row, T symmetry), $Ag_{56}Cu_{32}$ (second row, D3 symmetry), and $Ag_{62}Cu_{39}$ (third row, C5 symmetry). The chiral Cu core in each of the nanoalloys is shown in the first column. The color coding in the third column refers to the energy of the atoms

Settem M 2020 *J. Alloys Comp.* **844** 155816

4. Defect engineering

Mastering defects in NPs

A. Lappas et al. Phys. Rev. X 9, 041044 (2019)



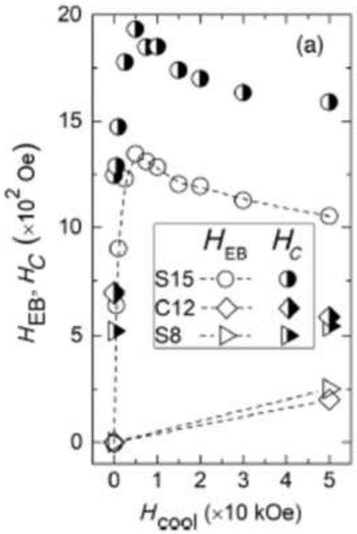


FIG. 2. High-resolution TEM images in the [001] zone axes for spherical S8 (a), S15 (c) and cubic C12 (b), C18 (d) morphology nanocrystals. The corresponding diffraction patterns (e, f and h, g) after FFT analysis of each micrograph are shown beneath. Green and yellow circles mark a set of reflections that could be indexed on the basis of either wüstite (green) or/and magnetite (yellow) rock-salt and cubic spinel crystal unit cells (see text for details). Representative real-space images of the (220) atomic lattice planes (inverse FFT synthesis; filtered from specific plane orientations) for the samples S8 (i), C12 (j), S15 (k), and C18 (l), respectively. Lattice planes have been colored with red (possible presence of atomic plane) and green (possible absence of atomic plane) pseudochrome acquired after the inverse FFT process. Lattice phase contrast images obtained by the GPA method (see text) after recentering the diffraction around one of the (220) reflections for samples S8 (m), C12 (n), S15 (o), and C18 (p).

5. Assembling 1D into structure

Particles move under electric field by:

- Electro-osmosis — Flow driven by the Coulomb force induced by an electric field on the net charge in the electrical double layer at the electrodes

- Electrophoresis — - Charged particle: linear interaction between the electric field and the surface charge
  - Polarized uncharged particle: non-linear (quadratic) interaction (Induced-Charge EP)

- Dielectrophoresis — Interaction of particle dipoles in a non-uniform field

$$\vec{F}_{dep}^{cons} = 2\pi a^3 \varepsilon_m \Re(\omega) \cdot \vec{\nabla} \left| \vec{E}_{rms} \right|^2$$

$$\vec{F}_{dep}^{non-cons} = 2\pi a^3 \varepsilon_m \Im(\omega) \cdot \vec{\nabla} \times \vec{W}_n$$ vector electromechanical potential

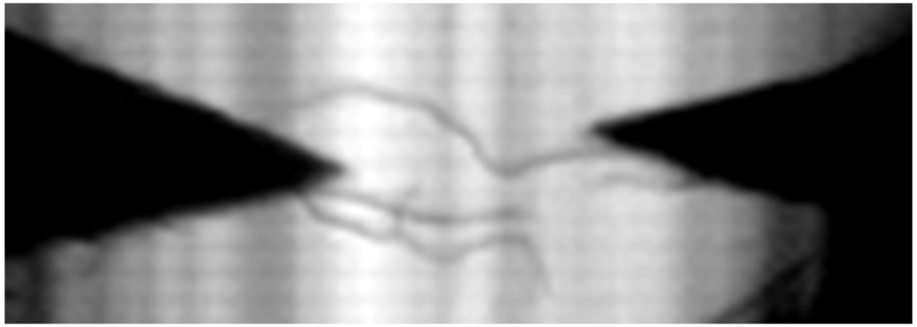
- Dipolophoresis — Spatially non-uniform electric fields are encountered, both DEP and ICEP contribute to the particle movement

5. Assembling 1D into structure

How to get 1D nano-objects by discharges in liquids?

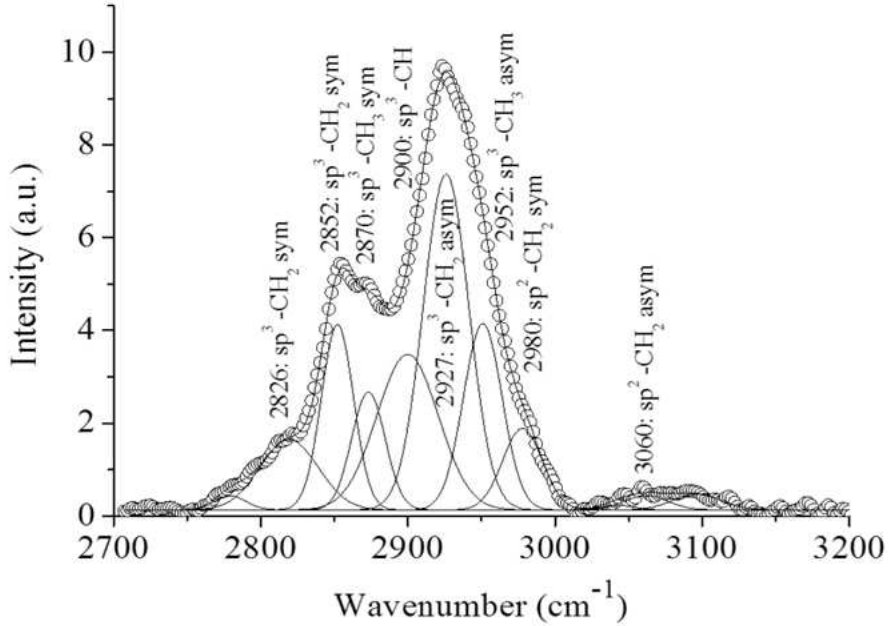
2-step process:

- Discharges in C_7H_{16} between Pt electrodes
- High-Voltage E-Field in C_7H_{16} loaded with NPs



Hamdan *et al.* 2014 *Mater. Lett.* **135** 115

Non-conductive wires

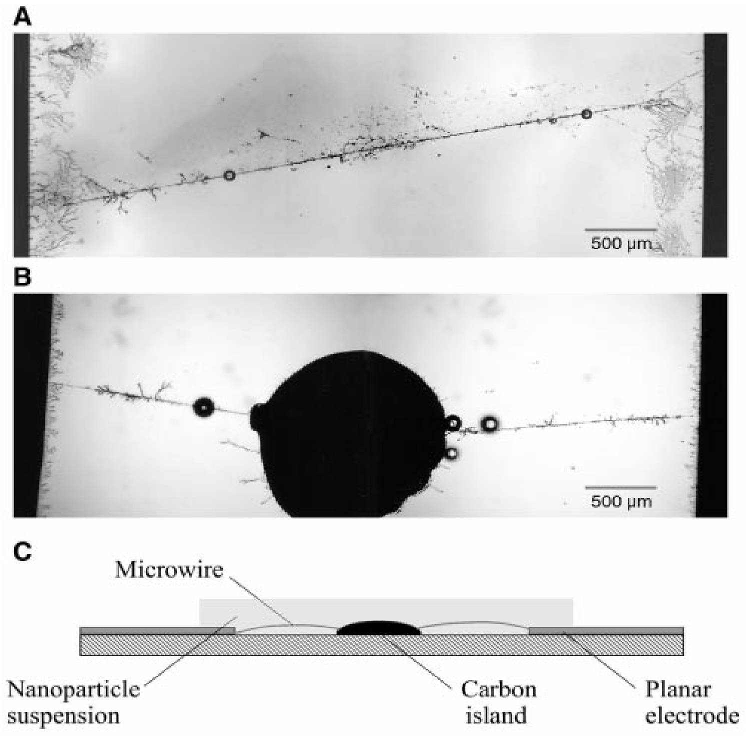


Pt-doped hydrogenated amorphous carbon

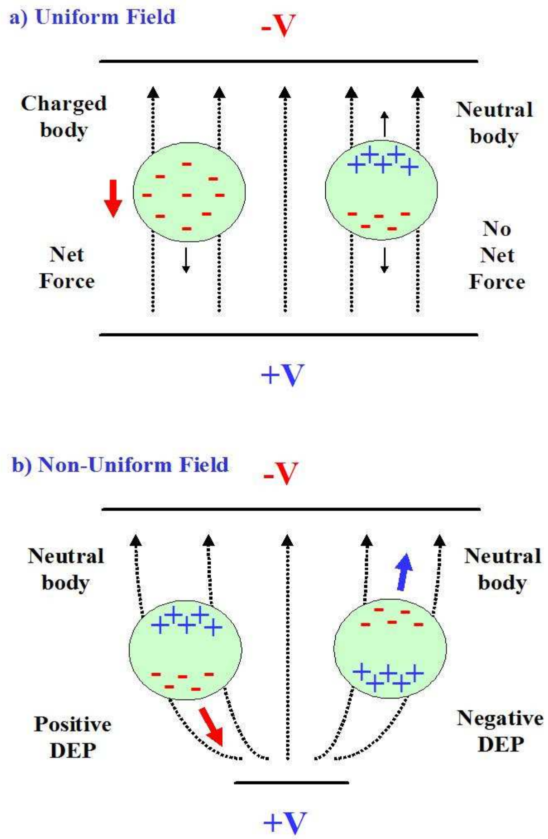
5. Assembling 1D into structure

How to get 1D nano-objects by discharges in liquids?

