Assembly of Nanoparticles in Multiscales and Multidimensions (Multiscale Architecturng): Platform for Convergence Technology

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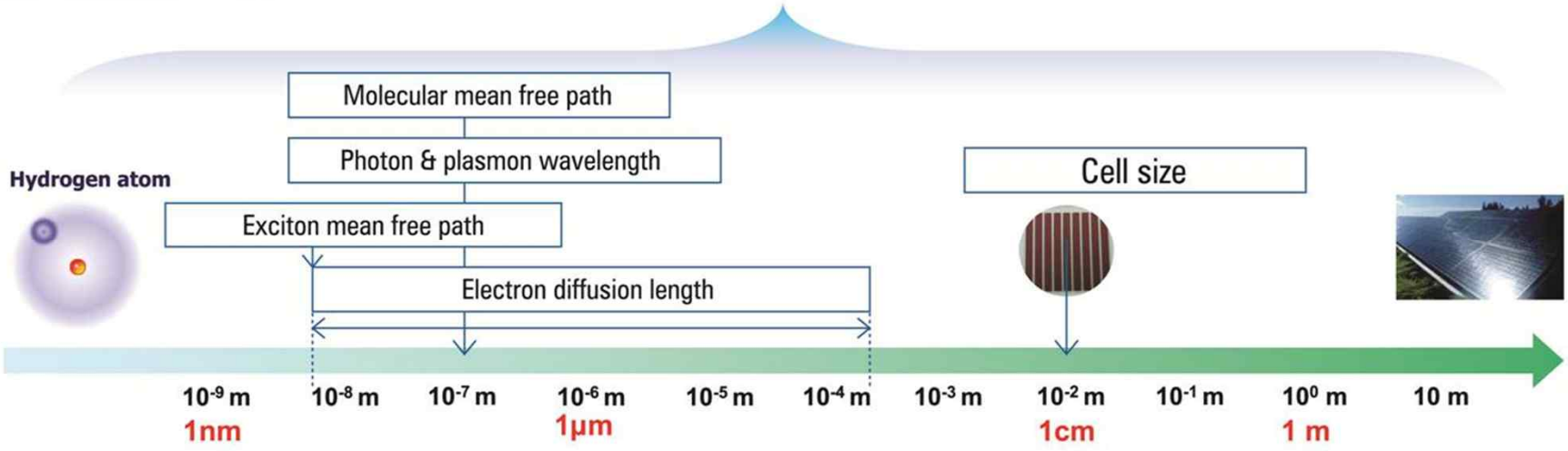
Why Multiscale ?

Example: Solar and Fuel Cells

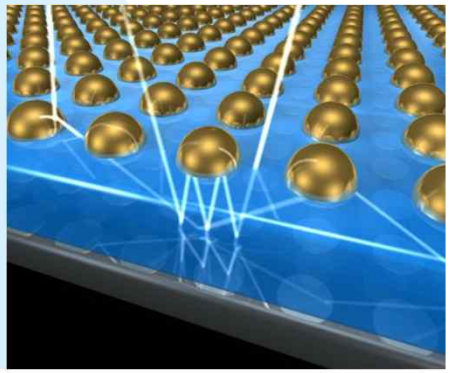
- Energy conversion and transfer in solar and fuel cells are multiscale phenomena
- Energy carriers: photon, electron, exciton, plasmon, molecule ion, phonon

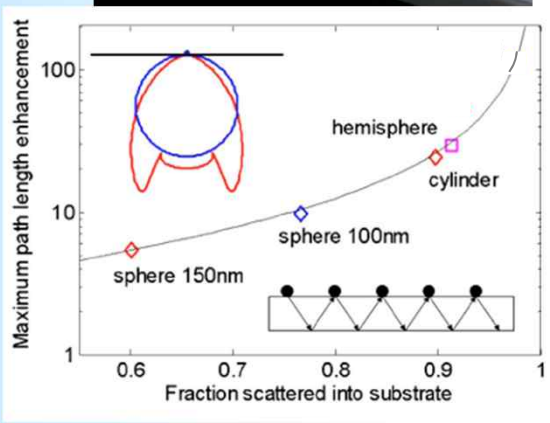
Multiscale approach integrating nano, micro and macroscales is needed to optimize the process.



Plasmonic solar cell utilizes multiscale metal nanoparticle patterns to enable physically thin but optically thick cells to maximize light trapping

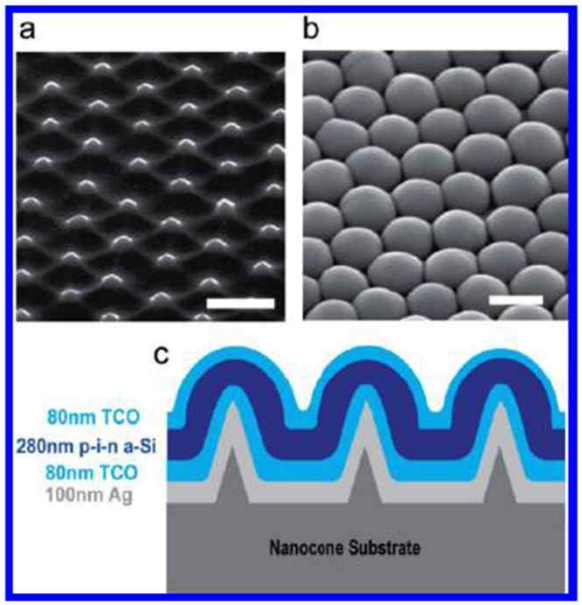
Optical path length enhancement



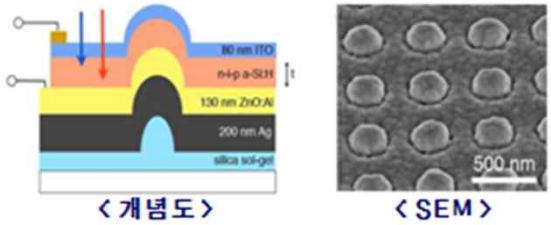


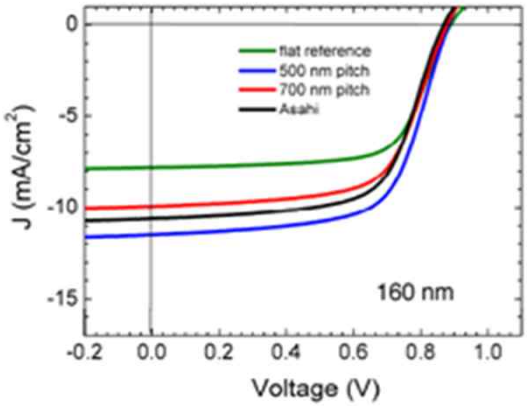
path length enhancement
Atwater et al., Nature Materials (2010)

Multiscale plasmonic solar cells



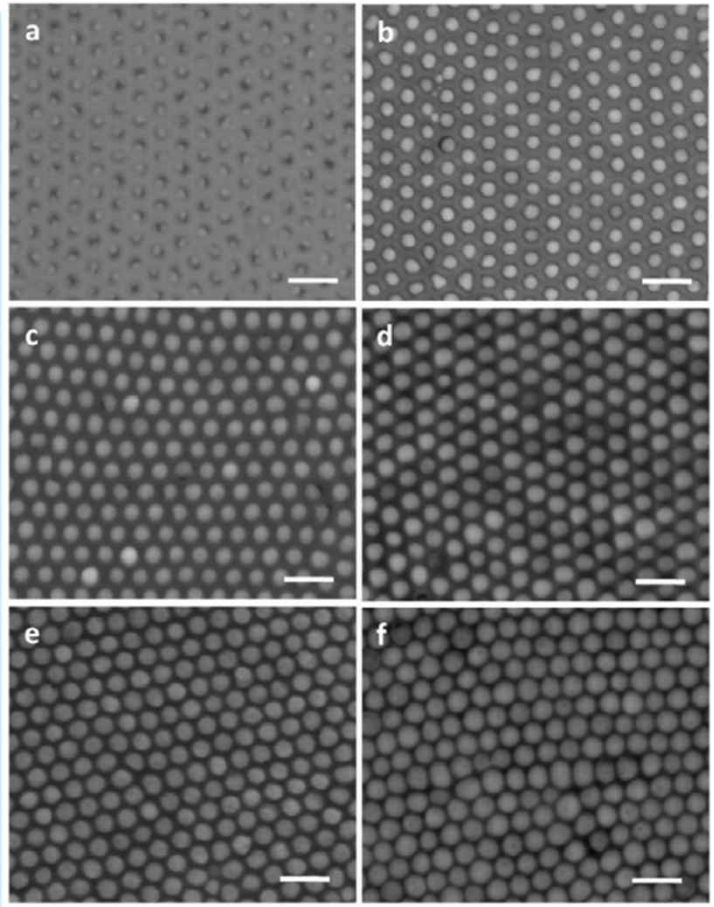
Cui et al., Nano Letters, 2010

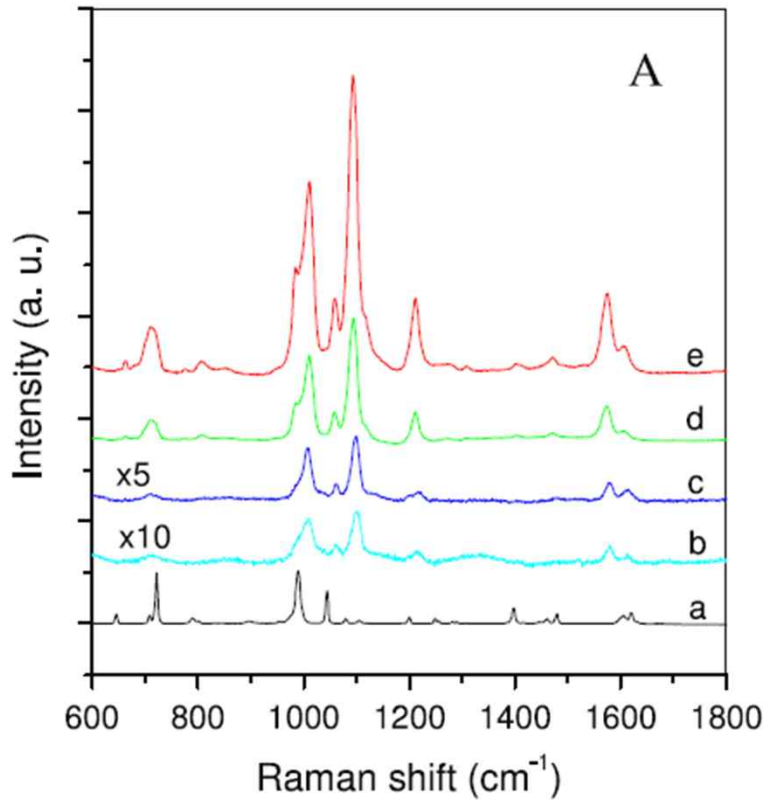




Polman and Atwater, Optical Society of America, 2010

Surface Enhanced Raman Scattering (SERS) based on nanoparticle patterns

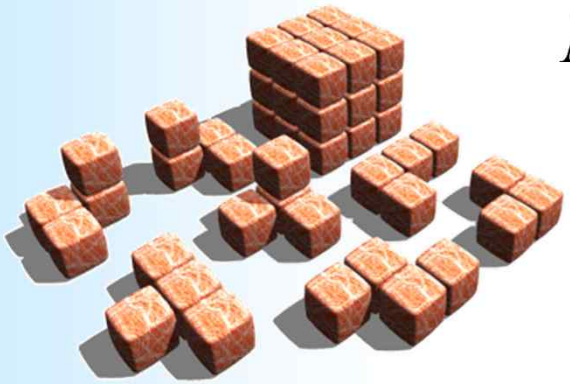




Mu et al. (2010),
***Nanotechnology.*, 21: 015604**

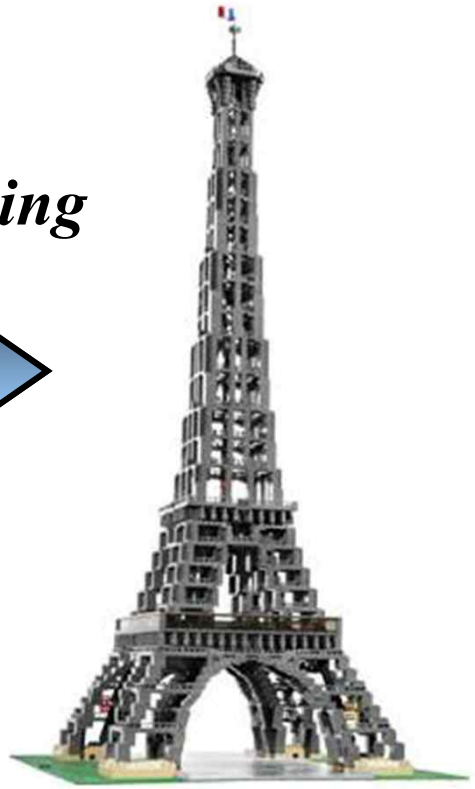
Nanoparticles: Building Blocks for Nanotechnology

- Nanoparticles have long been conceived as the fundamental ***building blocks*** for realizing ***nanotechnology***



Nanoparticles

Multiscale Architecturing

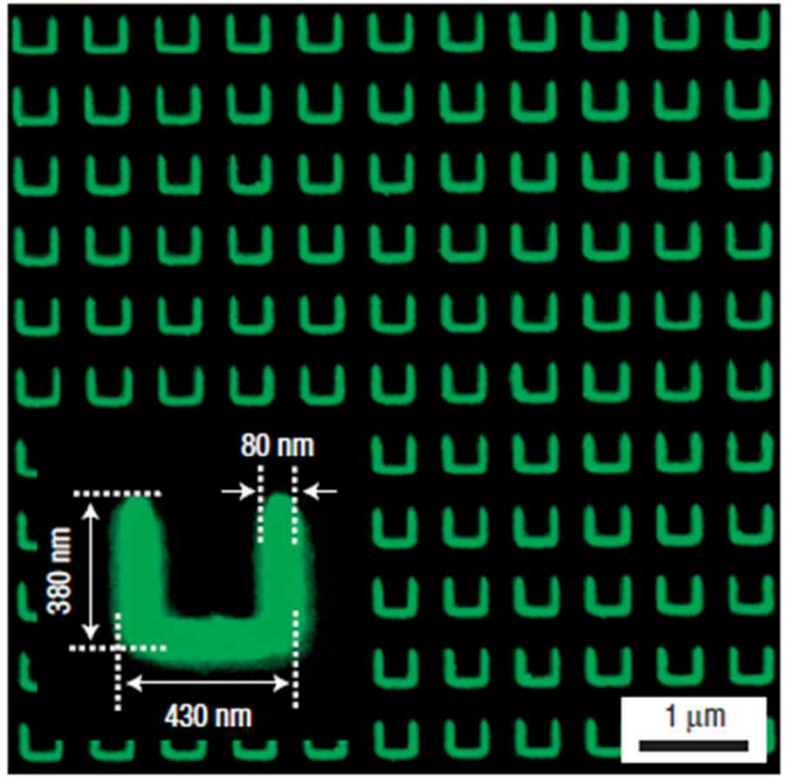


Nanotechnology

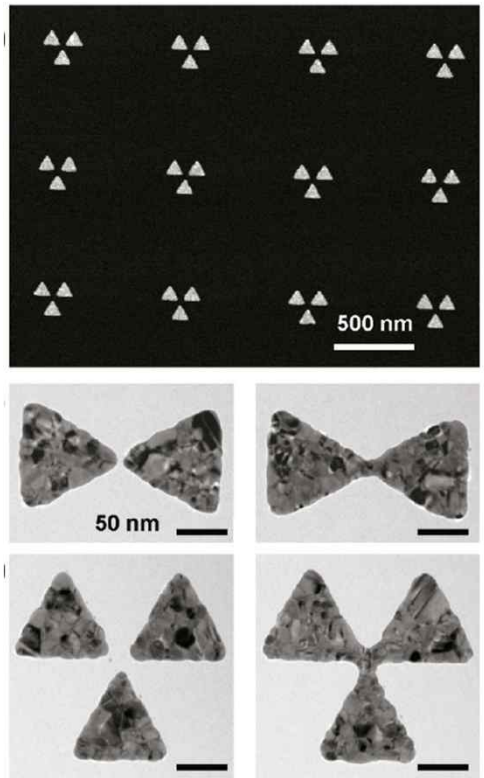
It remains challenging for a controlled way of nanoparticle assembly in multiscales and three dimensions.

