Novel Physical and Chemical Properties of Nanoparticles

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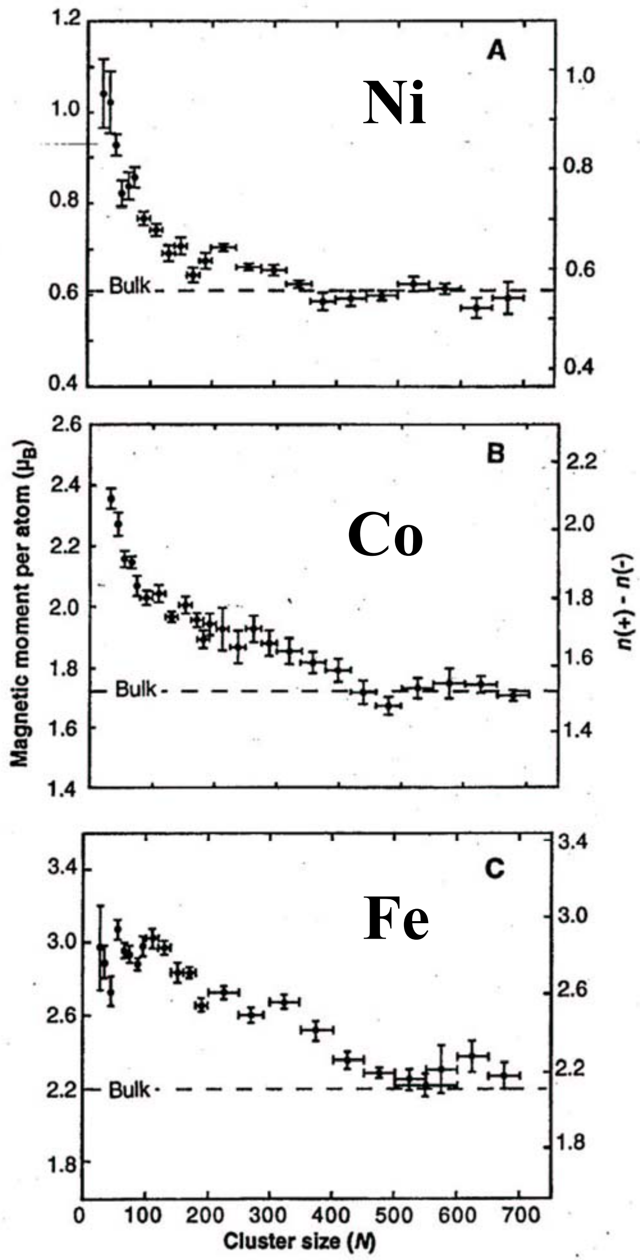
College Station, TX

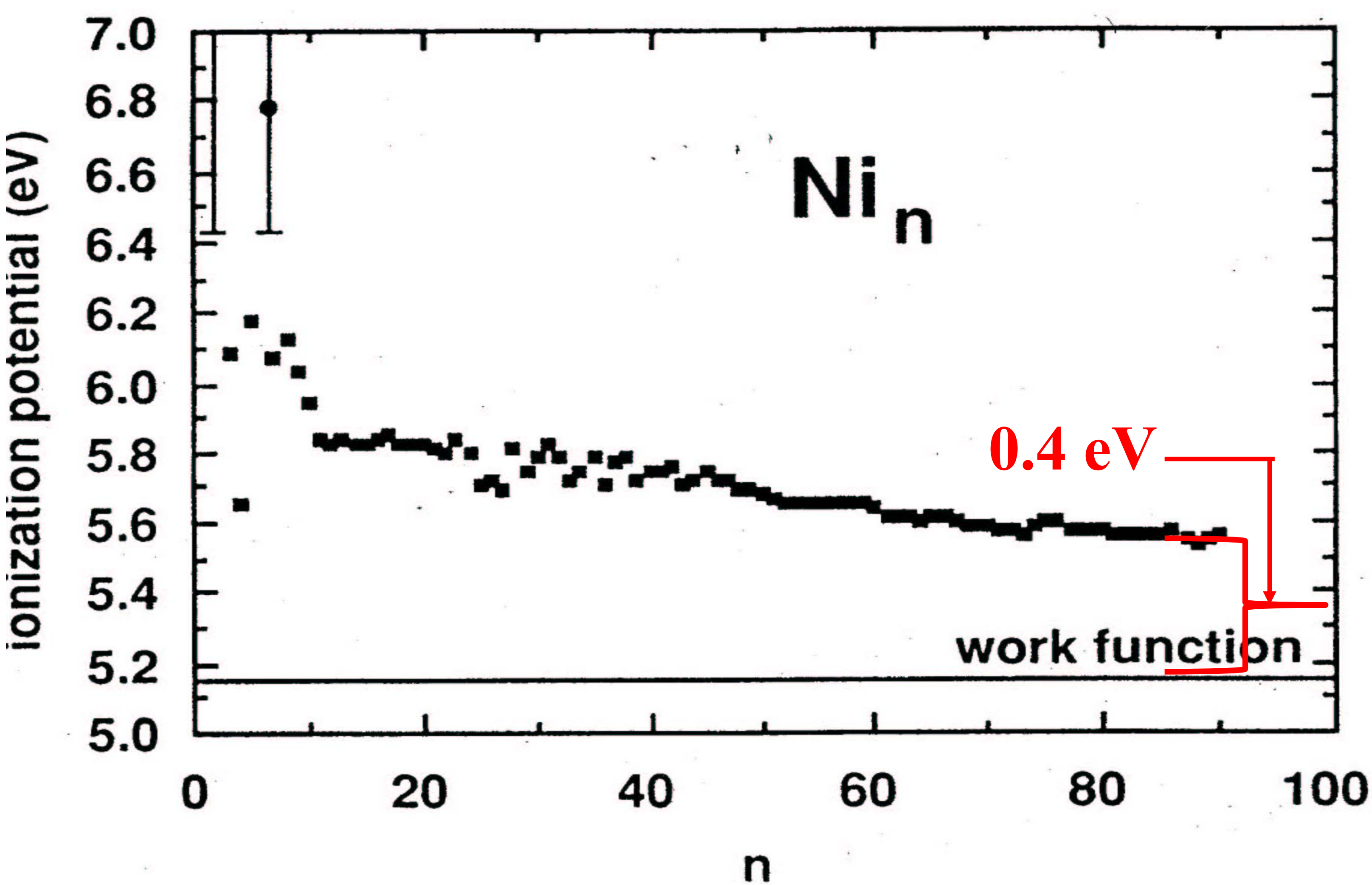
Magnetic Moments Versus Metal Cluster Size

From Gillas, Chatelain, and De Heer, Science (1994)



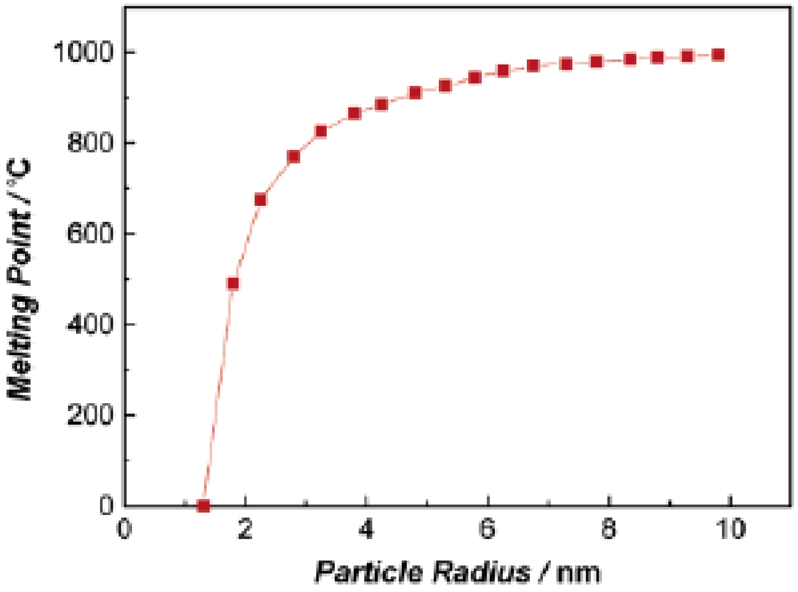
Ionization Potentials of Ni Clusters Versus Size

Knickelbein, Yang, Riley, JCP (1990)



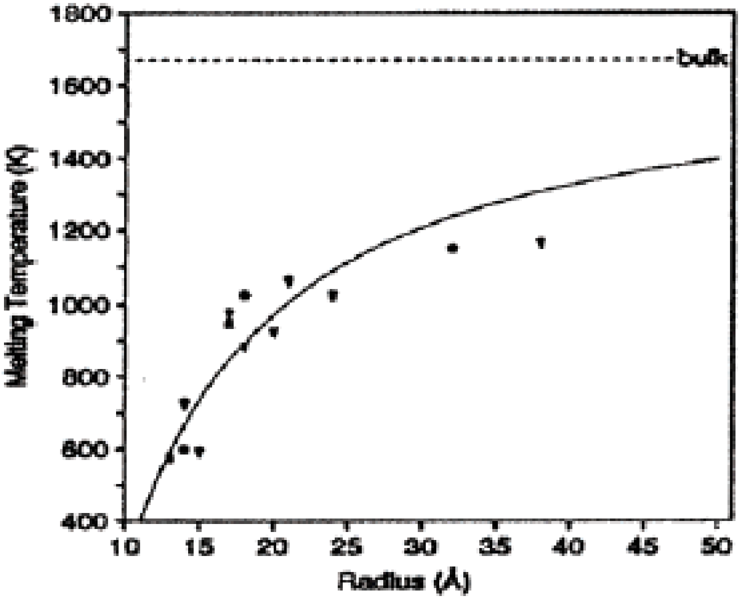
Relationship between melting points and particle sizes

