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# Highly-Ordered Molecular Nanoarchitectures: Concepts for Biosensors

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Many thanks to Andrei Ruckenstein  
«Quantitative Biology: The New, Cross-disciplinary Paradigm»  
If you come to a fork in the road, take it [quoting Yogi Berra]



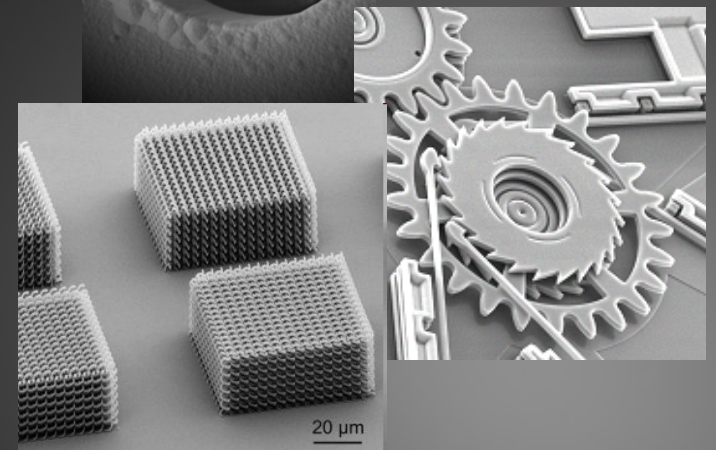
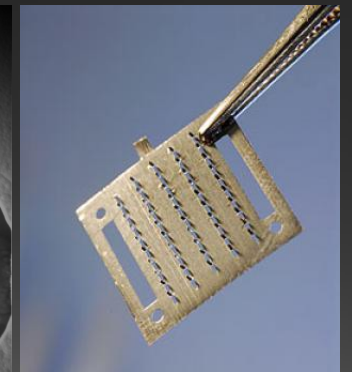
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# Why 3D Sensing Platforms and Direct 3D Structuring?

[Yogi Berra]:

I wish I had an answer to that because  
I'm tired of answering that question

- High surface-to-volume ratio for increased reactivity
- Functional platforms and membranes for 3D models
- Micro- and nanomachines for bottom-up fabrication
- **Highly-ordered, periodic structures...for sensing**





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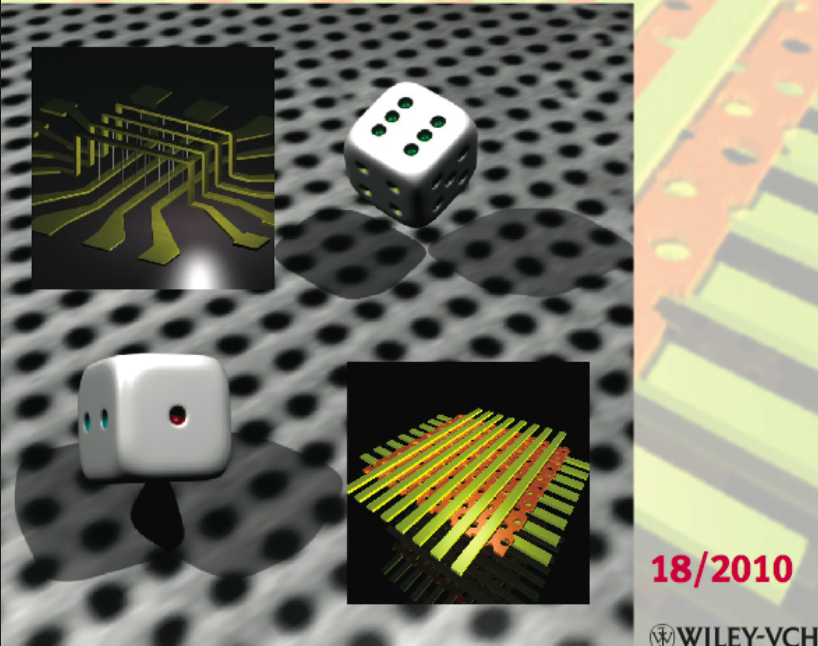
Volume 6 · No. 18 · September 20 2010

D15063

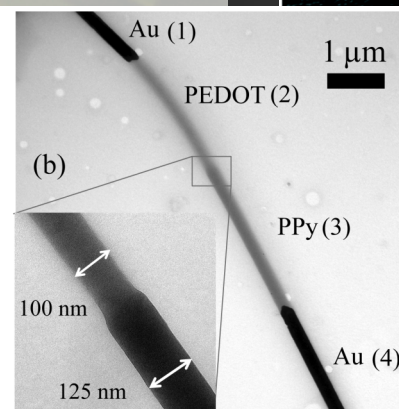
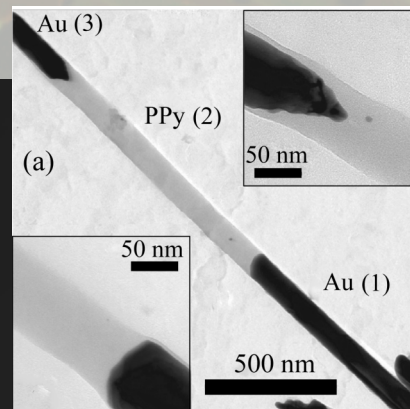
NANO MICRO

small

www.small-journal.com

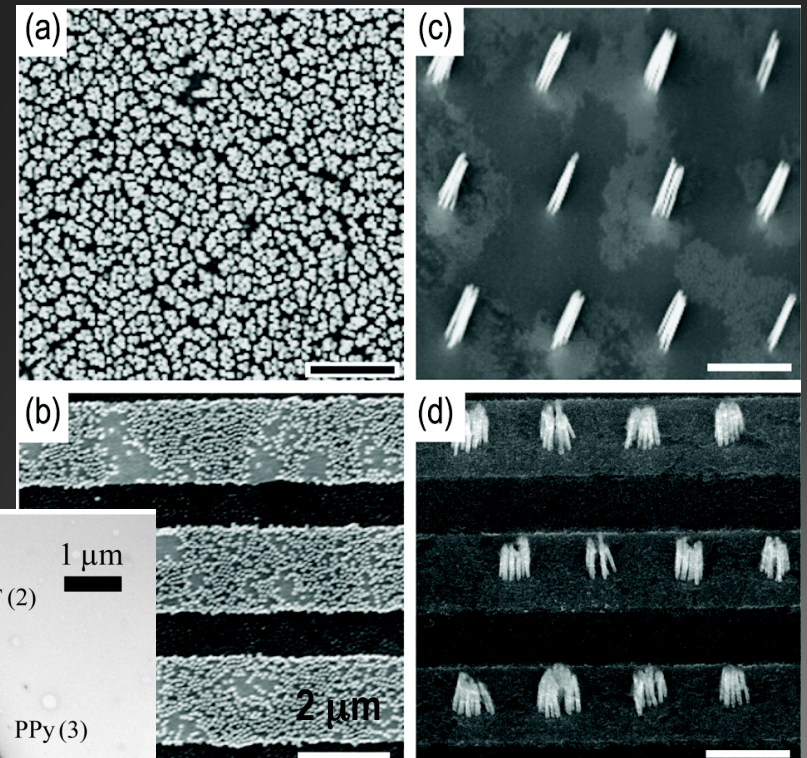


Vertical Nanowire Architectures: Statistical Processing of Porous Templates towards Discrete Nanochannel Integration  
S. Melinte et al.



# Nanowire Arrays

Small 5, 557 (2008)

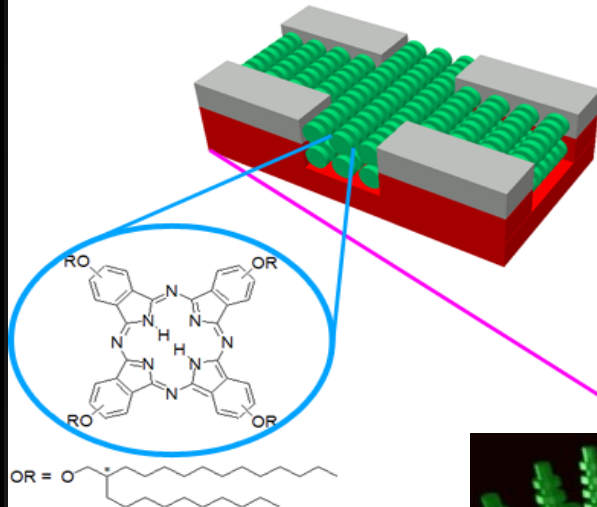


Chem. Mater. 21, 4241 (2009)

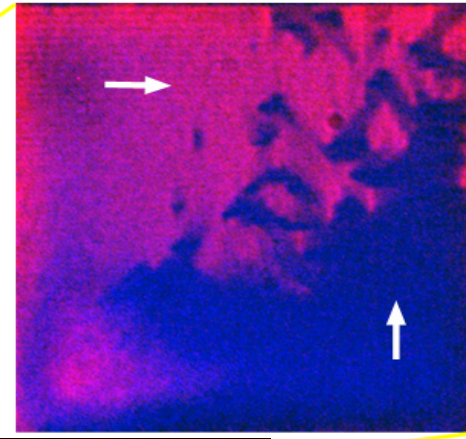
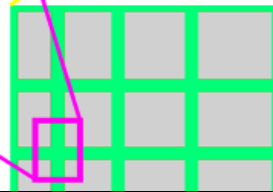


