Atomic structure and mass-production of size-selected nanoparticles (clusters)

Richard Palmer

Taylor & Francis Group
an informa business

Swansea University
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Feynman's conception of nanotechnology

- Dec. 1959, Feynman's lecture to the APS

  There's Plenty of Room at the Bottom

  An Invitation to Enter a New Field of Physics

"the problem of manipulating and controlling things on a small scale"

- Arranging the atoms
- Writing and reading information, stored in metal clusters – **"a bit of… 100 atoms"**

"But I am not afraid to consider the final question as to whether, ultimately – in the great future – we can arrange the atoms the way we want; the very atoms, all the way down!
What would the properties of materials be if we could really arrange the atoms the way we want them?"

Can we arrange the atoms (in clusters) the way we want?

Can we transform cluster science into a manufacturing technology?

Architecture on the Nanometre-Scale: Arranging the Atoms

February 14, 2010

Image of the Day: The World's Smallest Valentine

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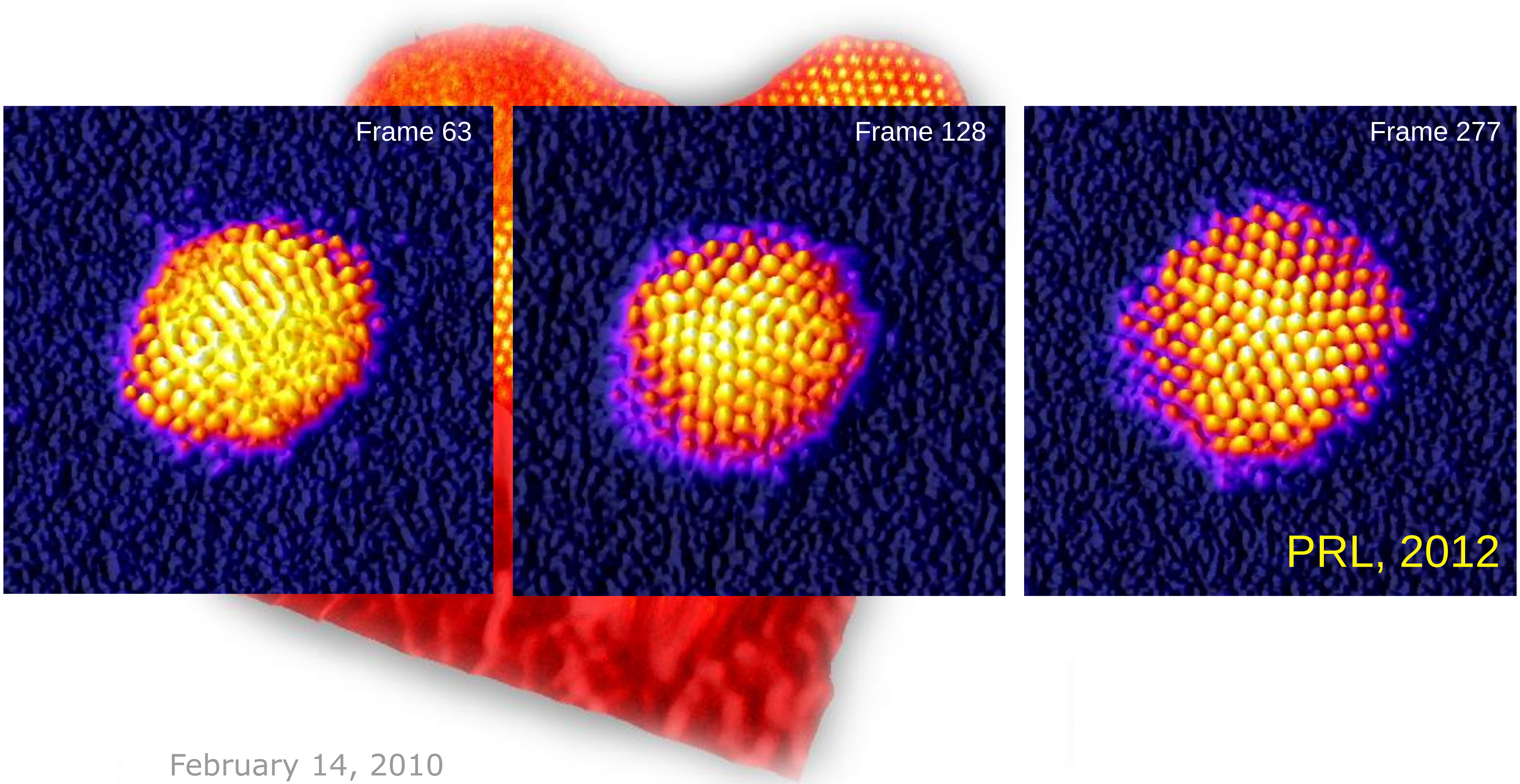
Architecture on the Nanometre-Scale: Arranging the Atoms



February 14, 2010
Image of the Day: The World's Smallest Valentine

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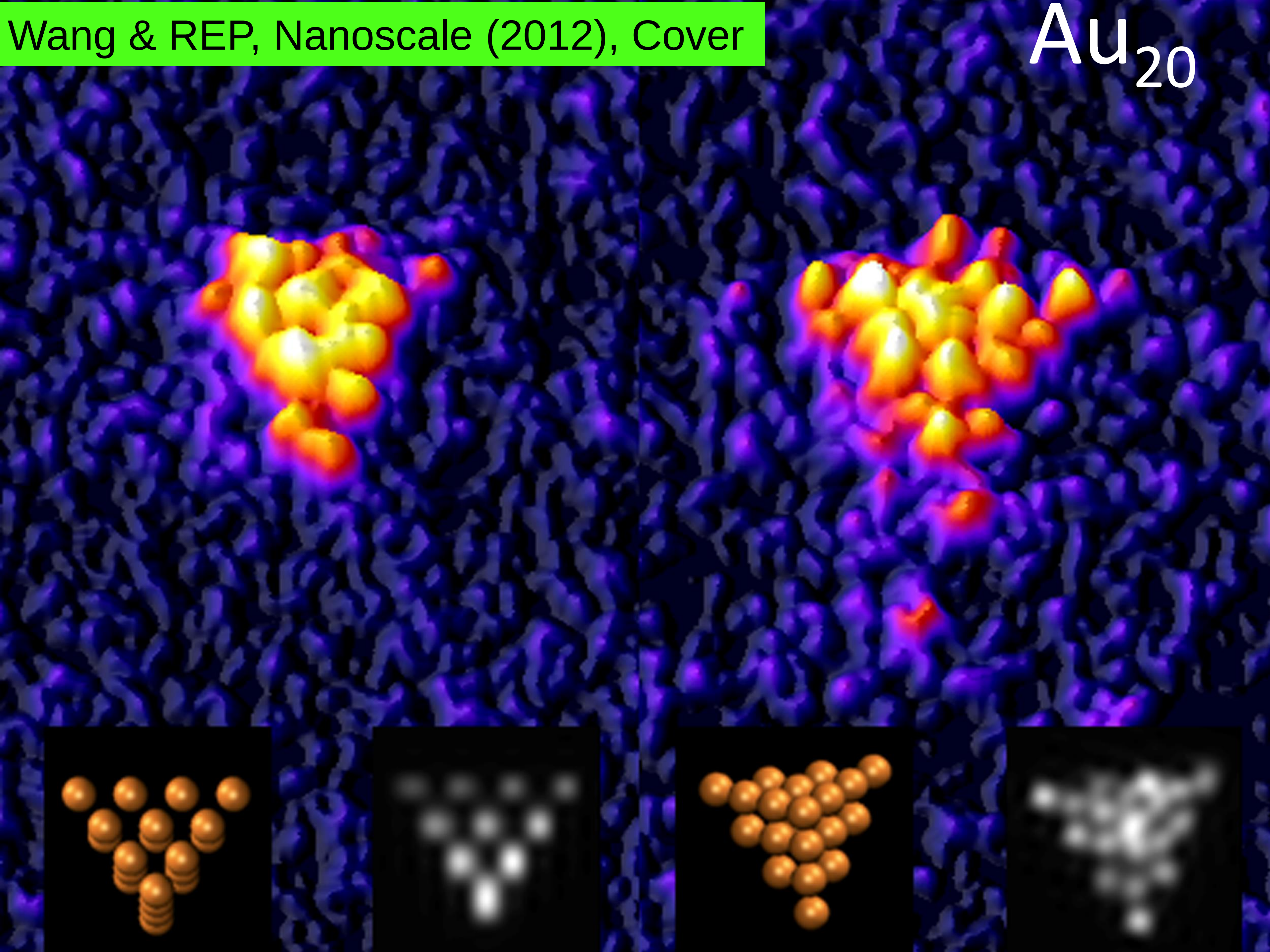
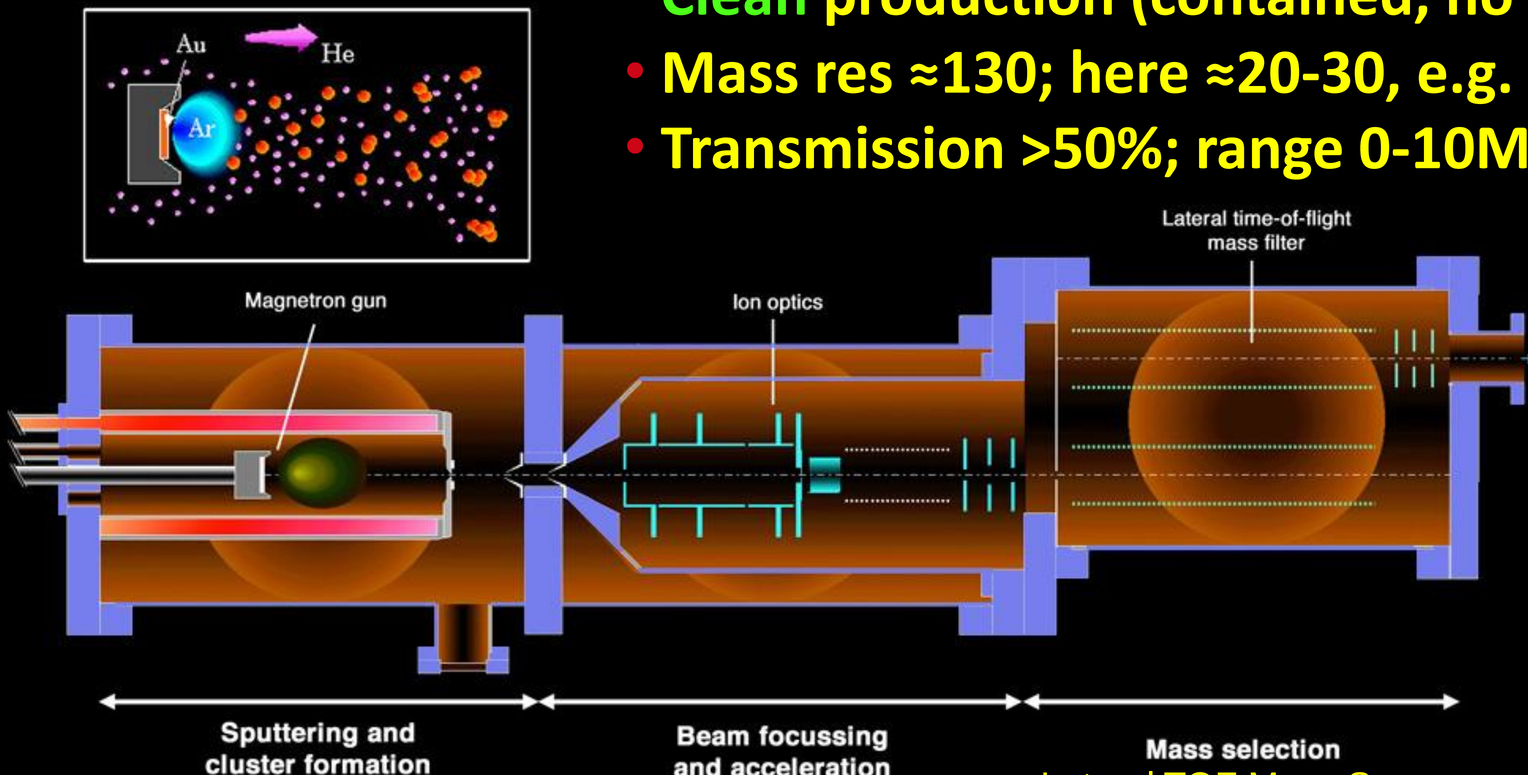
Wang & REP, Nanoscale (2012), Cover



Size-selected "cluster beam deposition" (CBD)

- Clean production (contained, no effluent)
- Mass res ≈130; here ≈20-30, e.g. 55±1
- Transmission >50%; range 0-10M amu



Cluster Source
Pratontep et al, RSI (2005)

Lateral TOF Mass Spec
von Issendorff and Palmer, RSI (1999)
US, Europe, Japan patents

0.1nA+

0.1 nanoAmp ≈ 10^9 clusters/second
= 10^{11} atoms/second for size N=100
≈ 0.1 microgram of Au clusters/hour

Some applications of cluster beams

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

(2) liquid and vapour phase **catalysis** and photocatalysis on the test-tube/flask scale [Johnson Matthey, Loughborough]

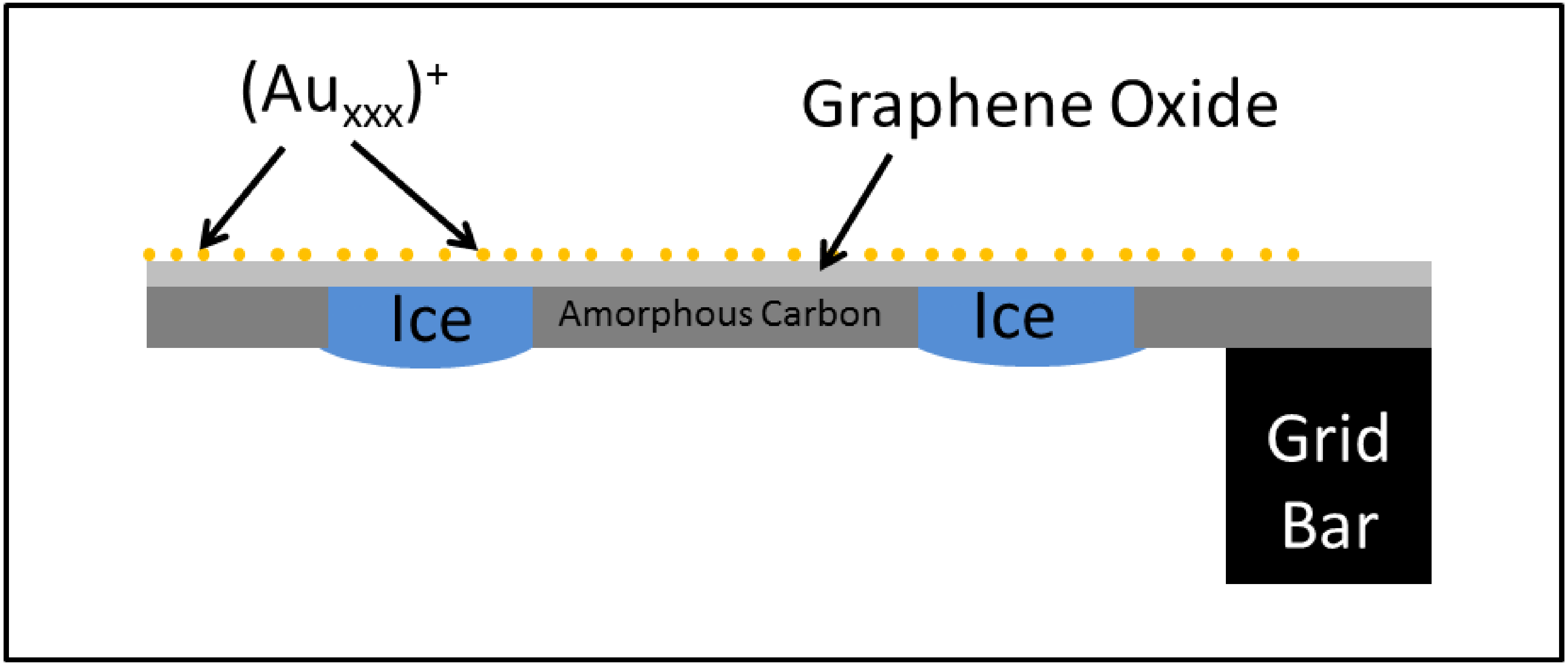
(3) nanostructured membranes for molecular filtration and **catalytic growth** of nanowires [Rome, Harvard]

(4) fiducial markers for electron **tomography** [Bristol, NIH]

(5) **reference** materials for nanometrology [NPL, PTB]

(6) production of **colloids** for diagnostics and radiotherapy

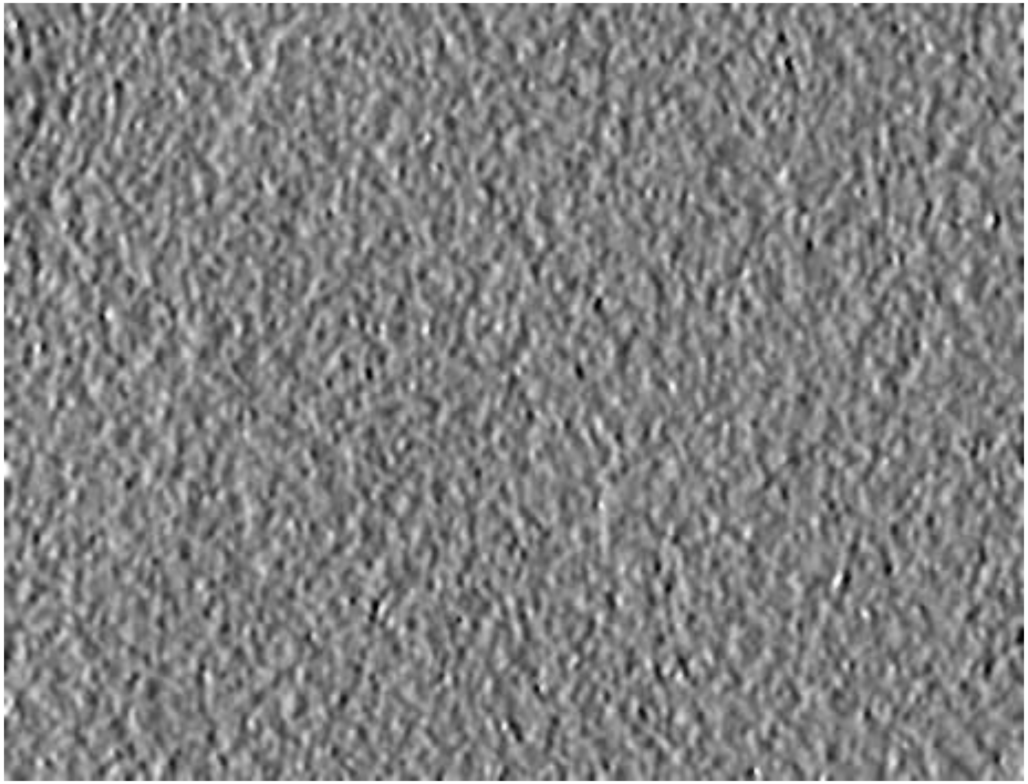
Fiducial Markers for CryoTomography



Schematic diagram showing the tomography electron microscopy grid (not to scale). Amorphous carbon with holes is covering a copper mesh electron microscopy grid. A graphene oxide film is supported on top of the amorphous carbon leaving just the graphene oxide over the holes. Au size-selected clusters are deposited on top of the GO film. Vitreous ice containing the sample can be placed on the other side for imaging through the holes.

Arkill et al, Sci Rep (2015)

Fiducial Markers for CryoTomography



Tomographic Reconstruction of TMV

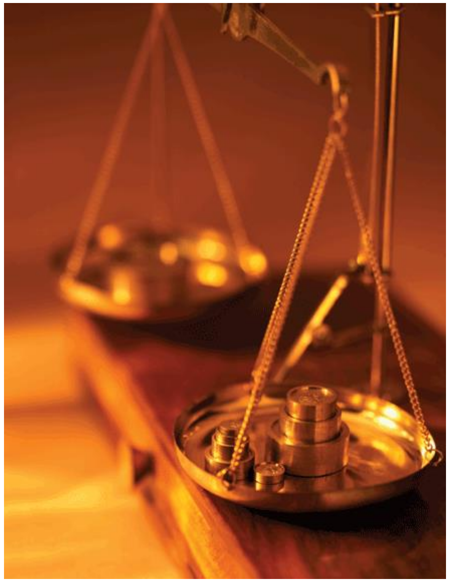
Arkill et al, Sci Rep (2015)

NanoBEE, PI JR Lead

Size-selected clusters as mass standards (HAADF STEM)

“a bit of… 100 atoms” *Richard Feynman*, 1959

Weighing Nanoparticles



nature nanotechnology

nature.com > Journal home > Table of Contents

Research Highlights

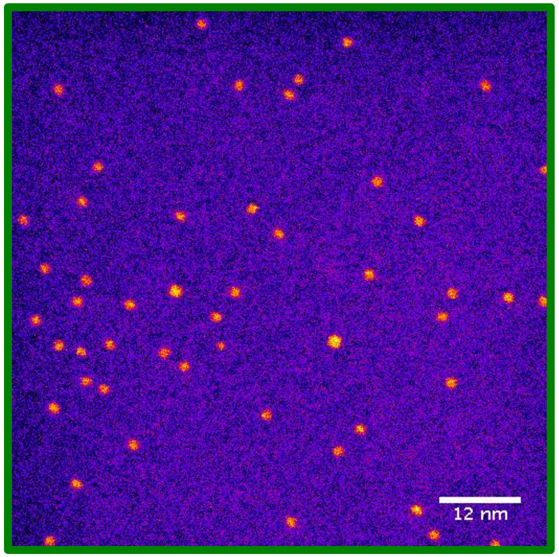
Nature Nanotechnology (19 December 2008) | doi:10.1038/nnano.2008.408

Nanoparticles: Gold standard

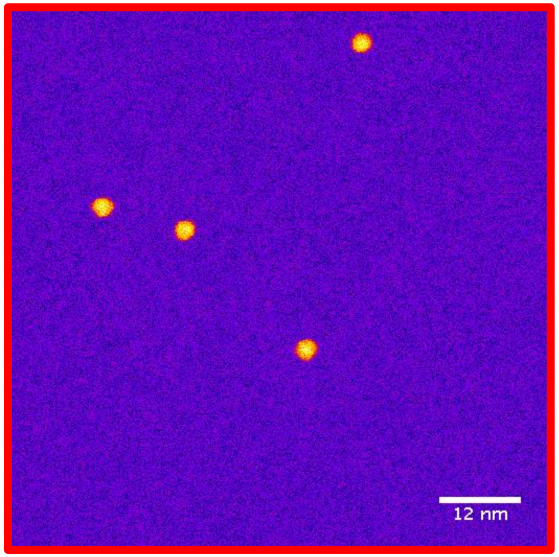
Tim Reid

Nanoparticles can have strikingly different properties depending on their size, so it is important to have effective ways of measuring them. Ziyou Li and colleagues at the University of Birmingham have developed mass standards that could provide a quick and easy way of weighing nanoparticles and gaining insight into their fine structure.

