The Big Picture

Intelligent Nanomaterials for Energy

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Nanoscale Energy and Surface Engineering

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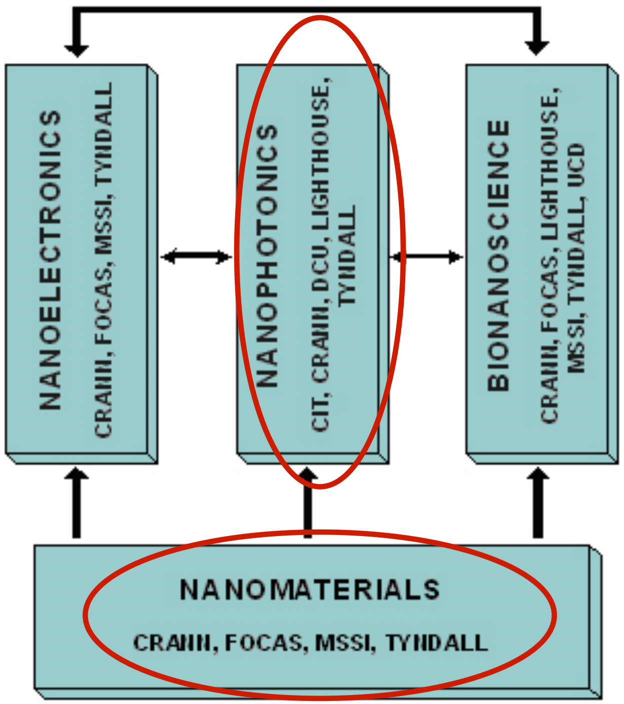
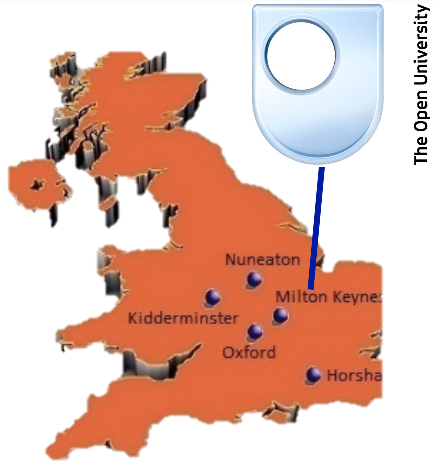




Education and Research Experience

Material Scientist, specialised in preparation and characterisation of wide range of micro and nano materials using soft x-ray spectroscopies

Post doctoral research/teaching experience (6 years)

•**2008 to 2012: Research Fellow**, Integrated Nanoscience Platform for Ireland, National Centre for Plasma Science and Technology, Energy Design Lab, Dublin City University (DCU), Dublin, Ireland.

• **2006- 2008: Research Fellow,** Centre for Research in Nanostructures and Nanodevices, Trinity College Dublin (TCD), Ireland

•**2004- 2006 : Post doctoral Research Fellow,** Soft X-ray Spectroscopy group, School of Physical Sciences, Trinity College Dublin (TCD), Ireland

•2001 -2004 (2006) : PhD on Synchrotron radiation studies on Nanostructured systems, University of Newcastle upon Tyne, UK.

Acknowledgements

Newcastle University

Dr. L. Siller and Dr. B. Horrocks, Dr.Y. Chao and Dr. Y. Butenko

Trinity College Dublin

Dr. C. McGuinness, Prof . JMD Coey, Prof G. Duesberg, Prof. Coleman and Dr. B. Kennedy

DCU

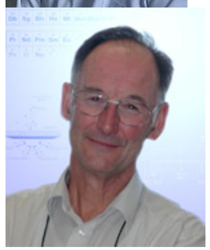
Dr. S. D. Daniels, Dr. J-P. Mosnier, Prof. Costello, Prof McNally, Dr. D. Brabazon, Dr. E, Marsili, Mr. D. Moore, Mr. S. Pheelan and Mr. J. Connolly

Berkeley Lab

Prof Jinghua Guo, Dr. Per Anders Glans and Mr. T. Learmonth

The University of Auckland New Zealand

Prof David E. Williams



Current Projects and Grants

1. **Ultrafast photonic processes and interactions for photovoltaic applications**: **Eu IRSES collaboration** between DCU, IIT Madras, IIT Delhi and University of Southampton, The Open University (2013-2017)

2.Smart Nanomaterials for bioenergy technology in collaboration, Department of Biotechnology, **IIT Madras** –, **DST Ireland, 2011- 2013**

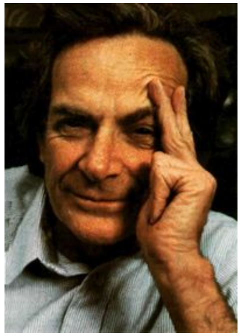
3.Development of novel materials, device structures and fabrication methods suitable for thin film solar cells and TCOs including organic photovoltaics, in collaboration, IIT Delhi DST Ireland, 2011 -2013

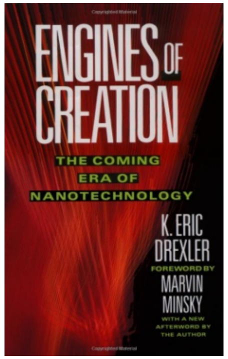
4.Novel transparent conductors for Microbial Fuel Cells (MFCs) for primary wastewater treatment at Northern Ireland (NI) water treatment plant. (2011-2014), QUESTOR Funding agent

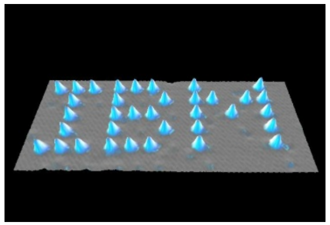
5.Probing the surface and interfaces of gold nitride nanoparticles on different substrates and surface characterisation of novel bio materials Science Foundation Ireland, 2006

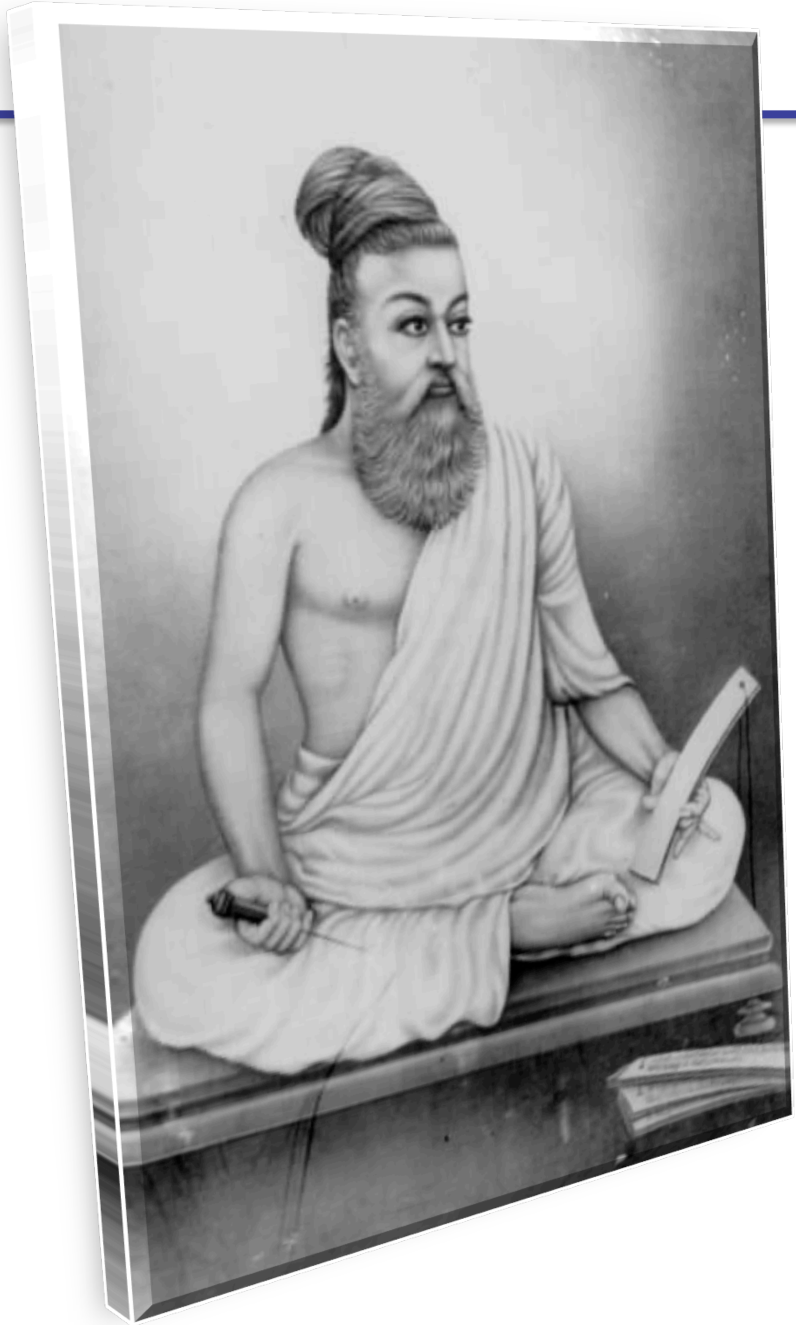
History of Nanotechnology

- **~ 2000 Years Ago** – Sulfide nanocrystals used by Greeks and Romans to dye hair
- **~ 1000 Years Ago (Middle Ages)** – Gold nanoparticles of different sizes used to produce different colors in stained glass windows
- **1959** – “There is plenty of room at the bottom” by R. Feynman
- **1974** – “Nanotechnology” - Taniguchi uses the term nanotechnology for the first time
- **1981** – IBM develops Scanning Tunneling Microscope
- **1985** – “Buckyball” - Scientists at Rice University and University of Sussex discover C_{60}
- **1986** – “Engines of Creation” - First book on nanotechnology by K. Eric Drexler. Atomic Force Microscope invented by Binnig, Quate and Gerbe
- **1989** – IBM logo made with individual atoms
- **1991** – Carbon nanotube discovered by S. Iijima
- **1999** – “Nanomedicine” – 1st nanomedicine book by R. Freitas
- **2000** – “National Nanotechnology Initiative” launched



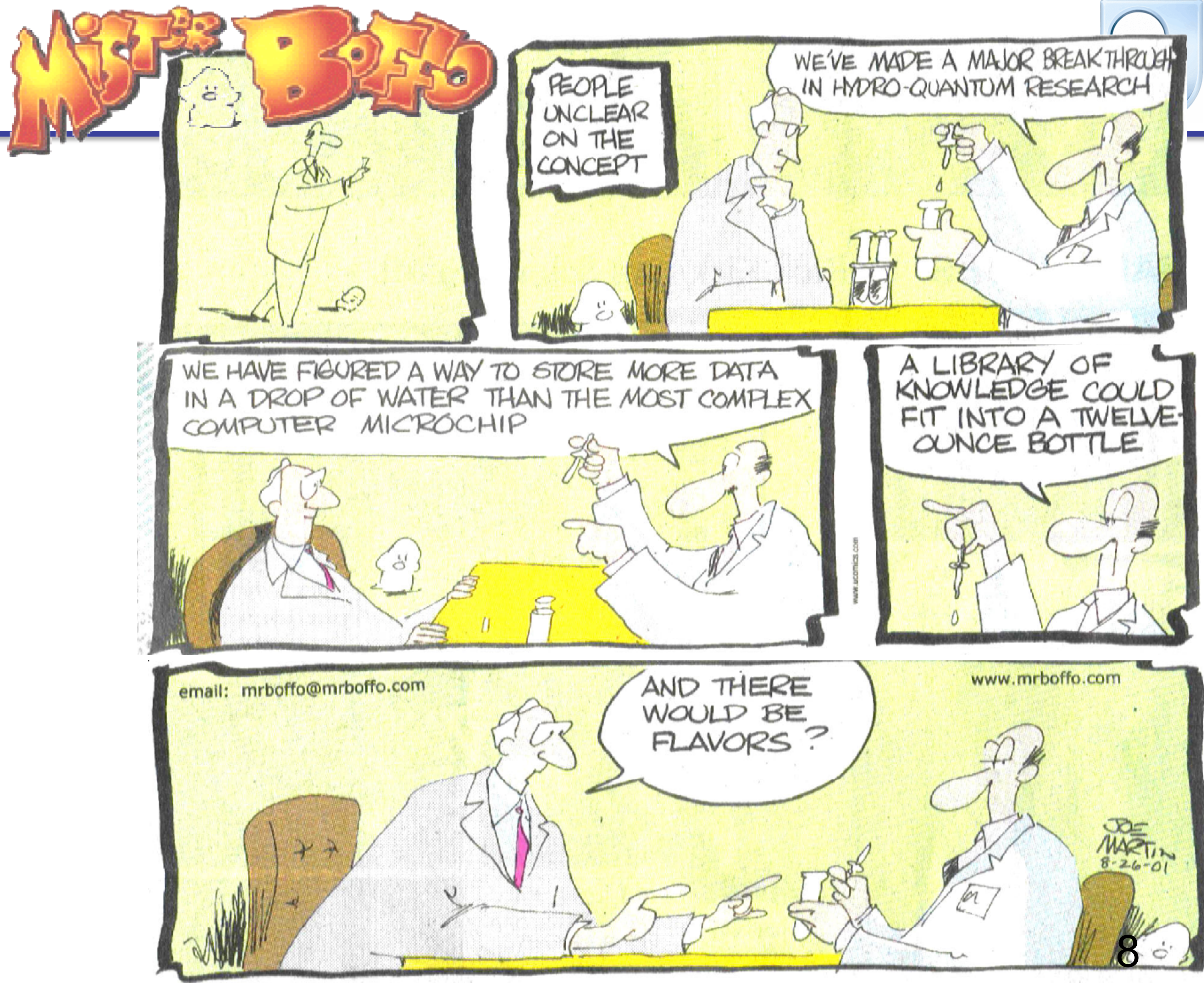






Thiruvaluvar- The famous poet from South India (Tamil Nadu)

Predicted the same 330 BC


MISTER BOFFO
PEOPLE UNCLEAR ON THE CONCEPT
WE'VE MADE A MAJOR BREAKTHROUGH IN HYDRO-QUANTUM RESEARCH
WE HAVE FIGURED A WAY TO STORE MORE DATA IN A DROP OF WATER THAN THE MOST COMPLEX COMPUTER MICROCHIP
A LIBRARY OF KNOWLEDGE COULD FIT INTO A TWELVE-OUNCE BOTTLE
email: mrboffo@mrboffo.com
AND THERE WOULD BE FLAVORS ?
www.mrboffo.com
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Overview

- Key nanostructures
- PNPA ??
- Why is each structure important?
- What industries use these structures?
- For what types of applications?
- Storage and policies

http://nanotechweb.org/cws/article/tech/17537

Nanoscience Research for Energy Needs

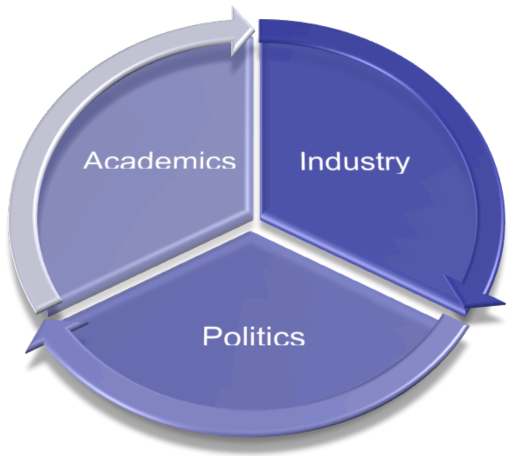
- Catalysis by nanoscale materials
- Using interfaces to manipulate energy carriers
- Linking structures and function at the nanoscale
- Assembly and architecture of nanoscale structures
- Theory, modeling, and simulation for energy nanosciences
- Scalable synthesis methods

Energy requires new strategies

Securing Energy Supplies for the Future has Top Priority

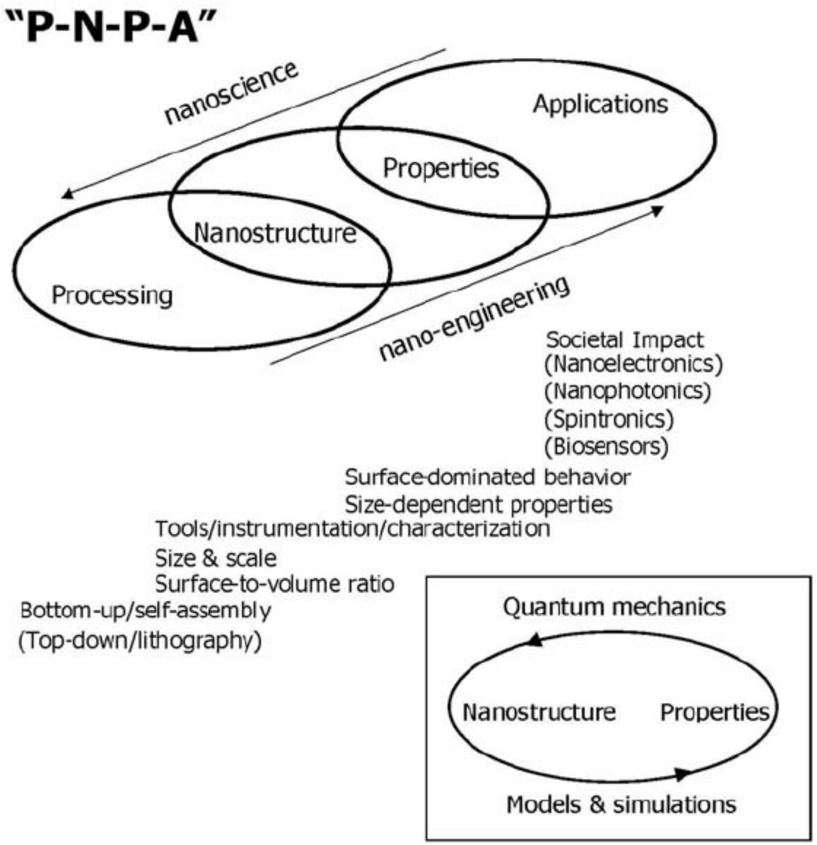
Nanotechnology Provides Materials for a Multitude of Applications

- Nanomaterials are essential for energy applications
- Long term sustainable solutions require disruptive technology
- Not incremental, innovative and substantial



PNPA is the HEART OF TECHNOLOGY

- Integrated nanomaterials engineering pedagogy
- Properties
- Applications
- Processing
- Nanostructure



The P-N-P-A Rubric for undergraduate nanomaterials engineering.

Five Grand Challenges:

Grand Challenge #1: How do we control materials processes at the level of electrons?

Grand Challenge #2: How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?

Grand Challenge #3: How do remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and how can we control these properties?

Grand Challenge #4: How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things?