Au



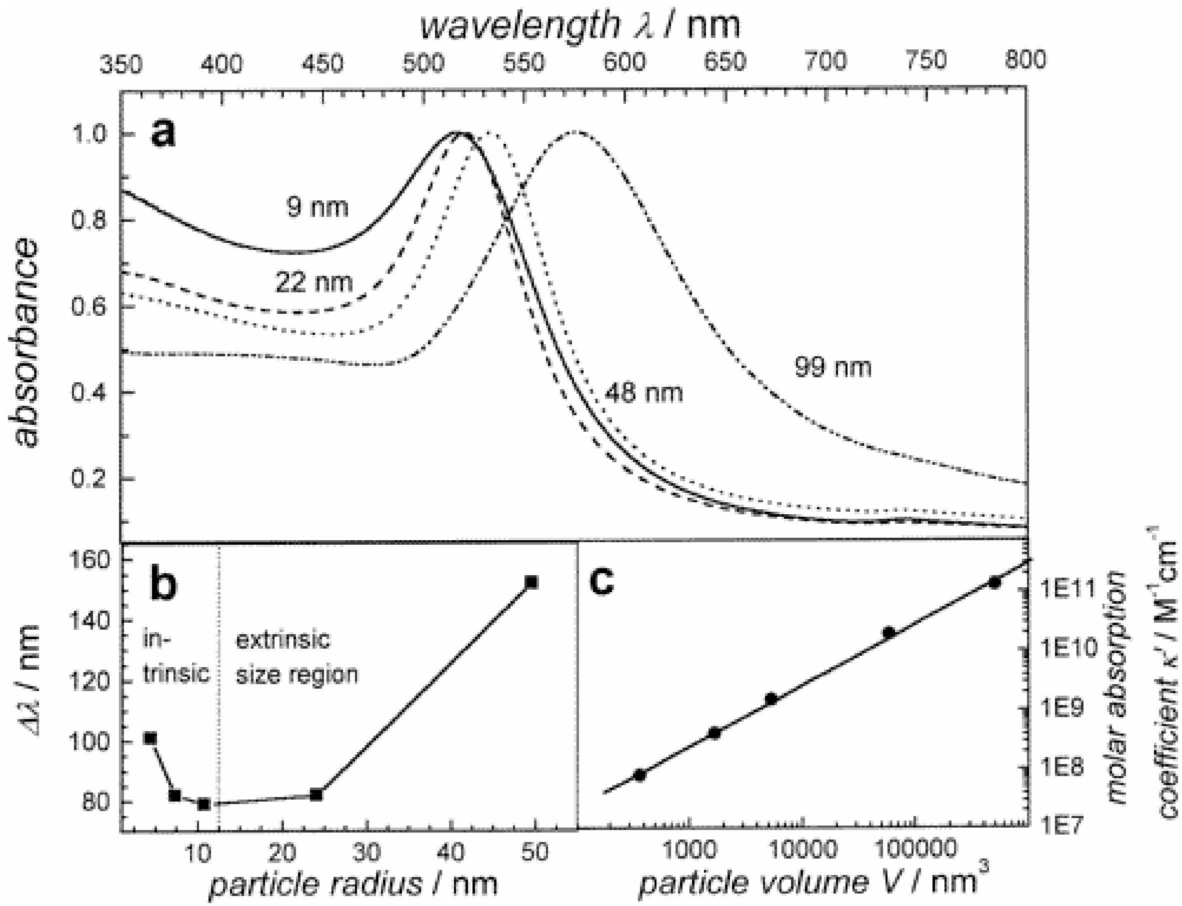
G. Schmid, in: Nanoscale Materials in Chemistry, Eds. K. J. Klabunde, Wiley-Interscience: New York, 2001; ch.2 p. 15.

CdS



A. P. Alivisatos, J. Phys. Chem. 100 (1996) 13226.

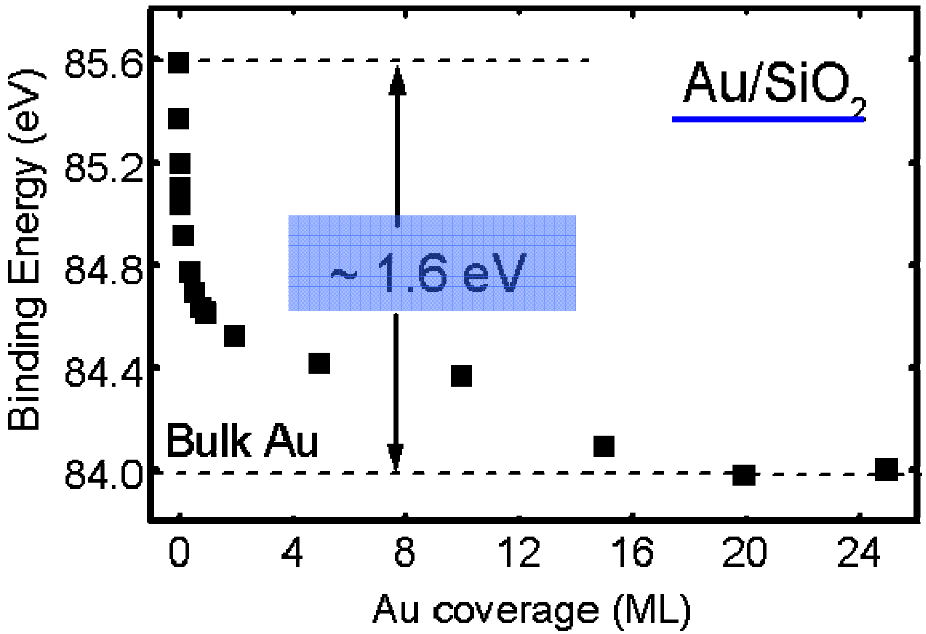
Surface plasmon vs. size of gold nanoparticles.

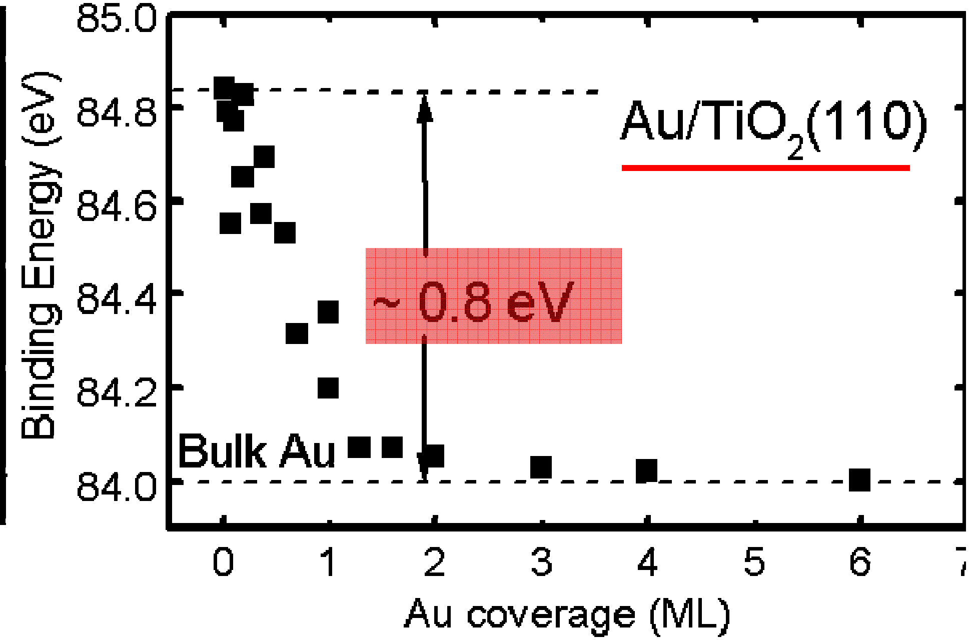


Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.

The UV-vis absorption spectra of colloidal solutions of gold nanoparticles with diameters varying between 9 and 99 nm show that the absorption maximum red-shifts with increasing particle size in part a, while the plasmon bandwidth follows the behavior illustrated in part b. The bandwidth increases with decreasing nanoparticle radius in the intrinsic size region and also with increasing radius in the extrinsic size region as predicted by theory. In part c the extinction coefficients of these gold nanoparticles at their respective plasmon absorption maxima are plotted against their volume on a double logarithmic scale. The solid line is a linear fit of the data points, illustrating that a linear dependence is observed, in agreement with the Mie theory.