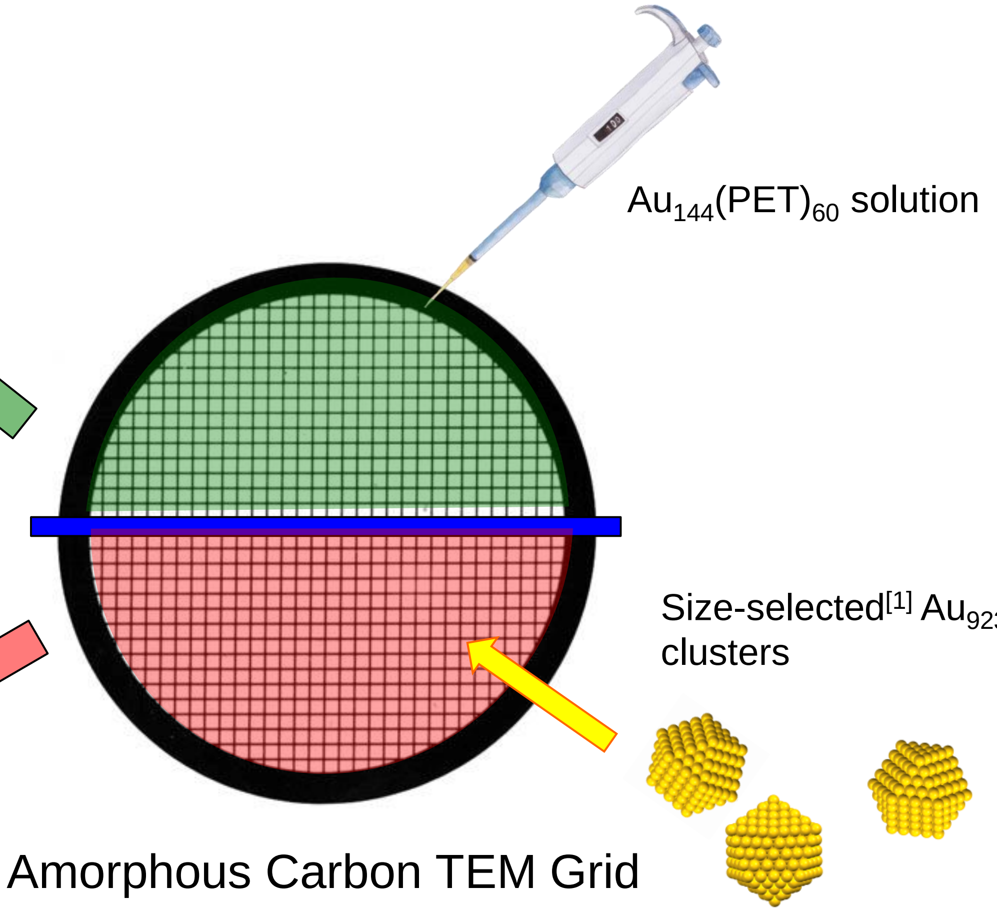
Atom Counting with Cluster Standards



$Au_{144}(PET)_{60}$ clusters

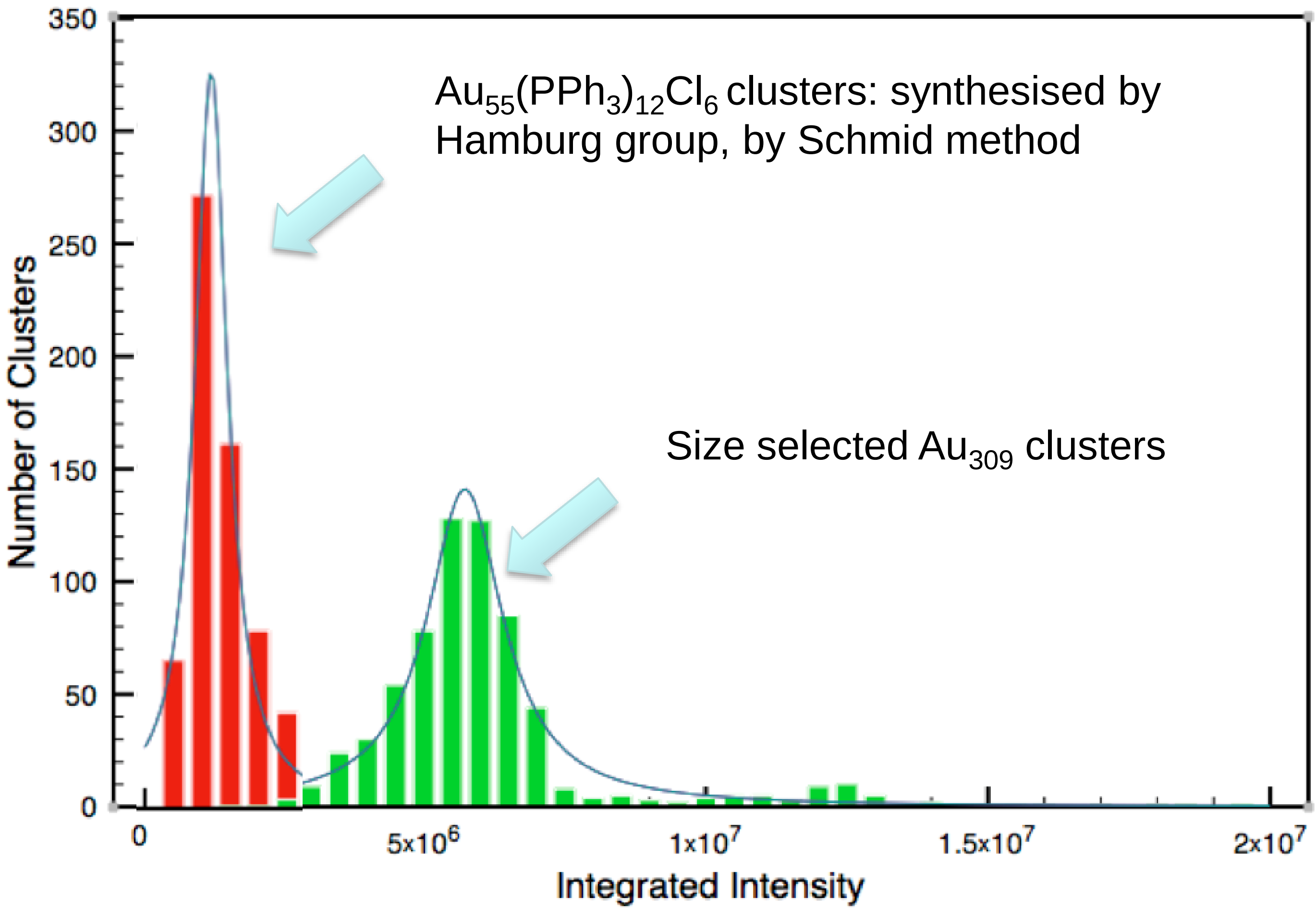


Size-selected Au_{923} clusters



[1] S. Pratontep, S. J. Carroll, C. Xirouchaki, M. Streun, and R. E. Palmer, Rev. Sci. Instrum., 2005, 76, 045103.

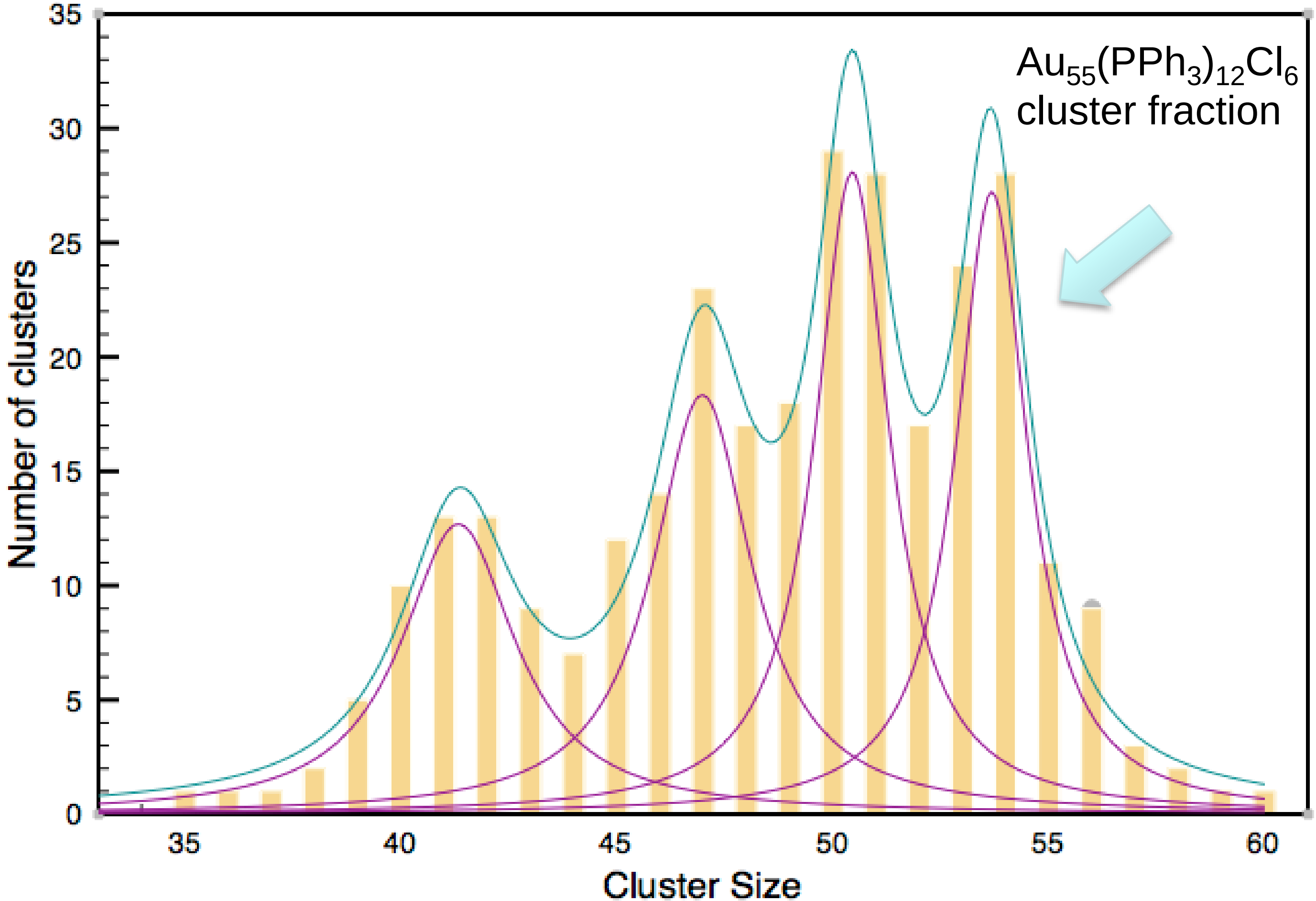
Schmid cluster: cluster weighing & "fractionation"



Weighing "$Au_{55}(PPh_3)_{12}Cl_6$" clusters against size-selected Au_{309} clusters

Nan Jian + Hamburg group

Schmid cluster: cluster weighing & “fractionation”

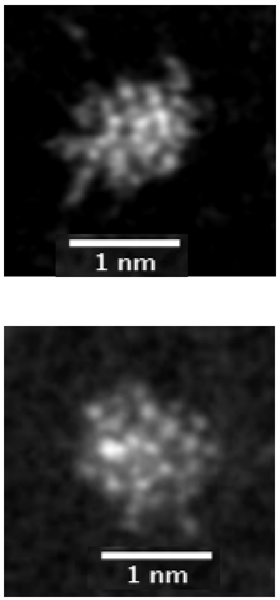


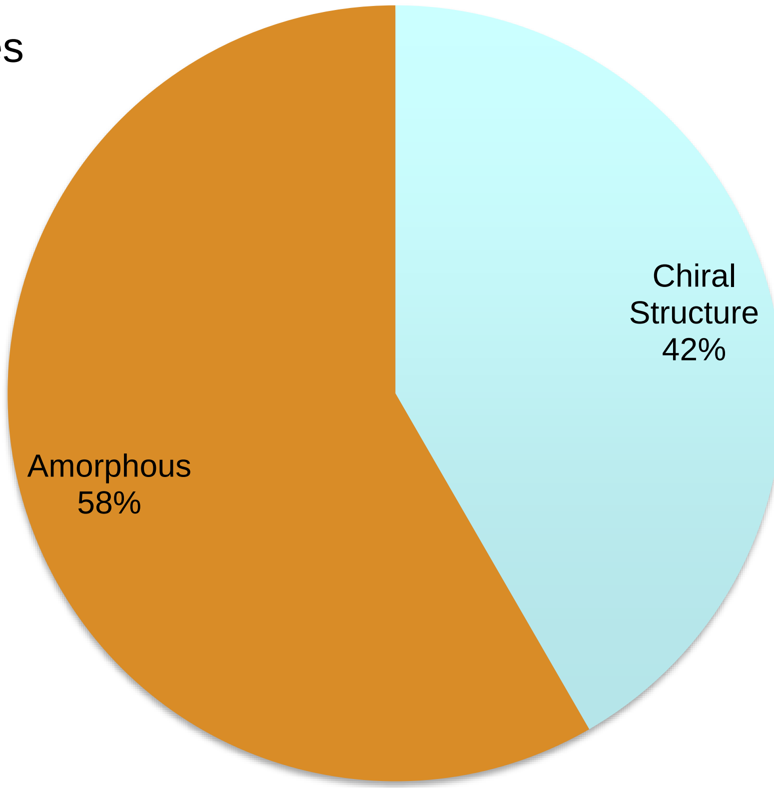
Fine distribution of “Schmid clusters”, the ligand contribution to the intensity has been eliminated. The fourth fraction at core-size n ~ 54 is assigned to $Au_{55}(PPh_3)_{12}Cl_6$.

Jian et al, Nanoscale (2014)

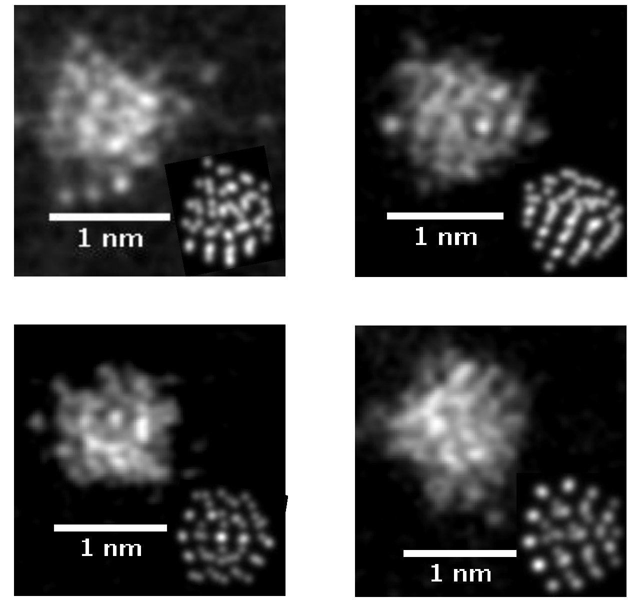
The Schmid cluster: Atomic structures of $Au_{55}(PPh_3)_{12}Cl_6$ clusters in the “purified” fraction

Amorphous structures



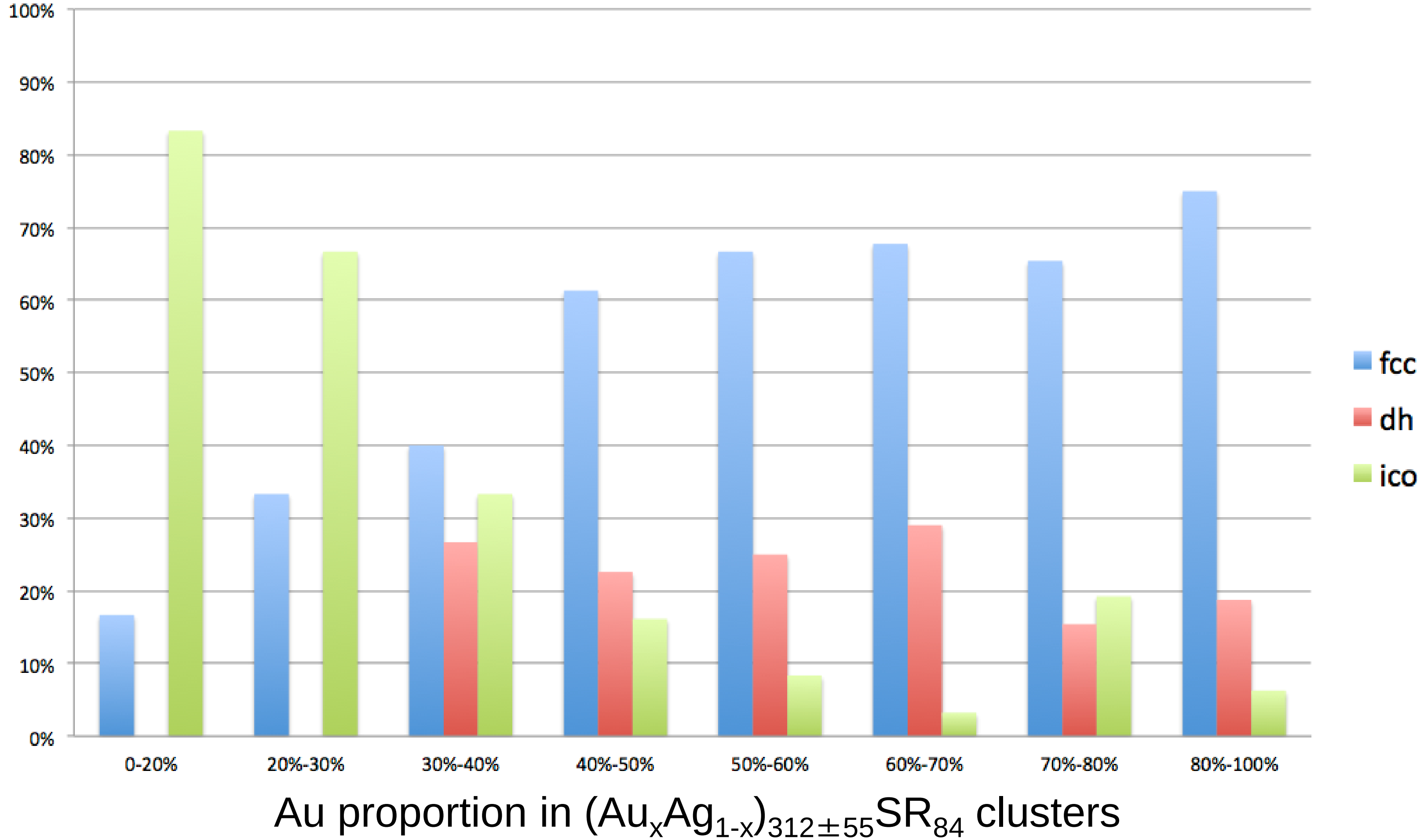


Clusters matching chiral structure



42% of clusters in the “purified” fraction match the hybrid (chiral) model structure; no matches to cuboctahedral, icosahedral or decahedral structures were found.

Atomic structure versus composition: $(Au_xAg_{1-x})_{312\pm55}SR_{84}$ clusters



The proportion of the fcc, Ino-decahedral and icosahedral motifs for thiolated $(Au\text{-}Ag)_{312\pm55}$ clusters with the composition varying from pure Ag(left) to pure Au (right).

Synthesis: Dass et al

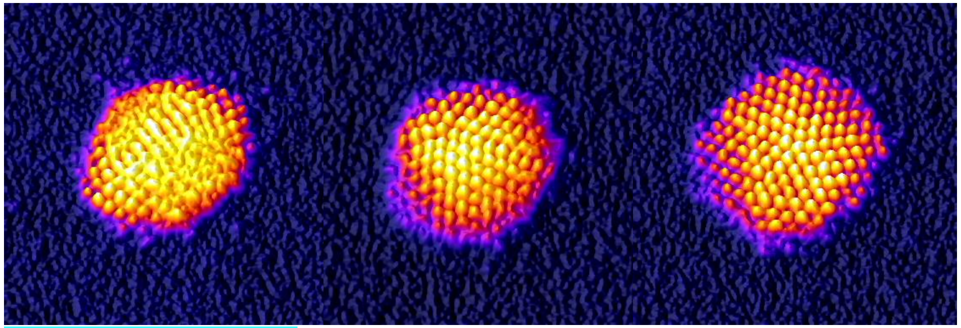
Nan Jian and REP, JPCC (2015)

Atomic structure and dynamics of size-selected clusters

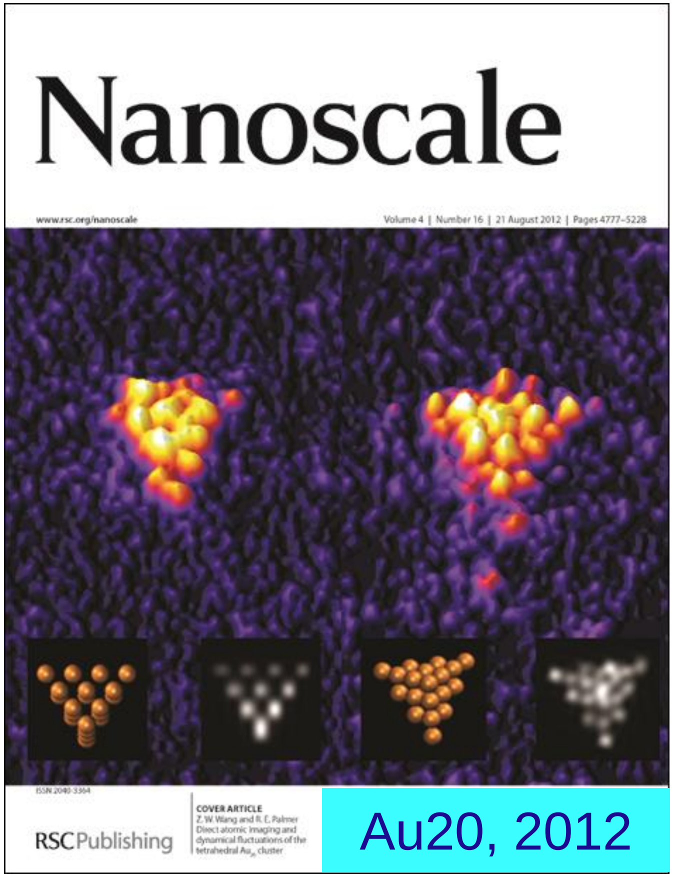
“a bit of… 100 atoms” *Richard Feynman*, 1959

Imaging size-selected Au clusters

11 Feb 1921 – 27 Aug 2014



Au923
PRL, 2012



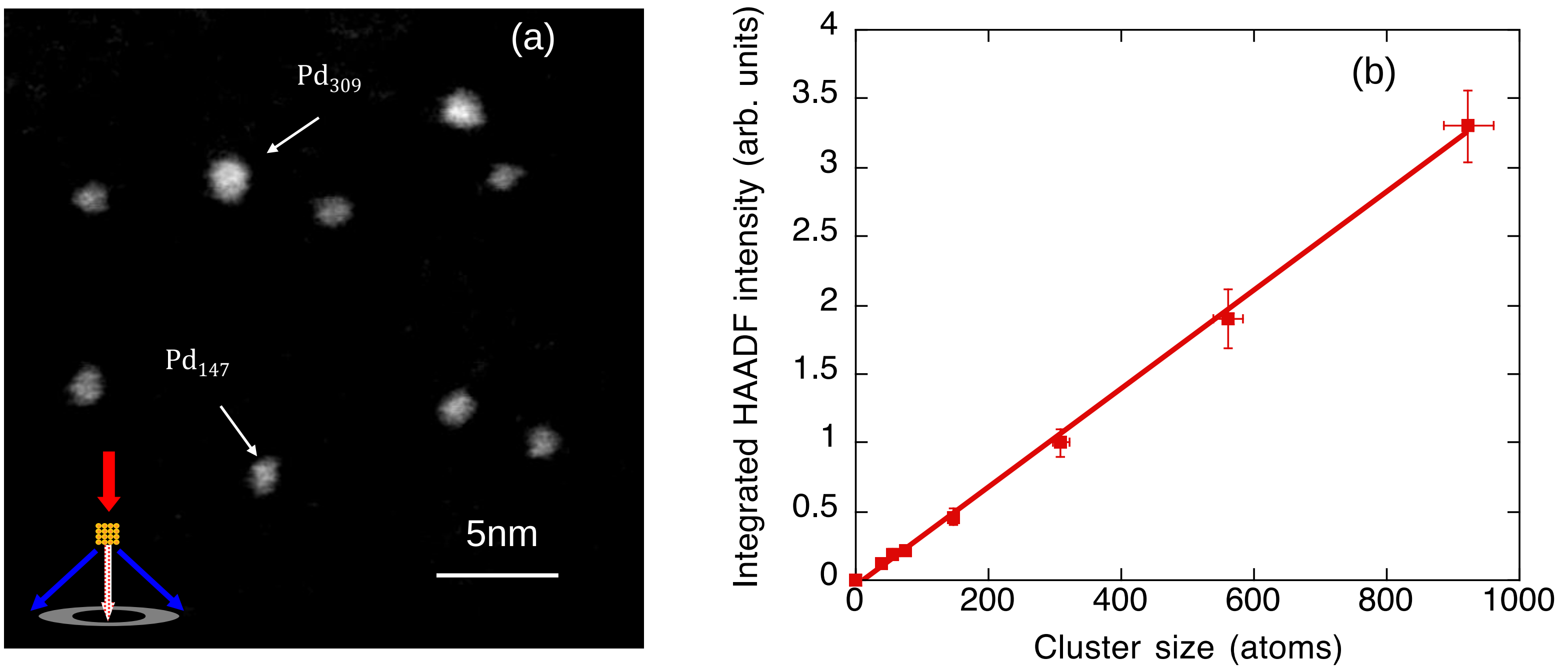
Au20, 2012

"one can also think of looking at the ***actual form of aggregates*** *of a few heavy atoms on light substrates"*

Jacques Friedel, Summary, ISSPIC-2 (1980)

Quantitative calibration of STEM with size-selected clusters

❑ Dependence of integrated HAADF-STEM intensity on cluster size



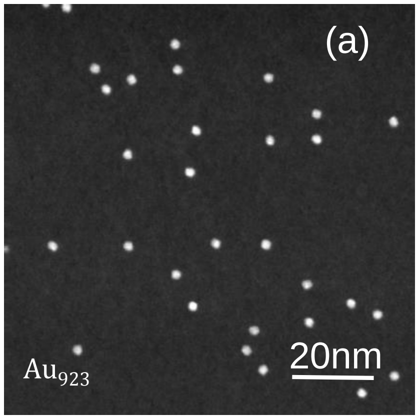
- ✓ Linear relationship between the integrated HAADF intensity and cluster size is observed with Pd clusters, as with Au[1].
- ✓ This relationship extends to smaller clusters (N<100)

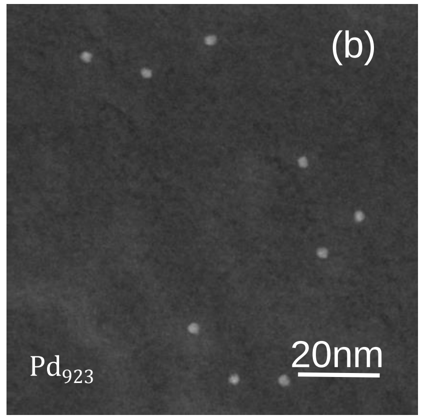
[1] Young, Li, Palmer et al, Phys. Rev. Lett., **101** 246103 (2008)

Zhiwei Wang

Quantitative calibration of STEM (Z dependence)