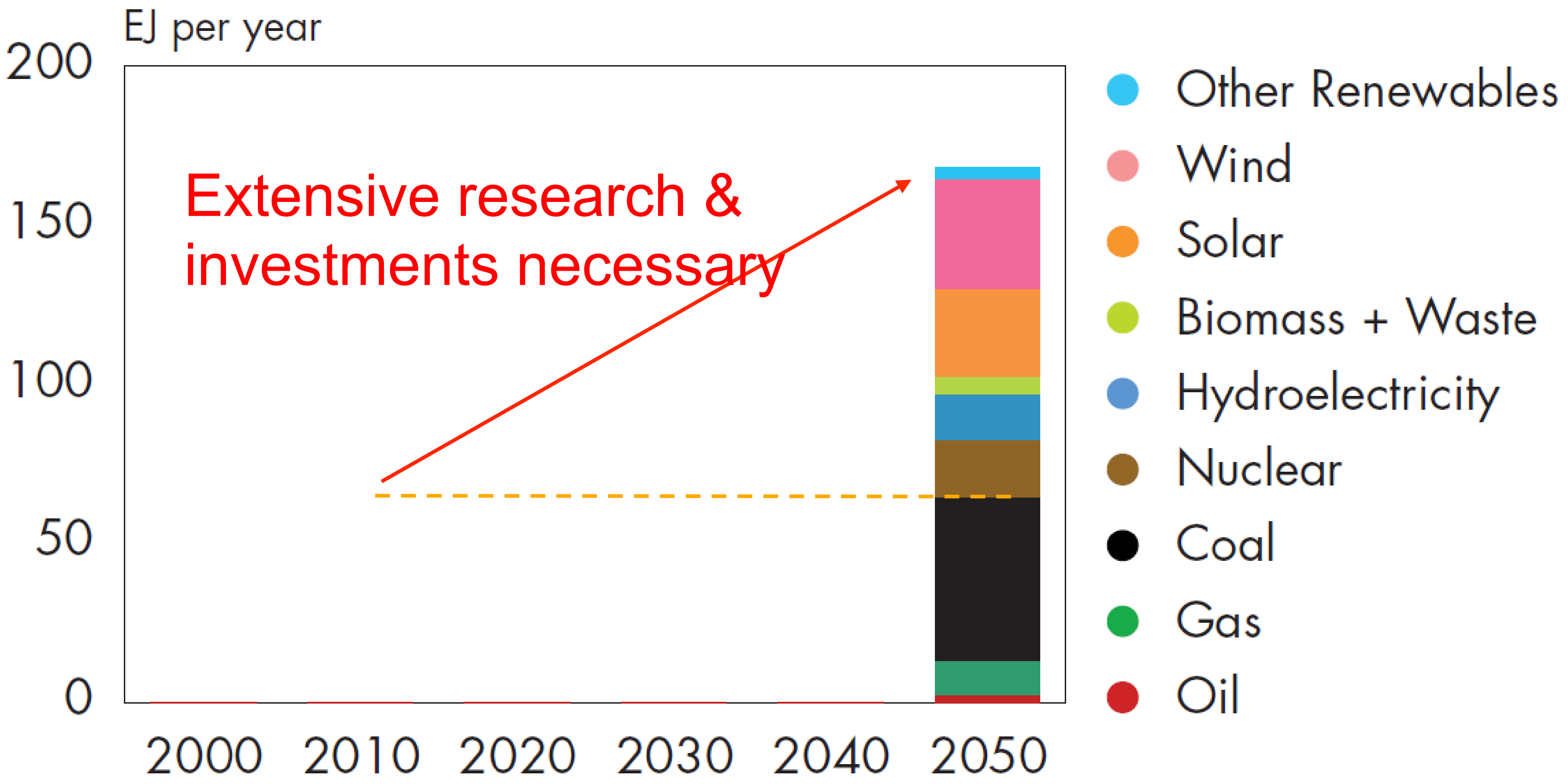
Grand Challenge #5: How do we characterize and control matter away - especially very far away - from equilibrium?

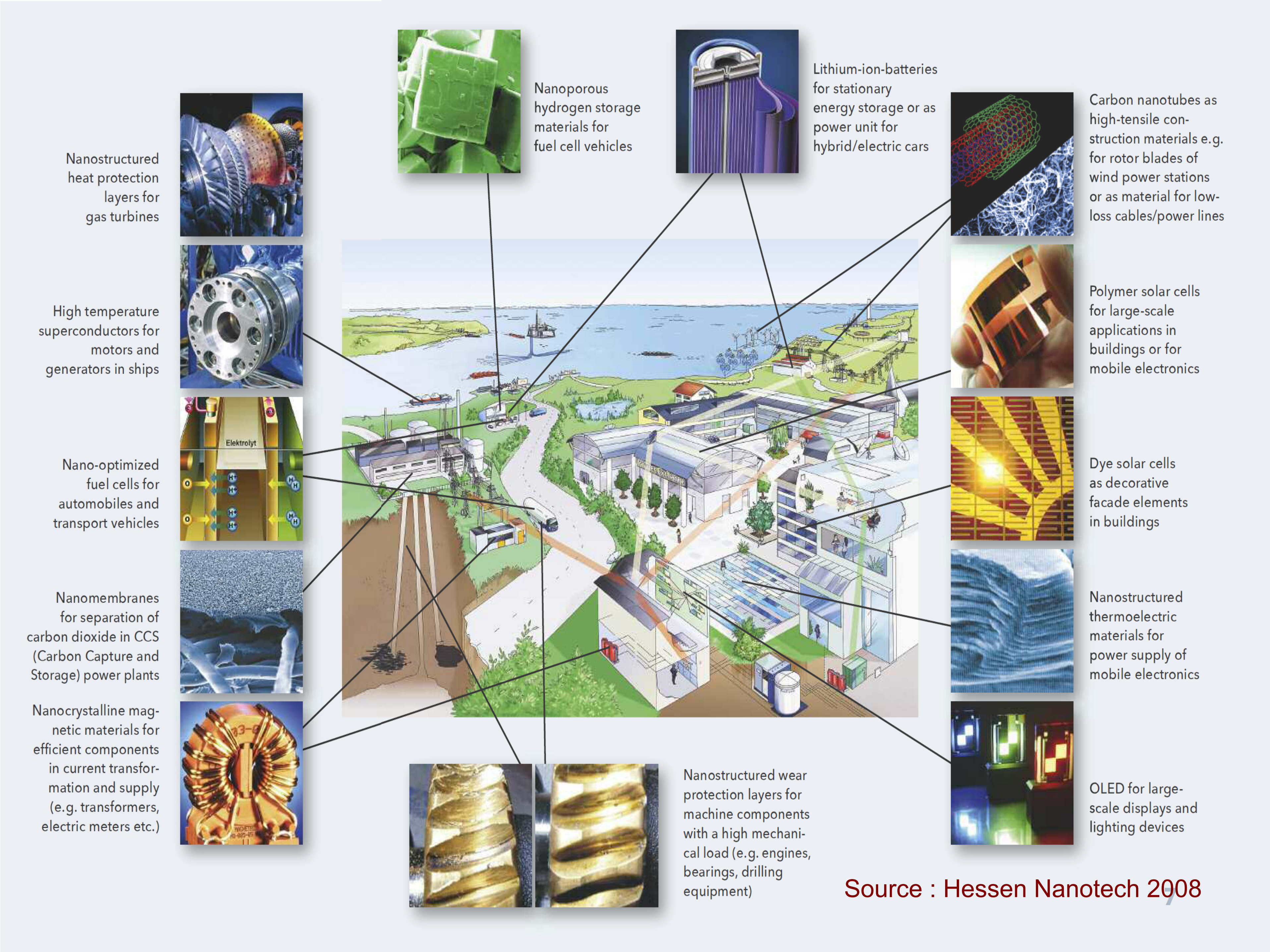
Materials Research for Energy Applications

Research topics

- **Solar Fuels**
- **Solar Cells**
- **Fuel Cells**
- **Lighting**
- **Piezoelectrics**
- **Thermoelectrics**
- **Thermal Insulation**
- **CO_2 separation/capture**
- **Fossil Fuels**
- **Related projects:**
  - Energy efficient electronics
  - Energy efficient processes

Energy consumption of electricity





Source : Hessen Nanotech 2008

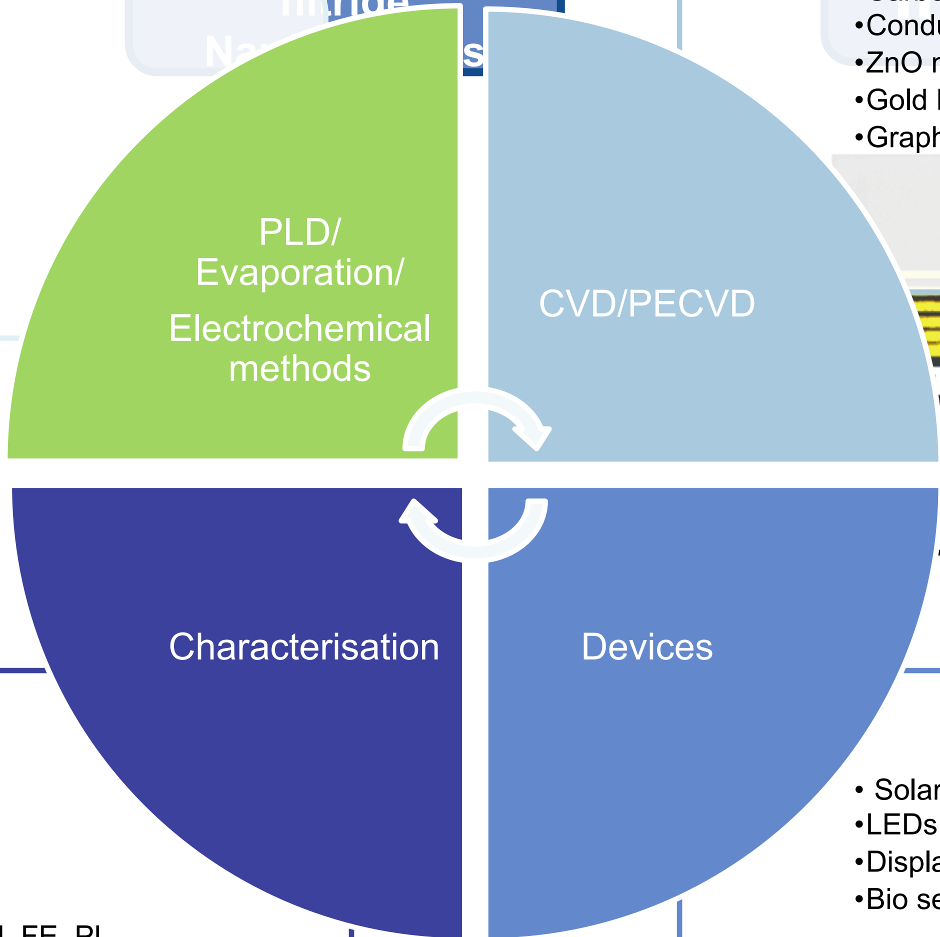
Materials Expertise and projects

Academic

- GaMnN
- Co doped ZnO
- Gold nitride
- Metal and Si nanoparticles
- Nanodiamond

Nano Si/ gold nitride

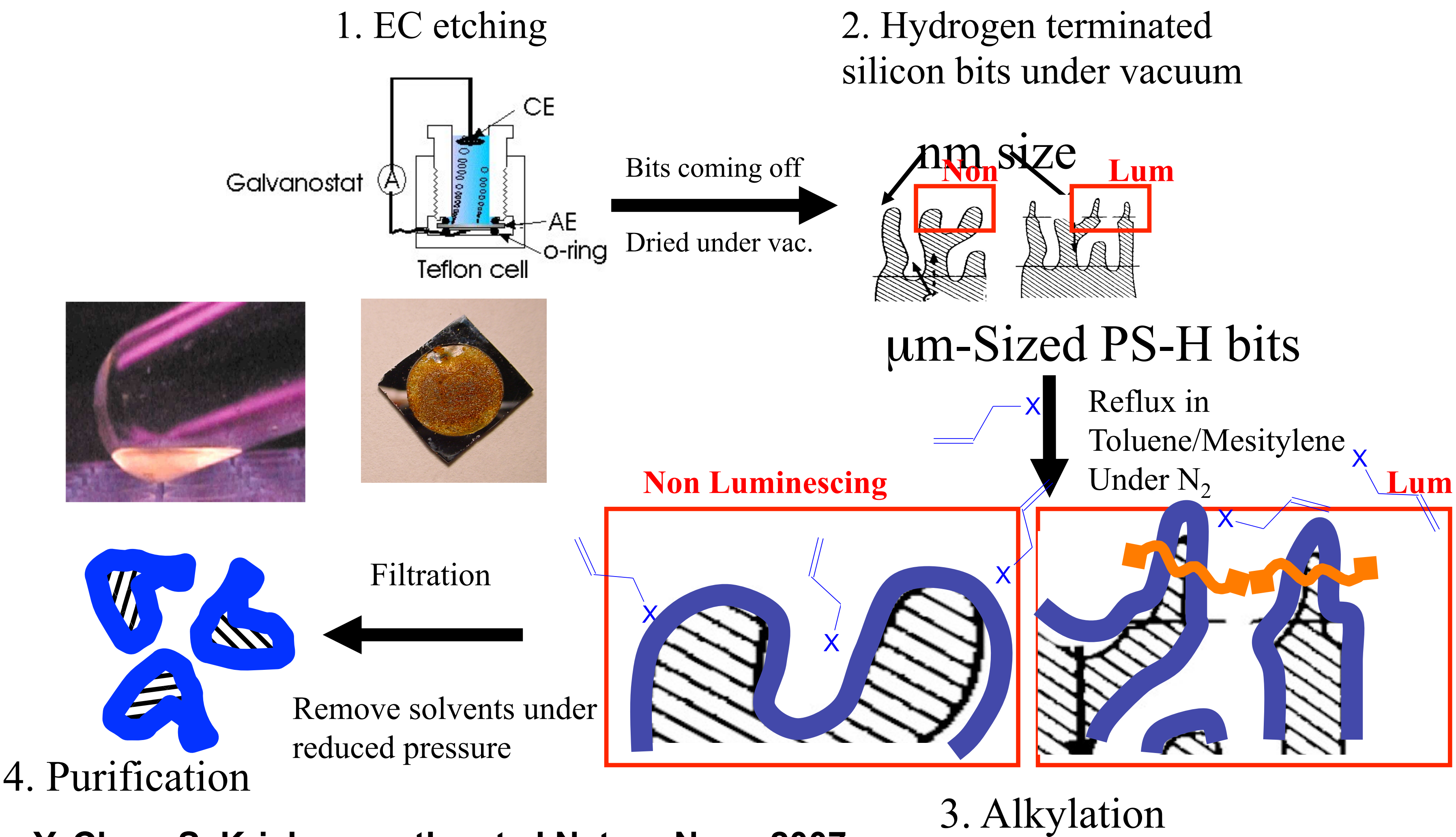
- Carbon Nanotubes
- Conducting carbon films
- ZnO nanorods
- Gold Nitride
- Graphene



- XPS
- XAS
- XRD
- Raman
- AFM, SEM, FE, PL

- Solar cells
- LEDs
- Displays
- Bio sensors

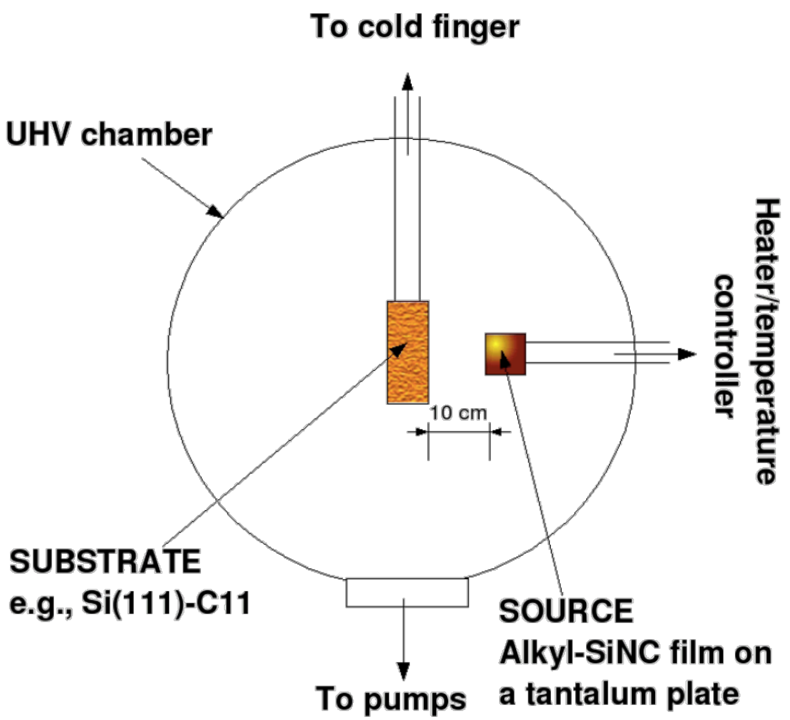
Low cost fabrication of Si nanocrystals for solar cell applications in lab scale

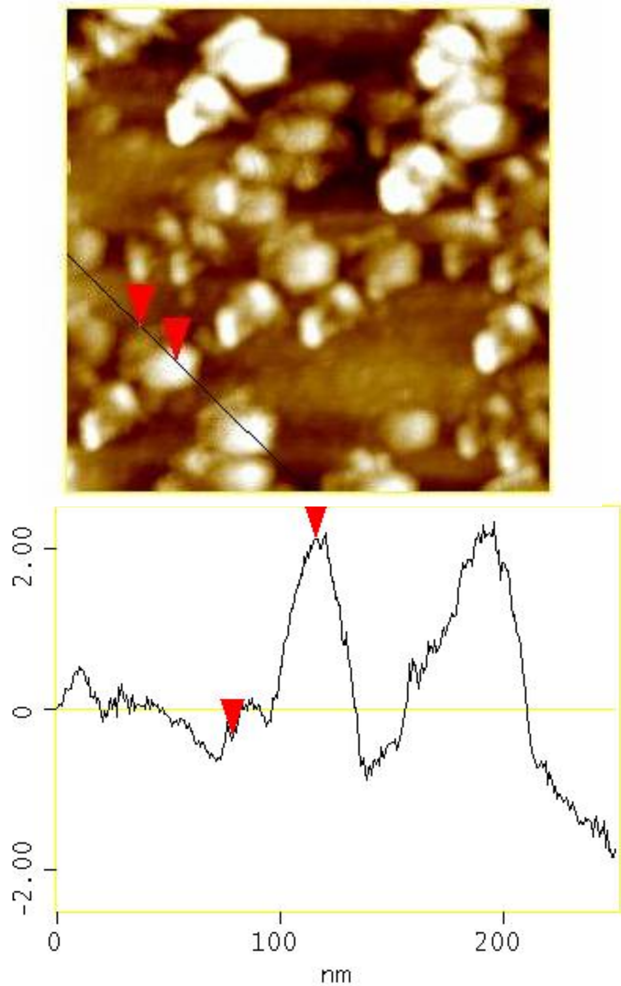


Y. Chao, S. Krishnamurthy et al Nature Nano 2007

S. Krishnamurthy PhD thesis , Y.Chao**, S. Krishnamurthy et al,** Journal of Applied Physics, 2005,065231

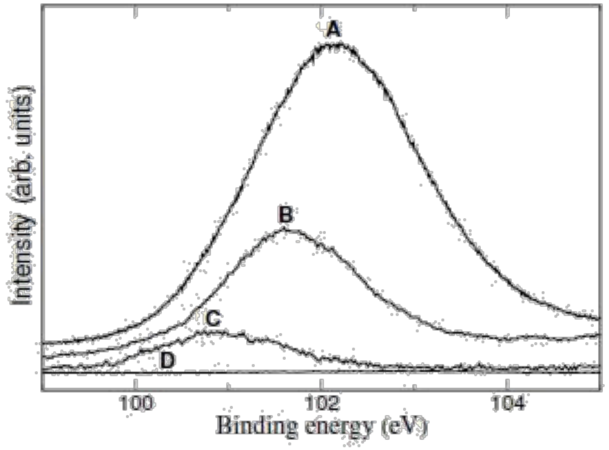
Evaporation of silicon nanocrystals

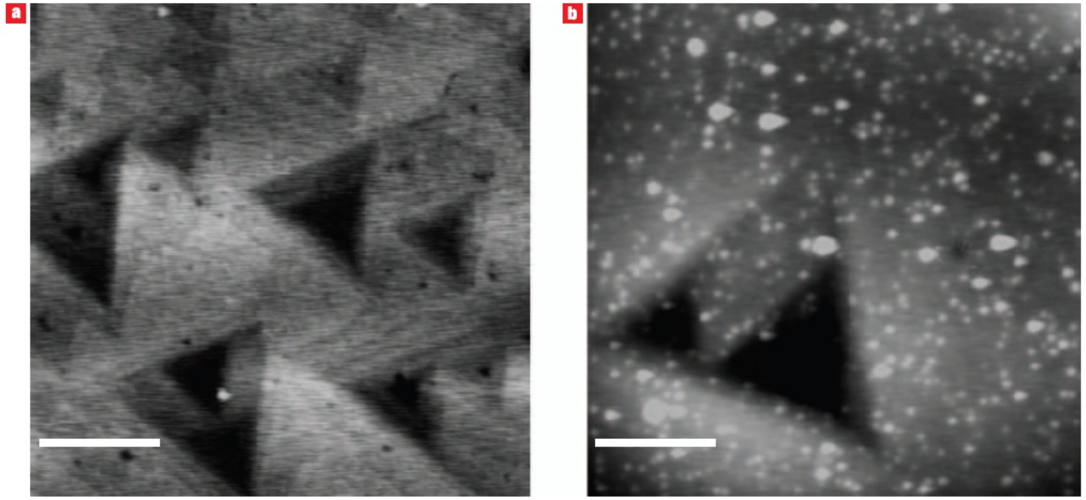




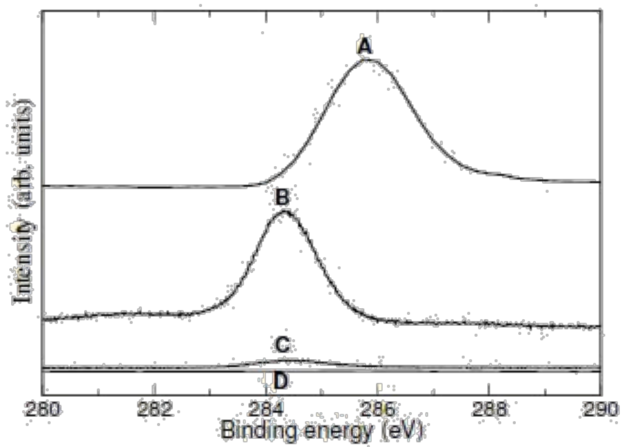
S. Krishnamurthy PhD Thesis and Y. Chao, L. Siller, **S. Krishnamurthy**, *et al* **Nature Nanotechnology** 2007, 2, 486,
L. Siller, **S. Krishnamurthy** et al J. Phys.: Condens. Matter 21,2009, 095005
S. Krishnamurthy et al, Applied Physics Letters, 2012 (revision submitted)