Some of Existing Nanoscale Patterning Methods

E-beam lithography (robust but serial approach)

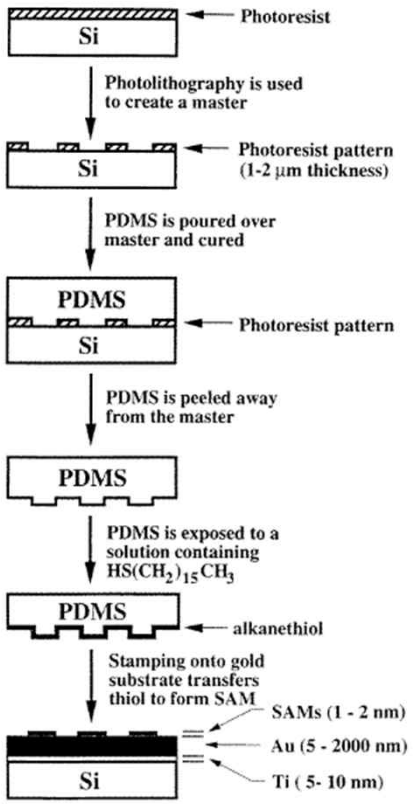


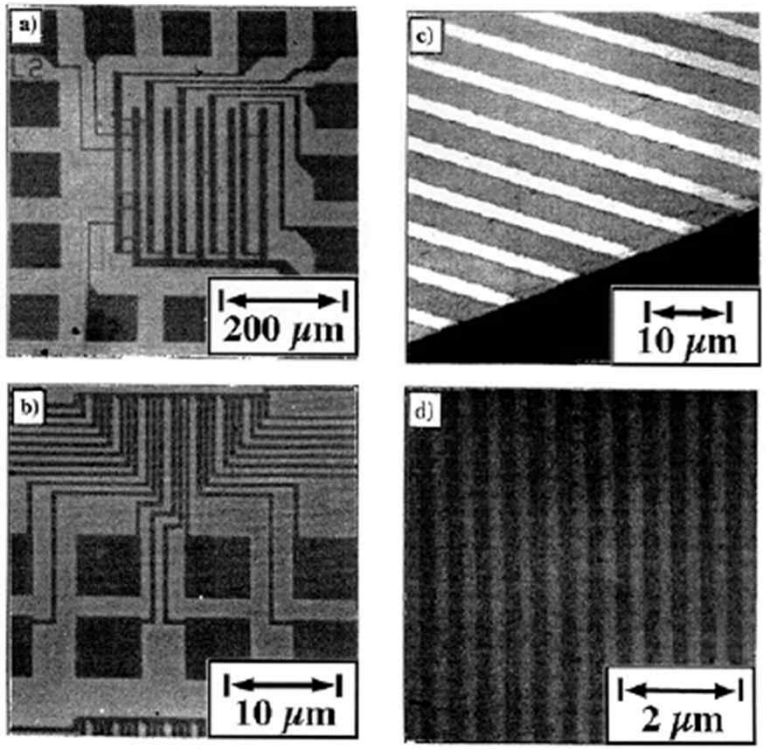
Liu et al., Nature Materials, 2007



Koh et al., Nano Letters, 2011

Micro-contact Printing (parallel but , uniform contact problem, difficulty in 3D architecturing) : Whitesides group

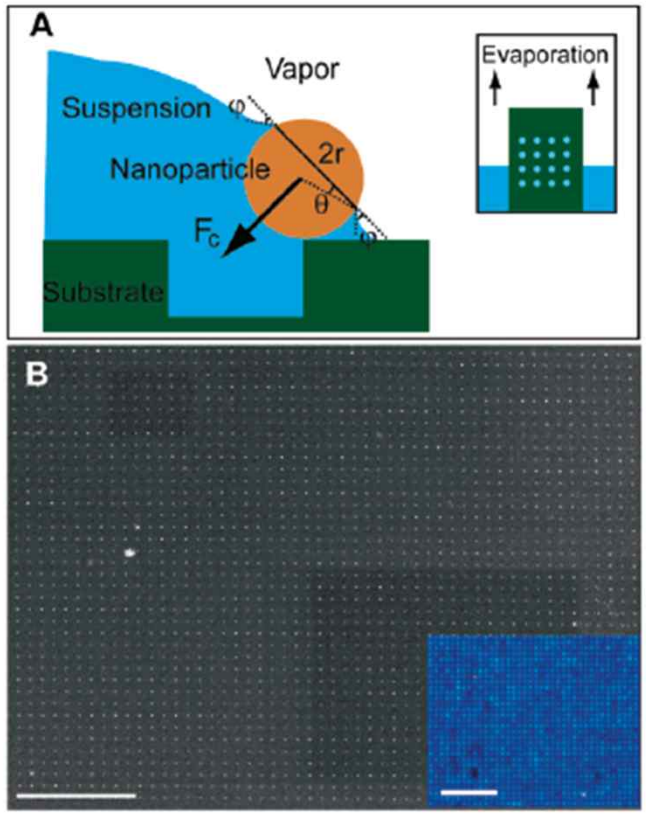


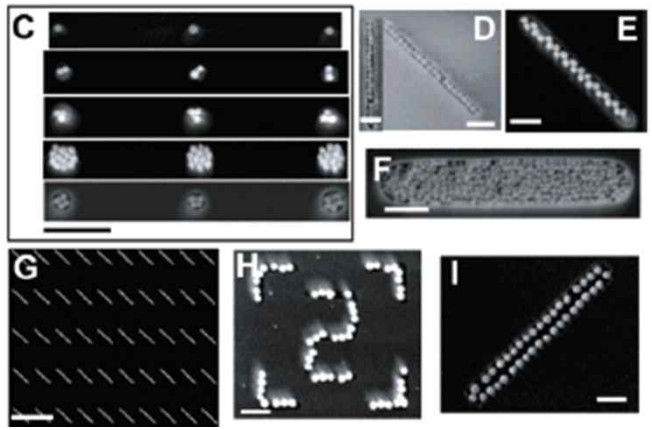


Wilbur et al., *Nanotechnology*, 1996

Capillary Force *A*ssembly

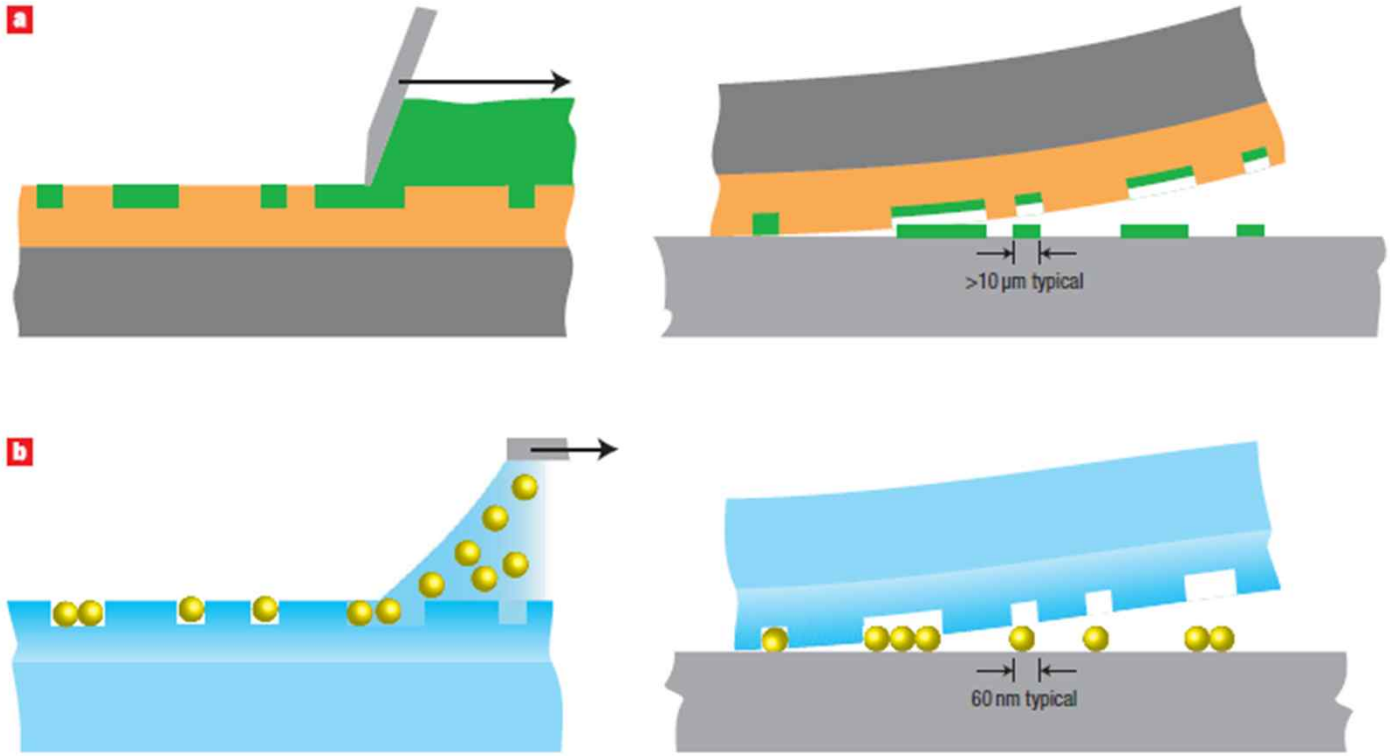
Cui et al., Nano Lett., Vol. 4, No. 6, 2004





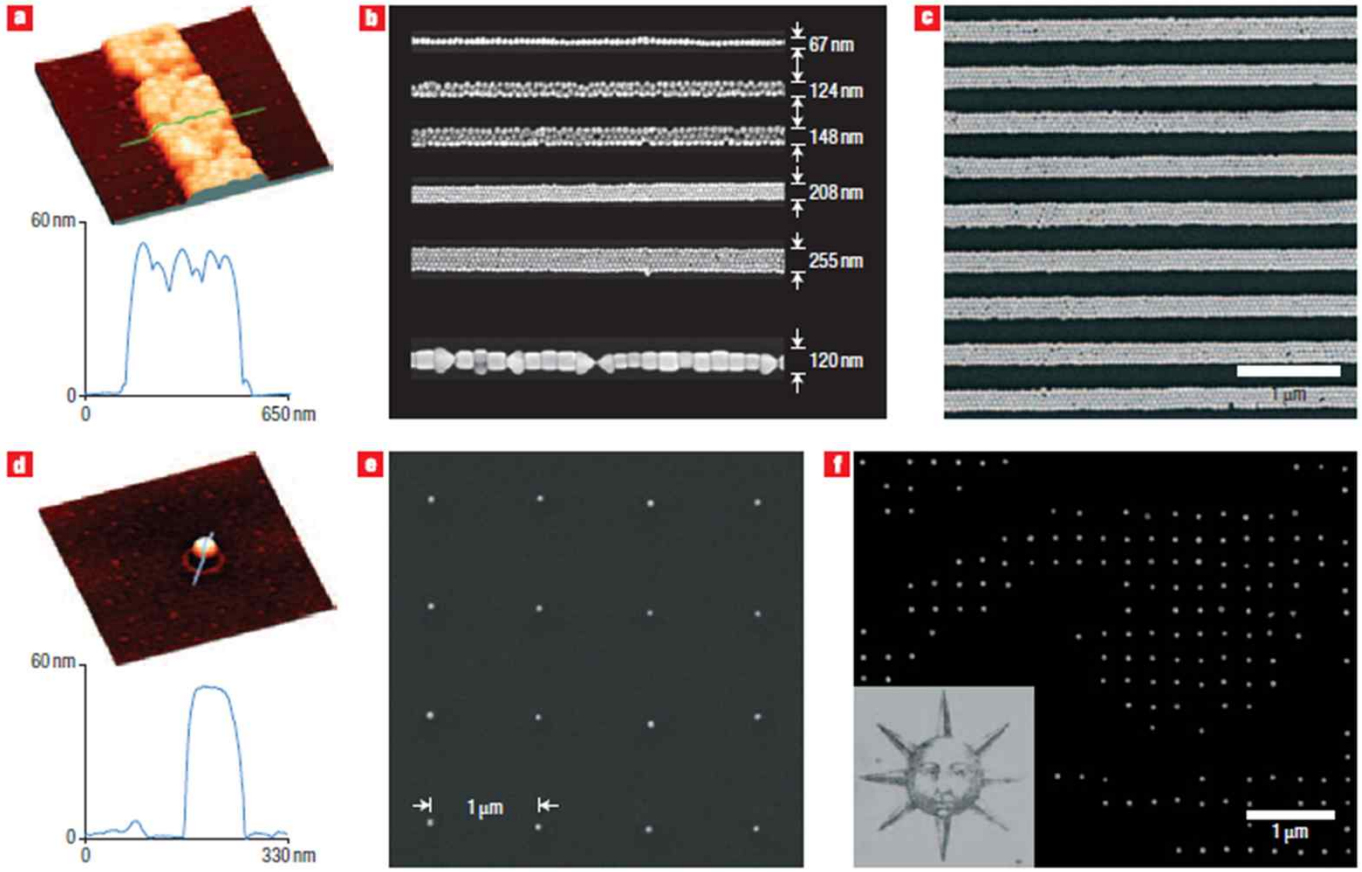
From traditional gravure printing to high-resolution particle printing

KRAUS et al. , Nature Nanotechnology, 2, 570 (2007)



Particle structures printed on flat Si substrates.

KRAUS et al. , Nature Nanotechnology, 2, 570 (2007)



Need to develop Cost-effective High-throughput Nano-Assembly Technique:

Multiscale, multidimensional assembly, Parallel, Atmospheric, Nanoscale resolution, Large surface area, Independent of substrates and materials

Our Method : Ion Assisted Aerosol Lithography(IAAL)

(Nature Nanotechnology(2006), Patents Registered in Korea and USA)

- Charged aerosol nanoparticles are precisely positioned on the desired location via ion-induced focusing electrostatic field.

- This is a parallel atmospheric process ensuring nanoscale resolution on large surface area.

Aerosol positioning and assembling of nanoparticles

- As particle size decreases, thermal driven random Brownian motion of nanoparticles becomes significant.

$$\sqrt{< x^2 >} = \sqrt{\frac{2k_B Tt}{f}} = \sqrt{2Dt}$$

$k_B : Boltzmann\_constant, T : Temperature,$

$f : friction\_coefficient$

$t : time, D : Diffusion\_coefficient\ of\ particle$

Aerosol Positioning and assembling of nanoparticles

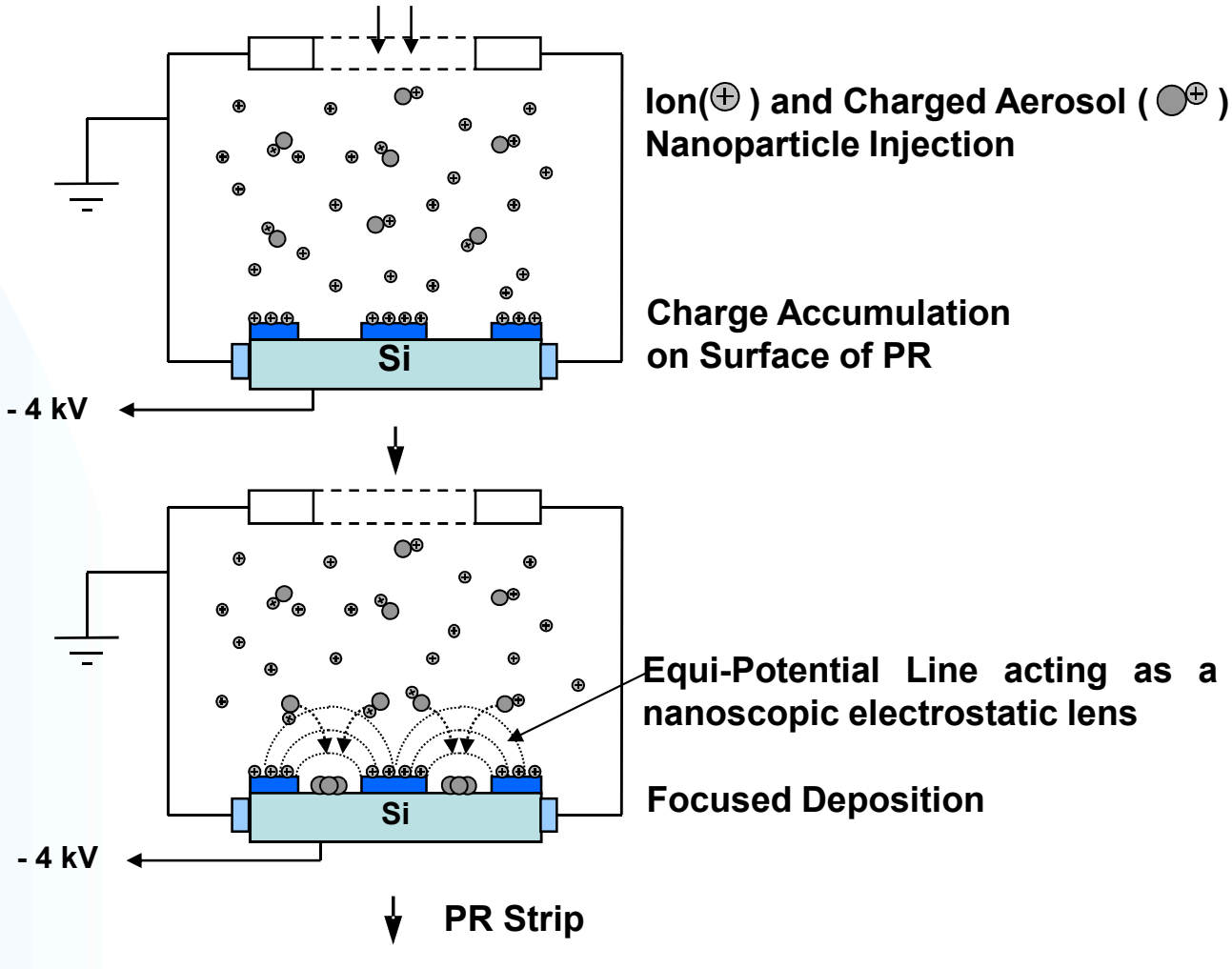
Particle size	**D** (cm^2/sec)	**Brownian random movement at 20°C in 1 second**
1μm	2.77×10^{-7}	7μm
100nm	6.75×10^{-6}	37μm
10nm	5.24×10^{-4}	320μm
1nm	5.14×10^{-2}	3200μm (= 3.2mm)

- Precise positioning of nanoparticles is required for nanoscale assembly of nanoparticles.

