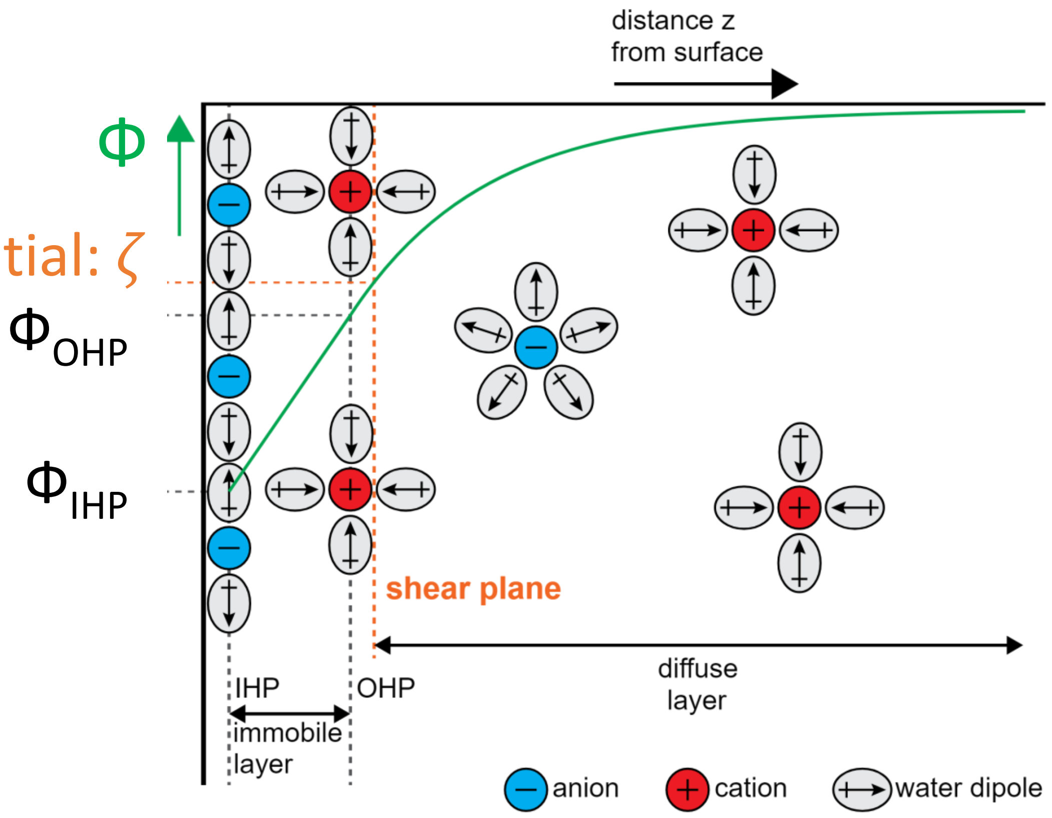
7 - Localized electrodeposition: from 3D parts to nanostructures

I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer



Zeta-potential: ζ

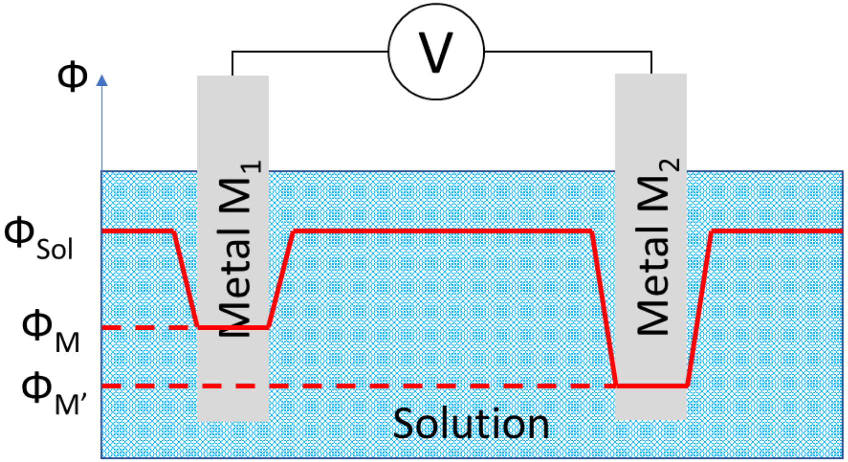
Determining factor
in electrophoresis

I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer

2) Equilibrium characterized by the Nernst equation

Need an additionnal electrode



$$\Delta \mathrm{E} = \Delta E^0 + \frac{RT}{z_1 F} ln[M_1^{z_1+}] - \frac{RT}{z_2 F} ln[M_2^{z_2+}]$$

$$\Delta \mathrm{E} = \sum \Delta\phi = \phi_M - \phi_{M'} = E_M^{eq} - E_{M'}^{eq}$$

ΔE is the difference of Nernst potentials

I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer

2) Equilibrium characterized by the Nernst equation

3) At equilibrium, there exists an exchange current

$$i_0 = zF\beta_{Red}[Red] \cdot exp^{\frac{-\Delta G^*_{\chi,\, Red}}{RT}} \cdot exp^{\frac{-\alpha zF\Delta\phi_{eq}}{RT}} = zF\beta_{Ox}[Ox] \cdot exp^{\frac{-\Delta G^*_{\chi,\, Ox}}{RT}} \cdot exp^{\frac{(1-\alpha)zF\Delta\phi_{eq}}{RT}}$$

I) Reminders

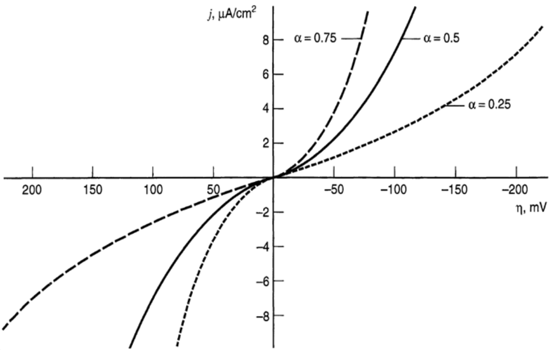
1) Electrode in an electrolyte: development of an electrical double layer

2) Equilibrium characterized by the Nernst equation

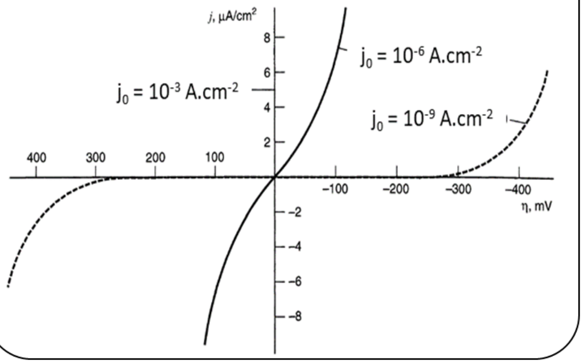
3) At equilibrium, there exists an exchange current

4) If the electrode potential is forced to a value $E < E^{eq}$ then electrons will be transfered from the cathode to metal cations → electrodeposition

Effect of the transfer coefficient α



Effect of the exchange current i_0



Out of equilibrium: $\Delta\phi = \Delta\phi_{eq} + \eta$

$$i = i_0\left(exp^{\frac{(1-\alpha)zF\eta}{RT}} - exp^{\frac{-\alpha zF\eta}{RT}}\right)$$

Butler-Volmer equation

I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer

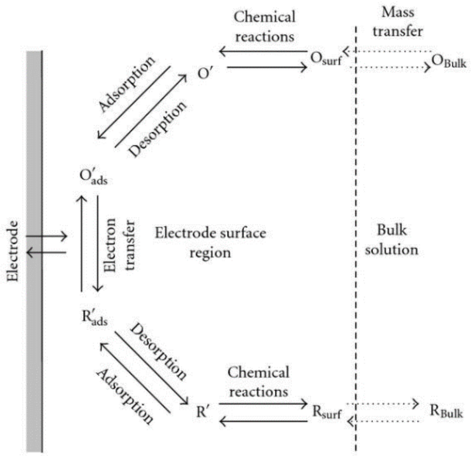
2) Equilibrium characterized by the Nernst equation

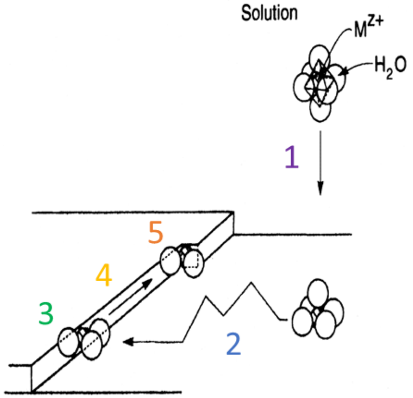
3) At equilibrium, there exists an exchange current

4) If the electrode potential is forced to a value $E < E^{eq}$ then electrons will be transfered from the electrode to metal cations → electrodeposition

5) Electrodeposition may involve five steps:

- Mass transfer to the interphase
- Chemical reactions
- Adsorption on planar surfaces
- Adion diffusion and dehydration
- Charge transfer/electrocrystallization





I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer

2) Equilibrium characterized by the Nernst equation

3) At equilibrium, there exists an exchange current

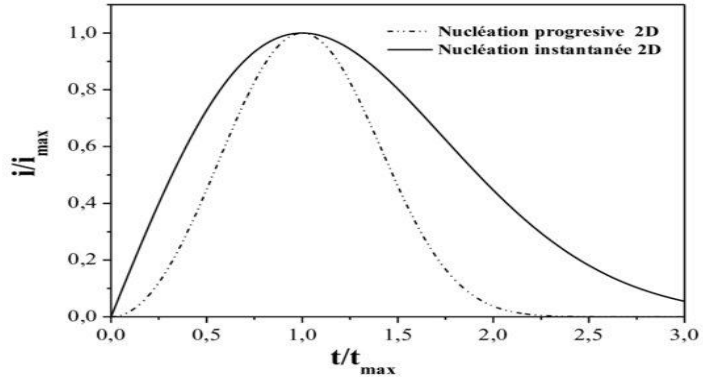
4) If the electrode potential is forced to a value $E < E^{eq}$ then electrons will be transfered from the electrode to metal cations → electrodeposition

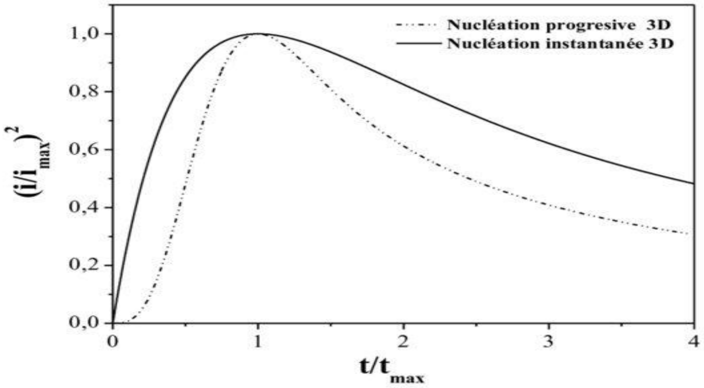
5) Electrodeposition may involve five steps

6) 3D or 2D Nuclei can be formed instantaneously or progressively:

3D/2D related to the interplay between η and $\Delta\sigma$

Density of nuclei N(t) related to η and the density of surface defects





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5) Electrodeposition may involve five steps

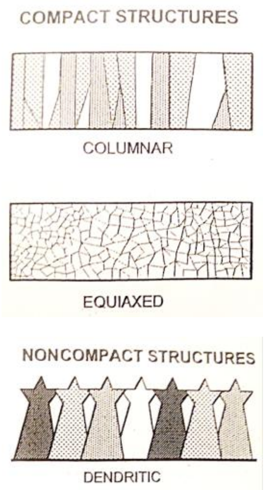
6) 3D or 2D Nuclei can be formed instantaneously or progressively

7) Deposit characteristics result from nucleation and growth regime

low η: low nuclei density, coarse grain compact coating

medium η: high nuclei density, fine grain structure

high η: oriented growth (dendrites) or powdery deposit



I) Reminders

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3) At equilibrium, there exists an exchange current

4) If the electrode potential is forced to a value $E < E^{eq}$ then electrons will be transfered from the electrode to metal cations → electrodeposition

5) Electrodeposition may involve five steps

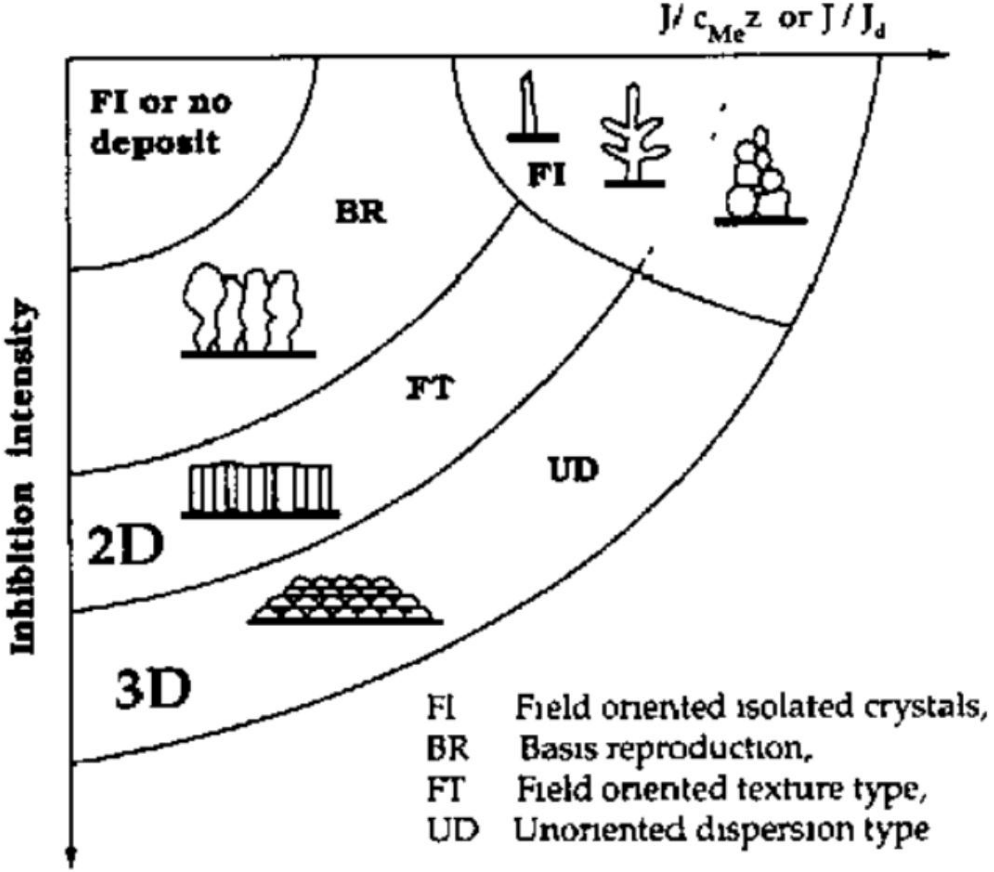
6) 3D or 2D Nuclei can be formed instantaneously or progressively

7) Deposit characteristics result from nucleation and growth regime

8) Several metal cations can be reduced simultaneously (supersaturated solid solutions possible)

Direct deposition
Codeposition and anomalous codeposition
Underpotential deposition of A on B then of B on A

I) Reminders



9) Tuning levers: electrical (η, j, pulses) and physicochemical ([C], T°, additives…)

II) Electrodeposition for micro and nanotechnologies

In a uniform overpotential field and uniform current density, electrodeposition occurs uniformly