Dielectrophoresis for insulating materials



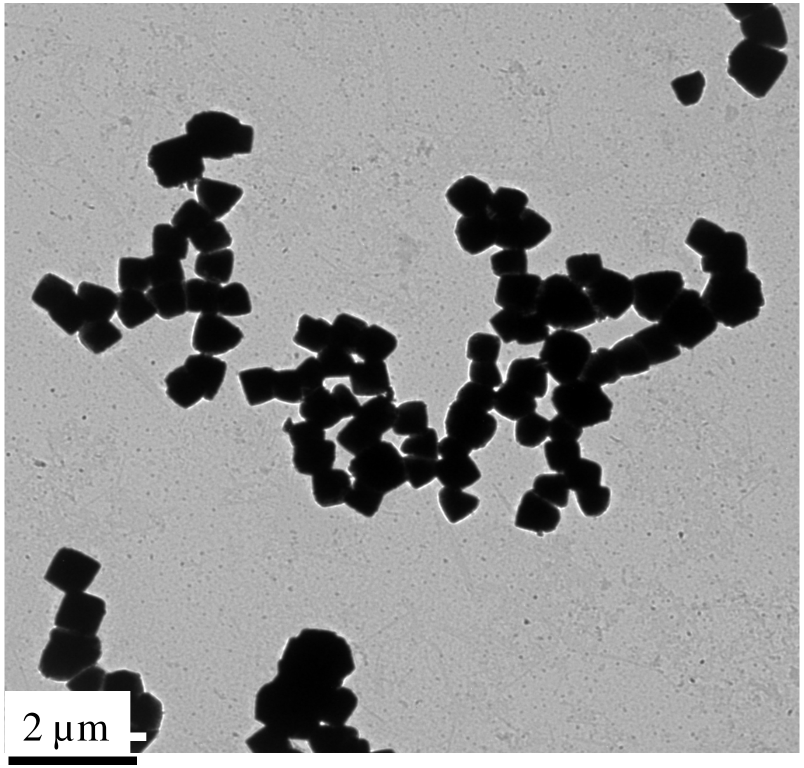
Hermanson *et al.* 2001 *Science* **294** 1082

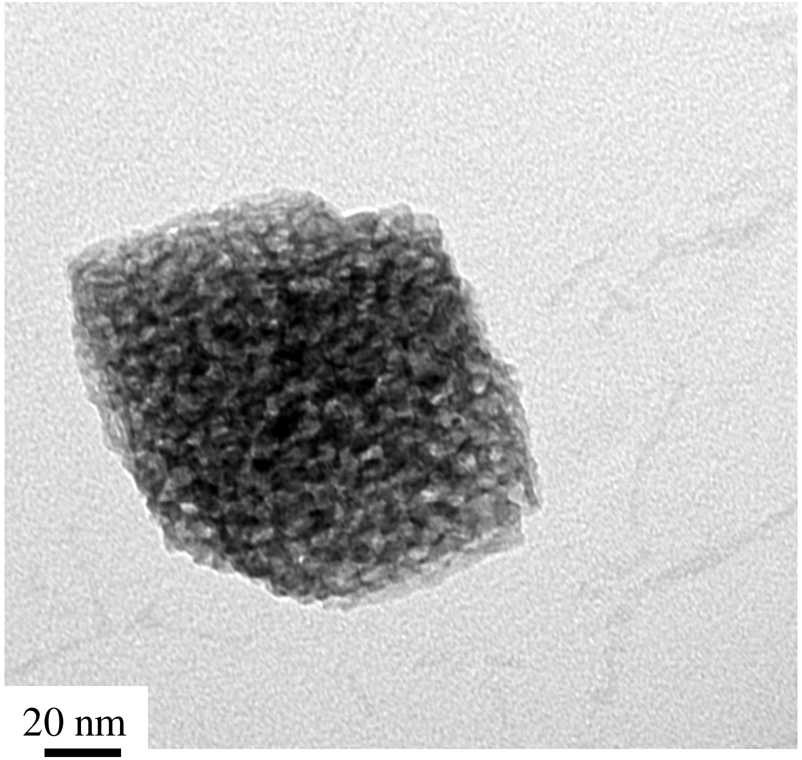


5. Assembling 1D into structure

Applied voltage: +4kV

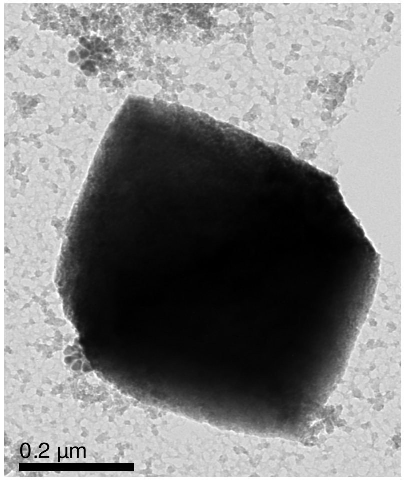
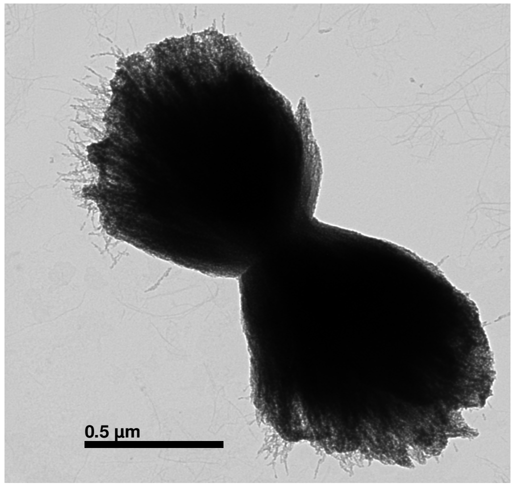
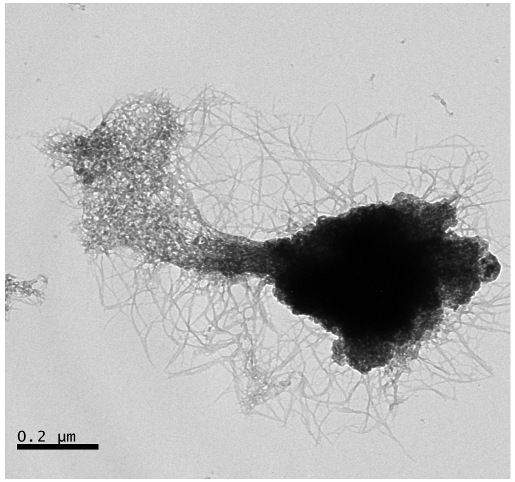
CdO micro-cubes