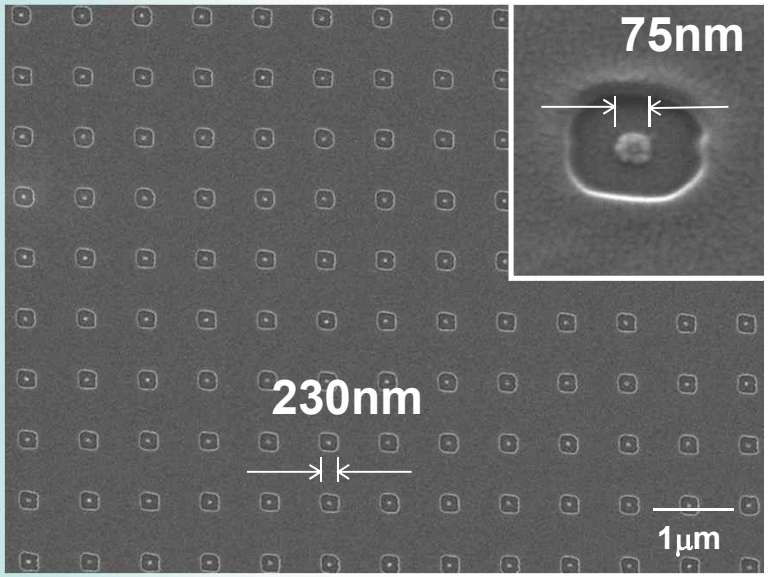
➡ Suppression of thermal motion of nanoparticles is necessary.

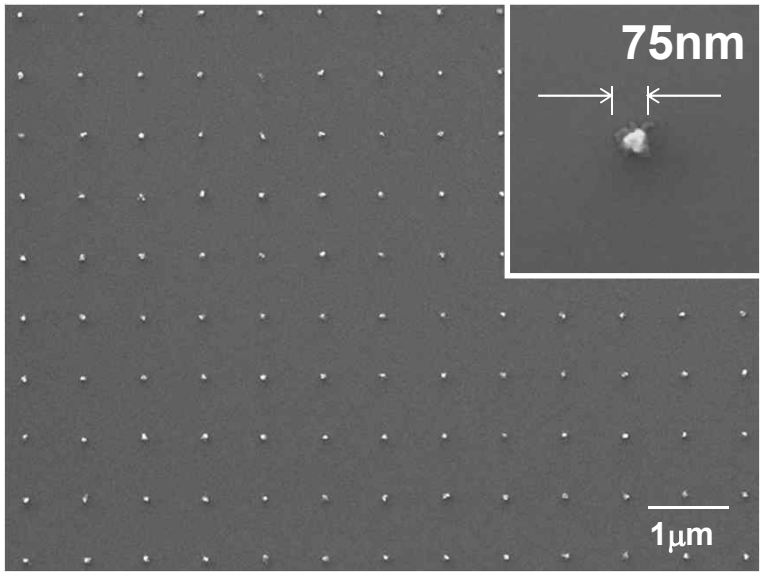
➡ Electrostatic force is utilized to suppress random Brownian particle deposition .

Ion Assisted Aerosol Lithography



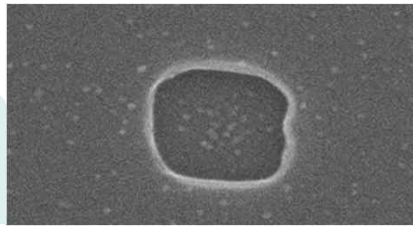
Through DMA, we select 10 nm silver nanoparticles.

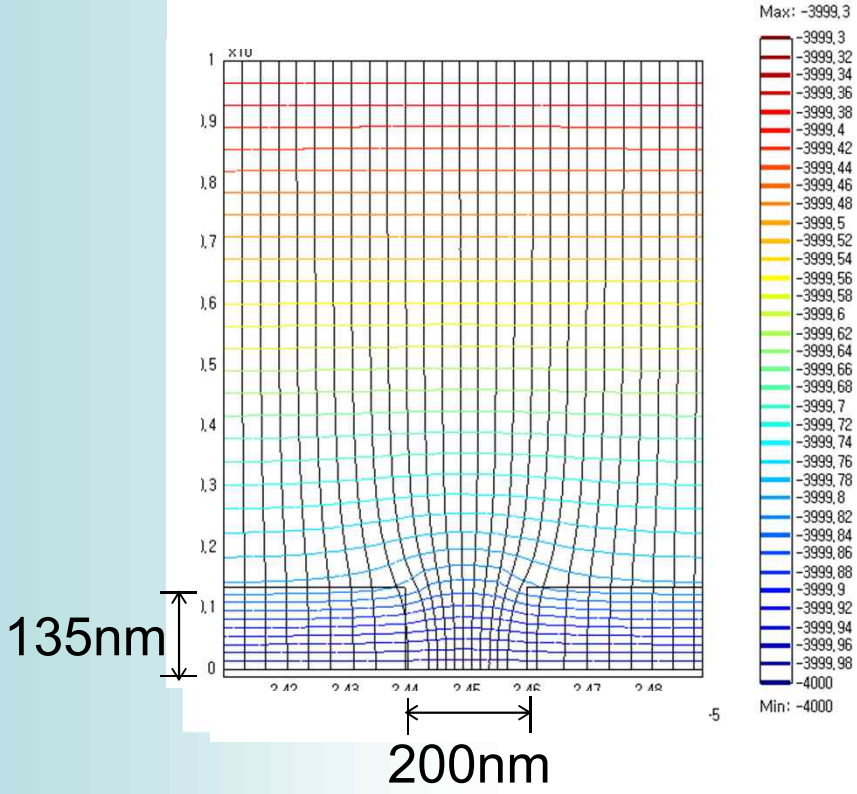




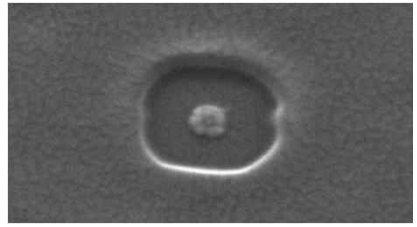
Nanoscopic electrostatic lenses

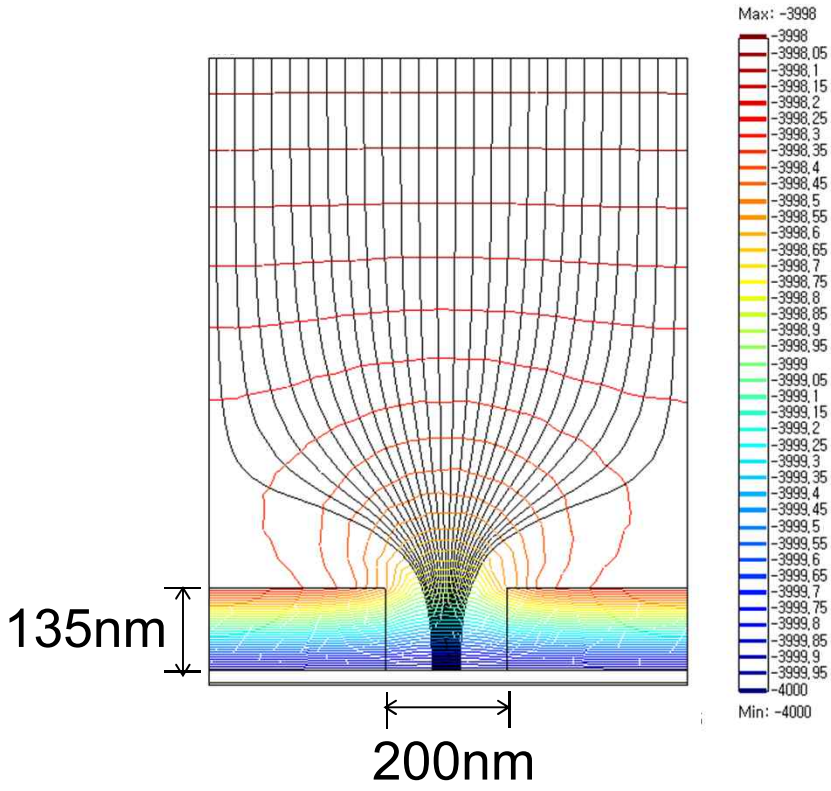
▶without ion injection





▶w/ ion injection (4lpm)



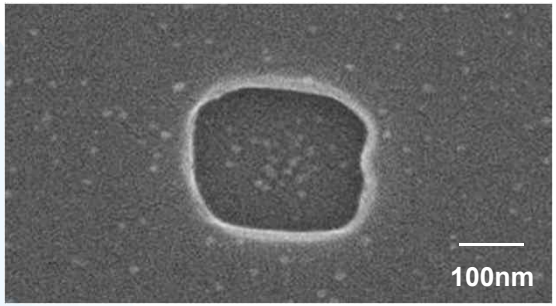


Ion mobility vs particle mobility

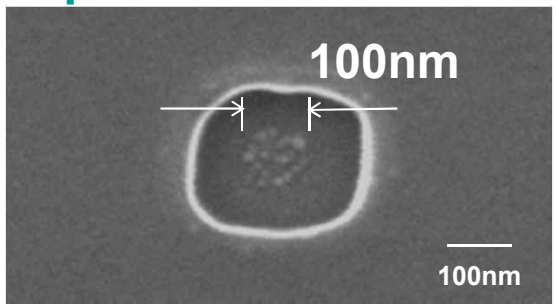
Focusing effect with the increase of ion flow rates

(Nature Nanotechnology,1, 117, 2006)

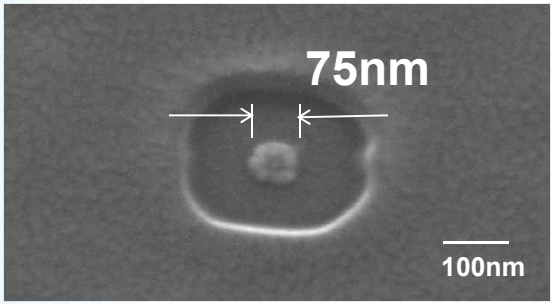
0lpm



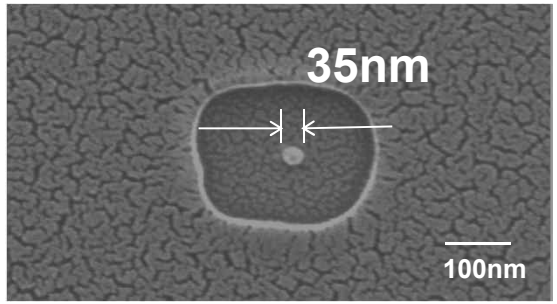
3lpm



4lpm



6lpm



Simulation of Electrodynamic Focusing of Charged Aerosols

- **Particle Trajectories : Langevin Equation**

$$m_p \frac{d\vec{v}_p}{dt} = \vec{F_D} + \vec{F_B} + \vec{F_E} + \vec{F_W}$$

$\vec{F_D}$: Fluid Drag Force

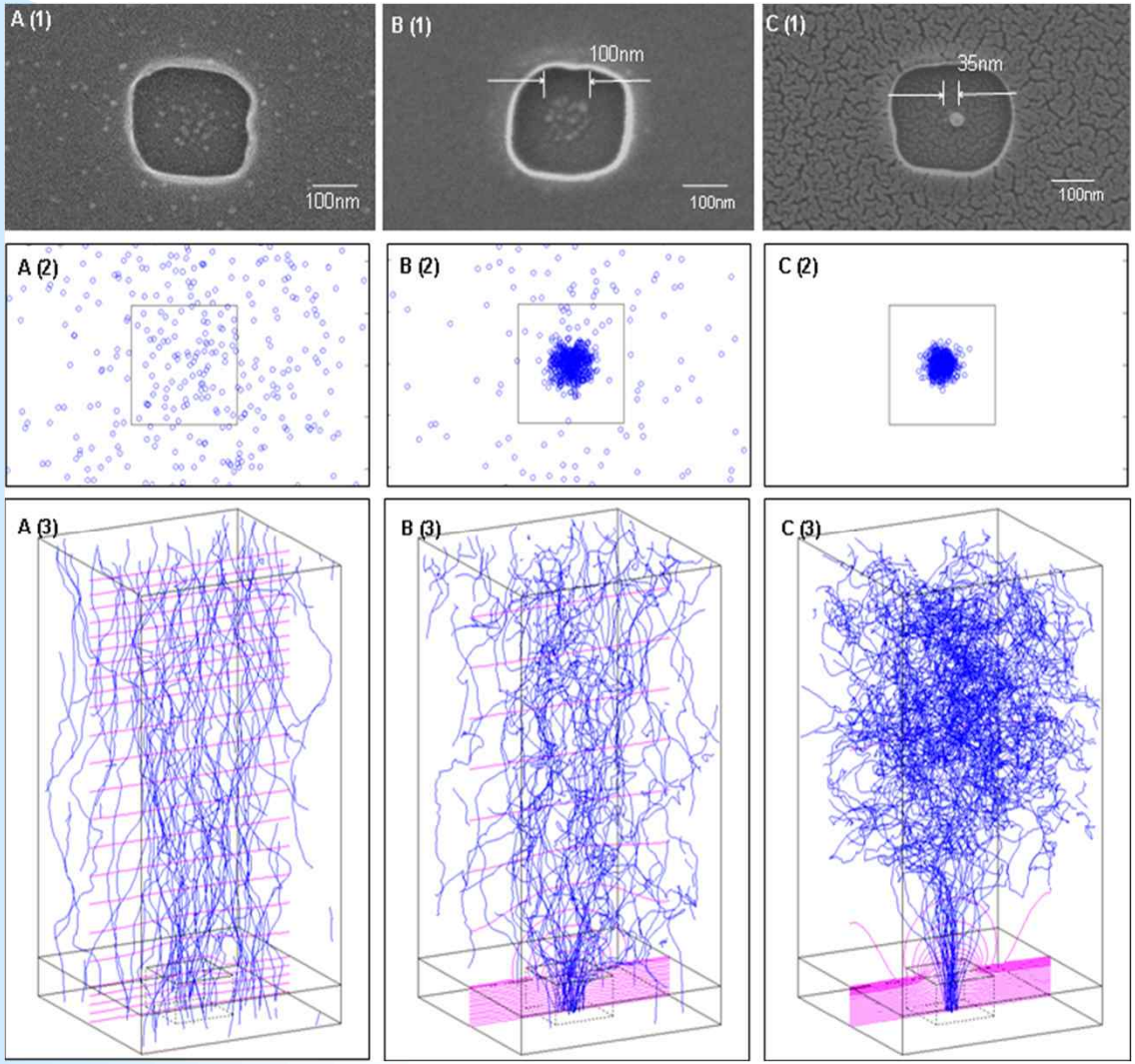
$\vec{F_B}$: Brownian random Force

$\vec{F_E}$: Electric Force

$\vec{F_W}$: Van der Waals Force

- **Electric Field : COMSOL CODE**

Simulation Results (Journal of Aerosol Science, Nov., 2007)



A. No ion injection

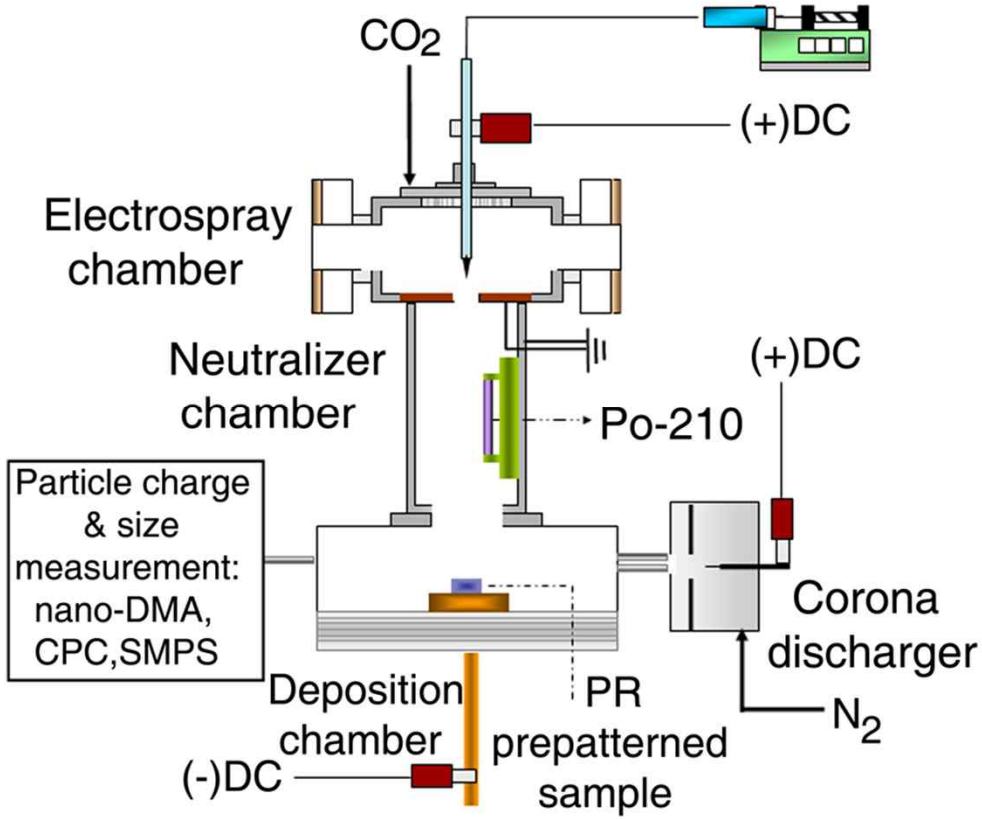
B. With ion injection, N_2 3lpm

C. With ion injection, N_2 6lpm

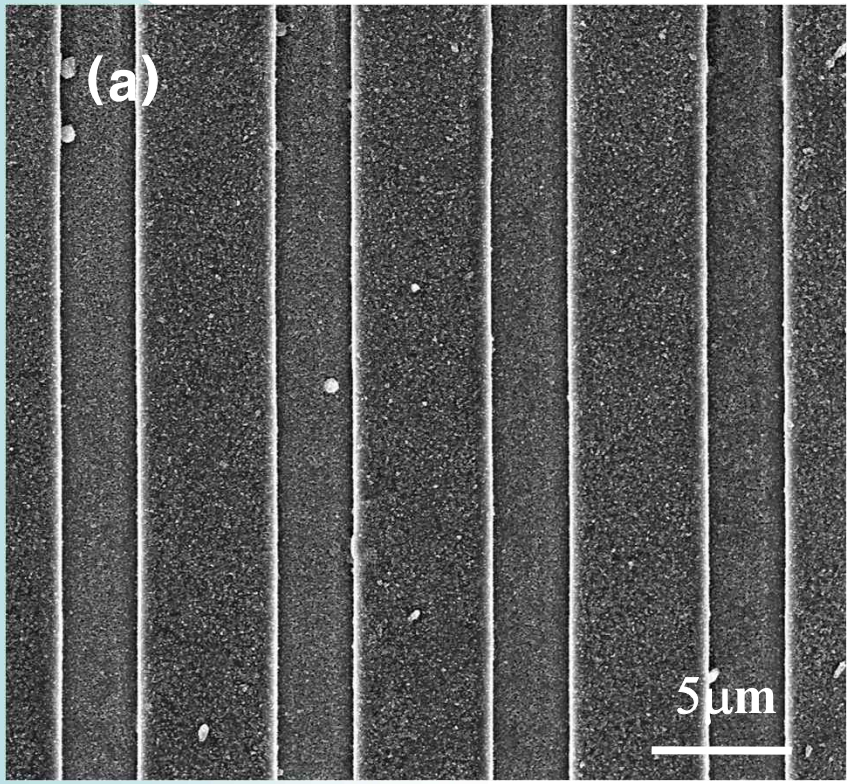
Patterning of nanoparticles that were already made