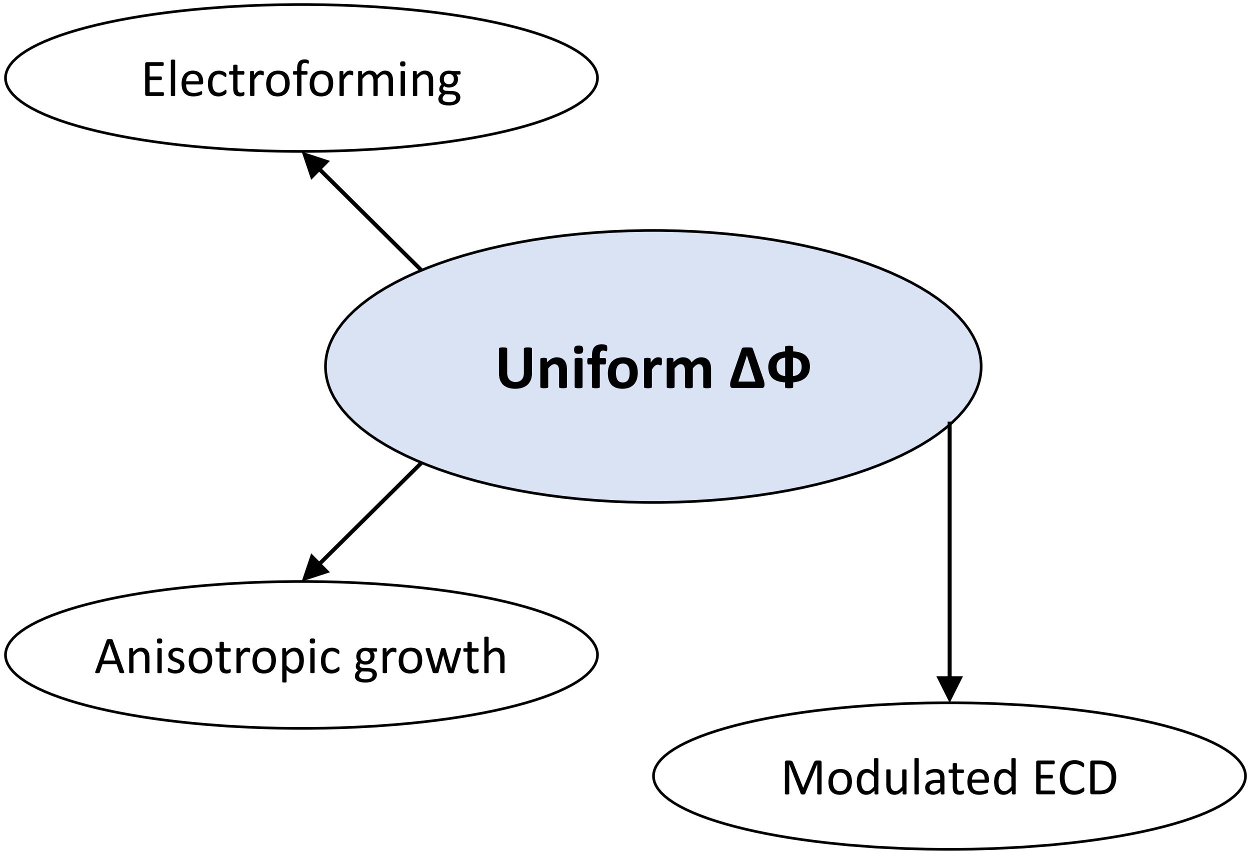
→ Localized electrochemistry

Synthetic electrochemistry:

An important tool for micro and nano fabrication!!!

II) Electrodeposition for micro and nanotechnologies

In a uniform overpotential field and uniform current density, electrodeposition occurs uniformly



Electroforming

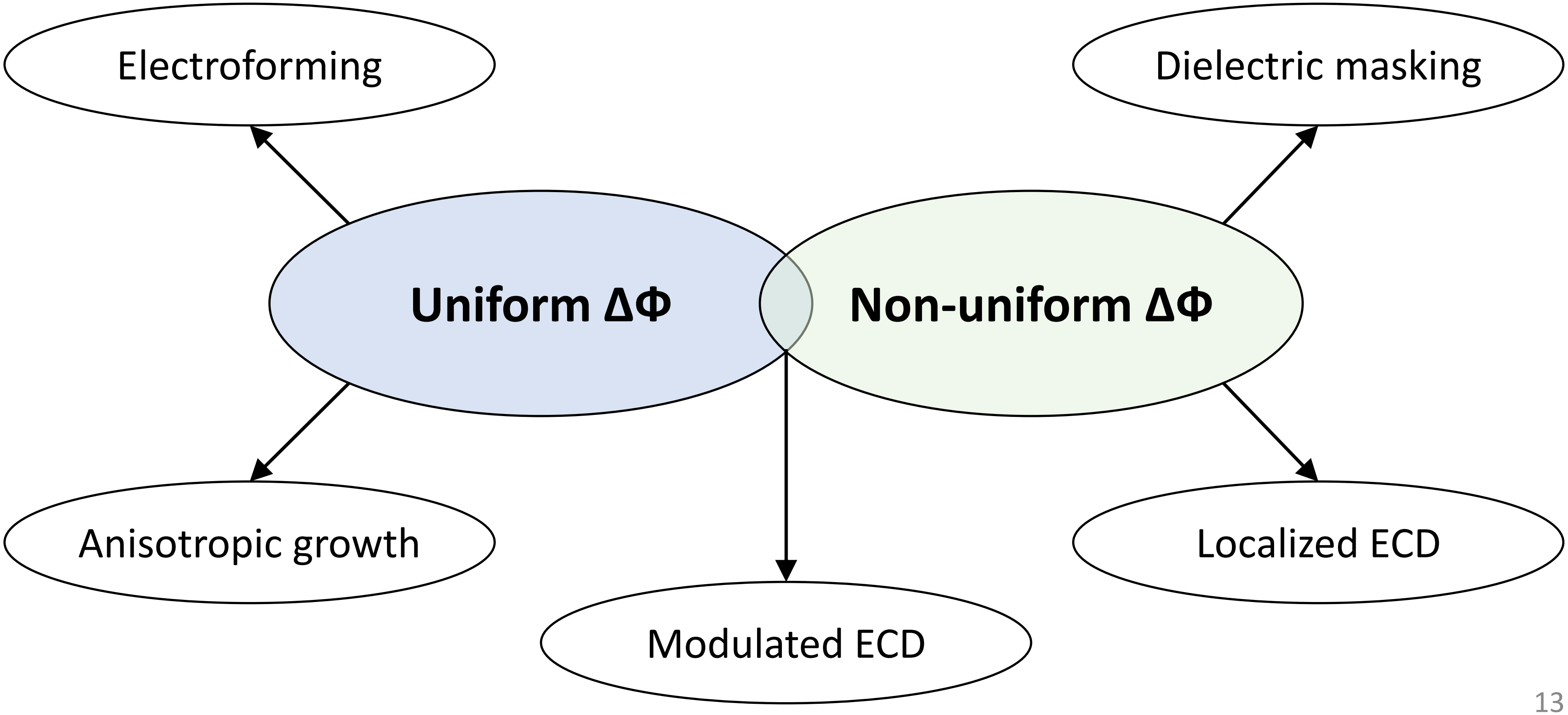
Uniform ΔΦ

Anisotropic growth

Modulated ECD

II) Electrodeposition for micro and nanotechnologies

In a uniform overpotential field and uniform current density, electrodeposition occurs uniformly



Electroforming

Dielectric masking

Uniform ΔΦ

Non-uniform ΔΦ

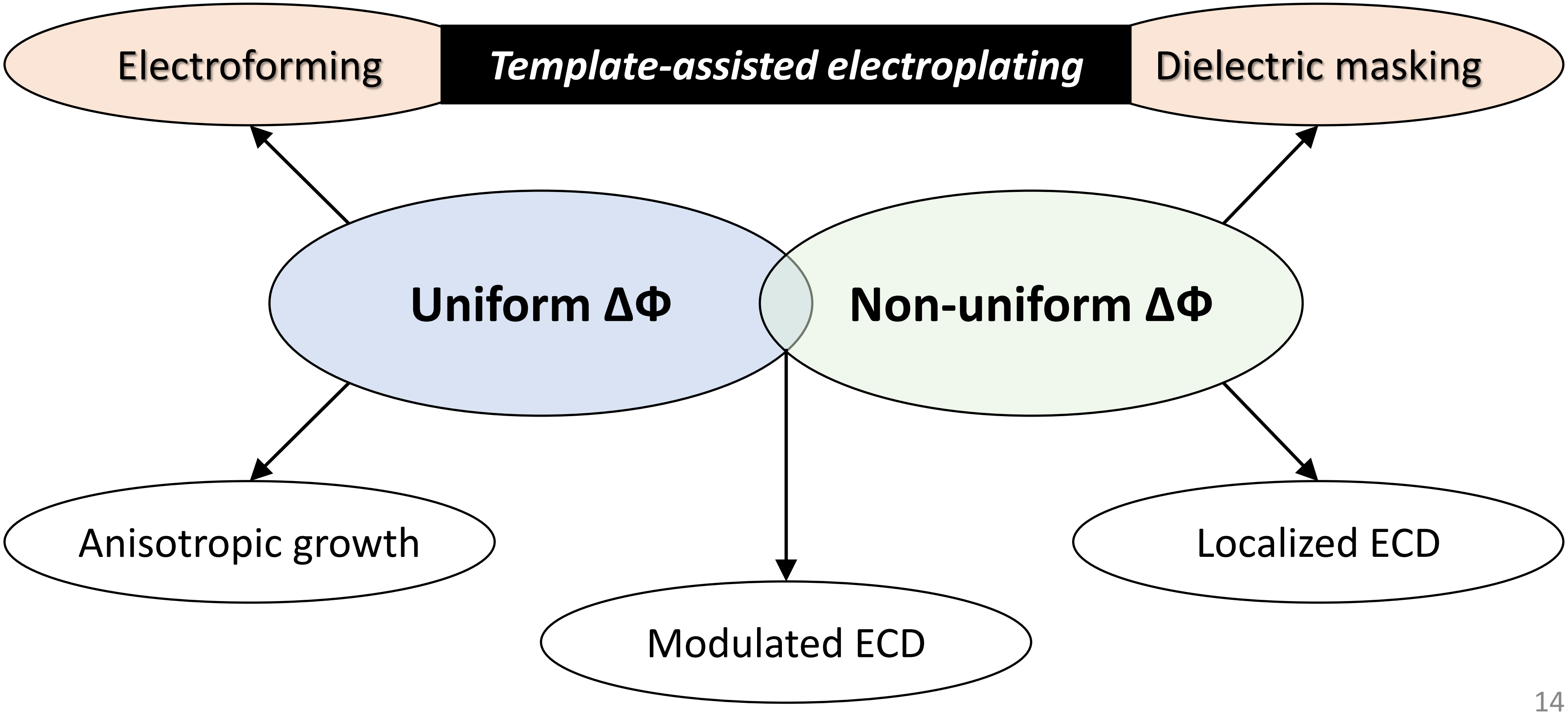
Anisotropic growth

Localized ECD

Modulated ECD

II) Electrodeposition for micro and nanotechnologies

In a uniform overpotential field and uniform current density, electrodeposition occurs uniformly



Electroforming

Template-assisted electroplating

Dielectric masking

Uniform ΔΦ

Non-uniform ΔΦ

Anisotropic growth

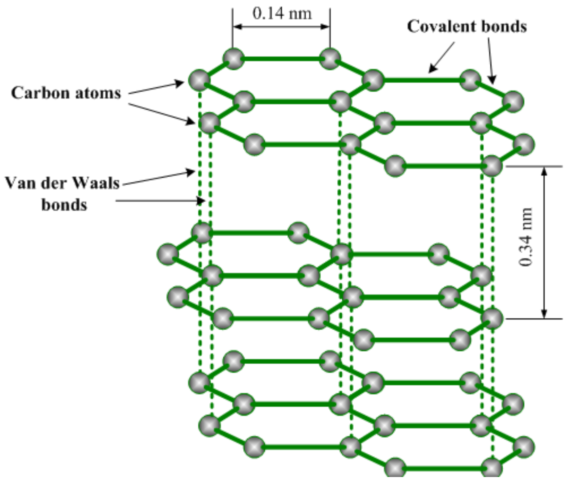
Modulated ECD

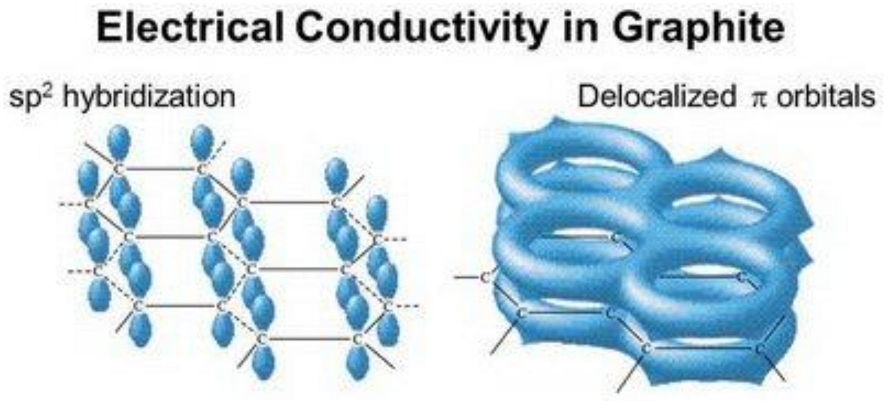
Localized ECD

III) Anisotropic growth

1) Anisotropic substrate

Highly Oriented Pyrolytic Graphite (HOPG)





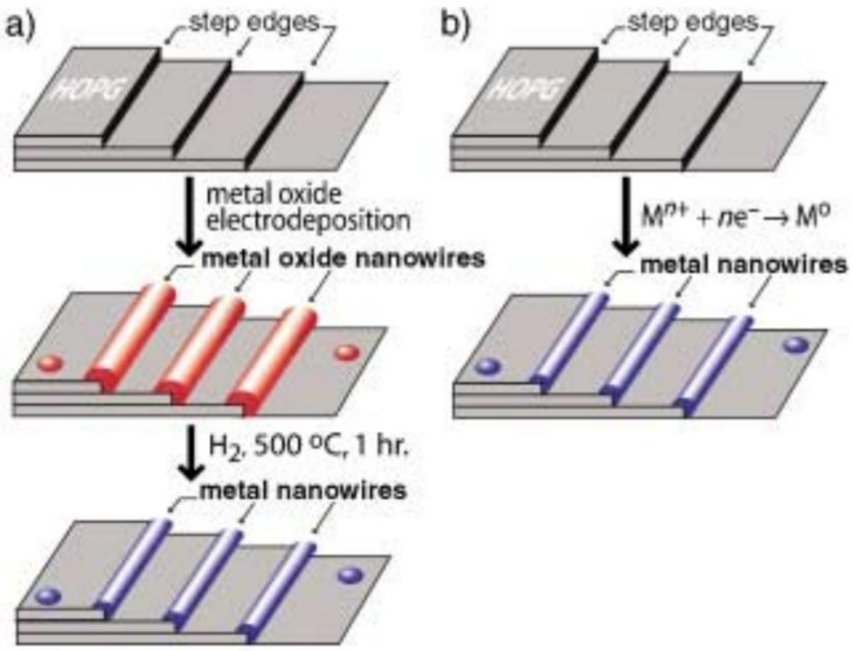
Basal plane: $\sigma_{//} \approx 3\times10^{5}$ S.cm^{-1}