XPS Core Level Shifts: Au/SiO_2 vs. Au/TiO_2





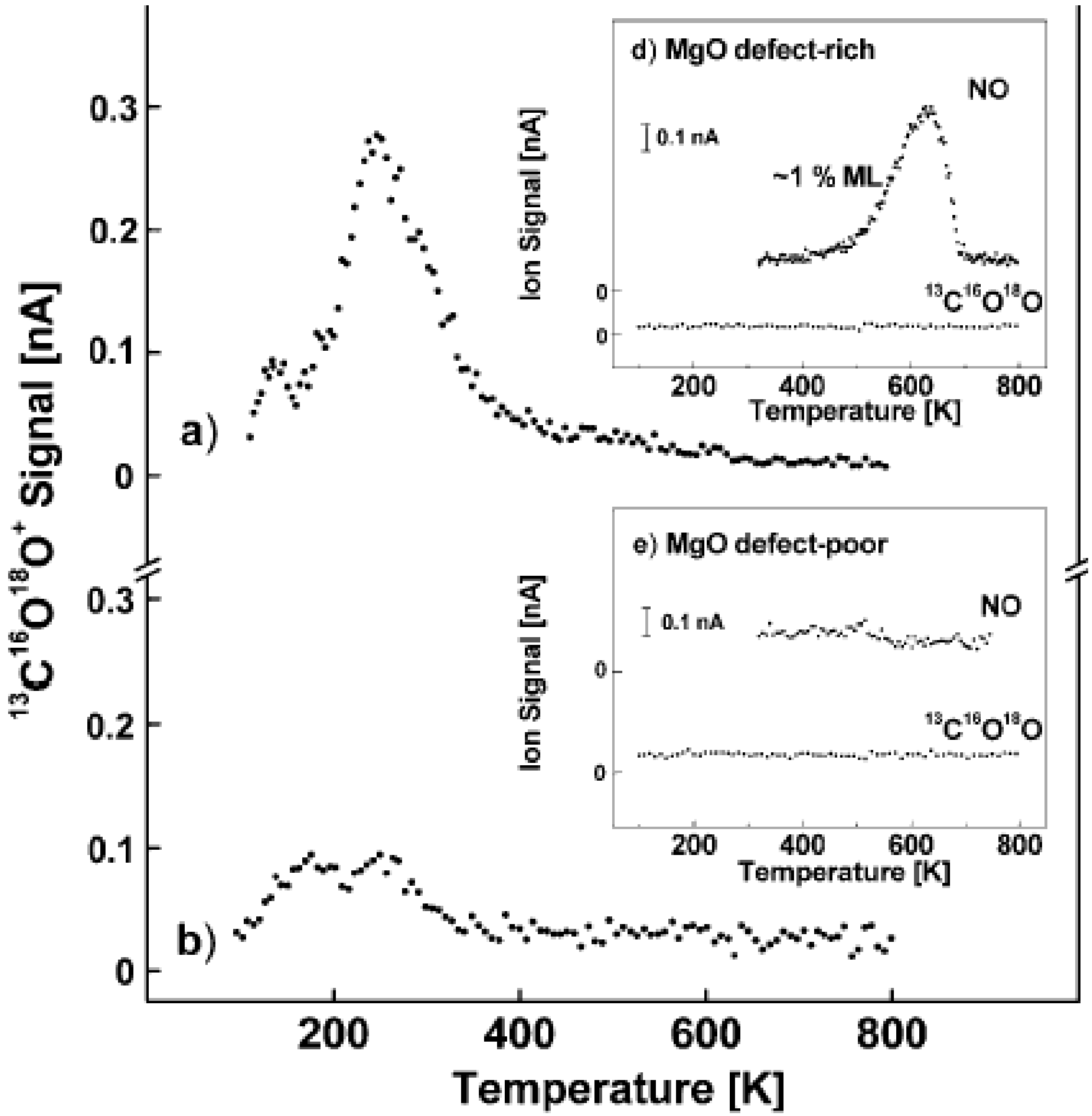
For Au/SiO_2: $BE_{small\ cluster} - BE_{bulk} = 1.6$ eV