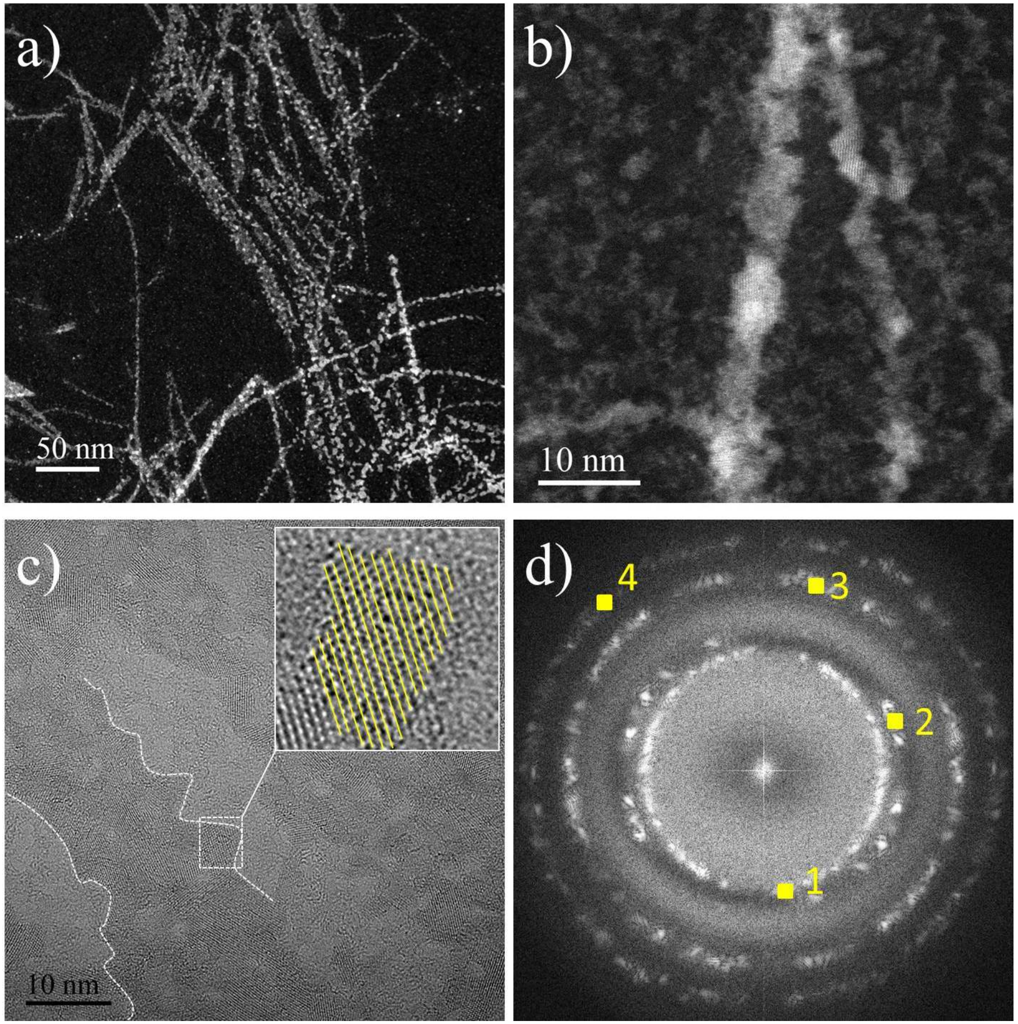


5. Assembling 1D into structure

Increasing voltage (+10 kV) and pulse duration

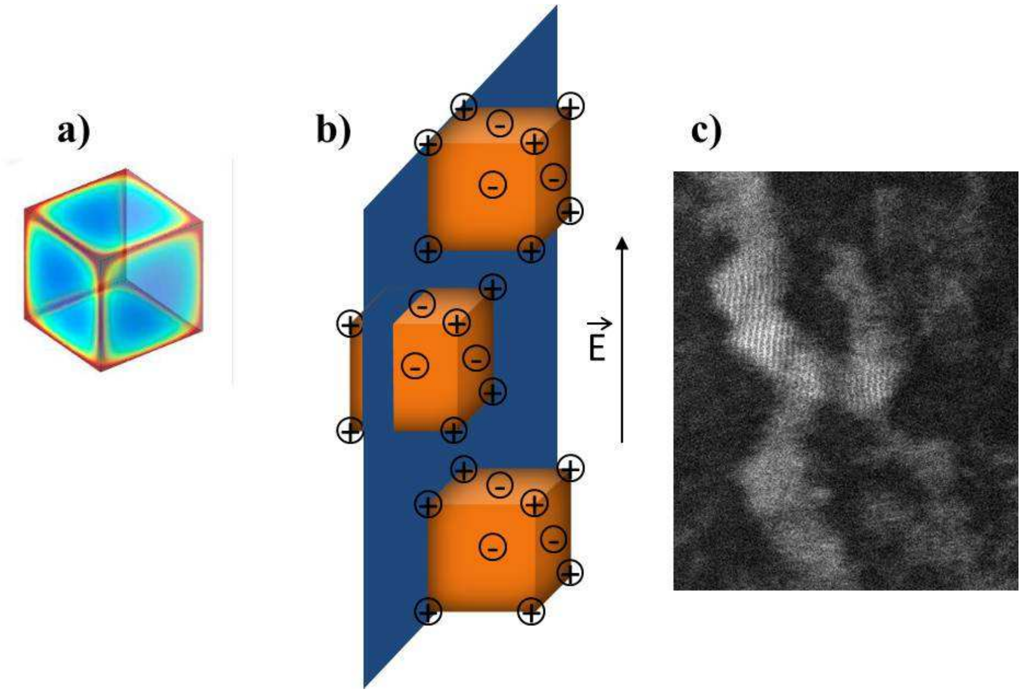
100 ns	500 ns	2500 ns
		
60 min	60 min	60 min

5. Assembling 1D into structure



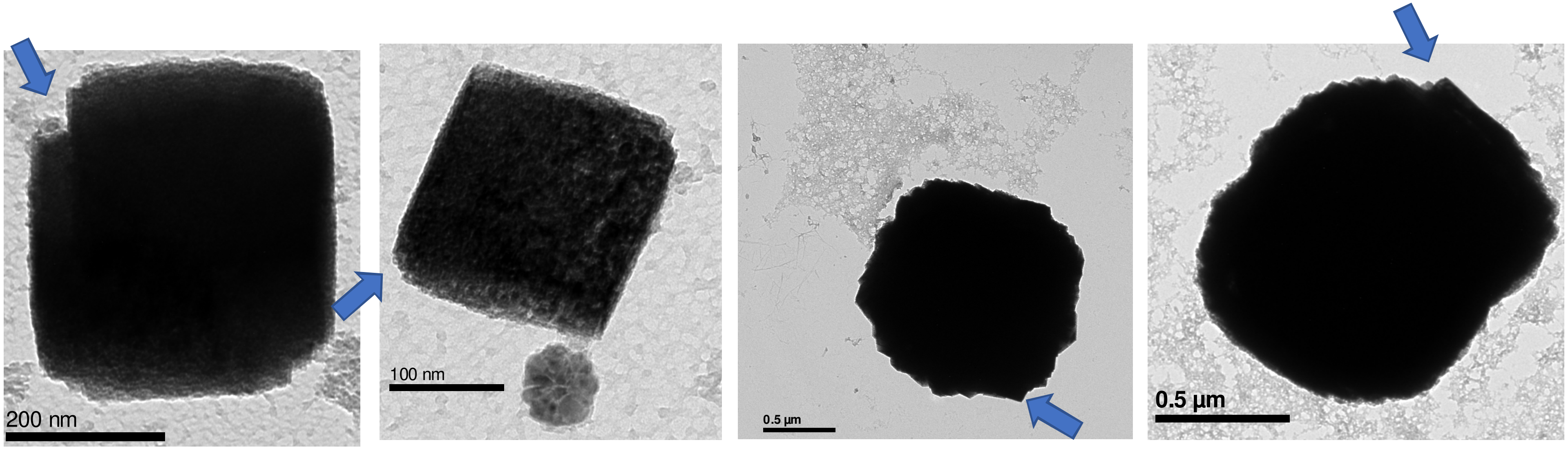
5. Assembling 1D into structure

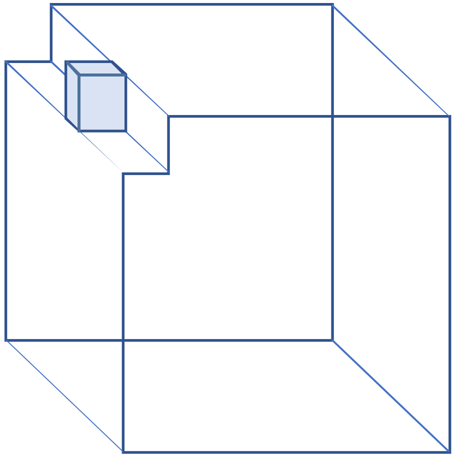
At high fields, Cd nanocubes are non-homogeneously charged