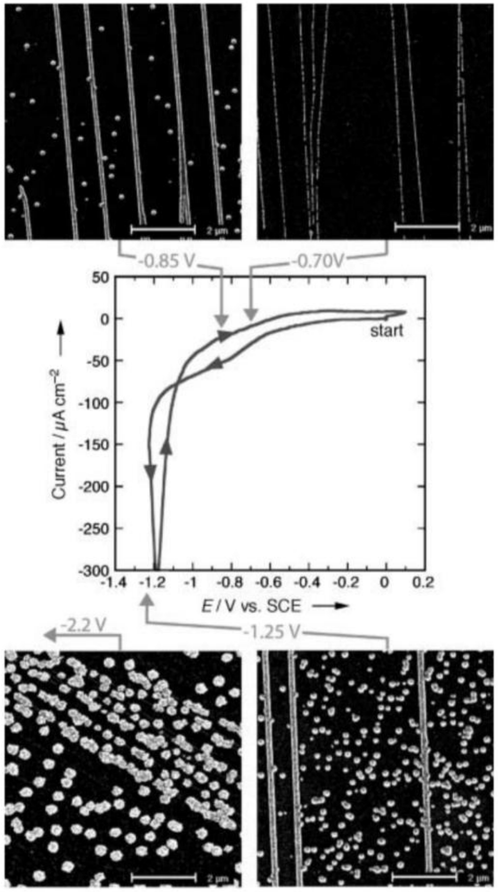
Transversal: $\sigma_{\perp} \approx 3.3\times10^{2}$ S.cm^{-1}

III) Anisotropic growth

1) Anisotropic substrate

Electrochemical Step Edge Decoration (ESED)



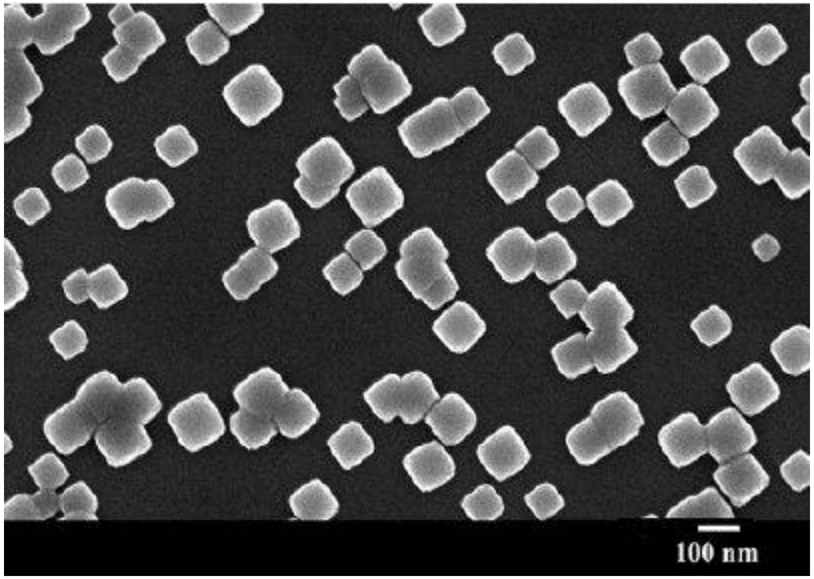


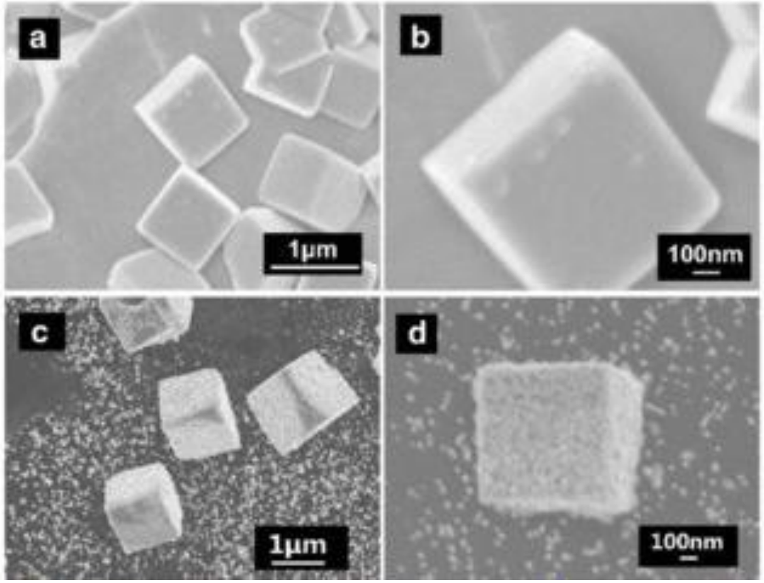
N(t) increases with increasing η

III) Anisotropic growth

2) Anisotropic electrodeposit

Electrodeposited Cu_2O nanocubes





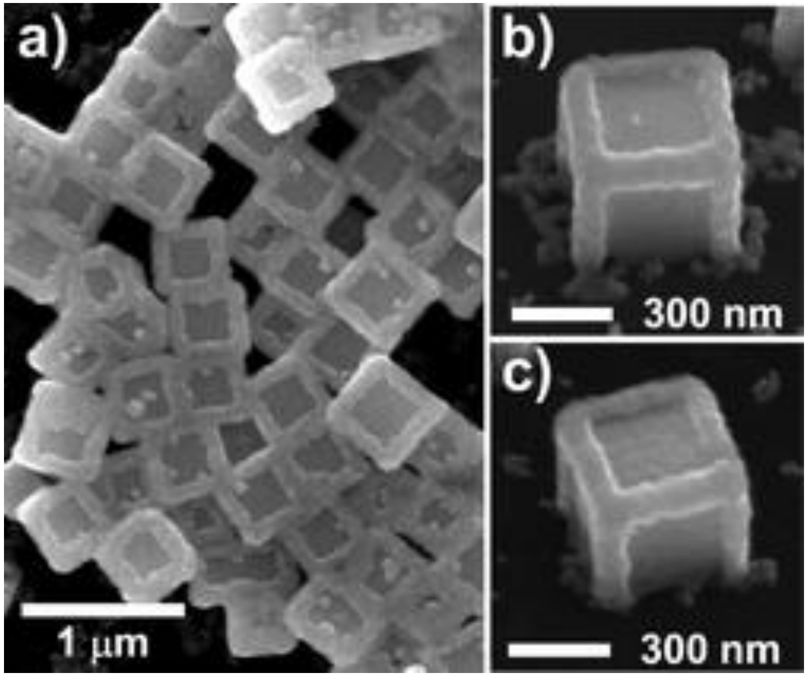
Minimization of surface energy → growth faster for high energy crystal planes

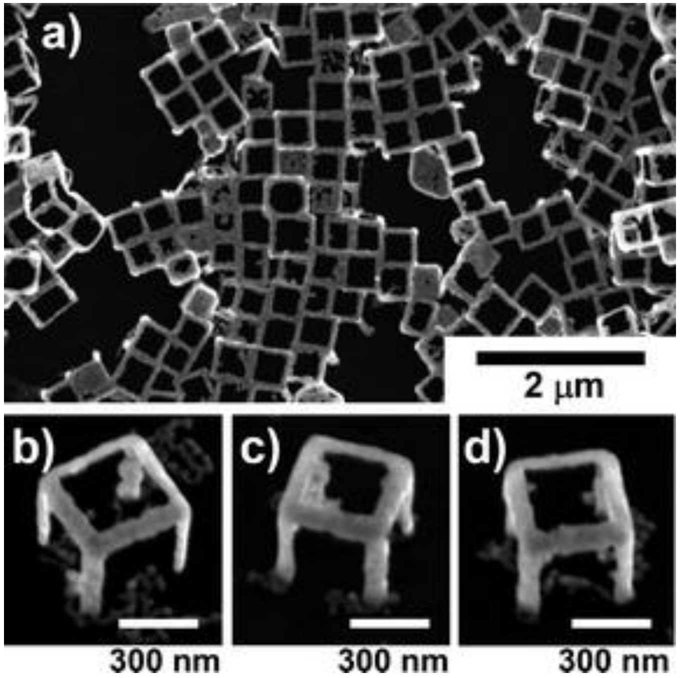
Nuclei geometry correspond to the crystal lattice symmetry

III) Anisotropic growth

2) Anisotropic electrodeposit

Electrodeposited Au nanocube frame





Au electroplating at edges and corners / electrodissolution of copper

Nanostructured Au has interesting surface plasmon resonance

III) Anisotropic growth

2) Anisotropic electrodeposit

Electrodeposited ZnO hexagonal nanorods

Step 1: Electrolytic production of OH^-

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
$2H_2O + O_2 + 2e^- \rightarrow H_2O_2 + 2OH^-$
$H_2O_2 + 2e^- \rightarrow 2OH^-$

Step 2: Precipitation of $Zn(OH)_2$

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$

Step 3: Spontaneous dehydration of $Zn(OH)_2$

$Zn(OH)_2 \rightarrow ZnO + H_2O$

III) Anisotropic growth

2) Anisotropic electrodeposit

Electrodeposited ZnO hexagonal nanorods

(001) plane is polar
$(1\bar{1}0), (100), and\ (010)$ are apolar

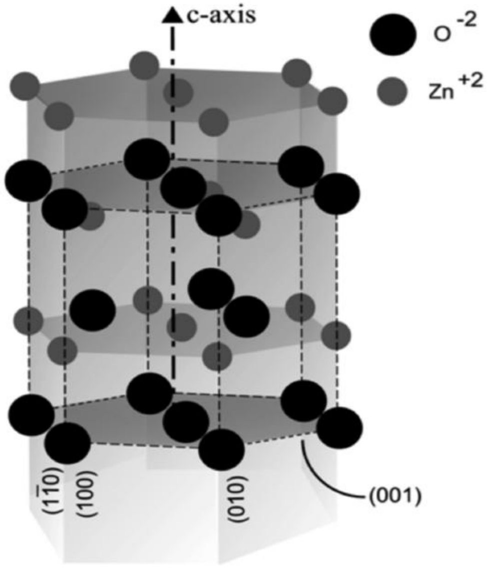
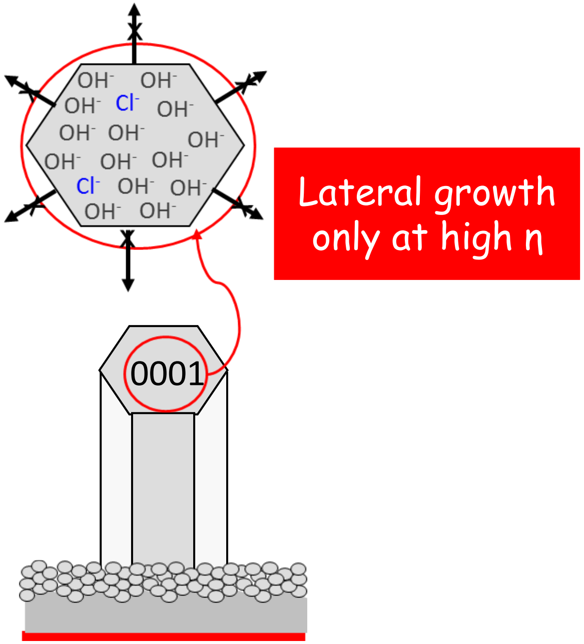


Figure 1. Schematic representation of the ZnO wurtzite structure.

