Assemblage et co-assemblage dirigé de nano-objets colloïdaux : Quid de la géométrie ?

Etienne PALLEAU
Maître de conférences (LPCNO)

epalleau@insa-toulouse.fr

LPCNO

Vendredi 14 juin 2019

Université de Toulouse

LPCNO
UMR 5215

Workshop « Géométrie et Matériaux » 2019, Toulouse

Outline

- ➢Definition: Self assembly vs Directed (self) assembly
- ➢Realization examples via directed assembly techniques
- ➢Directed co assembly: capabilities and interests
- ➢Looking for geometry in directed assembling : what for ?

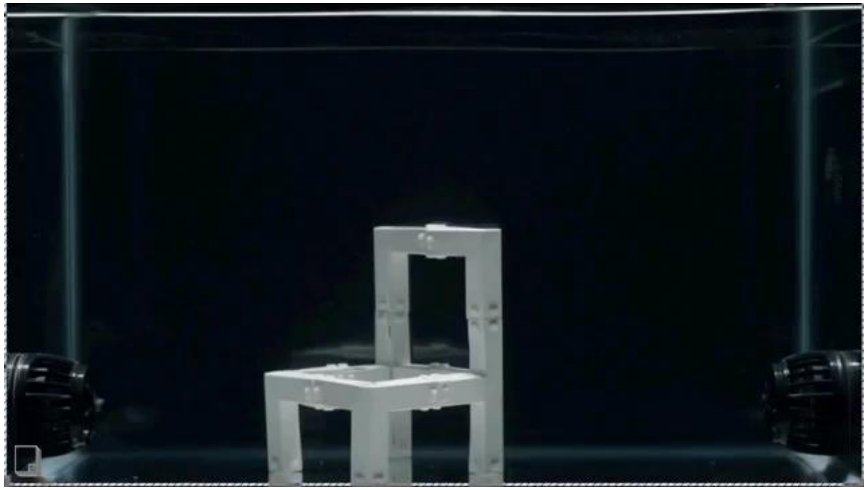
Definition:
Self assembly vs Directed assembly

Context

SELF ASSEMBLY

In general

« initial building block parts rearrange with each other without external assistance to form other structures »

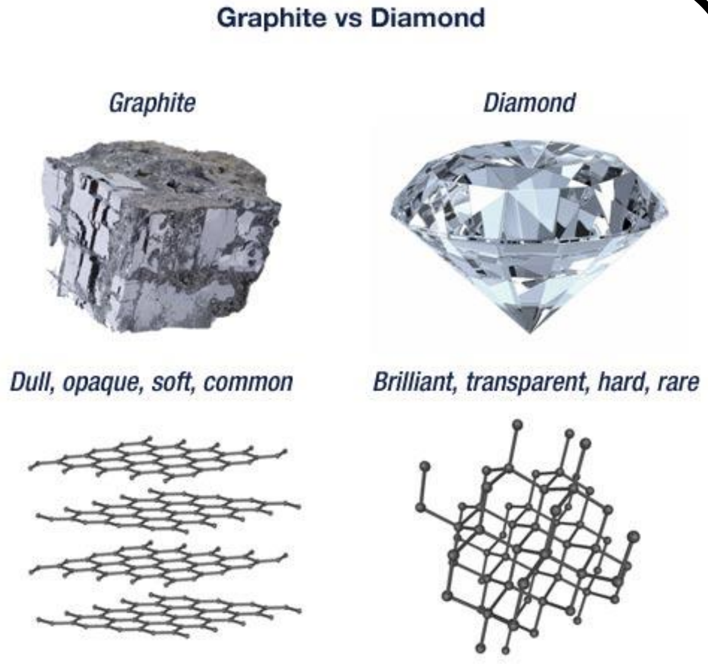


Self assembly lab at MIT (Skylar Tibbibs' group)

Context

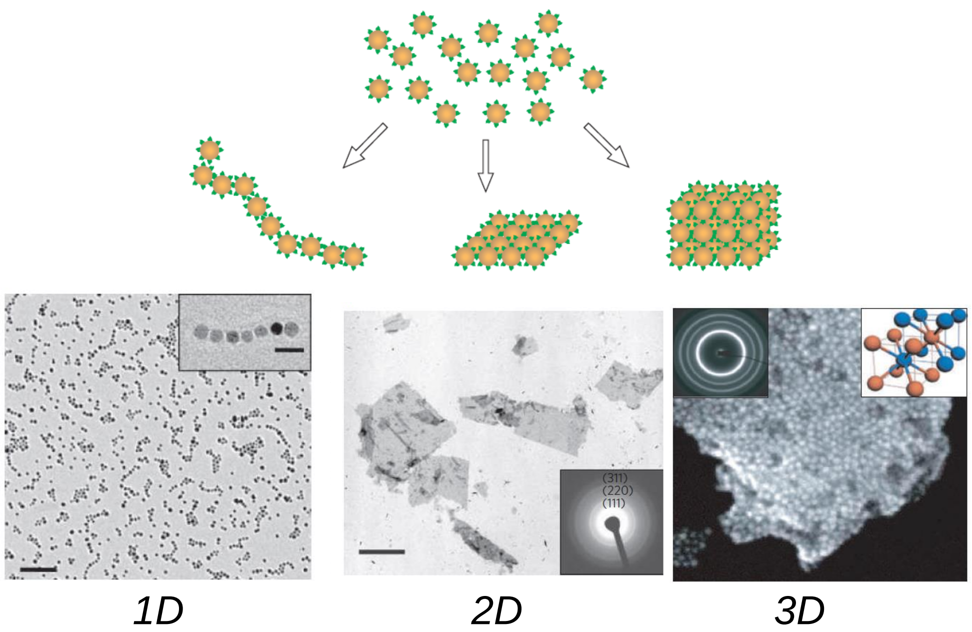
In P&C nanoscience

If the building block is an atom



http://www.philosophyib.com/3/wholebrain/diamond-vs-graphite

If the building block is a nanoparticle

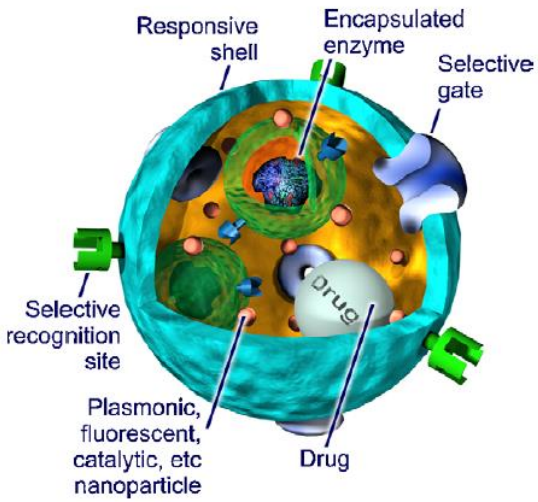


Nie et al, Nat. Nano., ***5 (2010)***

Molecular, VdW, RNA/DNA, Capillary interactions…

What about colloidal nano-objects as building blocks ?

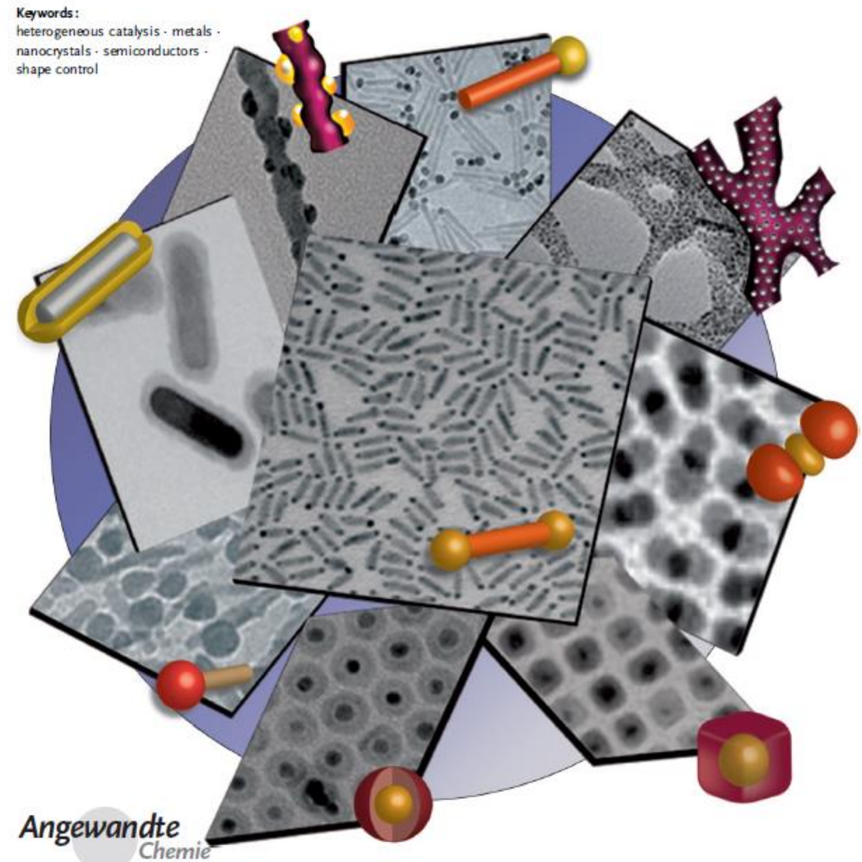
Nanogels



Motornov et al, Progress in Polymer Science , 35 ***(2010)***

Enviro-sensitive

Hybrid nano-objects



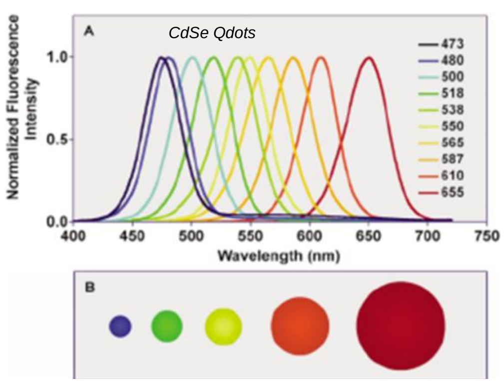
Costy et al, Angew. Chem. Int . Ed. , 49 ***(2010)***

Increase quantum yield, catalytic properties, photo stability,…

Metallic NPs

Magnetic NPs

QDots



Nie et al, Analyst, 8 ***(2004)***

Plasmonic, photoluminescent, thermal, mechanical, conductive, magnetic properties…

Assembling colloidal nano-objects on surfaces

Characterizing N-O properties or benefiting from their properties in new applications or devices

Assembling them on surfaces
at specific areas

Self assembly **Vs** <u>Directed assembly</u>

Random deposition
on surfaces

→ Most of the time:
% inefficient, time consuming

Addition of an extra external force to conduct specifically the assembly

Capillary,
Electrical,
Magnetic,
Chemical,
Optical forces…

A bit of help please !

Examples of directed assembly techniques

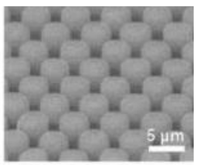
Examples

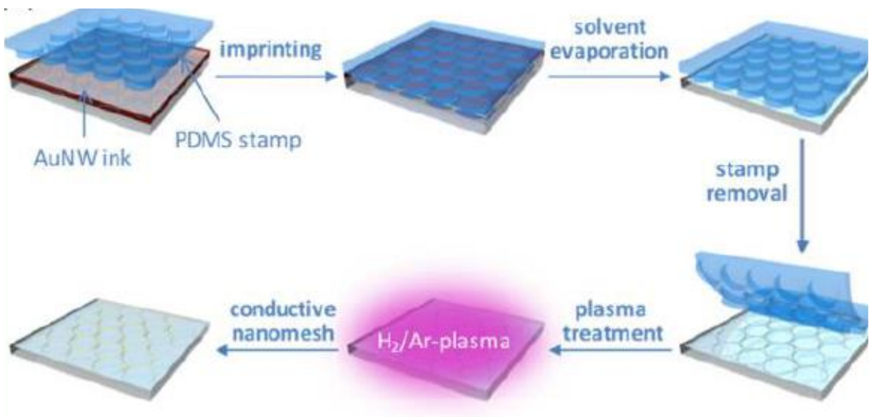
NANO LETTERS 2015 Letter
pubs.acs.org/NanoLett

Templated Self-Assembly of Ultrathin Gold Nanowires by Nanoimprinting for Transparent Flexible Electronics

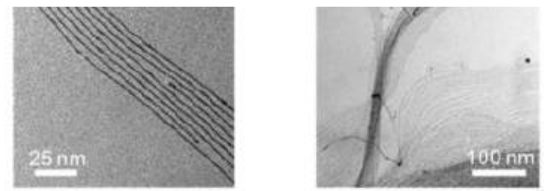
Johannes H. M. Maurer, Lola González-García,* Beate Reiser, Ioannis Kanelidis, and Tobias Kraus*
INM—Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany

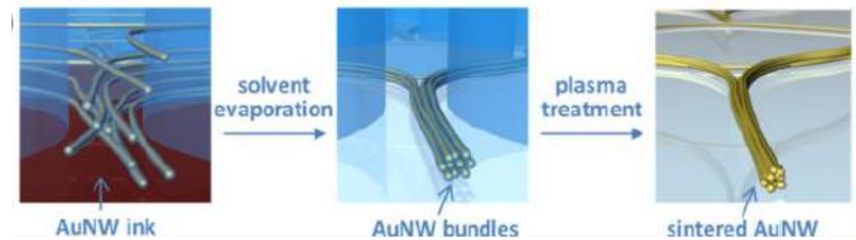
Using templates (structured surfaces)





Au NWs





☞ **Conductive, transparent, flexible metal grids → Electrodes / Touch screen**

Examples

Using optical forces

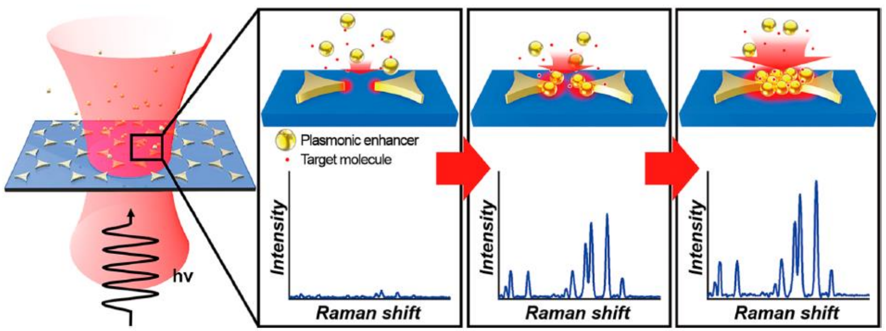
Autoenhanced Raman Spectroscopy via Plasmonic Trapping for Molecular Sensing

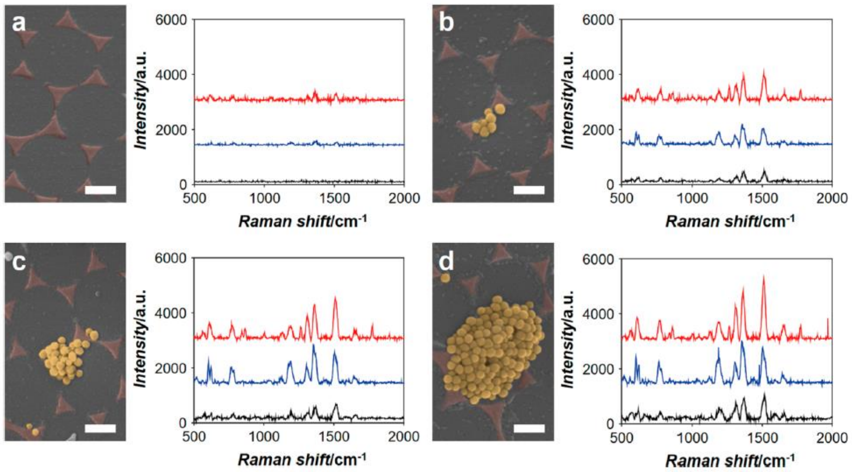
Soonwoo Hong,[†,‡] On Shim,[†,‡] Hyosung Kwon,[†] and Yeonho Choi*[,†,§]

[†]Department of Bio-convergence Engineering and [§]School of Biomedical Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

analytical chemistry

2016





☞ **Improvement of Raman spectroscopy / analysis**

Examples

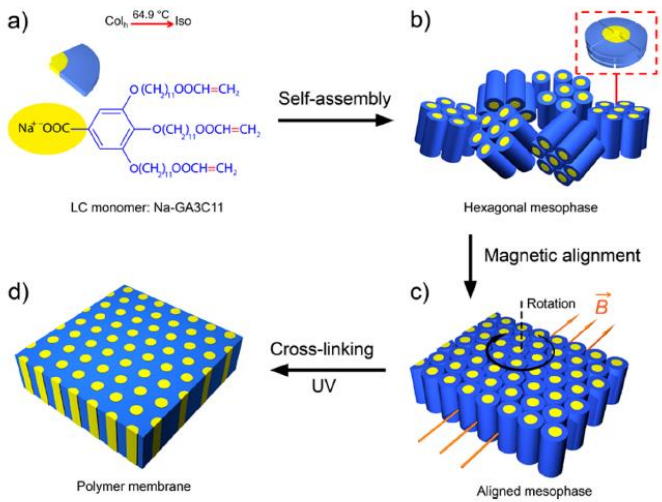
VOL. 8 ▪ NO. 12 ▪ 11977–11986 ▪ 2014 ACSNANO
www.acsnano.org