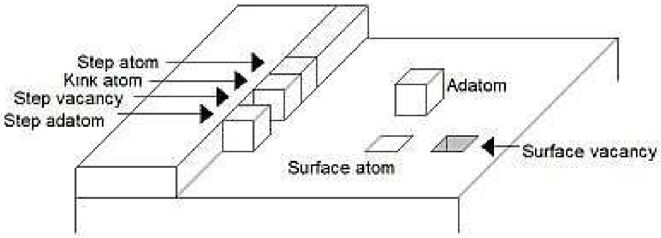
6. “2D” structures

Growth mechanism of Cd cubes

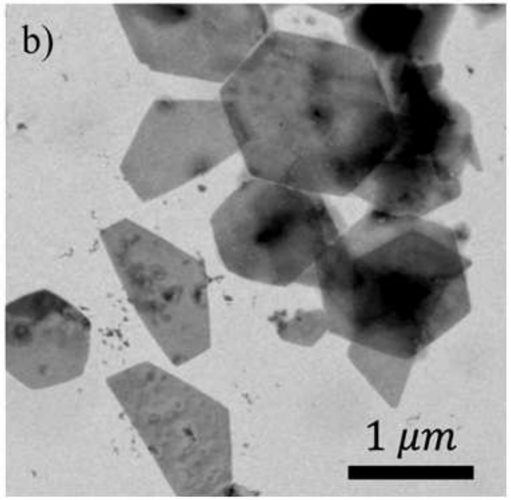


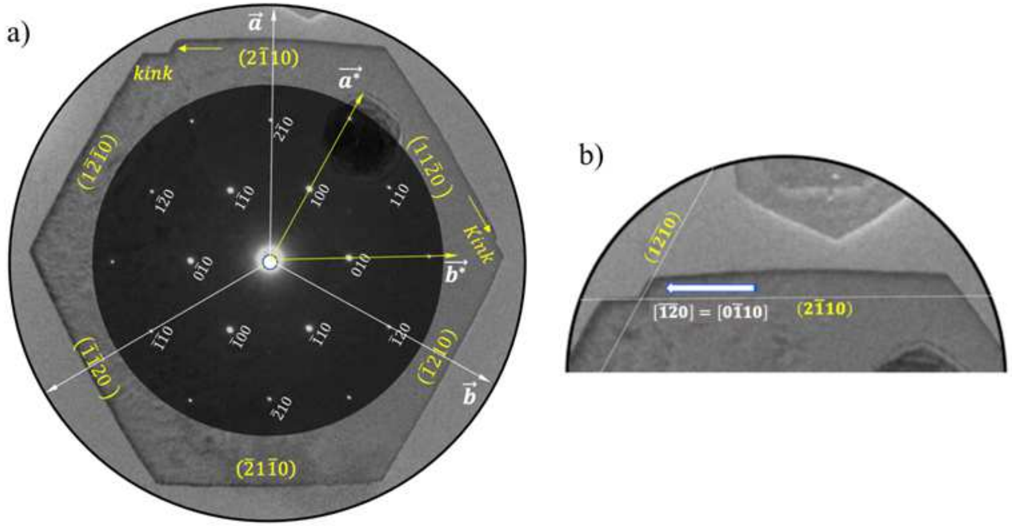


Terrace-Ledge-Kink growth model

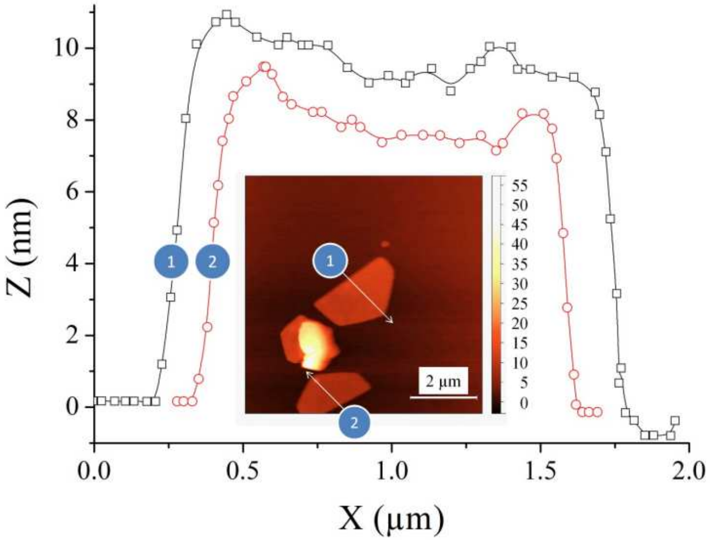


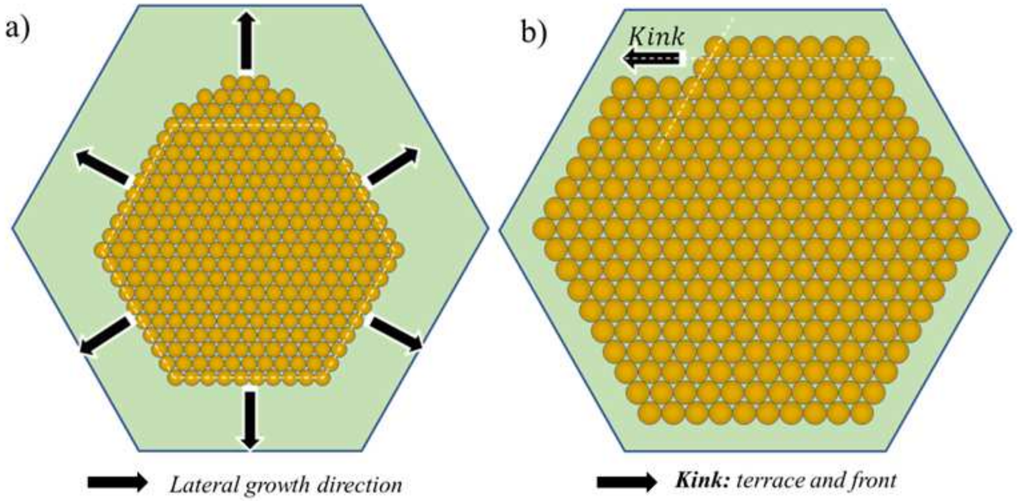
6. “2D” structures





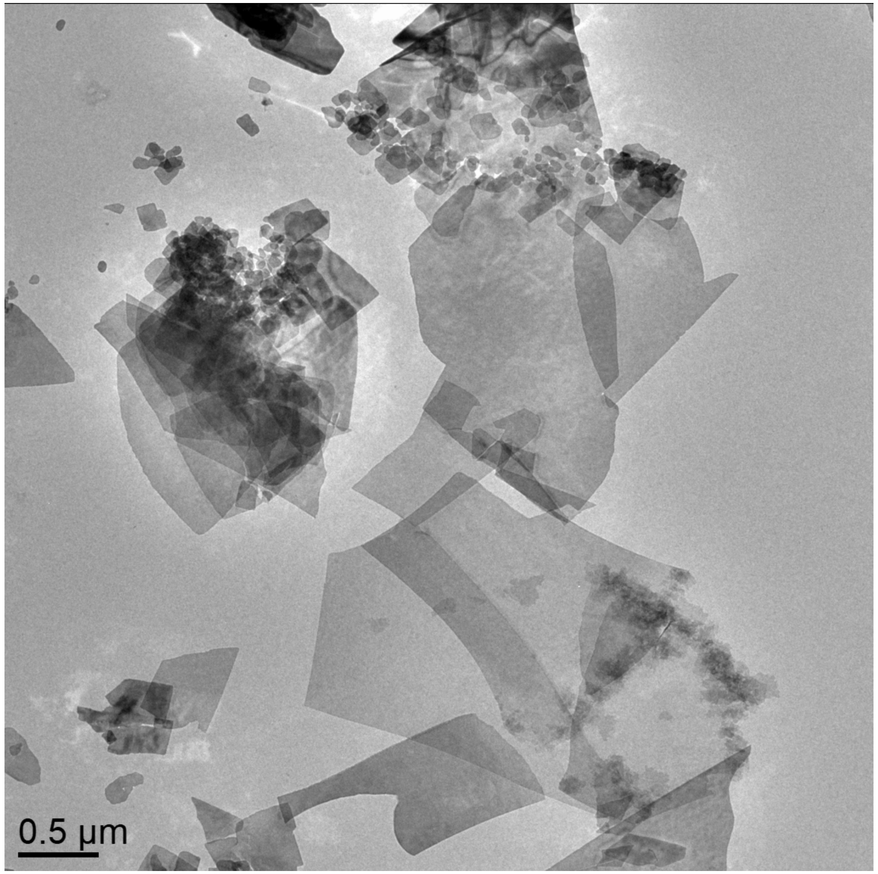
Lead nanosheets

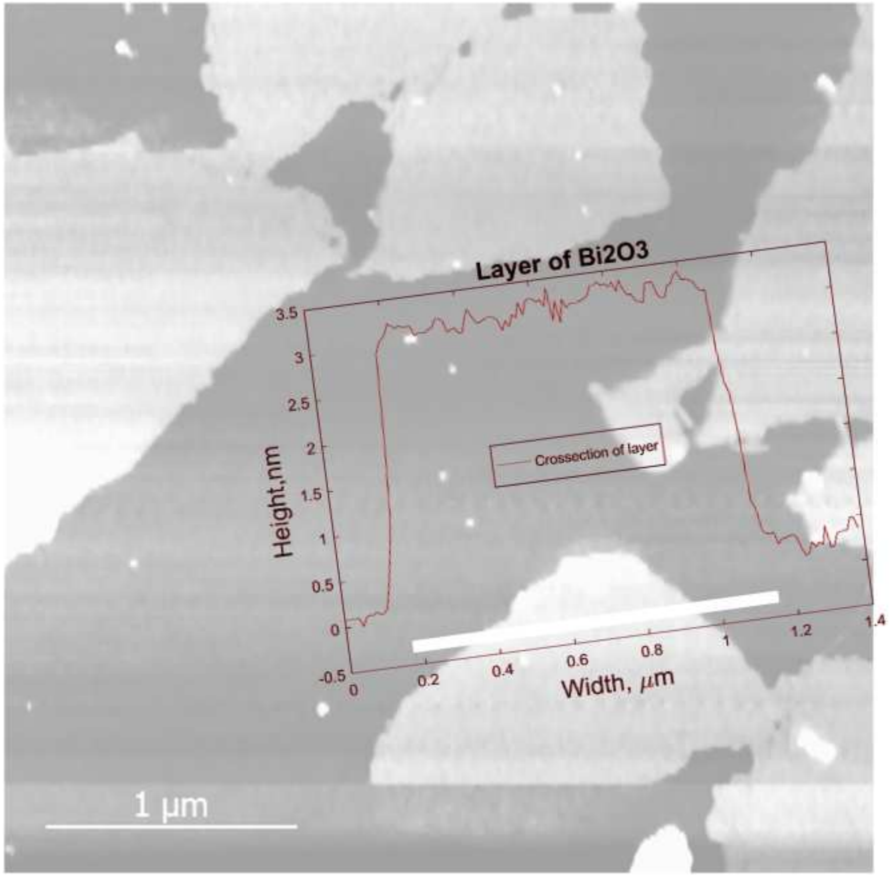




