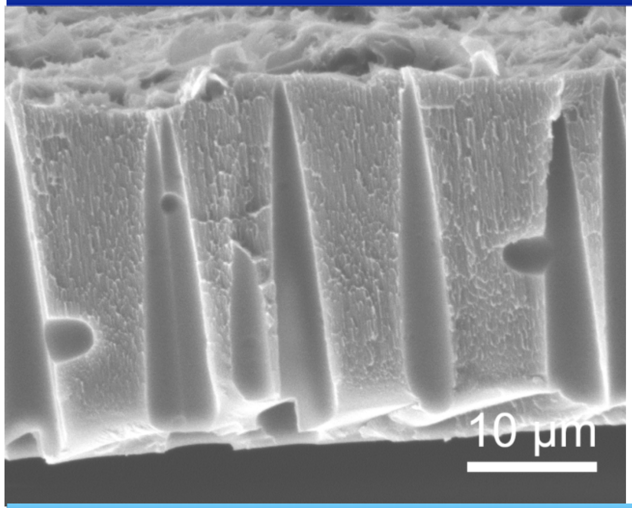
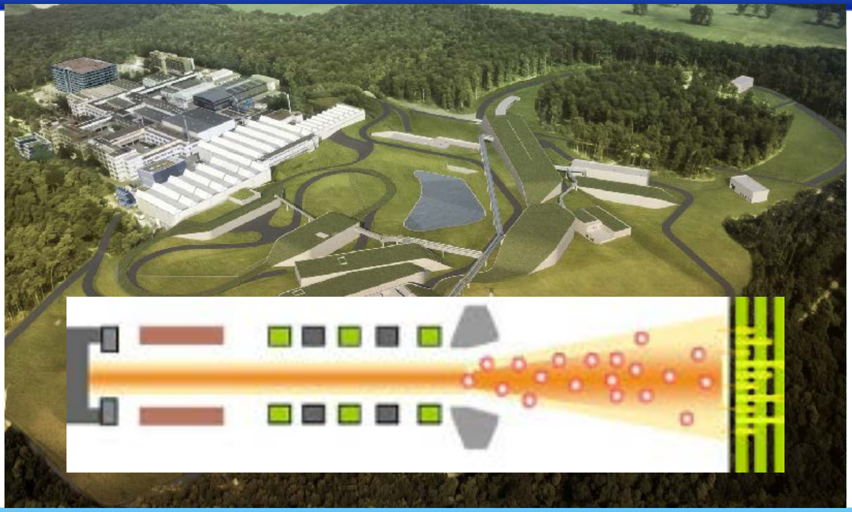
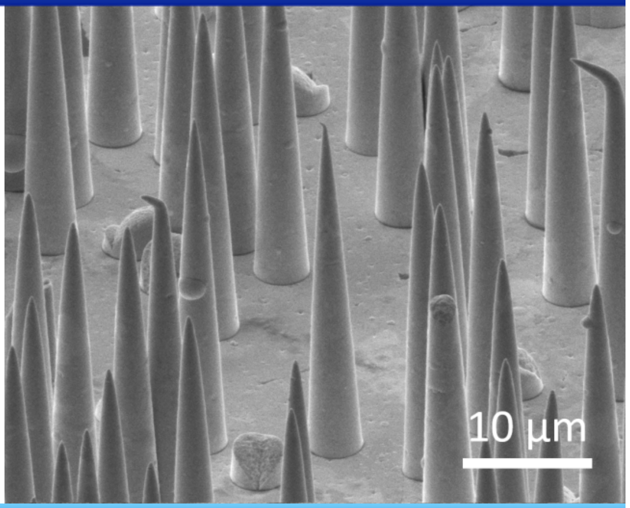
Ion-Track Nanotechnology With High-Energy Heavy Ions

M.E. Toimil-Molares and C. Trautmann

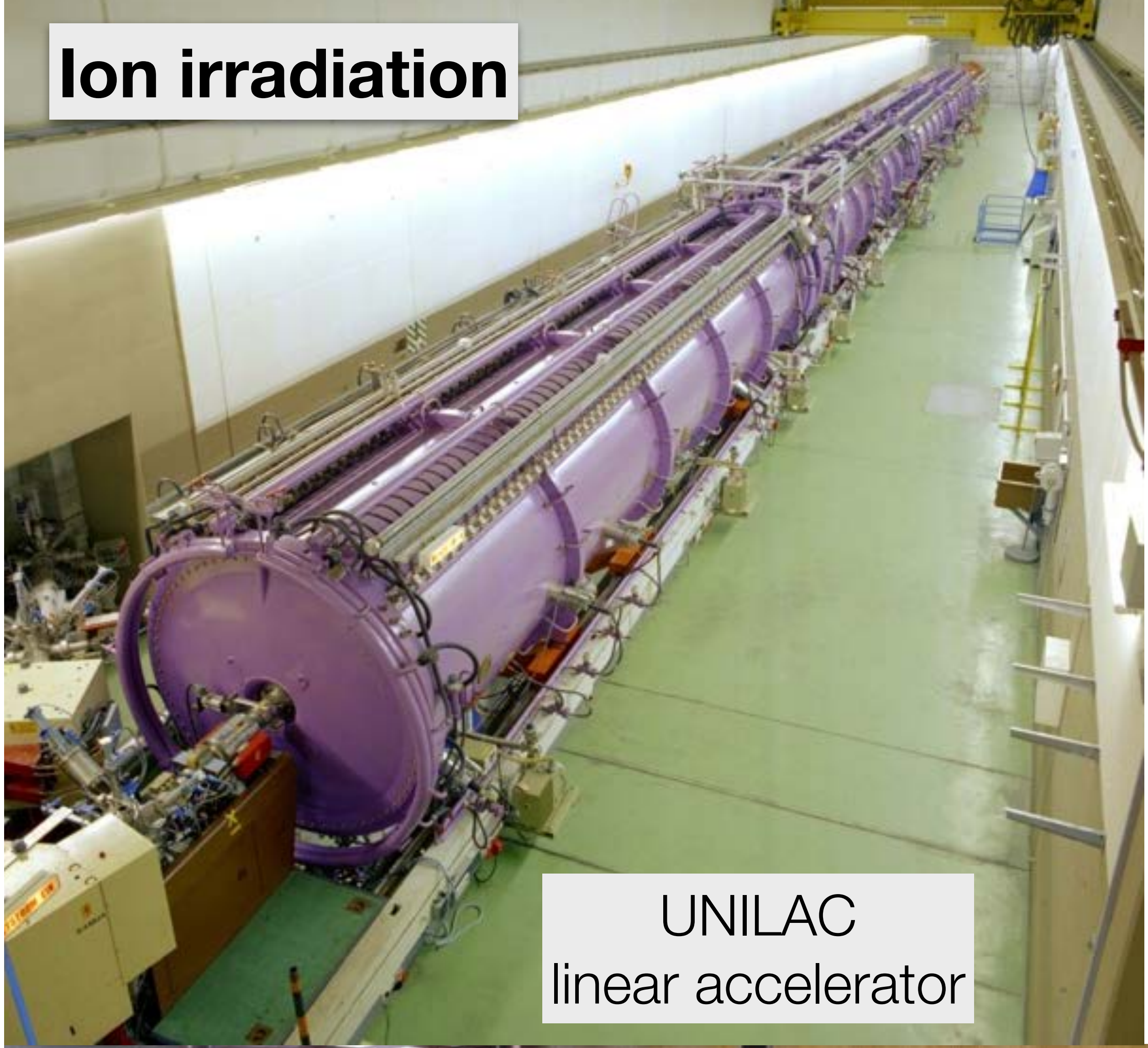
Materials Research Department
GSI Helmholtz Center for Heavy Ion Research
Darmstadt



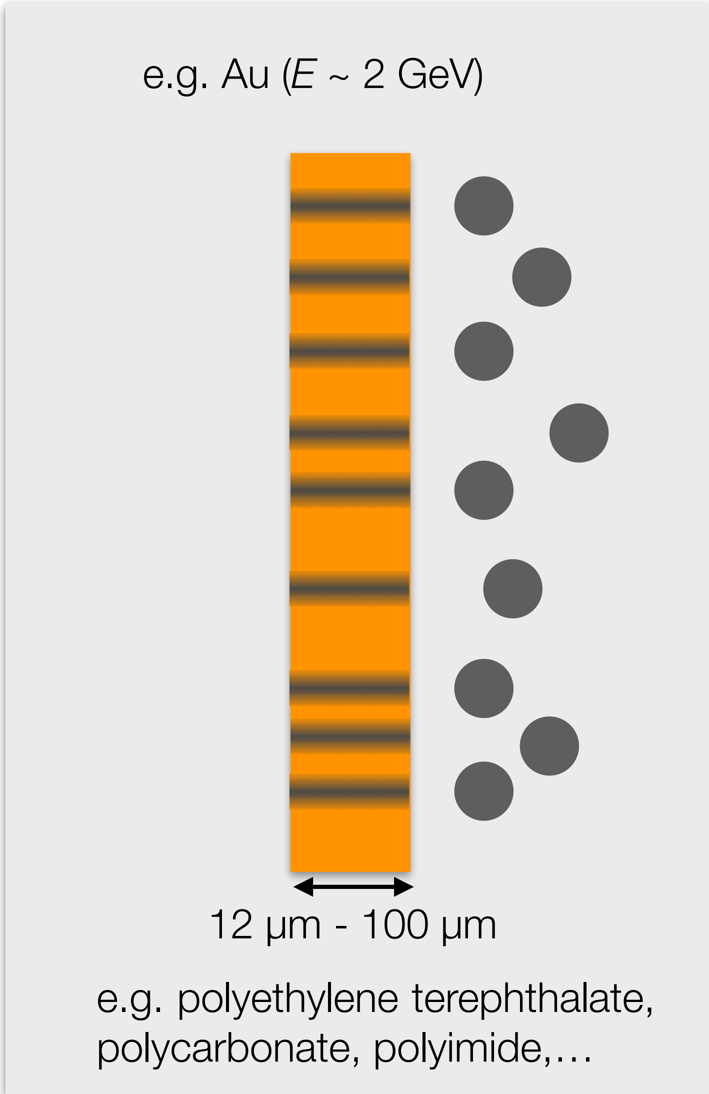




Ion irradiation



UNILAC
linear accelerator



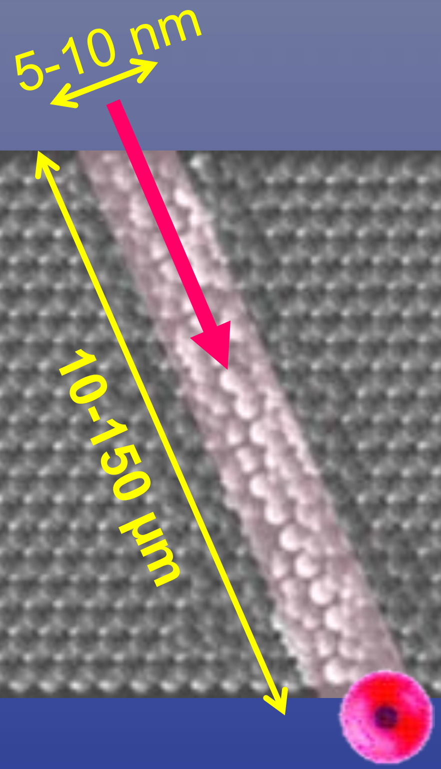
e.g. Au (E ~ 2 GeV)

12 µm - 100 µm

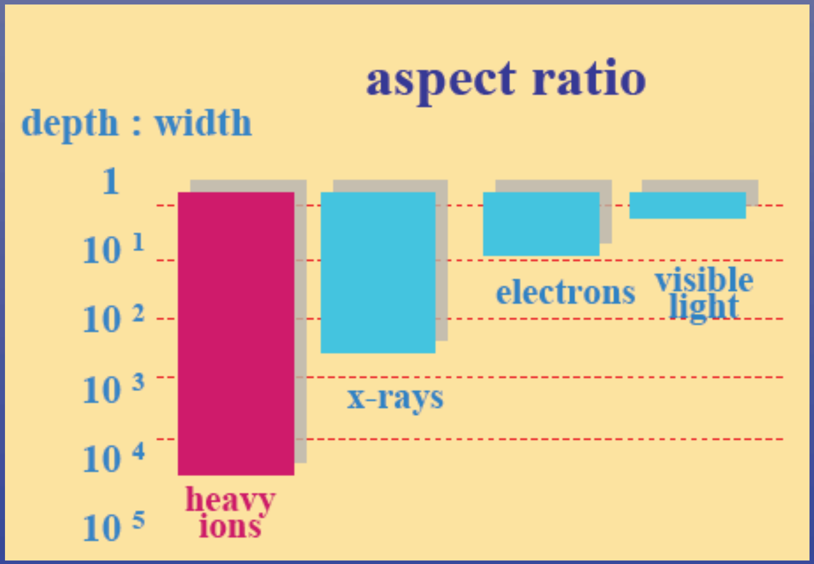
e.g. polyethylene terephthalate,
polycarbonate, polyimide,…

Control room

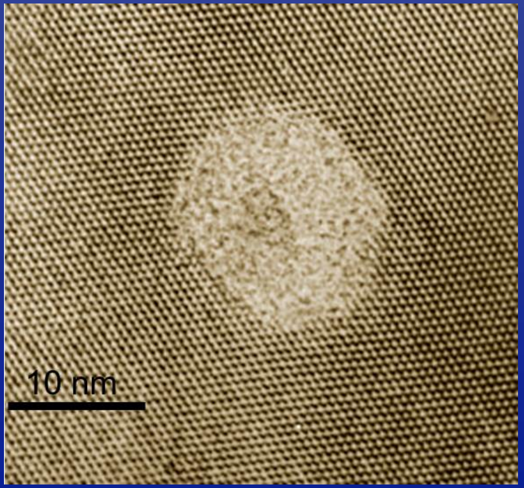
What is unique about heavy ions in matter?