OH^- preferentially produced on the polar place

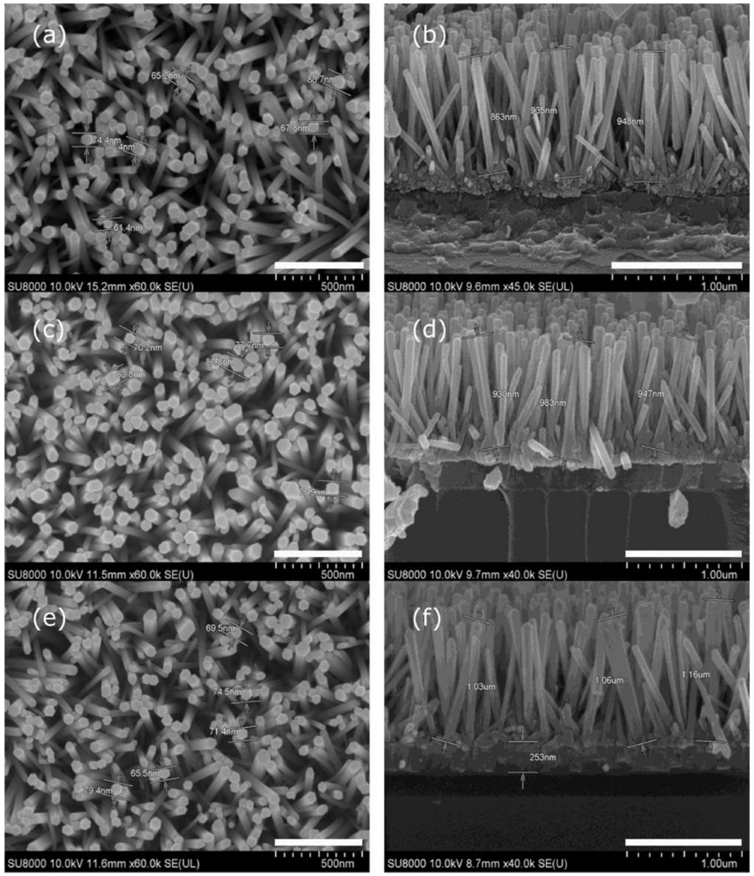


Lateral growth only at high η

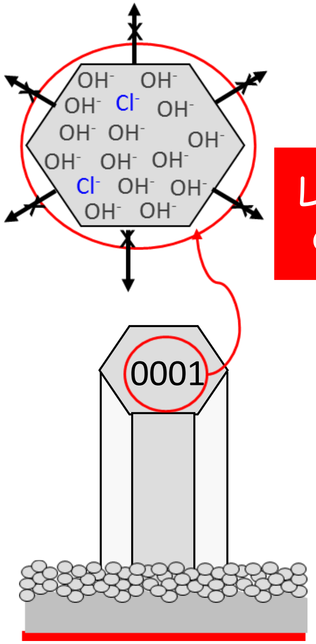
III) Anisotropic growth

2) Anisotropic electrodeposit

Electrodeposited ZnO hexagonal nanorods



OH^- preferentially produced on the polar place



Lateral growth only at high η

III) Anisotropic growth

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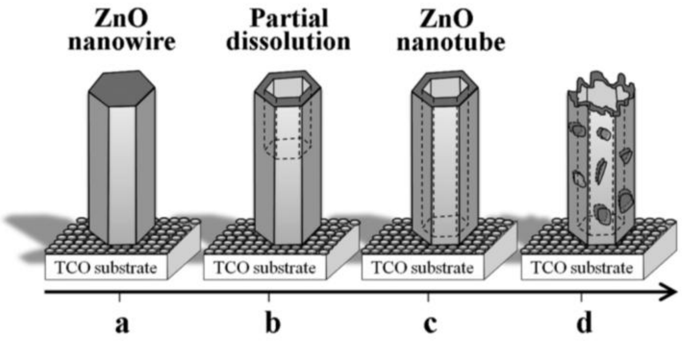
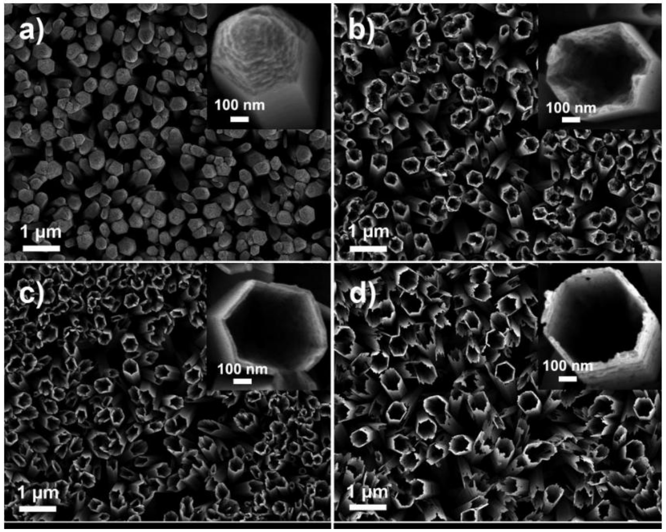
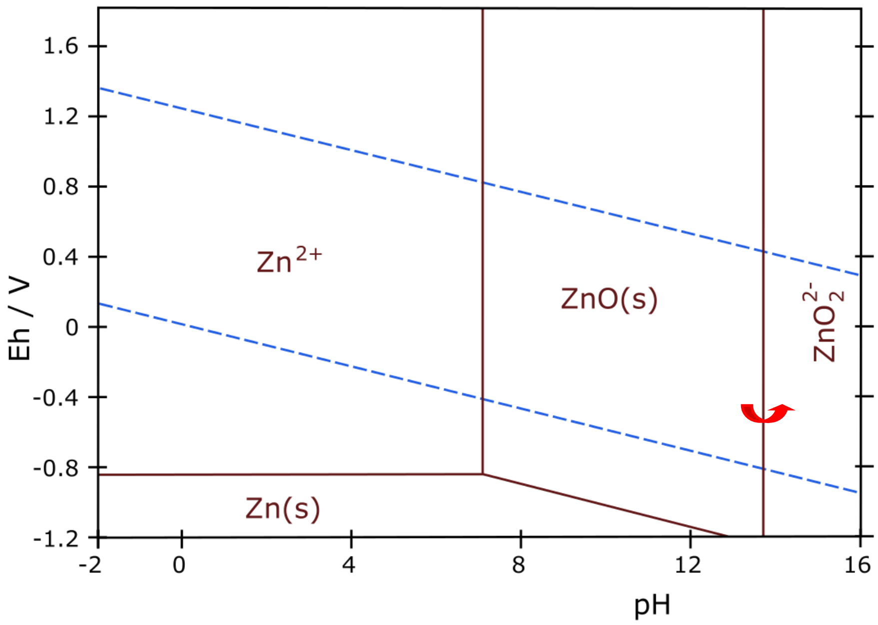
Electrodeposited ZnO hexagonal nanorods



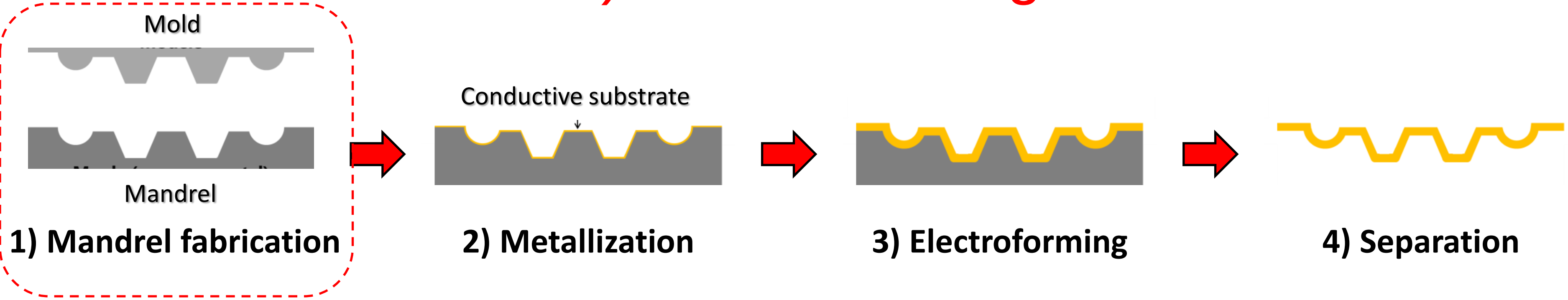


OH$^-$ preferentially produced on the polar place



III) Template-assisted electrodeposition

1) Electroforming



1) Mandrel fabrication

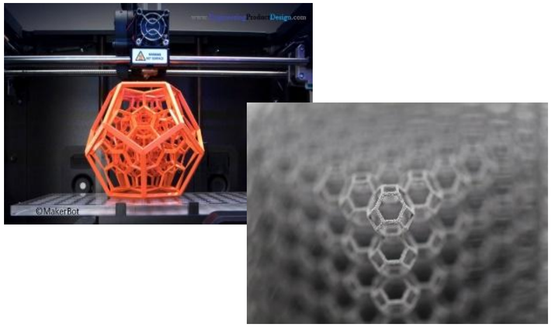
2) Metallization

3) Electroforming

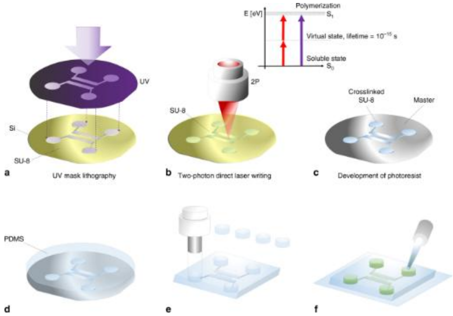
4) Separation

Natural materials:

Additive manufacturing:

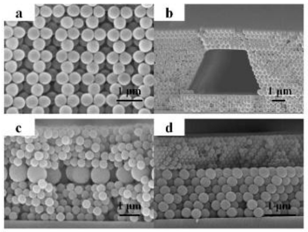


Photolithography:

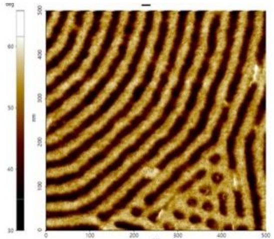


Machining — Molding — Stamping:

Self-assemblies:



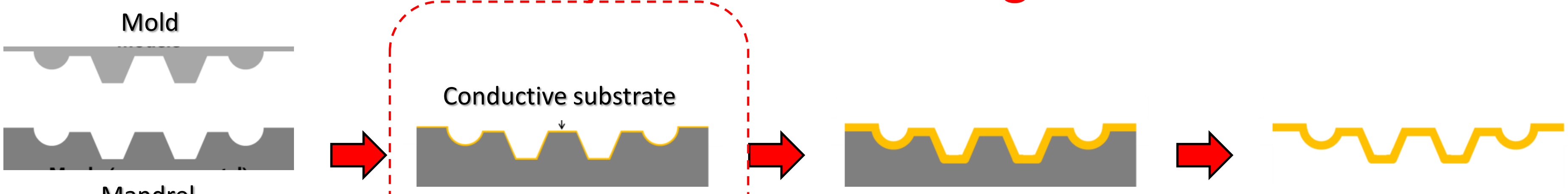
Colloidal crystals



Block copolymers

III) Template-assisted electrodeposition

1) Electroforming



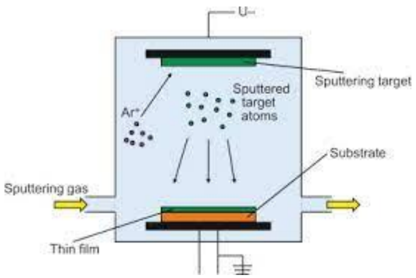
1) Mandrel fabrication

2) Metallization

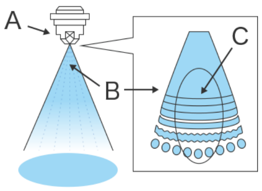
3) Electroforming

4) Separation

Physical deposition



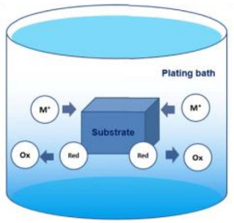
Physical vapor deposition



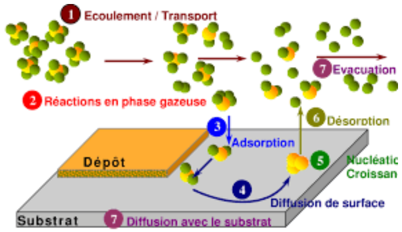
Spray coating

Chemical deposition

Electroless plating



Chemical vapor deposition



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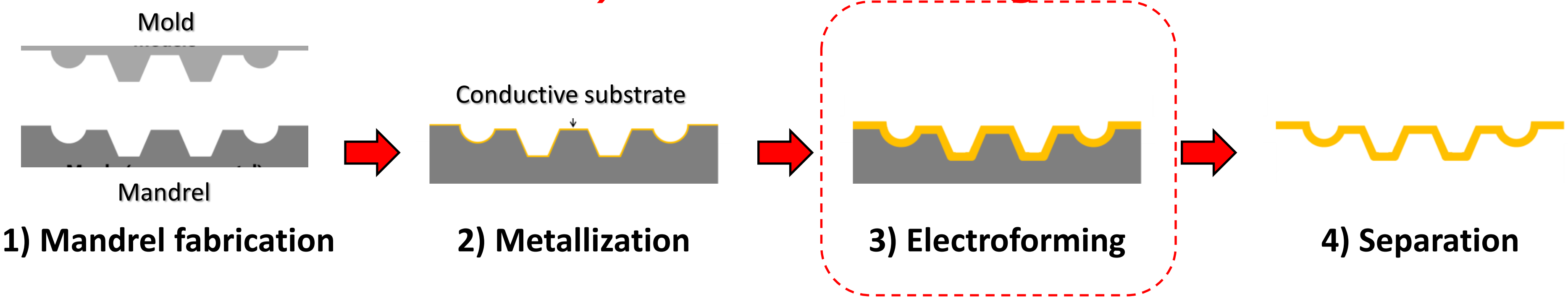
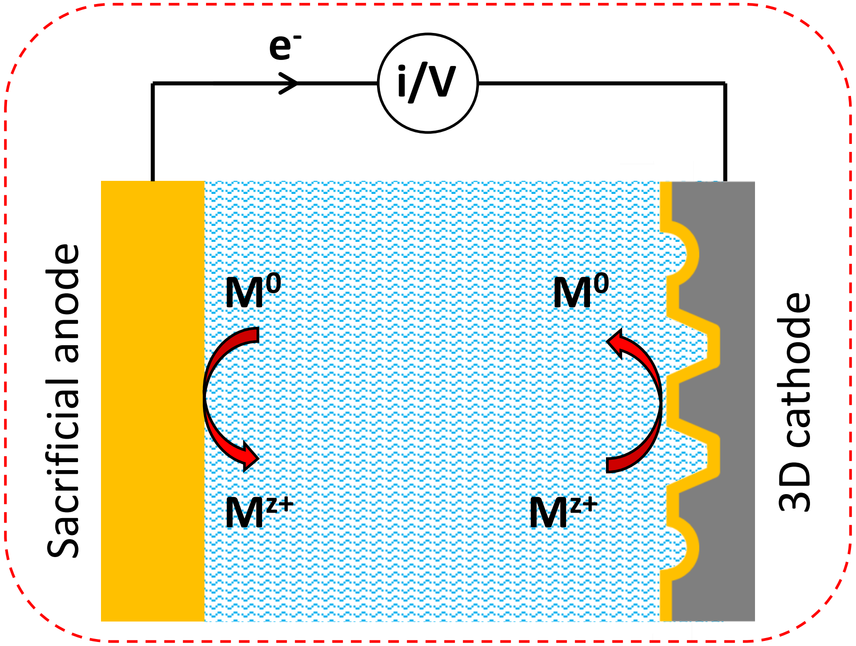
1) Electroforming



1) Mandrel fabrication **2) Metallization** **3) Electroforming** **4) Separation**



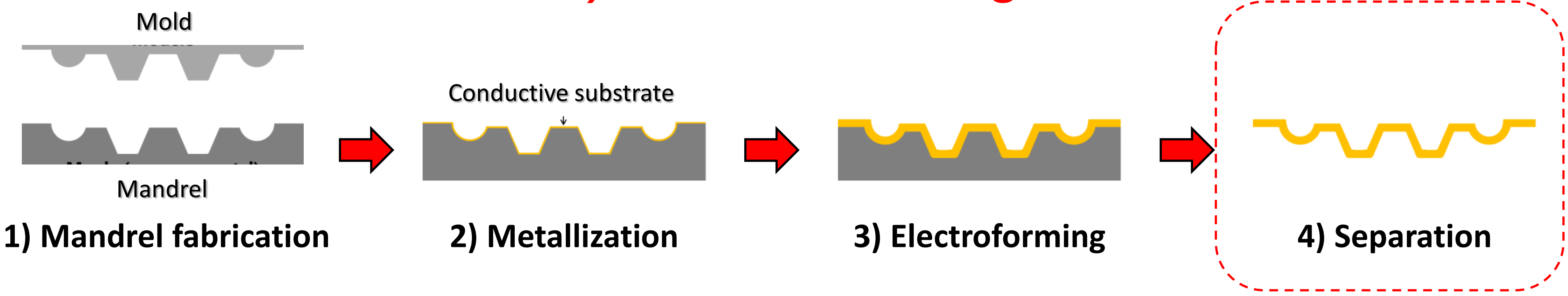
Influencing parameters:

- ❖ Bath composition *(pH, salts, additives)*
- ❖ Current and overpotential
- ❖ Temperature and agitation

- ✓ Substrate shape and properties
- ✓ Targetted thickness and throwingpower
- ✓ Electrodeposited metal or alloy

III) Template-assisted electrodeposition

1) Electroforming



Mechanical, thermal delamination

Dissolution of the seed layer

Mandrel can be reused

Dissolution of the mandrel

Mandrel is lost

Sometimes the mandrel is integrated in a final composite product

III) Template-assisted electrodeposition

1) Electroforming

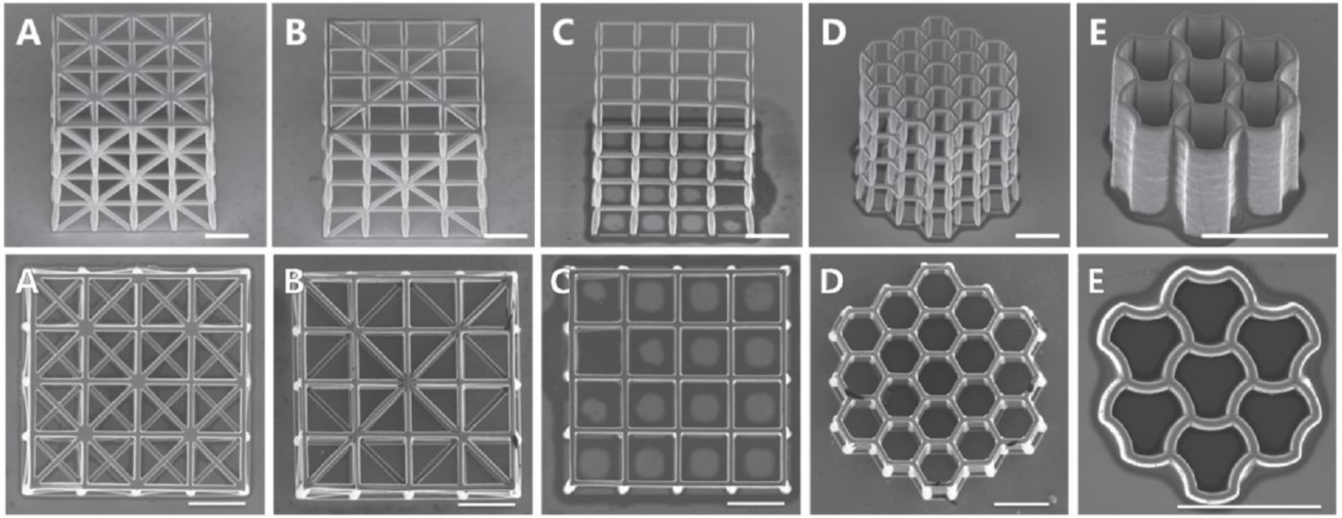
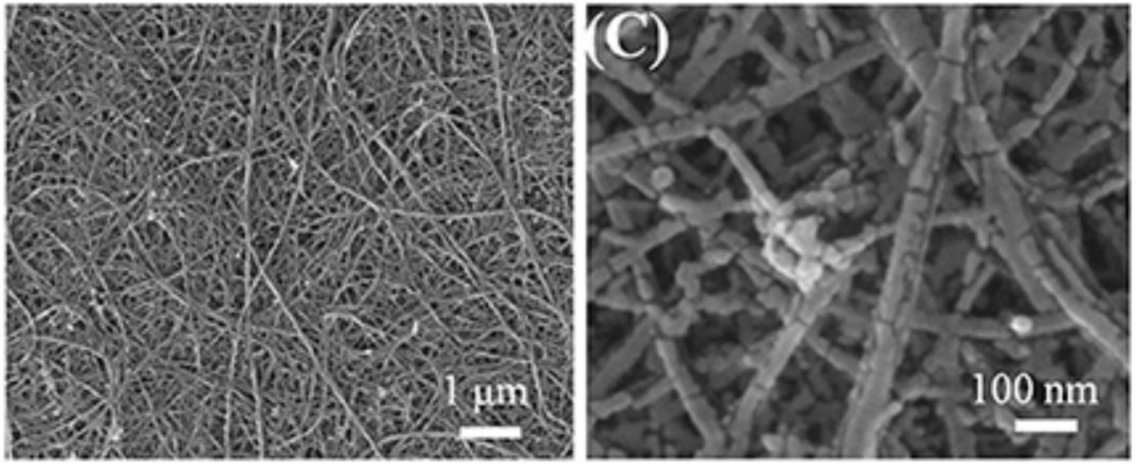


Figure 1. Tilted and top view SEM images of microcellular architectures after NiB metallization. The scale bar in all the images is 10 µm.