6. “2D” structures

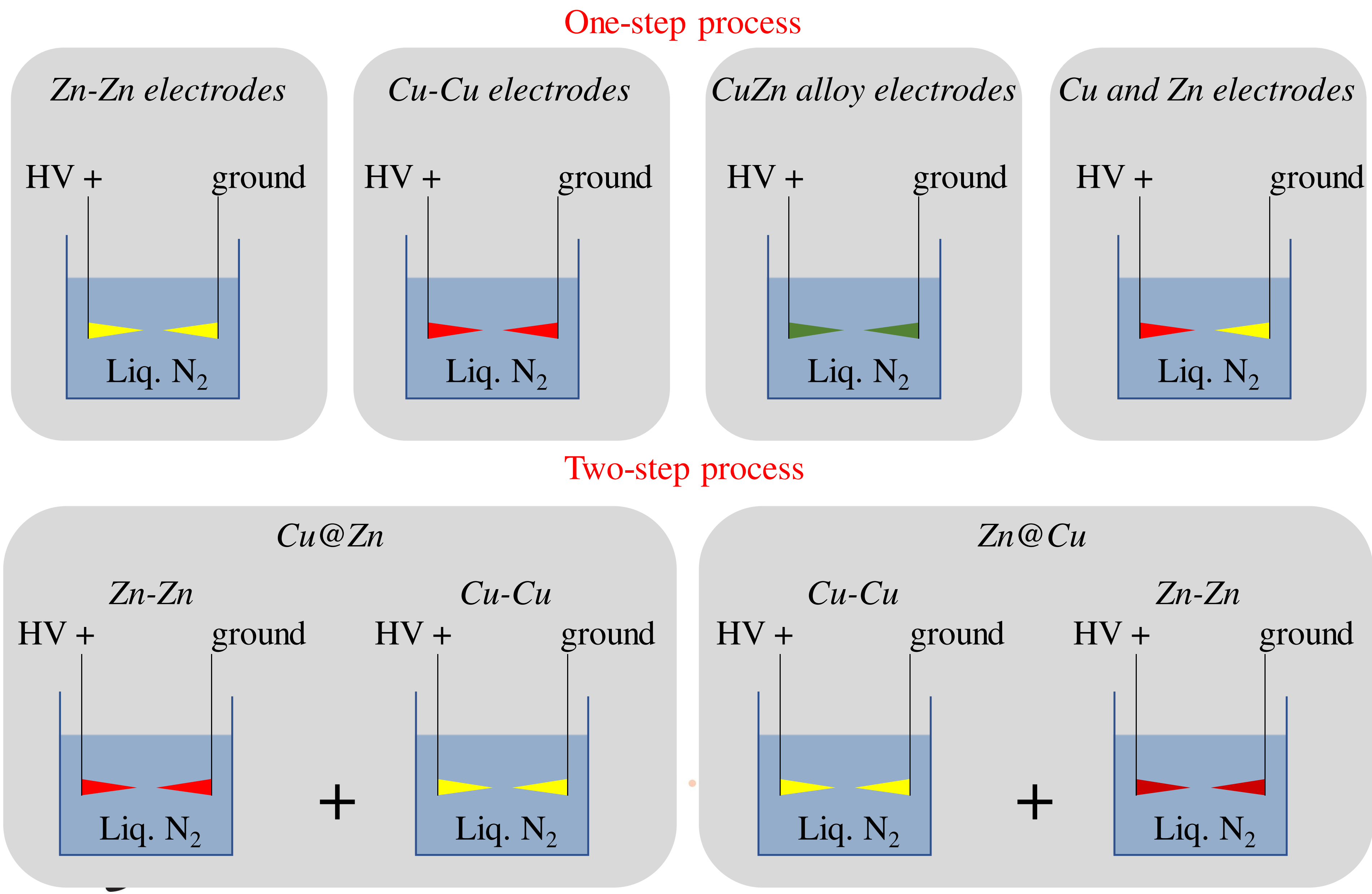
6 – 7 feuillets de δ-Bi_2O_3





Each step ~ 10^4 discharges

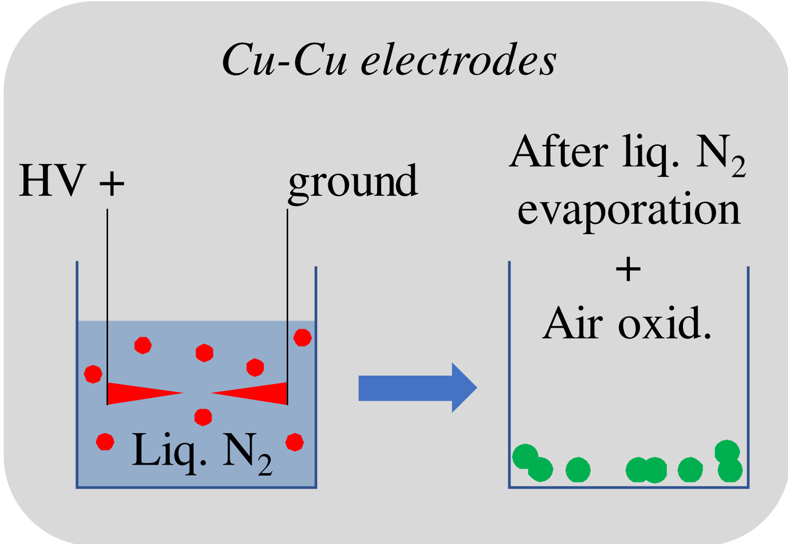
POSSIBLE ARRANGEMENTS



$m.p.(Cu) = 1358$ K
$m.p.(Zn) = 693$ K

Cu-Cu AND Zn-Zn ELECTRODES

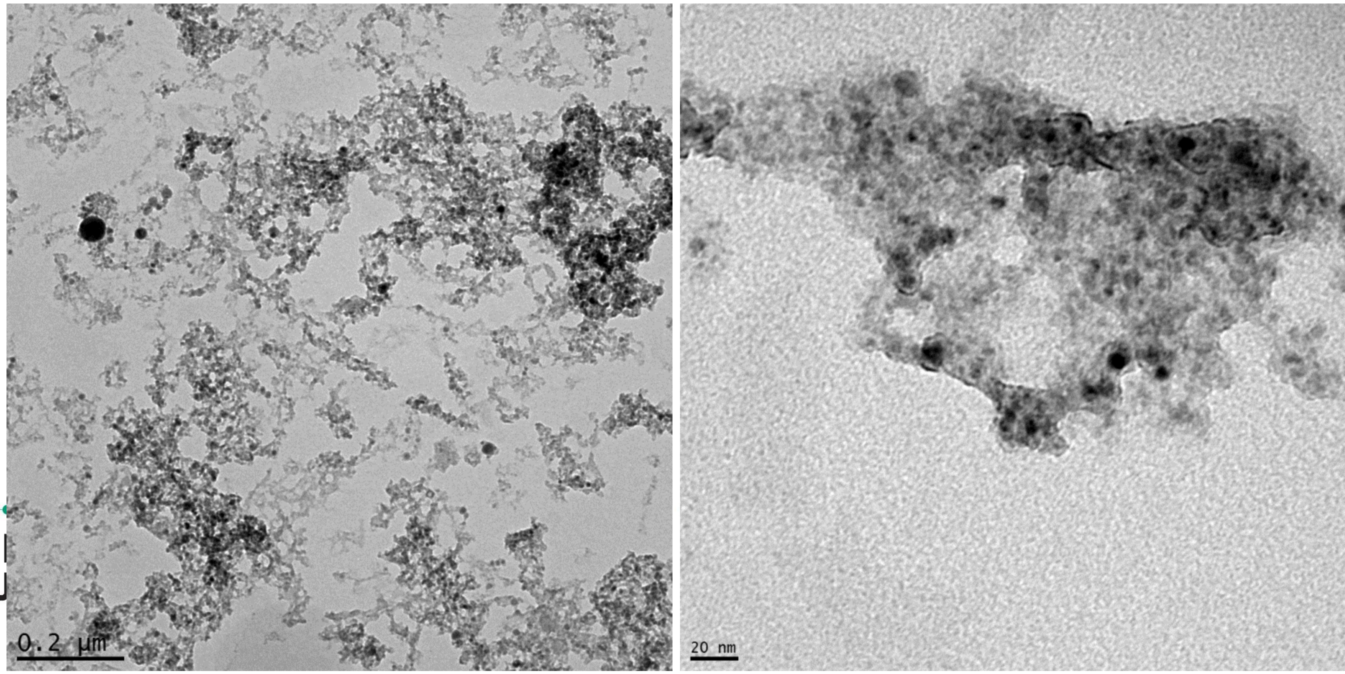
Metallic Cu



CuO

~10^4 discharges

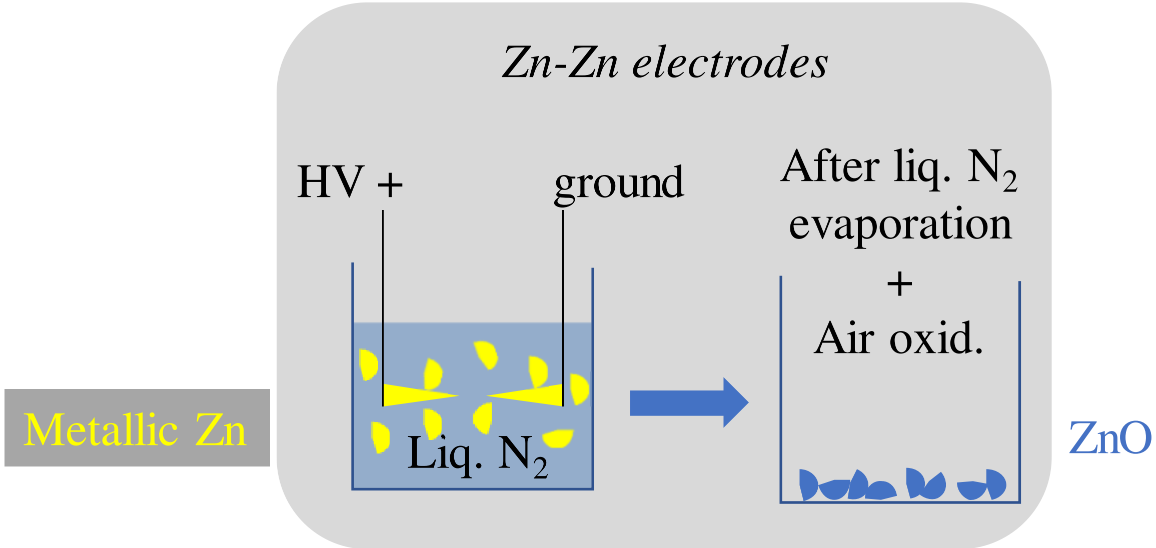
10 Hz → ~15-20 min

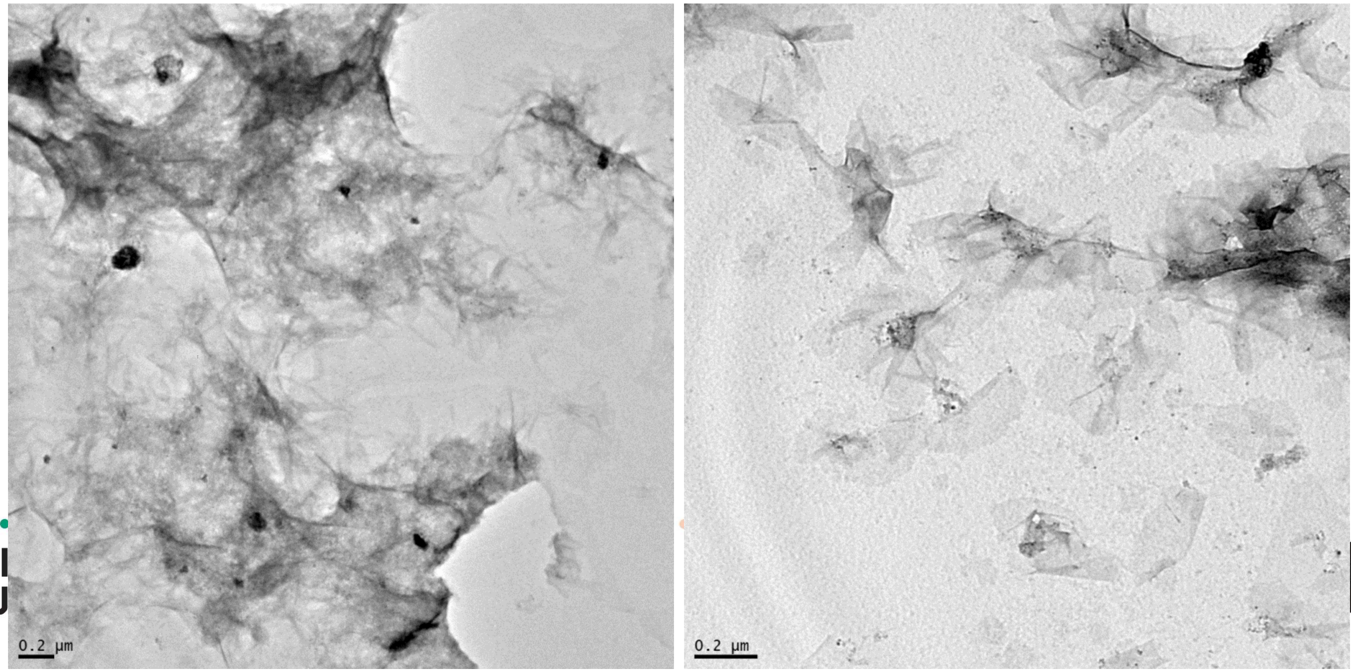