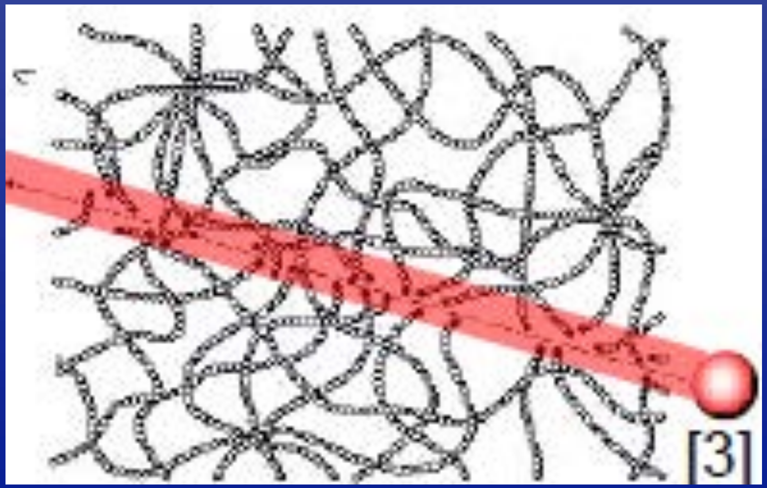


Very high aspect ratio



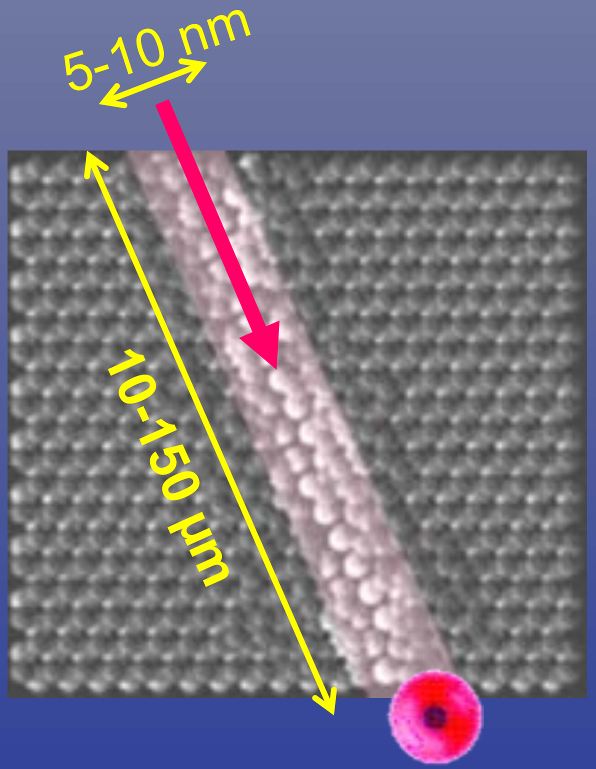
Ion track in mica



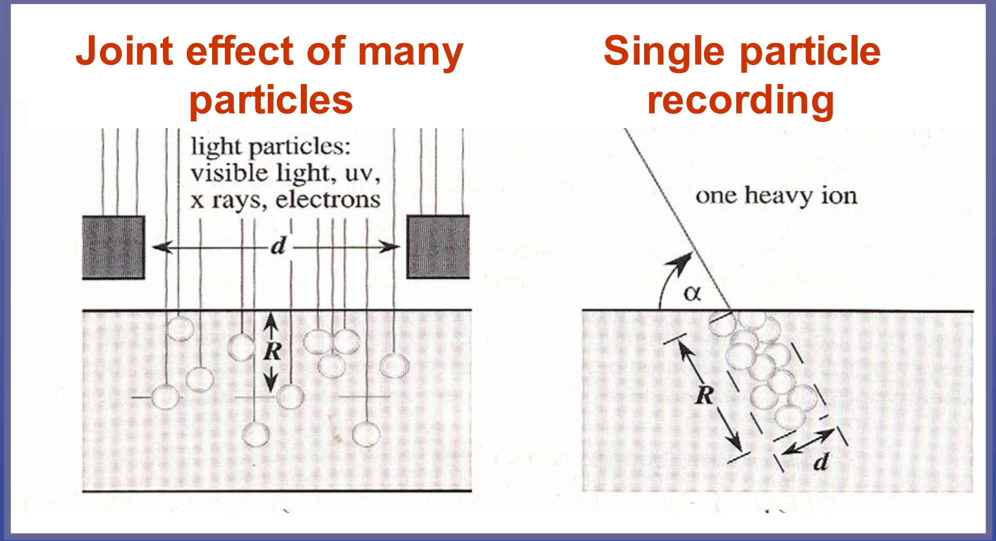


Ion track in polymer

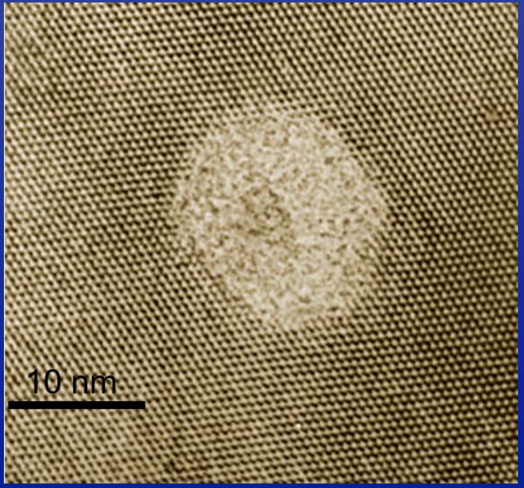
What is unique about heavy ions in matter?

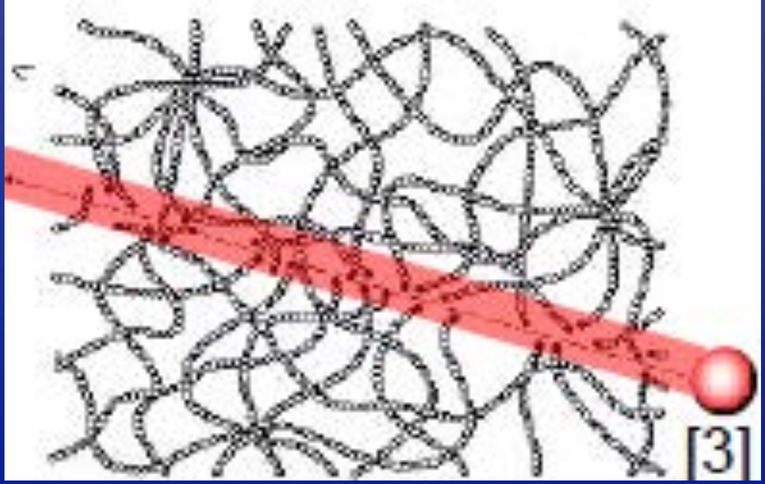


One ion = one track



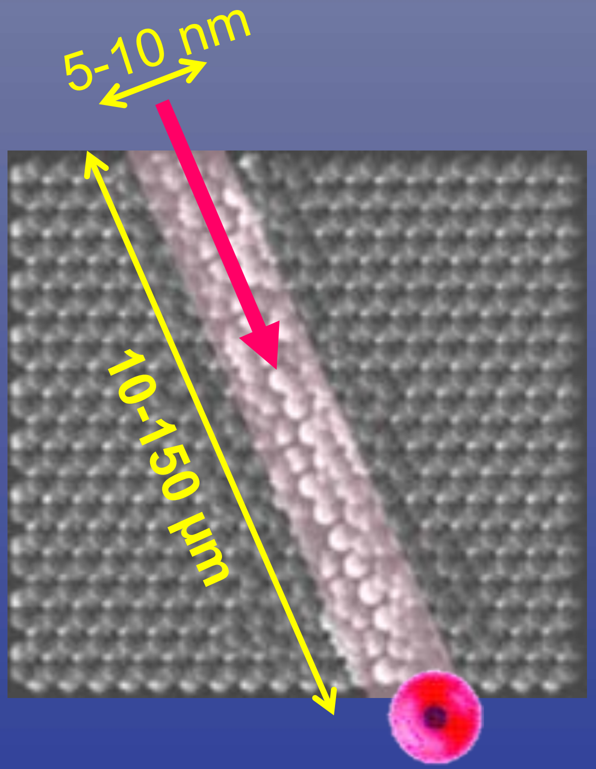
Ion track in mica



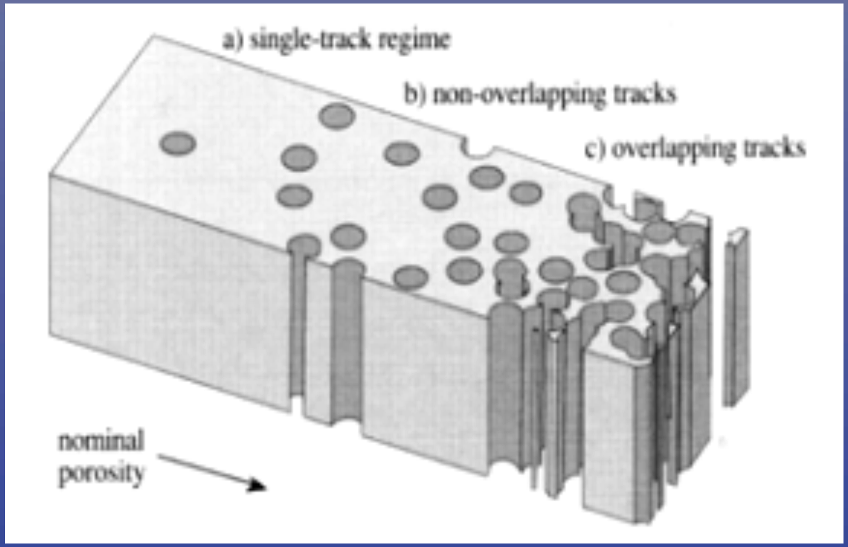


Ion track in polymer

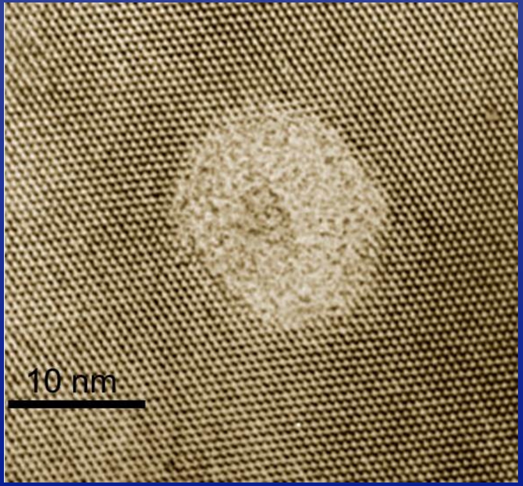
What is unique about heavy ions in matter?

