Universität Bielefeld

Fabrication and Imaging of 2D Nanomembranes and Graphene using Electron and Helium Ion Microscopes

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Outline:

Part I : Fabrication of 2D carbon nanostructures

Nanomembranes from SAMs

- Graphene and Graphenoids
- Nanoribbons and Nanosieves

Chemical Lithography

- Polymer Carpets
- Protein Biochips
- Janus Membranes

Part II : Helium Ion Microscopy

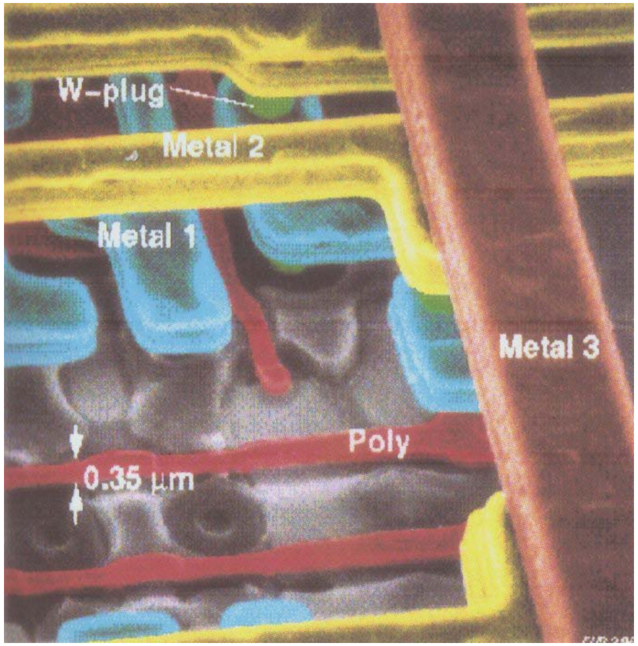
Basics

Nanomembranes and BioImaging

Concepts of Nanostructure Fabrication

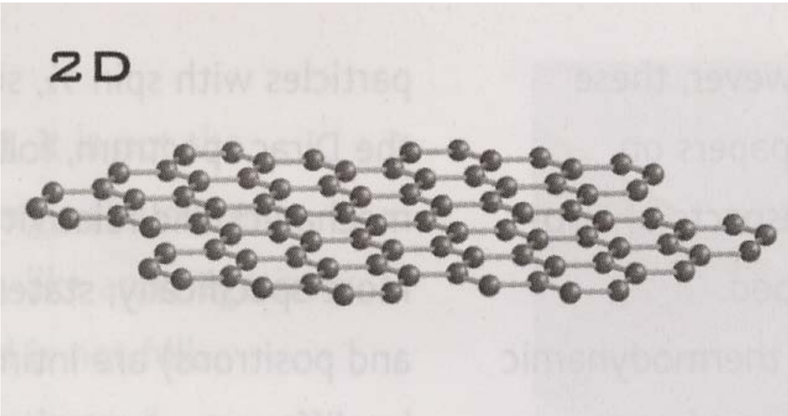
Integrated circuit
Lithography
(physics, engineering)

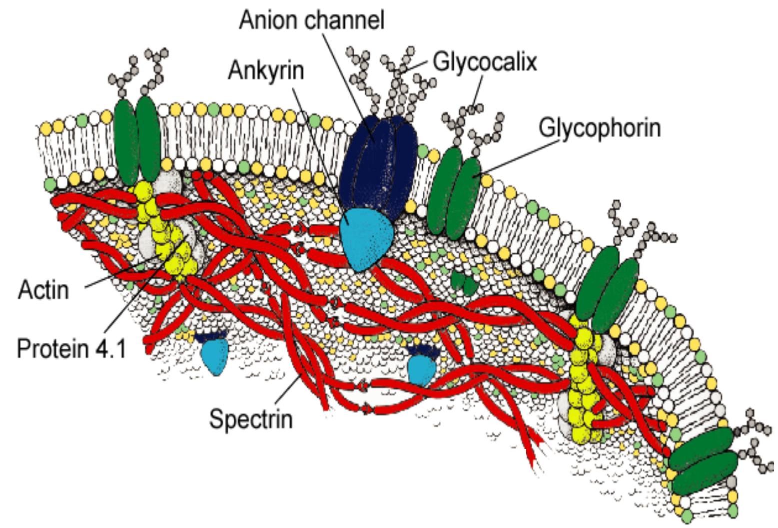
Eukaryotic cell
Self-assembly
(chemistry, biology)



Objective: Building (bio)functional molecular nanostructures with lithography and self-assembly

2-Dimensional Carbon Nanostructures





Graphene:

solid state, hard

Fabrication procedures :

- *Exfoliation of graphite/HOPG*
- *Epitaxy of SiC/TiC*
- *Oxidation/reduction of graphite*
- *CVD of hydrocarbons*

Hard to functionalize

Cell membranes:

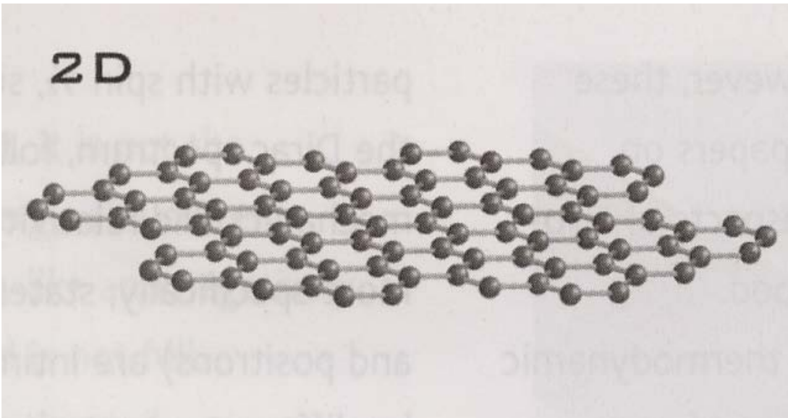
molecular, soft, directional

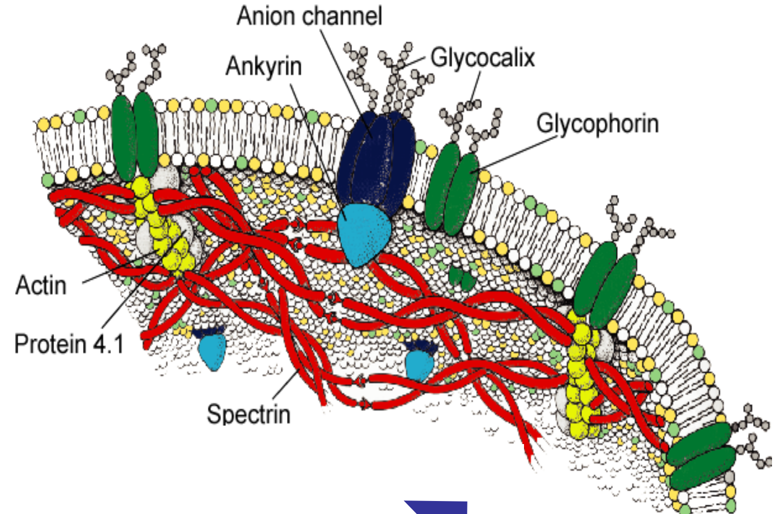
Fabrication procedures :

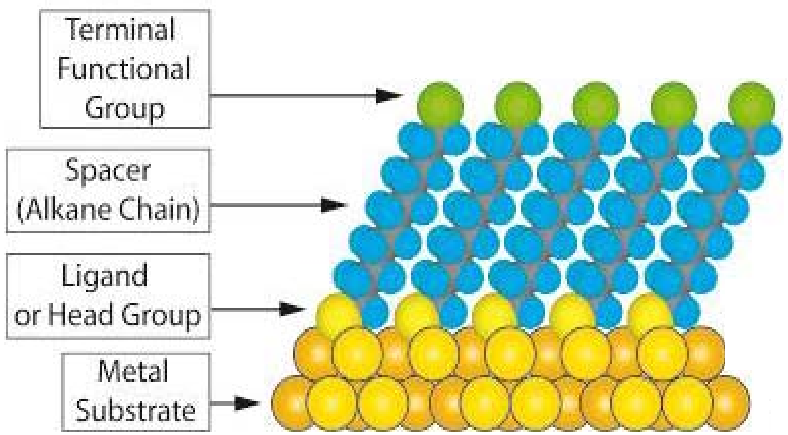
- *Self-Assembly*
- *Molecular recognition*
- *Enzymes*
- *Biology*

Functional

2-Dimensional Carbon Nanostructures







Self-Assembled Monolayer (SAM):

molecular, soft, directional

Fabrication:

Surface chemistry, Intermolecular interactions, lateral ordering, 2D-crystallization

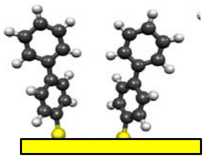
A molecular path to two-dimensional carbon nanostructures

Molecules

Solid substrates

self-assembly

Self-Assembled Monolayers (SAMs)

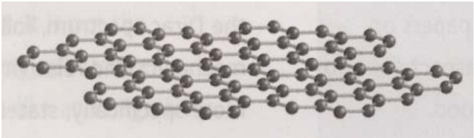


cross-linking by ***electron-beam***

Carbon Nanomembranes

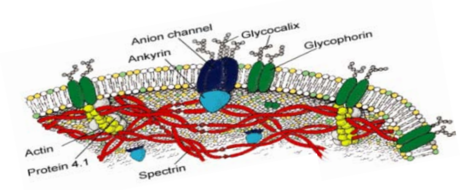
pyrolysis

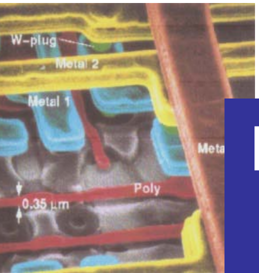
Graphene and Graphenoids



chemical, biological functionalization

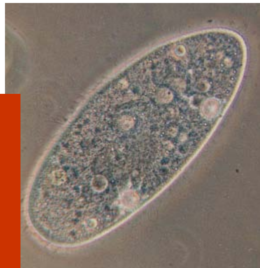
Functional Membranes





Electronics, NEMS, Sensors, …

Biomimetic, Medical, Biosensors,…

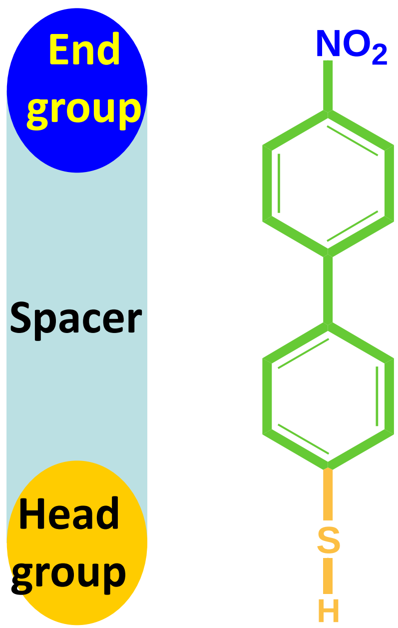


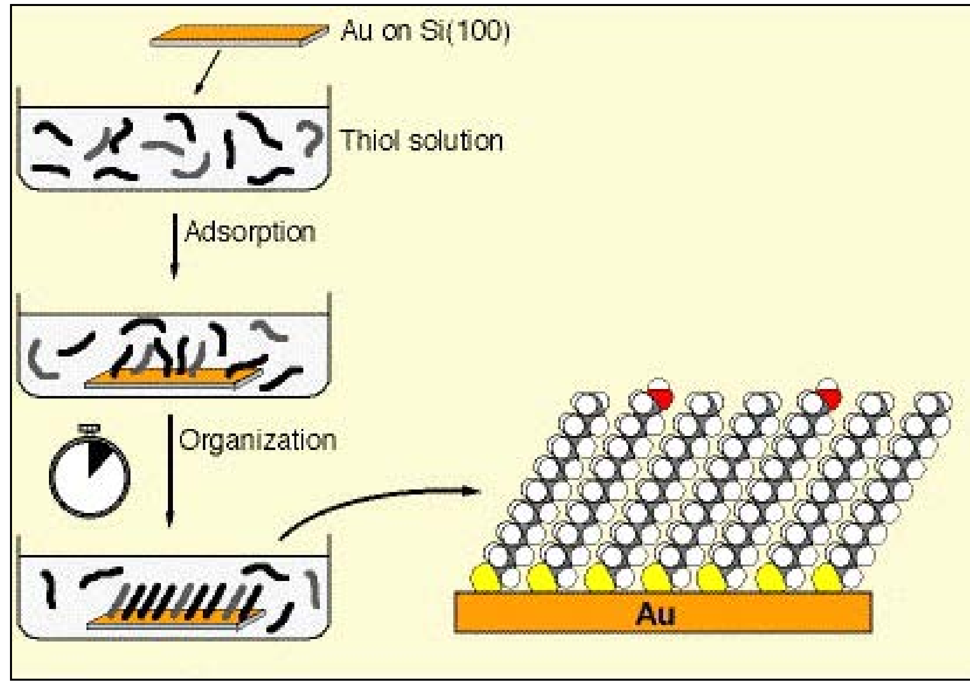
Self-Assembled Monolayers (SAMs)

-H
-OH
$-NO_2$
$-NH_2$
...

Alkyl
Phenyl
...

-SH
$-SiCl_3$
...





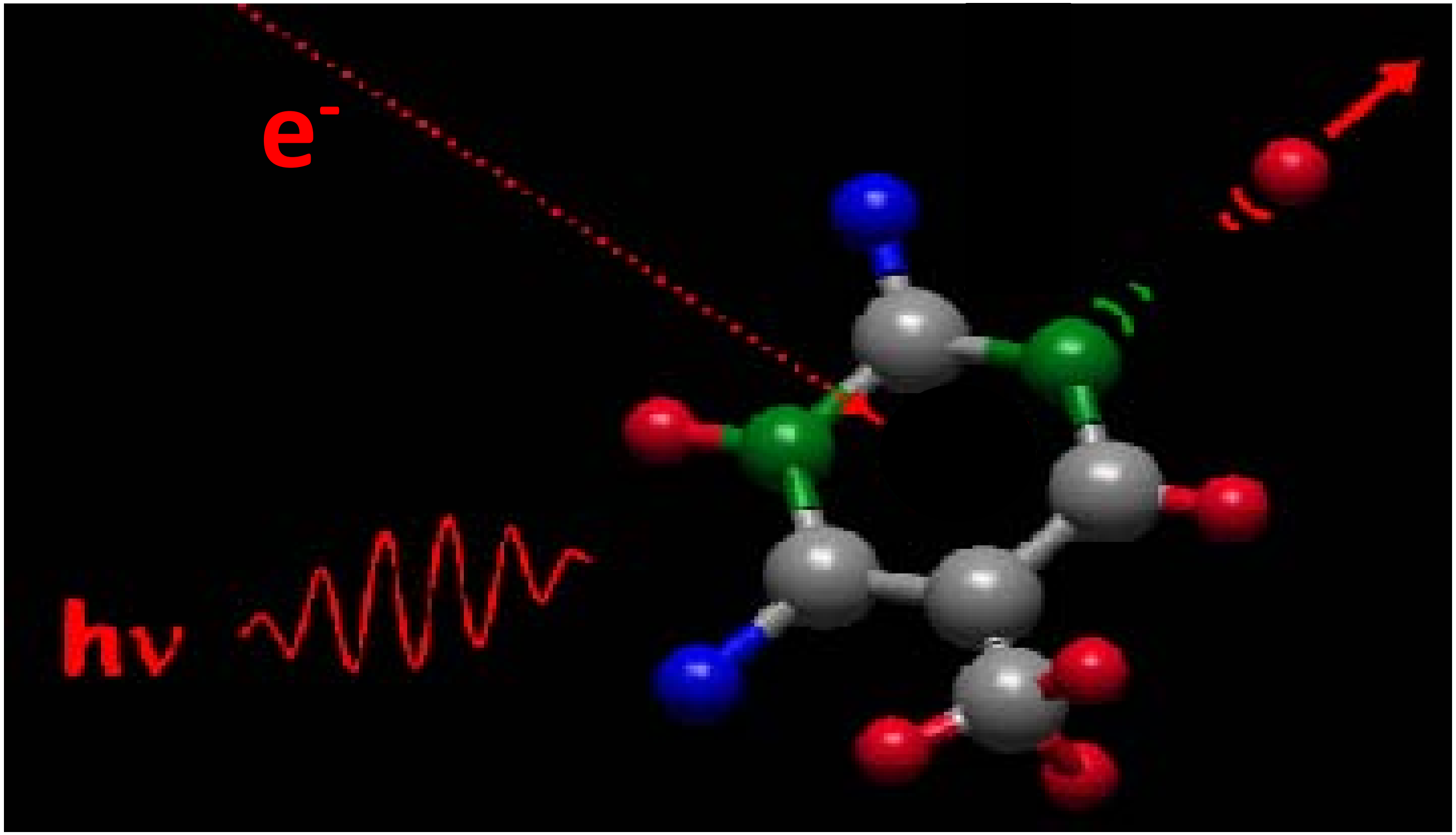
soft film on hard substrate

<u>Fabrication procedures and conditions:</u>

- *Liquid state, solutions*
- *ambient temperature and atmospheric pressure*
- *crystallization, equilibrium*

<u>Easy to functionalize by choice of molecules and substrate</u>

Electron and Photon induced Chemical Control

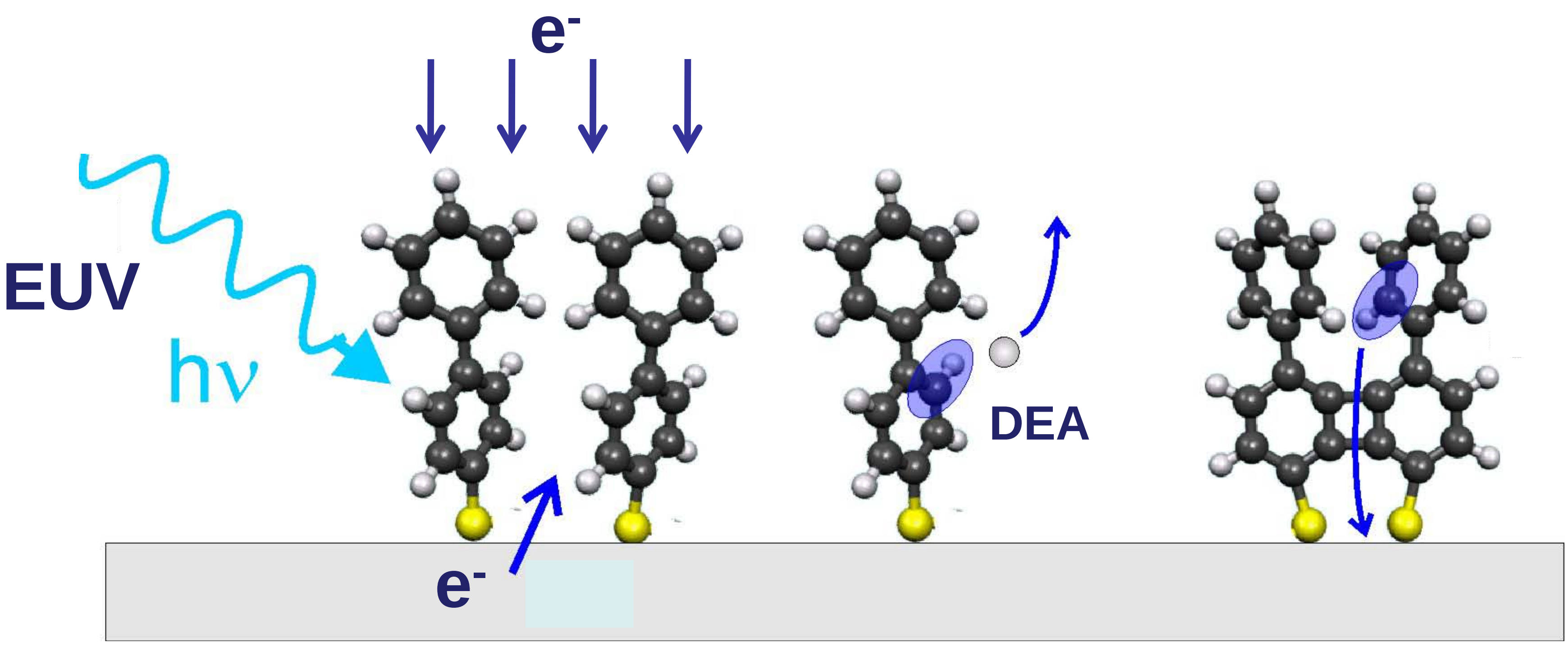


Electron-molecule interaction:

… Dissociative Electron Attachment (DEA) via Transient Negative Ion (TNI)

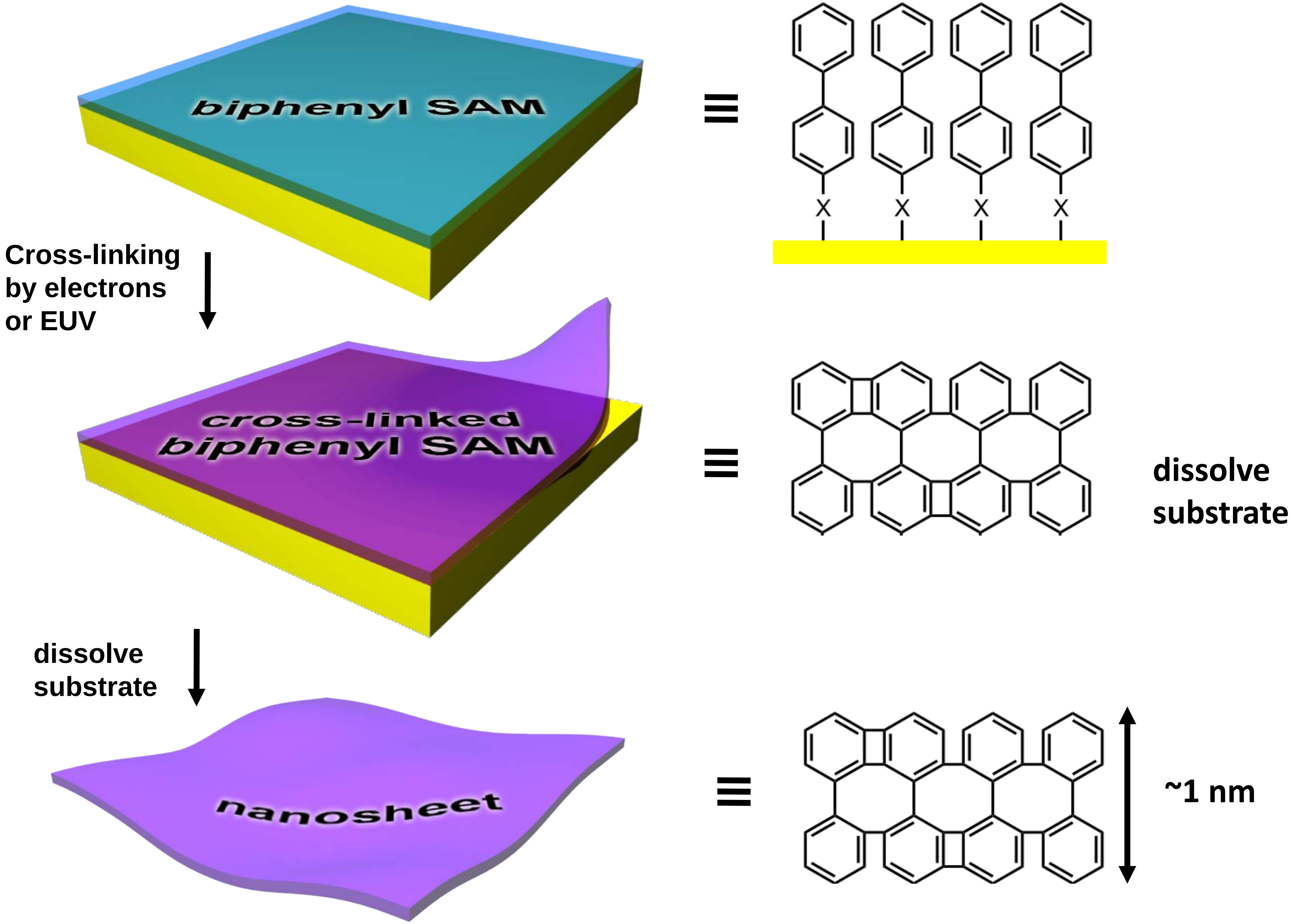
… requires low electron energies… typically below 10 eV

Electron and Photon induced Chemical Control in SAMs

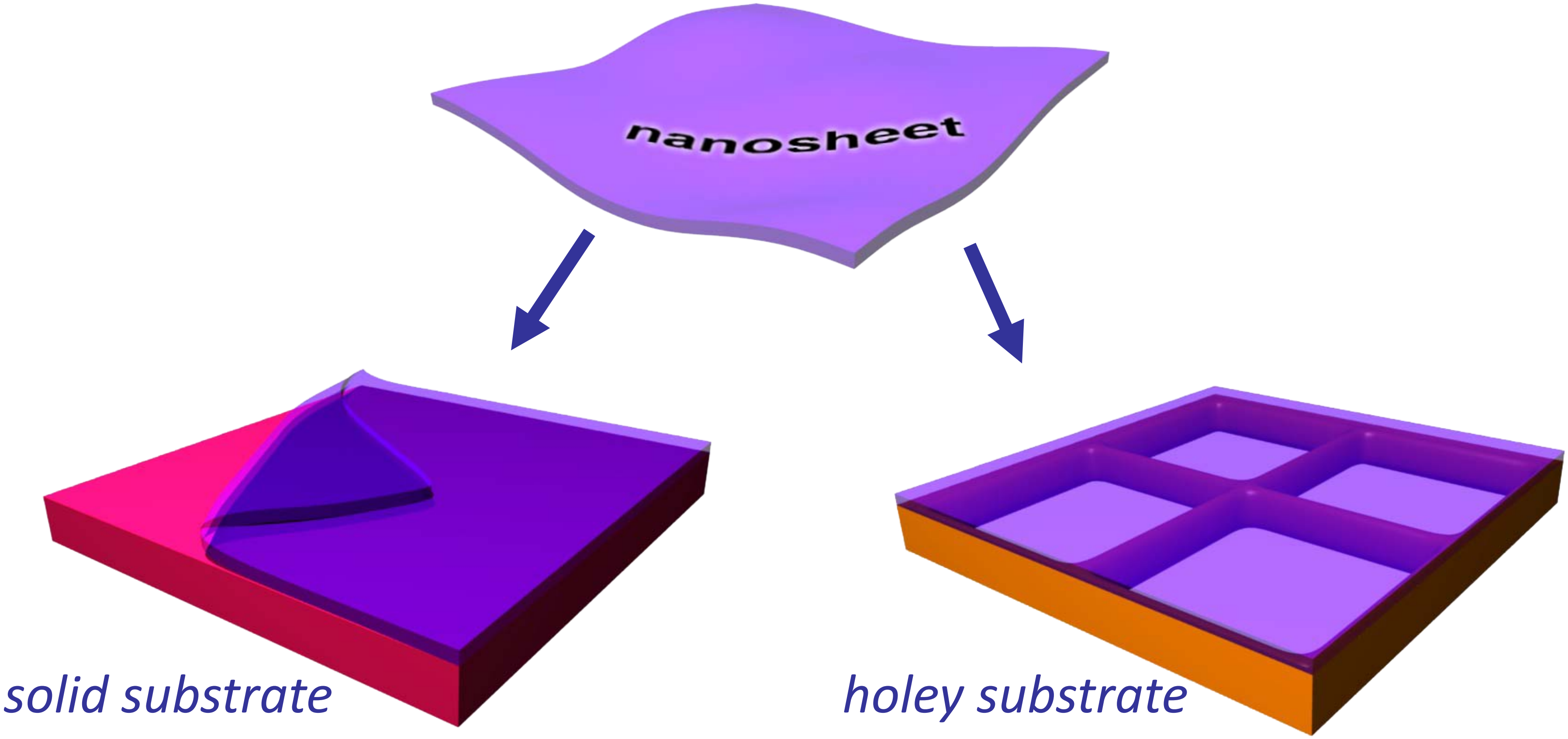


W. Geyer et al. Appl. Phys. Lett 75, 2401 (1999)
W. Eck et al. Adv. Mater. 12, 805 (2000)
A. Turchanin et al. Small 3, 2114 (2007)
A. Turchanin et al. Langmuir 25, 7372 (2009)

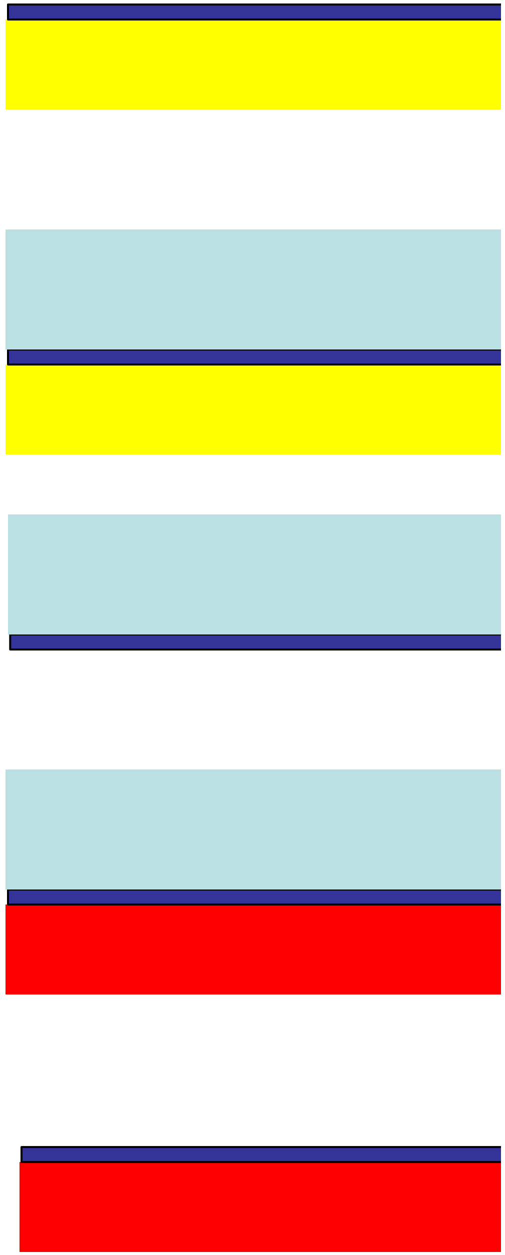
Preparation of Nanomembrane



Preparation of Nanomembrane



Transfer of carbon nanomembrane, process



CNM / Substrate 1 (Au, SiN, …)

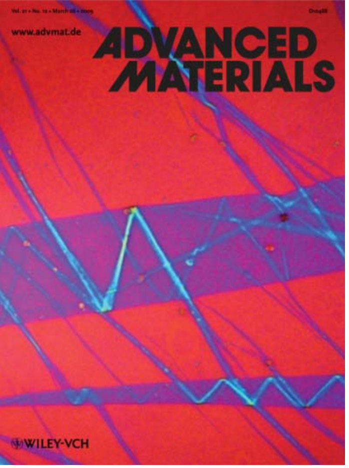
Coat with transfer medium

Dissolve substrate 1

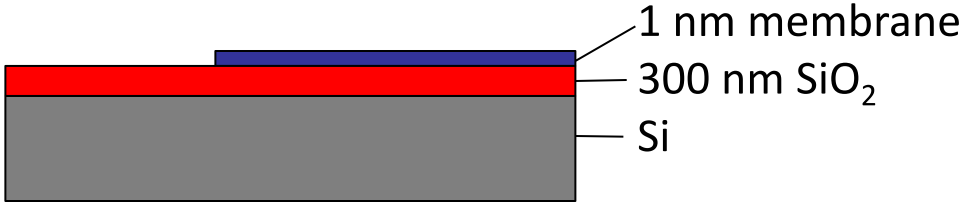
Place on substrate 2

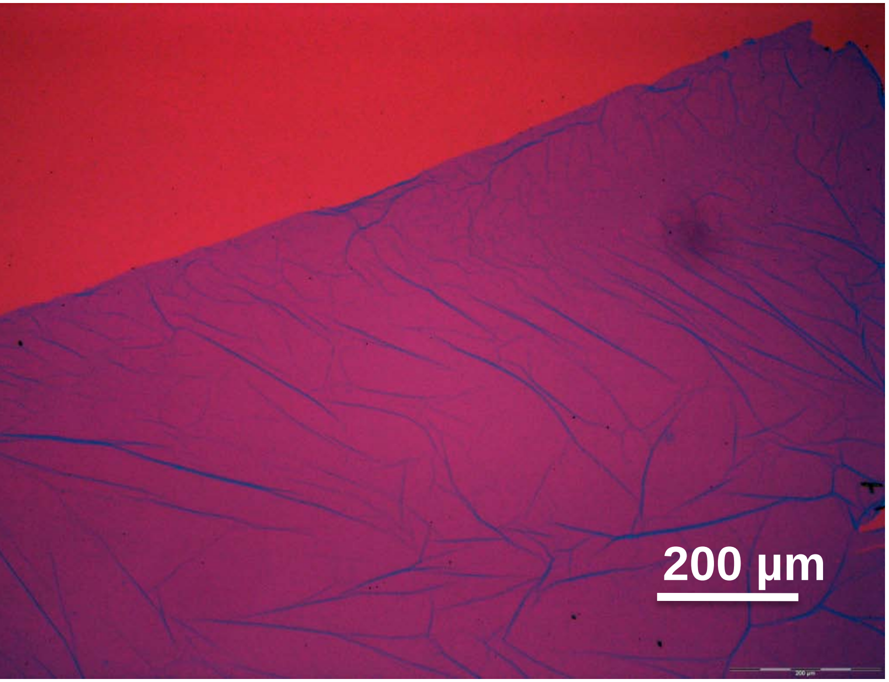
Dissolve transfer medium

CNM / Substrate 2 (SiO, Si, …)