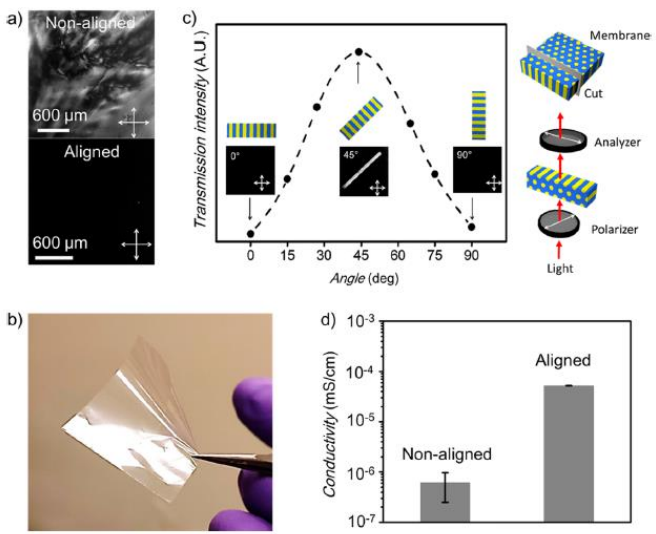
Via magnetic fields

Scalable Fabrication of Polymer Membranes with Vertically Aligned 1 nm Pores by Magnetic Field Directed Self-Assembly

Xunda Feng,[†] Marissa E. Tousley,[†] Matthew G. Cowan,[‡,§] Brian R. Wiesenauer,[‡] Siamak Nejati,[†] Youngwoo Choo,[†] Richard D. Noble,[§] Menachem Elimelech,[†] Douglas L. Gin,[‡,§] and Chinedum O. Osuji[*,†]

[†]Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States, [‡]Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, United States, and [§]Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309, United States





☞ **Large scale nanoporous membranes**

Examples

Via local dispensing/localization

LANGMUIR

Article

Cite This: *Langmuir* 2019, 35, 3256–3264

pubs.acs.org/Langmuir

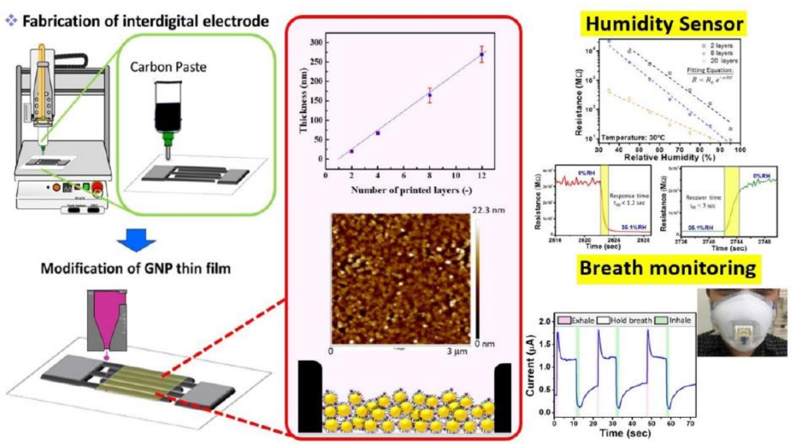
Highly Responsive PEG/Gold Nanoparticle Thin-Film Humidity Sensor via Inkjet Printing Technology

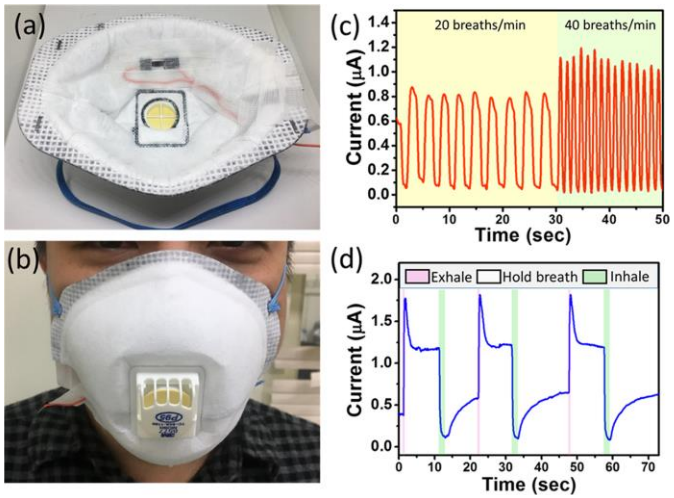
Chun-Hao Su,[†] Hsien-Lung Chiu,[†] Yen-Chi Chen,[†] Mazlum Yesilmen,[‡] Florian Schulz,[‡] Bendix Ketelsen,[‡] Tobias Vossmeyer,[‡] and Ying-Chih Liao[*,†]

[†]Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

[‡]Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany

- ✓ **E-jet printing**
- ✓ **Inkjet printing**
- ✓ **AFM**
- ✓ **…**

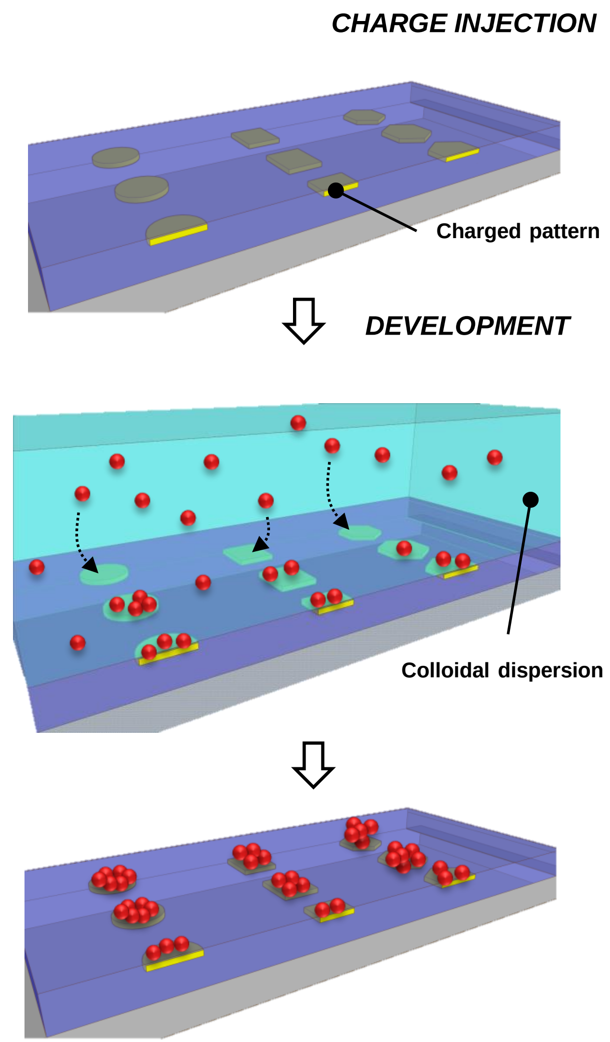




☞ **ΔR 10^5 times between 1,8 et 95 % RH !**

Focus on our work: nanoxerography

The process of Nanoxerography



1/ Inject electrostatic charges to form patterns of desired geometries into a substrate

2/ Acting as electrostatic trap for charged or polarizable colloidal nanoparticles in solution

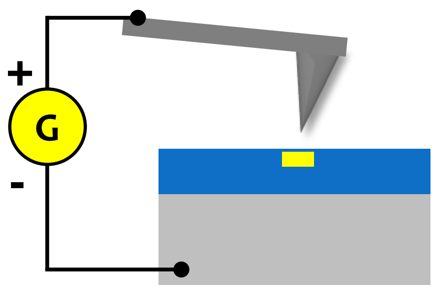
Focus on our work: Electrostatic charge injection

▶ What type of used materials/substrates for injection ? **Electret**

100 nm of PolyMethylMethAcrylate (PMMA) on highly doped silicon wafer

▶ How to inject charges ?

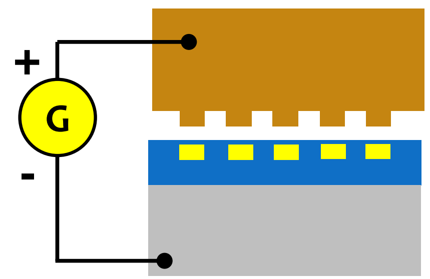
AFM tip



- High resolution (100 nm)
- Versatility

- Slow (10µm/s)
- Sequential
- Small area adressed

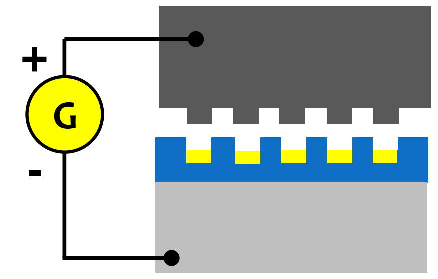
Electrical microcontact printing (e-µCP)



- Faster (45s /surface)
- Large area adressed

Lower resolution (6 µm)

Electrical nanoimprint (e-NIL)



- Topographical Structuration
- Large area adressed

Slower (15min/surf)

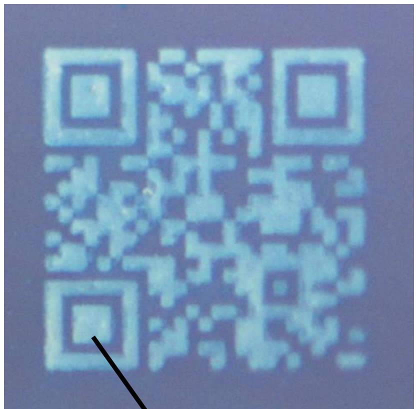
Focus on our work: anti counterfeinting nanotag

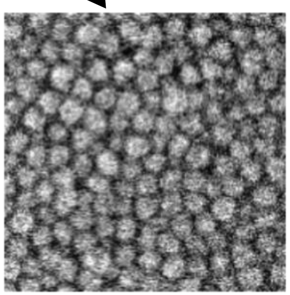
23 nm $NaYF_4$: Er^{3+},Yb^{3} NCs in hexane

By AFM nanoxerography

Optical microscope

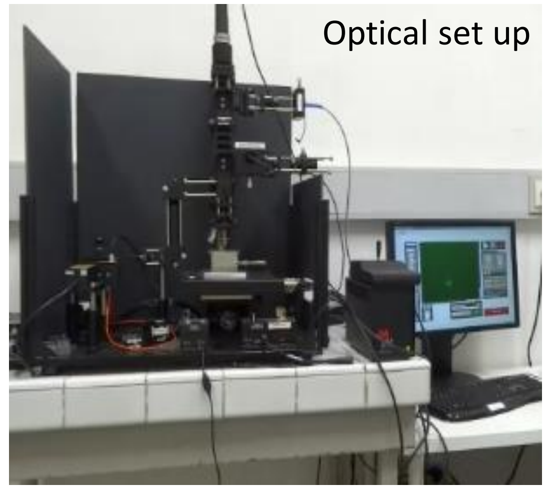
30 µm



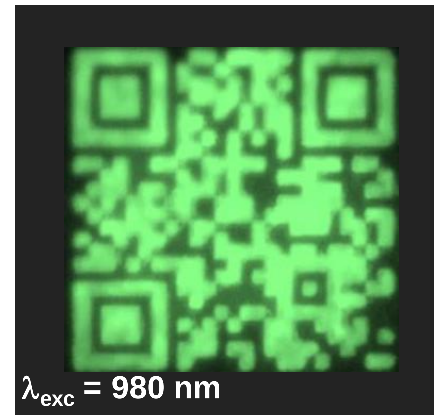


$NaYF_4$:Er^{3+},Yb^{3+} NPs (ϕ=22 nm)

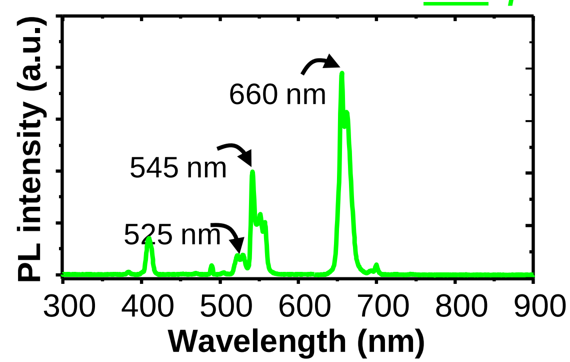
☞QR code 3 times smaller than a hair, visible using an optical microscope



Photoluminescence @ 545 nm



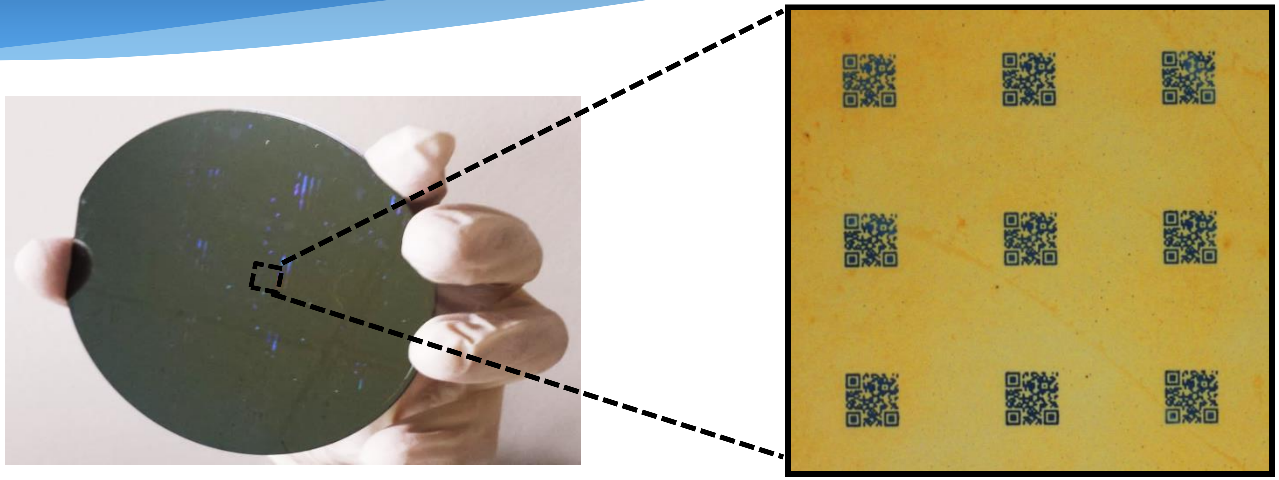
Low quantum yield 1 %



☞Luminescent signature solely accessible using a dedicated optical set up

Focus on our work: Large fabrication of nanotags

By e-NIL



☞ **Large scale fabrication of around 300 000 QR codes with 50 µm × 50 µm dimensions on a 4' wafer within a few minutes**

☞ **Transfer on transparent flexible film**

Diaz et al, *Nanotechnology*, 25 (**2014**)

***ANR** NanoTaggin (2015-18)*

« Simple » reading

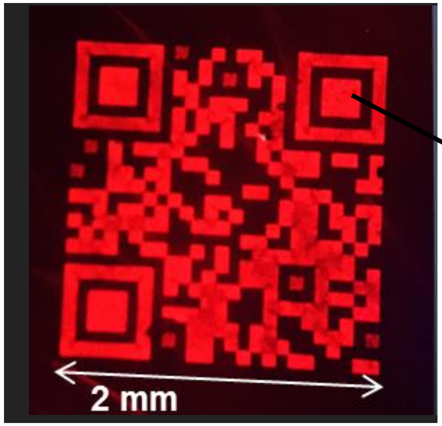
20nm CdSE@CdS Qdots in hexane

Luminescent Qr code based on CdSe@CdS NPs– « Simple » reading

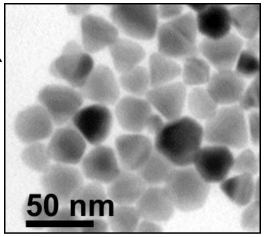
 +  = 

By e-µCP nanoxerography

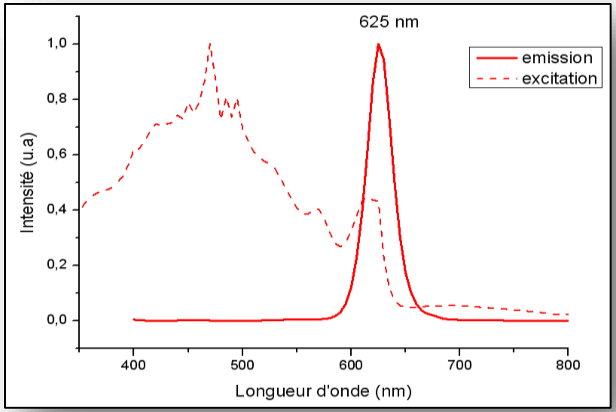
Photoluminescence @ 625 nm



λ_{exc} = 450 nm



CdSe@CdS NPs (ϕ=20 nm)



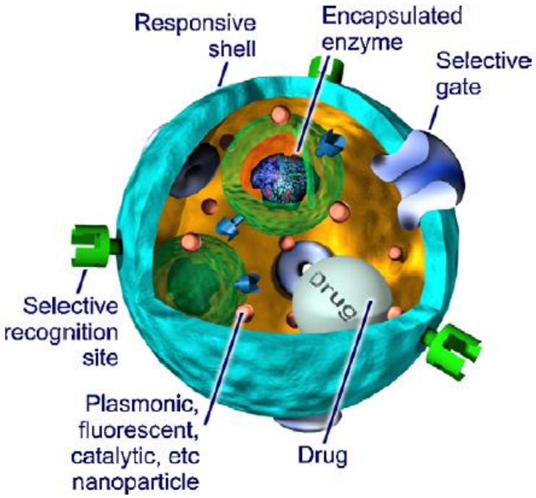
☞**Naked eye visible QR code using a simple blue LED excitation – reading through a regular smartphone application**