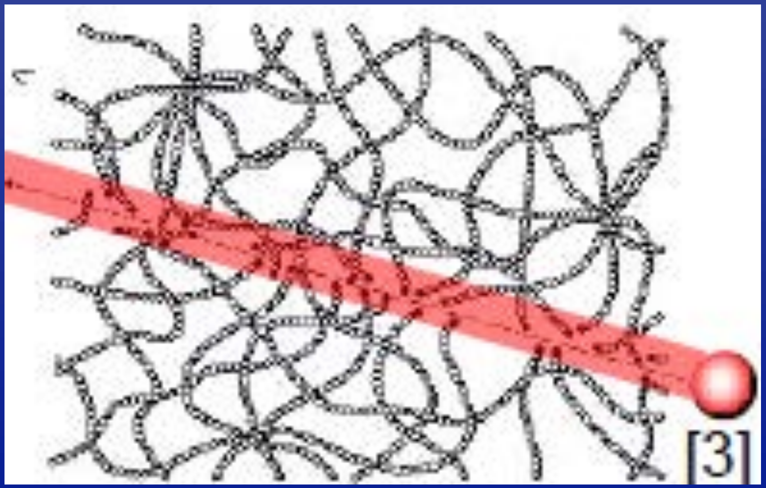


Adjustable fluence: 1 - 10^{11} cm^{-2}



Ion track in mica

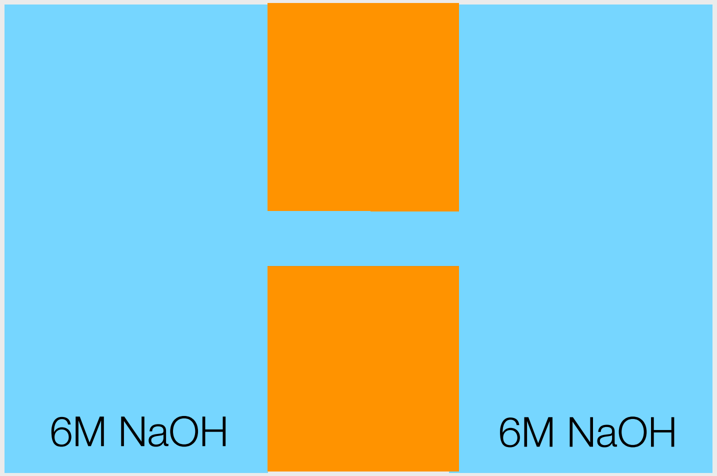




Ion track in polymer

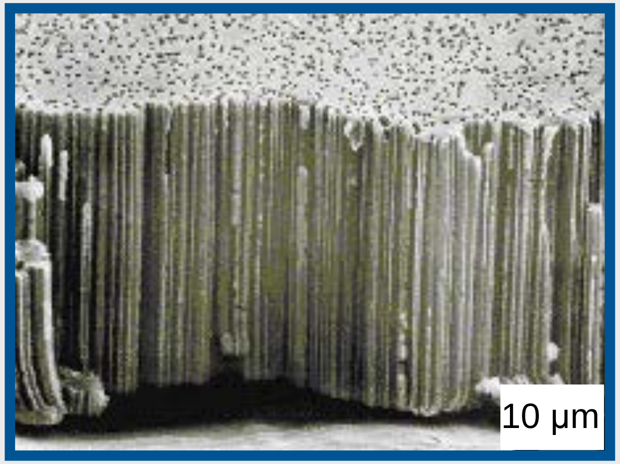
Chemical Etching

Symmetric

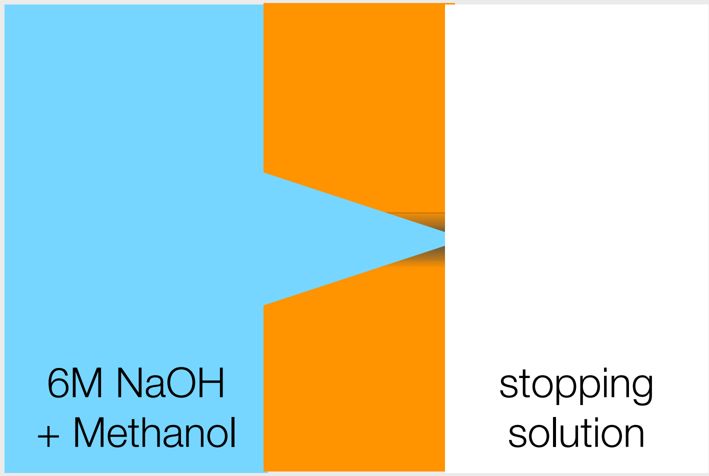


6M NaOH

6M NaOH

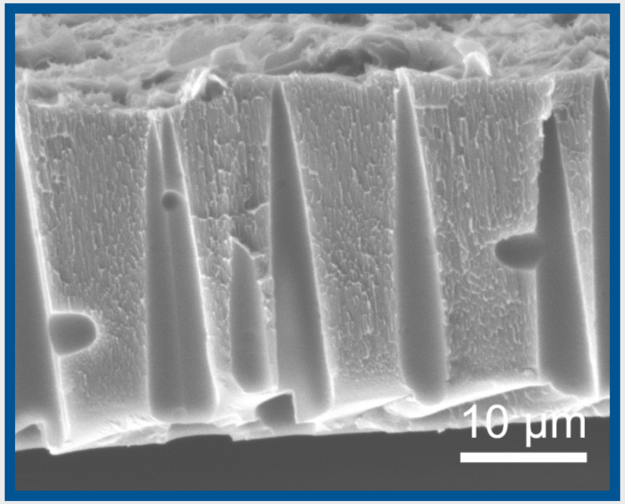


Asymmetric



6M NaOH
+ Methanol

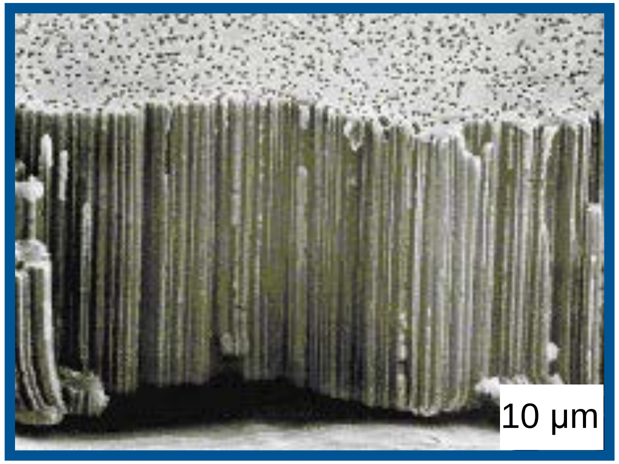
stopping
solution



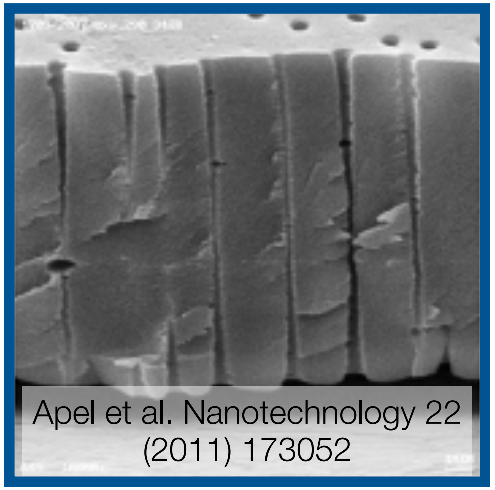
Etched Ion-Track Membranes

Polymeric

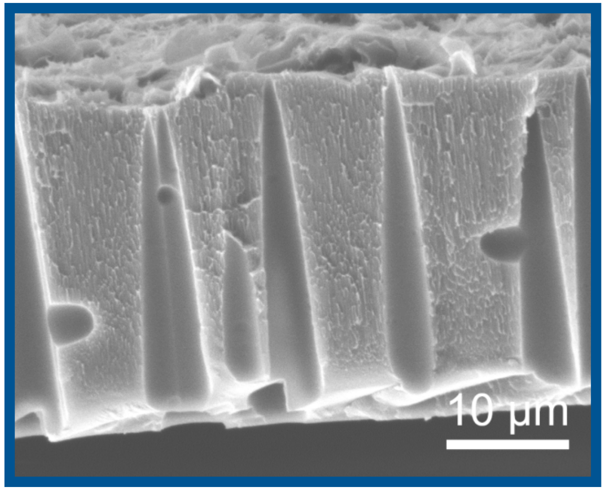
Cylindrical



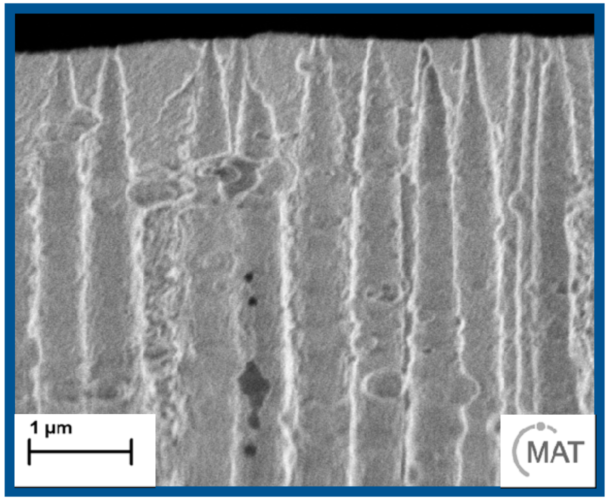
Biconical


Apel et al. Nanotechnology 22 (2011) 173052

Conical

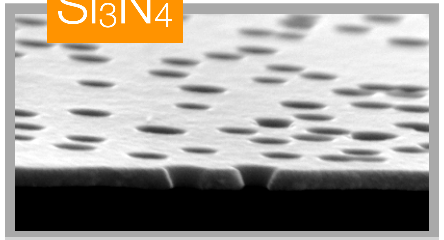


Bullet



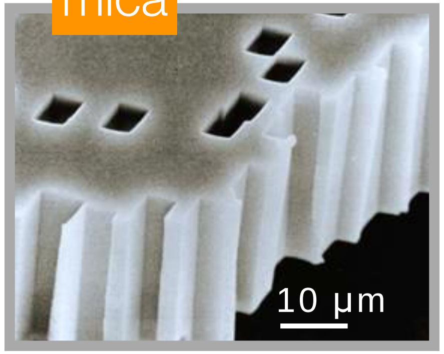
Inorganic

Si_3N_4


Vlassiouk et al. PNAS 15 (2009) 21039

glass

mica

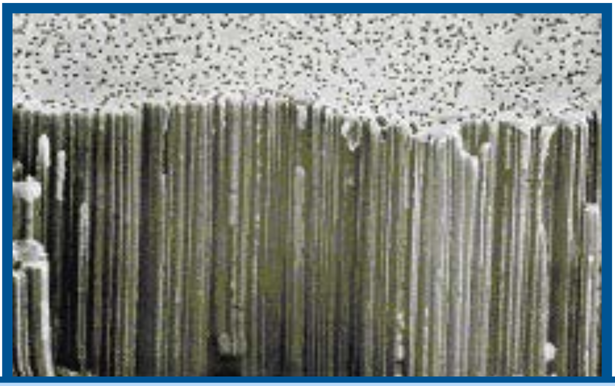


Fischer et al. Naturwissenschaften 75 (1988) 57

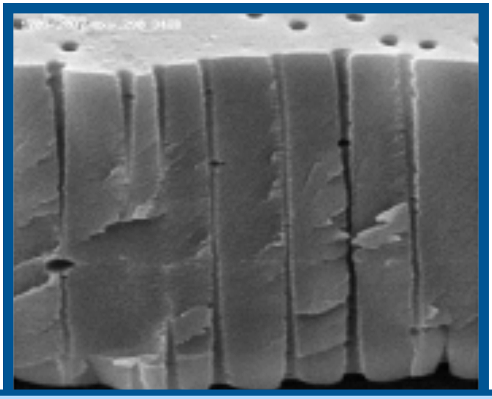
Etched Ion-Track Membranes

Polymeric

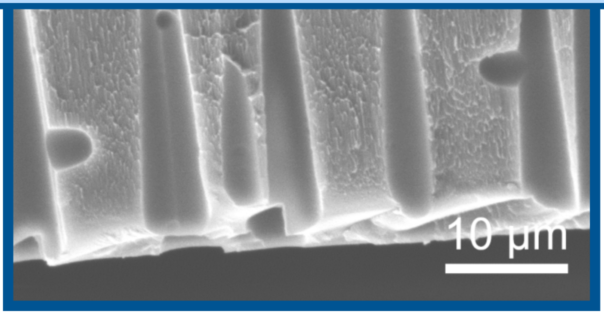
Cylindrical

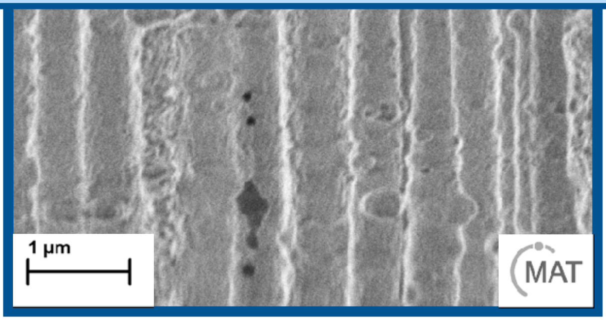


Biconical

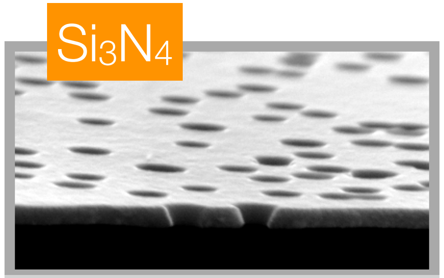


Various channel geometries
Diameter increases with etching time (~15 nm - µm)
Foil thickness up to 100 µm
Monodisperse channels
Highly parallel oriented channels





Inorganic



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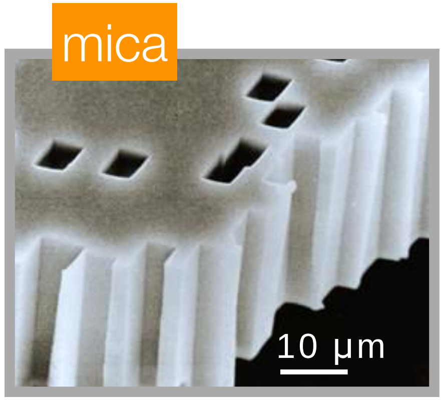
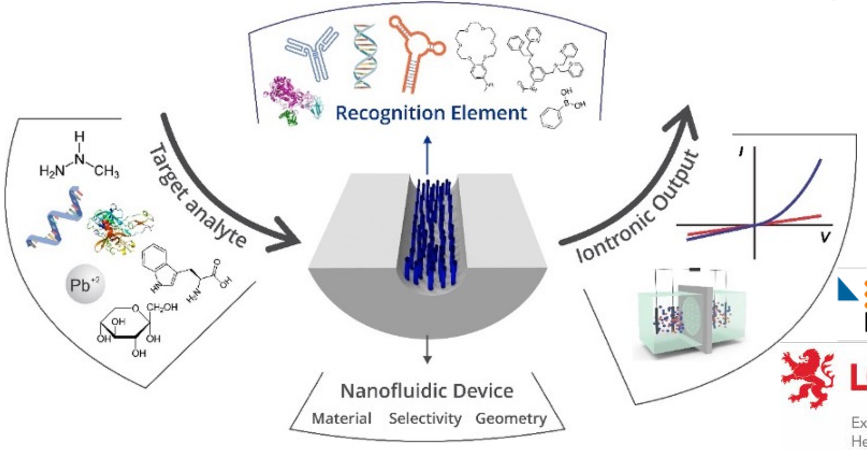


Fischer et al. Naturwissenschaften 75 (1988) 57

Ion-Track Nanotechnology at GSI:

1. Single nanochannel platform

- unique facility for single ion irradiation
- channel engineering and characterization
- more than 20 groups world-wide
- novel bio- and chemical nanopore sensors



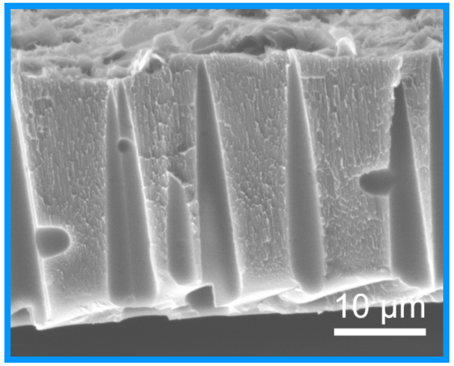
Laucirica, *Trends in Analytical Chemistry*, 144 (2021) 116425

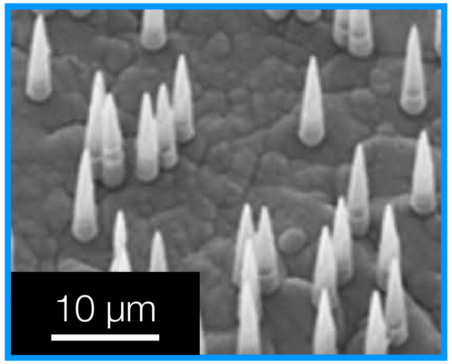
iNAPO

LOEWE
Exzellente Forschung
Hessens Zukunft

2. Tailored multichannel membranes

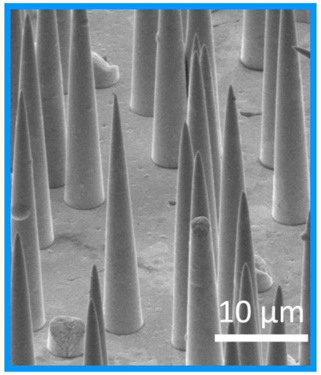
- special pore geometries
- new pore arrangements
- surface coatings

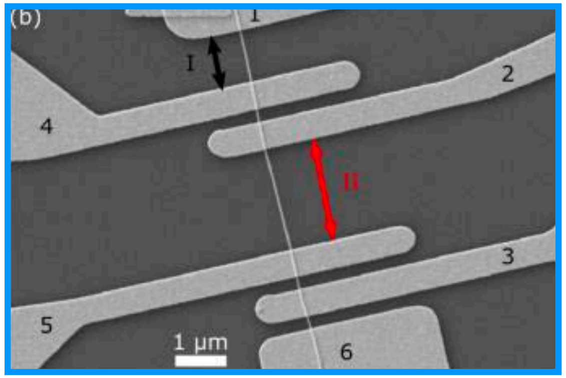




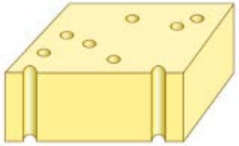
3. Electrodeposited nanowires

- tailored composition and crystallinity
- controlled geometry
- size-dependent properties





Tailored multichannel membranes



Can we conformally coat the polymer membranes by ALD?

