# Translating nanoscience into nanotechnology: The case of atomic clusters

HVM Graphene Conference 5 November 2013

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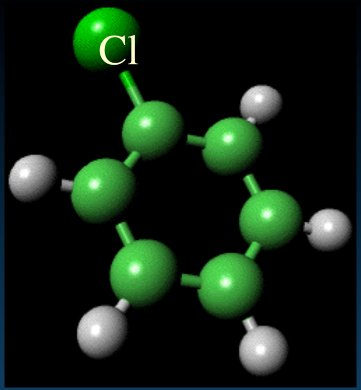
NPRL
Nanoscale Physics Research Laboratory
nprl.bham.ac.uk

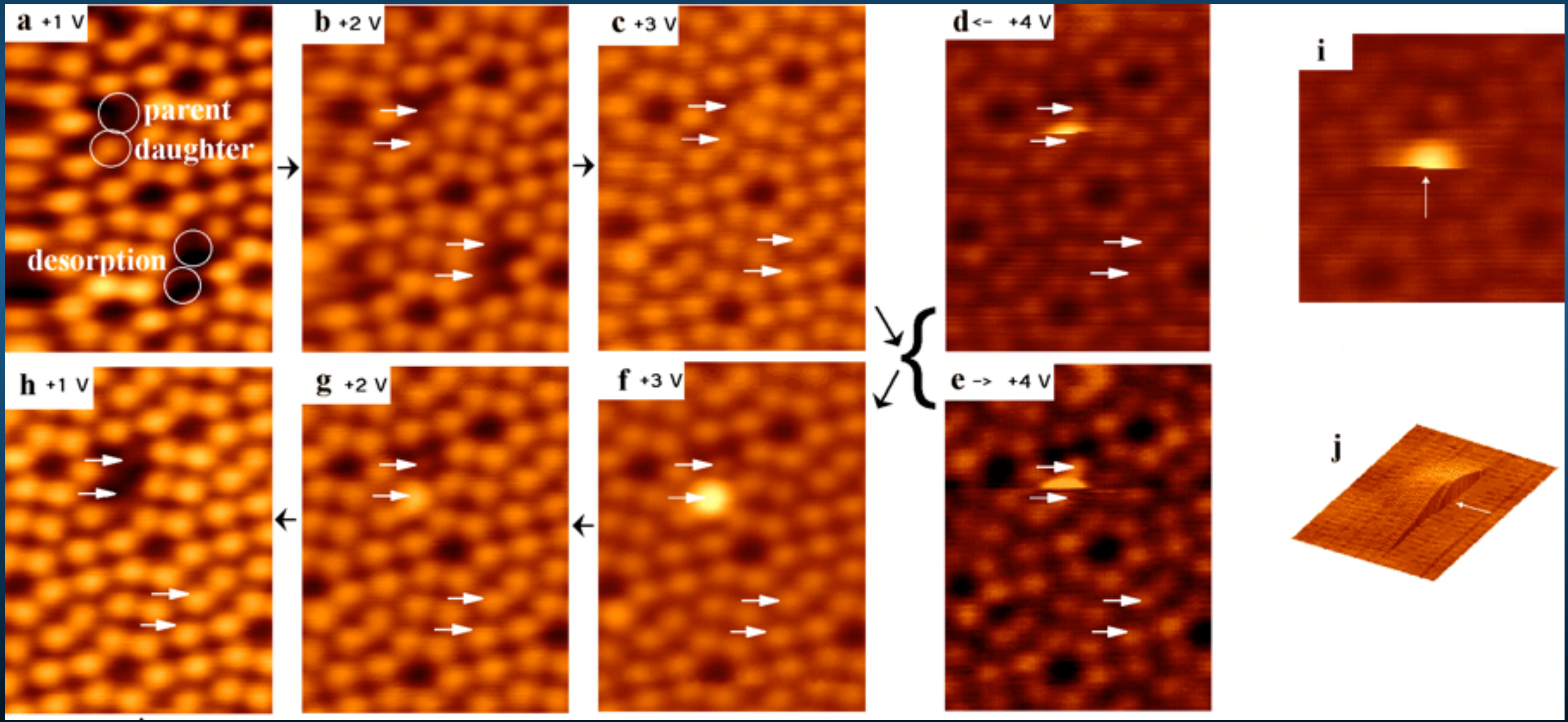
February 14, 2010

Image of the Day: The World's Smallest Valentine




# *STM Dissociation Images*

Sloan and Palmer, Nature (2005)



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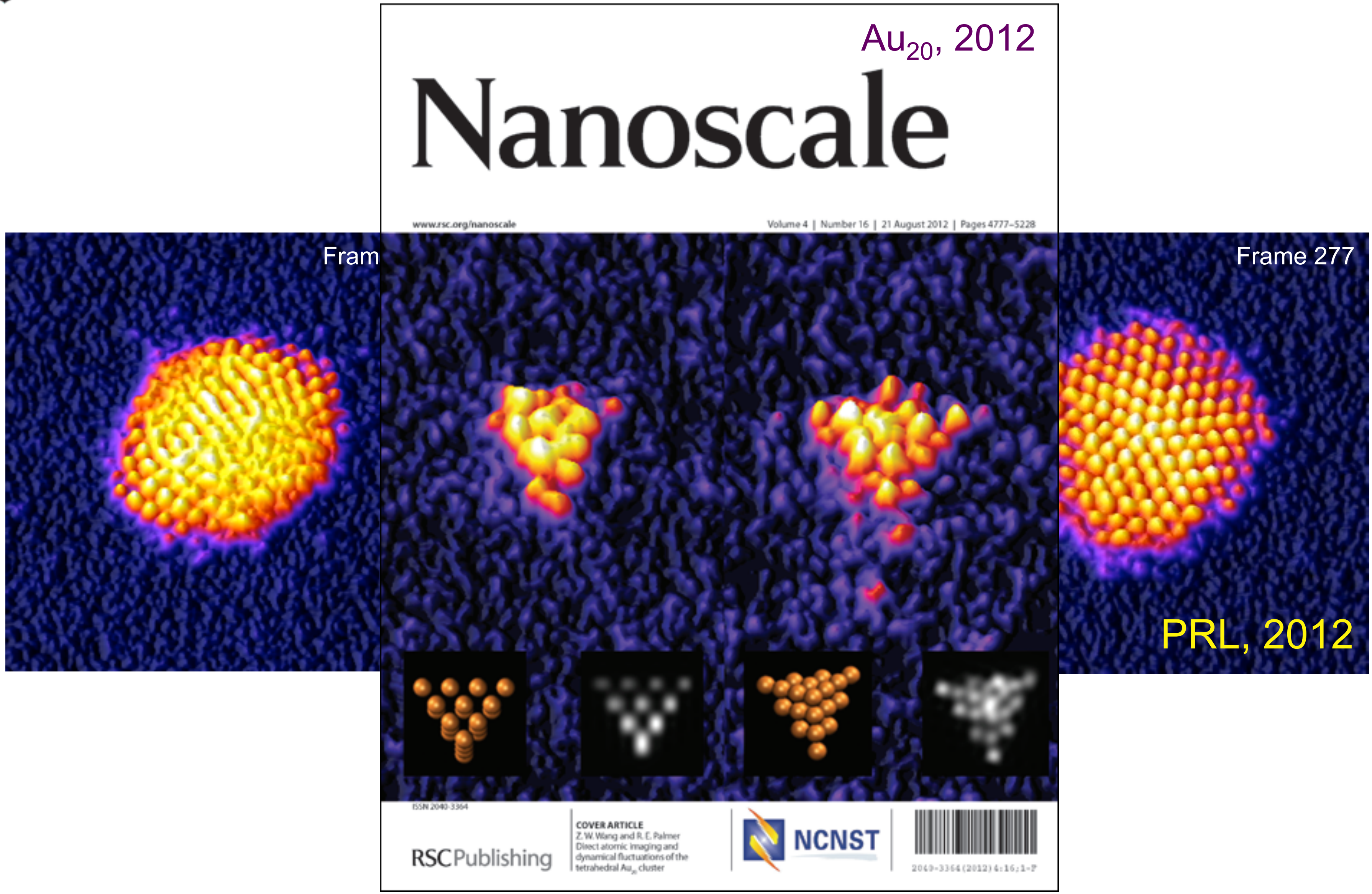


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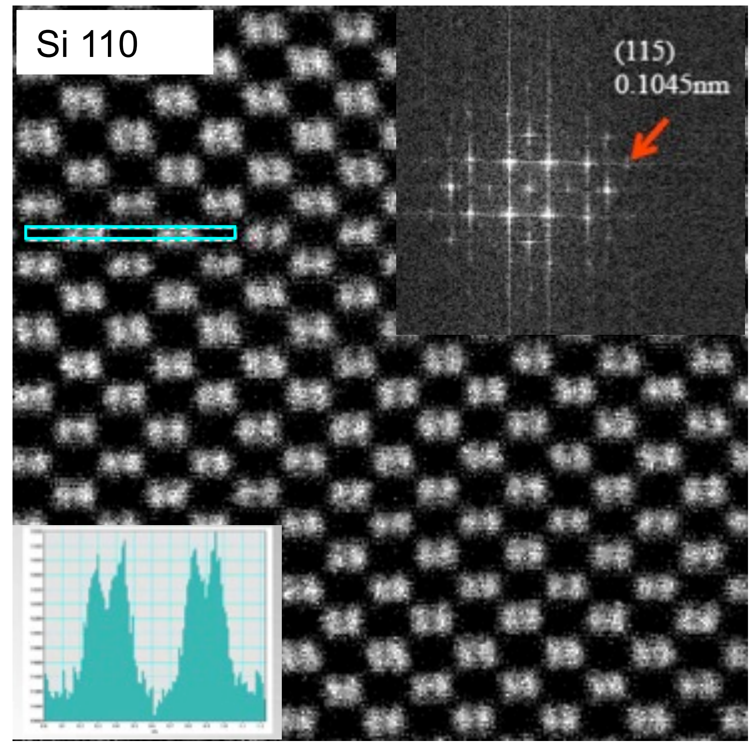
# Aberration-corrected STEM instrument

Cs−corrected JEOL 2100F: installed in NPRL, summer 2009

Angstrom or even sub-Å resolution obtainable

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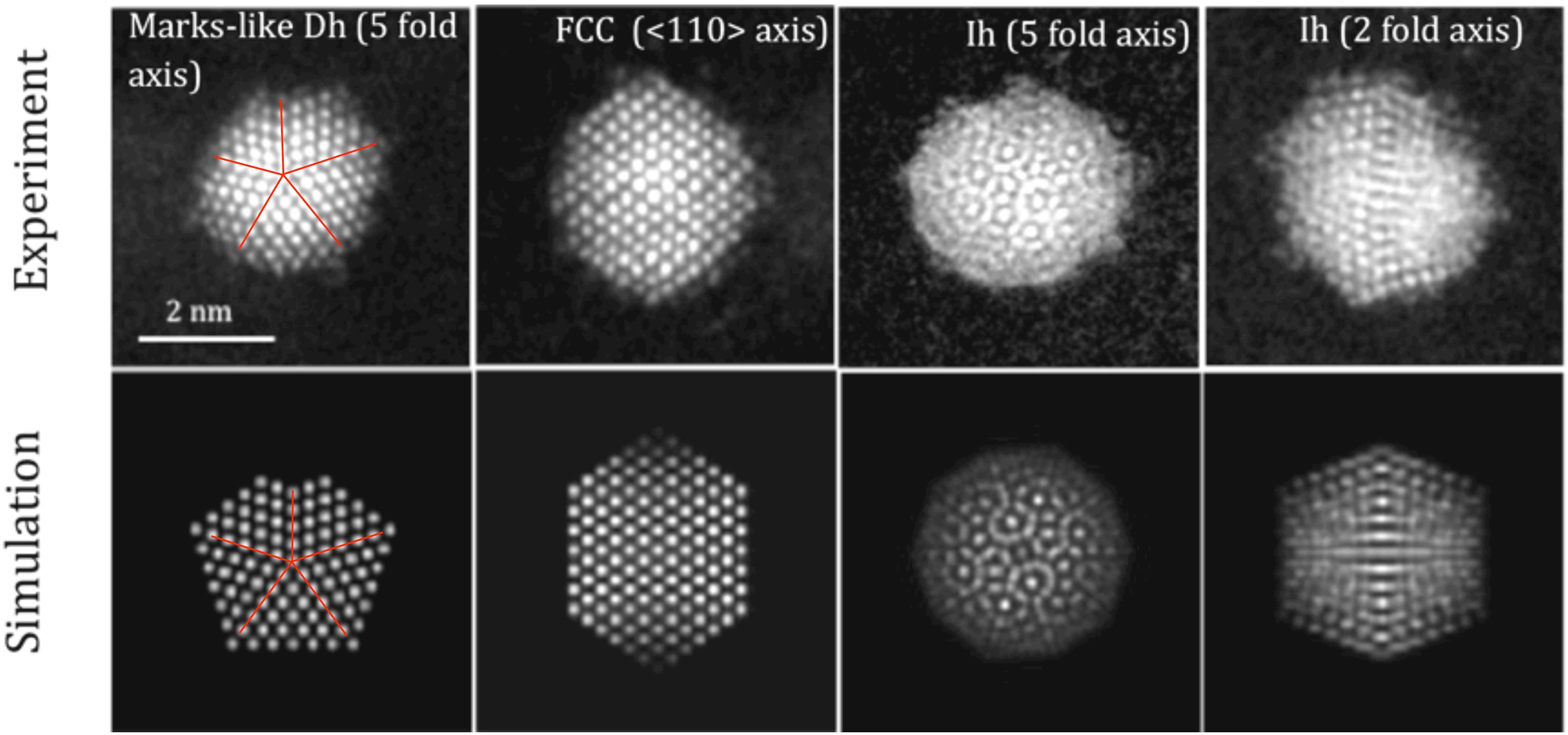
# $Au_{923}$: "Ground State" Structure?