❑ **Calibration of exponent "n" in Z^n dependent HAADF intensity**



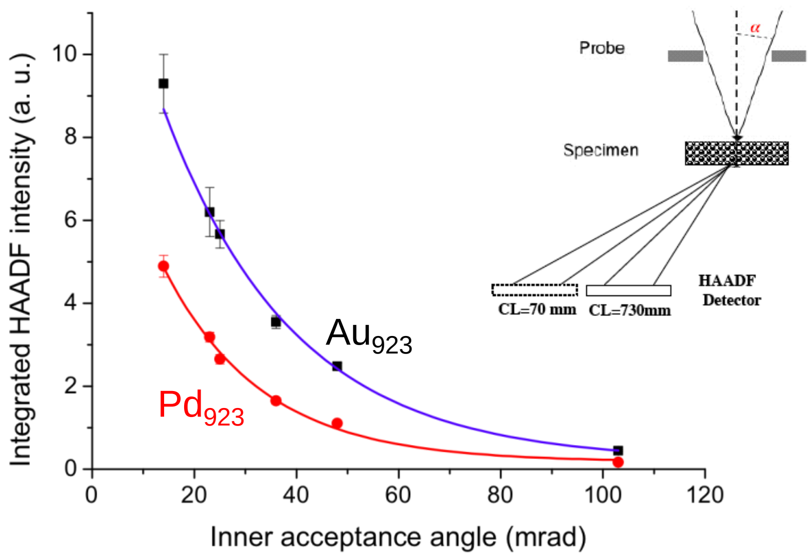


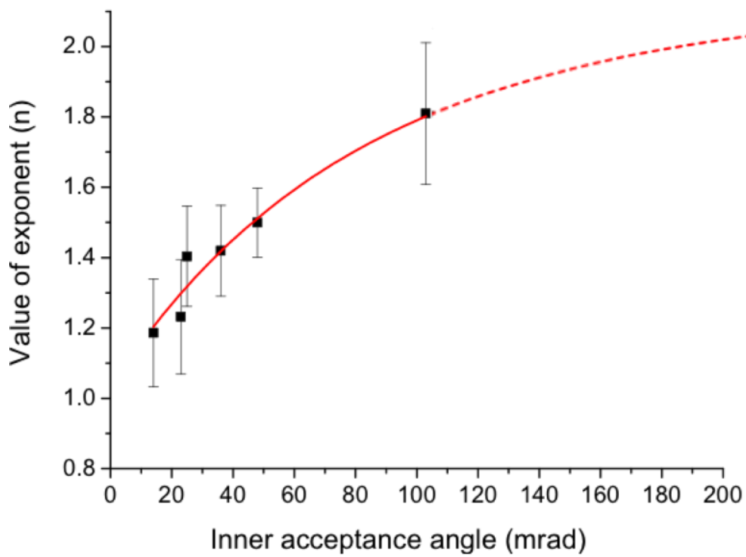
➢ Calibration principles

✓ *sample A and B have the same thickness*

✓ *imaged under the same conditions*

$$\frac{I_A}{I_B} = \left(\frac{Z_A}{Z_B}\right)^n$$



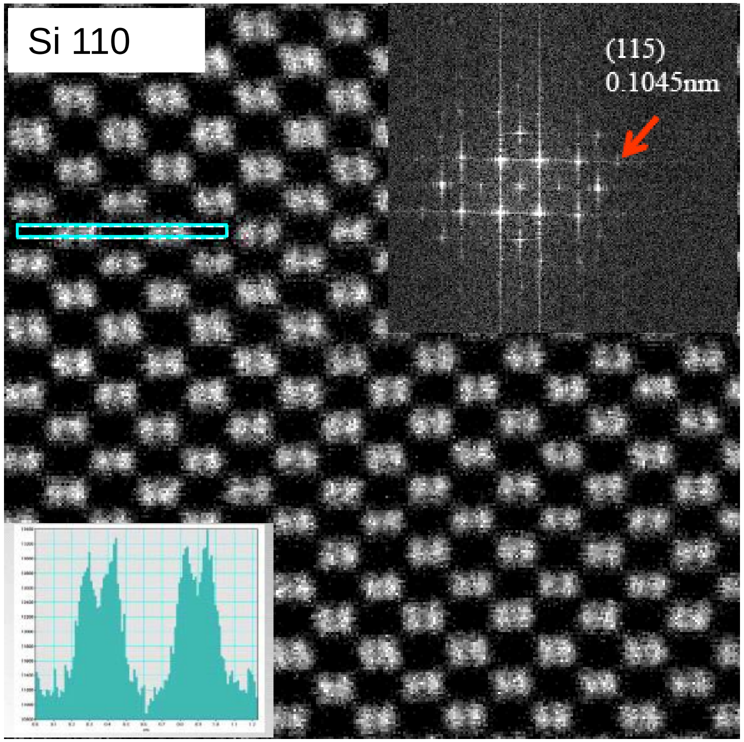


Wang et al, Phys Rev B, 2011

Aberration-corrected STEM instrument

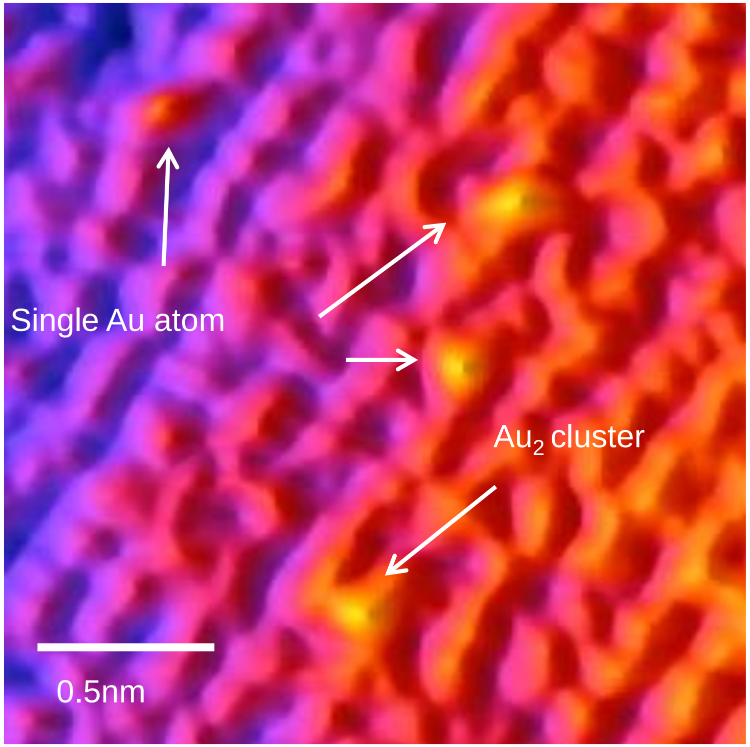
Cs–corrected JEOL 2100F: installed in NPRL, summer 2009

Angstrom or even sub-Å resolution obtainable

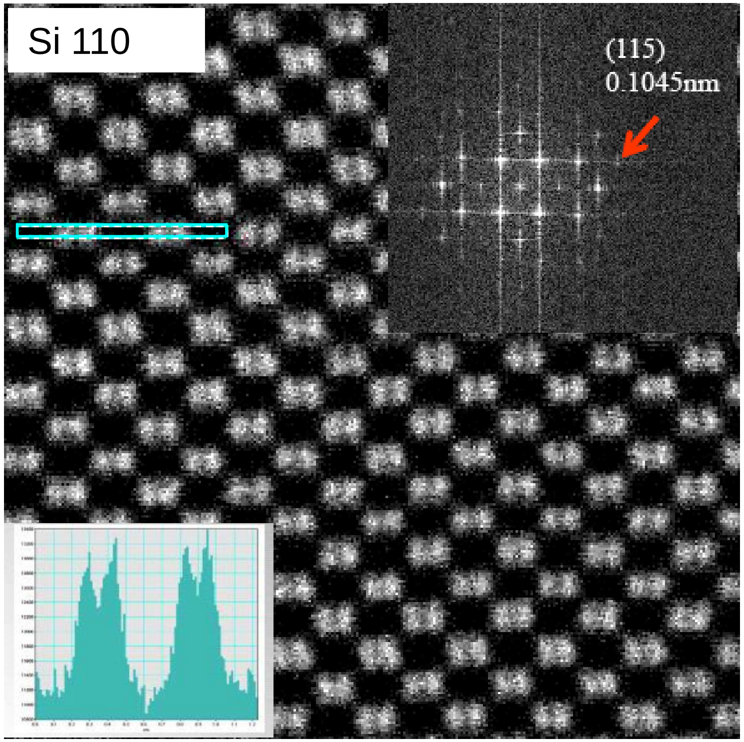


Aberration-corrected STEM instrument

Imaging single atoms



Angstrom or even sub-Å resolution obtainable



Nan Jian in Rogers et al,
ACS Catalysis 5 4377 (2015)

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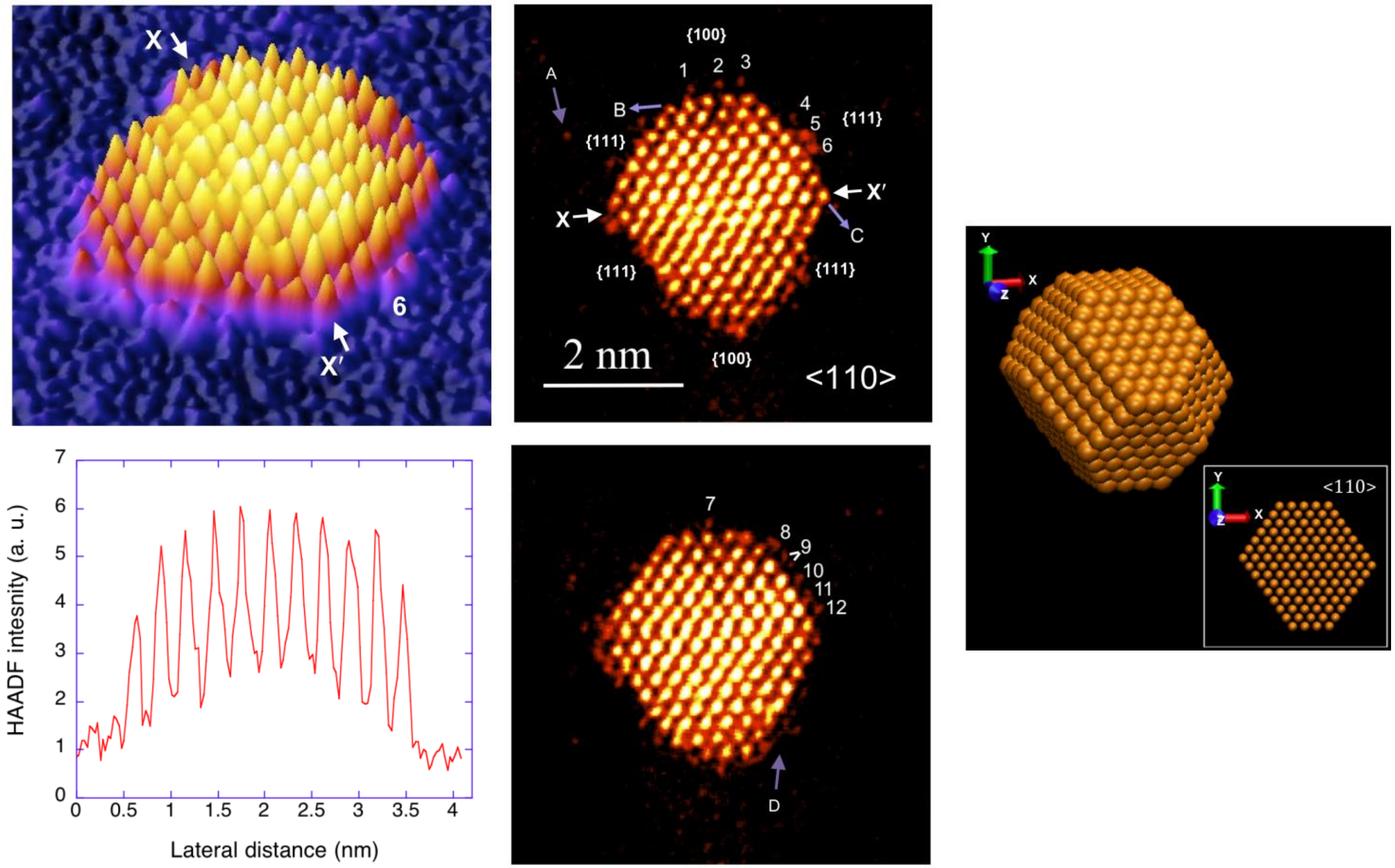
Au adatoms on the surface of Au_{923}

- **Direct visualization of surface adatoms**

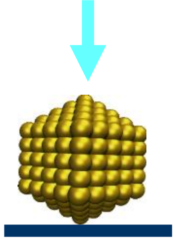


✓ Adsorbed species are clearly visible on the surface of the TO (fcc) cluster

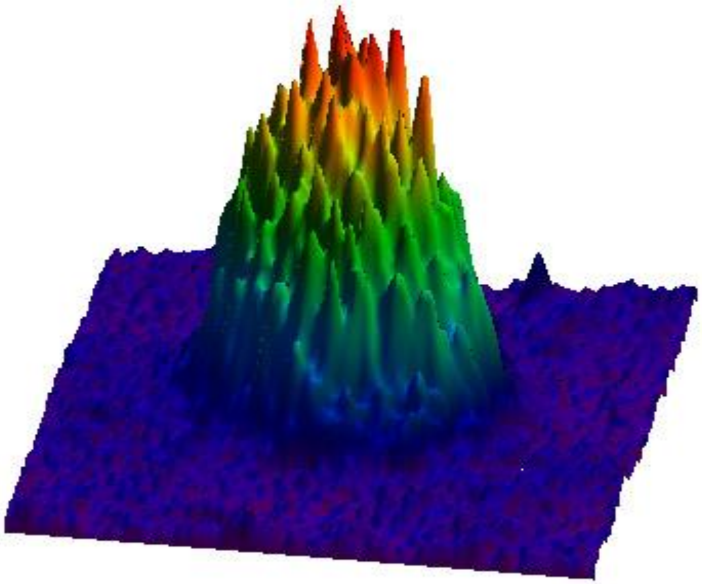
✓ The number and positions of surface species display significant changes

Wang & REP, Nano Lett (2012)

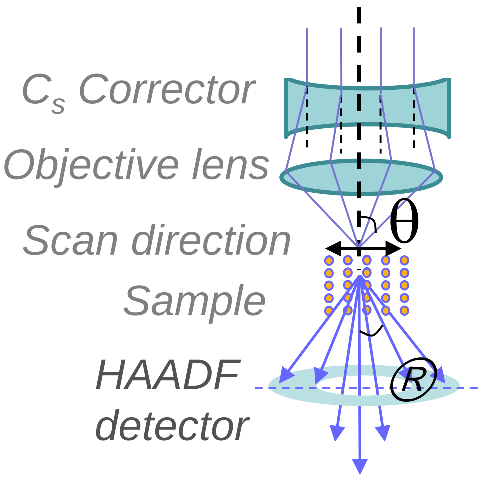
3D Atom Density Profile for Au_{309}

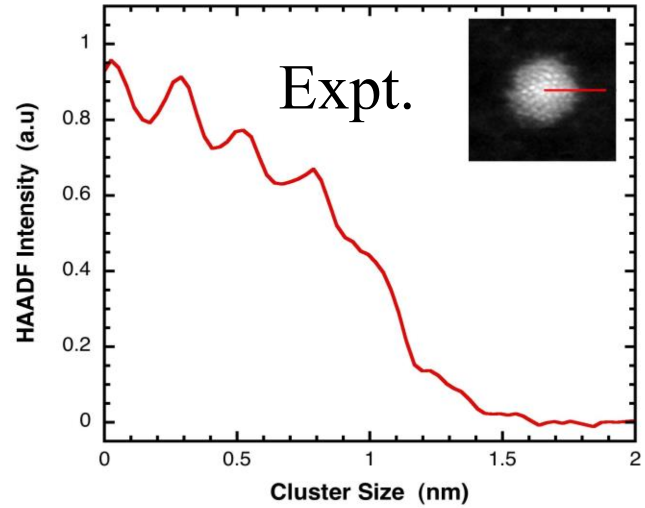


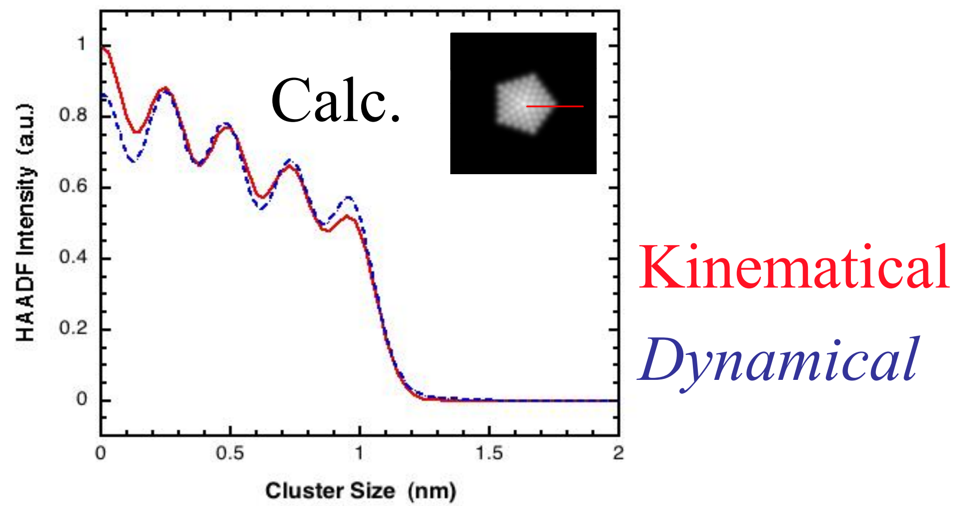
truncated decahedron



Probe-corrected STEM

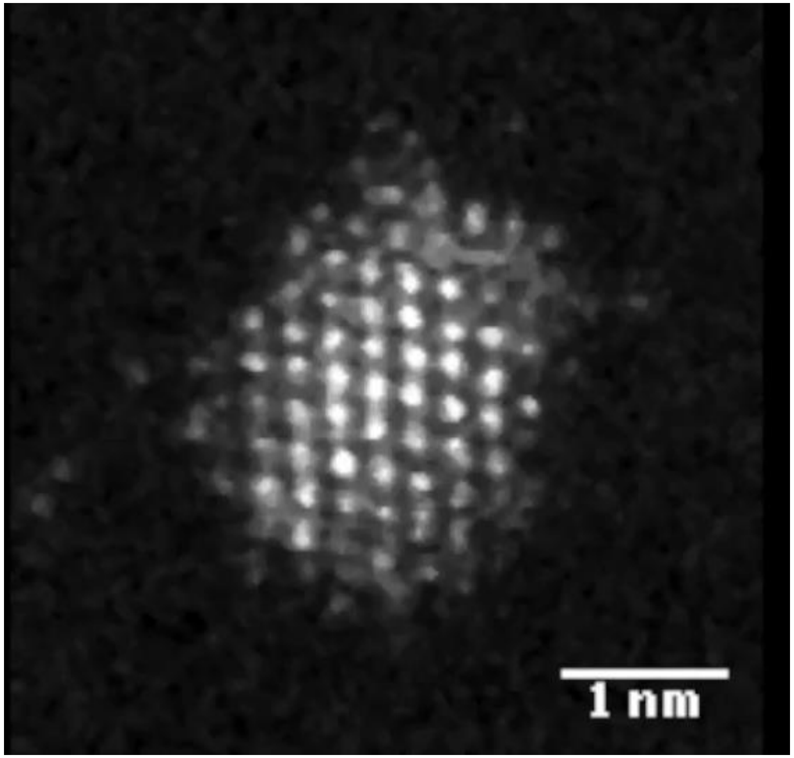






Li et al, Nature, 2008

Au_{309} structure oscillations



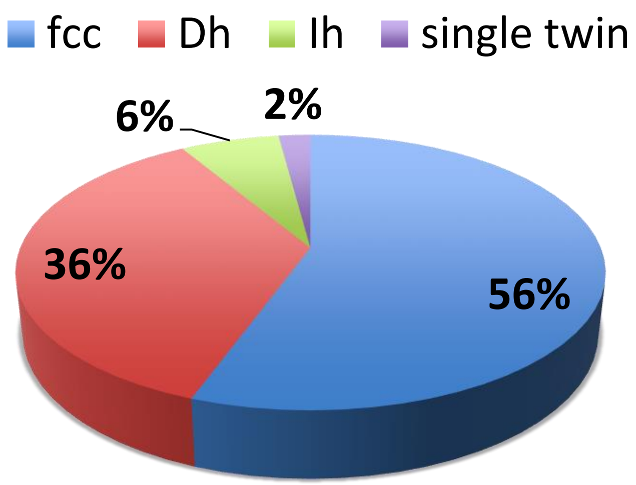
- Au_{309} clusters fluctuate between Dh and fcc during 'video imaging'
- Different behaviour from Au_{561}: Dh➔fcc transformation

Dose: 2.6×10^4 e^-/Angstrom^2/frame, 2.9 seconds per frame, 13.12nm × 13.12nm.

Dawn Wells

Au_{309} structure oscillations

- Frame by frame analysis of Au_{309} videos gives the proportion of structural isomers
- Images not in focus discounted
- Fcc is the most commonly observed structure



Can we use population ratios to map out the energy surface?

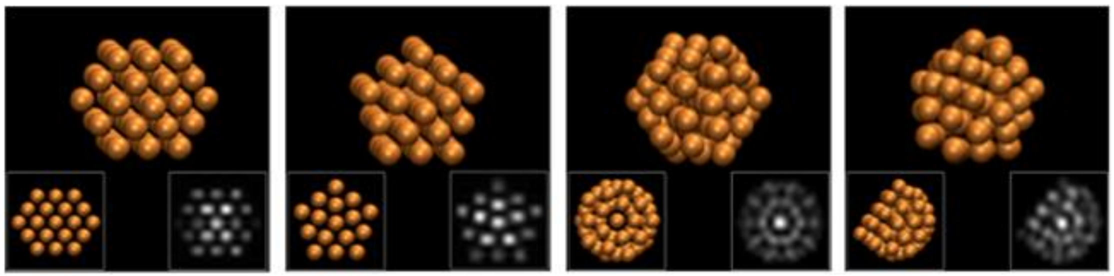
What temperature is the cluster under the e-beam?

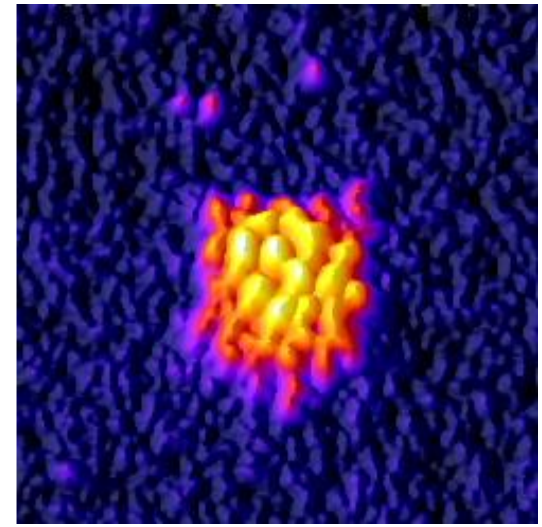
Dawn Wells

Au_{55} Simulation Atlas (QSTEM)

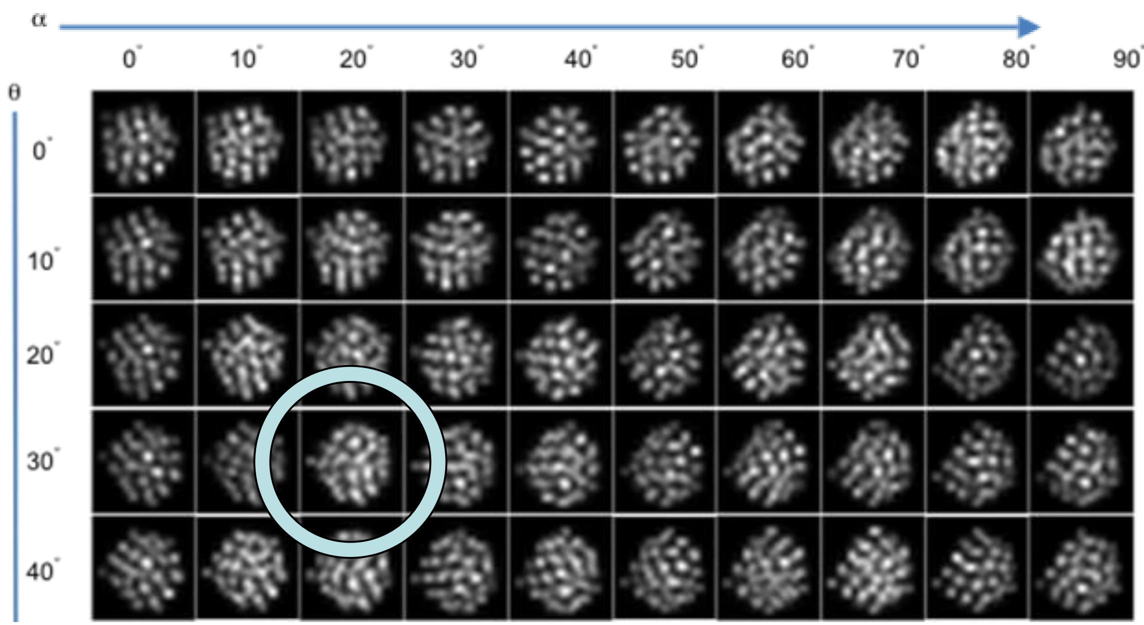
Systematic STEM simulations of Au_{55} clusters

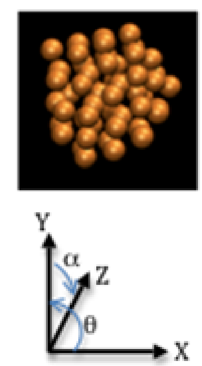
Ih **Dh** **FCC** **Chiral[1]**





Examples of the calculated images for the hybrid model

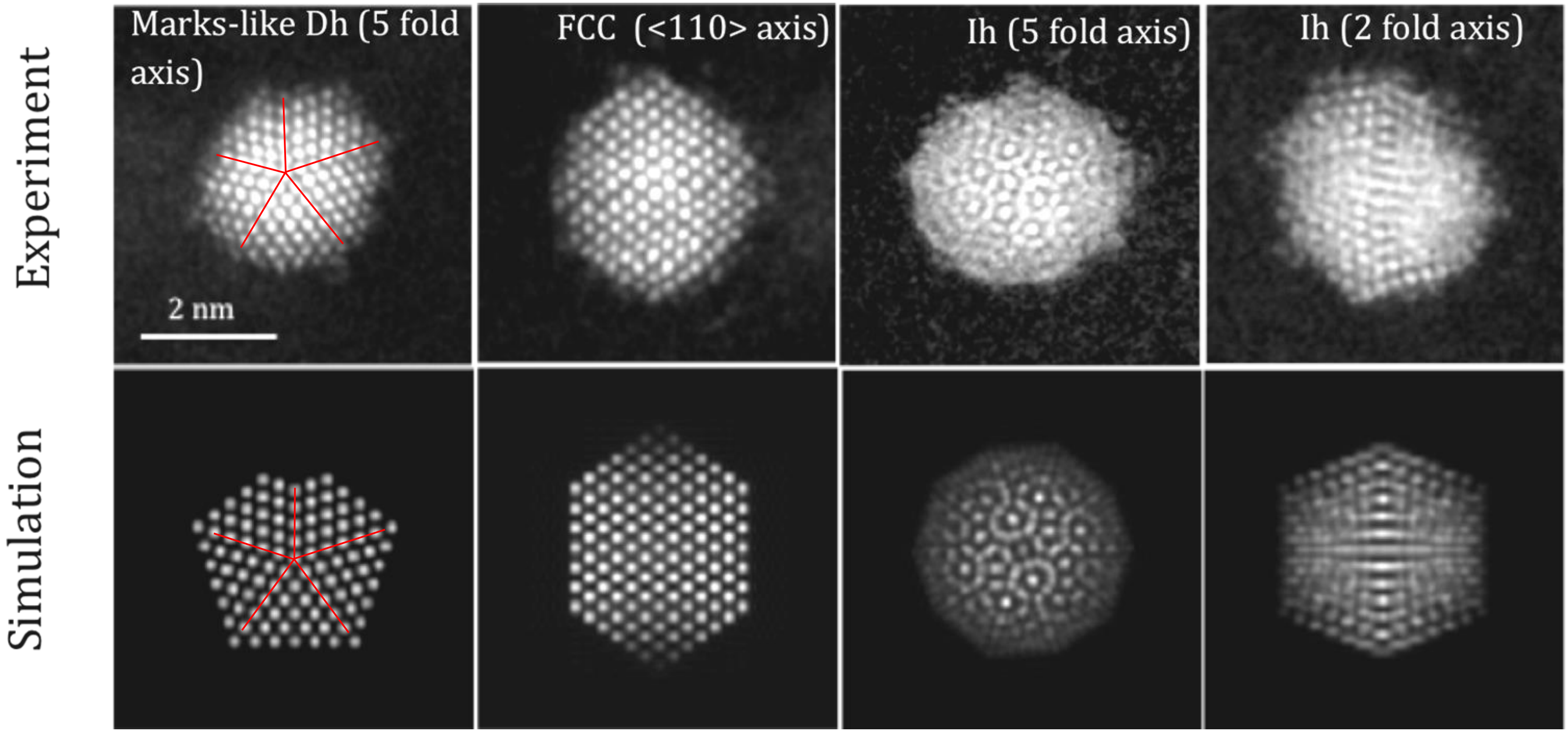




The simulation atlas allows us to identify structures frame-by-frame

[1] I. L. Garzon et al. PRL 97, 233401 (2006)

Au_{923}: "Ground State" Structure?