1 nm thick Membrane on SiO/Si: Interference Contrast



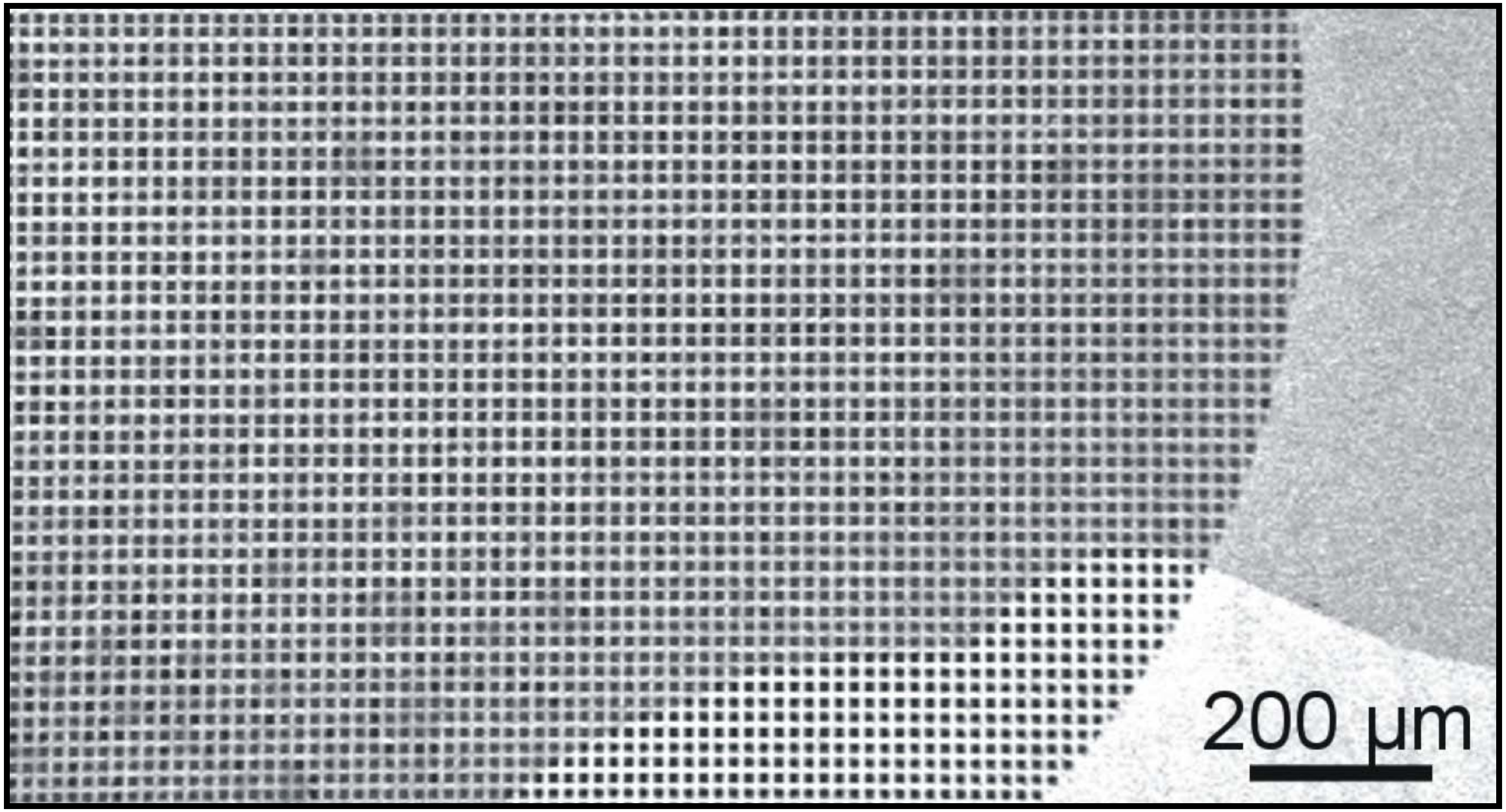


optical micrograph

photograph

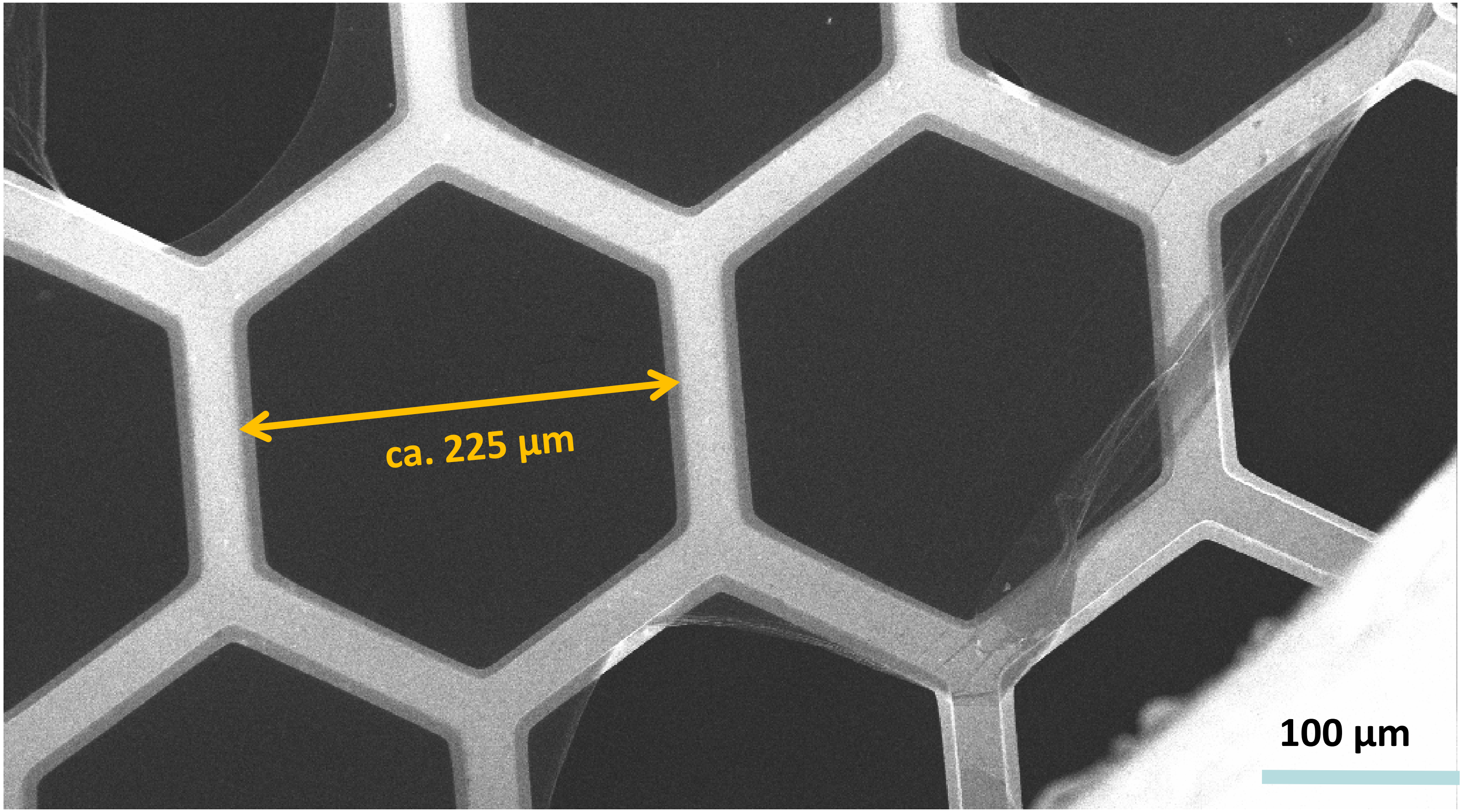
Nanosheet on TEM grid

TEM grid (Au 1500mesh), SEM Image



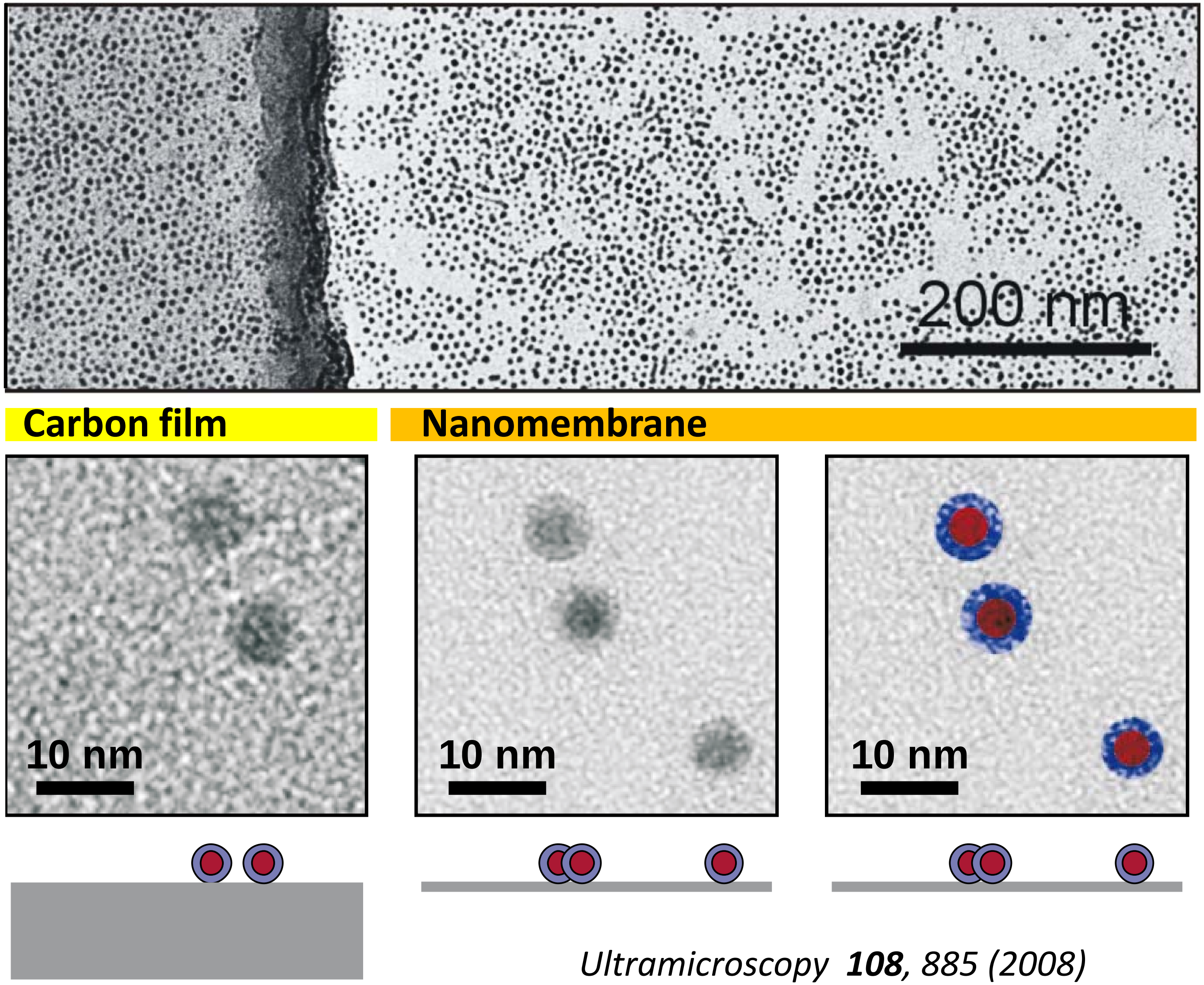
Nottbohm et al., Ultramicroscopy ***108****, 885 (2008)*

Large area Free-standing Nanomembrane



Nanomembrane transfered onto Cu TEM grid, imaged by SEM (A. Beyer)

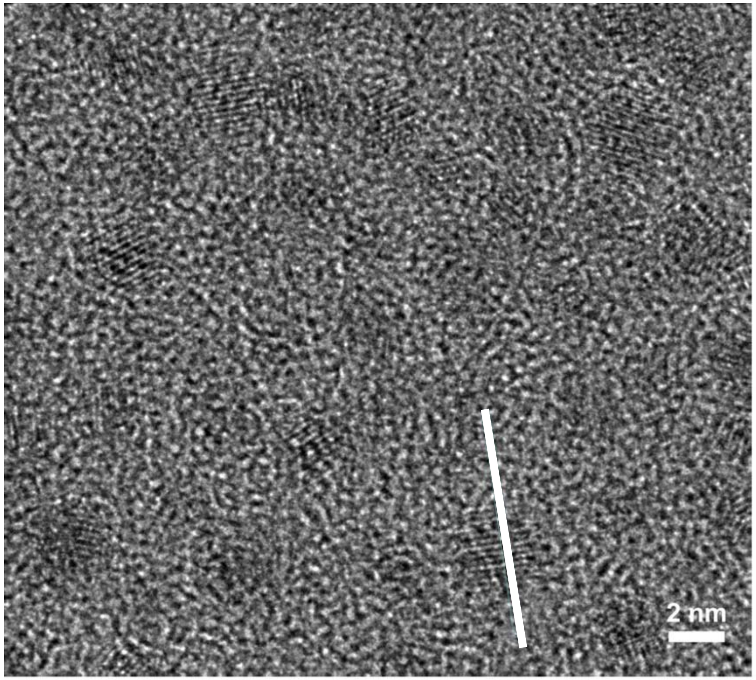
Nanomembrane supports for HRTEM: Imaging of - Co nanoparticles (ca. 4 nm)

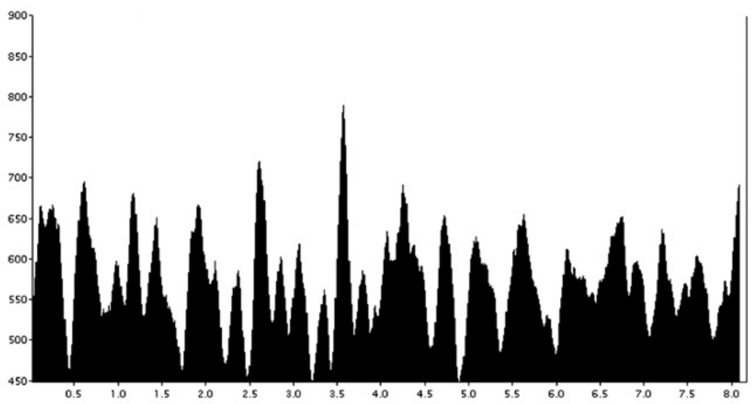


Ultramicroscopy ***108***, *885 (2008)*

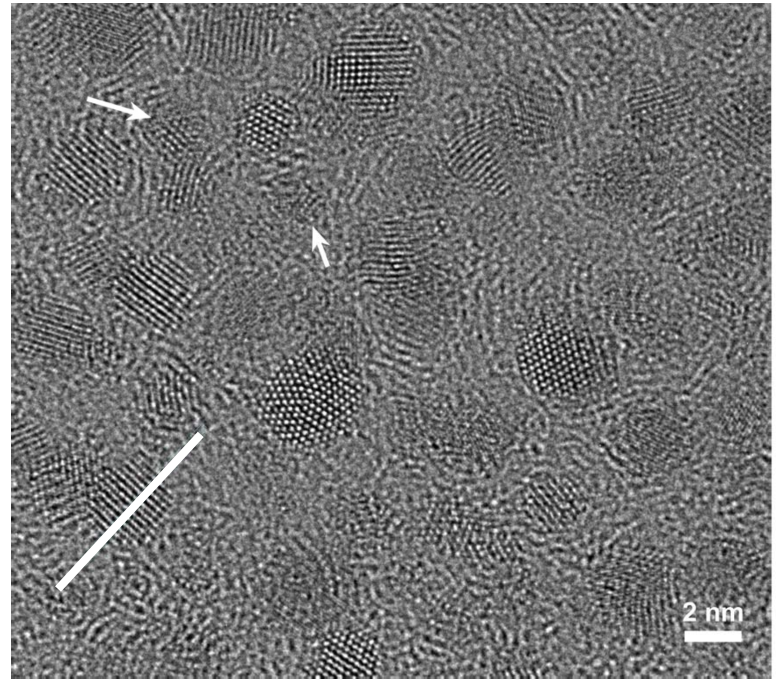
TEM - Au_{55} Cluster

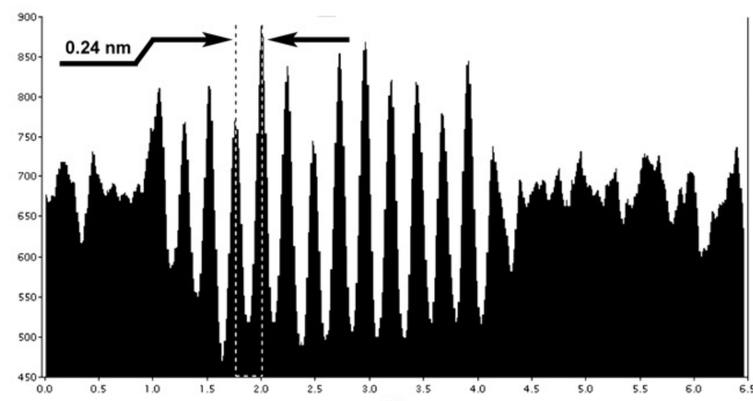
Carbon film





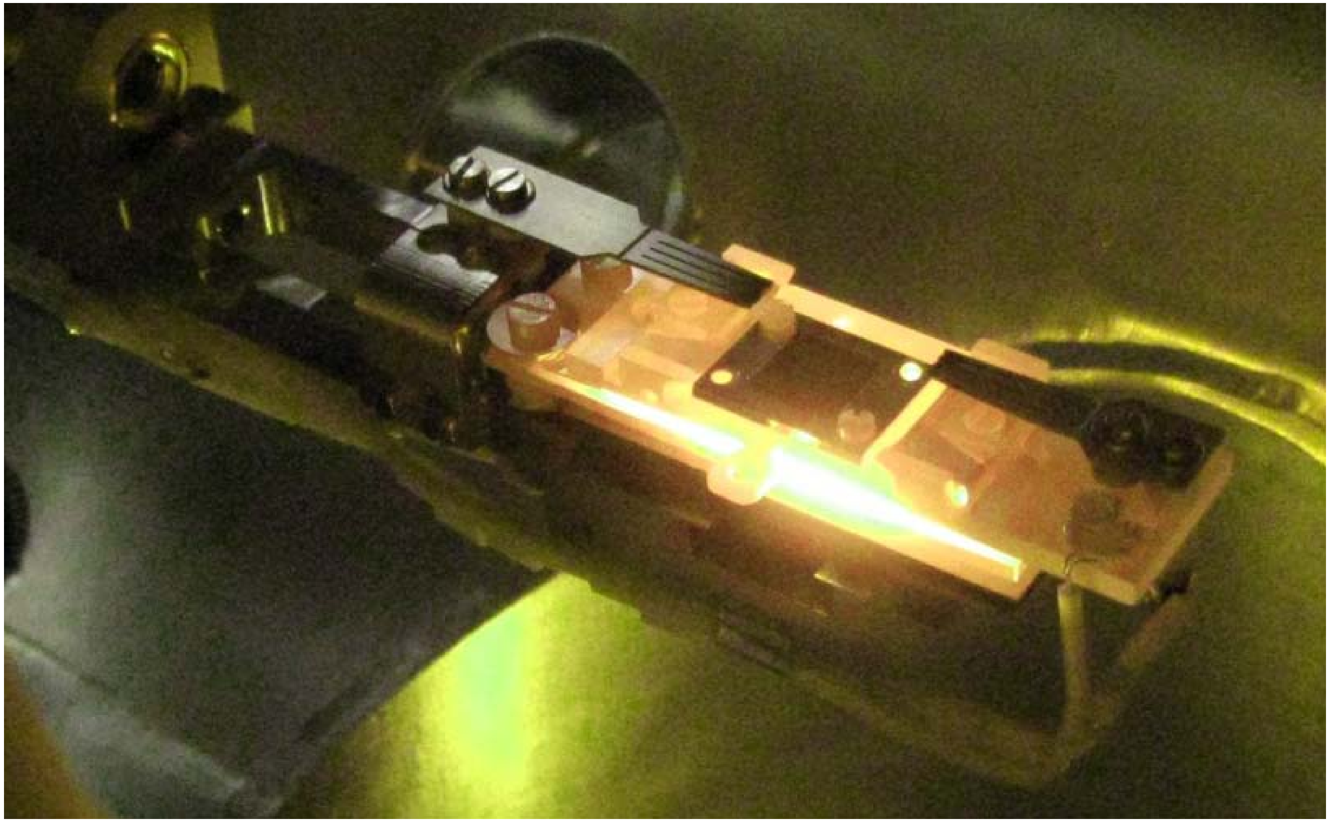
Nanosheet





(J. Mayer, A. Sologubenko, RWTH Aachen)

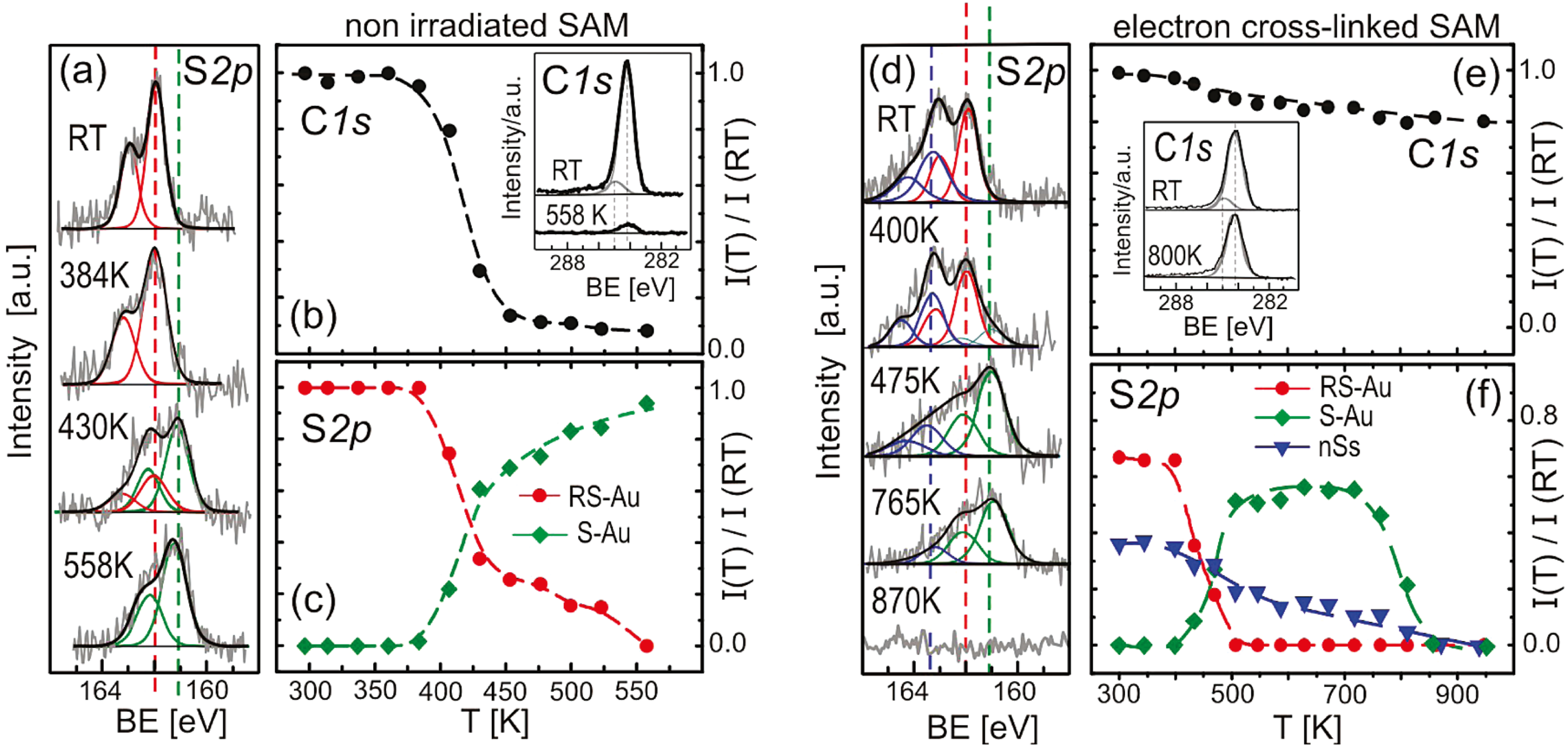
Thermal Properties of Carbon Nanomembranes



Heating of biphenylthiol nanosheet on SiO_2-Si in UHV

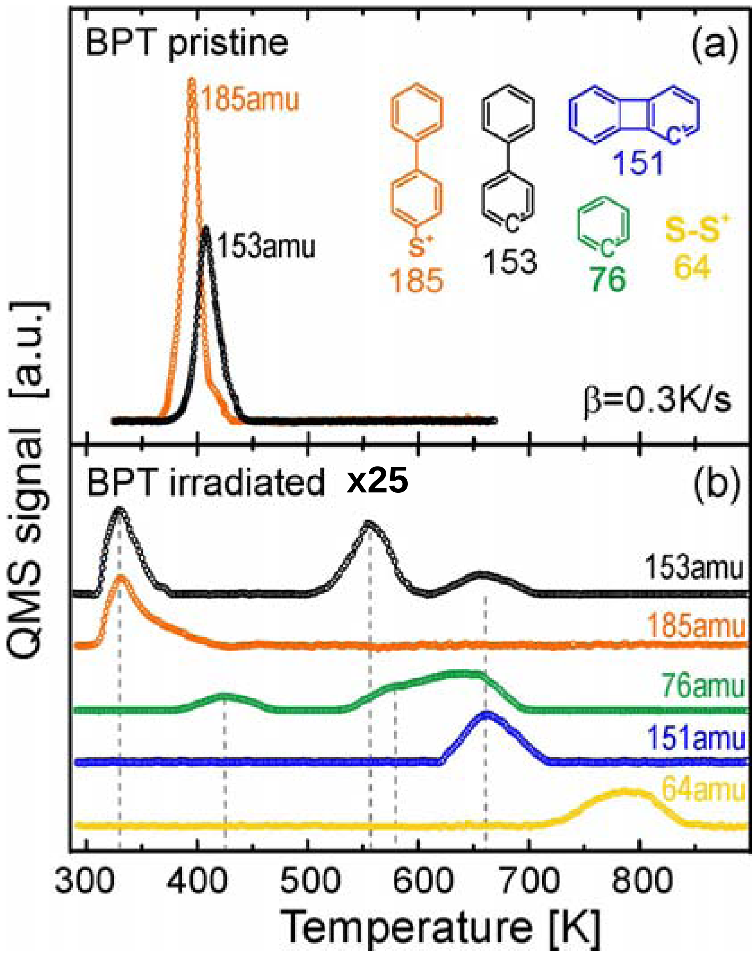
Appl. Phys. Lett. **90,** 053102 (2007)

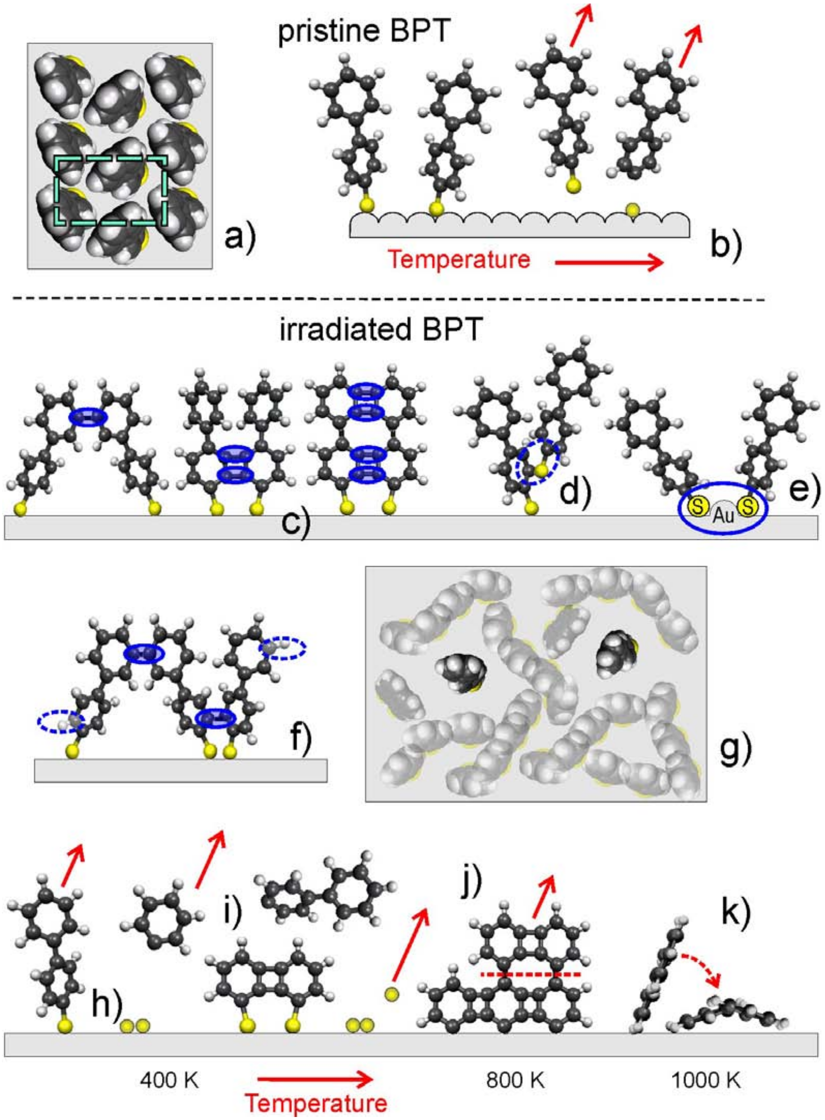
Heating of pristine and cross-linked BPT SAMs (XPS)



A. Turchanin et al. Langmuir 25, 7372 (2009)

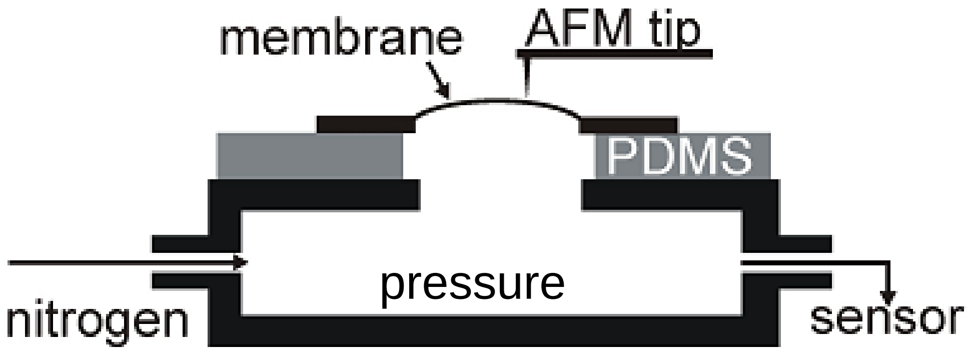
Heat induced molecular desorption

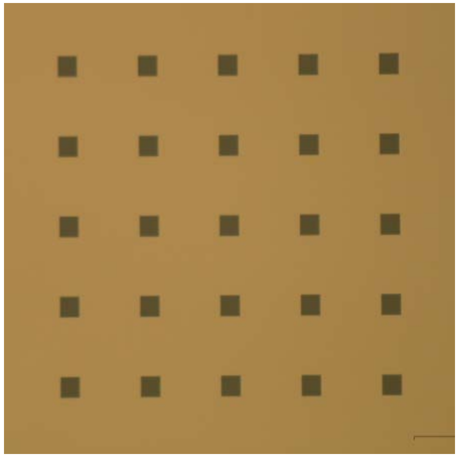




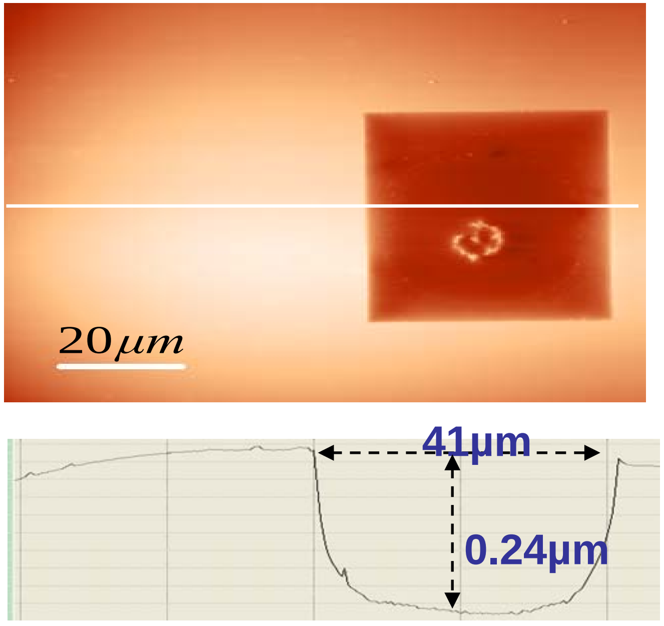
A. Turchanin et al. Langmuir 25, 7372 (2009)