For Au/TiO_2: $BE_{small\ cluster} - BE_{bulk} = 0.8$ eV

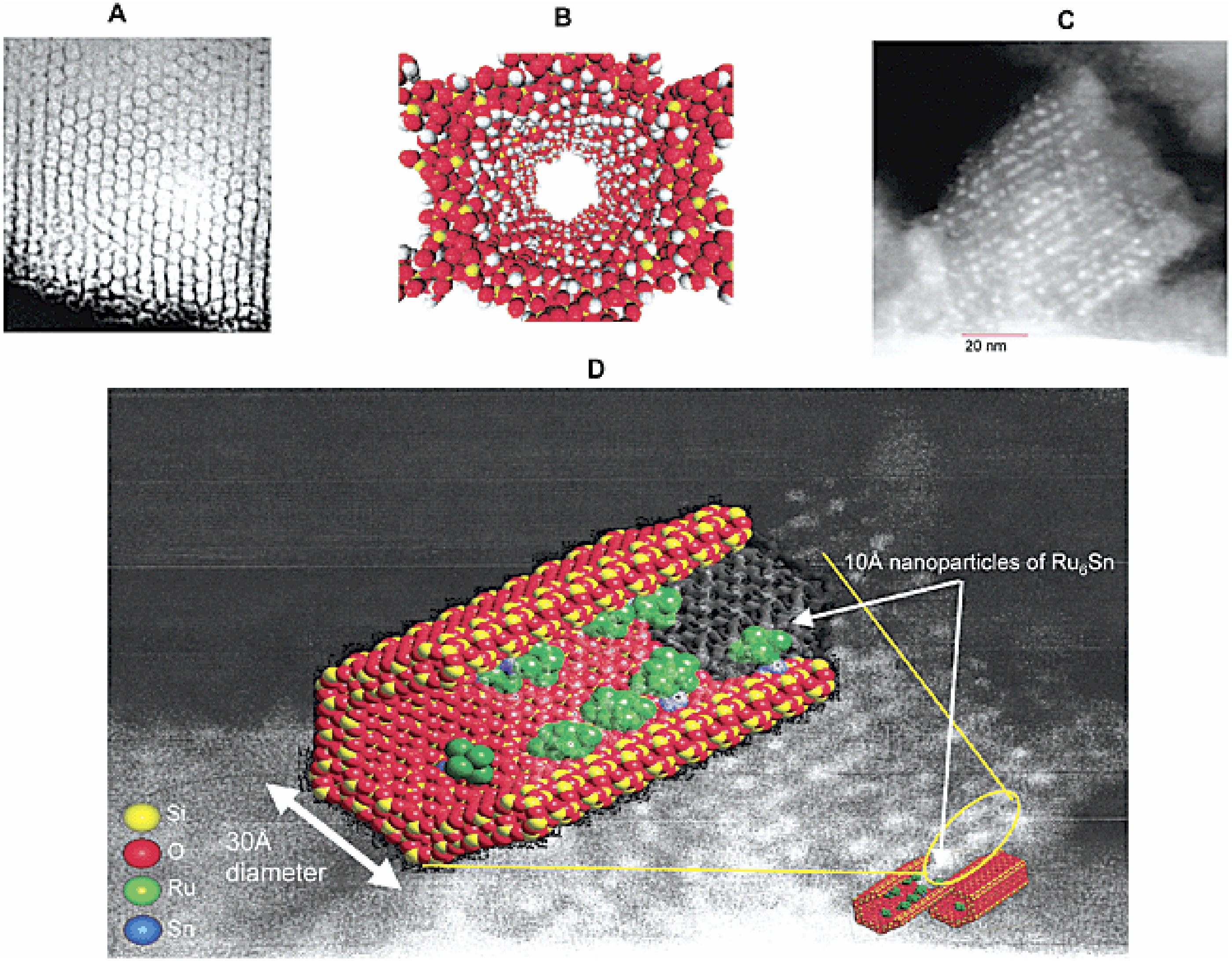
CO oxidation over Au_8 on MgO

Defect rich

Defect poor

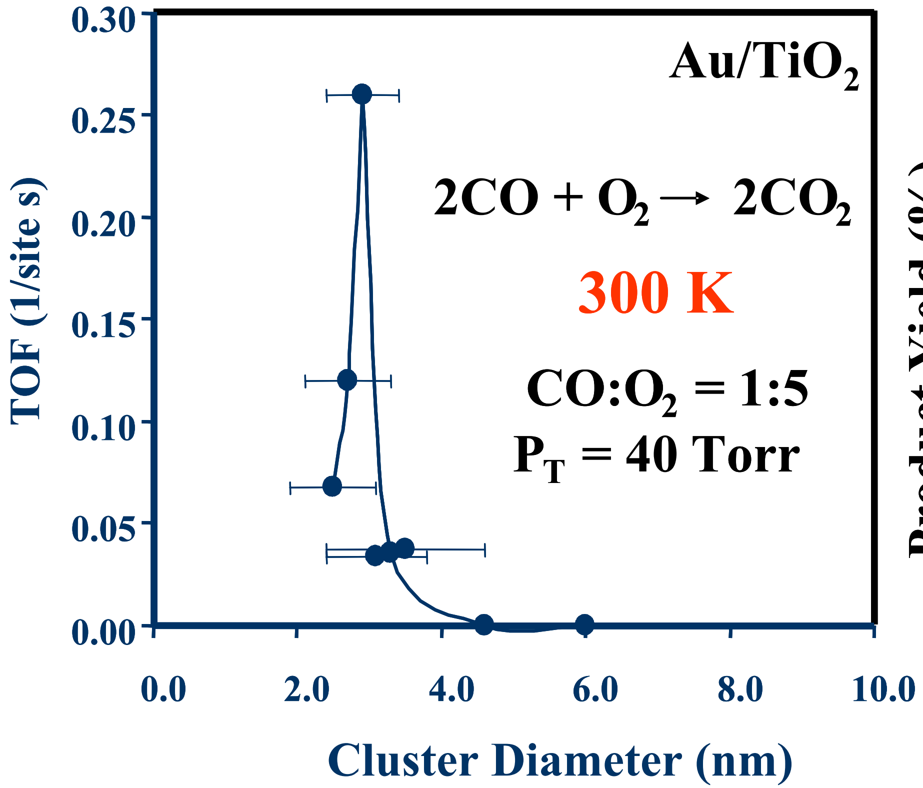


A. Sanchez, S. Abbet, U. Heiz, W. D. Shneider, H. Hakkinen, R. N. Barnett, U. Landman, J. Phys. Chem. A 103 (1999) 9573.

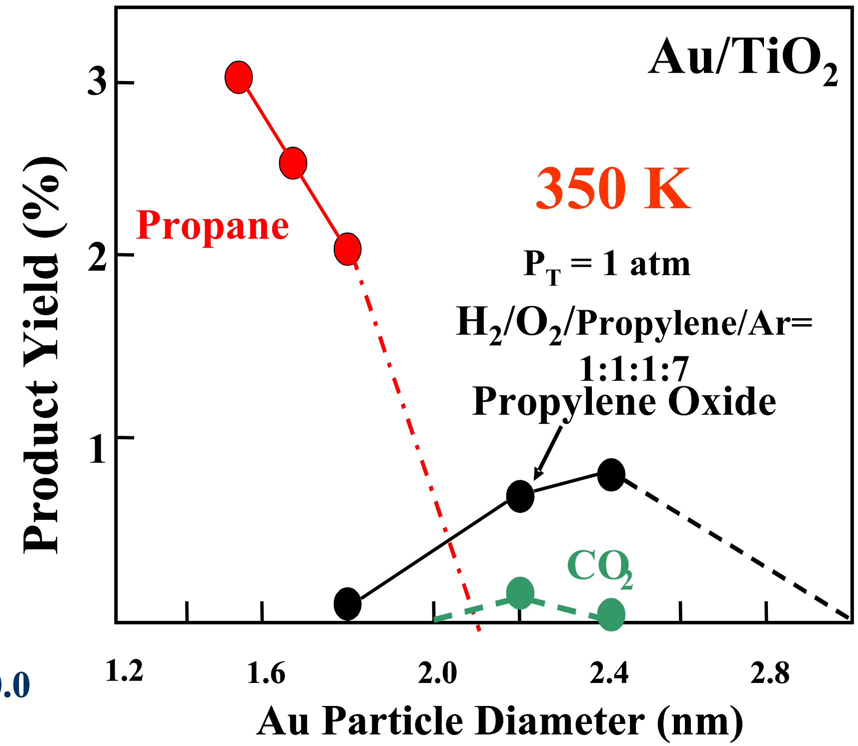


J. M. Thomas, B. F. G. Johnson, R. Raja, G. Sankar, P. A. Midgley, *Acc. Chem. Res.*, 36 (2003) 20.

Unique Catalytic Activity of Nanosized Gold Particles



from Haruta, et al., Catalysis Letters (1997)

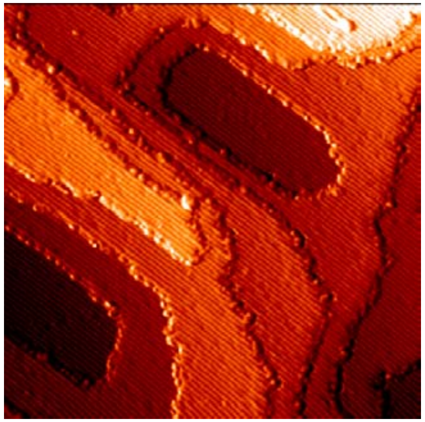


from Haruta, et al., Shokubai, Catalysts and Catalysis (1995)