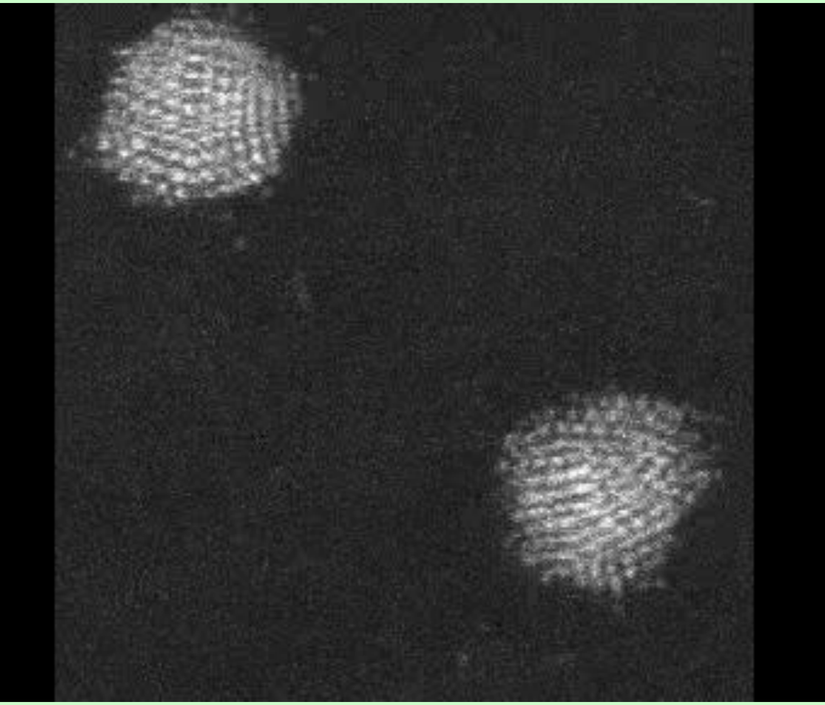
Three main structures observed for Au_{923}:

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

Wang & REP, PRL (2012)

Au_{561}

Dh ➔ fcc transformations



- Clusters irradiated in STEM
- Dose 3.1×10^4 e^-/A^2/frame
- 2.9 seconds per frame
- Field of view 13.12nm x 13.12nm

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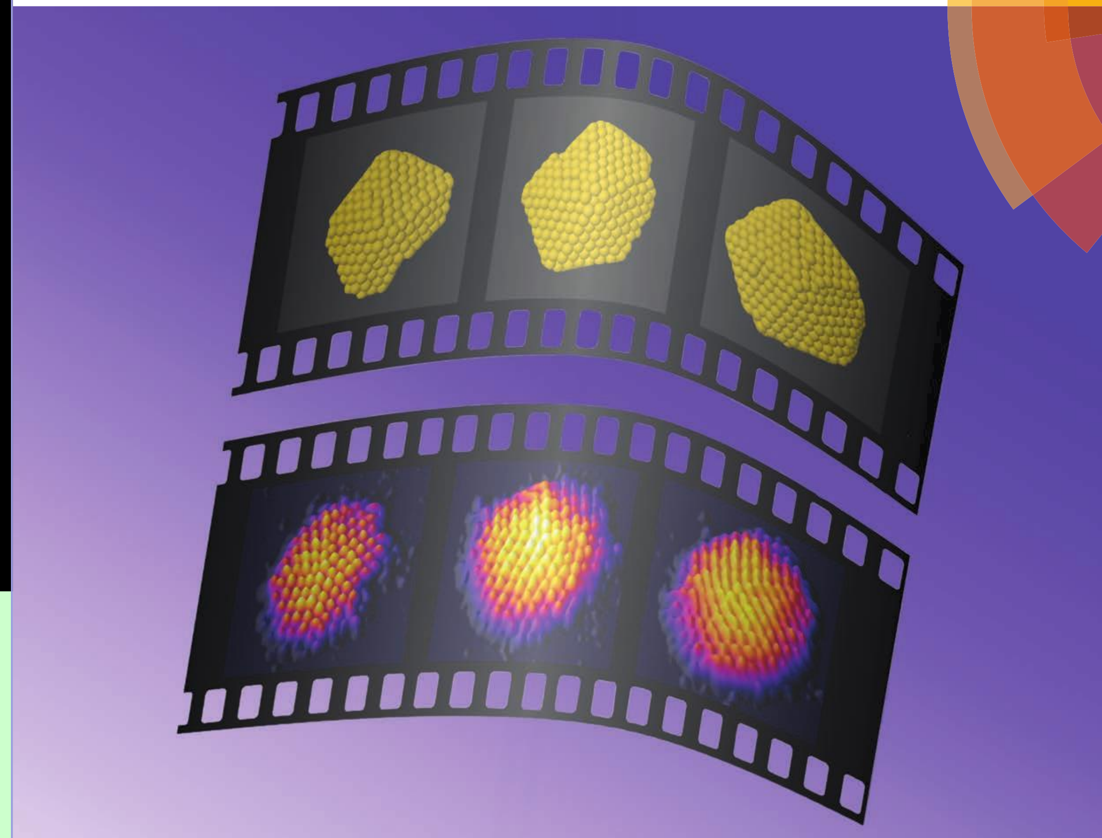
Volume 7 | Number 15 | 21 April 2015 | Pages 6391–6860

Nanoscale

www.rsc.org/nanoscale



ISSN 2040-3364

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PAPER

Richard E. Palmer *et al.*

Metastability of the atomic structures of size-selected gold nanoparticles

NCNST

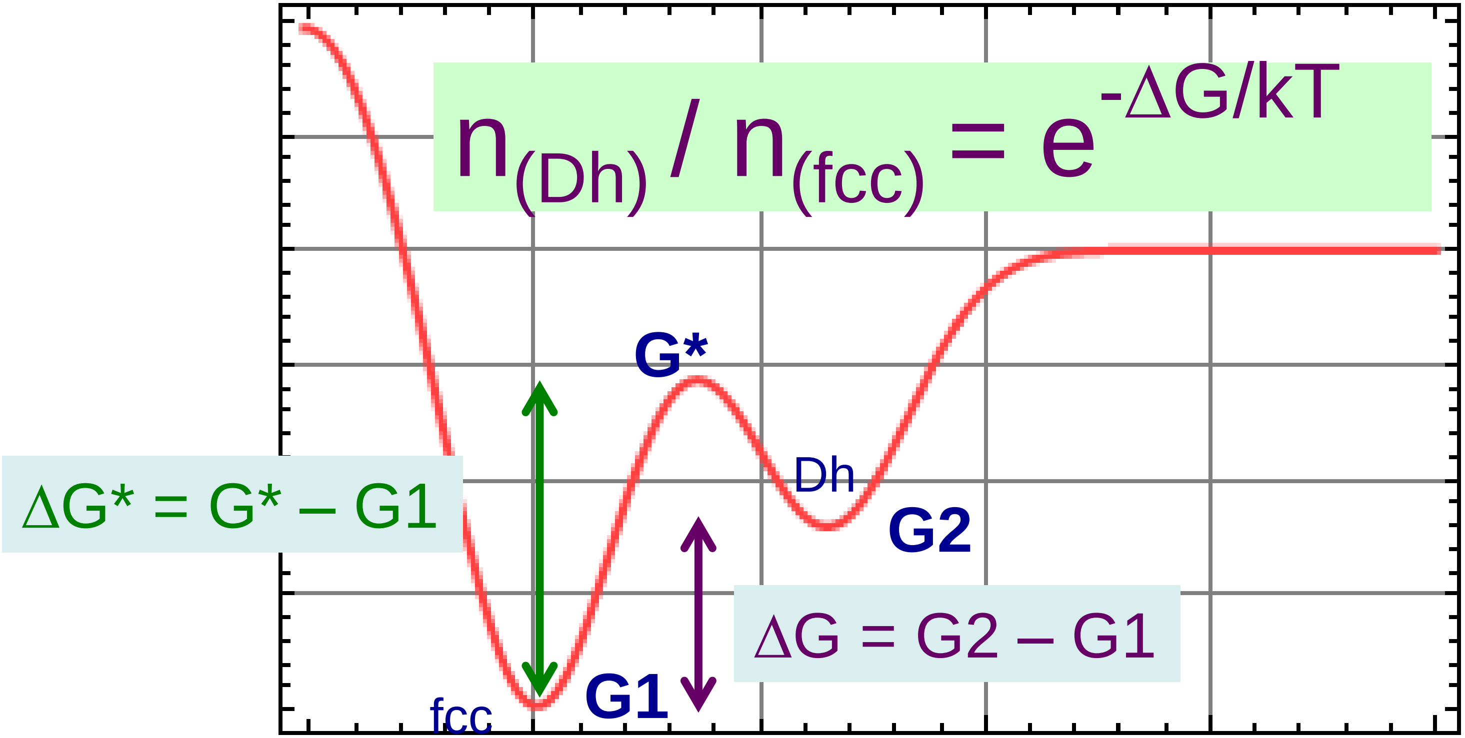
Au_{561} Structural Transformations

Initial state	Final state	(via)	Frequency
Dh ➔	Fcc	-	17
Dh ➔	Dh	-	2
Fcc ➔	Fcc	-	13
Fcc ➔	Fcc	(Dh)	2

- Clusters irradiated with STEM electron beam
- Dose of 1.4 – 3.1 $\times$ 10^4 e^-/Angstrom^2/frame
- Minimum of 50 frames
- 2.9 seconds per frame
- Field of view 15.74nm $\times$ 15.74nm or 13.12nm $\times$ 13.12nm
- Similar behaviour was seen for Au_{742}

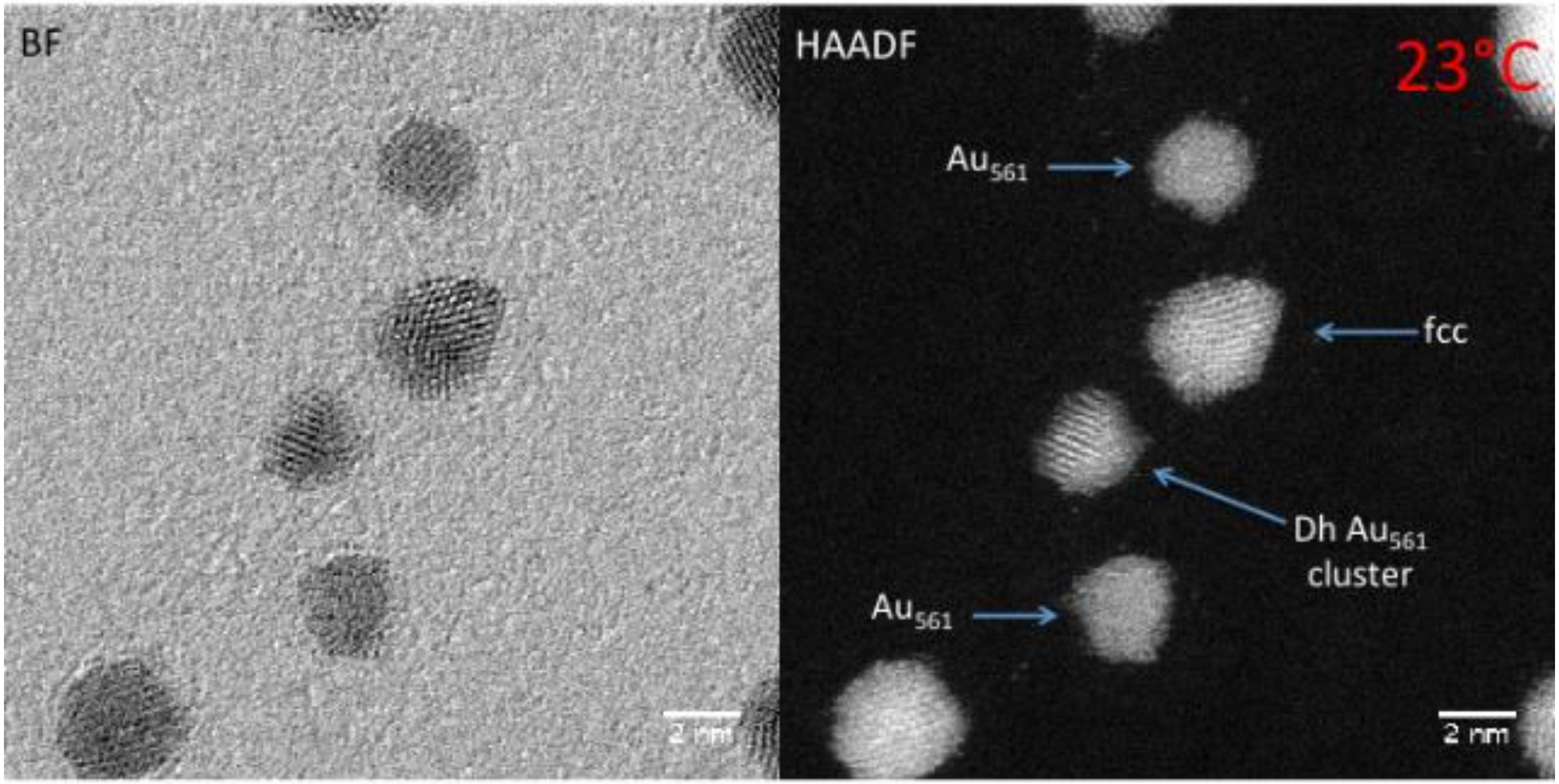
Wells & REP, Nanoscale (2015)

Equilibrium: relative populations of (two) isomers



- The **populations** of structural isomers observed as a function of temperature give the **energy difference** between them.
- (Do the **residence times** in each state versus T lead to the **activation energy** barriers between the states?)

Au_{561} In-situ Heating



- Au_{561} clusters deposited onto carbon 'windows' of thermal chip (DENS).
- Cluster in centre switches Dh ➔ fcc at 100 ° C then fcc ➔ Dh at 150 ° C.
- We **release** then **repopulate** higher lying isomer in 2-level system.
- Normal e-beam Dh ➔ fcc only. **Electron beam heats clusters to about 125 ° C.**
- (Cluster shape less angular from ~600° C – compare T_m ~ 800K for d = 2.5nm, Buffat & Borel (1976) – but ordered core structures persist above T_m).

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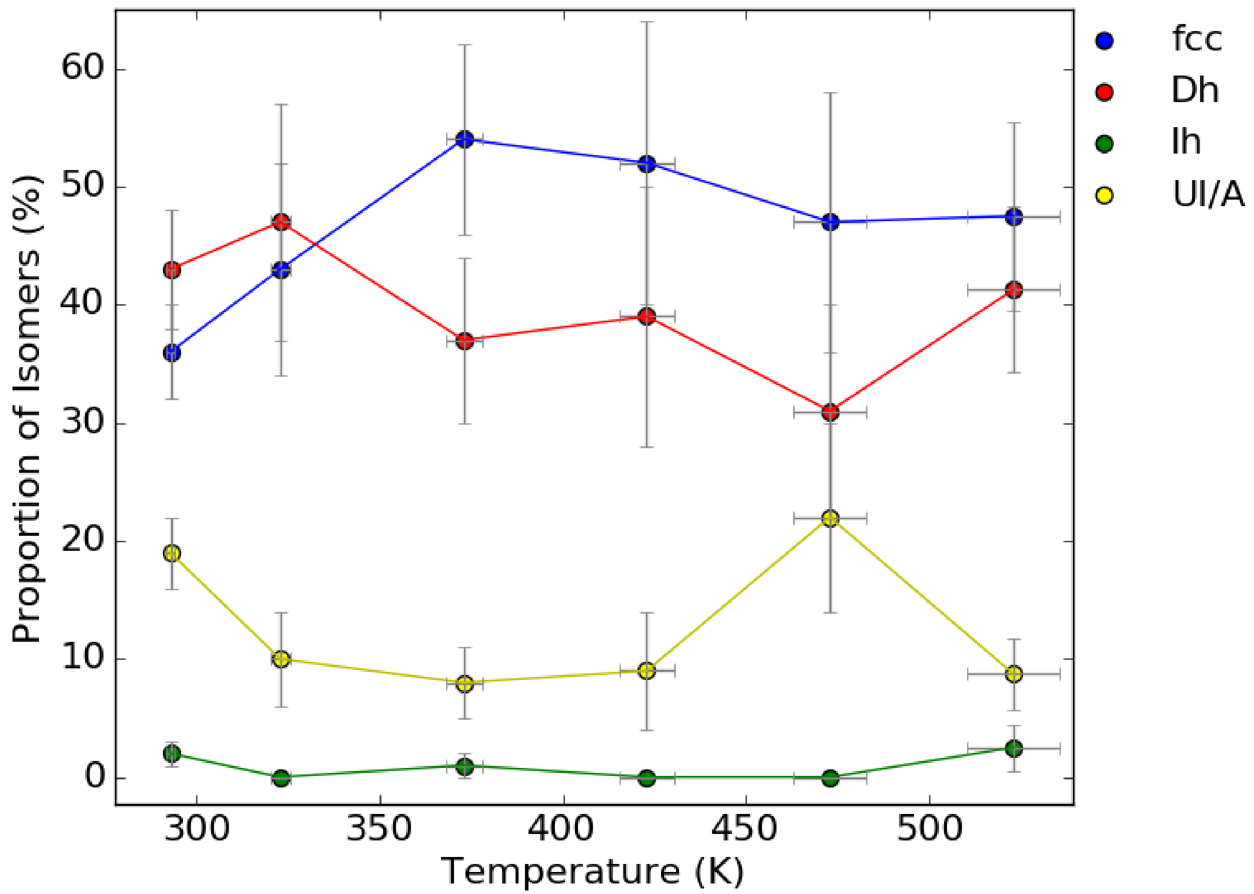
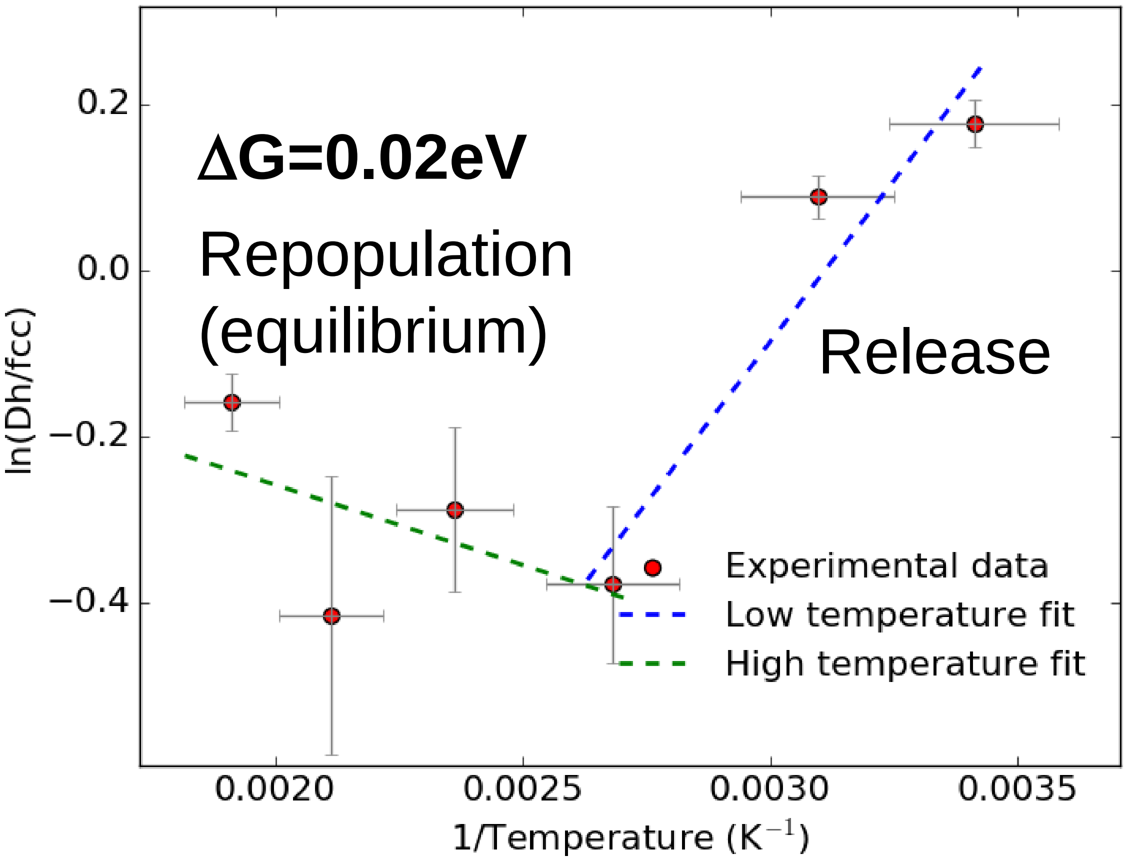
Measured populations vs T for Au_{561} on a:Si_3N_4



The proportion of structural isomers recorded from static HAADF STEM images of ensembles at temperatures ranging from 20-250° C.

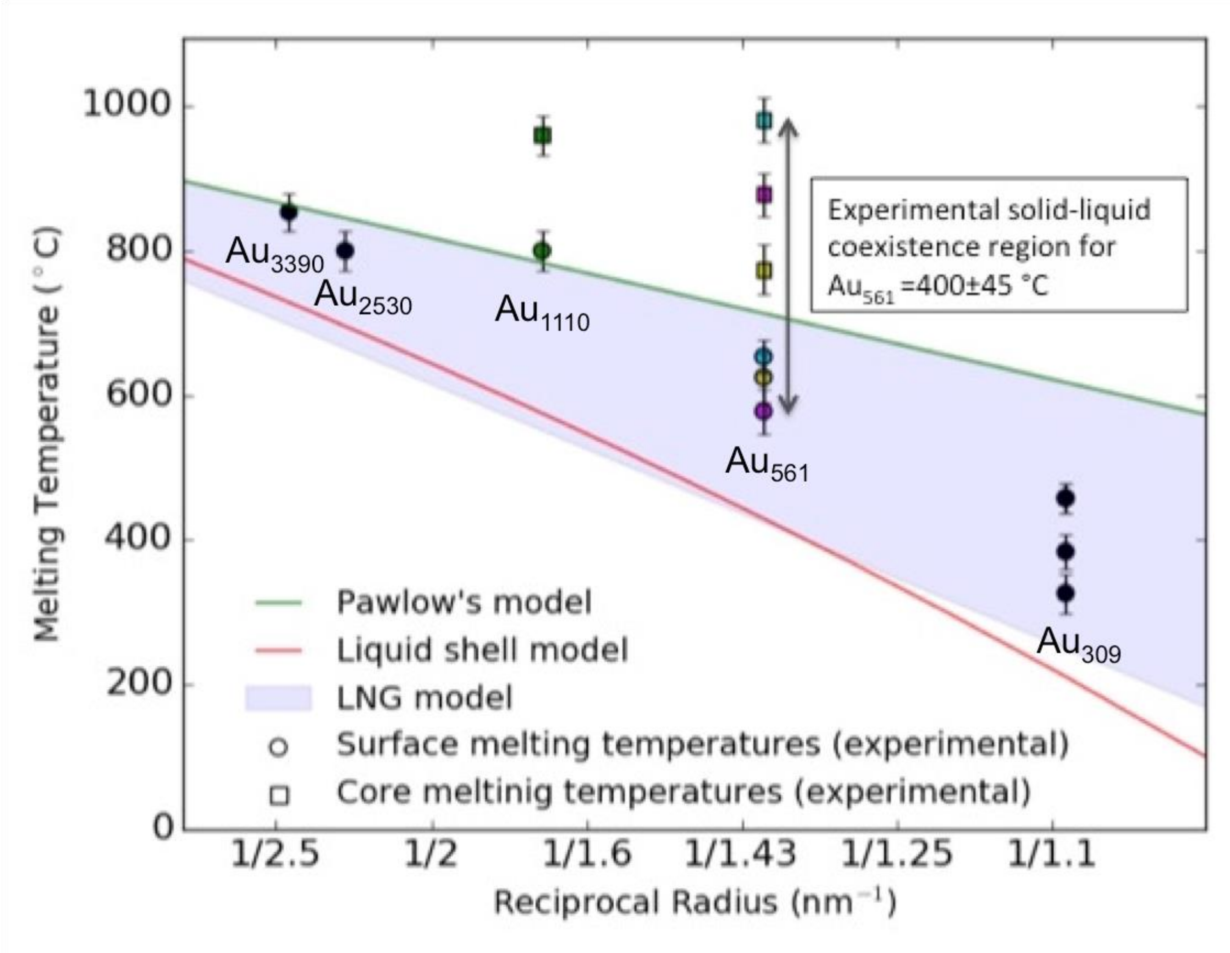
Proportions of D_h and fcc : Determining ΔG between isomers for Au_{561}



High Temp ← *Low Temp*

- **Van 't Hoff plot** of the ratio of Dh/fcc isomers for Au_{561}
- **Lower temperature range:** metastable Dh transform to fcc due to the elevated temperatures
- **Higher temperature range:** clusters are now in equilibrium (obvious from dynamic behaviour at these temperatures); as the temperature is increased the proportion of Dh increases slightly ➔ Dh higher in energy.
- **Dh only marginally higher (0.02eV) in energy than fcc**, the two structures are almost degenerate.

Surface & core melting temperatures of Au_N clusters on a:C



Experimental, single particle measurements of melting point suppression in Au nanoparticles, plotted alongside several models for melting point suppression.