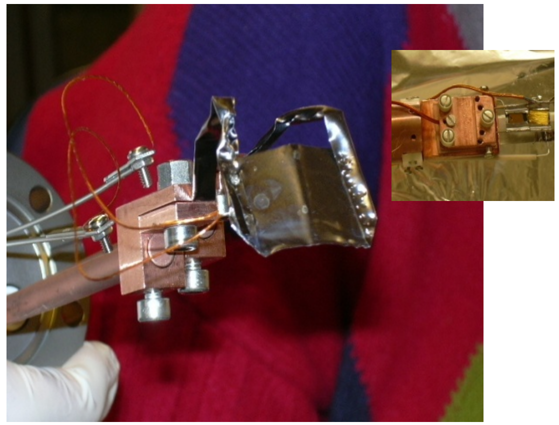
Photoemission and Microscopy of evaporated Si nanocrystals

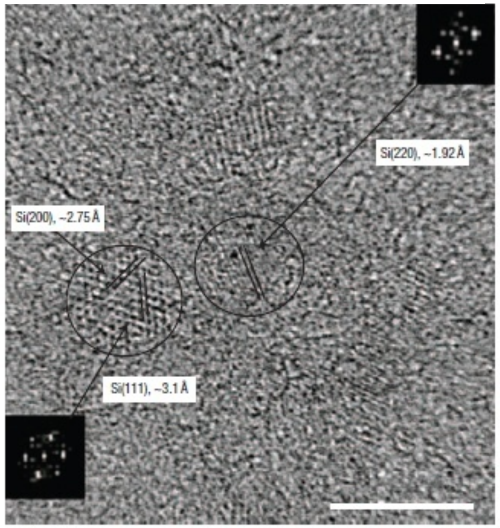




Scale bars- 250 nm.







Y. Chao, L. Siller, **S. Krishnamurthy**, *et al* **Nature Nanotechnology 2, 2007, 486 and this work has been cited in Science editors choice**

Sample growth and Characterisation Techniques

• **Sample growth techniques:** Ion implantation, Reactive ion etching, Pulsed Laser Deposition, PECVD, Electrochemical etching

Characterisation techniques

❖**PES** – for the identification of core levels and valence band for the PLD grown samples

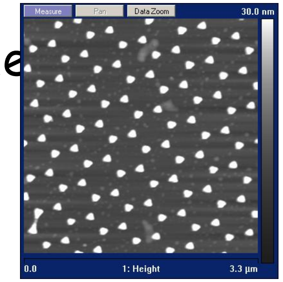
❖**XES and XAS-** Element specific spectroscopic technique gives necessary information about valence and conduction band – Partial Density of states

❖***AFM and SEM-*** To study the surface morphology, Roughness and distribution

❖**XRD, XRR and RHEED** to get necessary information regarding thickness of the PLD grown samples, orientation and crystallinity.

❖**Photoluminescence and Time resolved PL** spectroscopy to probe the luminescence features of nanocrystalline silicon

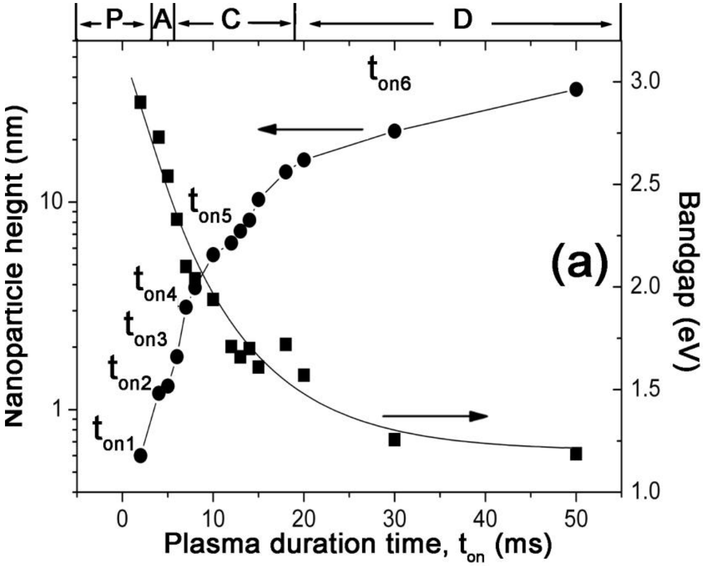
❖Lithography: e-beam lithography and Nanosphere Lithography



European Facilities

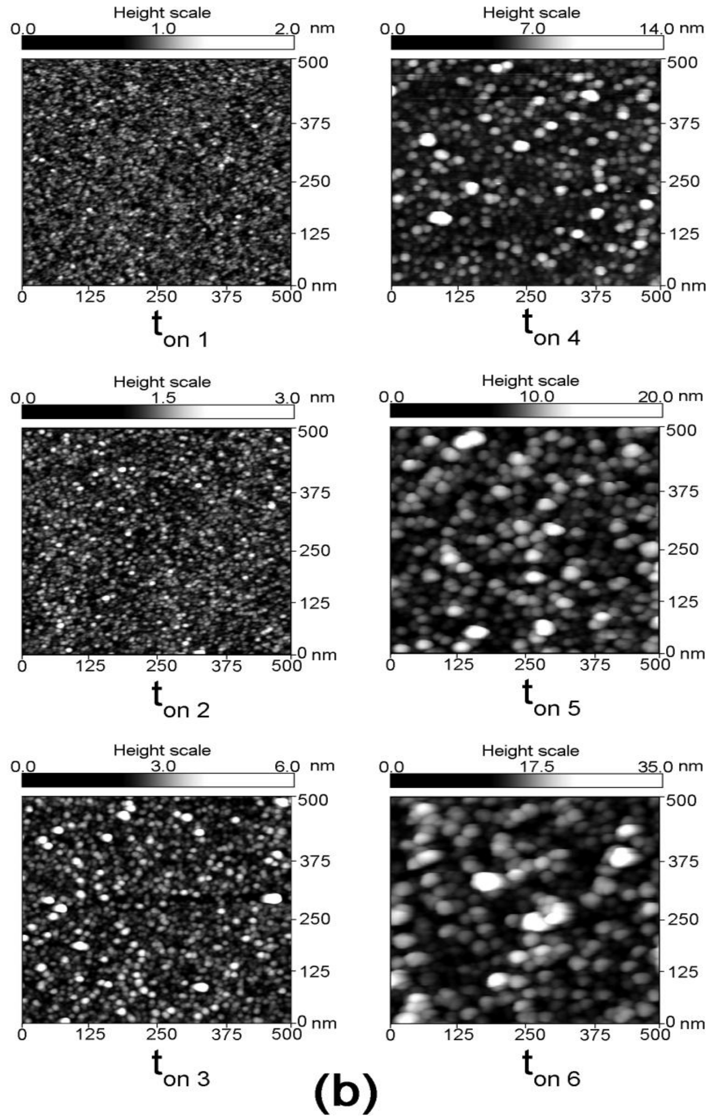
US Facilities

Large scale production of Si nanocrystals by PECVD at Berkeley



(a) Height of Si nanoparticles and bandgap value of the nc-Si films constituted by these nanoparticles as a function of the plasma duration time t_{on}. Regions P, A, C, and D correspond to polymerization, accumulation, coalescence, and surface deposition growth phases, respectively.

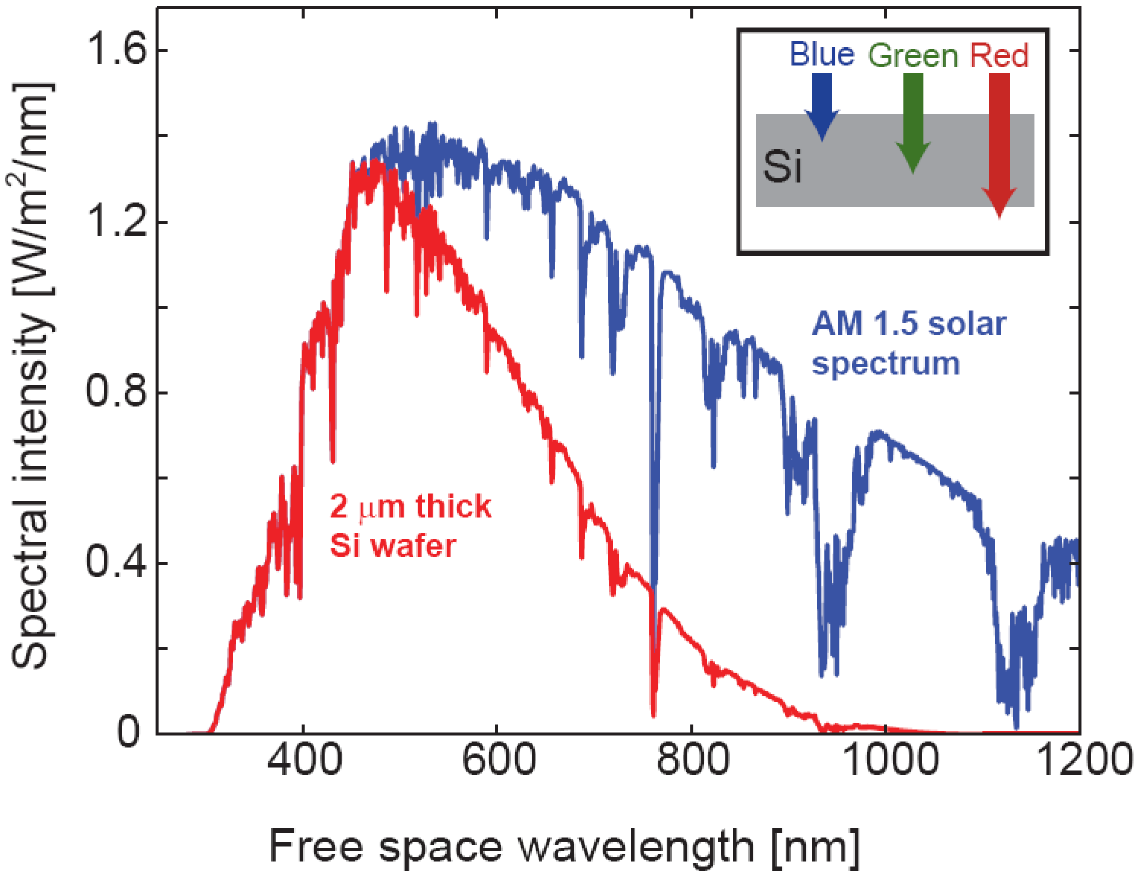
(b) AFM images corresponding to each experimental point related to a given plasma duration time, $t_{on\ i}$



S. Krishnamurthy et al unpublished

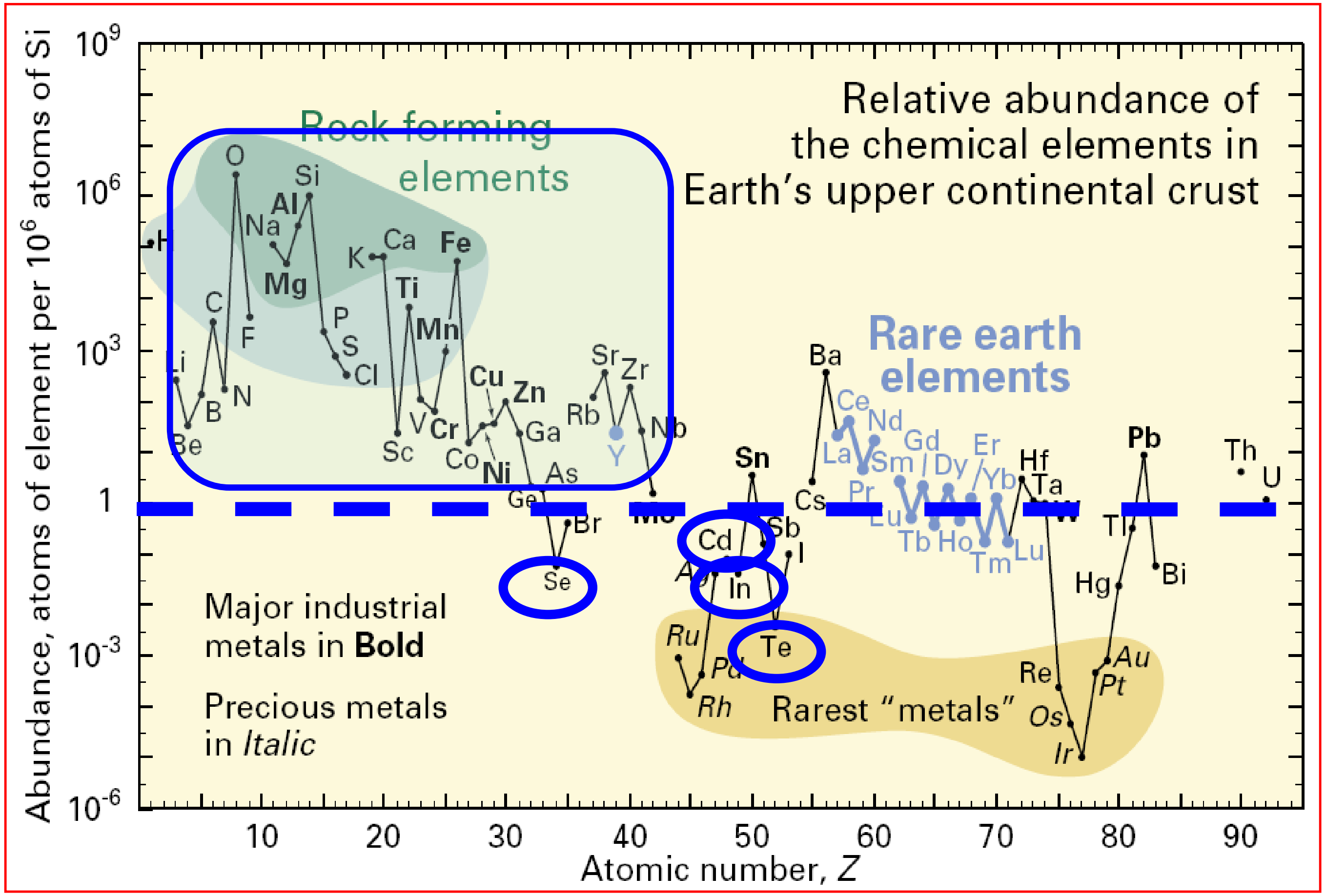
Silicon Solar cell for PV applications

Light is poorly absorbed in Silicon solar cells

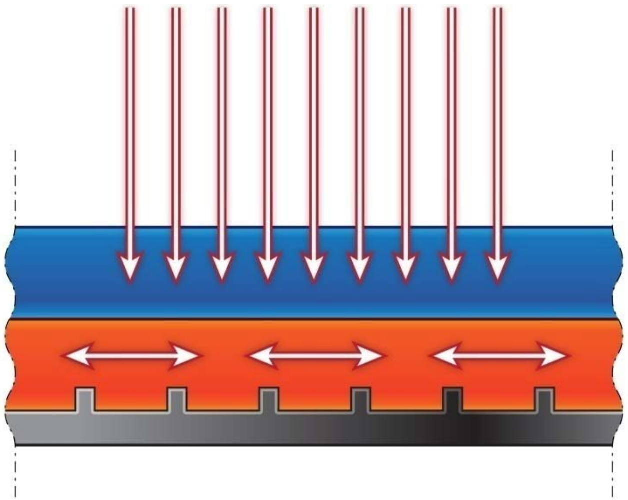


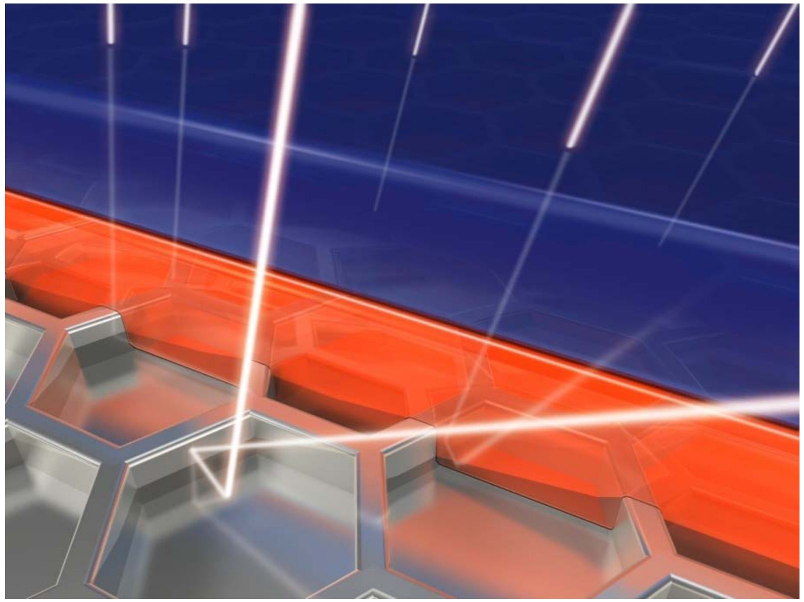
Why Si

Relative abundance of elements vs. atomic nr.

