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

Etienne PALLEAU
Maître de conférences (LPCNO)

epalleau@insa-toulouse.fr

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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
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)
In P&C nanoscience

If the building block is an atom

Graphite vs Diamond

Dull, opaque, soft, common
Brilliant, transparent, hard, rare


If the building block is a nanoparticle

Molecular, VdW, RNA/DNA, Capillary interactions…

What about colloidal nano-objects as building blocks?

Nanogels


Enviro-sensitive

Hybrid nano-objects

Keywords: heterogeneous catalysis, metals, nanocrystals, semiconductors, shape control

Metallic NPs


Increase quantum yield, catalytic properties, photo stability,

Magnetic NPs

Nie et al, Analyst, 8 (2004)

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

QDots

Nanogels

Responsive shell
Encapsulated enzyme
Selective gate
Selective recognition site
Plasmonic, fluorescent, catalytic, etc. nanoparticles
Drug

QDots

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  Directed assembly

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

Using templates (structured surfaces)

Conductive, transparent, flexible metal grids → Electrodes / Touch screen
Examples

Using optical forces

Autoenhanced Raman Spectroscopy via Plasmonic Trapping for Molecular Sensing

Soonwoo Heng,†,‡ On Shin,†,‡ 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

Improvement of Raman spectroscopy / analysis
Examples

Via magnetic fields

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


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

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 Vossmeier,* 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
✓ ...

$\Delta R \times 10^5$ 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 addressed

**Electrical microcontact printing (e-µCP)**
- Faster (45s/surface)
- Large area addressed
- Lower resolution (6 µm)

**Electrical nanoimprint (e-NIL)**
- Topographical Structuration
- Large area addressed
- Slower (15min/surf)
Focus on our work: anti counterfeinting nanotag

By AFM nanoxerography

Optical microscope

Optical set up

Photoluminescence @ 545 nm

23 nm NaYF$_4$: Er$^{3+}$,Yb$^{3+}$ NCs in hexane

NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ NPs ($\phi=22$ nm)

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

Luminescent signature solely accessible using a dedicated optical set up

Low quantum yield 1 %

Wavelength (nm)

PL intensity (a.u.)

$\lambda_{exc} = 980$ nm
Focus on our work: Large fabrication of nanotags

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

ANR *NanoTaggin* (2015-18)
« Simple » reading

Luminescent QR code based on CdSe@CdS NPs—« Simple » reading

By e-µCP nanoxerography

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

Photoluminescence @ 625 nm

CdSe@CdS NPs (\(\phi=20\) nm)

\(\lambda_{\text{exc}} = 450\) nm

Luminescent signature obtained on a dedicated optical set up

PhD work of David Poirot (2017)

« Enviro-intelligent » marking

Nanogels


Enviro-sensitive

By e-µCP

PhD work of Lauryanne Teulon (2018)

« Enviro-intelligent » marking

(a) Color changing

(b) Removable marking

(c) Persistent latent marking

(d) Recycling

(e) Examples of NG markers arrays
Verifying authenticity via latent marking

Color changing to validate/specify a process step

Recycling & new NG marking
Which technique to be selected?

Questions to be addressed...

***Sequential vs Parallel 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
**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
Applications on displays (RGB pixels...)
Applications in anticounterfeiting

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

Minli You,‡a 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 anticounterfeiting

AFM Charging

Concentration-dependent encryption

Looking for geometry in directed assembling: what for?
**Closed packed!**

> **Link between nanoparticles: promote the electrical conduction**

**Convective assembly**

- (a) polyimide film
- (b) Photoresist (S1805) deposition
- (c) Patterning by laser photolithography
- (d) 50 nm Au layer deposition
- (e) Sacrificial layer removal
- (f) Convective assembly technique
- (g) Final structure


**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

Nanosphere lithography / colloidal lithography
or not closed pack

Nanomachining, patterns on demand better than e-beam (speed, scale, cost, …)
or not closed packed!

Engineering Shadows to Fabricate Optical Metasurfaces

Tuning optical properties, light polarization etc…

Nanosphere lithography / colloidal lithography
Going 3D!

→ Enhance the properties of nanoparticles

Optics

23 nm NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ NCs in hexane

Nanoxerography

New security levels for anticounterfeiting

Going 3D!

Inverse opale

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, 99 Gajeo-Dong, Gwangjin-gu, Seoul 143-747, Republic of Korea

Optics

Low cost biocompatible temperature and pH sensors

Need matter if you want to turn it visible!
Going 3D!

Equipe Nanotech

Electrical properties by increasing conduction paths

Highly sensitive resistive strain gauges

CSA
Exotic hybrid assembly

Programmable colloidal molecules from sequential capillarity-assisted particle assembly

Songbo Ni,1,2 Jessica Leemann,1,2 Ivo Buttinoni,1 Lucio Isa,1* Heiko Wolf2*

[Diagram showing assembly direction and new colloidal molecules with images and graphs supporting the research article.]
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
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?? QUESTIONS ??
Back up
Properties of nanoparticles affected by the substrate?

For nanogels in solution

- COO⁻
  - pH(NIPAAm/AAc)
- NR₃⁺
  - pH(NIPAAm/APTAC)

- Hydrodynamic Diameter (nm)
- Electrophoretic Mobility (cm²/Vs)

⇒ Not really, same trend!

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

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

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

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

LAAS CNRS

Advanced Materials

www.advmat.de
Oriented assembly by using Paint!

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

-1.5 V

KFM

AFM

1.5 V

20 nm

100 nm de PMMA sur substrat Si dopé 10^16 cm^{-3}

Using a polarized AFM tip

Impulsions : ±30 V 1 ms 50 Hz

f ≈ 300 kHz

20 nm

Potentiel de surface (mV)

X (µm)
Mechanisms of nanoxerogaphy assembly

Coulomb Force

\[ F_{EP} = QE \]

Dielectrophoretic Force

\[ F_{DEP} = 2\pi\varepsilon_0\varepsilon_{Sol} \text{Re} \left( \frac{\varepsilon_{NP}^* - \varepsilon_{Sol}^*}{\varepsilon_{NP}^* + 2\varepsilon_{Sol}^*} \right) R_{NP}^2 \nabla E^2 \]

Positively charged NPs

Neutral NPs

E : Electric field  \hspace{1cm} \varepsilon_0 : vacuum permittivity
R_{NP} : NP radius  \hspace{1cm} \varepsilon_{Sol}^* : permittivity of dispersing media
\xi : NP zeta potential  \hspace{1cm} \varepsilon_{NP}^* : complexe permittivity of NP
Example of typical assembly

AFM Charge Injection

Development

ΔV → ΔE

Surface potential (V)

Height (nm)

Palleau et al, Nanotechnology, 22, (2011)
Example of typical assemblies

AFM charge injection

Development

14 nm Au negatively charged NPs in EtOH

Surface potential (V)

Height (nm)

Simulations of charge screening in solution

Need to increase the electrostatic force range
→ addition of an extra developing step
Single particle and binary assemblies

Palleau et al, ACS Nano, 5, (2011)
Going 3D!

Some requirements:

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

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

Extra degree of coding using binary assemblies
Transfer on transparent flexible film

Si substrate

Nanoparticles

PMMA

PVA

UV curable glue

Host transparent film

UV exposure

Water

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

Diaz et al, Nanotechnology, 25 (2014)