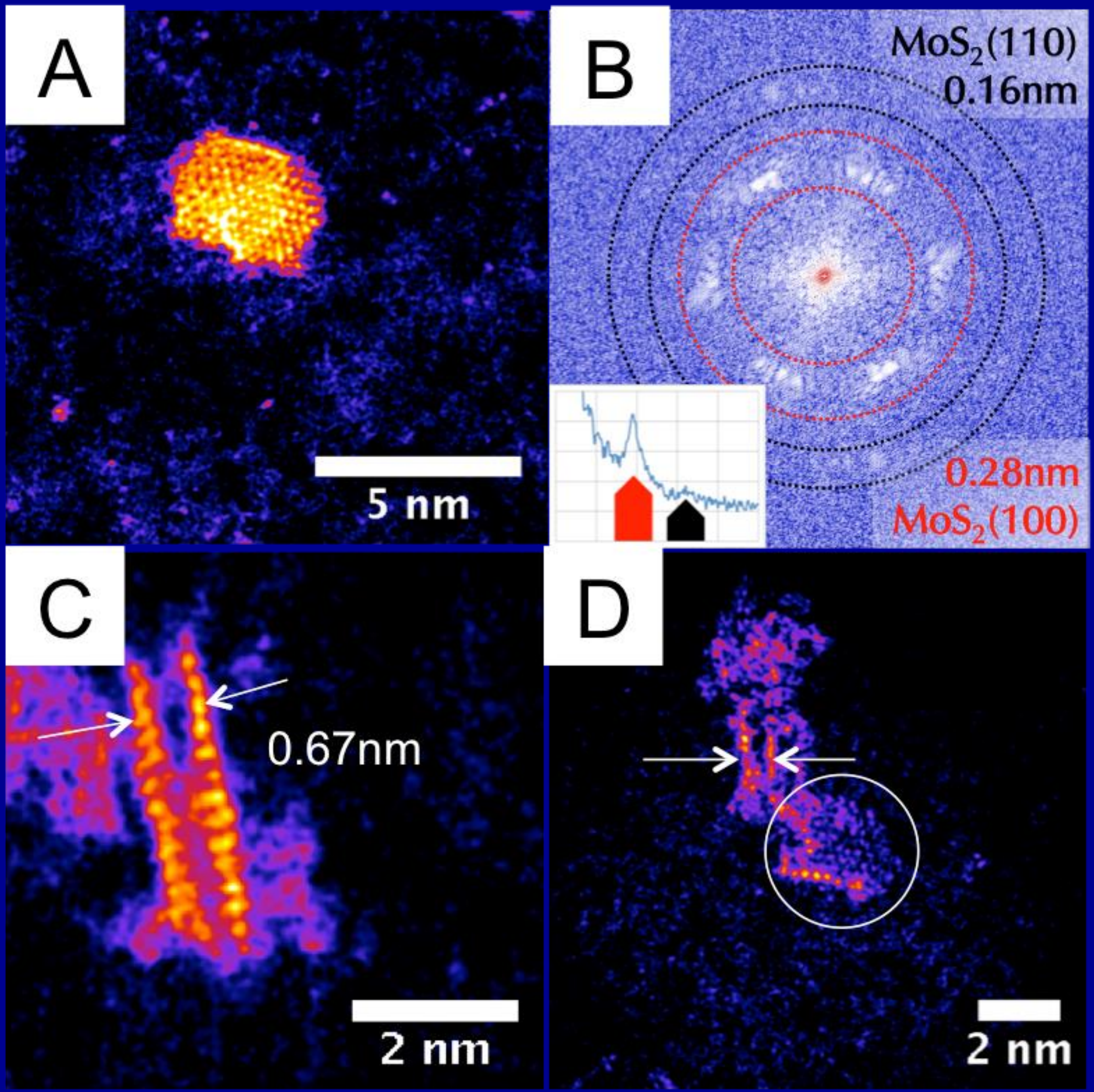
The experimental data is represented by scatter points, the circles show the surface melting temperatures and the squares the core melting temperatures.

The solid green line is Pawlow's model, the solid red line is the liquid shell model and the blue region is the liquid nucleation and growth model (melting sector).

Dawn Wells

Production of binary clusters

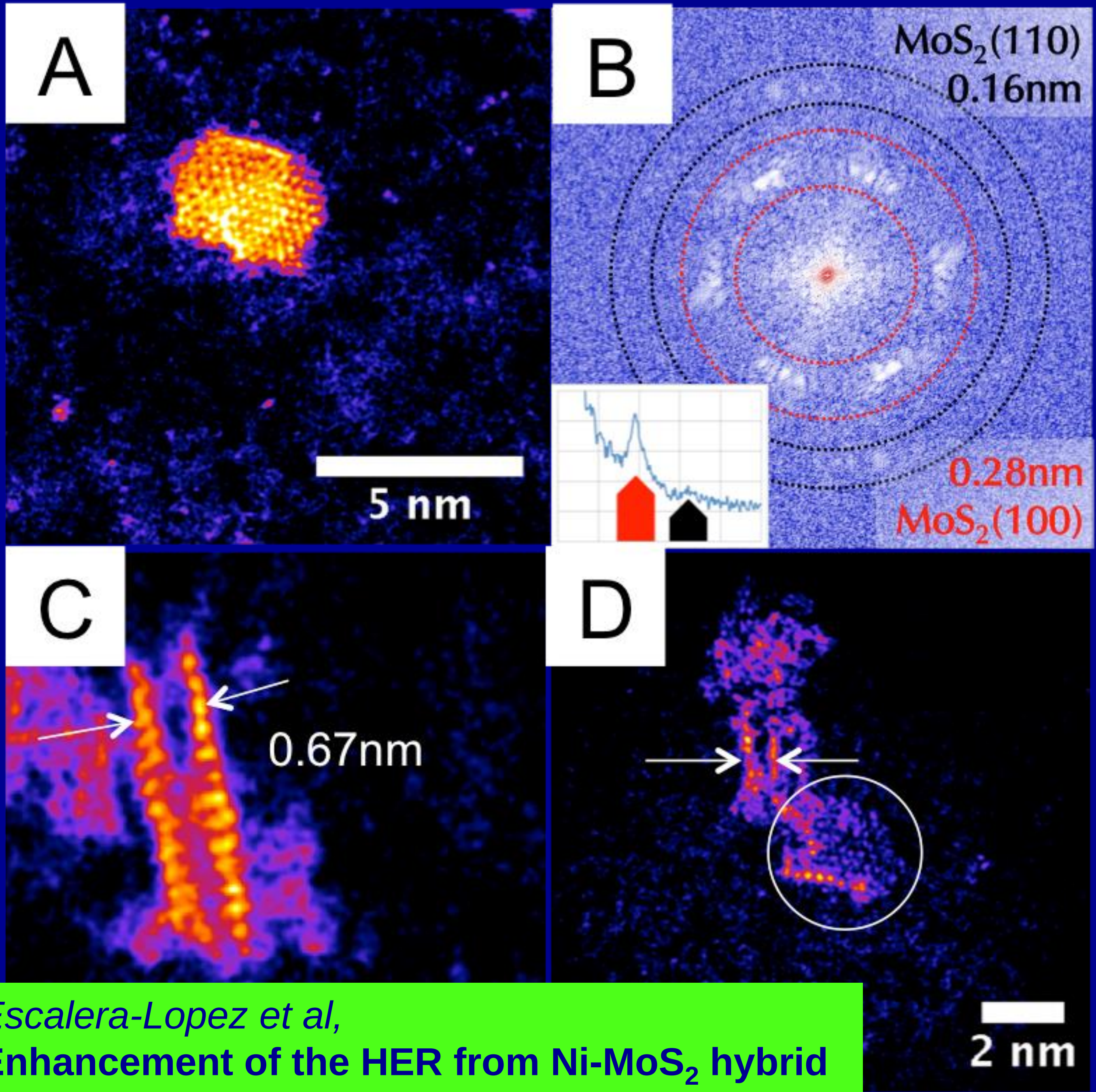
MoS_2



(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.

Cuddy et al, Nanoscale (2014)

MoS_2

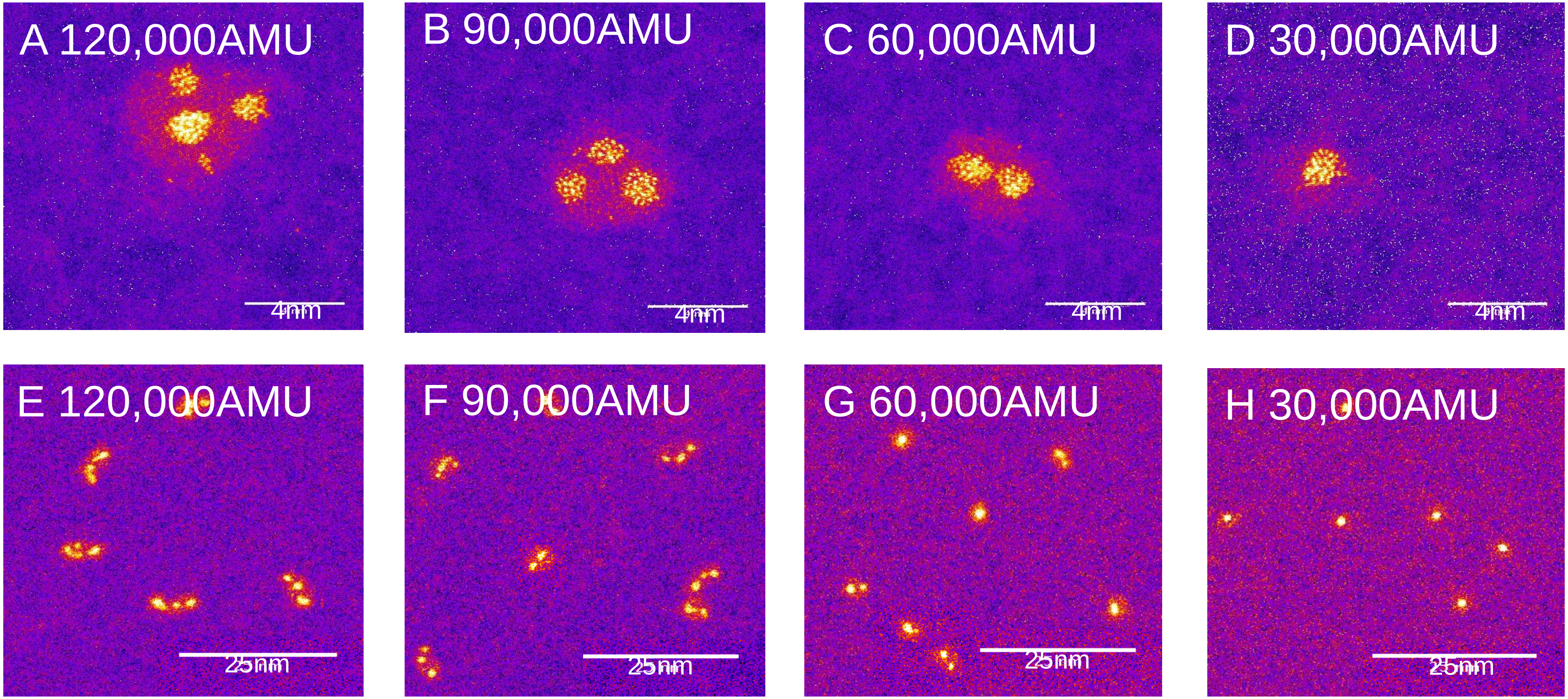


(A) (MoS2)500 trilayer and corresponding FFT (B) showing hexagonal crystal structure characteristic of bulk MoS2 basal plane, with radial intensity profile highlighting the spots (B-Inset). (C) (MoS2)650 side-on showing basal plane edges (002) and (D) another (MoS2)650 with features from both (100) and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

Cuddy et al, Nanoscale (2014)

Escalera-Lopez et al,
Enhancement of the HER from Ni-MoS_2 hybrid nanoclusters, *ACS Catalysis (2016)*

Imaging of Pt@Ti Clusters (air exposed)



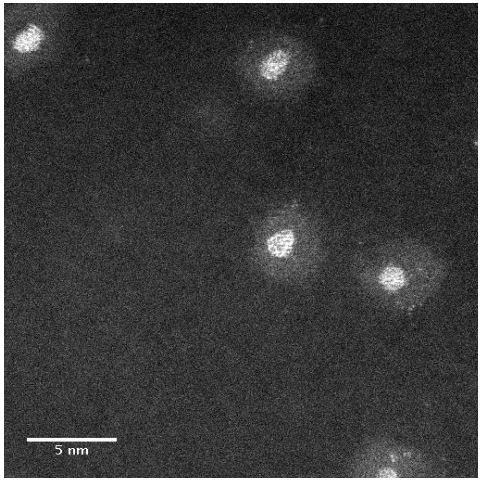
Pt Yellow, TiO_2 Pink, Background Purple

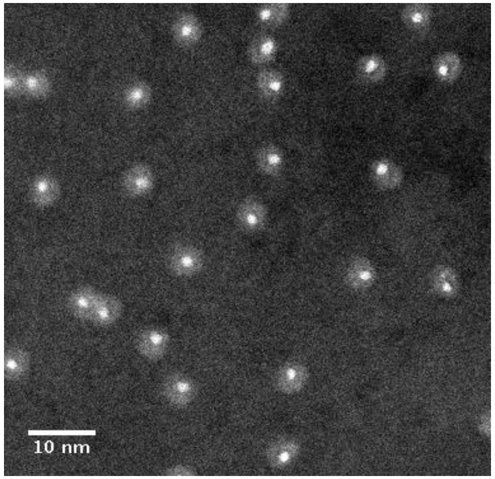
Large clusters contain **multiple cores** of Pt, small clusters only one core

Blackmore & REP, PCCP (15)

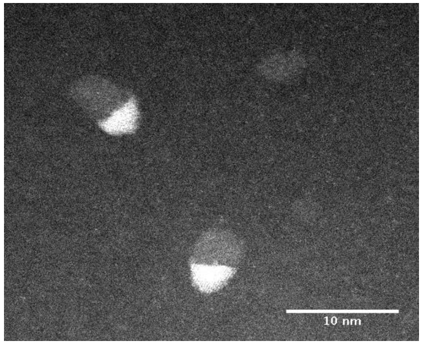
Structural modification of 90k amu Pt/Ti clusters by in vacuum annealing

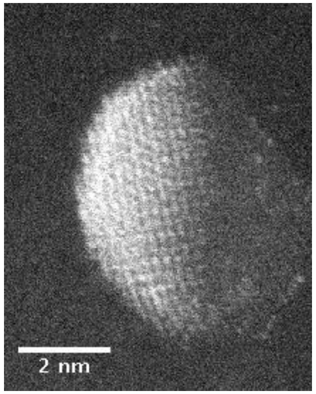
- Single core formation (annealing T ~ 130 C)





- Janus clusters (annealing T ~ 220 C)





Saeed Gholhaki

Scaling up cluster generation – a route to manufacturing?

Scale-Up

How many clusters needed for catalyst R&D?

10mg/hour = 1g catalyst at 1% loading is comfortable.

Thus 10μA cluster flux (cf. 0.1nA mass-filtered).

$$\times 10^5$$

Other research groups working on cluster beam scale-up…

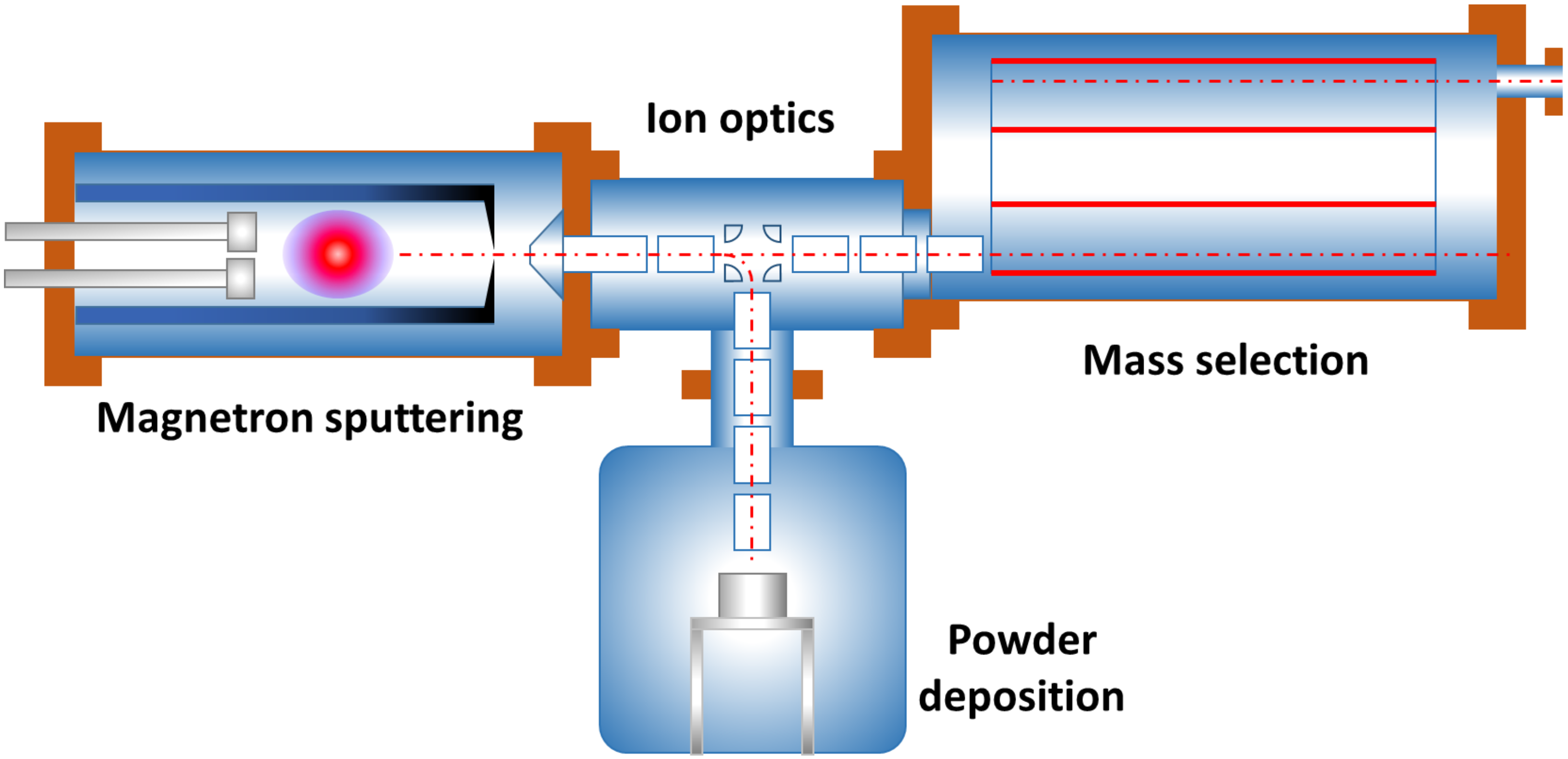
Heinz Hövel (Dortmund) Bernd von Issendorff (Freiburg)

Paolo Milani (Milan) Yves Huttel (Madrid)

We aim for 1 g/hr, ΔD ~ 10%, i.e. $\times 10^7$

Scale-Up: Size-*Controlled* Clusters (10 nA)

Ellis et al, Faraday Discussions 2016

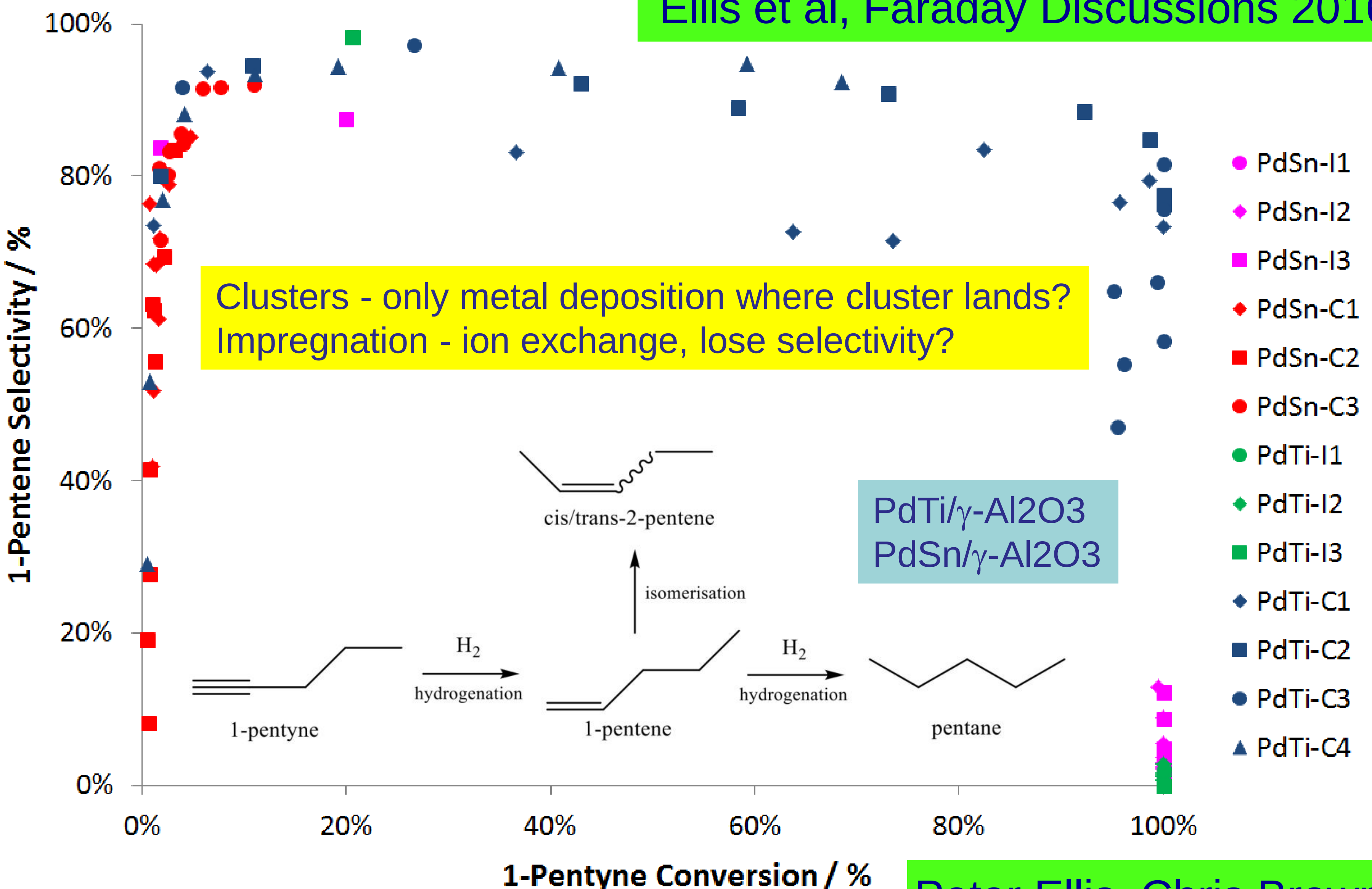


x10^2

Jin Yin, Kevin Cooke
(Teer Coatings Limited)

1-Pentyne Hydrogenation: Clusters vs Conventional Catalysts

Ellis et al, Faraday Discussions 2016

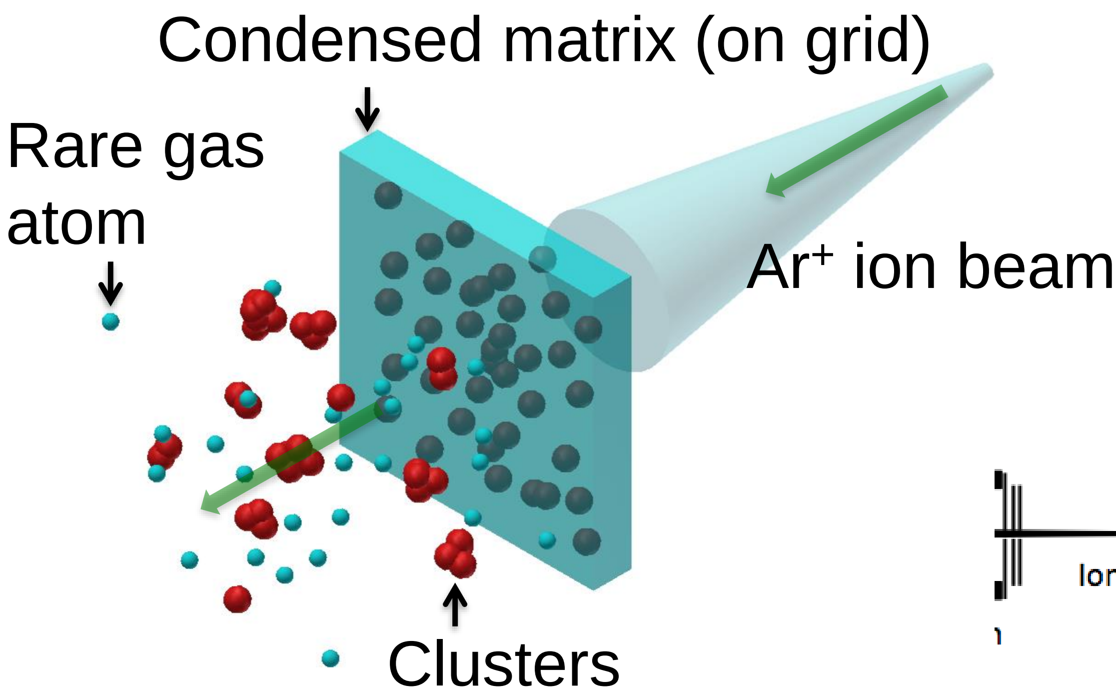


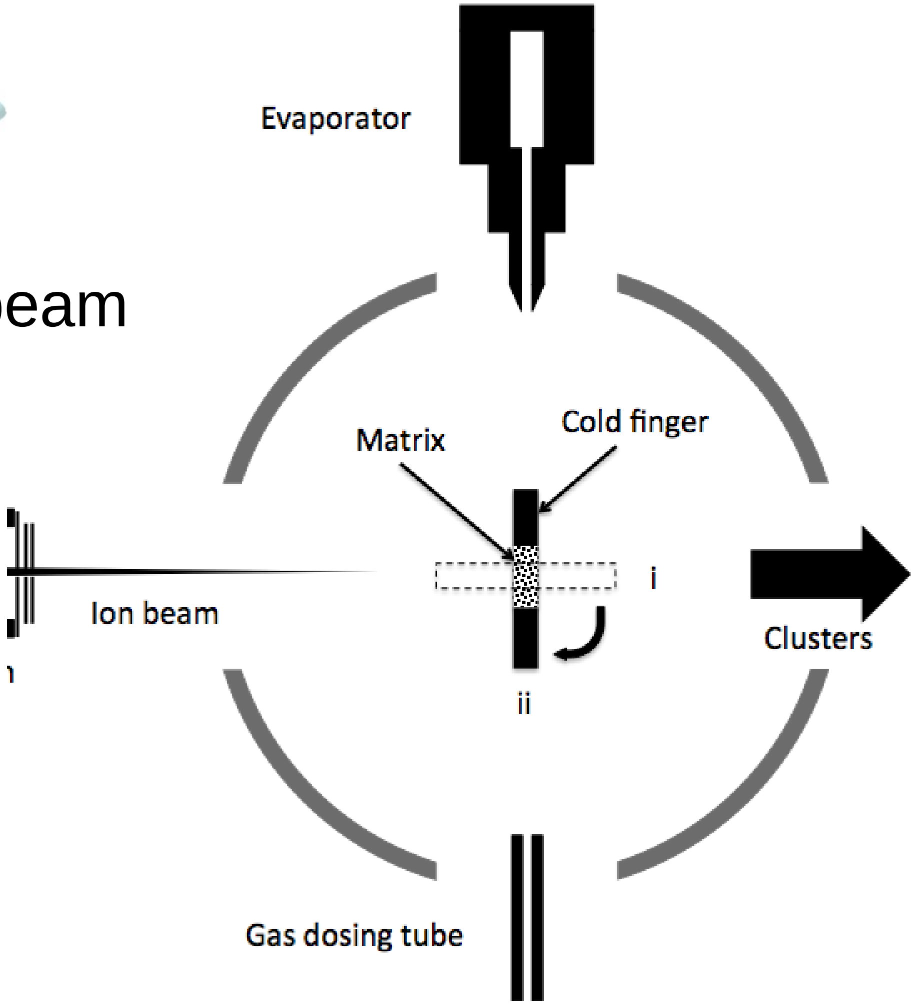
Clusters - only metal deposition where cluster lands?
Impregnation - ion exchange, lose selectivity?

