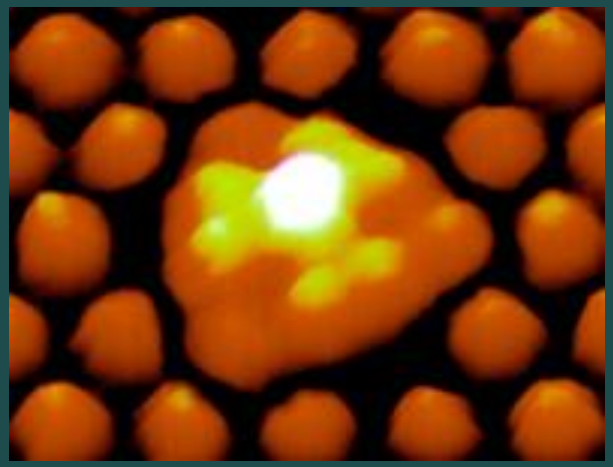
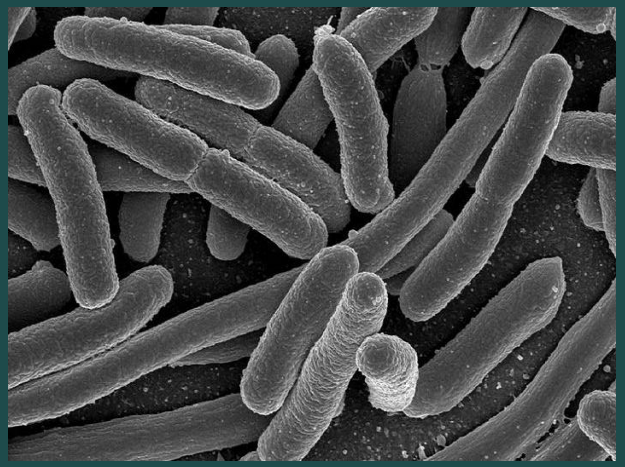
A Voyage from Atoms/Molecules and Clusters/Nanostructures to Bacteria and Planet-Human

Magic-Number Cluster (nm)



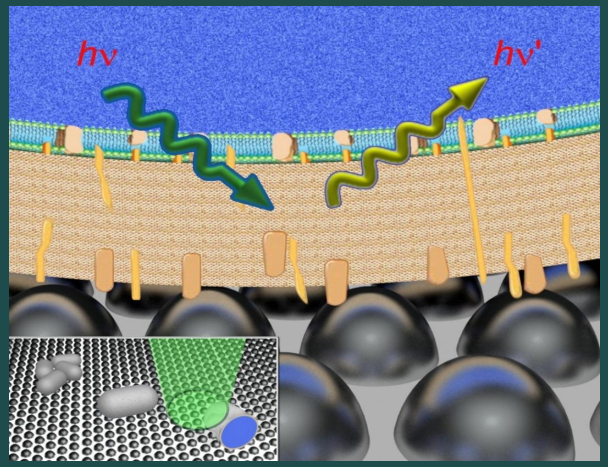
Bacteria (μm)



x10^6

Planet Human (m)

Ag-nanoparticles (10 nm)



Homo Sapiens (m)

x10^6

Planet Earth (Mm)

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IAMS (6/16//2015)

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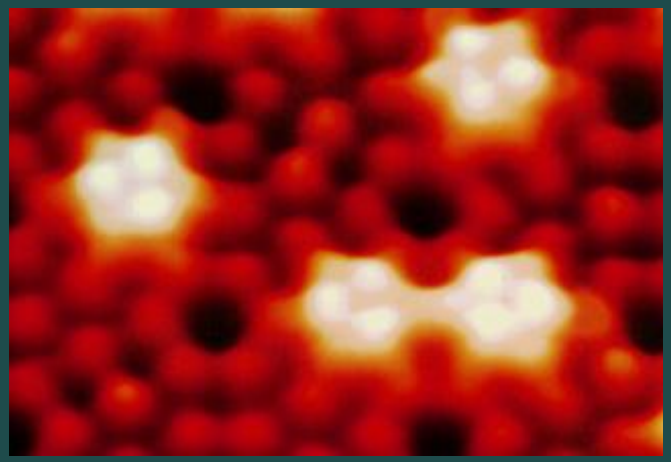
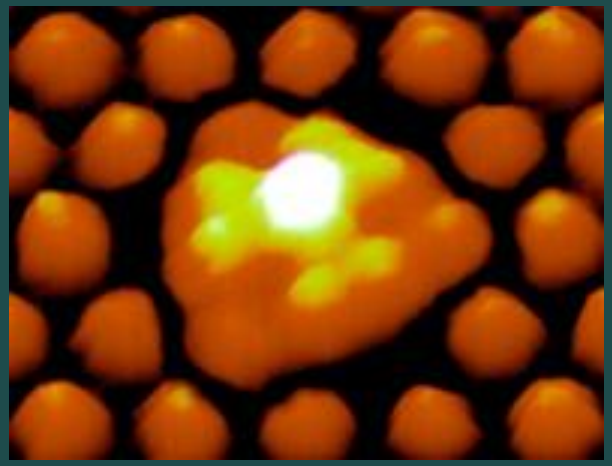
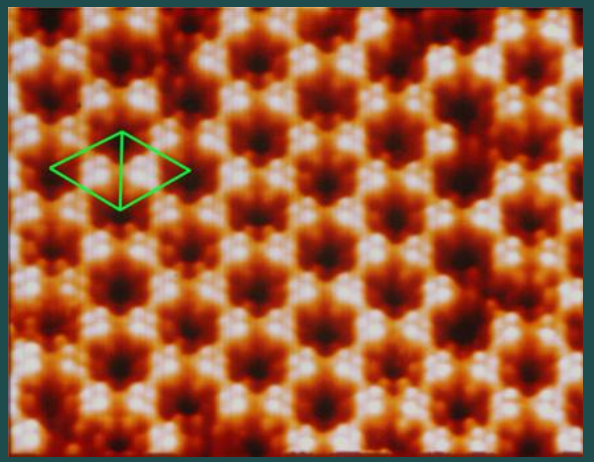


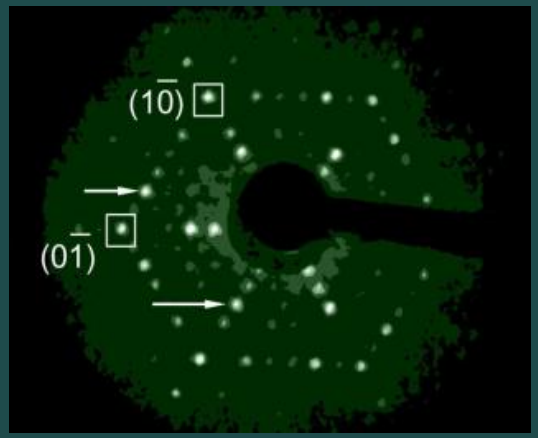
PRB 2001



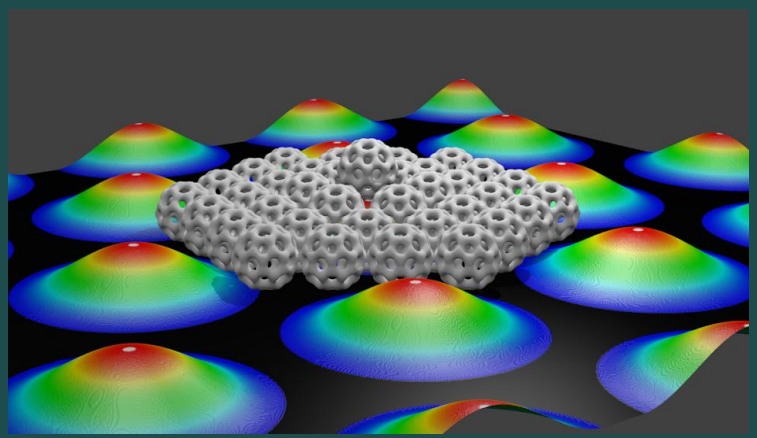
PRL 1998, PRB 1999



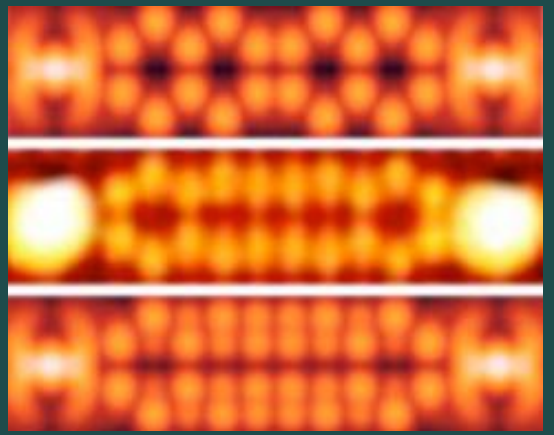
PRB 2001



PRL 2004



Nat. Comm. 2013



PRL 2011

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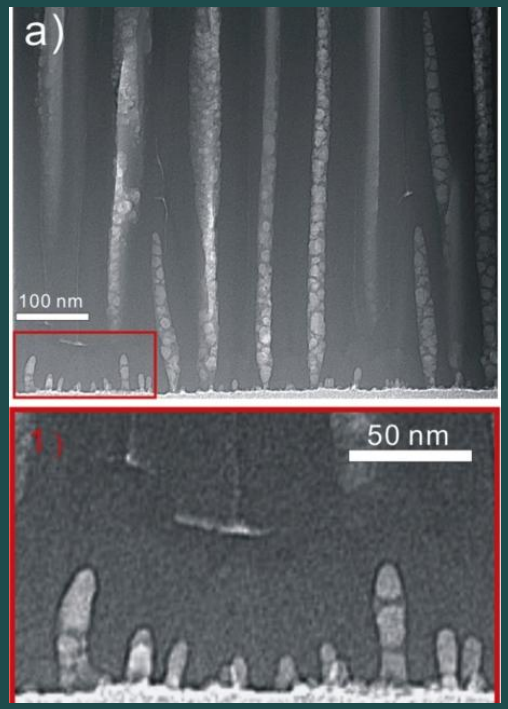

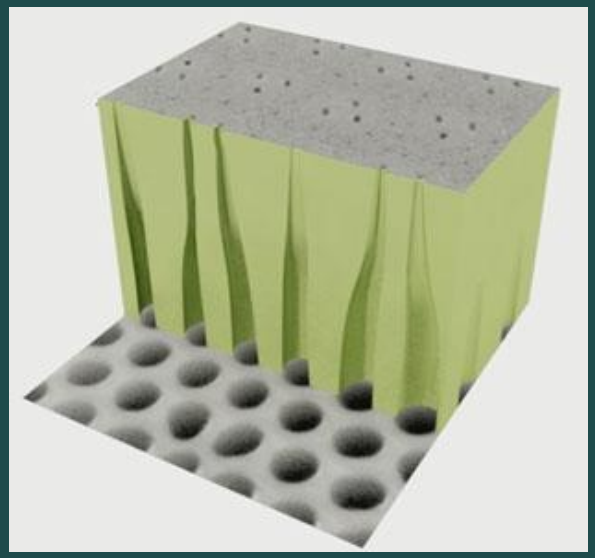

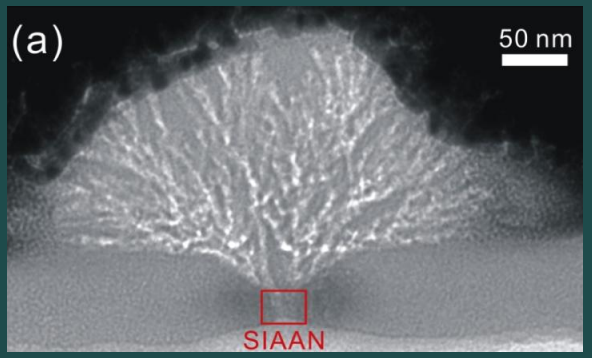

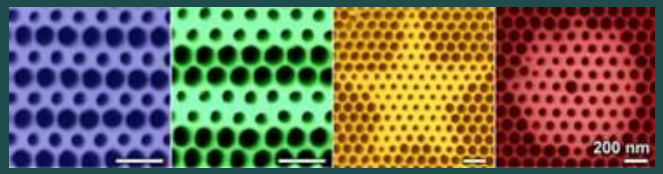

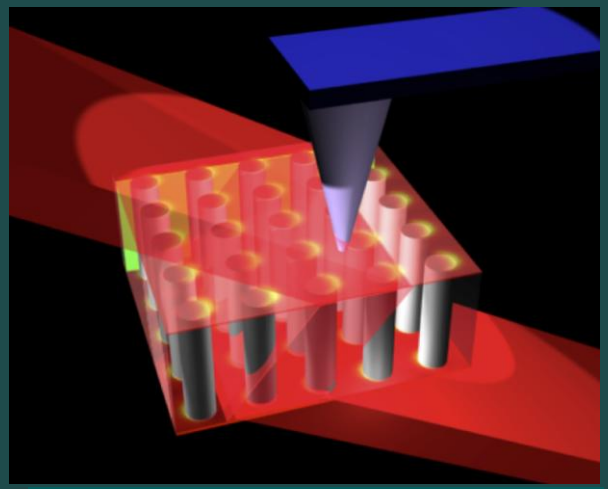

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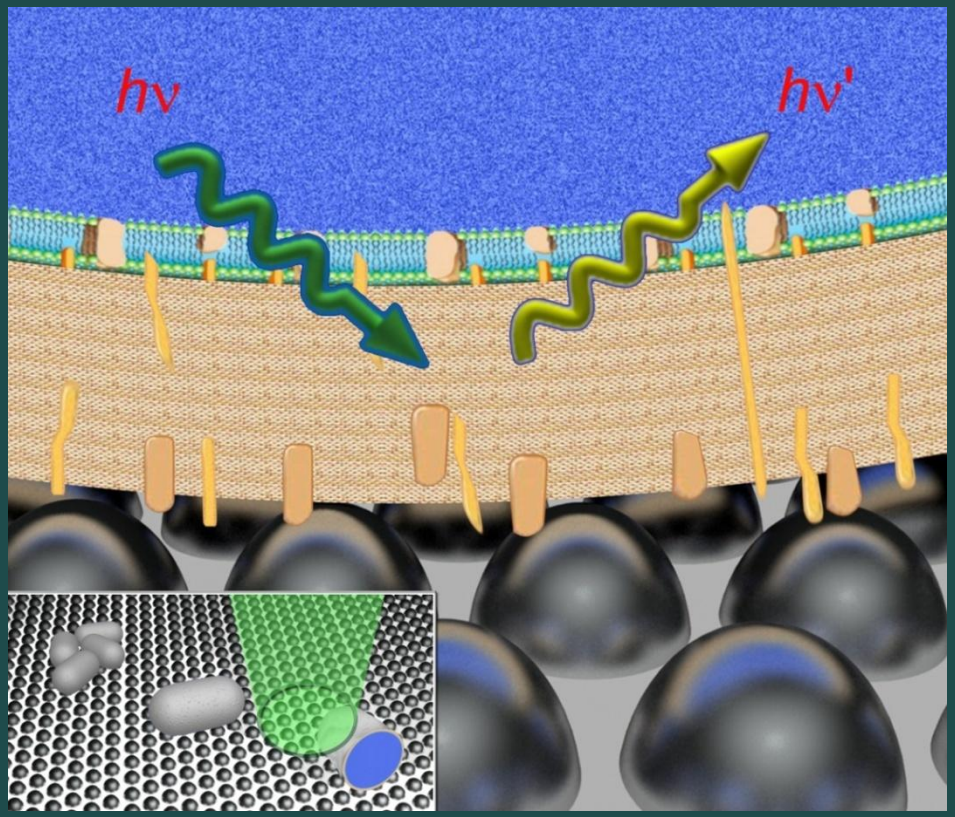
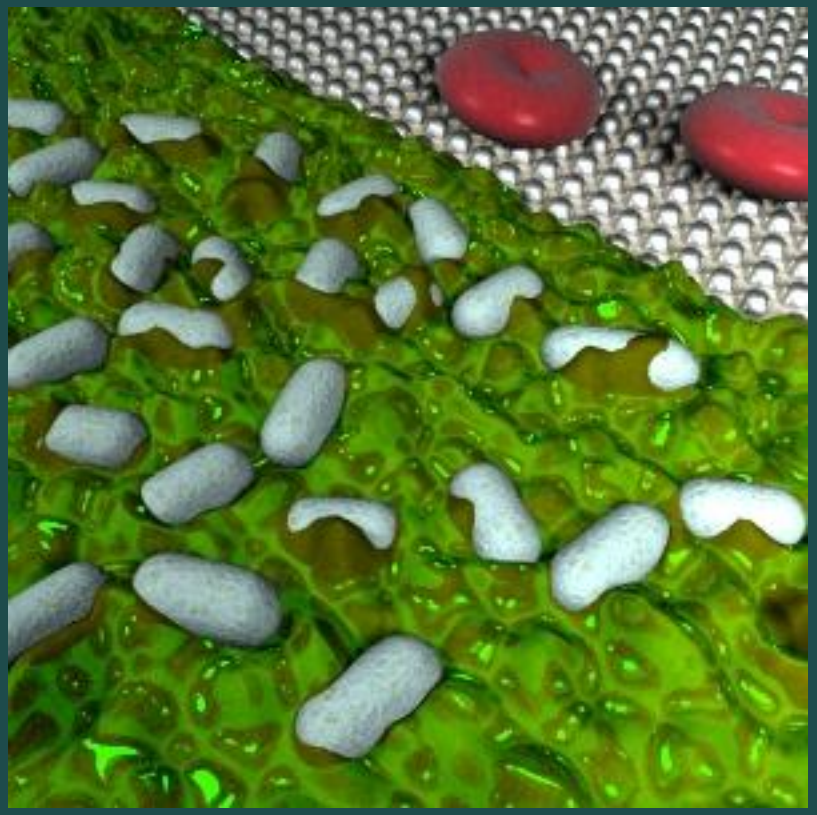


Plos One 2009



Nat. Comm. 2011

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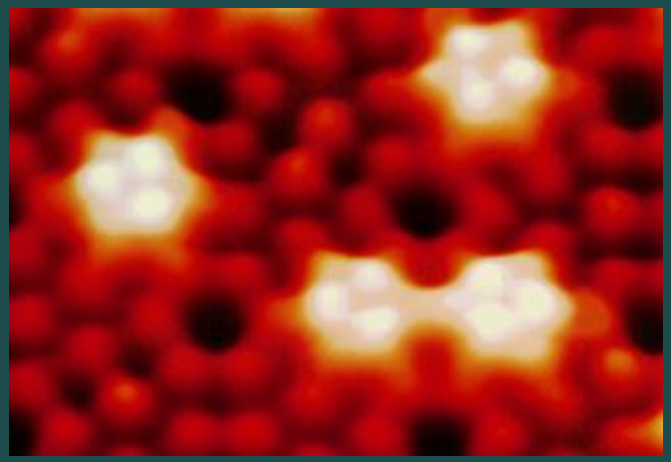
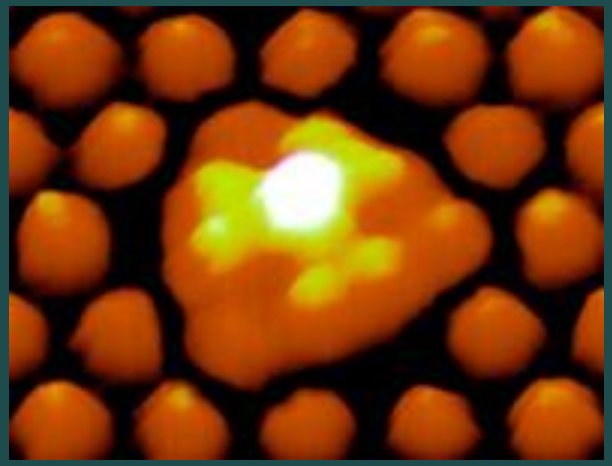
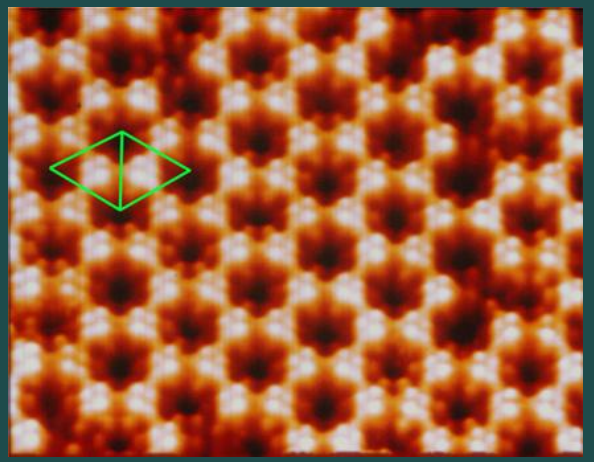


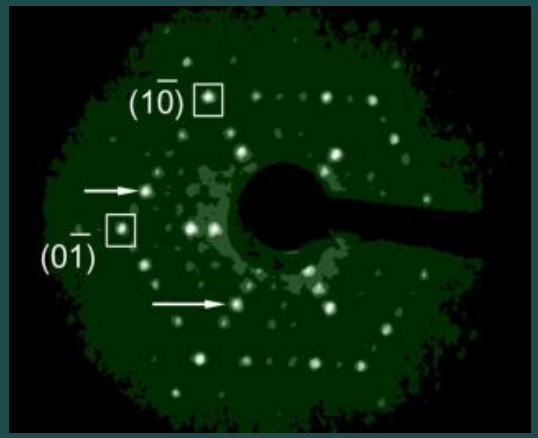
PRB 2001



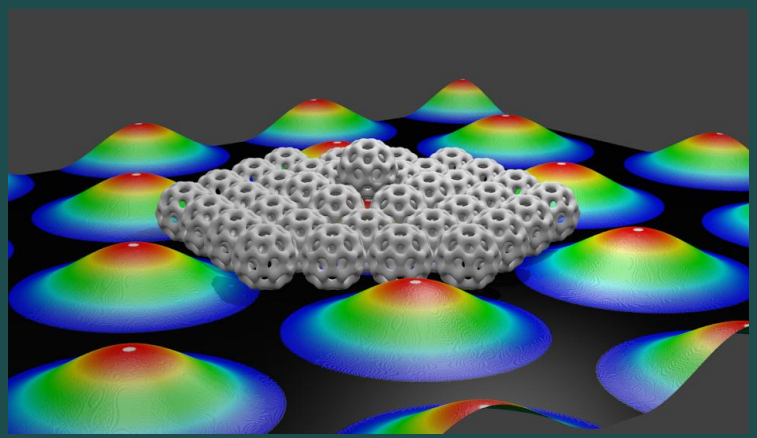
PRL 1998, PRB 1999



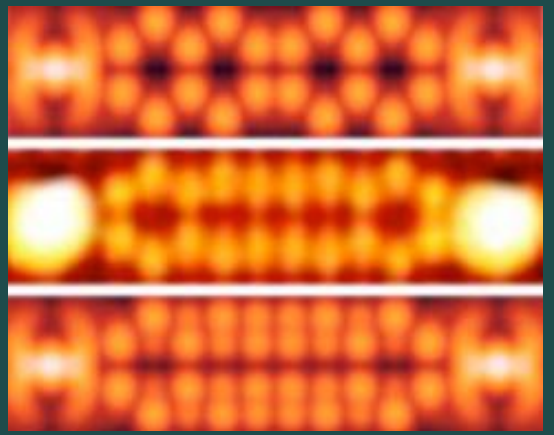
PRB 2001



PRL 2004



Nat. Comm. 2013



PRL 2011

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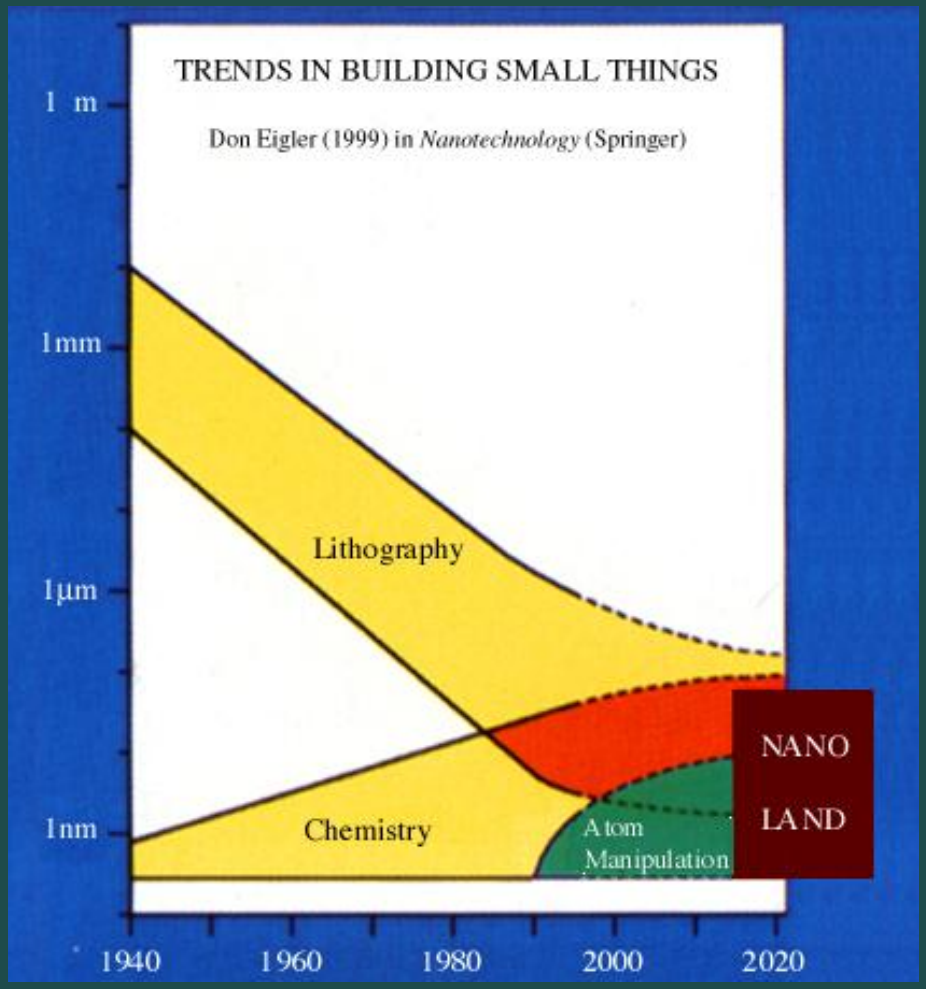
Why Bother Creating an Array of Mono-Dispersed Nanostructures?



For nonspecialists,

Nanotechnology is:

- The creation of <u>useful</u> materials, devices, and systems through the <u>control</u> of matter on the nanometer-length scale
- The exploitation of <u>novel</u> properties and phenomena at that scale

P. Alivisatos, M.C. Roco, &
R.S. Williams, IWGN Report (1999)

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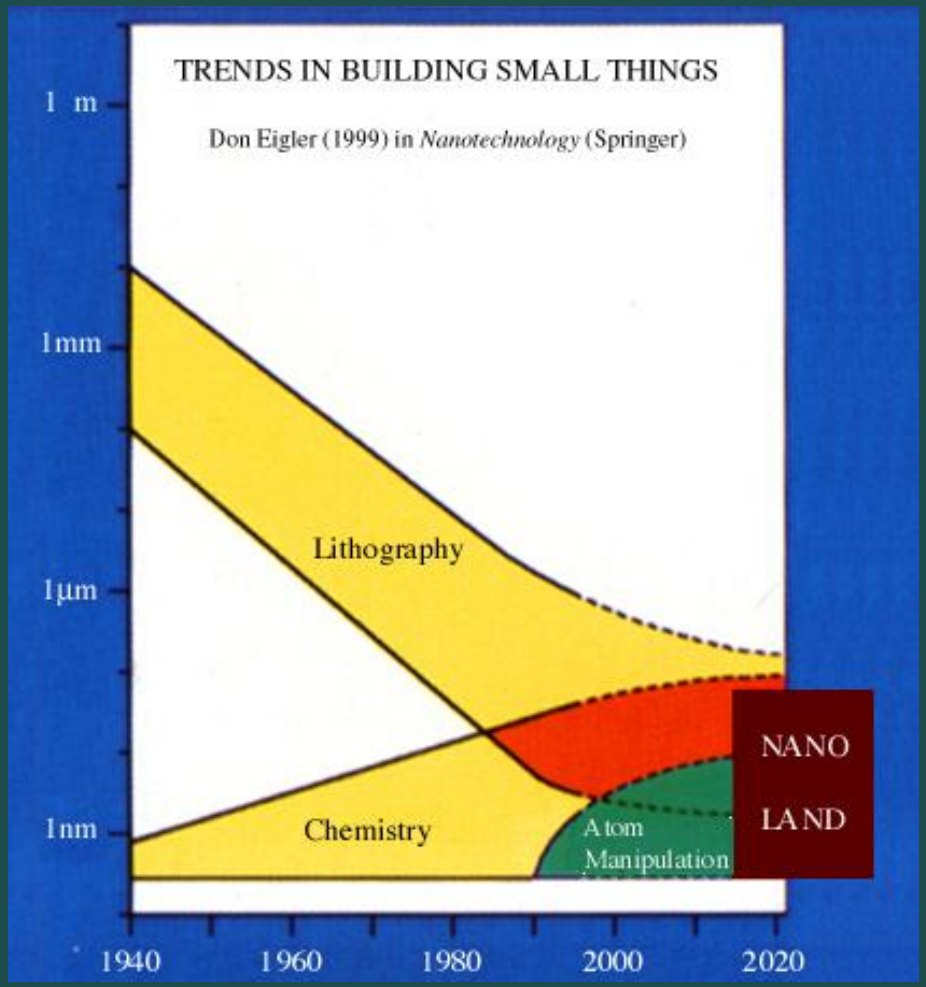

For specialists,

Nanostructures are the natural home of engineered quantum effects.

Novel properties are expected to originate from quantum size confinement, wave-like electron transport, and predominance of interfacial phenomena.