Model Oxide-Supported Metal Catalysts

e.g.
TiO_2

Oxide Single Crystal

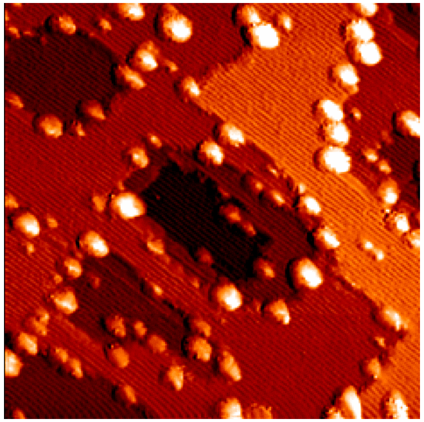


50 nm

$TiO_2(110)$

Metal Clusters
1.0-50 nm

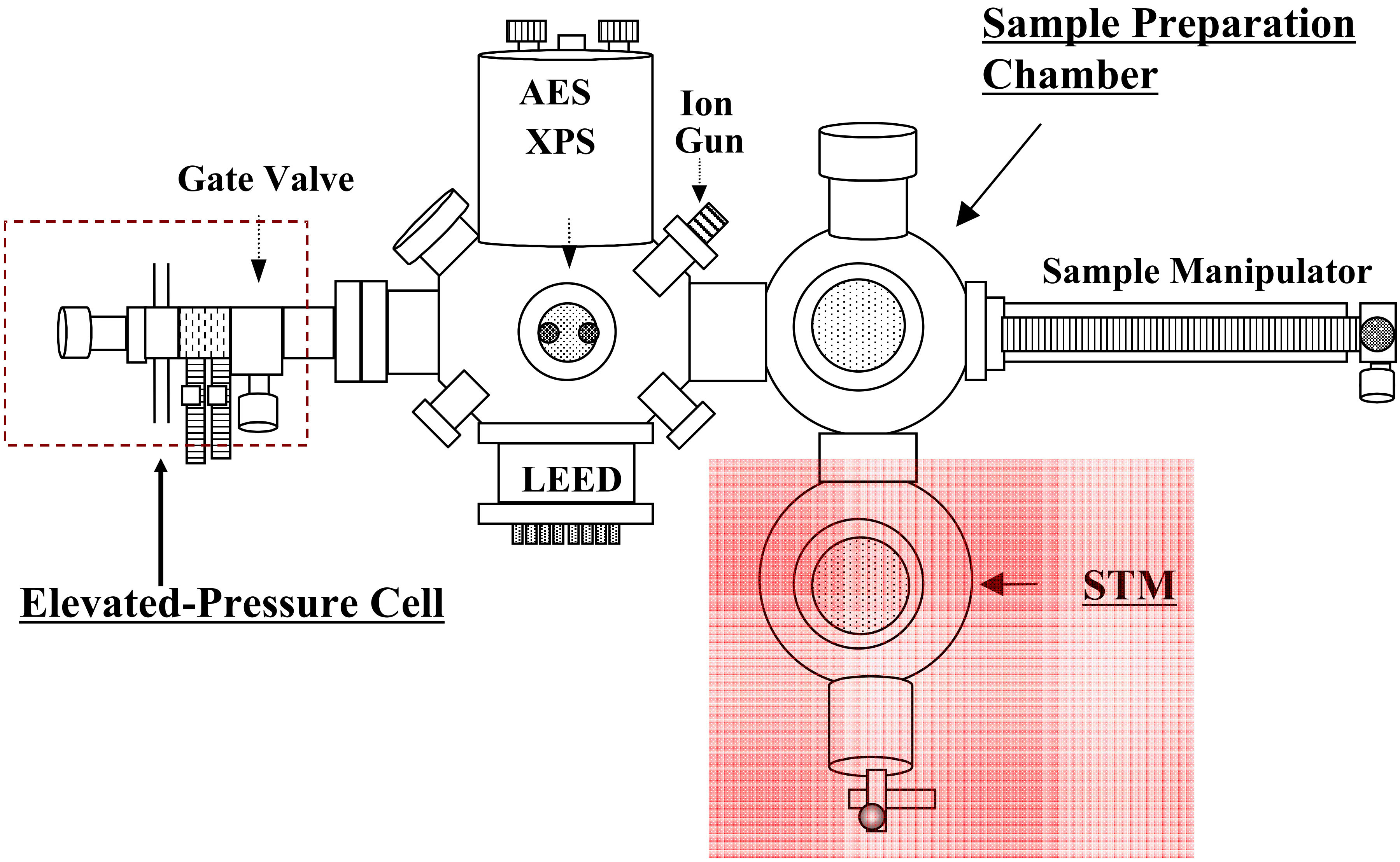
Oxide Single Crystal



50 nm

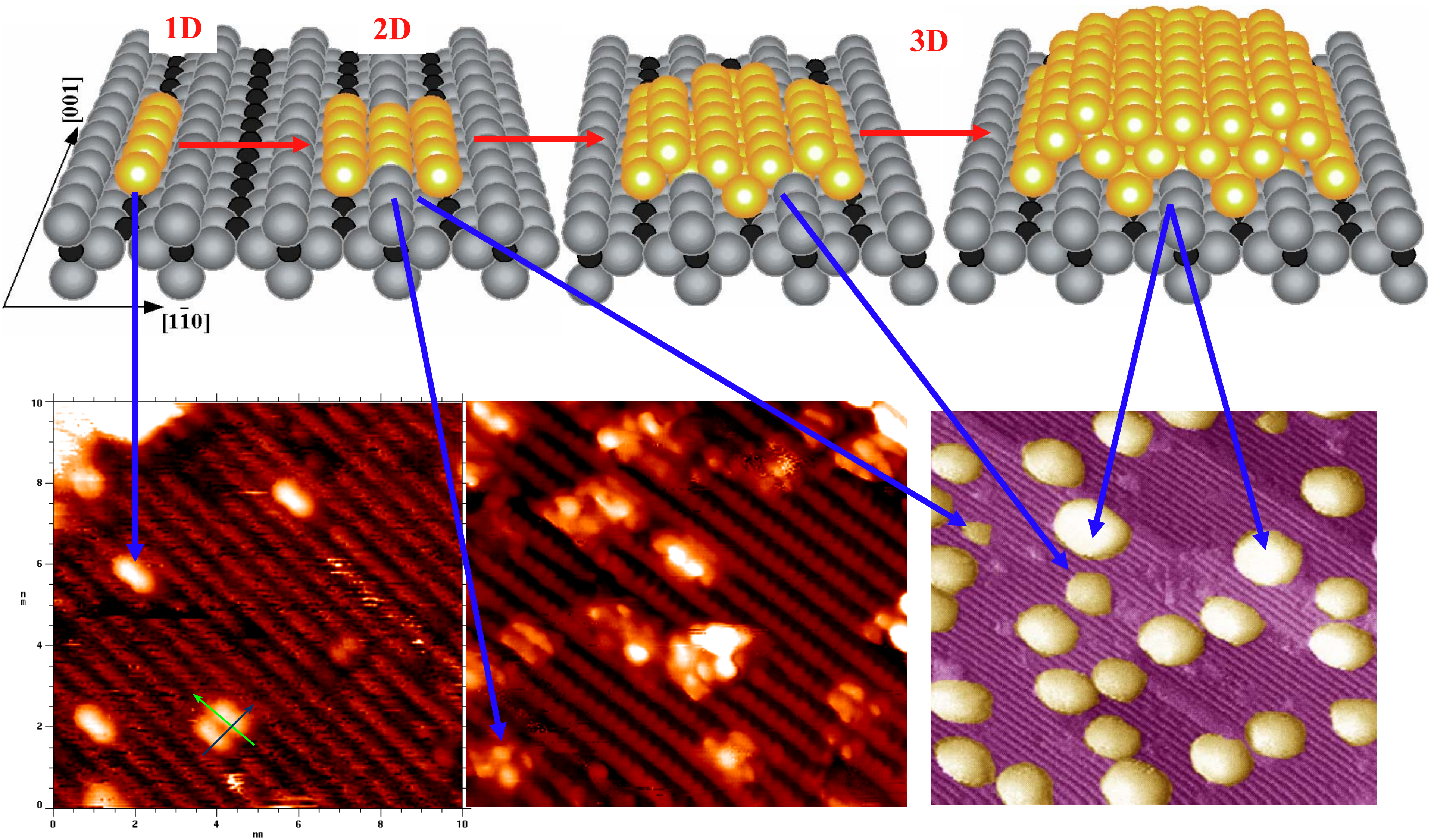
$TiO_2(110)$
+
0.25 Au

Apparatus



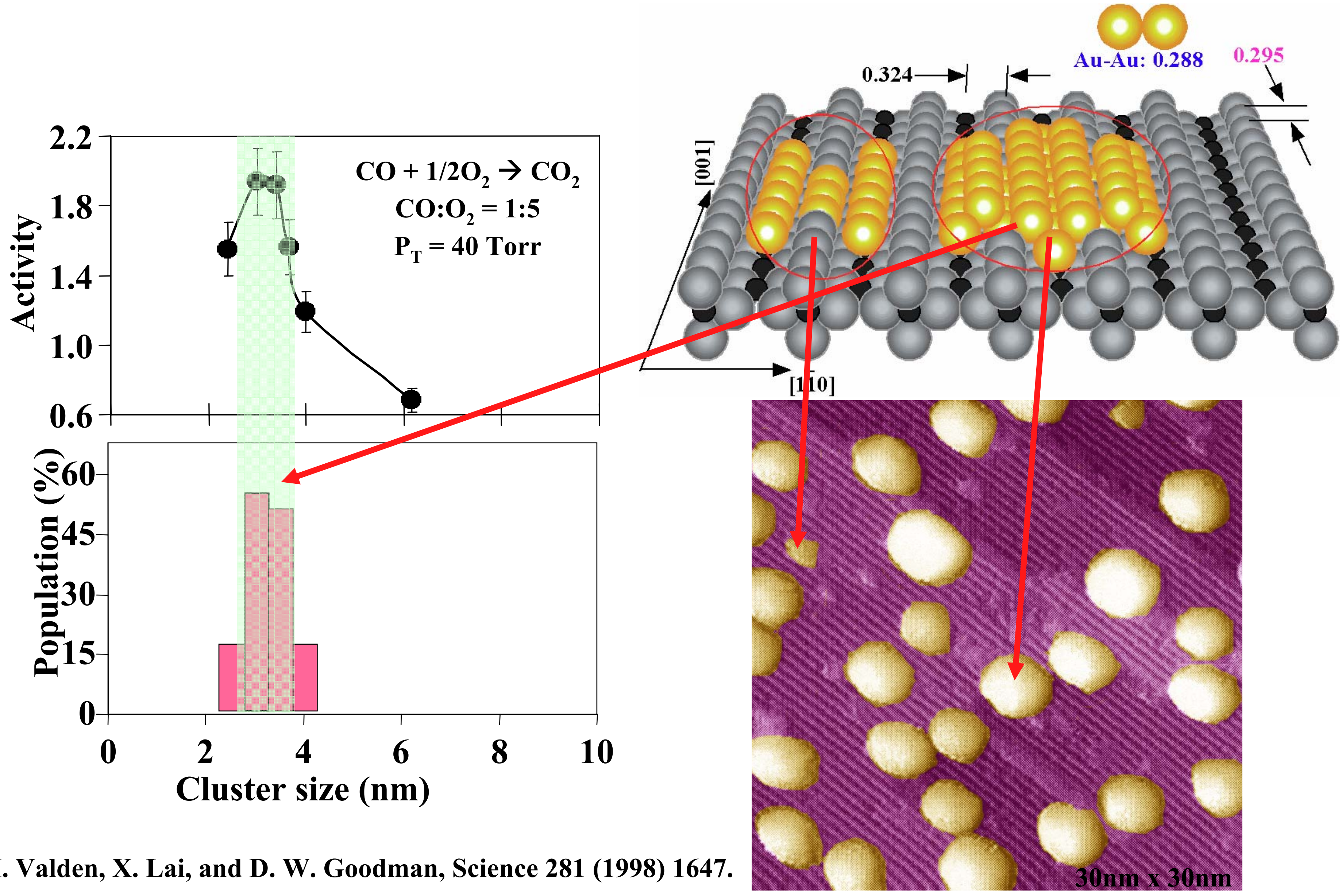
Sample Preparation Chamber
AES
XPS
Ion Gun
Gate Valve
Sample Manipulator
LEED
STM
Elevated-Pressure Cell

Au/TiO_2(110):1D→2D→3D



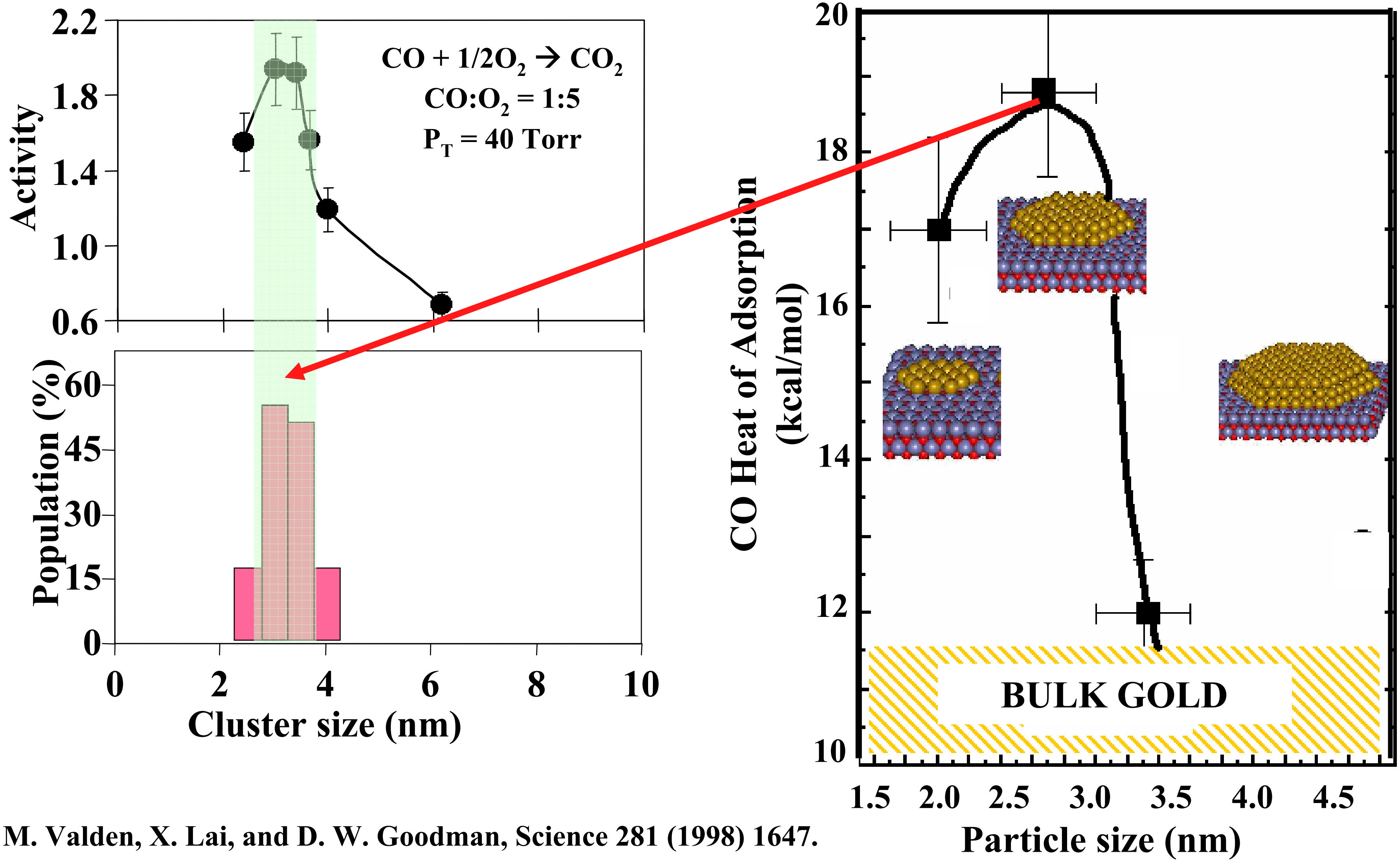
M. Valden, X. Lai, and D. W. Goodman, Science 281, 1647 (1998)