Membrane mechanics: Bulge Tests

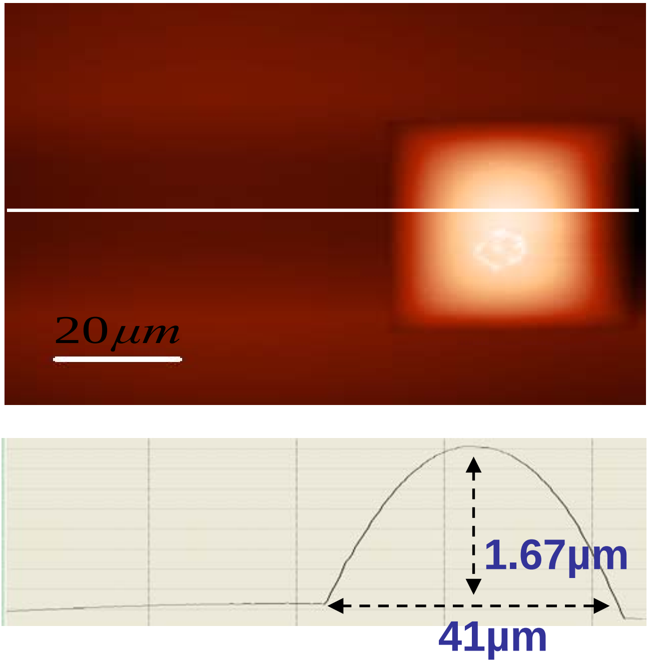




p=0



p=750Pa

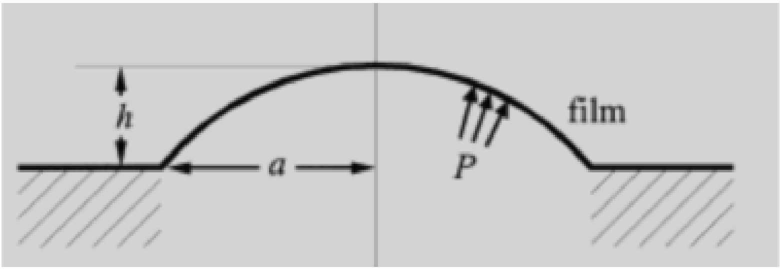


Mechanical properties of nanomembranes

Pressure-deflection relationship for a stressed nanomembrane:

$$P = P_1 + P_2 = \frac{Et}{a^4(1-\nu)}h^3 + \frac{\sigma_0 t}{a^2}h$$

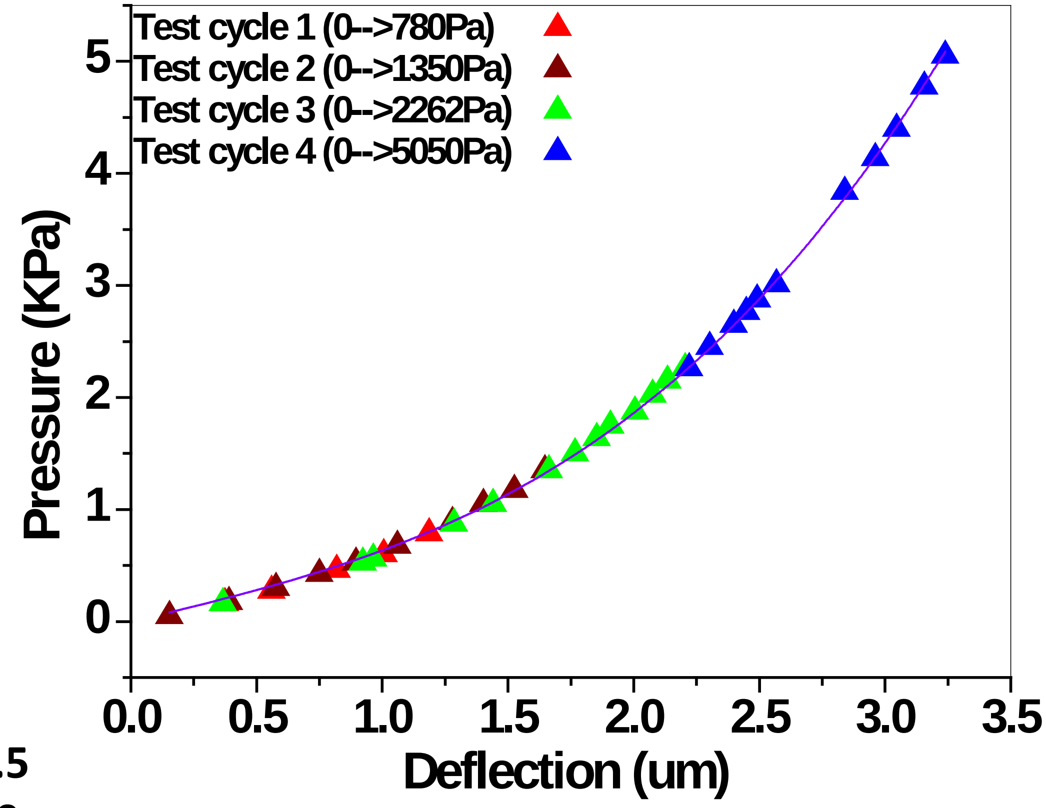
J.J.Vlassak and W.D. Nix, J. Mater. Res. 7 (1992) 3242



t=1.5nm: thickness
v=0.35: Poisson's ratio
E=Young's modulus
σ_0 = residual stress
a: half-width
b/a: aspect ratio

E = 10.0 GPa

σ_0 = 40.0 MPa



some E values (Gpa):
rubber 0.01….0.1, polystyrene 3.0…..3.5
copper 110… 130, diamond 1050…1200

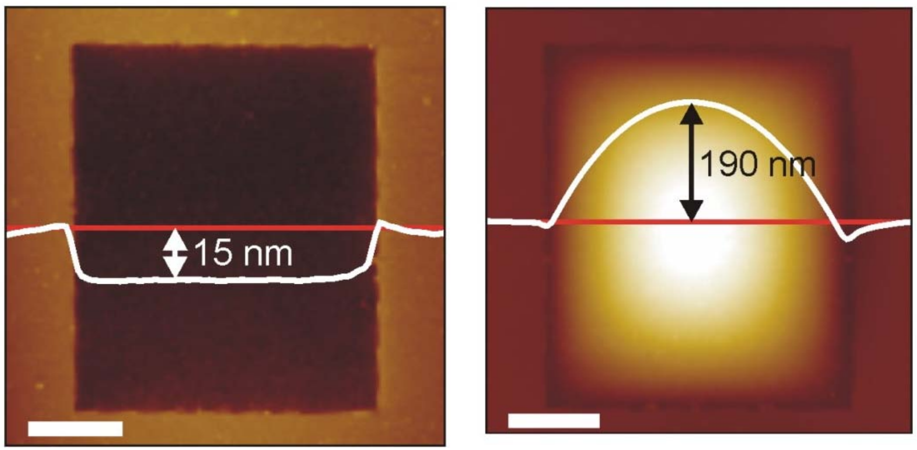
Comparison with other Free-standing Nanomembranes

Freestanding nanomembranes	Thickness (nm)	Fabrication Method	Young's Modulus (GPa)	Tensile Strength (MPa)
Nanocomposite membranes [1]	**55**	Spin-assisted layer by layer assembly	**8±3.5**	**40…100**
IPNs hybrid nanomembranes[2]	**35**	Spin-coating and polymerization	**N.A.**	**105**
Nanomembranes (epoxy resin)[3]	**20**	Spin-coating and baking	**N.A.**	**30**
Nanomembranes[4] (melamine,phthalic, rethane,epoxy)	**19…24**	Spin-coating, irradiation, baking	**1.2…3.5**	**10…22**
Carbon Nanomembrane	**1.5**	**Self-assembly & cross-linking**	**10**	**150…420**

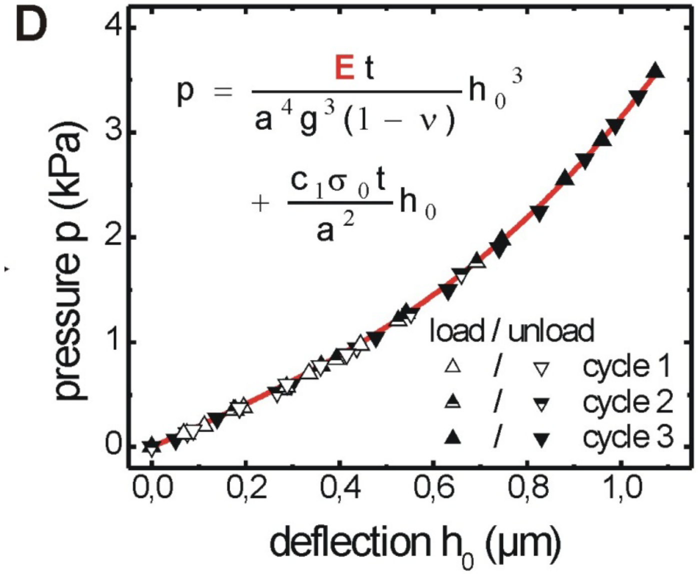
[1] Nature Materials 3 (2004) 721; Advanced Materials 17 (2005) 1669
[2] Nature Materials 5 (2006) 494
[3] Advanced Materials 19 (2007) 909
[4] Macromolecules 40 (2007) 1369

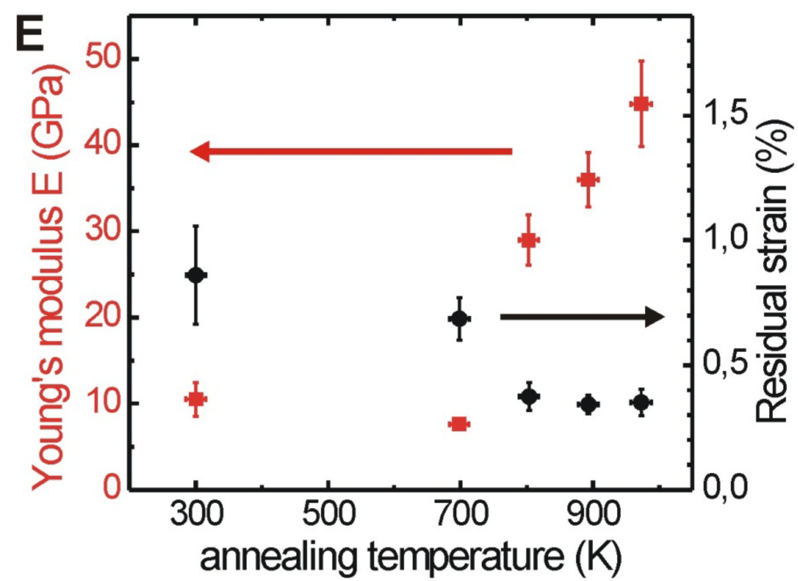
Effect of Annealing on Young's Modulus

P=0 Pa **P=450 Pa**



(annealed at ~900 K)



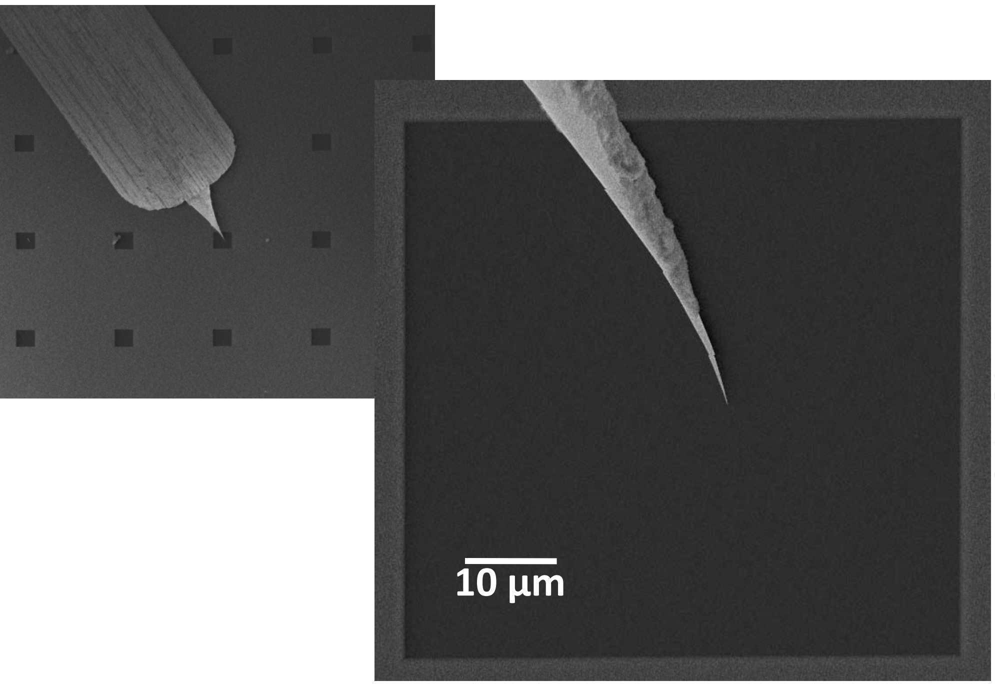


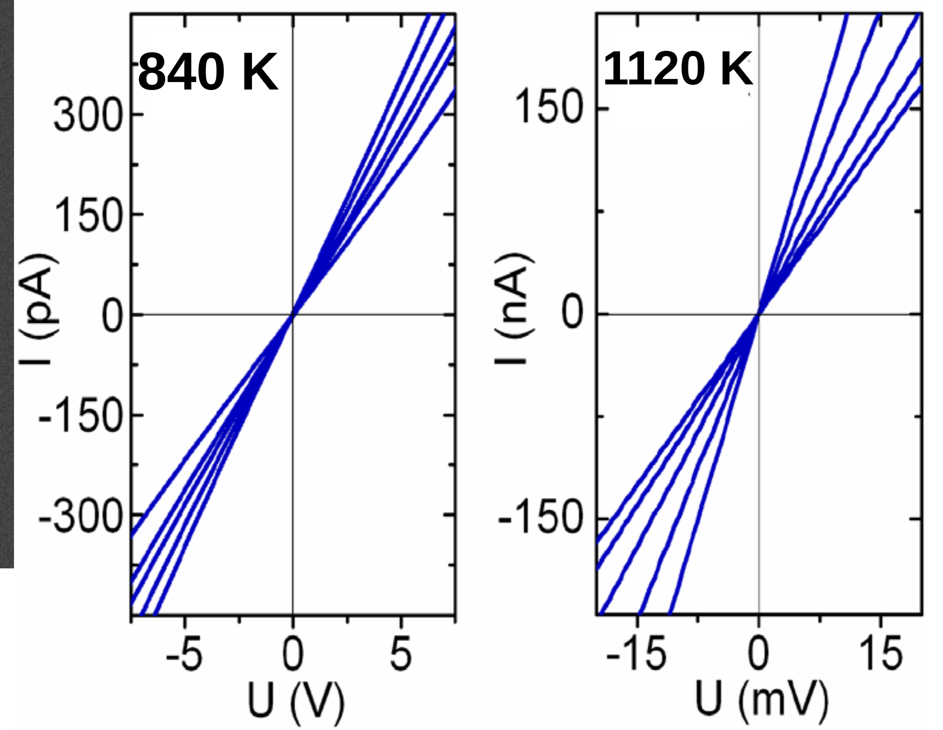
- **Young's modulus increase from ~10 GPa to ~45 GPa after heating at ~1000K**
- **Residual strain reduced from ~0.9 % to ~0.35 %**
- **Structural transformation**

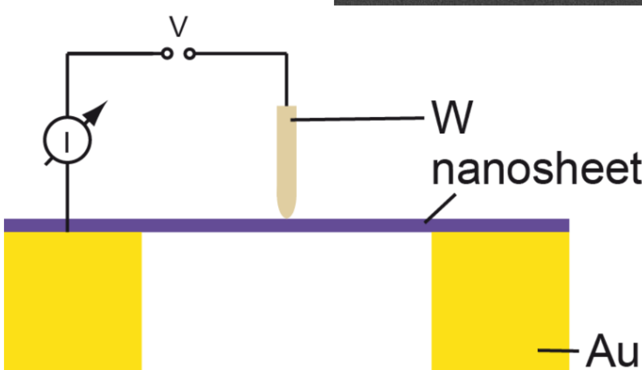
Adv. Mater. **21,** 1233 (2009)

Electrical Characterization of Nanomenbranes:

Electrical Characterization of Nanomenbranes: 2-point measurement of free-standing membrane in UHV SEM/STM

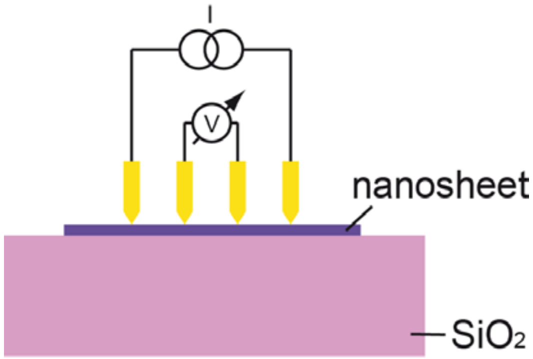




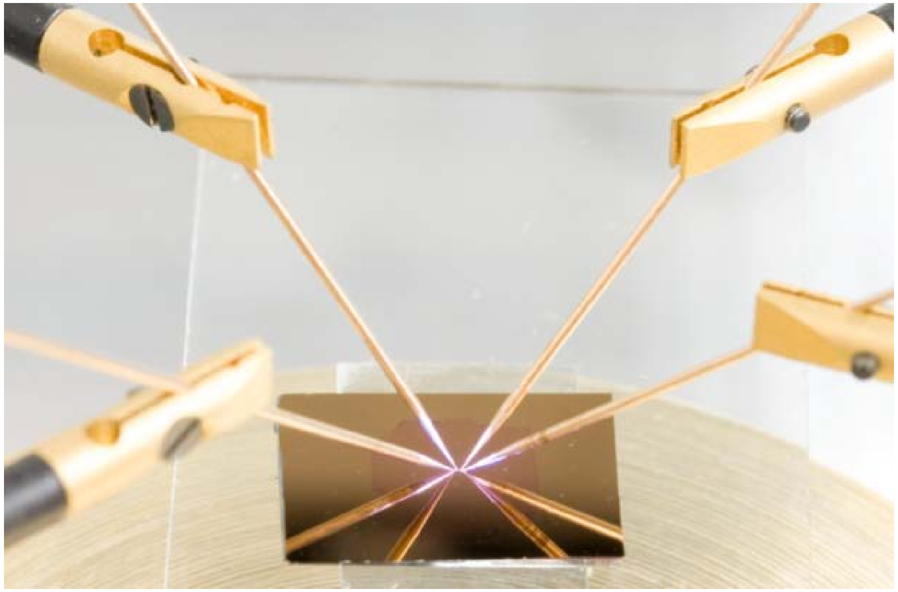


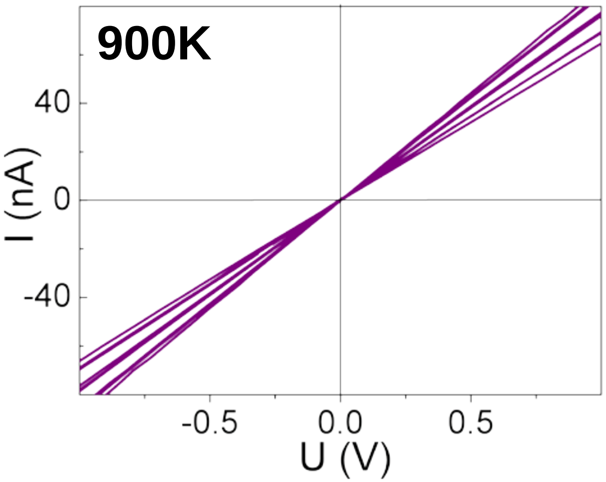
Turchanin et al. Adv. Mater. **21,** 1233 (2009)

Electrical Characterization of Nanomenbranes: 4-point measurement of supported membrane on SiO-surface

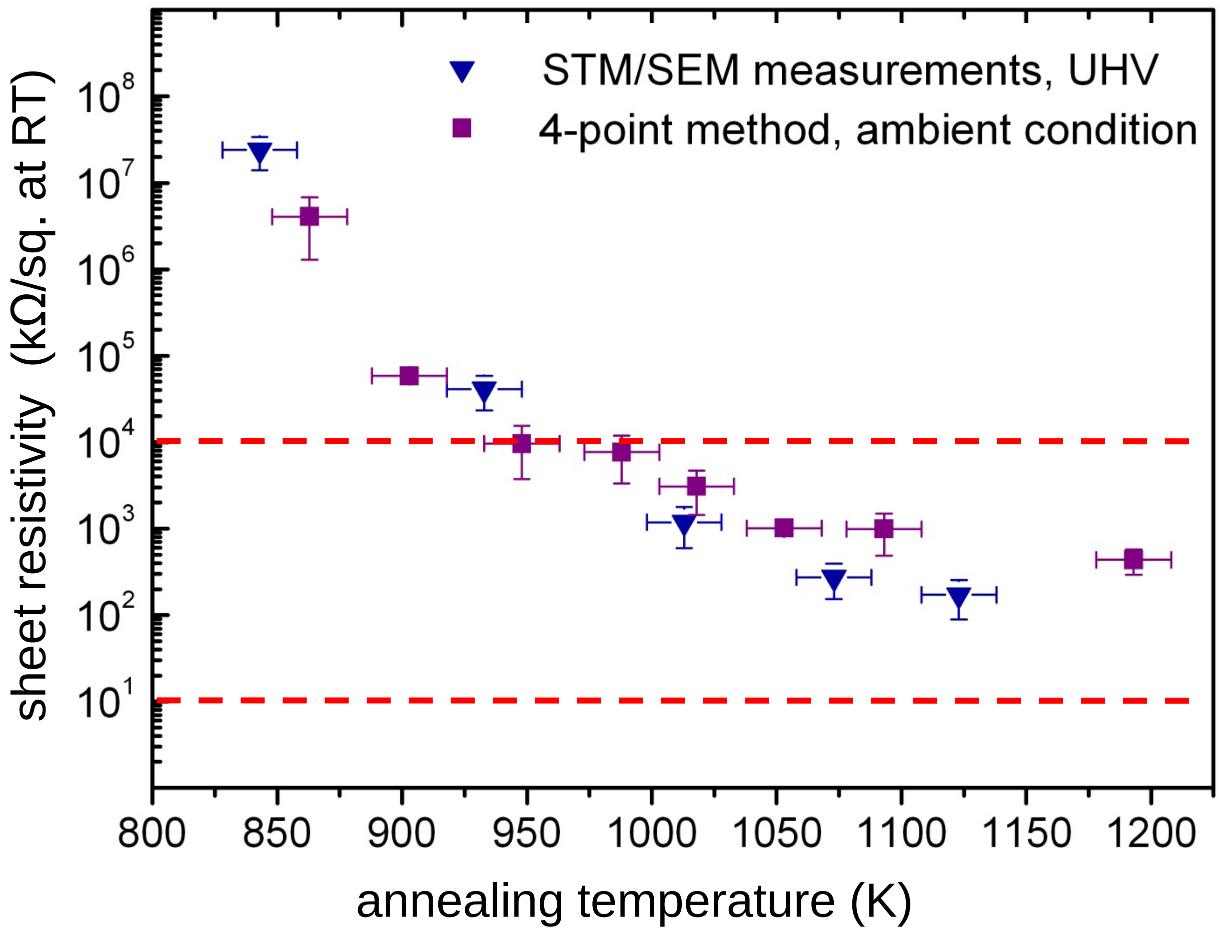


$$\rho_S = \frac{\pi}{\ln(2)}\frac{V}{I} = 4.532\frac{V}{I}\,\Omega/\text{square}$$





Electrical conductivity of nanomembrane:



1 layer chemically reduced graphene
Gómez-Navarro et al.
Nano. Lett . 7, 3499 (2007)

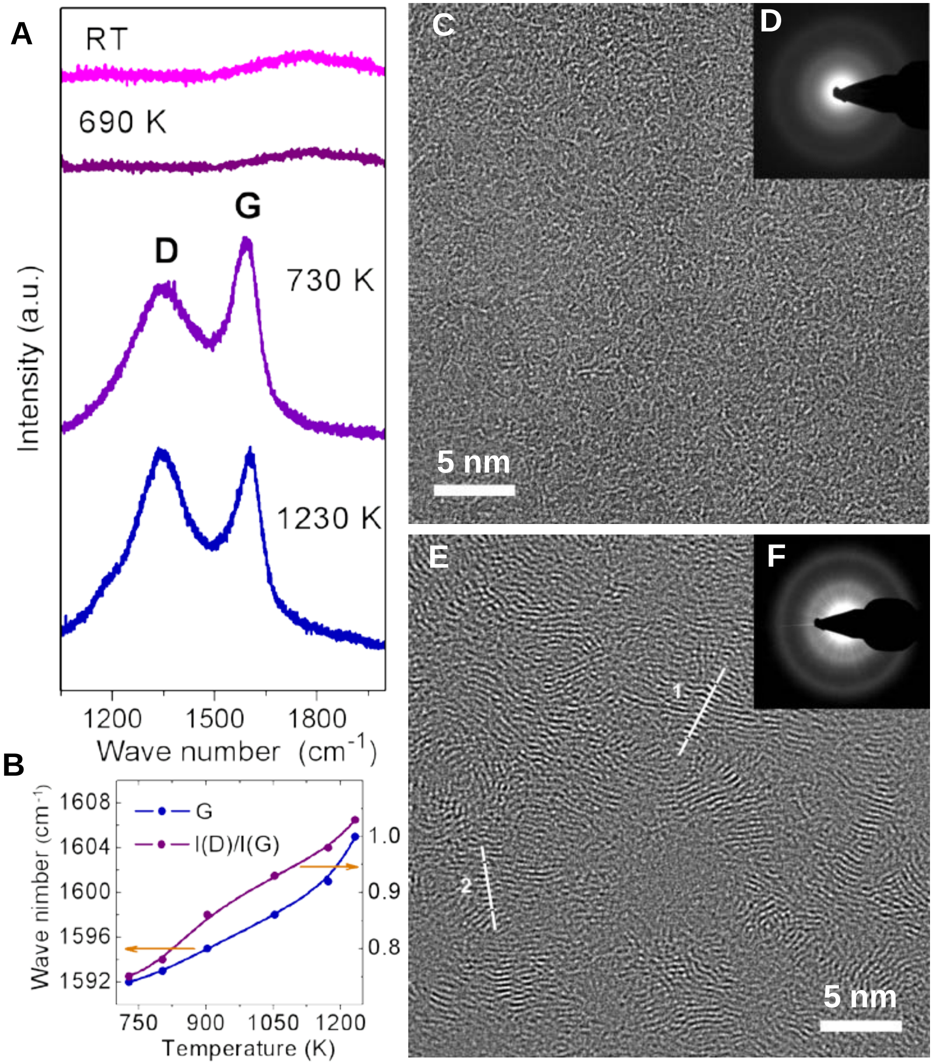
1 layer graphene
mechanical exfoliation
Novoselov et al.
Nature 438, 197 (2005)

⇒**Nanomembrane conductive after annealing**

⇒**Tunable electrical resistance !!**

Adv. Mater. **21,** 1233 (2009)

Structural transition (insulator to conductor) in nanomembrane (Raman spectroscopy and TEM):

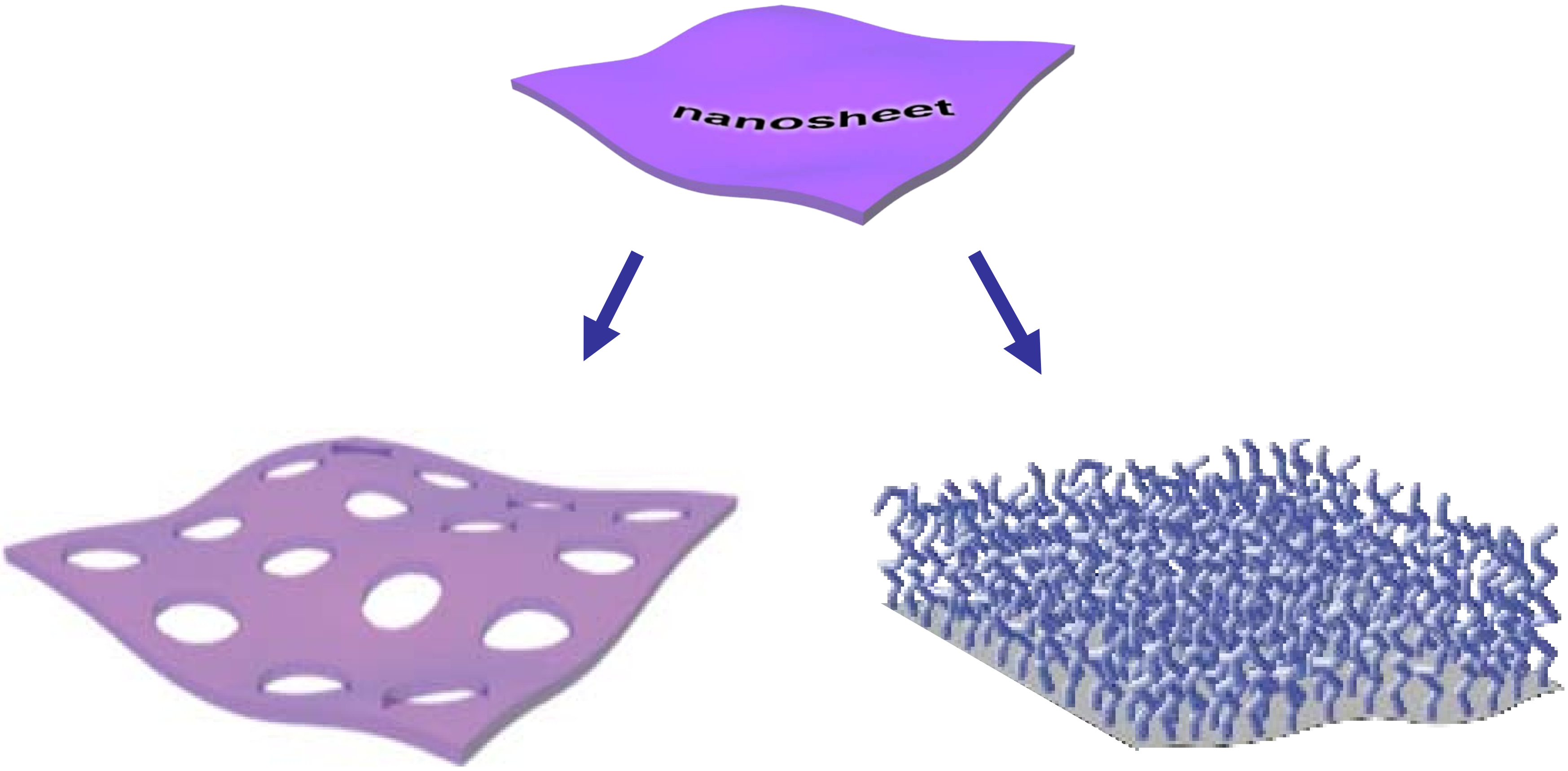


⇒**Formation of nanocrystalline graphene**

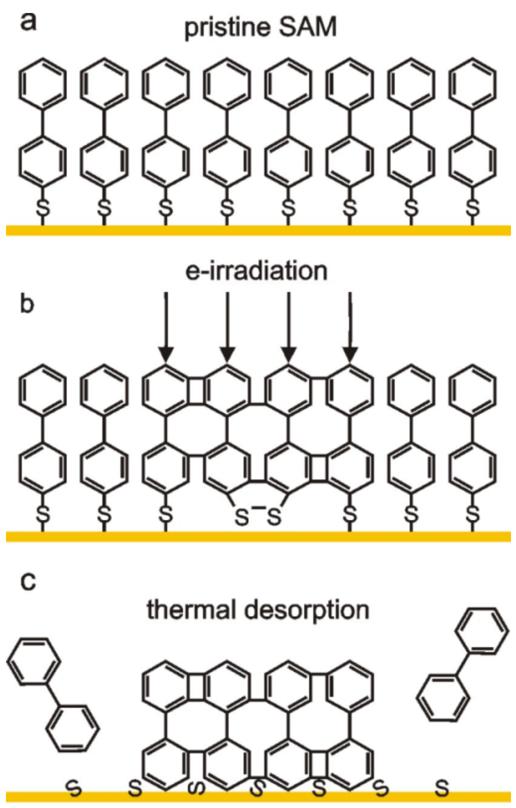
⇒**Tunable electrical properties !!**

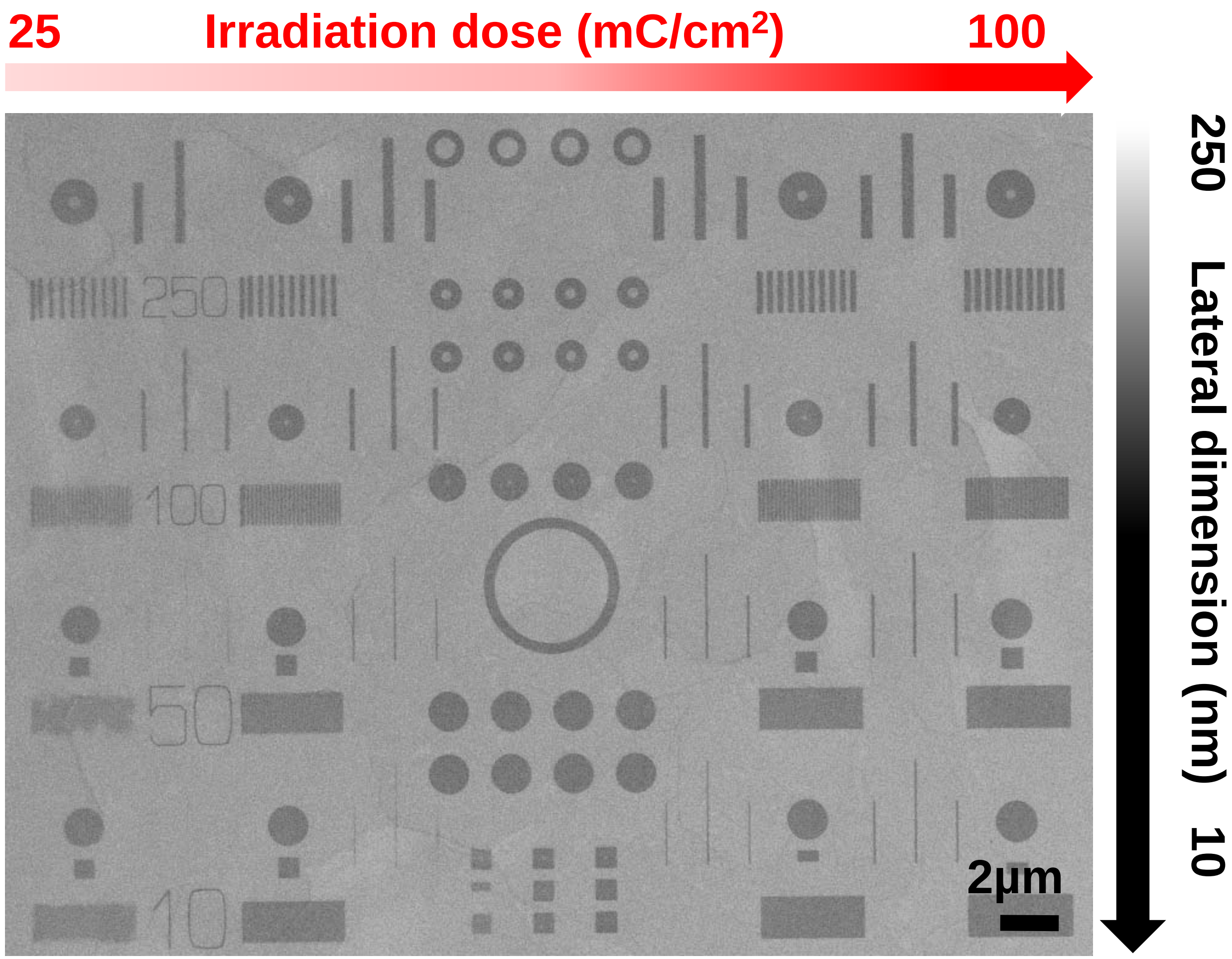
Adv. Mater. **21,** 1233 (2009)