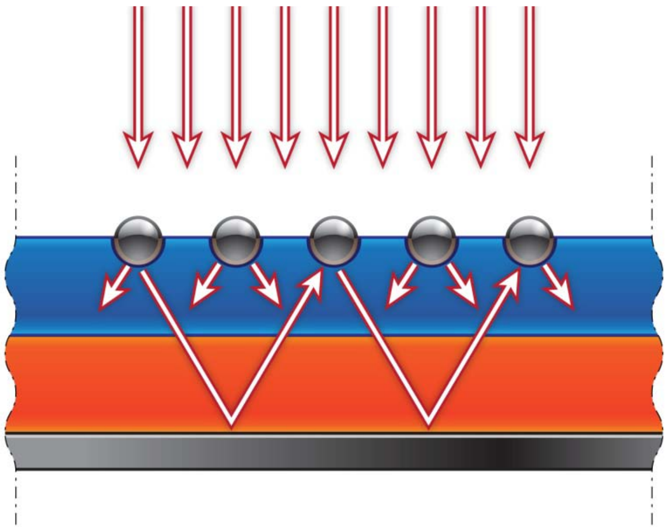


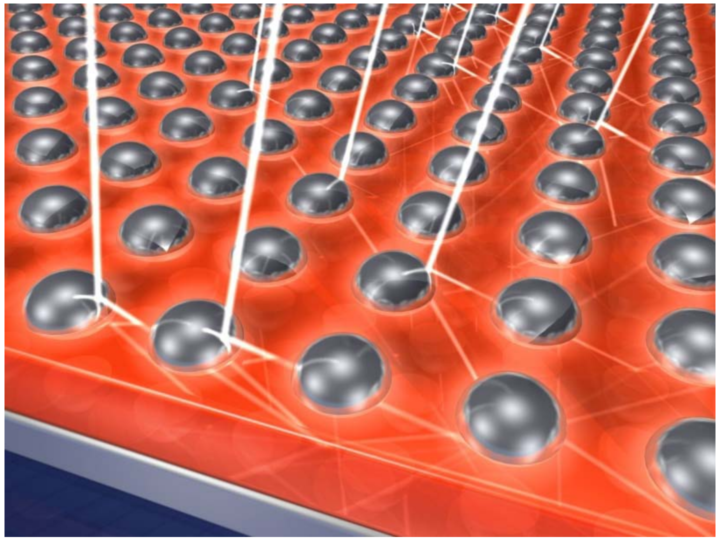
Light Trapping in Si



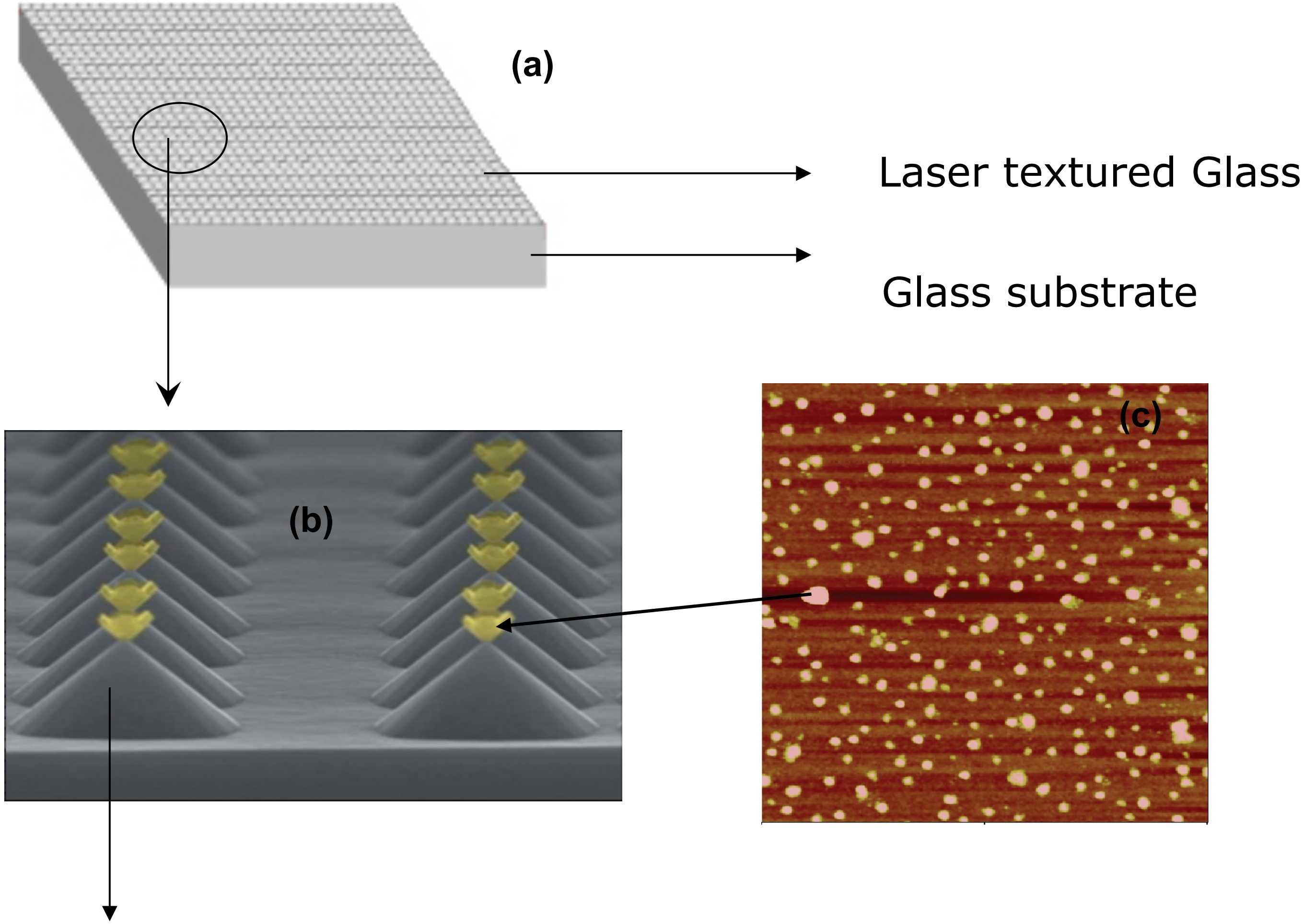


Model for light trapping





Commercialisation application in process for solar cells



PECVD deposited Si on Glass

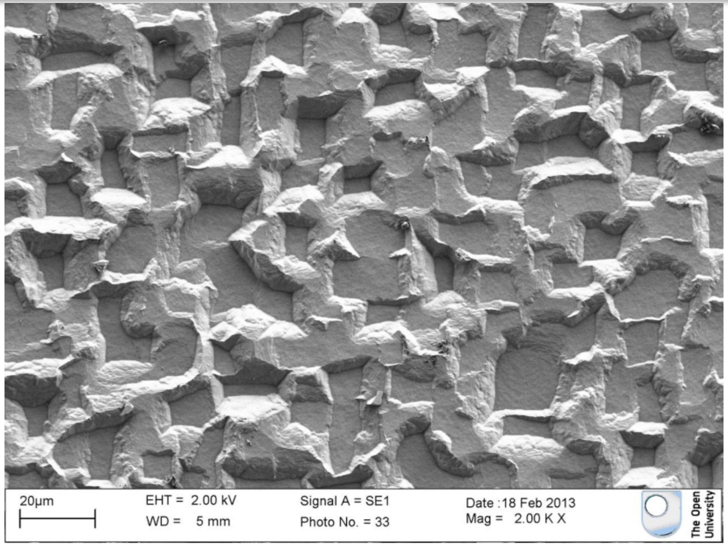
PECVD deposited Si on Glass

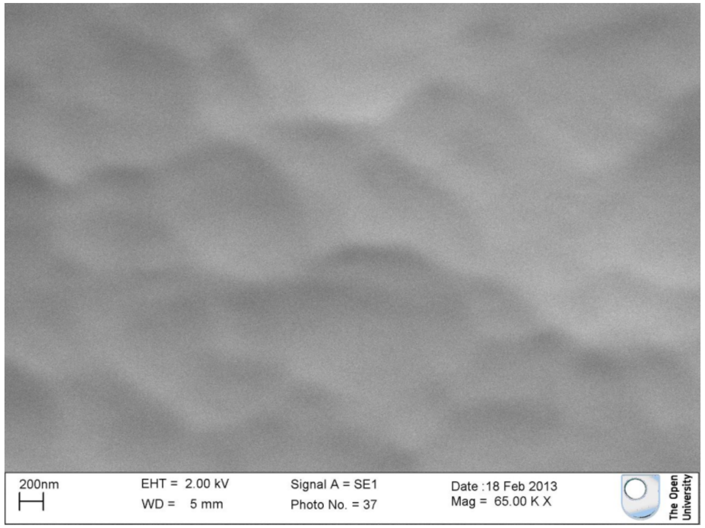
S. Krishnamurthy et al, J. Nanosci. Nanotech 2009, S. Krishnamurthy et al phys.stat.solidi 2011,

Commercialisation Grant to be submitted in collaboration with Dr. Dermot Brabazon and Prof Patrick McNally, Dublin City University