Funded by
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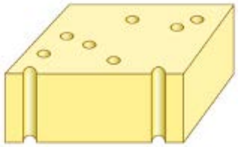
Spende, Sobel, Lukas, Zierold, Riedl, Gura, Schubert, Moreno, Nielsch, Stühn, Hess, Trautmann, Toimil-Molares, Nanotechnology 26 (2015) 335301.
Sobel, Hess, Lukas, Spende, Stühn, Toimil-Molares, Trautmann, Beilstein J. of Nanotechnol. 6 (2015) 472.

Tailored multichannel membranes



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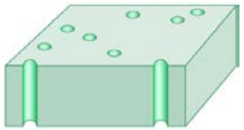
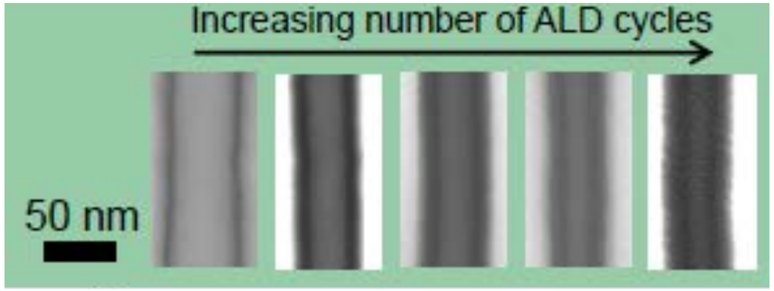
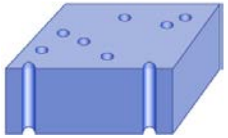
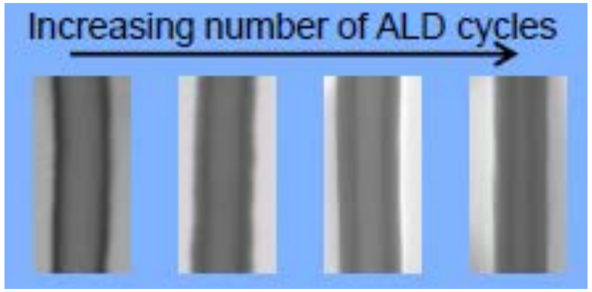


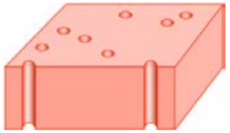
TiO_2



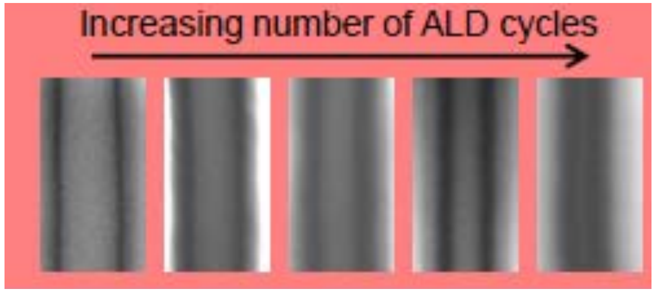


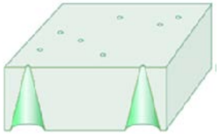
SiO_2

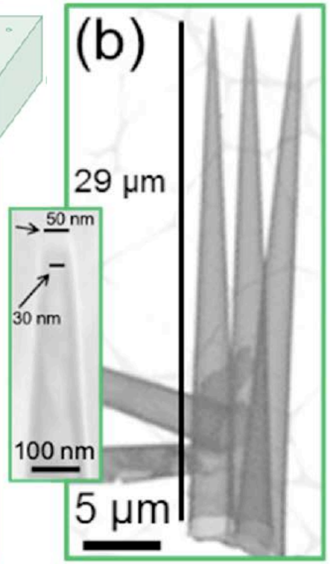


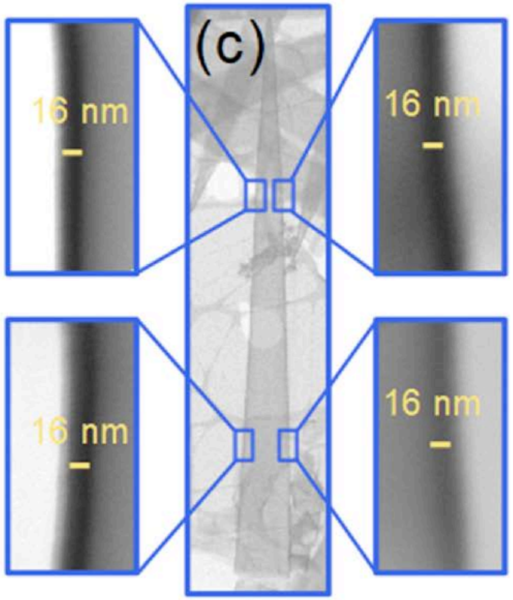


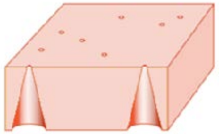
Al_2O_3

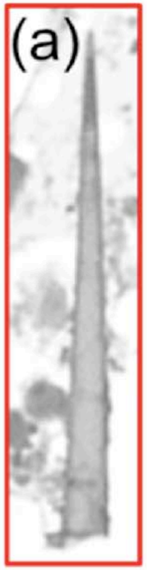












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Ulrich, Spende, Burr, Sobel, Hess, Schubert, Trautmann, Toimil-Molares, Nanomaterials 11 (2021) 1874.
Spende, Sobel, Lukas, Zierold, Riedl, Gura, Schubert, Moreno, Nielsch, Stühn, Hess, Trautmann, Toimil-Molares, Nanotechnology 26 (2015) 335301.
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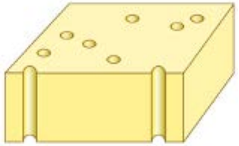
Tailored multichannel membranes



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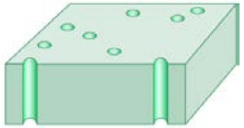
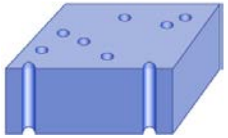


TiO_2



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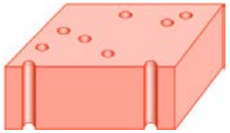

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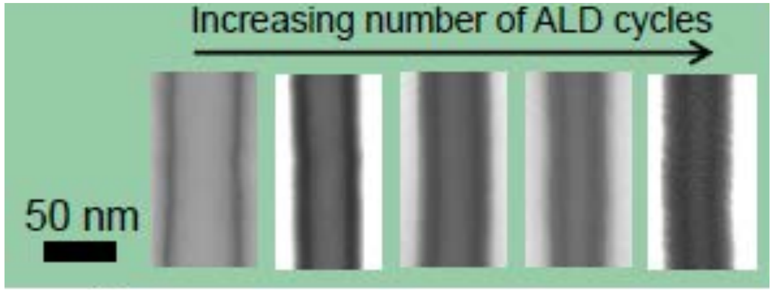
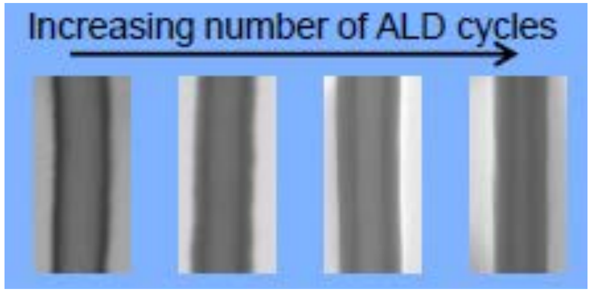
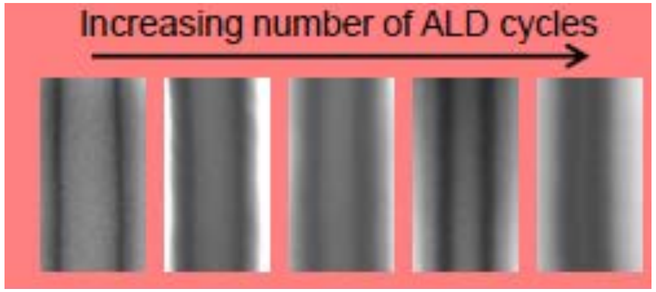


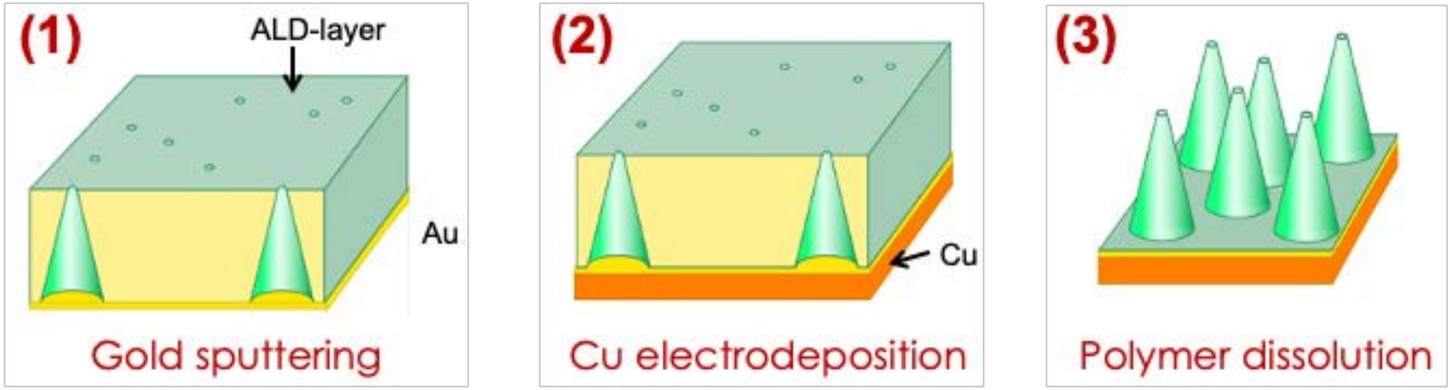


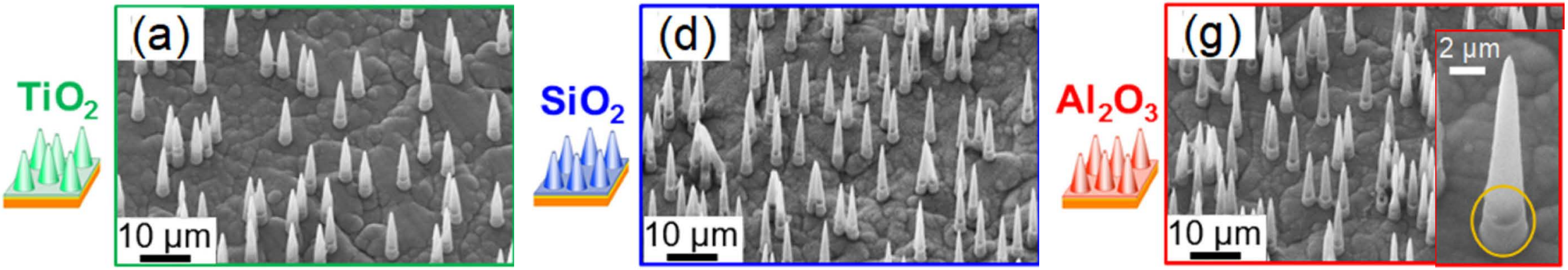


- controlled oxide layer thickness
- very small pore sizes (~ 6 nm)
- material determines isoelectric point of membrane surface
- new membrane applications e.g. for sensing, battery separators, …
- approach suitable for other materials

Lee, Thangavel, Guery, Trautmann, Toimil-Molares, Morcrette, *Nanotechnology* 32 (2021) 365401.
Ulrich, Spende, Burr, Sobel, Hess, Schubert, Trautmann, Toimil-Molares, Nanomaterials 11 (2021) 1874.
Spende, Sobel, Lukas, Zierold, Riedl, Gura, Schubert, Moreno, Nielsch, Stühn, Hess, Trautmann, Toimil-Molares, Nanotechnology 26 (2015) 335301.
Sobel, Hess, Lukas, Spende, Stühn, Toimil-Molares, Trautmann, Beilstein J. of Nanotechnol. 6 (2015) 472.