Microcellular architectures (2-photons lithography) coated with electroless NiB

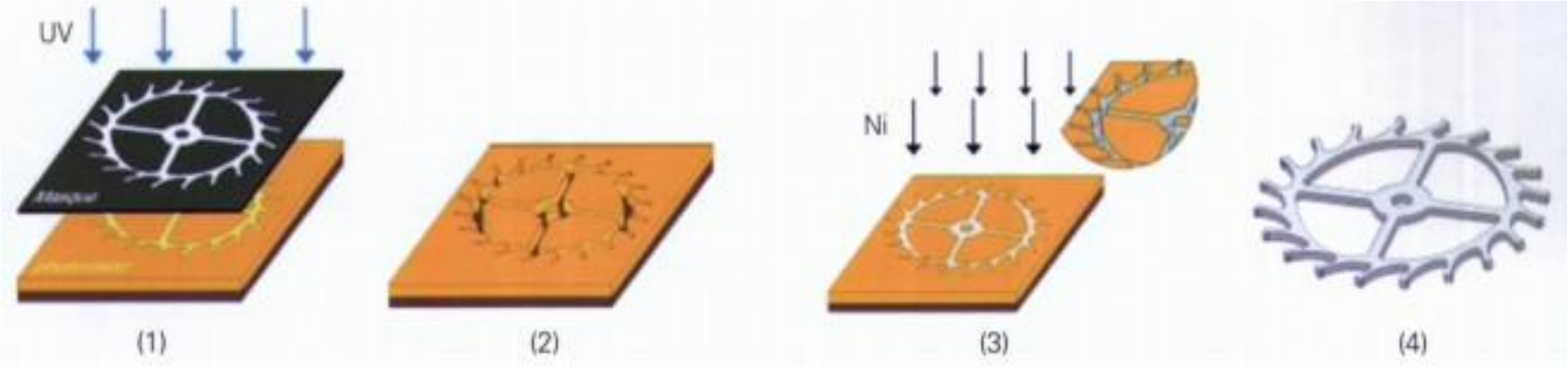
Silicon electrodeposited on carbon nanotubes



III) Template-assisted electrodeposition

2) Filling dielectric cavities

Micro ElectroMechanical Systems (MEMS): UV-LIGA



Exposure of a photosensitive resist spin-coated on a metallized Si-wafer

Electroplating: dissolution of the resist (exposed: positive; masked: negative)

Electroplating: bottom-up filling of the cavities by electrodeposition

Finishing: Thickness adjustment, polishing, dissolution of the template

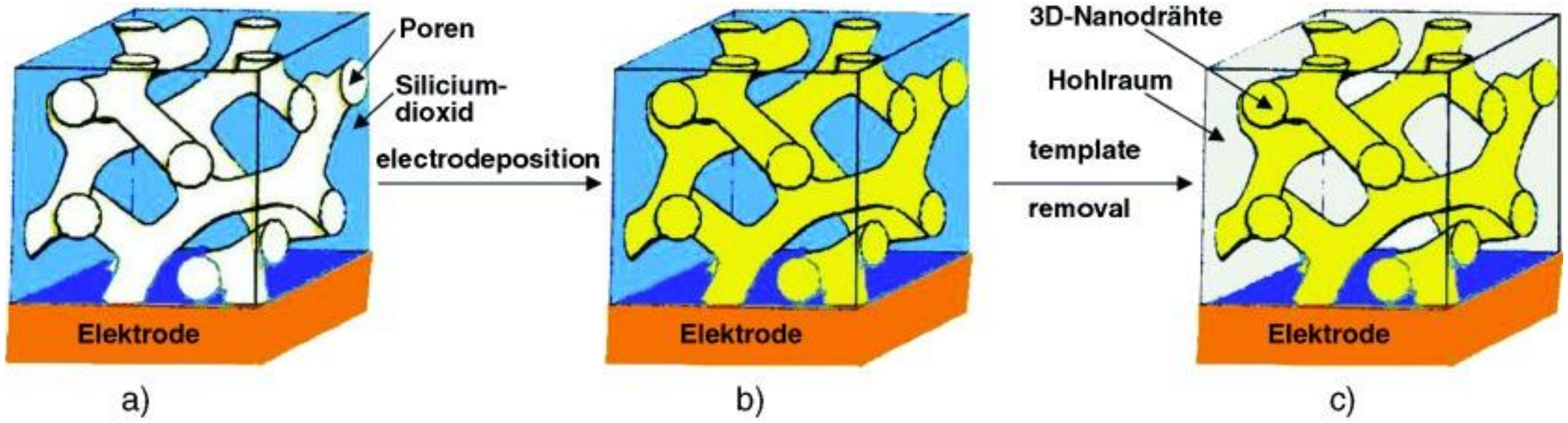
Positive photoresists: exposed resist is dissolved (UV light breaks polymer chains): PMMA

Negative photoresists: shadowed resist is dissolved (UV light reticulates the polymer): SU-8

III) Template-assisted electrodeposition

2) Filling dielectric cavities

Micro ElectroMechanical Systems (MEMS): UV-LIGA



Multilayered parts: repeat photolithography steps

3D microcomponents: 2-photon lithography

Positive photoresists: exposed resist is dissolved (UV light breaks polymer chains): PMMA

Negative photoresists: shadowed resist is dissolved (UV light reticulates the polymer): SU-8

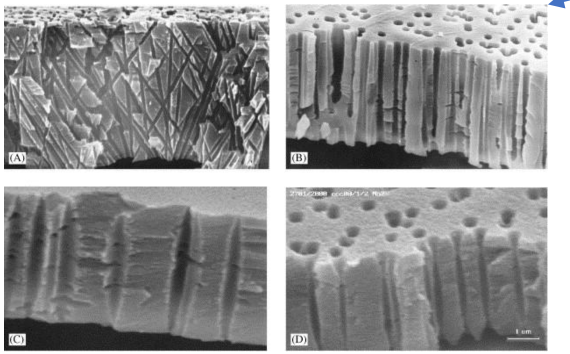
III) Template-assisted electrodeposition

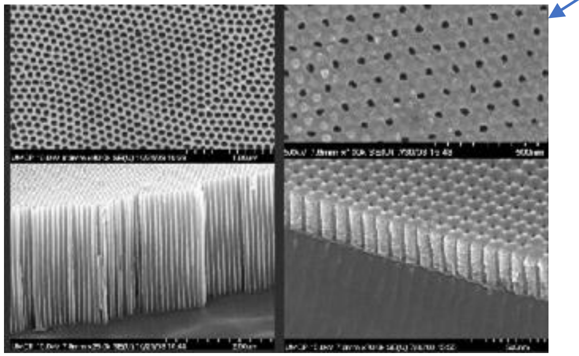
2) Filling dielectric cavities

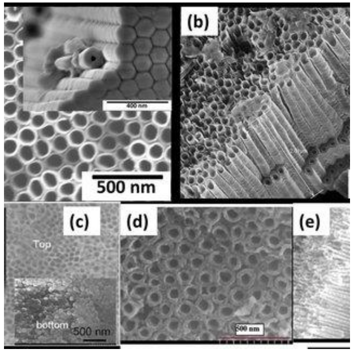
Nanowires, nanotubes, and quantum dots arrays:

Several alternative ways to pattern an electrode surface:

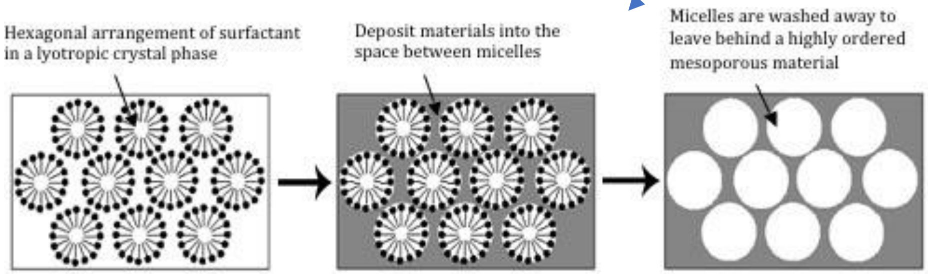
- Nanopore arrays: ion-track etched polymers, anodic oxides (alumina, titania)

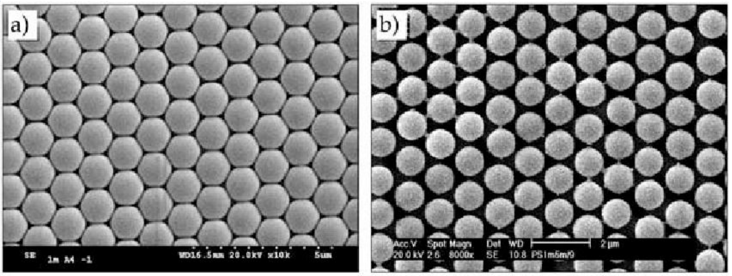






- Self-assembled structures: micelles, colloid monolayers, and block copolymers

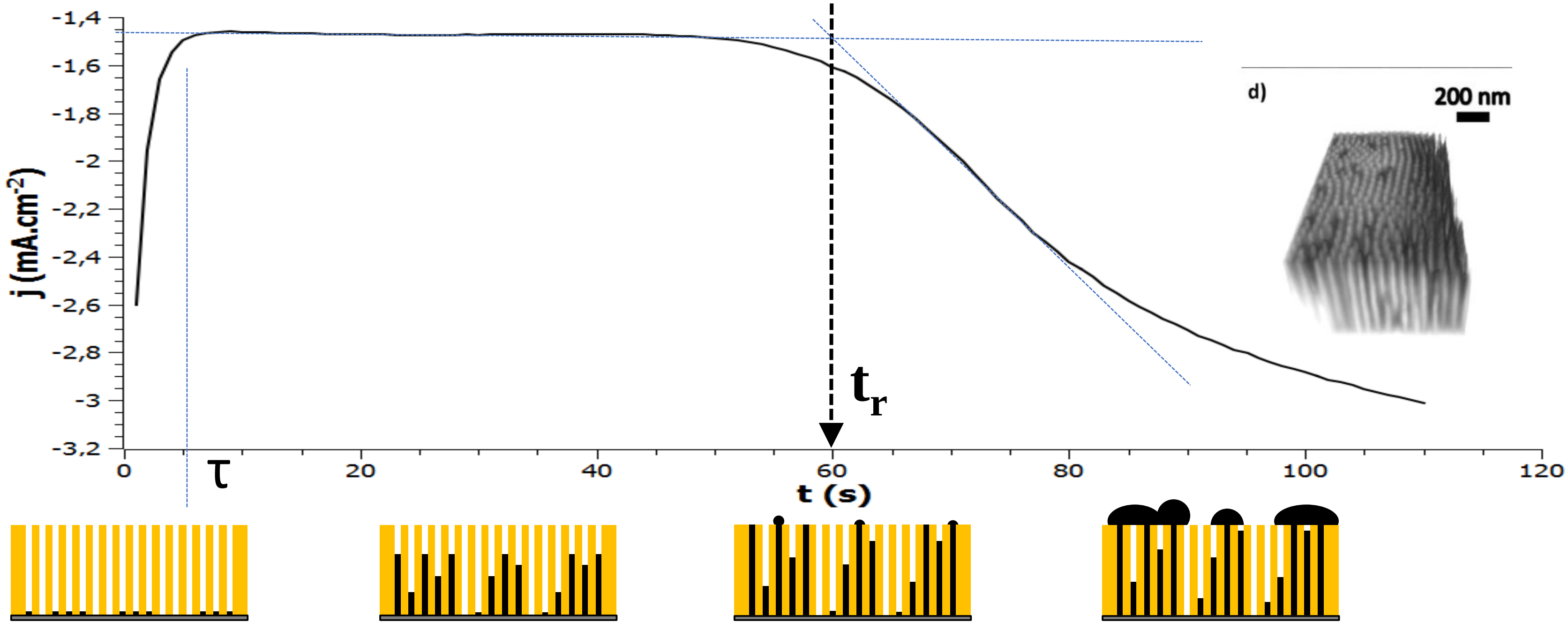




III) Template-assisted electrodeposition

2) Filling dielectric cavities

Nanowires in anodic alumina:



$0 < t < \tau$
DL charging
Nuclei induction

$\tau < t < t_r$
Confined growth
of nanowires

$t = t_r$
First pores
are filled

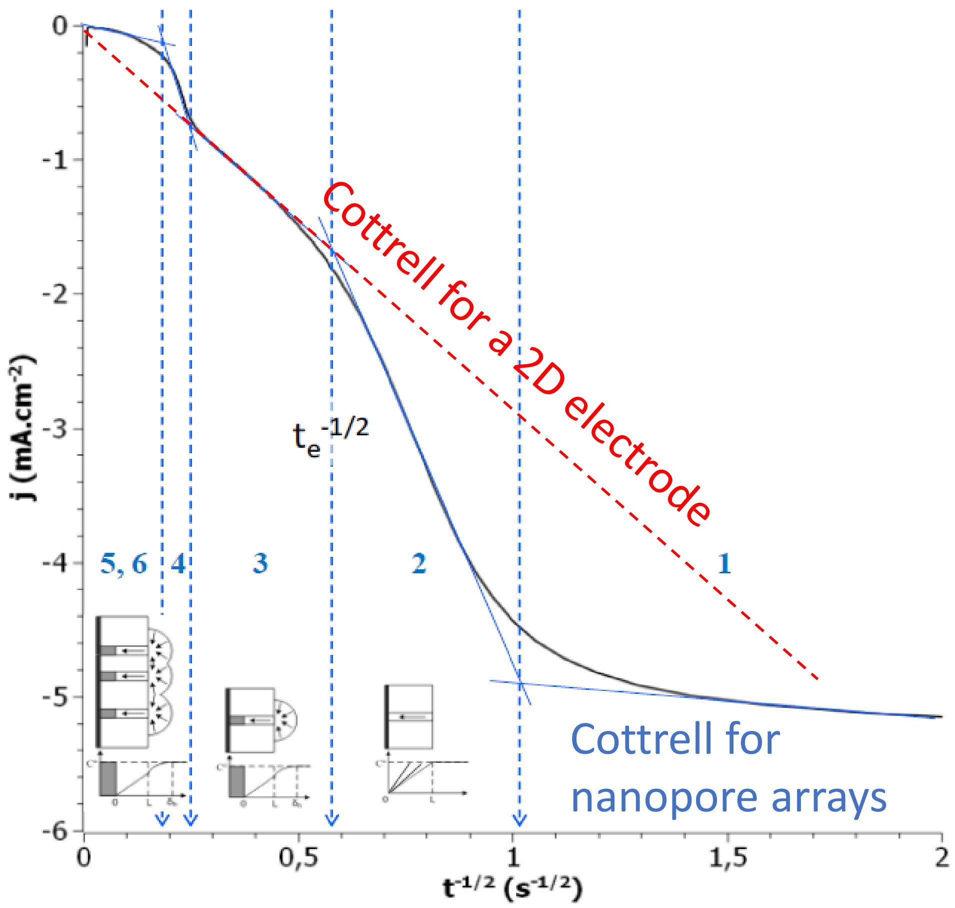
$t > t_r$
Overgrowth /
film formation

$$Filling\ ratio = \frac{V_{nw}}{V_{np}} = \frac{M}{z\rho F}\,\frac{\int_0^{t_r} i(t).dt}{N_{np}\pi R^2 L}$$

III) Template-assisted electrodeposition

2) Filling dielectric cavities

Nanowires, nanotubes, and quantum dots arrays:



1-2 $$i(t) = nFAC^\circ\sqrt{\frac{D}{\pi t}}$$

t_e $$\left.\begin{aligned}\delta &= \sqrt{\pi D t} = e - l\\ \delta &= e - \frac{M.\int_0^{t_3} i.dt}{nF\rho\pi r^2 NS}\end{aligned}\right\} D_p = \frac{(e-l)^2}{\pi t_e}$$

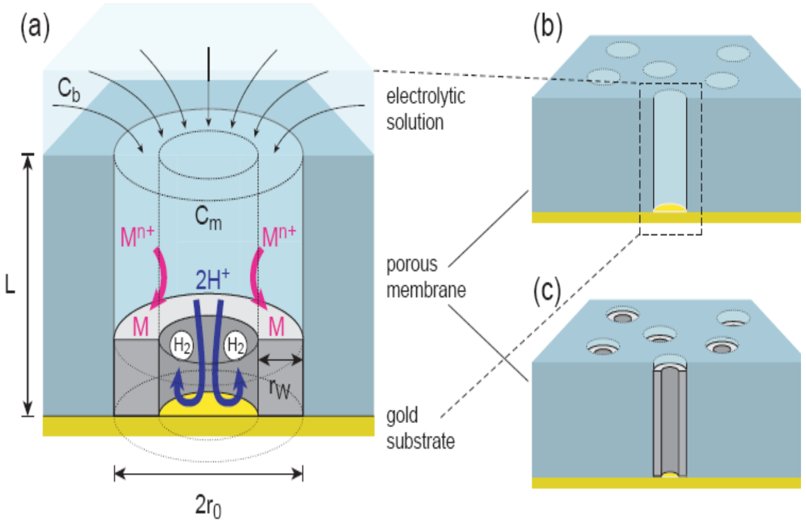
3 $$i_{lim} = \frac{nFADC_L}{L} + \frac{nFDA(C^\circ - C_L)}{\delta_h} = \frac{nFADC^\circ}{L+\delta_h}$$

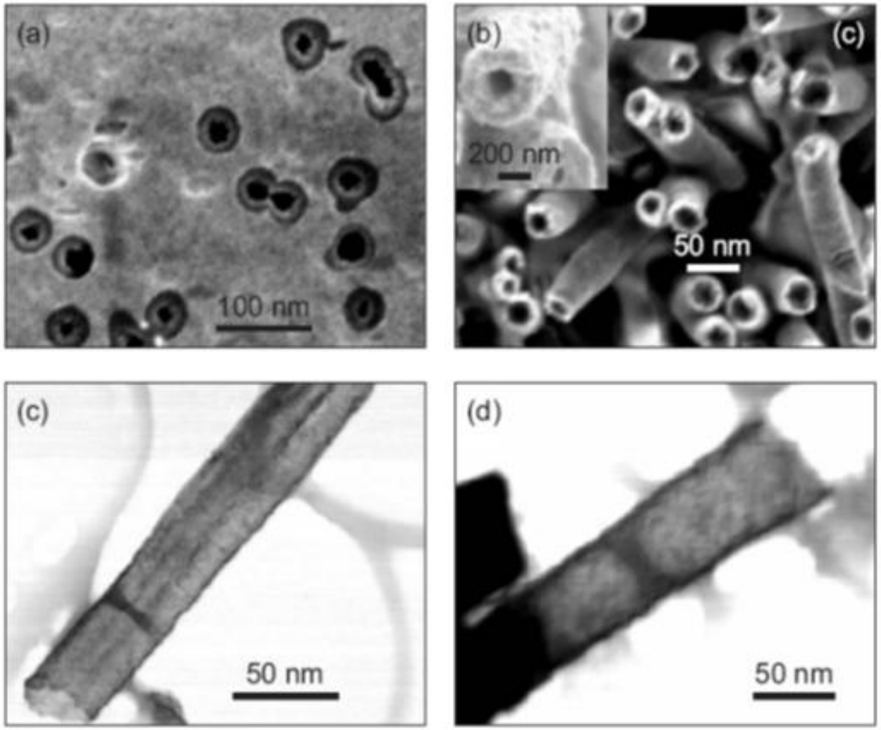
$$\text{avec } \delta_h = \frac{\pi R}{4}$$

III) Template-assisted electrodeposition

2) Filling dielectric cavities

Nanotubes in ion-track etched membranes:





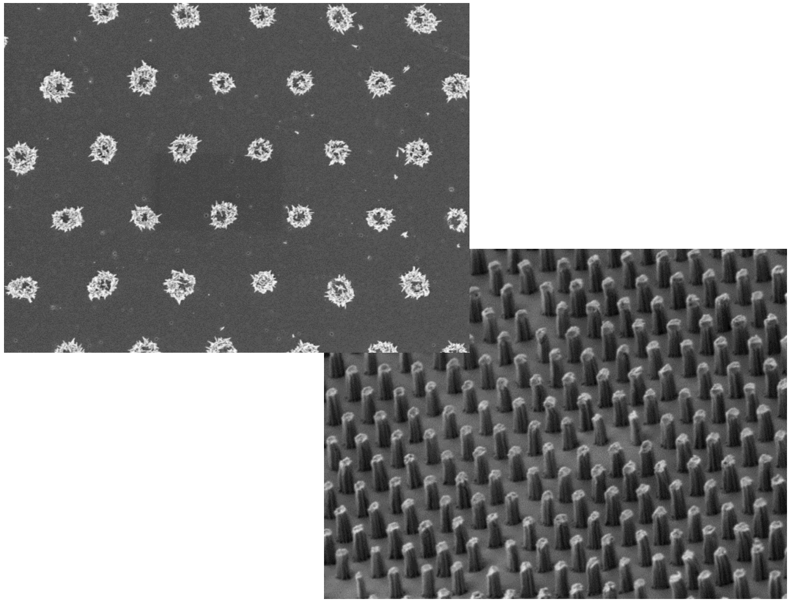
Enhancing growth at the pore walls:

1) ***High surface diffusion of cations***
2) ***Hydrogen bubbles***

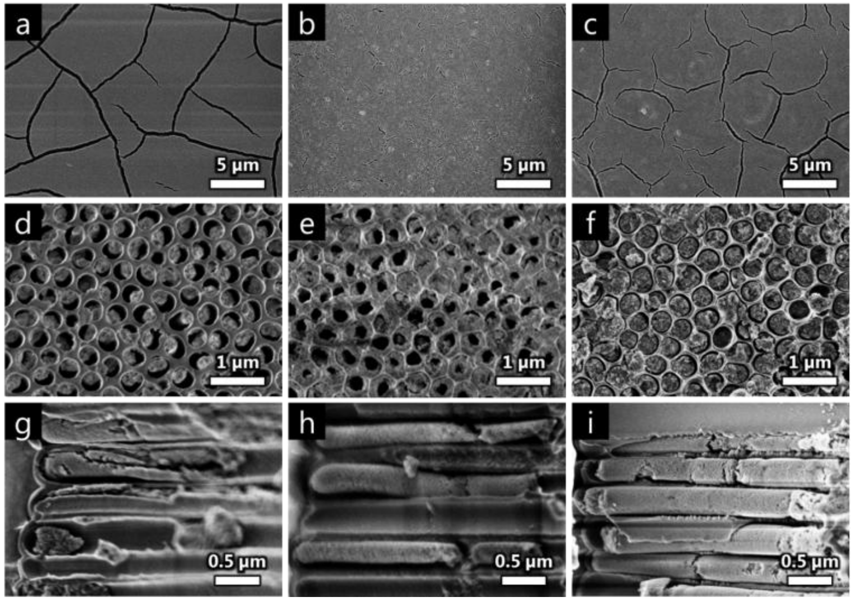
III) Template-assisted electrodeposition

2) Filling dielectric cavities

Quantum dots arrays in anodic alumina:



Short electrodeposition at the bottom of ordered nanopores



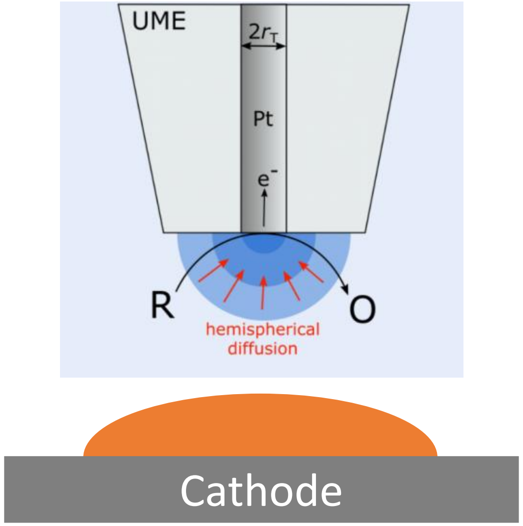
Electrophoretic deposition of nanoparticles inside nanochannels

IV) Localyzed electrochemistry

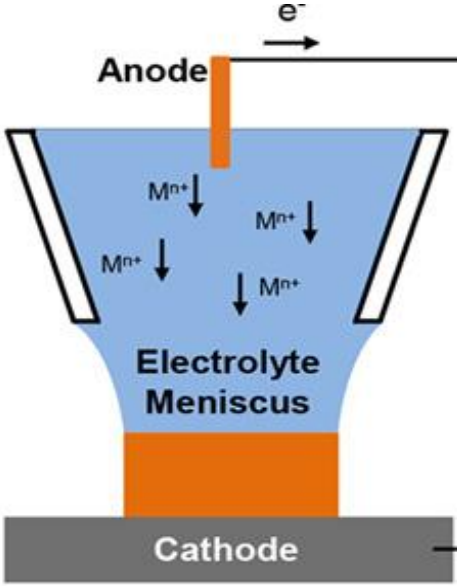
Electrochemical Additive Manufacturing (ECAM)

The working region is limited by electrochemical conditions

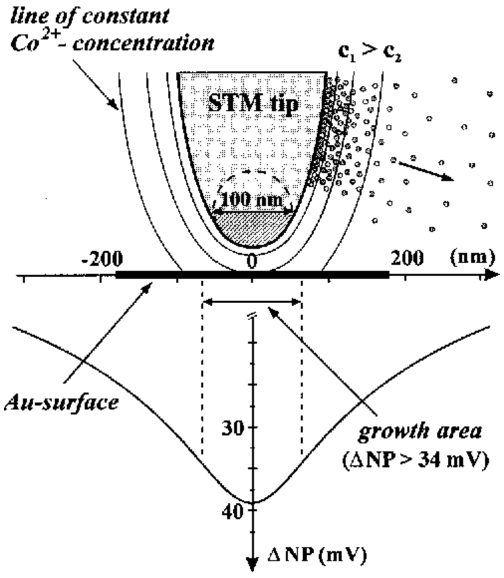
Overpotential field lines are not aligned: charge transfer is localized



Scanning Probe Electrodeposition:
SPECD
Non-uniform electric field in a uniform electrolyte



Meniscus-Confined ECD
MCECD
Uniform electric field in a non-uniform electrolyte

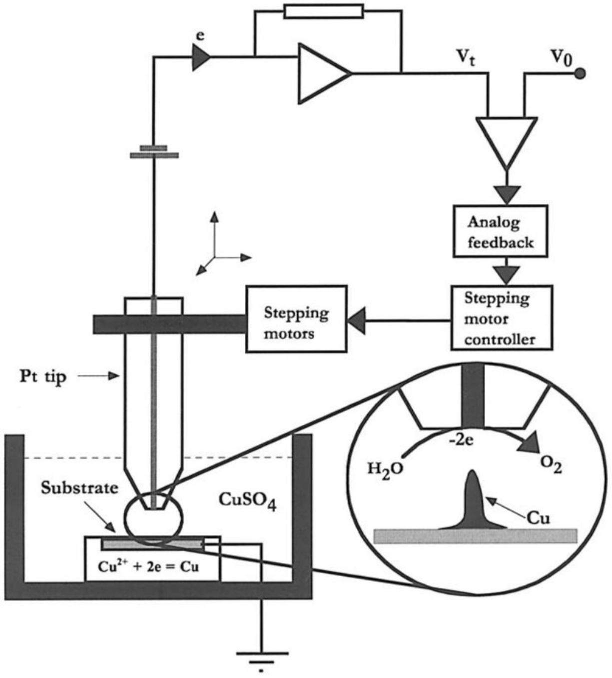


Sacrificial STM Anode
STECD
Non-uniform electric field in a non-uniform electrolyte

IV) Localyzed electrochemistry

Electrochemical Additive Manufacturing (ECAM)

Scanning Probe Electrodeposition:



Scanning Probe Electrodeposition: SPECD

Non-uniform electric field in a uniform electrolyte

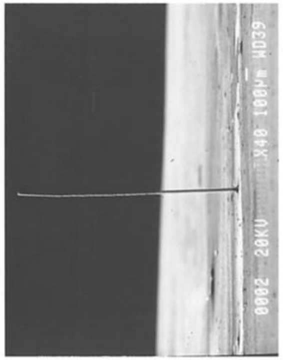
Electric field: Poison distribution:

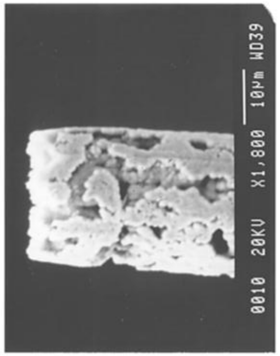
$$\nabla^2\phi = \frac{\varrho}{\varepsilon} = \frac{charge\ density}{permitivity}$$