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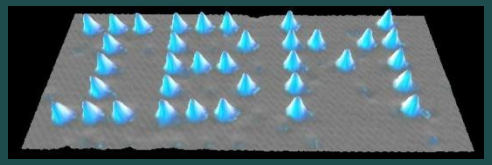
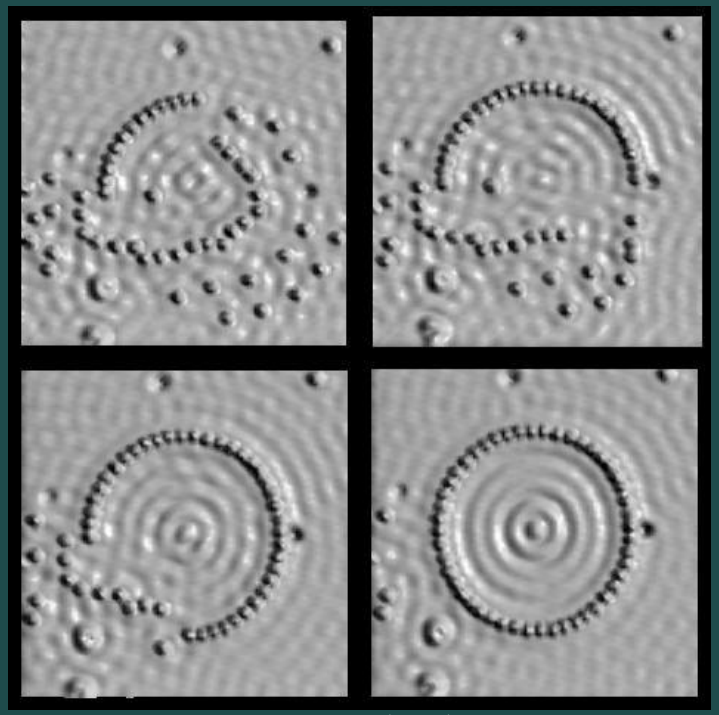
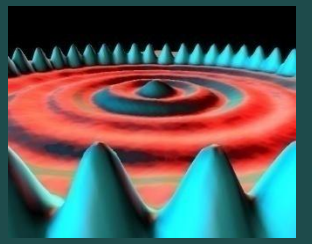
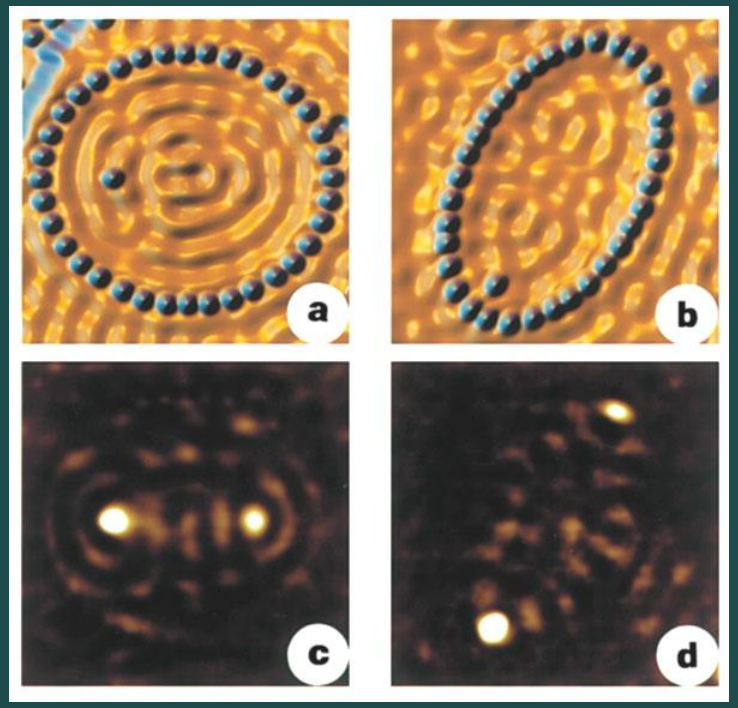
The Art and Science of Atomic Manipulation: from Quantum Corral to Quantum Mirage



Xe/Ni(111)
D.M. Eigler
E.K. Schweizer
Nature 344
(1990) 524







Fe/Cu(111)
M.F. Crommie, C.P. Lutz, D.M. Eigler
Science 262 (1993) 218

Co/Cu(111)
H.C. Monoharan, C.P. Lutz, D.M. Eigler
Nature 403 (2000) 512

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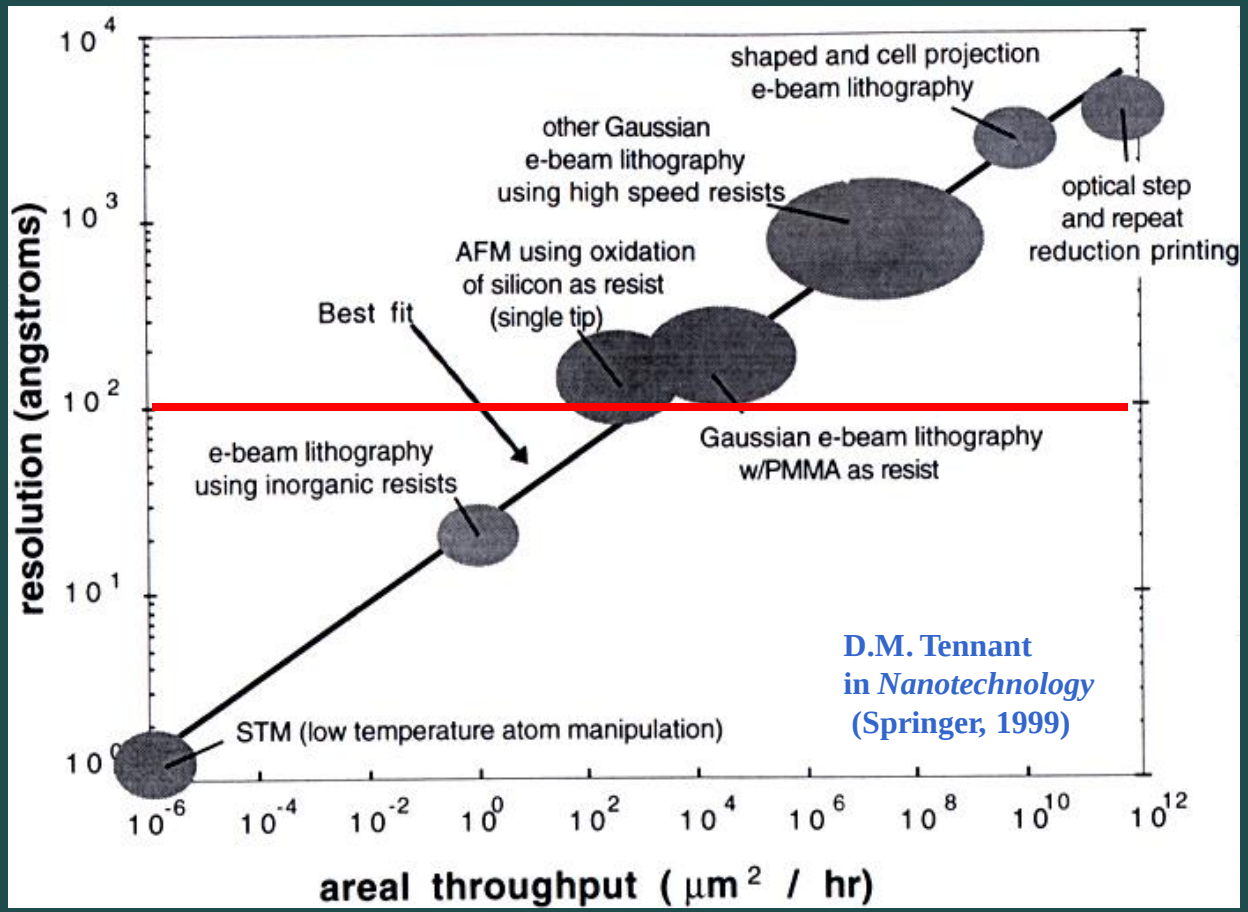

Beautiful Art & Science → Profitable Technology

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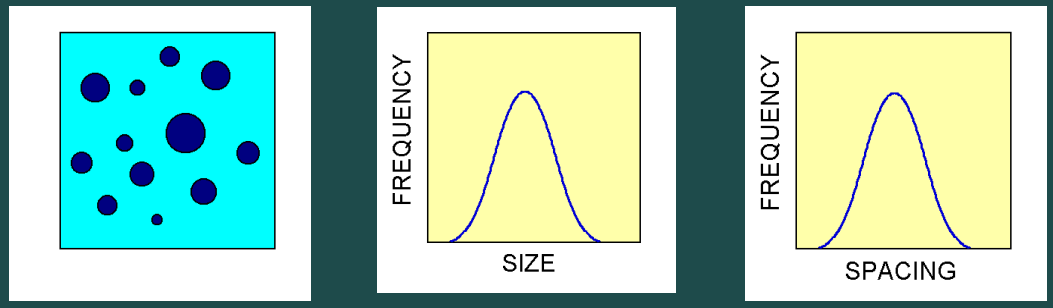
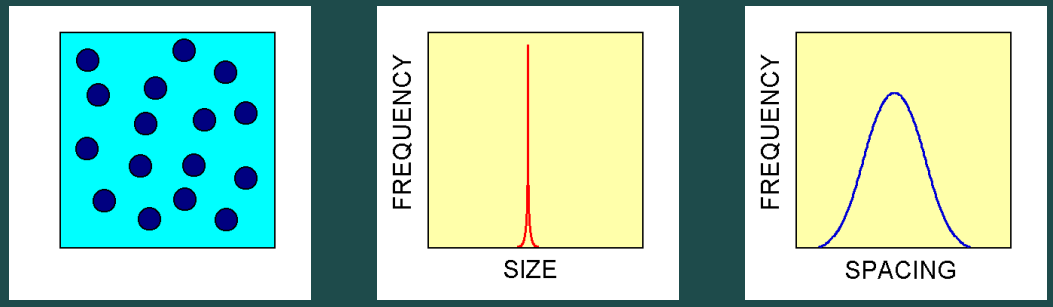
Size and Spacing Dispersion of an Array of Nanoclusters

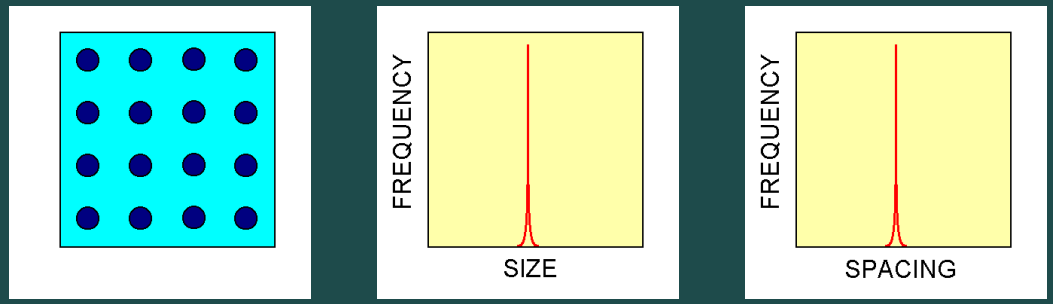
Random cluster array



Random array of identical (magic) clusters



Ordered array of identical (magic) clusters



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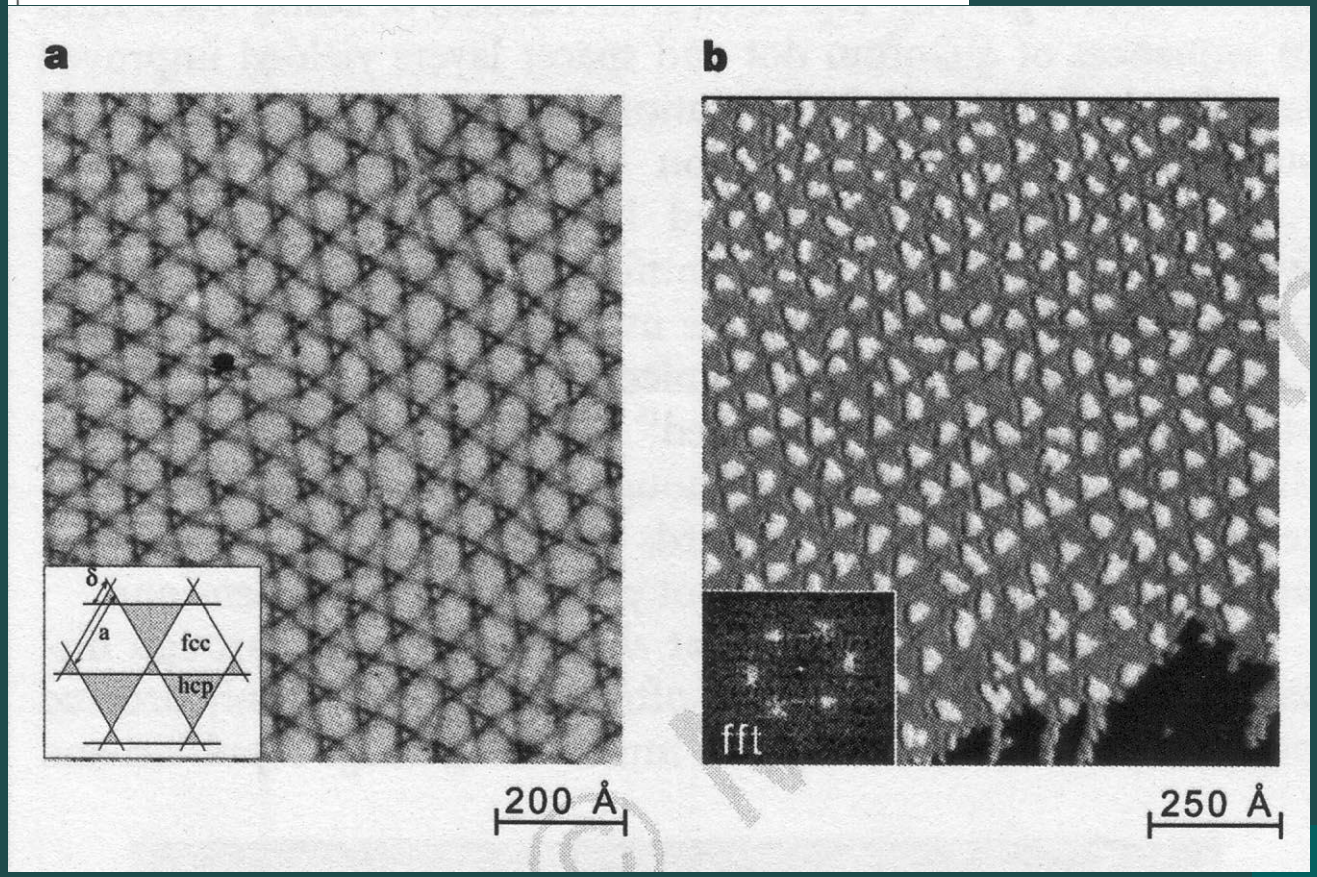
Self-organized growth of nanostructure arrays on strain-relief patterns

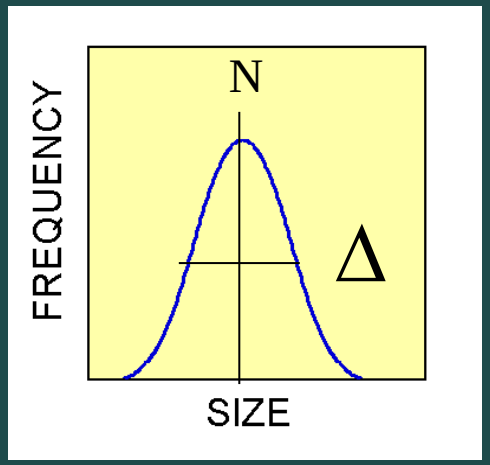
Harald Brune, Marcella Giovannini, Karsten Bromann & Klaus Kern

Institut de Physique Expérimentale, EPF Lausanne, CH-1015 Lausanne, Switzerland

Dislocation networks on 2-ML Ag/Pt(111) substrate surface.

Ag-nanoclusters formed by depositing 0.1 ML of Ag at 110K.





$$\Delta \sim (N)^{1/2}$$

Nature 394 (1998) 451

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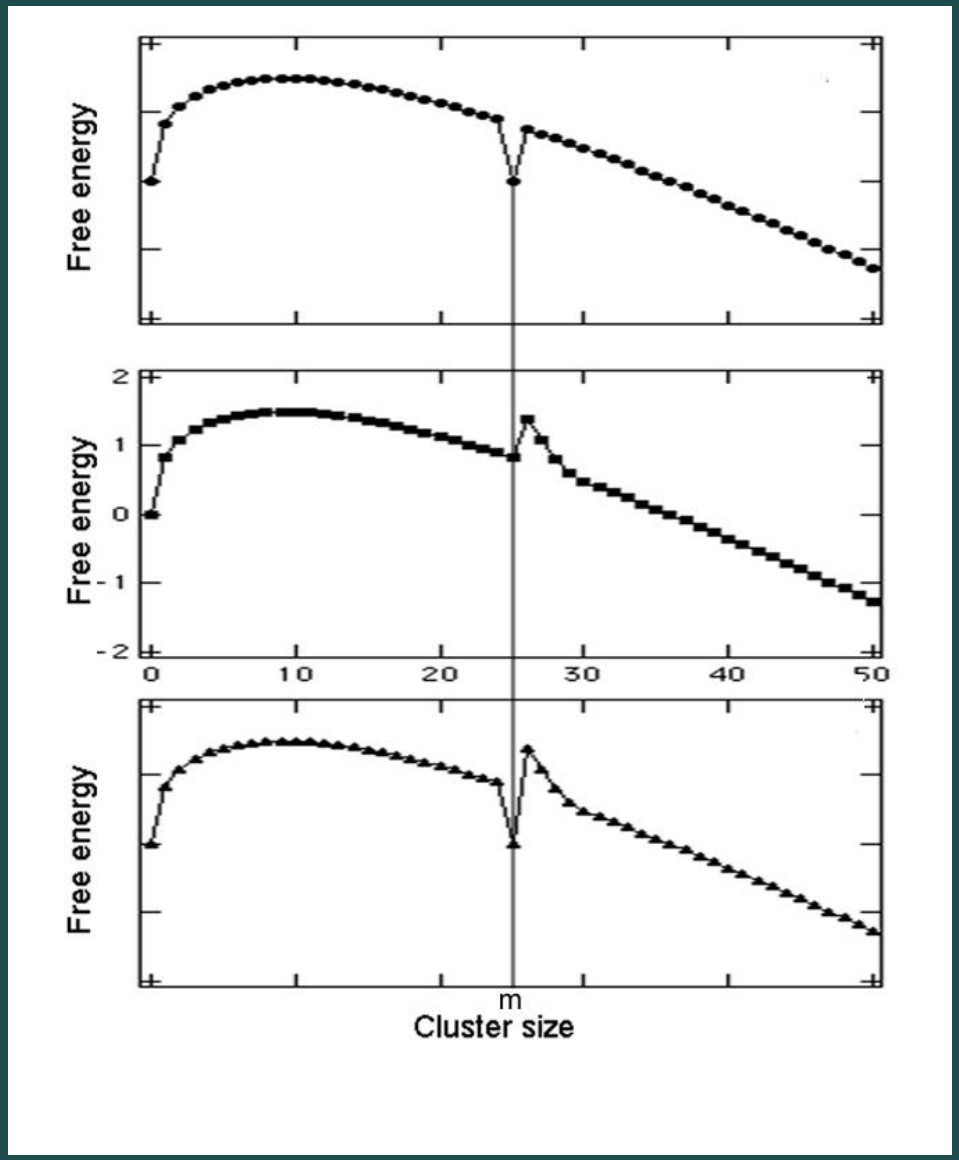
Free energy of clusters formation



in 3d

$\Delta G = -ar^3 + br^2$

$-a'N + b'N^{2/3}$

in 2d

$\Delta G = -ar^2 + br$

$-a'N + b'N^{1/2}$

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Electronic Shell Closure of Magic-Number Cluster

VOLUME 52, NUMBER 24 PHYSICAL REVIEW LETTERS 11 JUNE 1984

Electronic Shell Structure and Abundances of Sodium Clusters

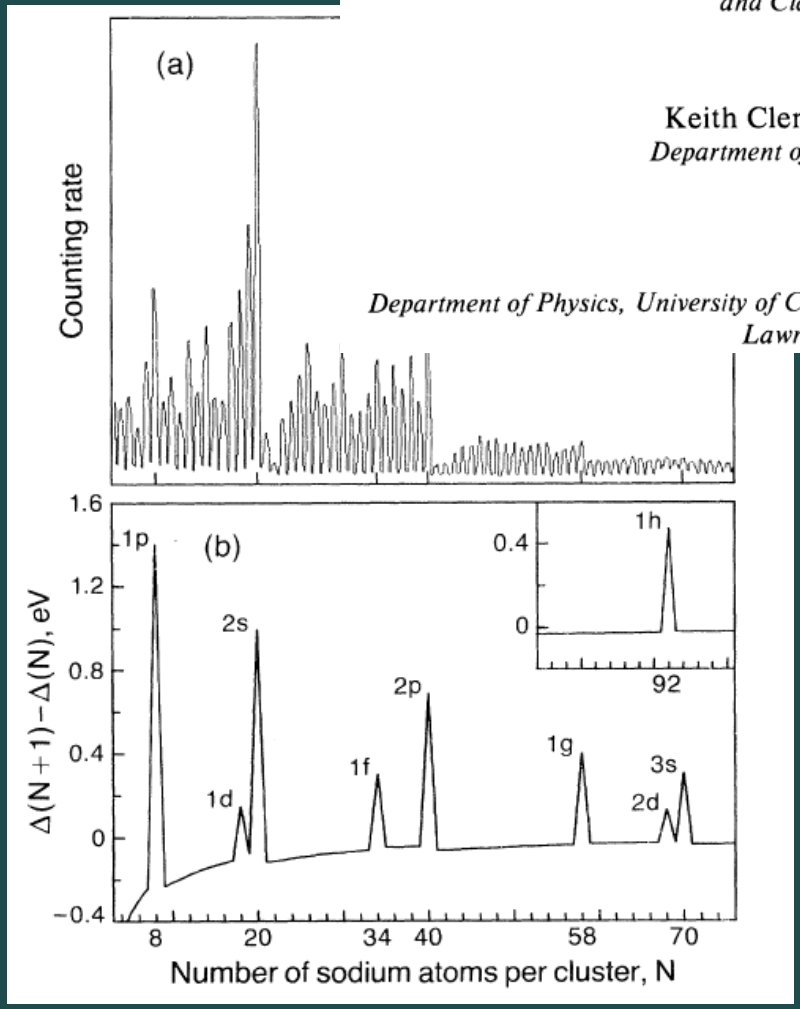
W. D. Knight
Department of Physics, University of California, Berkeley, California 94720, [a]
and Clarendon Laboratory, Oxford OX1 3PU, United Kingdom

and

Keith Clemenger, Walt A. de Heer, and Winston A. Saunders
Department of Physics, University of California, Berkeley, California 94720

and

M. Y. Chou and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720



$$U(r) = -\frac{U_0}{\exp[(r - r_0)/\epsilon] + 1}$$

Mei Yin Chou
Director
IAMS (2011~)

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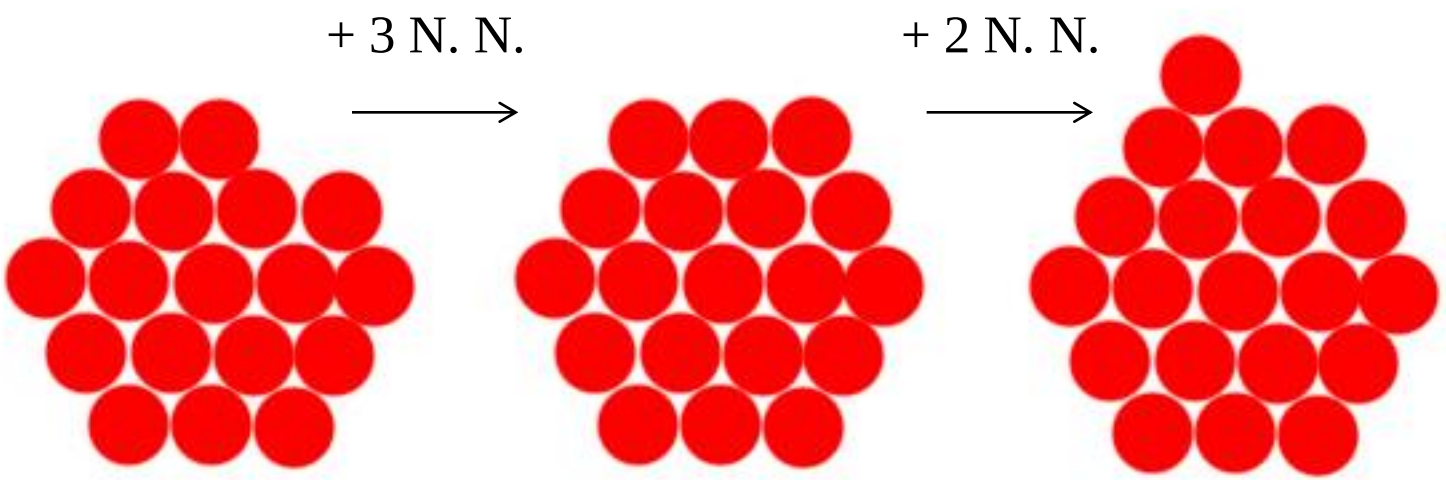
Geometric Shell Closure Magic-Number Cluster



Geometrically Closed

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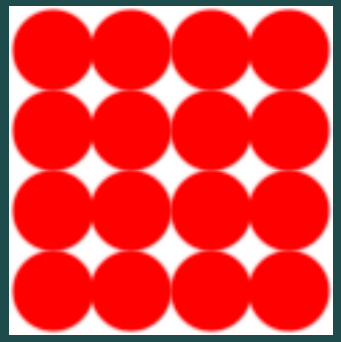
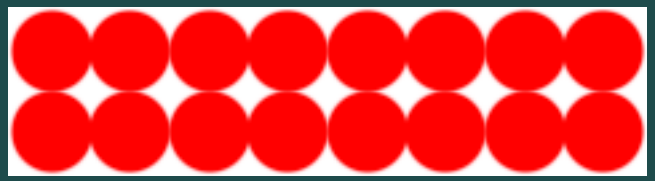
Geometric Shell Closure

NNN = 24



NNN = 16x(4/2) - (12x1- 4x1)
= 24

NNN = 22



NNN = 16x(4/2) - (16x1 - 4x1)
= 22

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Self-Assembly of C_{60} Islands on the Si(111)-√3×√3-(Au,In)

Experimental Observations

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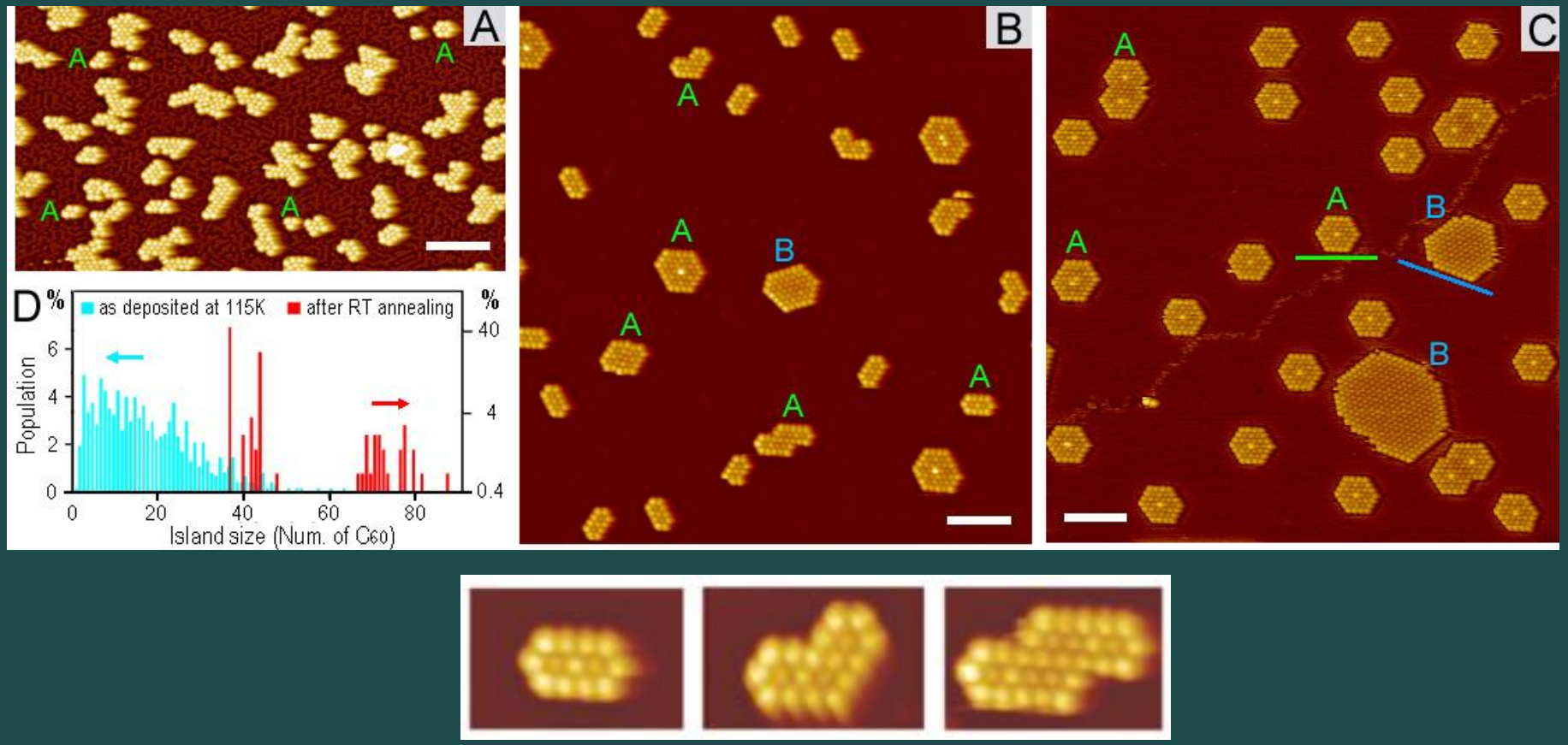
Upon slow heating to RT, random C_{60} islands coarsen into the islands with regular shape



100×100 nm^2 (V_{tip}=-1.9 V I_t=200 pA)

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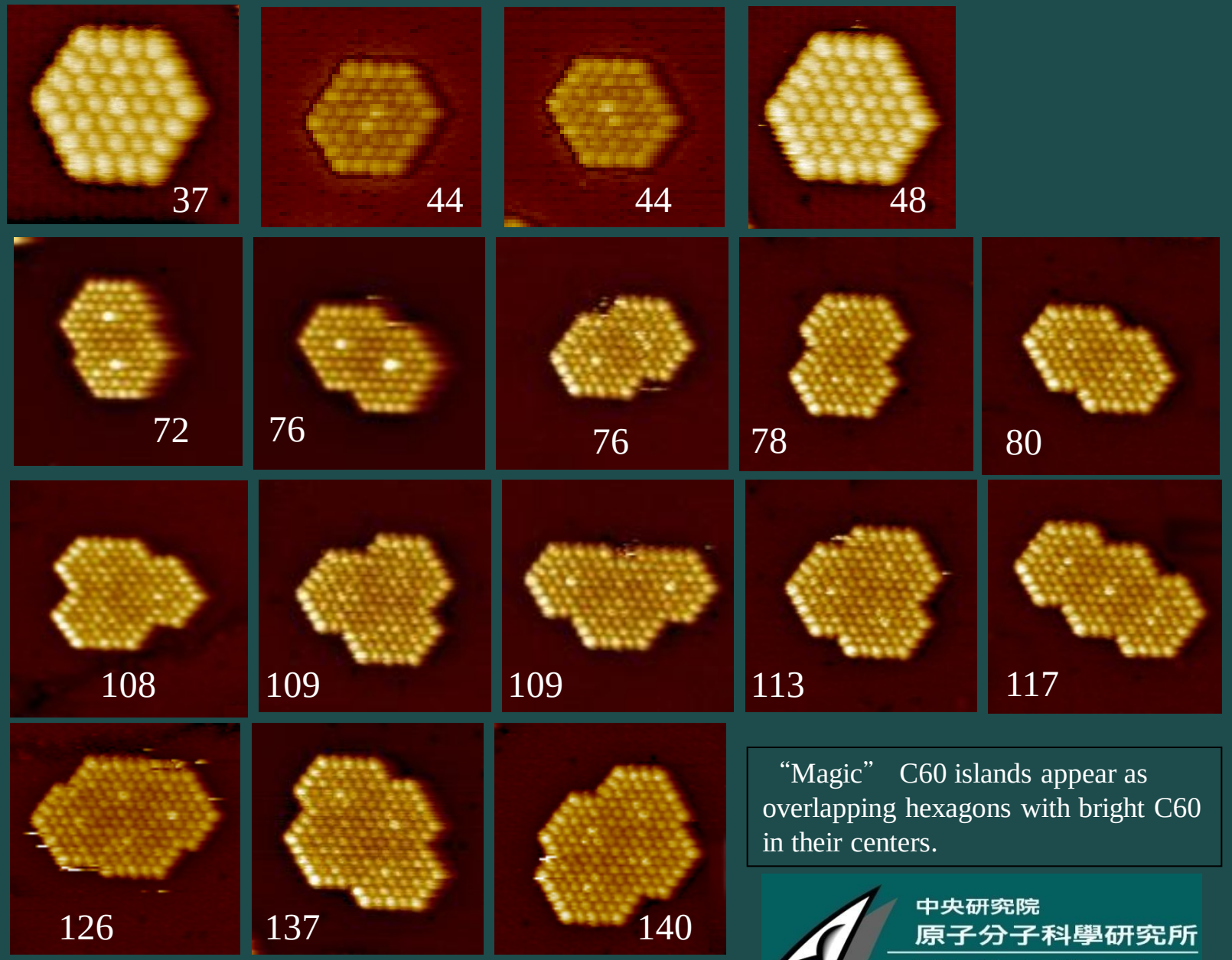
C_{60} on Si(111)-√3×√3-(Au,In): "magic" C_{60} islands



"Magic" C60 islands appear as overlapping hexagons with bright C60 in their centers.

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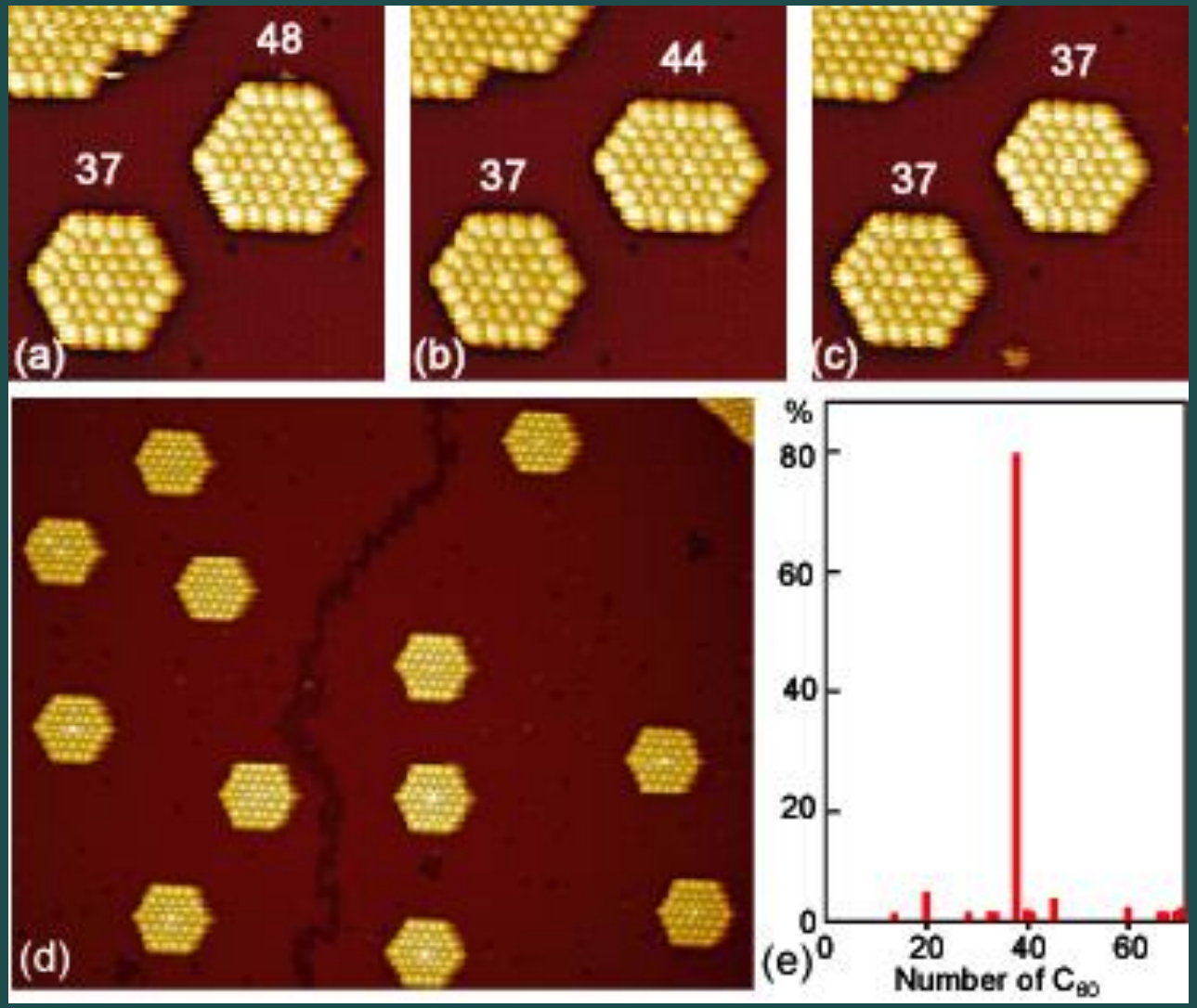
Prolong RT annealing leads to the formation of “magic” 37-mer islands



37mer is the most stable 1st-generation C60 island.