Oxide nanotube assemblies





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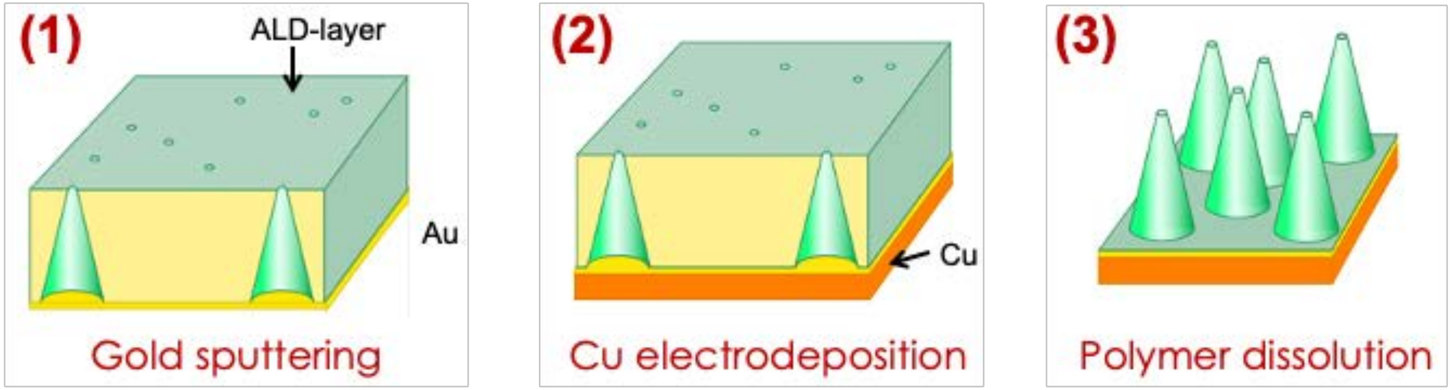
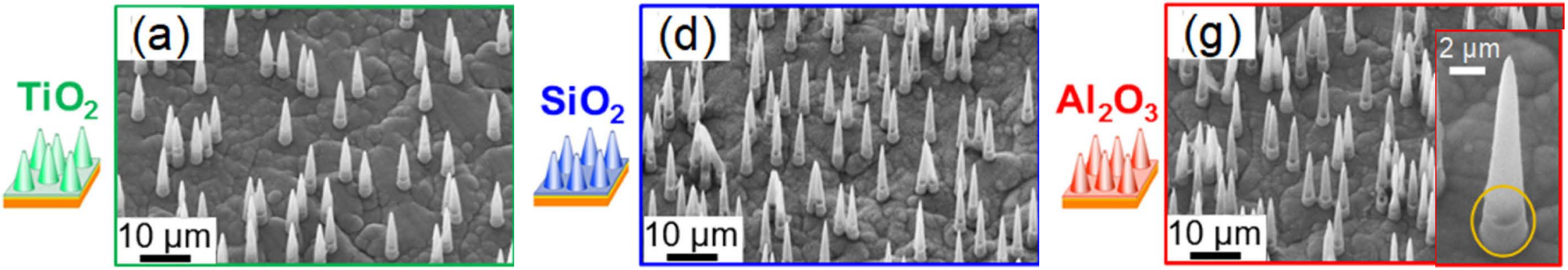
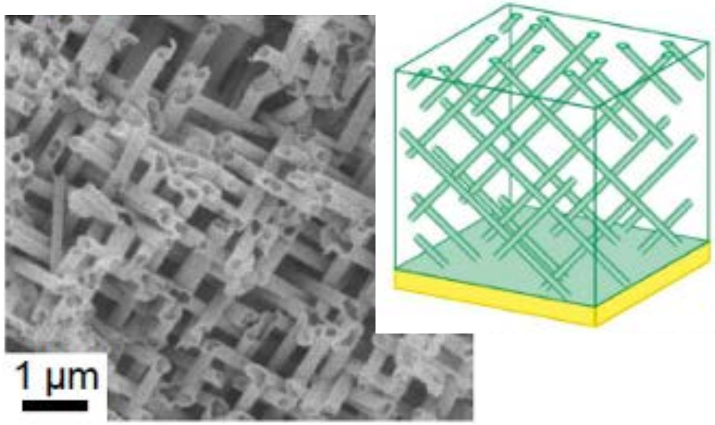
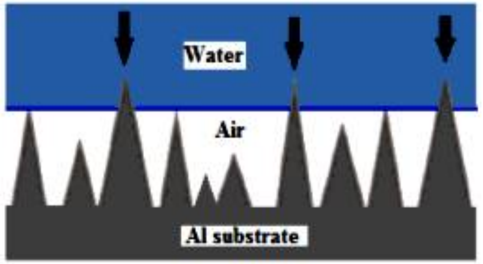
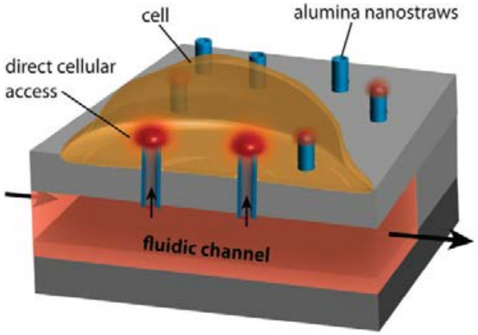






Applications: hydrophobic surfaces, drug delivery, etc.

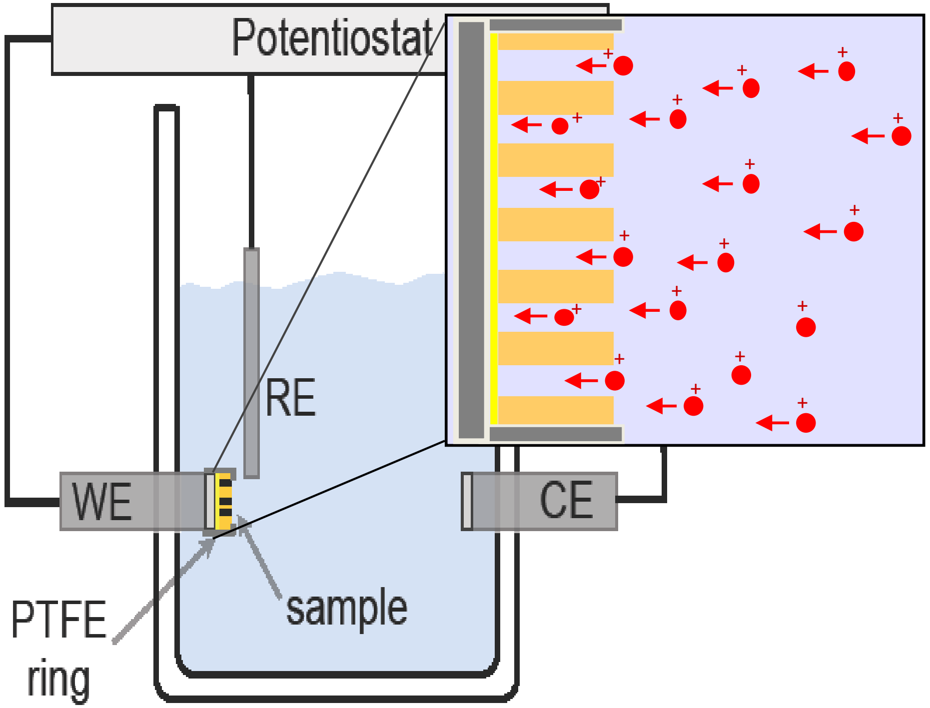


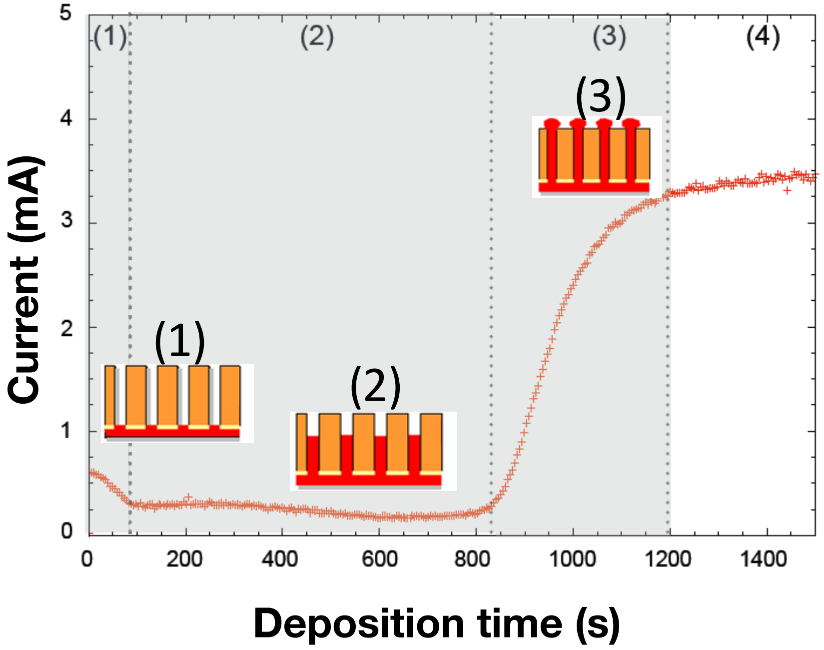


Van Dersarl et al., Nano Lett. **12** (2012) 3881

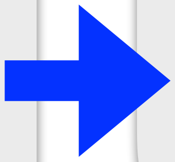
Ulrich, Spende, Burr, Sobel, Hess, Schubert, Trautmann, Toimil-Molares, Nanomaterials 11 (2021) 1874.

Tailoring and designing nanowires





Nanowires adopt size and shape of hosting channel: control on size and geometry



Parameters:

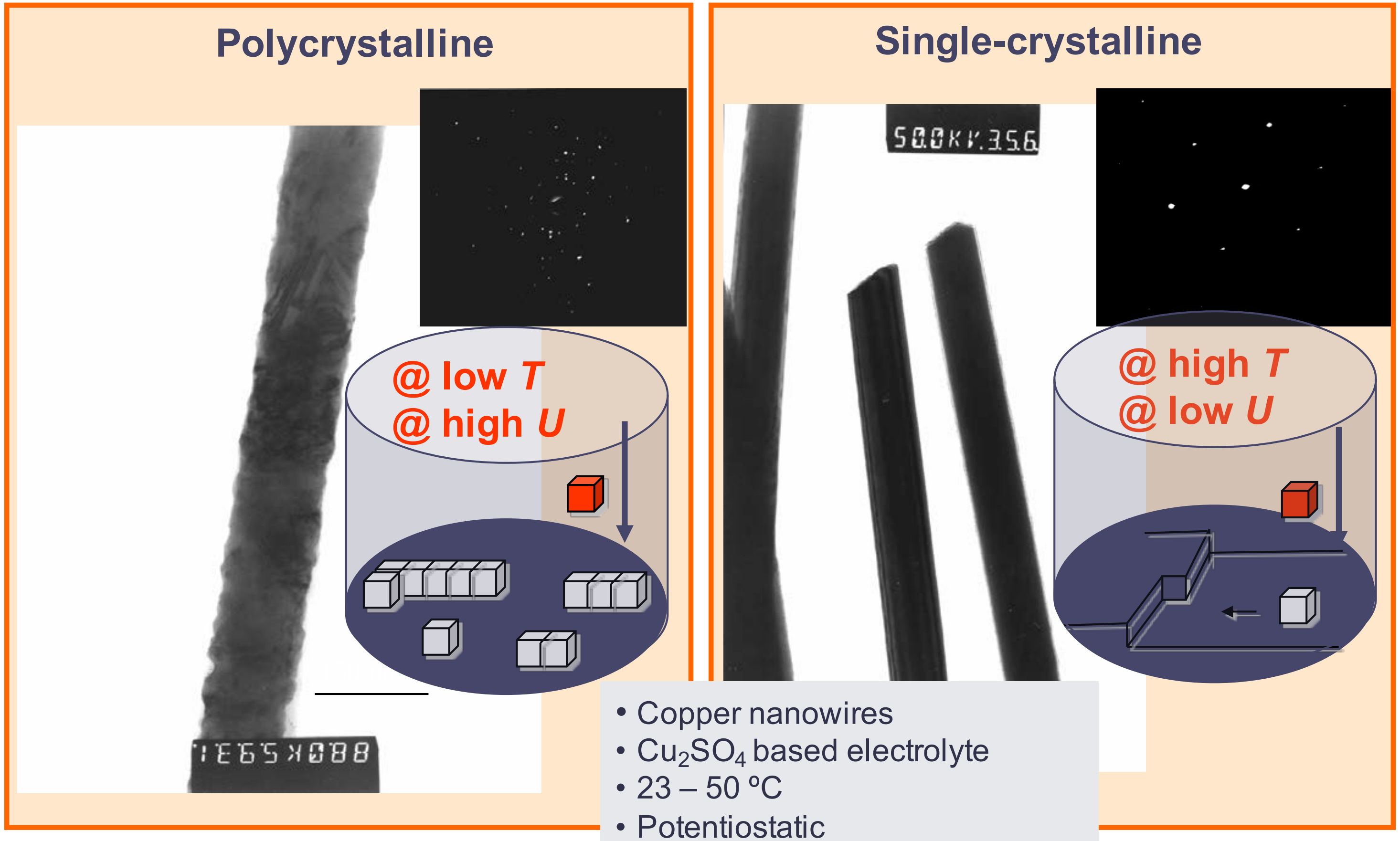
Temperature
Electrolyte
Potential
Convection
Electrodes
Cell geometry

Control:

Composition
Crystallinity
Roughness

Control on crystalline structure

Crystallinity and crystallographic orientation controlled by deposition conditions



- Copper nanowires
- Cu_2SO_4 based electrolyte
- 23 – 50 ºC
- Potentiostatic

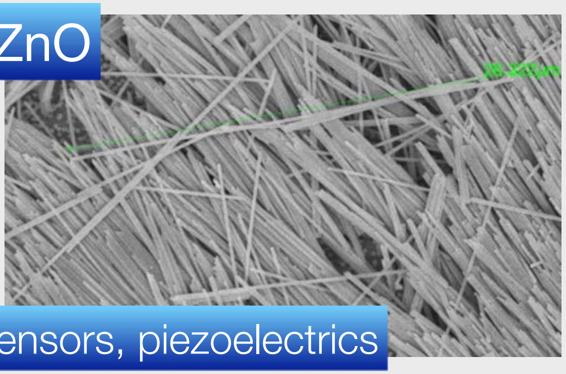
- Applied to study:
  - Crystal growth in confinement
  - Influence of grain size on electrical conductivity, thermal stability, etc.
- Applied to various materials: copper, gold, bismuth, antimony, etc.