Wang & REP, Phys Rev Lett, 2012




Three main structures observed for $Au_{923}$:

Decahedron (Dh), Icosahedron (Ih) and FCC polyhedron (TO etc)

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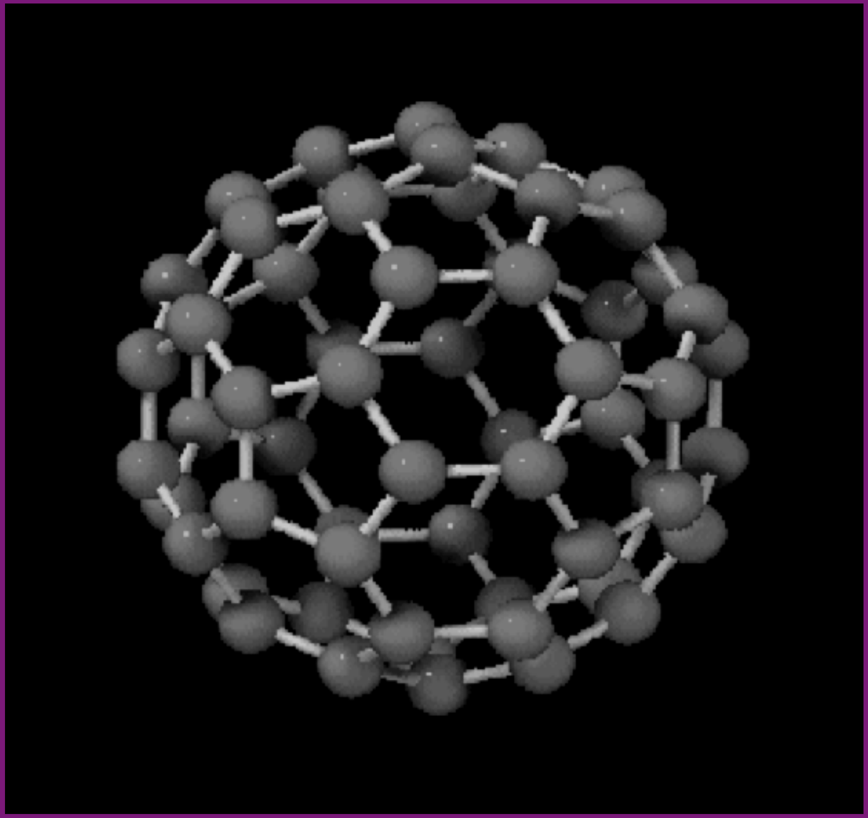
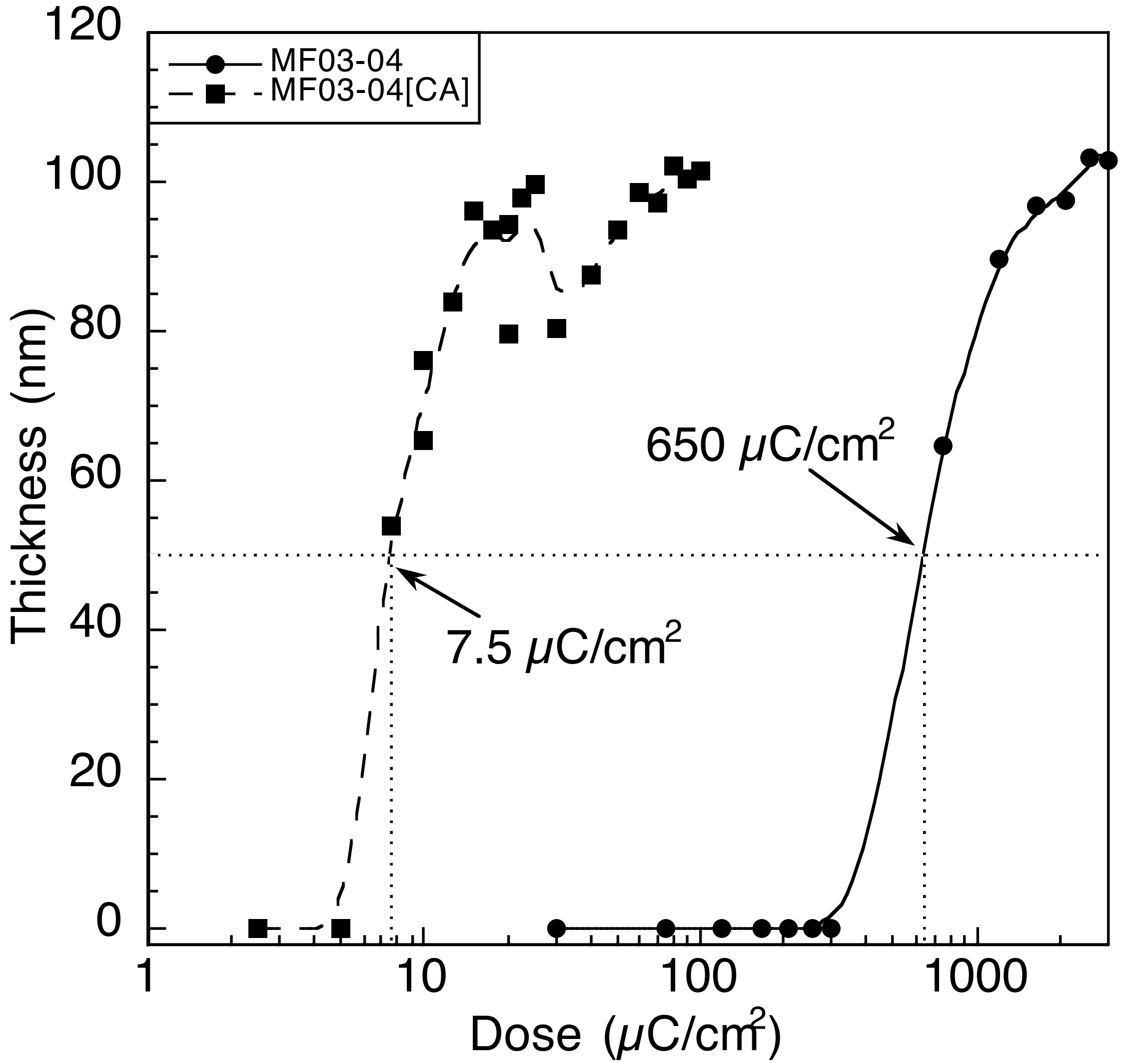
# *$C_{60}$ - Buckminsterfullerene*

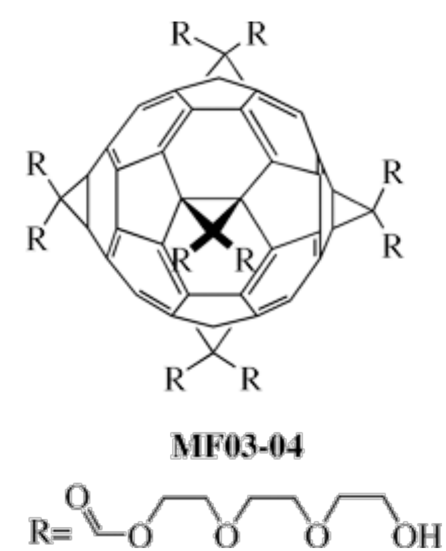


# Chemically Amplified Fullerenes

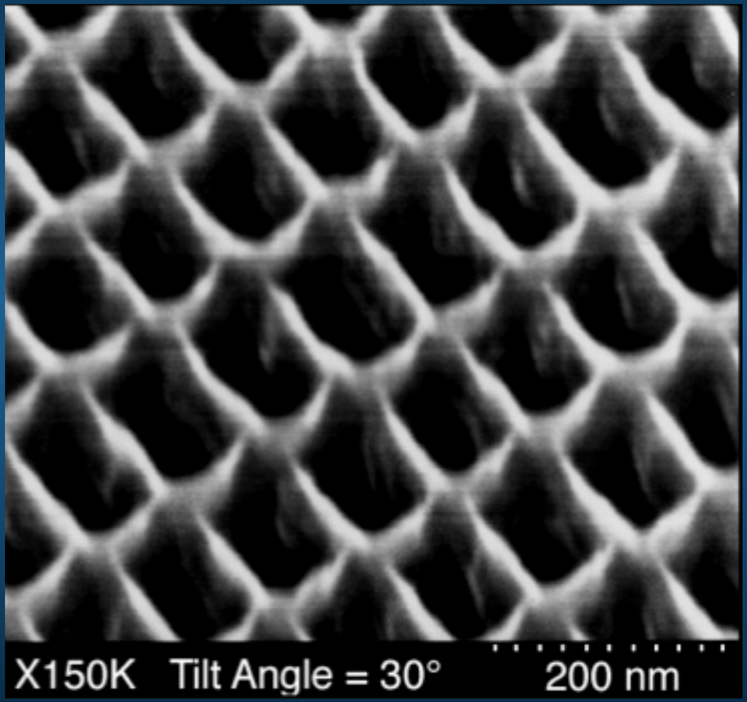



MF03-04:PAG:HMMM
1 mg :0.23 mg:1.5 mg

20 keV Exposure
PEB = 100 °C / 60 s
10 s MCB Development



# *High Aspect Ratio Structures*




Grating in silicon; wall width is 20 nm and hole depth is 160 nm

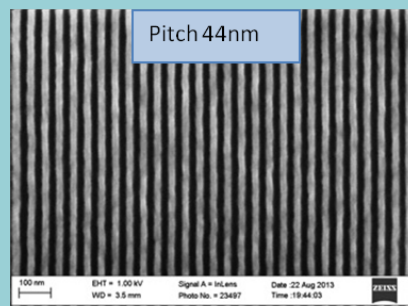
## Confidential Progress update – Irresistible Materials EUV resist materials

The advantages of EUV resist materials based on derivatives of fullerene are well documented, and include:

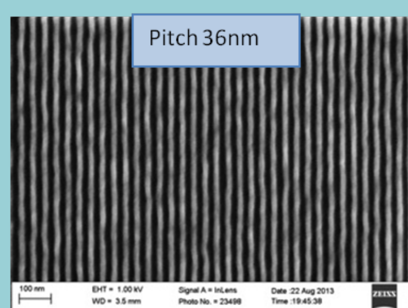
- High resolution features
- High aspect ratio etching
- Familiar processing techniques

Latest/ recent results and performance comparison to champion LER resist

IM-EUV-45

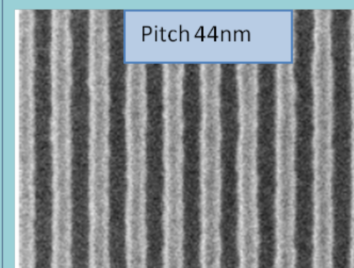



Dose: 33.1 mJ/cm²
LER: 2.5 nm

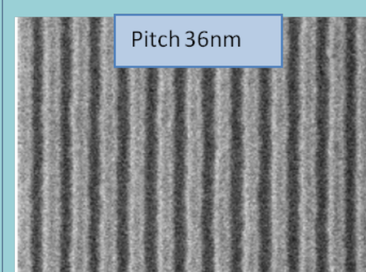



Dose: 25.6 mJ/cm²
LER: 3.2 nm

'Champion' LER Resist – Resist R [1]




Dose: 39.5 mJ/cm²
LER: 2.6 nm



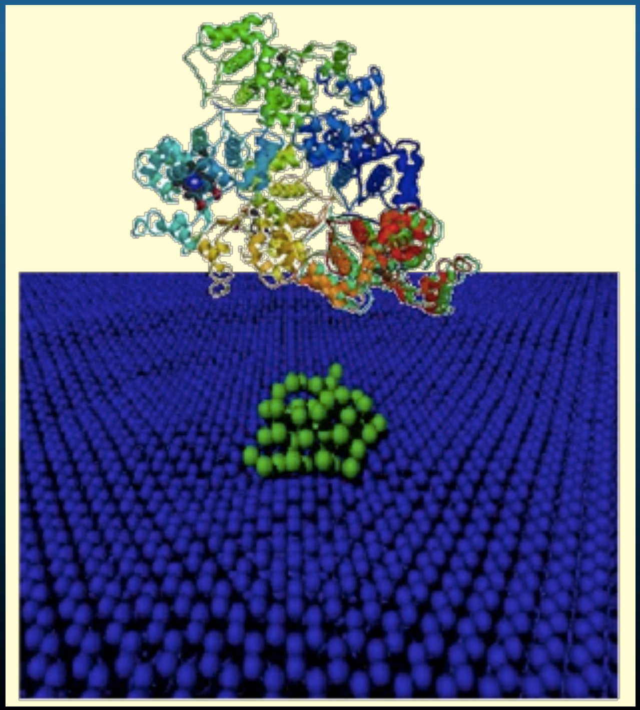

Dose: 24.8 mJ/cm²
LER: 3.0 nm *(with FIRM™ rinse)*

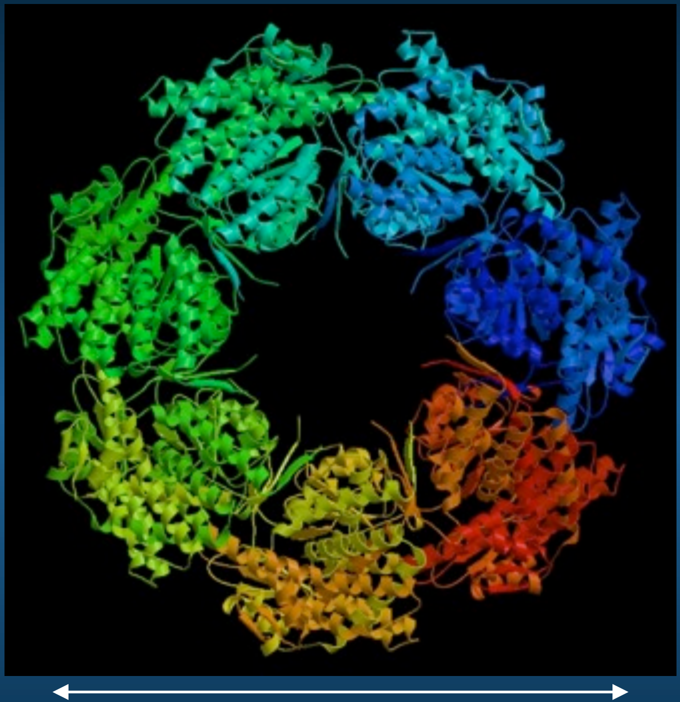
# *Protein Molecules*

Proteomics

- "Soft and flexible nanomachines"
- Structure from X-ray diffraction
- Hard to crystallise proteins (70%?)