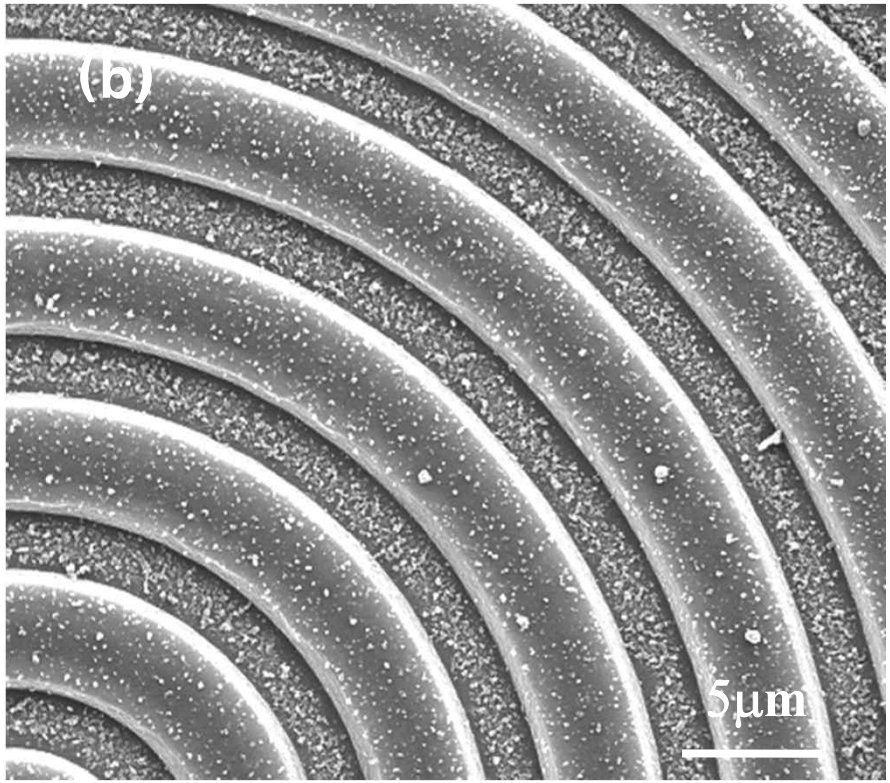
Electrospray of nanoparticle suspension

(Applied Physics Letters, 94, 053104, 2009)



30nm Polystyrene nanoparticles

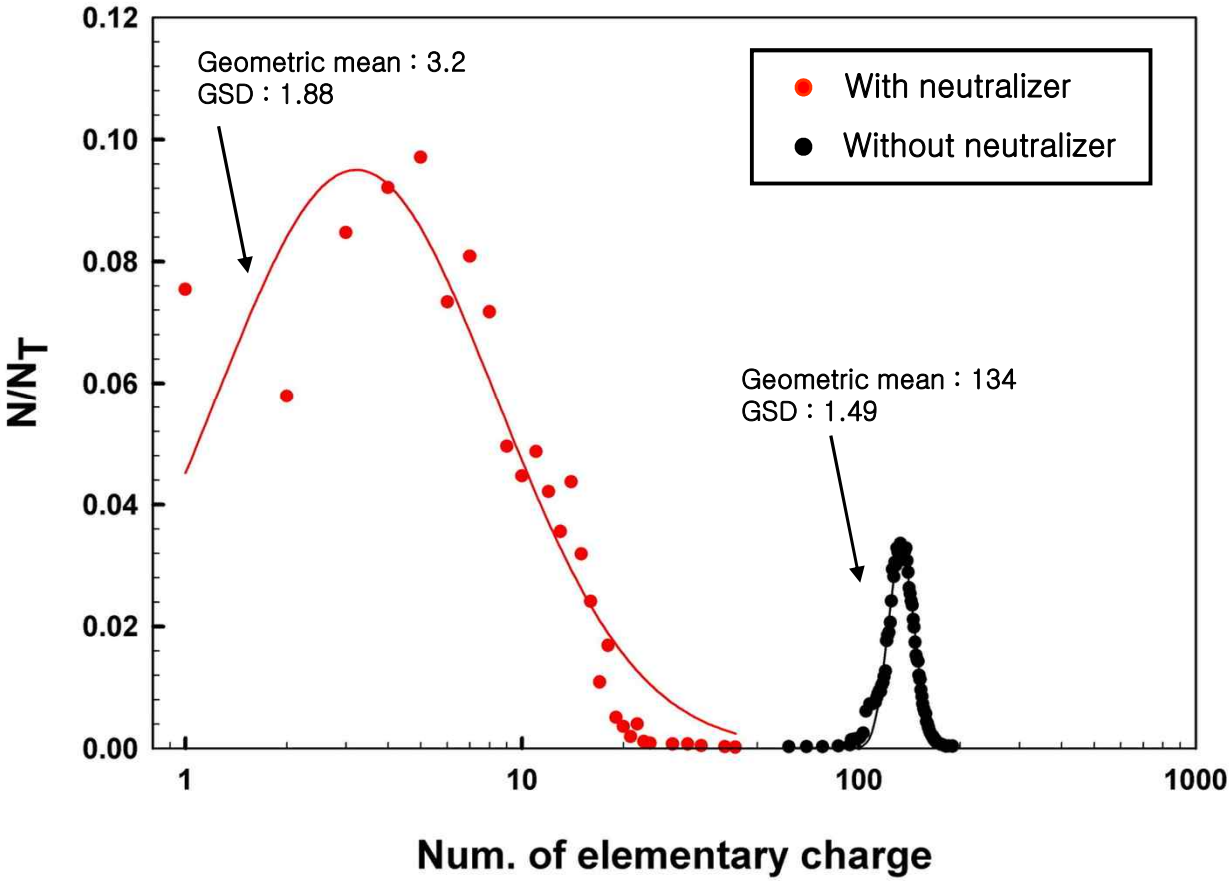




Ion shower 30min,
Deposition 30min,
Without neutralizer

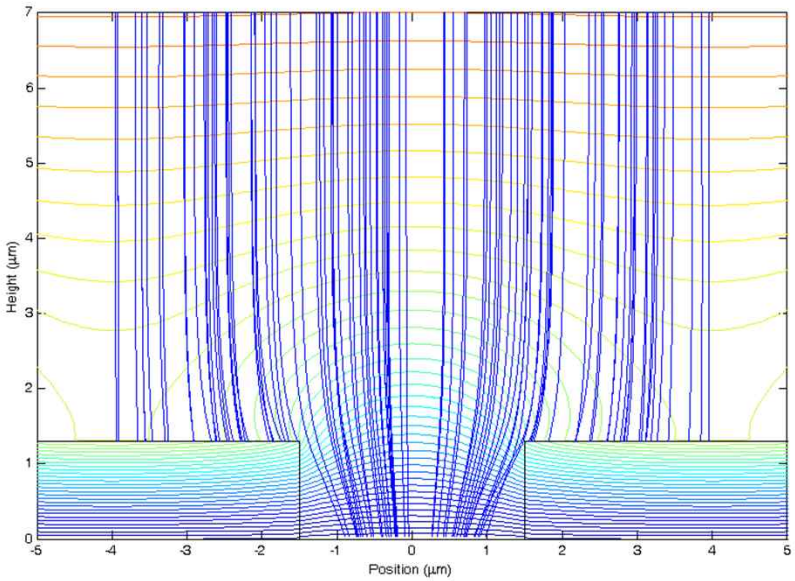
V_s=-
4kV

Results – Charge Distribution

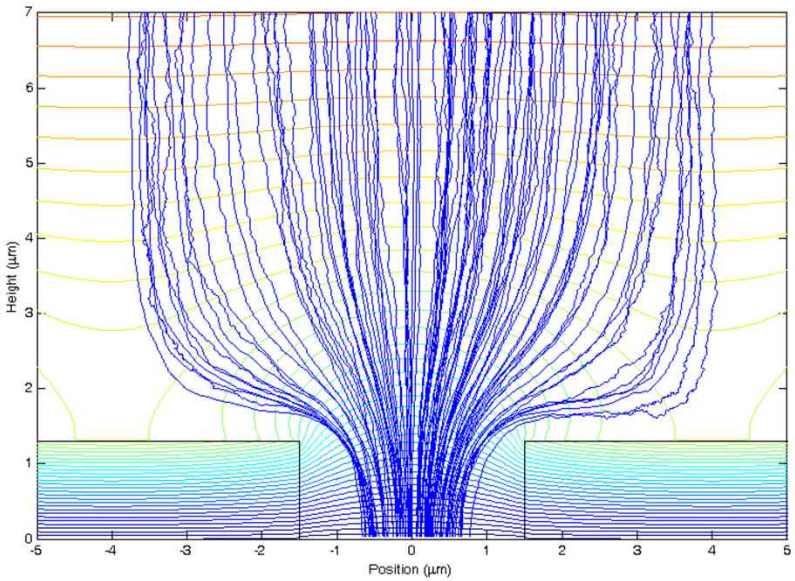


Inertial effect of 10 nm particles: Too high charge, too high velocity

(a)



(b)