☞**Luminescent signature obtained on a dedicated optical set up**

Poirot, D et al *Applied Nano Materials* ,1, **(2018)**

« Enviro-intelligent » marking

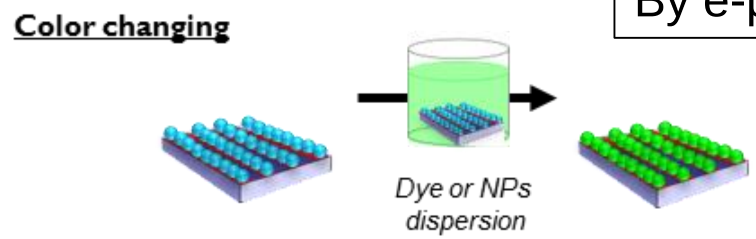
Nanogels



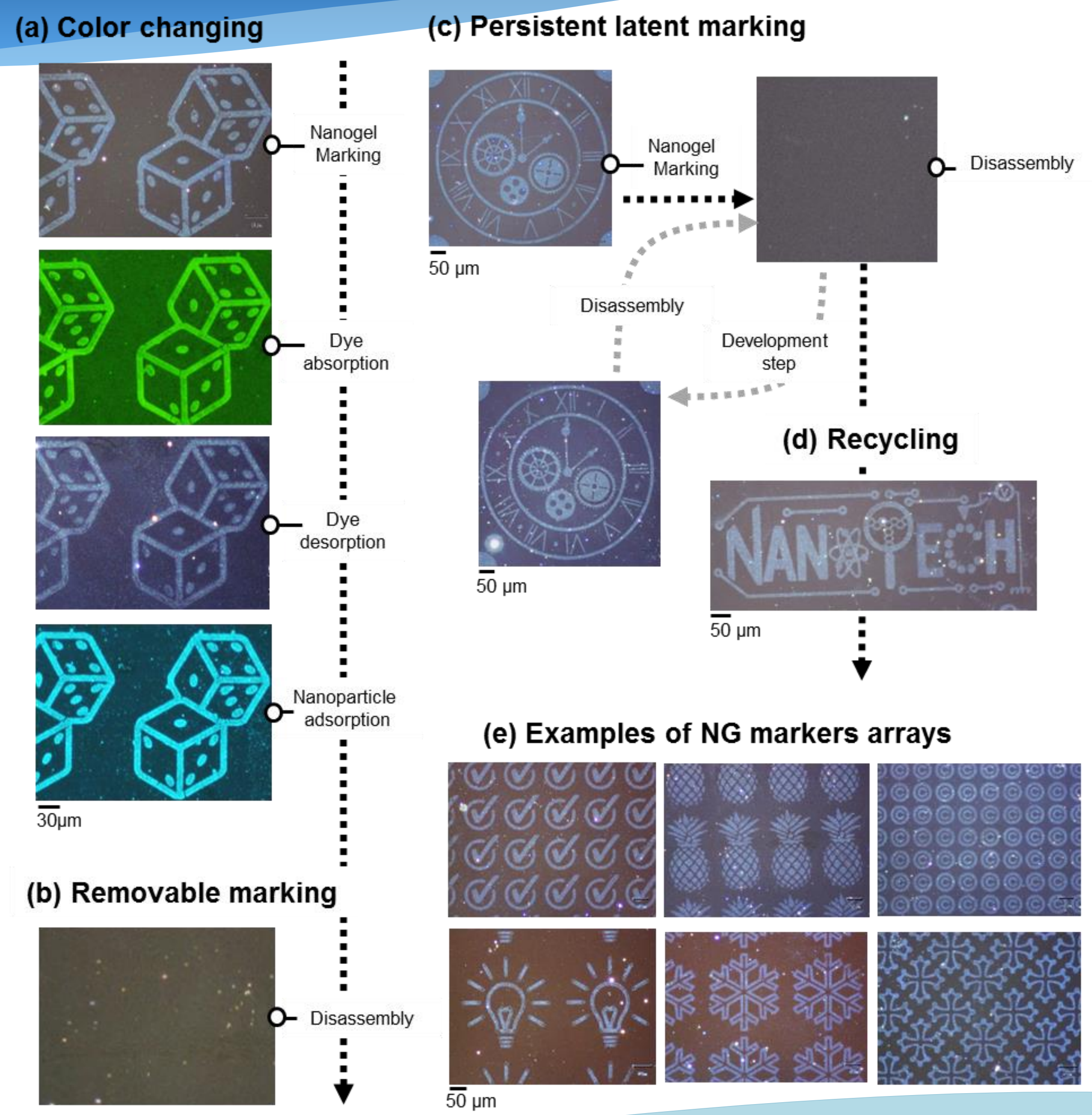
Motornov et al, Progress in Polymer Science , 35 ***(2010)***

Enviro-sensitive

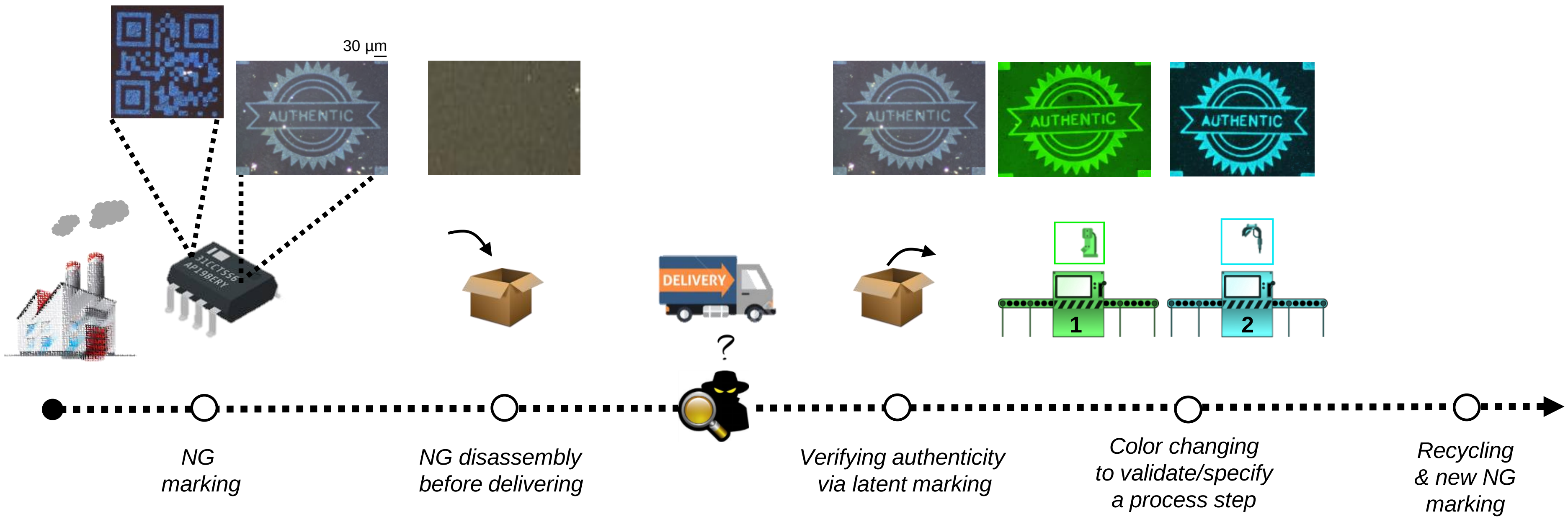
By e-µCP



« Enviro-intelligent » marking



« Enviro-intelligent » marking



Which technique to be selected ?

➢ Questions to be adressed…

***Sequential vs Parrallel technique ?

Resolution, speed, versatility, scale,…

***External force to be introduced ?

Integration, set up, specificity, resolution,…

➢ Nothing is perfect, there is always a compromise…

Directed co assembly: capabilities and interests

Definition

Co assembly = assembly of various (at least 2) types of nanoparticles on the same surface

simultaneous or sequentially

+

Directed = on specific sites of a rigid or flexible substrate

Interests:

Combination of geometries and properties on the same support

Multifunctions/Multiplexing

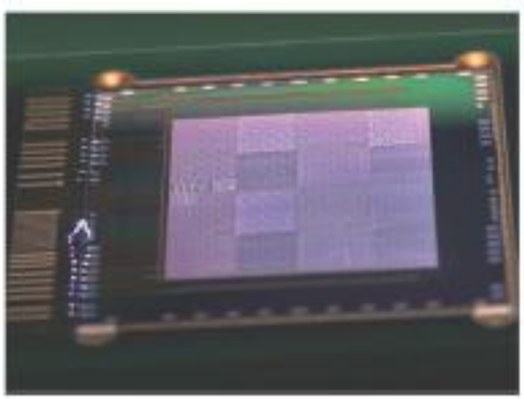
- Multiplexing analyses on the same support
- Surfaces with multi-functionnalities

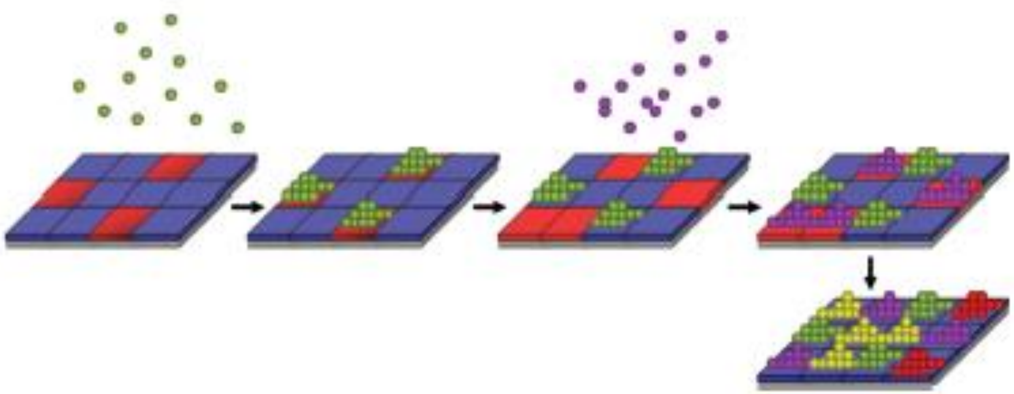
FEATURE ARTICLE 2017 ADVANCED FUNCTIONAL MATERIALS

Particle Patterning www.afm-journal.de

Combinatorial Particle Patterning

*Clemens von Bojnicic-Kninski, Roman Popov, Edgar Dörsam, Felix F. Loeffler, Frank Breitling, and Alexander Nesterov-Mueller**





Applications on displays

npj | Flexible Electronics 2018 www.nature.com/npjflexelectron

REVIEW ARTICLE OPEN

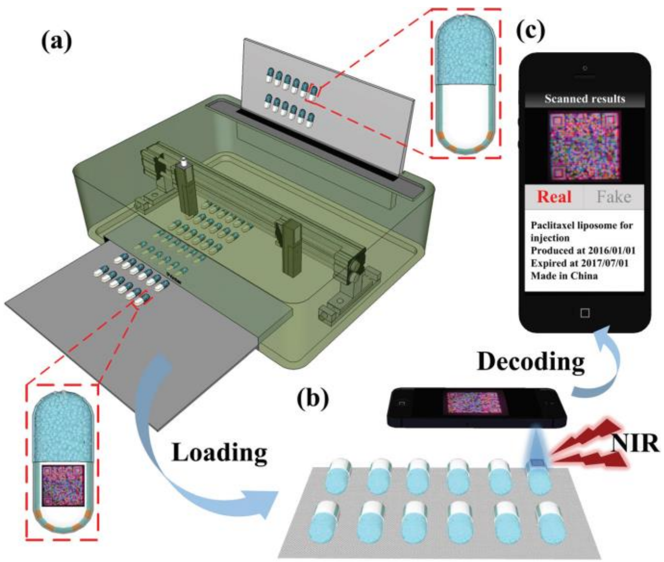
Flexible quantum dot light-emitting diodes for next-generation displays

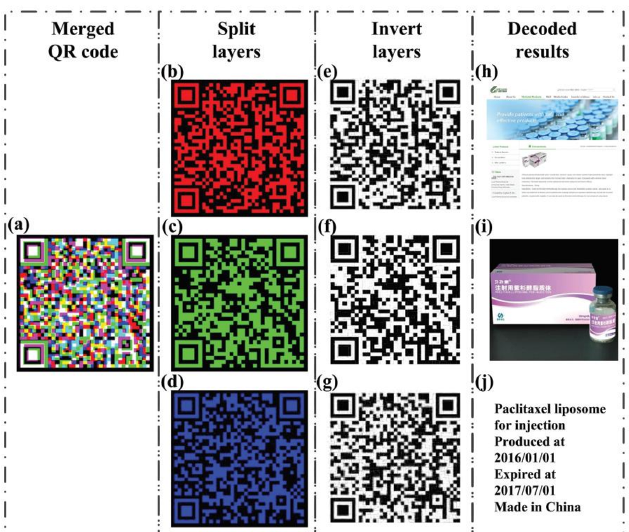
Moon Kee Choi[1,2], Jiwoong Yang[1,2], Taeghwan Hyeon[1,2] and Dae-Hyeong Kim[1,2]

- Applications on displays (RGB pixels…)

e

Applications in anticounterfeiting





Nanoscale

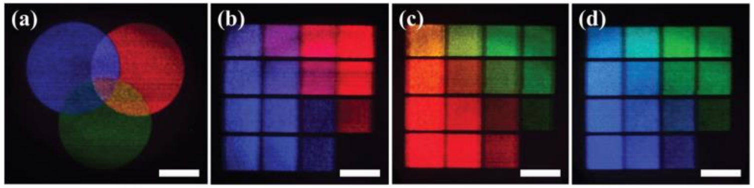
PAPER

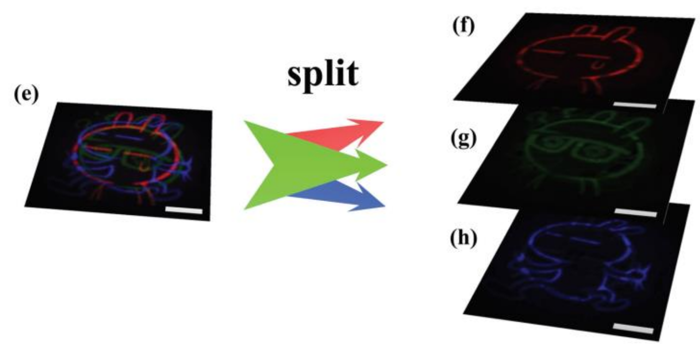
View Article Online
View Journal | View Issue

Cite this: *Nanoscale*, 2016, **8**, 10096

Three-dimensional quick response code based on inkjet printing of upconversion fluorescent nanoparticles for drug anti-counterfeiting†

Minli You,[a,b] Min Lin,*[a,b] Shurui Wang,[a,b] Xuemin Wang,[a,b] Ge Zhang,[b] Yuan Hong,[b] Yuqing Dong,[a,b] Guorui Jin[a,b] and Feng Xu*[a,b]

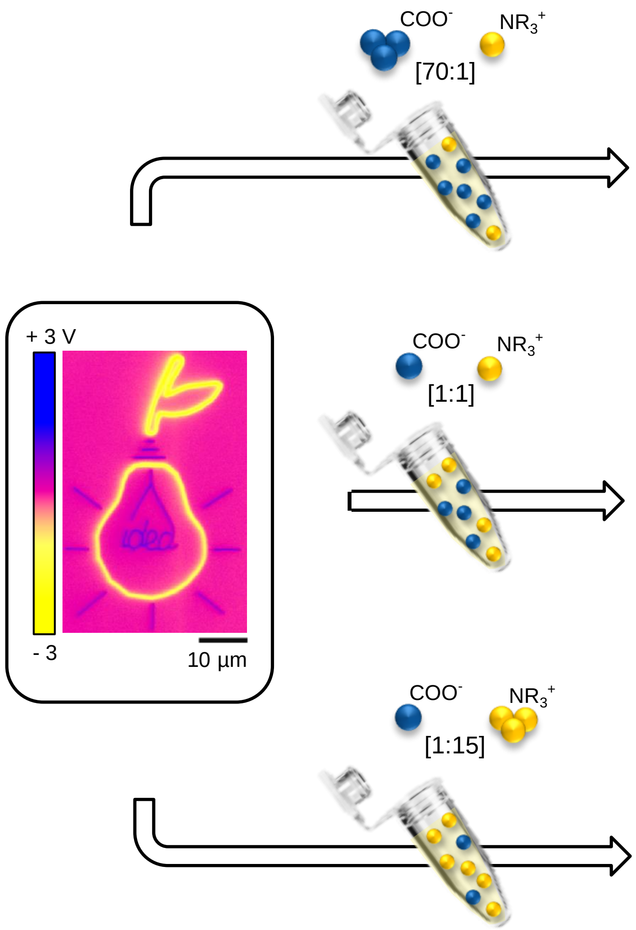




☞ **Specific optical signature**

Applications in anticounterfeinting

AFM Charging



☞ **Concentration-dependant encryption**

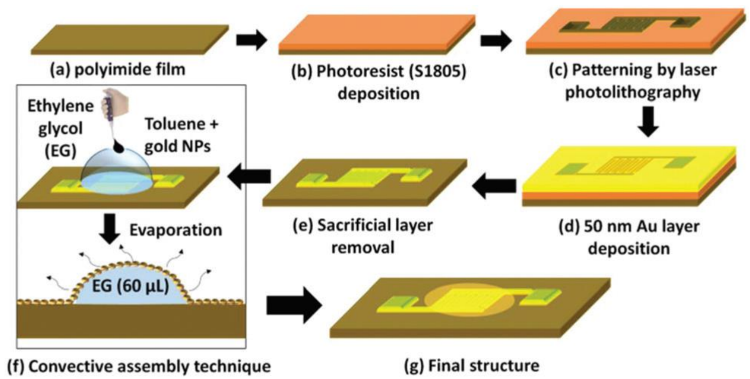
Teulon et al, *Langmuir*,*4*,(**2018)**

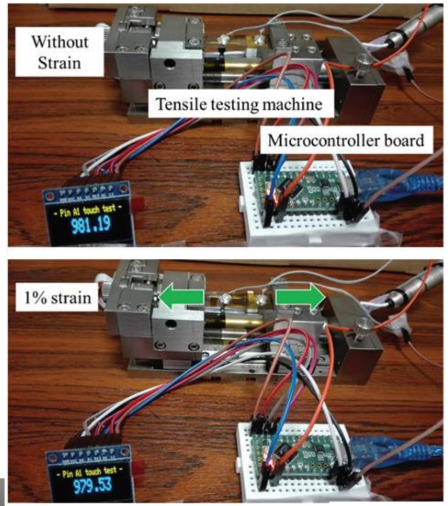
Looking for geometry in directed assembling : what for ?