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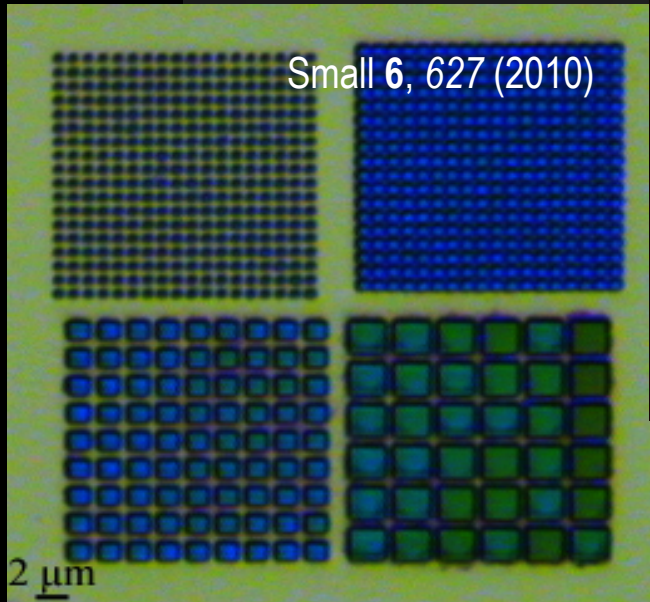
Nano Letters 7, 2838 (2007)



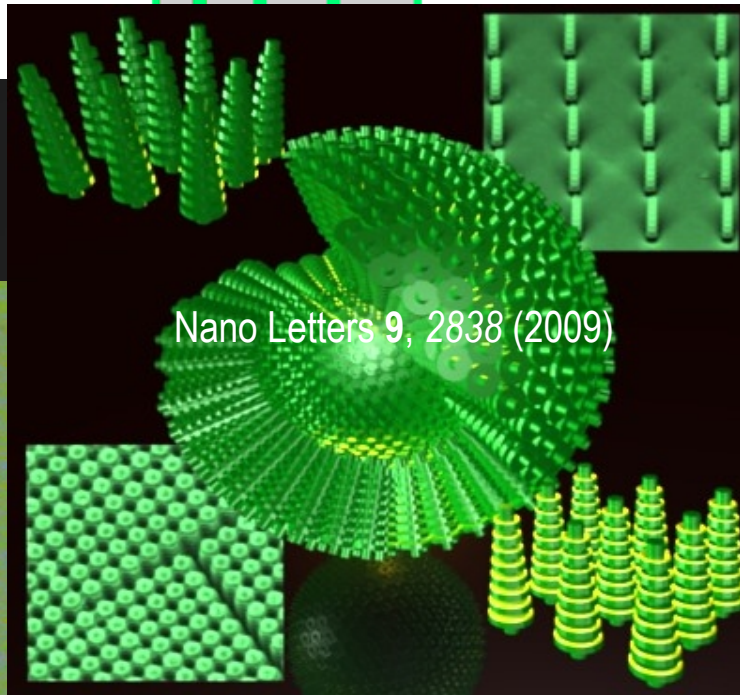
High-throughput screening of uniaxial alignment



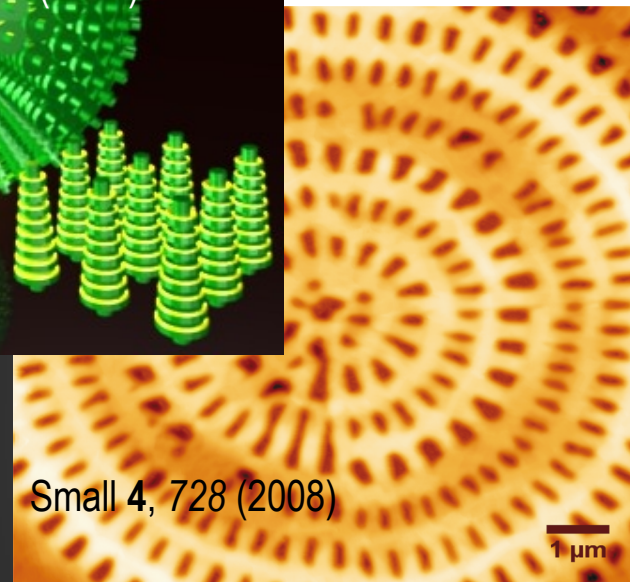
Small 6, 627 (2010)



Nano Letters 9, 2838 (2009)



Small 4, 728 (2008)



NANO MICRO  
**small**

Second  
ISI Impact Factor  
**6.4**

6/2008

WILEY-VCH

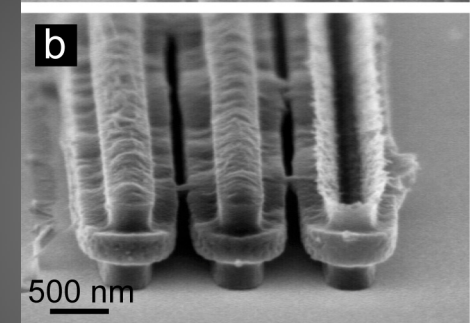
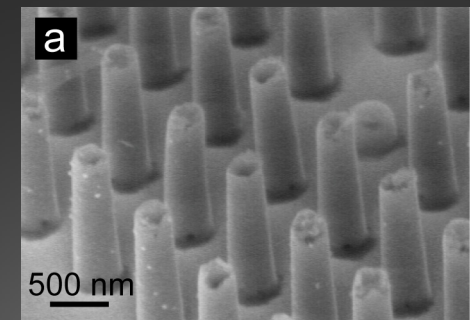
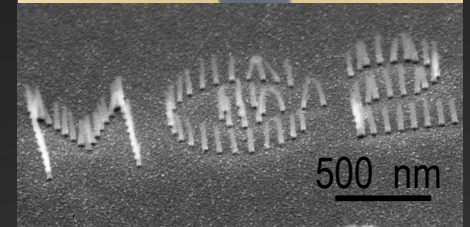
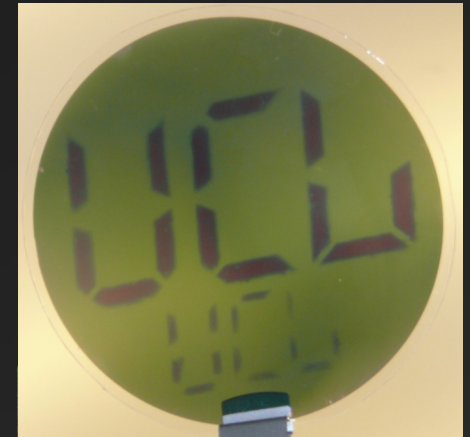
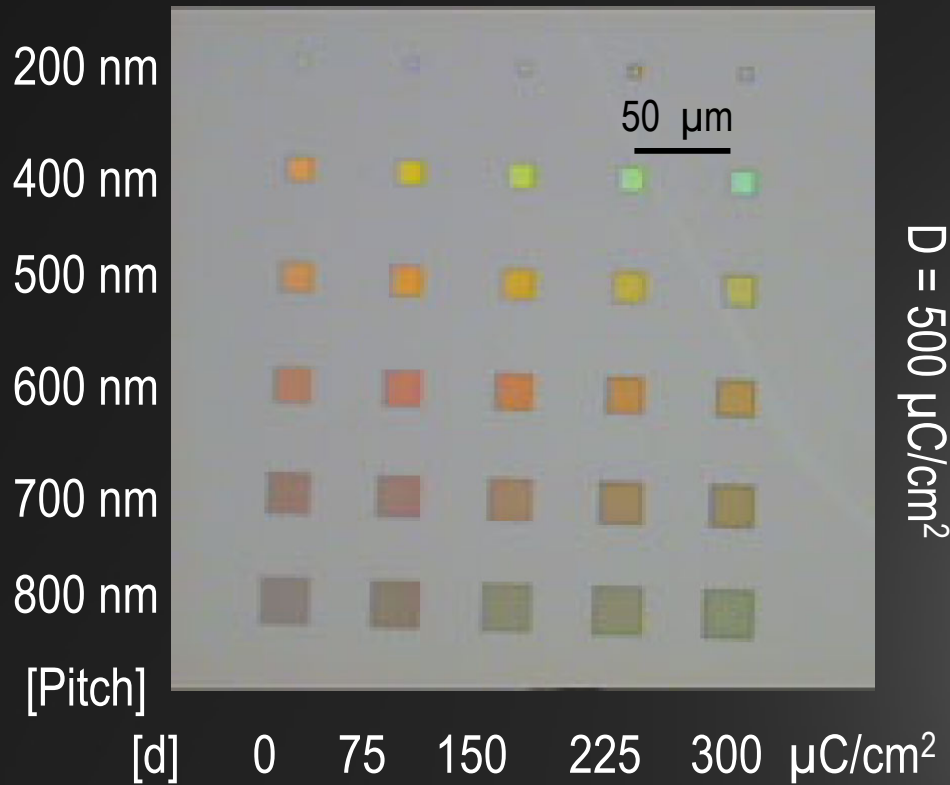


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## Electroless Polymerization of Aniline

## Template Confined Growth of Polyaniline (PANI)

## Direct Electron-Beam Writing of 3D Polymer Structures





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# Patterning PANI: Current Status