Toimil-Molares, Beilstein J. of Nanotechnology 3 (2012) 860.
Picht, Müller, Rauber, Alber, Lensch-Falk, Medlin, Neumann, Sigle, Toimil-Molares, J. Phys. Chem. B 116 (2012) 5367.
Cornelius, Brötz, Chtanko, Dobrev, Miehe, Neumann, Toimil-Molares, Nanotechnology 16 (2005) 246.

Control on geometry and composition

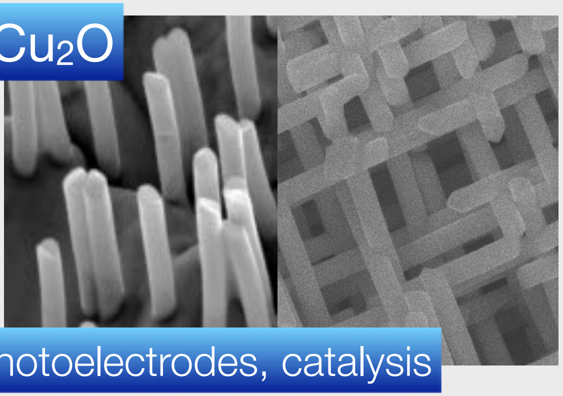
Semiconductors

ZnO



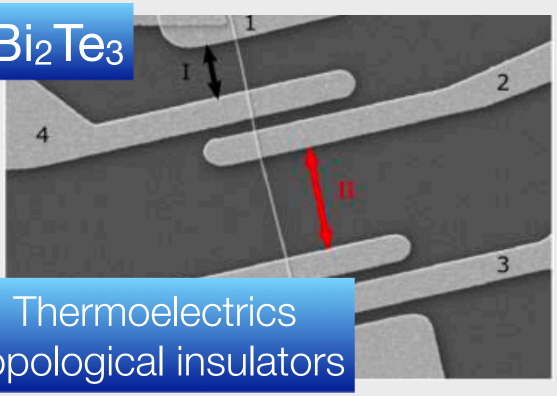
Sensors, piezoelectrics

Cu_2O



Photoelectrodes, catalysis

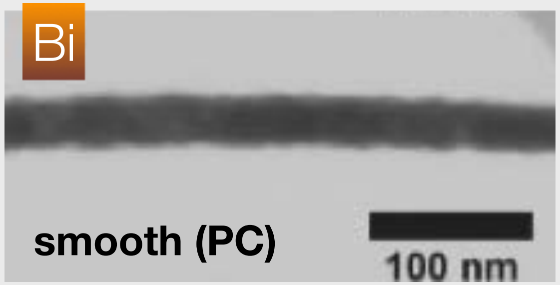
Bi_2Te_3



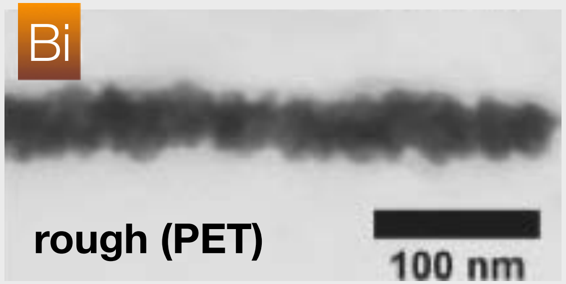
Thermoelectrics
Topological insulators

Semimetals

Bi

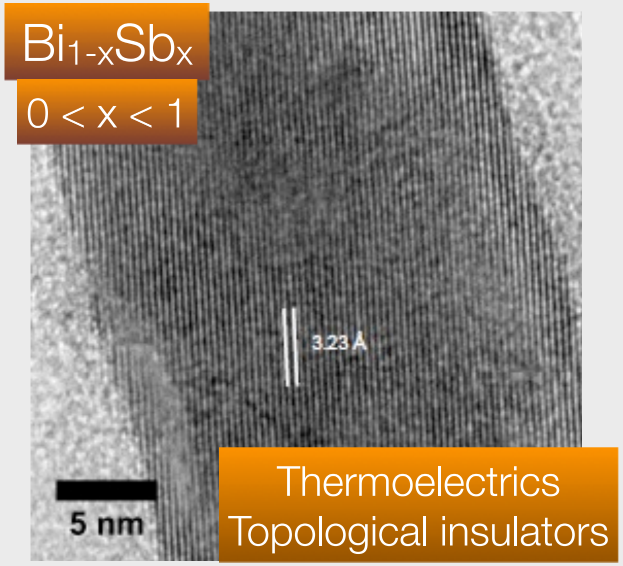


Bi



$Bi_{1-x}Sb_x$

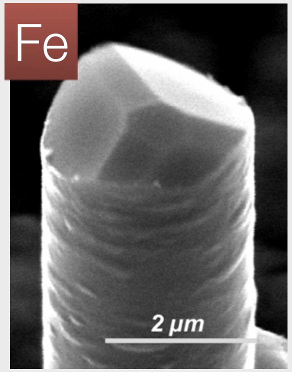
$0 < x < 1$



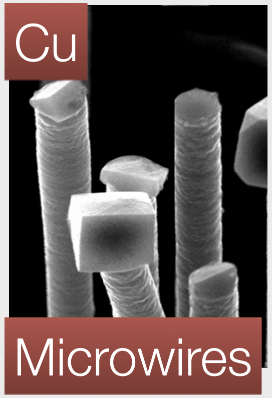
Thermoelectrics
Topological insulators

Metals

Fe

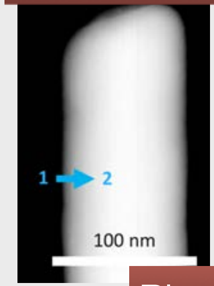


Cu

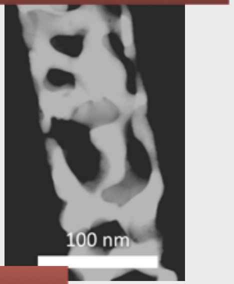


Microwires

$Au_{0.4}Ag_{0.6}$

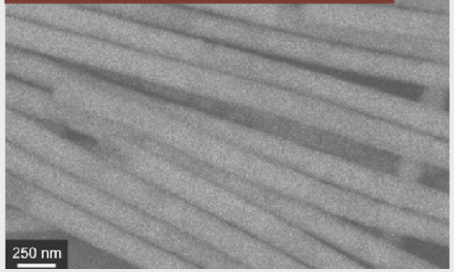


Porous Au



Plasmonics

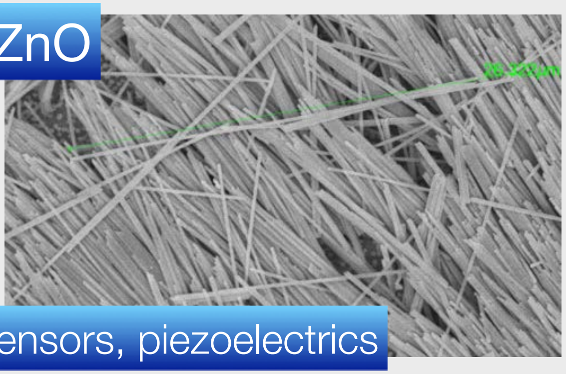
Cu → $Cu_3(BTC)_2$



Control on geometry and composition

Semiconductors

ZnO

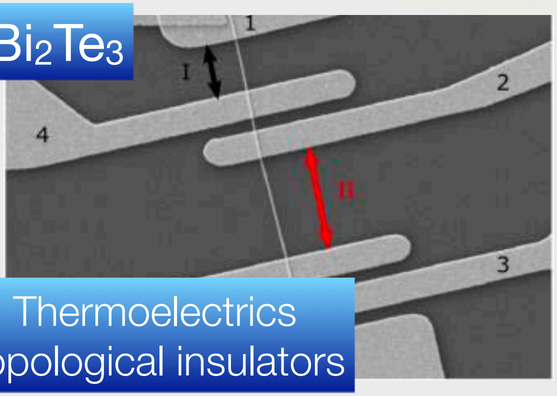


Sensors, piezoelectrics

Cu$_2$O

Photoelectrodes, catalysis

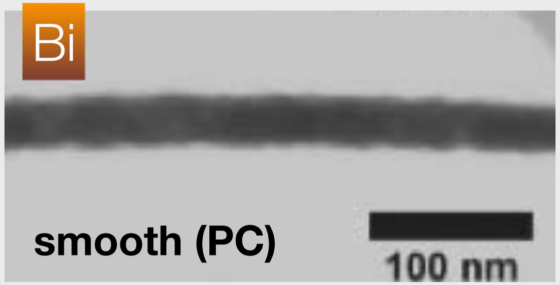
Bi$_2$Te$_3$



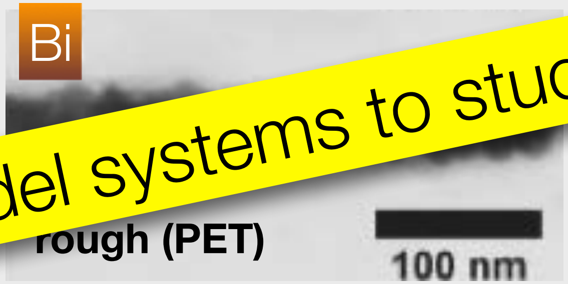
Thermoelectrics
Topological insulators

Semimetals

Bi

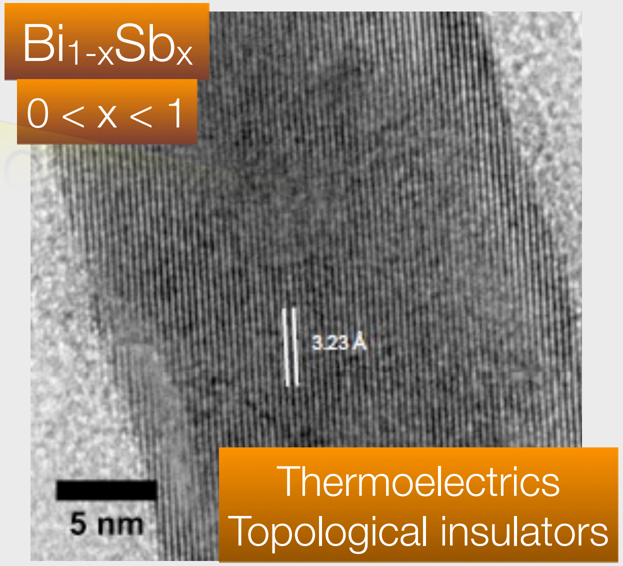


Bi



Bi$_{1-x}$Sb$_x$

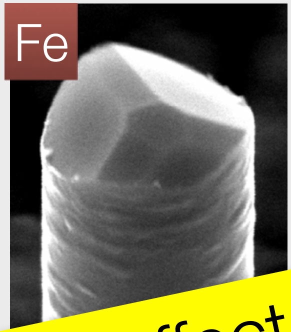
$0 < x < 1$



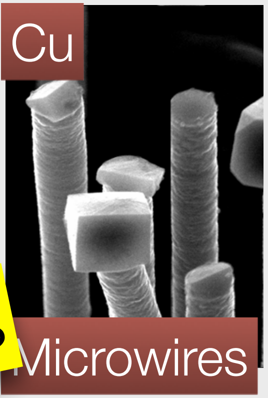
Thermoelectrics
Topological insulators

Metals

Fe

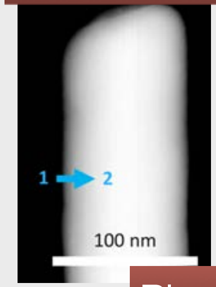


Cu

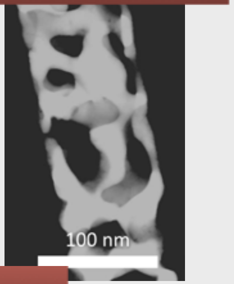


Microwires

Au$_{0.4}$Ag$_{0.6}$

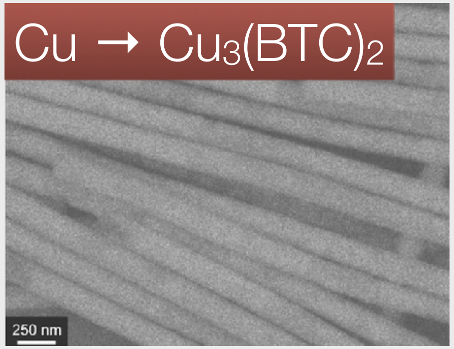


Porous Au



Plasmonics

Cu → Cu$_3$(BTC)$_2$

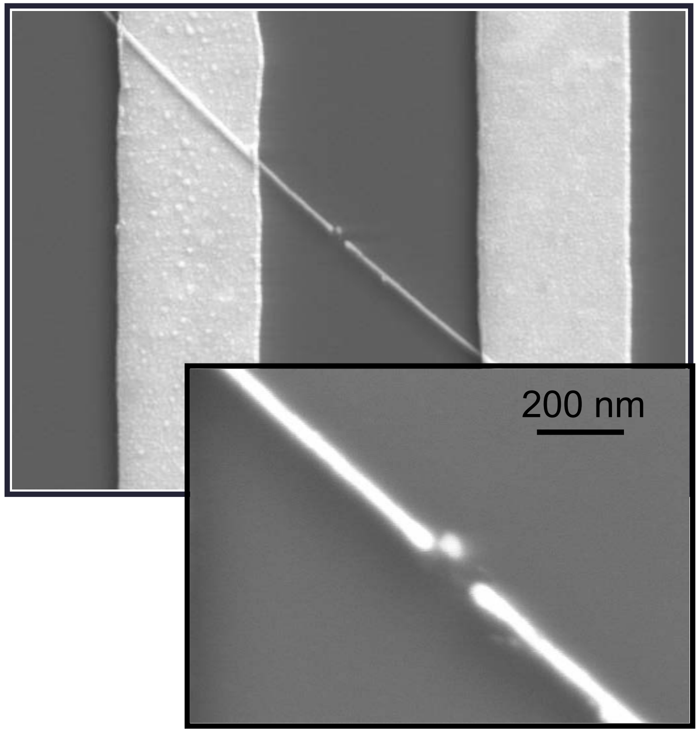


Excellent model systems to study size-effects

Investigations of size effects

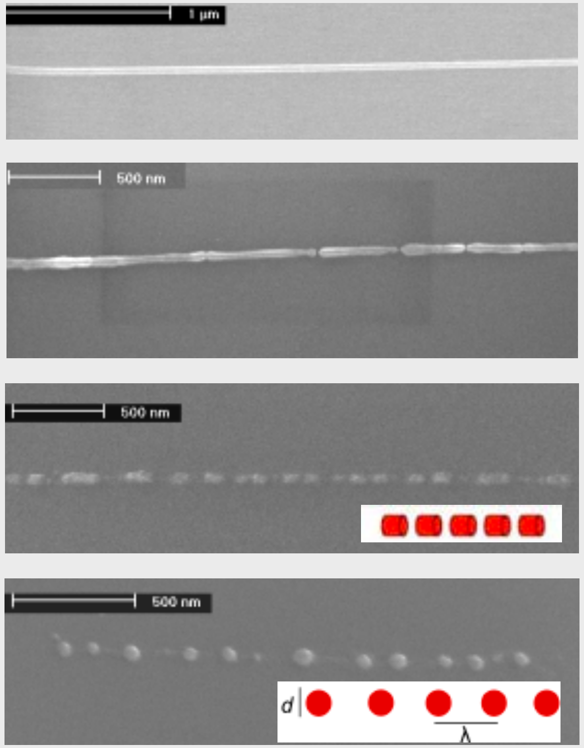
Some examples…

Rayleigh Instability



Nanowires break during electrical measurements due to Joule heat and electromigration