Unique catalytic activity of $Au/TiO_2(110)$



M. Valden, X. Lai, and D. W. Goodman, Science 281 (1998) 1647.

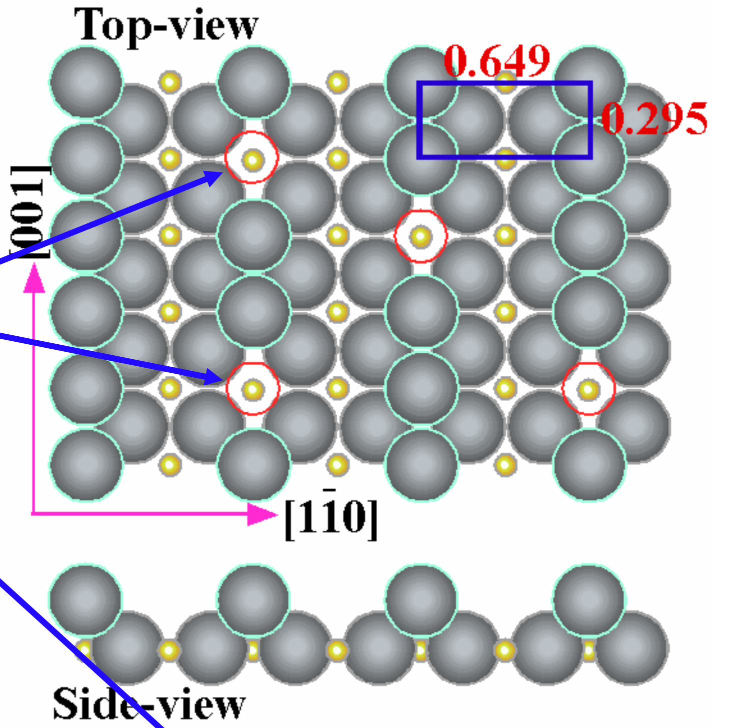
Unique properties of $Au/TiO_2(110)$

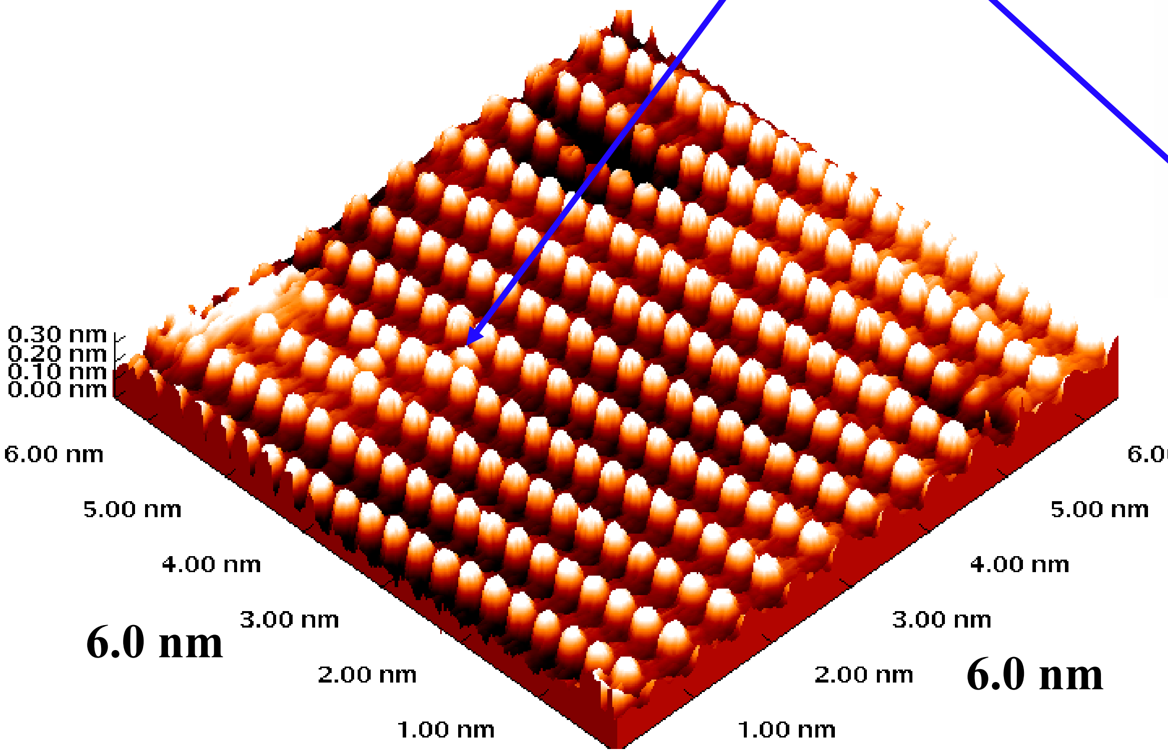


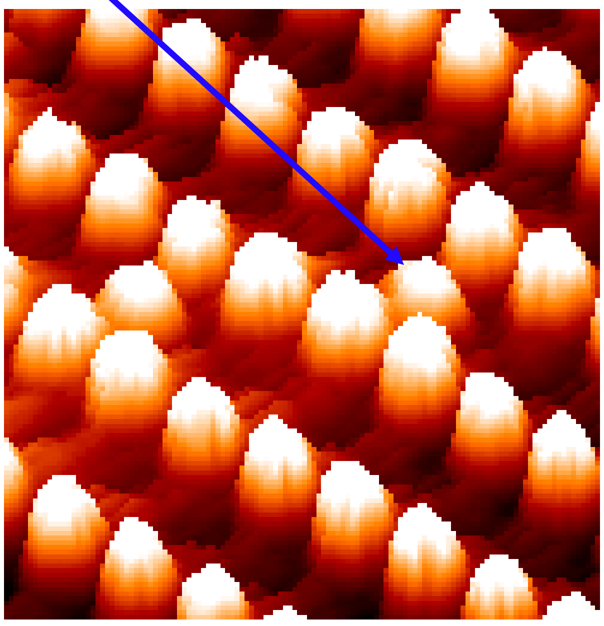
M. Valden, X. Lai, and D. W. Goodman, Science 281 (1998) 1647.
D. C. Meier, D. W. Goodman, J. Am. Chem. Soc. 126 (2004) 1892.