Bare Silicon

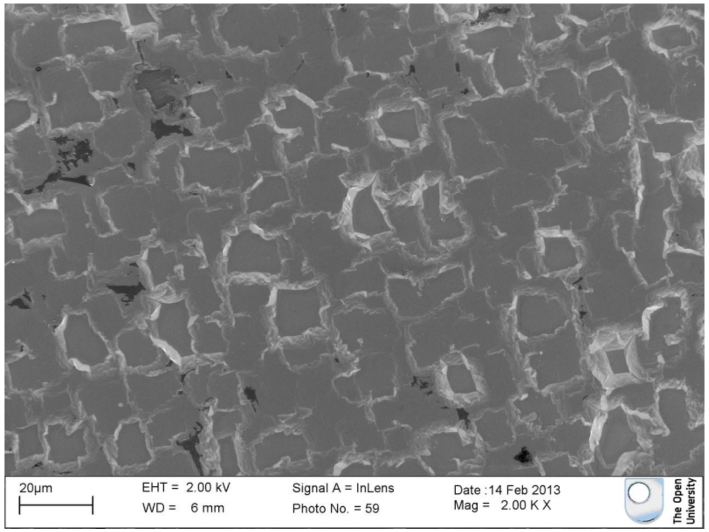
Bare Silicon

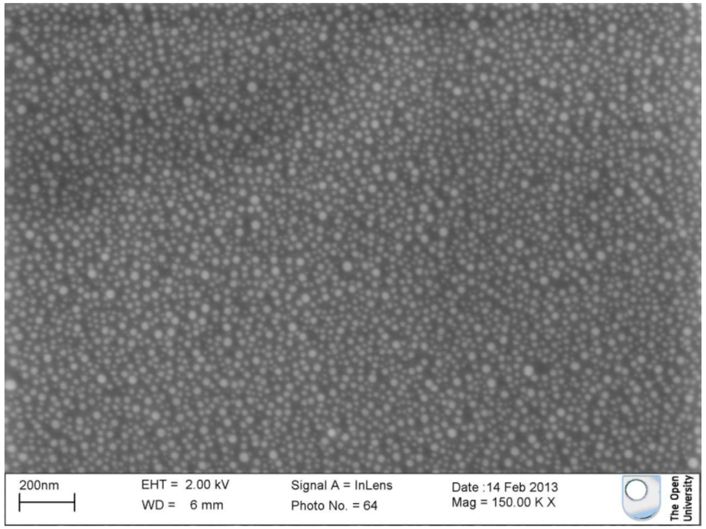




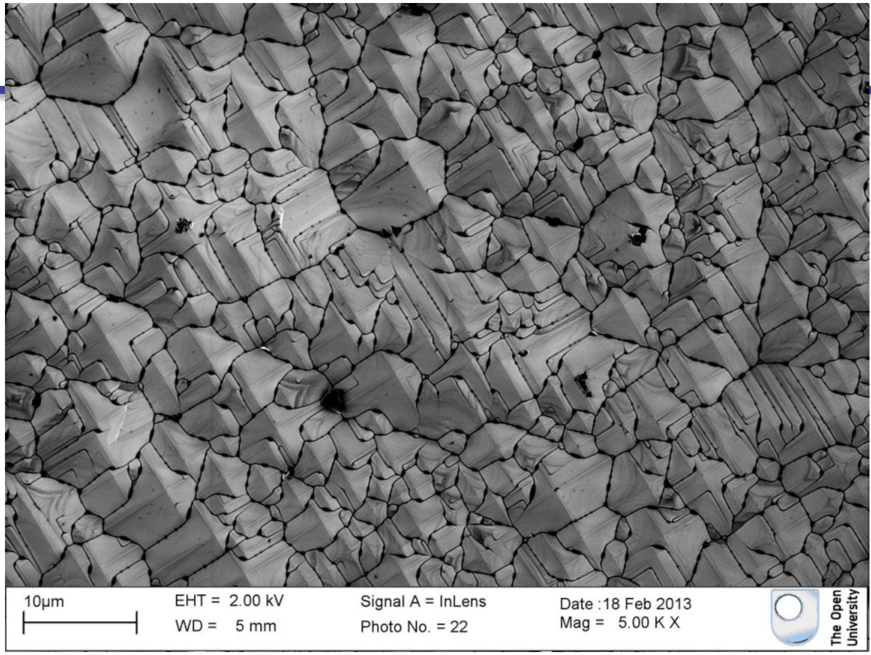
Ag nanoparticles on Si

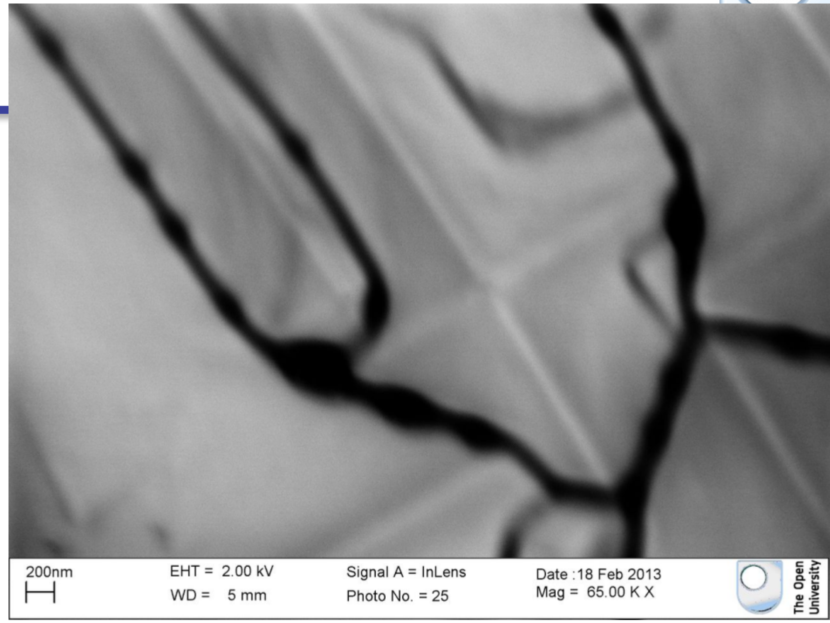
Ag nanoparticles on Si

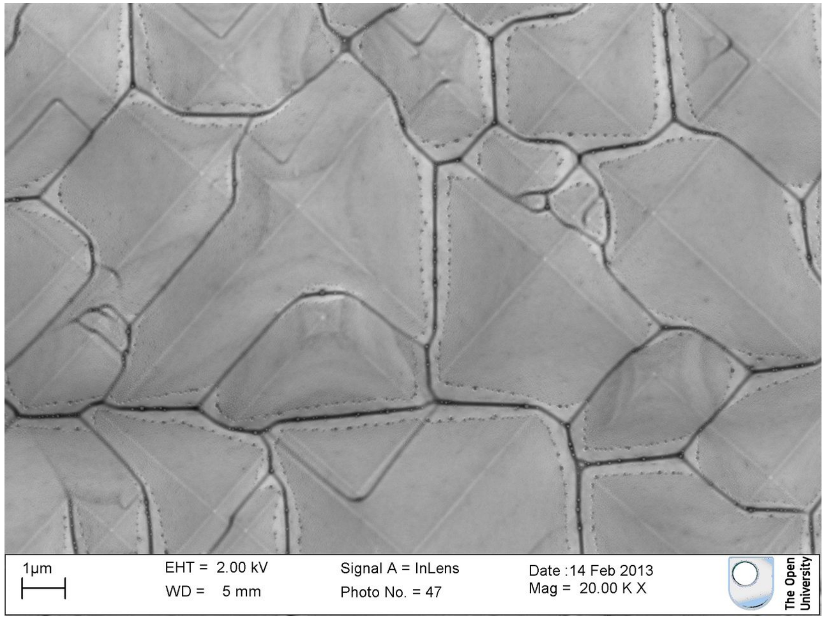


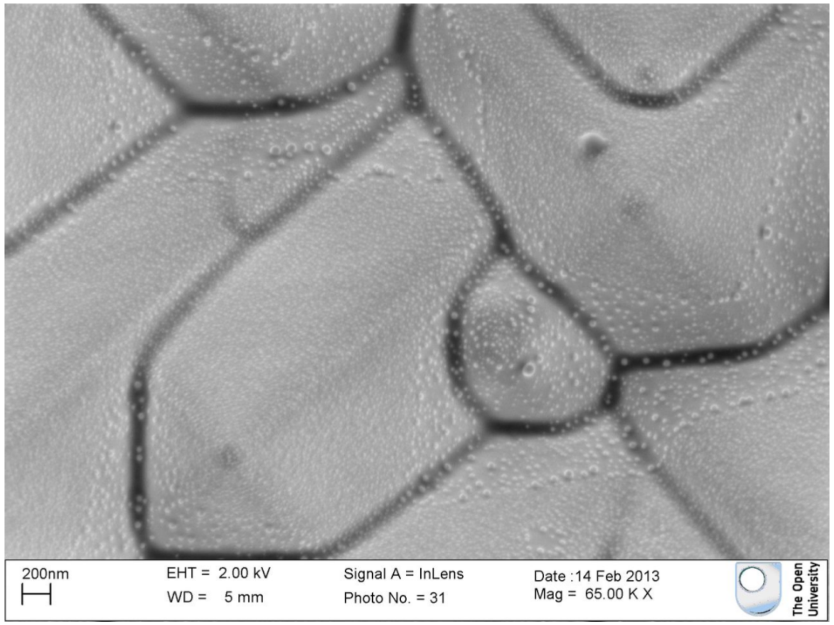


Bare PNJ on the top and Ag nanoparticles deposited on

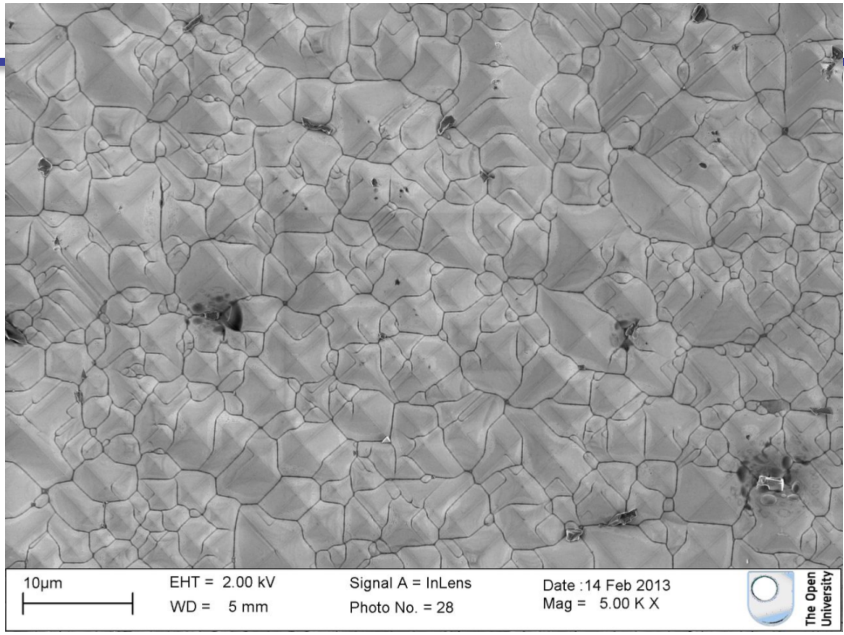


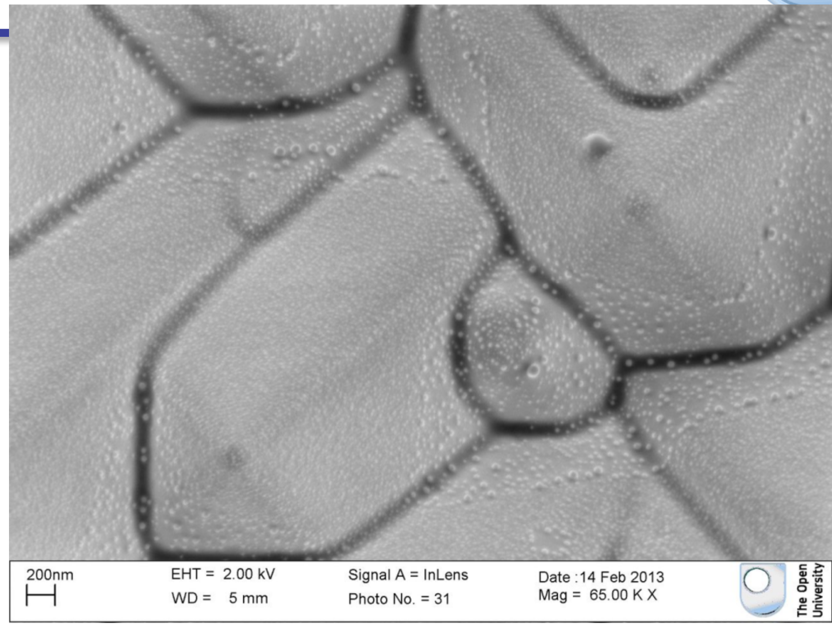


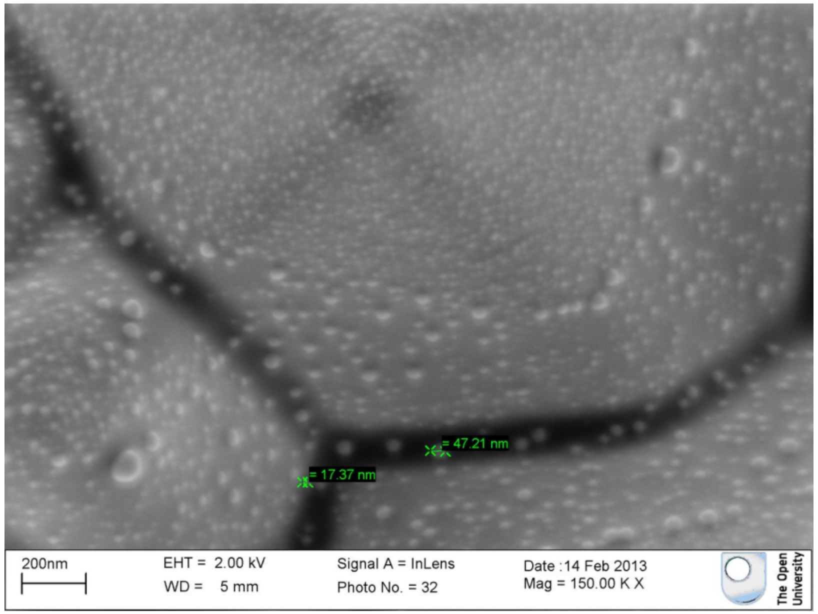


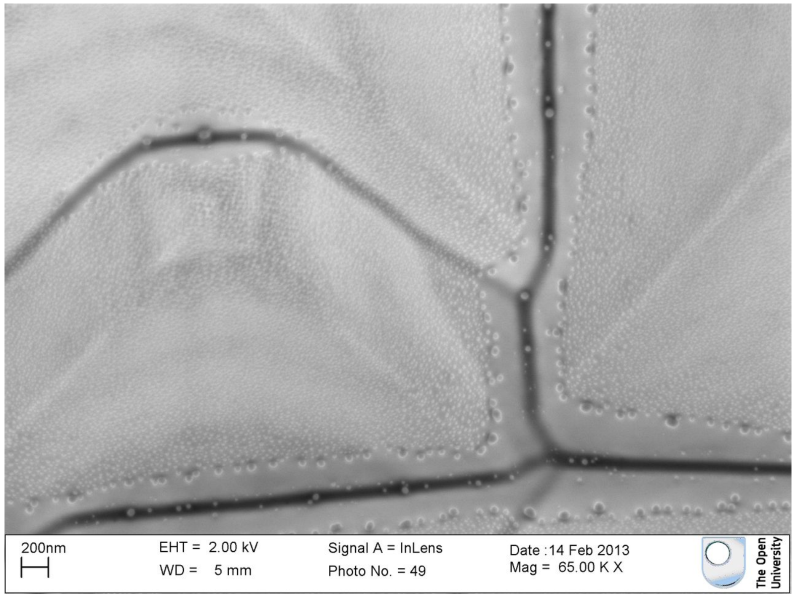


Nanoparticle on pnj on annealing for 35 s





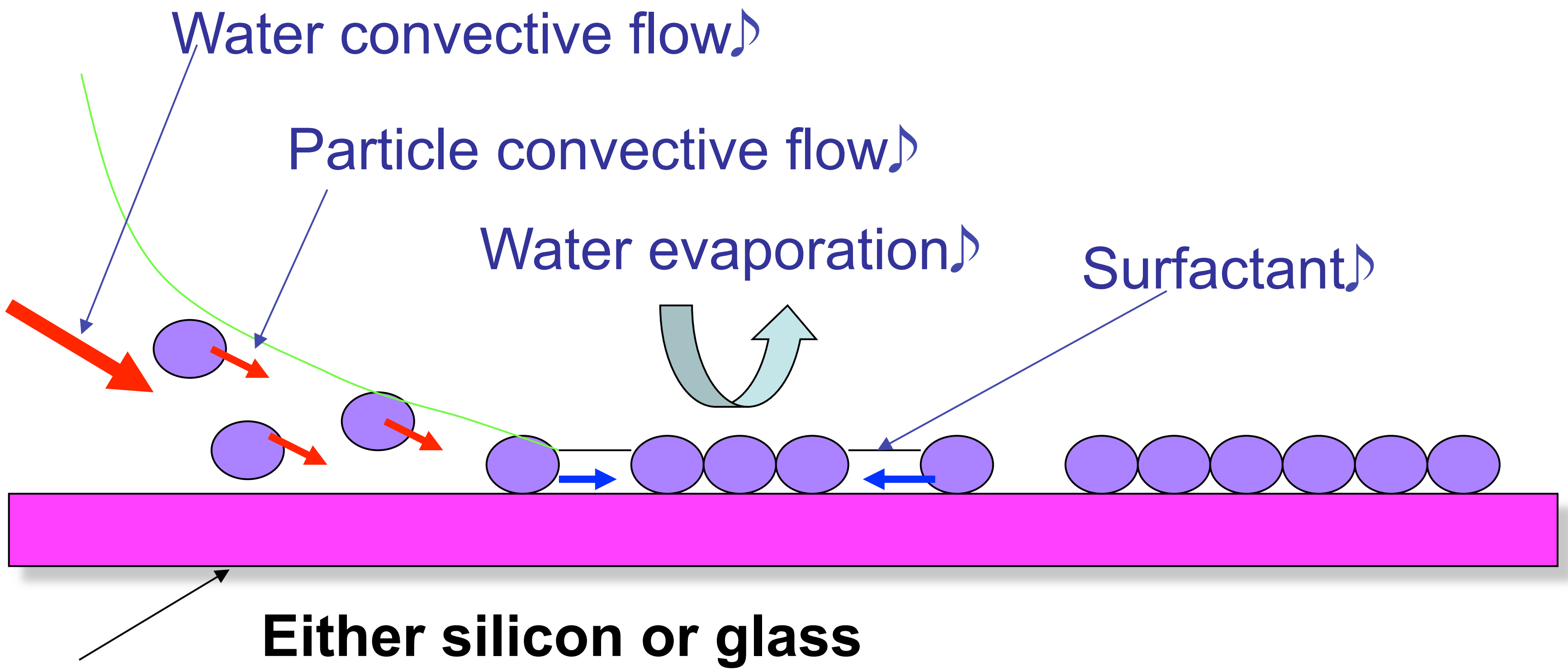




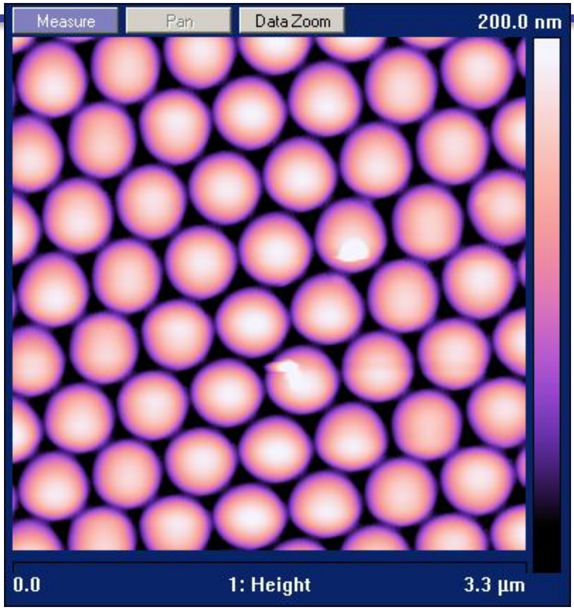
Nanosphere Lithography♪

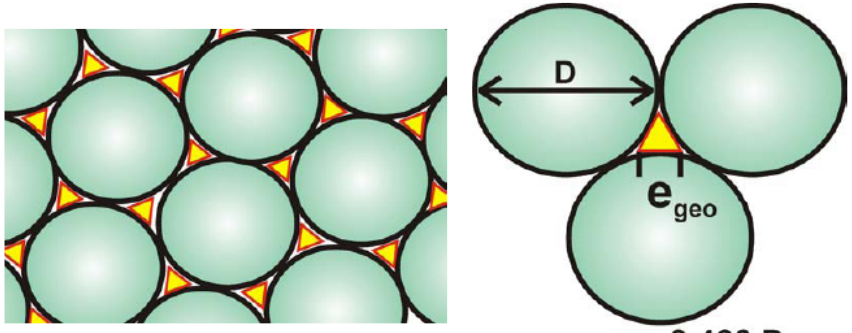
Produced by Surfactant

- Capillary force (Surface tension)due to meniscus formation
- Convective flow due to water evaporation

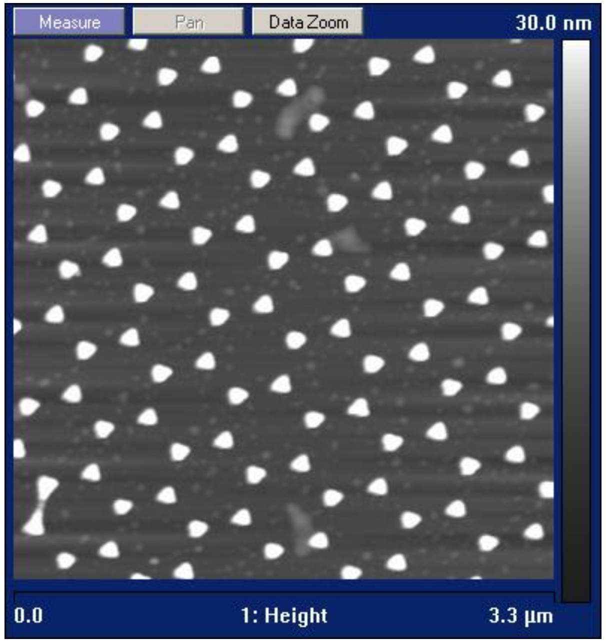


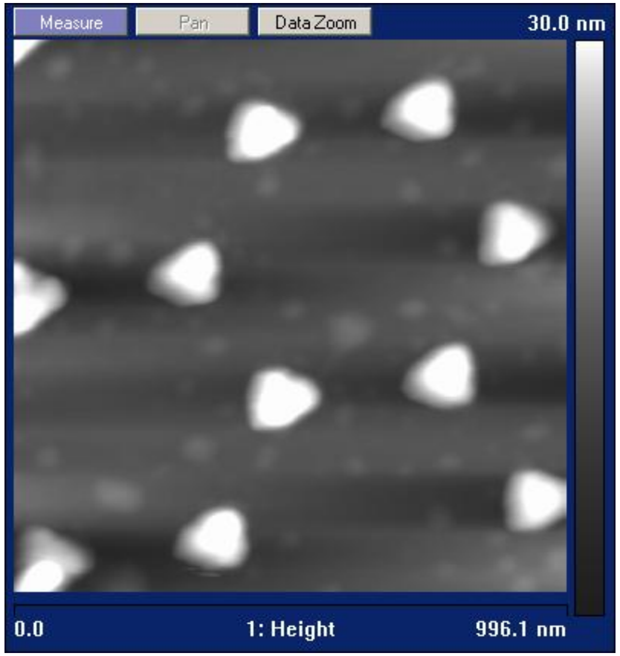
AFM and SEM Images of the patterned surfaces