Perforating and functionalizing carbon nanomembranes



Thermal Desorption Lithography (TDL): Fabrication of Graphenoid Nanoribbons



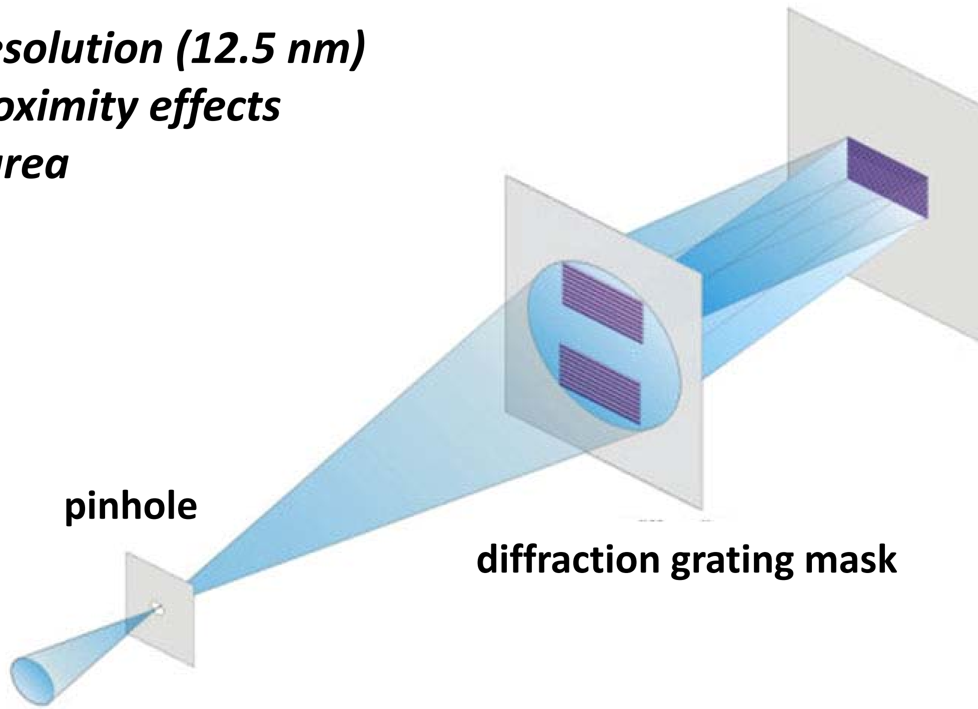


C.T. Nottbohm et al., J. Vac. Sci. Technol. B 27, 3059 (2009)

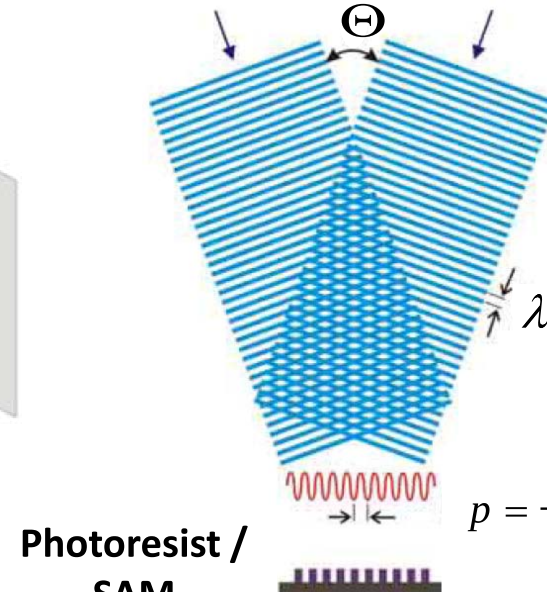
Perforated Nanomembranes by EUV Interference Lithography

Extreme UV Interference lithography (EUV-IL):

- ***high resolution (12.5 nm)***
- ***low proximity effects***
- ***large area***



focused synchrotron irradiation
(92.5 eV, 13.5 nm)

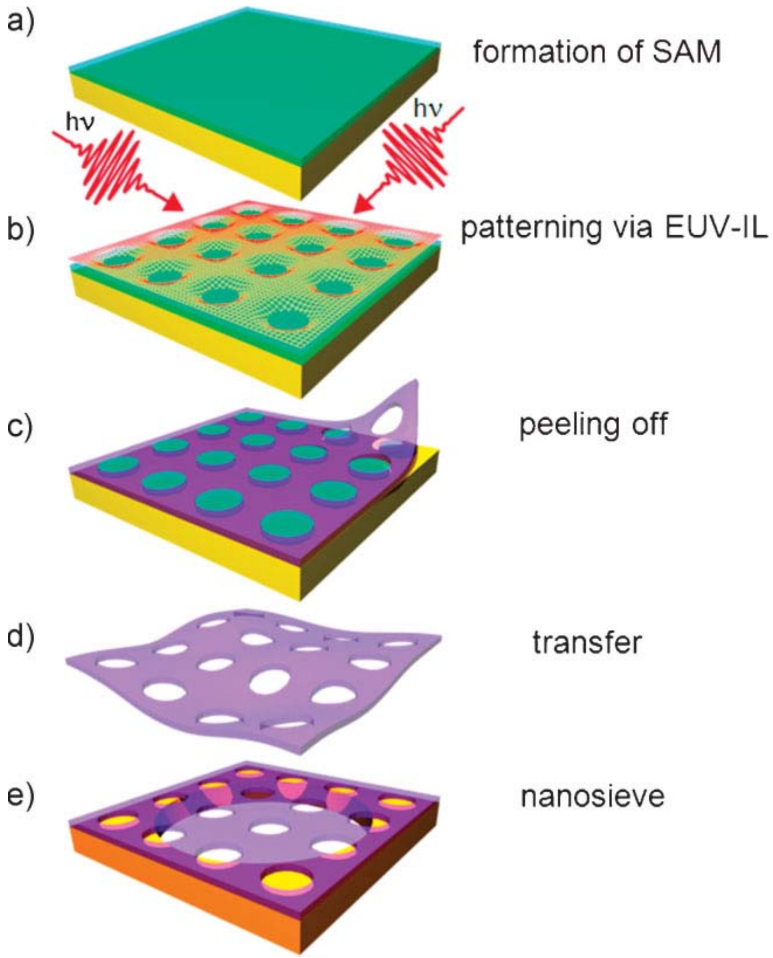


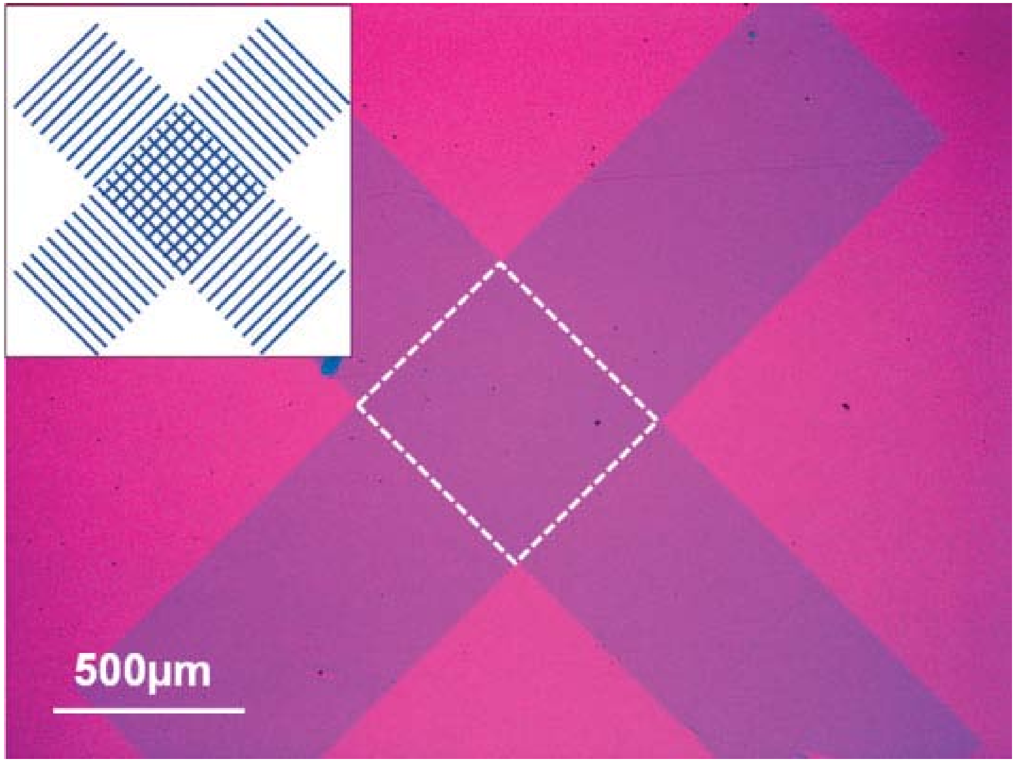
$$p = \frac{\lambda}{2 \sin \frac{\Theta}{2}}$$

Two coherent beams are forming a linear fringe pattern with a sinusoidal intensity distribution.

H. H. Solak, Paul Scherrer Institut

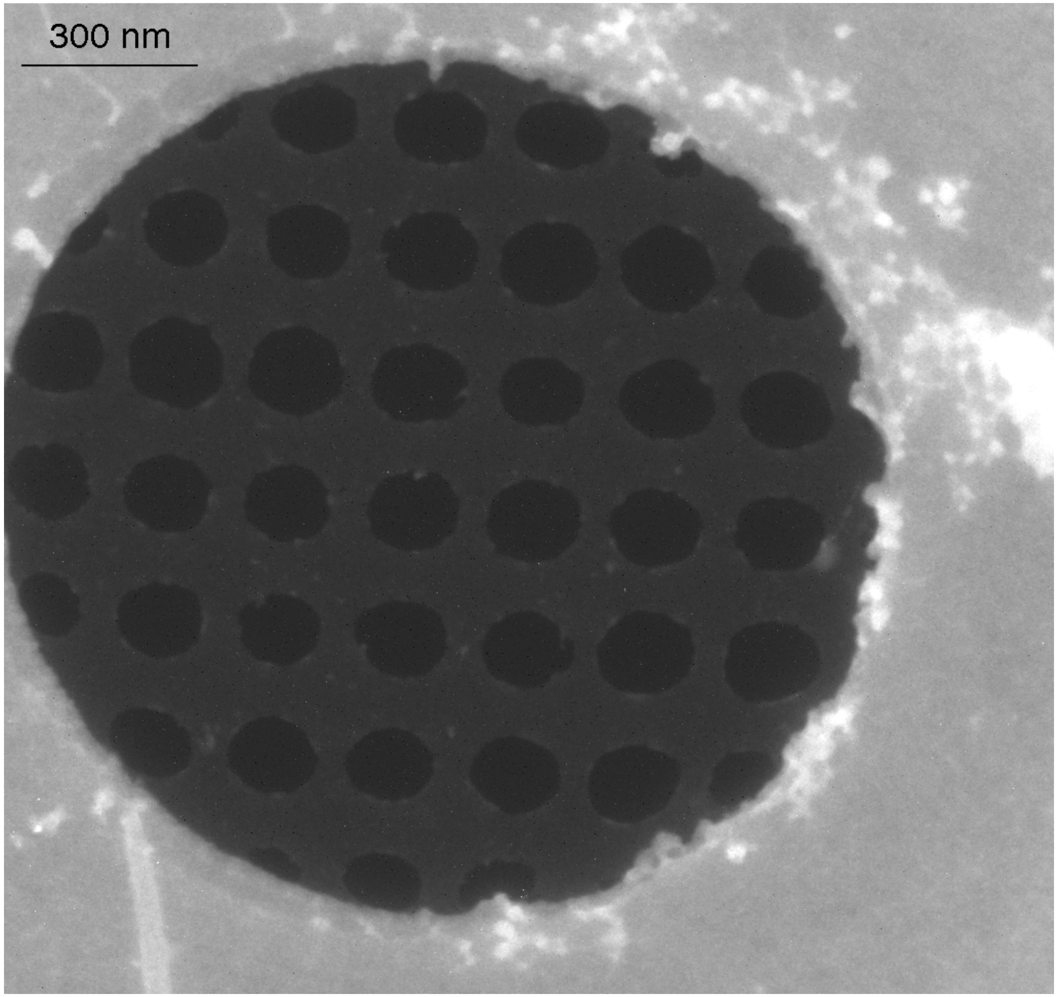
Nanosieve fabrication by EUV-IL





M. Schnietz et al., Small 23, 2651 (2009)

Nanosieve membranes with a thickness of 1 nm via EUV-IL

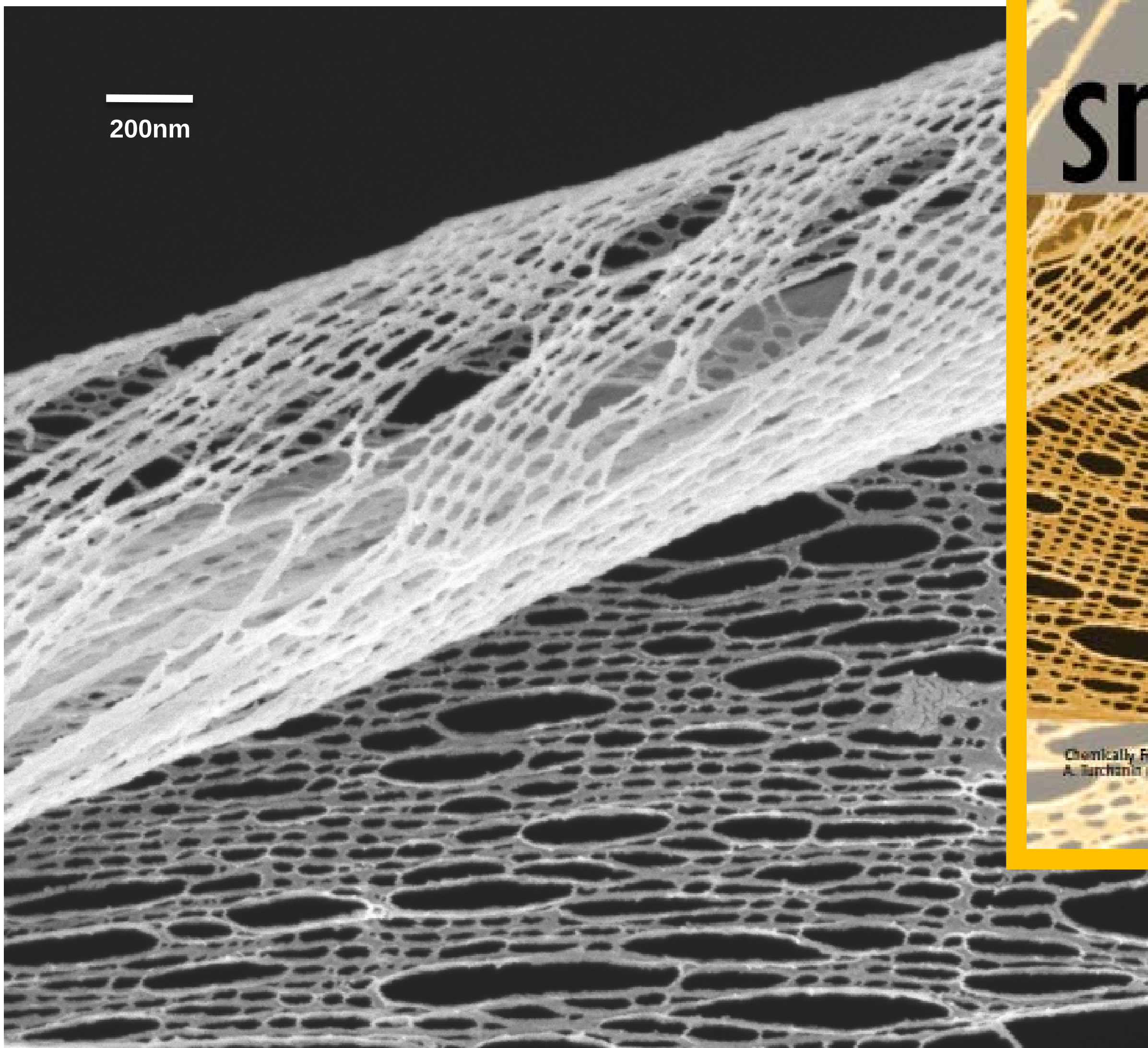


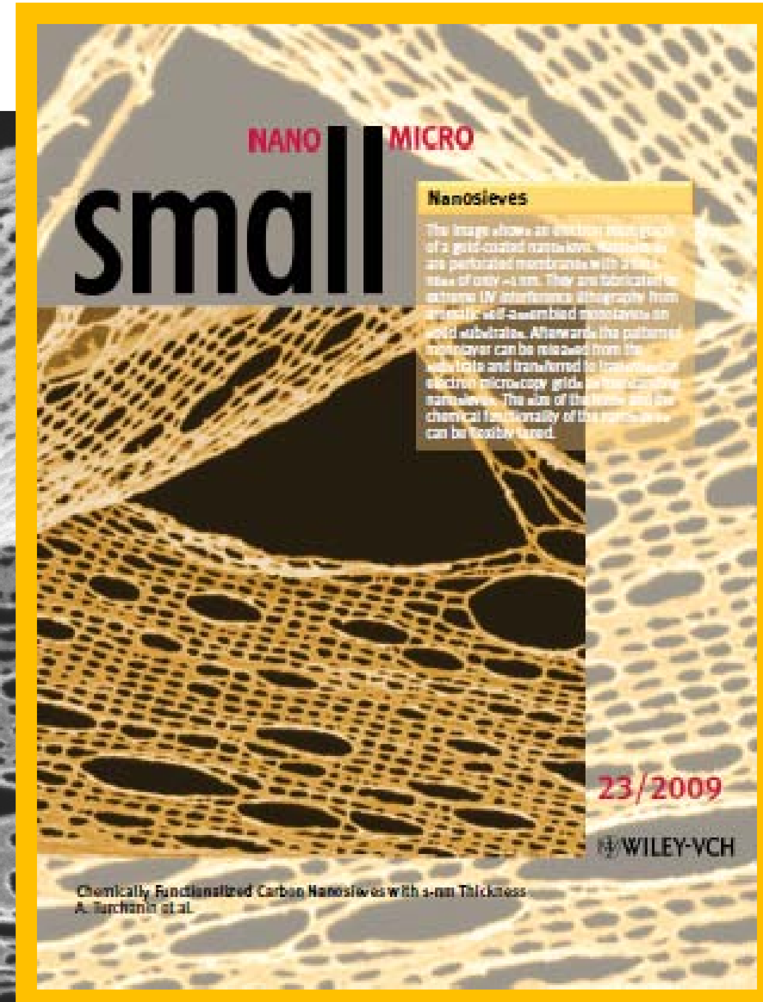
200 x 225 nm period,

hole diameter = 138 ± 17 nm

M. Schnietz et al., Small 23, 2651 (2009)

Freestanding nanosieve coated with 5 nm Au

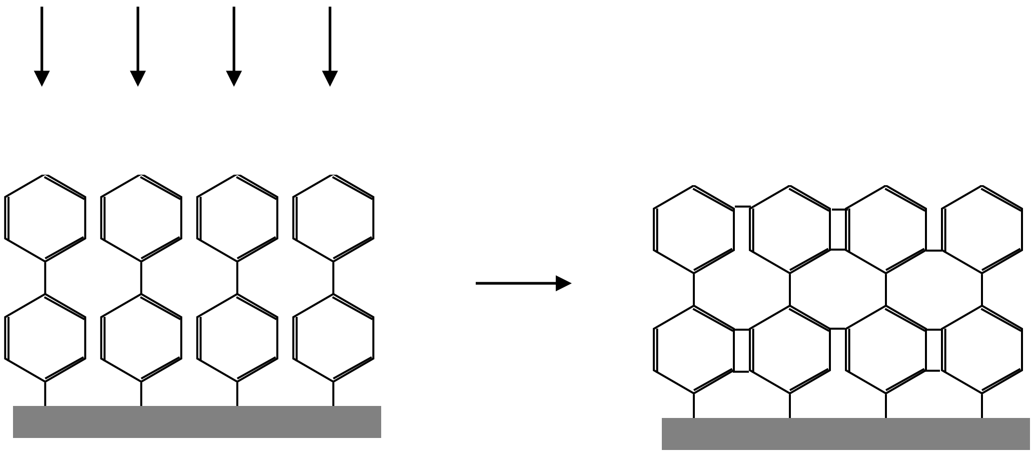




M. Schnietz et al.,
Small 23, 2651 (2009)

Electron induced cross-linking

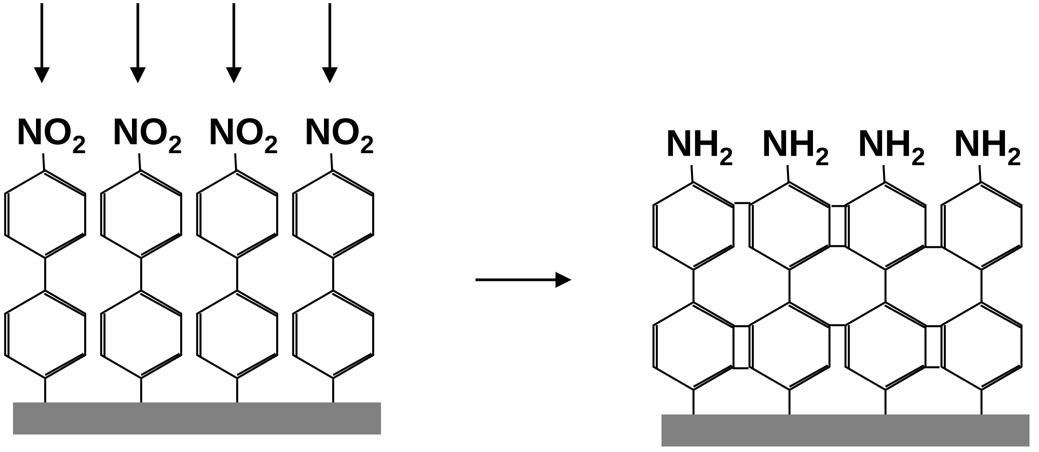
Electrons, 10 -500 eV
area dose: 1 -10 mC / cm^2



Appl. Phys. Lett. **75**, 2401 (1999)

Electron induced cross-linking and NO_2 to NH_2 conversion "Chemical Lithography"

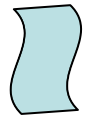
Electrons, 10 -500 eV
area dose: 1 -10 mC / cm^2



Appl. Phys. Lett. **75**, 2401 (1999)

Adv. Mater. **12**, 805 (2000)

Electron induced cross-linking and NO_2 to NH_2 conversion: Chemical lithography and subsequent functionalisation

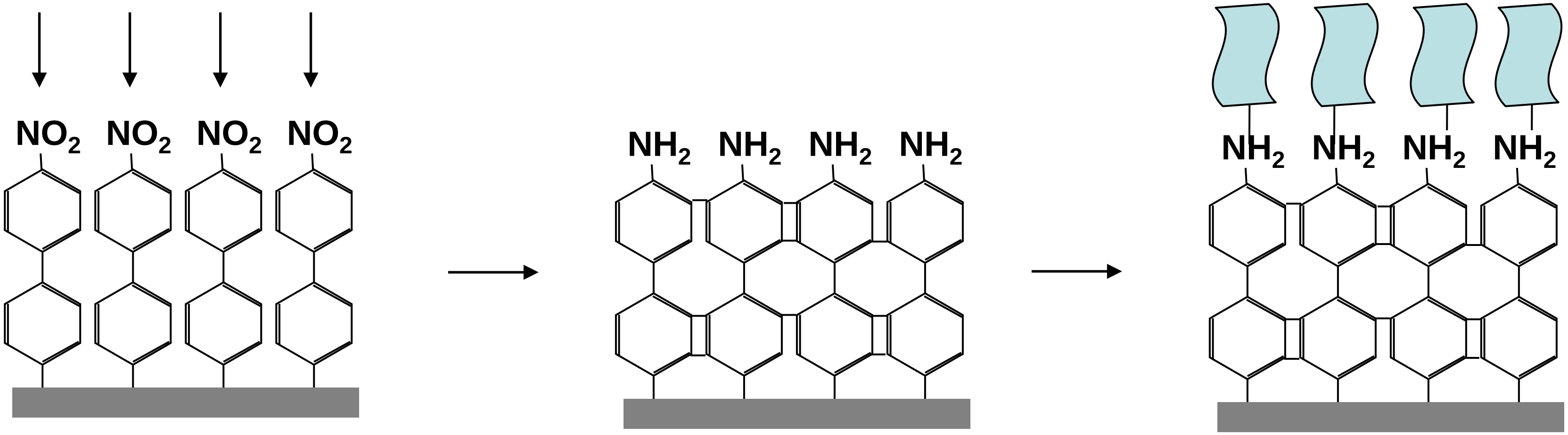


=

Molecules binding to NH_2 group

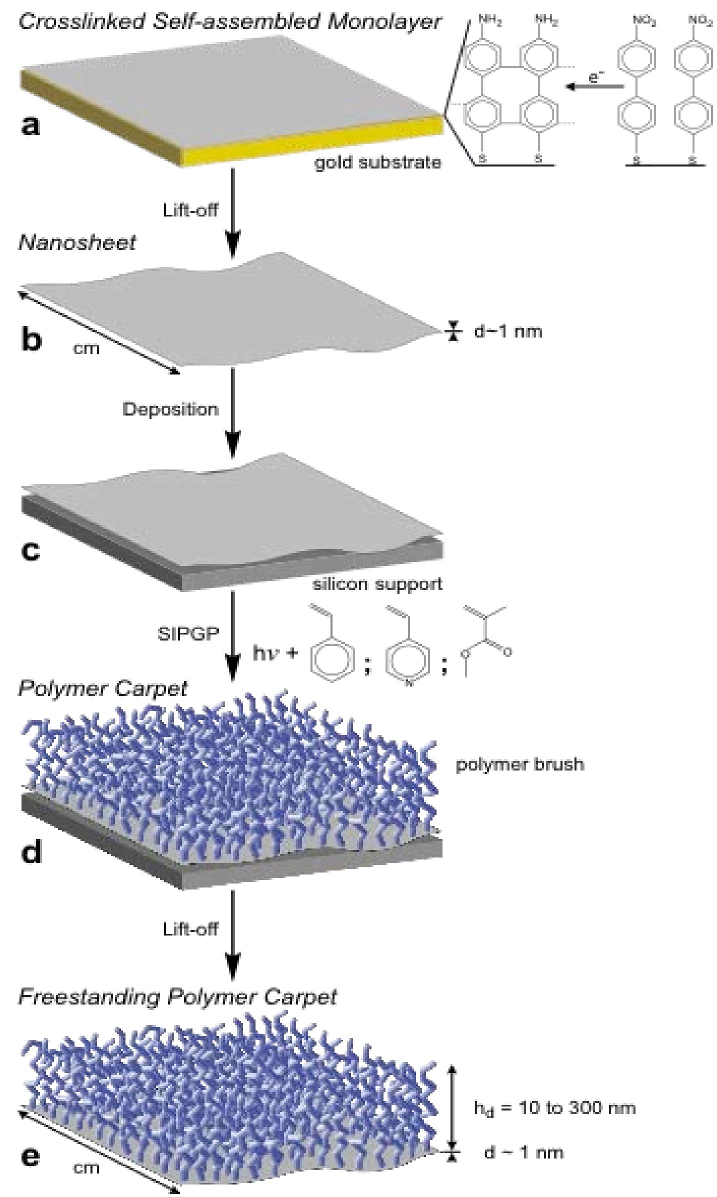
- **polymers**
- **proteins**
- **dyes**
- **...**

Electrons, 10 -500 eV
area dose: 1 -10 mC / cm^2



Adv. Mater. **12**, 805 (2000)
Small **3**, 2114 (2007)