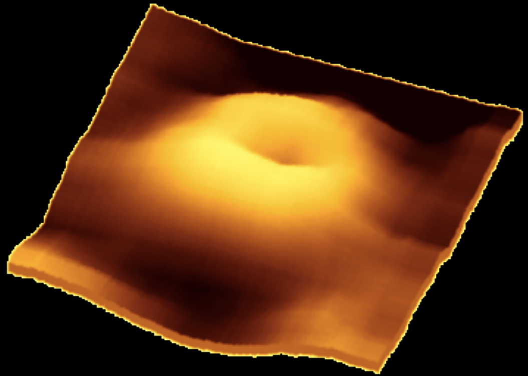
$\Rightarrow$ Single molecule approach





15 nm

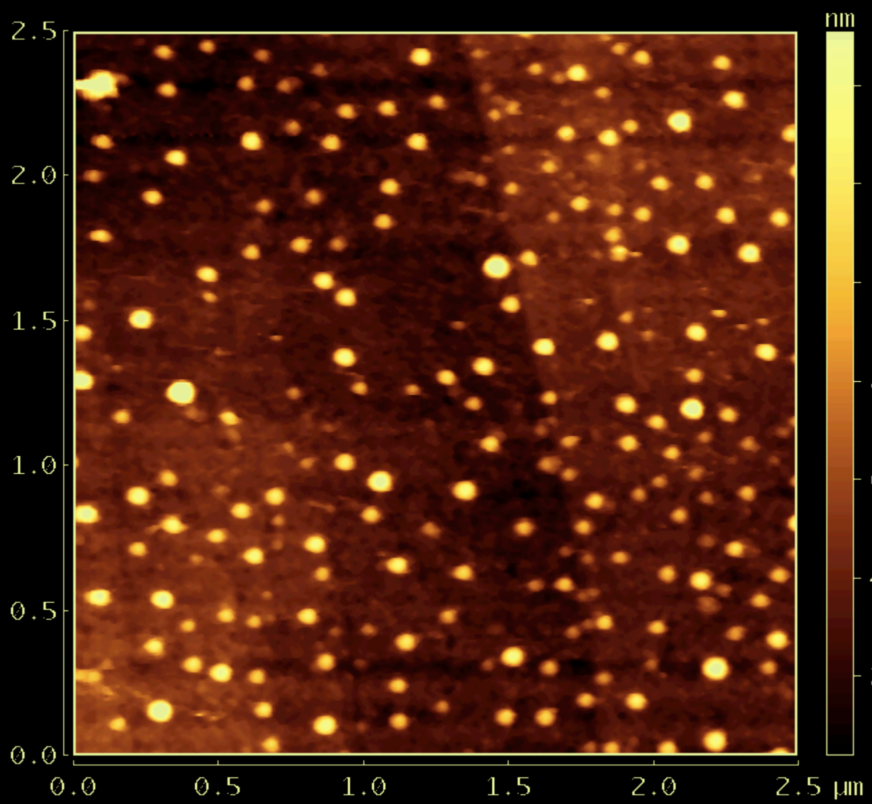
Chaperonins: Molecular structure of GroEL protein ring assembly from *E. Coli*.

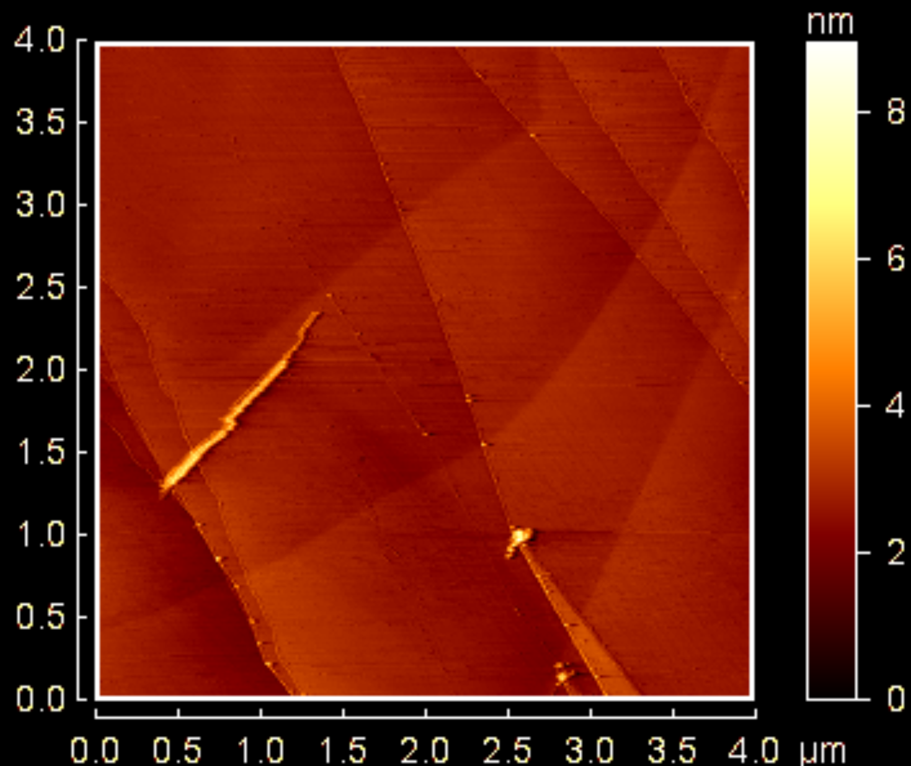


# *Chaperonins*

Immobilisation by $Au_{55}$ clusters on graphite (*Nature Materials, 2003*)

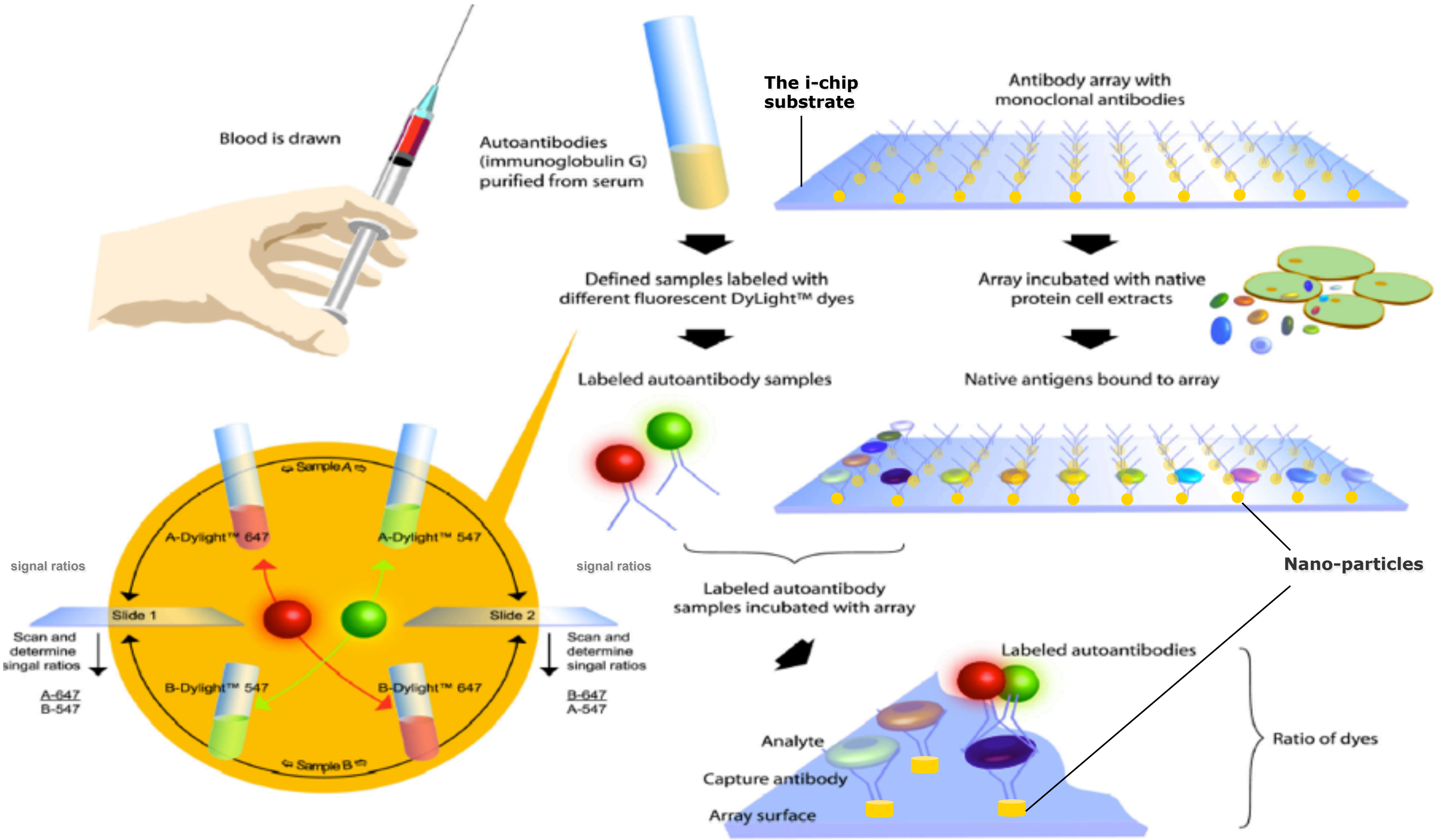
Deposition on bare graphite - *Protein diffusion?*



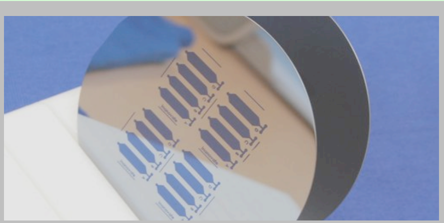



# 'Auto-antibody' based reverse-capture cancer diagnosis

## *i-Screen by Inanovate*



# The Bio-ID™



**A New Solution to Protein Detection and Measurement**

## Product Highlights

- Quantitative measurement of multiple proteins across an unprecedented concentration range from a single dilution.
- High multiplexing flexibility, enabling the development of biologically relevant multiplexes.
- In built QC that helps differentiate non-specific protein binding from targeted (specific) interactions.
- Automated assay processing through fluidic cartridges.
- Market leading sensitivity and consistency.
- Low cost disposable cartridges.
- High multiplexing capacity.

**For more information:**

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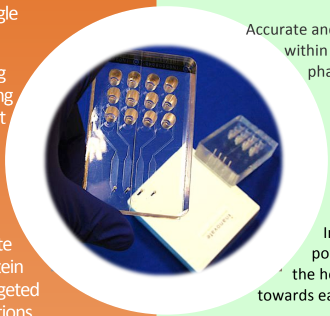


# The Bio-ID™

## A new solution to protein detection and measurement

Accurate and cost effective detection and measurement of multiple proteins within a single test is set to become a key driver of growth within the pharmaceutical and diagnostics industries through the next 15 years.

However, existing solutions to multiplexed protein screening are often complex, costly and inaccurate. Inanovate has developed a proprietary technology to address these limitations - ***Longitudinal Assay Screening (LAS).***

First developed in 2010, LAS has since been integrated into Inanovate's first product – The Bio-ID 400 (see below inset); a powerful and unique technology platform designed to help move the health-care industry away from late stage, high cost treatment, towards early stage, accurate diagnosis and lower cost therapy.

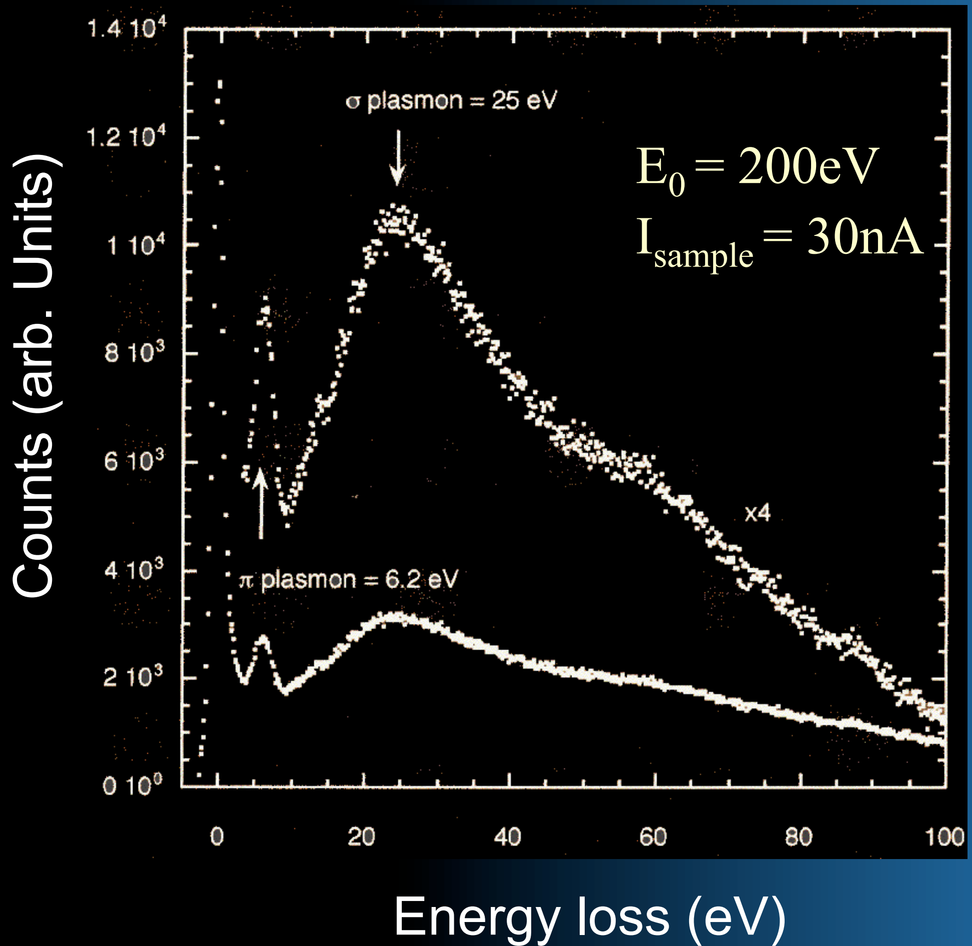
Driving the development of LAS were ***three significant technical limitations of existing state-of-the-art platforms*** that continue to hold back the true potential of multiple protein detection and measurement. These are:

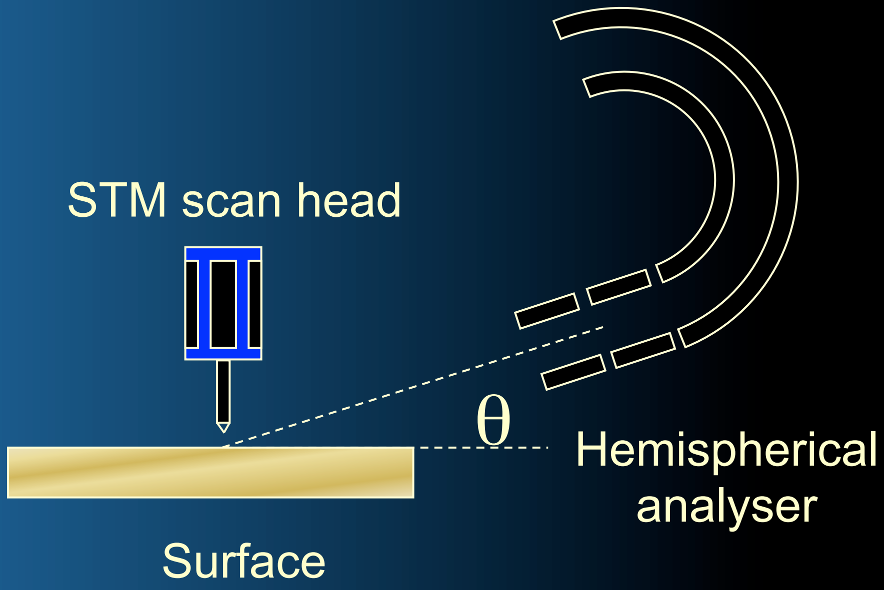
**1. Limited detection range:** A lack of capacity to screen across a wide range of protein concentrations in one test, requiring complex, costly, and time-consuming repeat experiments and repeated use of precious samples.

**2. Limited biological relevance:** Rather than developing assays around biological needs, the limited detection range of existing state-of-the-art platforms means multiplexed assays are typically confined to a selection of proteins known to be present in samples at similar concentration ranges. This severely restricts the 'biological relevance' of many multiplexed assays.

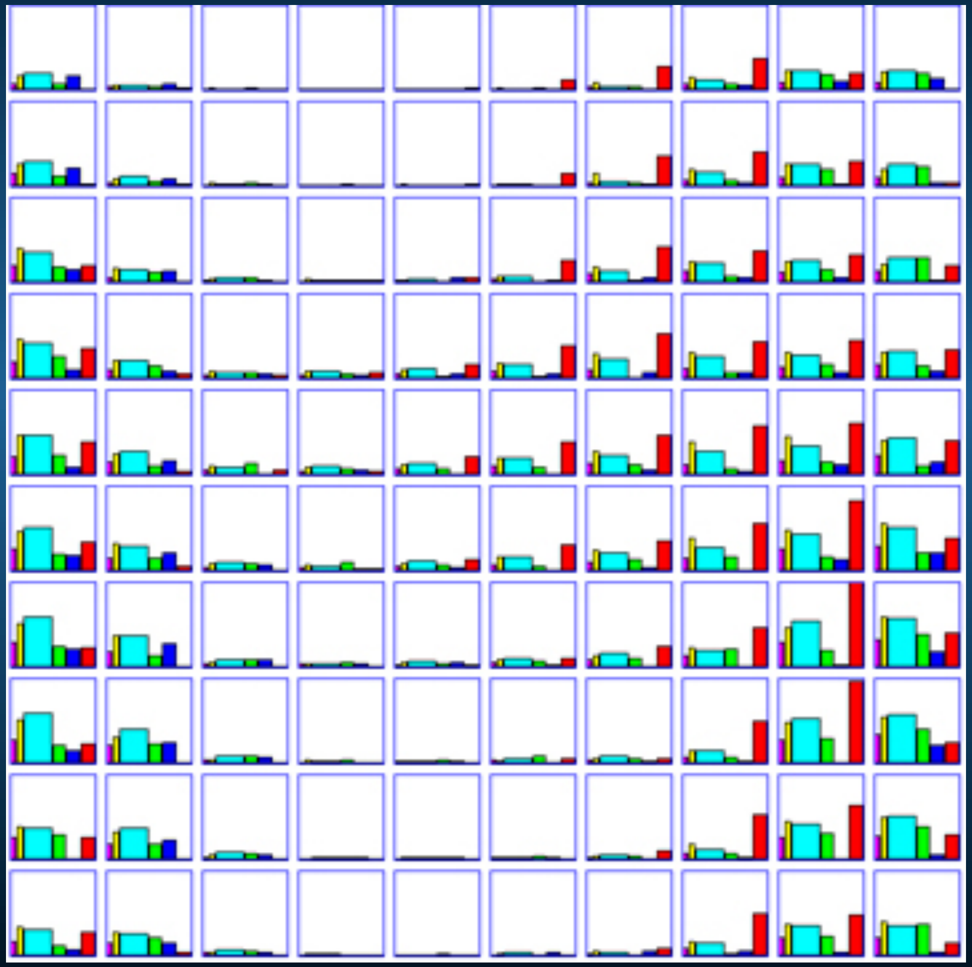
**3. Limited data accuracy:** A lack of consistency and reproducibility of multiplexed data, with high levels of 'false' signals caused by non-specific protein to protein interactions, bringing assay/test results into question.

# *Scanning Probe Energy Loss Spectroscopy (SPELS)*



# *2D Spectral Map of Silicon*



- Local EELS spectra
- 50x50 nm squares
- Spatial resolution < 50 nm

*Festy & Palmer, APL*

# Size-selected cluster deposition

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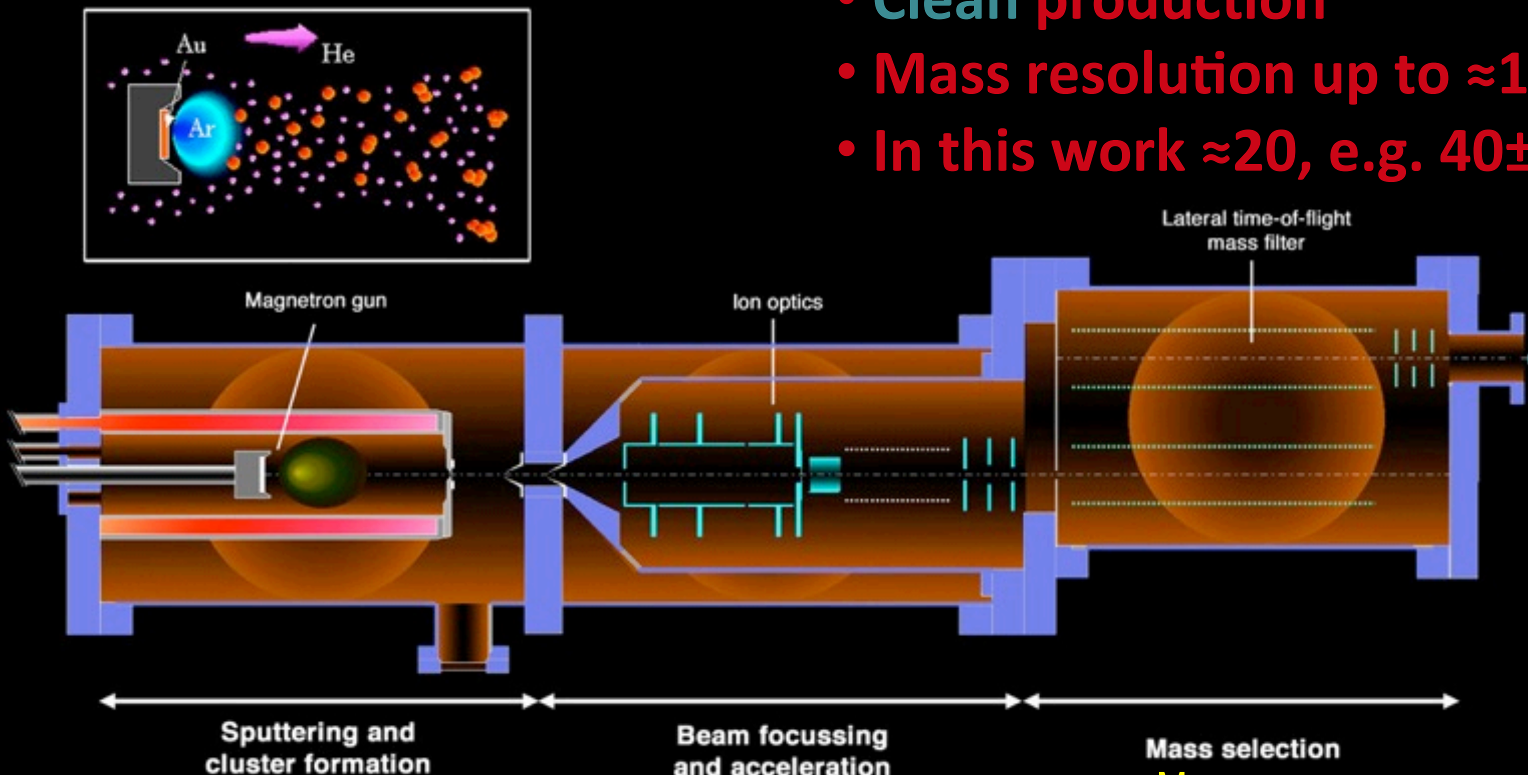
- Clean production
- Mass resolution up to ≈130
- In this work ≈20, e.g. 40±1



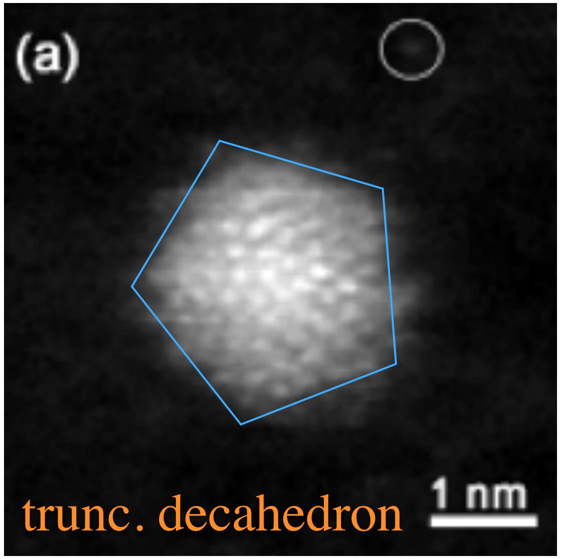

Cluster source
Pratontep et al, RSI (2005)

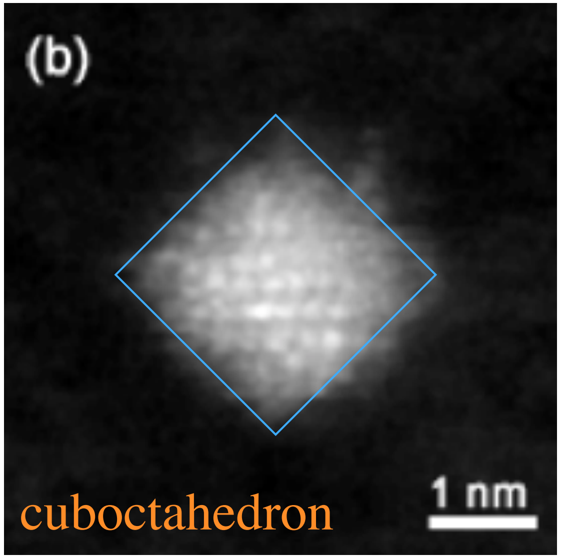
Mass spec
von Issendorff and Palmer, RSI (1999)
US, Europe, Japan patents

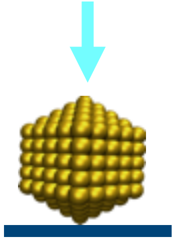
**1nA**

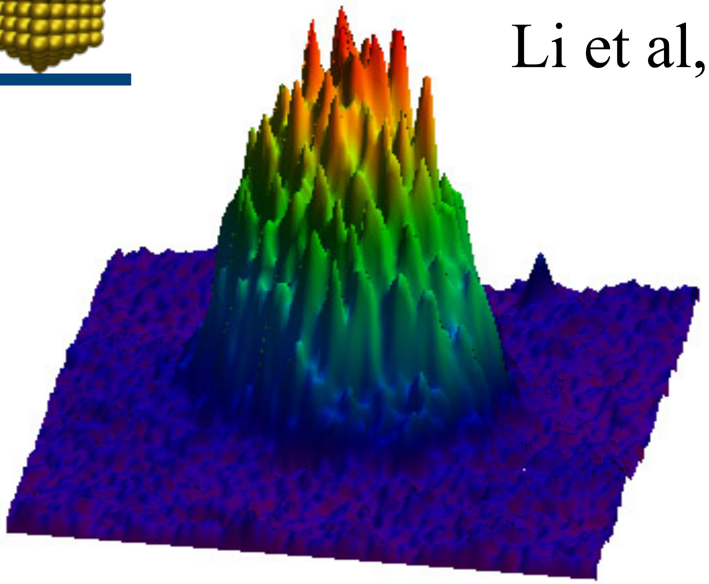
1 nanoAmp ≈ $10^{10}$ clusters/second
= $10^{12}$ atoms/second for size N=100
≈ 1 microgram of Au clusters per hour