Ion shower 30min, Deposition 30min, W/O neutralizer

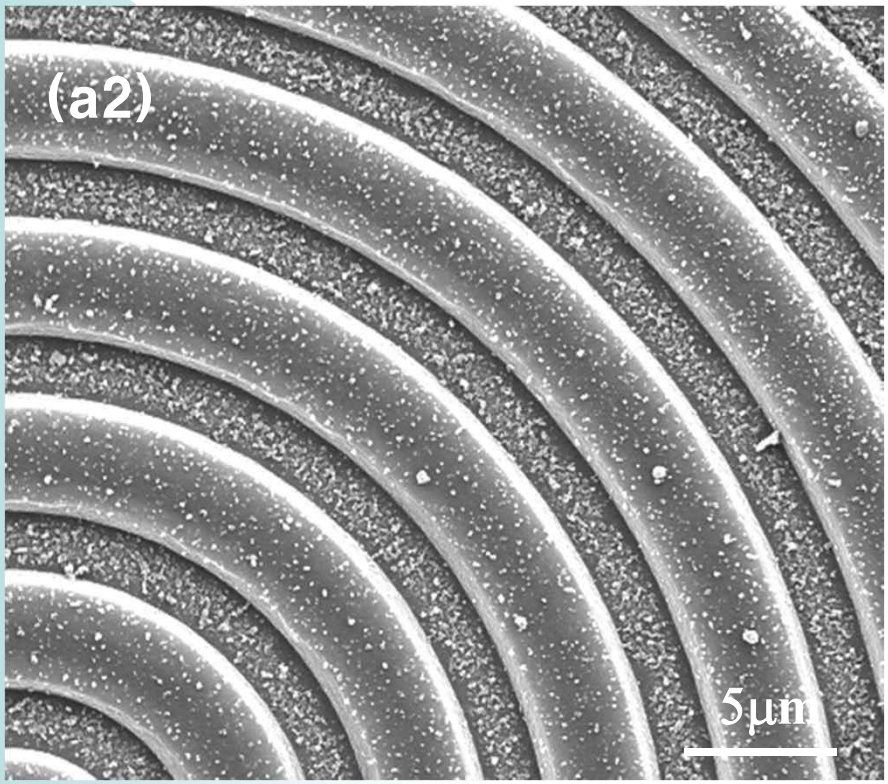
V_s=−4kV

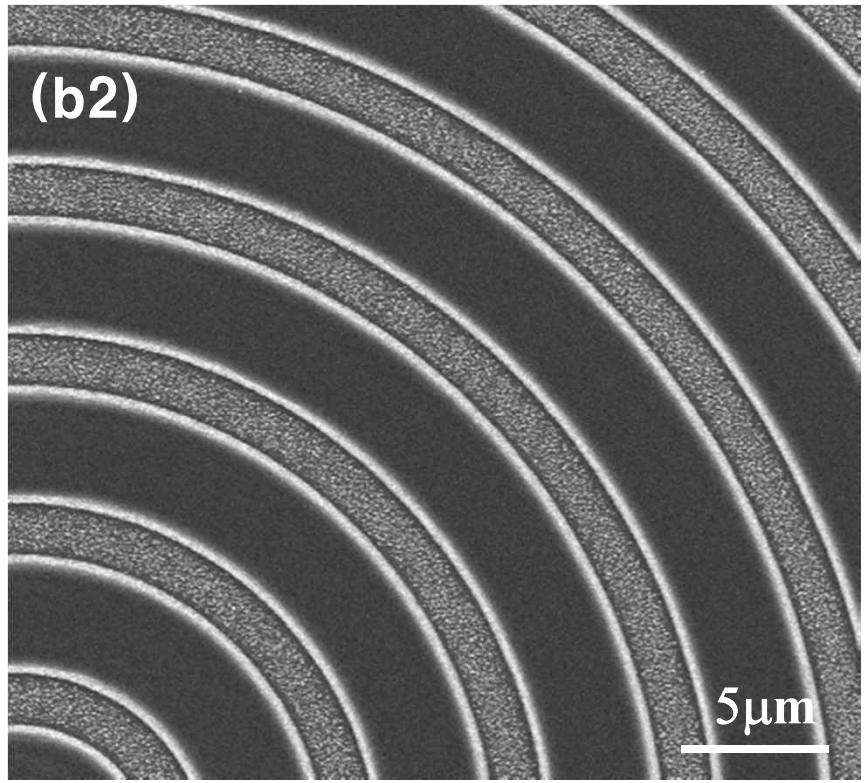
<3um line pattern>

Ion shower 30min, Deposition 30min, W/ neutralizer

V_s=−4kV

Results – Effects of neutralizer 2



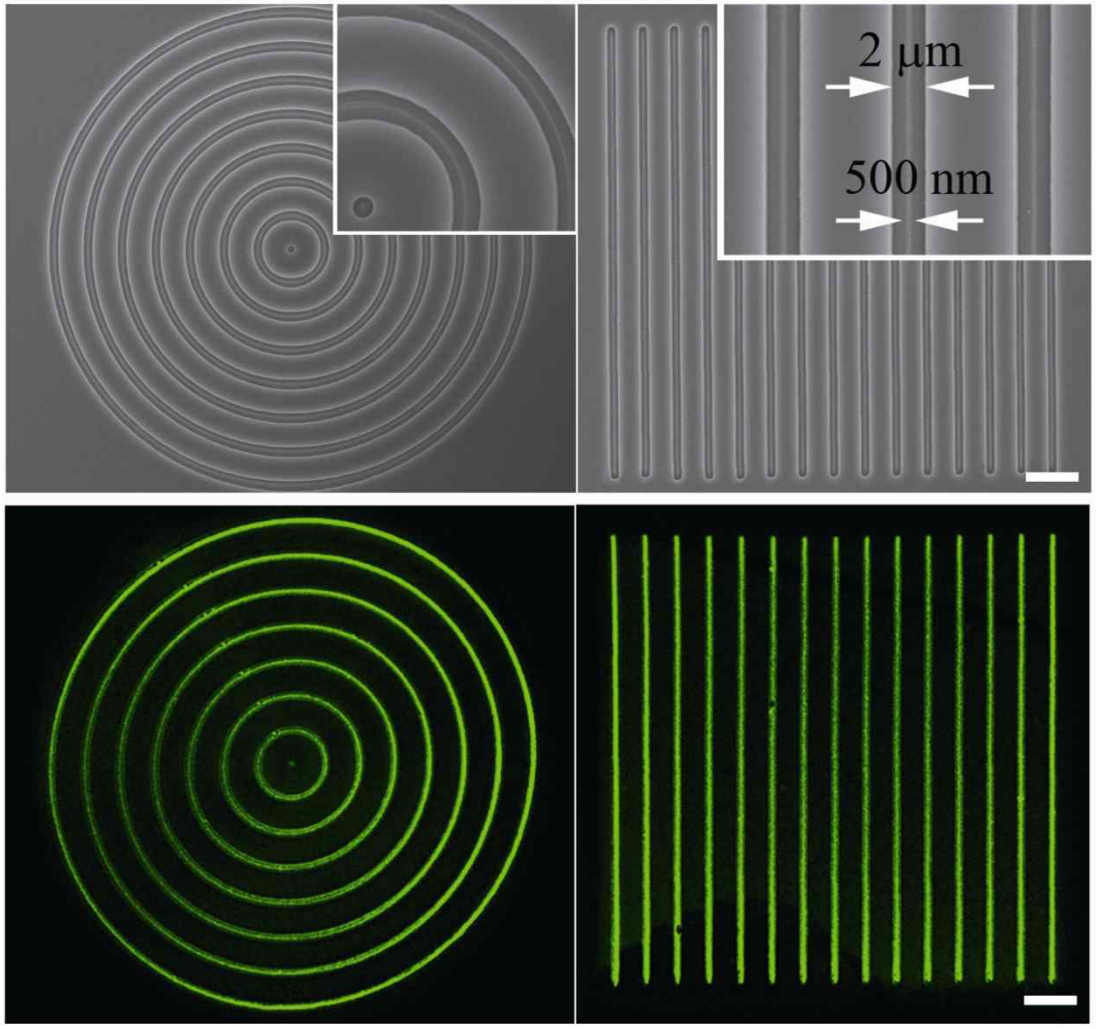


Ion shower 30min,
Deposition 30min,
W/O neutralizer
V_s=-4kV

<2um circle pattern>

Ion shower 30min,
Deposition 30min,
W/ neutralizer
V_s=-4kV

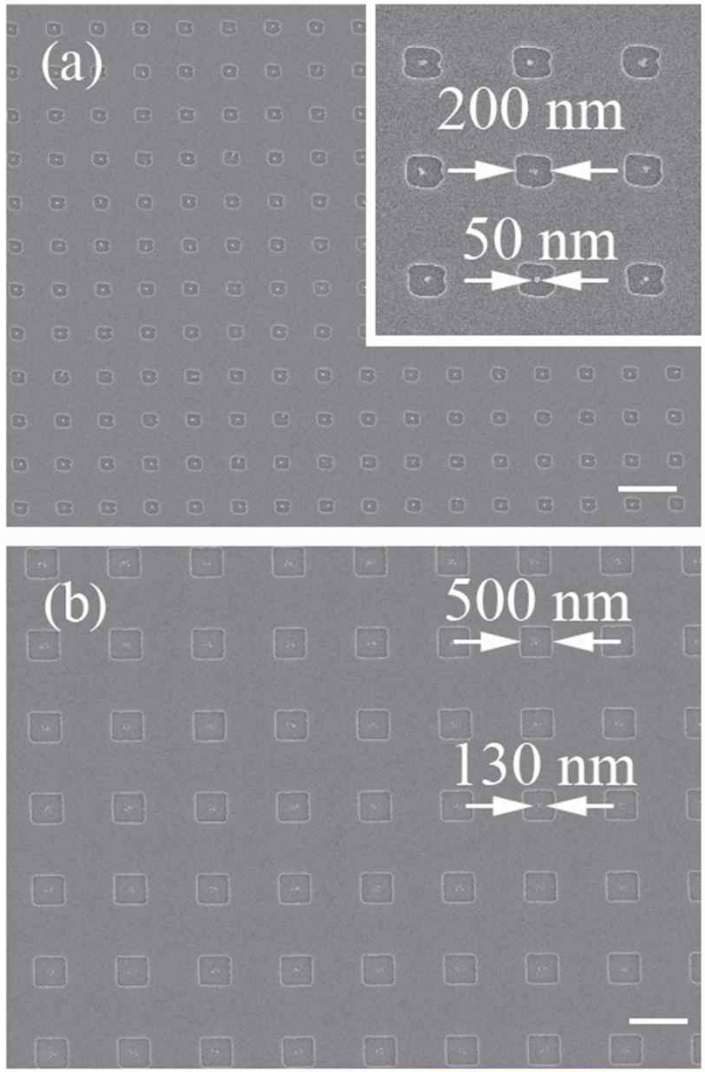
Protein Patterning(Human IgG)(Small, 7, 1790, (2011))



<scale bar = 10 μm>

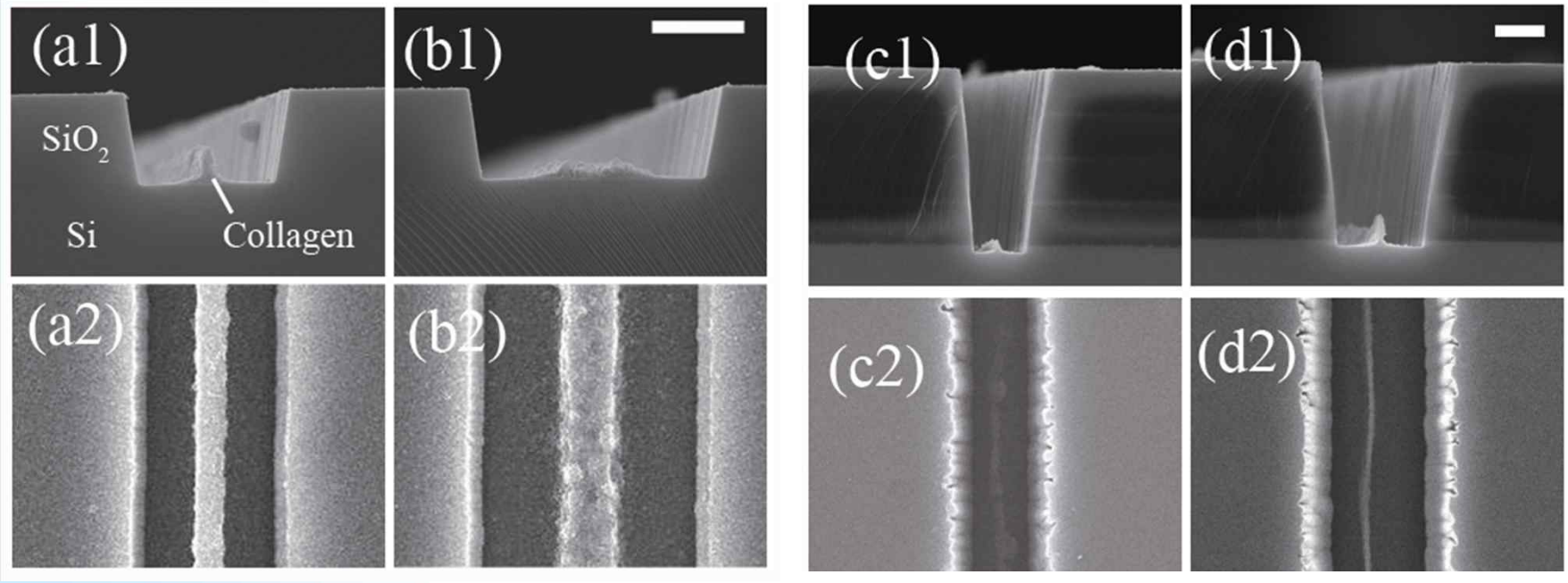
Protein Patterning – nanoscale, parallel method

(Small, 2011)

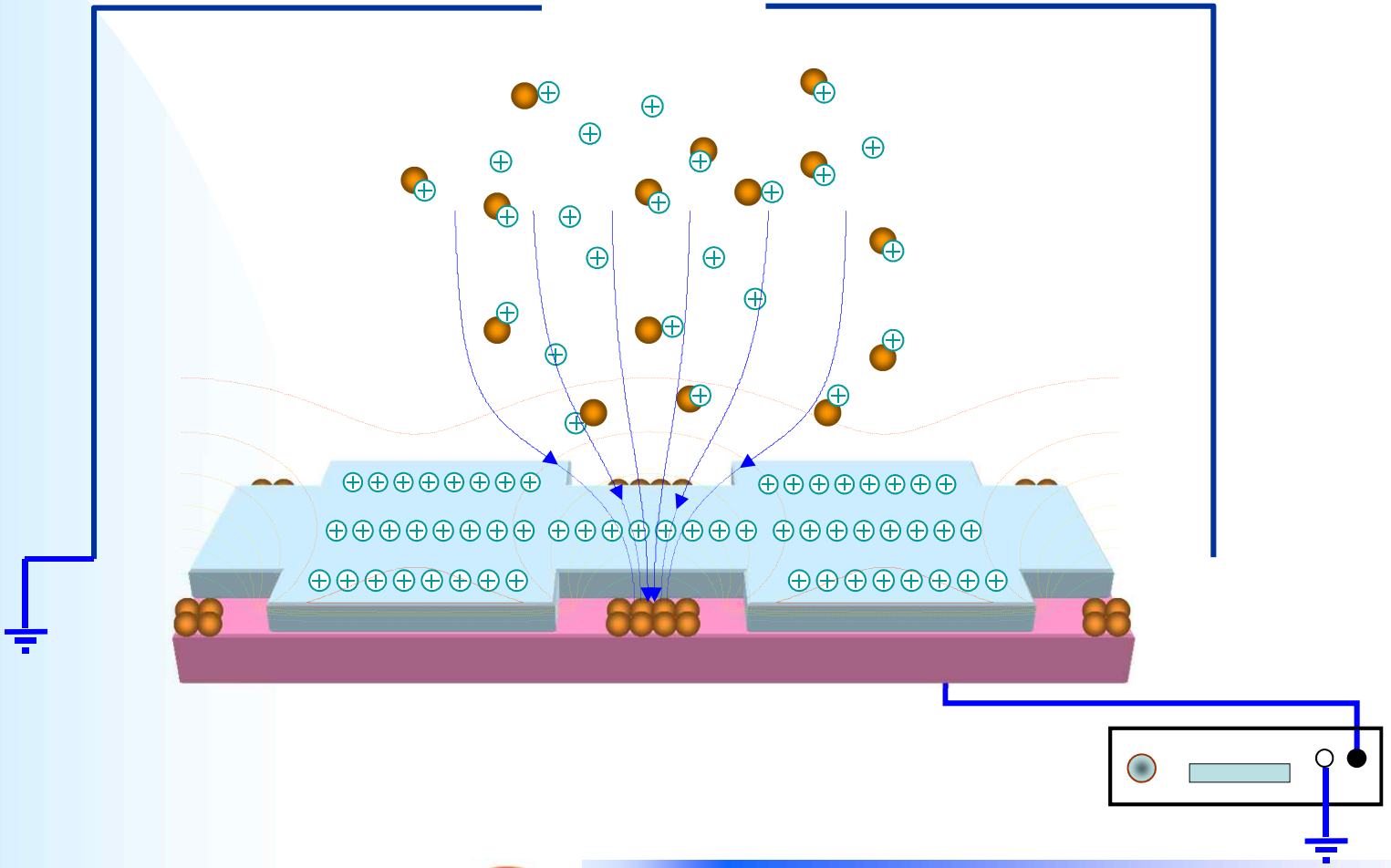


<scale bar = 1 μm>

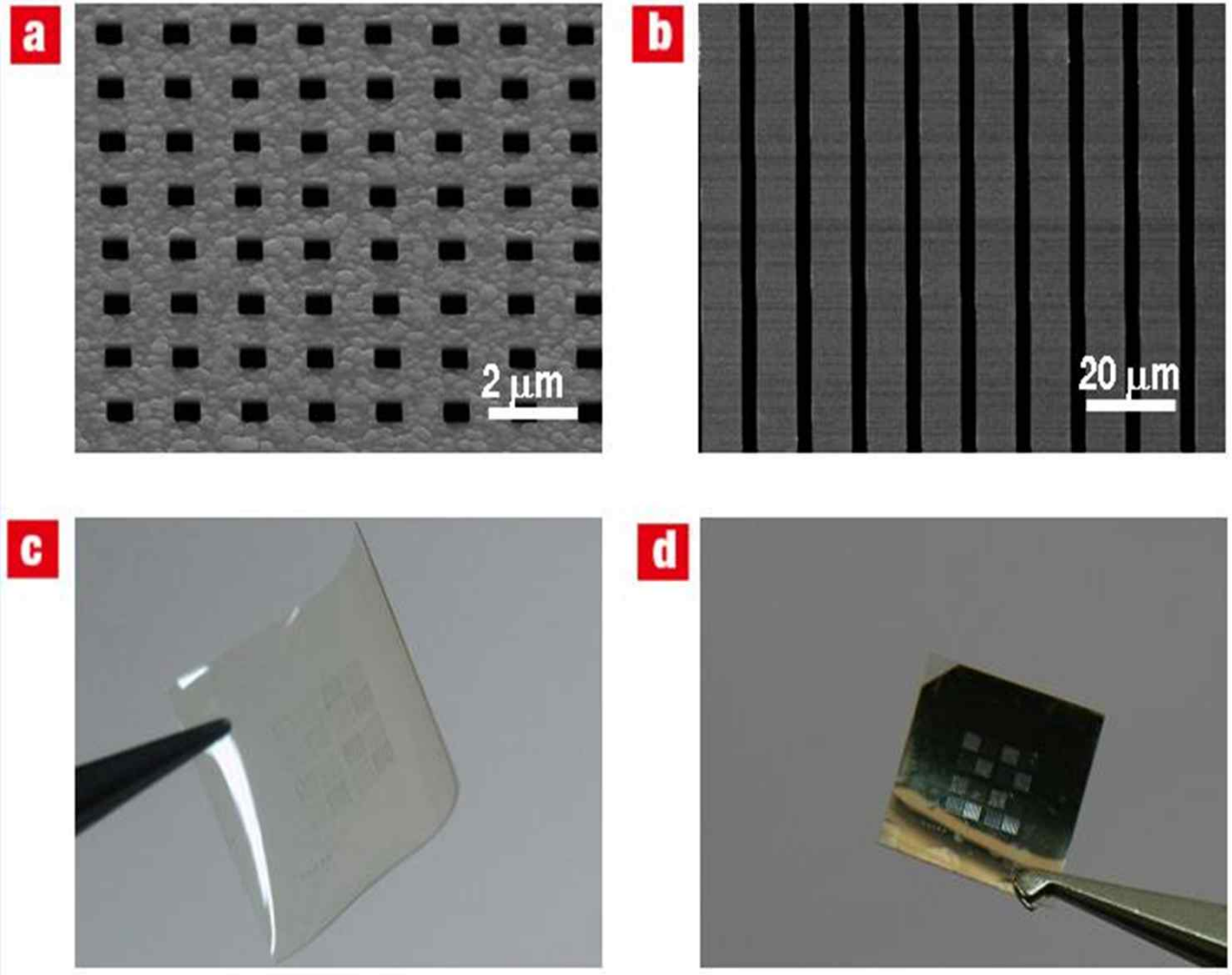
Protein Patterning in microfluidic channels



Do we need resist prepatterning ? Can we eliminate this process ? Solution : **Nanoparticle Focusing Mask** (***Small ,Vol. 6, p 2146, 2010***)



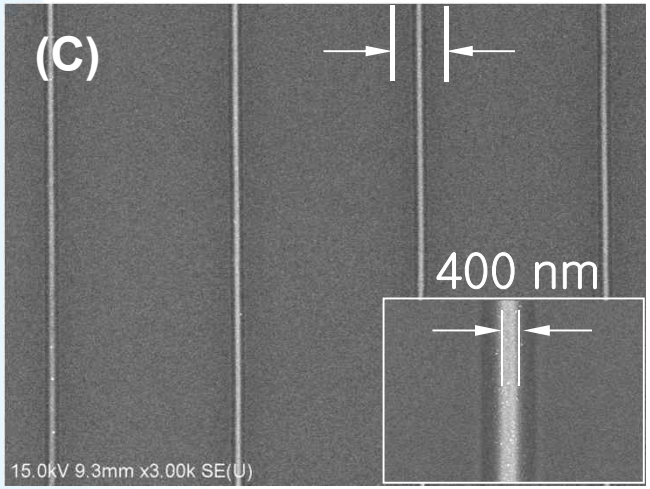
Nanoparticle Focusing Mask

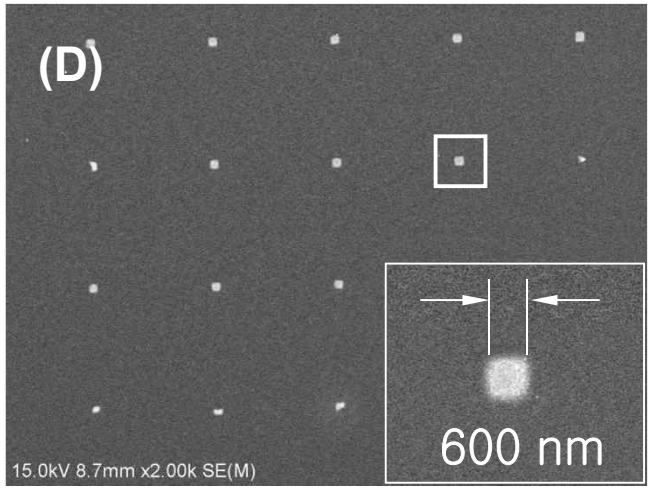


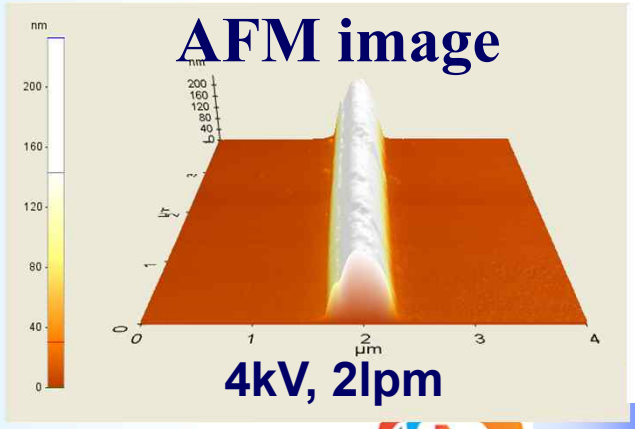
Nanoparticle Focusing Mask : Silicon Nitride Mask