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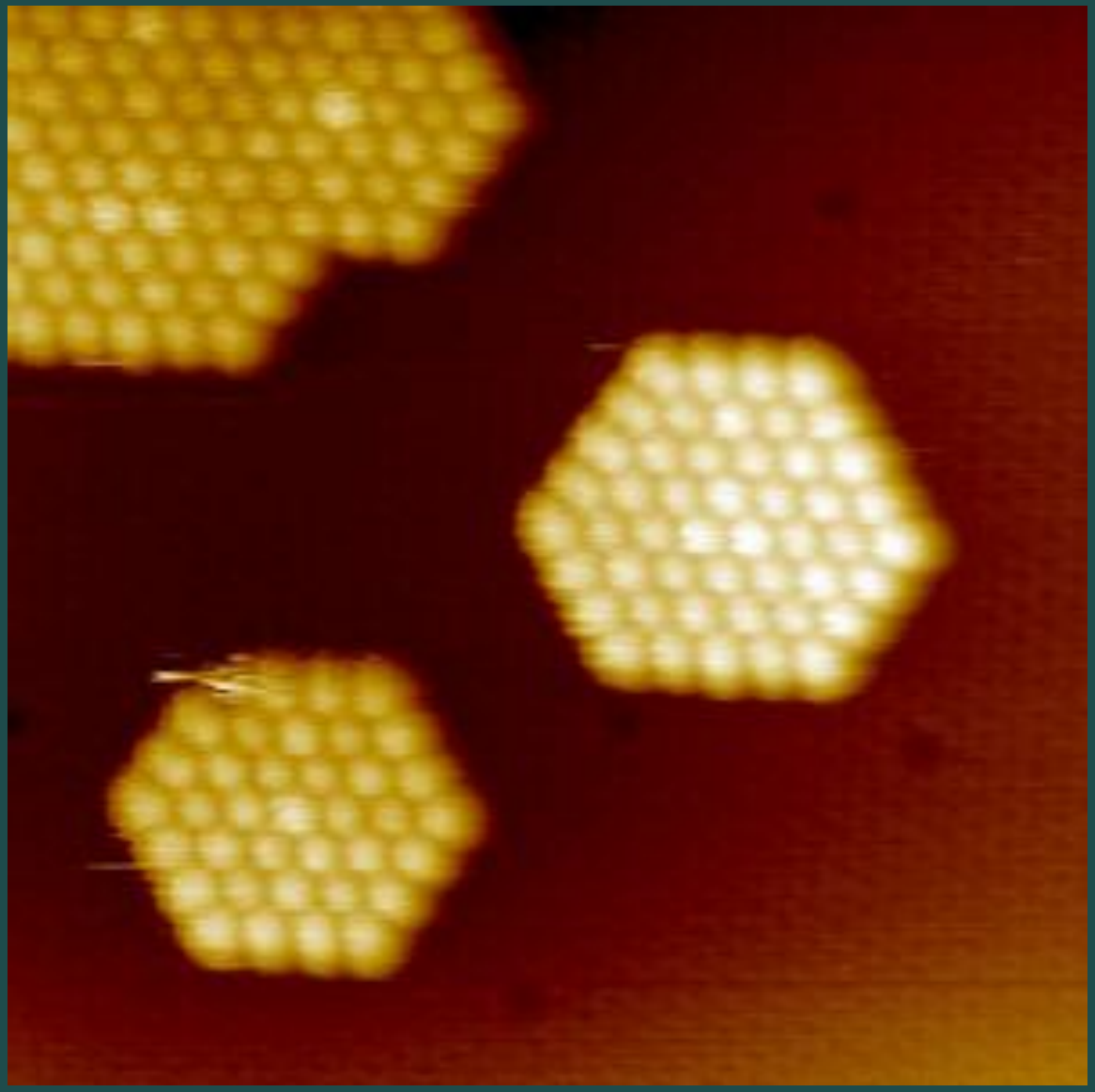
STM movie showing a magic 37-mer and a 48-mer turning into a 37-mer



Snapshots illustrating the dynamic process of C_{60} island ripening towards the more stable forms. Observations are taken at room temperature and C_{60} flux is switched off.

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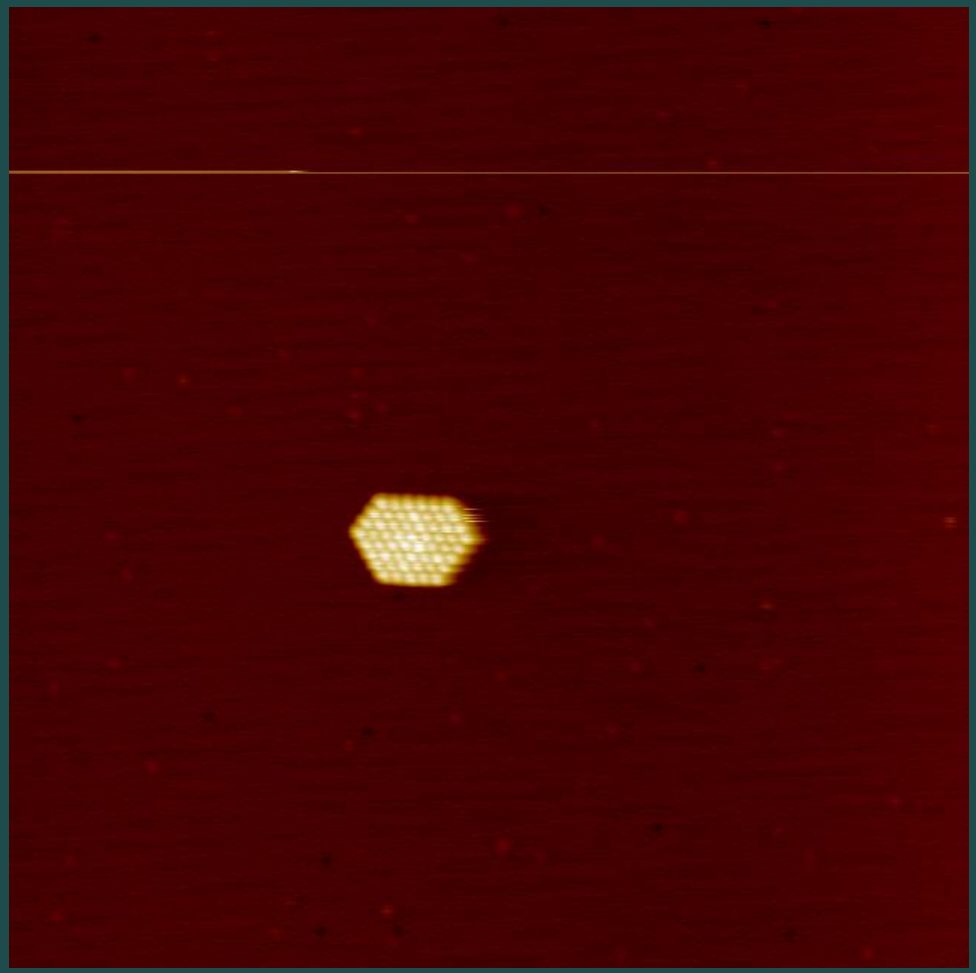
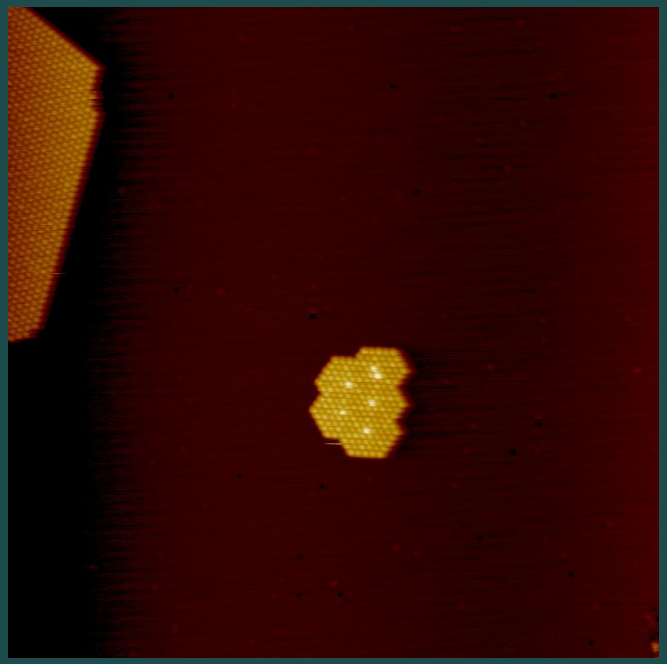
STM movie showing the stepwise growth of a C_{60} Island



When C_{60} flux is switched on, the 56-mer starts to grow through the successive formation of the high-generation magic islands. This growth in the island size exhibits a stepwise dependence versus C_{60} deposition time.



The ‘magic’ C_{60} island grows predominantly from the right lower side due the presence of a huge 19.1º-rotated C_{60} island from its upper side, which acts as a strong sink for mobile C_{60}.

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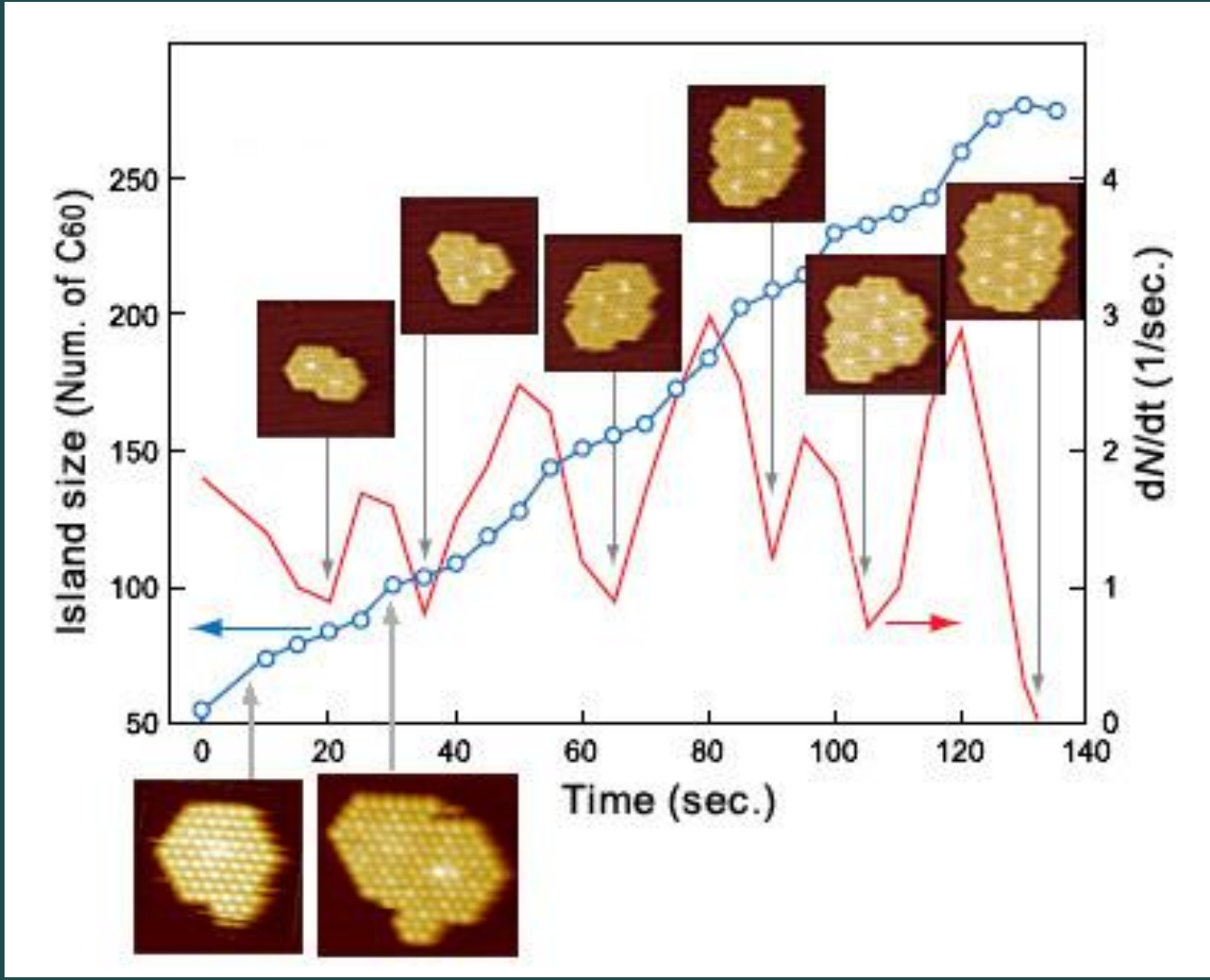

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Formation of C_{60} Surface Magic Clusters (SMC) on the Si(111)-√3×√3-(Au,In)

Theoretical Understanding

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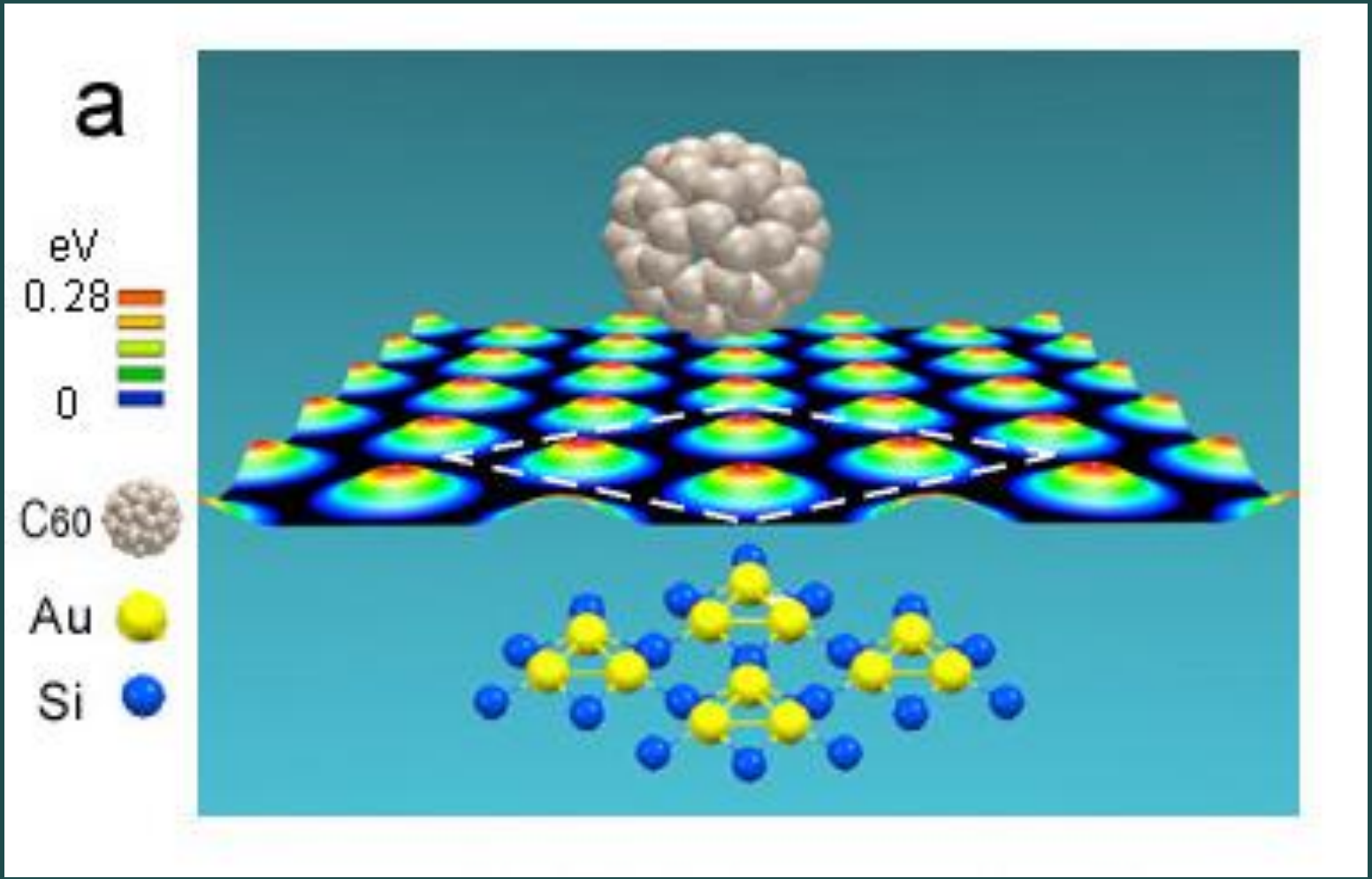
Adsorption Energy of C_{60} on the Si(111)-√3×√3-(Au,In) surface



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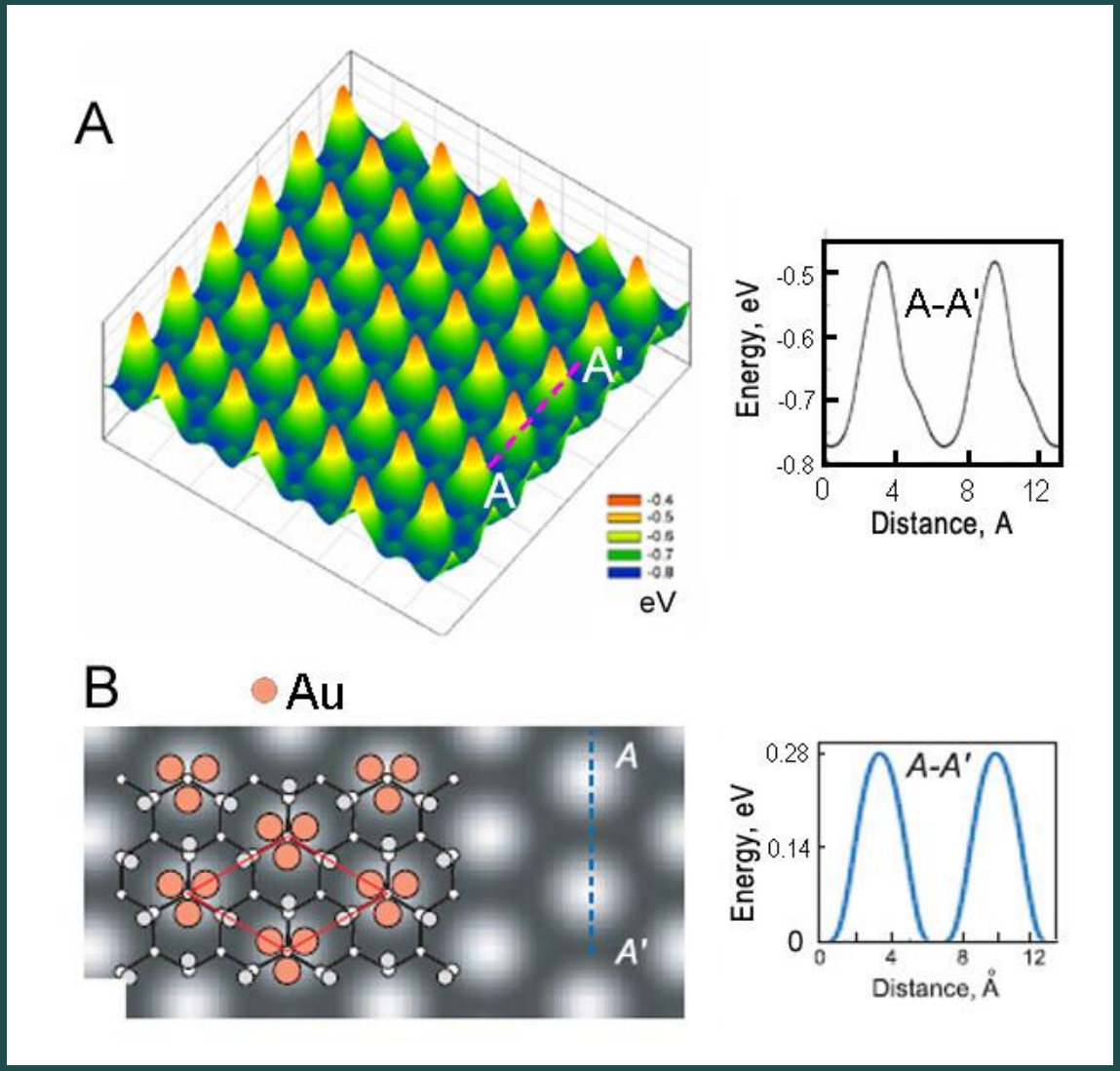

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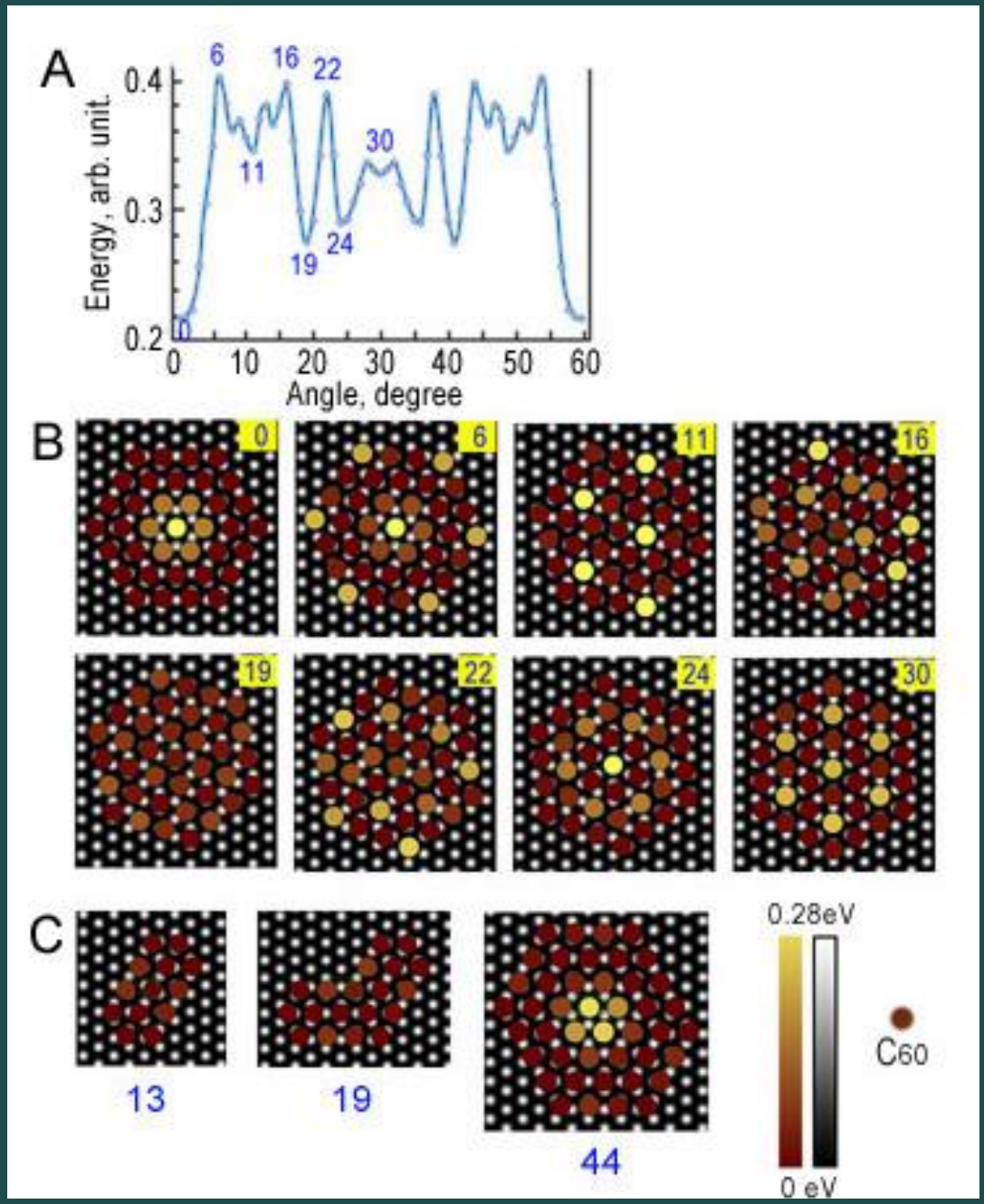

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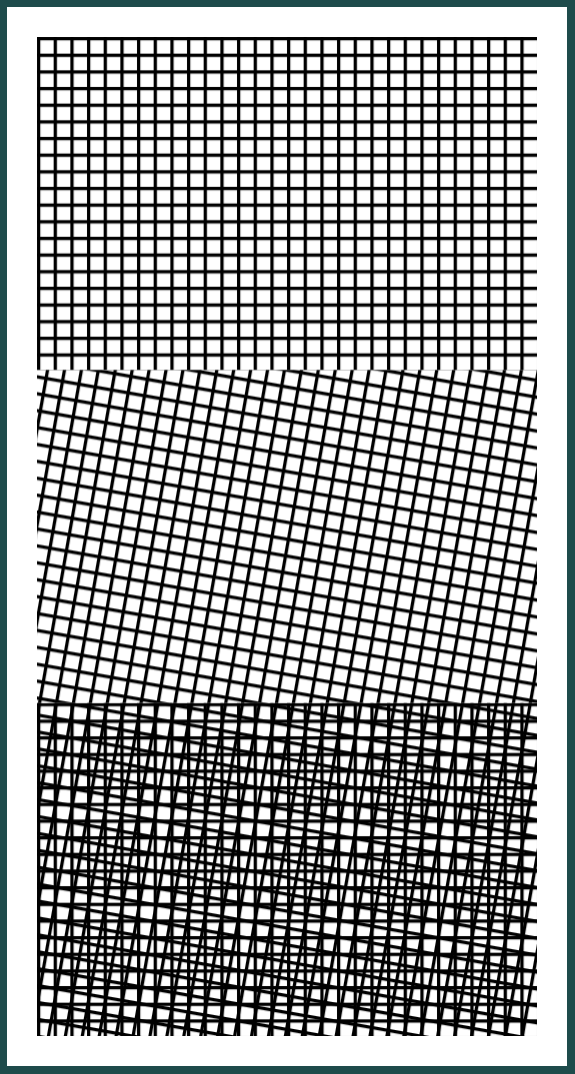
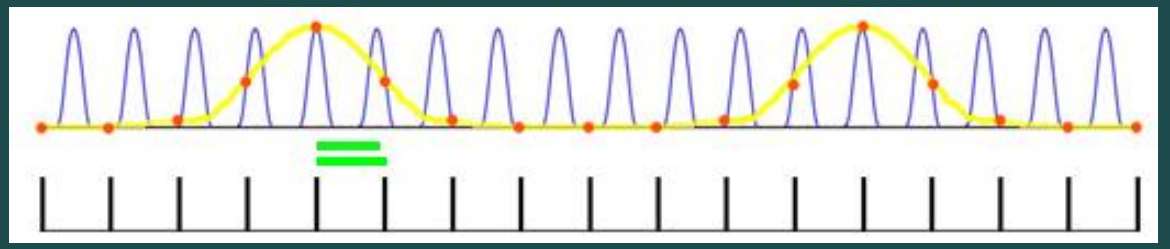
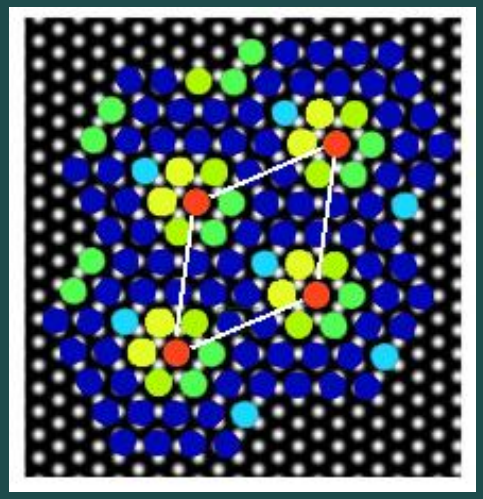
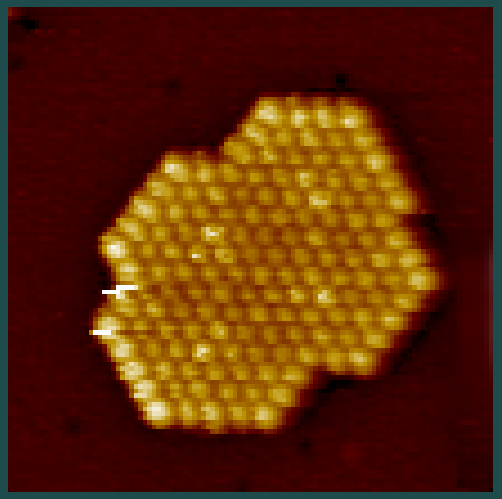
Moiré Pattern & Moiré Magnifiers





http://en.wikipedia.org/wiki/Shape_moiré





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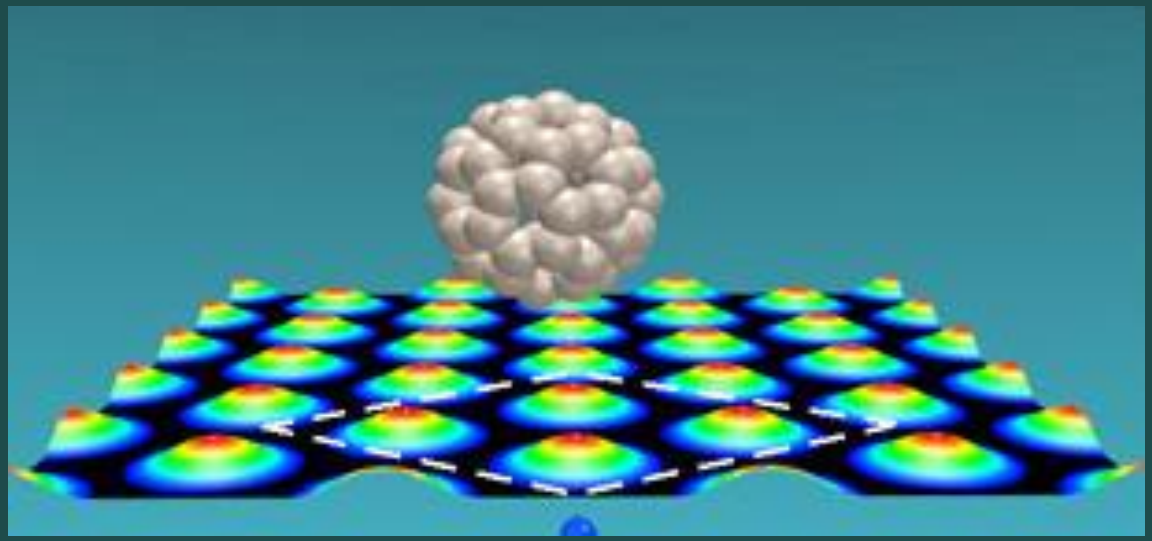
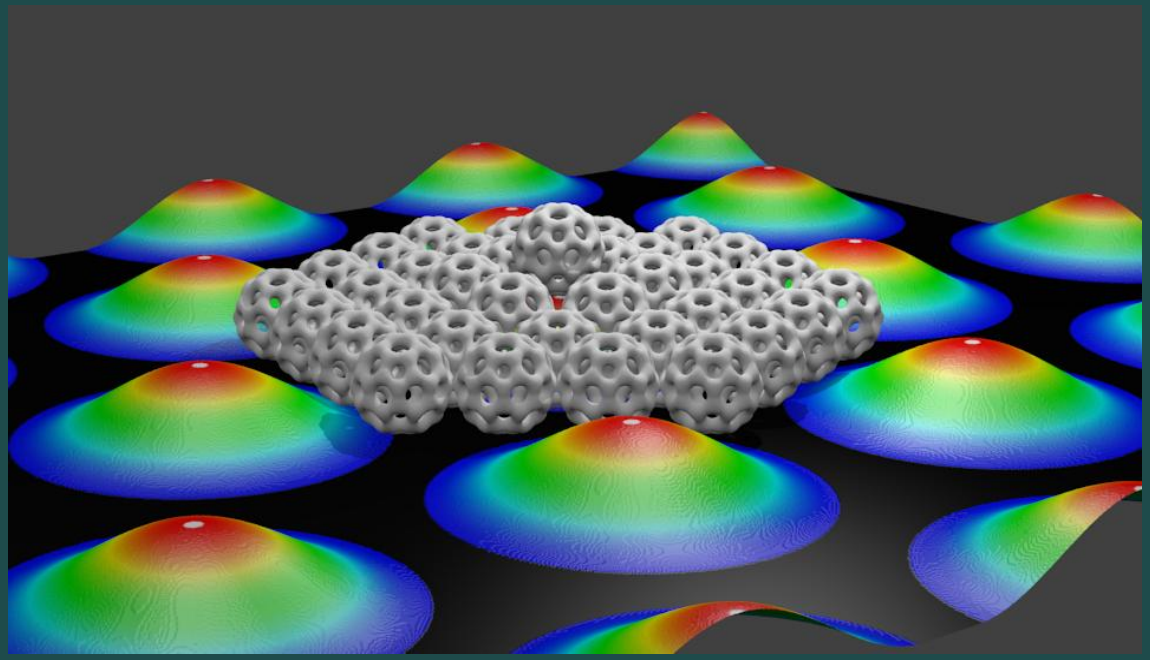
Atomic Scale Moiré Magnifiers



length scale is scaled up by a factor of $\sqrt{19}/(\sqrt{3}\times 0.384)$, ~6.5