CuO nanodots

$m.p.(Cu) = 1358$ K
$m.p.(Zn) = 693$ K

Cu-Cu AND Zn-Zn ELECTRODES

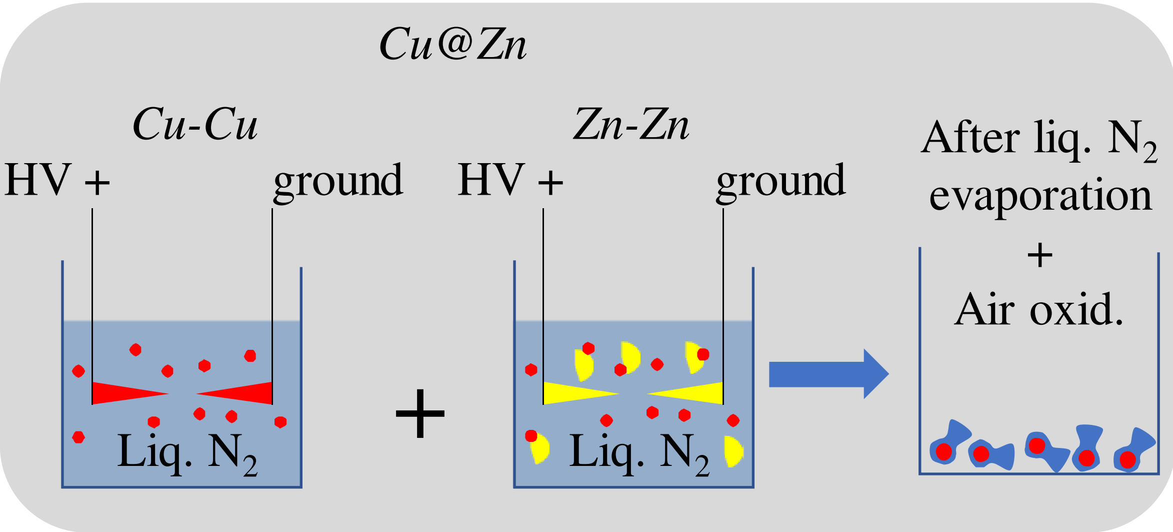


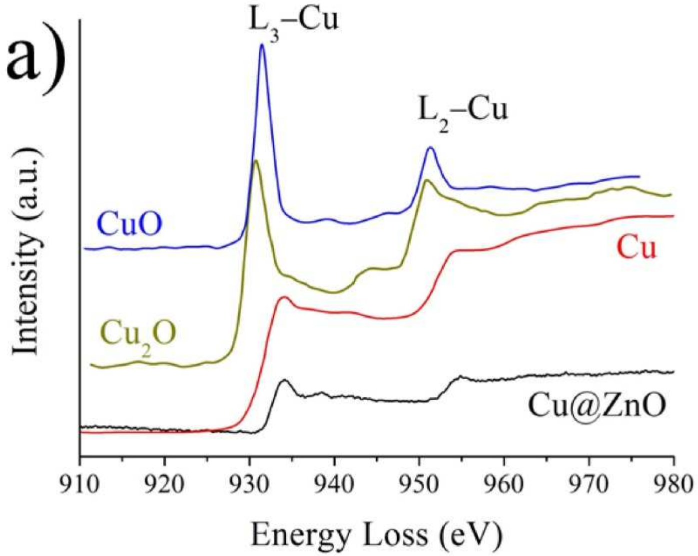


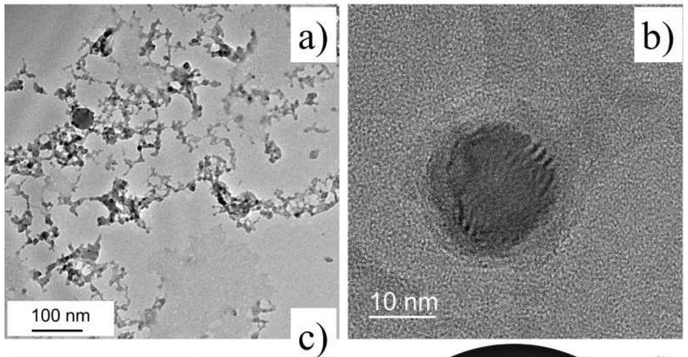
ZnO nanosheets

m.p.(Cu) = 1358 K
m.p.(Zn) = 693 K

CORE-SHELL NPs

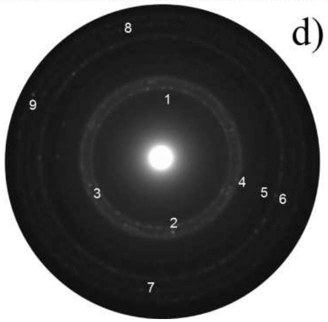


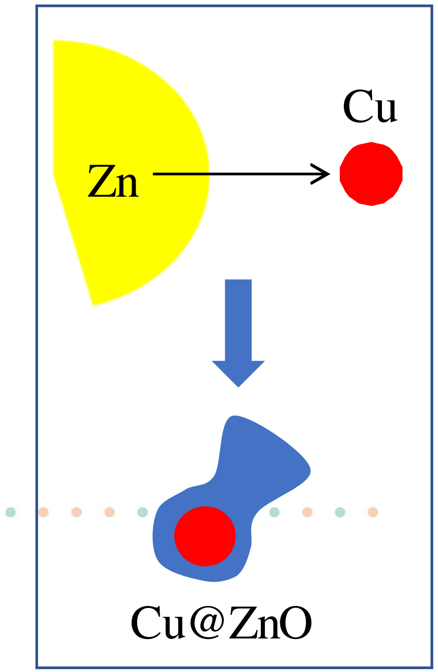


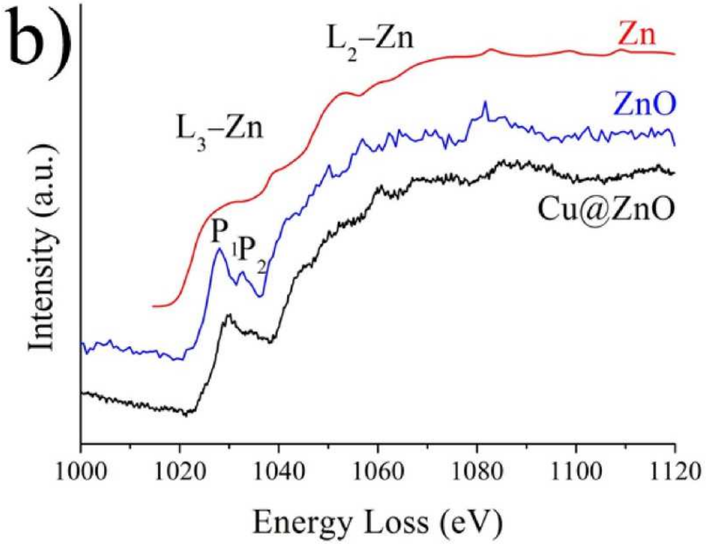


c)