# 3D Atomic Structure of Clusters: $Au_{309}$/Carbon

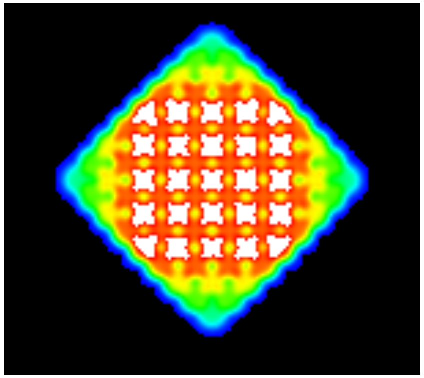




Li et al, Nature (2008)

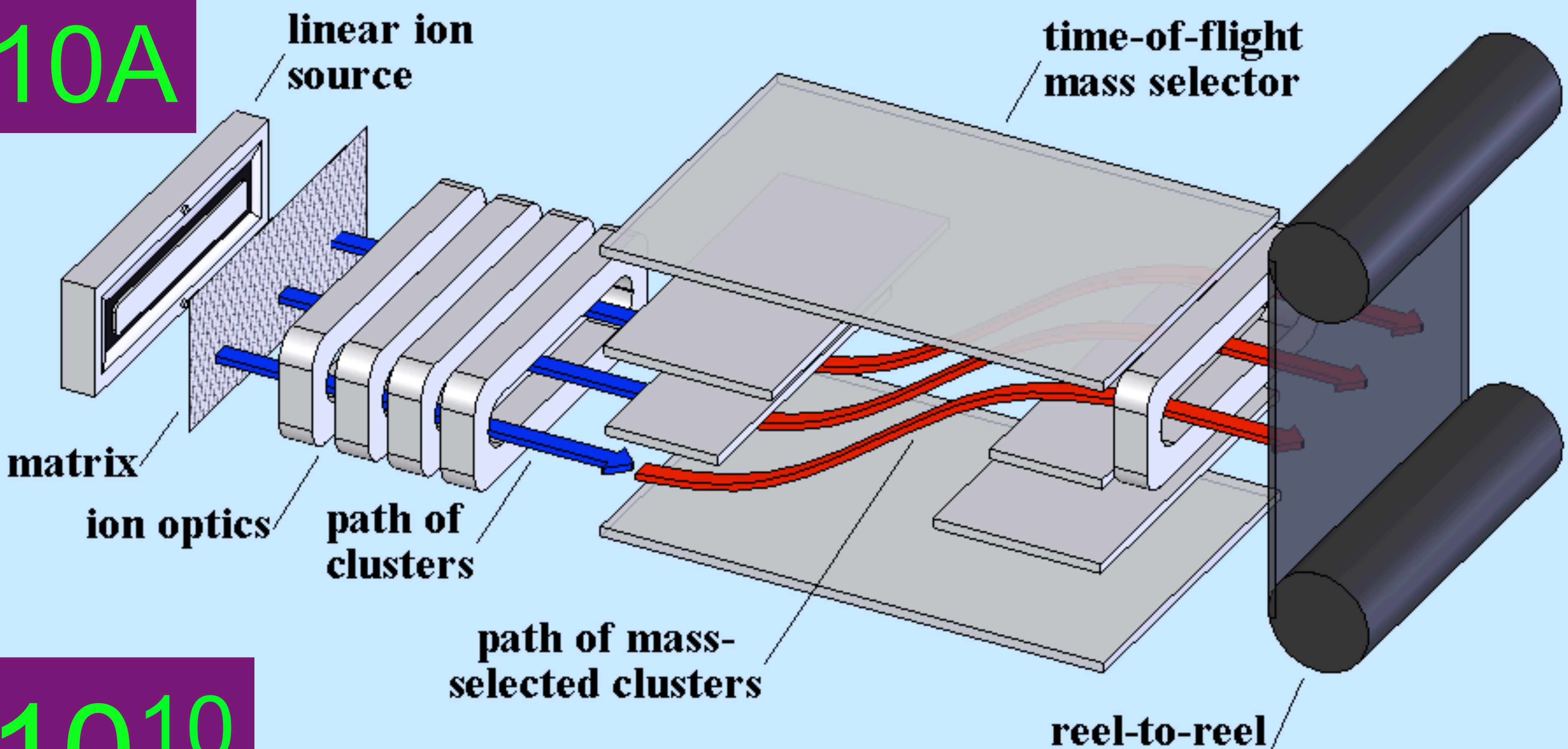


**False Colour Z-Contrast Simulation: Cuboctahedral [001]**

*(Curley & Johnston, Gupta Potential, Kinematic Scattering)*

# Matrix Assembly Cluster Source (MACS)

10A




$10^{10}$

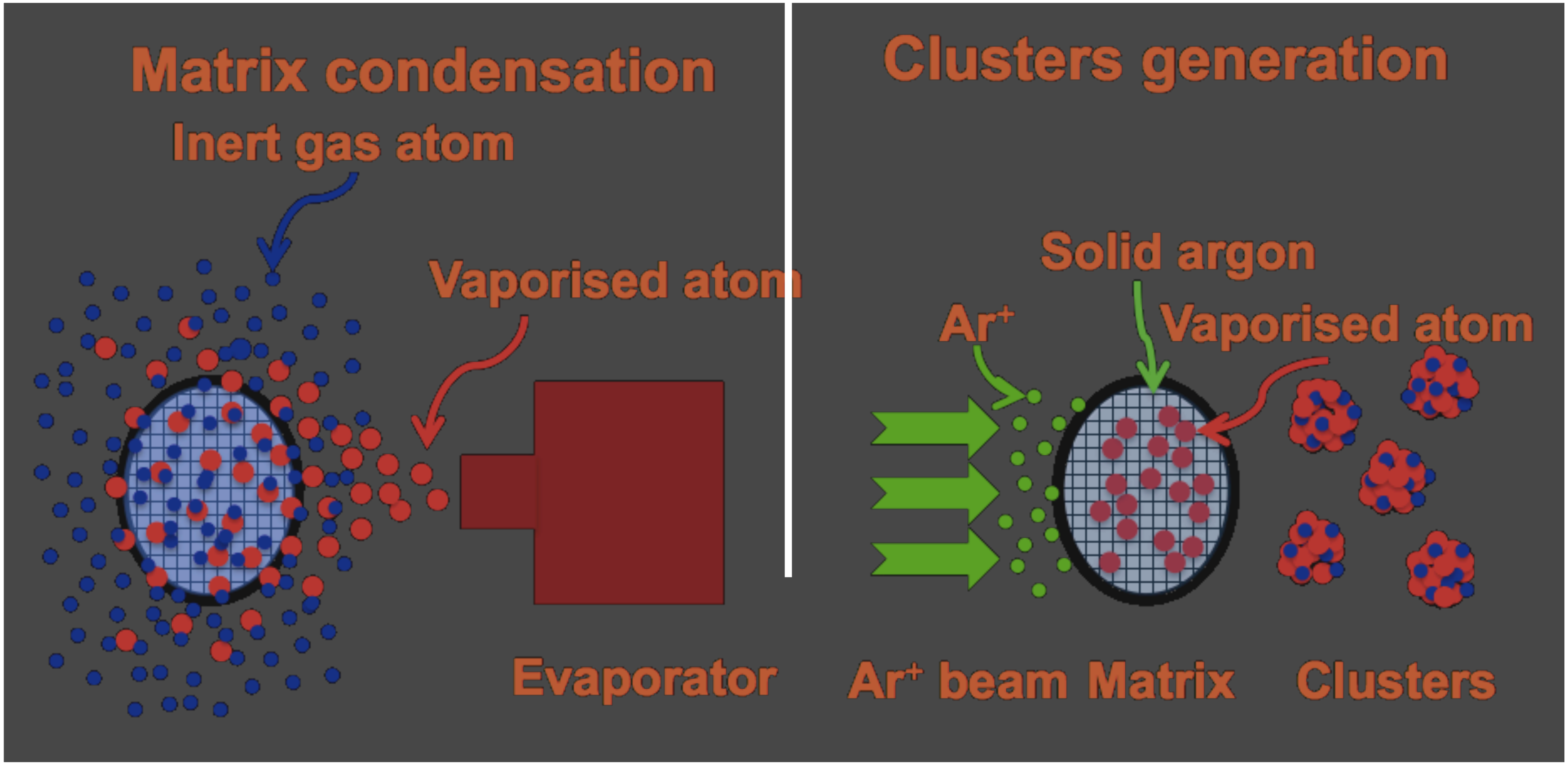
≈ 10kg of Au clusters per hour

Target 10g per hour

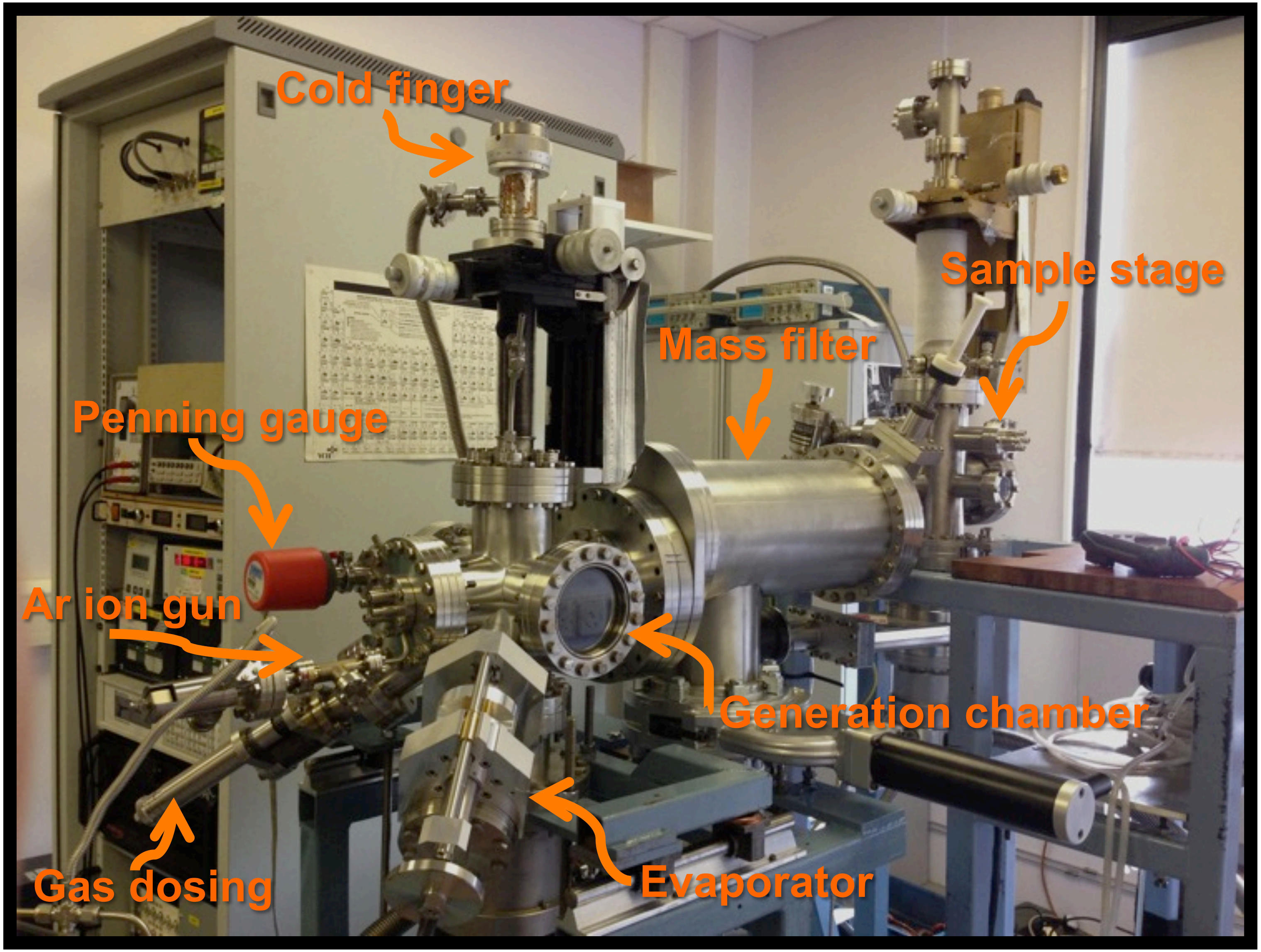
RE Palmer, UK Patent Application (2011), PCT Application (2012)

# Principle of MACS

- **The Matrix is formed by vaporized target atoms and inert gas co-condensed on a semi-transparent matrix support e.g. a grid**
- **Clusters are produced by argon ion beam "transmission sputtering" of the matrix (spike regime); back sputtering should also work…**



# Matrix Assembly Cluster Source

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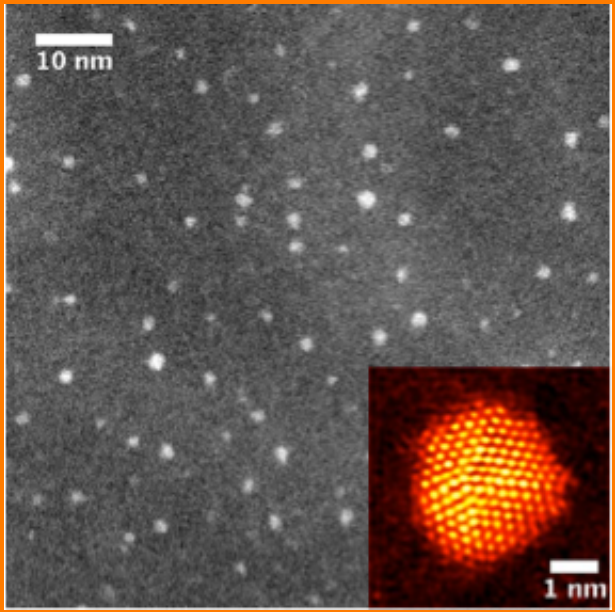
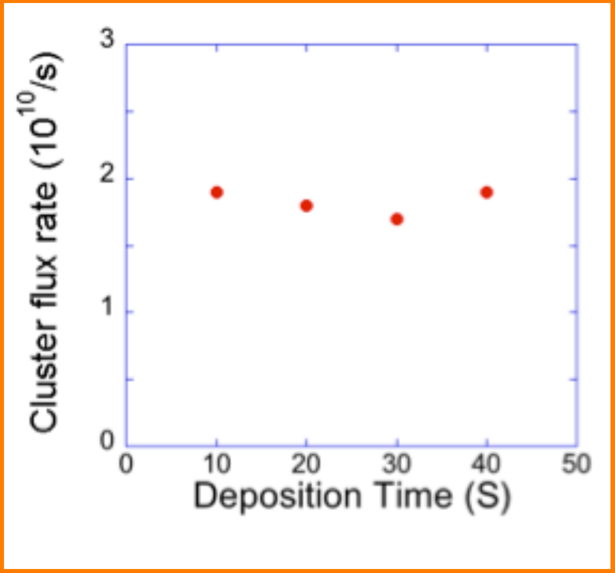
# MACS: Proof of Principle

- **Figure 1** STEM images of Ag cluster production, 3.3×10$^{10}$ clusters/sec (5.3nA).
  - Matrix transparency 14% (quantifoil), $Ar^+$ current on holes ~25 nA.
  - Ag evaporation rate 1.5 Å/s, deposition time 5s.
  - **Conversion efficiency ~20% (+).**

- **Figure 2** Sustained cluster deposition (~3 nA) by replenishing the matrix.
  - Matrix support quantifoil
  - Ag evaporation rate 1.5 Å/s
  - $Ar^+$ beam on matrix ~ 15nA.