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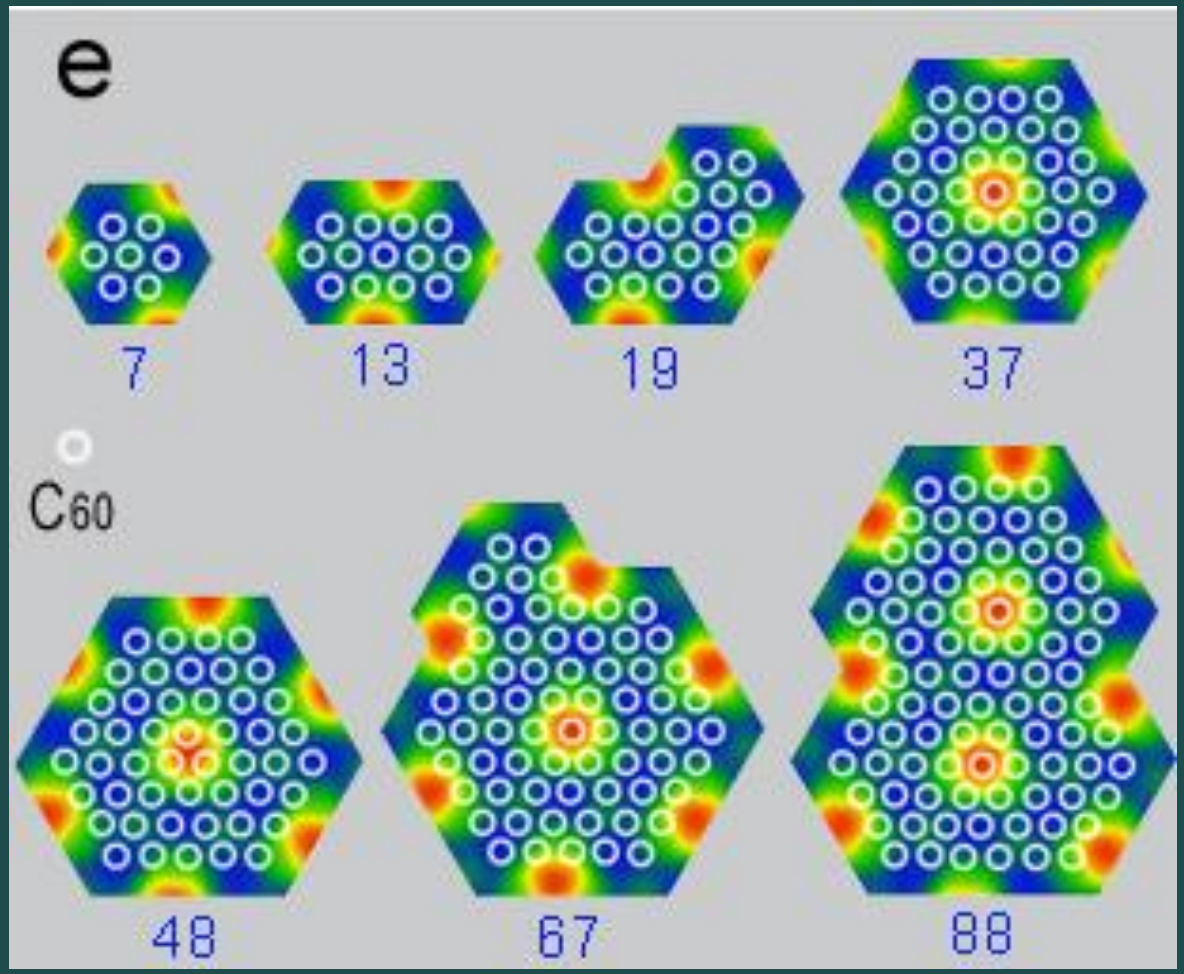
Size Selection of C_{60}-Islands Mediated by by Atomic Scale Moiré Magnifiers



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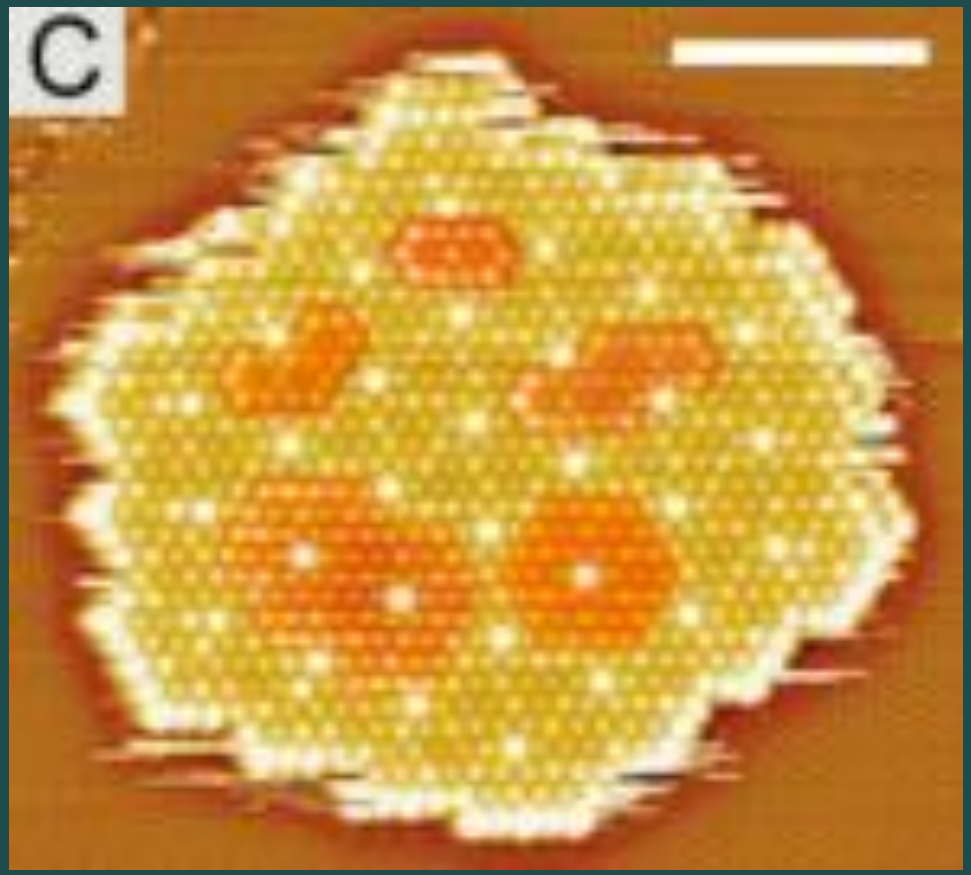
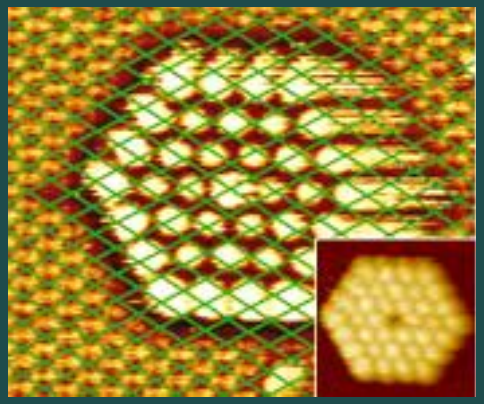
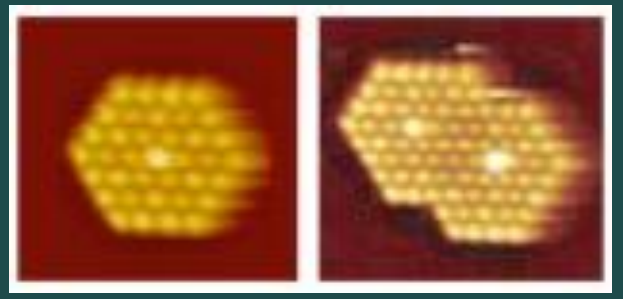
Size Selection of C_{60}-Islands Mediated by by Atomic Scale Moiré Magnifiers







Scale bar is 10 nm

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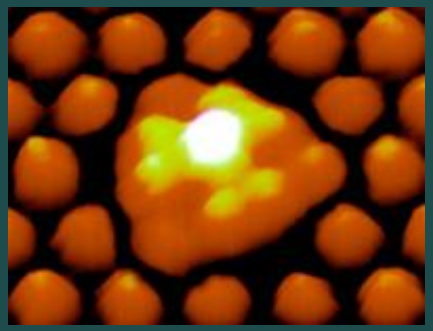
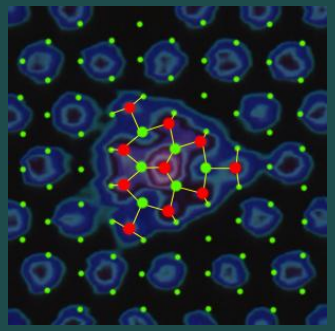
Conclusions

The moiré interference pattern between the C_{60}-layer and the In-Au/Si(111) substrate surface constrain the self-organization process of $C_{60,}$ leading to the size selection of 37-mer magic-number cluster of C_{60}.

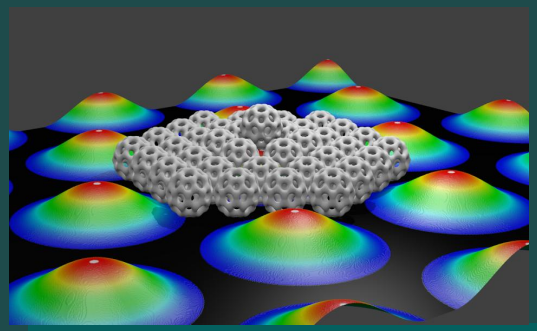
The concepts of moiré-shell-closure and moiré magnifier could be exploited for the creation of mono-dispersed atomically precise nanostructures by self-assembly.





10 Ga

37 C_{60}= 2220 C



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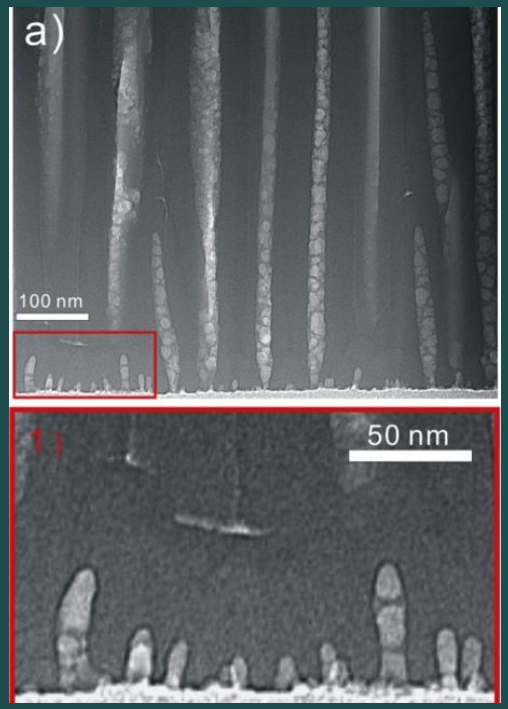
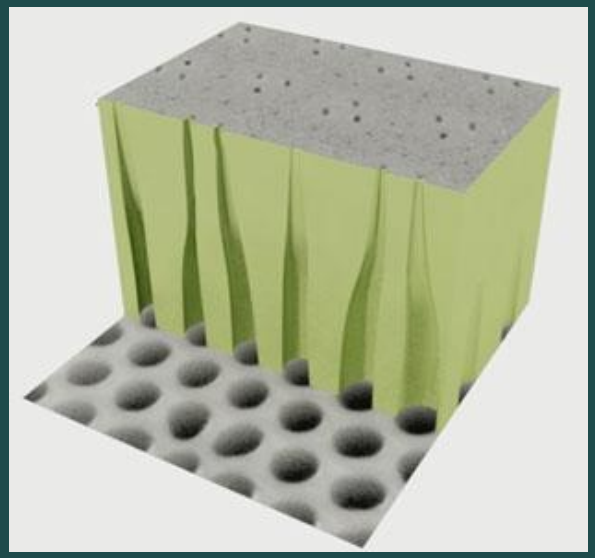
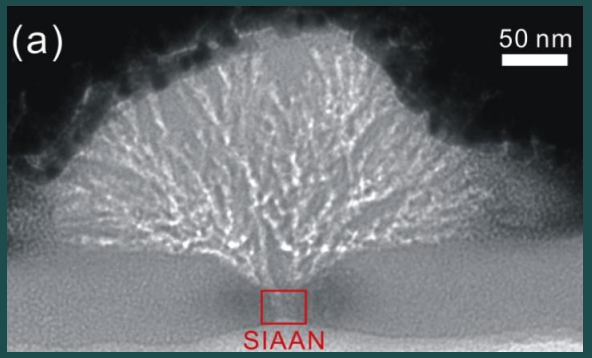
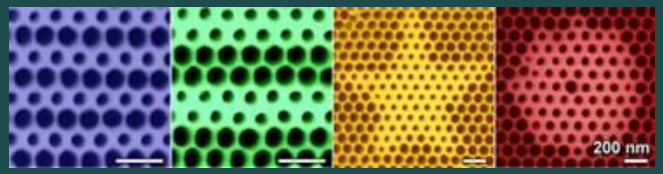
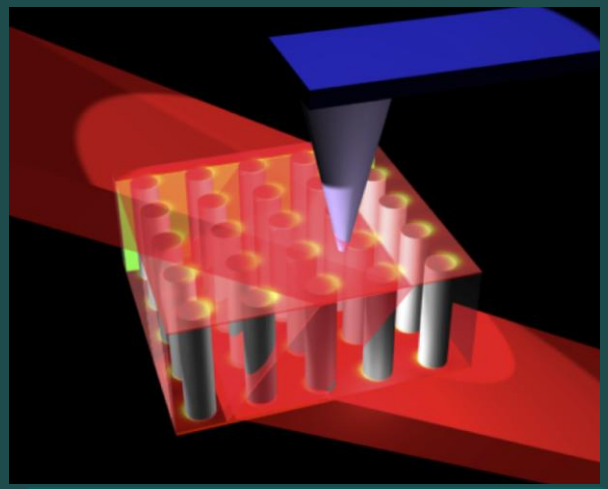
A Voyage from Atoms/Molecules and Clusters/Nanostructures to Bacteria and Planet-Human











Yuh-Lin Wang (王 玉 麟)
IAMS, Academia Sinica & Dept. of Physics, NTU
IAMS (6/16//2015)

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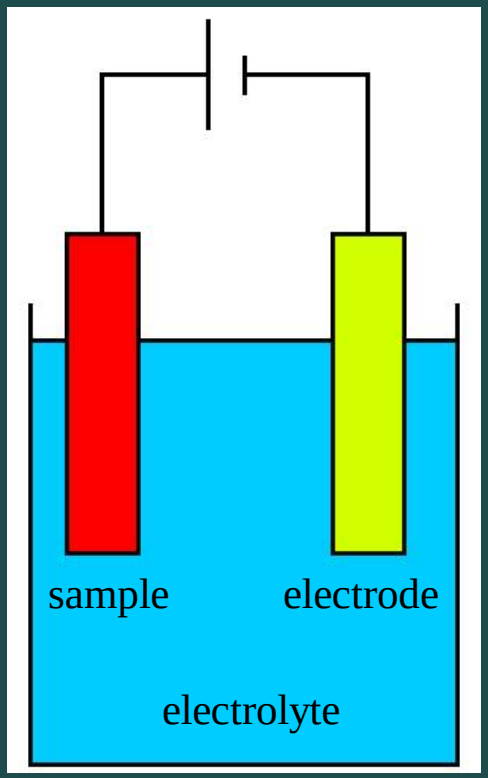
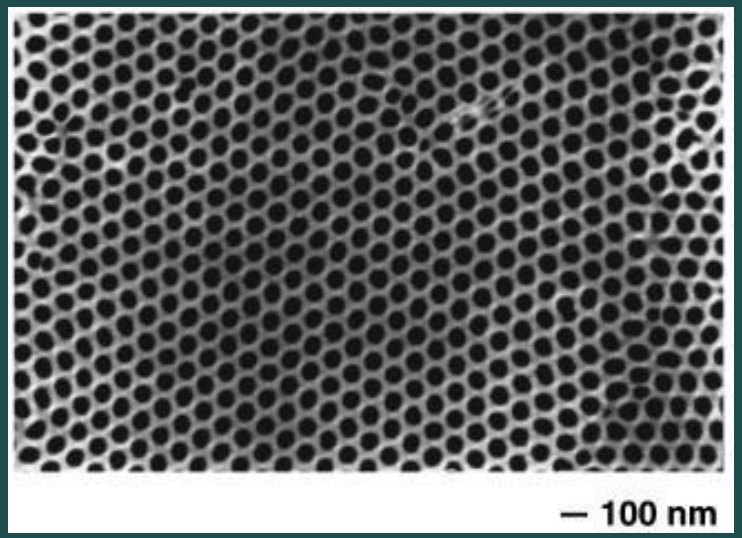
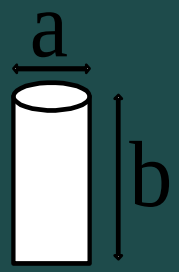
Anodization of Metal Leading to Porous Oxide: an Example of Material Self-organization in 1~100 nm Scale

example: Al $\longrightarrow$ Al_2O_3 (Anodic Alumina)





O. Jessensky, F. Müller, U. Gösele
Appl. Phys. Lett. **72**, 1173 (1998)



- Range of diameter is between several to a few hundreds of nm
- High aspect ratio: b/a can be larger than 1000

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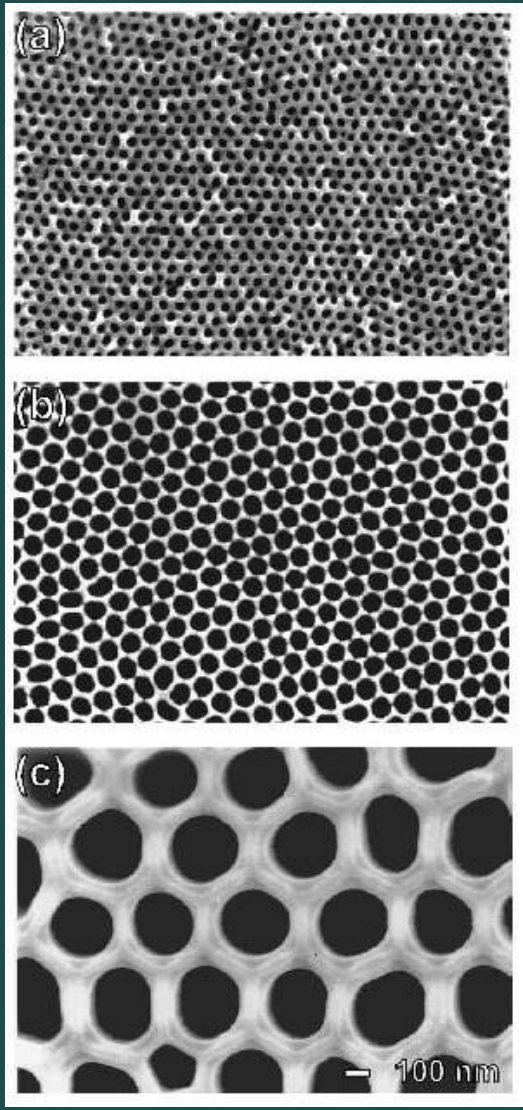
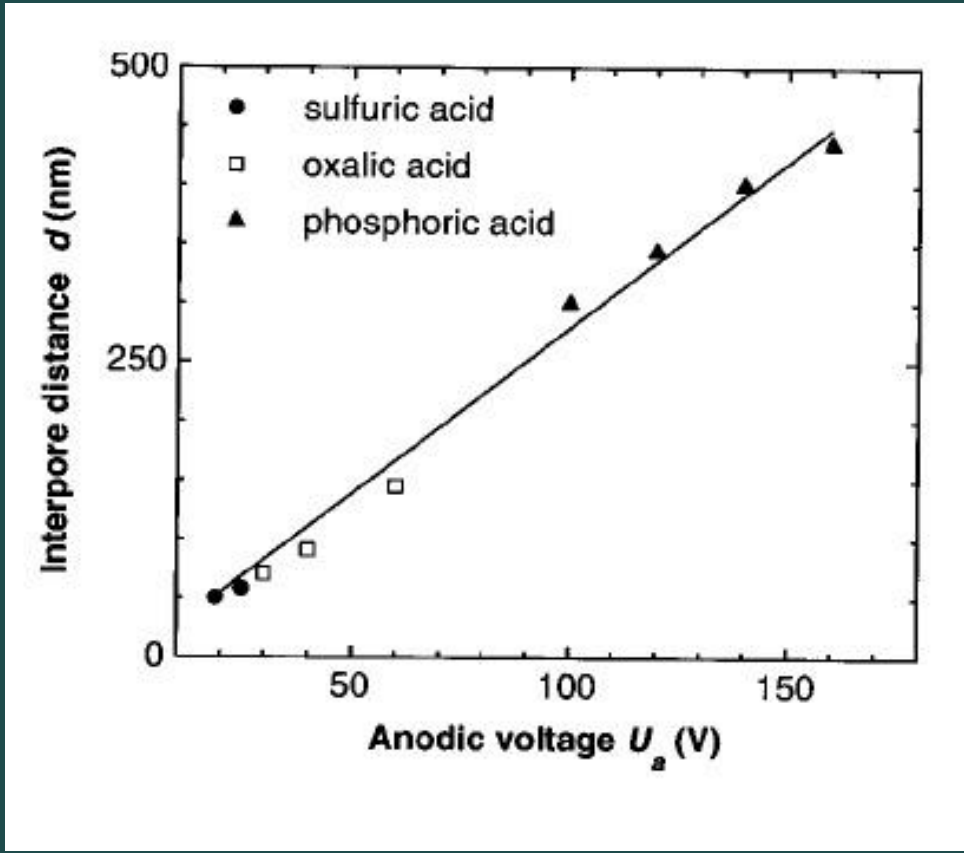
H_2SO_4
25V

$H_2C_2O_4$
40 V

H_3PO_4
160 V

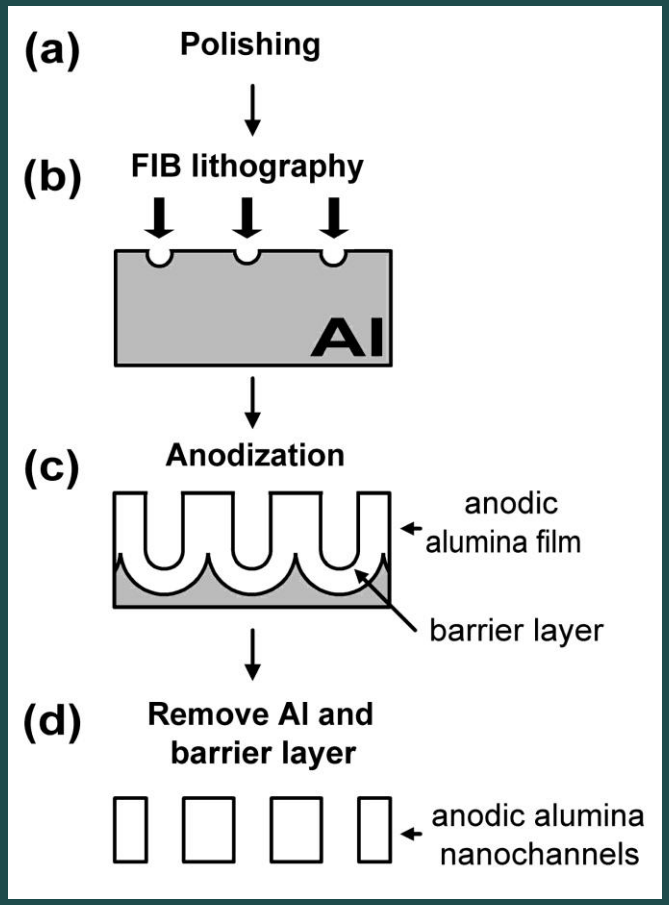


2.5 nm/V



A. P. Li *et al.* J. Appl. Phys. **84**, 6023 (1998)

Constraining the growth of anodic alumina nanochannel arrays with focused ion beam (FIB) lithography



- Anodic alumina film with ideally ordered nanochannels are grown on aluminum surfaces that have been pre-patterned by FIB lithography

- The period and arrangement of the lithographic pattern must be similar to that of the self-organized ordered array of nanochannels.

App. Phys. Lett. **78**, 120-122 (2001).

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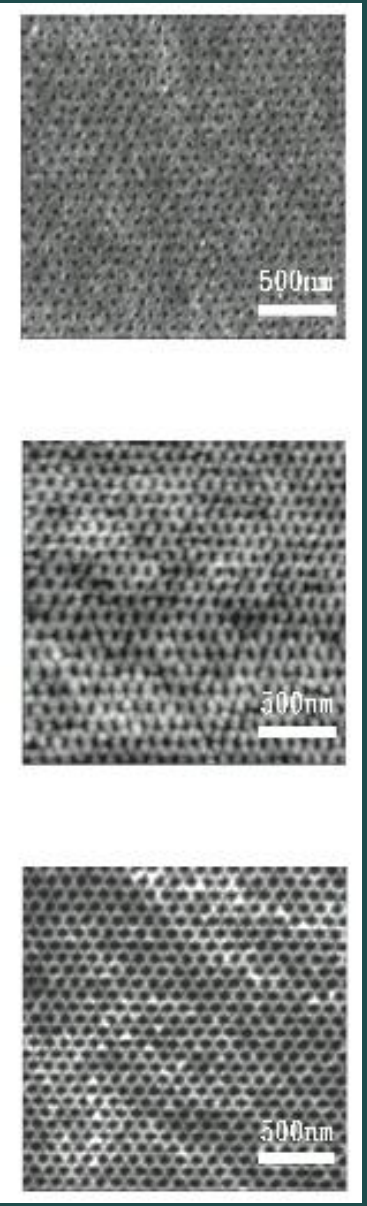
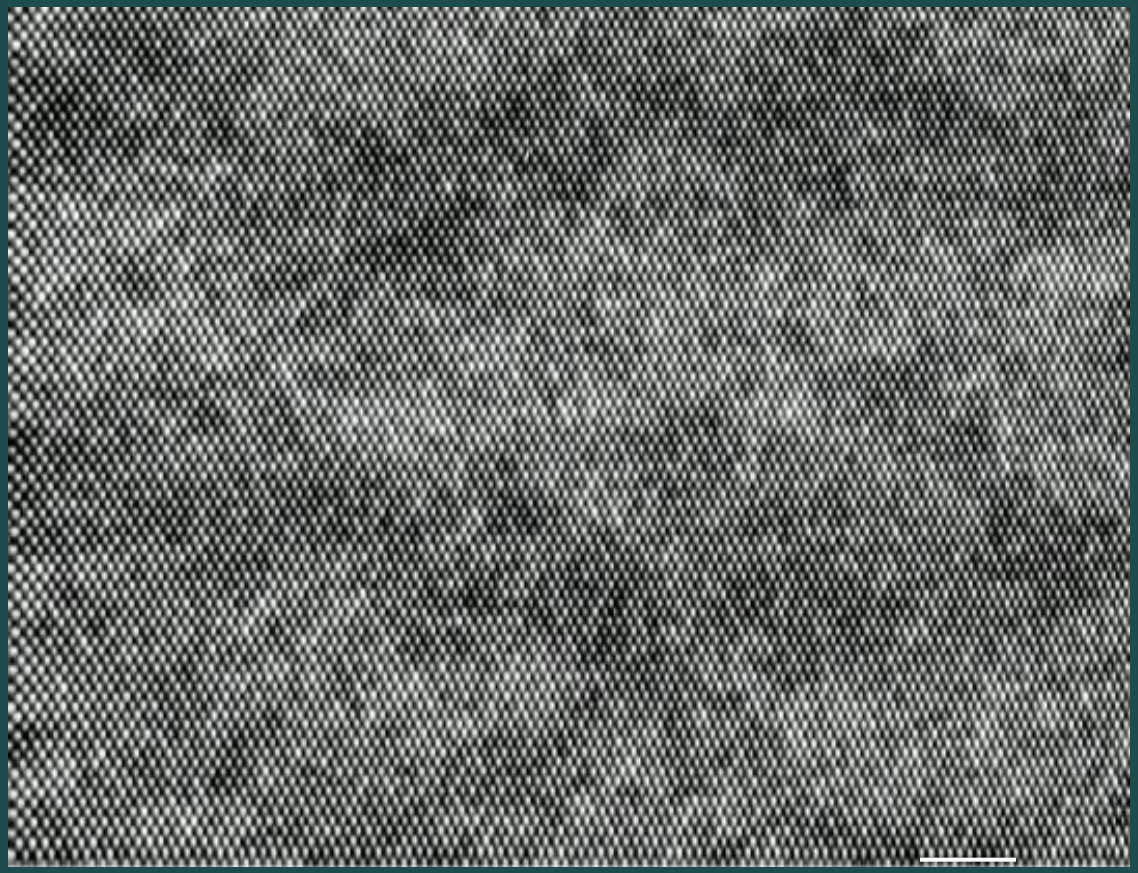
FIB pattern on Al

top view of the channels

bottom view of opened channels



AFM image of the barrier layer
V = 40 V, Period = 100 nm



1 um

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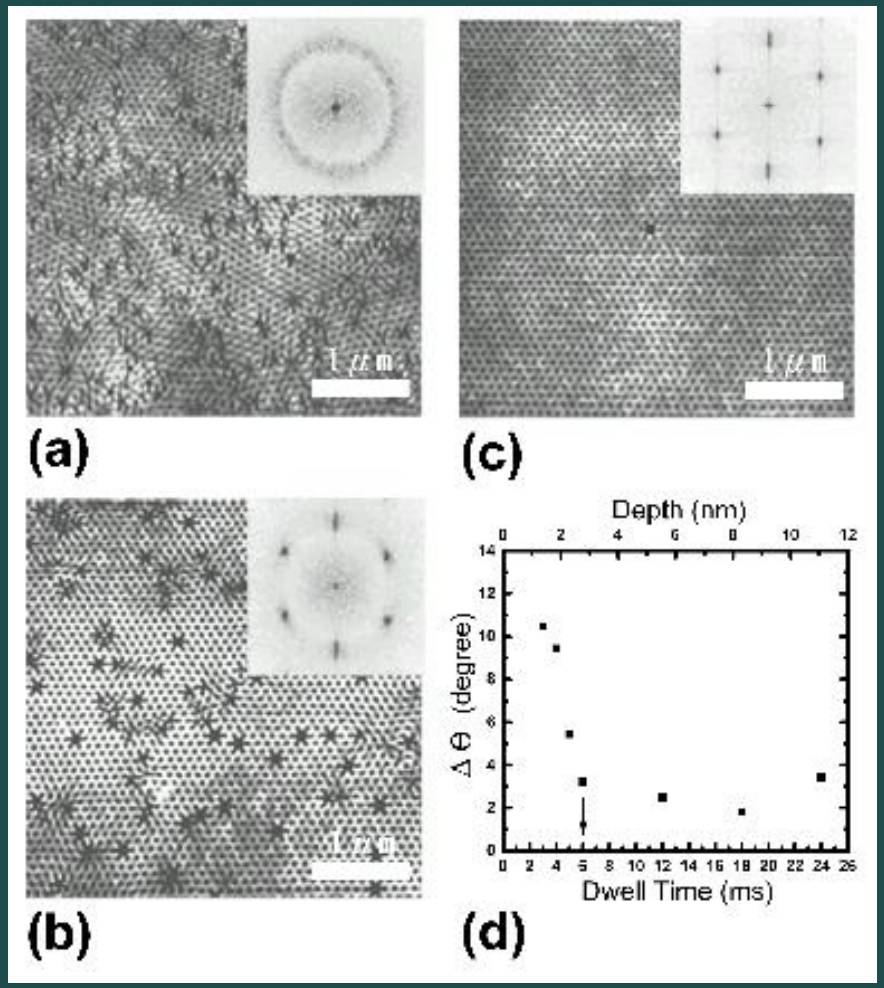
Effect of FIB dose on the order of nanochannel



AFM images of the backside of the nanochannels created by (a)2×10^{15} (1 ms), (b) 9×10^{15} (6 ms), and (c) 2×10^{16} (12 ms) ions/cm^2. The insets show the corresponding Fourier transforms of the images. (d) Angular spread of the intensity peaks ($\Delta\theta$) as a function of FIB dwell time.