Spot#	d-Spacing (nm)	Element	h k l
1	0.2821	ZnO	1 0 0
2	0.2593	ZnO	0 0 2
3	0.2580	ZnO	0 0 2
4	0.2480	ZnO	1 0 1
5	0.1921	Cu	1 1 0
6	0.1626	ZnO	1 1 0
7	0.1484	ZnO	1 0 3
8	0.1469	Cu	2 0 0
9	0.1380	ZnO	1 1 2

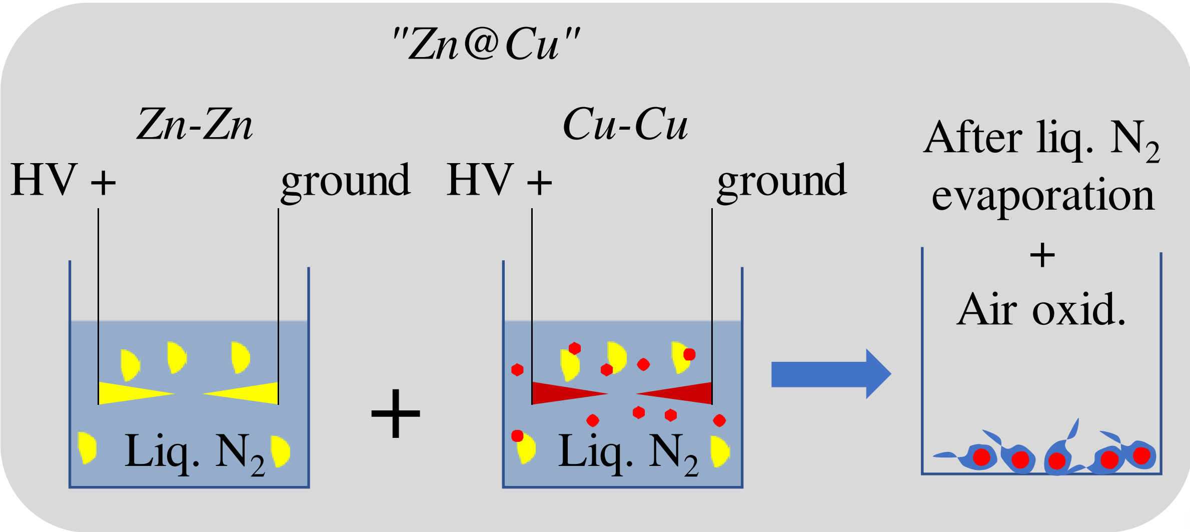


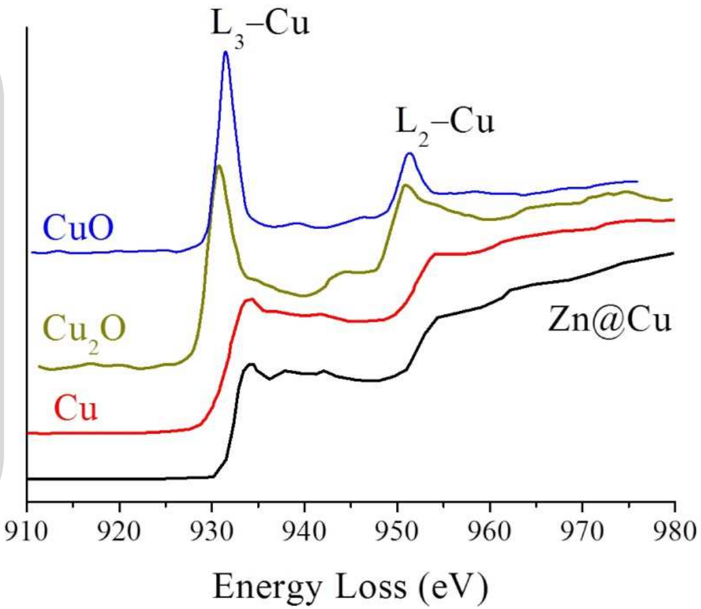


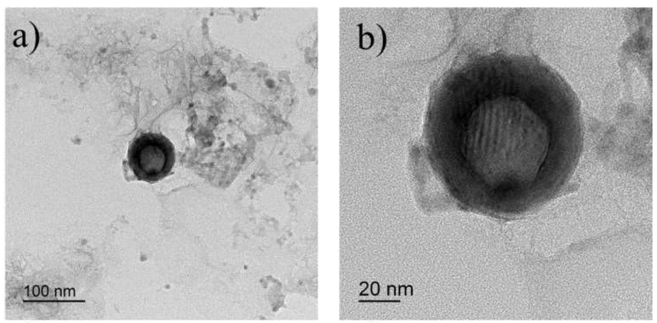


$m.p.(Cu) = 1358$ K
$m.p.(Zn) = 693$ K

CORE-SHELL NPs



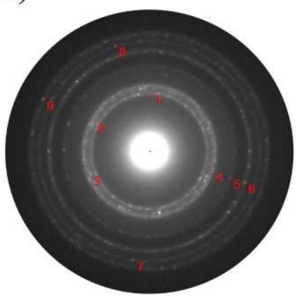


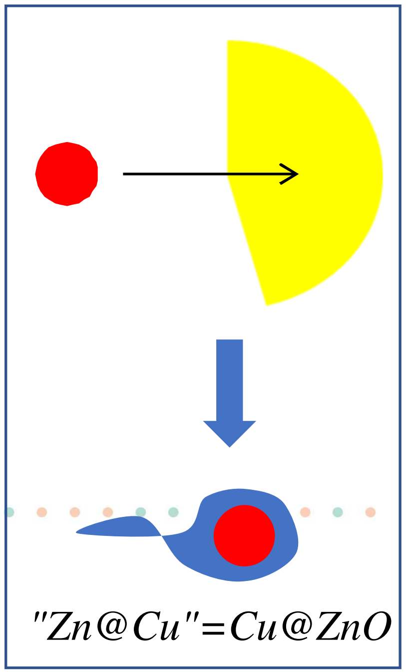


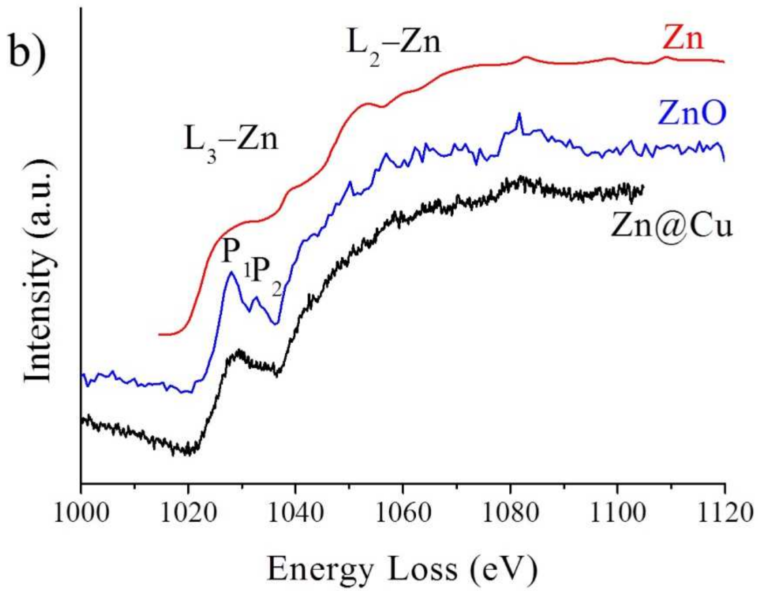
c)

Spot#	d-Spacing (nm)	Element	h k l
1	0.2821	ZnO	1 0 0
2	0.2593	ZnO	0 0 2
3	0.2580	ZnO	0 0 2
4	0.2480	ZnO	1 0 1
5	0.1921	Cu	1 1 0
6	0.1626	ZnO	1 1 0
7	0.1484	ZnO	1 0 3
8	0.1469	Cu	2 0 0
9	0.1380	ZnO	1 1 2

d)