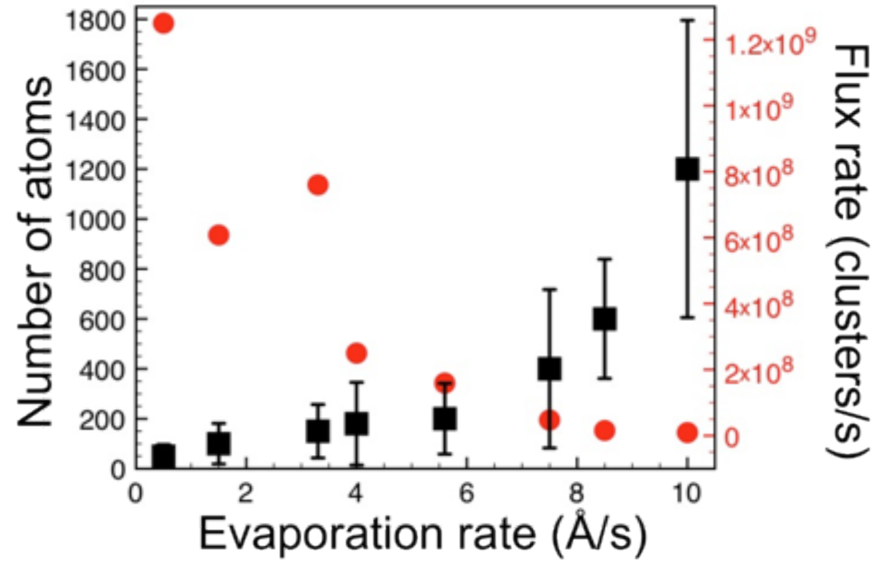
*Lu Cao, Feng Yin, Will Terry, Simon Plant, Graham Kirkby, REP*



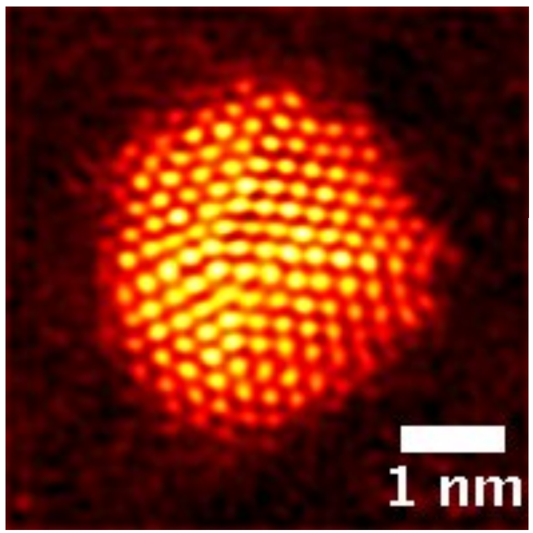



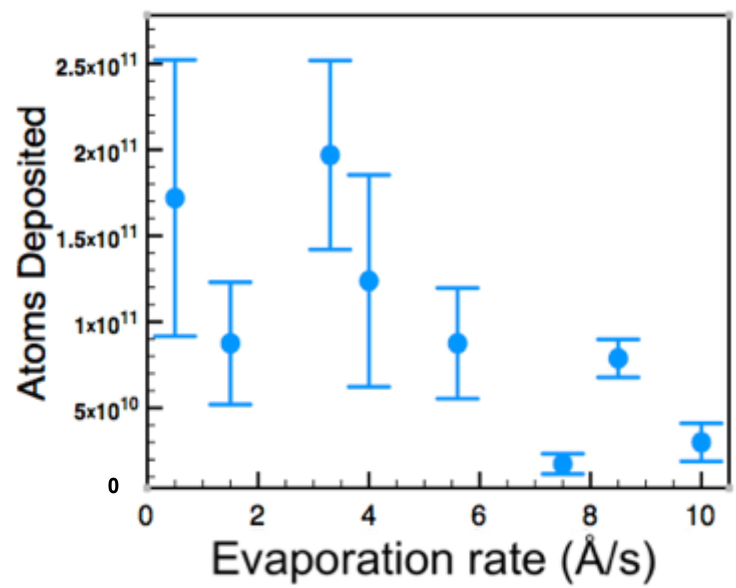
# Cluster size versus metal loading

- **Cluster size (black squares) increases with metal concentration.**
- **Cluster flux (red) falls; total number of Ag atoms (blue) falls slowly.**




- 400 mesh EM grid
- 950eV $Ar^+$
- ~2nA $Ar^+$ on matrix
- 200s condensation
- 60s sputtering

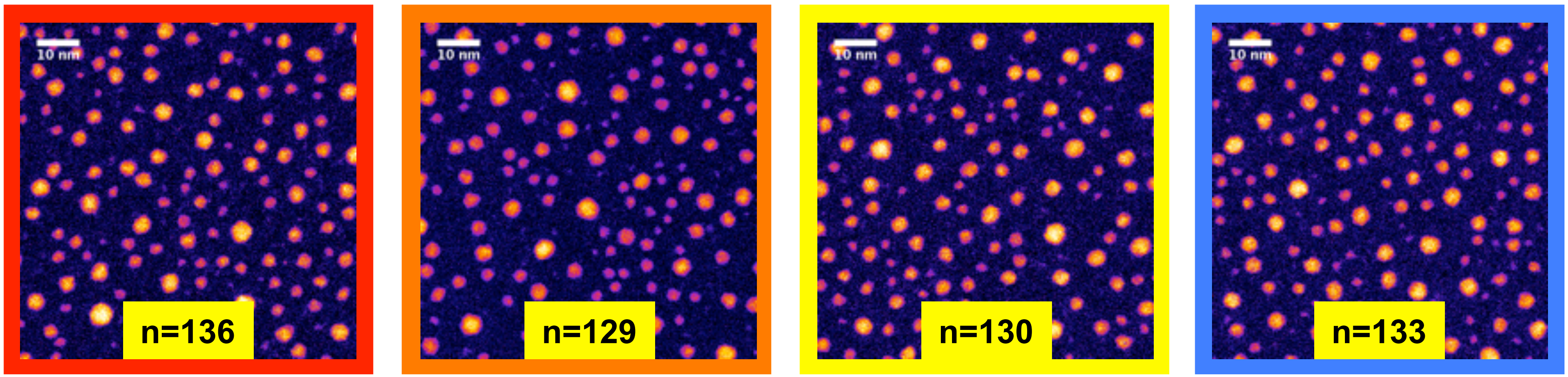



| | Positive | Negative | Neutral |
|---|---|---|---|
| Percentage | 47% | 42% | 11% |

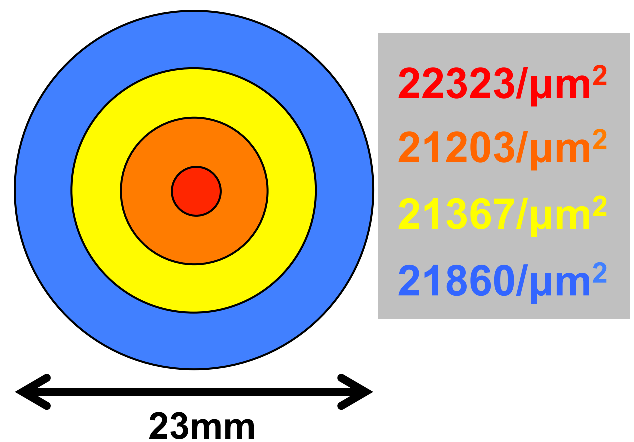
# Highest flux samples to date

- Clusters can be collected from a 23mm circular area by a cross array of TEM grids
- Density of clusters produced is similar among all samples and total flux is equivalent to **93.1nA**




*Frame size (78nmx78nm)*

Gas dosing pressure: 3.0E-6mbar (9.5E-6mbar RT); Evaporation rate: 0.4Å/s; Matrix condensation time: 200s; Metal concentration: 11%; Ar beam: 0.4mA(-1000V bias), 5keV; Deposition time: 15s.




Density of clusters

# Some applications of clusters

*Objective 4 from new EPSRC research grant*

To demonstrate the utility of size-selected clusters, with focus on:-

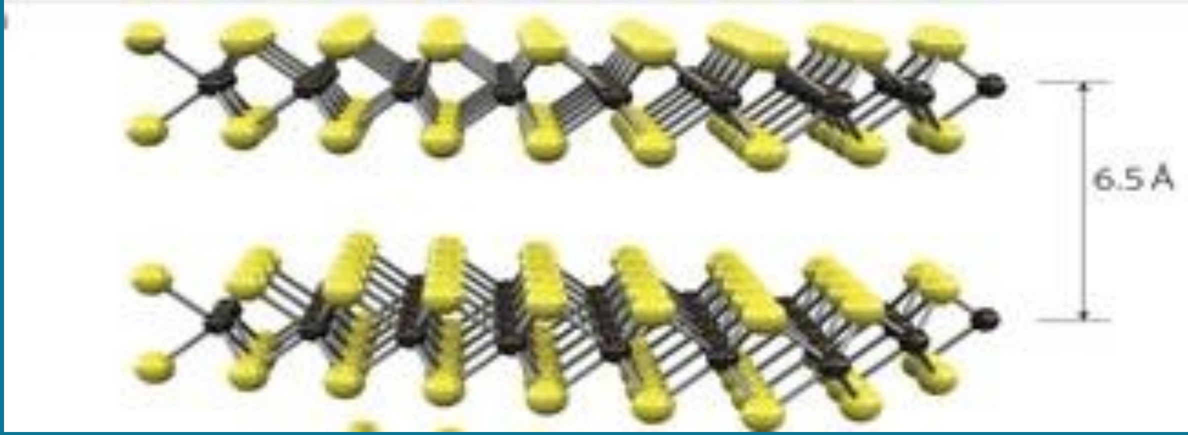
(a) creation of large area and/or multilayer optical, electronic, magnetic and *biological coatings [Inanovate]*,

(b) production of colloidal bioprobes and environmental reference materials

(c) liquid and vapour phase catalytic and photocatalytic chemistry on the test-tube/flask scale,

(d) nanostructured membranes for molecular filtration and catalytic growth of nanowires.

# $MoS_2$ Nanoclusters for Water Splitting (Solar Photocatalysis)



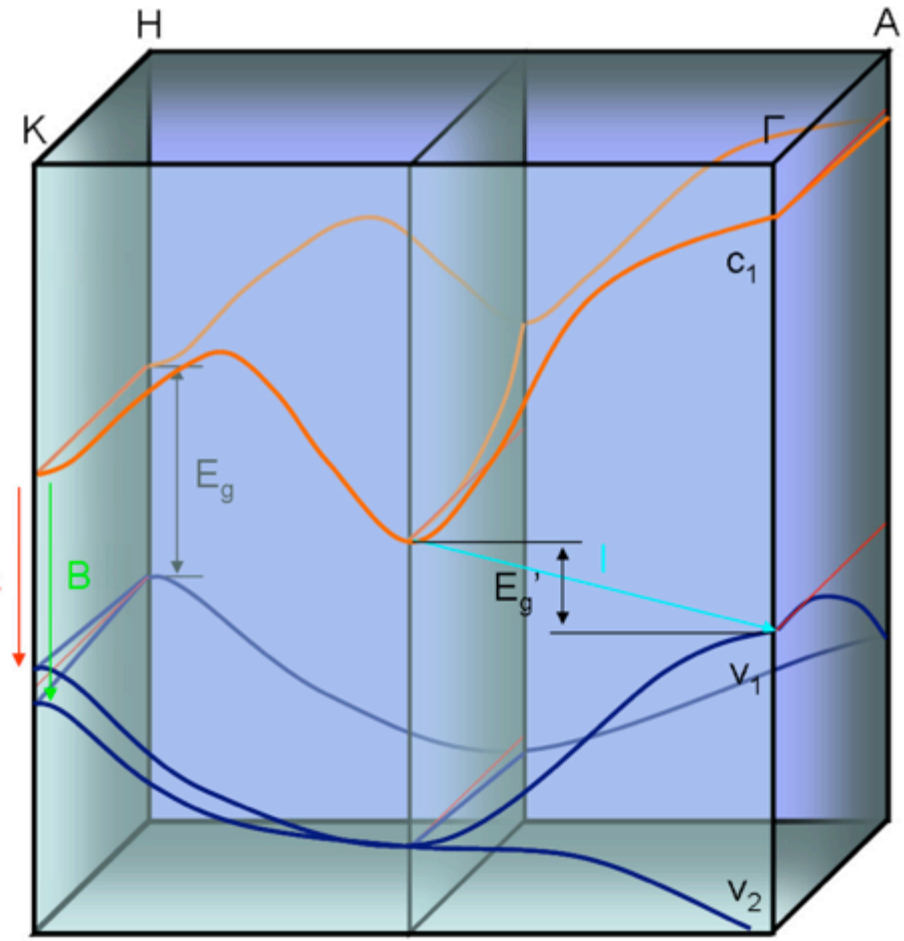

*earth abundant and thus cheap;*
*lubricant, desulphurisation catalyst;*
*electronics, photonics, photocatalyst*