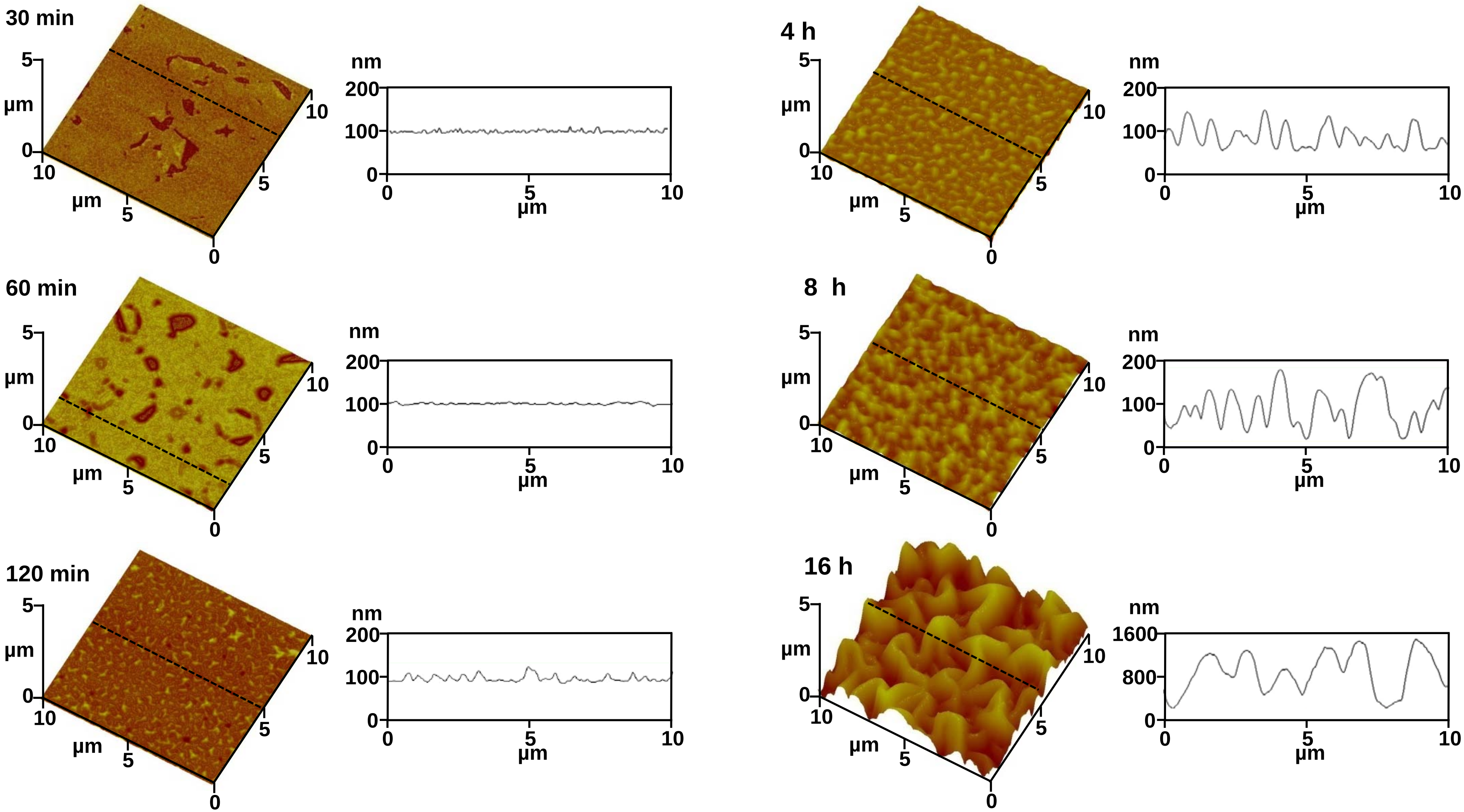
Polymer Carpets



Small 6, 1623 (2010)

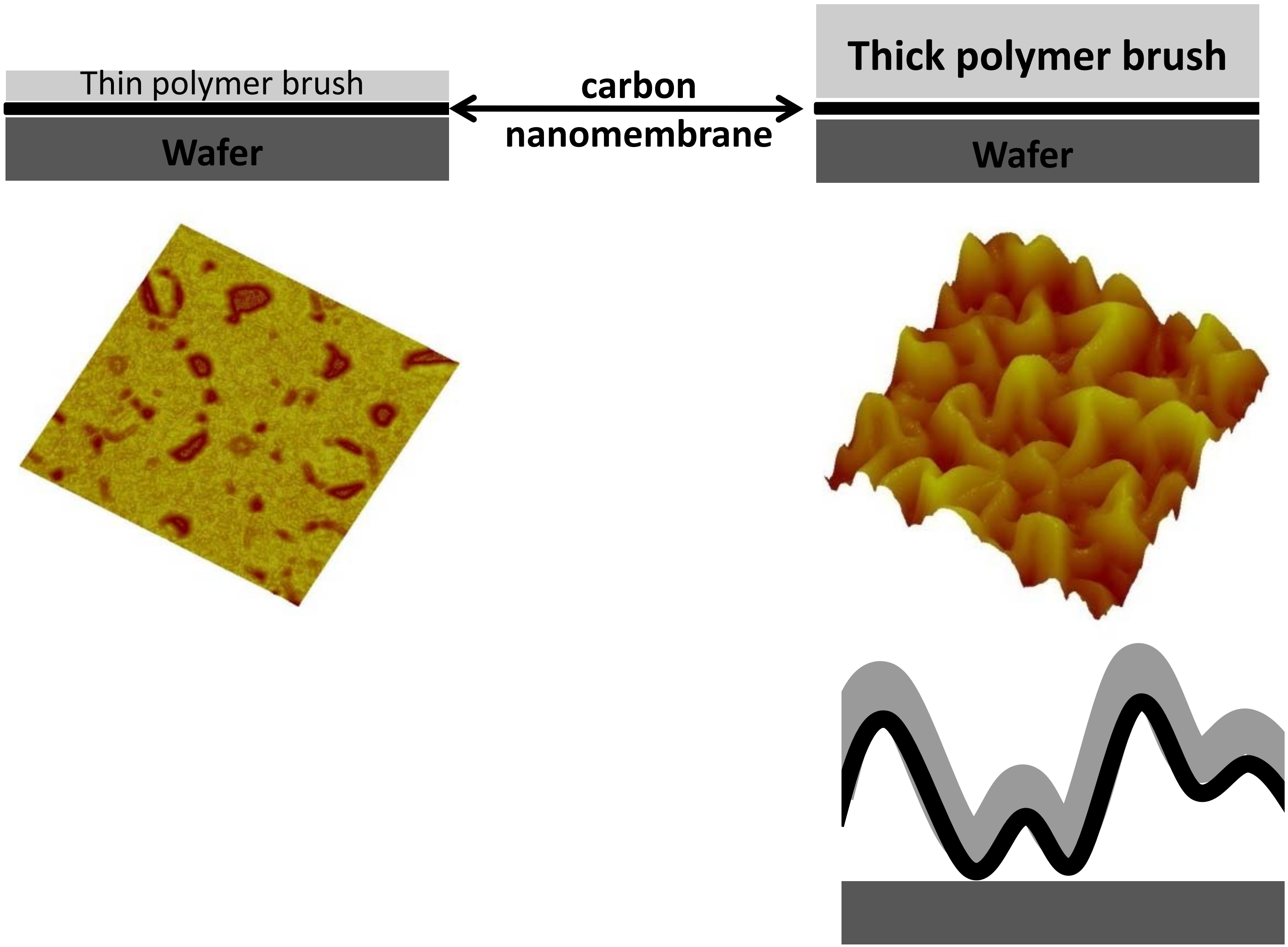
Polymer Carpets: Thickness of Polymer Brush as a Function of Polymerization Time

True-to -scale 3d AFM images of polystyrene carpets on nanosheet/Si

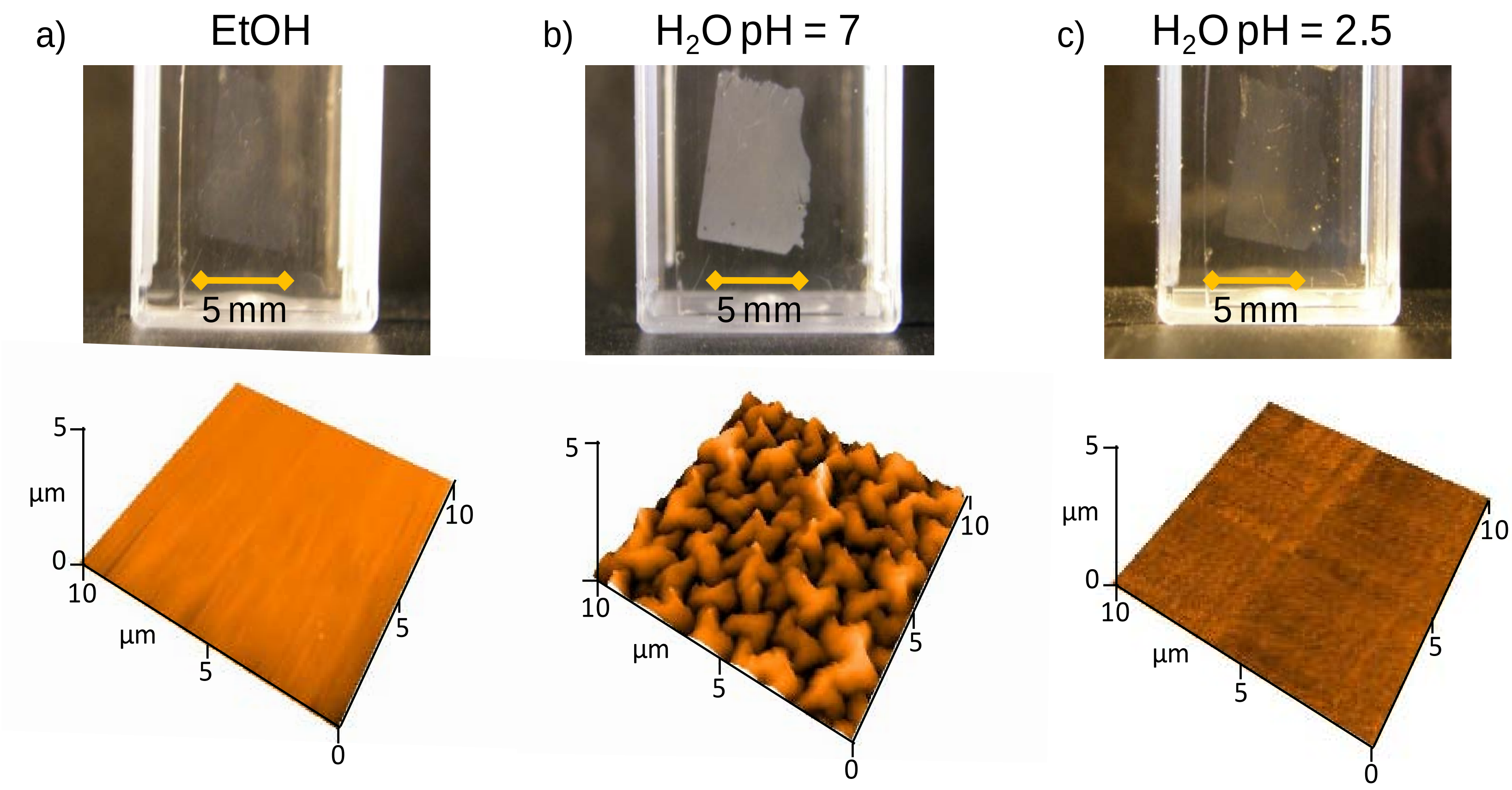


Small 6, 1623 (2010)

Buckling of Polymer Carpets



Building a Sensor (and Actuator) by Buckling of Polymer Carpet



Photographs and AFM measurements of P4VP carpets in a) ethanol, b) water at pH 7 and c) water at pH 2.5.

Small 6, 1623 (2010)

Electron Transmission through freestanding Polymer Carpets

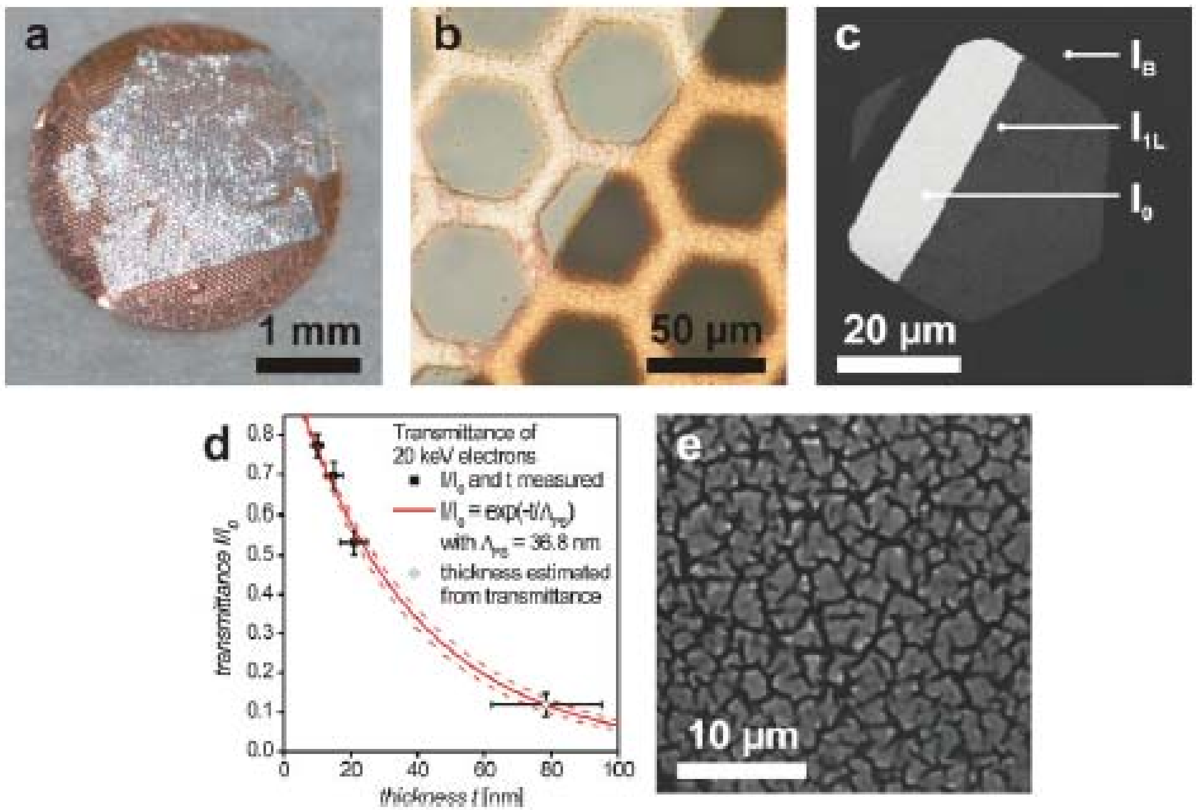
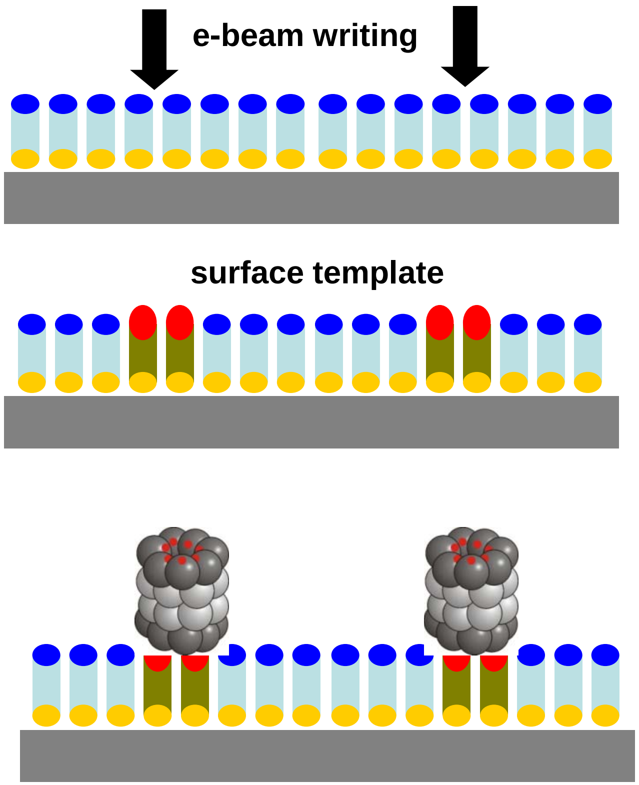


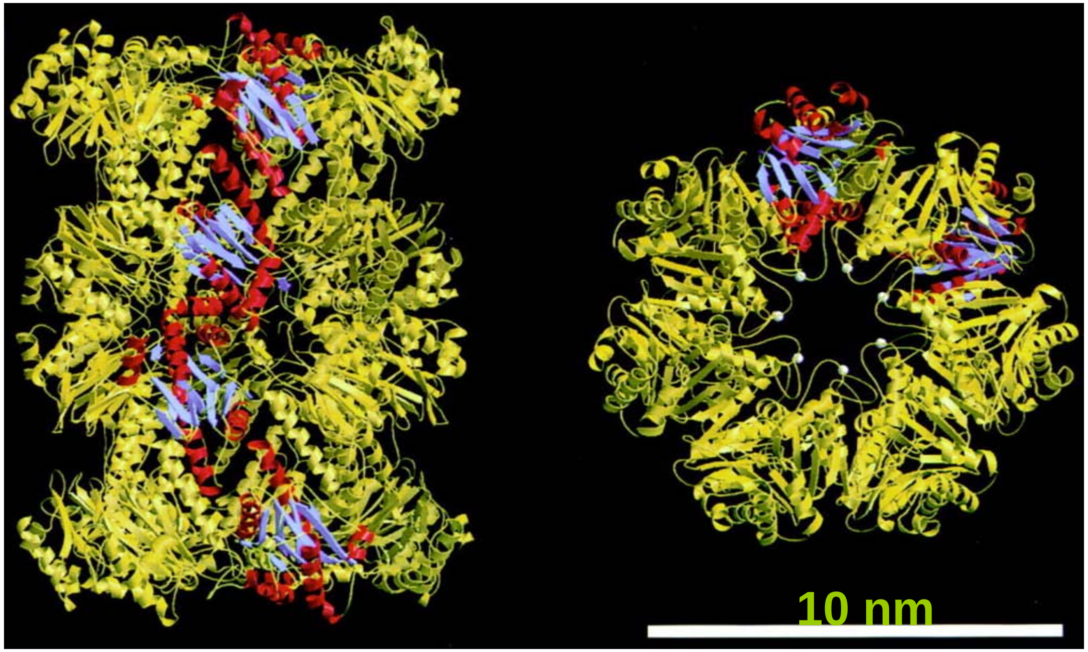
Figure 7. a) Photograph, b) optical micrograph, and c) STEM image of freestanding PS carpets. d) The transmittance of 20 keV electrons was determined from STEM images of PS-carpet edges, such as in (c). An attenuation length of 36.8 nm (solid red line) ±2.6 nm (dashed lines) was calculated. e) STEM image of a freestanding PS carpet at higher magnification.

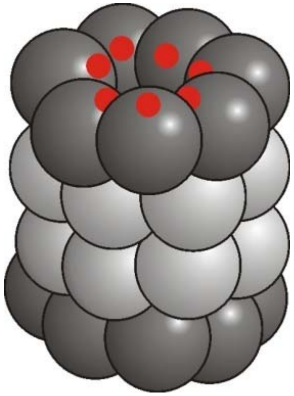
Small 6, 1623 (2010)

Immobilization of biomolecules



20S Proteasome - Nanocompartment for Cellular Protein Degradation – Model system for AFM studies

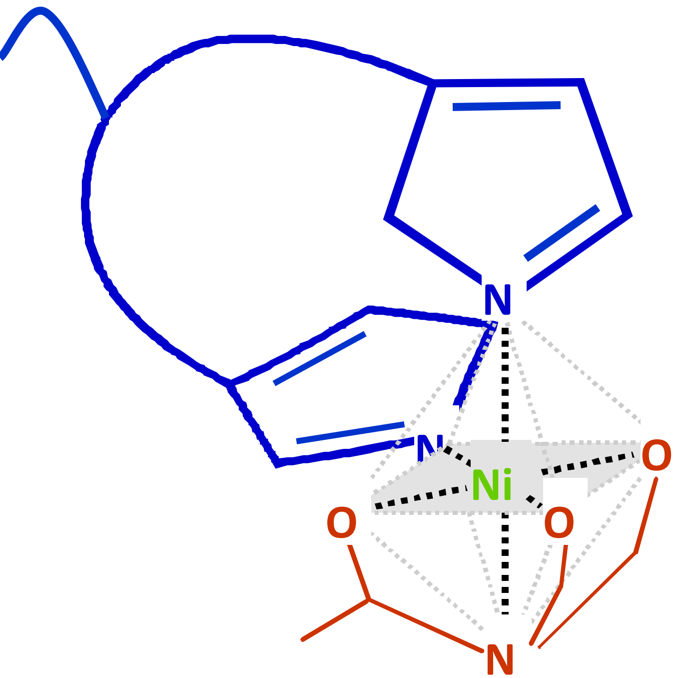




Thermoplasma acidophilum
700.000 Da
11 x 15 nm

(with R. Tampé, U Frankfurt)

NTA/His-tag interaction: molecular tweezers



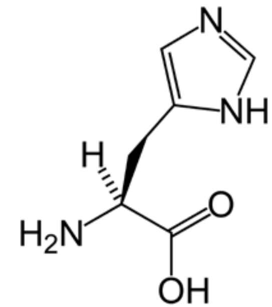
histidine tag (His-tag)

- *easily introduced into proteins by genetic engineering*

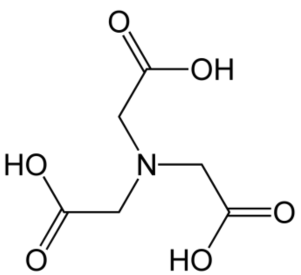
nitrilotriacetic acid (NTA)

- *high specificity for neighboring histidine residues*
- *easily functionalized*

histidine



NTA



reversible binding

imidazole
ETDA
low pH

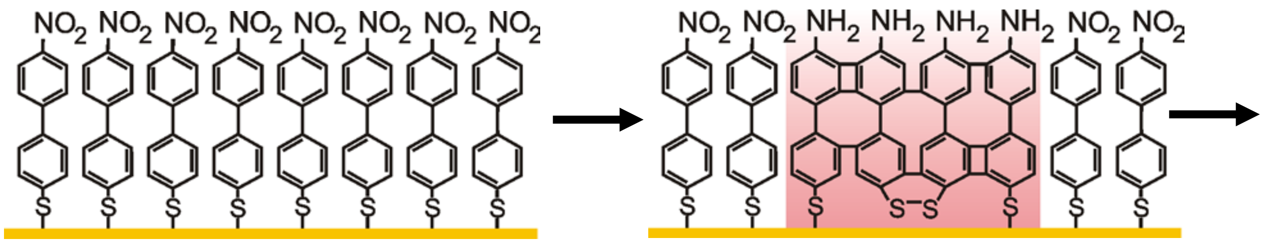
high affinity by utilization of

multivalent chelators: *bis-NTA, tris-NTA*

F.H. Arnold, Metal-affinity protein separations, Academic Press, 1992
S. Lata, A. Reichel, R. Brock, R. Tampé, J. Piehler, JACS 127 (2005) 10205

Assembly of the structured chips: schematic representation

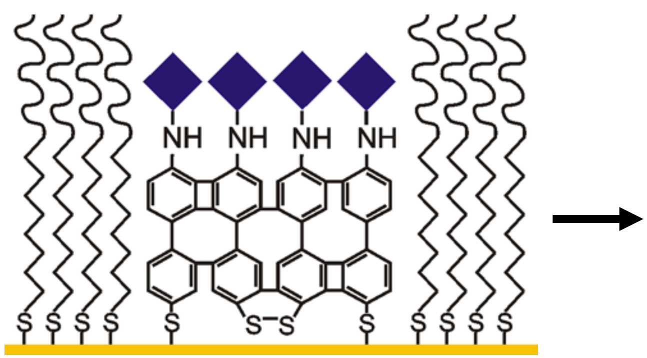
SAM formation **e-beam/EUV lithography**

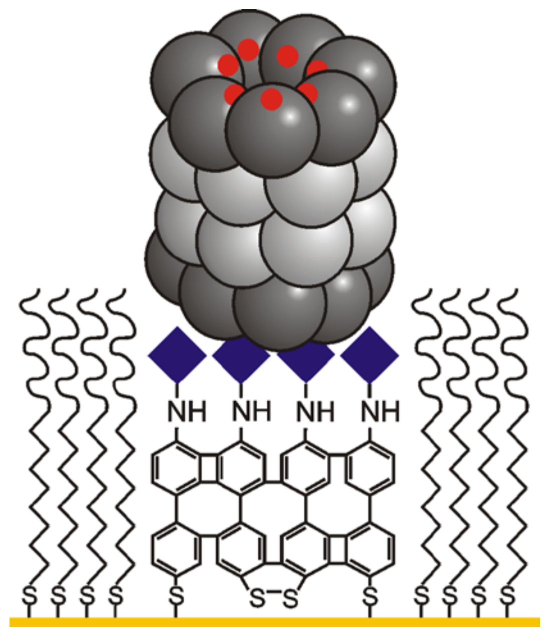


molecular self-assembly
e-beam/EUV lithography
chemical biology
molecular recognition

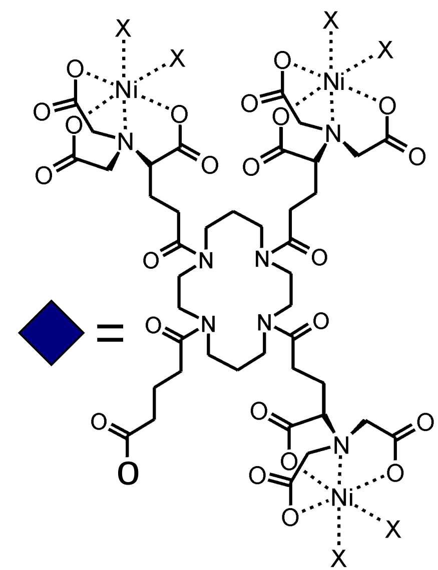
functional immobilization of His$_6$-taged proteins

grafting of multivalent chelators and generation of the protein repellent matrix

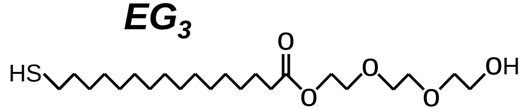




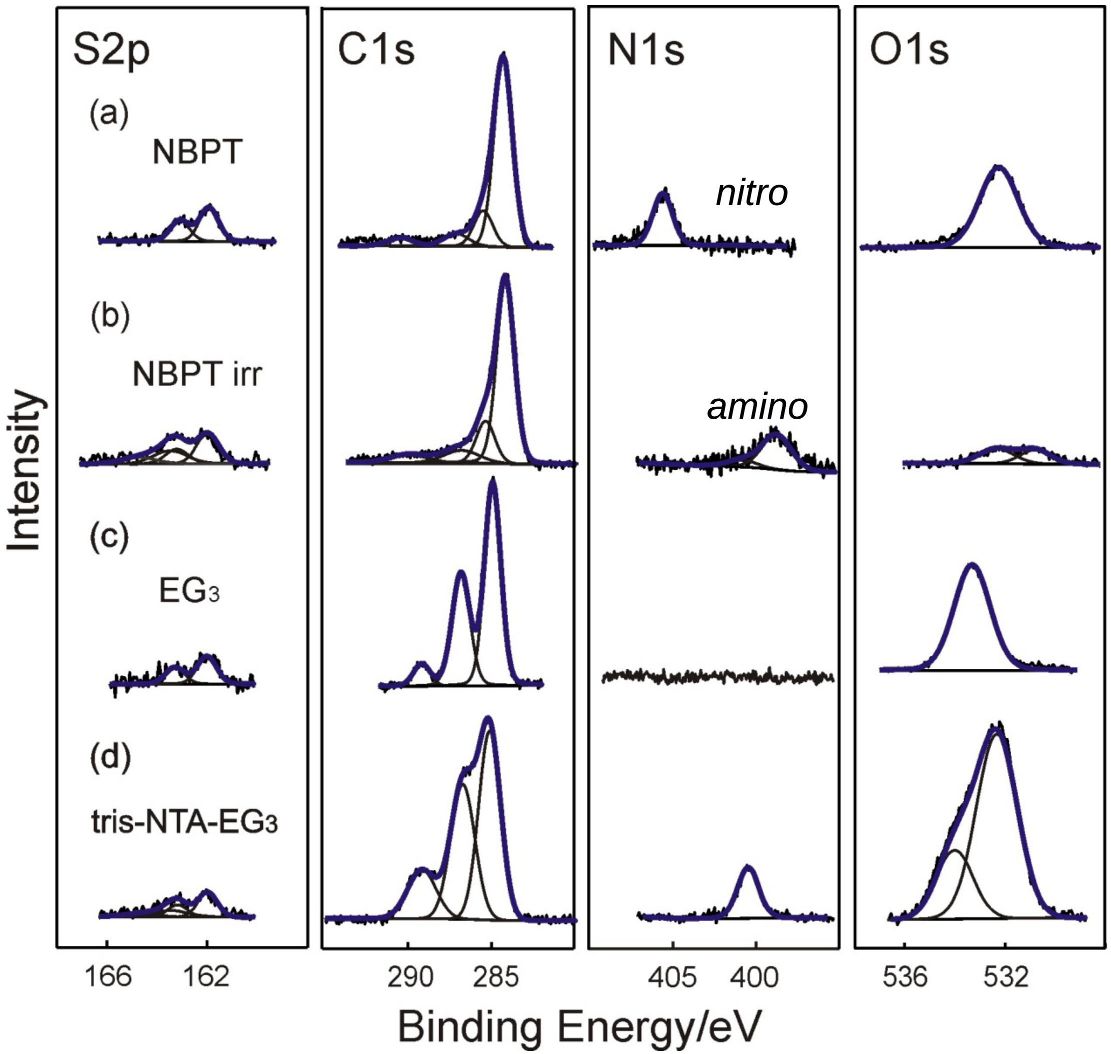
tris-NTA



EG$_3$



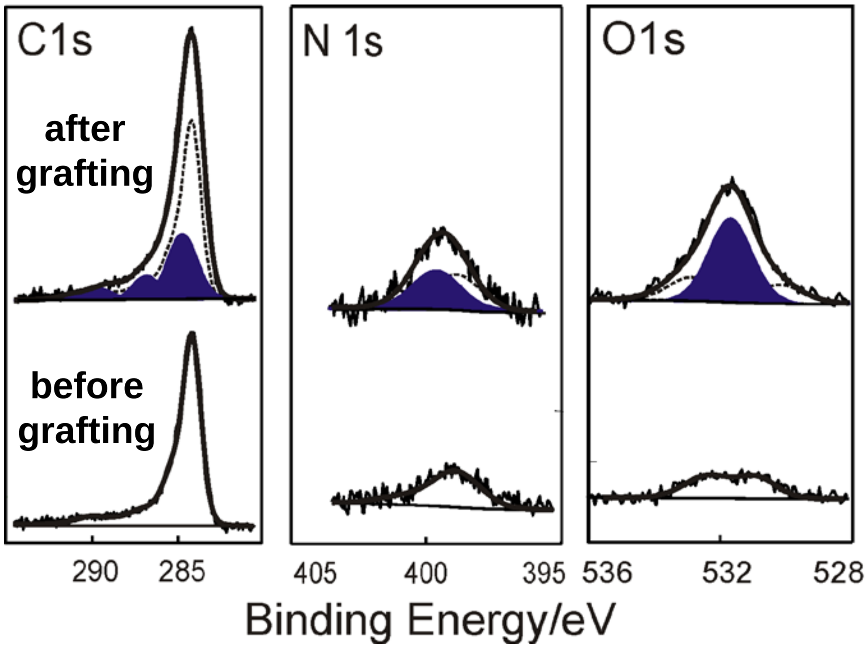
XPS characterization of the elemental components of the chip' surface

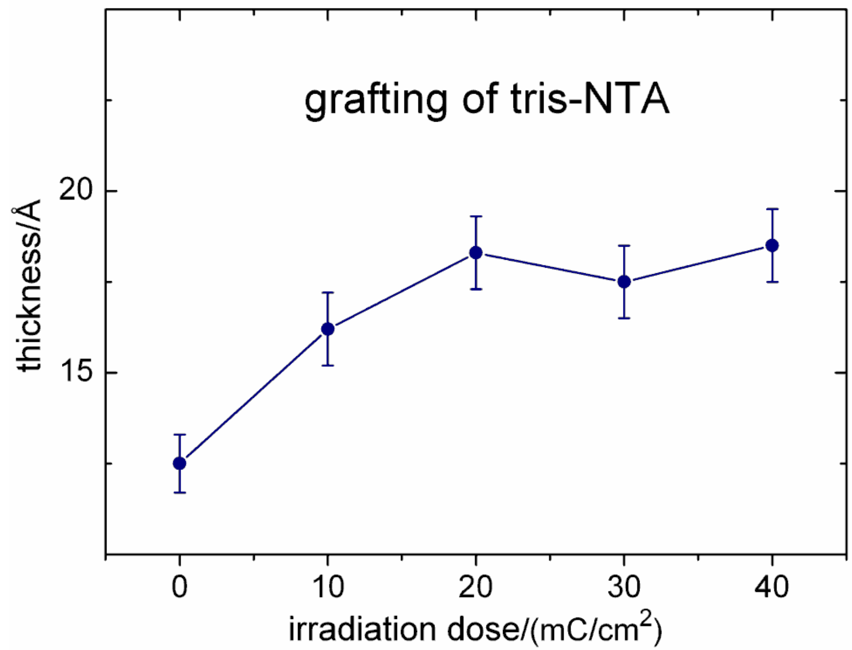


different types SAMs

A.Turchanin, A. Tinazli, M. El-Desawy, H. Großmann, M. Schnietz, H. H. Solak, R. Tampé, A. Gölzhäuser, Adv. Mater. 20, 471 (2008)

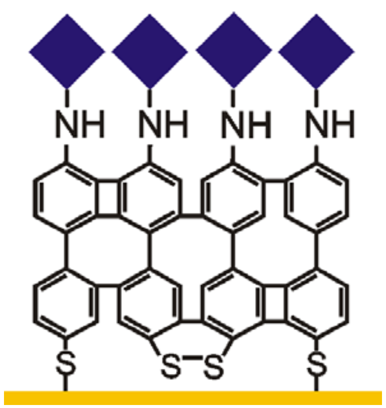
Grafting of multivalent chelators (tris-NTA)