App. Phys. Lett. **78**, 120-122 (2001).

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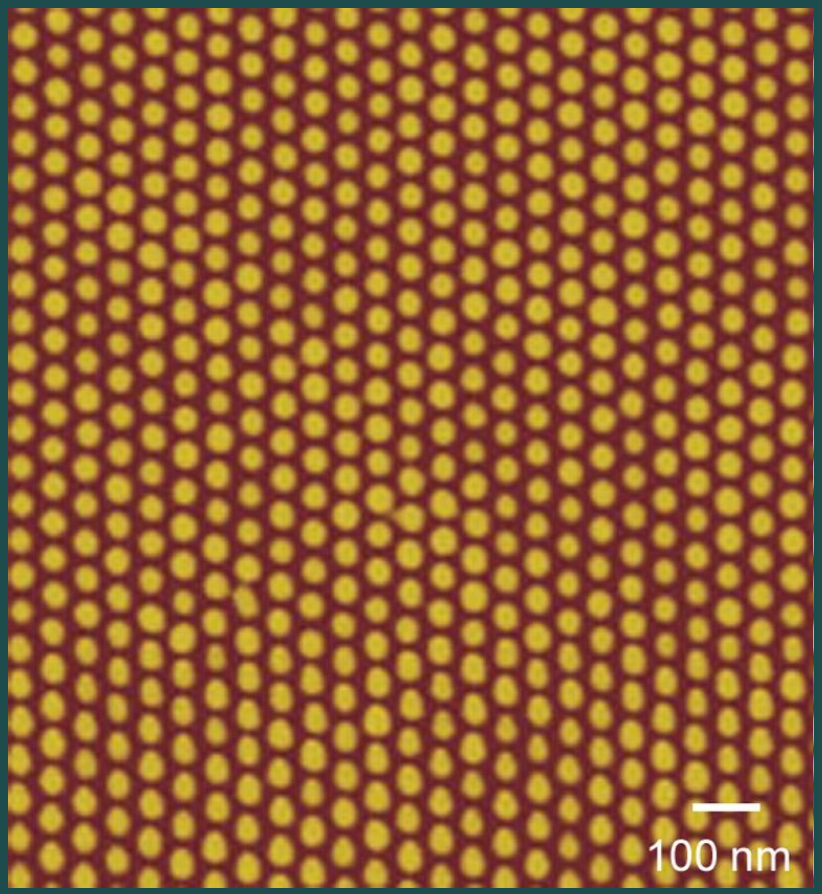

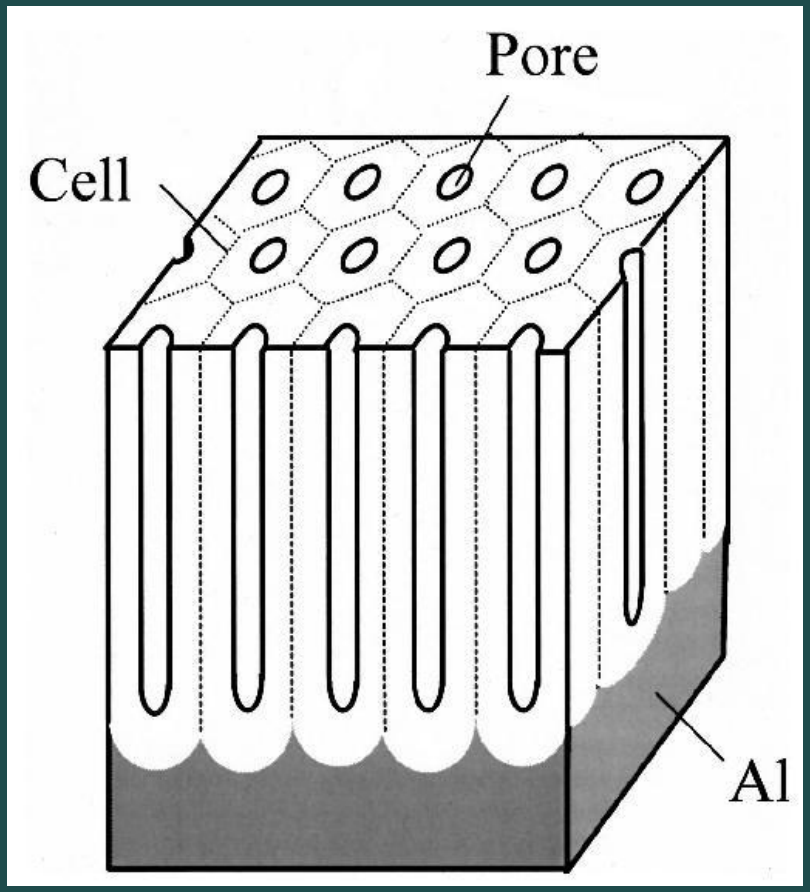

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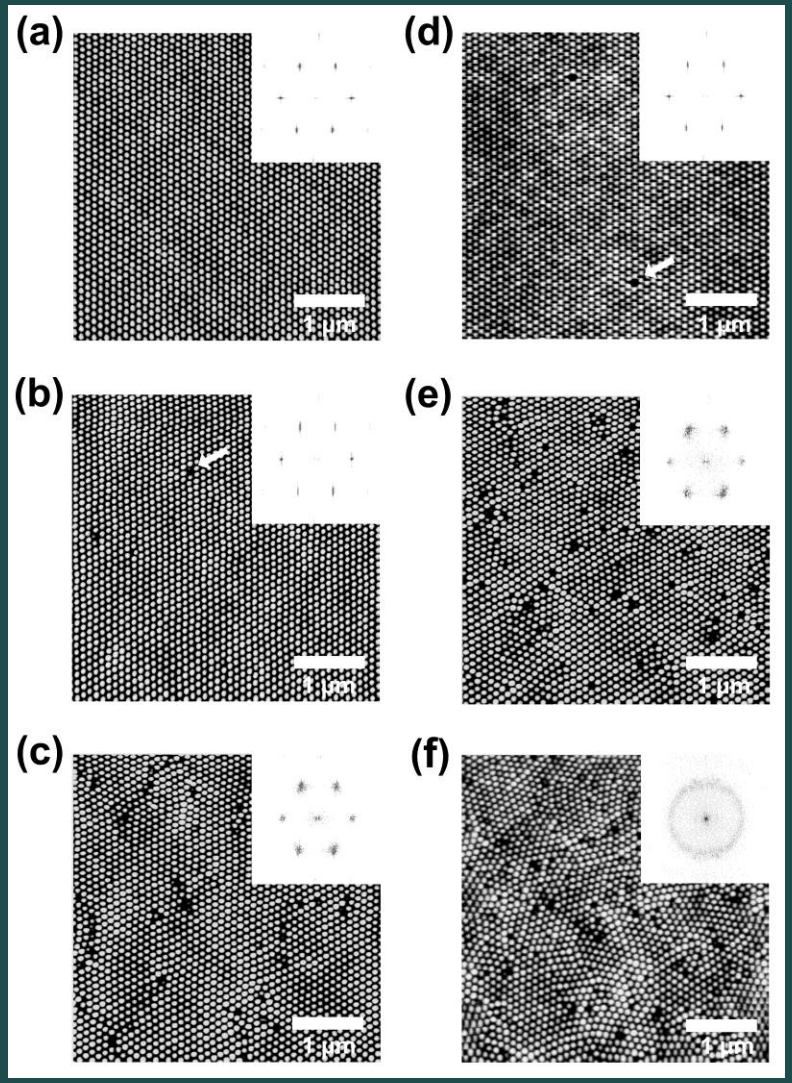
Effects of ‘lattice mismatch’



Barrier layer of arrays fabricated using a confining lattice with various ‘lattice mismatch’.

(a) 0 %
(e) 2 %
(c) 6 %
(d) -2 %
(e) -8 %
(f) is a self-organized structure

The insets show the 2D power spectra of corresponding array.

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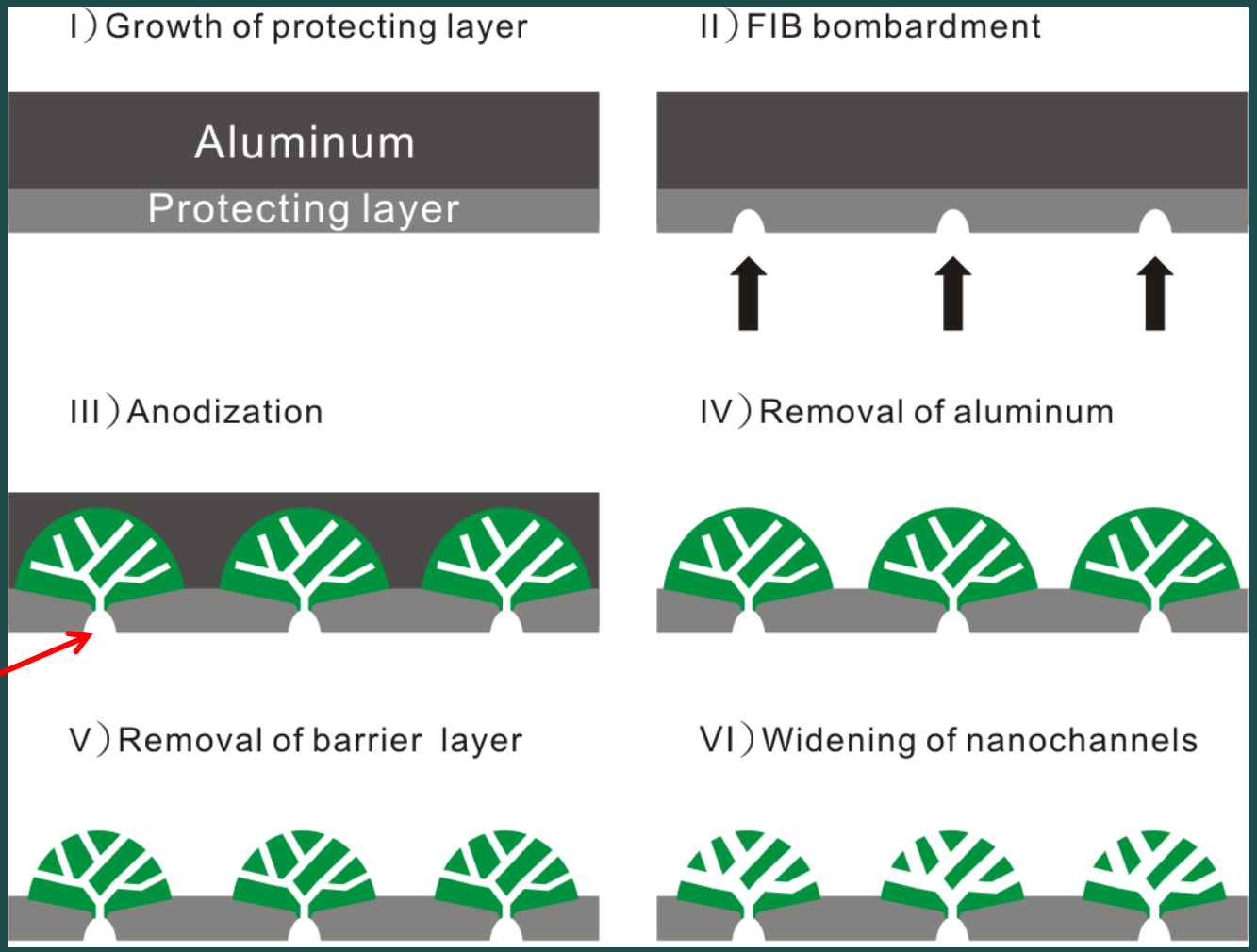
What is the natural growth behavior of a single isolated anodic alumina nanochannel (SIAAN)



原分所
陳師詠博士

FIB: focused ion beam

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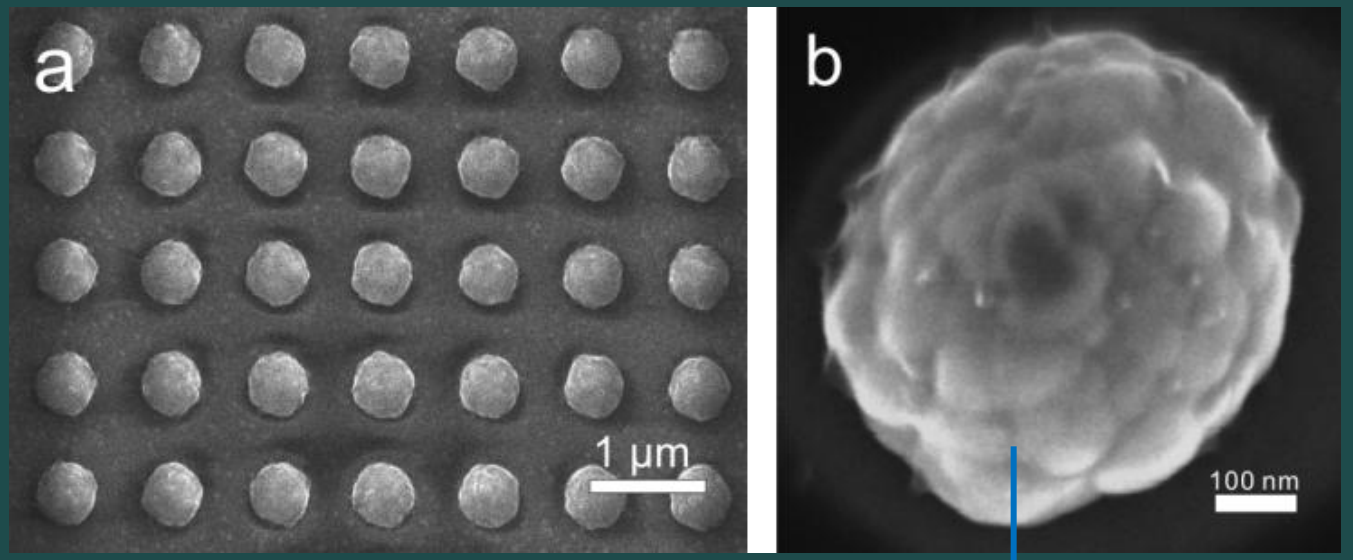
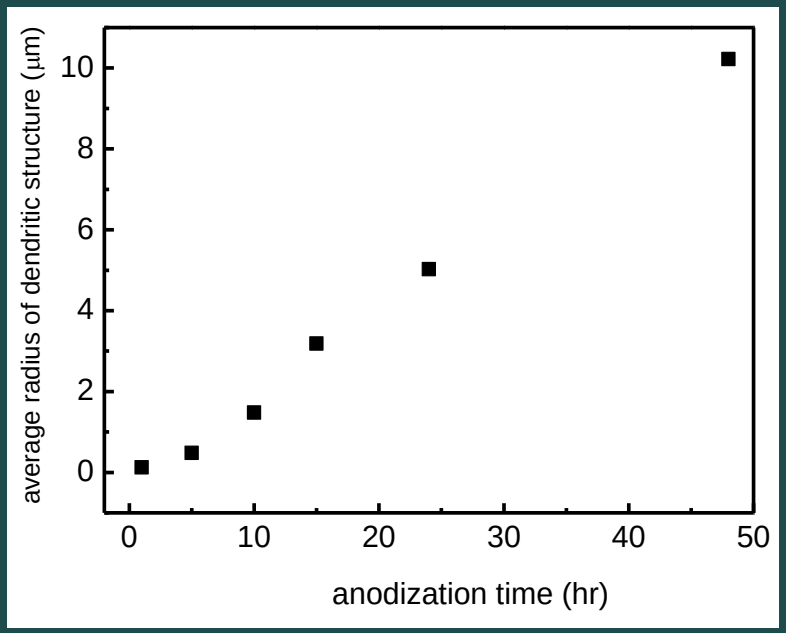
Array of Isolated Alumina Evolved from SIAANs



Protrusion ~ 100 nm



Nanotechnology, **22**, 365303 (2011)

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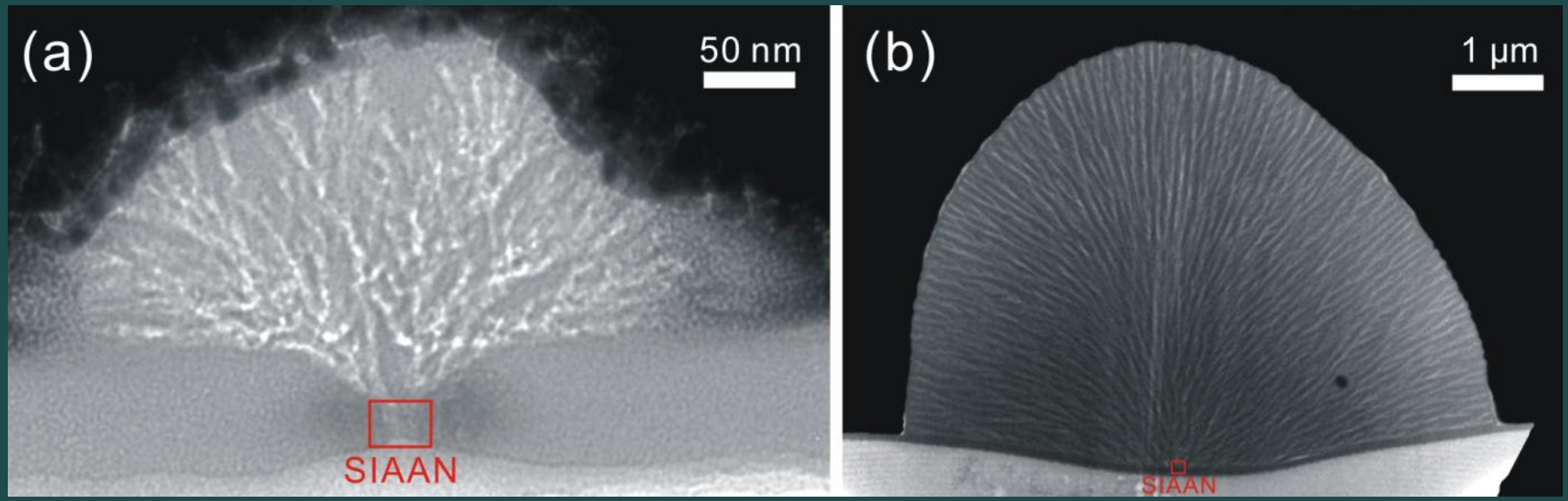
Cross-sectional TEM Images of Structures Grown from a SIAAN at Different Stages



1 hour anodization

24 hour anodization

spontaneous branching

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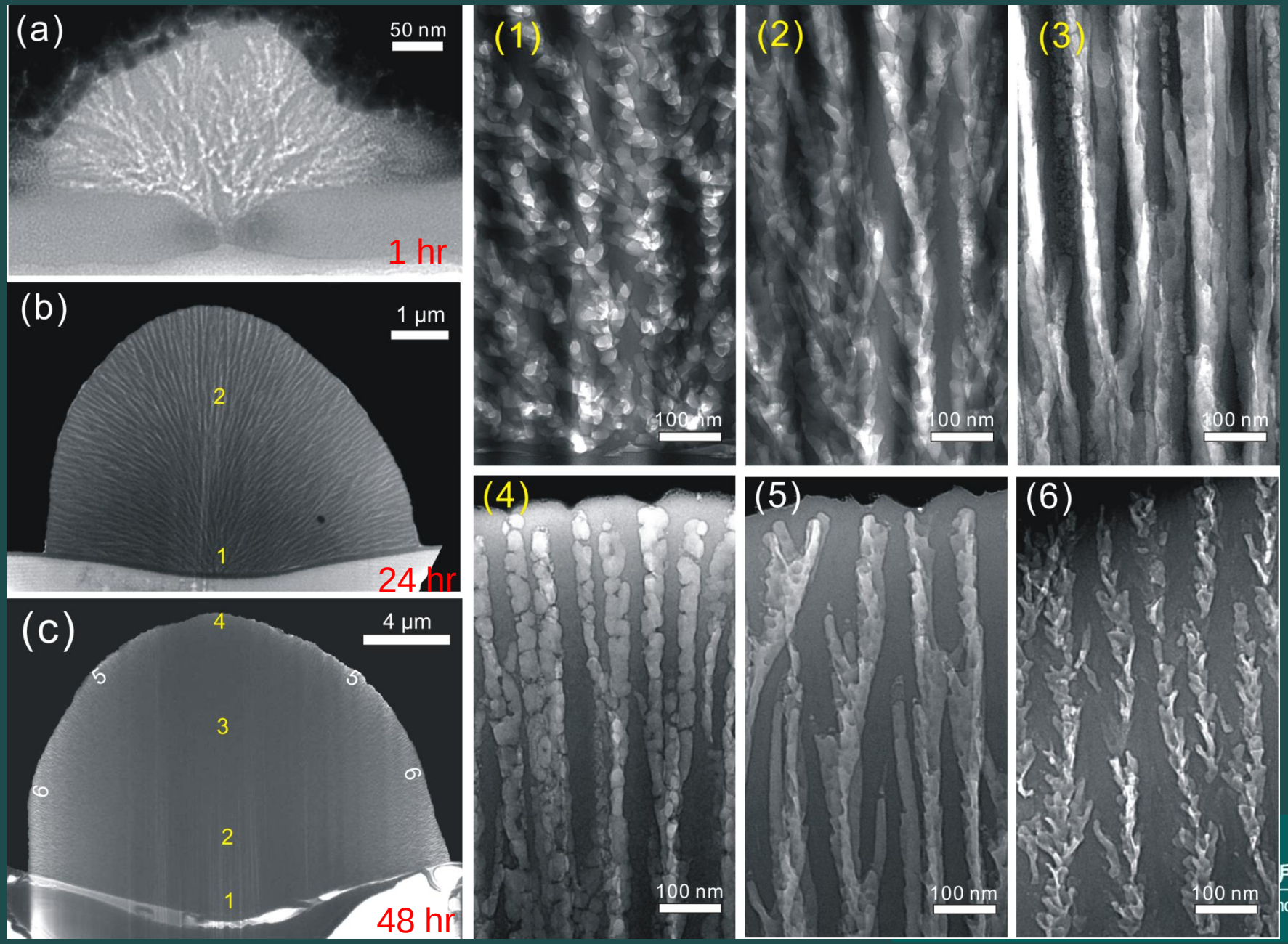
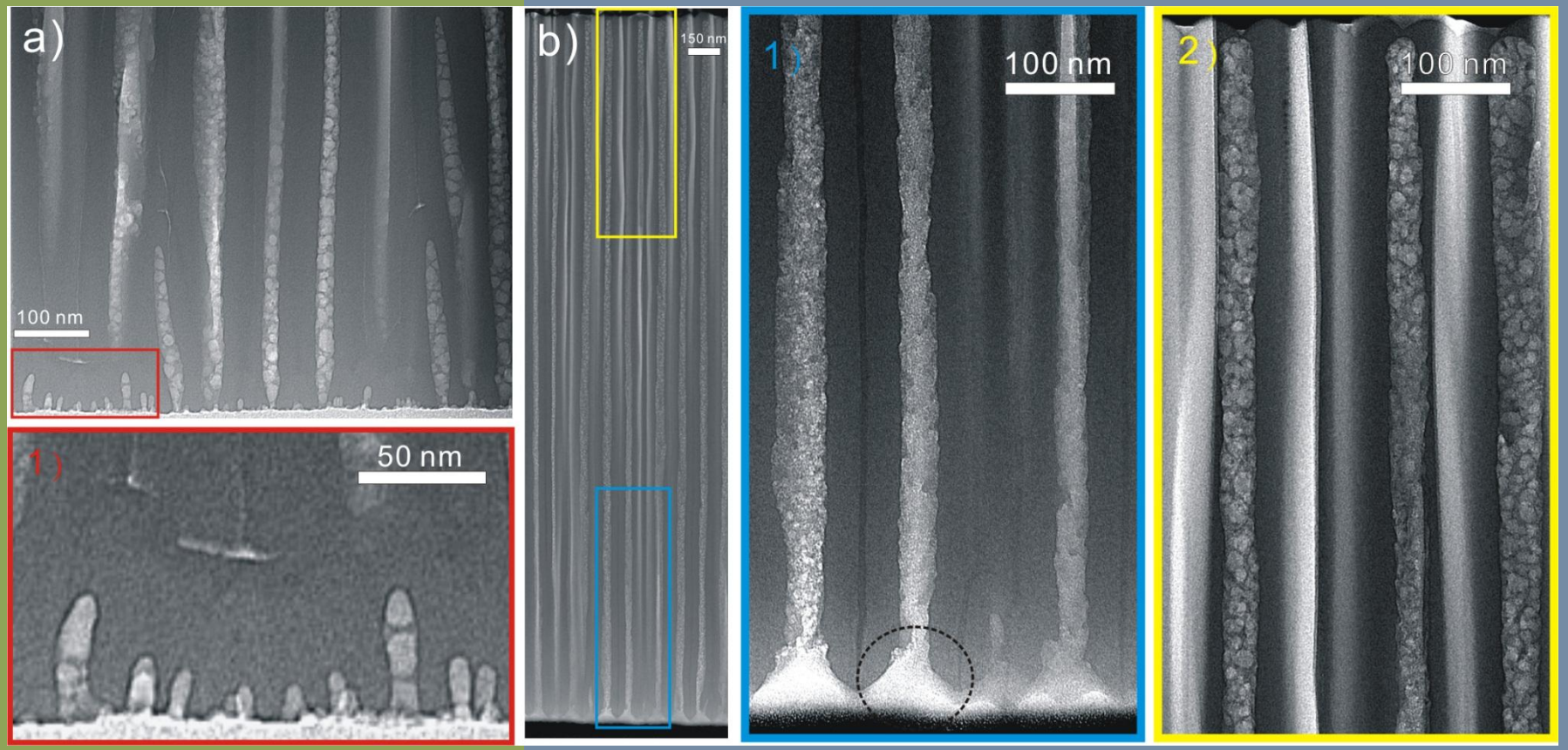
Morphological Evolution of Porous Nanostructures Grown from a SIAAN



Cross-sectional TEM Images of Arrayed AAO Nanochannels

Nanotechnology, **22**, 365303 (2011)



one-step anodization

two-step anodization

characteristic size ~ 30 nm

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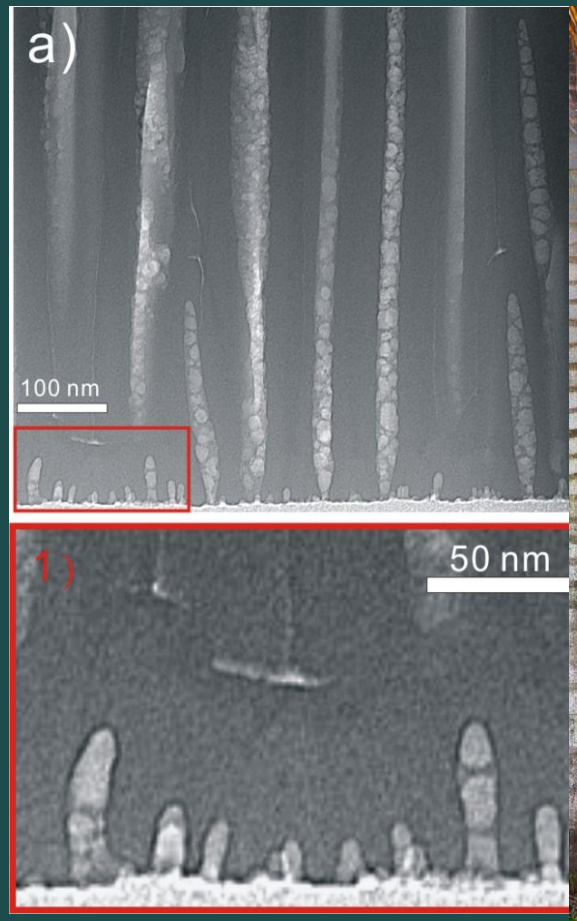
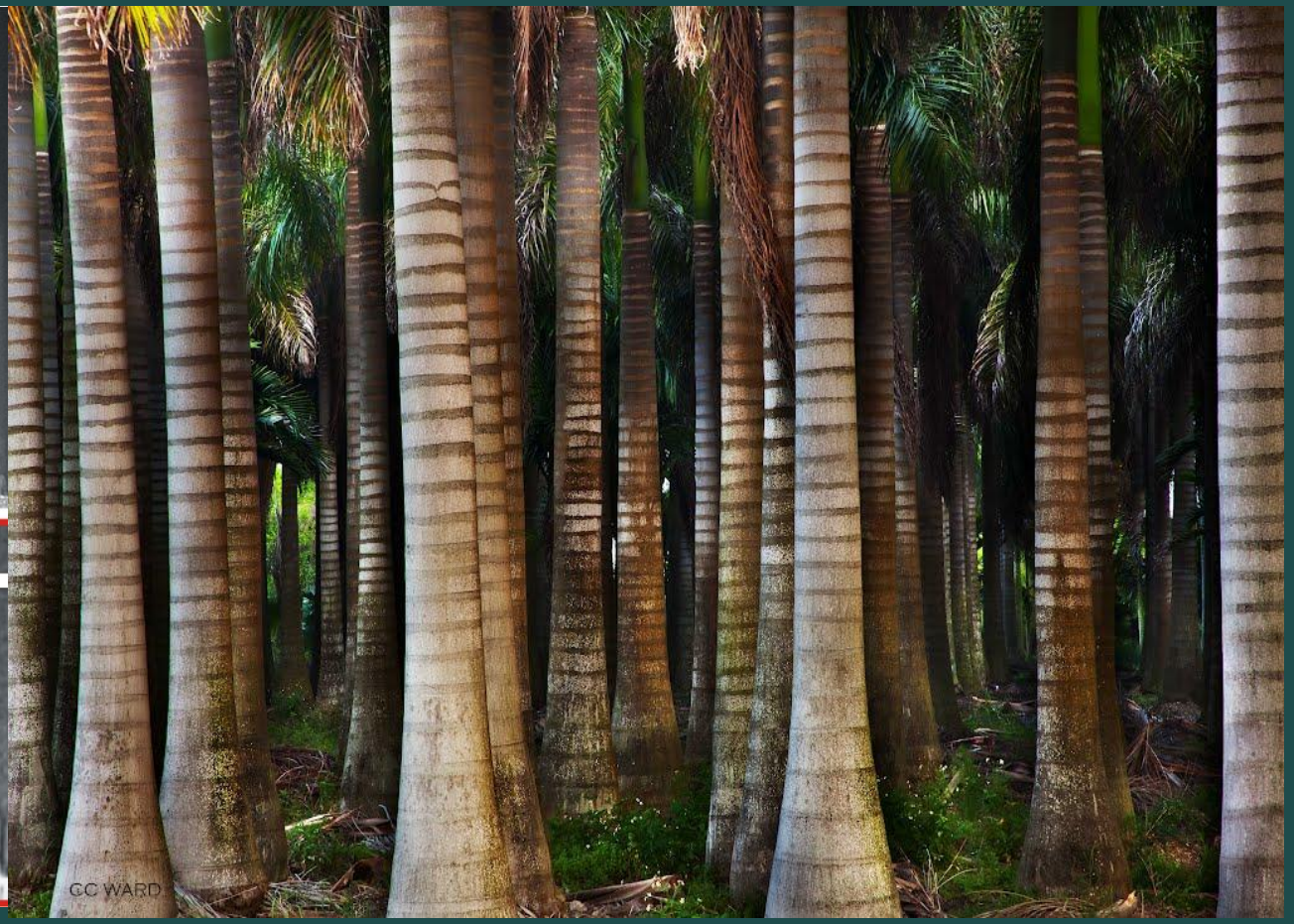
Growth Behavior of Arrayed AAO Nanochannels