Surface defects on $TiO_2(110)$

Oxygen vacancies

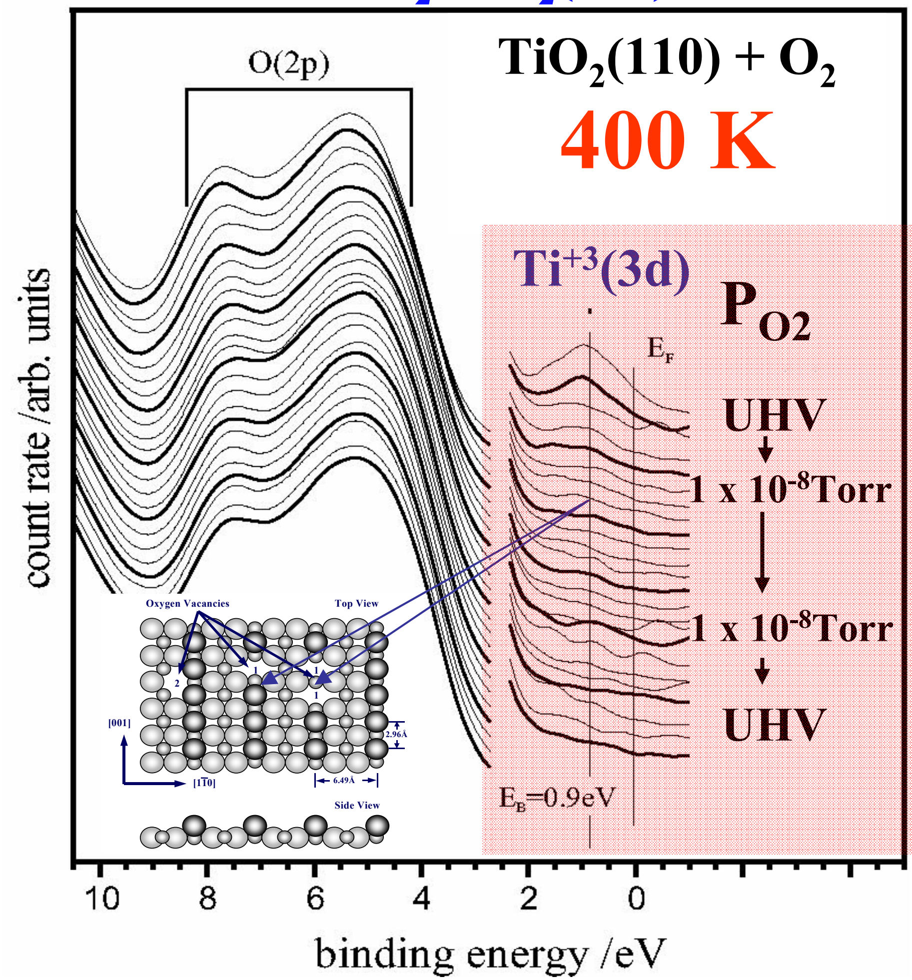






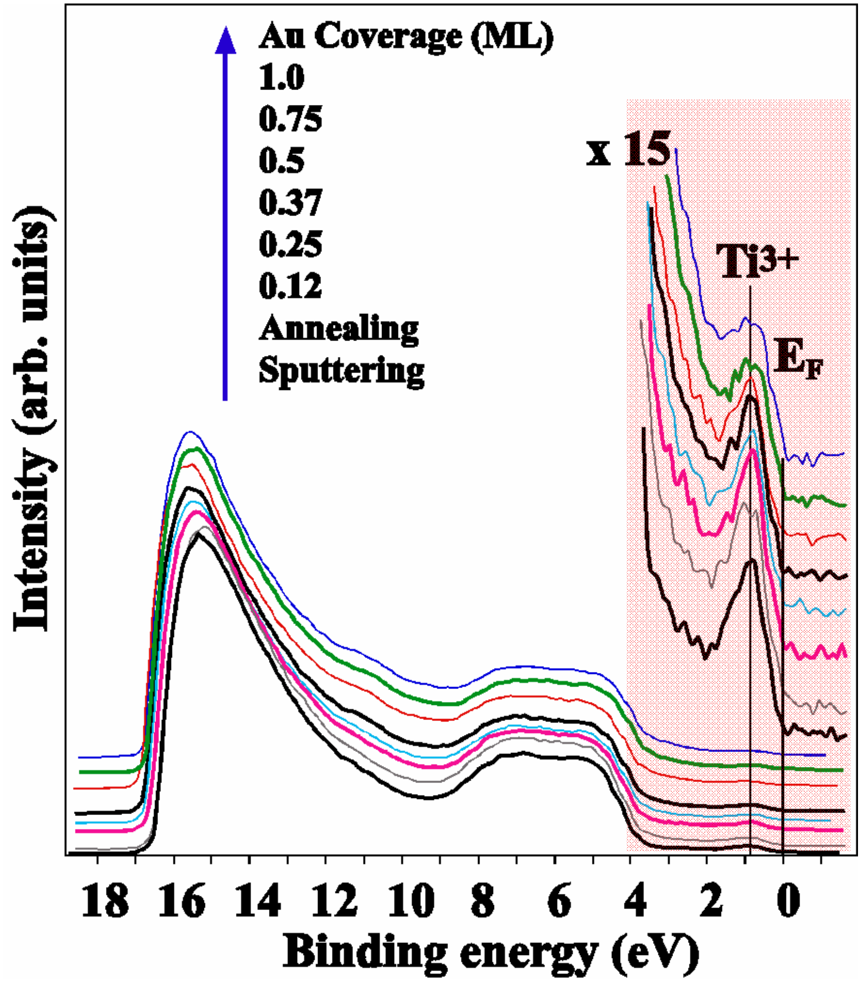
Ultraviolet Photoelectron Spectroscopy (UPS): Defects on $TiO_2(110)$

$O_2/TiO_2(110)$



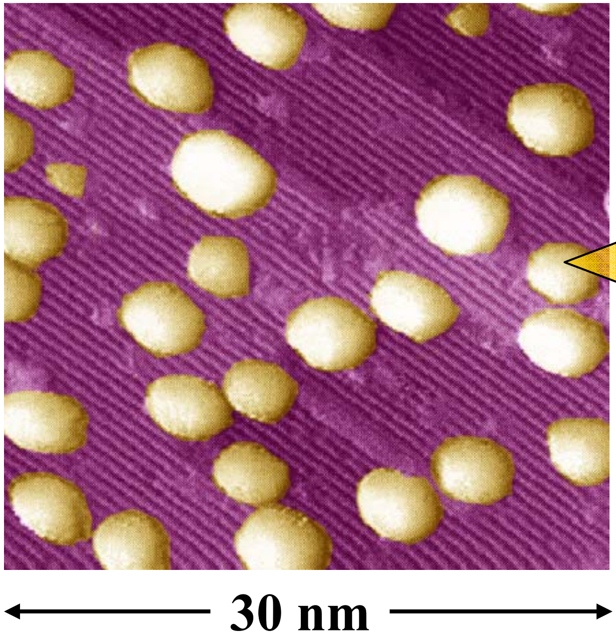
Krischok, Guenster, Goodman, Hoefft, and Kempter, 2005

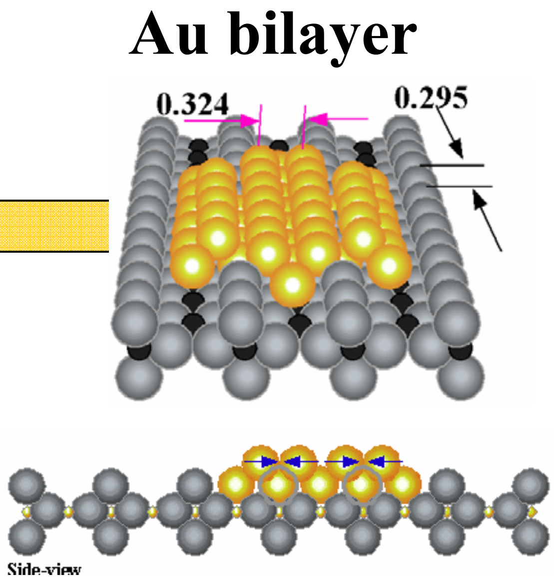
$Au/TiO_2(110)$



Chen and Goodman, 2005

Au Cluster Growth on TiO_2(110): Defects as Anchors for Clusters





Au nanoparticles promote the exchange of oxygen vacancies between the surface and bulk of titania