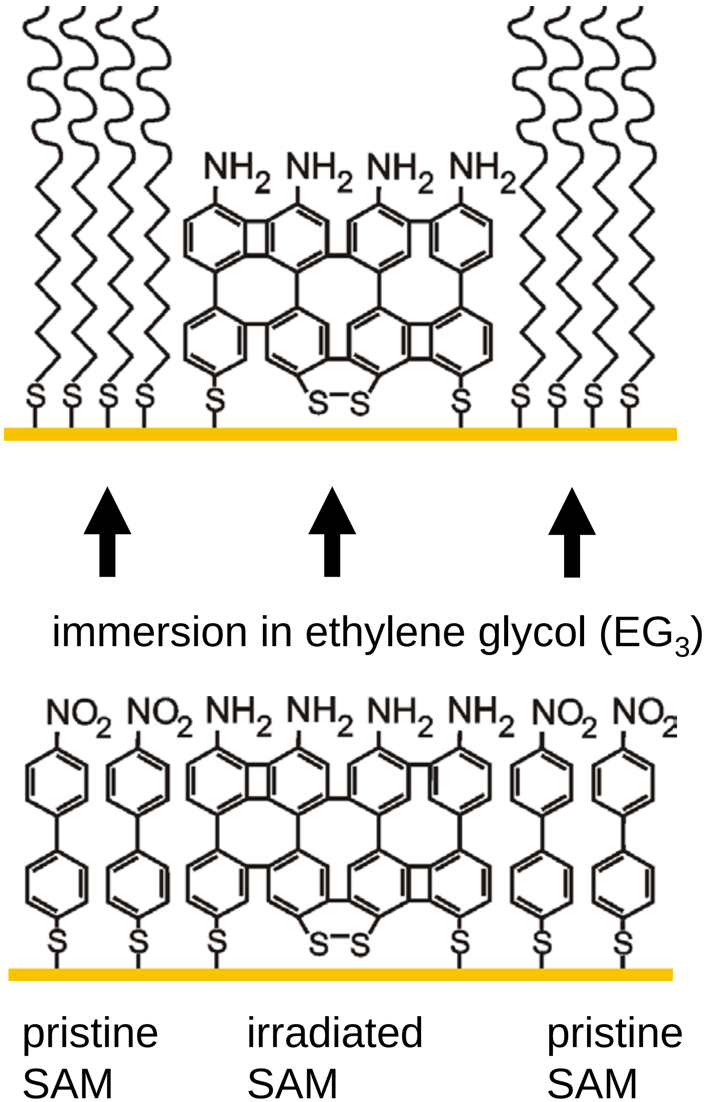
thickness increase ~6 Å
tris-NTA:NBPT~1:9
experimental C:O:N =11.2:3.5:1
theoretical C:O:N =11.1:3.4:1

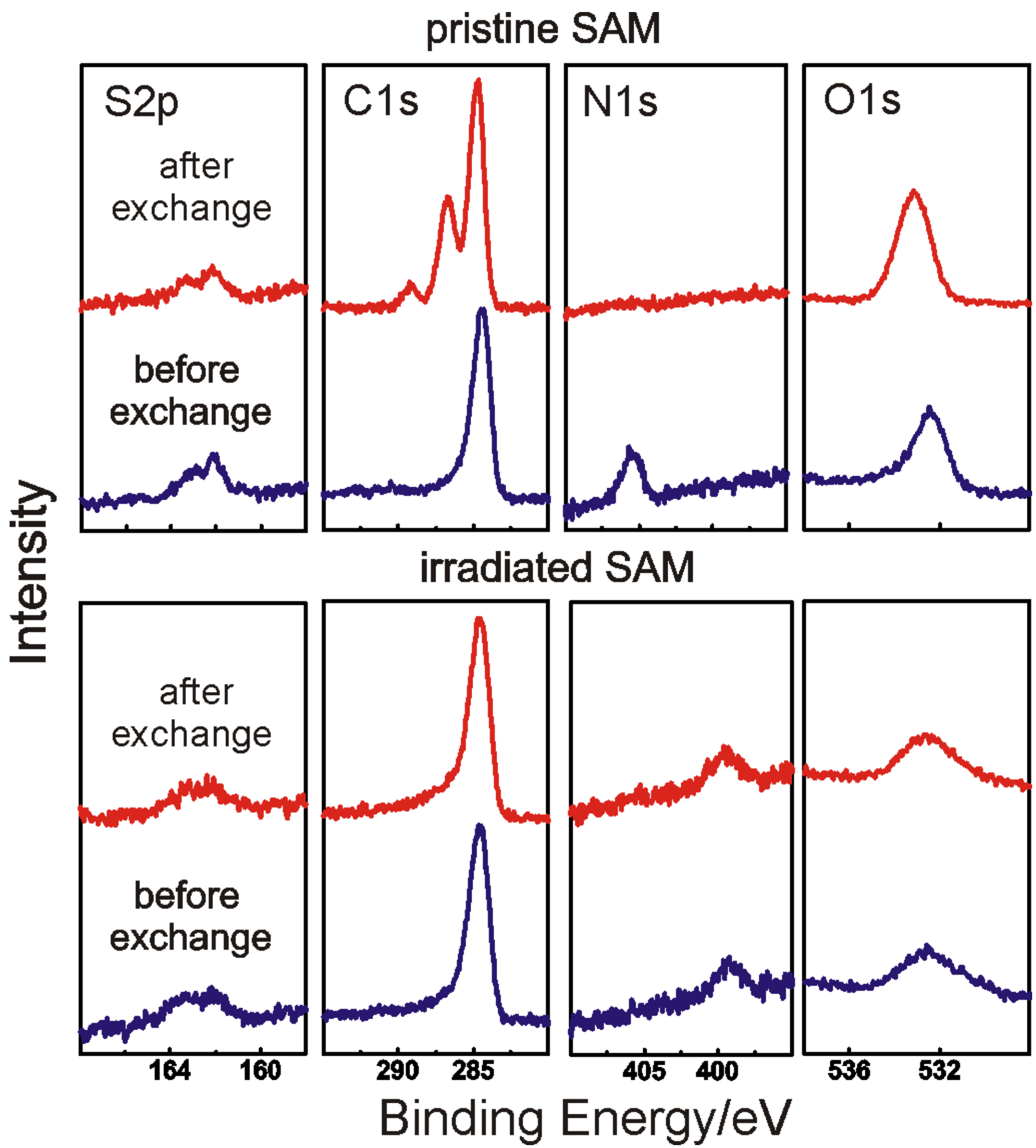
C1s^{I} 284.9 eV (alkane-like groups)
C1s^{II} 286.8 eV (N-C bonds)
C1s^{III} 288.9 eV (carboxylic groups)
N1s 399.8 eV (amine groups)
O1s 531.9 eV (carboxylic groups)



Adv. Mater. 20, 471 (2008)

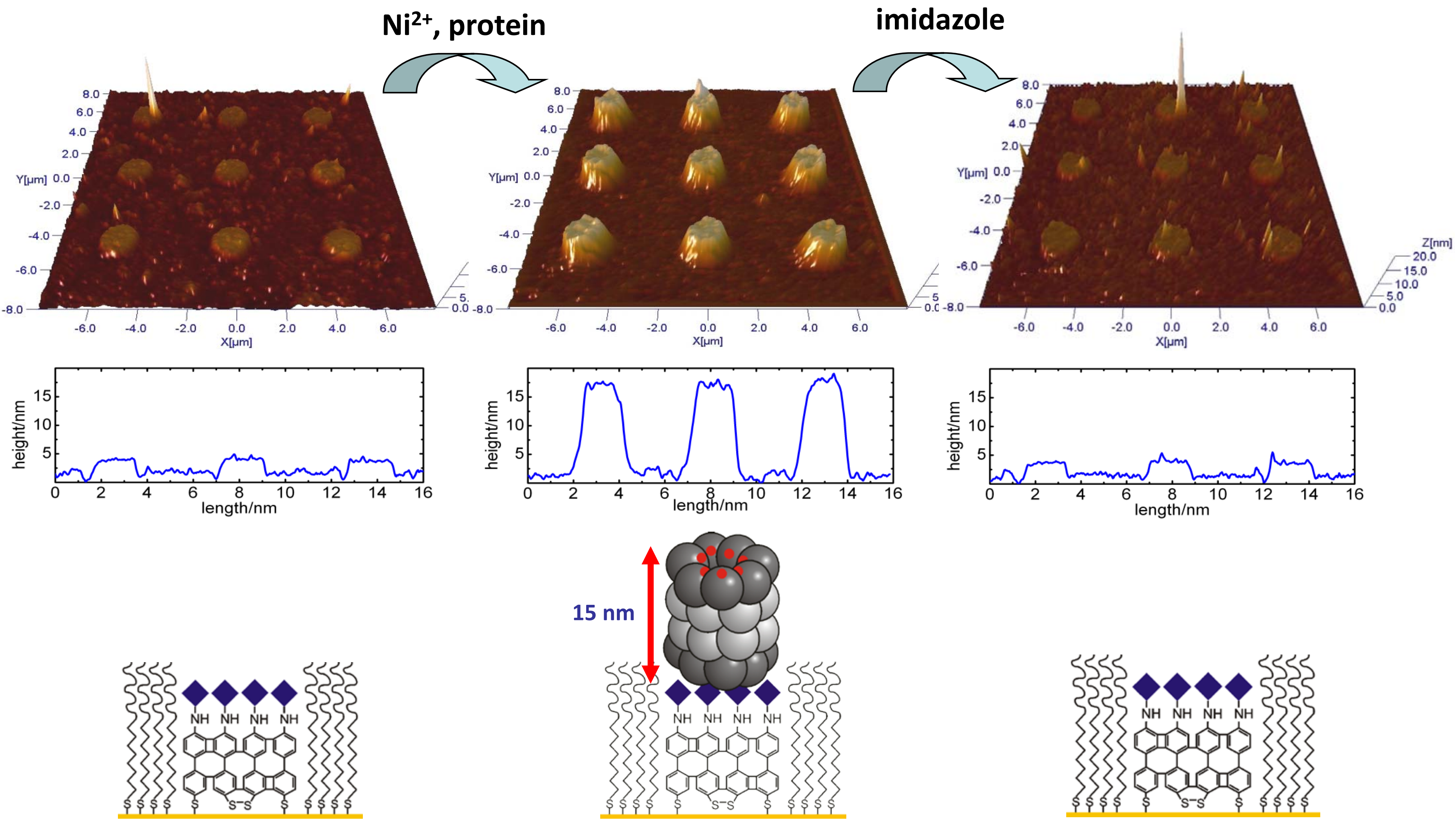
Generation of protein repellent matrix by exchange





Protein chip functioning: an *in situ* AFM study

Chips' surface in buffer | **Immobilization of proteins** (20S His_6-tagged proteasome) | **Regenerated chip**

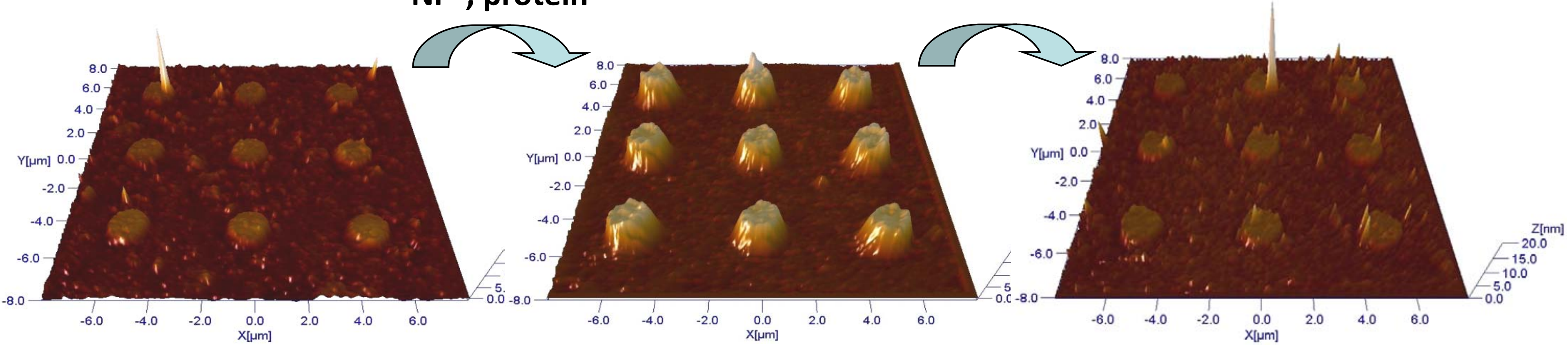


Protein chip functioning: an *in situ* AFM study

Chips' surface in buffer | **Immobilization of proteins** (20S His_6-tagged proteasome) | **Regenerated chip**

Ni^{2+}, protein

imidazole



structured

specific

highly parallel

highly affine

oriented

reversible

immobilization of protein micro arrays

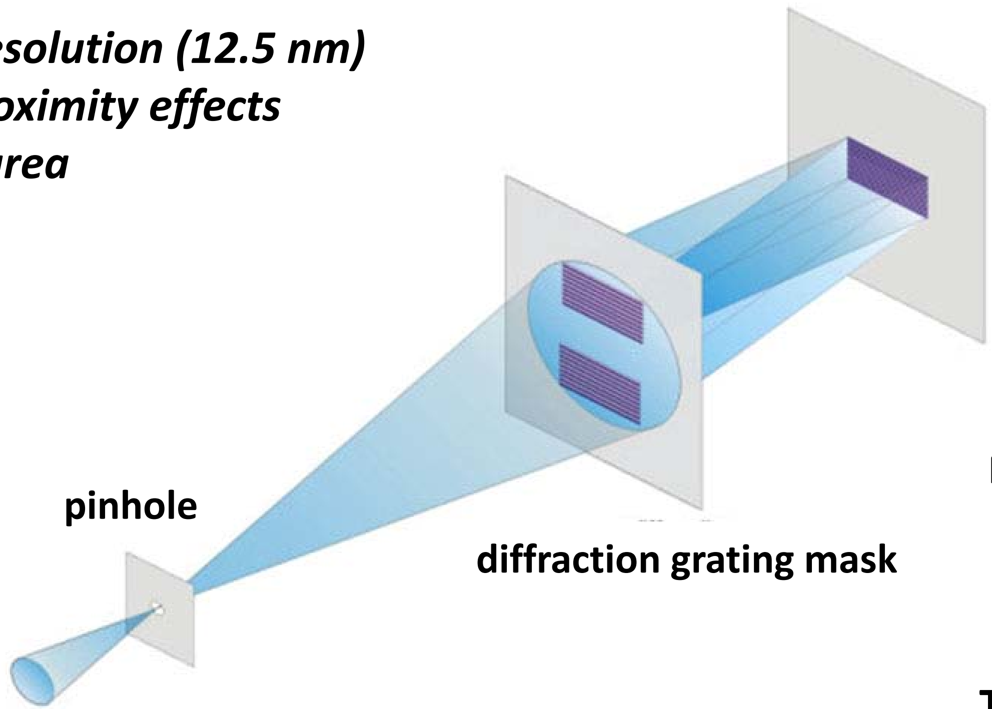
Down to the single molecular resolution?

A.Turchanin et al.
Adv. Mater. 20, 471 (2008)

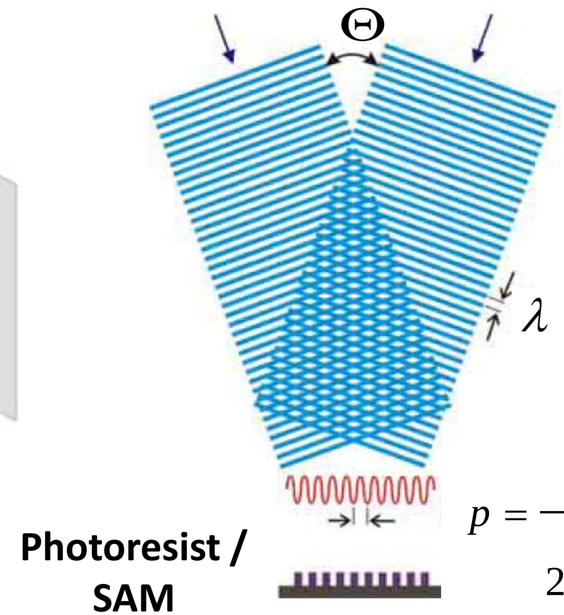
Protein nanopatterns by EUV Interference Lithography

Extreme UV Interference lithography (EUV-IL):

- ***high resolution (12.5 nm)***
- ***low proximity effects***
- ***large area***



focused synchrotron irradiation (92.5 eV, 13.5 nm)



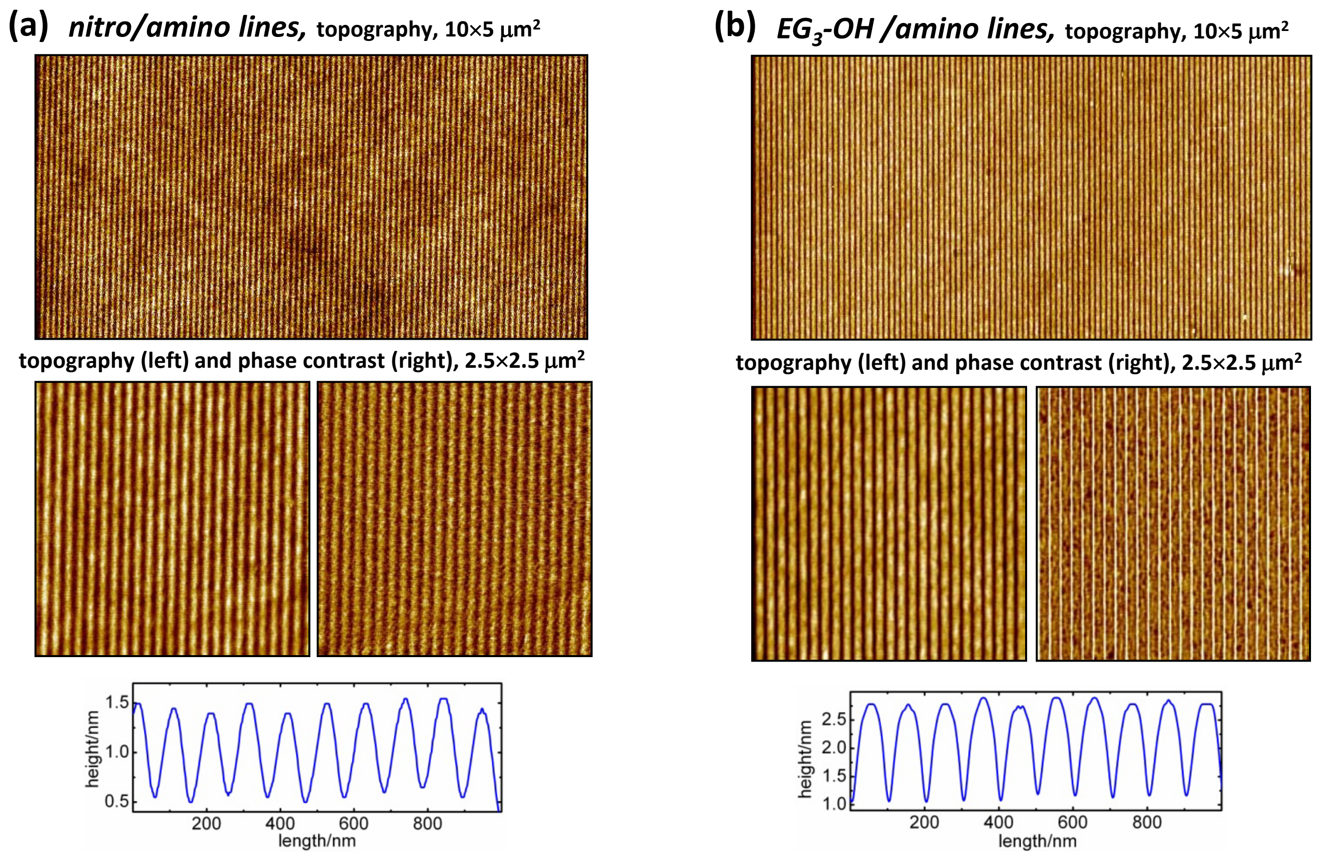
$$p = \frac{\lambda}{2\sin\frac{\Theta}{2}}$$

Two coherent beams are forming a linear fringe pattern with a sinusoidal intensity distribution.

H. H. Solak, Microelectronic Engineering 78-79 (2005) 410-416

High resolution chemical patterns by EUV-IL: AFM

50 nm lines

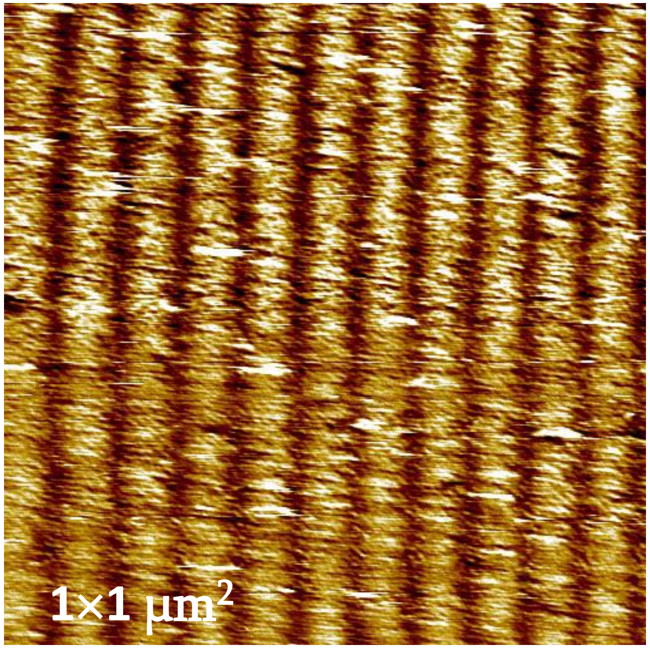


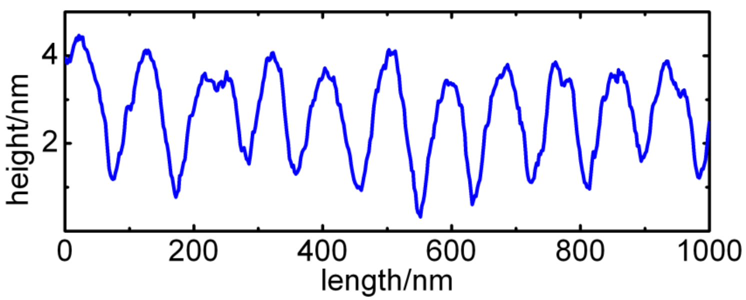
A. Turchanin, M. Schnietz, M. El-Desawy, H. H. Solak, C. David, A. Gölzhäuser, Small 3, 2114 (2007)

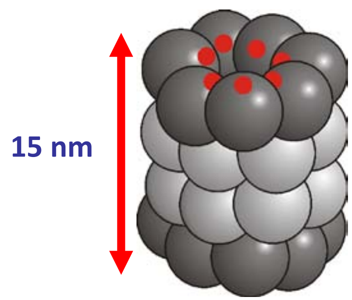
Immobilization of protein nanoarrays : *in situ* AFM characterization

Proteasome lines

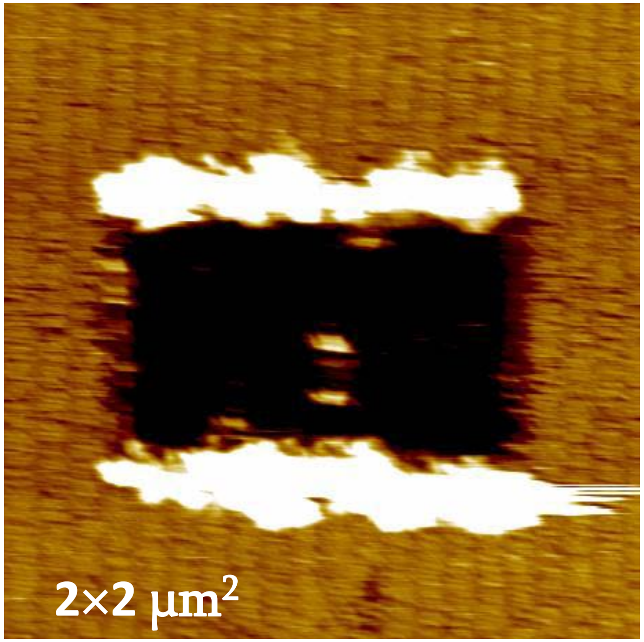
100 nm period

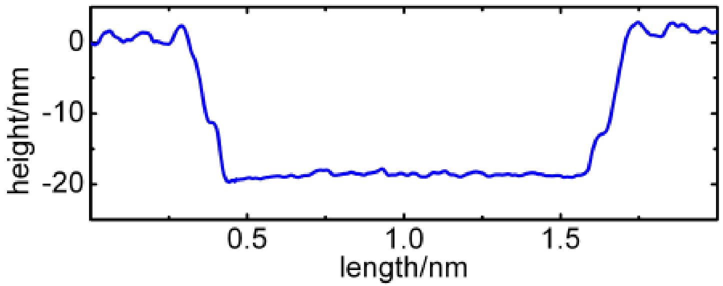






Protein lithography

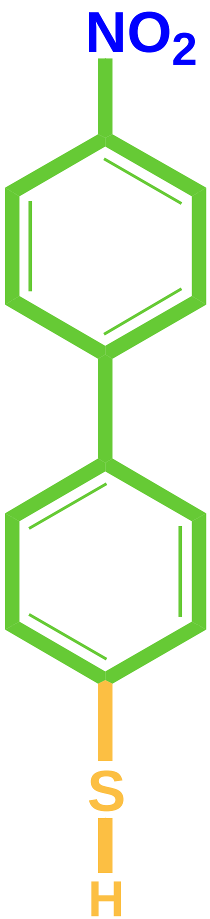


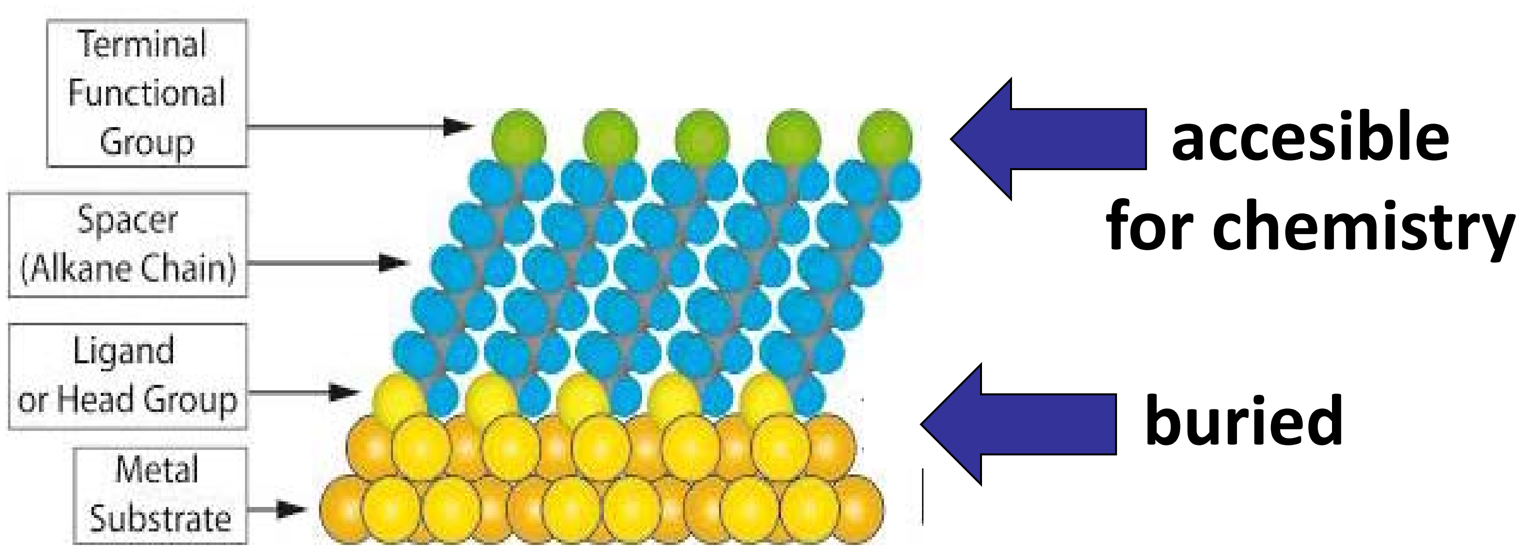


A.Turchanin et al., Adv. Mater. 20, 471 (2008)

Bifunctional Nanomembranes: „Janus Membranes“

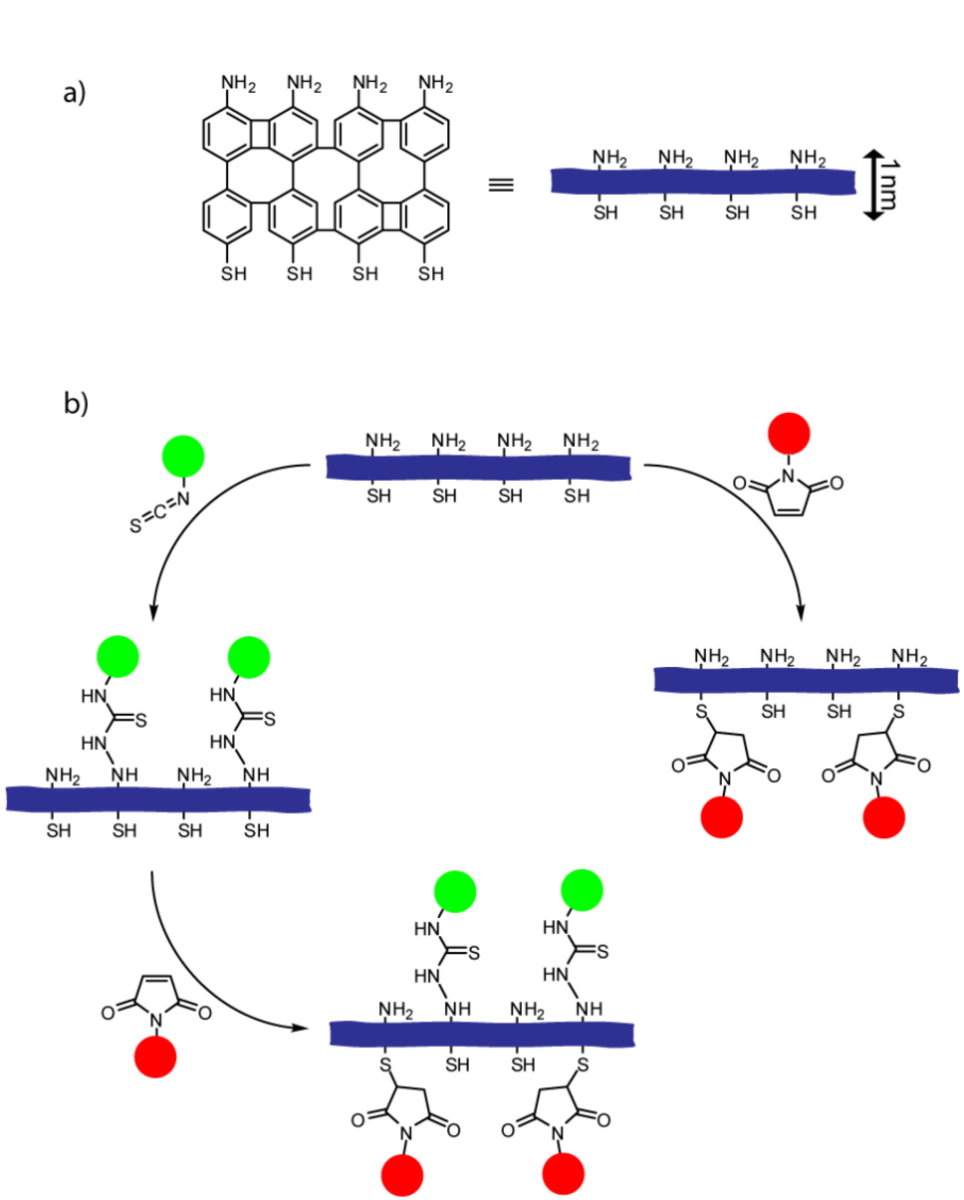
SAMs have 2 functional groups!

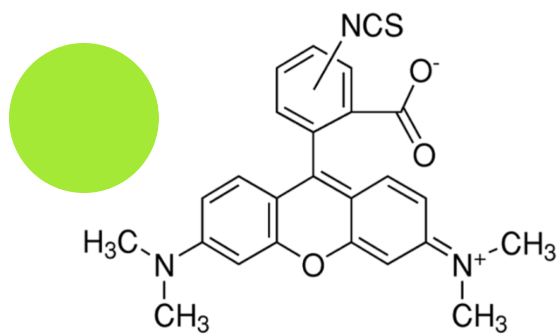




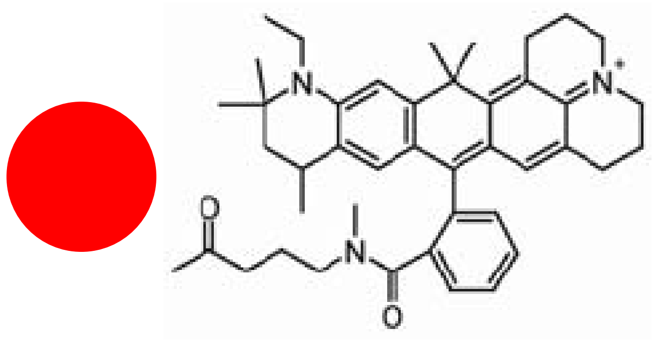
Converting the directionality of the SAM into the directionality of a 2D nanomembrane....