one-step anodized channels
characteristic size ~ 30 nm



palm forest
characteristic size ~ 30 cm

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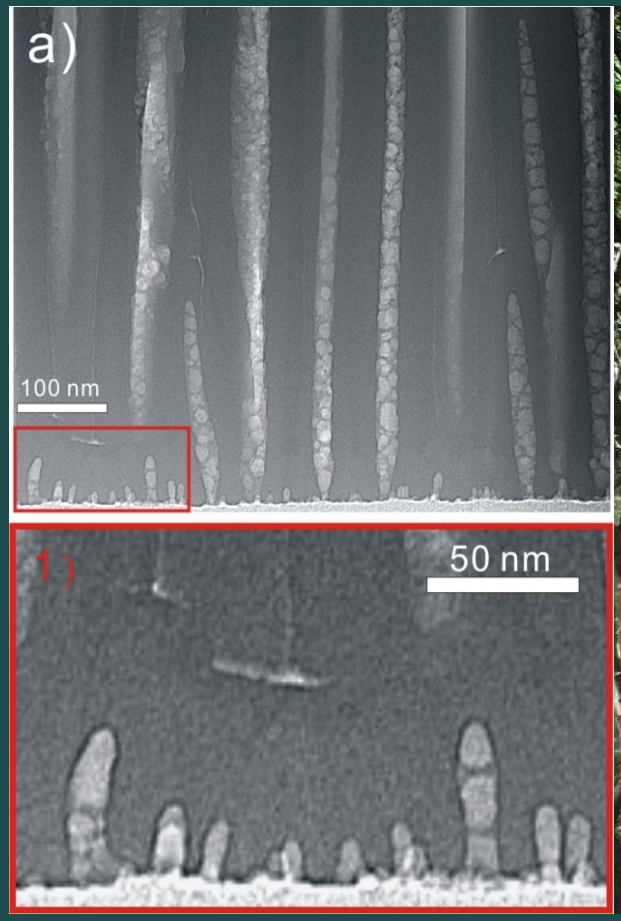
Growth Behavior of Arrayed AAO Nanochannels



one-step anodized channels
characteristic size ~ 30 nm

shrub forest (mangrove)
characteristic size ~ 10 cm

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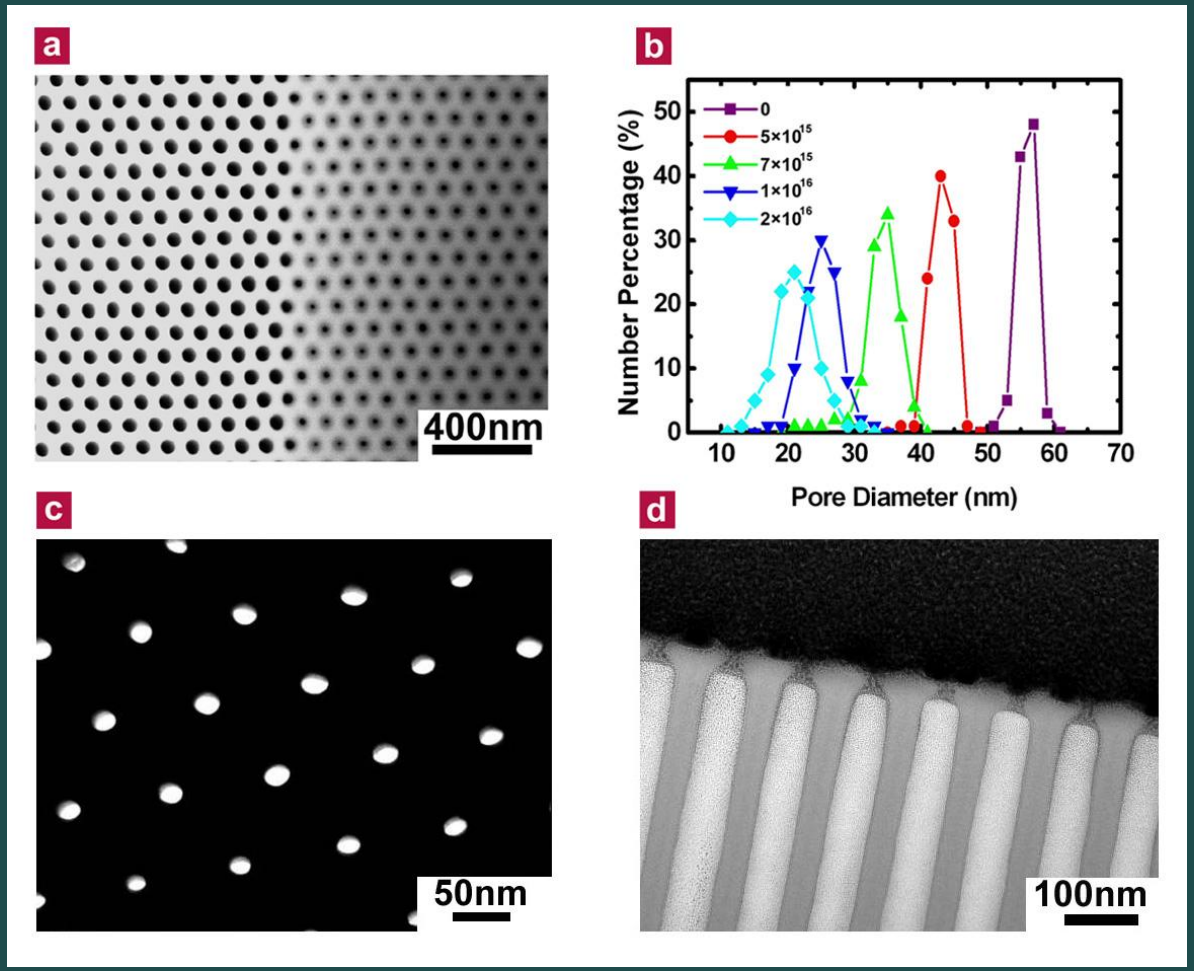
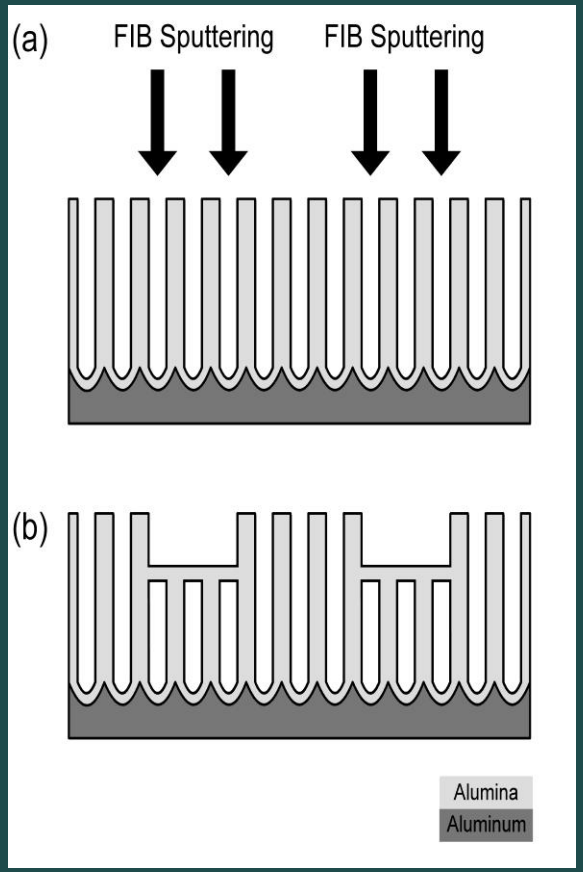
Closure of Nanochannels by FIB bombardment





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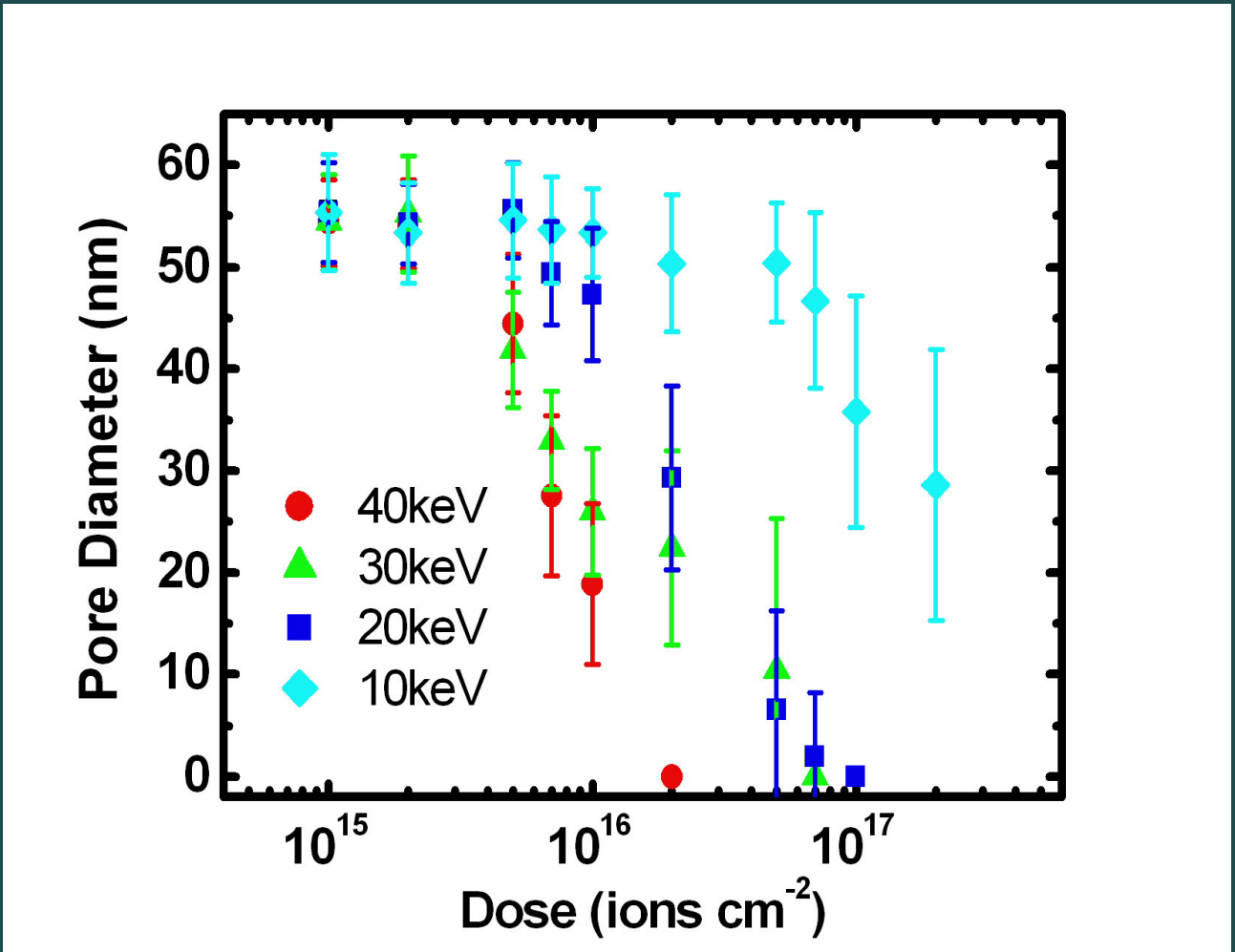
Channel Closure by FIB of Different Energies



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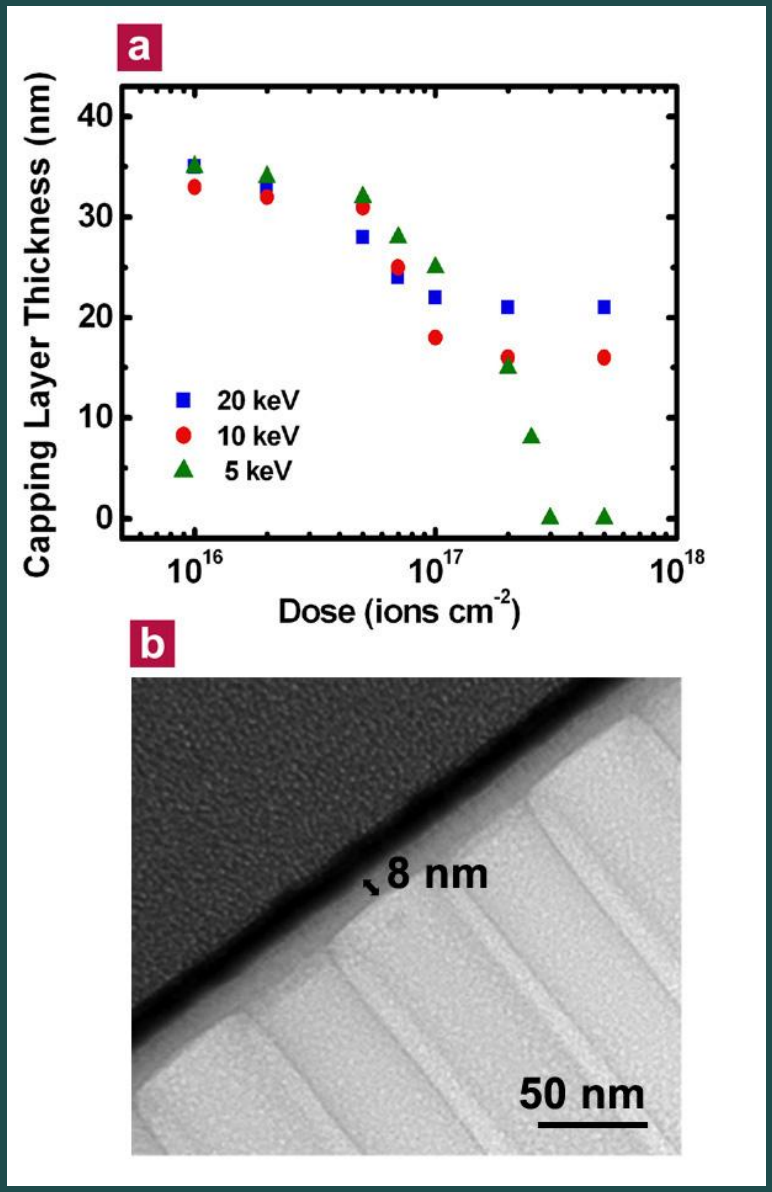
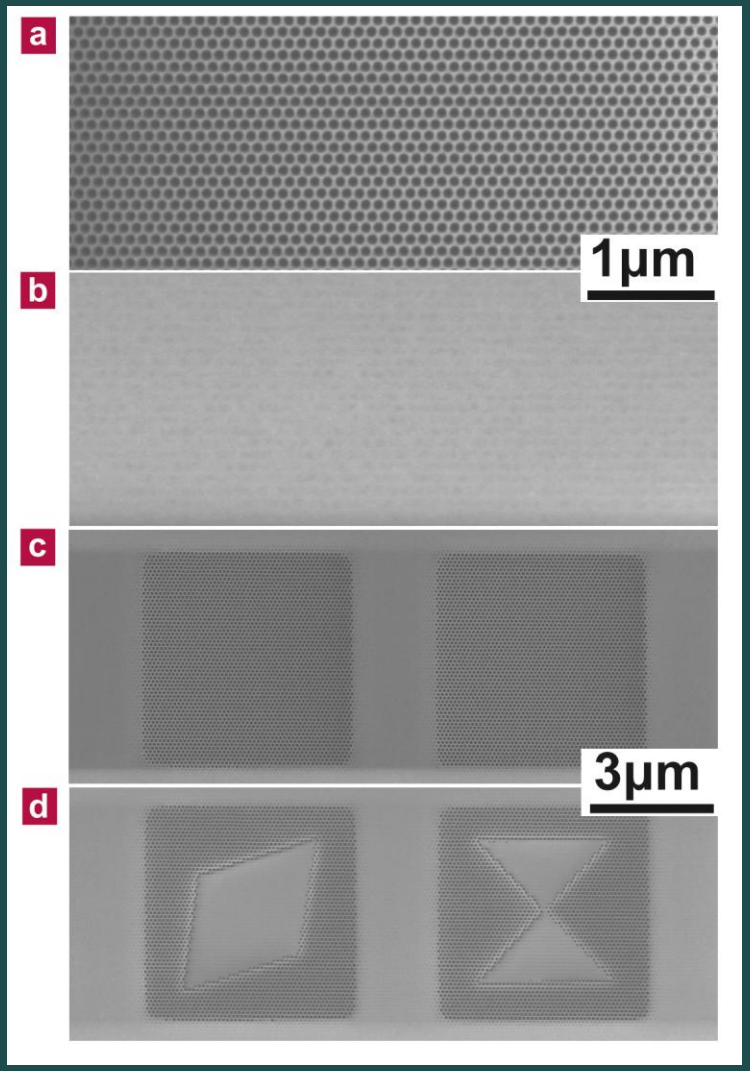
Channel Re-opening by FIB bombardment





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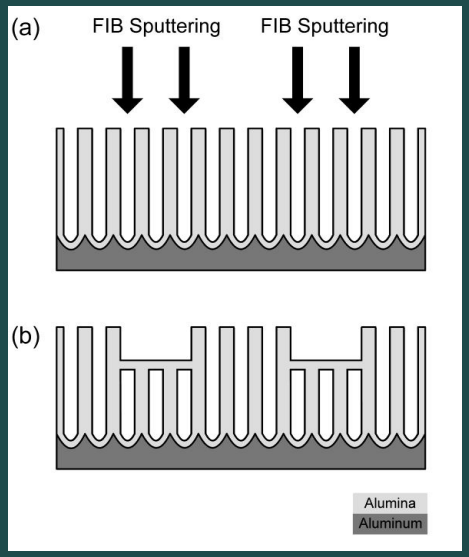
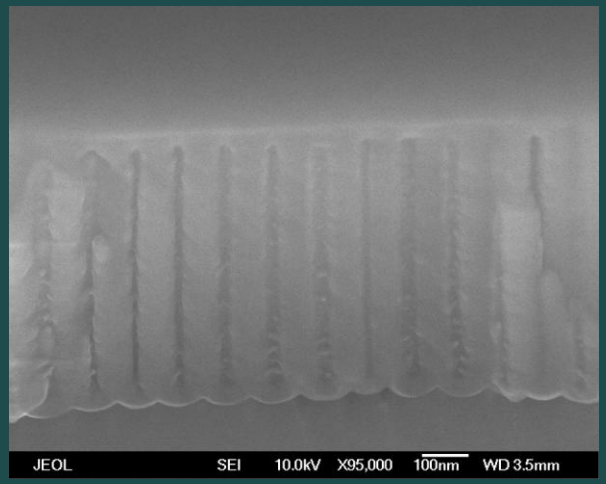
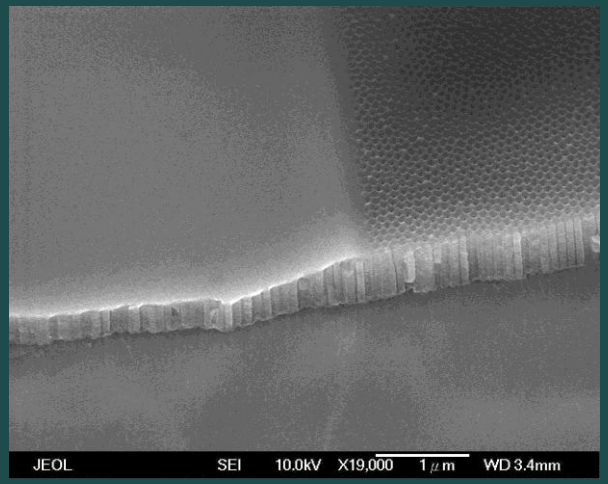
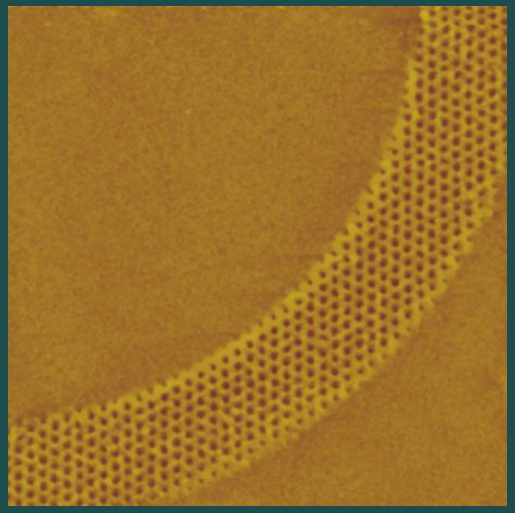
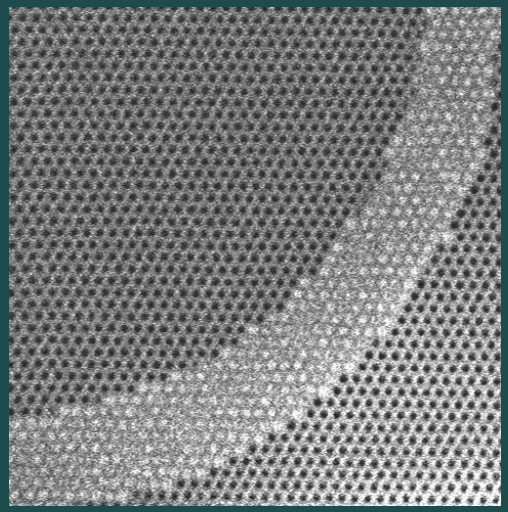
Custom-Designed Array of Nanochannels & Ag-Nanoparticles

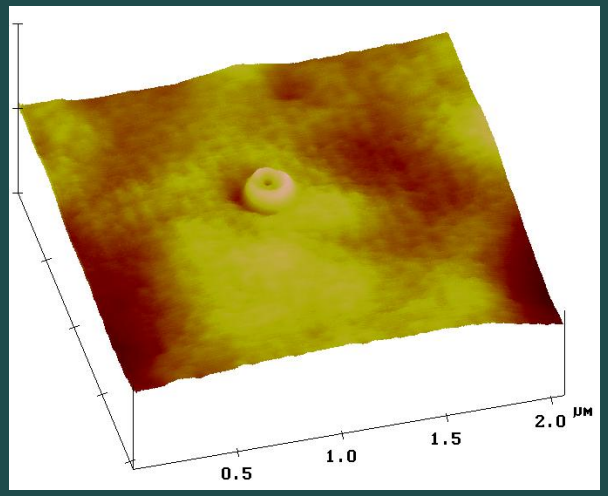












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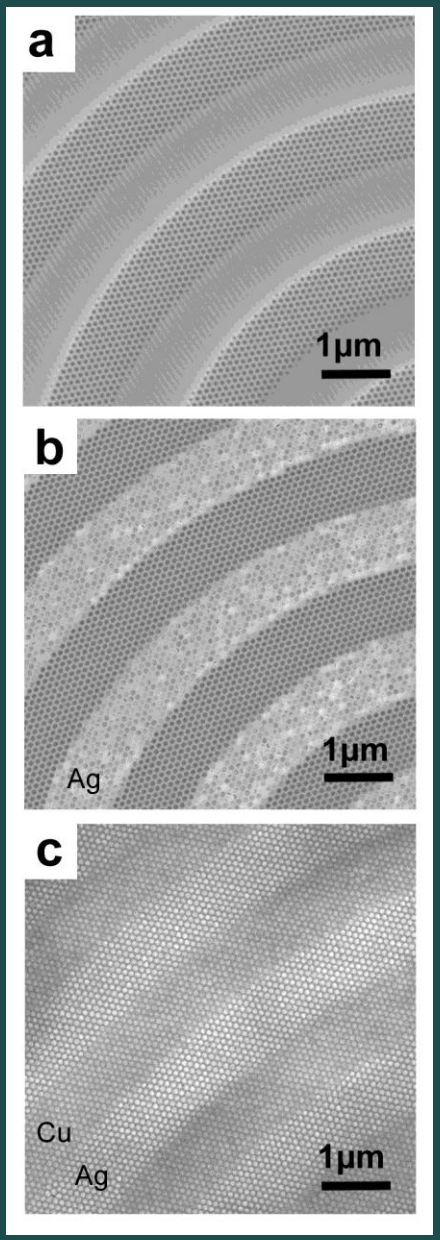
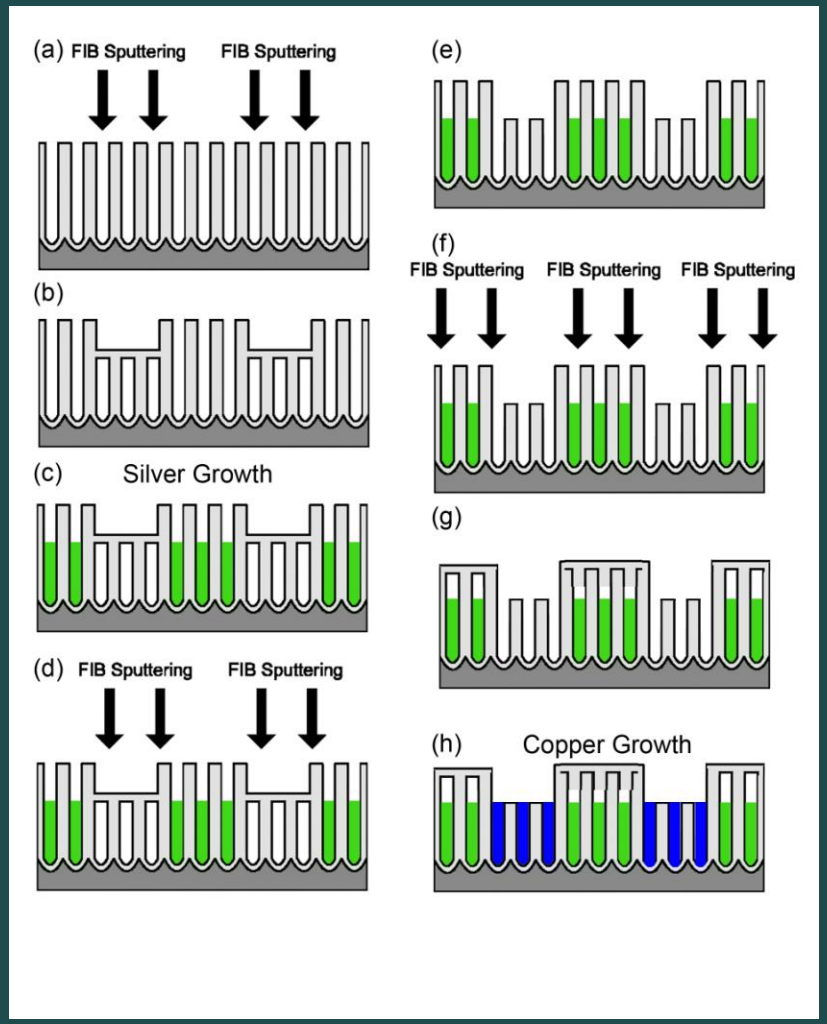
Custom-Designed Array of Multi-Element Nanowires





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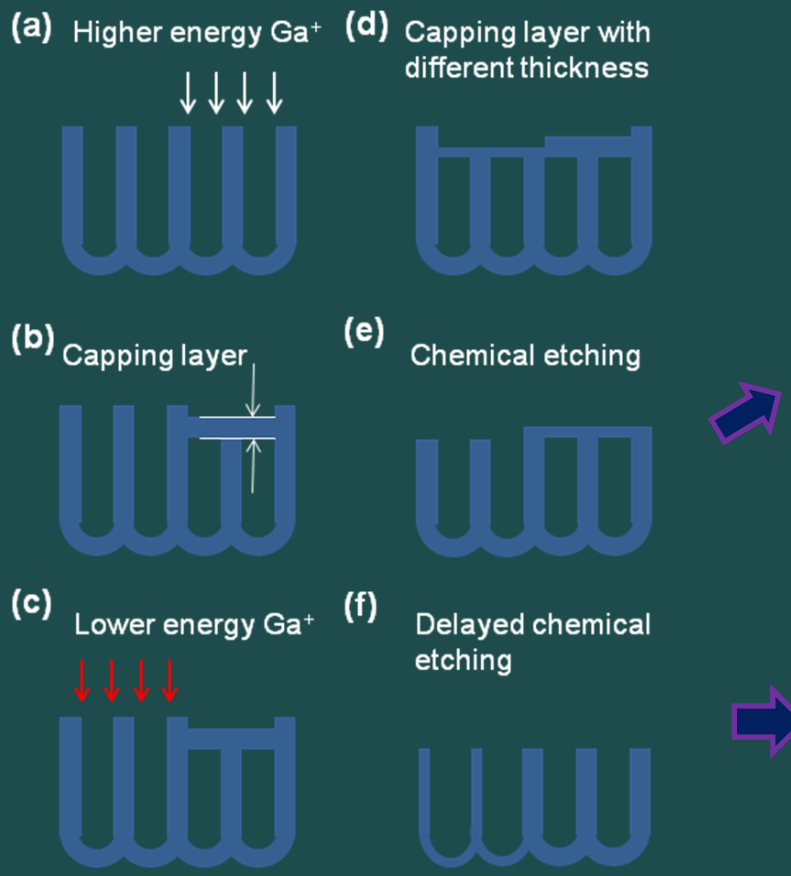
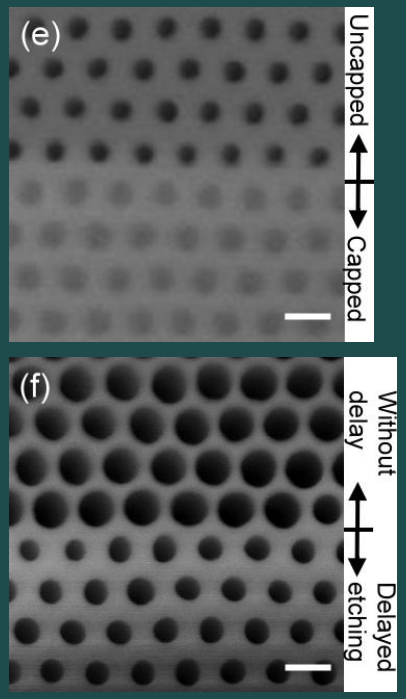
An array of anodic alumina nanochannels with variable

原分所蔡焜棟博士



Contrast generation on pore diameters (>40nm)



(Scale bar: 100nm)

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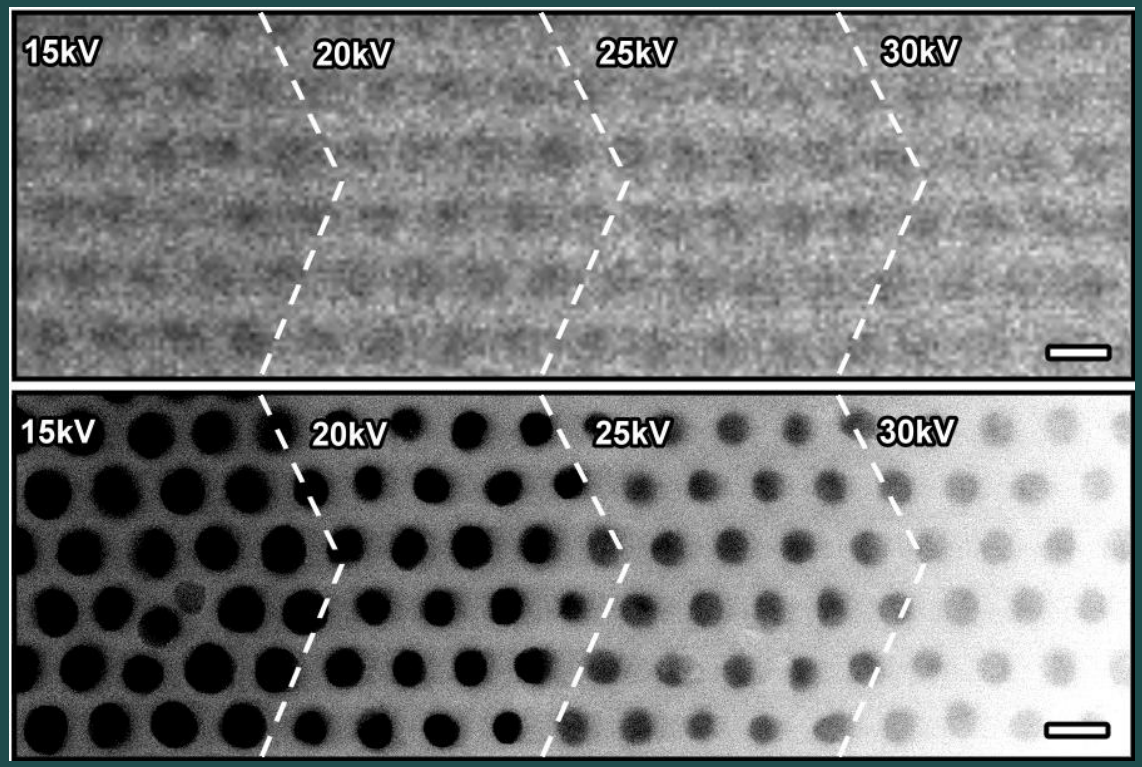
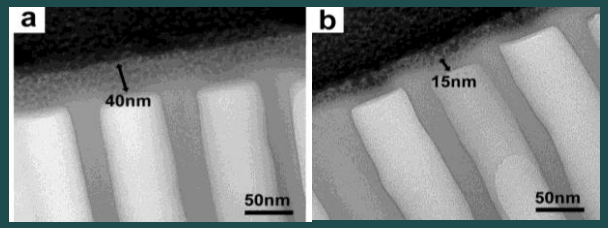
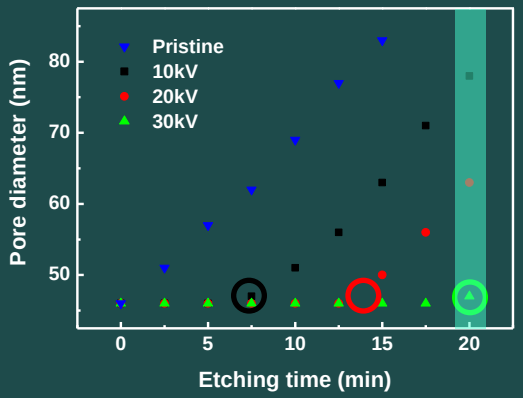
Creation of nanochannels with tunable diameters