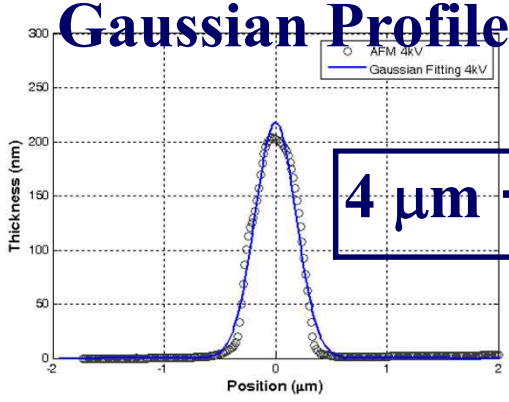
4 μm aperture mask

N_2 ion flow rate of 2 l/min





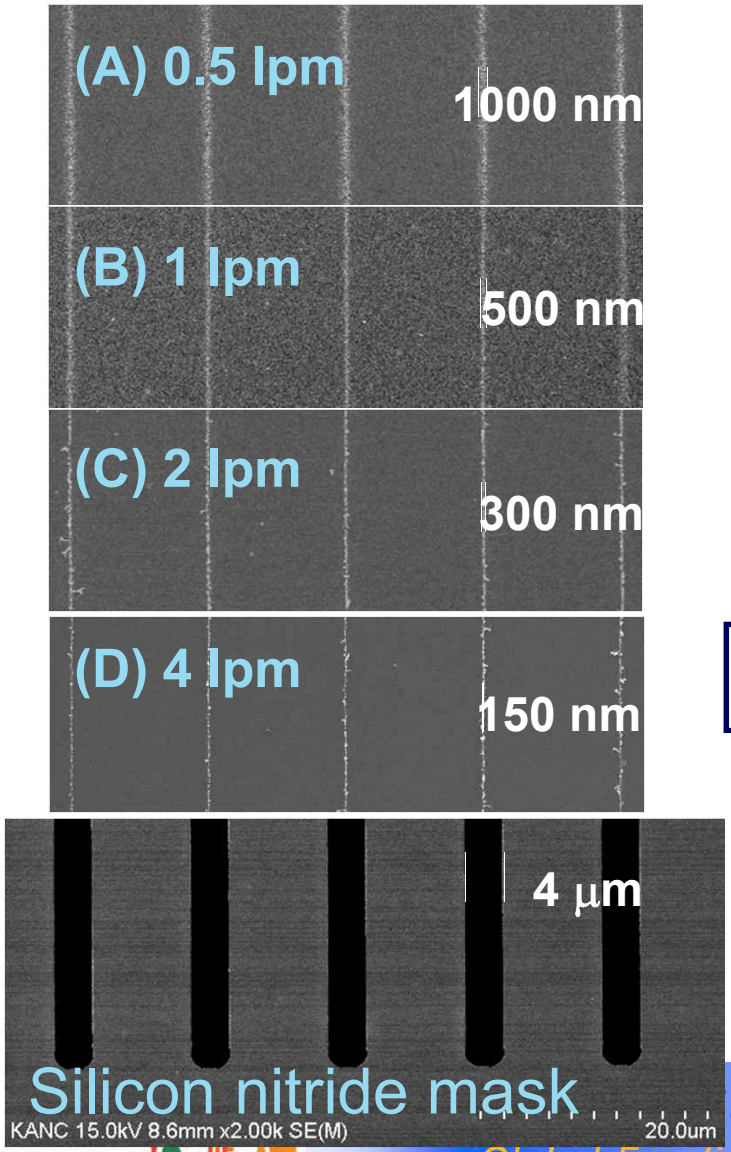




4 μm → 0.4 ~ 0.6 μm

Size Control by Ion Flow Rate

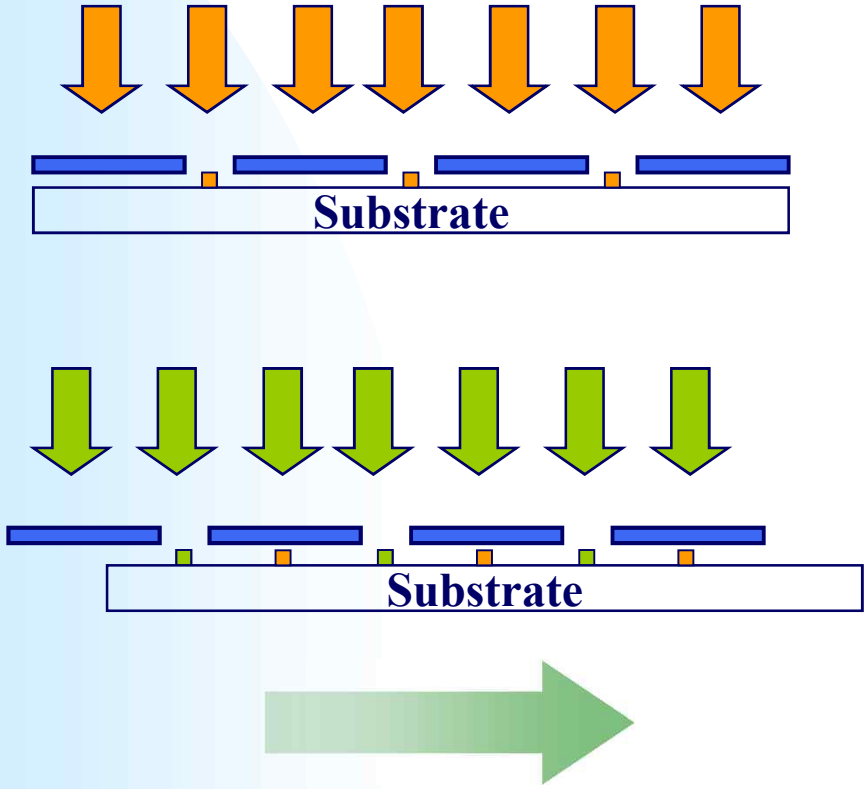
(Small ,Vol. 6, p 2146, 2010)

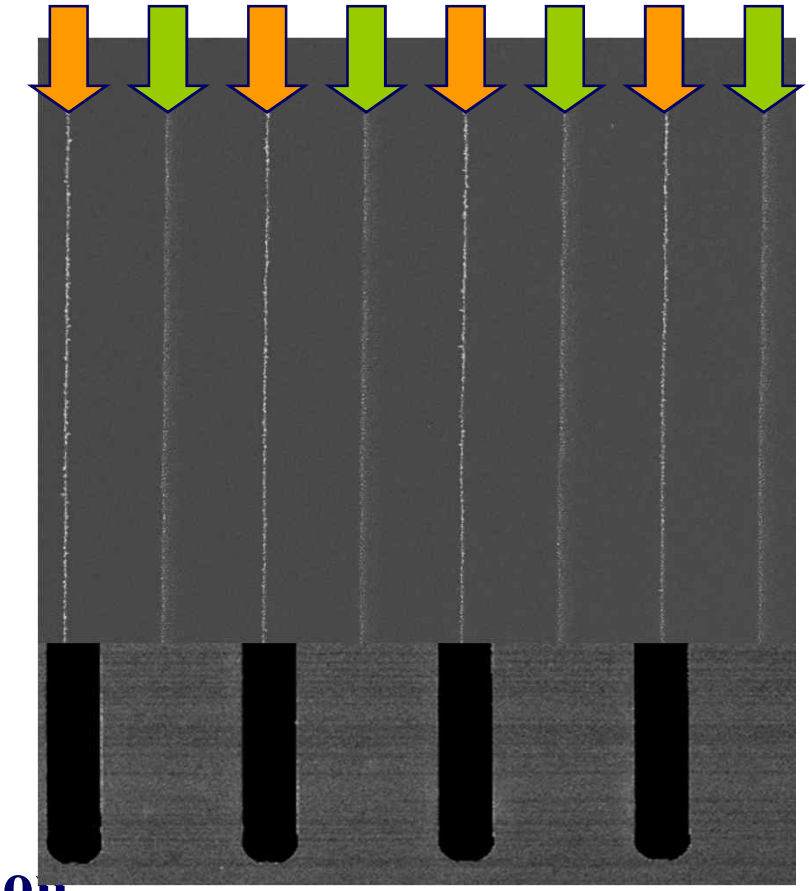


4 μm → 0.15 ~ 1 μm

Sequential Deposition

Control the space between patterns by sequential deposition

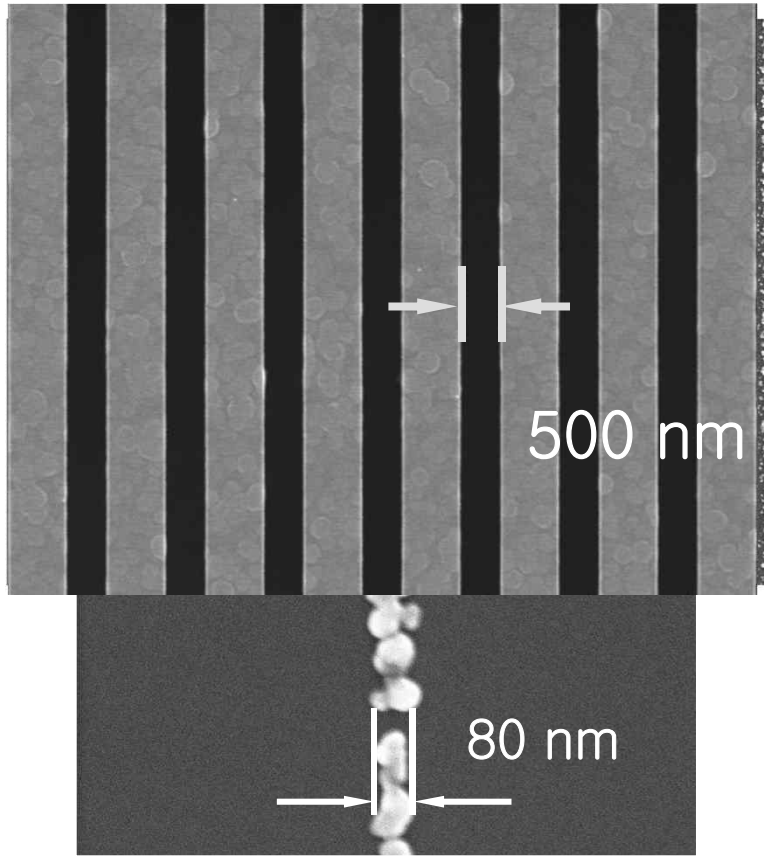




Schematic of stencil translation

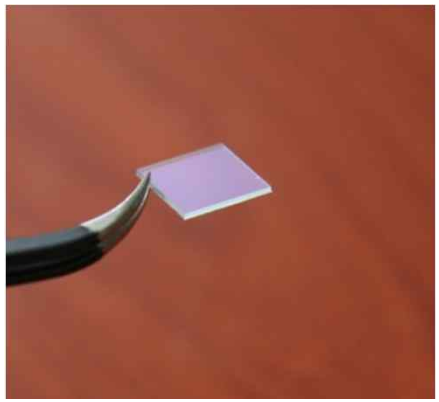
Focusing Nano-Mask

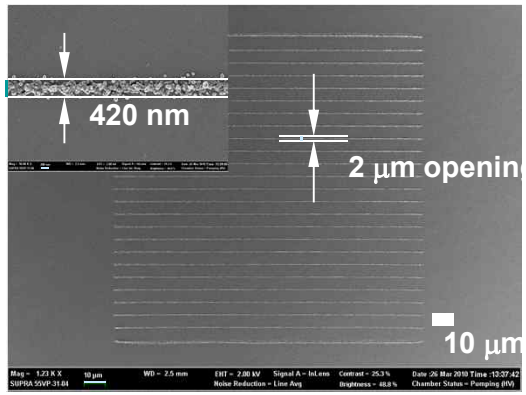
Focusing Mask with 500 nm line openings (manufactured by e-beam lithography)



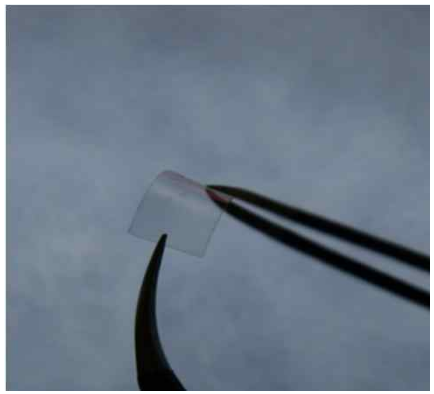
Focused patterning on thick non-conducting substrates (*Small ,Vol. 6, p 2146, 2010*)

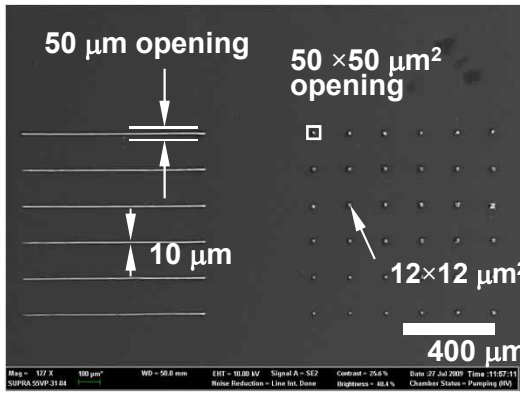
Patterning of electrosprayed 30 nm PSL particles on thick glass(~ 0.7 mm)



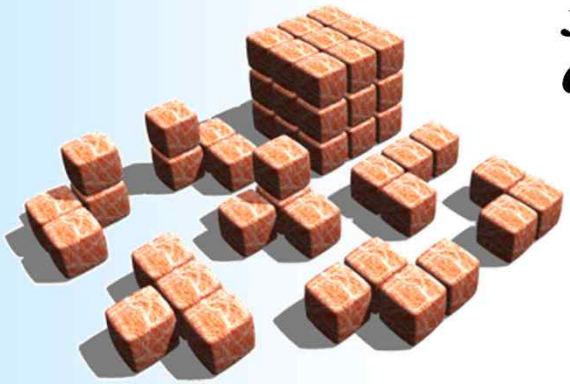


Patterning of electrosprayed 100 nm PSL particles on a flexible PET film (thickness ~ 0.1 mm)



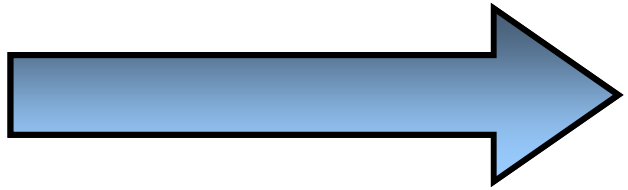


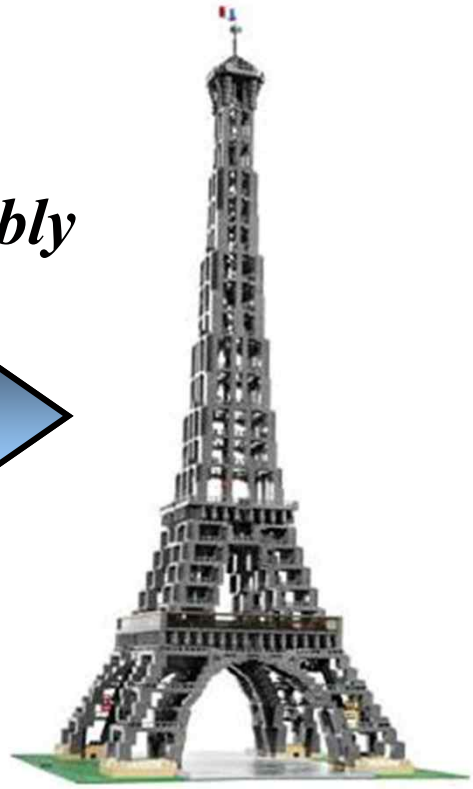
Is it possible to assemble nanoparticles in three dimensions using IAAL(Ion Assisted Aerosol Lithography) ?