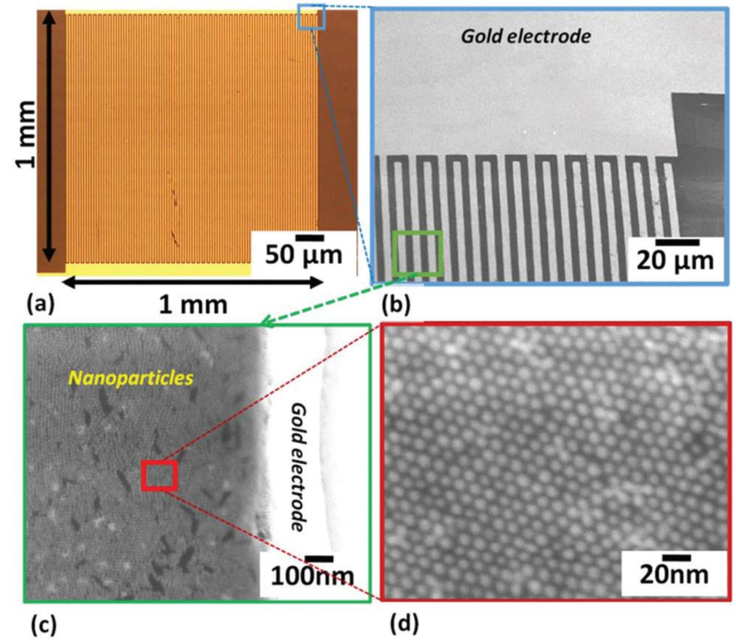
Closed packed !

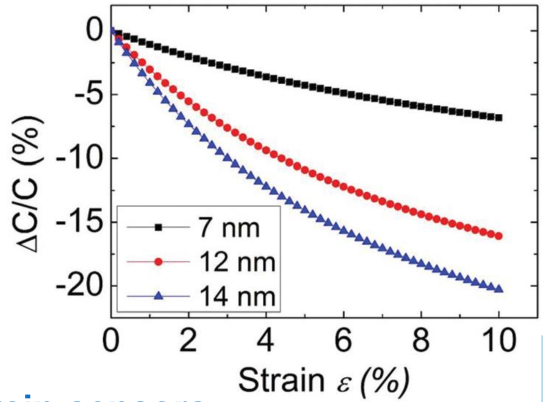
→ Link between nanoparticles: promote the electrical conduction

Convective assembly









H. Nesser et al, *Nanoscale*, 10 (**2018**)

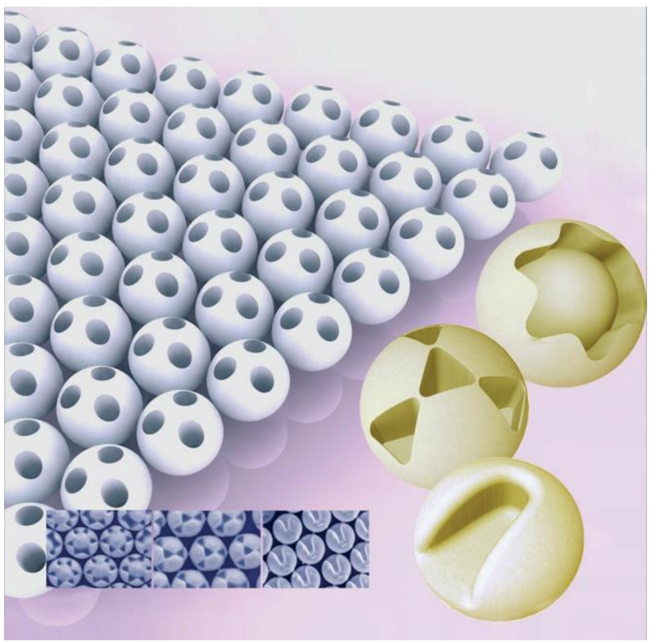
☞ **Wireless low consumption capacitive strain sensors**

or not closed packed!

→ **Controlling the interparticle distance and combining multiple nanoparticle types and processes**

Nanomachining by Colloidal Lithography

Seung-Man Yang, Se Gyu Jang, Dae-Geun Choi, Sarah Kim, and Hyung Kyun Yu*

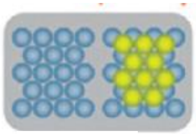


NANO small MICRO

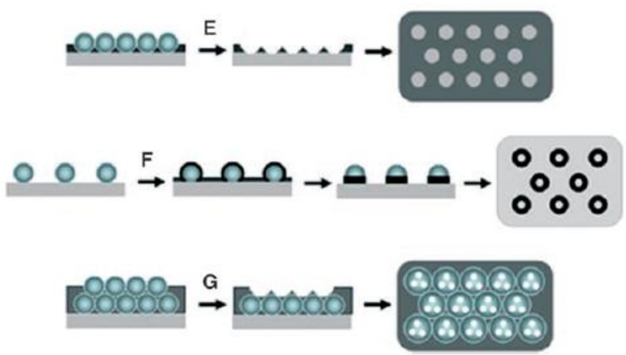
www.small-journal.com

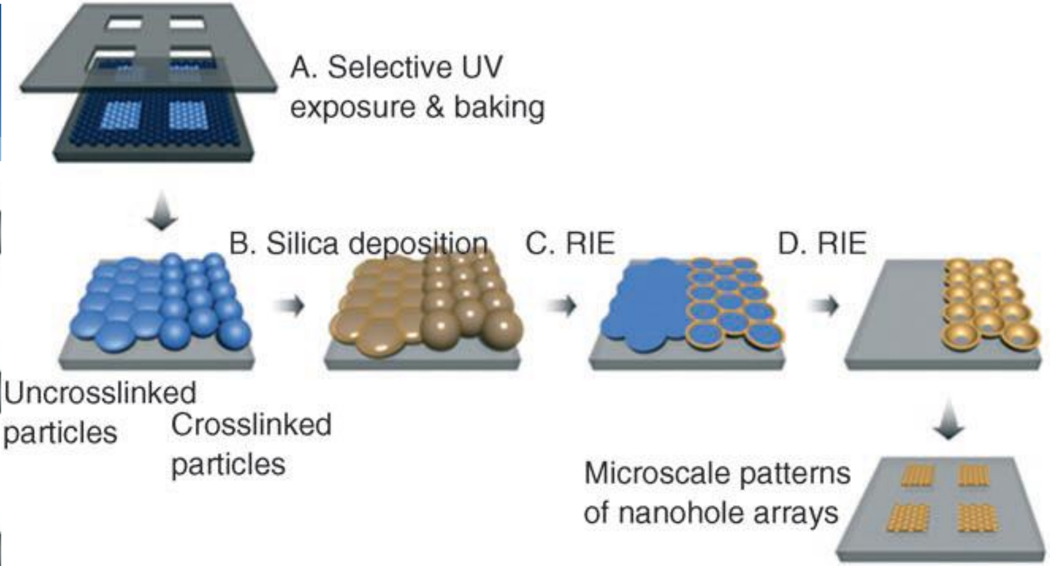
Nanosphere lithography / colloidal lithography

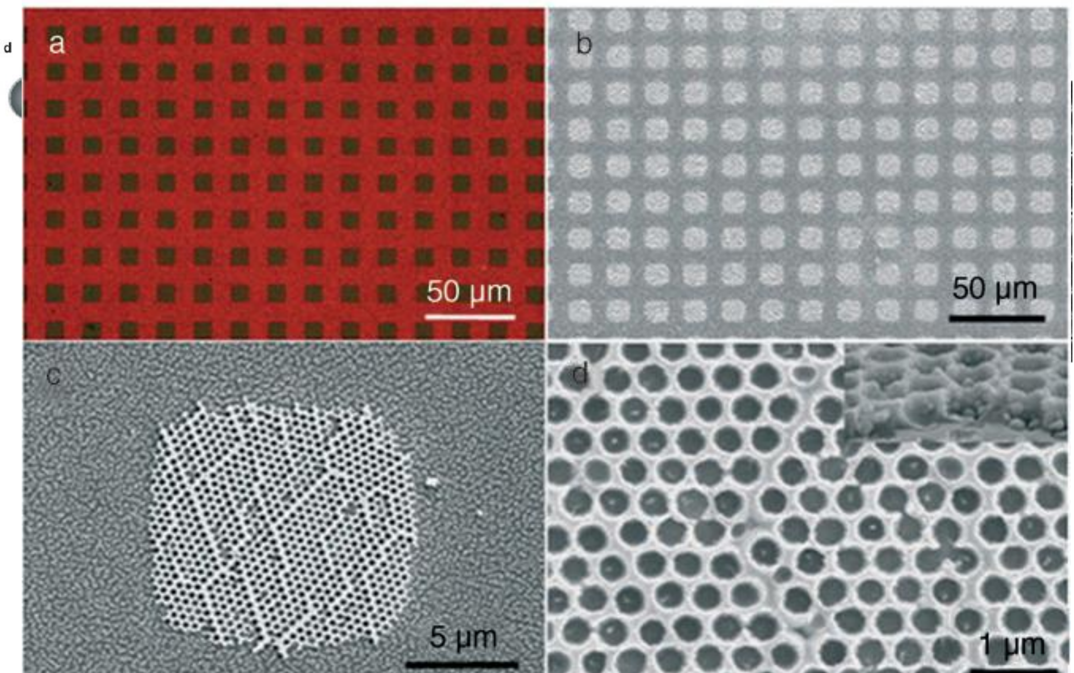
or not closed pack



Nanodot array
Nanowire growth
QD array
Nanodiode array
Patterned media







☞ **Nanomachining, patterns on demand better than e-beam (speed, scale, cost,…)**

Materials Views
www.MaterialsViews.com
2010
ADVANCED MATERIALS
www.advmat.de

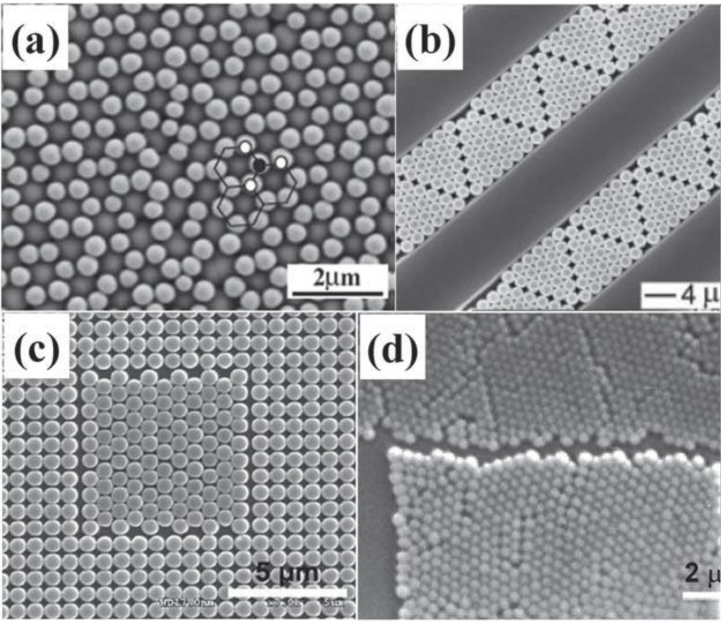
Colloidal Self-Assembly Meets Nanofabrication: From Two-Dimensional Colloidal Crystals to Nanostructure Arrays

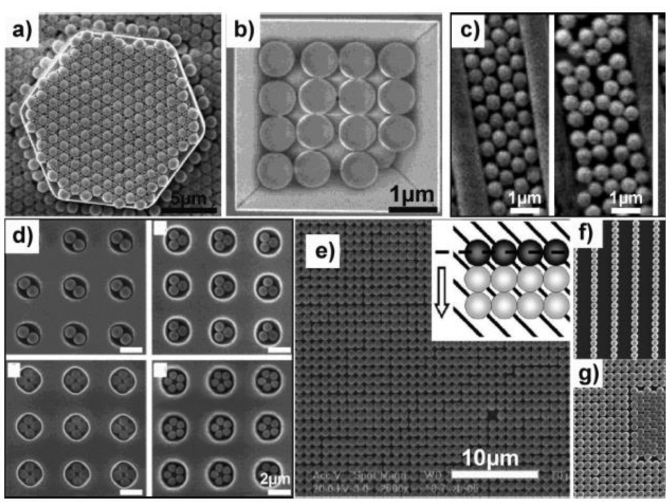
By *Junhu Zhang, Yunfeng Li, Xuemin Zhang,* and *Bai Yang**

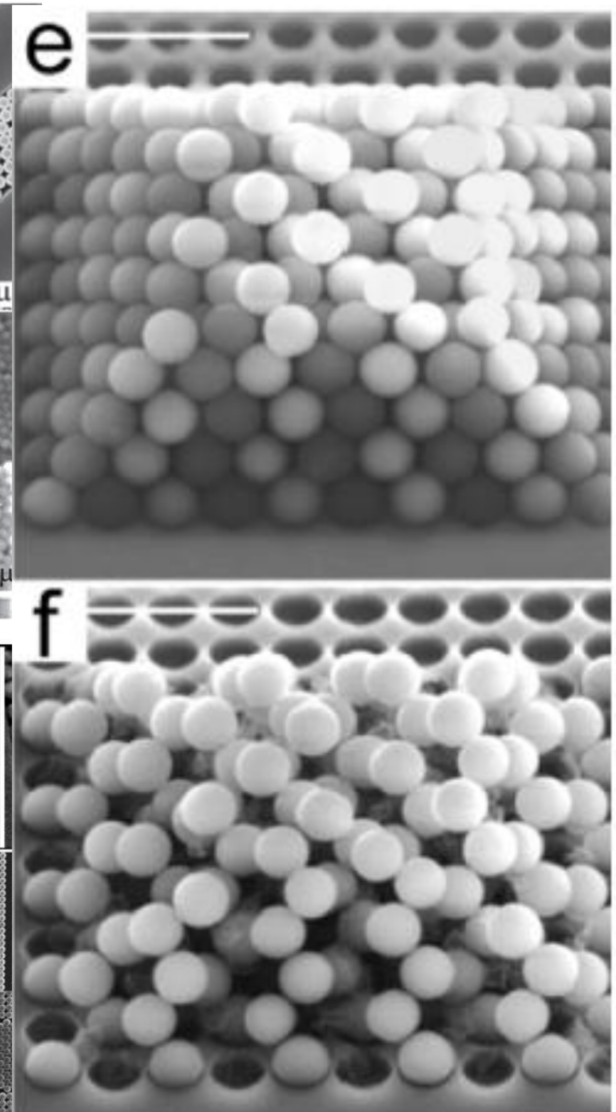
CHEMICAL REVIEWS
Review
2015
pubs.acs.org/CR

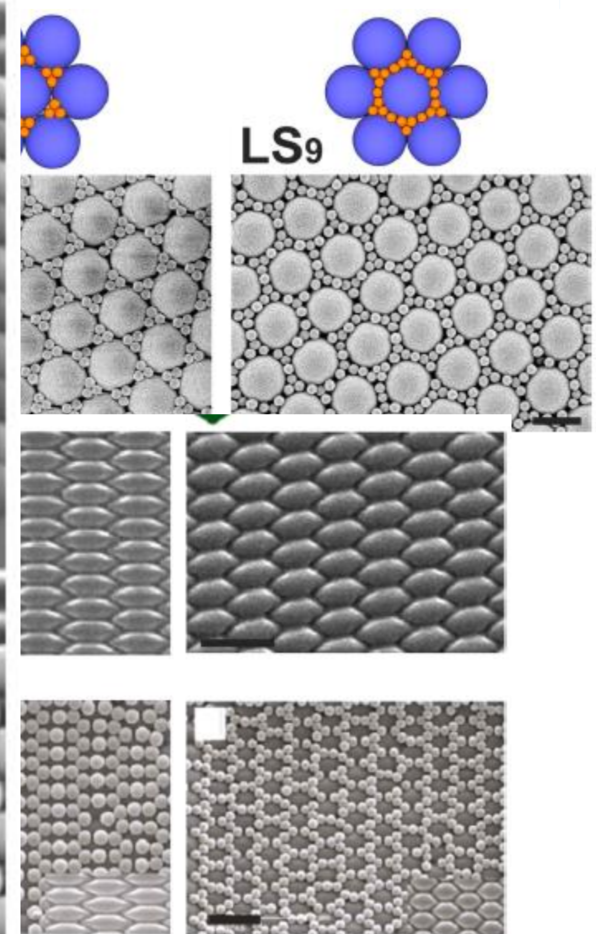
Advances in Colloidal Assembly: The Design of Structure and Hierarchy in Two and Three Dimensions

Nicolas Vogel,*,†,‡,^ Markus Retsch,*,§,^ Charles-André Fustin,‖ Aranzazu del Campo,⊥ and Ulrich Jonas*,∇,#

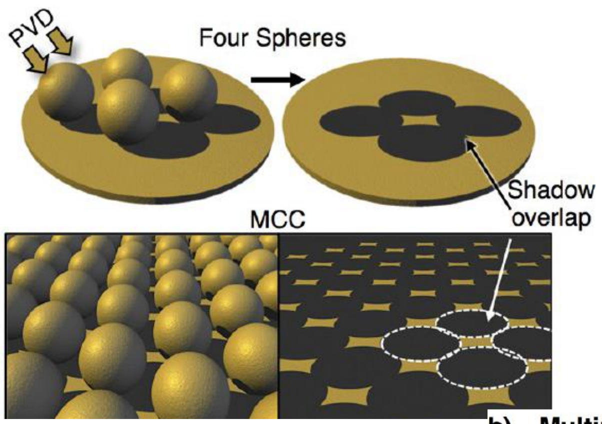








or not closed packed!