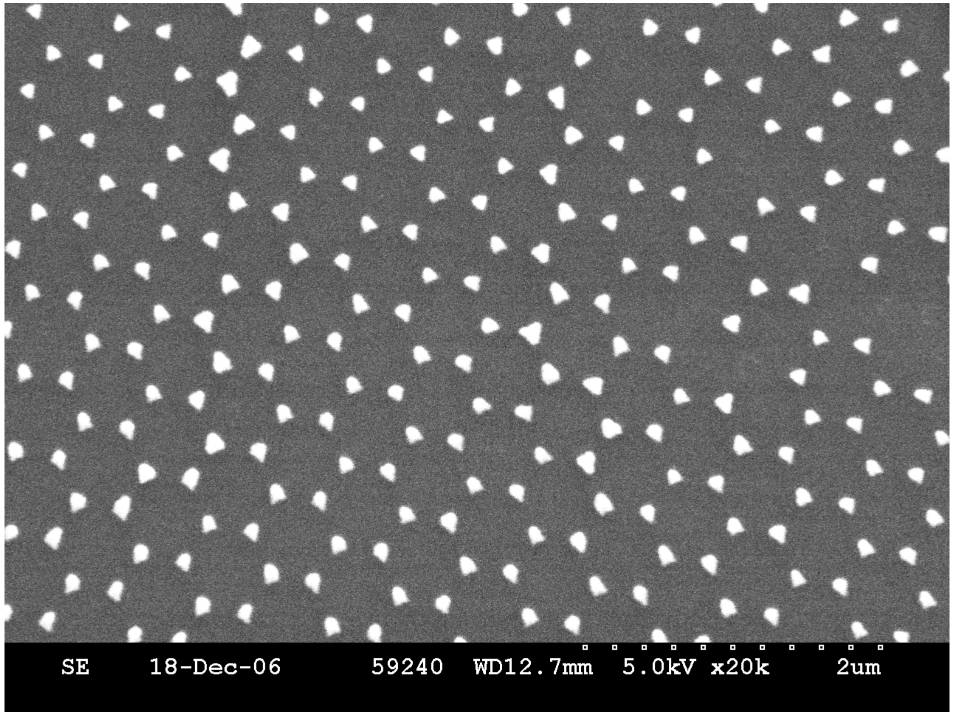
$$e_{geo} = \frac{0.466\ D}{\tan 60}$$





Patterned nanorods for energy harvestingon glass

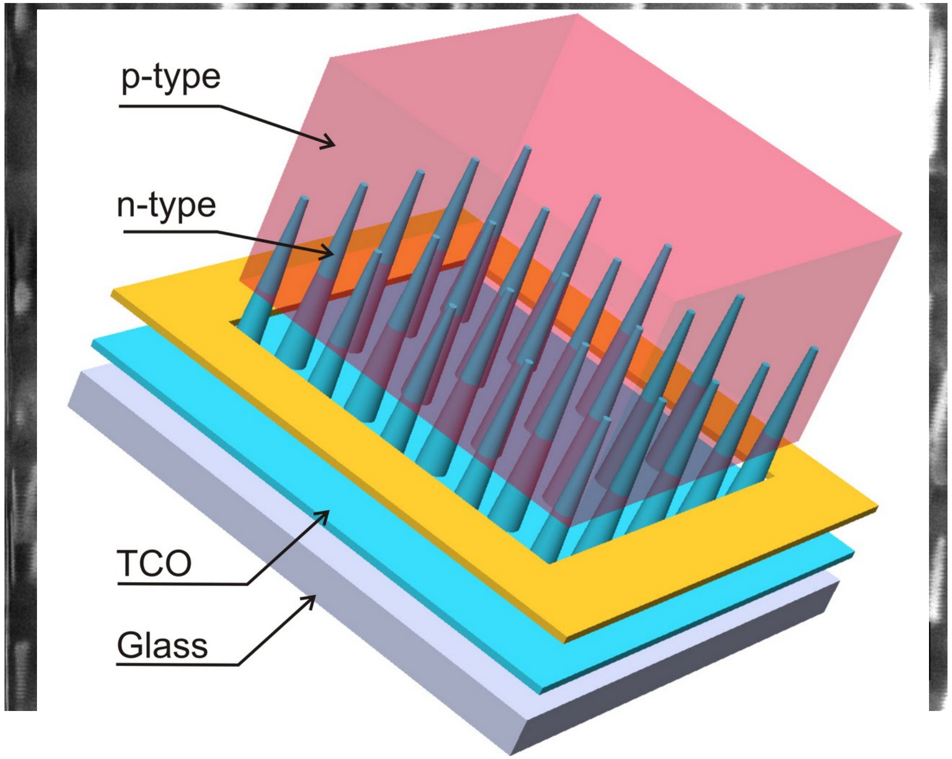
Gold nanostructures by NSL



Krishnamurthy et al unpublished

Si Nanorods for solar cells

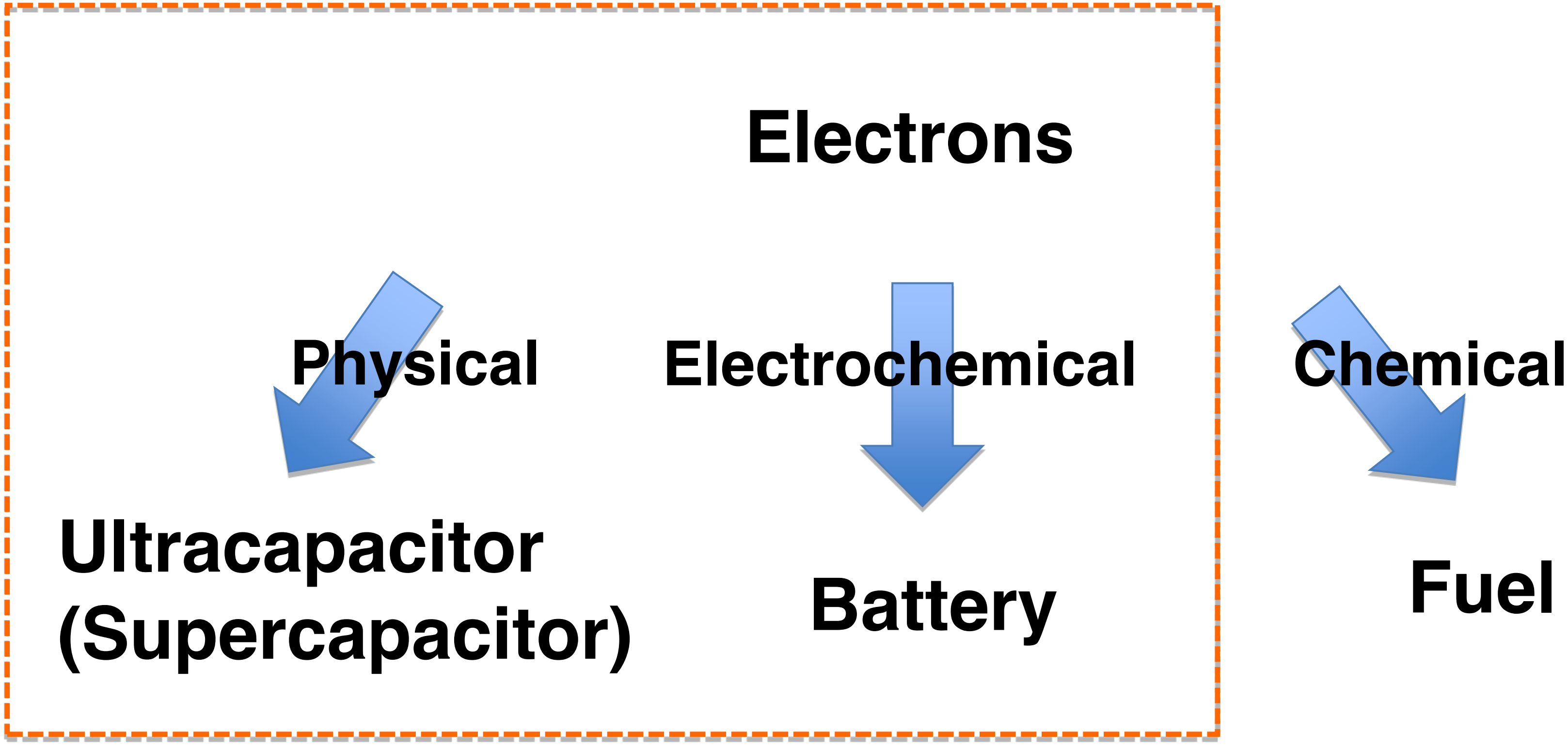
Si nanorods grown on NSL



Si nano rods – n type
Semiconductor- p type

Energy Storage

Electrical Energy Storage

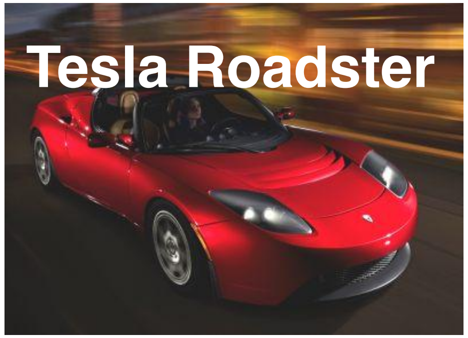


Energy Storage - Challenges

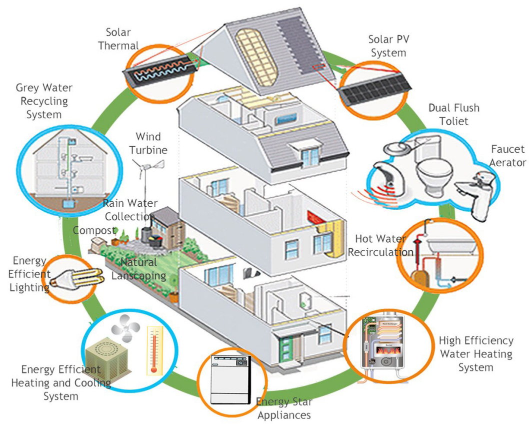
Portable applications: energy density




Electrical Vehicles



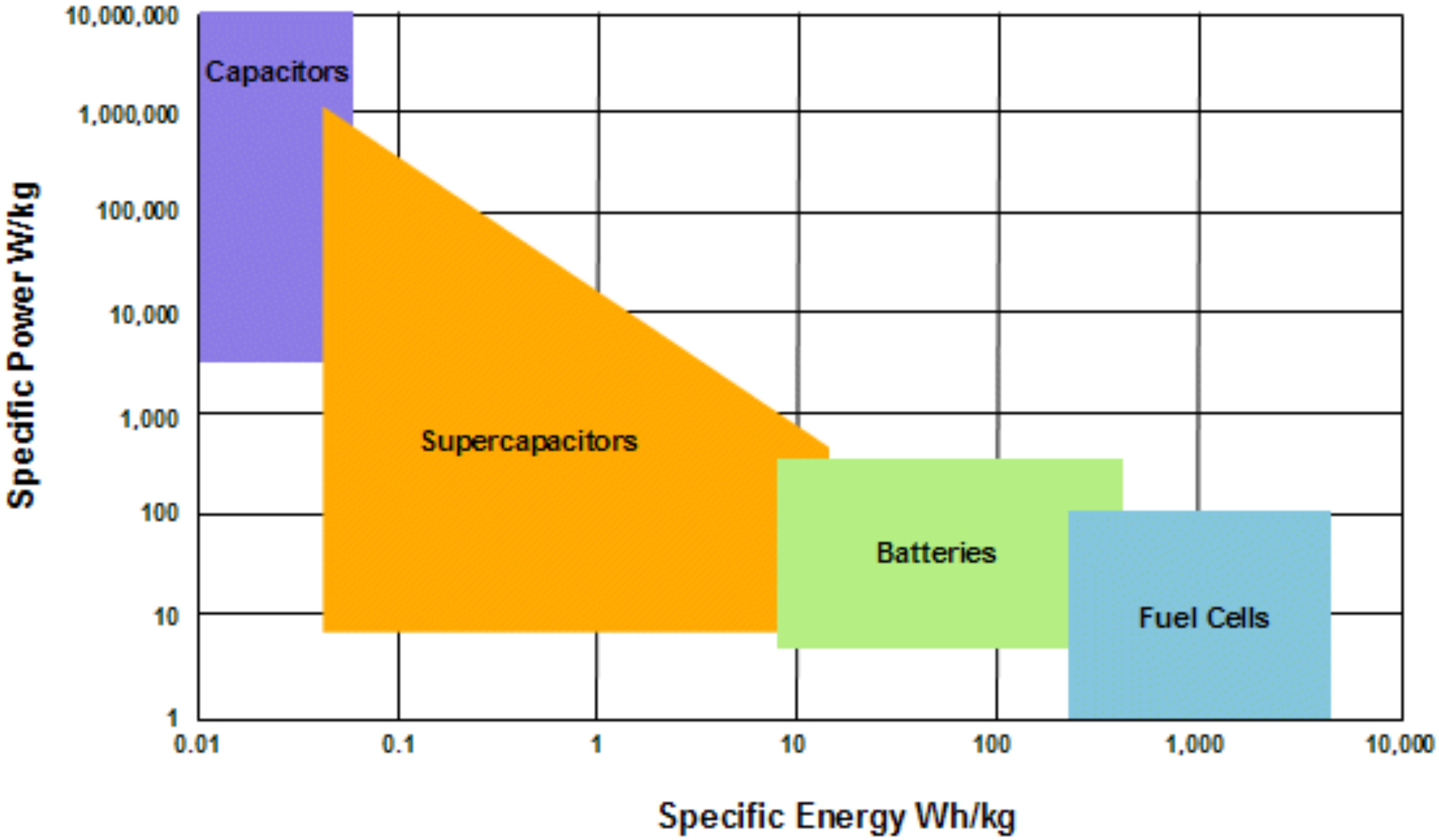
Stationary applications: cost, power



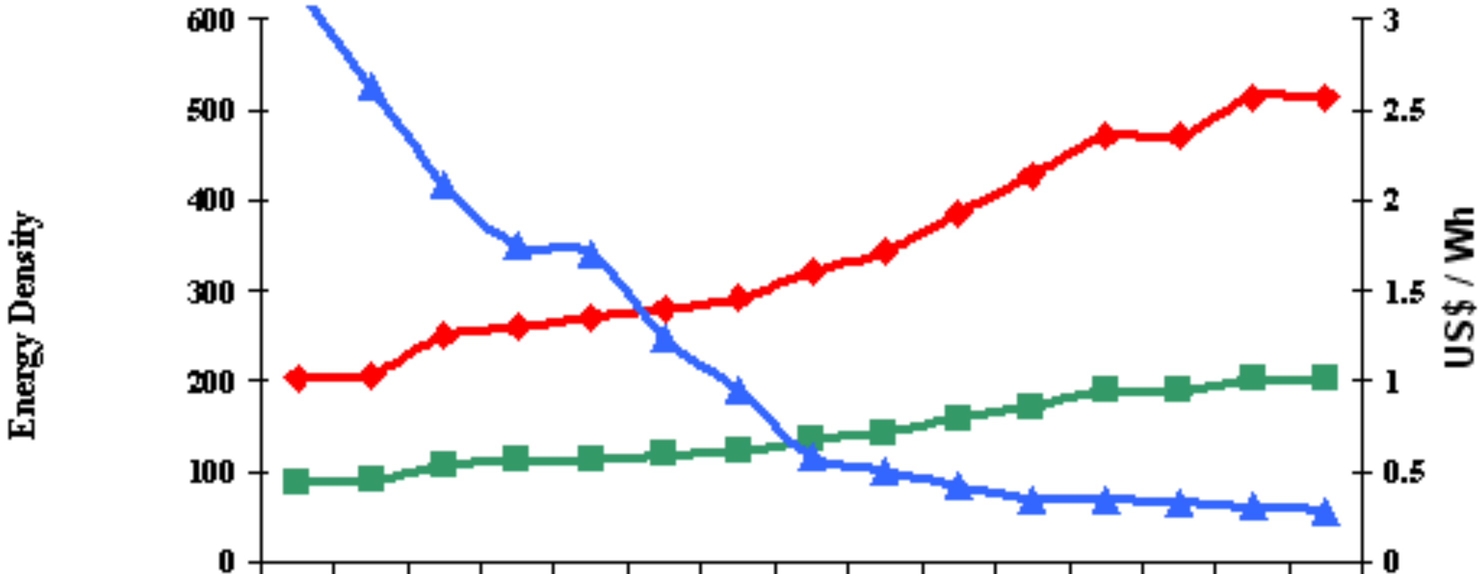
Parameters of Energy Storage

- Energy density (volume); Specific Energy (weight)
- Power density; Specific power
- Cycle life, calendar life
- Safety
- Cost
- Round trip energy efficiency

Comparison of Energy Storage



Energy density and price



	'91	'92	'93	'94	'95	'96	'97	'98	'99	'00	'01	'02	'03	'04	'05
Wh/l	204	208	250	260	271	281	292	321	343	386	428	471	471	514	514
Wh/kg	88	90	108	113	114	119	123	135	143	159	172	189	189	202	202
US$/Wh	3.17	2.63	2.09	1.75	1.71	1.24	0.95	0.59	0.51	0.42	0.35	0.35	0.33	0.31	0.28

Improvement only 8% per year hence new materials needed to manage the gap

Electrode materials determine the specific energy.

$$\text{Specific Energy} = \frac{\text{Voltage} \times \text{\# of movable Li ions in electrodes}}{\text{Battery weight}}$$

Negative electrode
Graphite: 370 mAh/g

Positive electrode
$LiCoO_2$ 150 mAh/g
$LiMn_2O_4$ 140 mAh/g
$LiFePO_4$ 170 mAh/g

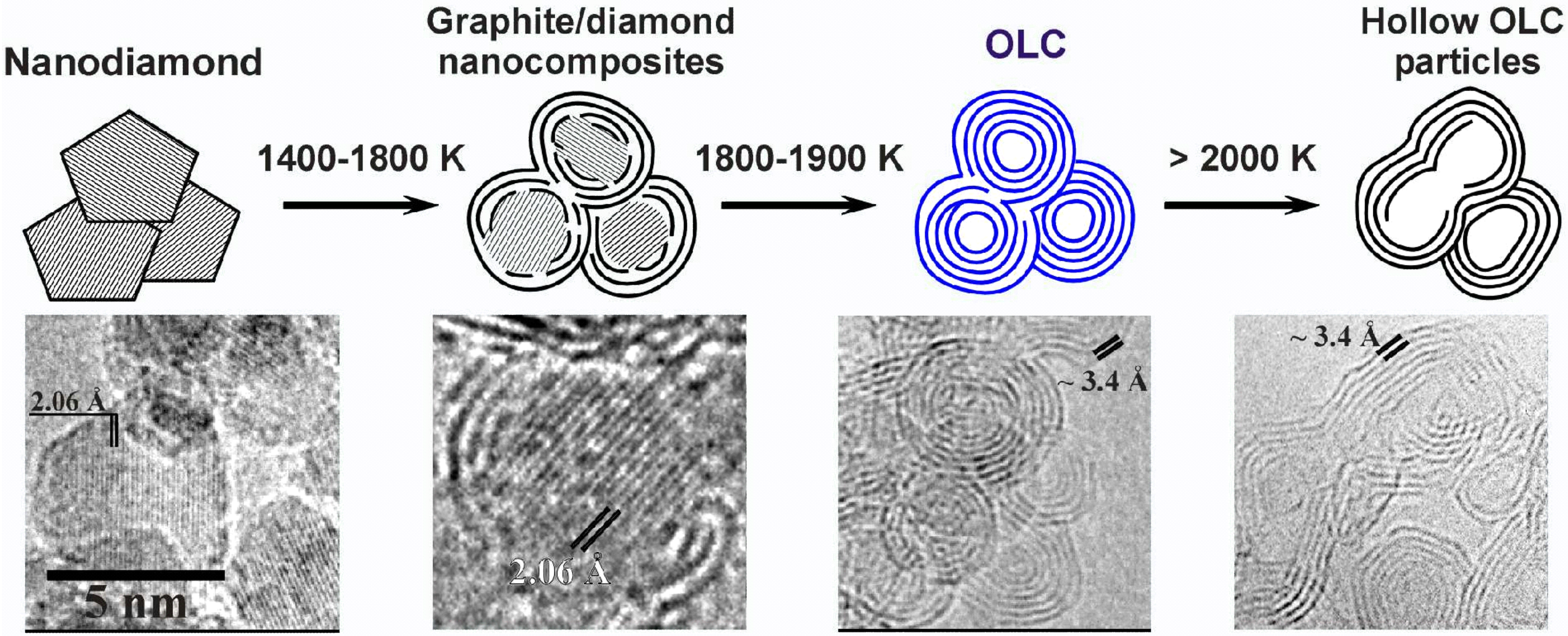
Future high capacity materials

Negative electrode
- Si (4200 mAh/g)
- Sn (900 mAh/g)
- Li metal

Positive electrode
- Sulfur (1673 mAh/g)
- Air (very high)

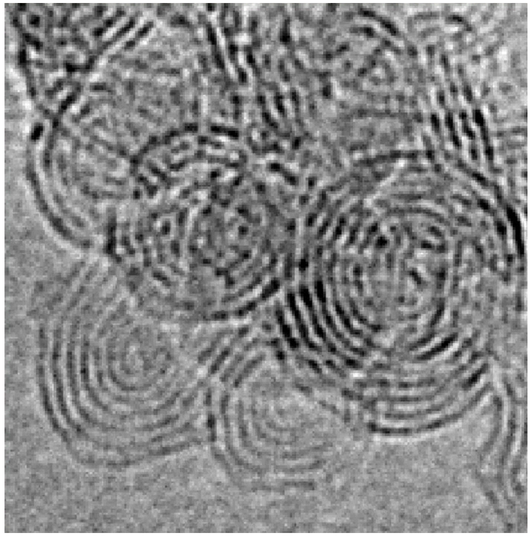
Carbon onion from Nanodiamond

We developed technique, which allows producing hundreds of grams OLC by heat treatment of NANODIAMOND (ND)



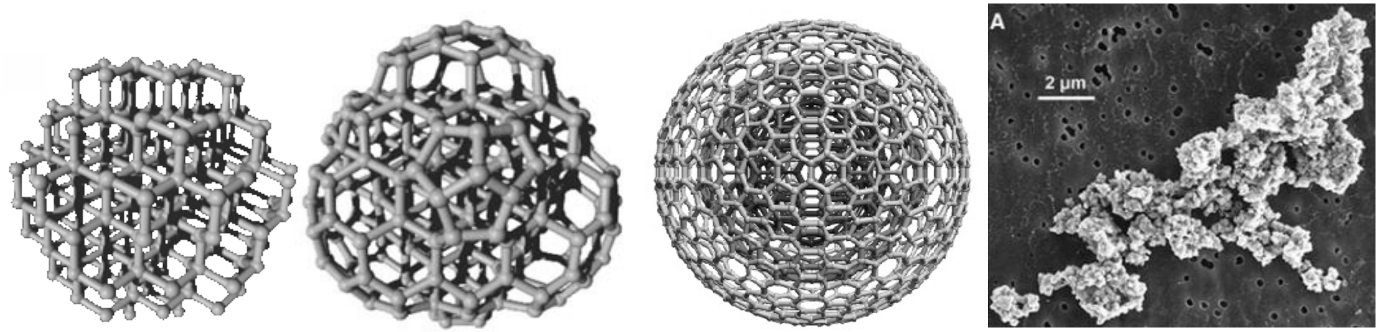
V.L. Kuznetsov, A.L. Chuvilin, Yu.V. Butenko, et al., *Chem. Phys. Lett.* 222 (**1994**) 343.
Yu.V. Butenko, V.L. Kuznetsov, A.L. Chuvilin, et al., *J.App.Phys.*, 88 (**2000**) 4380.

CARBON ONION



Possible OLC formation and applications

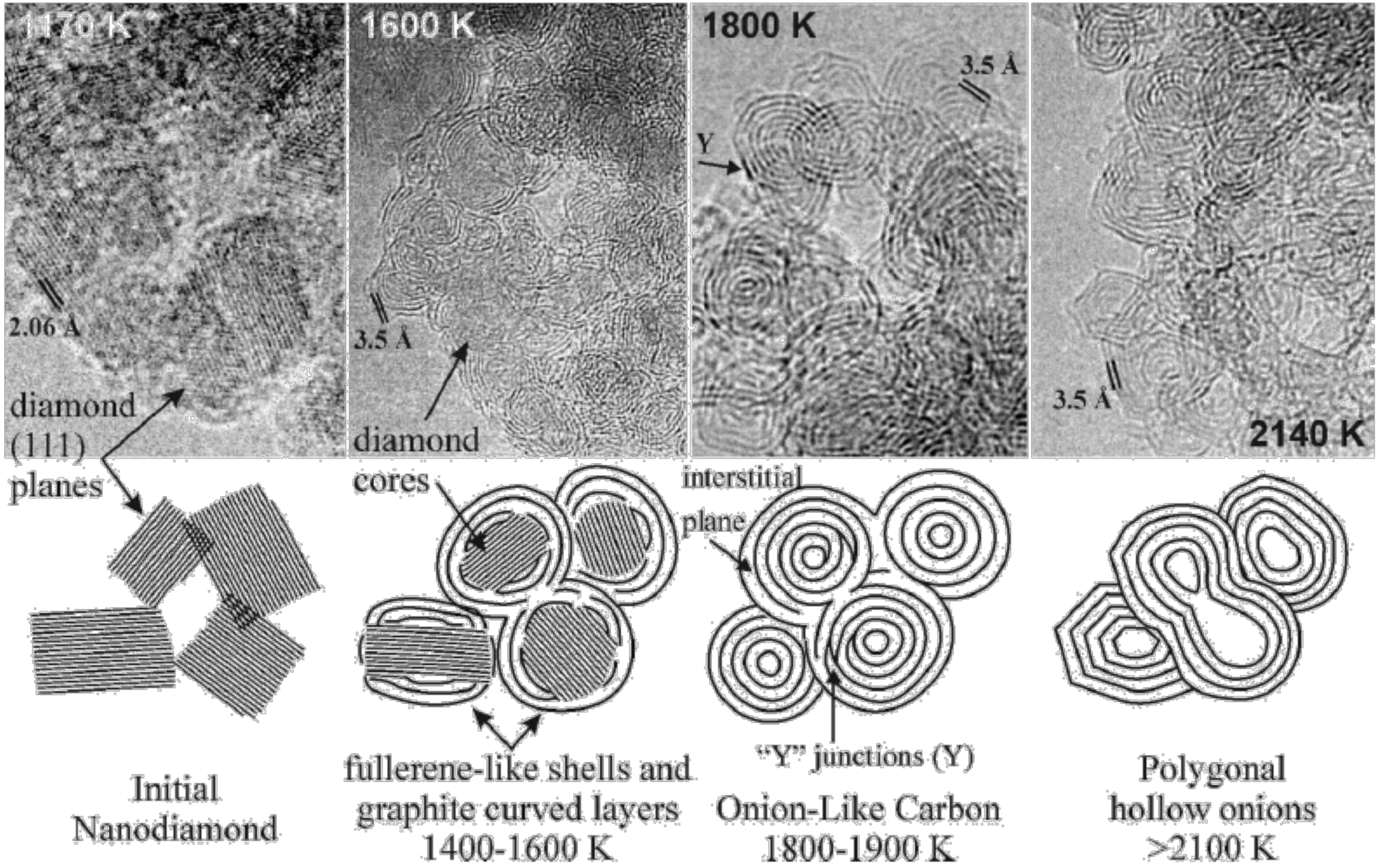
(a) (b) (c) (d)