PdTi/γ-Al2O3
PdSn/γ-Al2O3

Peter Ellis, Chris Brown
(Johnson Matthey)

Matrix Assembly Cluster Source (MACS)

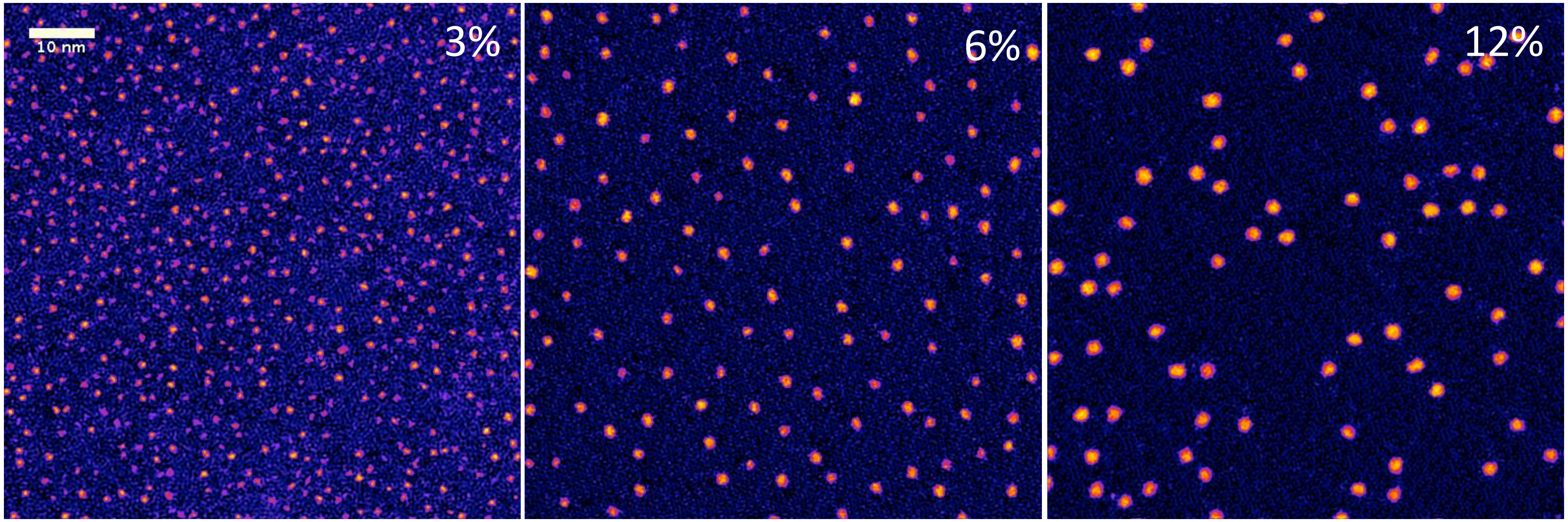




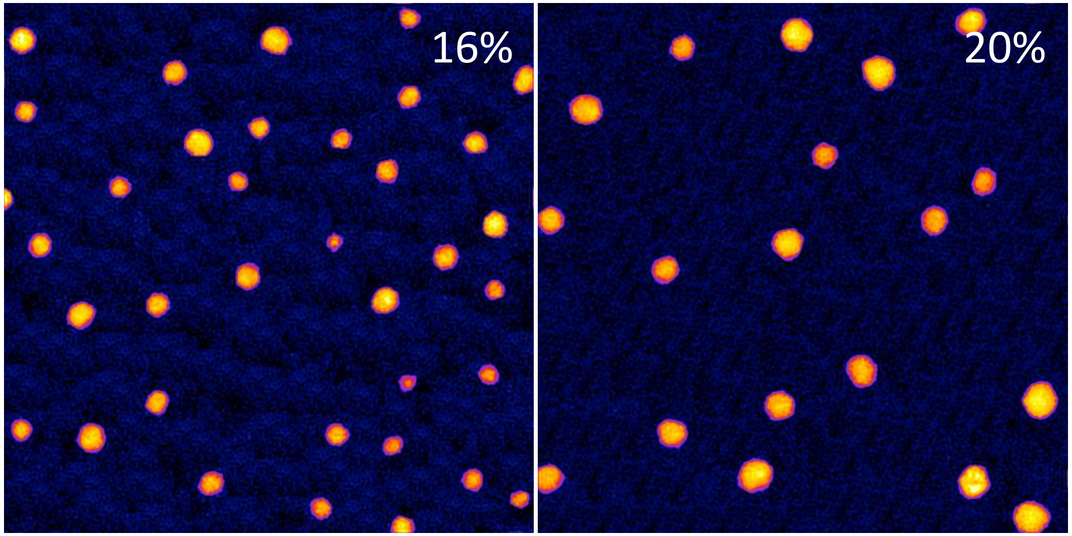
Schematic diagram of the MACS apparatus. The matrix support grid is mounted on a rotatable cold finger in the centre of the chamber. The grid first faces towards the evaporator for matrix preparation (i), then is rotated to face the ion beam for cluster production (ii).

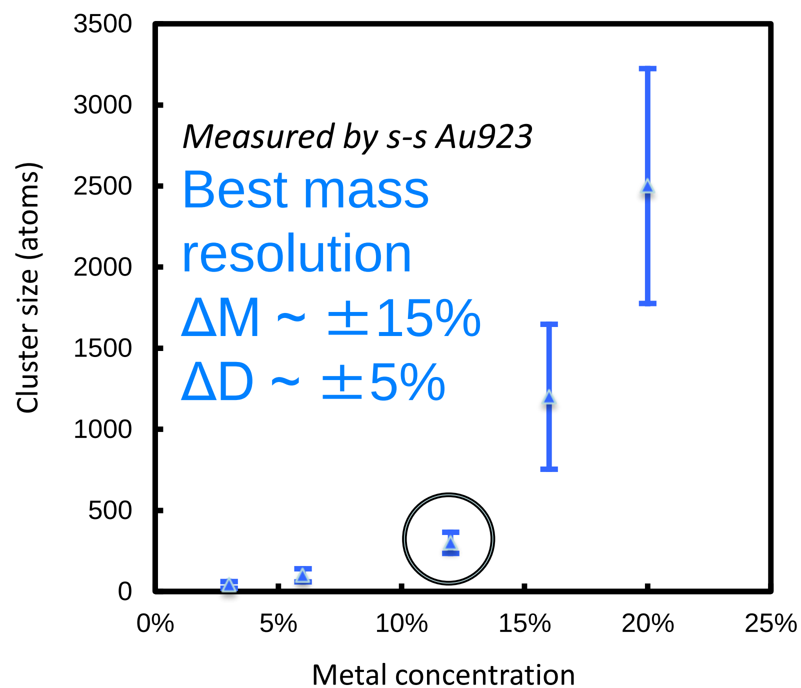
REP, Lu Cao, Feng Yin, Rev Sci Instrum (2016)

Au cluster size versus metal loading



x10



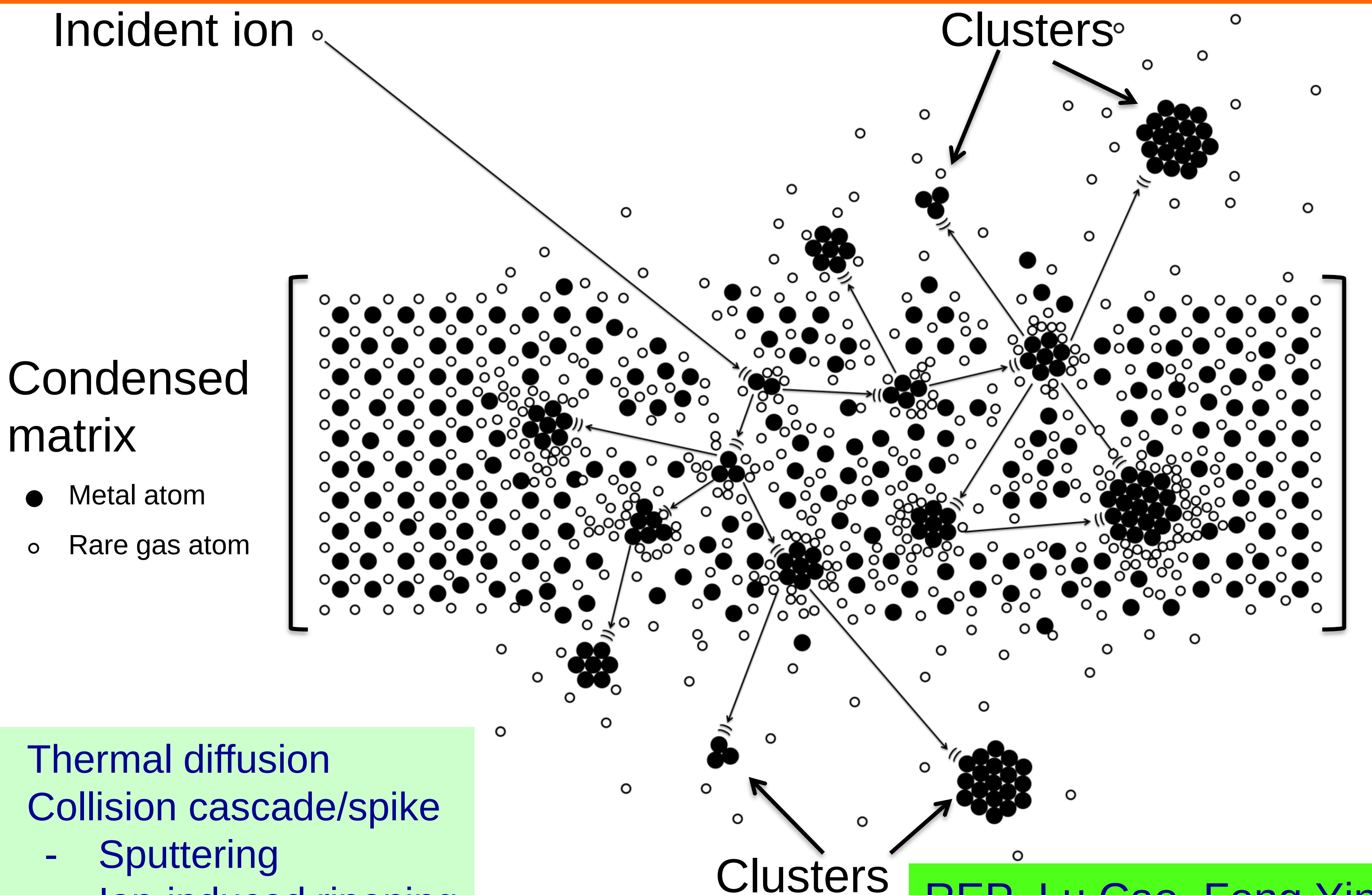


Ar beam energy: 1keV, ion current: 10μA, dep time: 1 min, matrix temp: 9K.

clusters/ion = 3% (transmission)

Lu Cao, Richard Balog

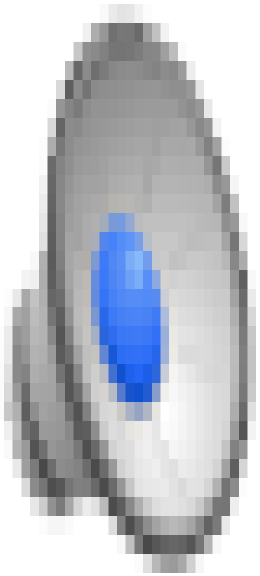
Matrix Assembly Cluster Source (MACS)



- Thermal diffusion
- Collision cascade/spike
  - Sputtering
  - Ion-induced ripening
  - **Multiple impacts**

REP, Lu Cao, Feng Yin
Rev Sci Instrum (2016)

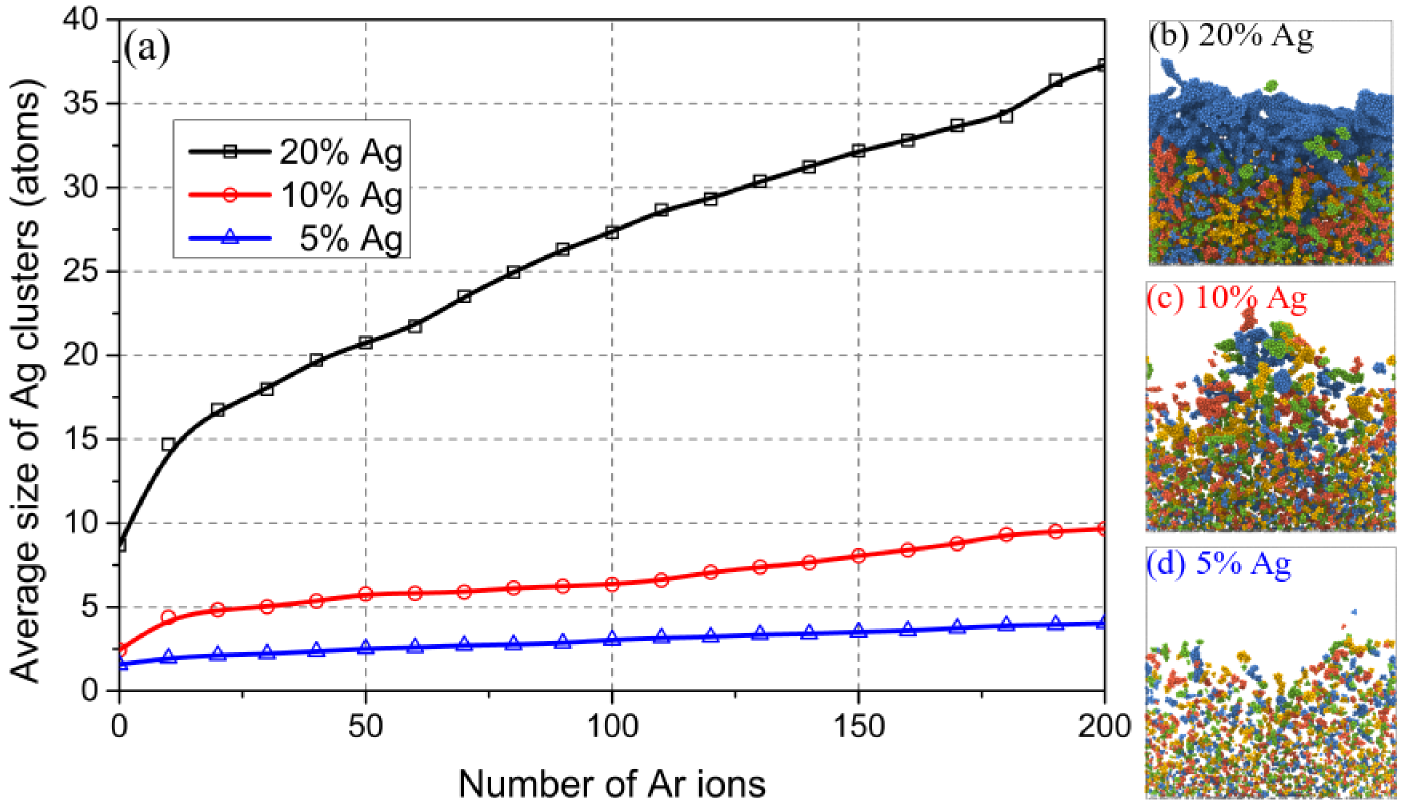
Helsinki Simulations



Movie. An example of the movement of Ag clusters during one irradiation. The cyan-coloured Ag atoms and yellow trajectories show that small Ag clusters move as a unit during the thermal spike.

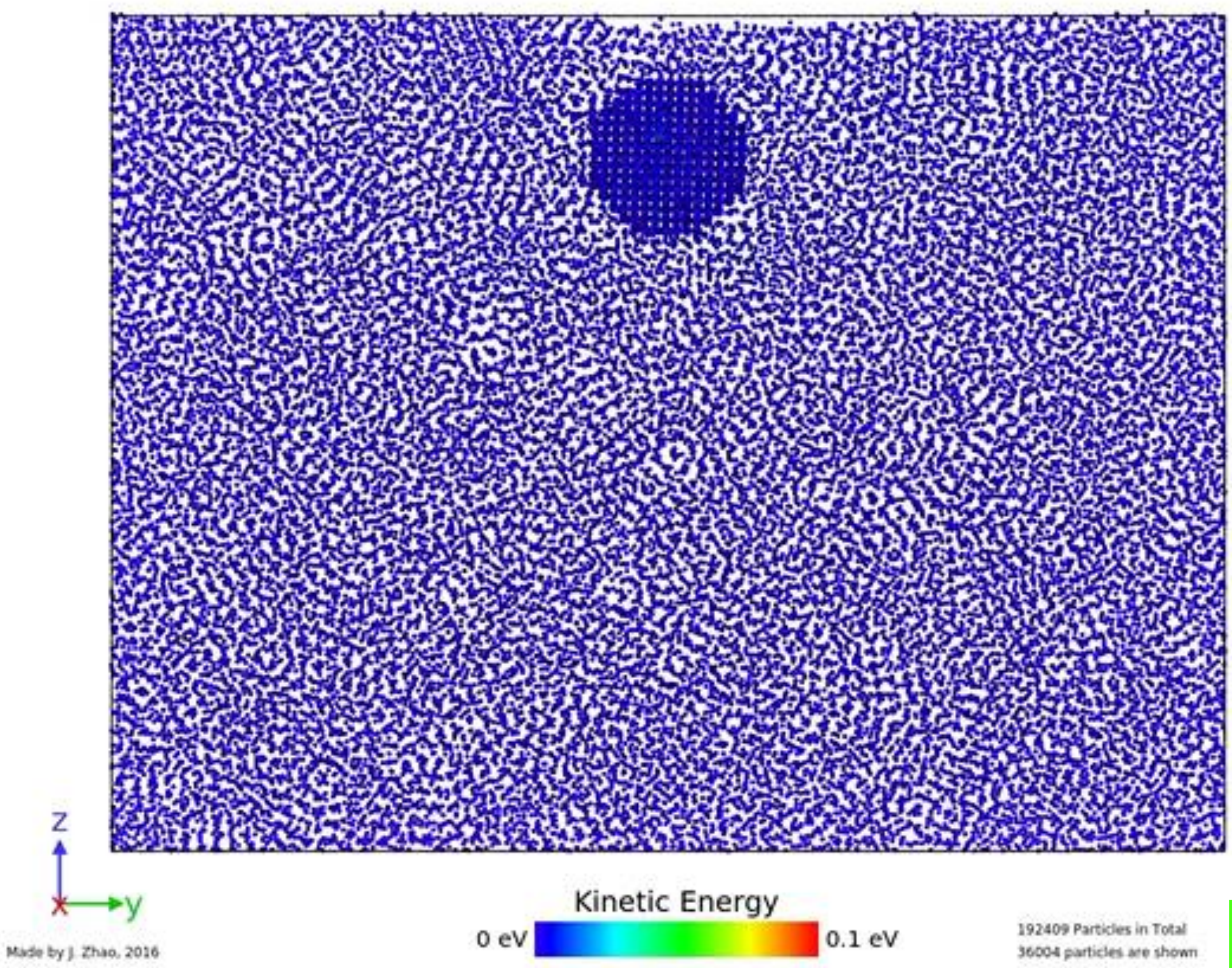
Junlei Zhao
Flyura Djurabekova
Kai Nordlund

Helsinki Simulations (molecular dynamics)



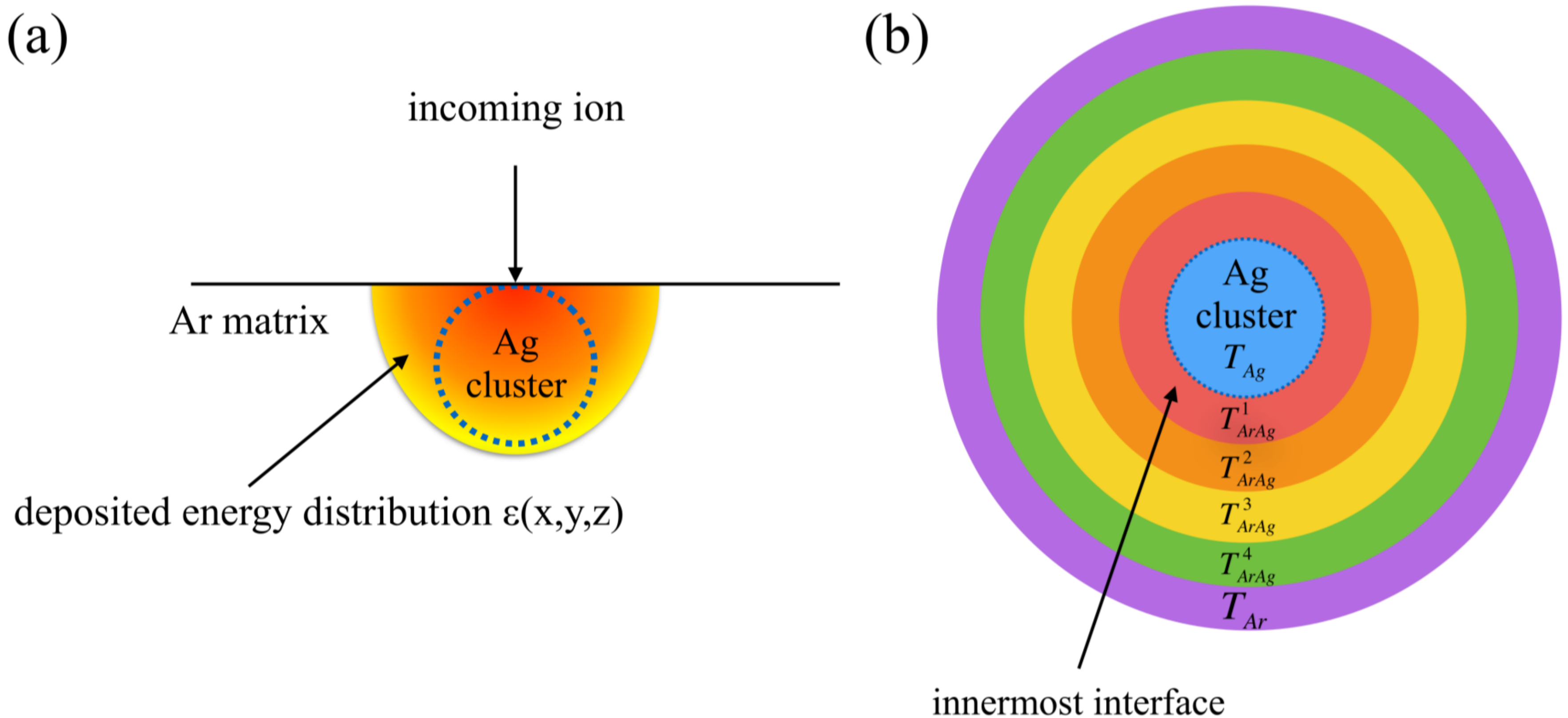
(a) Evolution of the average size of Ag clusters agglomerated in the matrix as a function of the number of incoming Ar ions. (b – d) Simulation snapshots of the matrix with different concentrations of Ag atoms after 200 ion impacts. Four-colour coding is used to distinguish separate clusters.