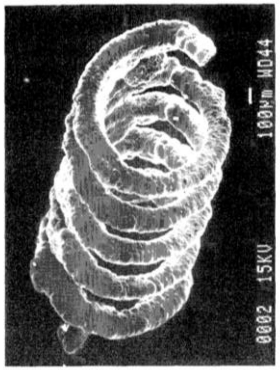
Spatial resolution depends on:

- The probe dimensions and distance
- The electrolyte conductivity
- The applied potential difference

Adapted to 3D structures of several microns



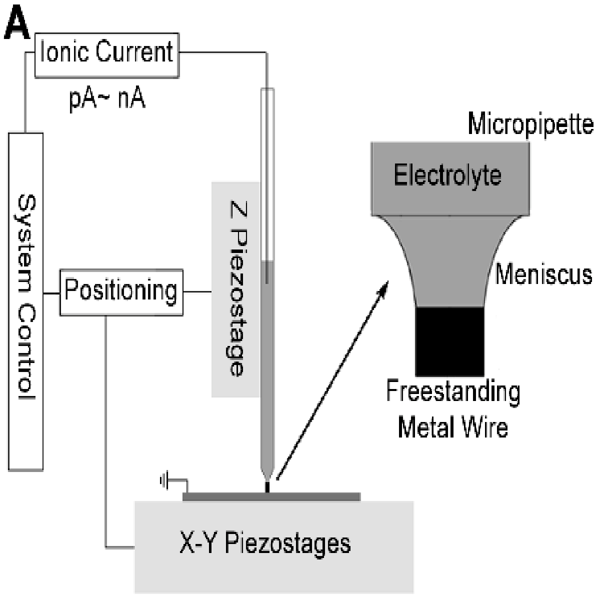




IV) Localyzed electrochemistry

Electrochemical Additive Manufacturing (ECAM)

Meniscus-Confined Electrodeposition:

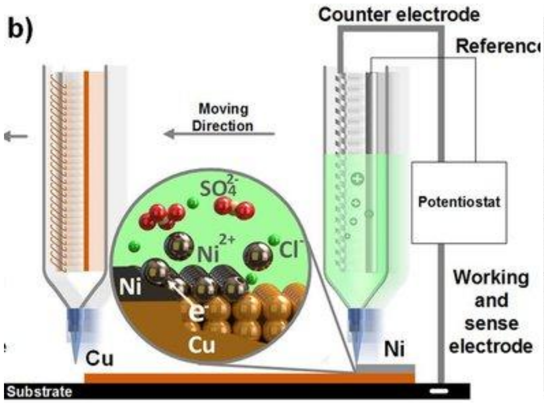


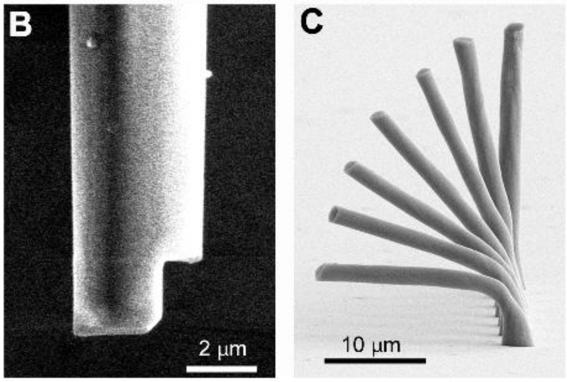
Resolution only depends on the meniscus size:
- Micro-capillary dimension
- Surface tension

Adapted to 3D structures of few microns

Possible to electrodeposit multi-metallic structures

Meniscus-Confined ECD
MCECD
Uniform electric field in a
non-uniform electrolyte

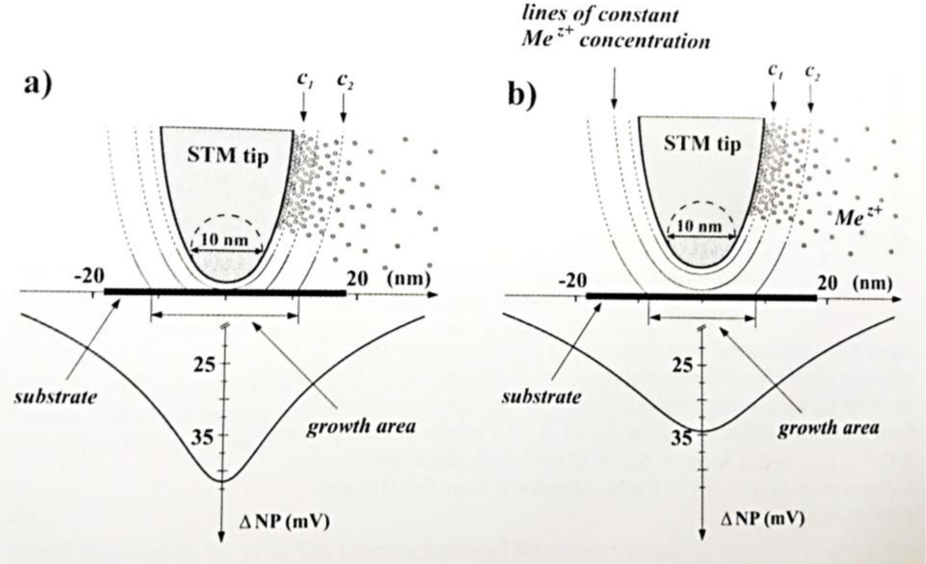




IV) Localyzed electrochemistry

Electrochemical Additive Manufacturing (ECAM)

Sacrificial STM Anode:



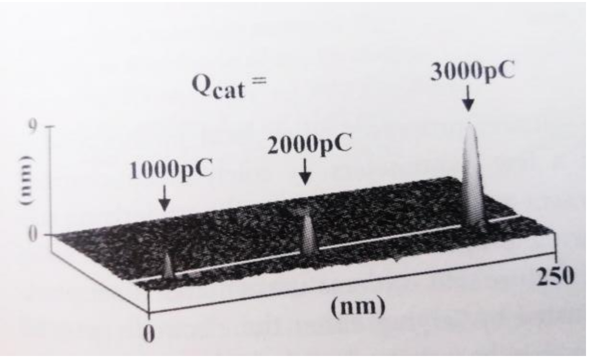
Spatial resolution depends on the overpotential distribution:

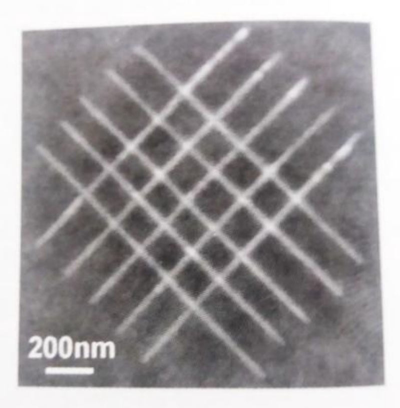
- Tip-electrode distance
- Nernst potential distribution vs [M^{z+}]
- Applied potential

Adapted to short structures of few nm

Nanoscale surface patterning

Sacrificial STM Anode
STECD
Non-uniform electric field in a
non-uniform electrolyte



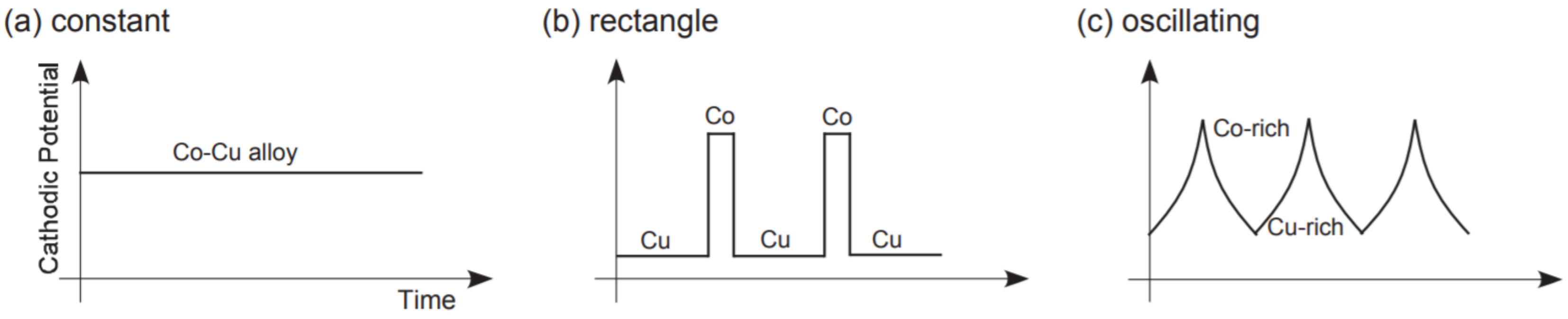


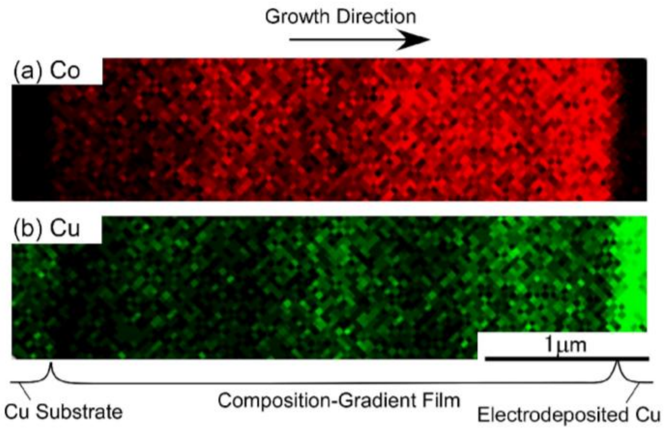
V) Modulated electrochemistry

1) Single electrolyte

Multilayers, composition gradients, nanocomposites:

Simple, multilayer, and composition gradients by modulated potential



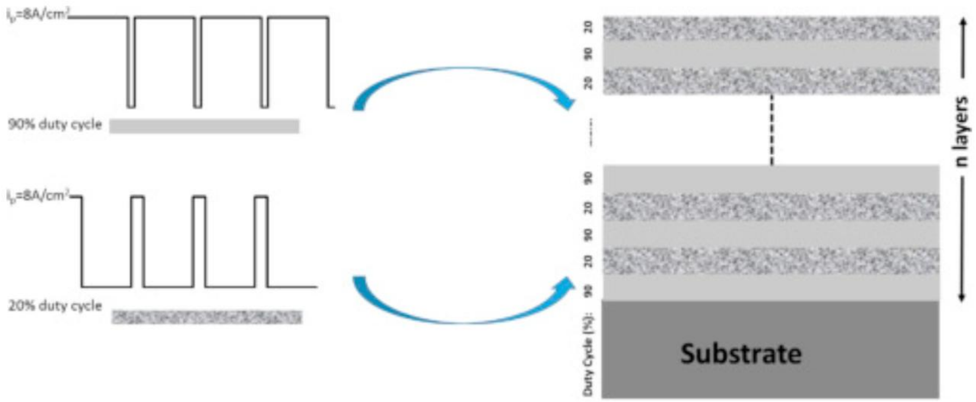


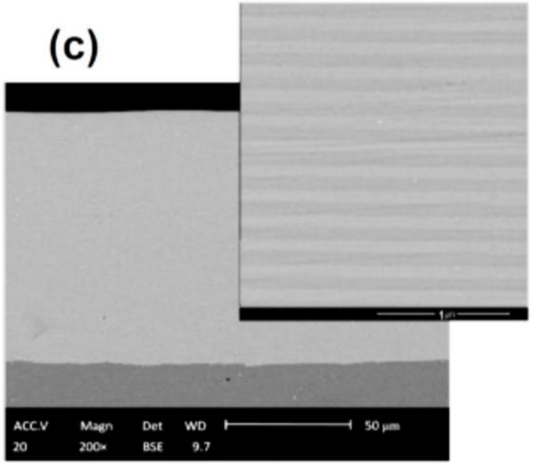
V) Modulated electrochemistry

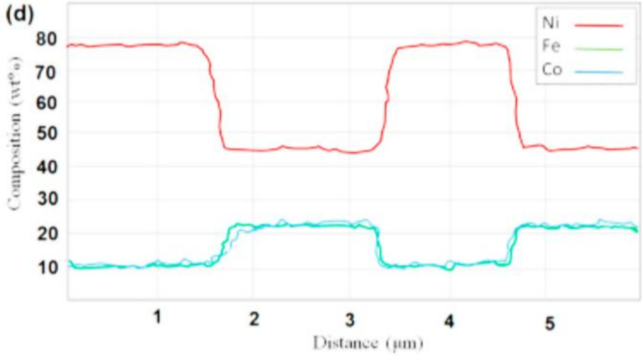
1) Single electrolyte

Multilayers, composition gradients, nanocomposites:

Multilayer by modulated pulse deposition



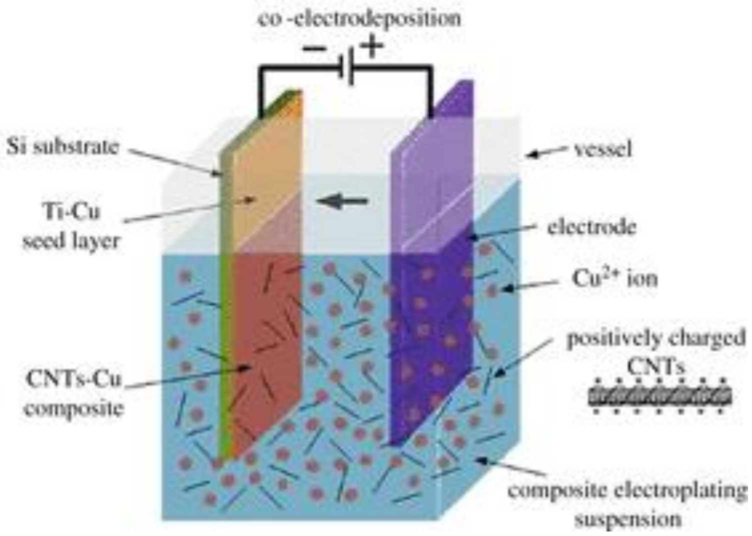




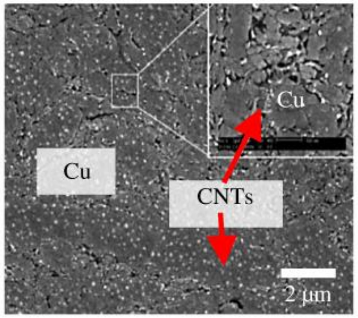
V) Modulated electrochemistry

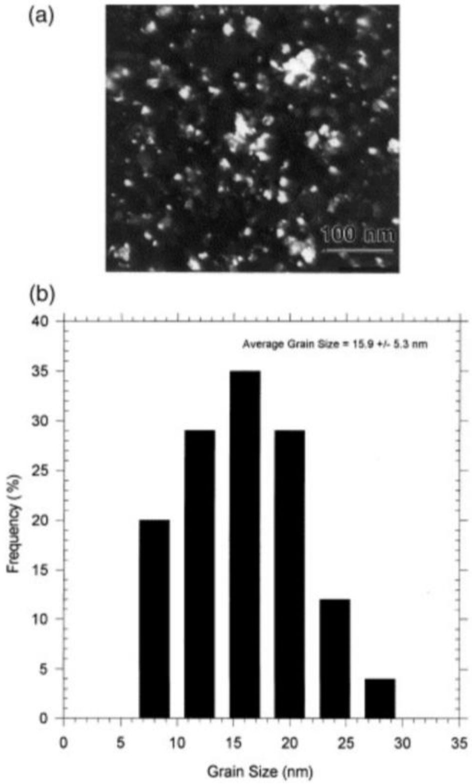
1) Single electrolyte

Multilayers, composition gradients, nanocomposites:



Heterogeneous electrolyte with suspended nanostructures



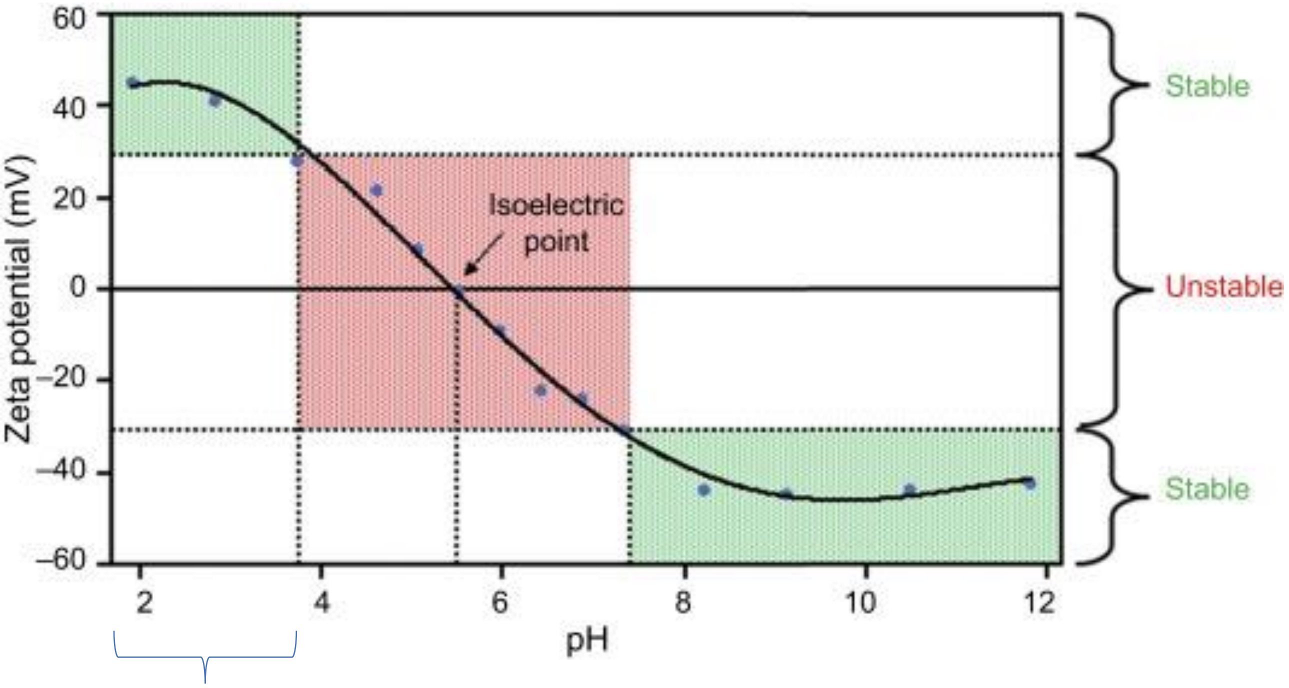


Ni electrodeposit with SiC nanoparticles

V) Modulated electrochemistry

1) Single electrolyte

Multilayers, composition gradients, nanocomposites:



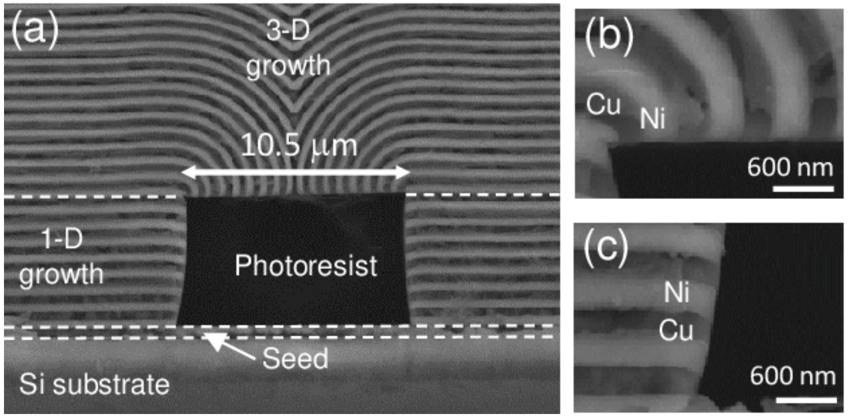
Zeta potential $\zeta > 0$: cathodic electrophoresis
Zeta potential $|\zeta| > 30$ mV: stable colloïds

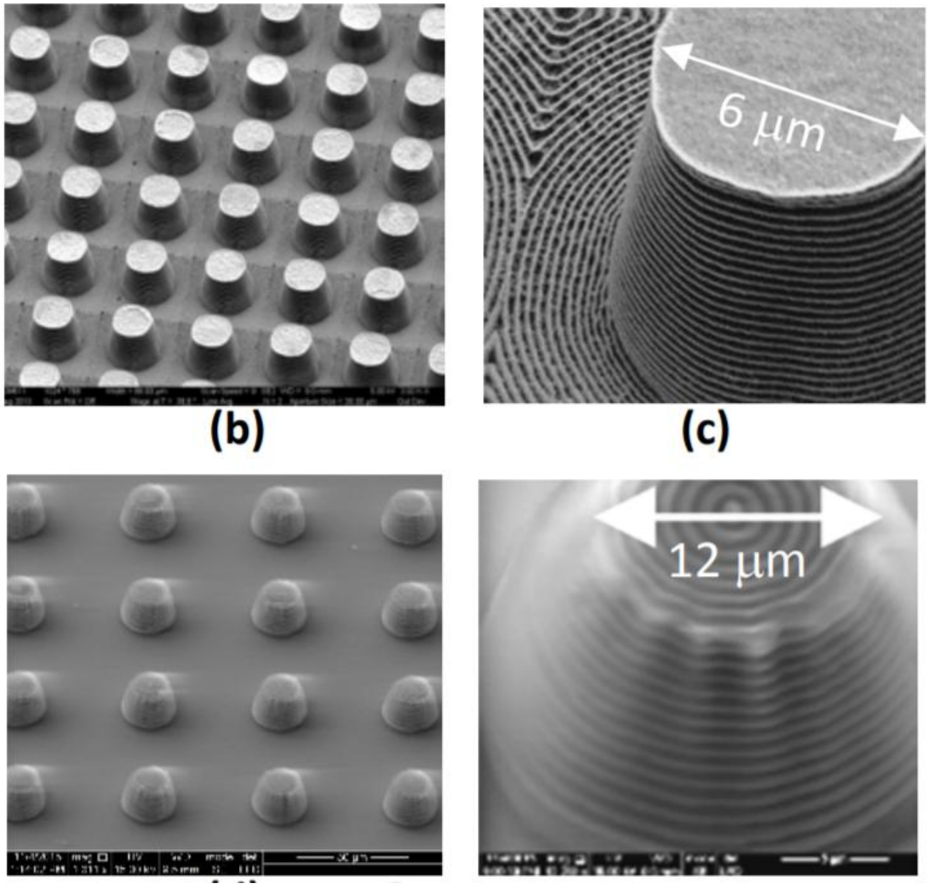
Need to destabilize suspended particles (high $\Delta\phi$ or local pH increase)

V) Modulated electrochemistry

2) Multiple electrolyte

Superlattices and ECALE:





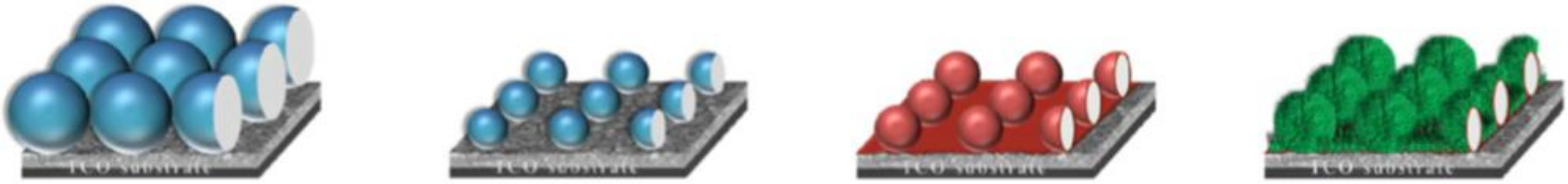
(b)

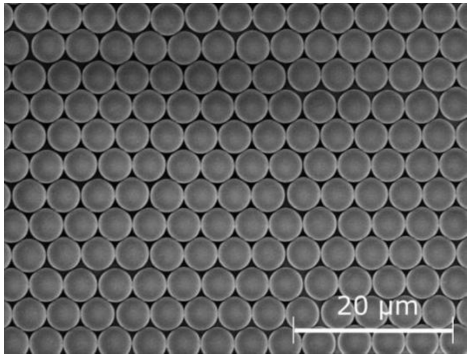
(c)

Nickel-copper multilayer by sequential electrodeposition from different electrolytes

VI) Multiscale structuring

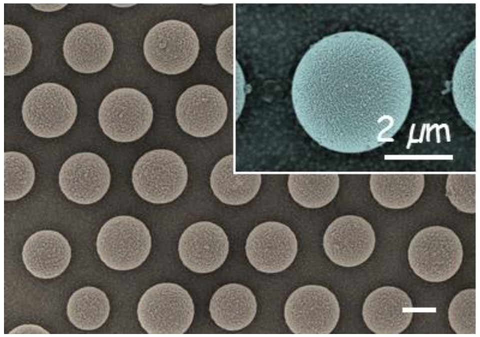
1) Anisotropic growth + colloid monolayer



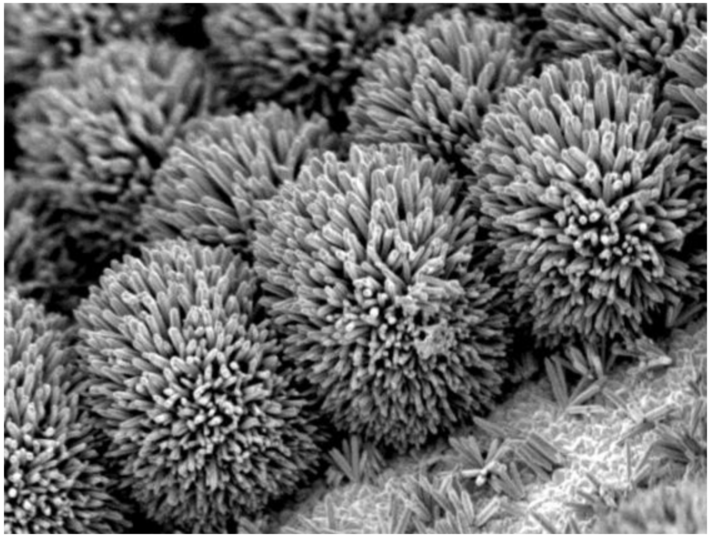


Self assembly of polystyrene micro-beads

Reactive plasma etching

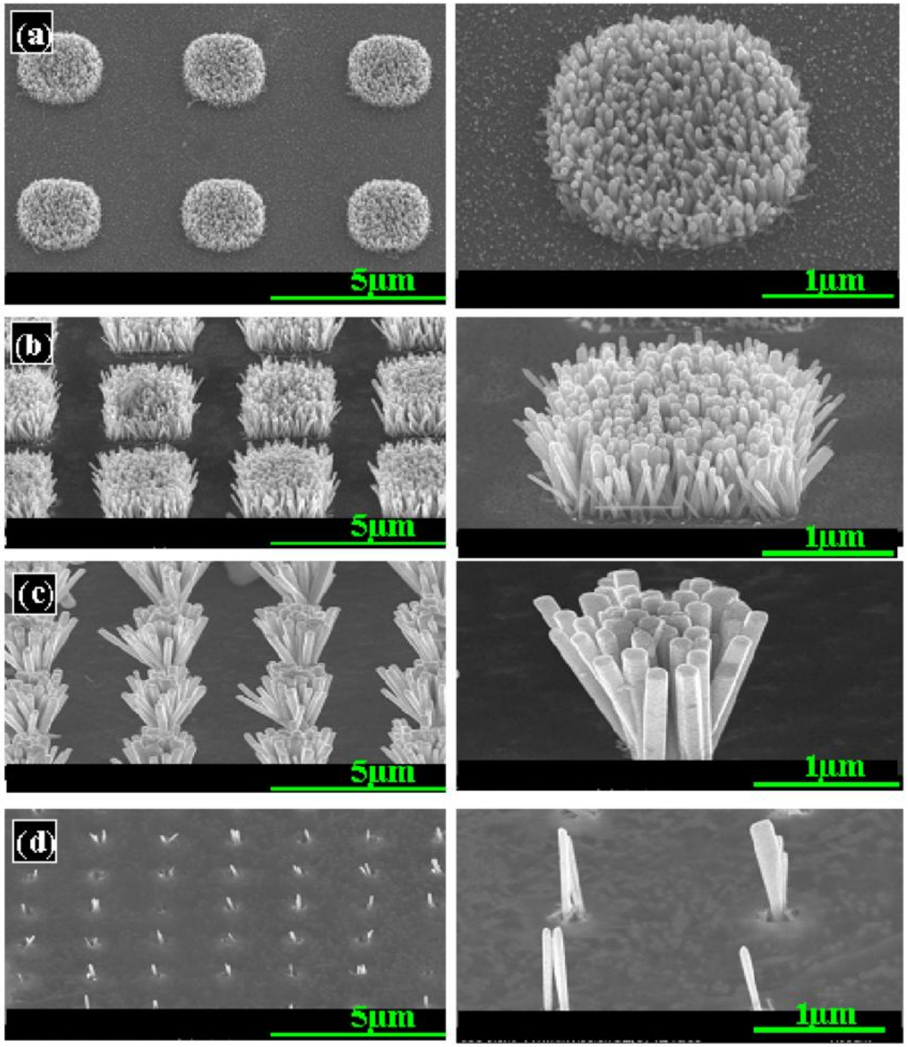


Surface activation and growth of urchin-like ZnO



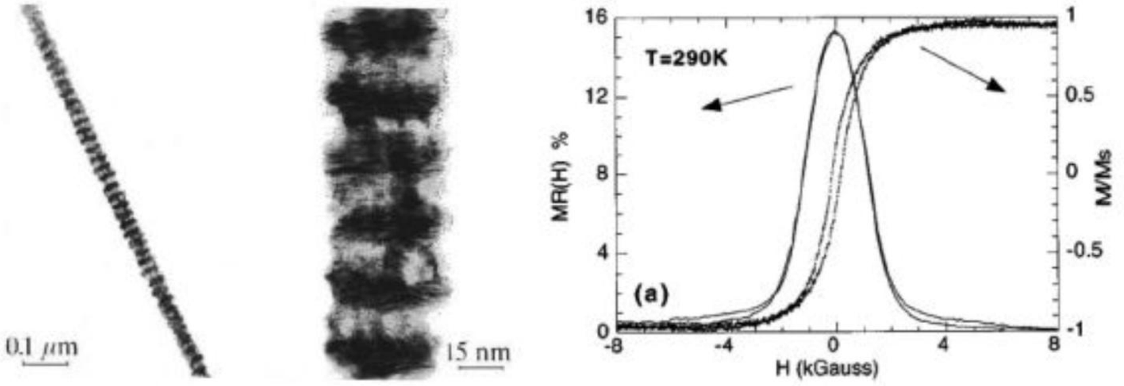
VI) Multiscale structuring

1) Anisotropic growth + dielectric saving



VI) Multiscale structuring

1) Nanopore + multilayer



(a) (b) (c)

Co/Cu multilayer nanowire by voltage modulation
Giant MagnetoResistance

Bi_2Te_3/Sb multilayer nanowire by voltage modulation
Thermoelectric nanostructure