## Why polyaniline?

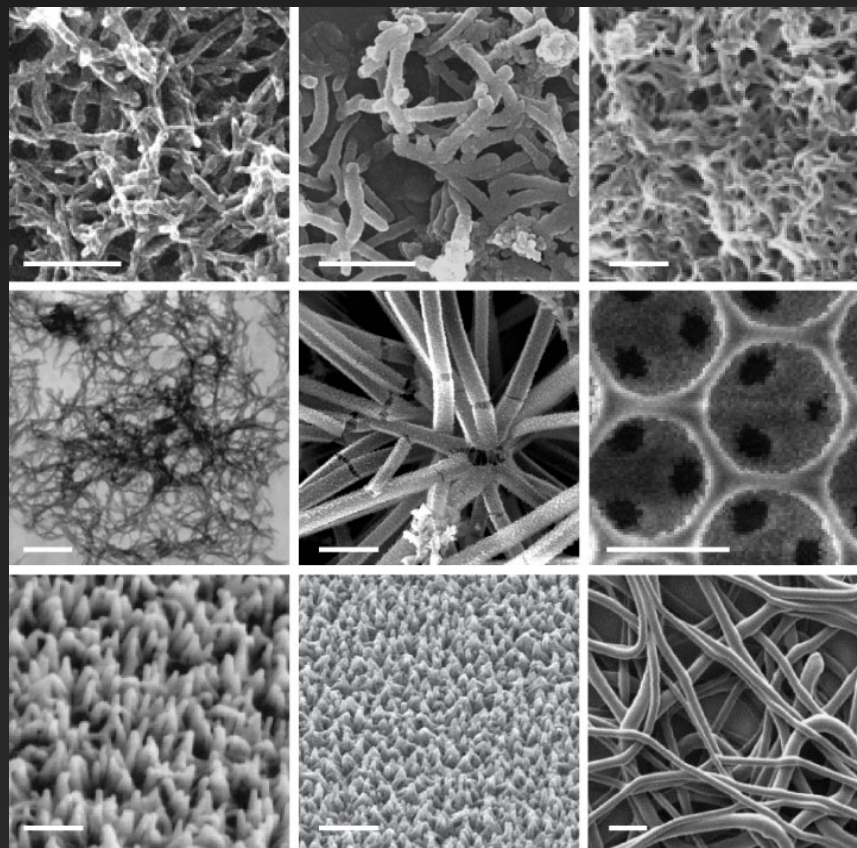
- tunable opto-electronic properties
- electrical bistability
- actuation

## Developed Approaches

- interfacial polymerization
- surfactant assisted polymerization
- seeding polymerization
- oligomer assisted polymerization
- template confined chemical and electrochemical growth
- diluted polymerization
- electro spinning

## Our approach

- higher resolution patterning
- precise positioning
- multi-directional alignment



Angew. Chem. Intl. Ed. 41, 3665 (2002);

JACS 126, 851 (2004); JACS 126, 2278 (2004);

JACS 126, 4502 (2004); Nat. Nanotechnol. 2, 354 (2007)



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# Electroless Polymerization of PANI: Mechanism

Ingredients:

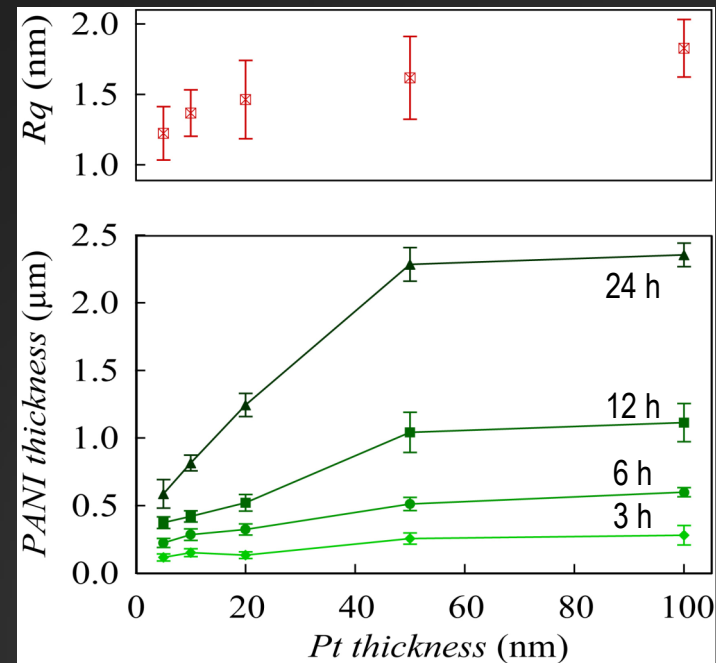
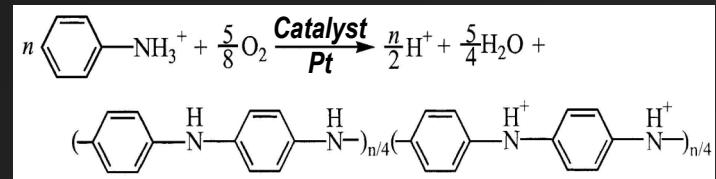
- $C_6H_5NH_2$  and  $H_2SO_4$  in  $H_2O$
- $O_2$  saturated solution
- Pt as catalyst

Mechanism:

- oxygen reduction } at Pt surface
- aniline oxidation }

Kinetics:

- linear time dependence
- exponential temperature dependence
- surface rather than bulk dependence



Electrochemical process without any external charge supply



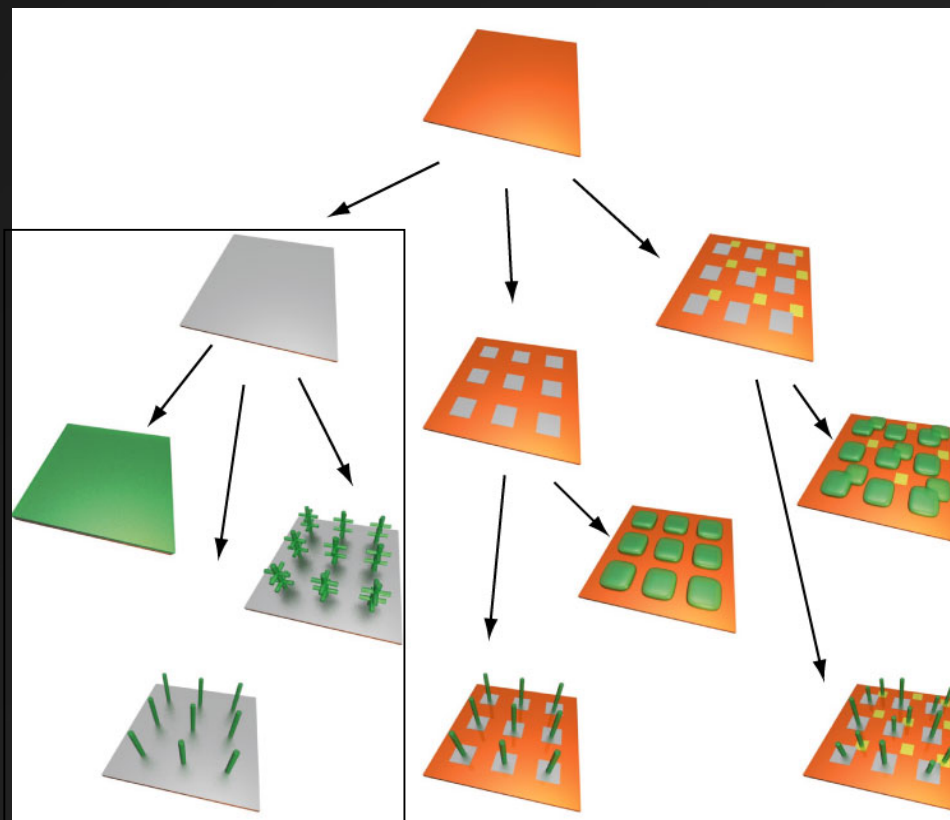
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# PANI: Hierarchical Nanoscale Structuring