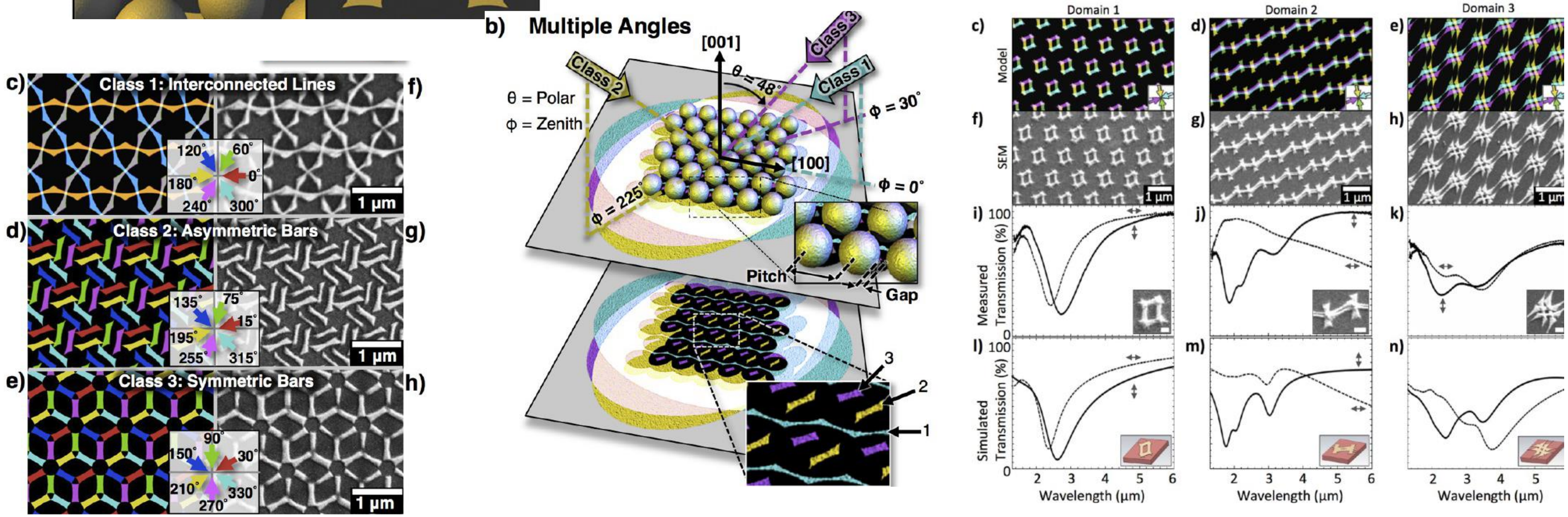


Engineering Shadows to Fabricate Optical Metasurfaces

Alex Nemiroski,[†] Mathieu Gonidec,[†] Jerome M. Fox,[†] Philip Jean-Remy,[†] Evan Turnage,[†] and George M. Whitesides[†,‡,§,*]

2014 ACS NANO
www.acsnano.org

Nanosphere lithography / colloidal lithography



☞ **Tuning optical properties, light polarization etc…**

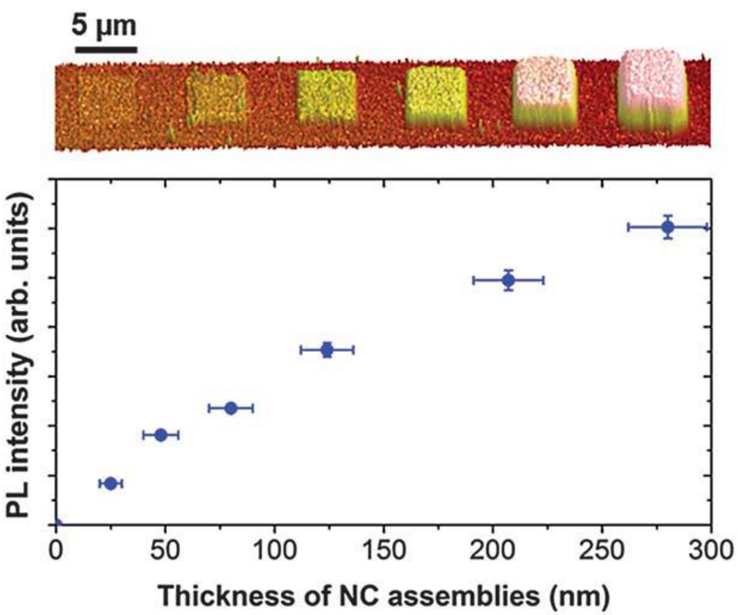
Going 3D !

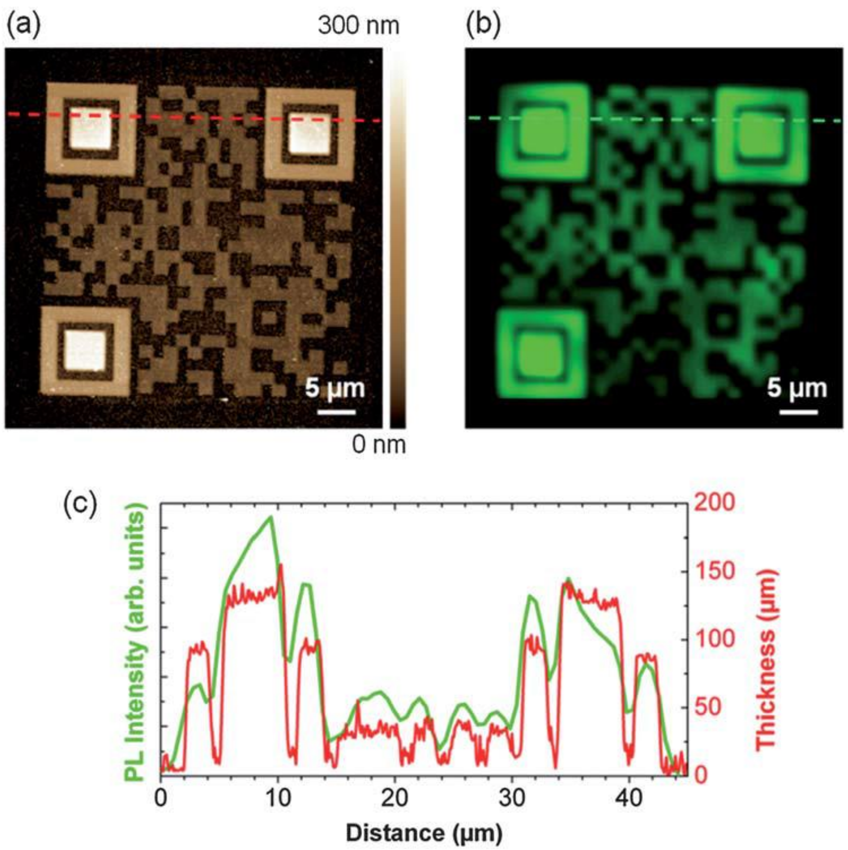
Optics

→ **Enhance the properties of nanoparticles**

23 nm $NaYF_4$: Er^{3+},Yb^3 NCs in hexane

Nanoxerography





☞ **New security levels for anticounterfeinting**

Sangeetha et al, *Nanoscale*, 5, (**2013**)

Going 3D !

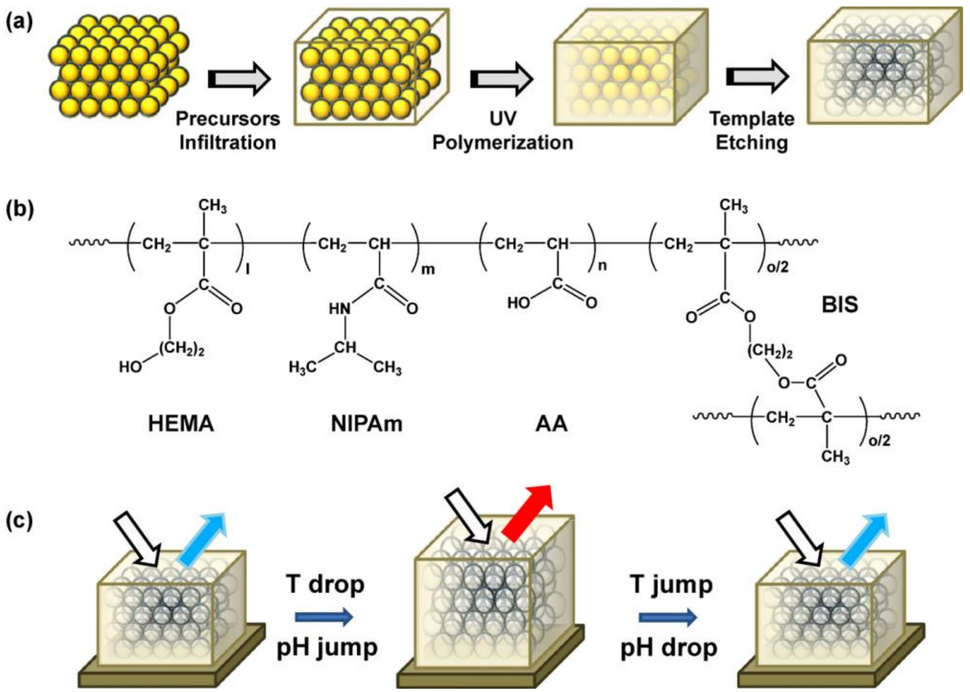
Contents lists available at SciVerse ScienceDirect
Sensors and Actuators B: Chemical
journal homepage: www.elsevier.com/locate/snb
2012

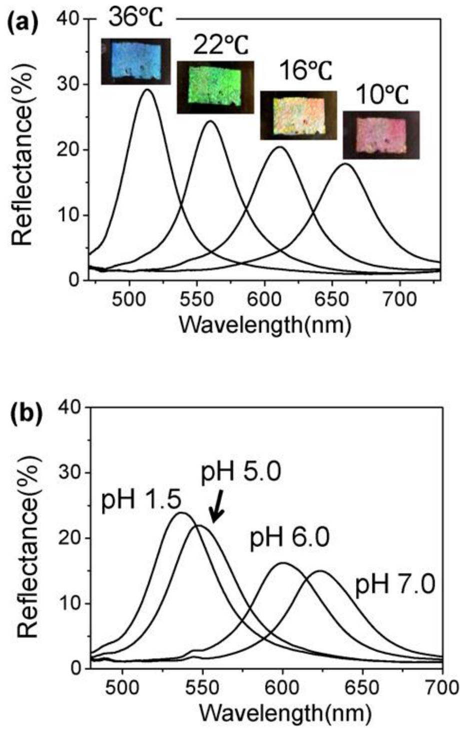
Dually tunable inverse opal hydrogel colorimetric sensor with fast and reversible color changes

Jinsub Shin, Sung Gu Han, Wonmok Lee*
Department of Chemistry, Sejong University, 98 Gunja-Dong, Gwngjin-gu, Seoul 143-747, Republic of Korea

Inverse opale

Optics





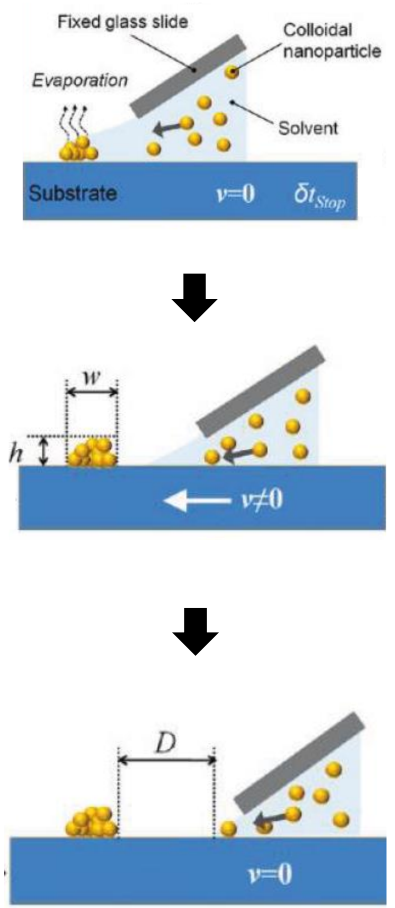
☞ **Low cost biocompatible temperature and pH sensors**

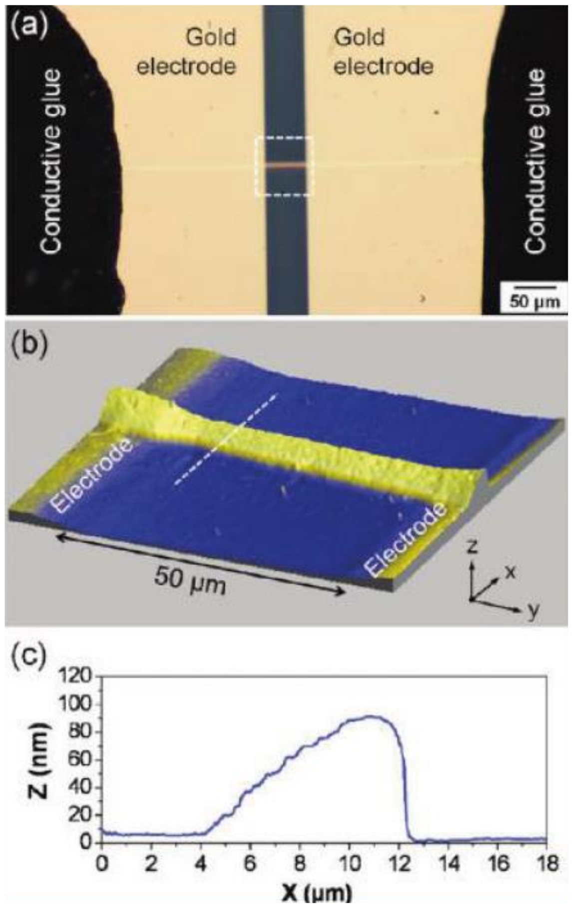
Need matter if you want to turn it visible !

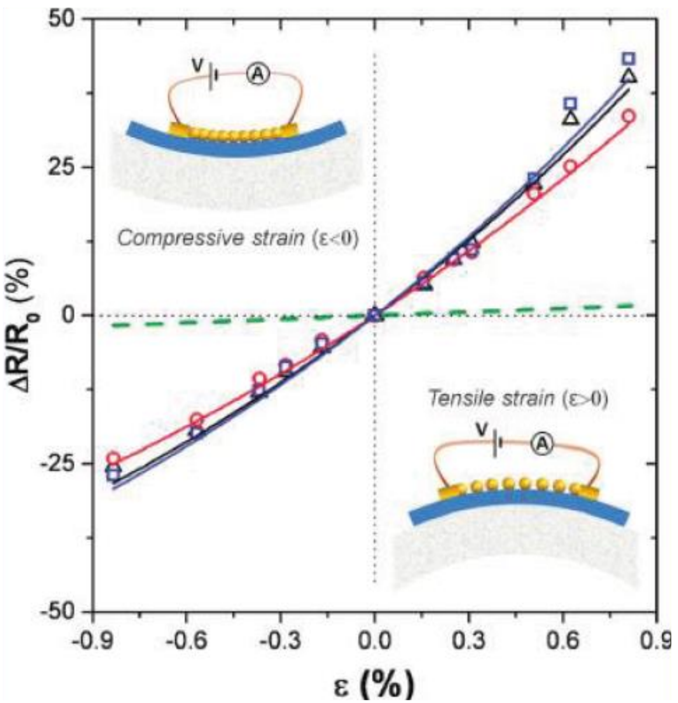
Going 3D !