Scale bar:100nm



20kV 30kV



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Creation of nanochannels with tunable diameters

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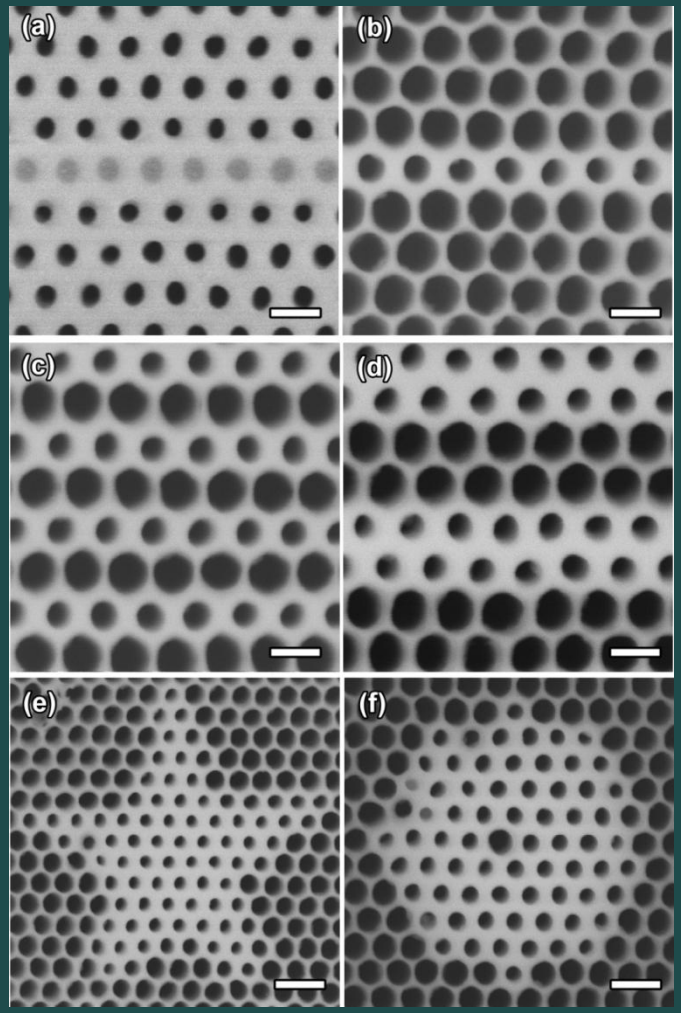

← Single line

← Grating-like

← Individually addressable

Scale bar:100nm

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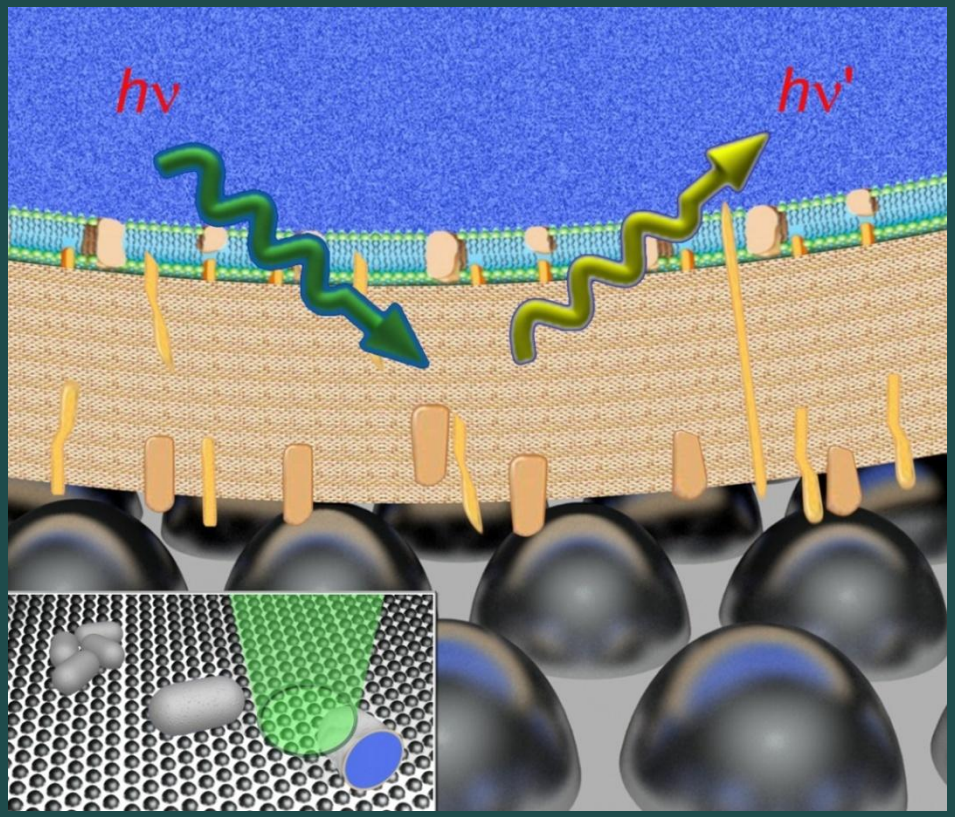
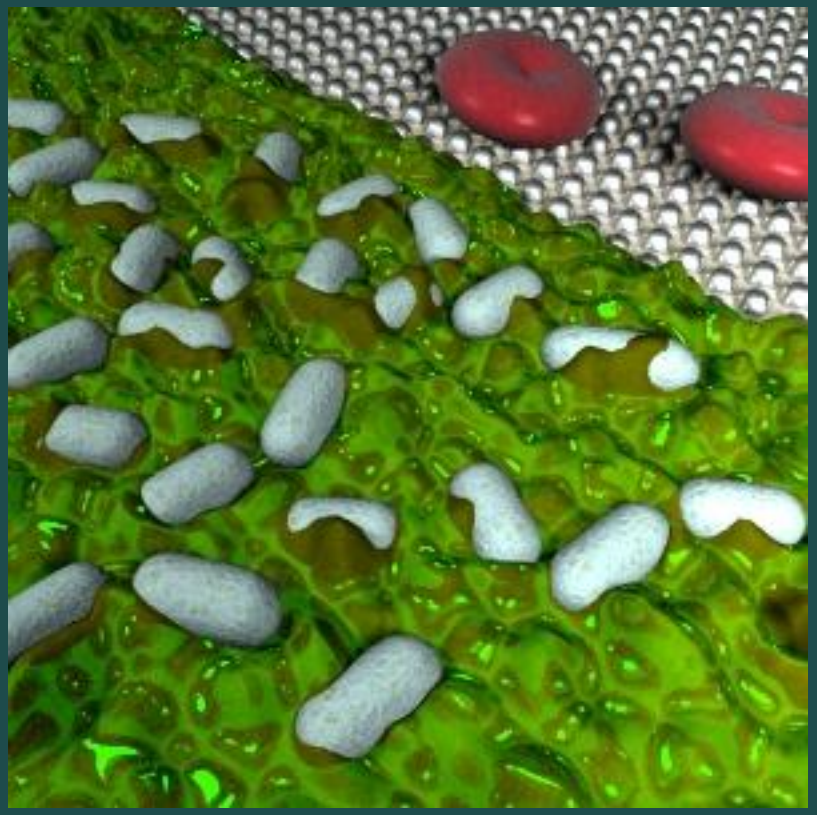
A Voyage from Atoms/Molecules and Clusters/Nanostructures to Bacteria and Planet-Human



Plos One 2009



Nat. Comm. 2011

Yuh-Lin Wang (王 玉 麟)
IAMS, Academia Sinica & Dept. of Physics, NTU
IAMS (6/16//2015)

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A High Speed SERS-Based Platform for Bacteria, Food and Environment-related Studies

1. Antibiotic susceptibility: To delineate bacteria's response to antibiotic treatments (Yang-Ming University, NTU Hospital)
2. Differentiation of *Mycobacterium tuberculosis* (TB) and *non-tuberculosis Mycobacteri*a (Center for Disease Control, Taiwan)
3. Fake olive and other food oils (Yang-Ming University)
4. Probiotics: *Lactobacillus reuteri* and *Lactobacillus johnsonii* (IAMS)
5. Environmental contaminants (Environmental Analysis Lab, EPA)

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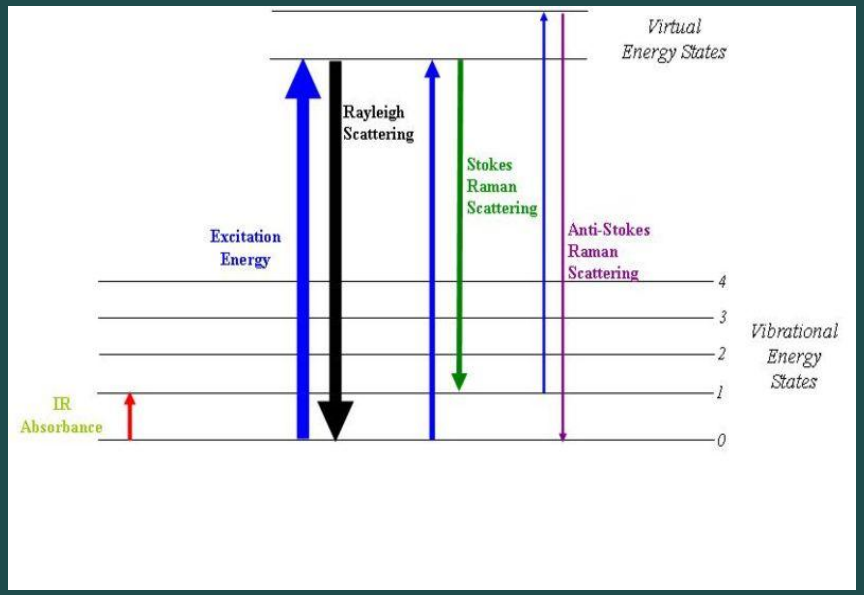
Raman Scattering



Chandrasekhara Venkata Raman was born at Trichinopoly in Southern India on November 7th, 1888.
His father was a lecturer in mathematics and physics so that from the first he was immersed in an academic atmosphere.
In 1922 he published his work on the "Molecular Diffraction of Light", the first of a series of investigations with his collaborators which ultimately led to his discovery, on the 28th of February, 1928, of the radiation effect which bears his name ["A new radiation", *Indian J. Phys.*, 2 (1928) 387], and which gained him the 1930 Nobel Prize in Physics.

Sir Venkata Raman died on November 21, 1970.

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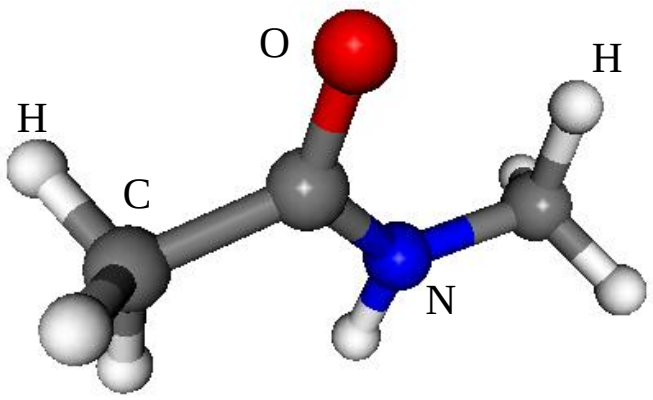
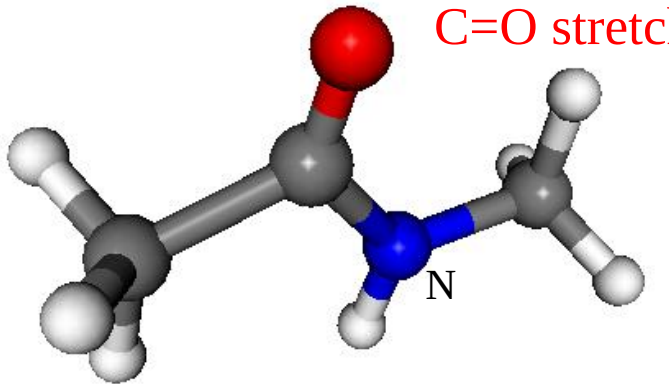
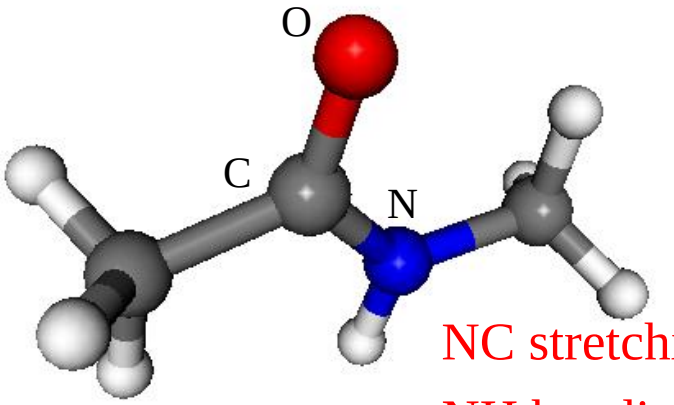
Raman Scattering & Molecular Vibration



CH_3 umbrella

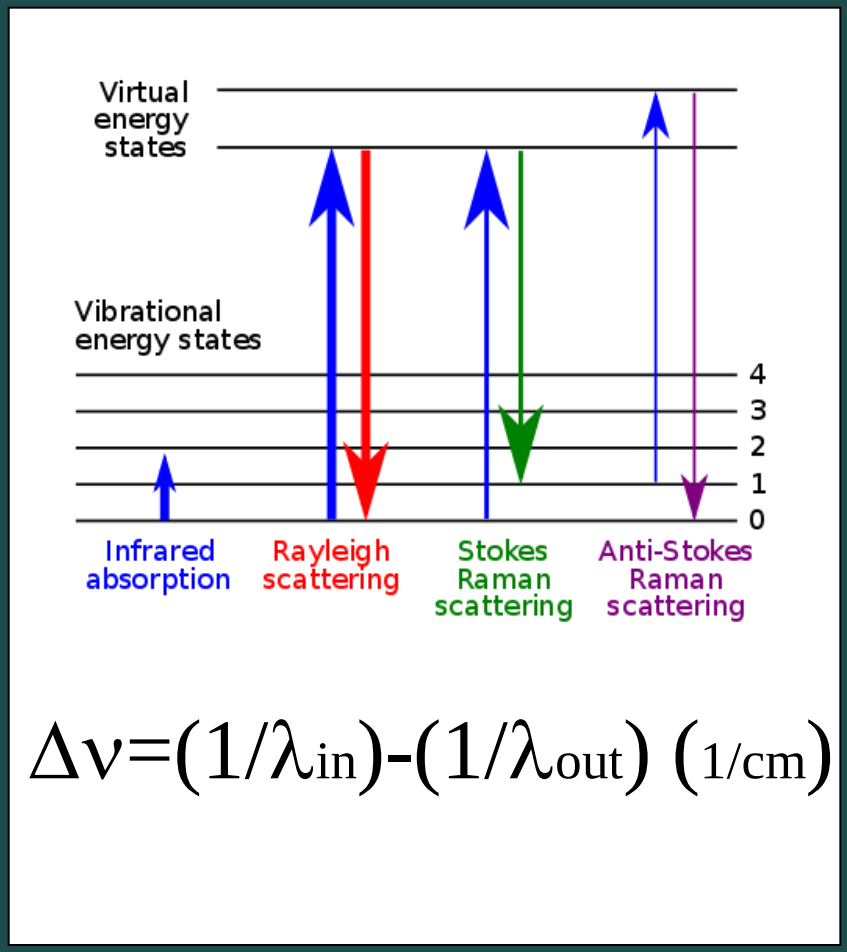
C=O stretching





NC stretching

NH bending



$$\Delta\nu=(1/\lambda_{in})-(1/\lambda_{out})\ (1/cm)$$

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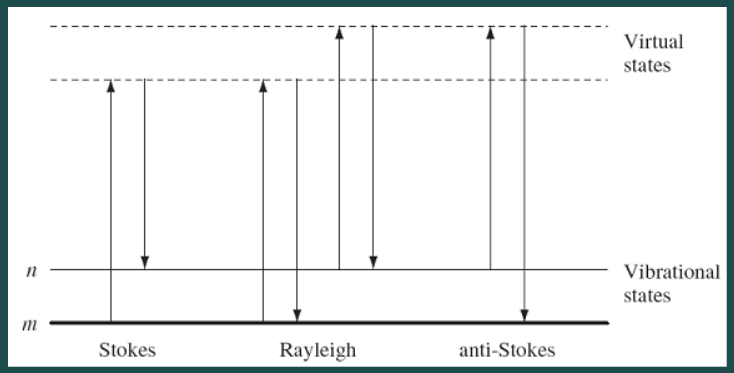
Surface Enhanced Raman (SERS)

σ (fluorescence) ~ 10^{-16} (cm^2/molecule)
σ (Raman) ~ 10^{-32} (cm^2/molecule)



First Observation of SERS

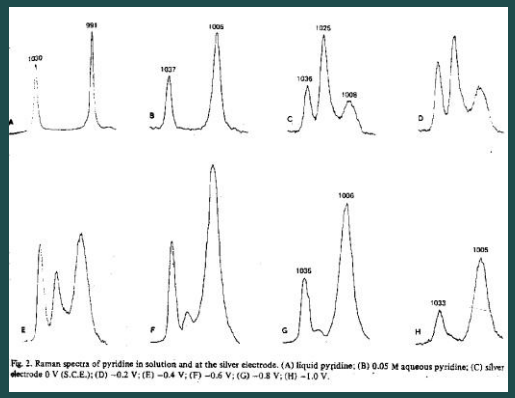
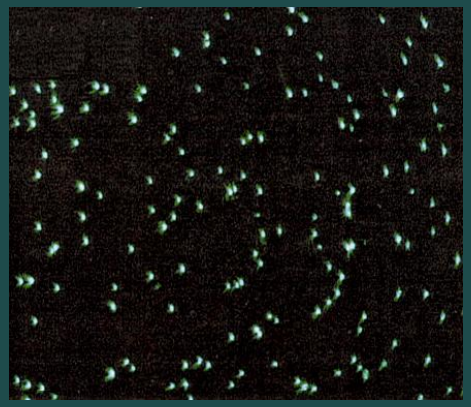


Fig. 2. Raman spectra of pyridine in solution and at the silver electrode. (A) liquid pyridine; (B) 0.05 M aqueous pyridine; (C) silver electrode 0 V (S.C.E.); (D) −0.2 V; (E) −0.4 V; (F) −0.6 V; (G) −0.8 V; (H) −1.0 V.

M. Fleishmann, P. J. Hendra, A. J. MacQuillan, Chem. Phys. Lett. 26 (1974) 163

First Direct Observation of 'Hot-Spots' in SERS



S. Nie and S. R Emory Science 275(1997)1102

Exploit field enhancement to increase the Raman signal, facilitating optical spectroscopic detection and study of bio-molecules

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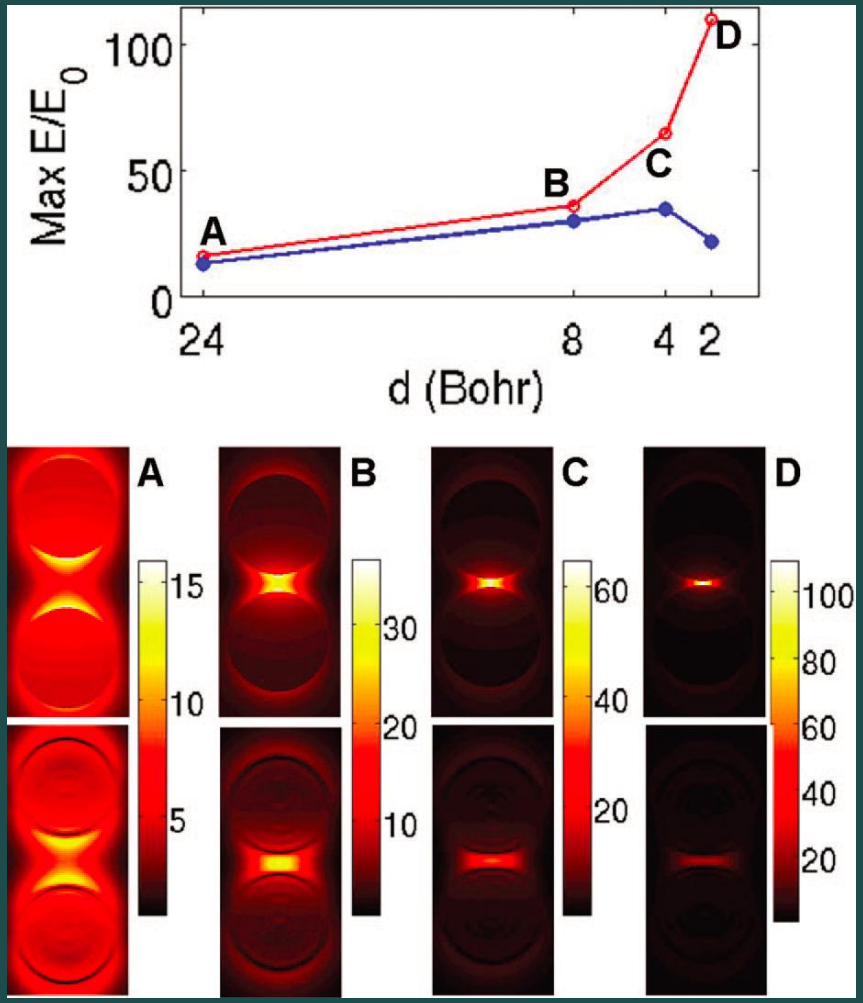
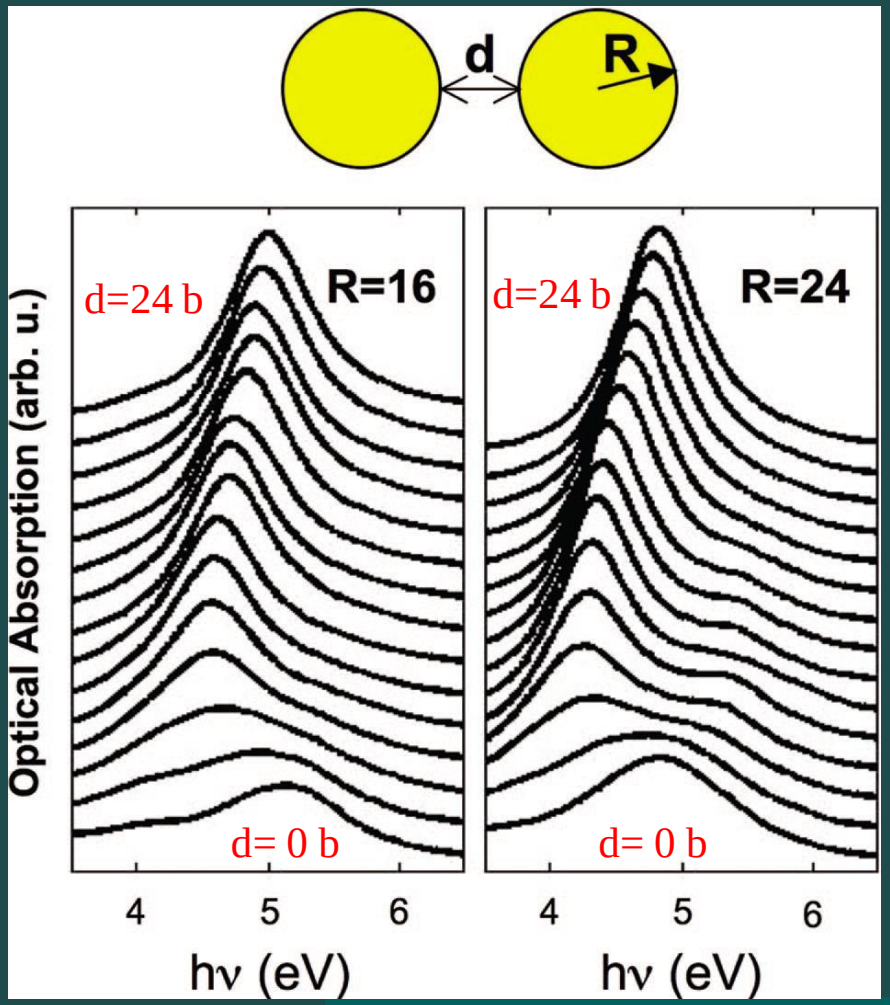
Exploiting Field Enhancement a 'Hot-Junctions' for Surface Enhanced Raman Spectroscopy (SERS)





Jorge Zuloaga, Emil Prodan, and Peter Nordlander
Nano Lett. 9 (2009) 887.

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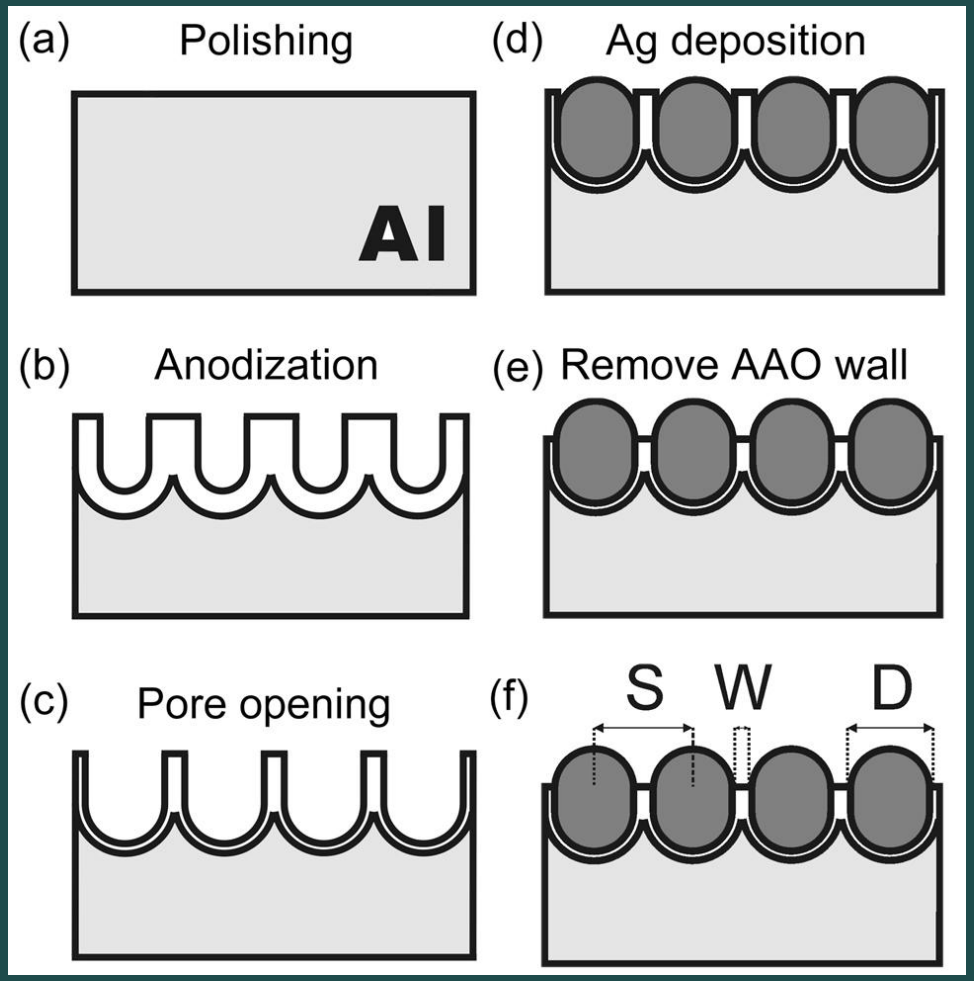
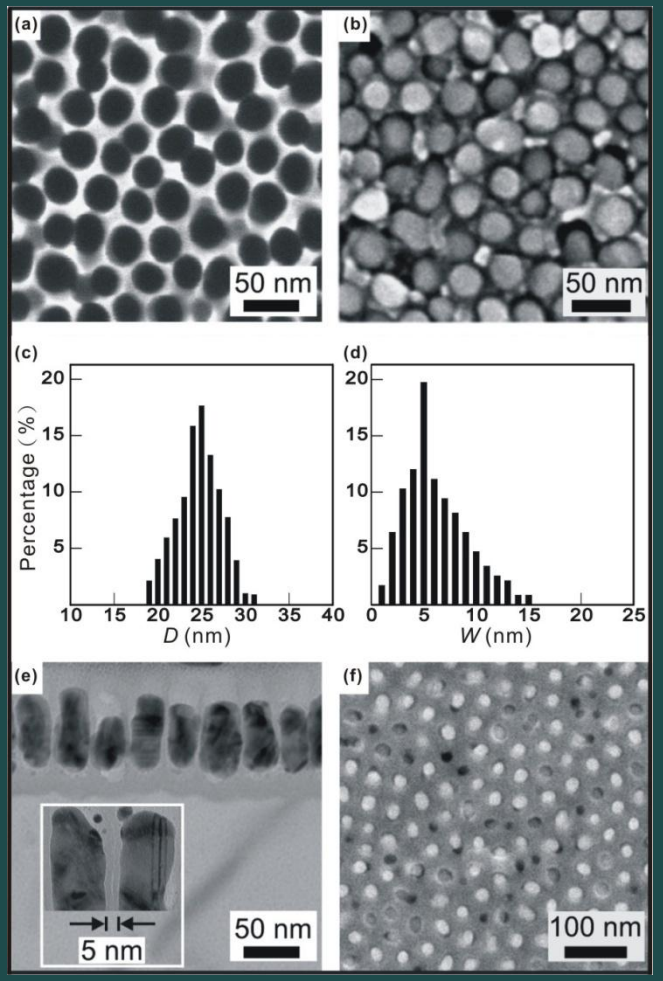
利用「氧化鋁奈米管」陣列製造「表面增強光譜」奈米光學晶片





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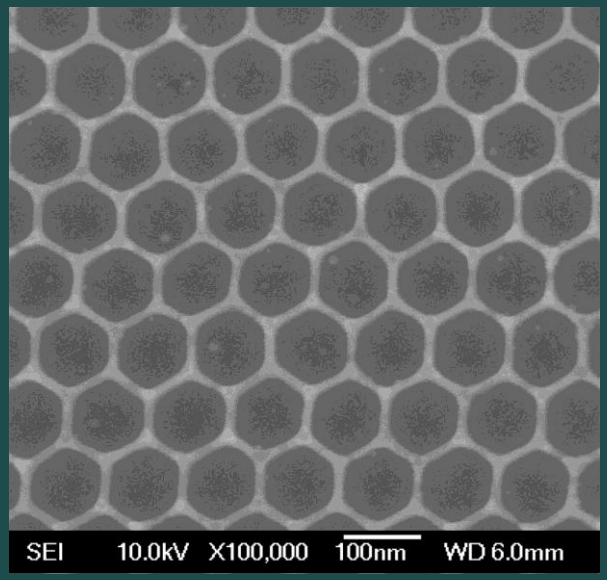
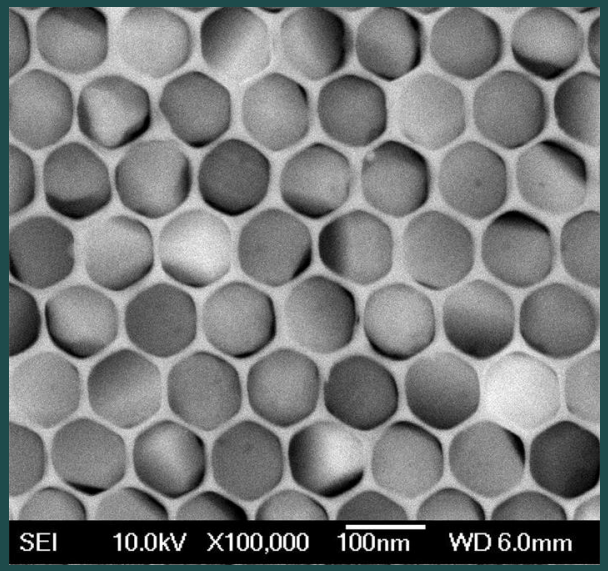
Fabrication of Ordered Array of Ag-nanoparticles

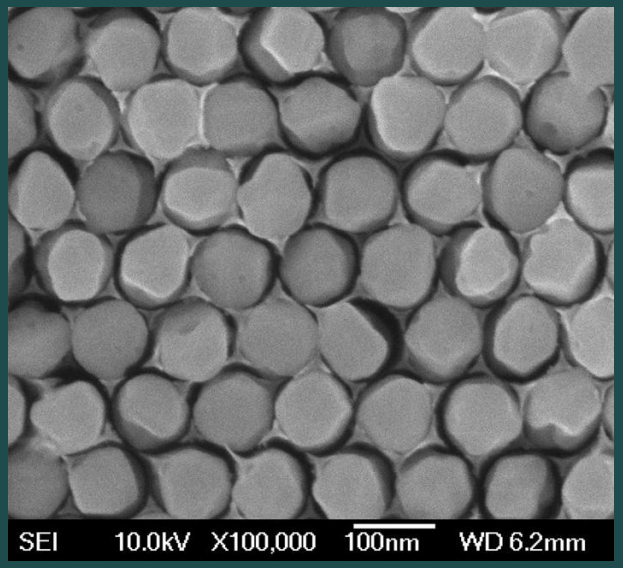
AAO nanochannel array with 10 nm channel wall



AAO nanochannel array partially filled with Ag



AAO nanochannel array filled with Ag nanocrystals



- USA Patent granted, 2008
- SERS substrate fabrication nanotechnology transferred to MA-tek, 2009

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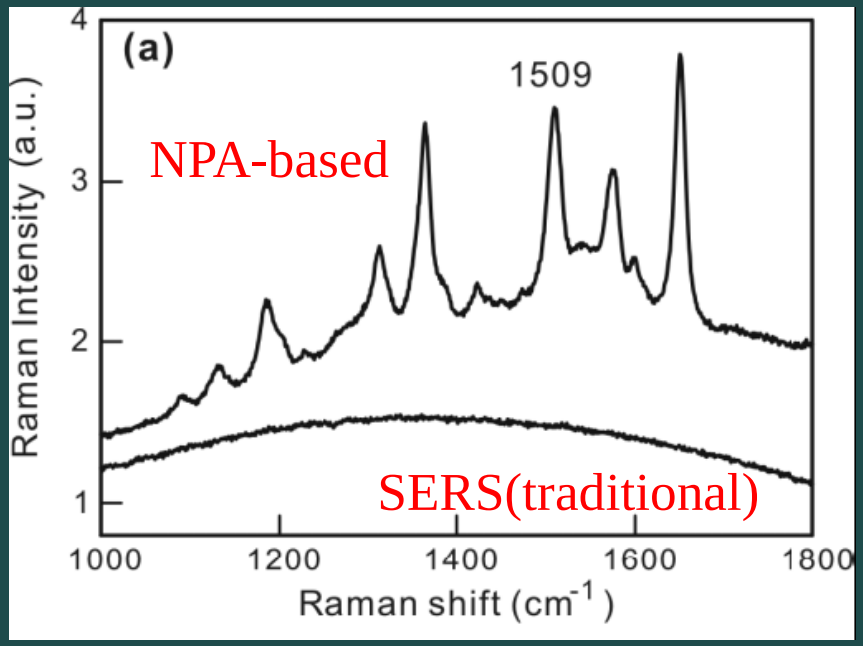
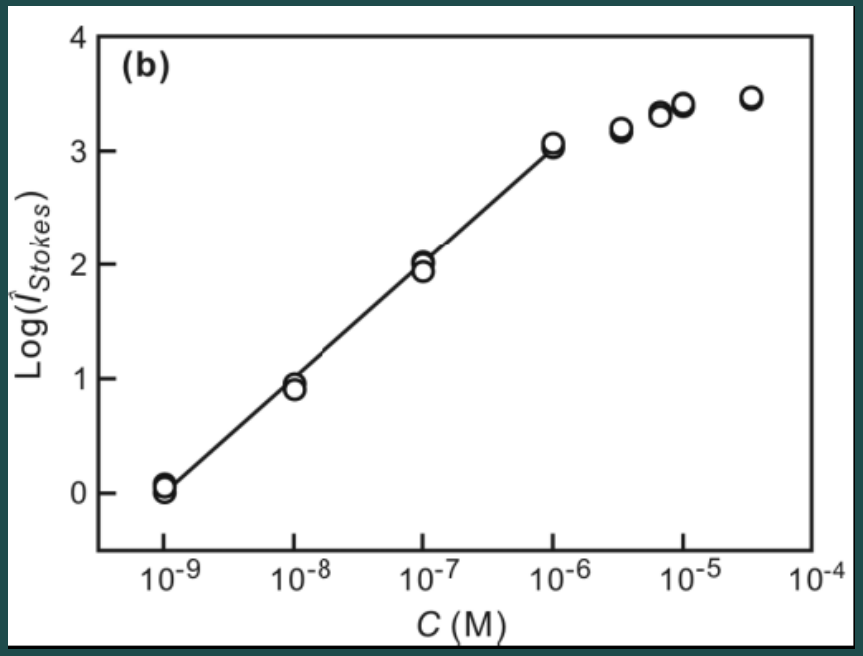
Comparison between NPA-based and Traditional SERS





a) NPA-based SERS of 10–6 M R6G solution (top) and on a typical SERS substrate prepared by depositing ~ 30 nm Ag on Si (bottom); b) NPA-based SERS at 1509 cm^{-1} as a function of the molecular concentration on a logarithmic scale.