**I**  
Substrate choice

**II**  
Catalyst coating

**III**  
Nanostructuring



Thin-film metal  
catalysts

Single-metal  
nanocatalysts

Dual-metal  
nanocatalysts

A. Vlad *et al.*, *Nano Letters* **9**, 2838 (2009); A. Vlad *et al.*, *Small* **6**, 627 (2010)

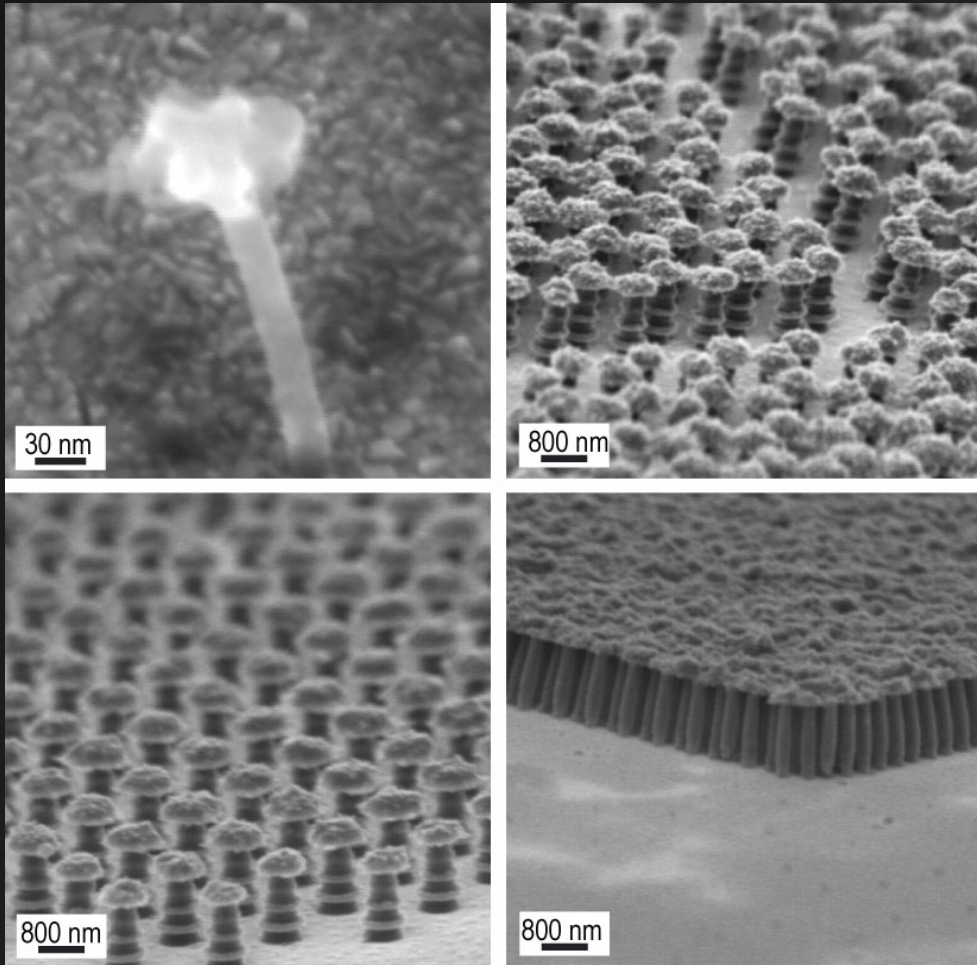




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# Template Confined Polymerization

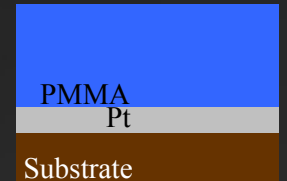
Partially connected



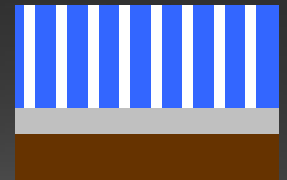
Mushroom-type

Continuous film

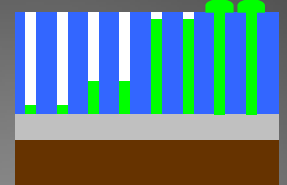
Spin PMMA  
Aspect ratio



EBL  
Pattern design



Electroless growth  
Template removal



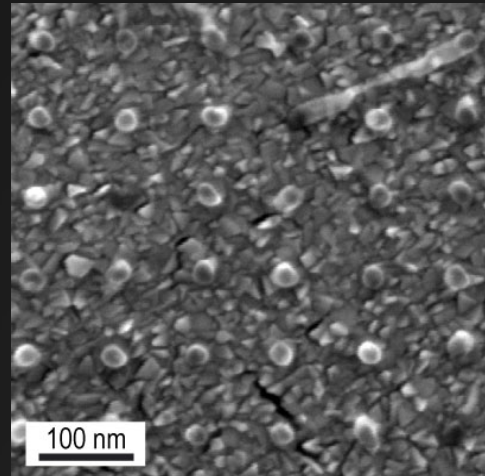


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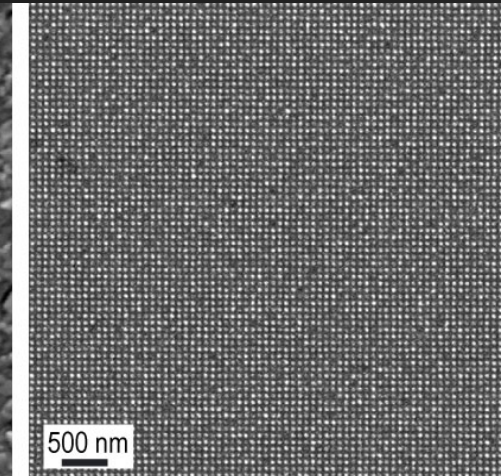
# PANI 2D Nanostructuring: High-Areal Patterning Density

## PANI Nanodots

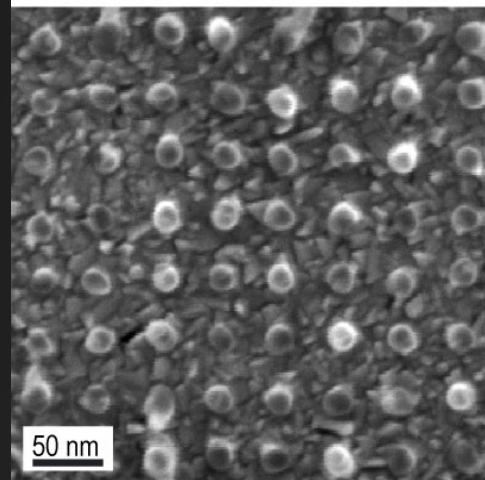
100 nm pitch  
0.07 Tdot/inch<sup>2</sup>



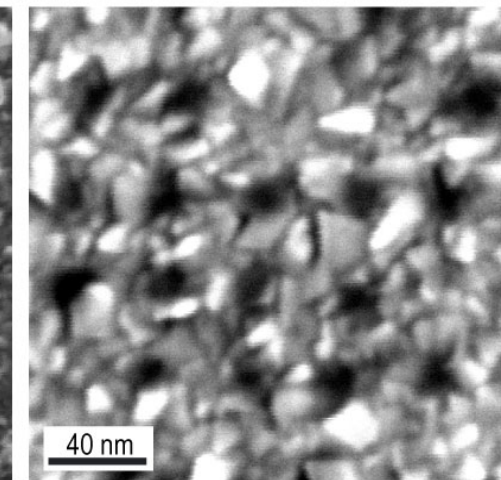
75 nm pitch  
0.13 Tdot/inch<sup>2</sup>



50 nm pitch  
0.28 Tdot/inch<sup>2</sup>



40 nm pitch  
0.44 Tdot/inch<sup>2</sup>



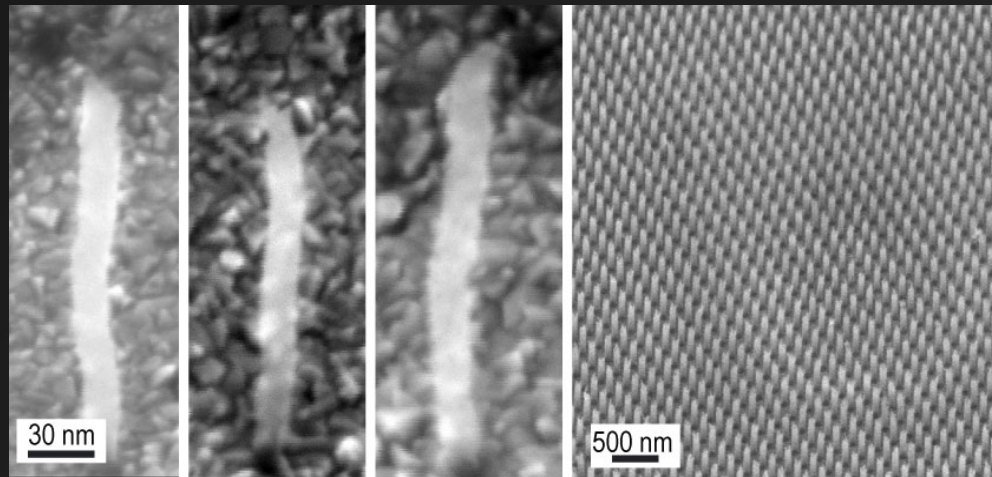


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# PANI 2D Nanostructuring: High-Aspect Ratio

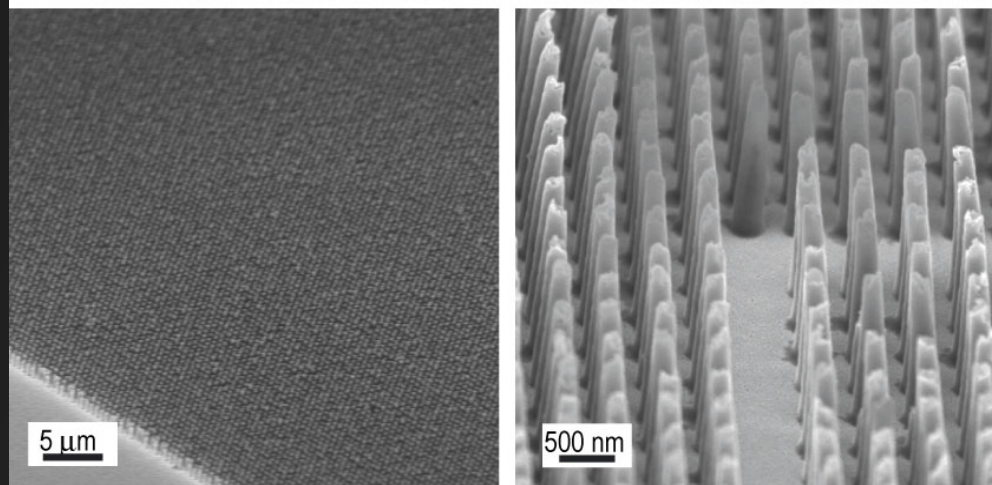
## PANI Nanowires

~ 15 nm  
nanowires



Nanowires  
array

Large-area  
structuring



Photonic  
architectures



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# PANI 3D Nanostructuring: E-Beam Lithography (EBL)