CSA

Electrical properties by increasing conduction paths







☞ **Highly sensitive resistive strain gauges**

Exotic hybrid assembly

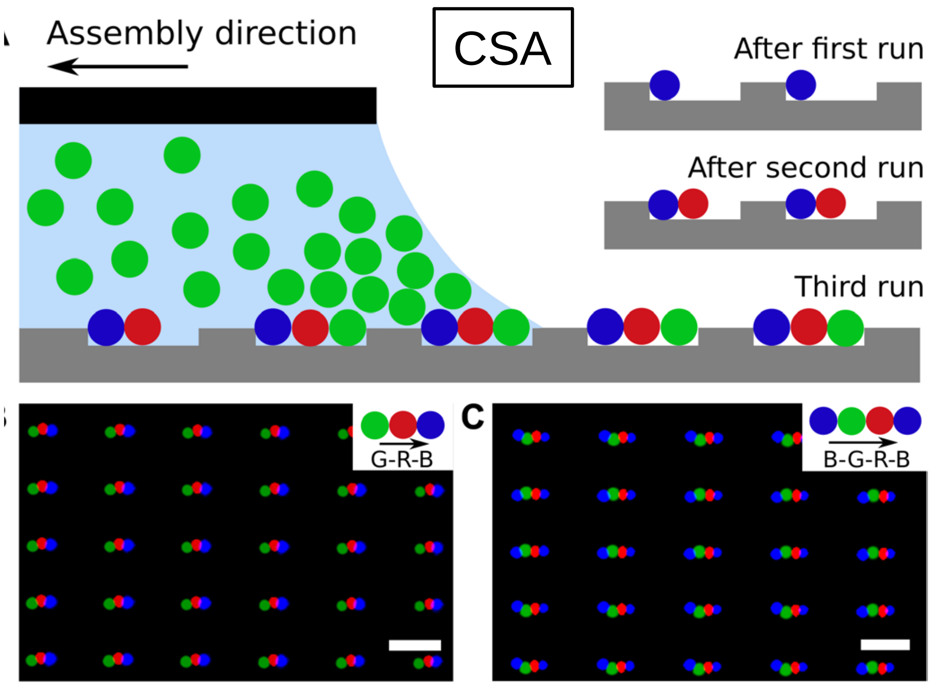
RESEARCH ARTICLE

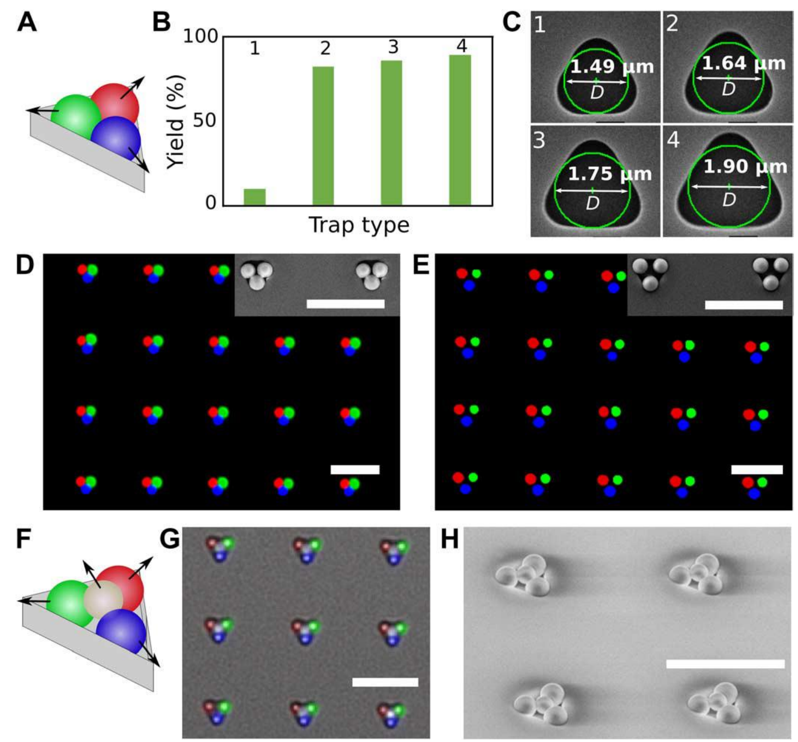
MATERIALS ENGINEERING

Programmable colloidal molecules from sequential capillarity-assisted particle assembly

Songbo Ni,[1,2] Jessica Leemann,[1,2] Ivo Buttinoni,[1] Lucio Isa,[1]* Heiko Wolf[2]*

10.1126/sciadv.1501779





☞ **New colloidal molecules**

GENERAL CONCLUSION

→ Definition of directed assembly of colloidal nanoparticles on surfaces

→ Directed co assembly : multiplying combinations and so properties !

→ Geometry in assembling is important :

** Controlling the interparticle distance

** Shapes/structures on demand : nanofabrication / nanomachining with colloidal lithography

** Arrangement and order for default free properties

** 3D for more matter and so more capabilities !

Thank you !

Permanent


Jérémie Grisolia


Laurence Ressier


Etienne Palleau


Delphine Lagarde


Benoit Viallet


François Guérin


Pierre Moutet

PhD students


Lauryanne Teulon

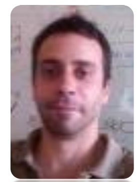

David Poirot

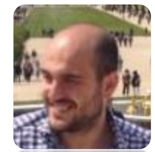

Romain Platel


Sangeetha Neralagata

Postdocs


Louis Vaure


Simon Raffy


Hussein Nesser


Thomas Alnasser

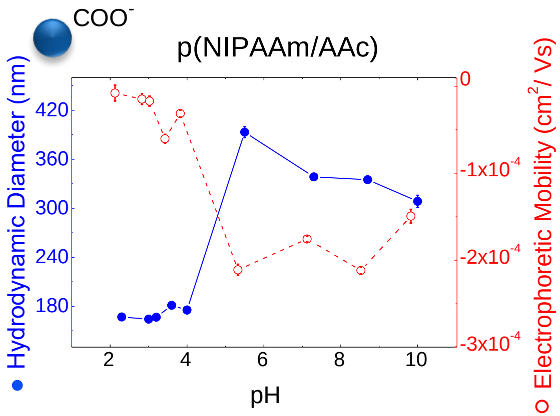
LPCNO ANR AGENCE NATIONALE DE LA RECHERCHE RÉGION MIDI-PYRÉNÉES otech TOULOUSE TECH TRANSFER Nanolike NEXT nano | mesures extrêmes | théorie

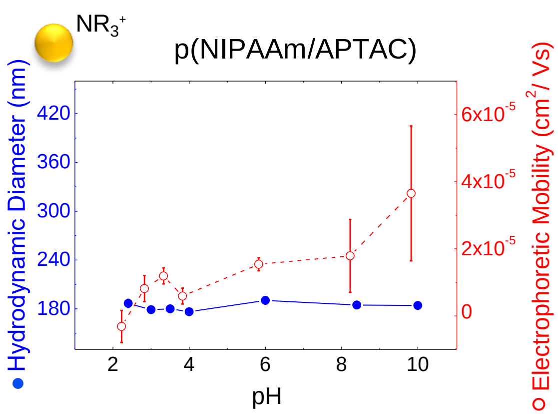
?? QUESTIONS ??

$$\boxed{\textbf{Back up}}$$

Properties of nanoparticles affected by the substrate ?

For nanogels in solution

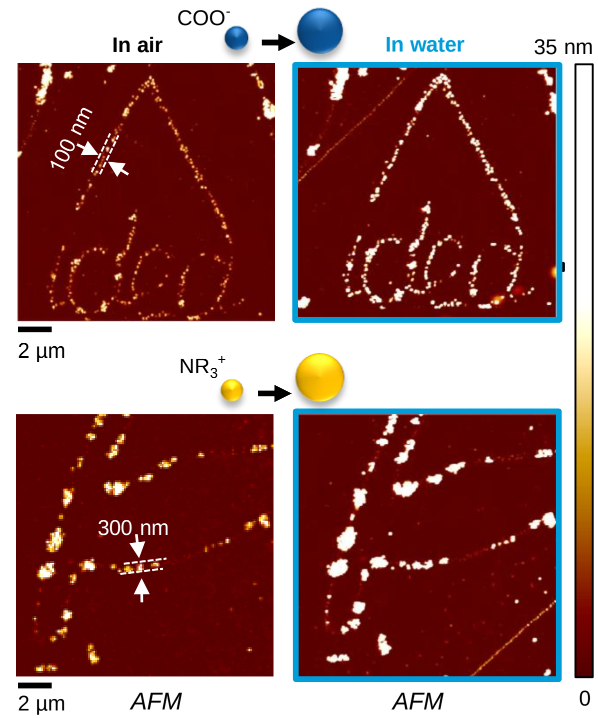


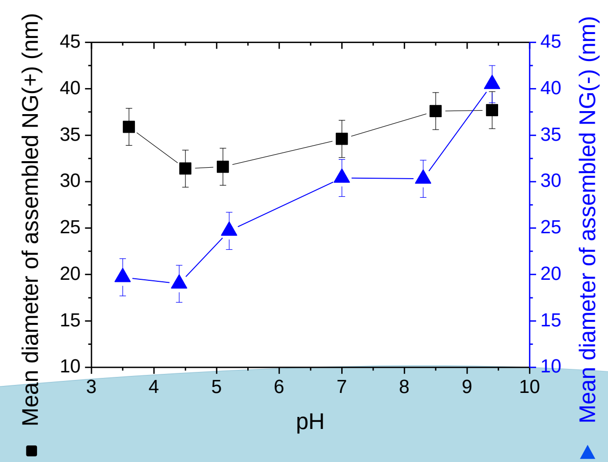


➔ Not really, same trend !

Teulon et al, submitted to *Langmuir*, (**2017**)

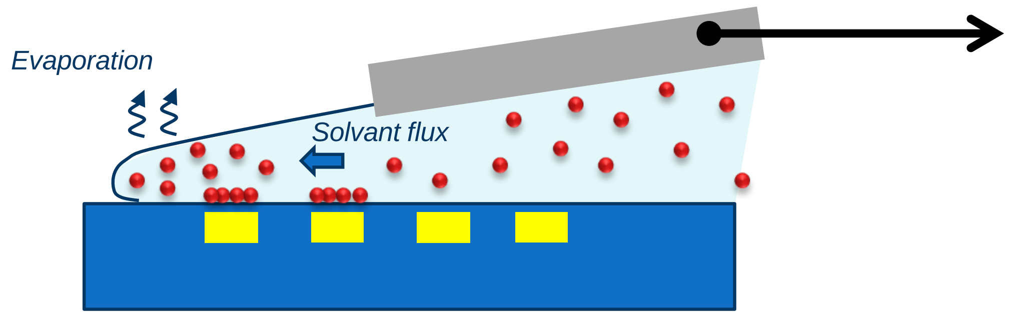
Once assembled





2st : quid of large nano-objects (>500nm) ?

Coupling of 2 directed assembly techniques :
Nanoxerography + Convective Self Assembly



Teulon et al, in preparation, (**2017**)

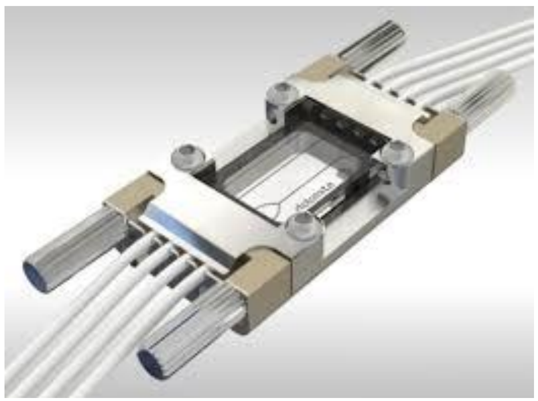
Increase of the electrostatic force range by controlling the triple line motion
Control of the nanoparticle reservoir/distribution

Directed and **oriented** assembly

Work with anisotropic nano-objects

Addition of the contribution of hydrodynamic forces

→ via flow injection or controlled evaporation



New microfluidic set up in progress

New properties depending on the orientation + observations in situ
→ better understanding of assembly theory and mechanisms

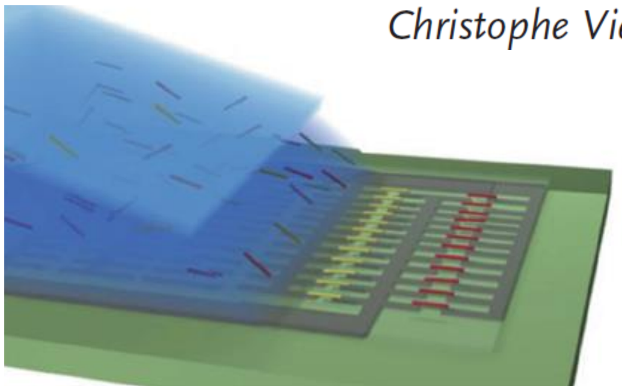
A « local » example

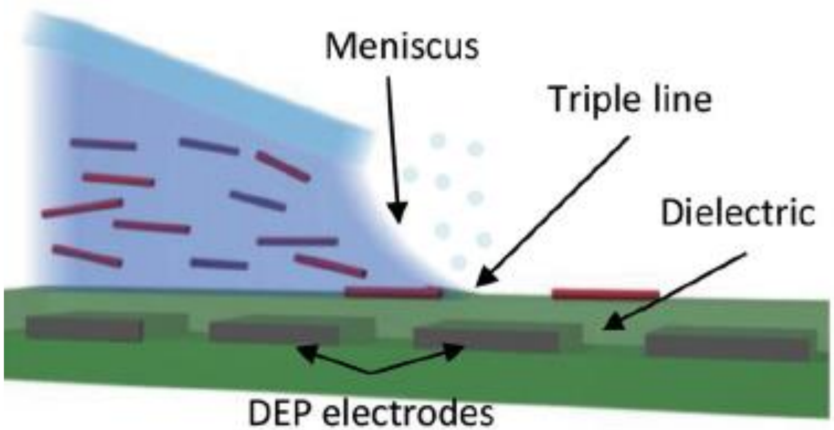
ADVANCED MATERIALS
www.advmat.de

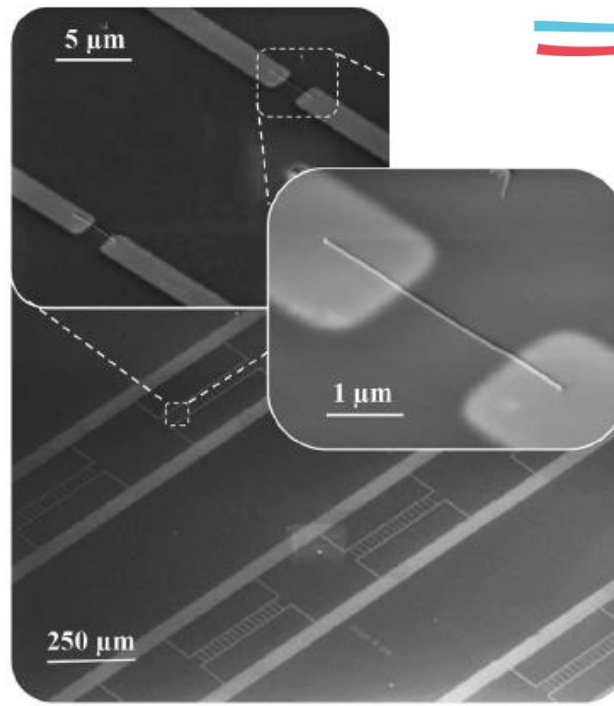
Large-Scale Assembly of Single Nanowires through Capillary-Assisted Dielectrophoresis 2015

*Maéva Collet, Sven Salomon, Naiara Yohanna Klein, Florent Seichepine, Christophe Vieu, Liviu Nicu, and Guilhem Larrieu**

LAAS CNRS

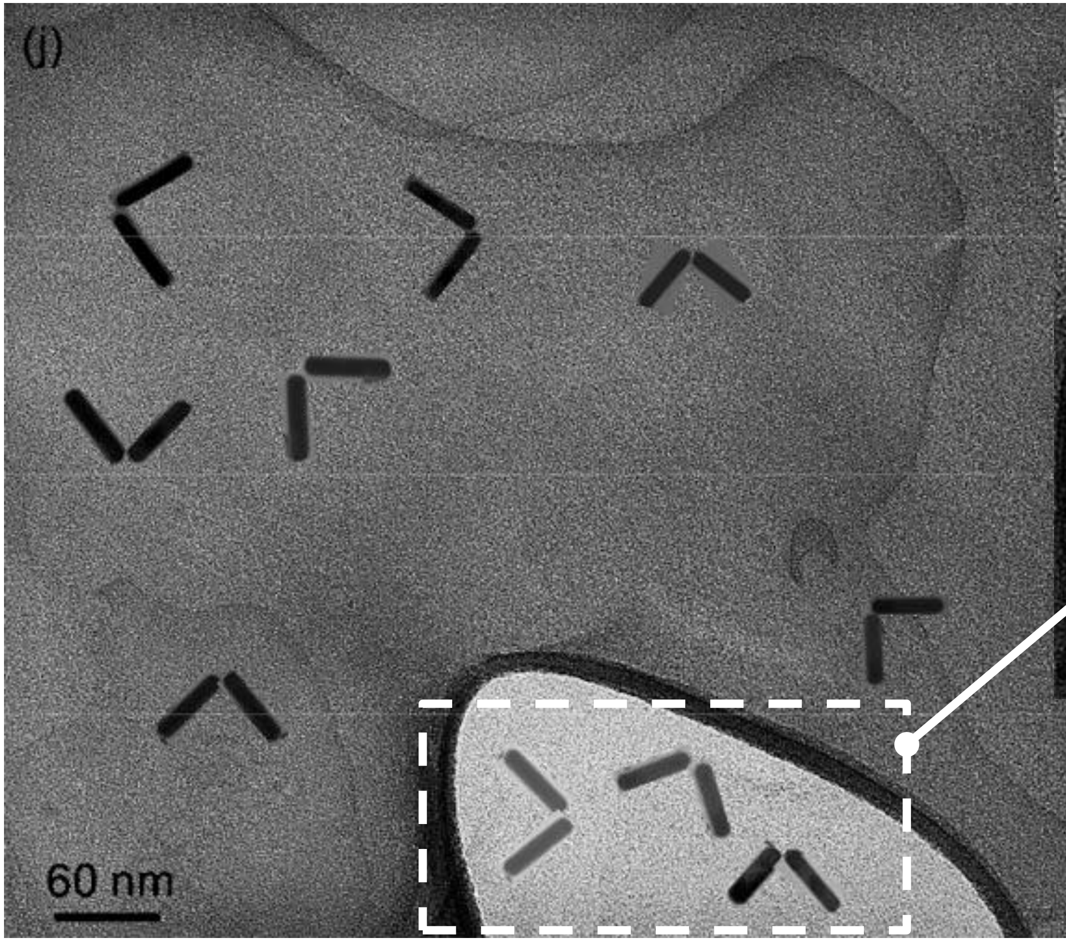






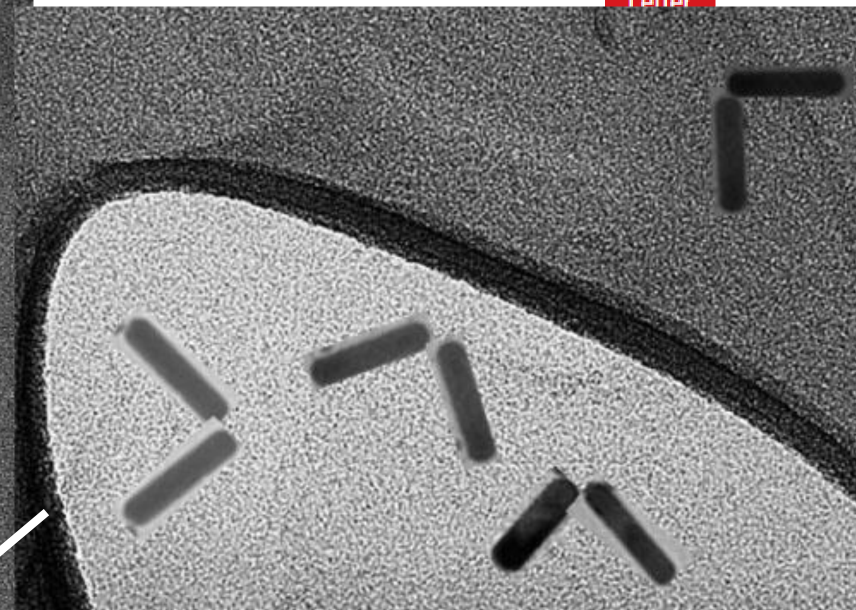
Oriented assembly by using Paint !