Helsinki Simulations of MACS



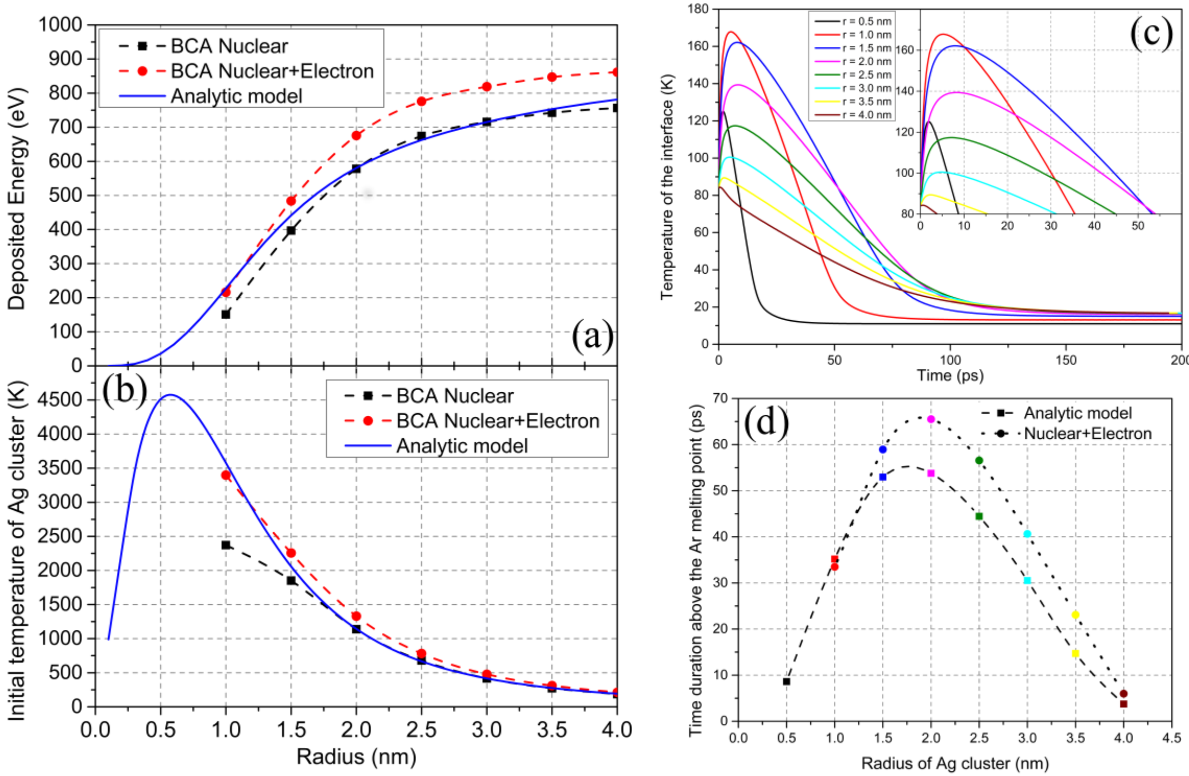
Junlei Zhao
Flyura Djurabekova
Kai Nordlund

Helsinki Simulations (exit, analytical model)



A schematic illustration of the analytical model. (a) Energy deposition: The Ag cluster (the dashed-line circle) is placed right below the surface of the Ar matrix. The shape of the distribution of the deposited energy is a Gaussian hemi-ellipsoid (orange region). The ion impact point and origin of the distribution is at the centre of the cross section of the cluster and at the surface of the matrix. (b) Thermal transmission: The Ag cluster is surrounded by the Ar matrix. The temperature evolution of five layers of Ar/Ag interface is calculated.

Helsinki Simulations (exit probability vs size)



"monochromator"

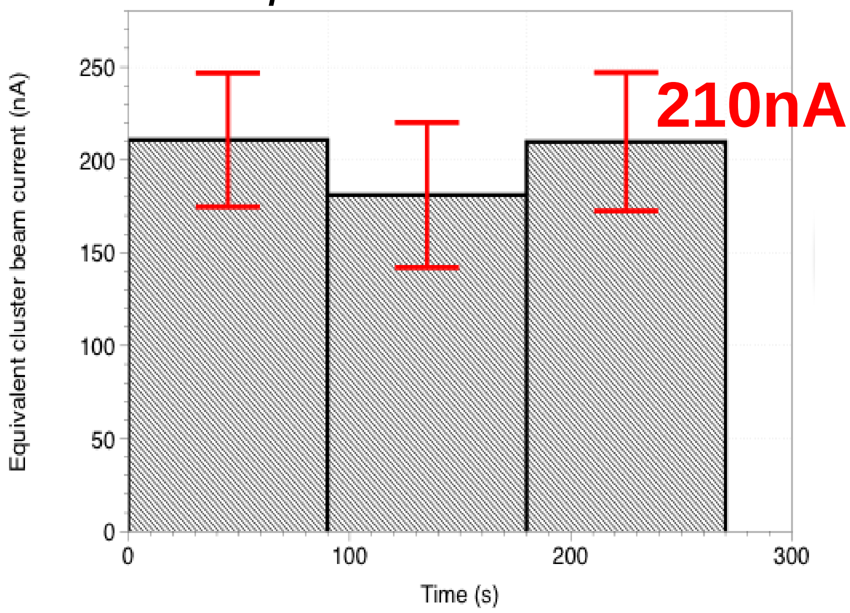
Resonant behaviour

Heat capacity, Conduction rate

*(a-b) Energy deposited E_p (top) and initial temperature (bottom) as a function of radius of the Ag cluster. Blue curve is analytical model from Equations 1, 2 and 3. Red and black dashed curves calculated from binary collision approximation (BCA) code with and without electronic stopping power, respectively. The two methods show very good agreement on the energy deposition. (c) Temperature evolution of the interface. The inset shows the time interval during which the interface temperature is above the melting point of Ar. (d) Time duration for which the cluster-matrix interface stays in the liquid phase as function of size of the Ag cluster. Two different initial conditions are calculated with analytical and BCA models. Colour code corresponds to the curve colours in **(c)**.*

MACS 2 Sustained Operation (~100 nA)

30μA Ar^+ beam current

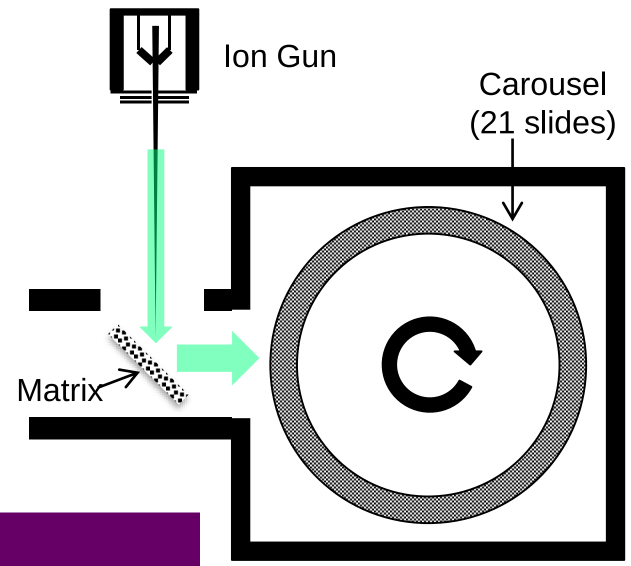


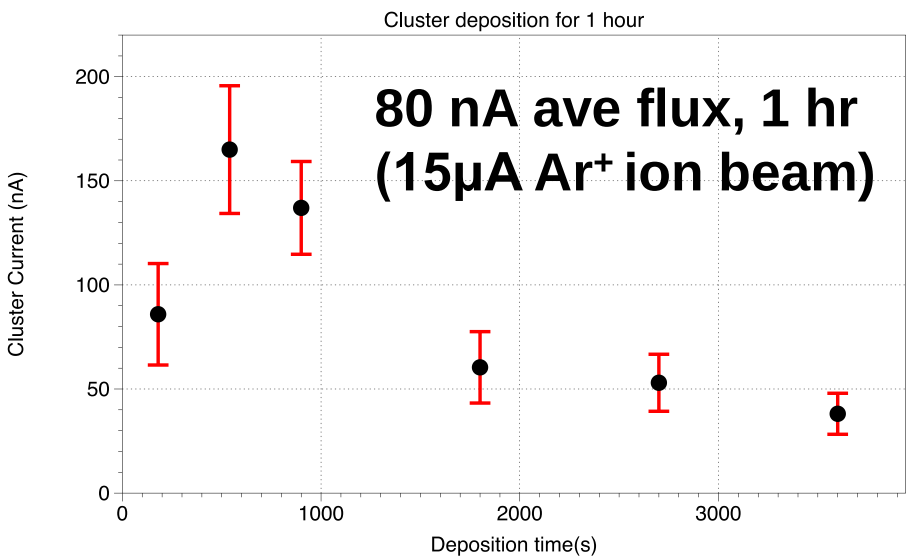
Ellis et al, Faraday Discussions 2016

MACS 2 cluster samples produced in **batches** (21 glass slides).

With 30μA Ar^+ beam, an equivalent cluster beam current of **210nA** was achieved (**clusters/ion ~ 1%**).

Average equivalent beam current of **80.9nA was produced over an hour long deposition.**



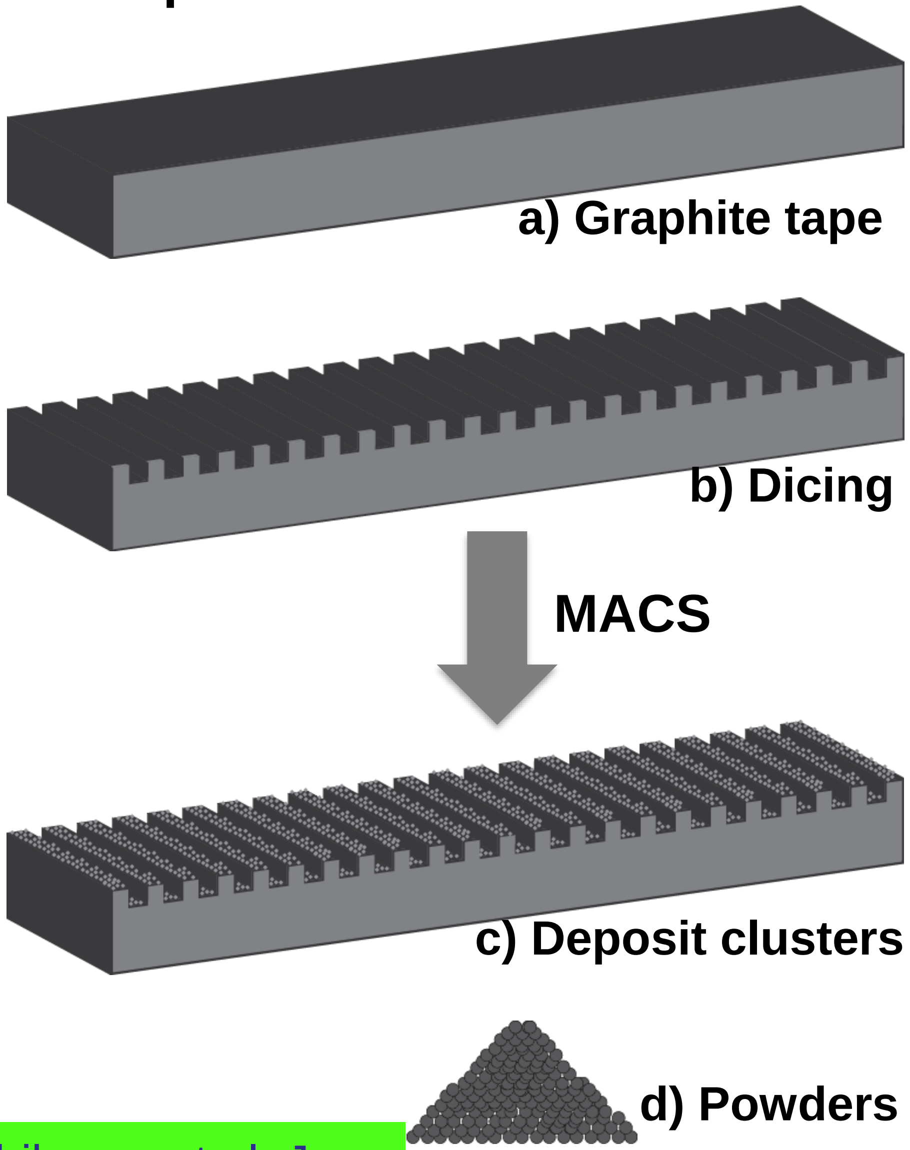


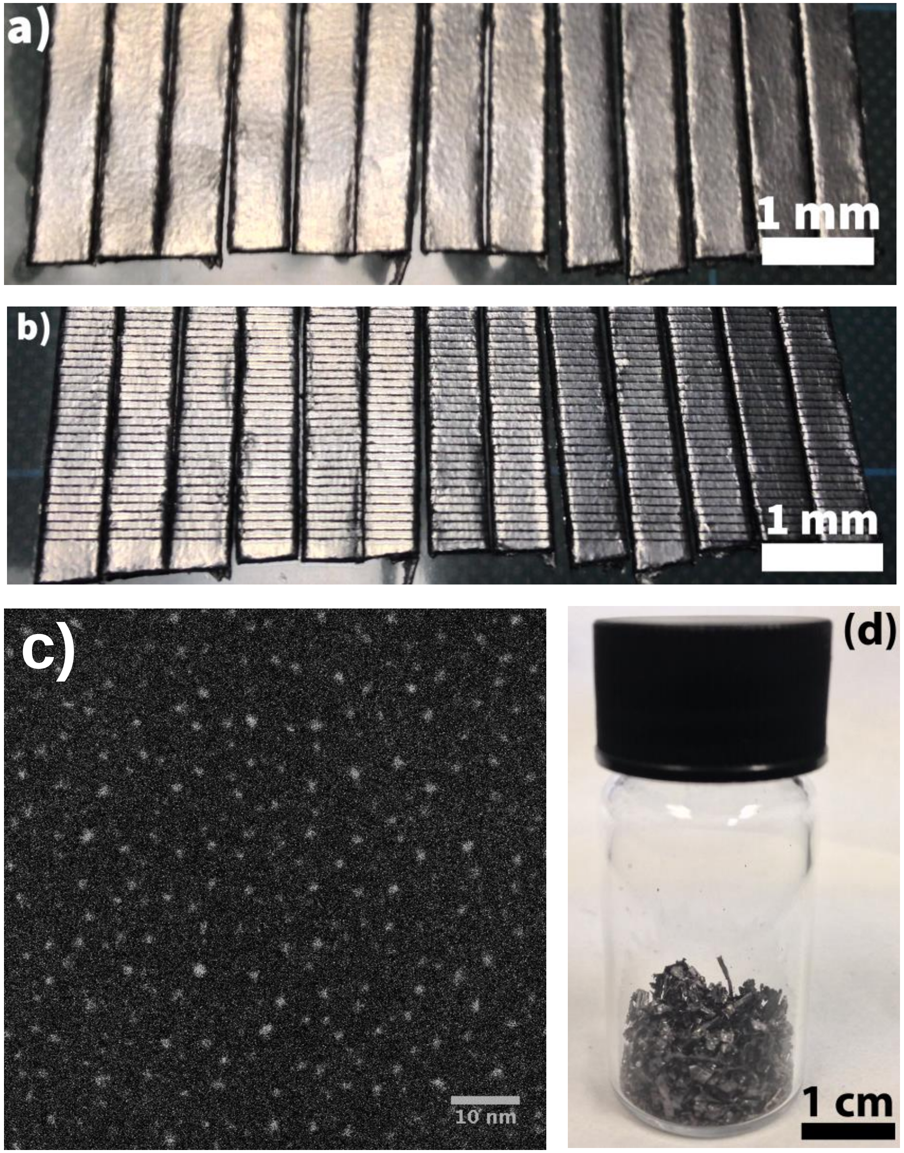
x10^3

Will Terry

Dicing carbon tapes to make cluster powders

➢ **The process:**

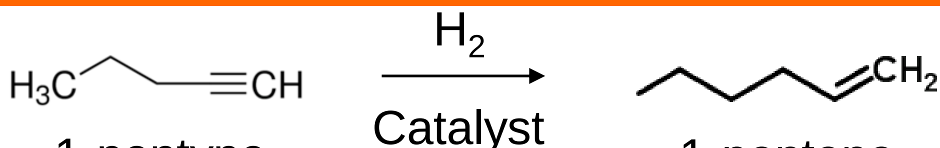




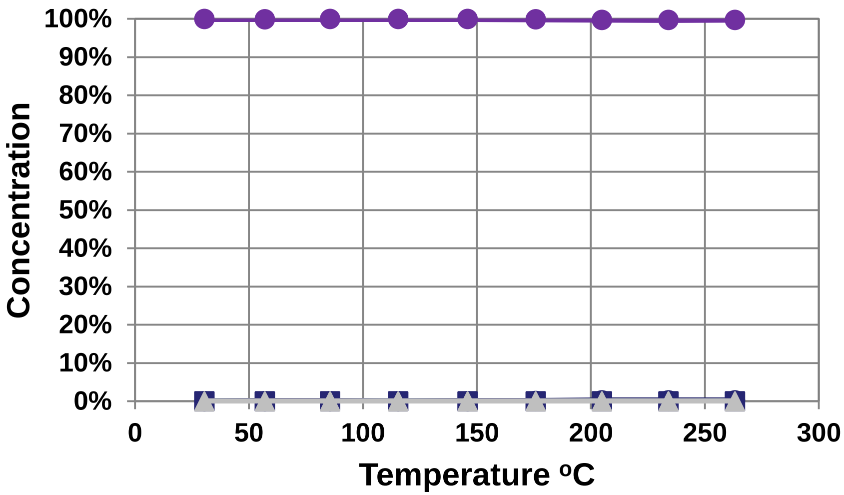
Habibpour et al, J Phys Chem C (2012)

Rong Cai, Thibaut Mathieu, Vitor Oiko

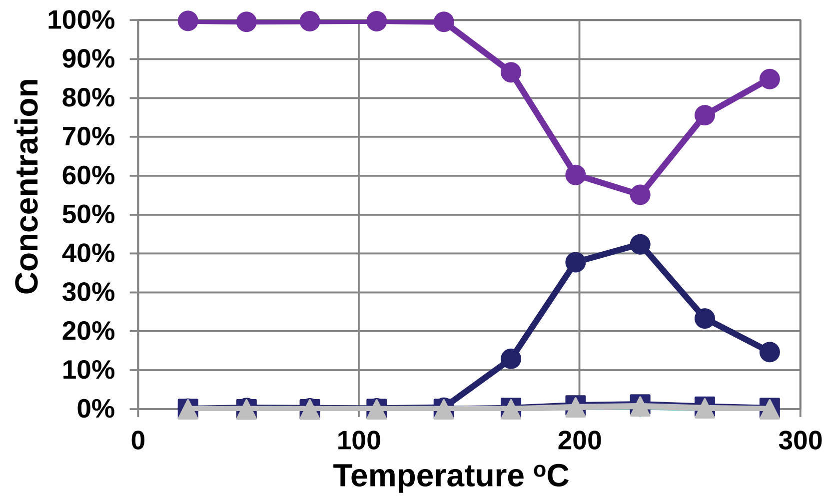
1-pentyne hydrogenation



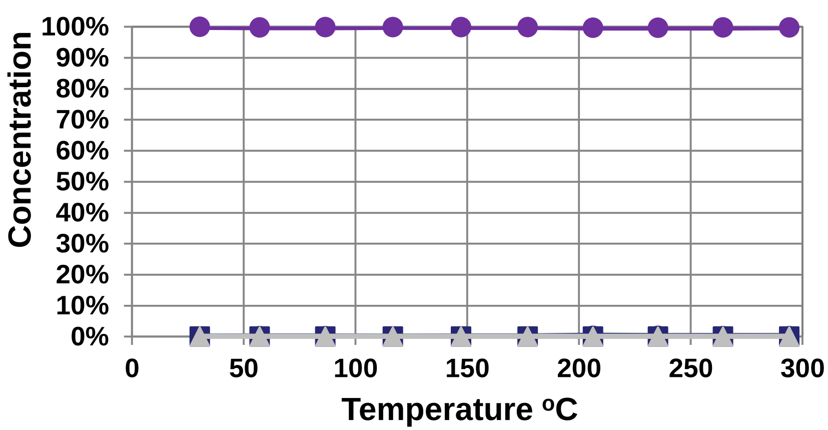
1-pentyne 1-pentene



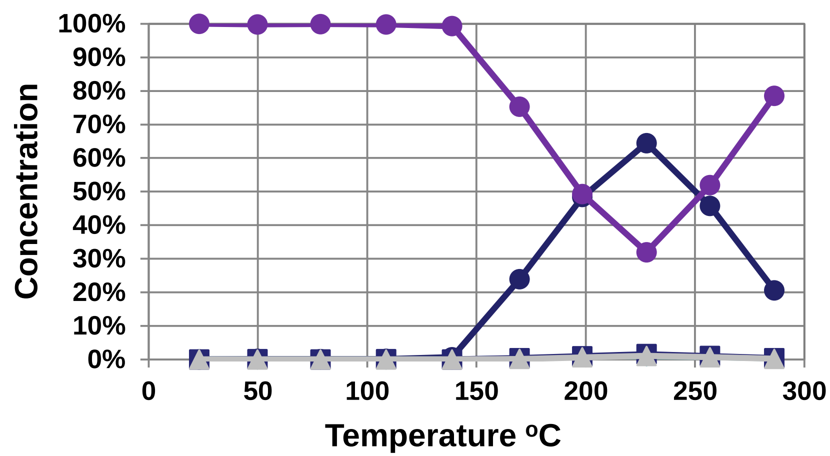
Blank carbon tape



Pd/Au cluster on carbon tape



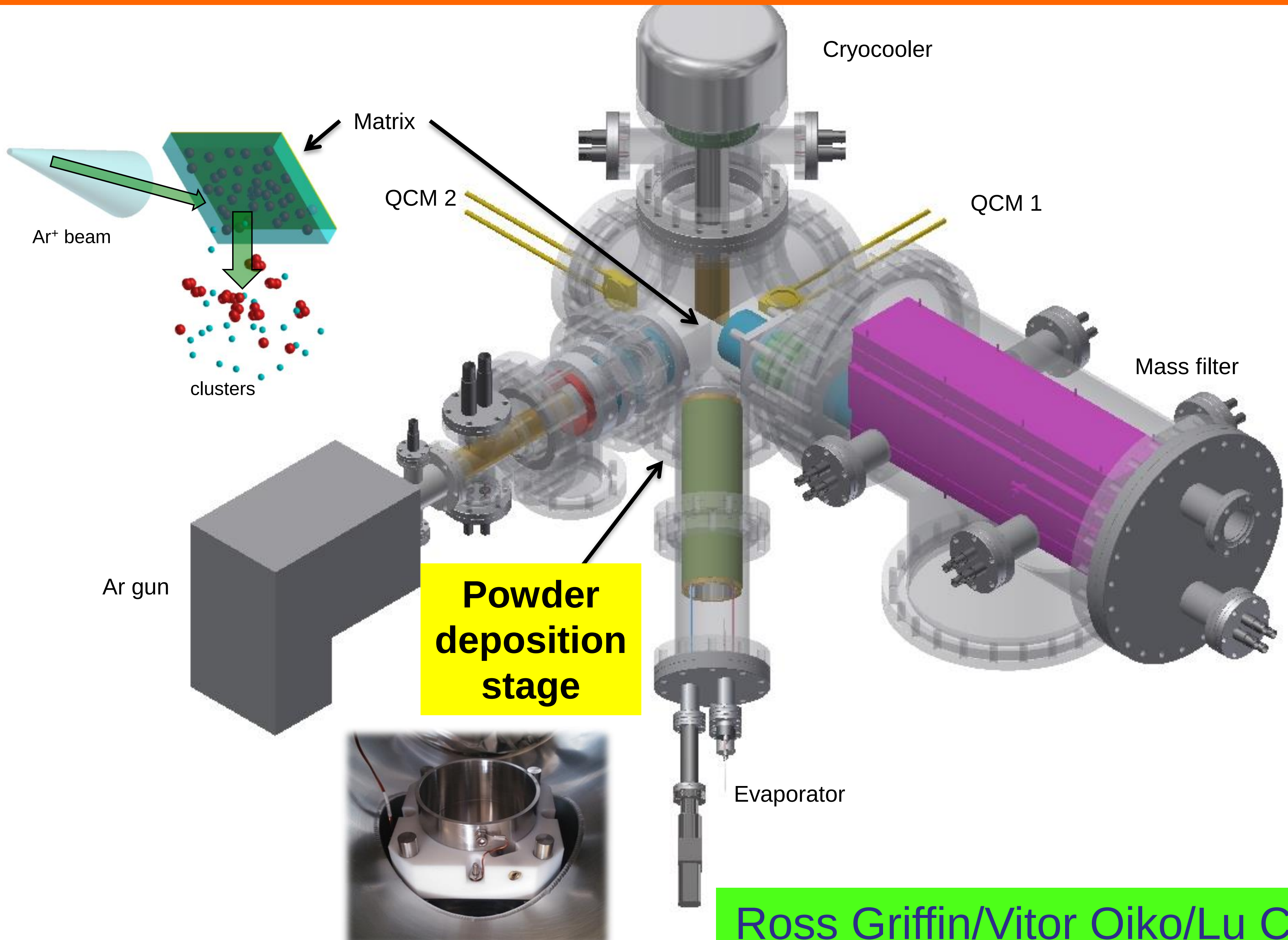
Au cluster on carbon tape



Pd cluster on carbon tape

Rong Cai/JM

The MACS 1+

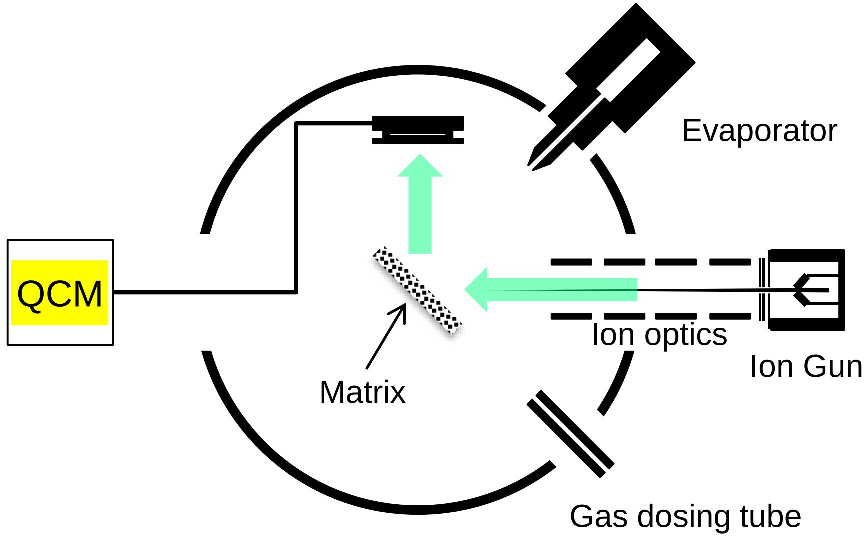


Ross Griffin/Vitor Oiko/Lu Cao

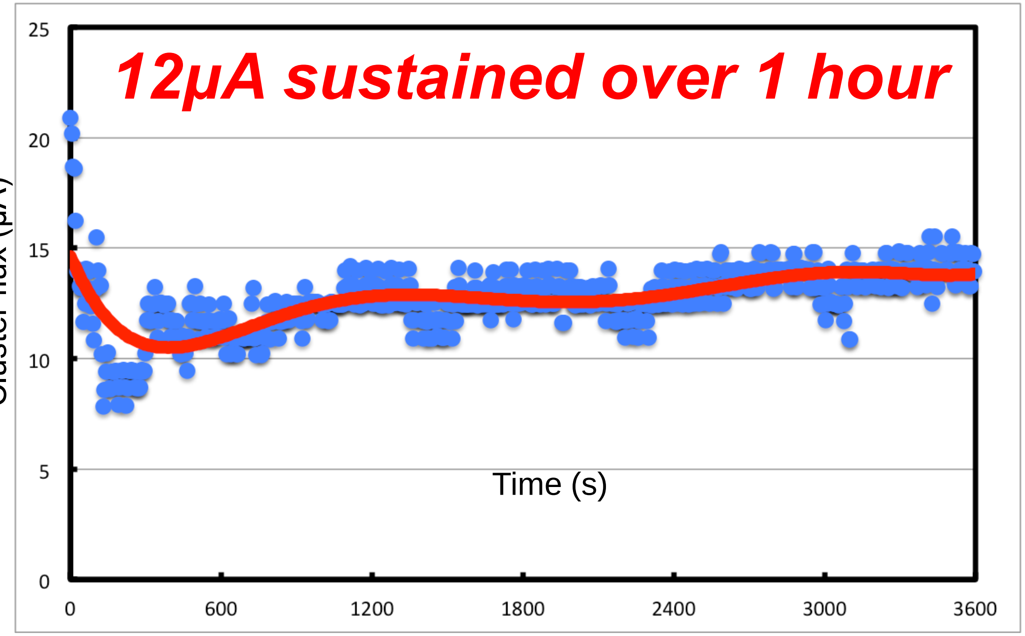
Breaking the 10μA barrier (MACS I, Ag_N)