Resist and Dose Modulated EBL

Spin multilayer: PMMA - PMMA/PAA

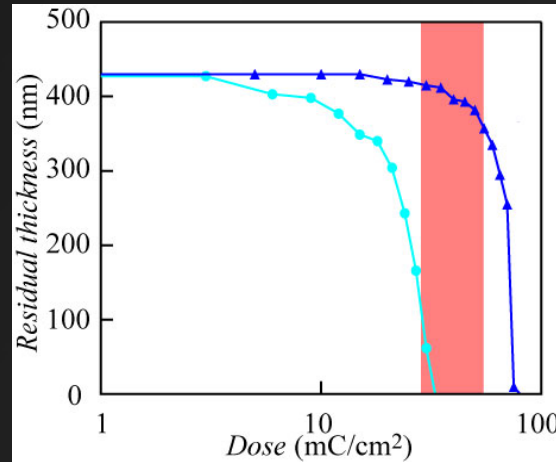


Dose Modulated Exposure

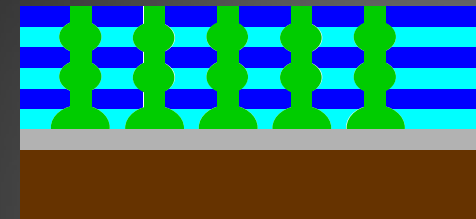
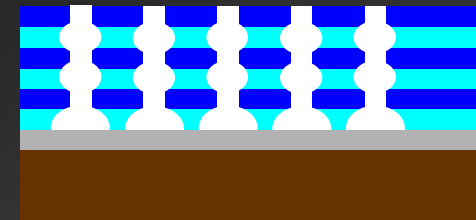


PANI Growth

D [central dose]  
d [side lines dose]



Resist Modulated EBL



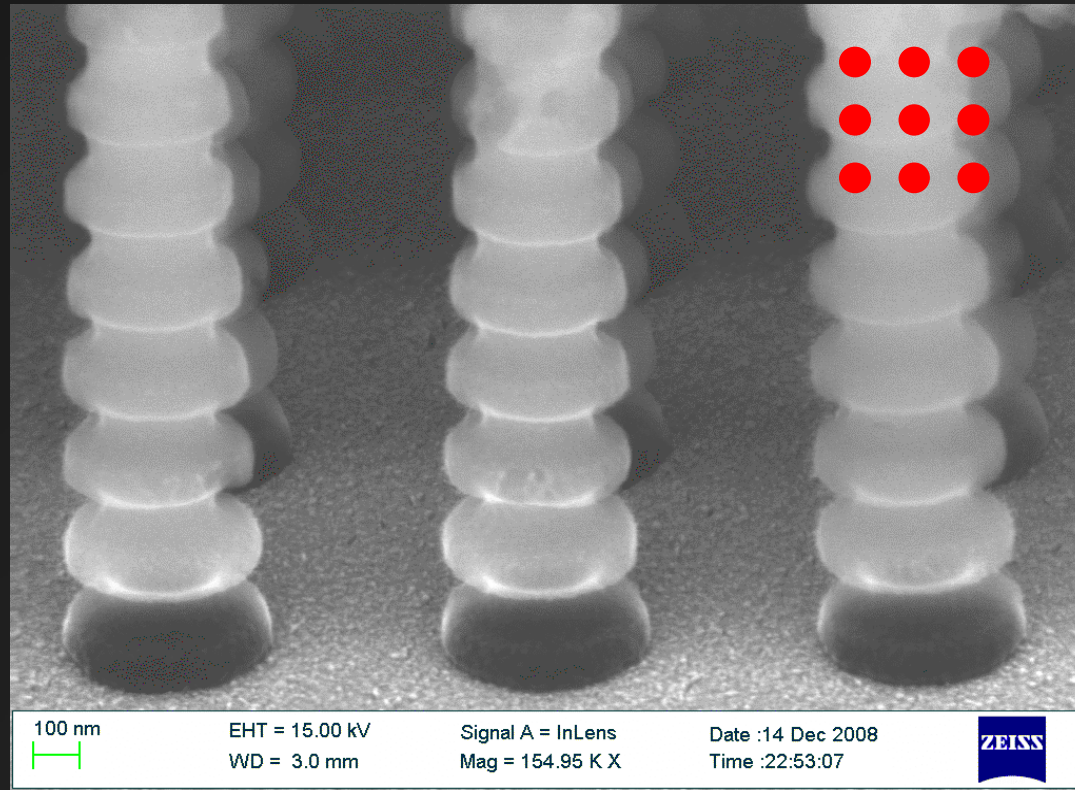


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# Resist and Dose Modulated EBL: Operation Principle

$$D = 500 \mu\text{C}/\text{cm}^2; d = 0 \mu\text{C}/\text{cm}^2$$

8 x [100 nm x 100 nm]



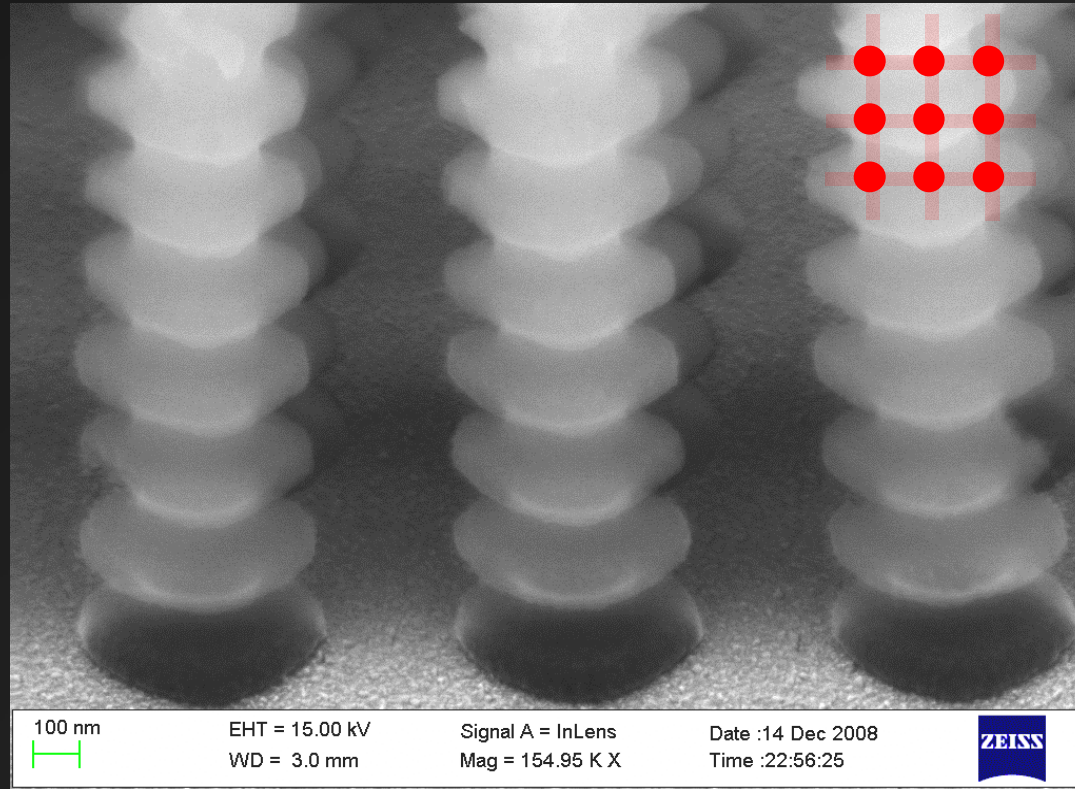


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# RDM-EBL: Operation Principle

$$D = 500 \mu\text{C}/\text{cm}^2; d = 75 \mu\text{C}/\text{cm}^2$$

8 x [100 nm x 100 nm]



100 nm  


EHT = 15.00 kV  
WD = 3.0 mm

Signal A = InLens  
Mag = 154.95 K X

Date :14 Dec 2008  
Time :22:56:25



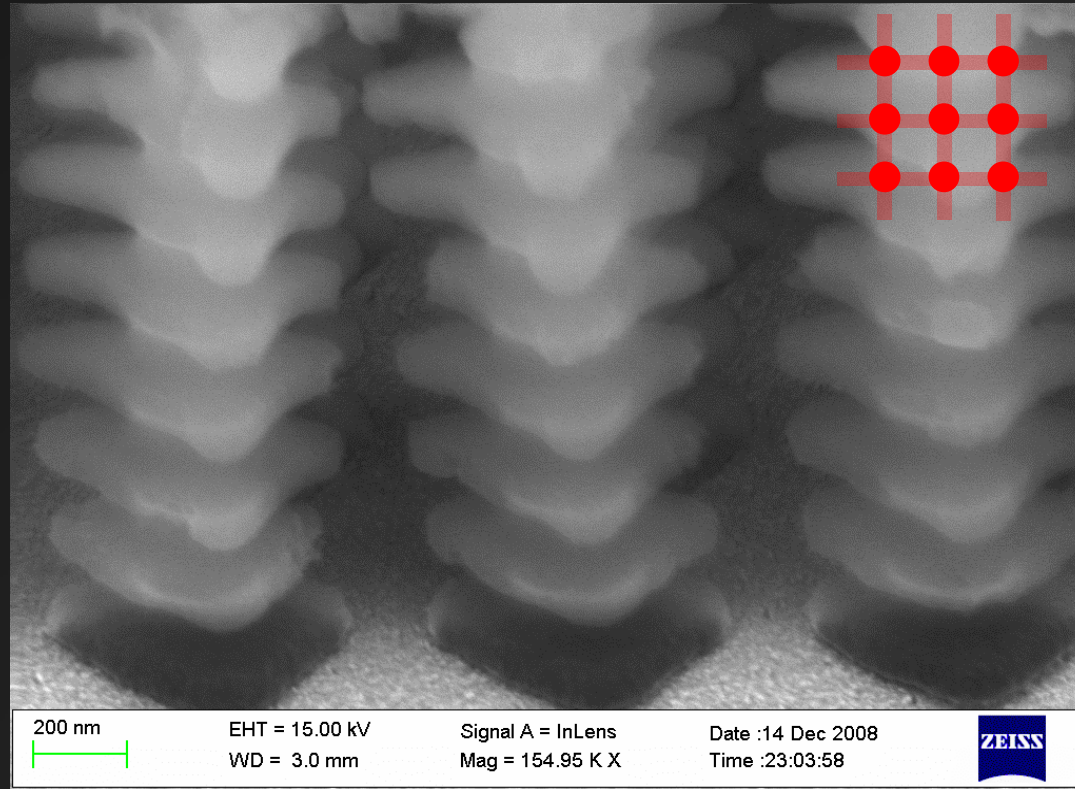


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# RDM-EBL: Operation Principle