Nanoparticles

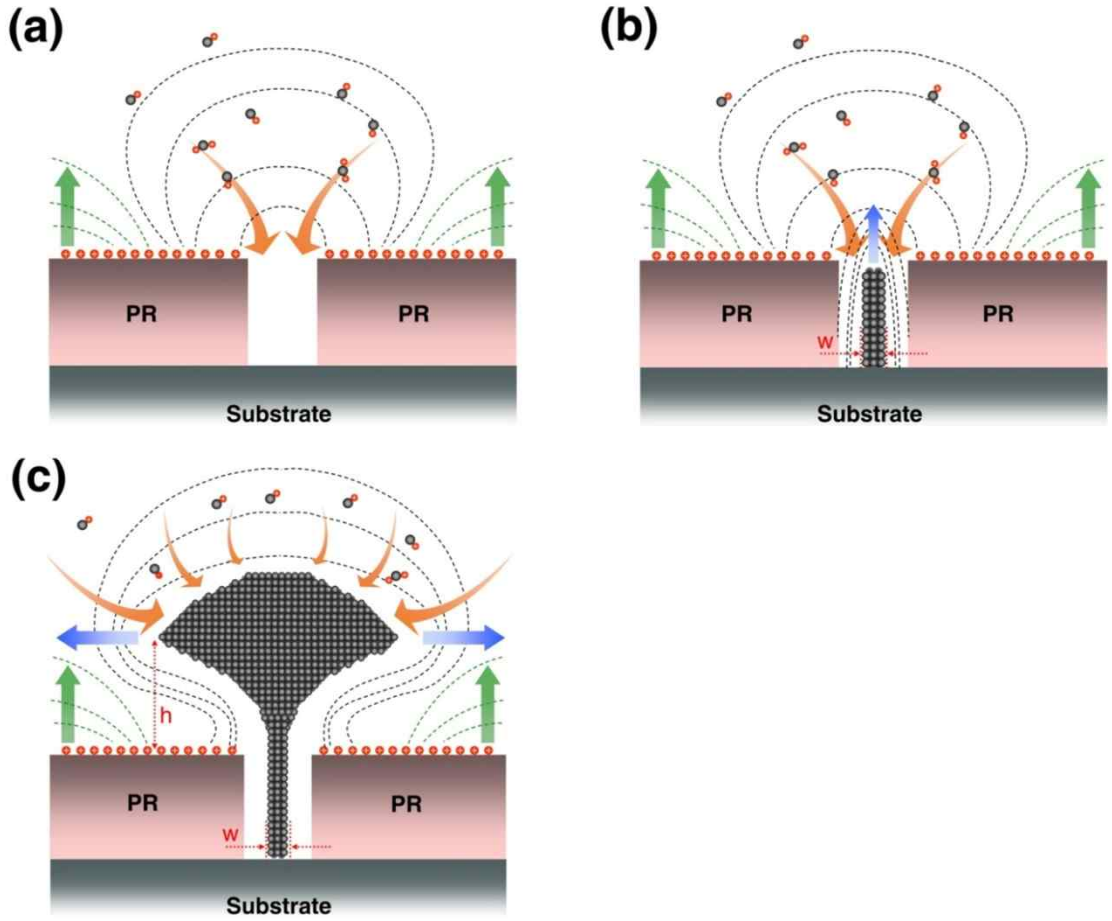
3 Dimensional Assembly of Nanoparticles ?





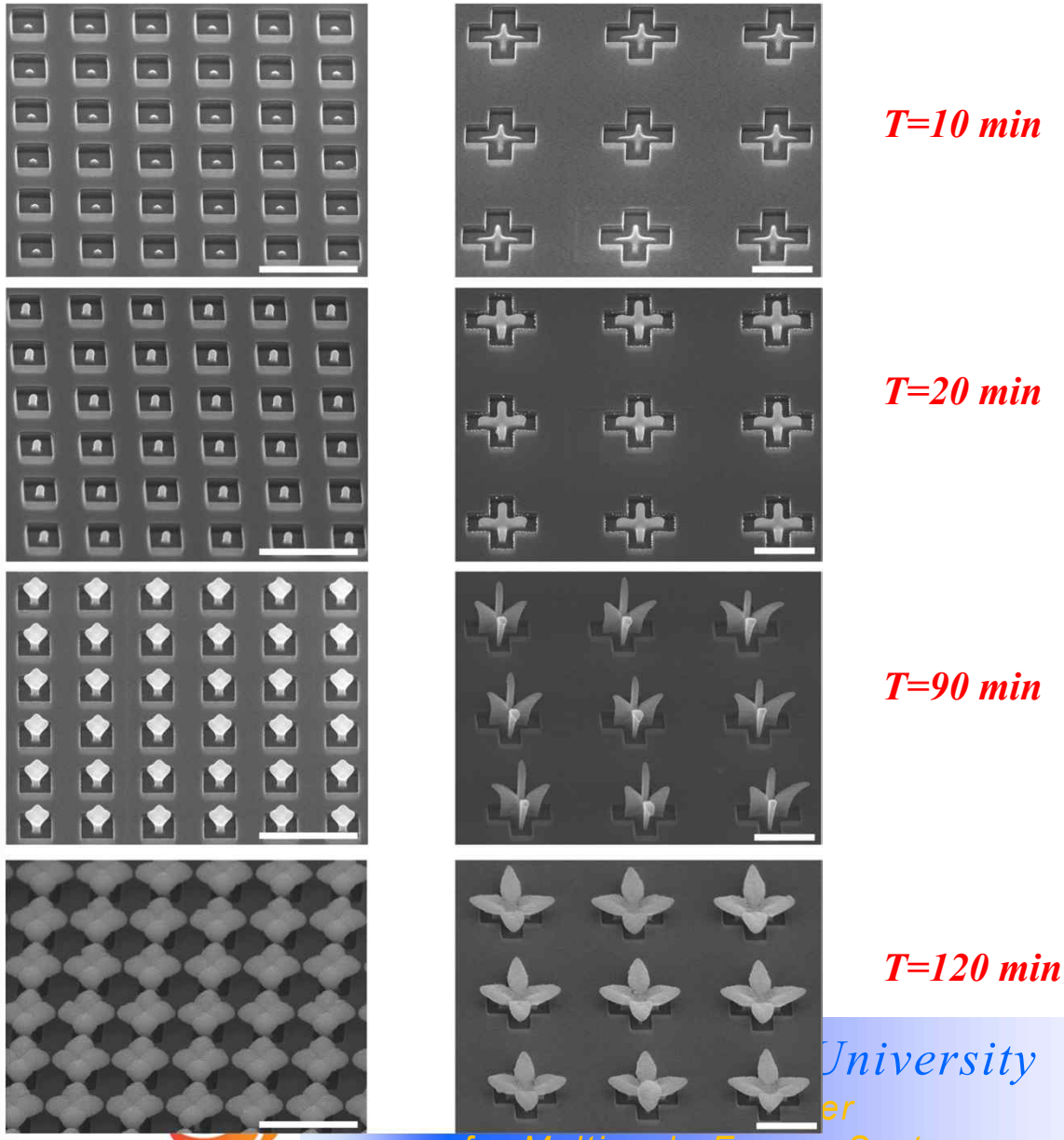
Nanotechnology

Scheme for 3D Assembly of Nanoparticles



Time Dependent Growth of 3D Nanoparticle Structures Arrays

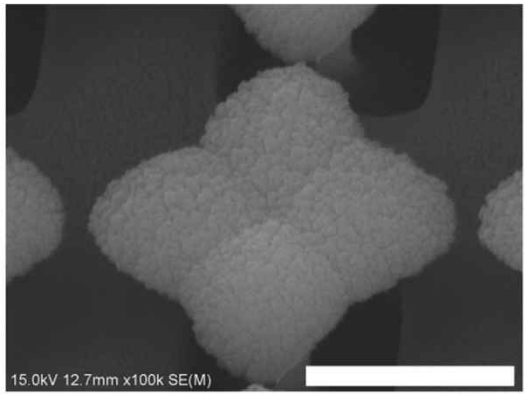
(Presented at 2008 AAAR Conference , Orlando, Abstract book, 2D. 04.)



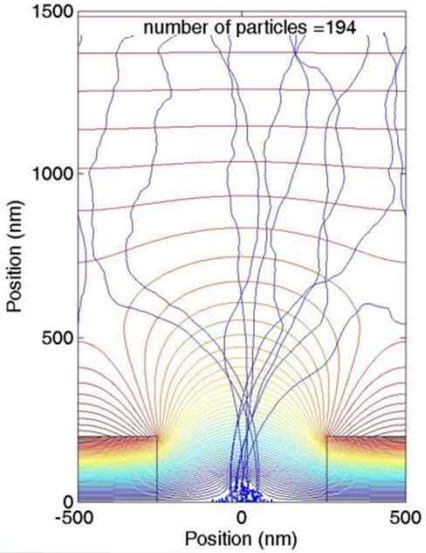
Scale bar : 1.5 μm

Numerical Calculation of Particle Trajectory and Deposition

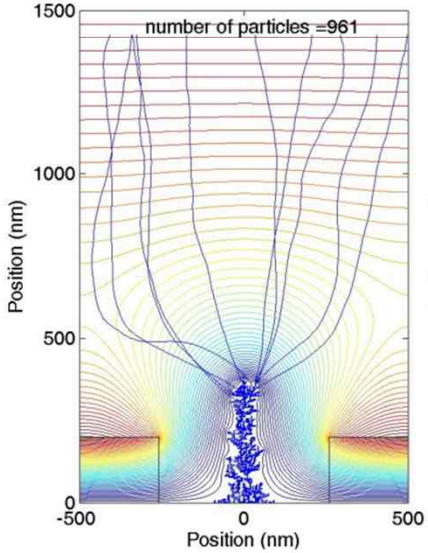
(a)



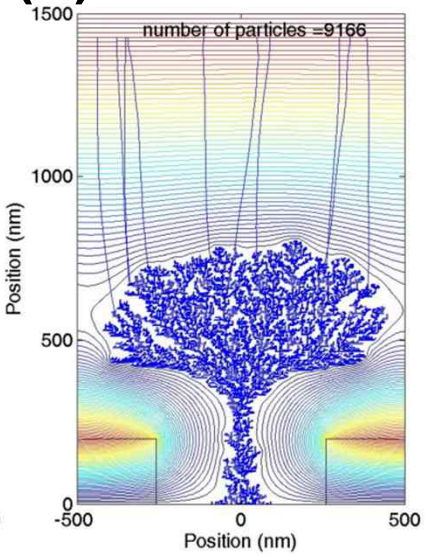
(b)



(c)



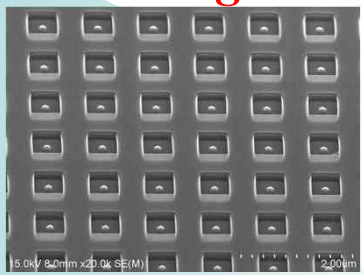
(d)

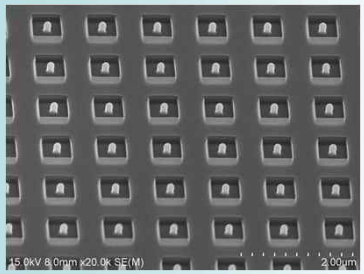


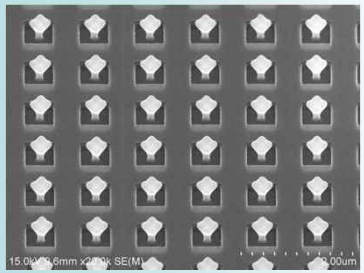
Scale bar : 500 nm

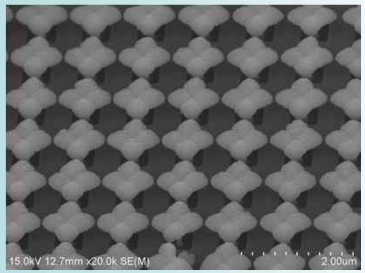
Growth of Nanoparticle Structure

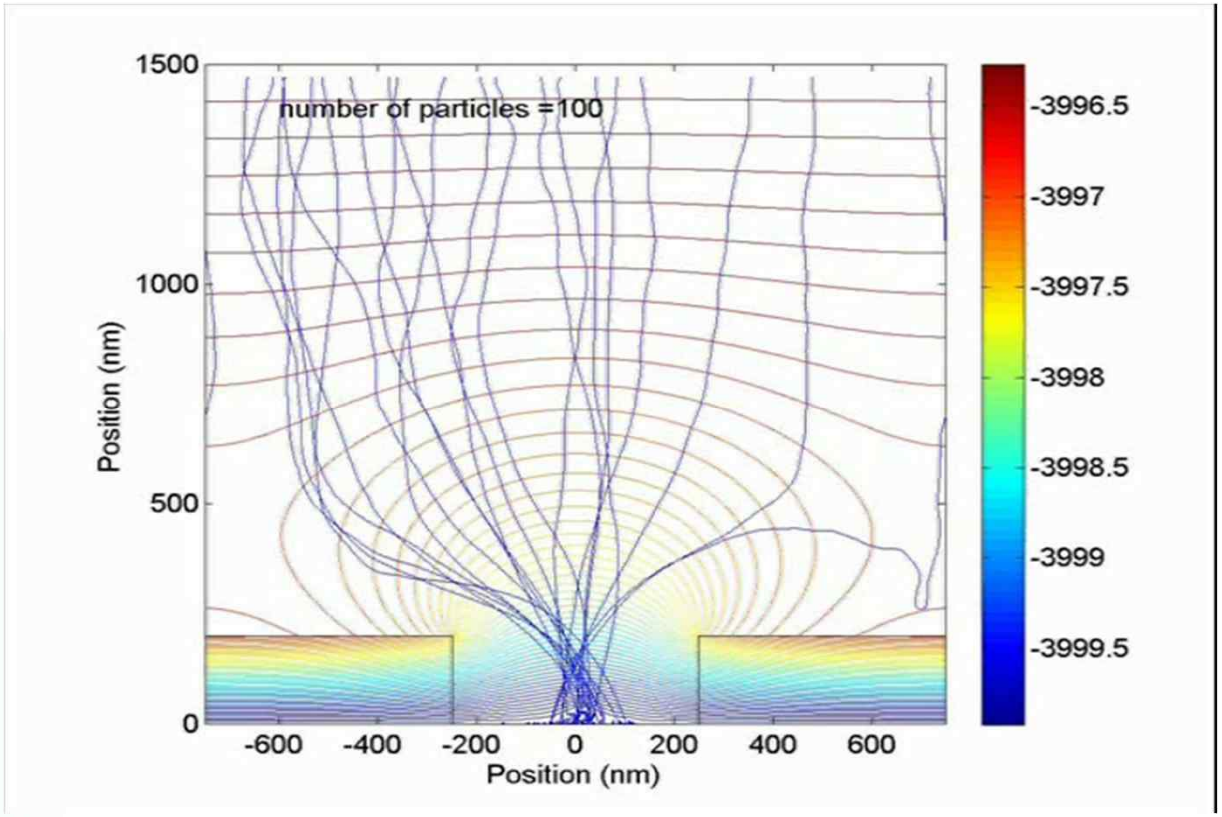
(Nano Letters, "Three dimensional assembly of nanoparticles from charged aerosols", Vol.11, 119, 2011)



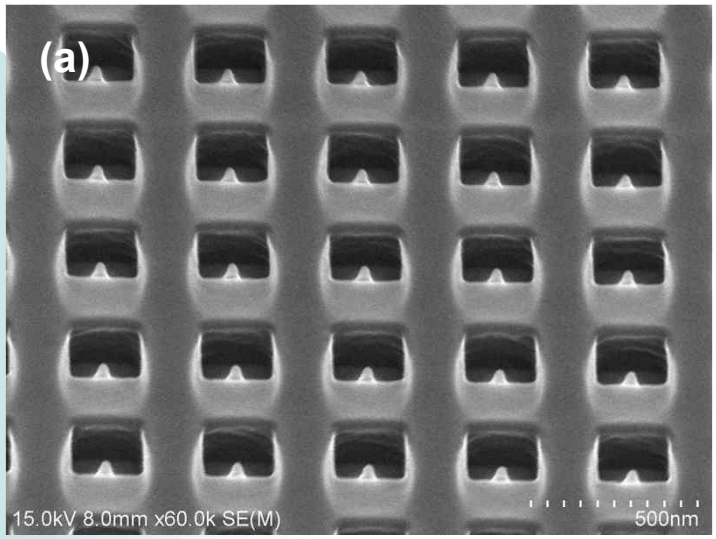


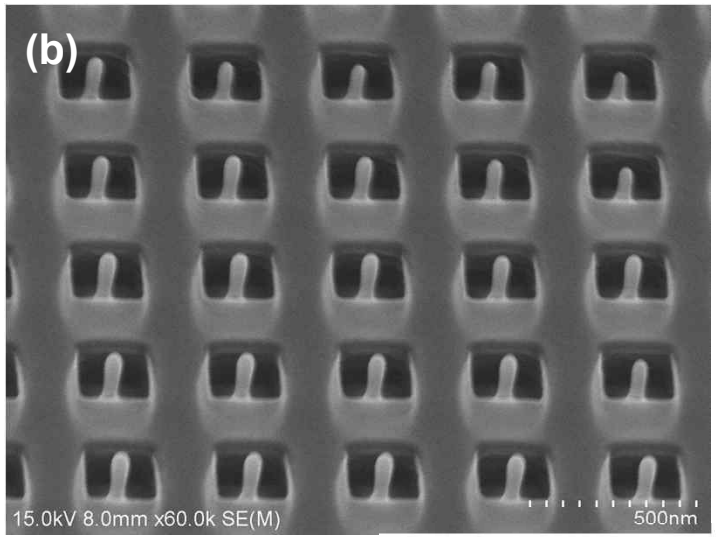


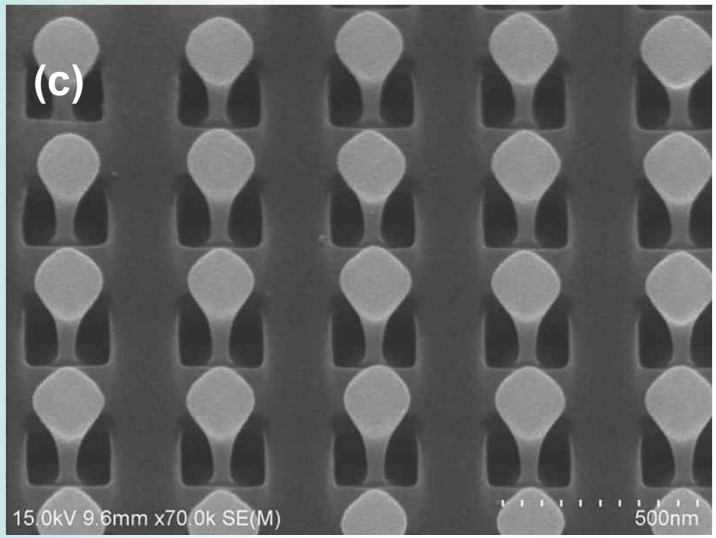


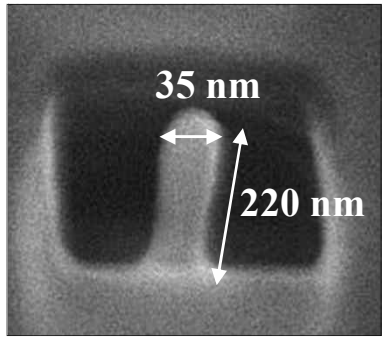


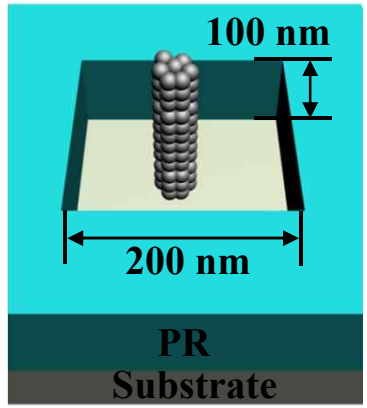
Array of 3D nanostructure of nanoparticles