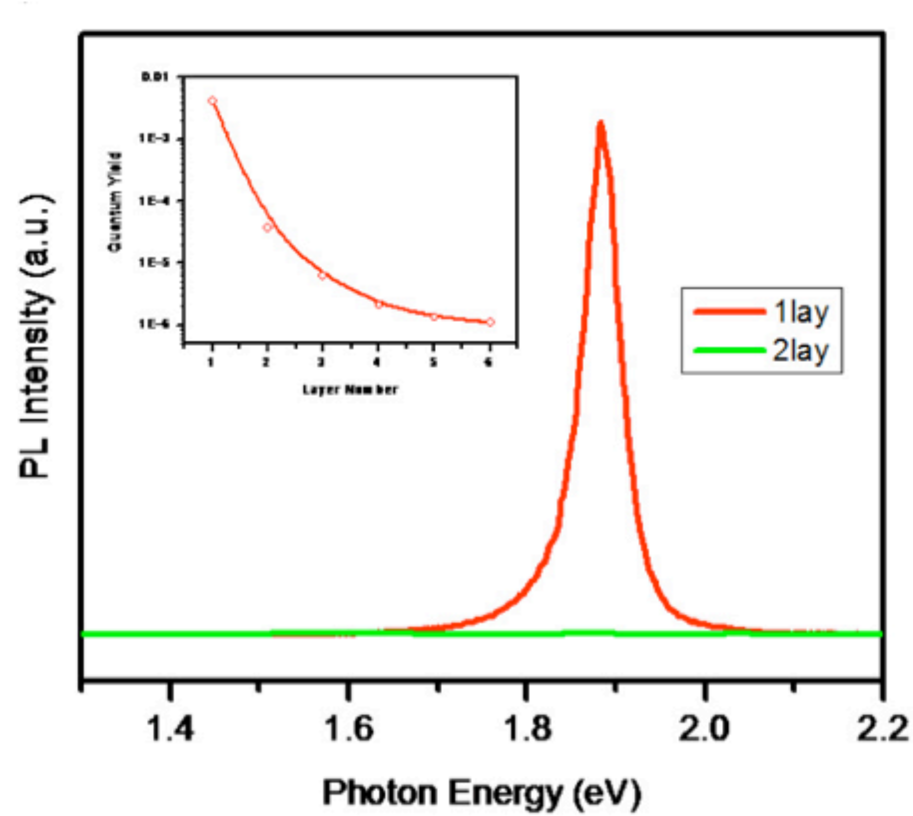
http://actu.epfl.ch/news/a-material-to-revolutionize-electronics-2/

# Atomically Thin $MoS_2$: A New Direct-Gap Semiconductor

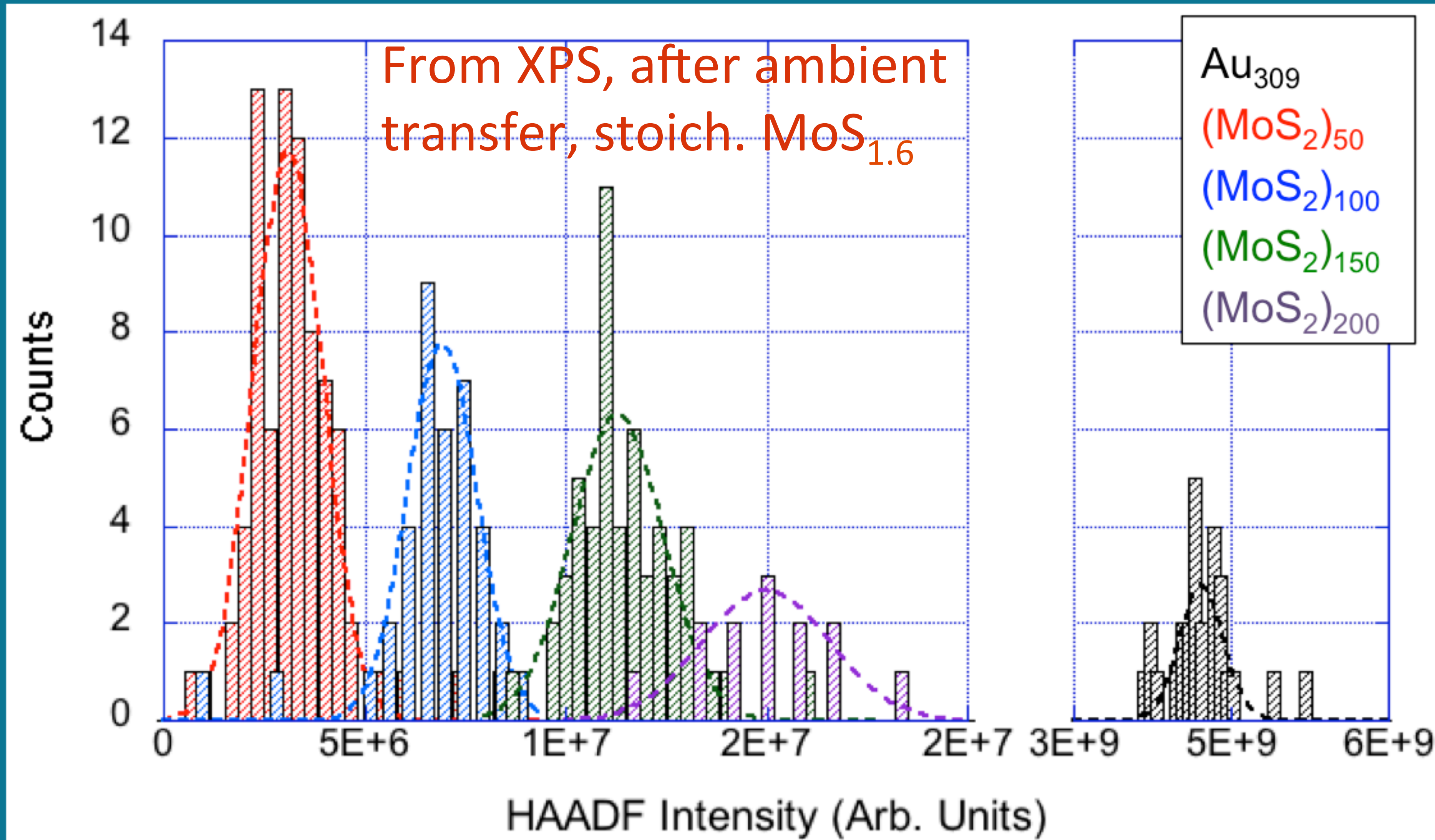
Phys. Rev. Lett. 105, 136805 (2010)

Kin Fai Mak, Changgu Lee, James Hone, Jie Shan, and Tony F. Heinz

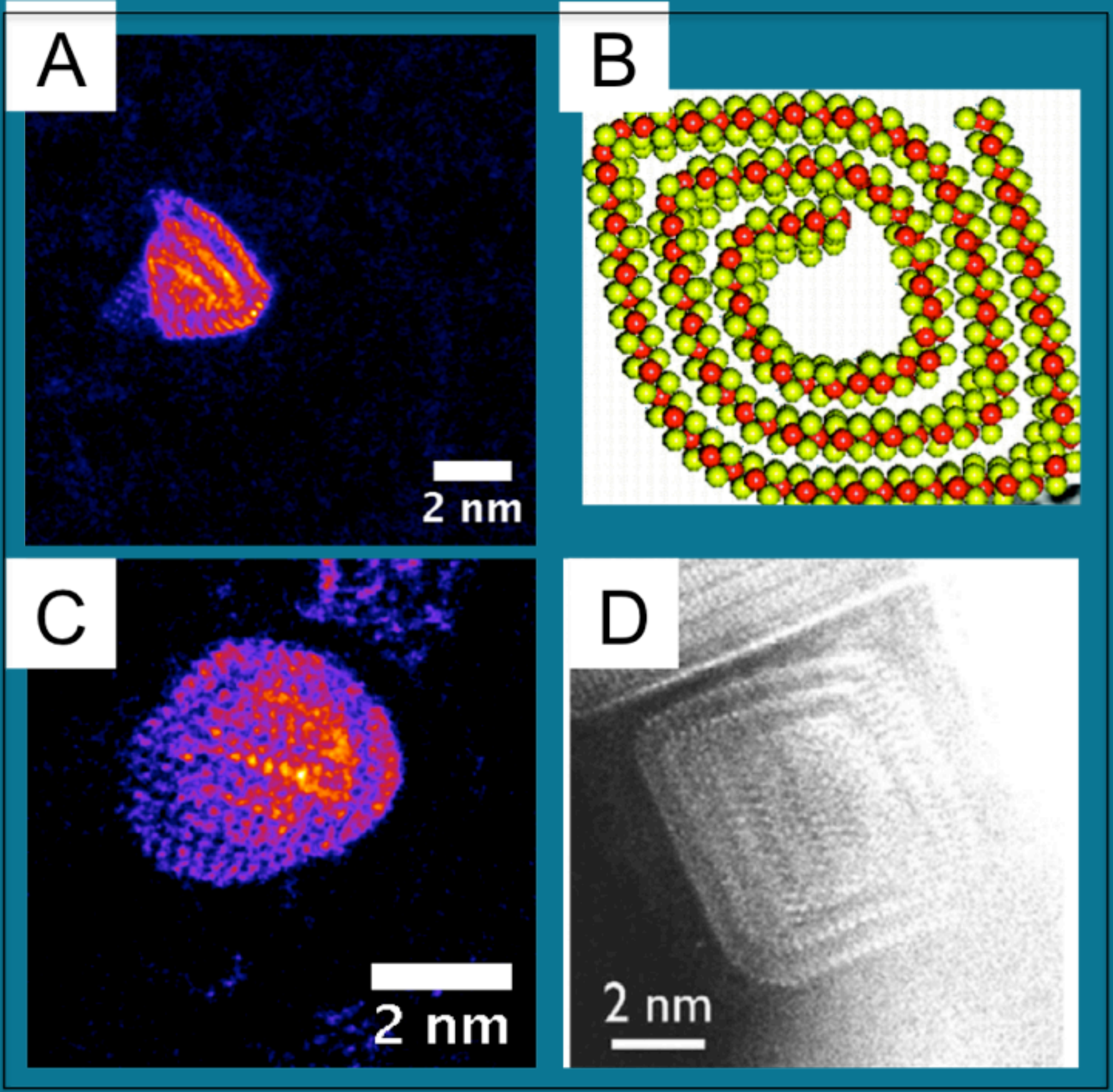



Also possible quantum confinement laterally in 2D flake of limited size



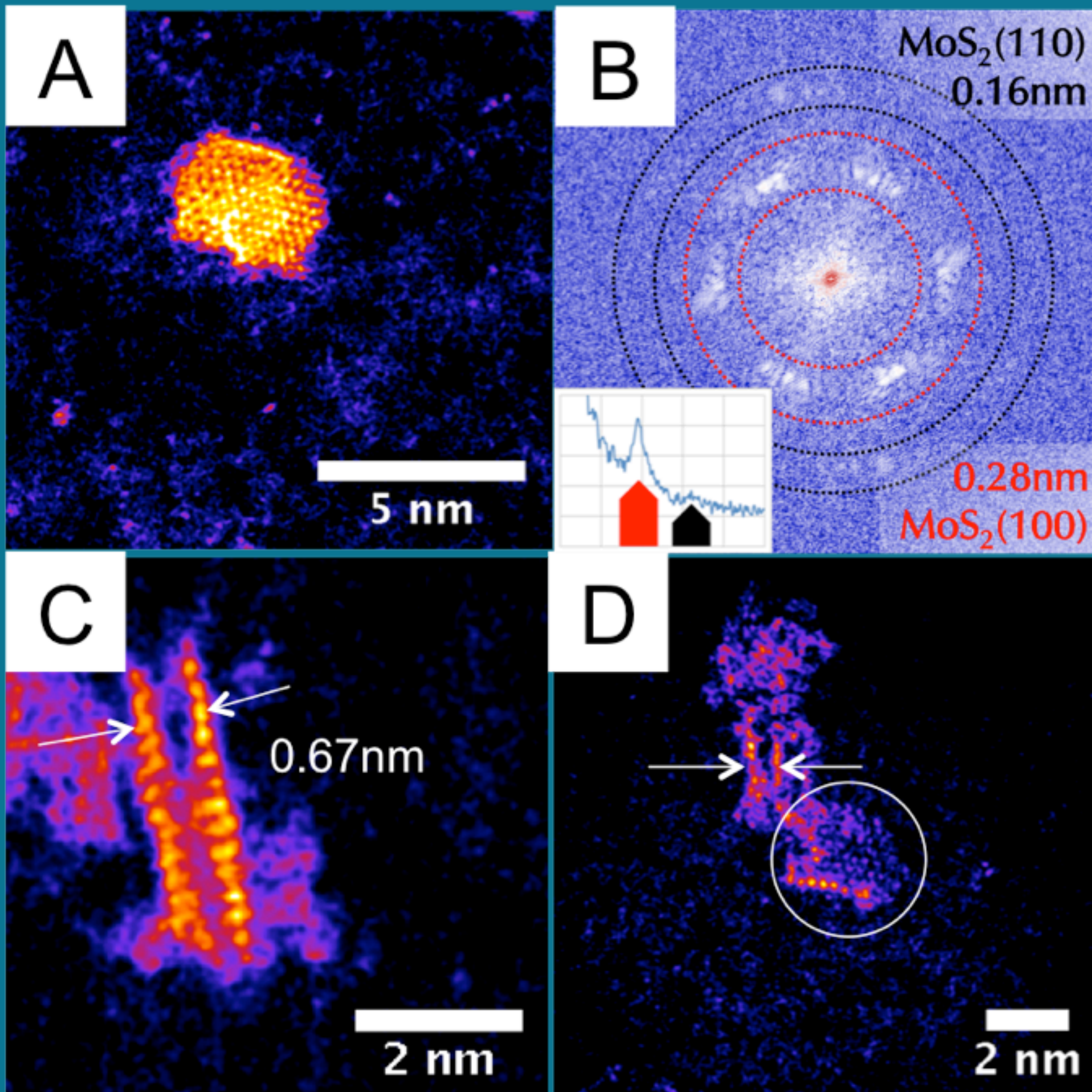

MoS2 cluster and Au mass standard distributions, with Gaussian fits to negate the effect of outliers. FWHM of peaks, δm/m: Au309, 5.0%; (MoS2) 50, 27.9%; (MoS2)100, 12.5%; (MoS2)150, 10.1%; (MoS2)200, 10.5%.