$$D = 500 \mu\text{C}/\text{cm}^2; d = 150 \mu\text{C}/\text{cm}^2$$

8 x [100 nm x 100 nm]



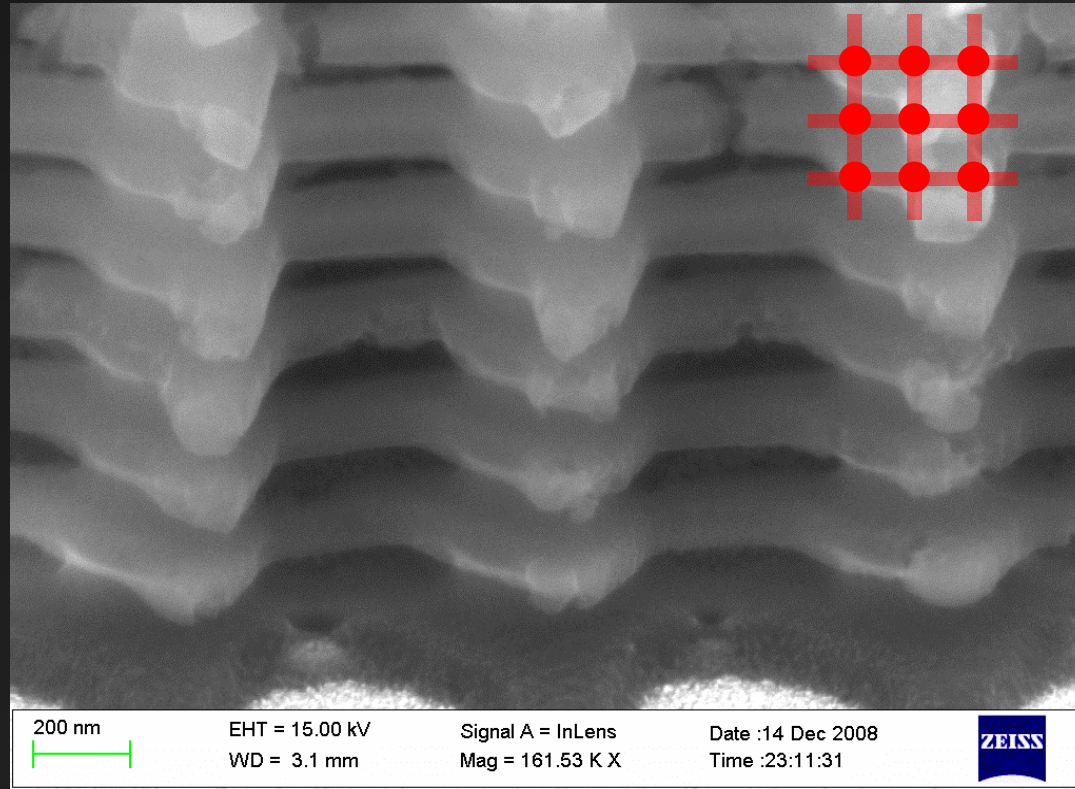


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# RDM-EBL: Operation Principle

$$D = 500 \mu\text{C}/\text{cm}^2; d = 225 \mu\text{C}/\text{cm}^2$$

8 x [100 nm x 100 nm]



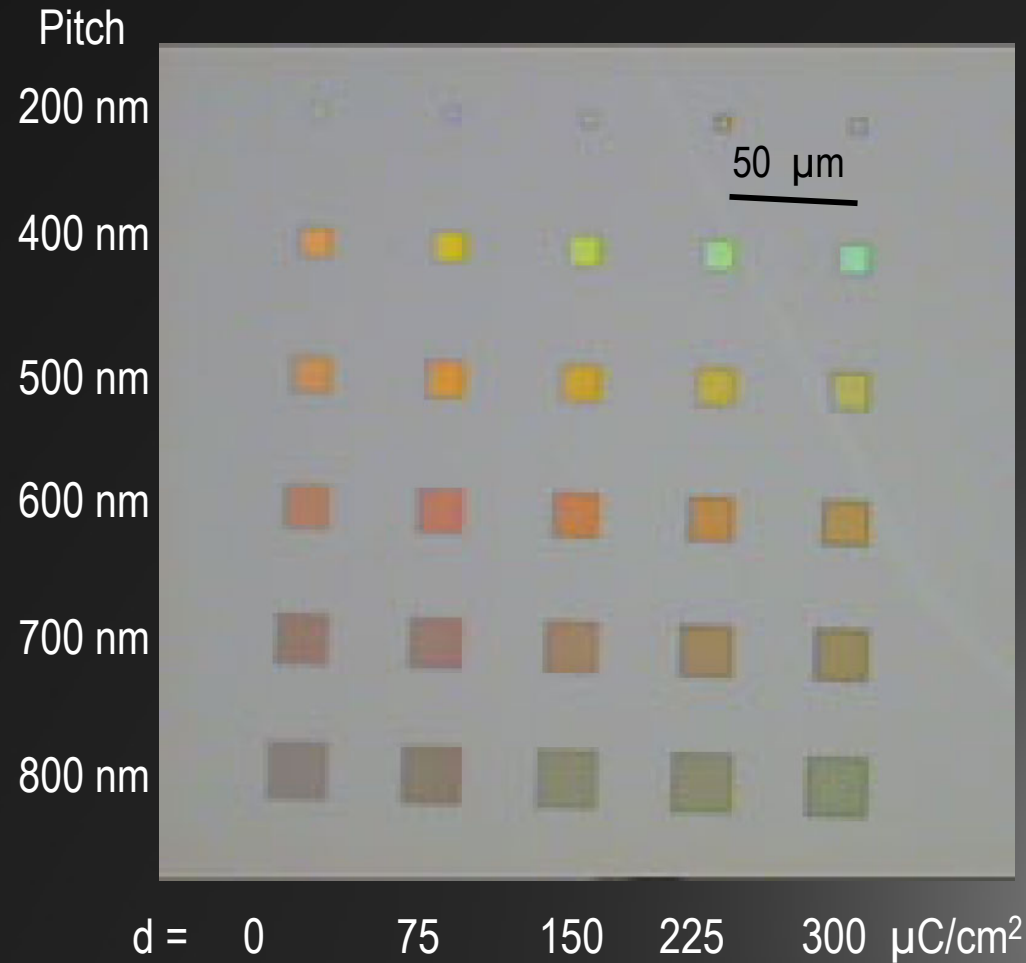




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# Direct Writing of 3D Photonic Lattices

6 X [100 nm **PMMA** + 100 nm **PMMA/MAA**]



$D = 500 \mu\text{C}/\text{cm}^2$

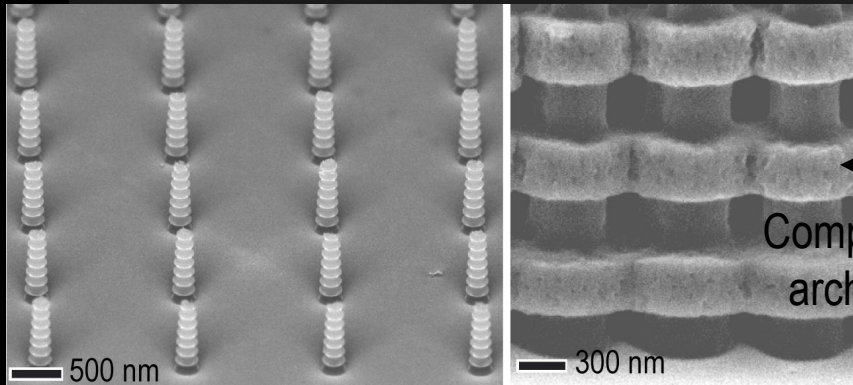
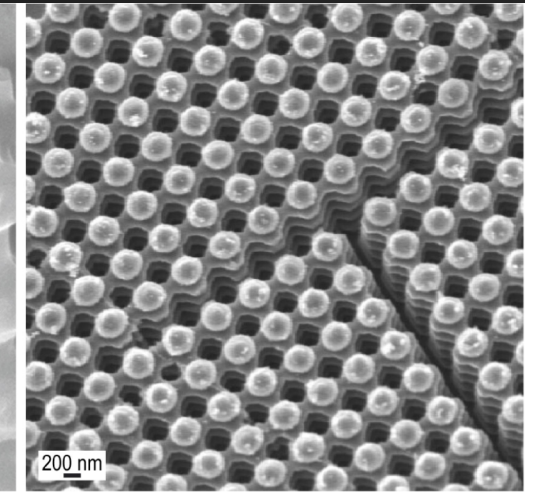
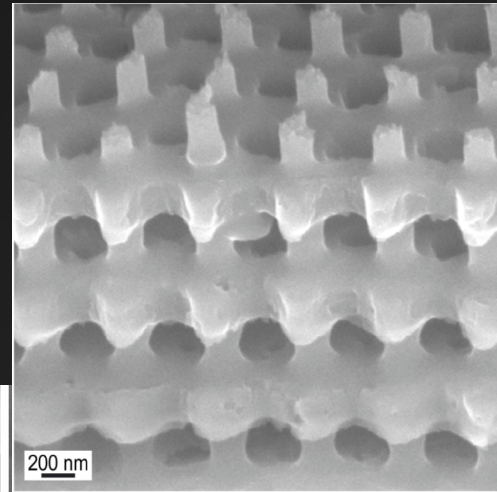