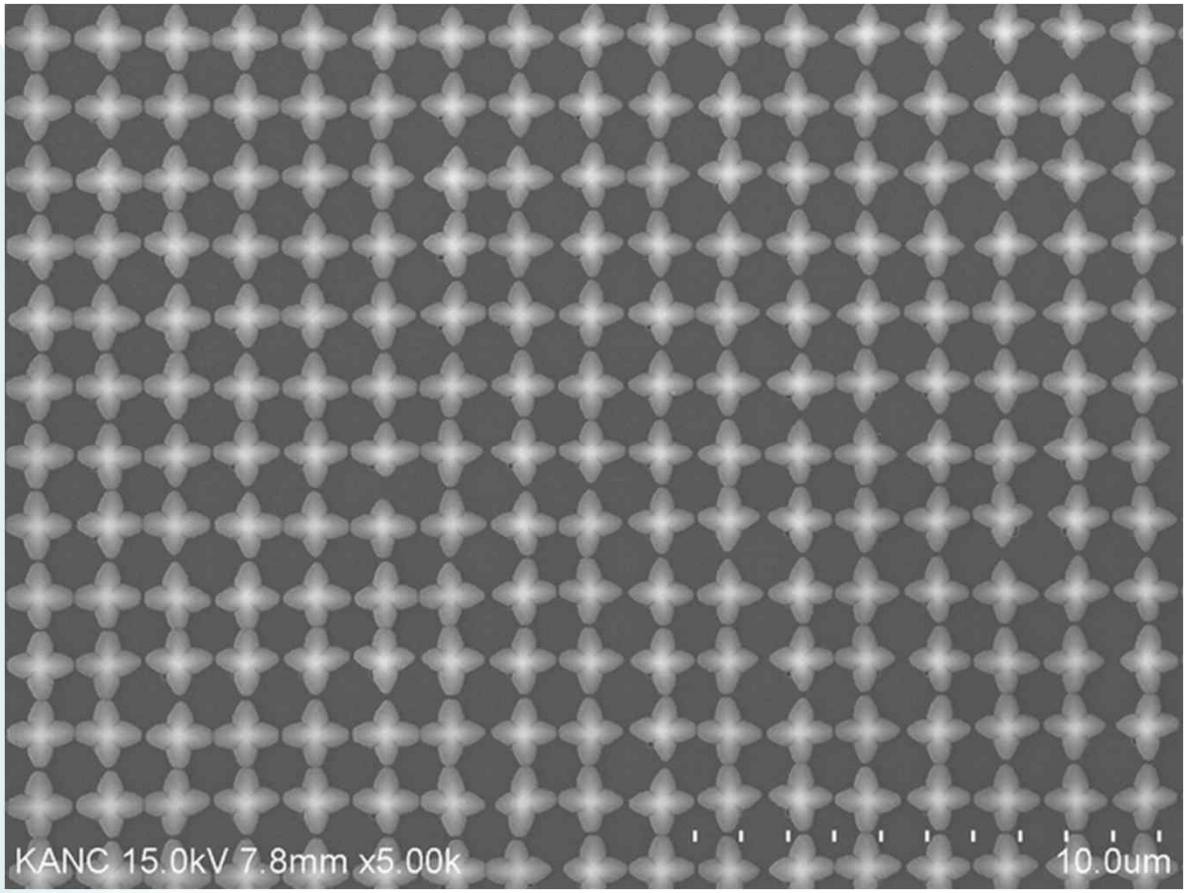


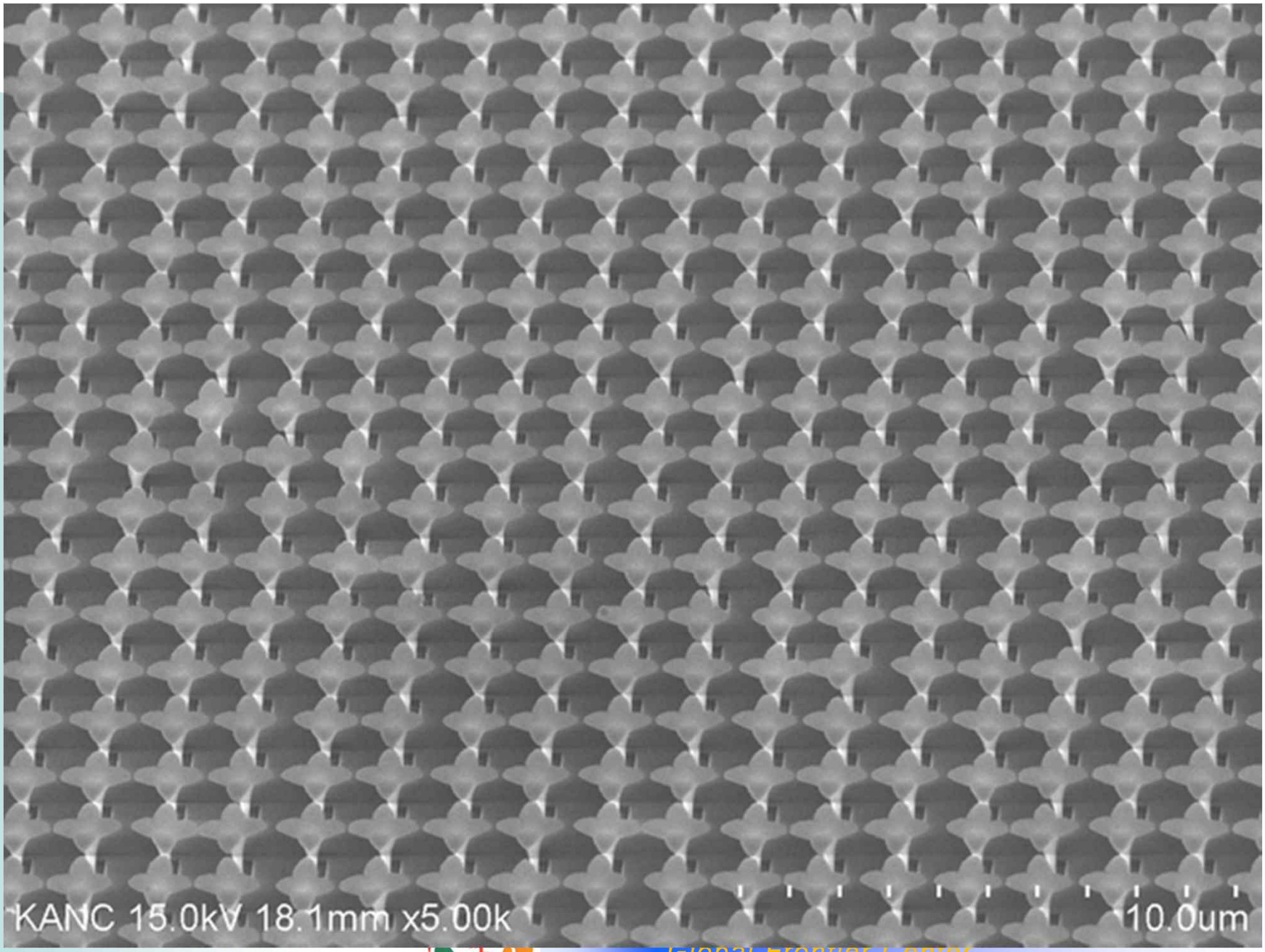






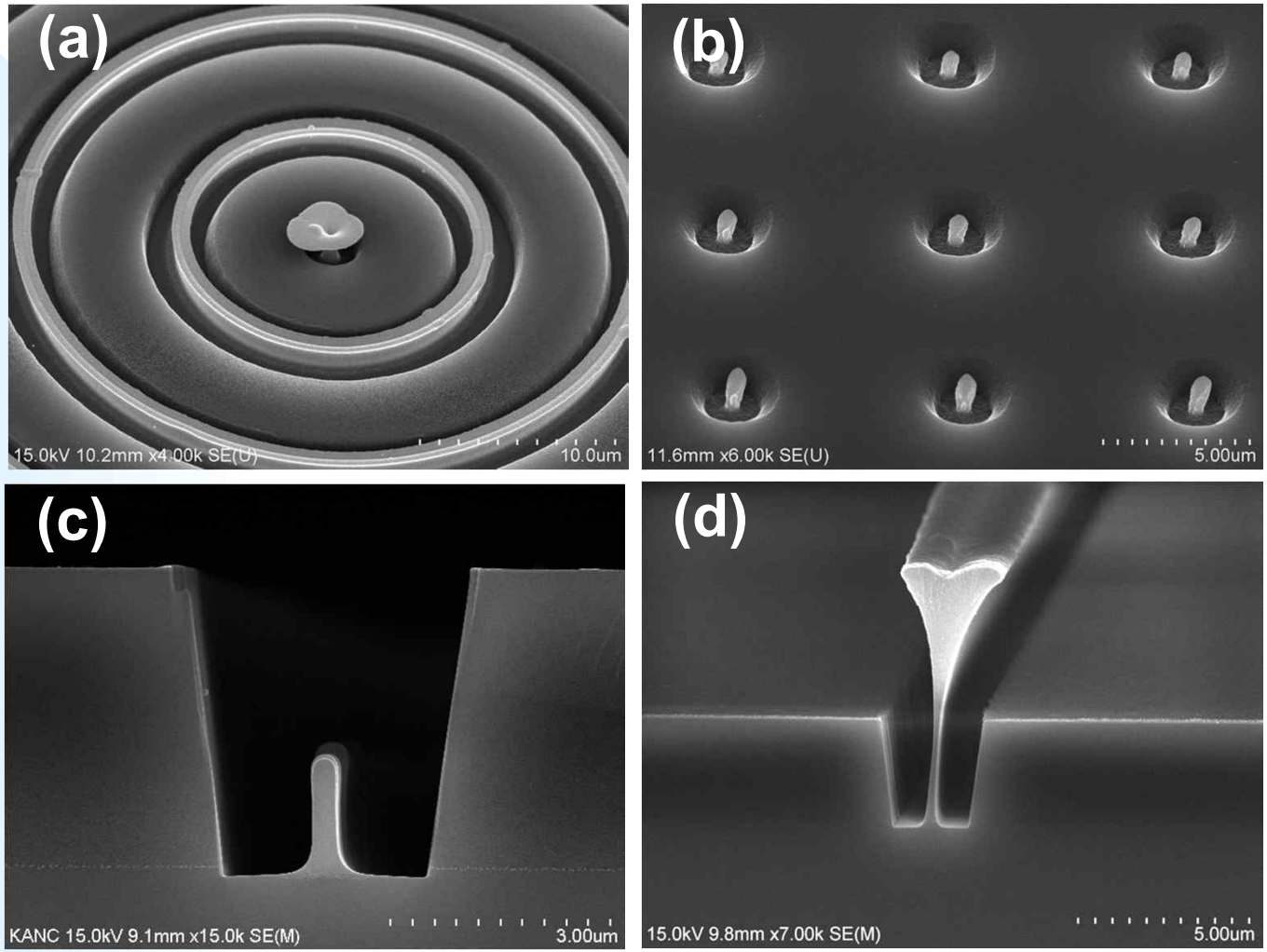
Four-leaf clover like 3D nanostructure array of nanoparticles (Nano Letters, vol. 11, 119)



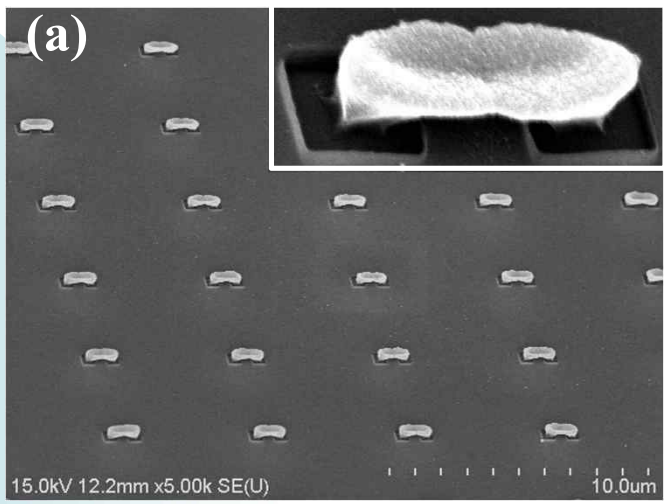

KANC 15.0kV 18.1mm x5.00k
10.0um

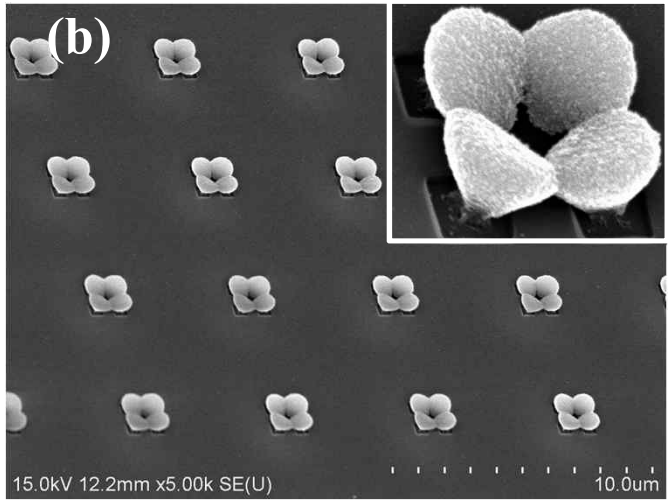
3D Nanoparticle Structures within Micron Scale SiO_2 Patterns

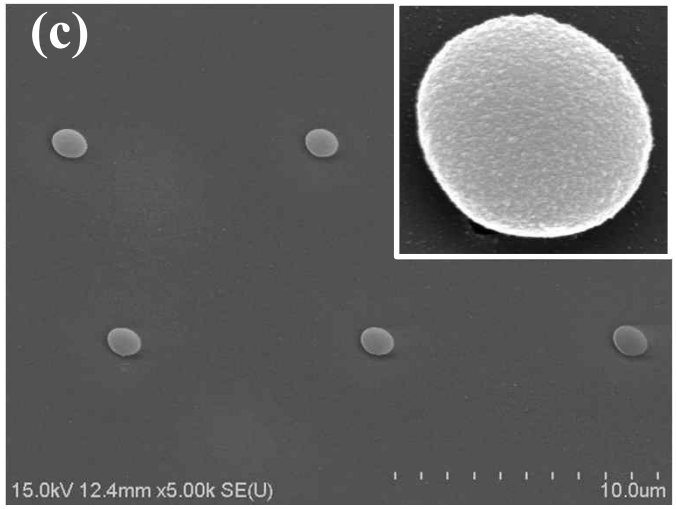
(2008 AAAR Conference, Orlando)



Asymmetric and Isolated Nanoparticle Structures (Nano Letters, 2011)







Pattern width : 500 nm

Applications of Aerosol Assembly of Nanoparticles

: Nanodevices based on 3D nanoparticle array.

Summary

- Aerosol engineering plays an important role for multiscale architecturing which can be a platform for convergence technology.

- "Ion Assisted Aerosol Lithography (IAAL)" is a general methodology of multiscale 3D architecturing: parallel, large area, nanoscale resolution on the surface regardless of metallic or dielectric or flexible film or thick glass at atmospheric pressure.
- Various nanodevices based on 3D nanoparticle assembly such as 3D gas sensors, 3D SERS, 3D solar cells were demonstrated.

Acknowledgements

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