THE UNIVERSITY OF UTAH



013

Letter



Photoshop is much better !!

Conclusion

Nanoxerography

=

Fast, versatile, scalable electrostatic directed assembly technique for a large range of colloidal nano-objects

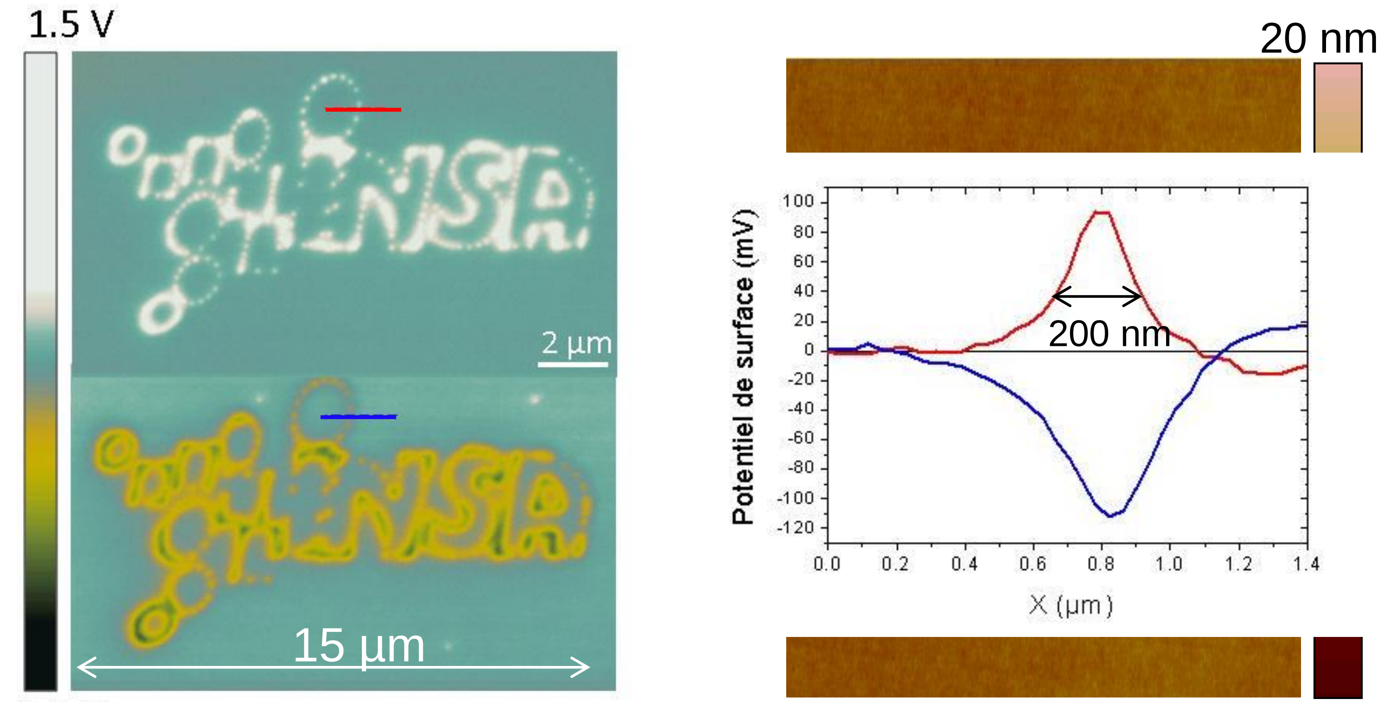
Multiple applications

(secured marking, sensing, etc…)

Always looking for new building blocks/applications

Example of charge injection/characterization

Using a polarized AFM tip



KFM ***AFM***

Mechanisms of nanoxerogaphy assembly

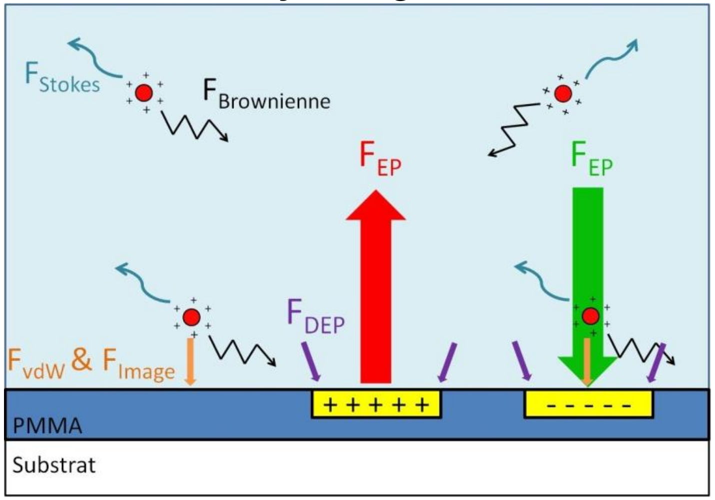
Coulomb Force

$$F_{EP} = QE$$

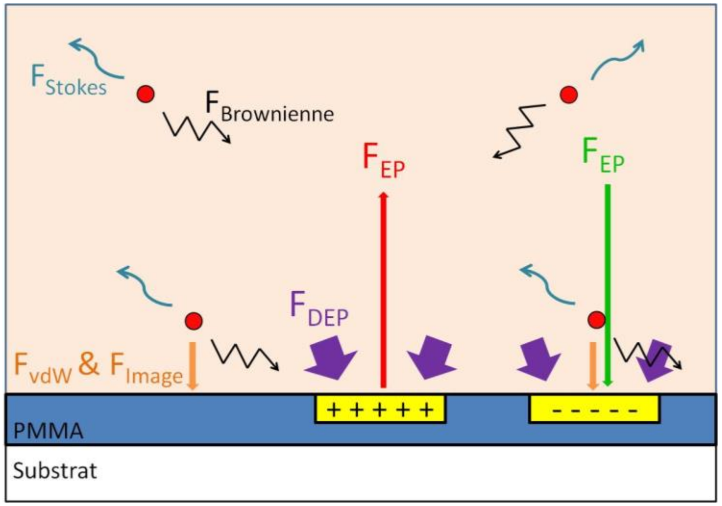
Dielectrophoretic Force

$$F_{DEP} = 2\pi\varepsilon_0\varepsilon_{Sol}\,\mathrm{Re}\left(\frac{\varepsilon^*_{NP} - \varepsilon^*_{Sol}}{\varepsilon^*_{NP} + 2\varepsilon^*_{Sol}}\right)R_{NP}^3\nabla E^2$$

Positively charged NPs



Neutral NPs



E : Electric field
R_{NP} : NP radius
ξ : NP zeta potential

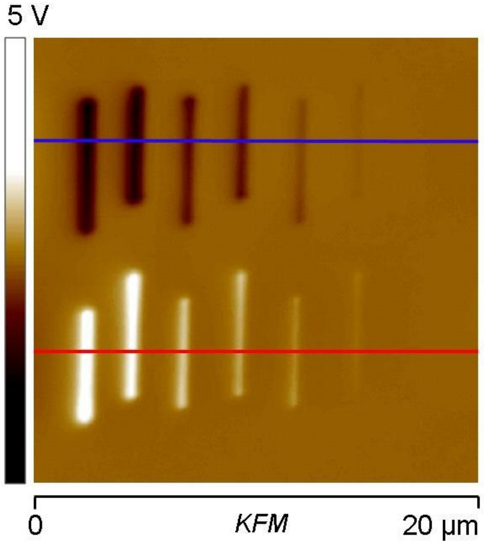
ε_0 : vaccum permitivity
ε^*_{Sol} : permitivity of dispersing media
ε^*_{NP} : complexe permitivity of NP

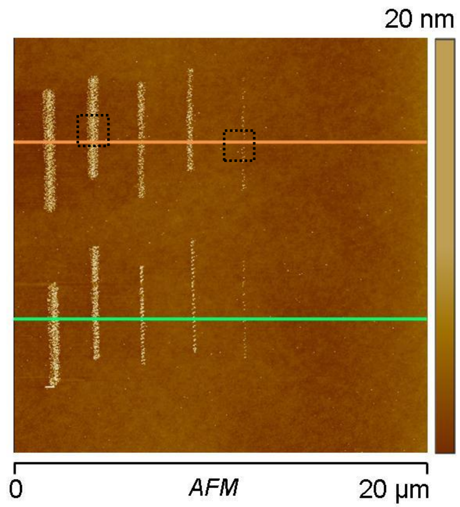
Example of typical assembly

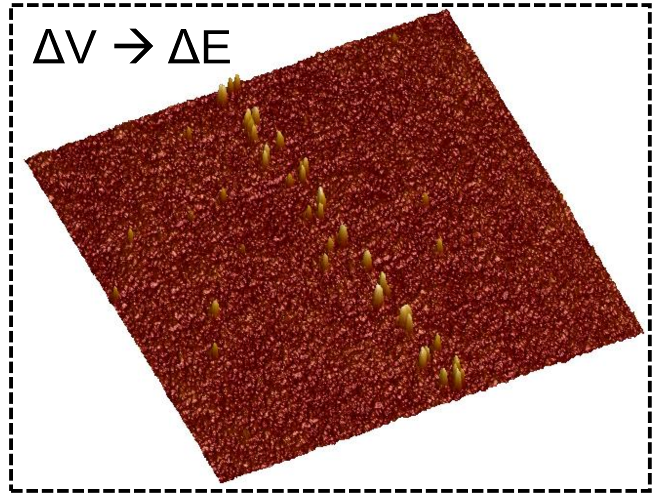
- NPs 10 nm neutral Ag NPs in hexane

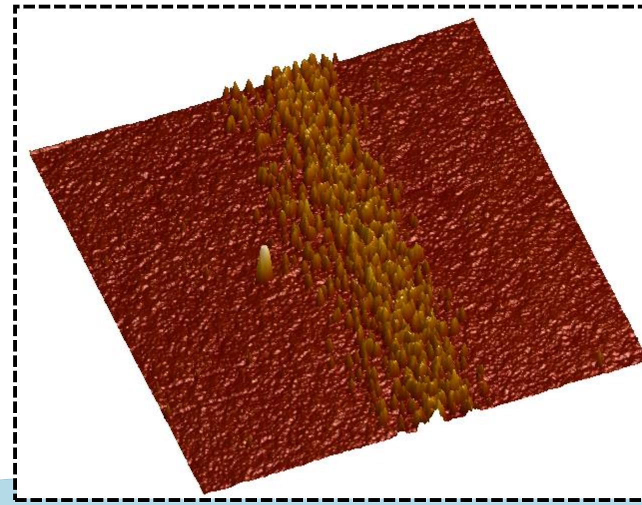
Development

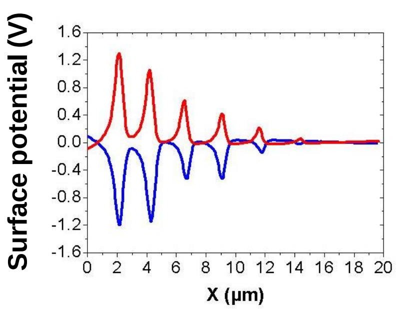
AFM Charge Injection

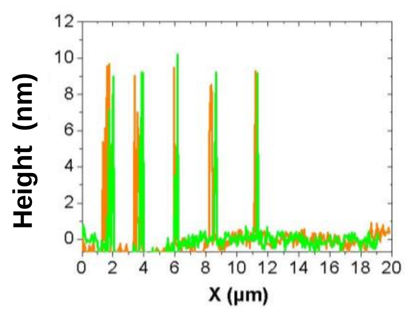










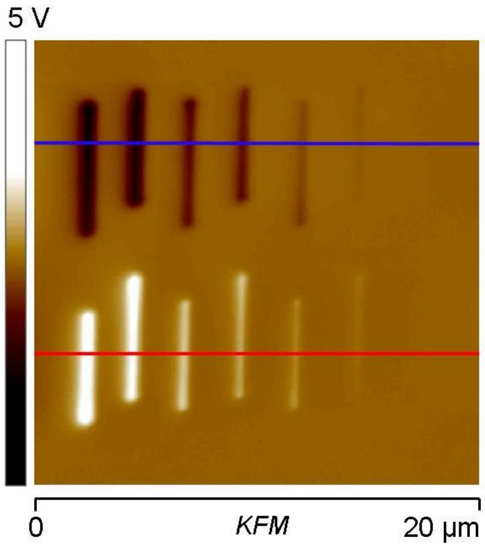


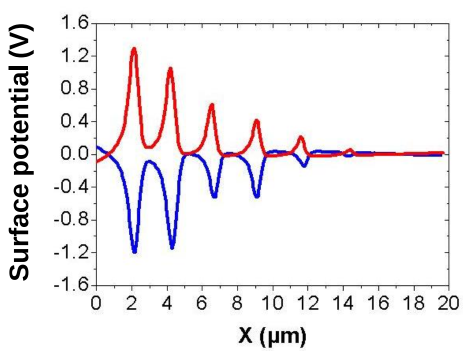
Palleau et al, *Nanotechnology*, 22, **(2011)**