Cu **r_i ~30 nm**



cylindrical Cu wire

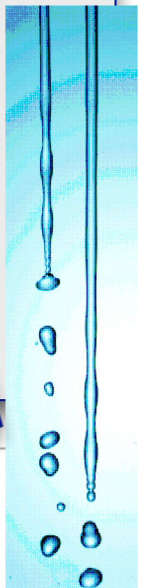
400 °C
wire fragmentation

500 °C
cylindrical sections

600 °C
spheres

D_s = 73 (9) nm ~3.78 r_i
l = 165 (57) nm ~8.89 r_i

surface diffusion
at T << $T_{melting}$



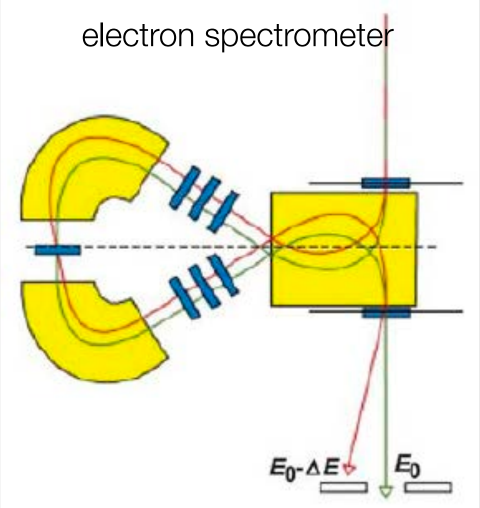
Cassinelli et al. Physica status solidi (a) 213 (2016) 603.
Toimil-Molares et al. Adv. Funct. Materials 22 (2012) 695.
Toimil-Molares et al. Appl. Phys. Lett. 85 (2004) 5337.

Lord Rayleigh. Proc. London Math
Nichols, Mullins, Trans. Metall. Soc 233, 1840.

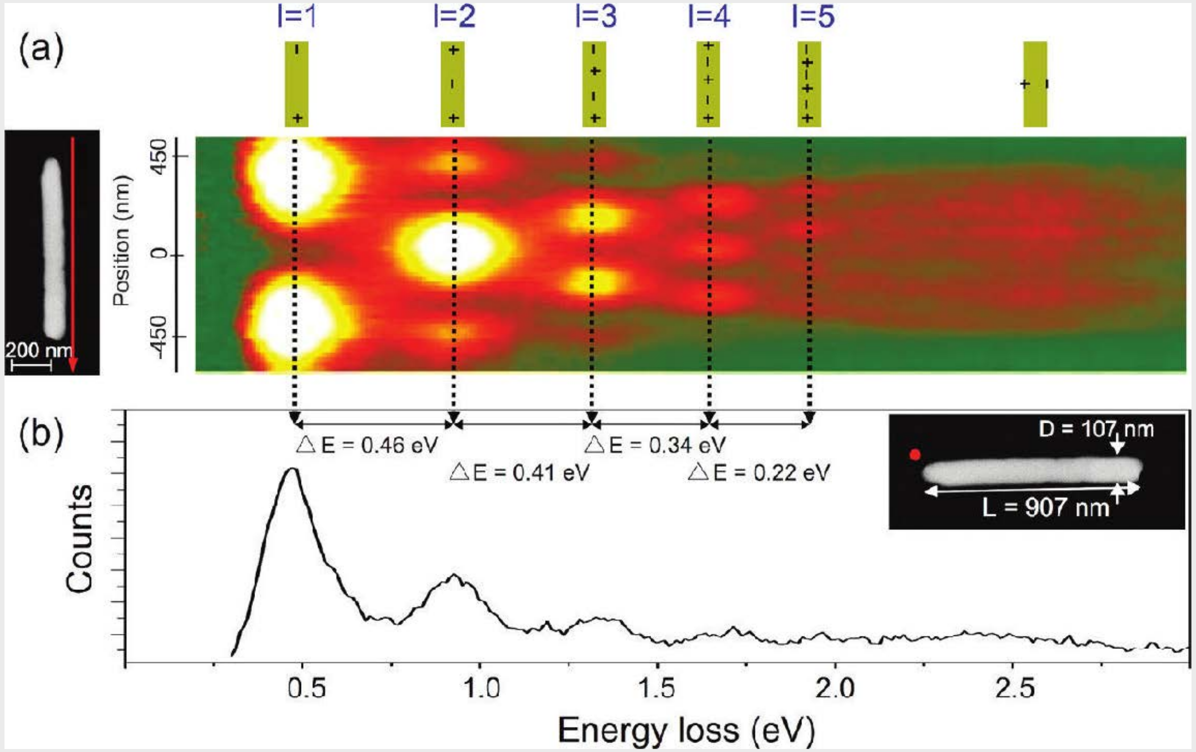
Plasmonic properties of Au nanowires

Some examples…

@ Stuttgart Center for
Microscopy, MPI for Solid
State Research



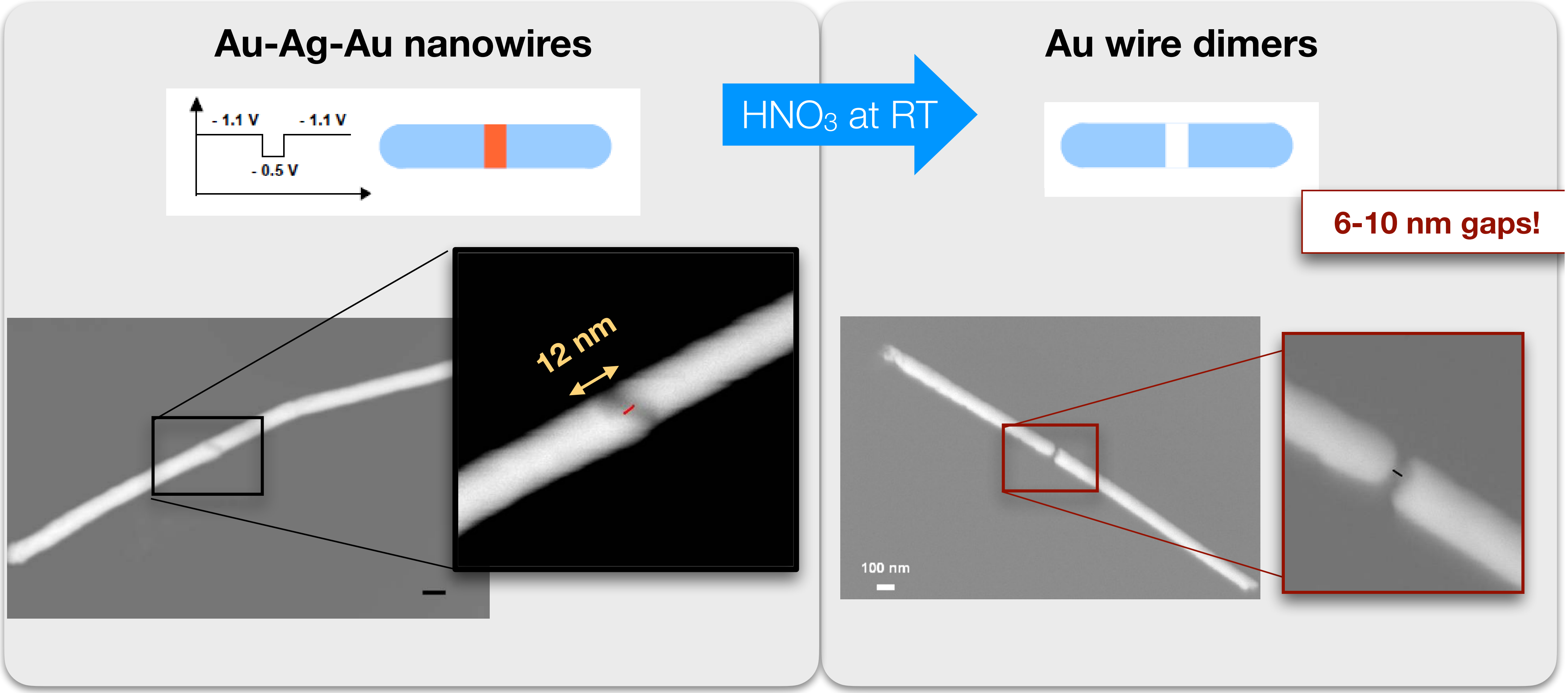
Sigle, Ann. Rev. Mater. Res. 35 (2005) 239



- Plasmonic resonances by electron energy loss spectroscopy (EELS).
- longitudinal resonances up to 5th order.
- Energy difference between two consecutive modes decreases.
- Resonance energy shifts with nanowire length, diameter, and substrate.

Alber, Sigle, Müller, Neumann, Picht, van Aken, Toimil-Molares, ACS Nano, 5 (12) (2011) 9845.

Nanowire Dimers and Nanogaps



Au-Ag-Au nanowires

HNO_3 at RT

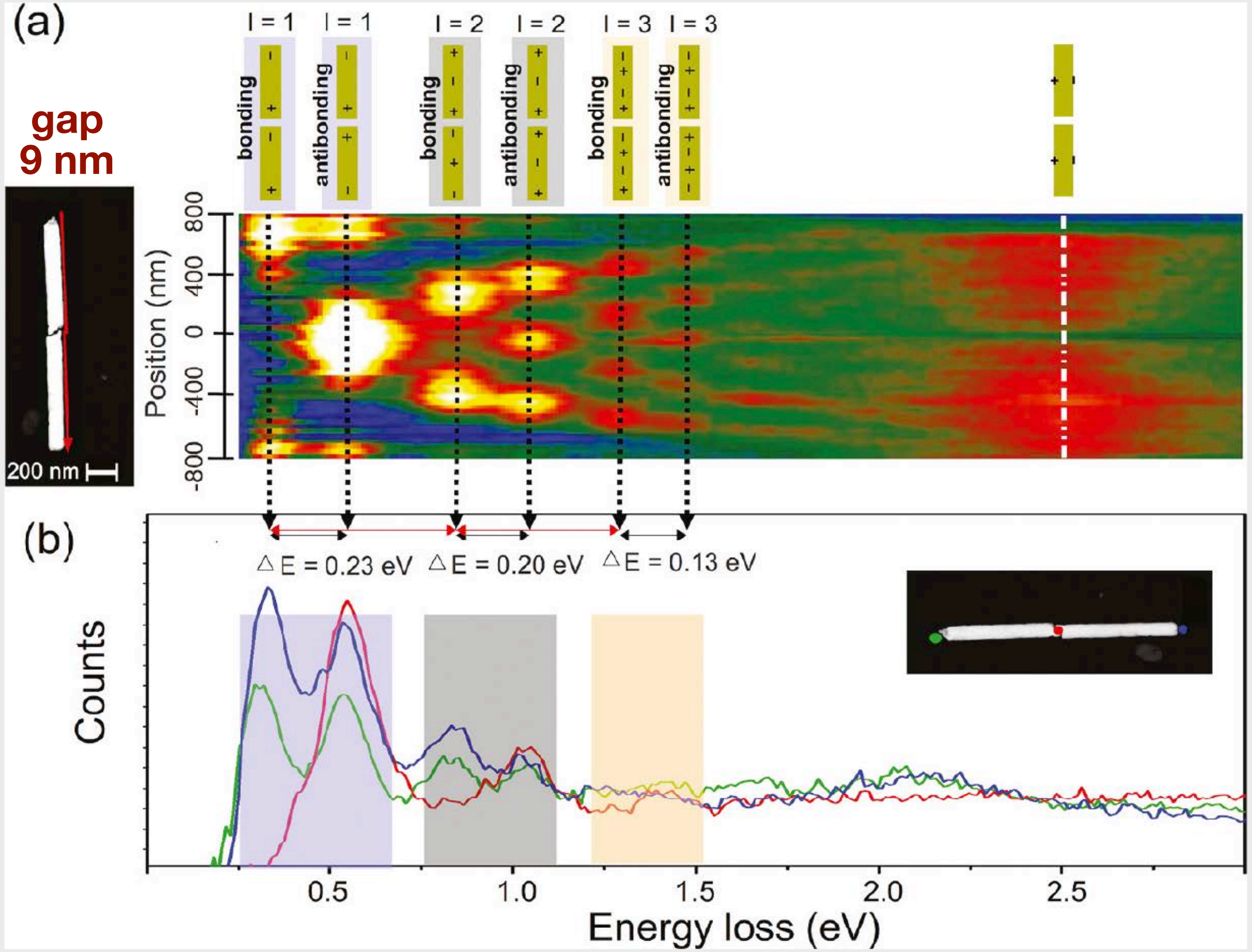
Au wire dimers

6-10 nm gaps!