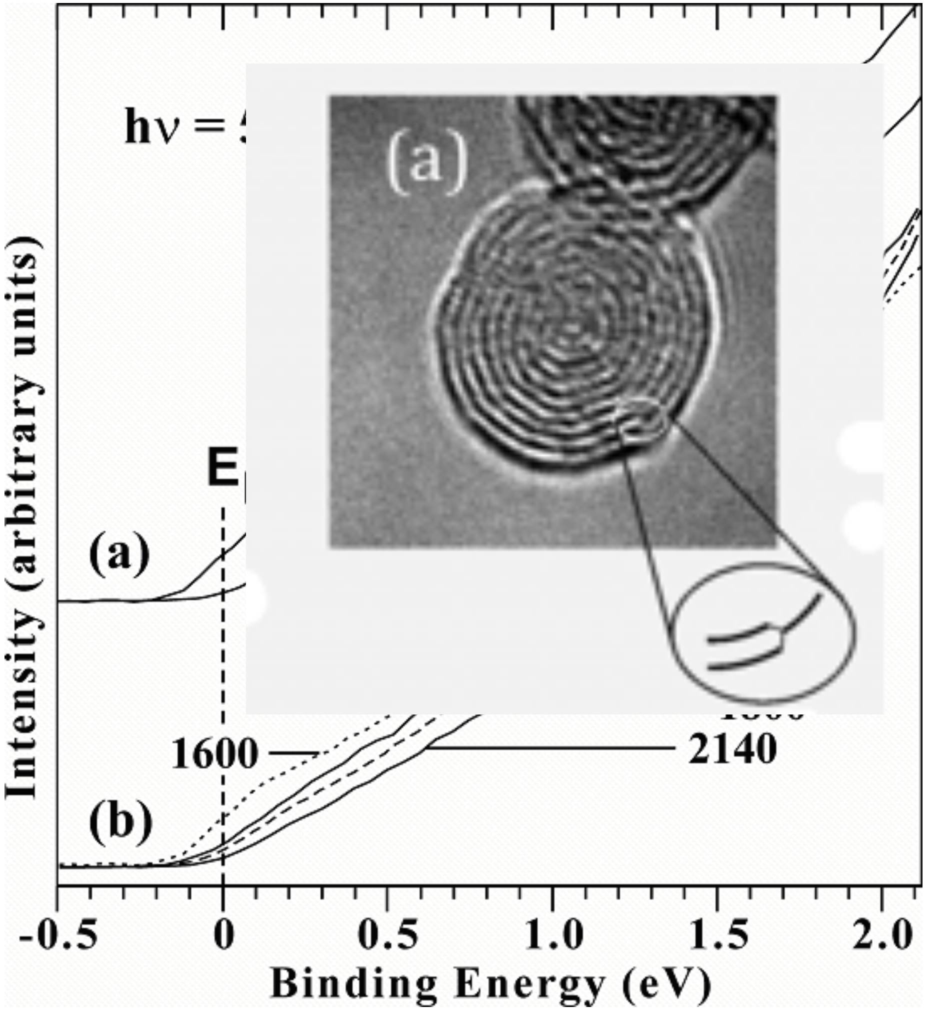
(Nanodiamond) (Diamond –core Fullerene like shells Outside) (Onion-like carbon) (Interstellar-dust)

- OLC has high surface area- hence can be used as a support for catalyst for **fuel cells applications**
- Defects in OLC causes the electron hoping phenomena and hence shows the existence of magnetic moments.
- It could be used as a lubricant in motor industry.

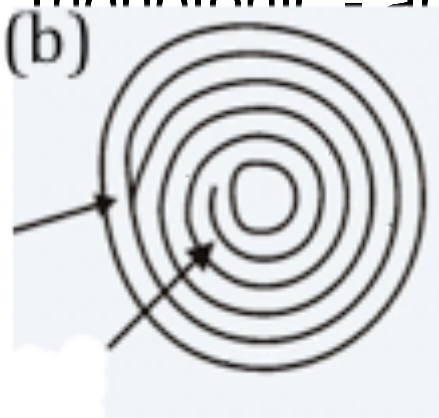
OLC Via annealing nanodiamond



Yu. V. Butenko, **S. Krishnamurthy et al**, Physical Review B, 71,075420 and **S. Krishnamurthy** et al Carbon 2013

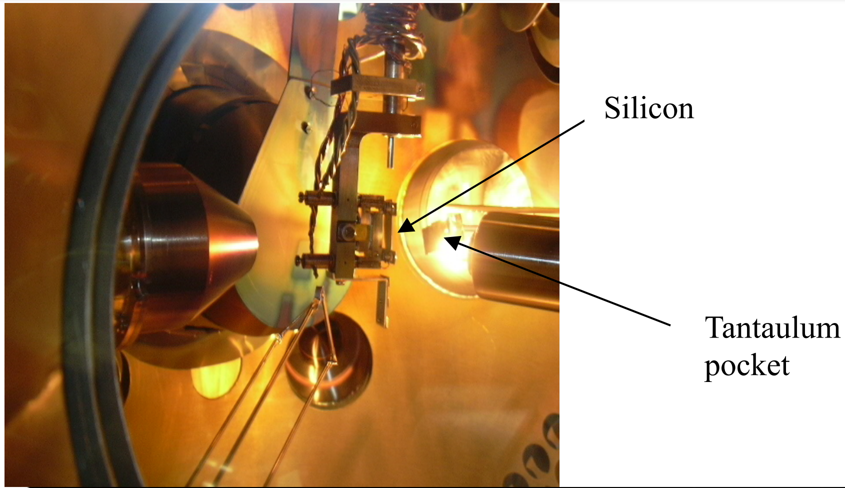


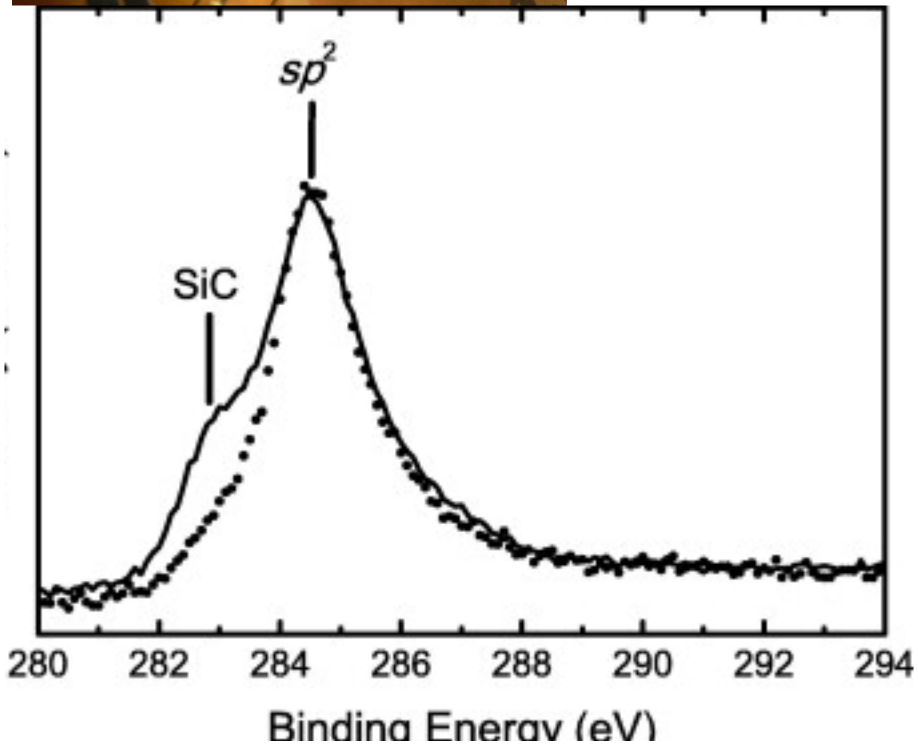
However, the process is not

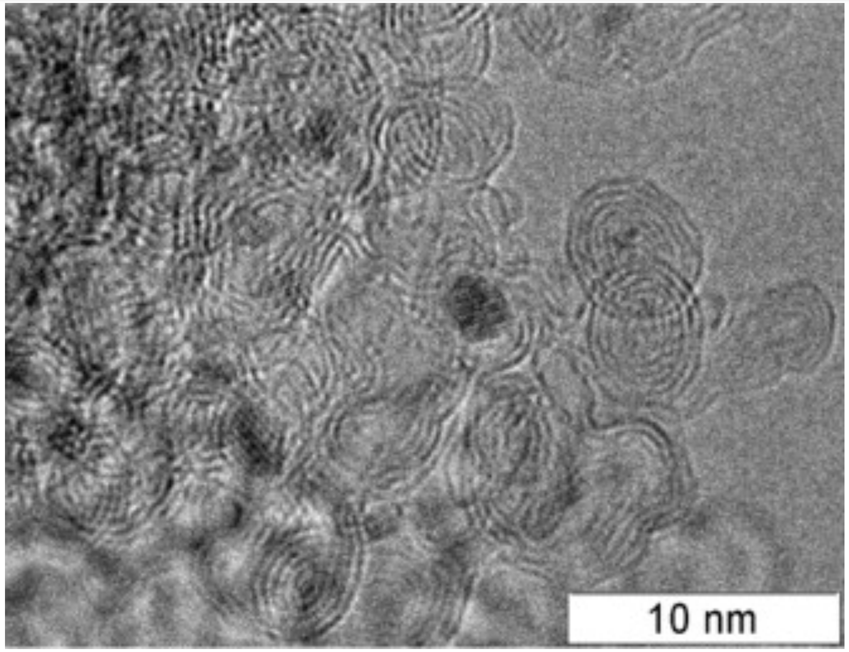


Possible reason for these may be the defects such as Y- Junctions or seven membered rings or multiple defects.

Insitu evaporation of OLC

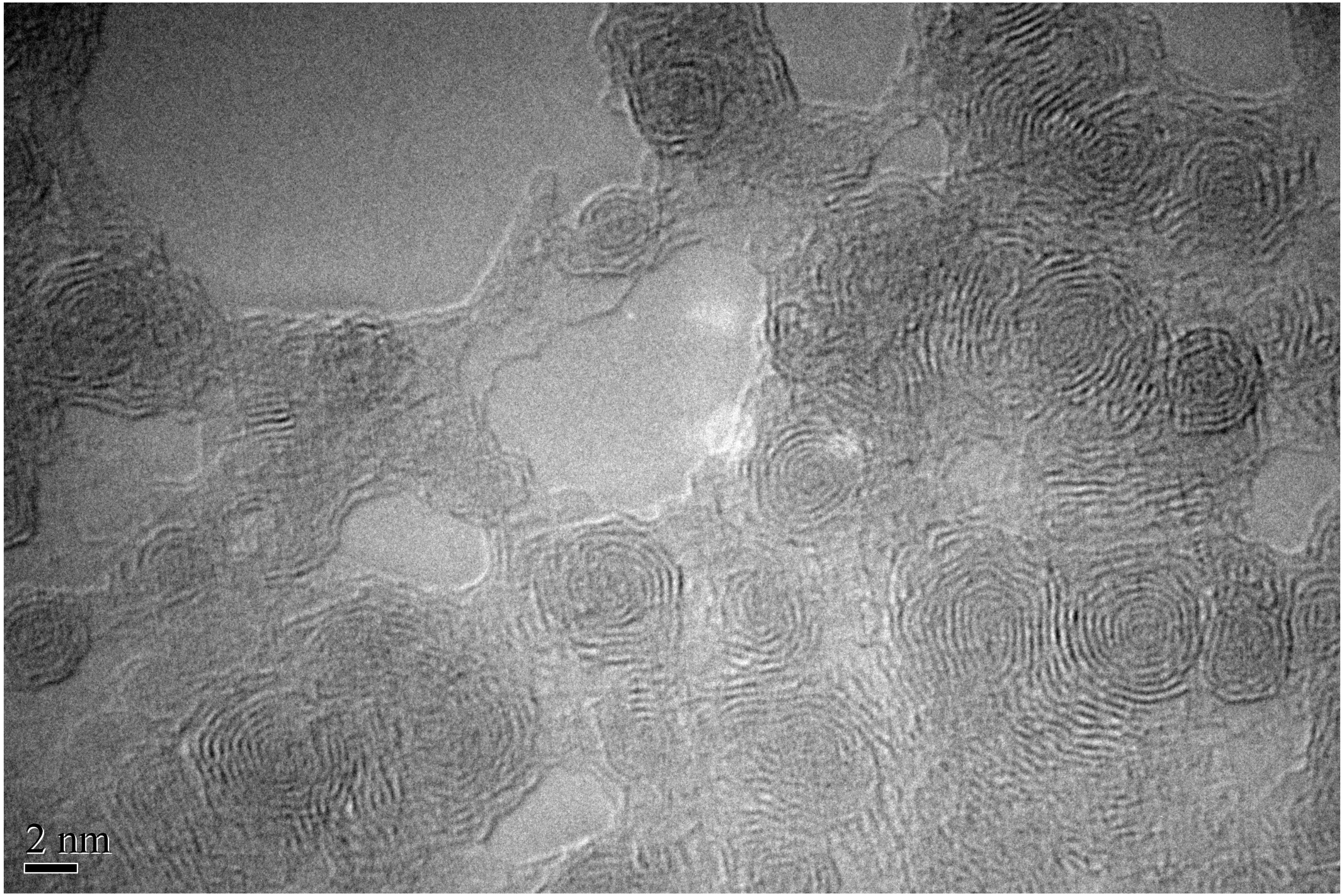






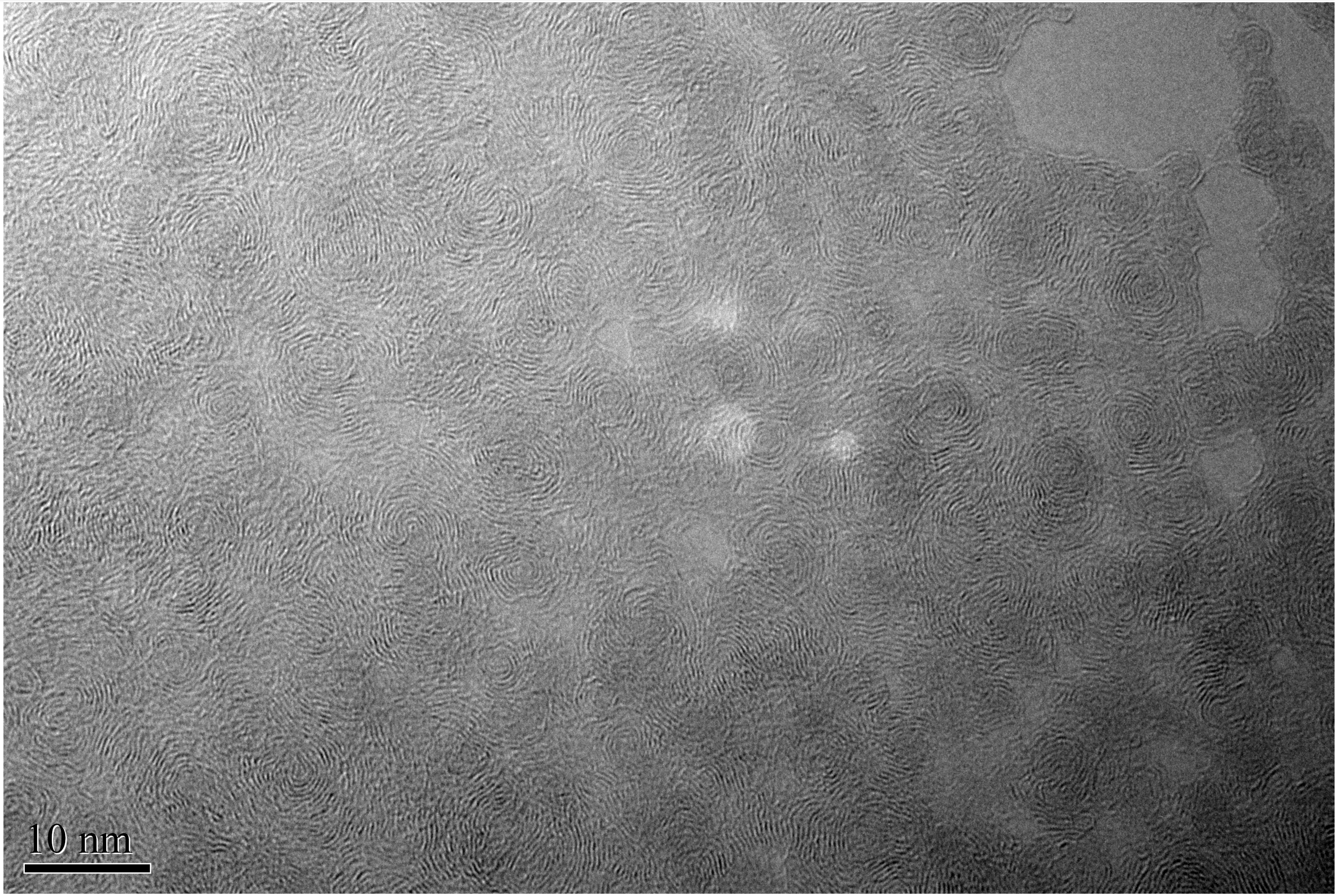
S. Krishnamurthy et al Carbon, 52, **2013**, 145

Annealing and plasma modification of surfaces to prepare homogenous growth of OLC