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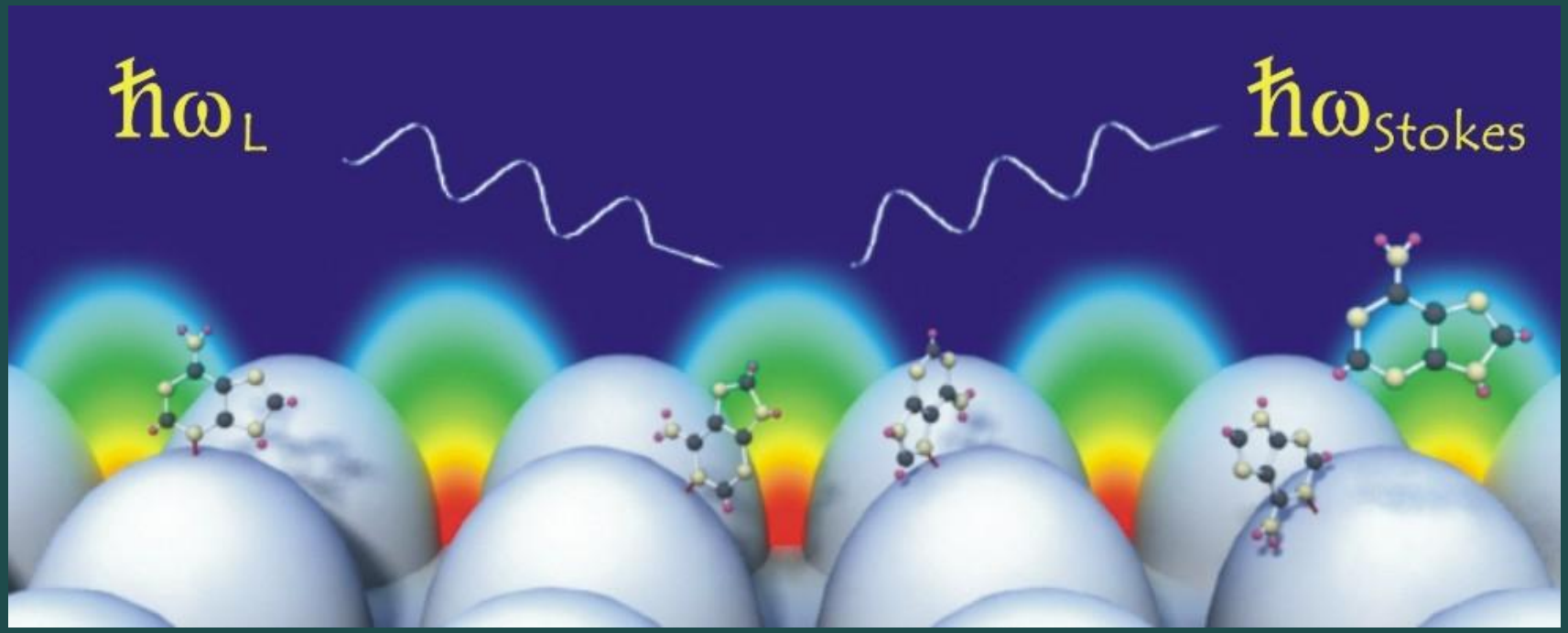
Nanoparticle-Array-based Surface Enhanced Raman Scattering (NPA-based SERS)



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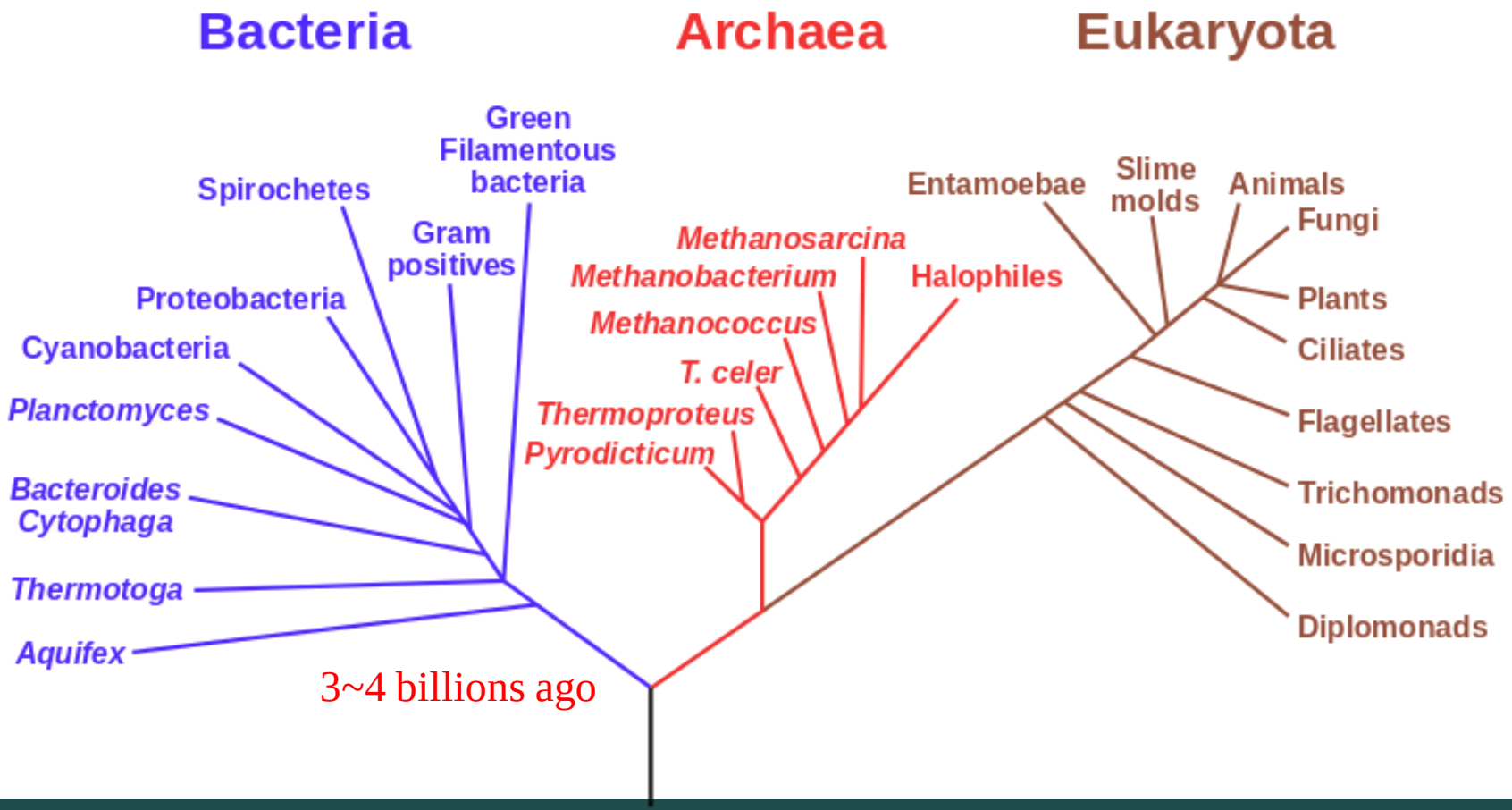
Phylogenetic Tree of Life



Life on earth started 4~5 Byrs, bacteria started 3~4 Byrs, plants & animals started ~1 Byrs, Homo sapiens started 3~4 Myrs ago

# of inhabitants on a ‘planet human’ is 10 times its cells #(10^{13}), their gene # is 100 times its genes # ($2x10^4$)

科學人2012年7月號

In other words:
We are 10% human
90% microorganism!!
We are 1% human
99% microorganism!!
Our microorganism weigh ~ 1.5 kg
Gut microbes: 400~40000 species
this ‘virtual organ’ improves energy harvest from food, synthesis of essential vitamin, degradation of complex plant polysaccharides…)

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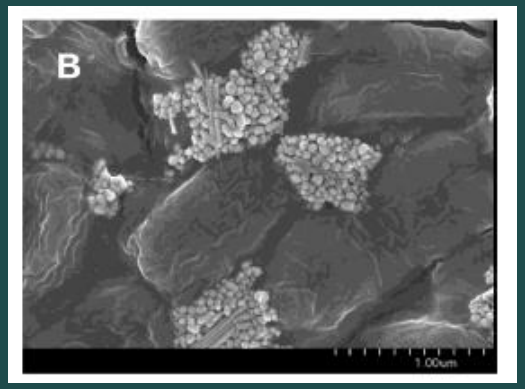
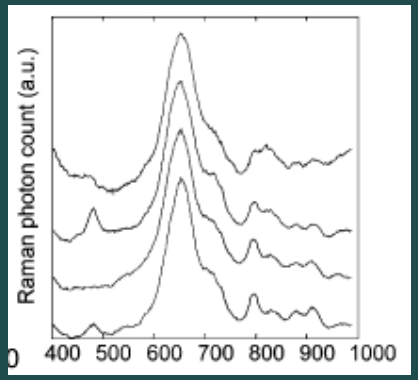
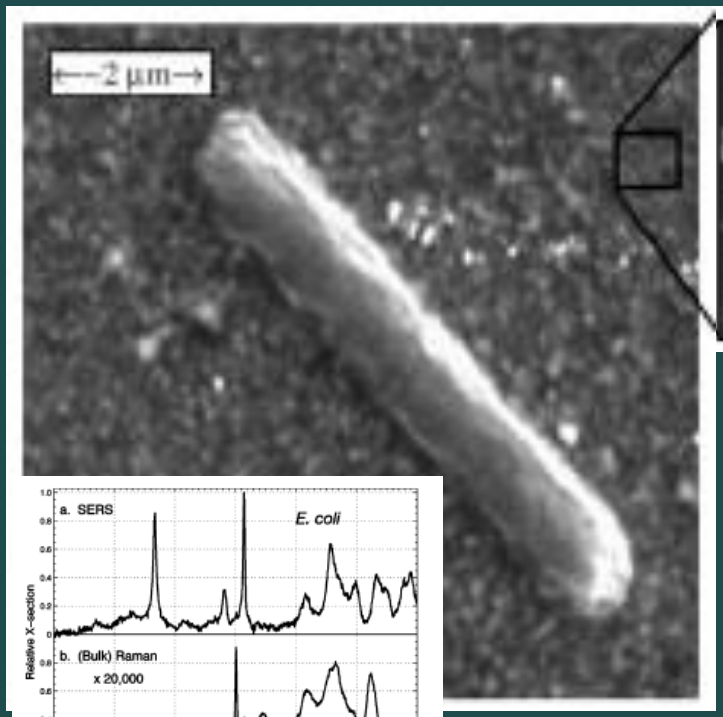
Comparison between previous and our ONPA-SERS substrates for bacteria studies

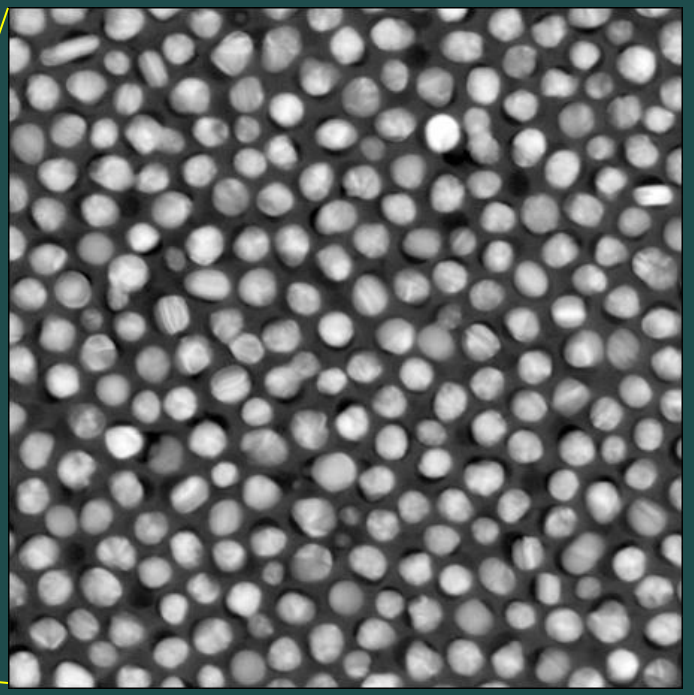




SERS achieved by mixing Au-nanoparticles with bacteria
Anal. Chem. 2004, 76, 40-47

ONPA-SERS substrate by IAMS/MA-tek





F. S.= 650 nm

SERS from a substrate with random Au-NP
Chem. Soc. Rev., 2008, 37, 883-884

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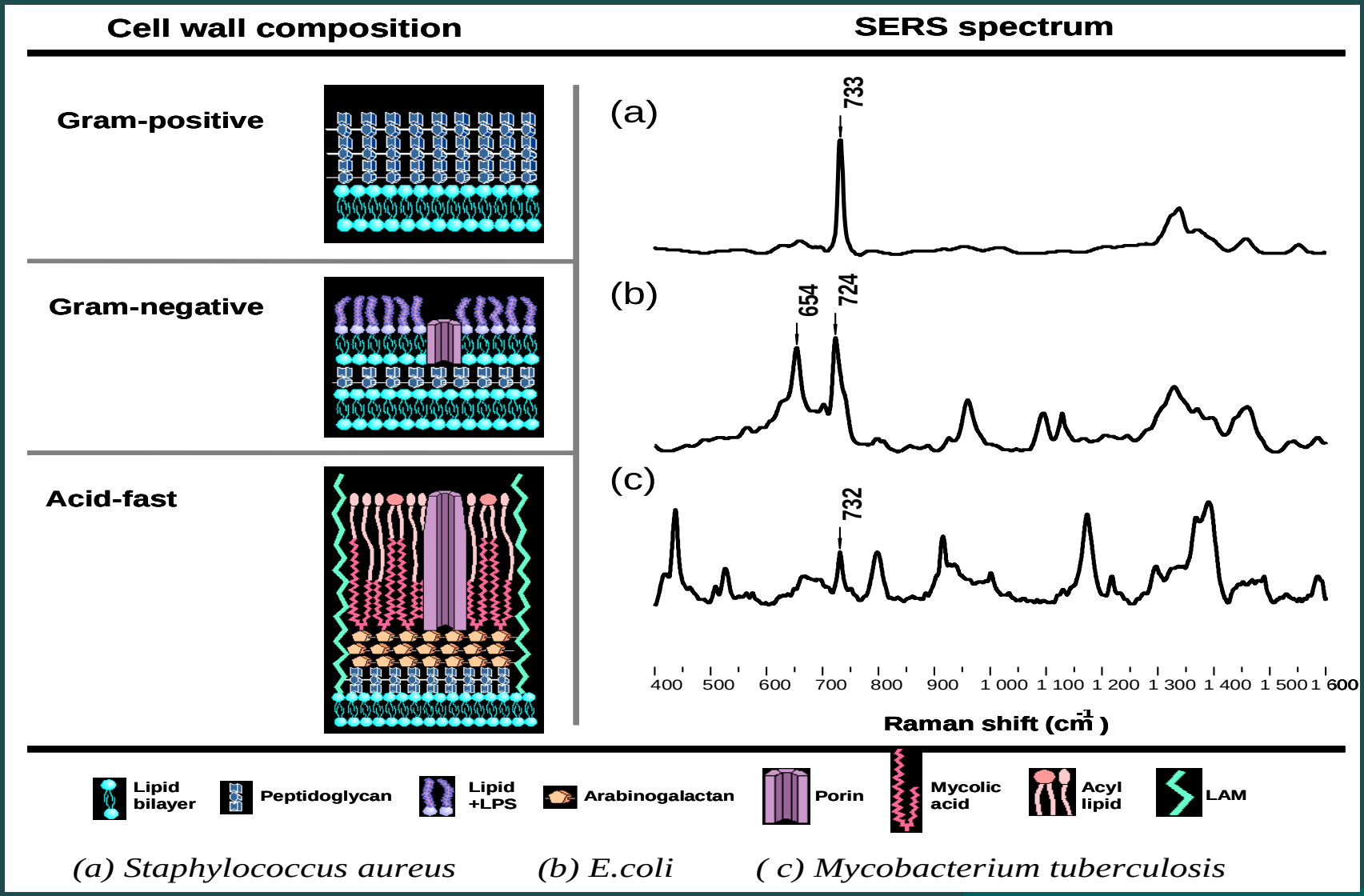
Three Typical SERS of Bacteria



(a) Staphylococcus aureus *(b) E.coli* *(c) Mycobacterium tuberculosis*

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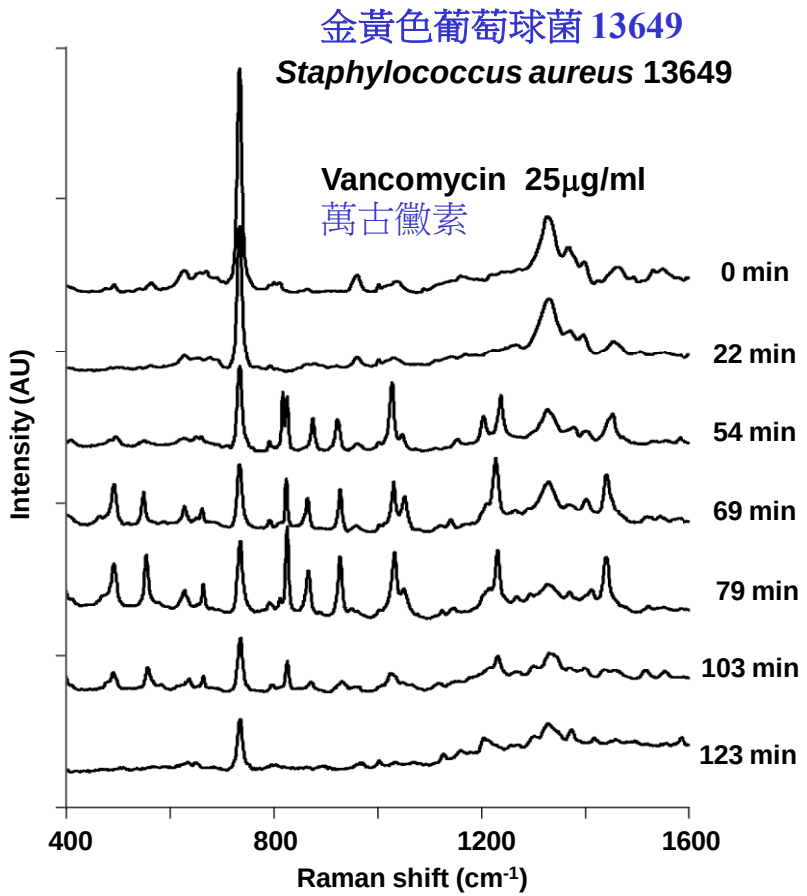
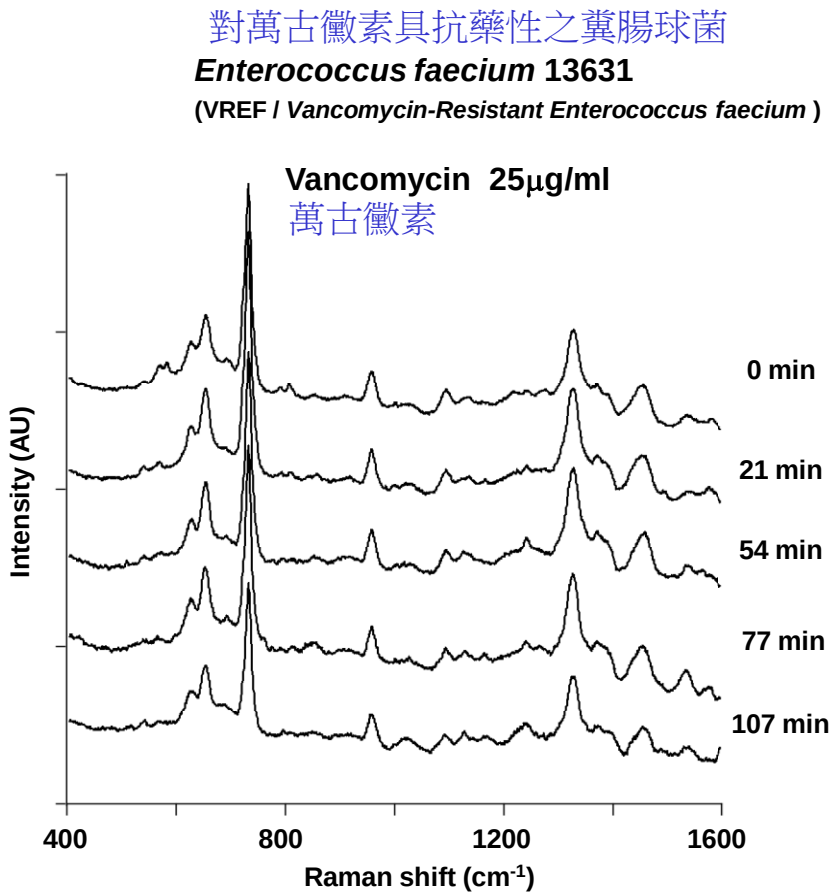
Changes of SERS from Bacteria during Antibiotic Treatment





Upon the treatment of vancomycin, the spectra of *Staphylococcus aureus* 13649 (vancomycin-susceptible) was dramatically shifted. But the spectra of *Enterococcus faecium* (vancomycin-resistant) 13631 had no changes.

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Conclusion

We have exploited the concept of 'constrained self-organization' to create an ensemble of identical magic-number clusters of atoms/molecules on crystal surfaces. The concept has also been exploited for the growth of AAO nanochannels with desired sizes and geometric arrangement, which can be used to create metamaterials with novel physical properties and SERS-active substrates with important biomedical applications.

However, to realize the dream of nanotechnology: precisely and promptly manipulating materials on the nanometer scale, we still have a very long way to go.

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Nano-Science/Technology Based on Anodic Aluminum Oxide (AAO) Templates

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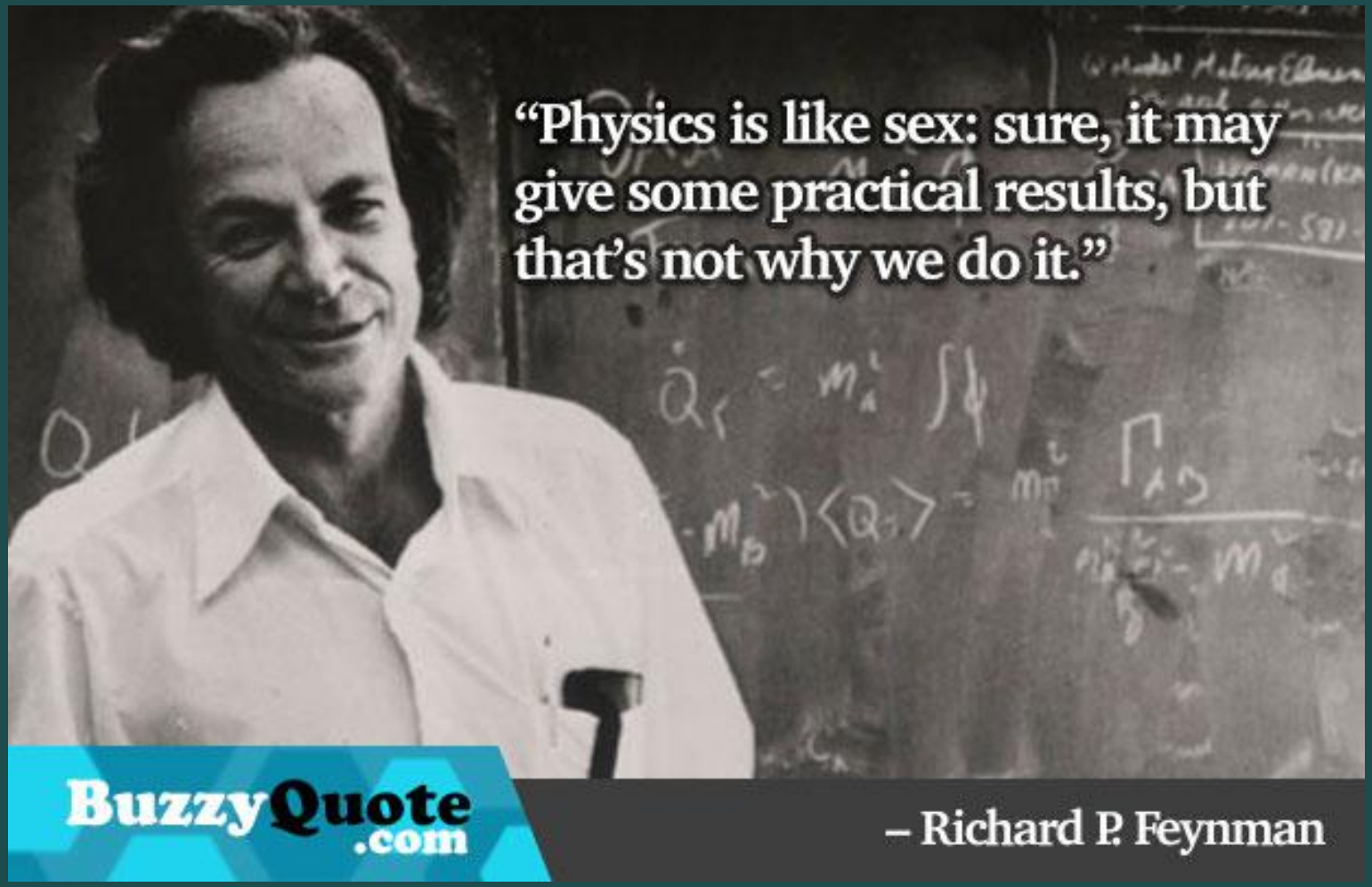

Why should tax payer pay physicists to have fun?

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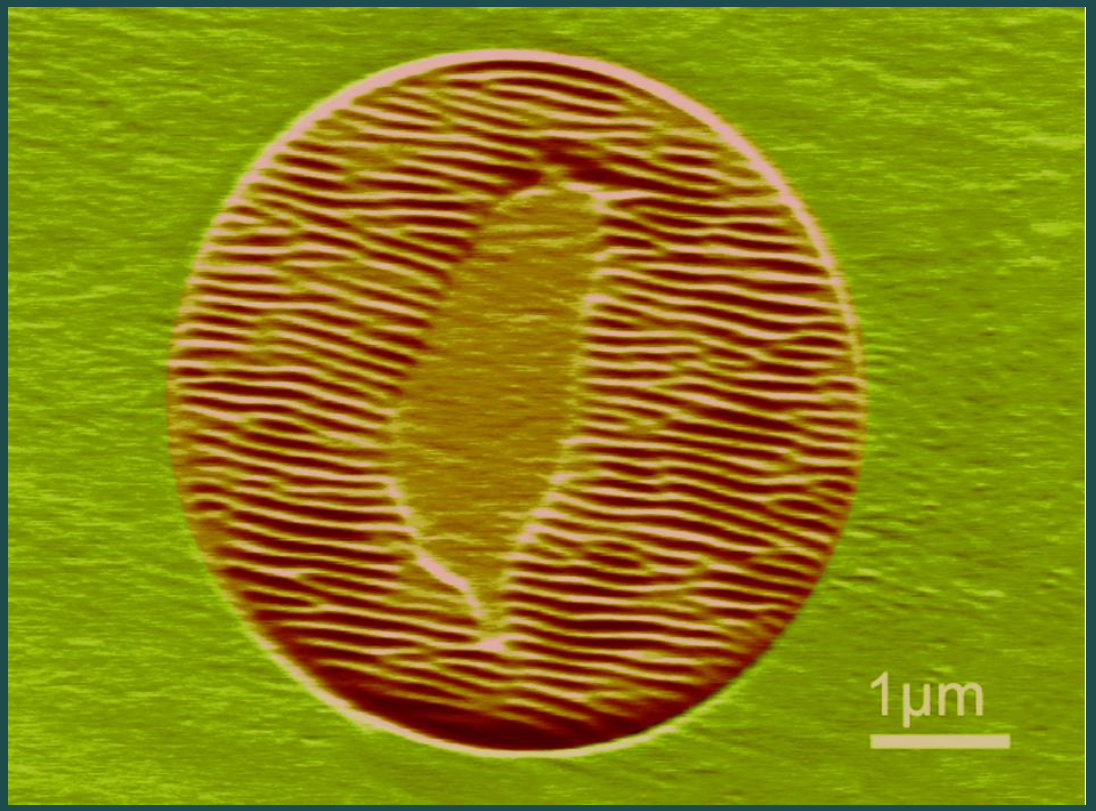
Thank You for Your Attention



‘Certification of diamond using an irreproducible nano-textured pattern fabricated by FIB induced self-organization

(Taiwan, R.O.C. Patent Number I 203406, April 24, 2006)

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