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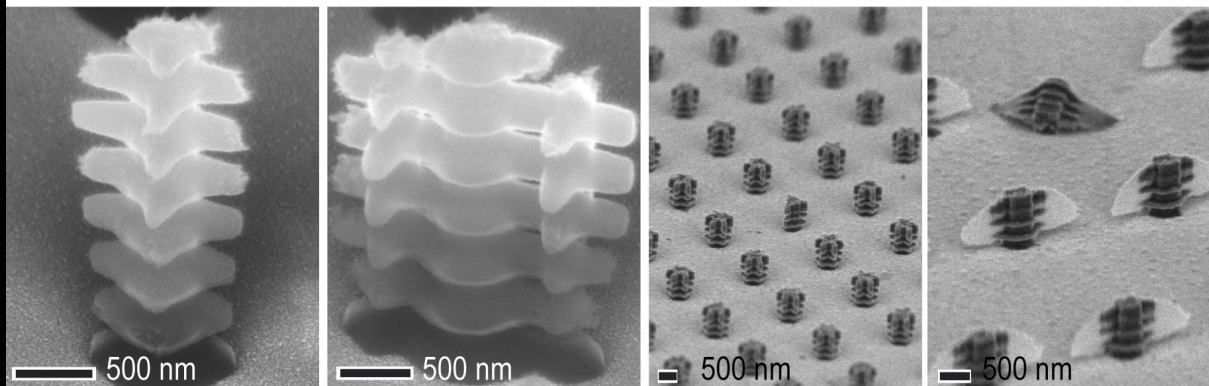
# 3D Structuring

Cubic vs tetragonal lattice

Diameter modulated nanopillars



Complementary architectures



Nano pagodas

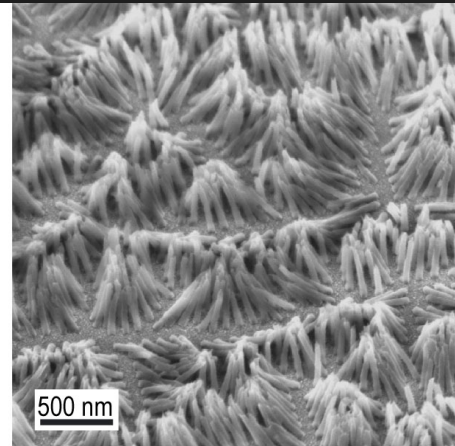
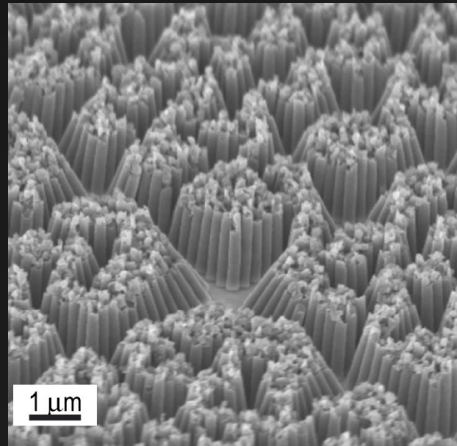




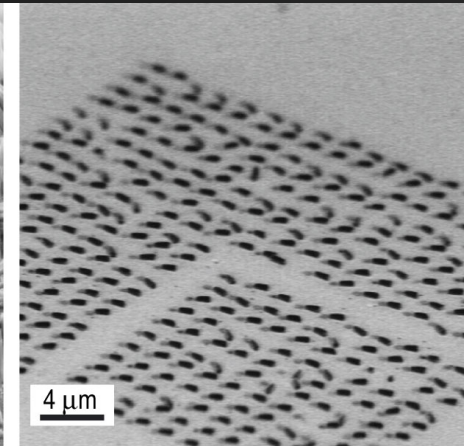
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# 2D and 3D Macroassemblies

Isotropic  
liquid front removal



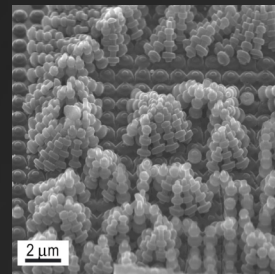
Anisotropic  
liquid front removal



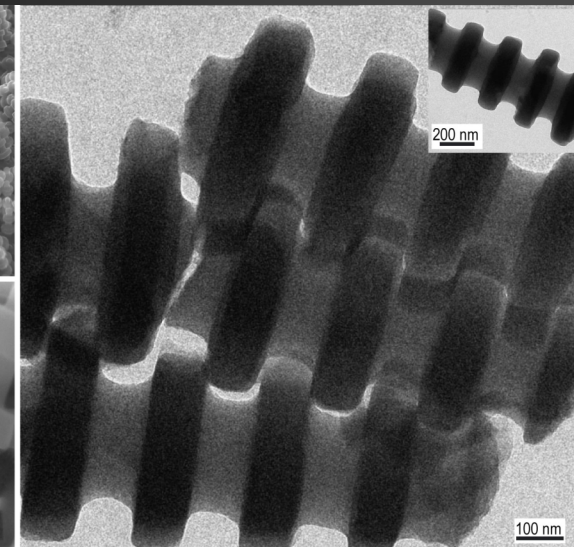
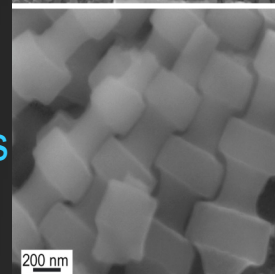
Bristle-like morphologies

Unidirectional alignment

Re-entrant features:



Key-locked type architectures

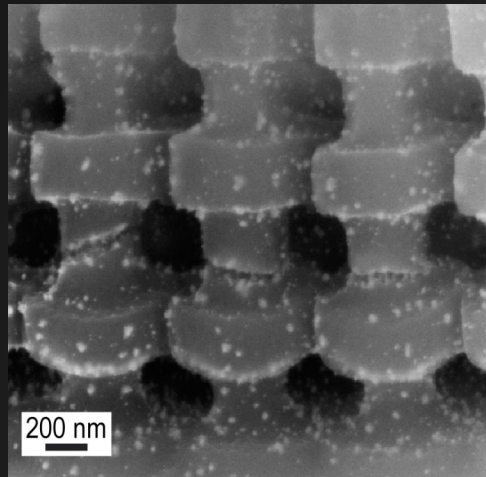




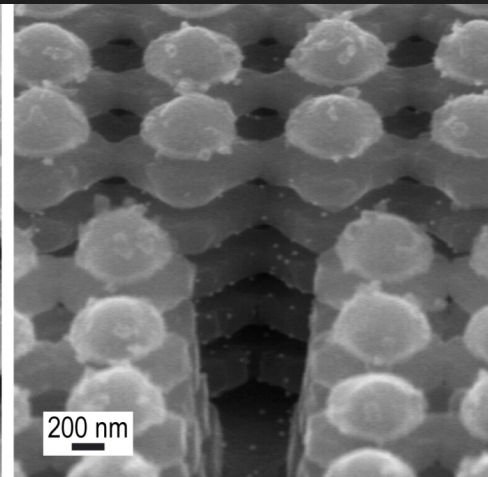
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# 3D PANI Nanocomposites

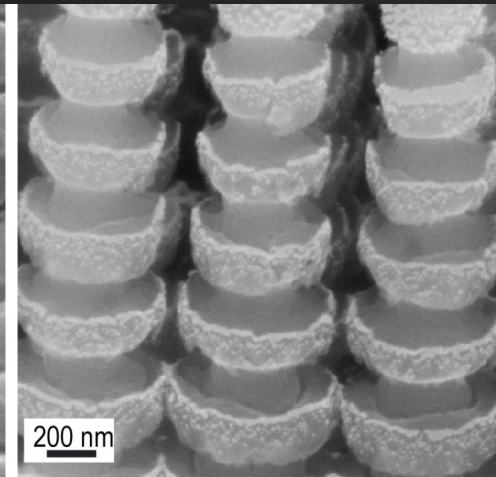
One step functionalization



[HAuCl<sub>4</sub>]  
in-situ reduction



Au nanoparticles  
grafting



Self-aligned shadow  
metal deposition

[Mercaptosuccinic acid capped  
40 nm particles]