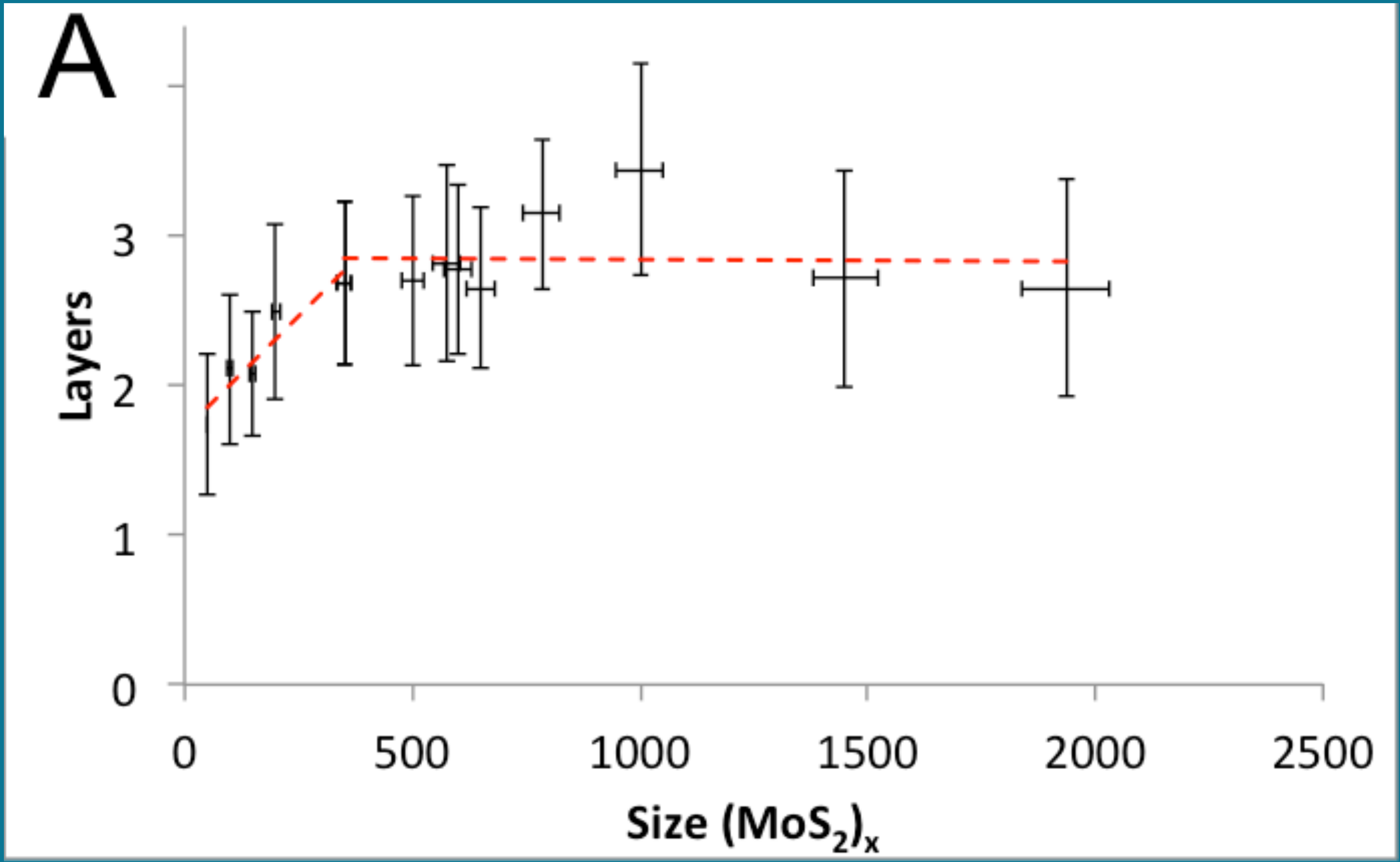

(A) STEM micrograph of seashell type (MoS2), compared with (B) a simulated seashell structure [1]. (C) STEM micrograph of (MoS2)650 fullerene candidate cluster and (D) other MoS2 fullerene clusters in literature [102].

1. A. N. Enyashin, et al, Chemistry of Materials, vol. 21, p. 5627, 2009.

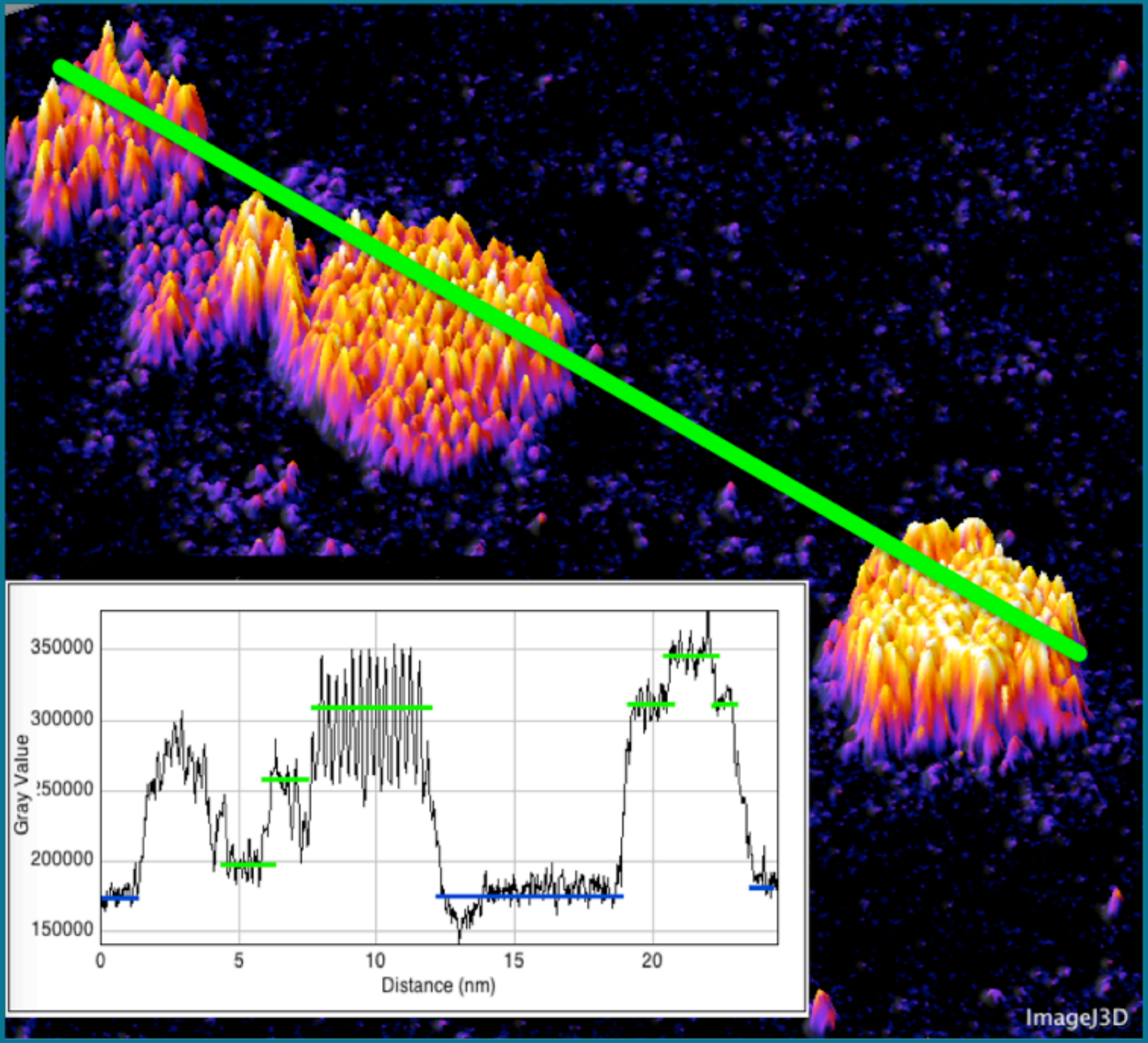
2. M. Bar Sadan et al, PNAS, vol. 105, p. 15643, 2008.




(A) (MoS2)500 trilayer and corresponding FFT (B) showing hexagonal crystal structure characteristic of bulk MoS2 basal plane, with radial intensity profile highlighting the spots (B-Inset). (C) (MoS2)650 side-on showing basal plane edges (002) and (D) another (MoS2)650 with features from both (100) and (002) faces, probably assembled from smaller clusters in gas phase.



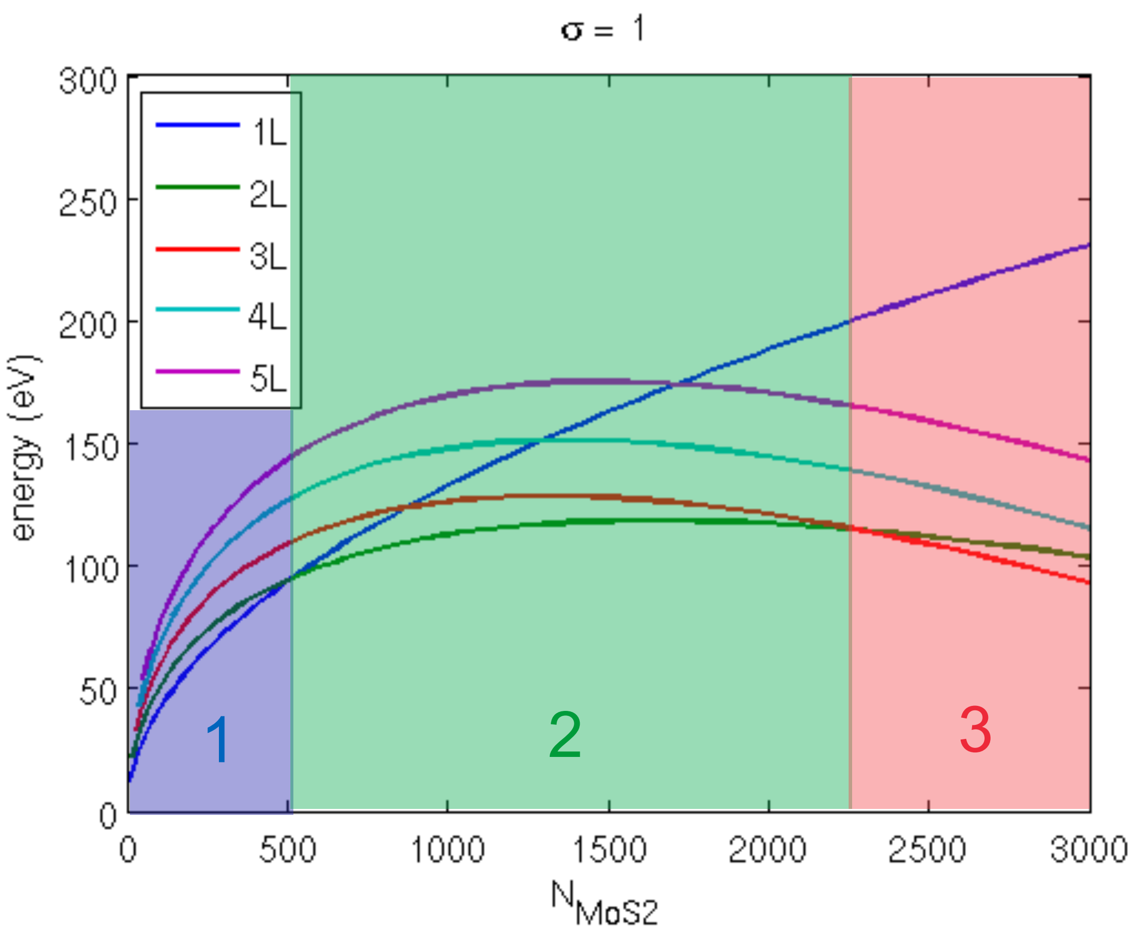

Layer height as a function of cluster size (derived from selected size + measured cluster footprint, both in MoS2 units). The values derived are in agreement with observed line profiles from STEM micrographs.




3D projection from a STEM micrograph of (MoS2)500 clusters. (Inset) Line profile along the clusters showing layered structure (4 layers).

# Number of layers as function of cluster size

- For each size, compare different numbers of layers.
- 1-3 layers, in good agreement with experiment
- About one more than experiment
- Role of defects in nucleation of new layers?



# Conclusions

- Size-selected $(MoS_2)_n$ clusters generated in range n = 50 to 2000 [slightly sub-stoichiometric?]
- Most clusters are quasi-2D sheets, bulk atomic structure, 1-3 layers high
- Average number of layers increases with size
- Consistent with DFT calculations (edge energy vs interlayer binding)
- Speculate that point defects enhance interlayer surface binding/nucleation
- Promising candidates for photocatalysis
- Need to manage contamination of reactive sites

# THE END