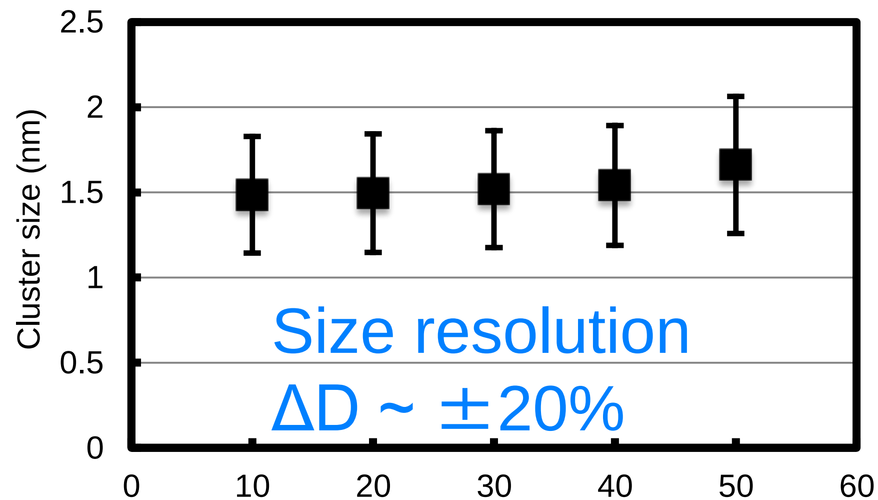
x10^5

- QCM measurement = mass of material over area of 0.8cm diameter in the centre
- Cluster flux on QCM calculated from average cluster size (~120 atoms)
- Integrated cluster flux from beam profile



QCM = Quartz Crystal Microbalance



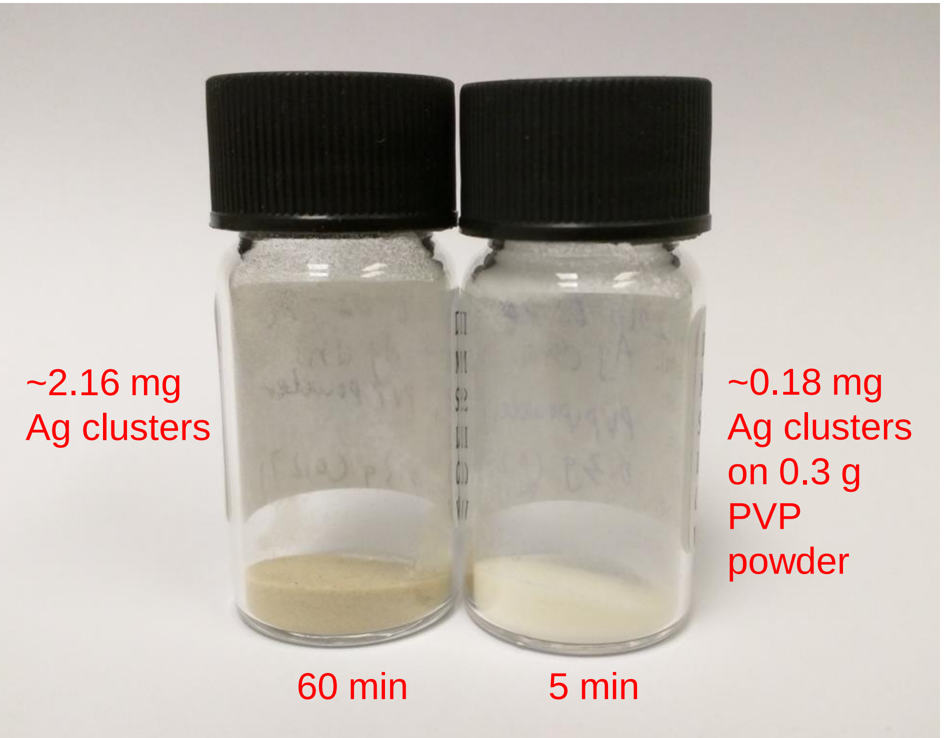


Ross Griffin, Vitor Oiko, Lu

The product: Ag clusters on TiO_2 powders

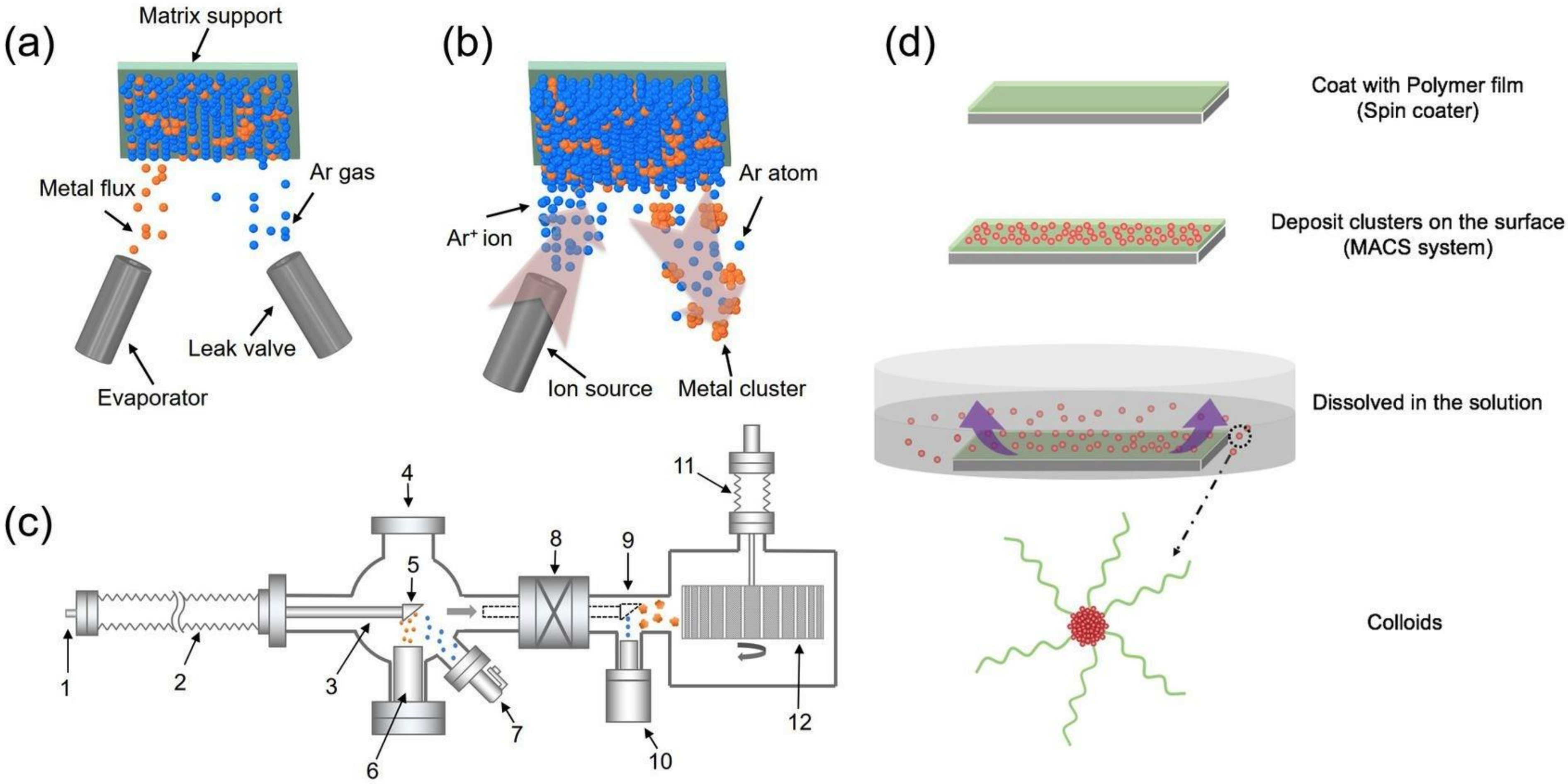
1 gram TiO_2 powder, 1% loading Ag clusters (10 mg), mean size 1.5nm.

Production in MACS 1+, deposition time 2 hours.



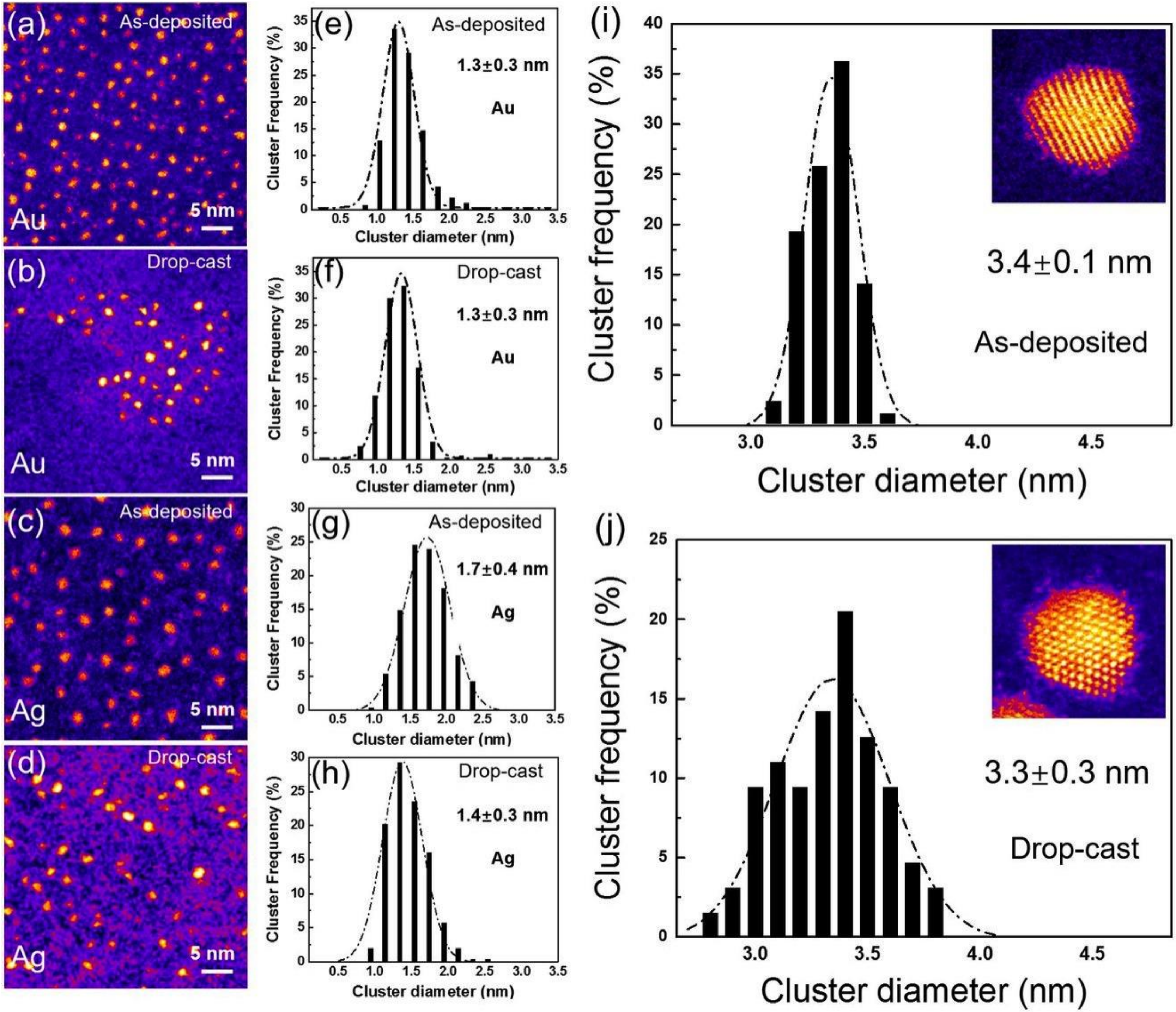
Ross Griffin, Lu Cao

Creating Colloids from Deposited Clusters

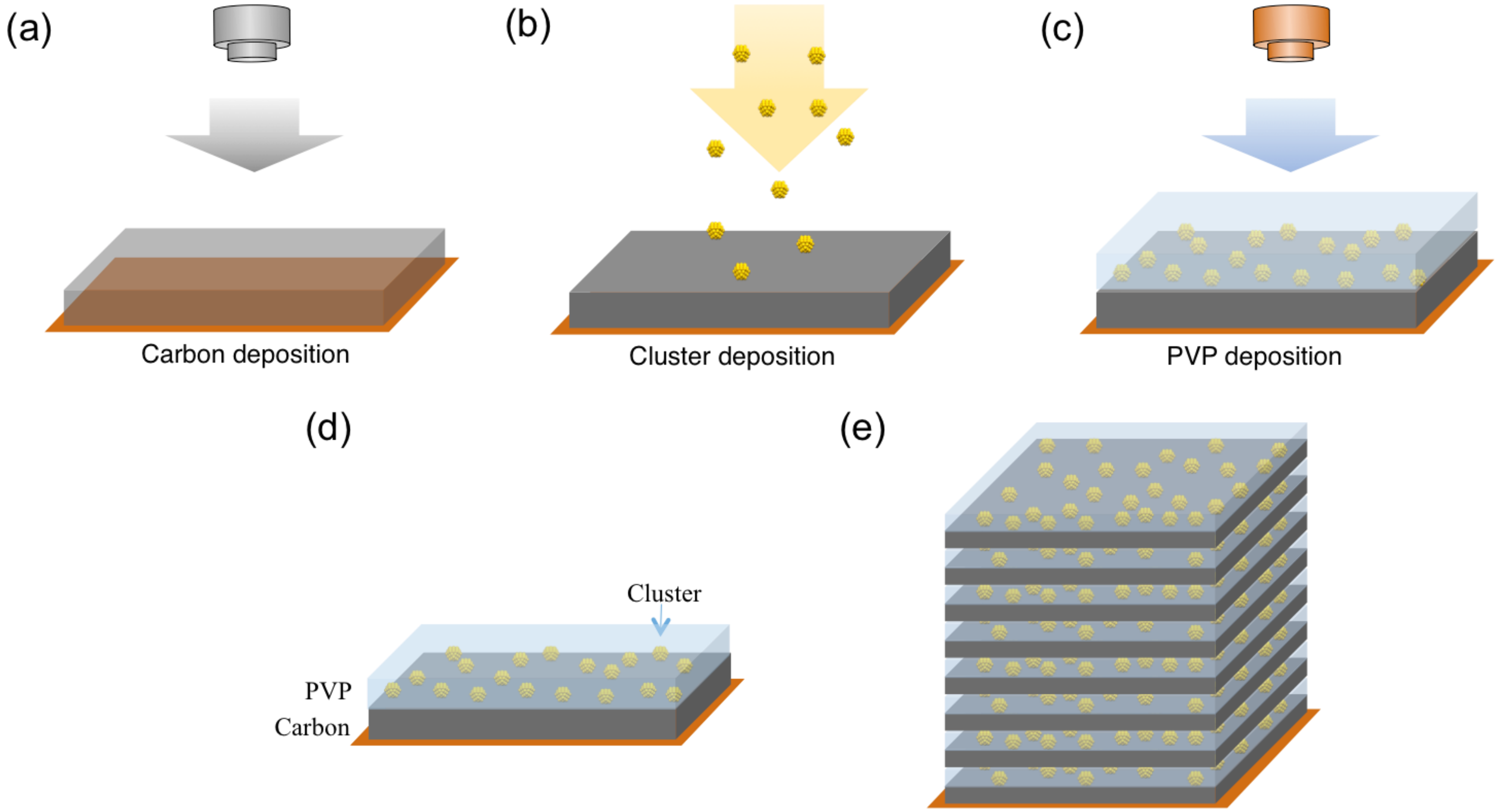


APL Mats (2017)

Rong Cai, Nan Jian, Jian Liu, Shane Murphy

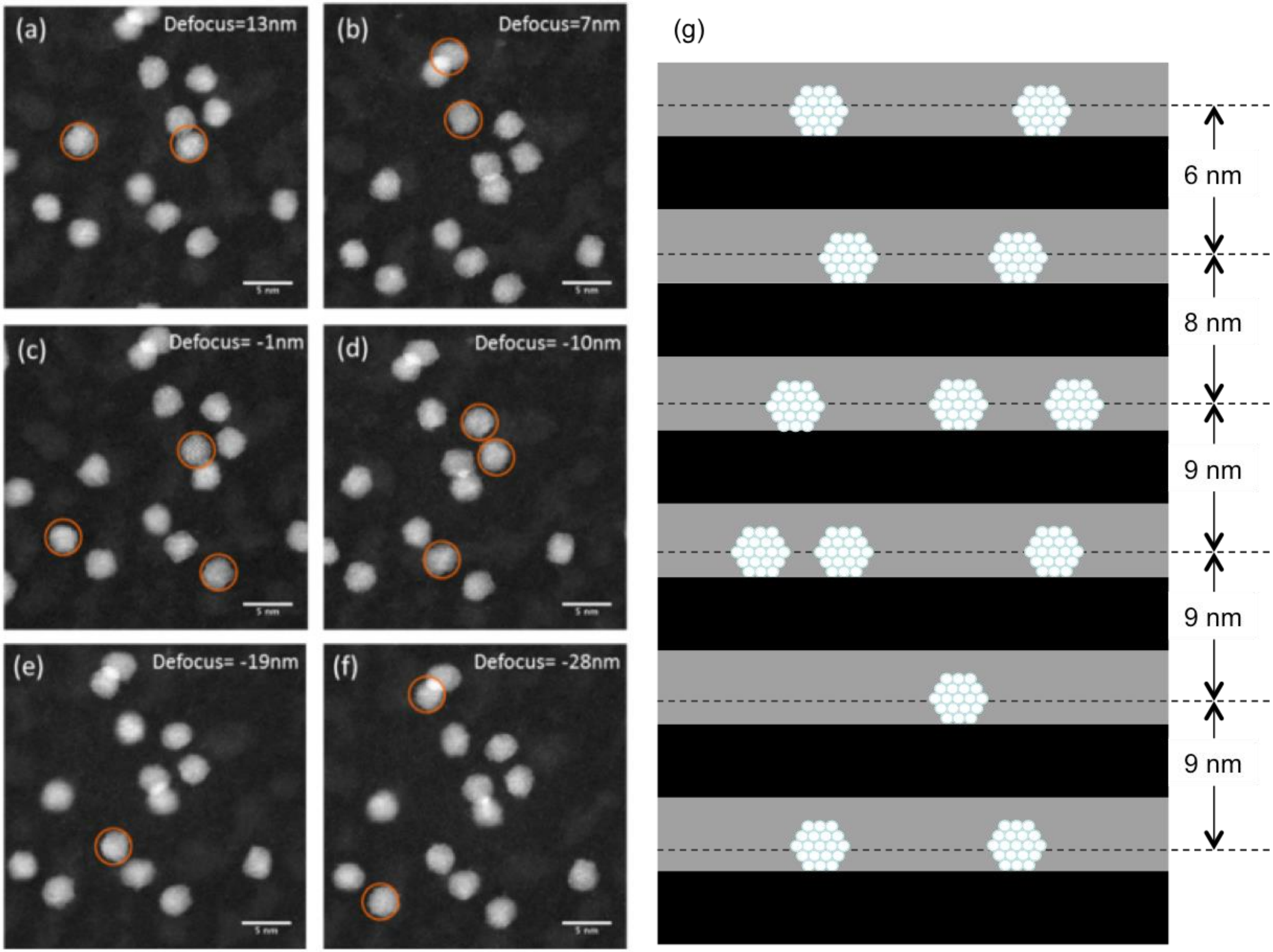

(a)
As-deposited
Au
5 nm
(b)
Drop-cast
Au
5 nm
(c)
As-deposited
Ag
5 nm
(d)
Drop-cast
Ag
5 nm
(e)
As-deposited
1.3±0.3 nm
Au
(f)
Drop-cast
1.3±0.3 nm
Au
(g)
As-deposited
1.7±0.4 nm
Ag
(h)
Drop-cast
1.4±0.3 nm
Ag
Cluster Frequency (%)
Cluster diameter (nm)
(i)
3.4±0.1 nm
As-deposited
(j)
3.3±0.3 nm
Drop-cast
Cluster frequency (%)
Cluster diameter (nm)

Multilayer stacks of clusters



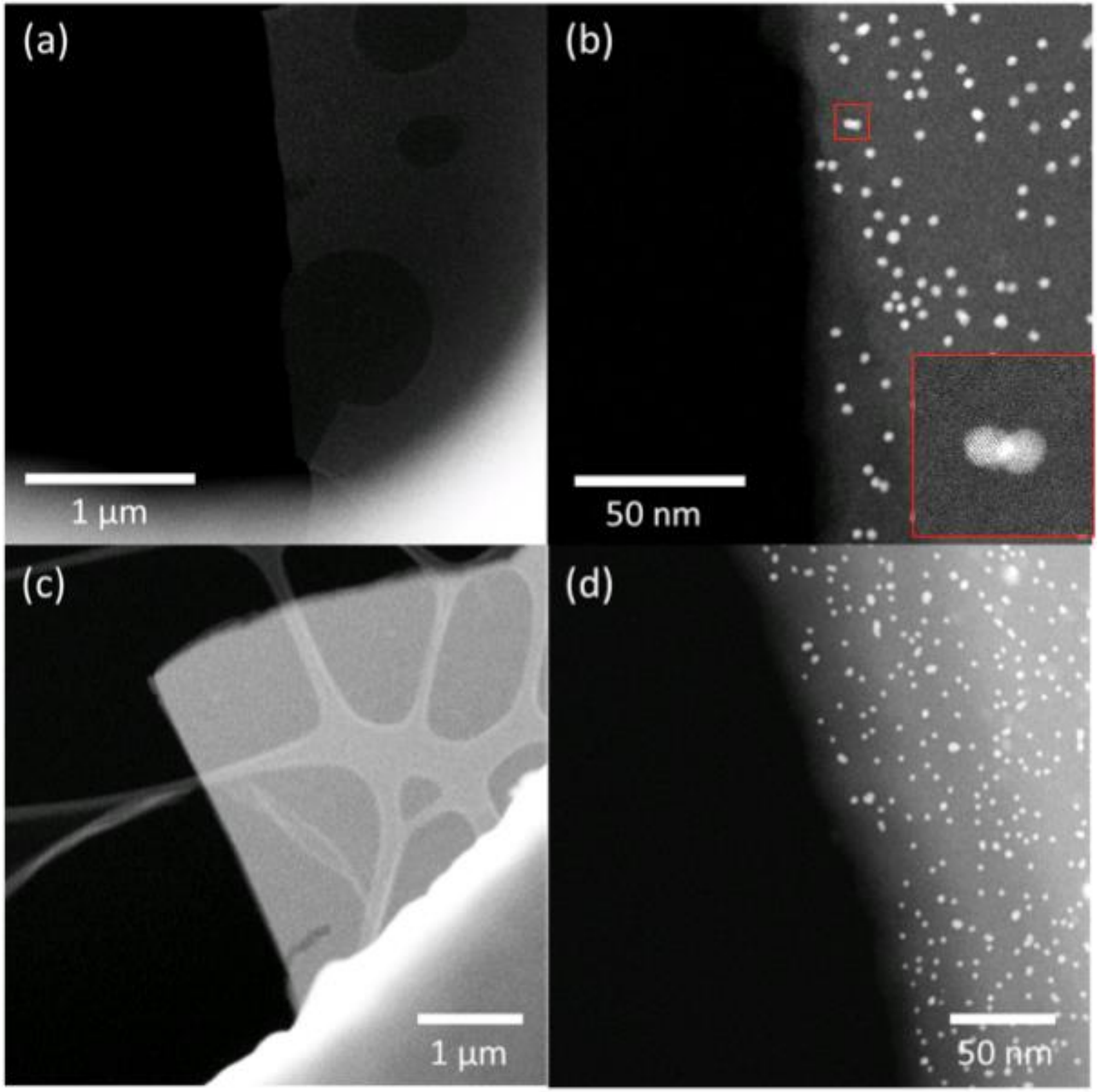
Nan Jian, Karl Bauer

Multilayer stacks of clusters



Nan Jian, Karl Bauer

Dicing of multilayer stacks of clusters



Nan Jian, Karl Bauer

Summary

(1) Size-selected nanoparticles have diverse applications.

(2) Feynman's **vision** of "arranging the atoms" is becoming a **reality** in cluster science!

(3) Cluster Beam Deposition (CBD): **size-selected** nanoparticles from **wide variety of materials** – elemental, binary, ternary…

(4) **Atomic structure, metastability, PES (**and **melting**) of clusters come from ac-STEM imaging plus heating: e.g. Au_N

(5) **MACS**: a promising route to **scale-up** by 5 orders of magnitude; 2 more orders of magnitude possible in lab? Size-controlled (best $\Delta D \sim \pm 5\%$).

(6) **Catalysis**, **theranostics** and **nanometrology** can exploit <10nm cluster deposition. **Photonics/photovoltaics?**

(7) We need innovations in cluster **processing** (dicing, powders, colloids, multilayers, etc) and **integration**…