Different fluorescent molecules on top and bottom of membrane





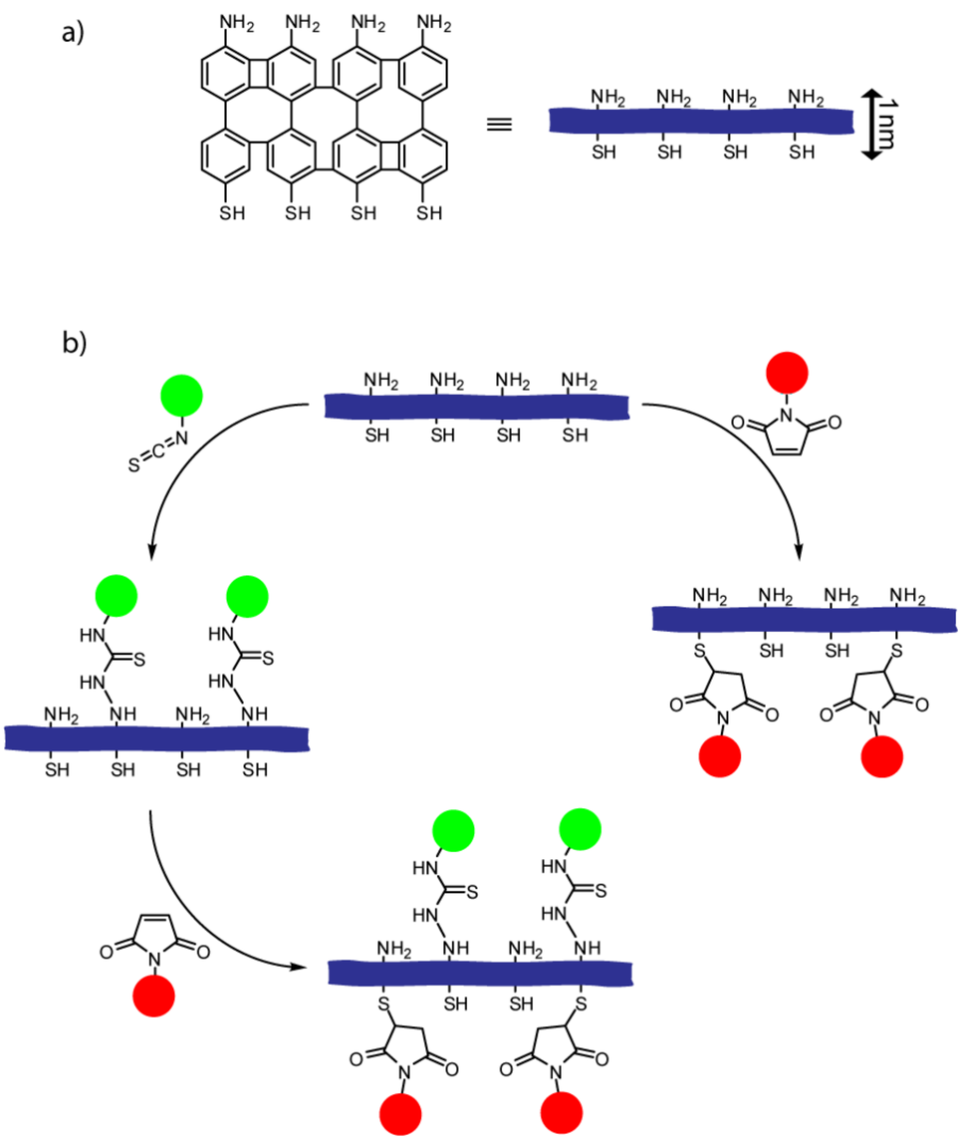
tetramethylrhodamine isothiocyanate (TMR)

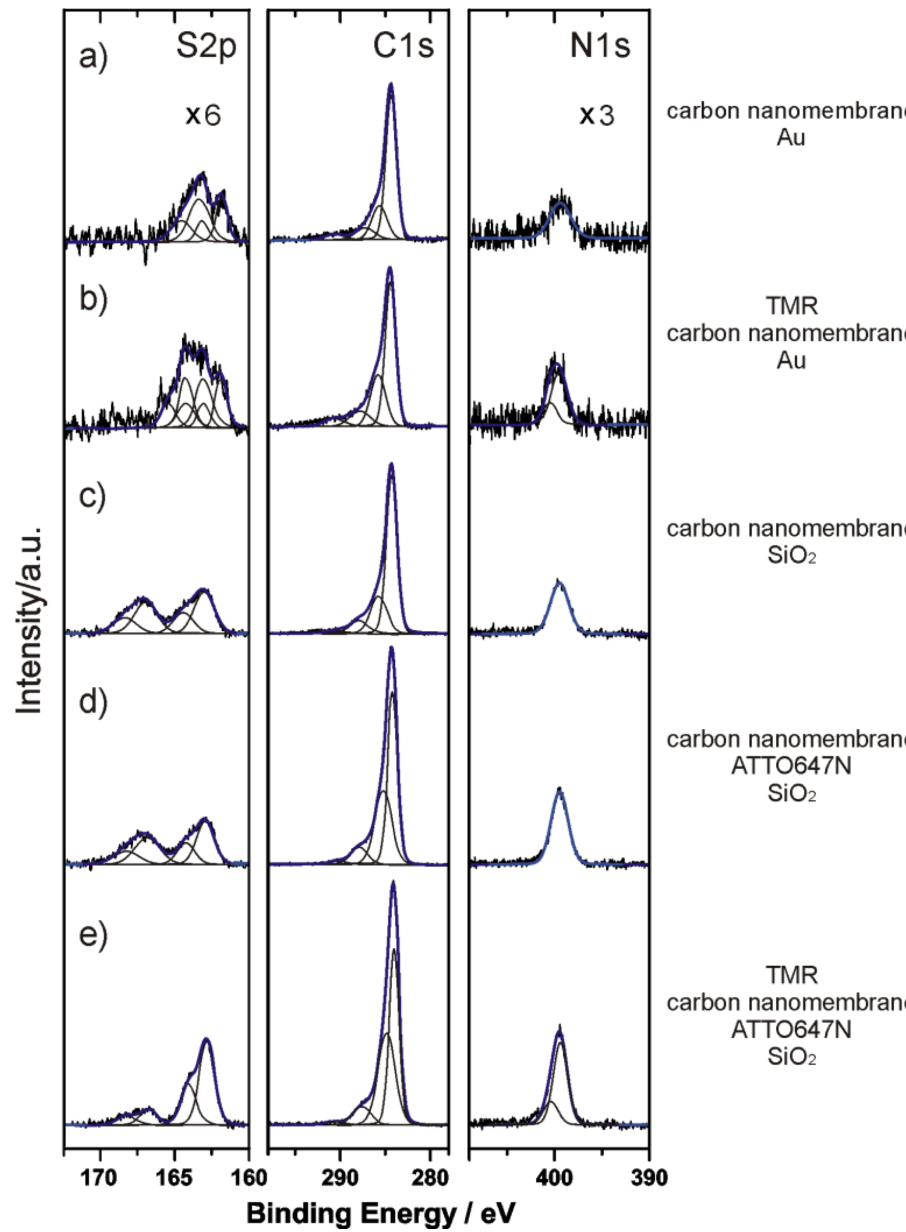


ATTO647N

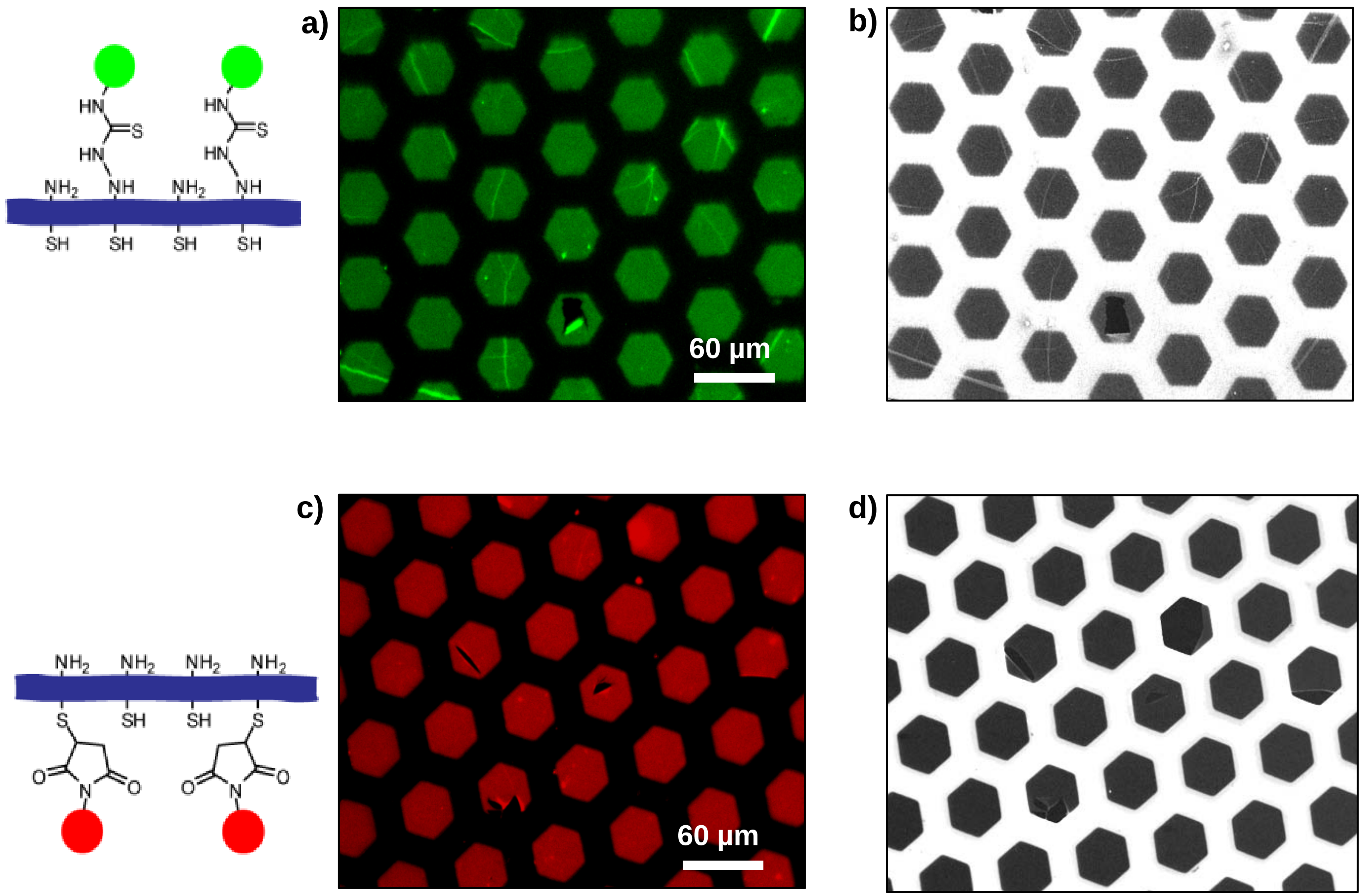
Zinkun Zheng et al., Angewandte Chemie, in press

Monitoring molecular coupling by XPS



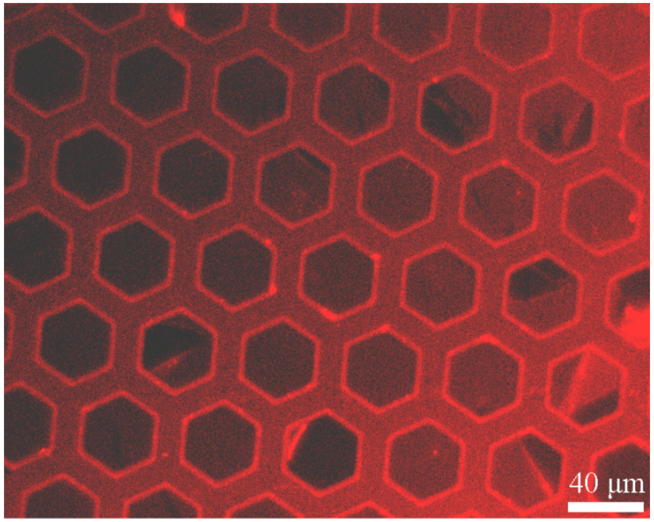


Flourescence detection of TMR and ATTO

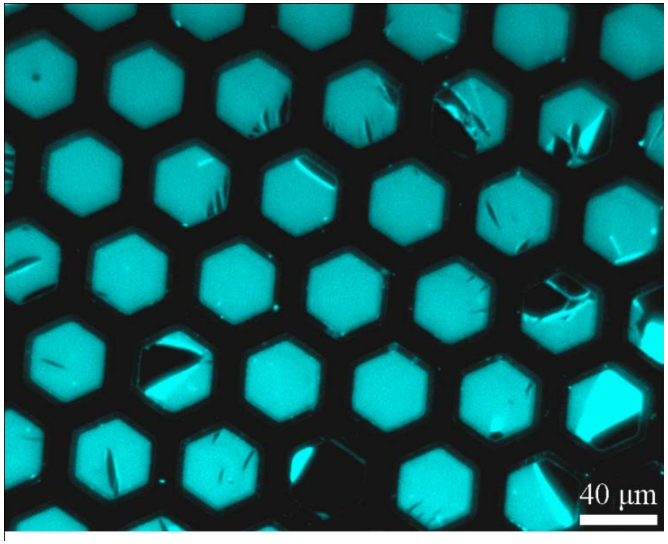


Step 3: Coupling of TMR to Top and ATTO647N to Bottom

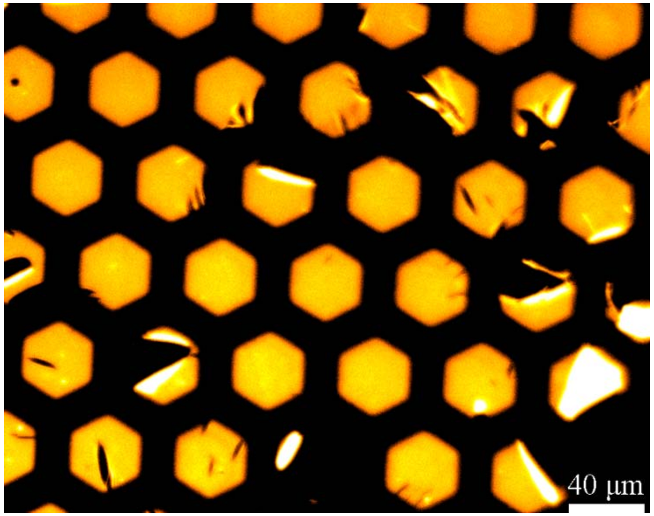
Fluorescence TMR



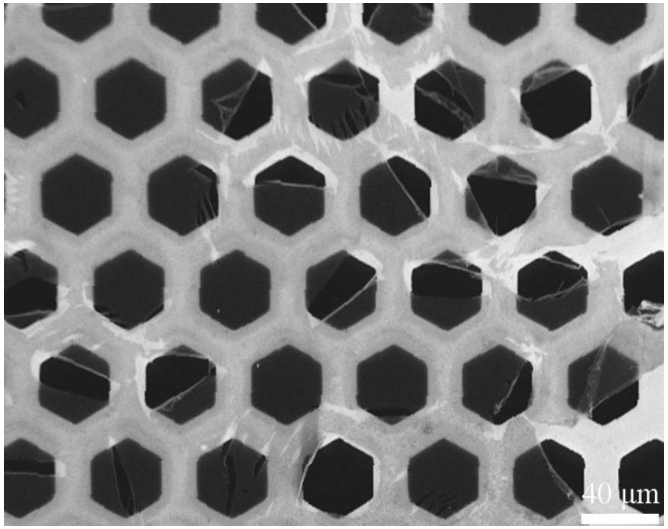
Fluorescence ATTO647N



FRET (Förster Transfer)

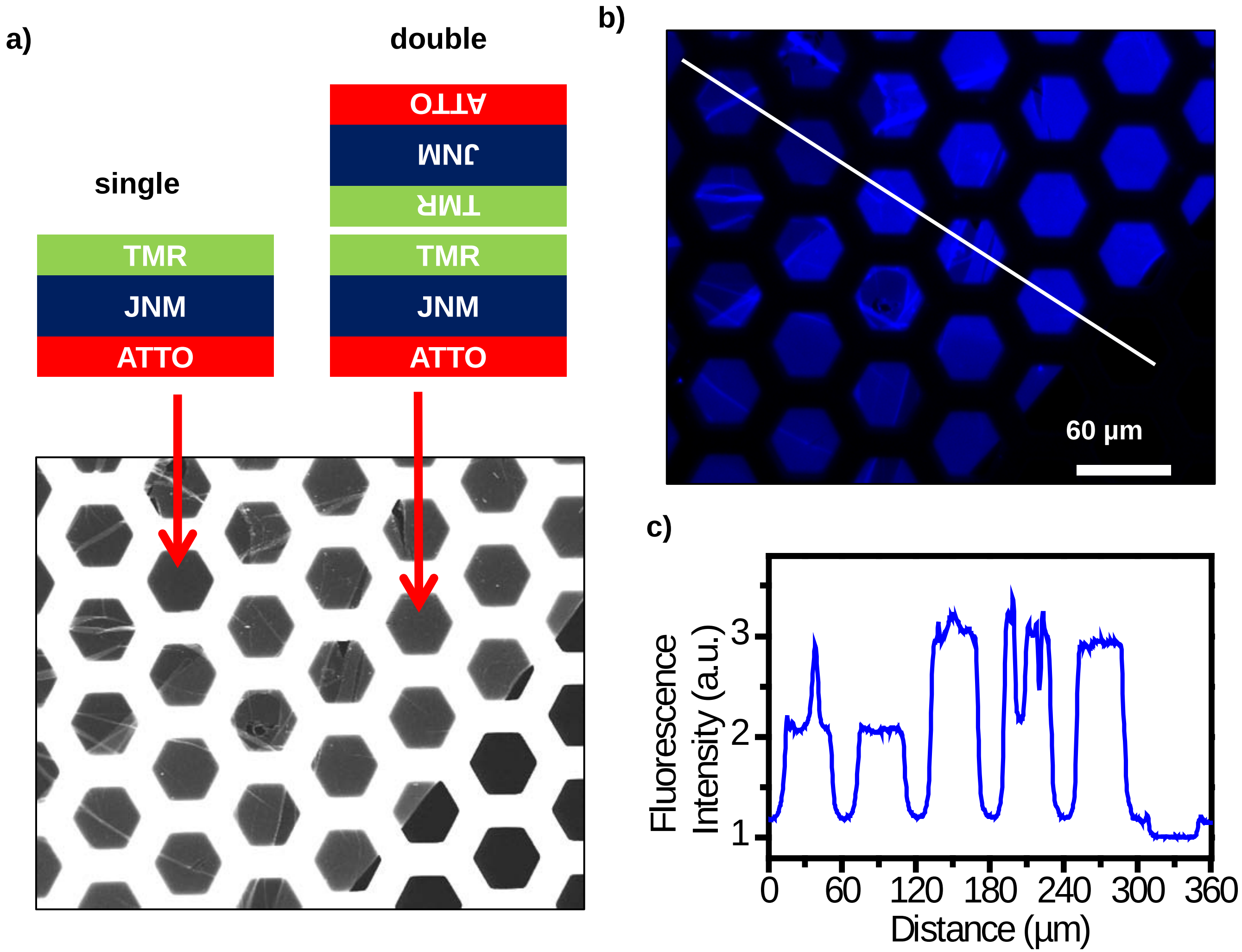


SEM



Angewandte Chemie, In press

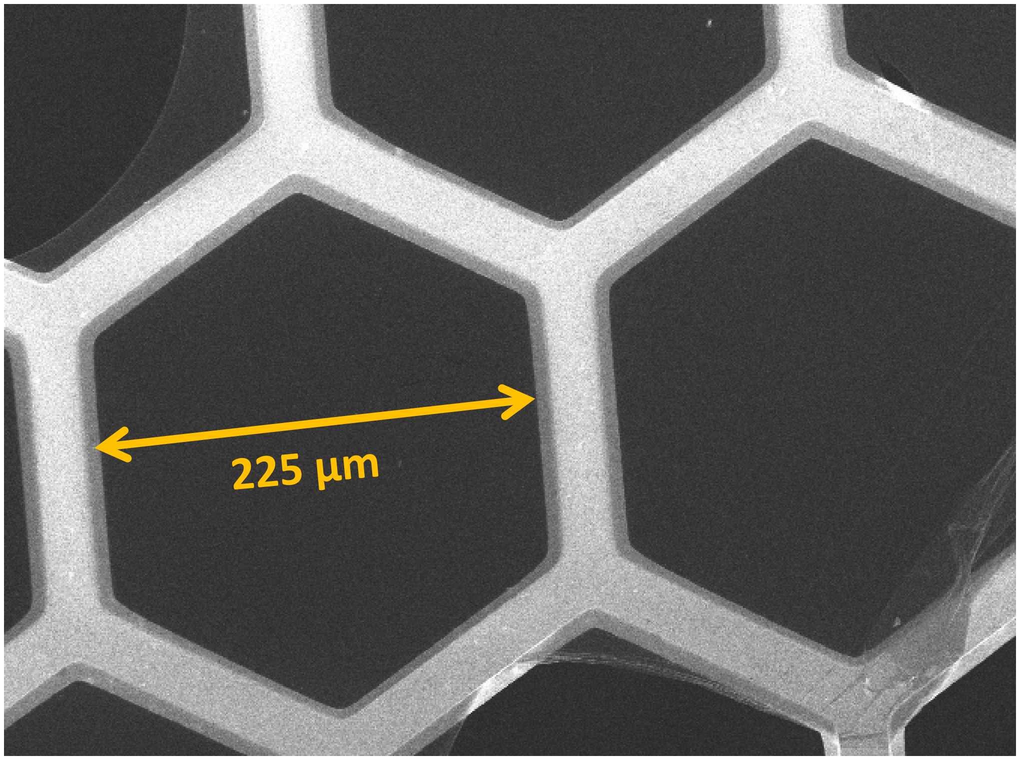
Single and double layers



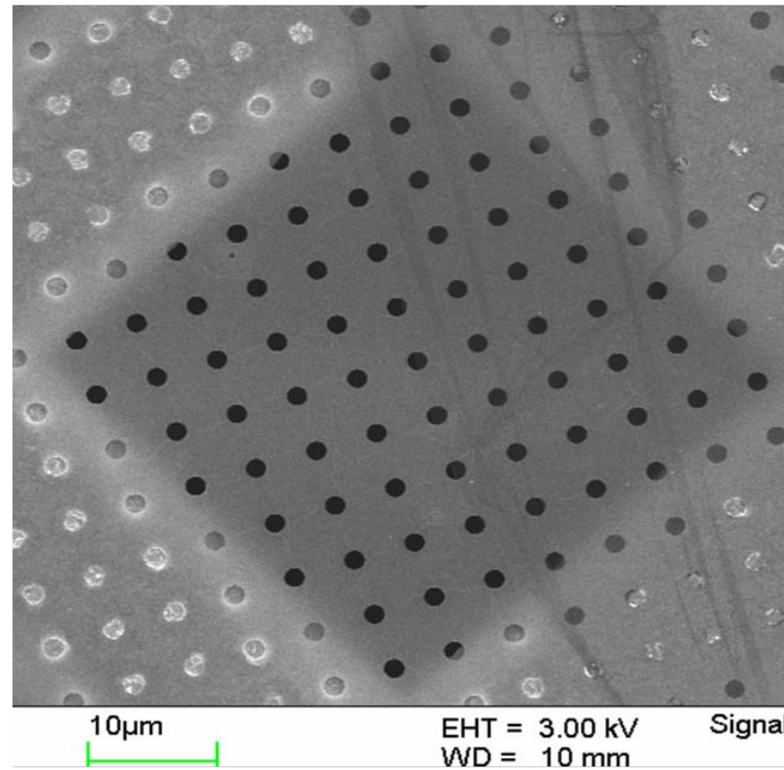
Angewandte Chemie, In press

Visualizing 2-dimensional Nanomembranes by scanning electron microscopy

on Cu grid



on perforated C foil



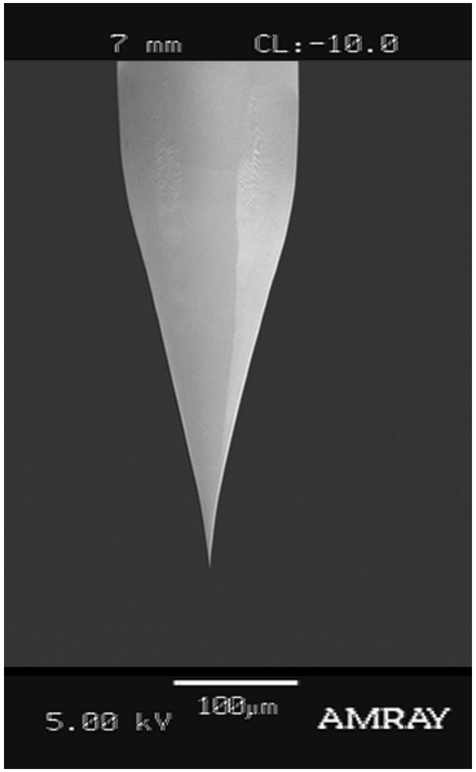
SEM produces acceptable pictures,
but low contrast and time consuming (2-3h/image)

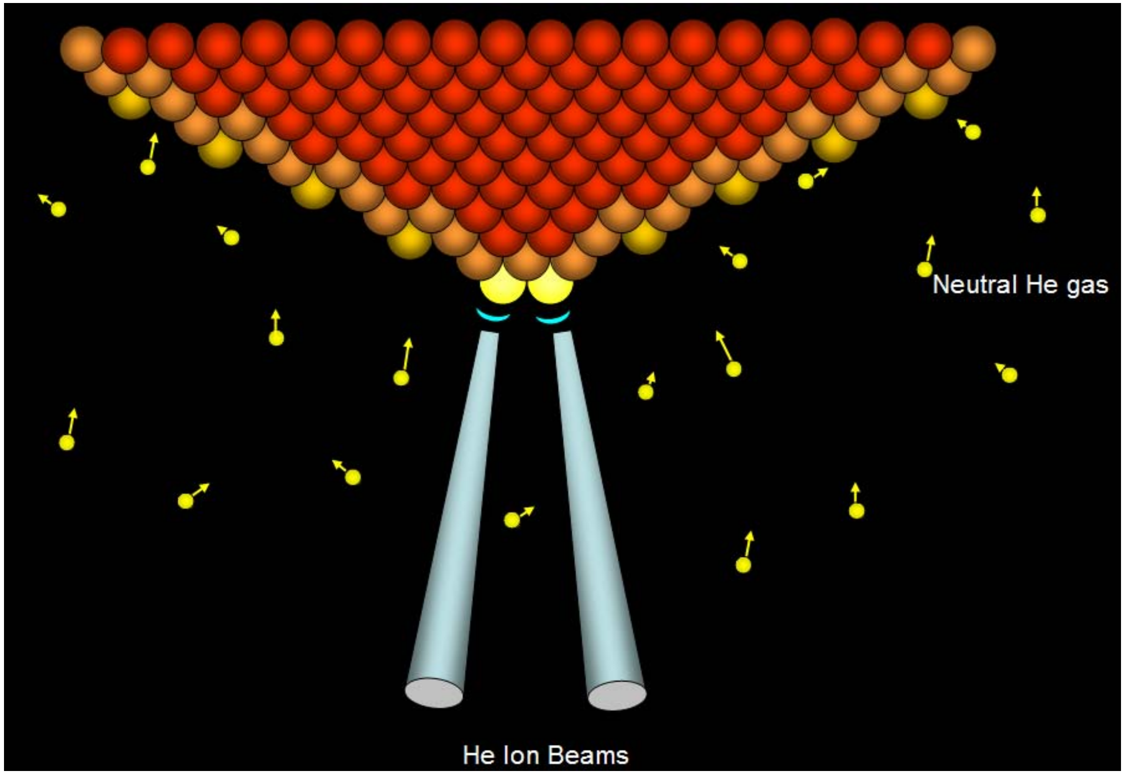
Is there a better imaging technique ?