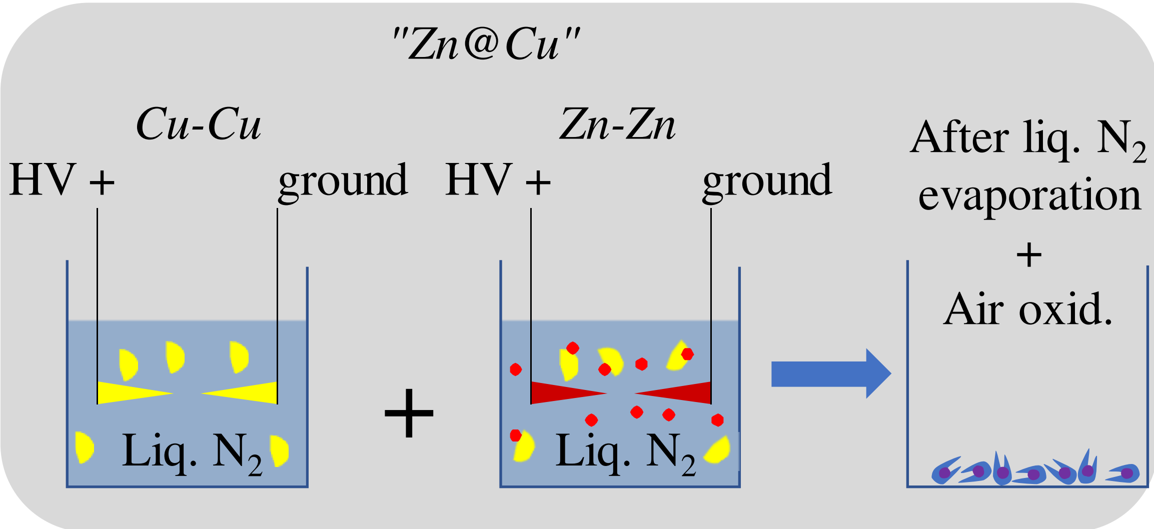






$m.p.(Cu) = 1358$ K
$m.p.(Zn) = 693$ K

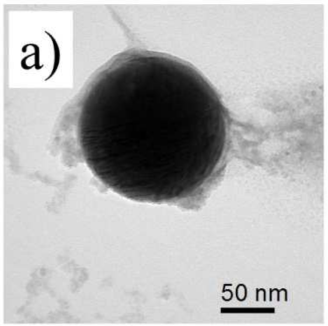
CORE-SHELL NPs

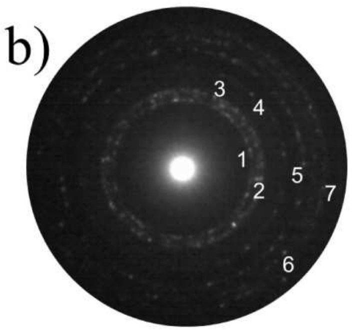


Presence of $Cu_2O@ZnO$ NPs

(to a much lower extent)

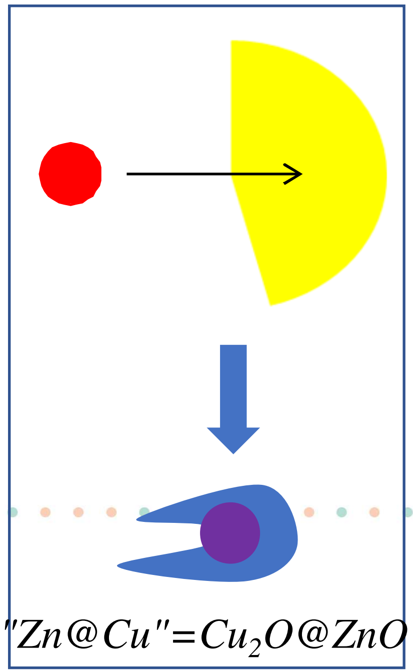
Failure in the film?

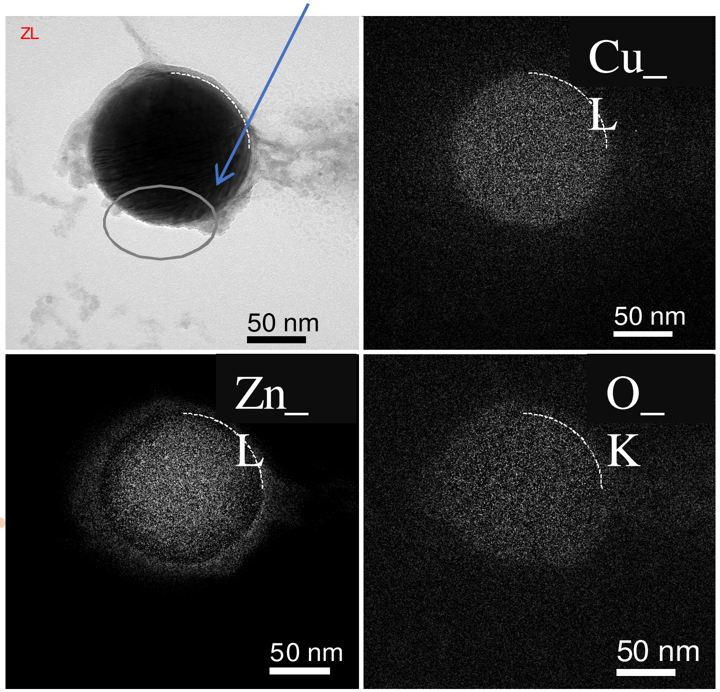




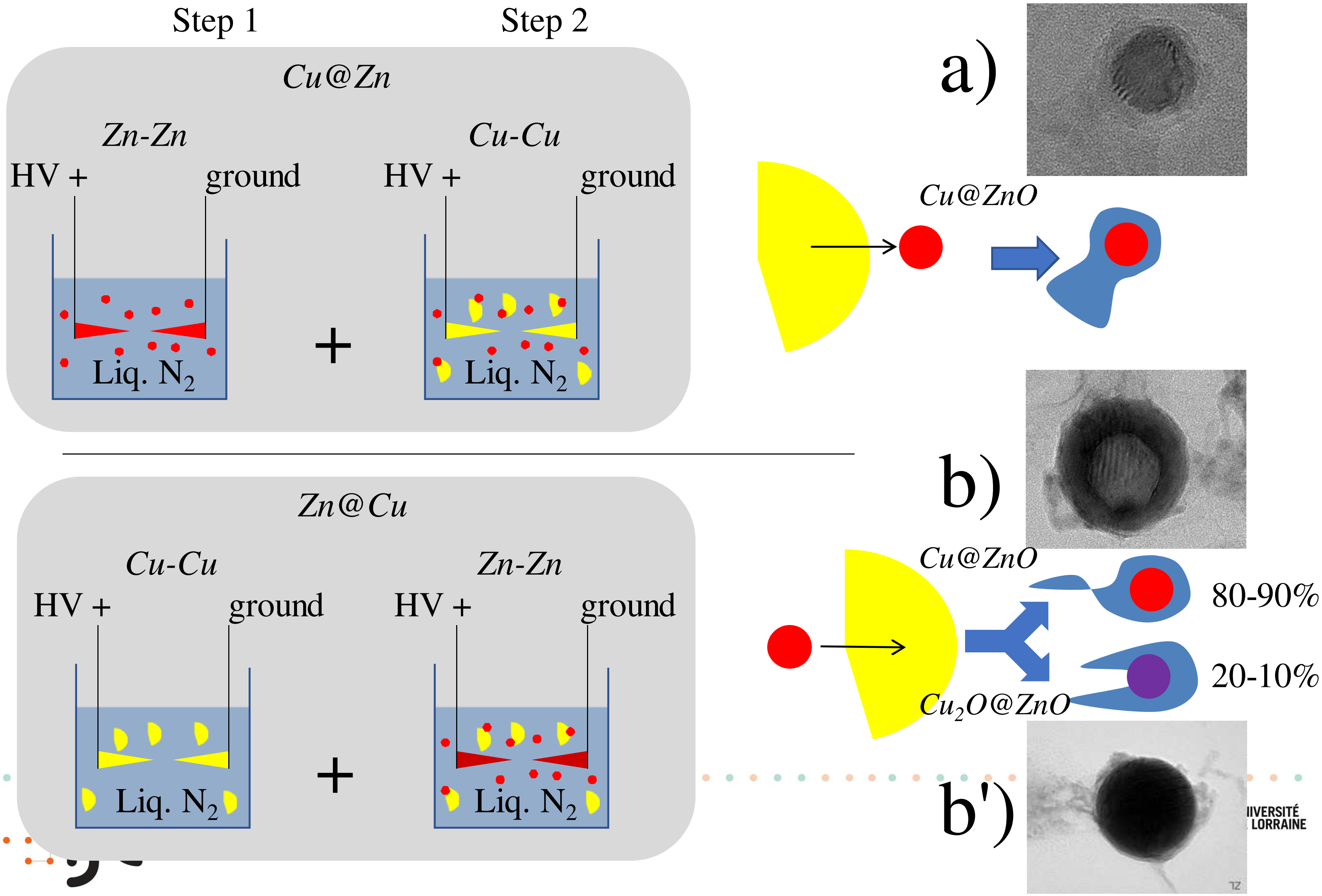
c)

Spot#	d-Spacing (nm)	Element	h k l
1	0.2834	ZnO	1 0 0
2	0.2657	ZnO	0 0 2
3	0.2488	ZnO/Cu_2O	1 0 1/ 1 1 1
4	0.1927	ZnO	1 0 2
5	0.1637	ZnO	1 1 0
6	0.1501	Cu_2O	2 2 0
7	0.1398	ZnO	1 1 2





CORE-SHELL NPs: SUM-UP



3. Conclusion

Ultrahigh quenching rates can be achieved = formation of amorphous structures

Segregation occurs all the time due to:

- Non-sufficient cooling rates
- Segregation phenomena driven by oxidation or surface segregation

The most important parameter to keep is the segregation distance over which phases split

However, properties are also dependent on defects, whose engineering is difficult to achieve… Another topic !

Thank you for your attention

Cette présentation est dédiée à la mémoire de Jean BRETAGNE

Wei-wei's masterpiece