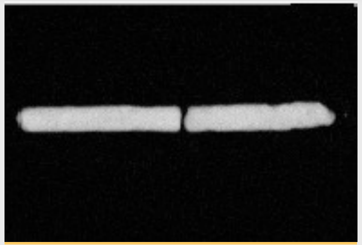
- Gap size down to few nm.
- Interesting as electrical contacts or hot spots.

Schubert, Burr, Trautmann, Toimil-Molares, Beilstein J. of Nanotechnology 6 (2015) 1272.

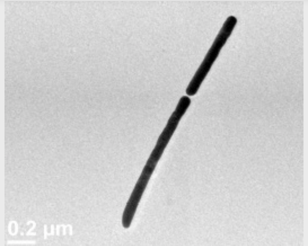
Plasmonic properties of nanowire dimers



symmetric dimers



asymmetric dimers



Relevant for, e.g. sensors based on SEIRA (surface enhanced IR-absorption spectroscopy)

- Splitting into bonding and antibonding modes up to 3rd multipole order.
- Energy splitting decreases with increasing multipole order.

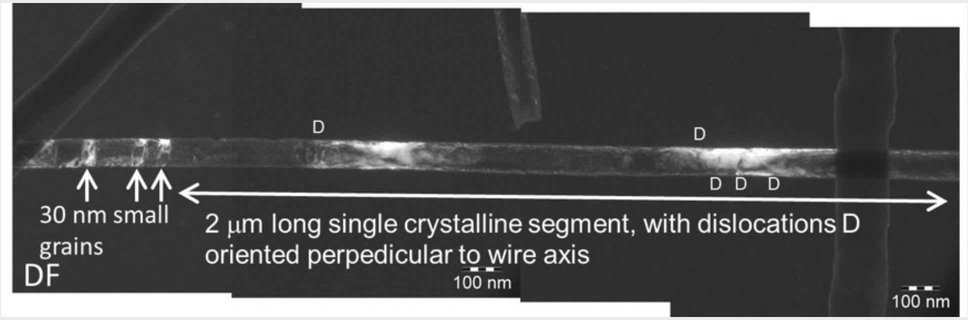
Schubert, Huck, Kröber, Neubrech, Pucci, Toimil-Molares, Trautmann, Vogt, Adv. Opt. Mater. 4 (2016) 1838.
Schubert, Sigle, van Aken, Trautmann, Toimil-Molares, Nanoscale 7 (2015) 4935.
Alber, Sigle, Müller, Neumann, Picht, van Aken, Toimil-Molares, ACS Nano, 5 (2011) 9845.
Alber, Sigle, Demming-Janssen, Neumann, Trautmann, van Aken, Toimil-Molares, ACS Nano 6 (2012) 9711.

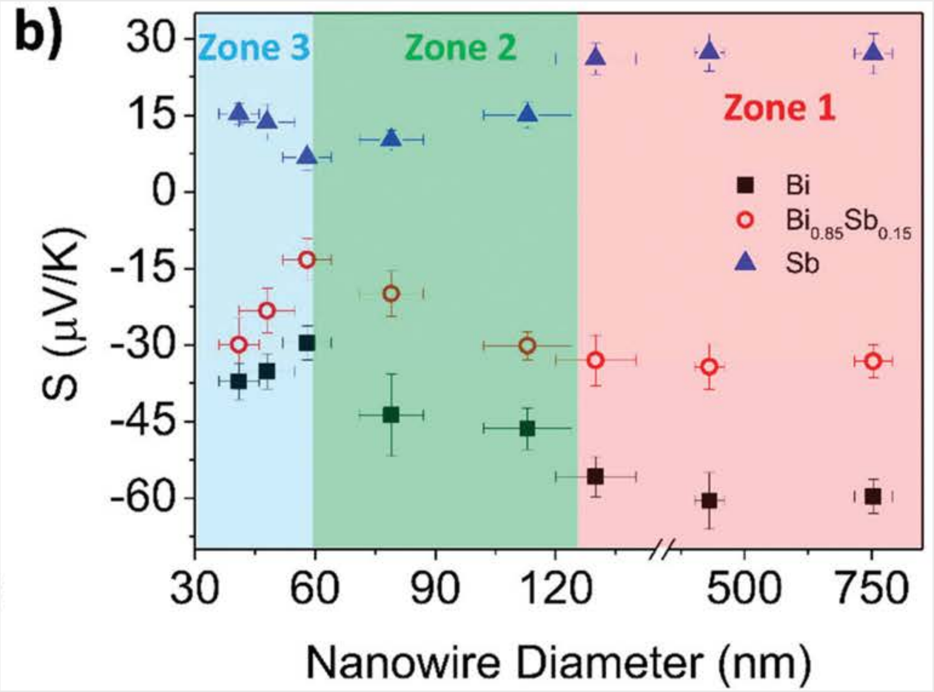
Size-dependent Seebeck coefficient

- $Bi_{1-x}Sb_x$ excellent model system
  - electron mean free path l_{el} ~100 nm
  - phonon mean free path l_{ph} ~10-100 nm
  - Fermi wavelength λ_F ~ 40 nm
- finite- and quantum size effects
- thermoelectric properties
- transport properties

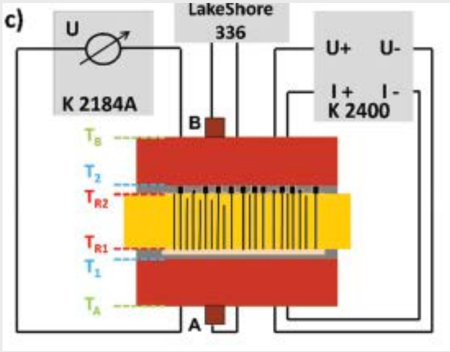
Synthesis

- Bi, Sb, and $Bi_{1-x}Sb_x$ nanowires
- crystallographic orientation and grain size (TEM, XRD)





$S = -\Delta V/\Delta T$



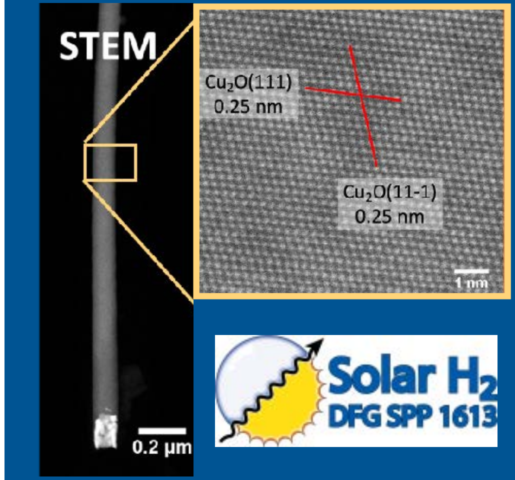
- Non-monotonic S as a function of wire diameter attributed to surface states, and finite and quantum size effects

Wagner, Paulus, Voss, Trautmann, Völklein, Toimil-Molares, Adv. Electron. Mater. 7 (2021) 3.
Cassinelli, Müller, Voss, Trautmann, Völklein, Gooth, Nielsch, Toimil-Molares, Nanoscale 9 (2017) 3169.
Cassinelli, Müller, Aabdin, Peranio, Eibl, Trautmann, Toimil-Molares, Nucl. Instr. and Meth. in Phys. Res. B 365 (2015) 668.
Müller, Schötz, Picht, Sigle, Kopold, Rauber, Alber, Neumann, Toimil-Molares, Crystal Growth and Design 12 (2012) 615.

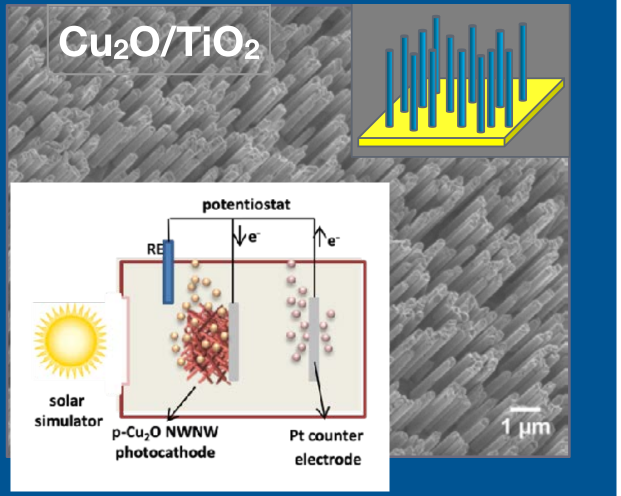
Funded by DFG SPP1386

From single wires… to nanowire assemblies

Cylindrical arrays as photoelectrodes

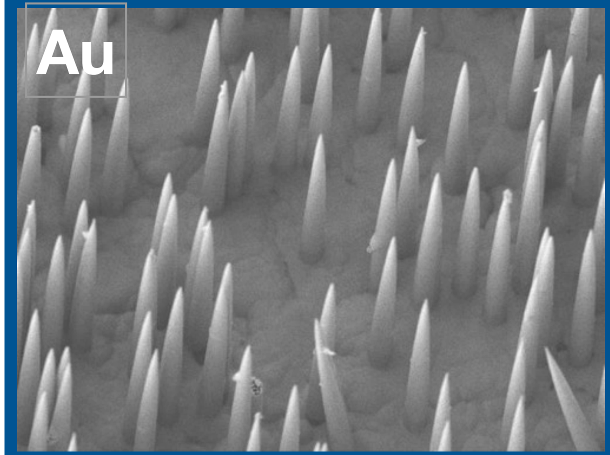


Solar H_2
DFG SPP 1613



Movsesyan, Yang, Kaiser, Jaegermann, Toimil-Molares et al., *Nanomaterials* (2018) 8, 693.
Yang, Schröck, Toimil-Molares et al. , *Zeitschrift für Physikalische Chemie* 234 (2020) 1205.

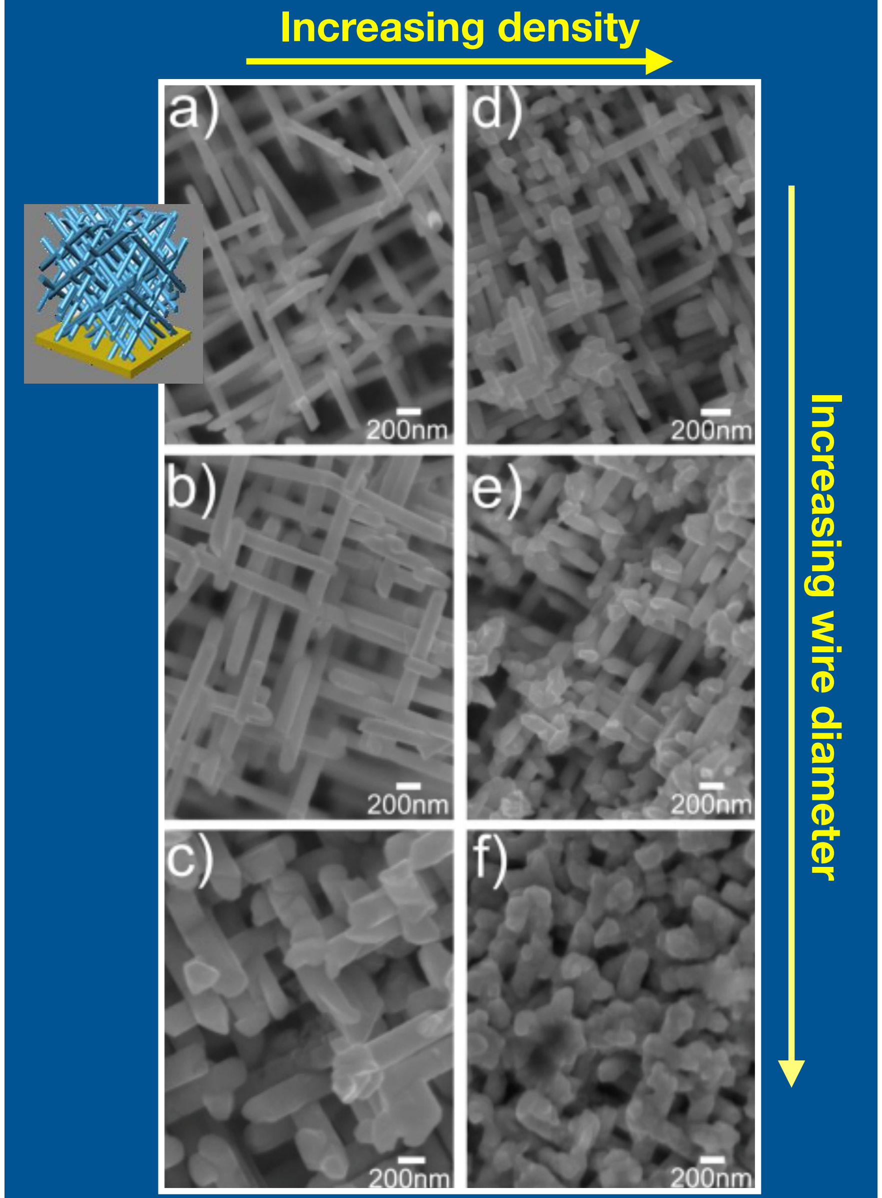
Conical arrays



- base ~µm
- tip ~few tens nm
- up to 100 µm
- all same height
- excellent thermal & electrical contact to base
- mechanically very stable

Burr et al. In preparation

Thermoelectric networks



Wagner et al., *Physica Status Solidi (a)* 213 (2016) 610.

FAIR

Thanks!

GSI

Materials Research at GSI

iNAPO

LOEWE
Exzellente Forschung für Hessens Zukunft

HELMHOLTZ
ASSOCIATION

BEILSTEIN INSTITUT

DAAD
Deutscher Akademischer Austausch Dienst
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Solar H_2
DFG SPP 1613

DFG SPP 1666

DFG SPP 1386

DFG SPP 1165