Example of typical assemblies

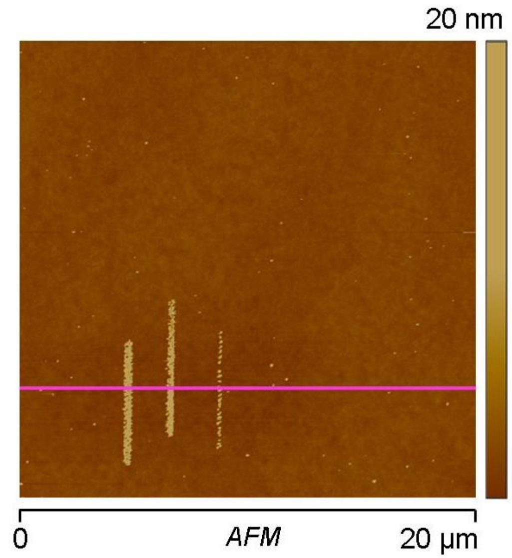
14 nm Au negatively charged NPs in EtOH

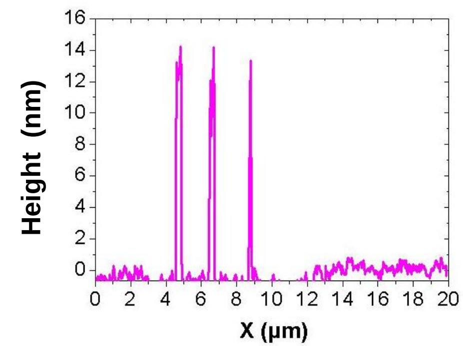
AFM charge injection





Development

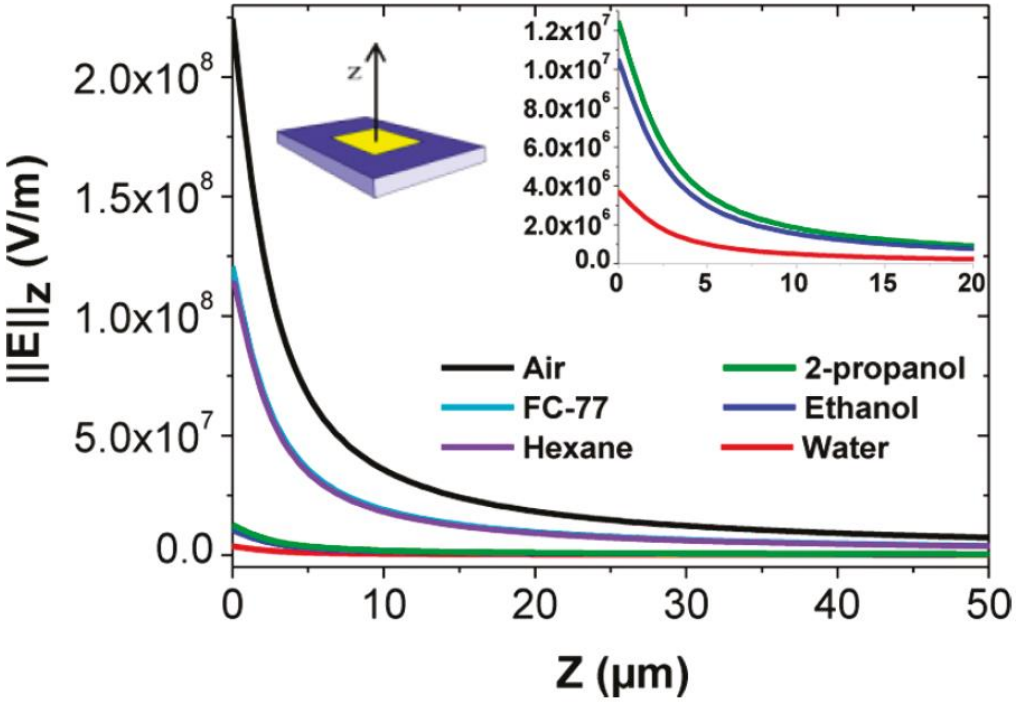




Palleau et al, *Nanotechnology*, 22, 2011

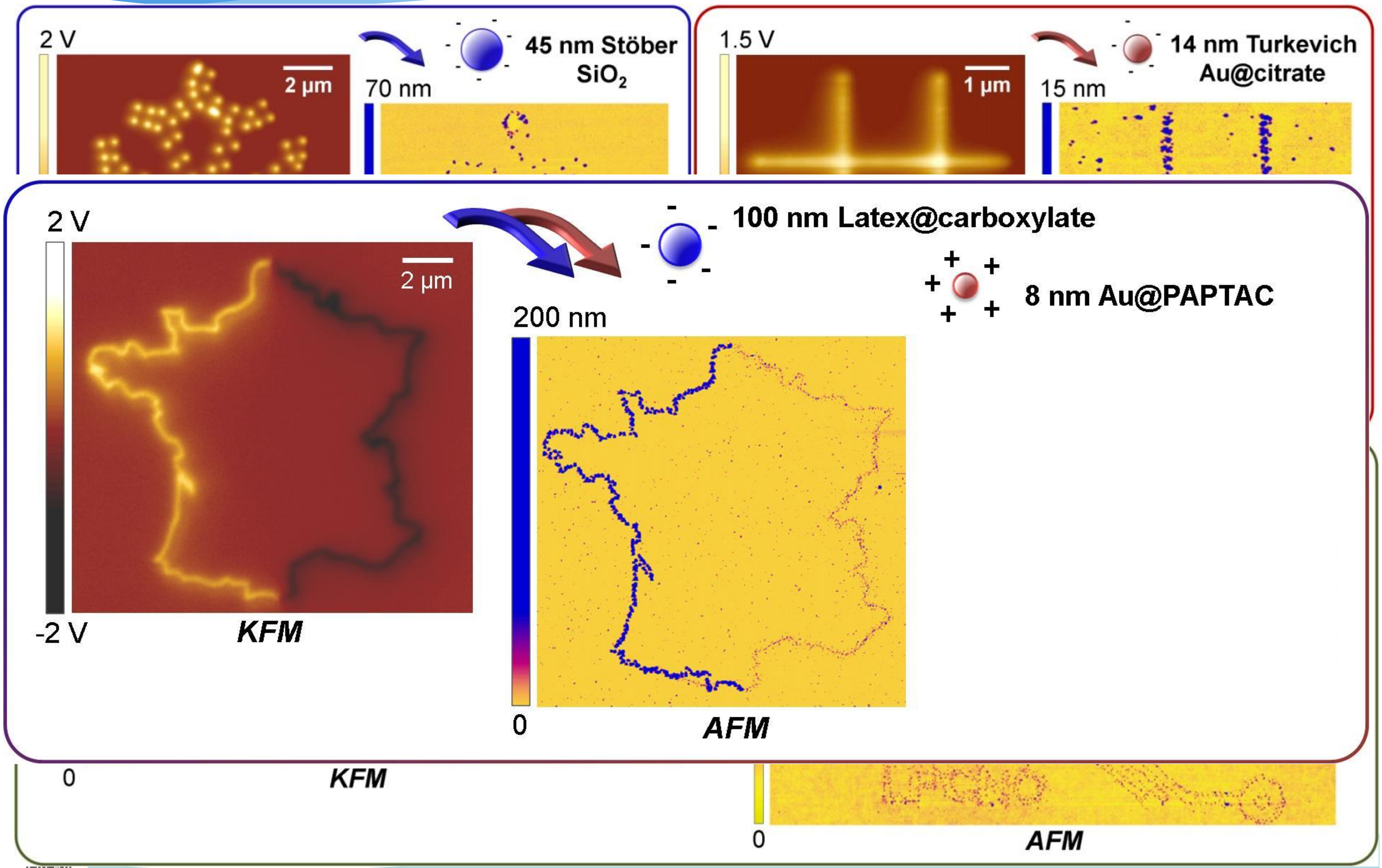
1st : quid of aqueous dispersions ?

Simulations of charge screening in solution



Need to increase the electrostatic force range
→ addition of an extra developping step

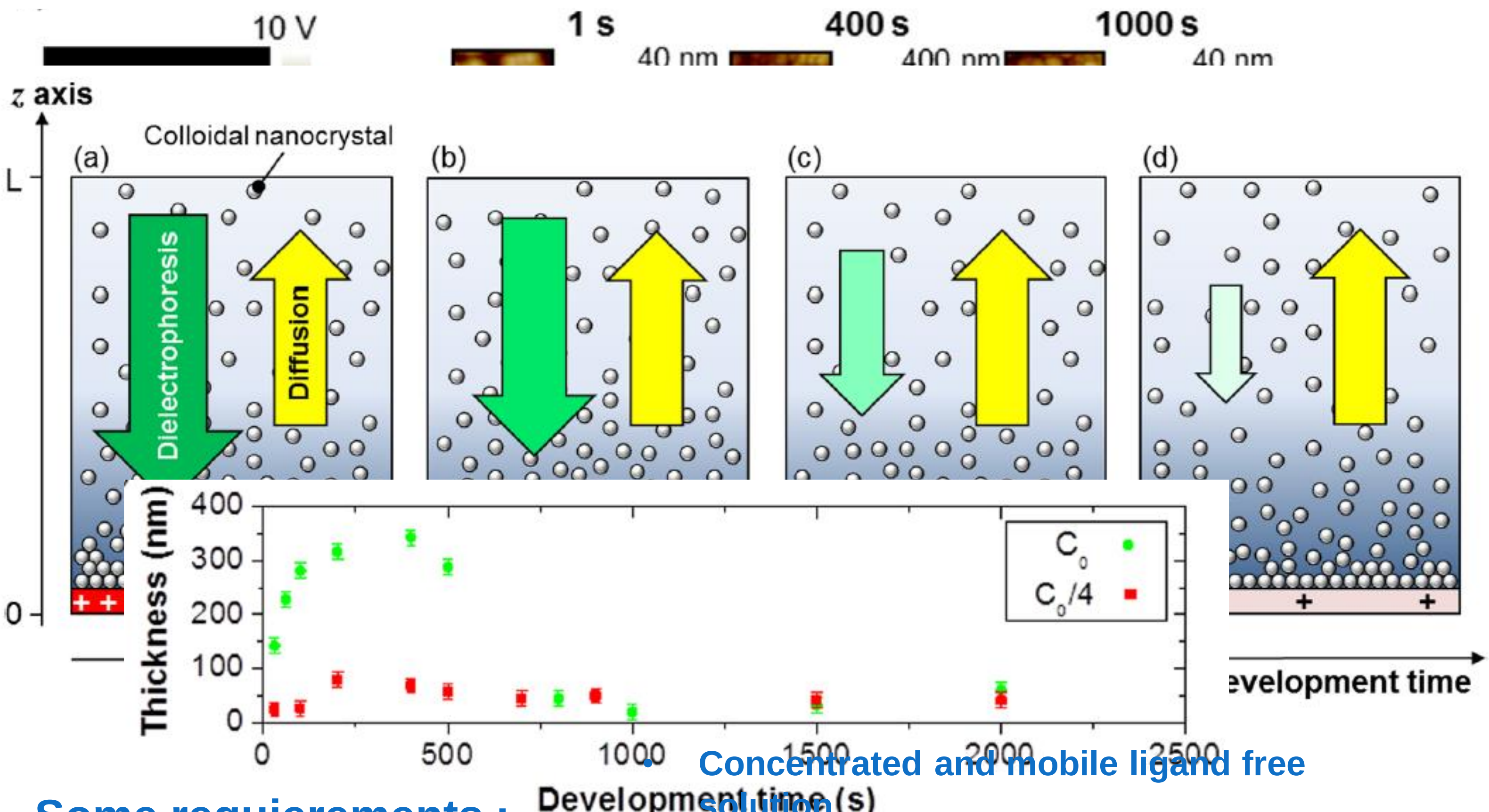
Single particle and binary assemblies



Palleau et al, *ACS Nano*, 5, (**2011**)

Going 3D !

23 nm $NaYF_4$: Er^{3+},Yb^{3} NCs in hexane

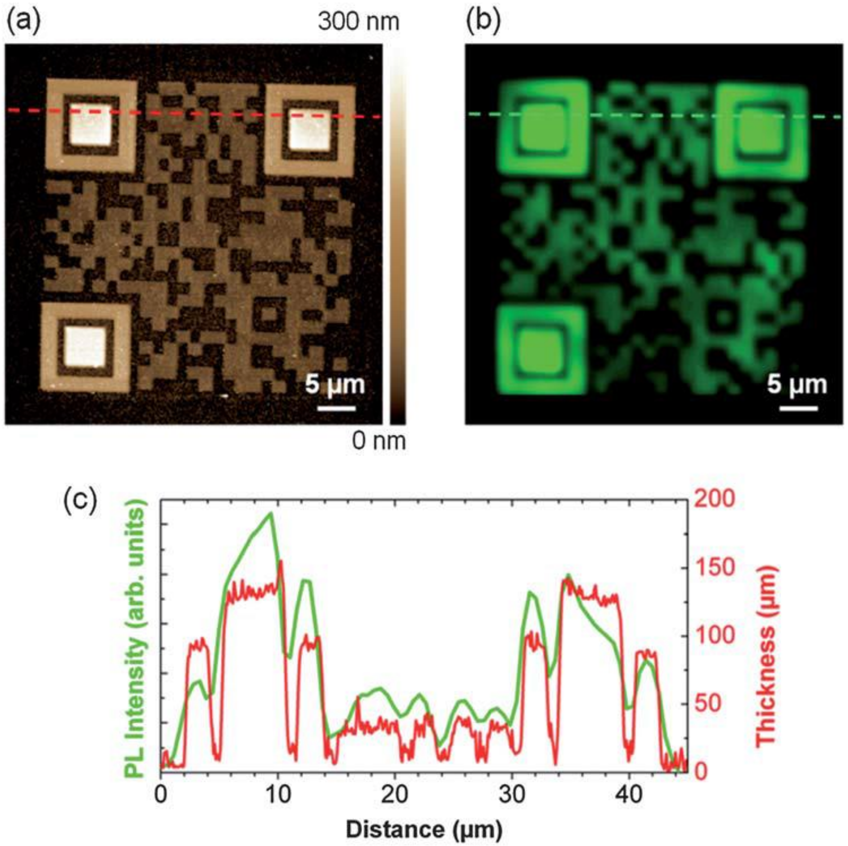


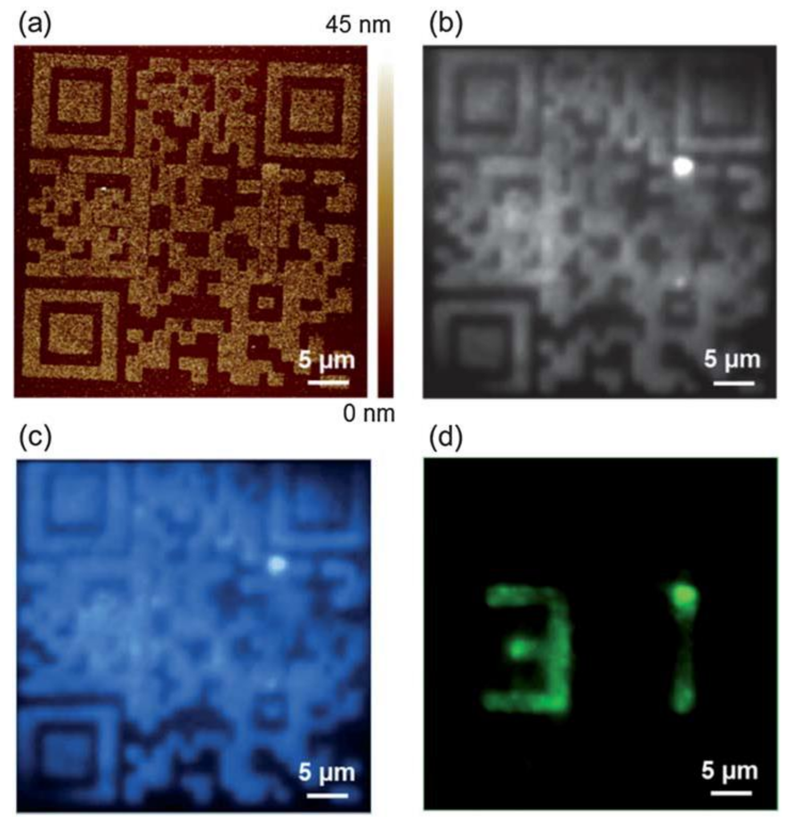
Some requierements :

- **Concentrated and mobile ligand free solution**
- **Neutral nano-objects**
- **NP Dimension around 20 nm**

« Complex » reading

23 nm $NaYF_4$: Er^{3+},Yb^{3} NCs in hexane



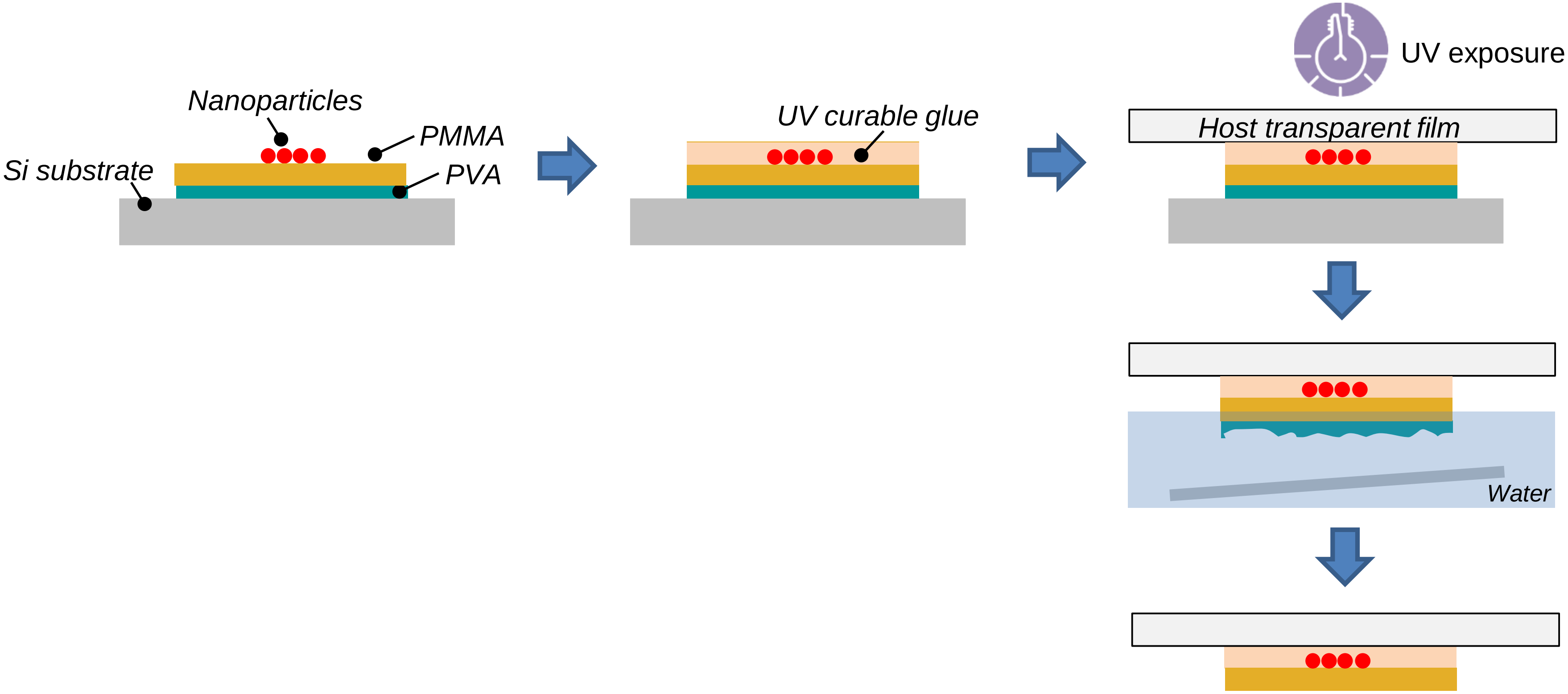


☞**Extra degree of coding using 3D assemblies depending on code intensity**

☞**Extra degree of coding using binary assemblies**

Transfer on a product

Transfer on transparent flexible film



➔ Encapsulated nanotags, easy to integrate inside/onto a product !

Diaz et al, *Nanotechnology*, 25 (2014)