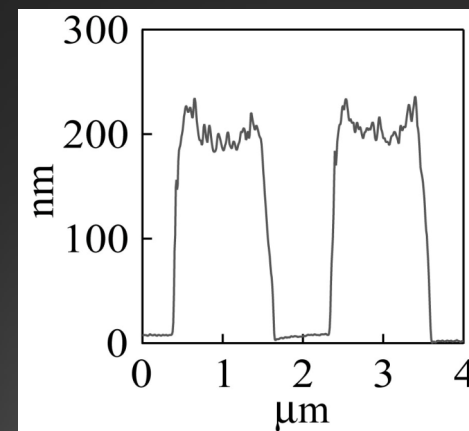
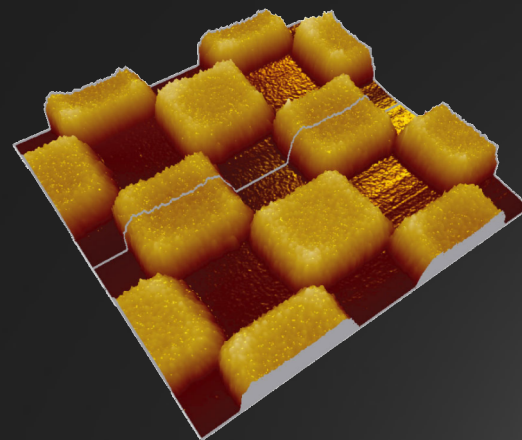
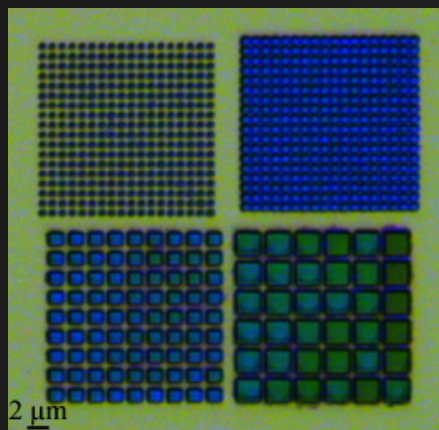
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# Nanoscale Chemistry: Single Metal Catalysts

Electrochemical process without any external power supply



Sub-picogram synthesis



0.83 fg/min *per catalyst unit*  
Difficult to realize otherwise

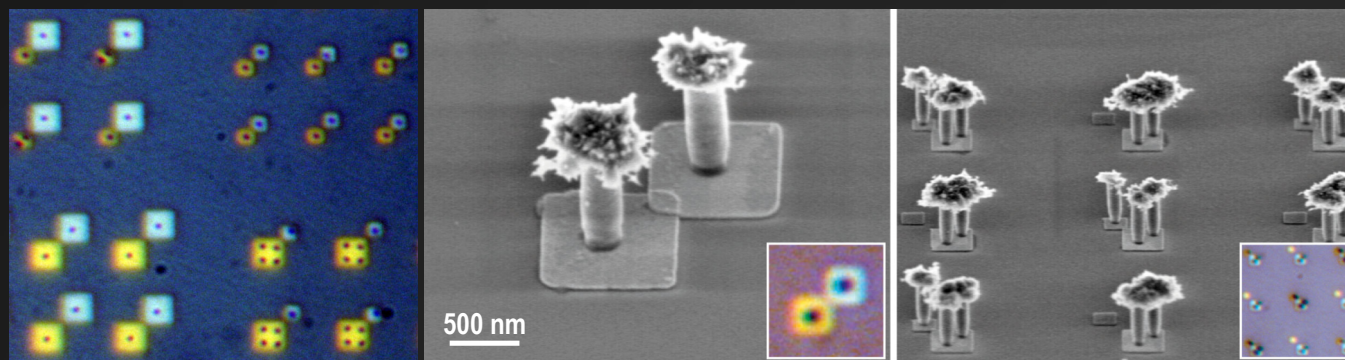
A. Vlad *et al.*, *Small* **6**, 627 (2010)



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# Nanoscale Chemistry: Dual Metal Catalysts

Electron beam lithography of single nanopores



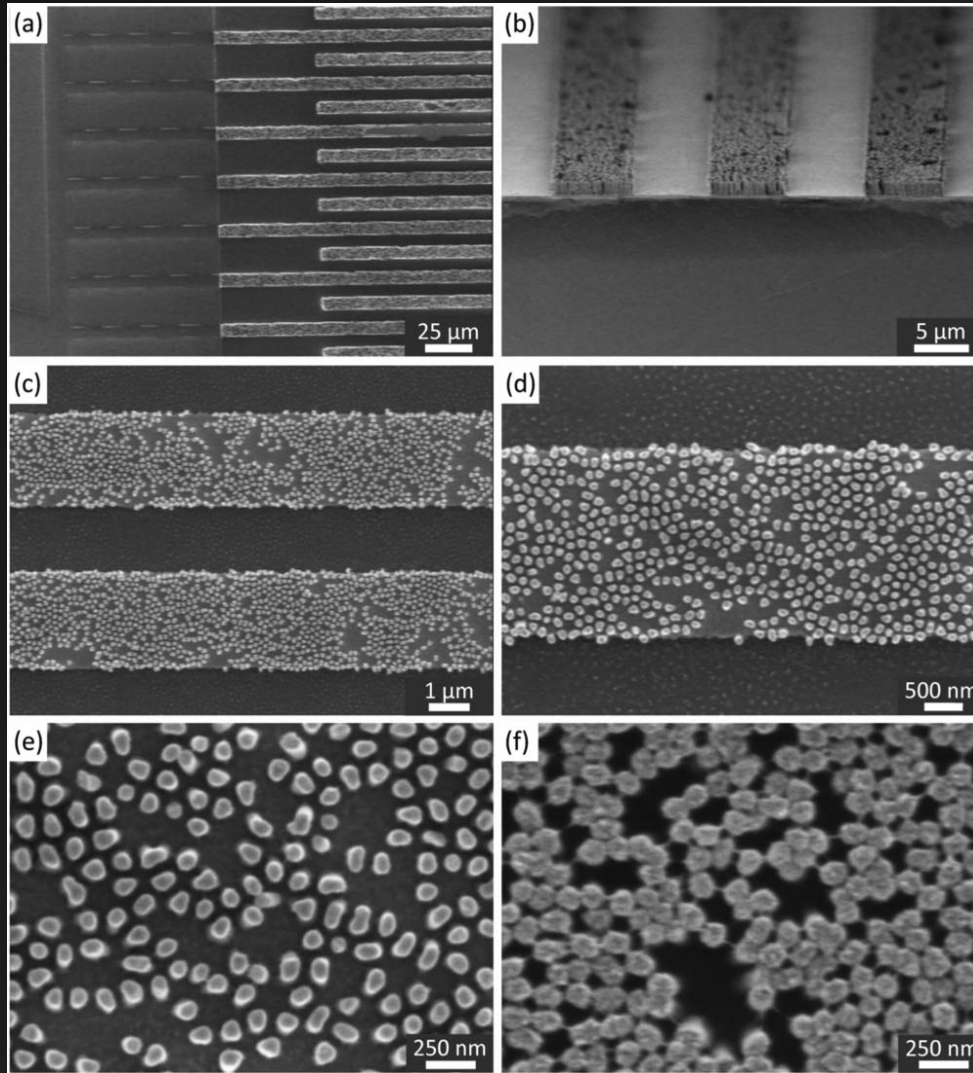
Configuration		● - ●	○ - ●	● - ○	○ - ○
		Pt - Au	Pt - Au	Pt - Au	Pt - Au
Pt - Au	In contact	Pt(+) - Au(+)	Pt(-) - Au(-)	Pt(+) - Au(-)	Pt(-) - Au(-)
	Not in contact	Pt(+) - Au(-)	Pt(-) - Au(-)	Pt(+) - Au(-)	Pt(-) - Au(-)

Work featured in *Research Highlights* by P.S. Dittrich - *Lab Chip* **10**, 811 (2010)

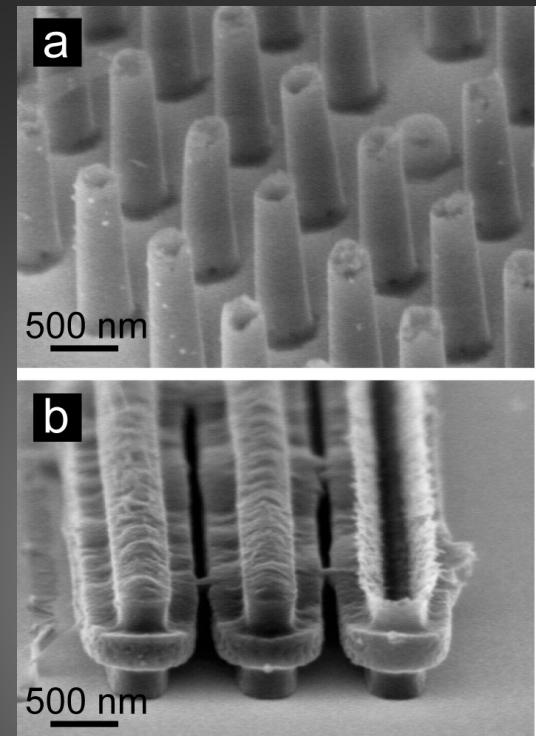


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# Bioanalytics



tubular structuring



pH sensors: V.A. Antohe *et al.*, APL **94**, 073118 (2009)



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*Thank You for Your Attention*

Work supported by Communauté Française de la Belgique, Wallonia Region  
and MC2 Access Programme as part of "Research Infrastructure Action" FP6