Helium Ion Microscope

- World's first commercially available Helium Ion Microscope (Carl Zeiss)
- Analogous to a SEM but uses Helium ions instead of electrons
- Image formed using secondary electrons and backscattered ions

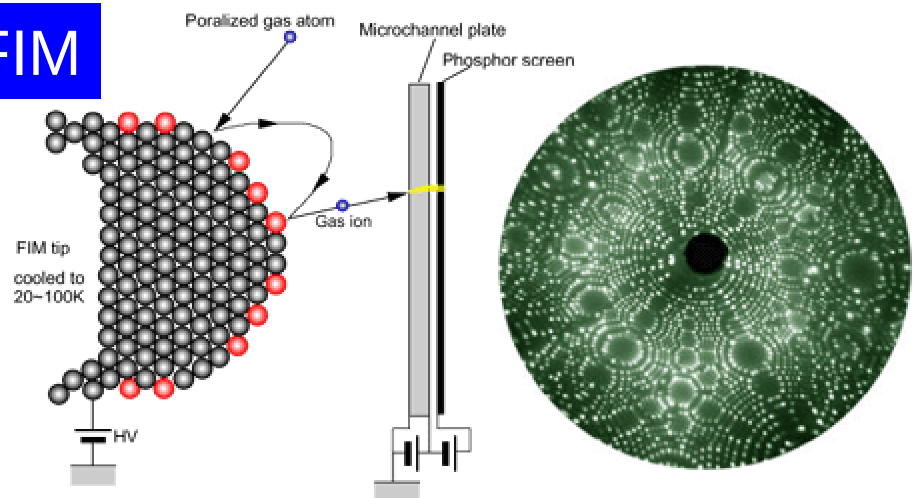
ALIS – Atomic Level Ion Source



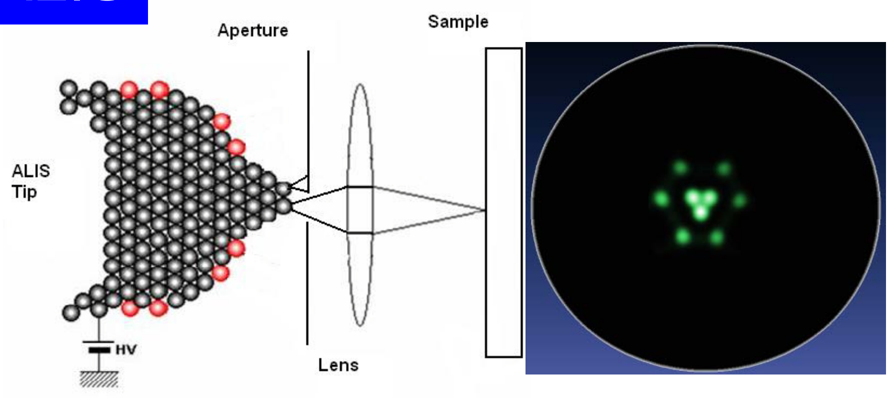


ALIS – Atomic Level Ion Source

FIM



ALIS



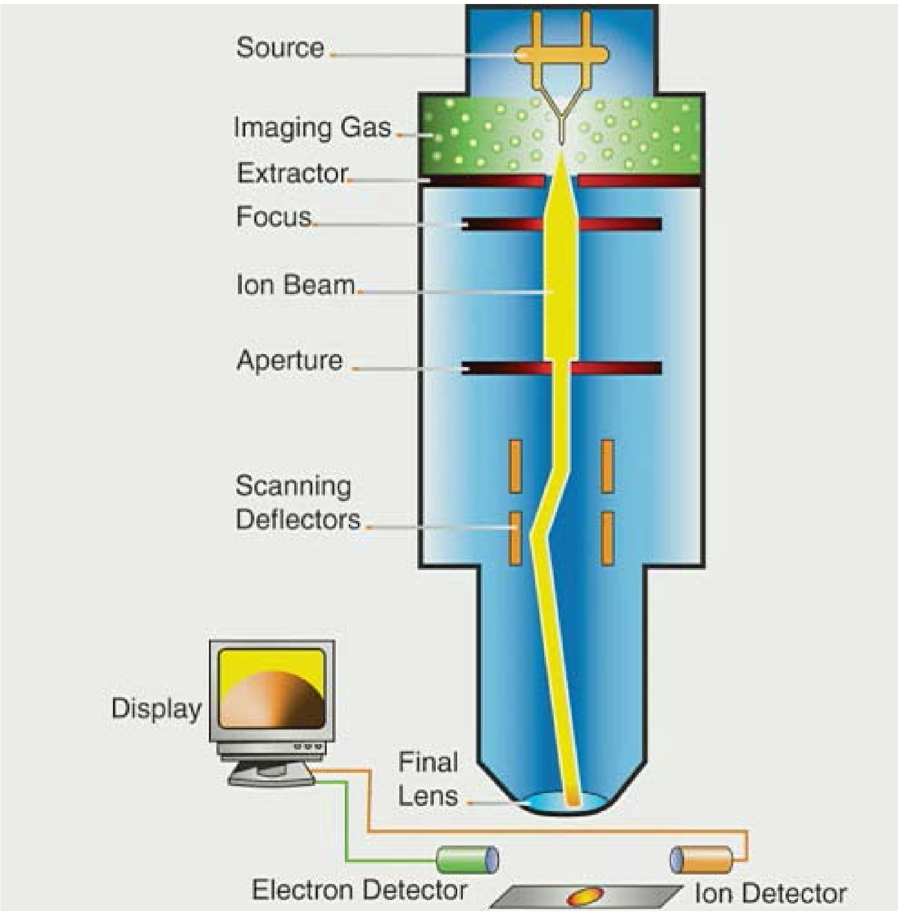
Field Ion microscope:

- Small emitters
- Beam current shared among hundreds or thousands of atom

ALIS:

- 3 atom shelf called the “trimer” created through field evaporation
- Single atom selected for final probe
- Source size < 1 Atom diameter

Column Architecture & Uniqueness



Architecture:

- Electrostatic optics similar to SEM / Ga FiB

Unique:

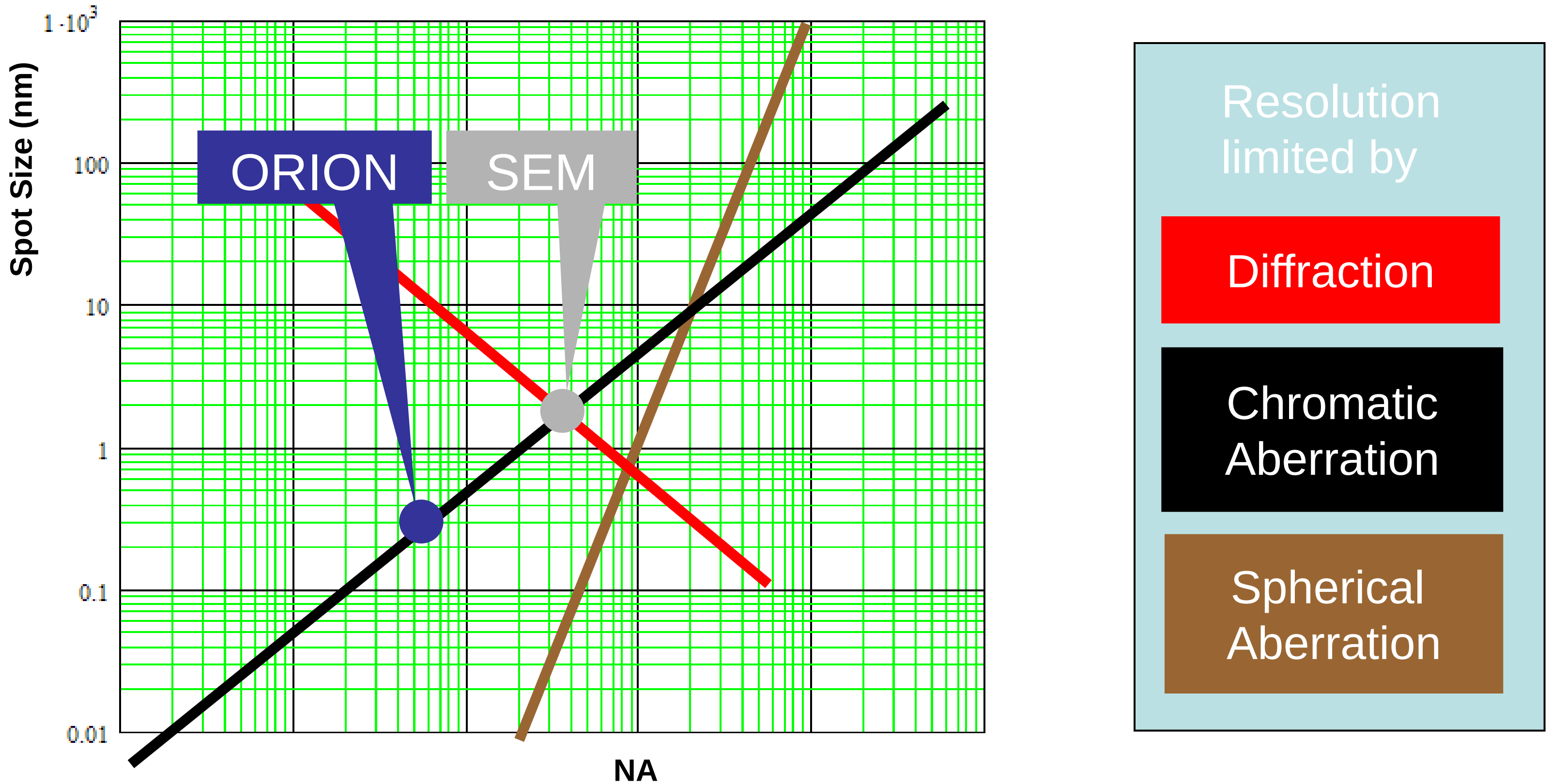
- He Ions:
    - Wave Length (Resolution)
    - Sample Interaction
    - Contrasts
    - Surface Sensitivity
    - Charging

- Source:

Brightness (Resolution/DoF)

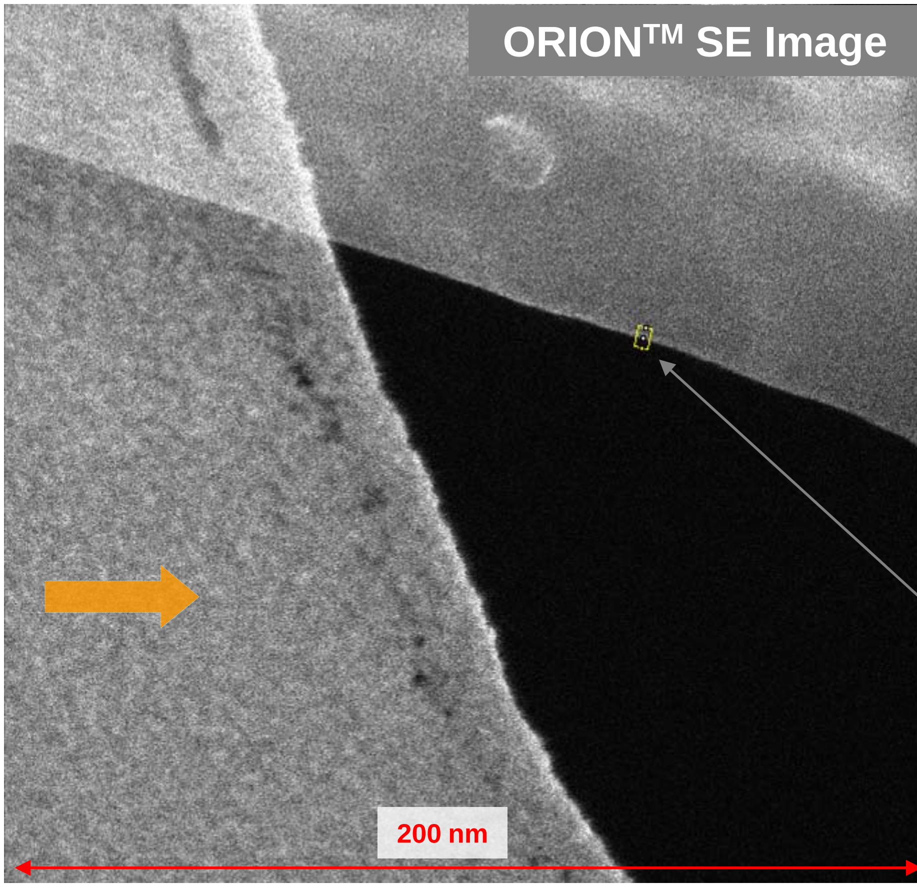
ORION™ HIM Ultra High Resolution

Down to 0.2 nm Probe Size



5-10x smaller NA (better Depth Of Field)

ORION™ Resolution Recent Status Update
0.24 nm resolution demonstrated in R&D lab

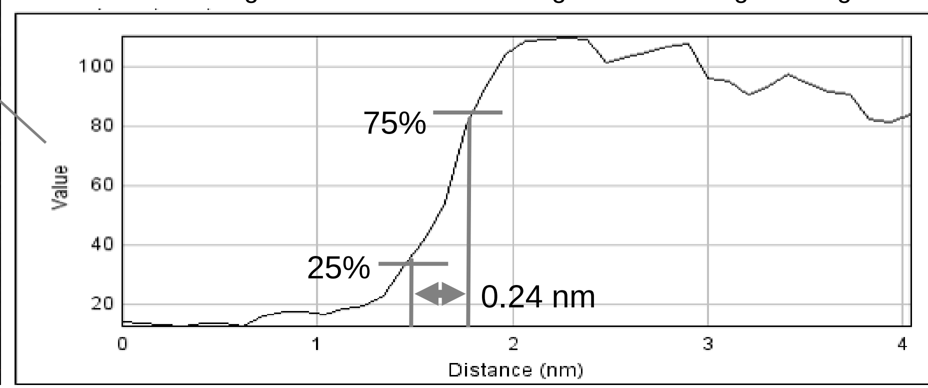


Specimen „Asbestos fibre“ on holy carbon

SE Imaging World Record
Resolution 0.24 nm (+/- 0.04 nm)

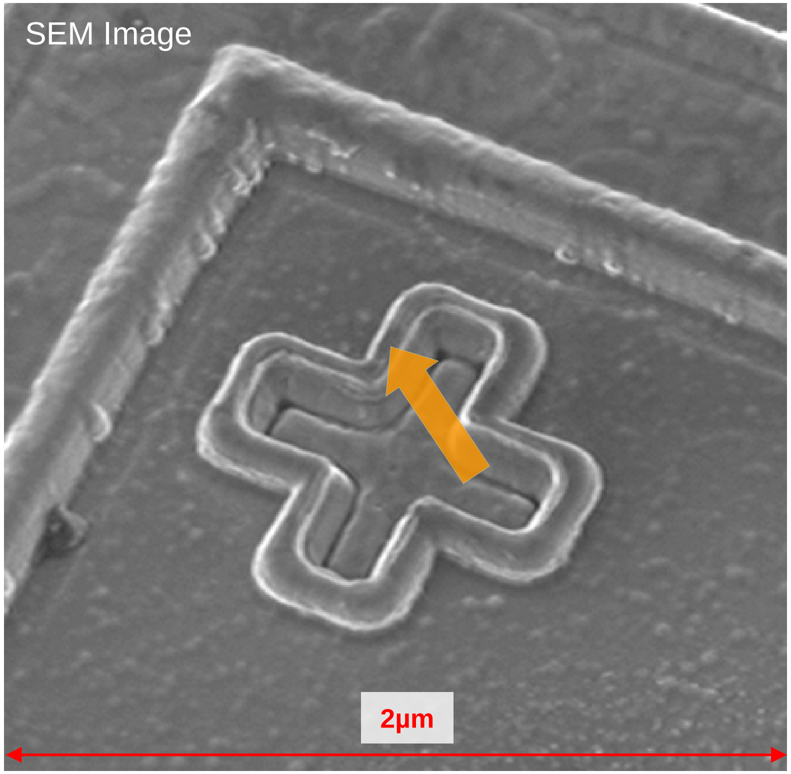
- Working Distance: 6 mm
- TEM like „salt and pepper pattern“ visible on carbon foil
- 0.24 nm resolution measured repeatedly on ORION R&D System

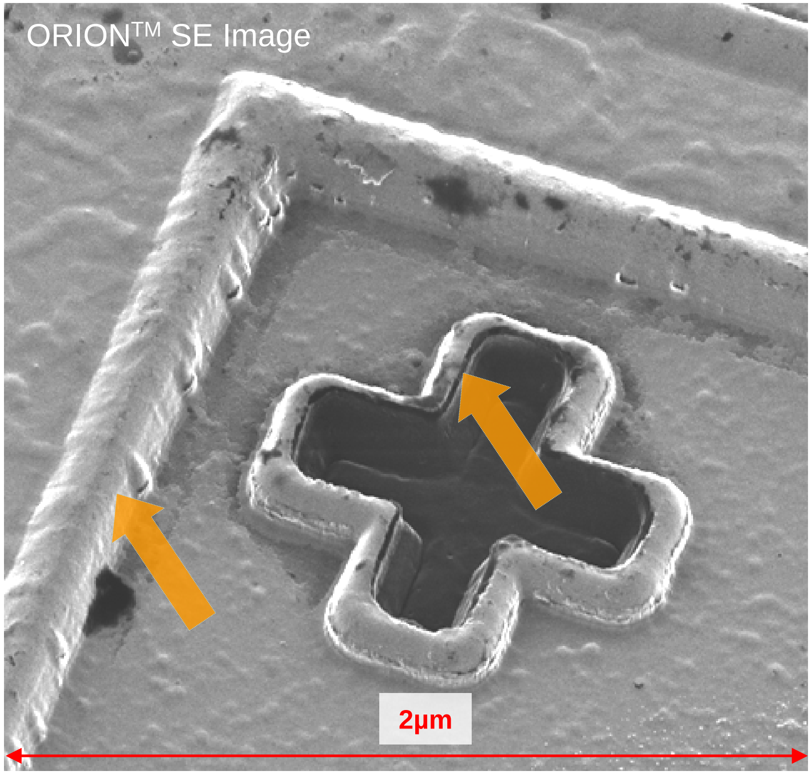
Linescan from edge of Asbestos fibre averaged over 20 neighbouring lines



***upgrade path will be available for Orion Plus customer**

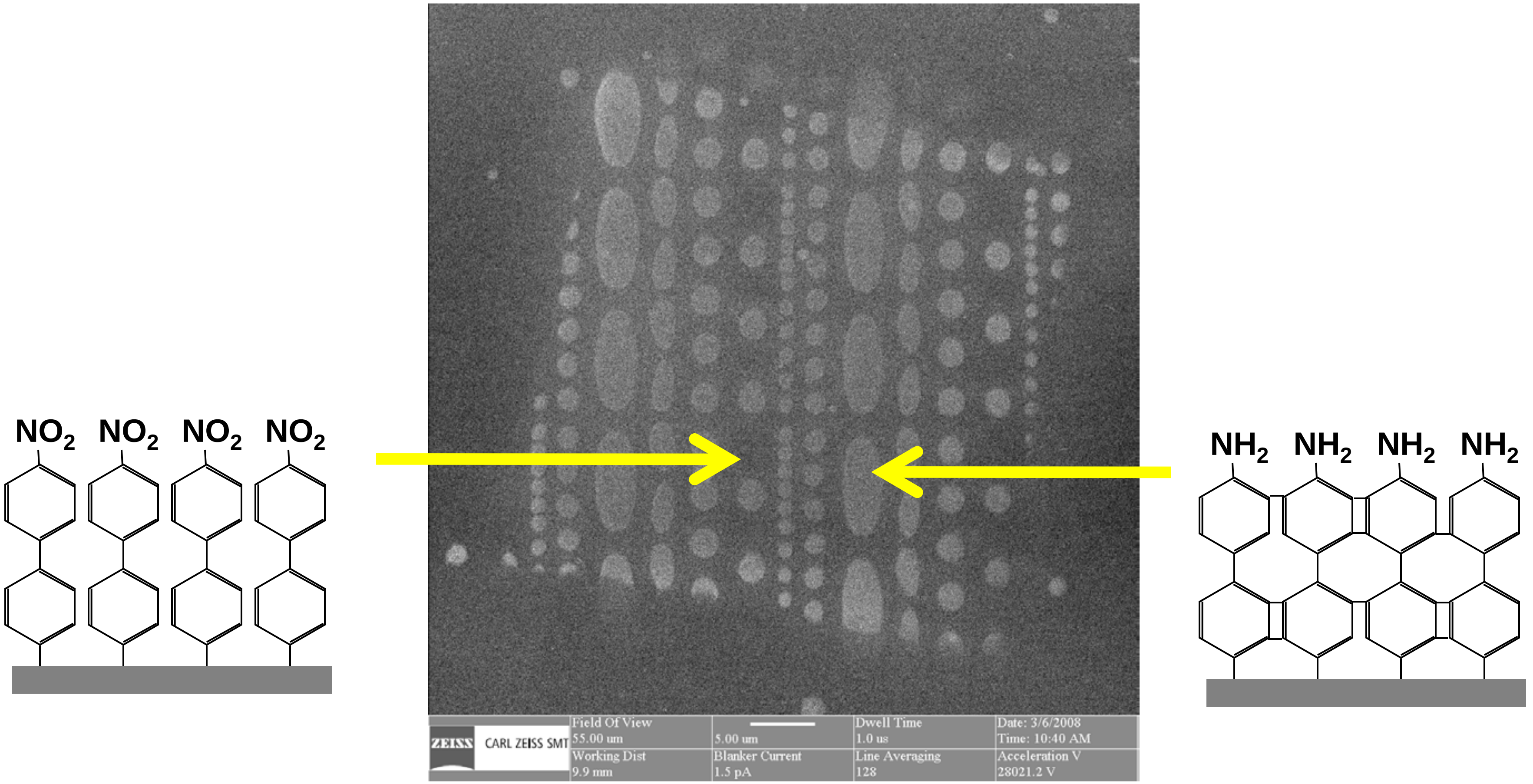
Unique Material Contrast





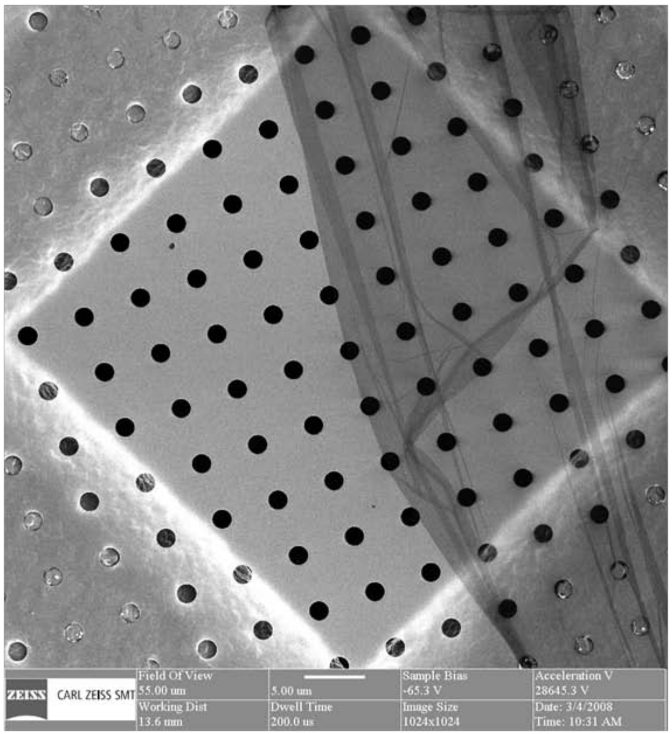
Secondary Electron image from the ORION™ shows superior material contrast in addition to surface detail

Imaging of SAM/Au Surface after Chemical Lithograpy

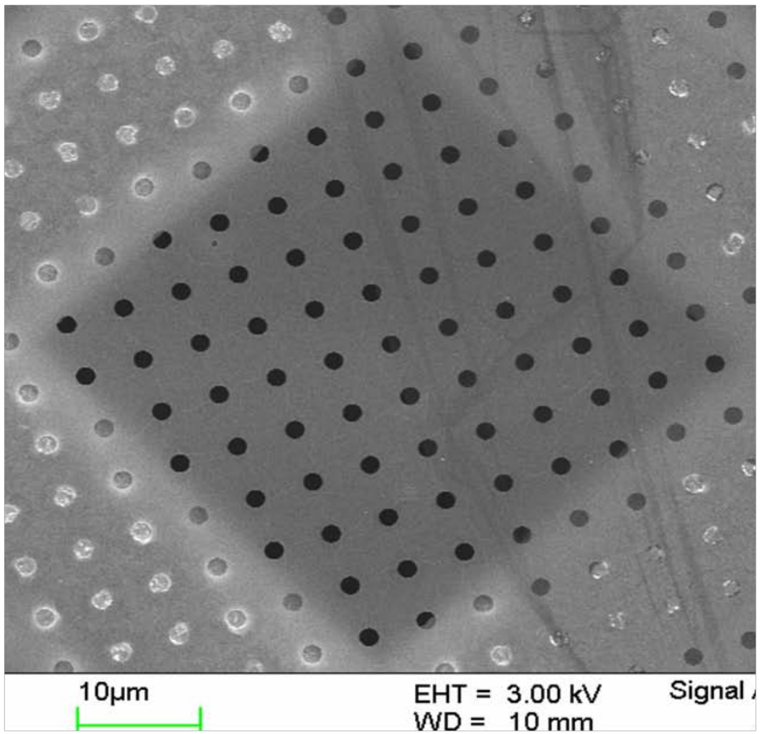


Visualizing 2-dimensional Nanomembranes

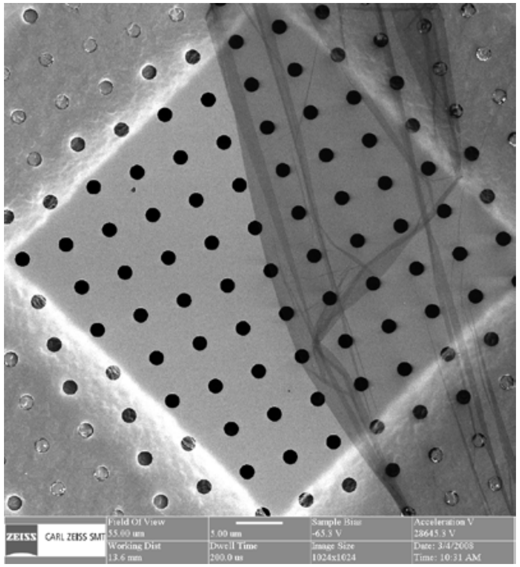
HIM

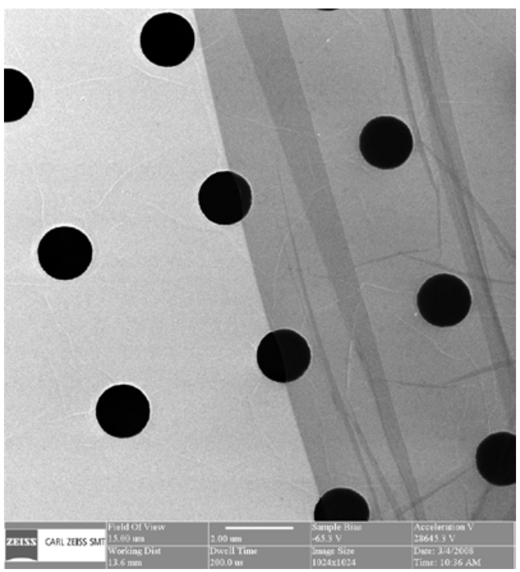


SEM

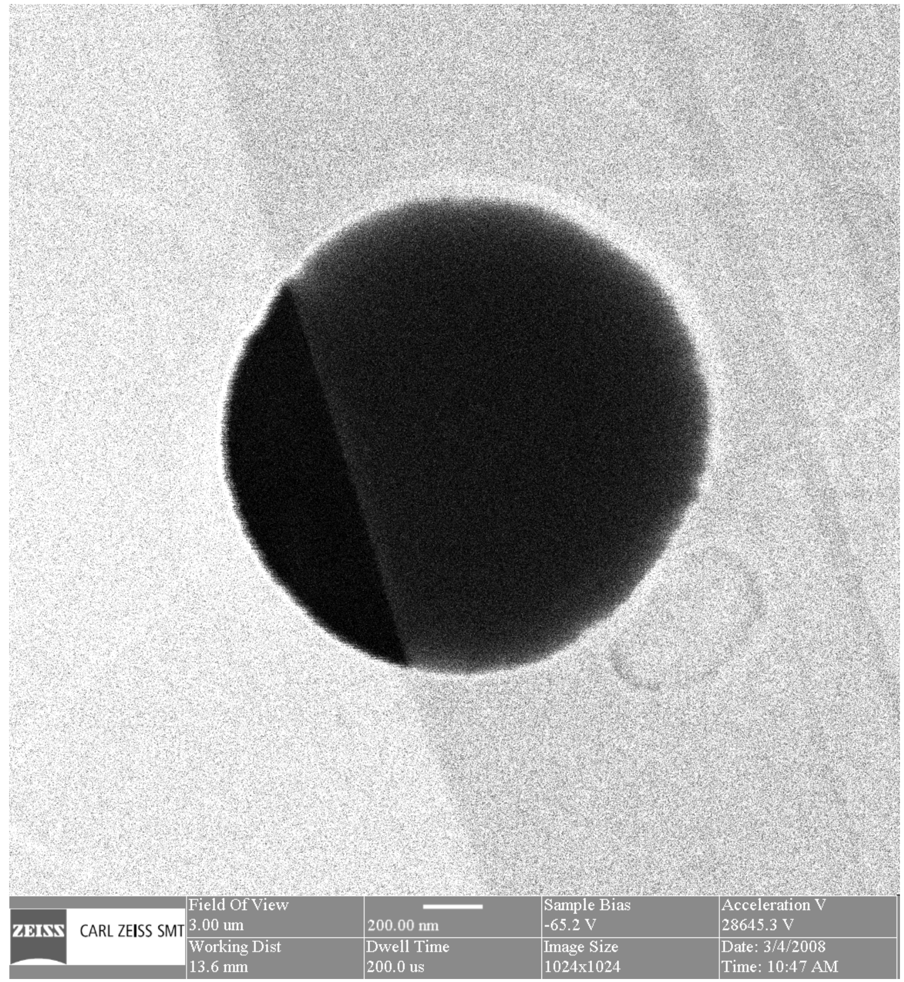


Freestanding nanomembranes on holey carbon foil





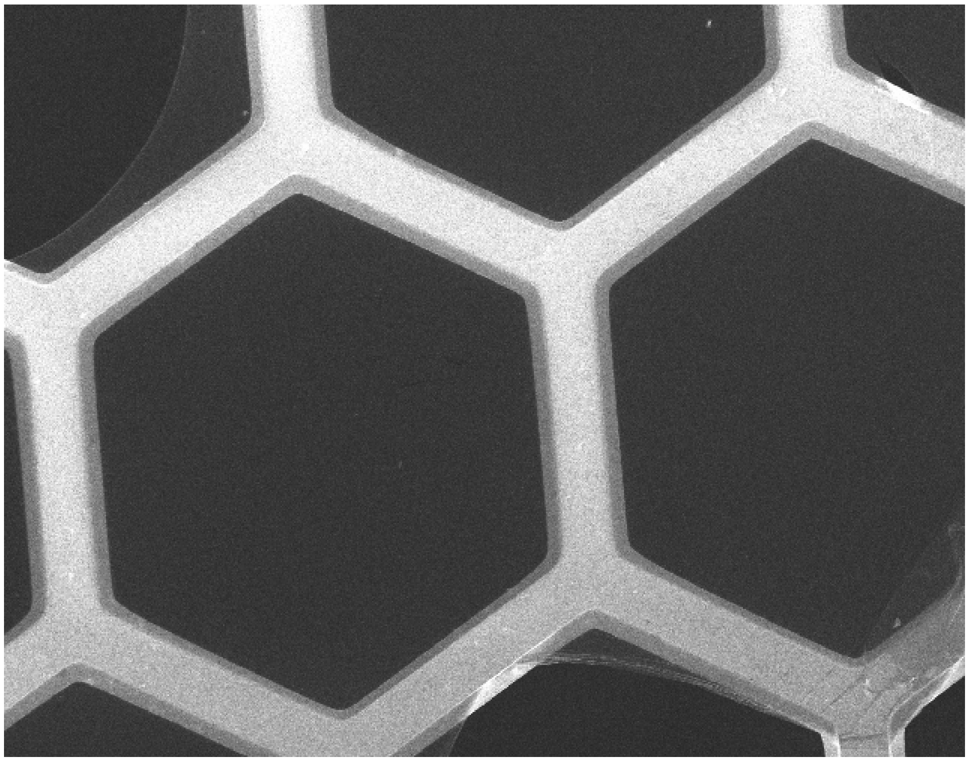
Quantifoil Holey Carbon Film, He$^+$ Ion Image



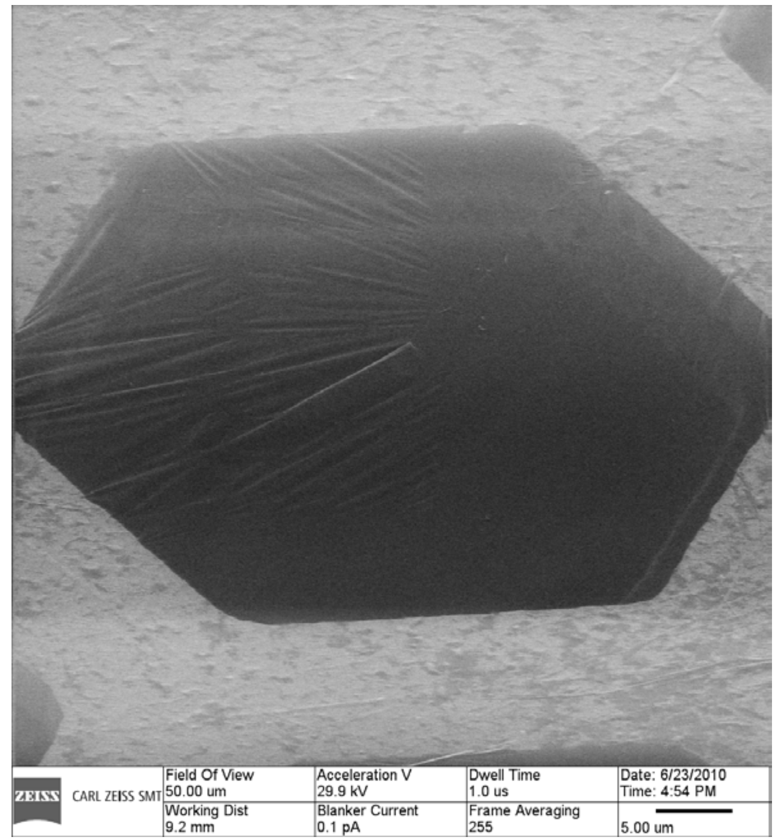
(A. Beyer)

Visualizing 2-dimensional Nanomembranes

SEM



HIM



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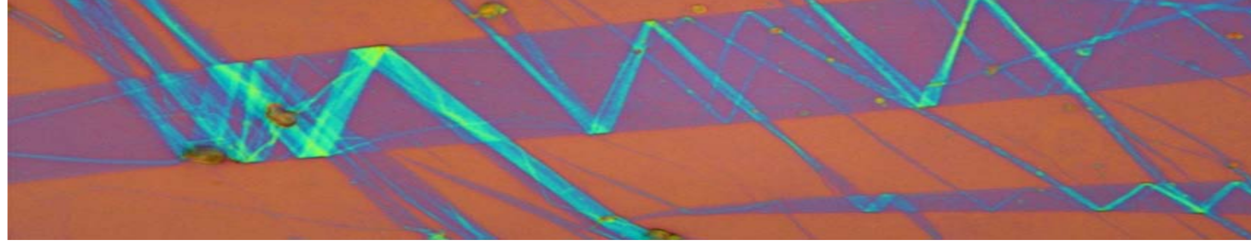
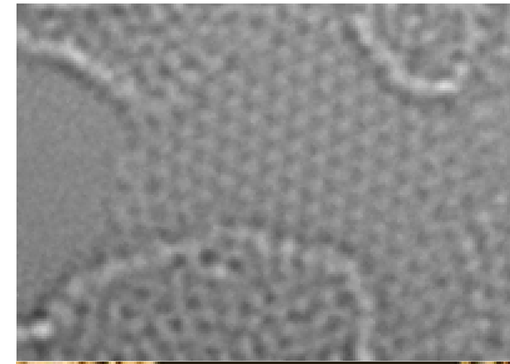
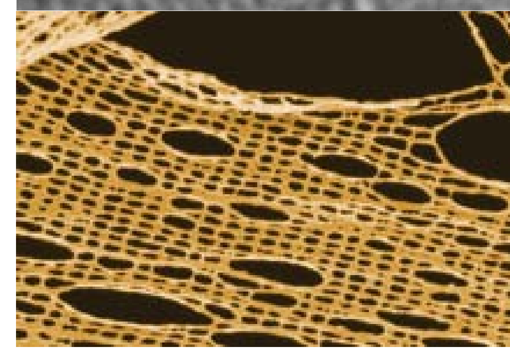
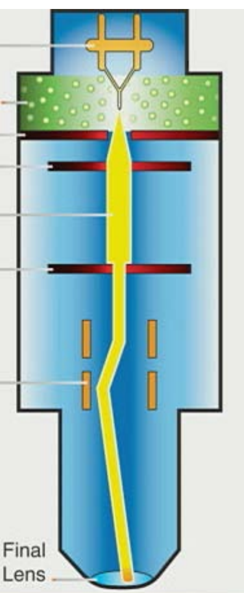


Nanomembranes from SAMs





- 1 nm thick freestanding
- Transition to Graphene
- Polymer carpets
- Nanosieves
- Janus Nanomembranes



Helium Ion Microscopy

- Imaging with He^+
- Chemical contrast
- High resolution

Universität Bielefeld

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