Emer Dufffy, Krishnamurthy et al in preparation

Monolayer production of onion-like carbon



Future onion work on supercacitors

LETTERS NATURE NANOTECHNOLOGY DOI: 10.1038/NNANO.2010.162

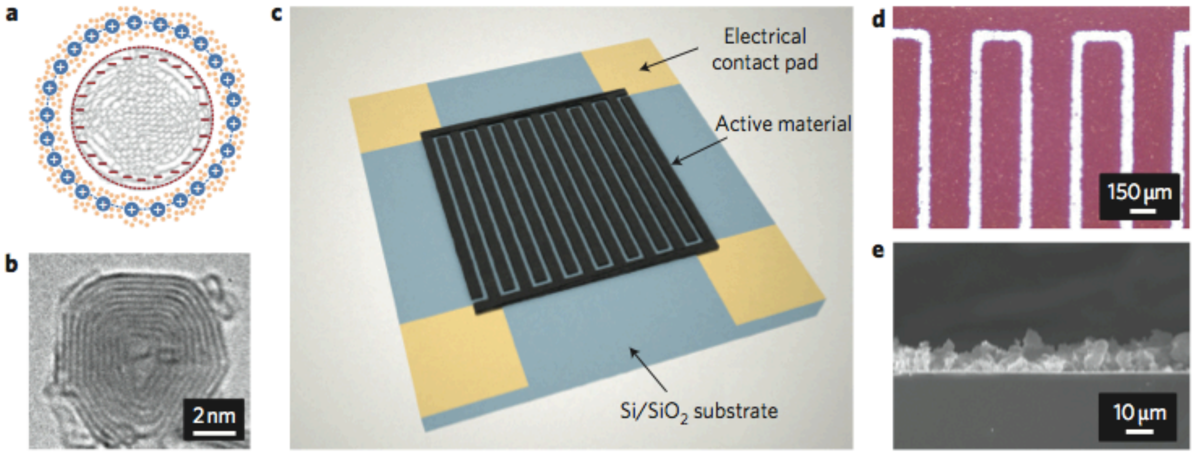
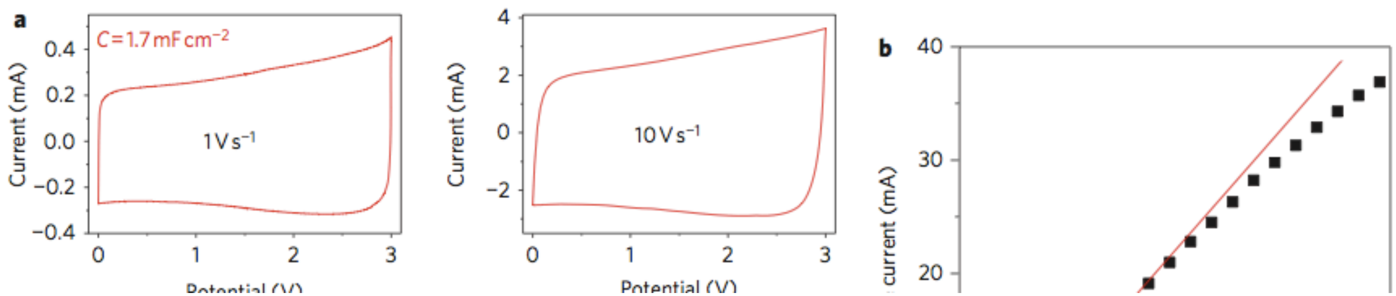
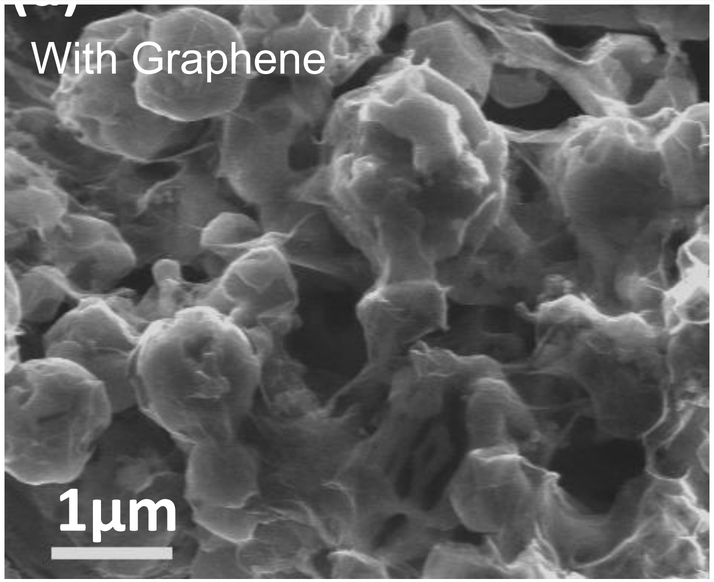
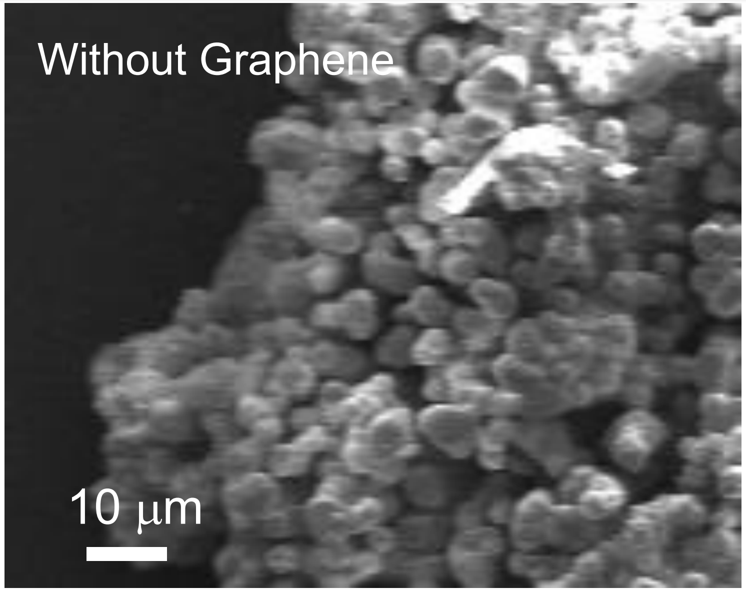


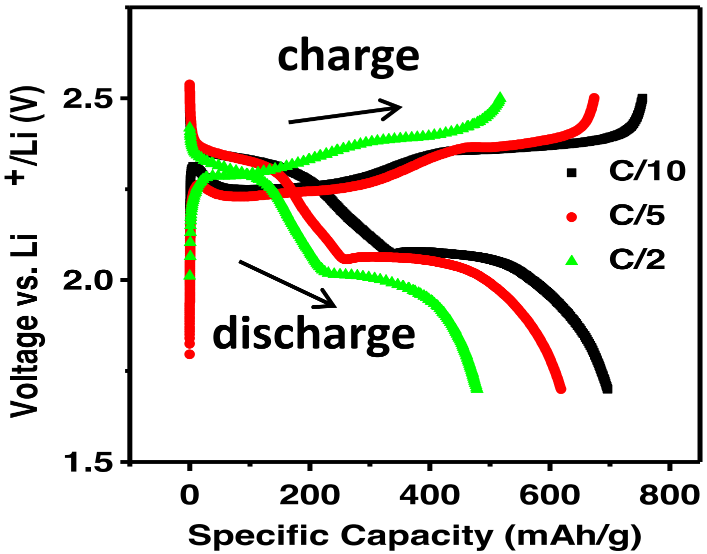
Figure 1 | Design of the interdigital microsupercapacitor with OLC electrodes. a, Cross-section of a charged zero-dimensional OLC (grey) capacitor, consisting of two layers of charges (blue and pink) forming the inner and outer spheres, respectively. **b**, Transmission electron microscopy image of a carbon onion produced at 1,800 °C. Lattice spacing between the bent graphitic layers in the onions is close to 0.35 nm. **c**, Schematic of the microdevice (25 mm^2). Two gold current collectors made of 16 interdigital fingers were deposited by evaporation on an oxidized silicon substrate and patterned using a conventional photolithography/etching process. Carbon onions (active material) were then deposited by electrophoretic deposition onto the gold current collectors. **d**, Optical image of the interdigital fingers with 100-µm spacing. **e**, Scanning electron microscope image of the cross-section of the carbon onion electrode. A volumetric power density of 1 kW cm^{-3} was obtained with a deposited layer thickness in the micrometre range, not the nanometre range.

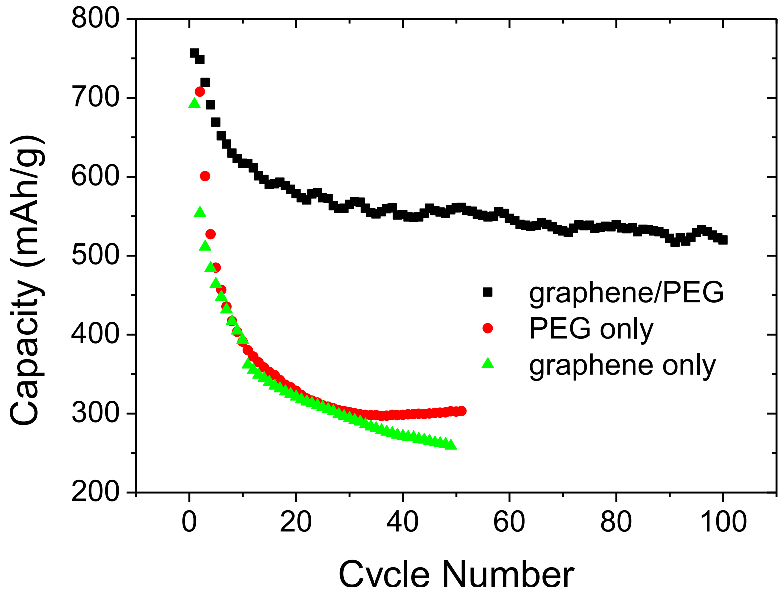


Graphene-Encapsulated Sulfur Cathodes









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↓

Future high capacity materials

Negative electrode

- Si (4200 mAh/g)
- Sn (900 mAh/g)
- Li metal

Positive electrode

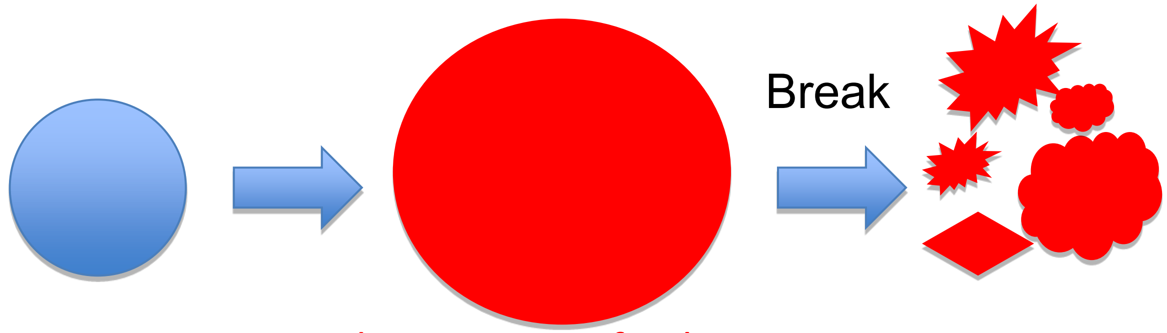
- Sulfur (1673 mAh/g)
- Air (very high)

Silicon nanowires for super capacitors

New anode materials (0-0.6V)

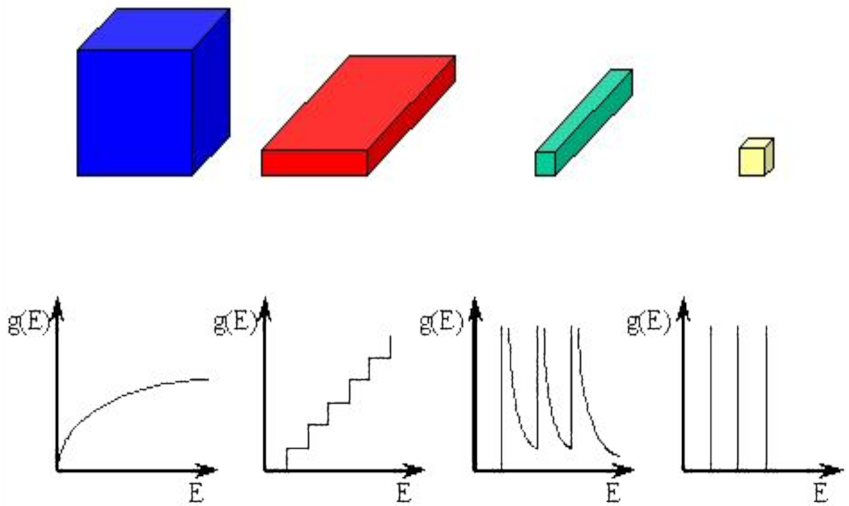
Si: 4200 mAh/g, 10X higher

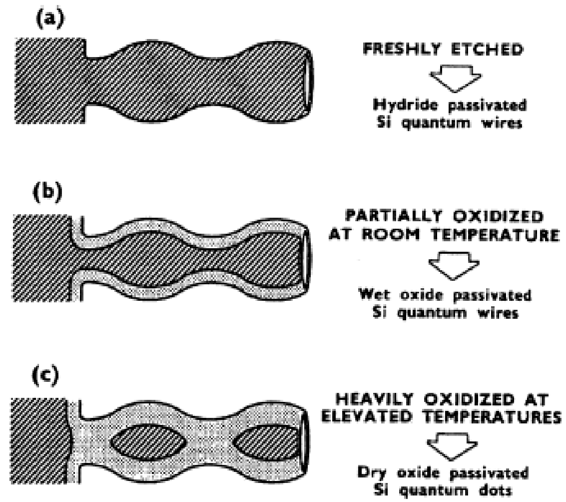
$Si \longleftrightarrow Li_{4.4}Si$



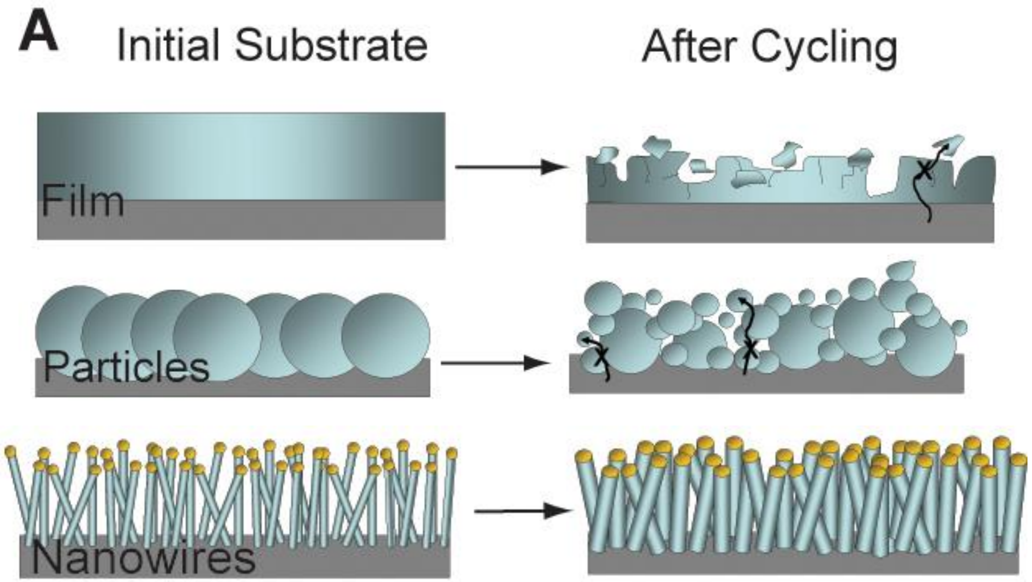
For Si: expand to 4 times of volume.

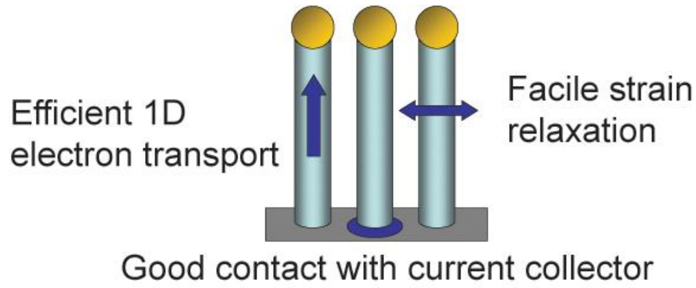
In Nanometer scale Mechanical strength is much higher





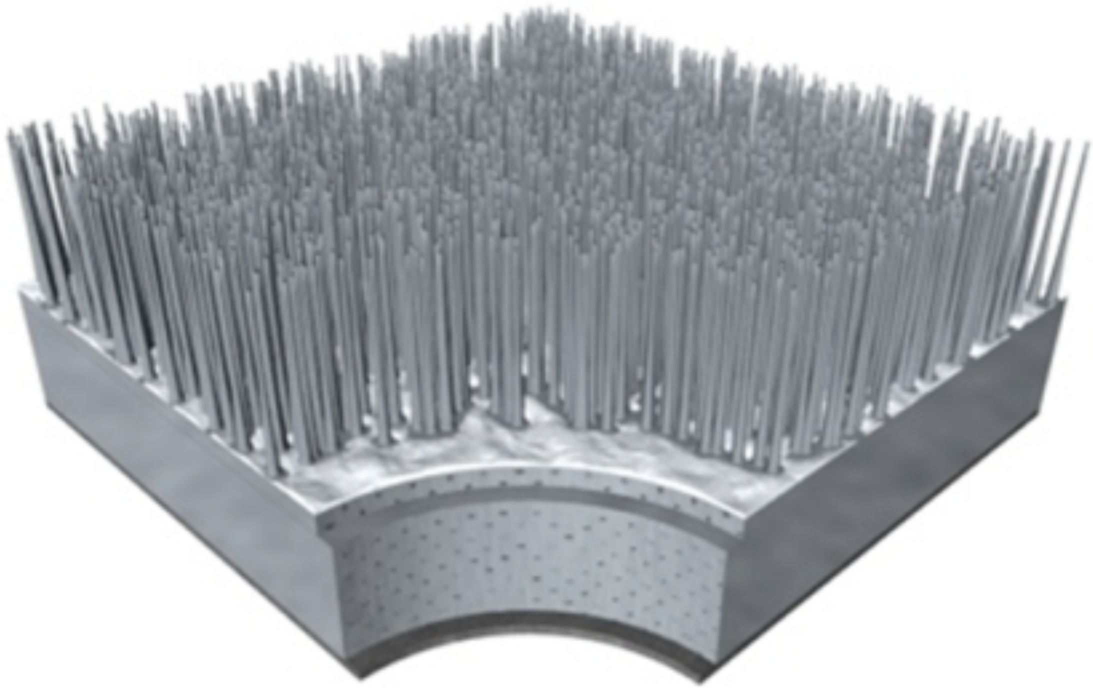
New Nanomaterials for current collector



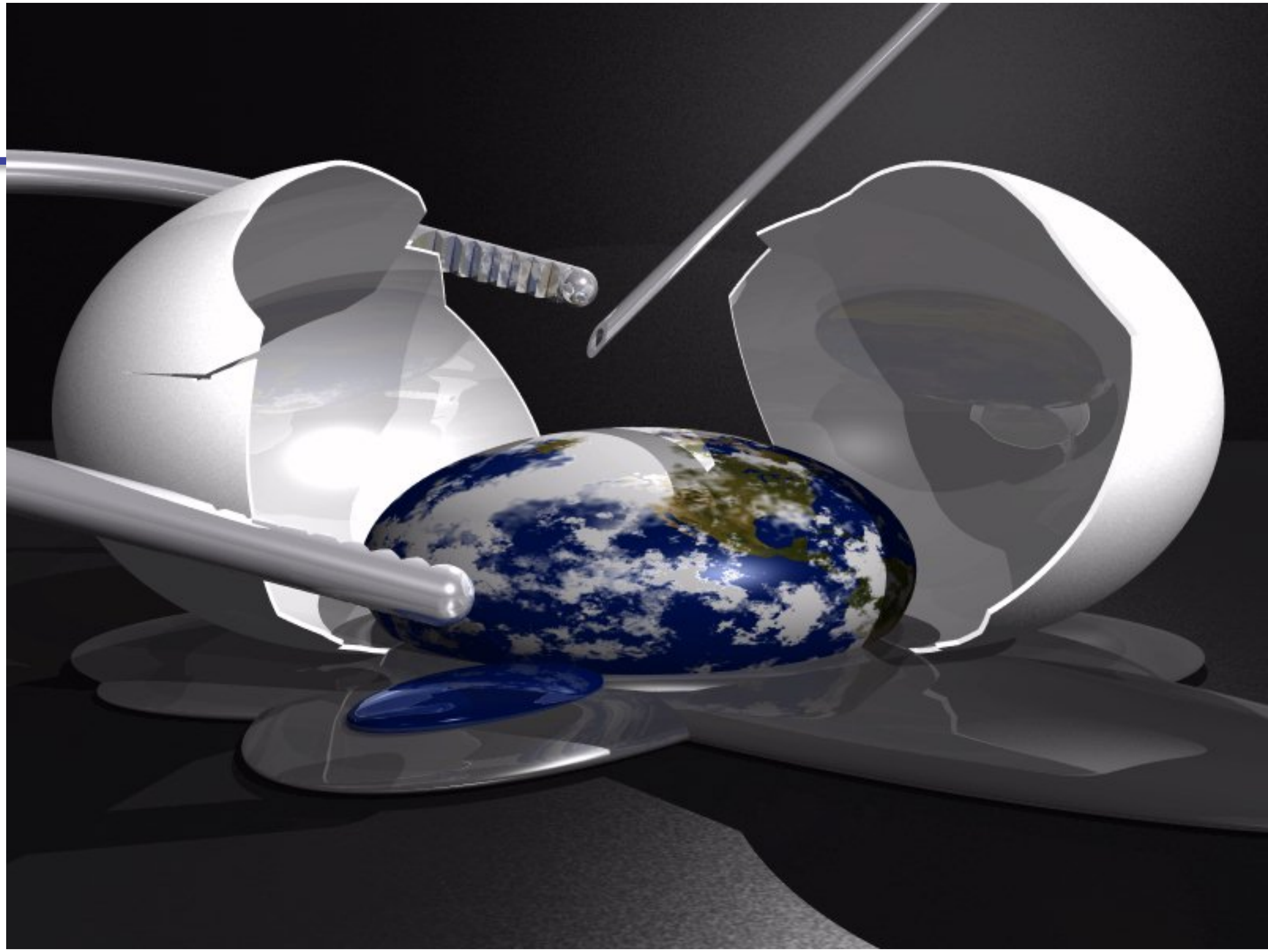


What nanowire can offer:
- Shorter distance for Li diffusion (high power).
- Good strain release and interface control (better cycle life).
- Continuous electron transport pathway (high power).

Capactiance test is encouraging and further tests are on



Electrode fabrication will look like this



In the end because of the advent of nanotechnology – whole world could be kept in egg shell