Rodriguez et al, J. Am. Chem. Soc., 124 (2002) 5242

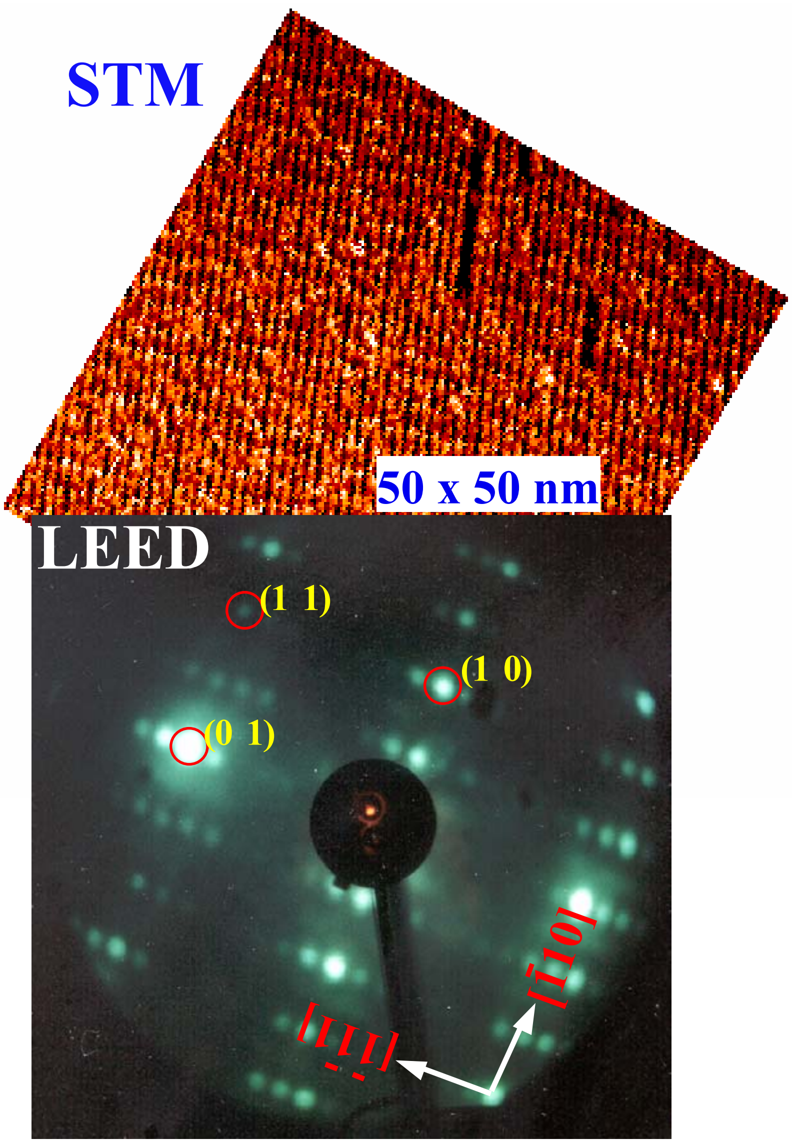
and

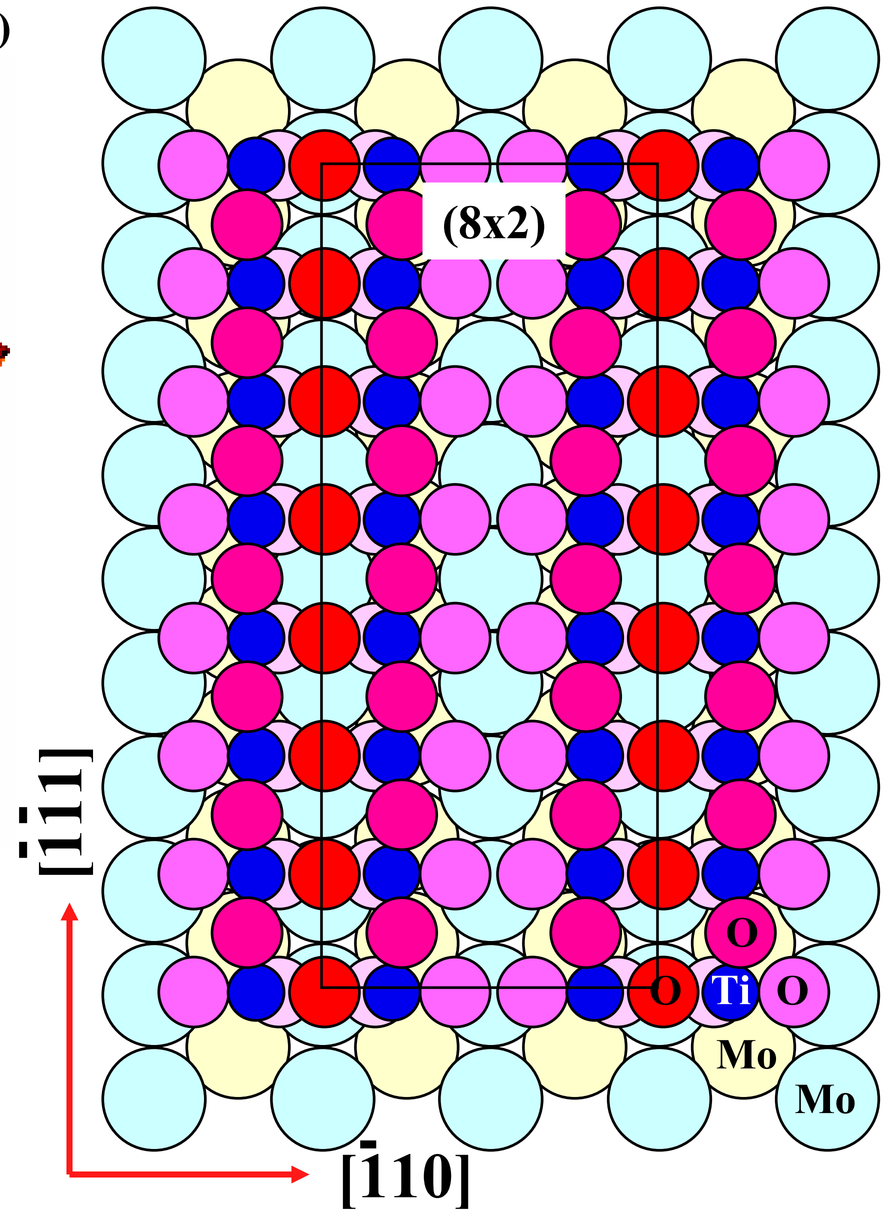
Single oxygen vacancy can bind 3 Au atoms on average

E. Wahlstroem, N. Lopez, R. Schaub, P. Thostrup, A. Ronnau, C. Africh, E. Laegsgaard, J. K. Norskov, and F. Besenbacher, Phys. Rev. Lett. 90, 101 (2003)

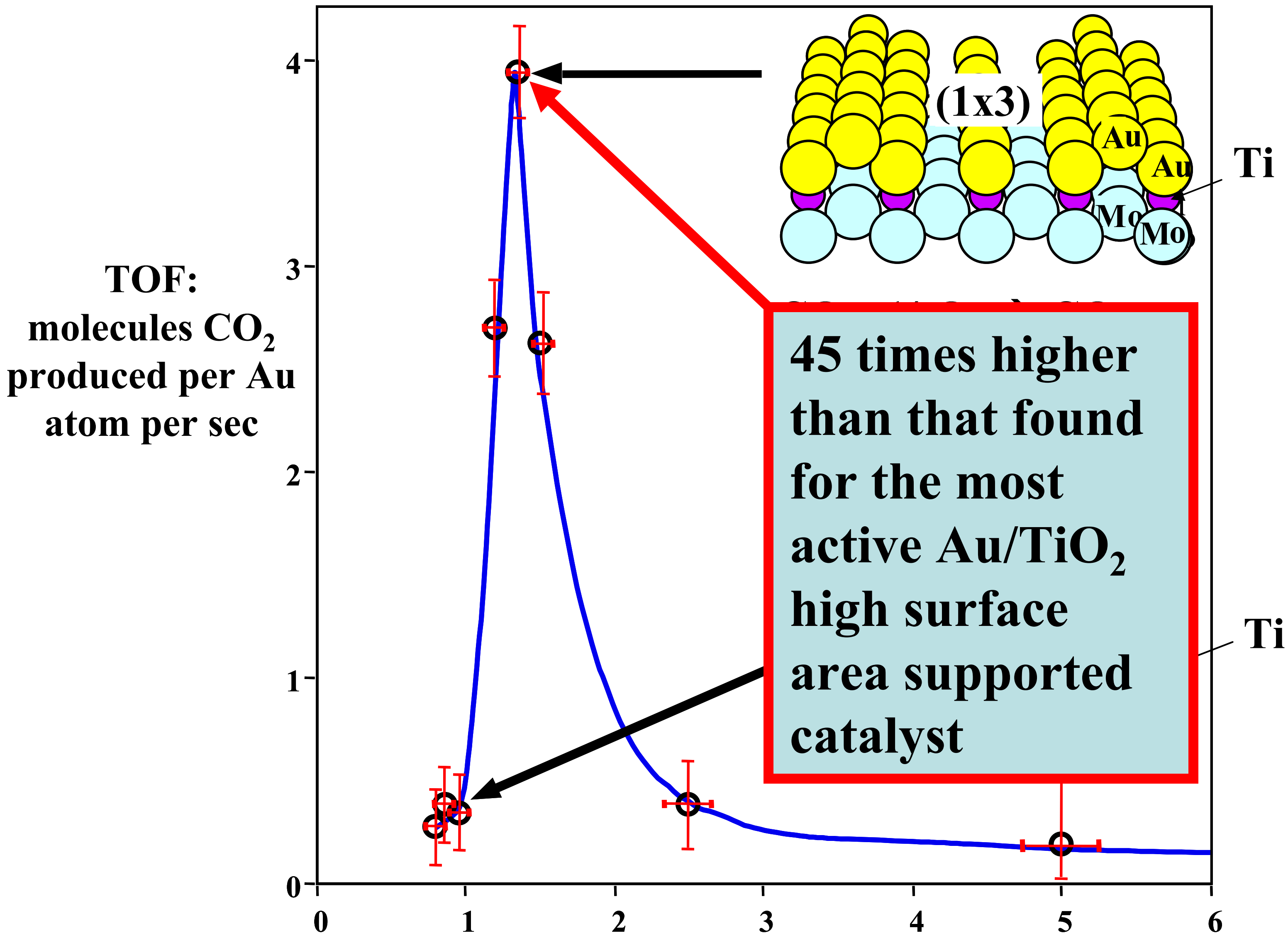
Thin oxide film: Mo(112)-(8x2)-$Ti^{3+}O_x$

Chen, et al., Science, 306, 252 (2004)



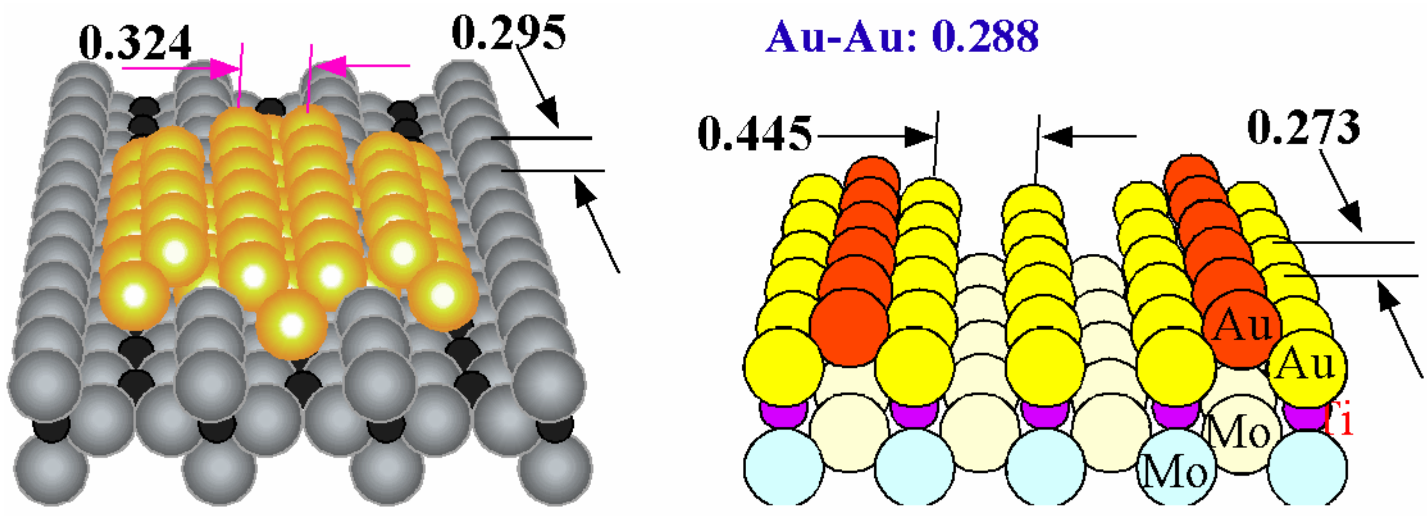


Relative Catalytic Activity of Mono- and Bi-layer Au/TiO_x



Chen, et al., Science, 306, 252 (2004)

Similarity of Au nanoparticles & the (1x3) ordered bilayer



Au(2~3 nm)/TiO_2(110)   Mo(112)-(1x3)-(Au,TiO_x)

Both form 1D-like chain for the topmost Au atoms!

Experimental and Theoretical Challenges

Structure of free and matrix isolated bare clusters, theory + measurements: insulators, semiconductors, metals.

Structure of supported clusters (thin films) and role of support in altering the free cluster structures.

Variation of chemical (catalytic), electronic, and structural properties through bulk to non-bulk transition, including 1D→2D→3D transition in thin films.

Role of point defects, steps, dislocations, low-coordination sites, etc., in defining chemical, electronic, and structural properties.

Surface versus bulk composition of multi-component clusters; deviation of surface phase diagram through bulk to non-bulk transition.

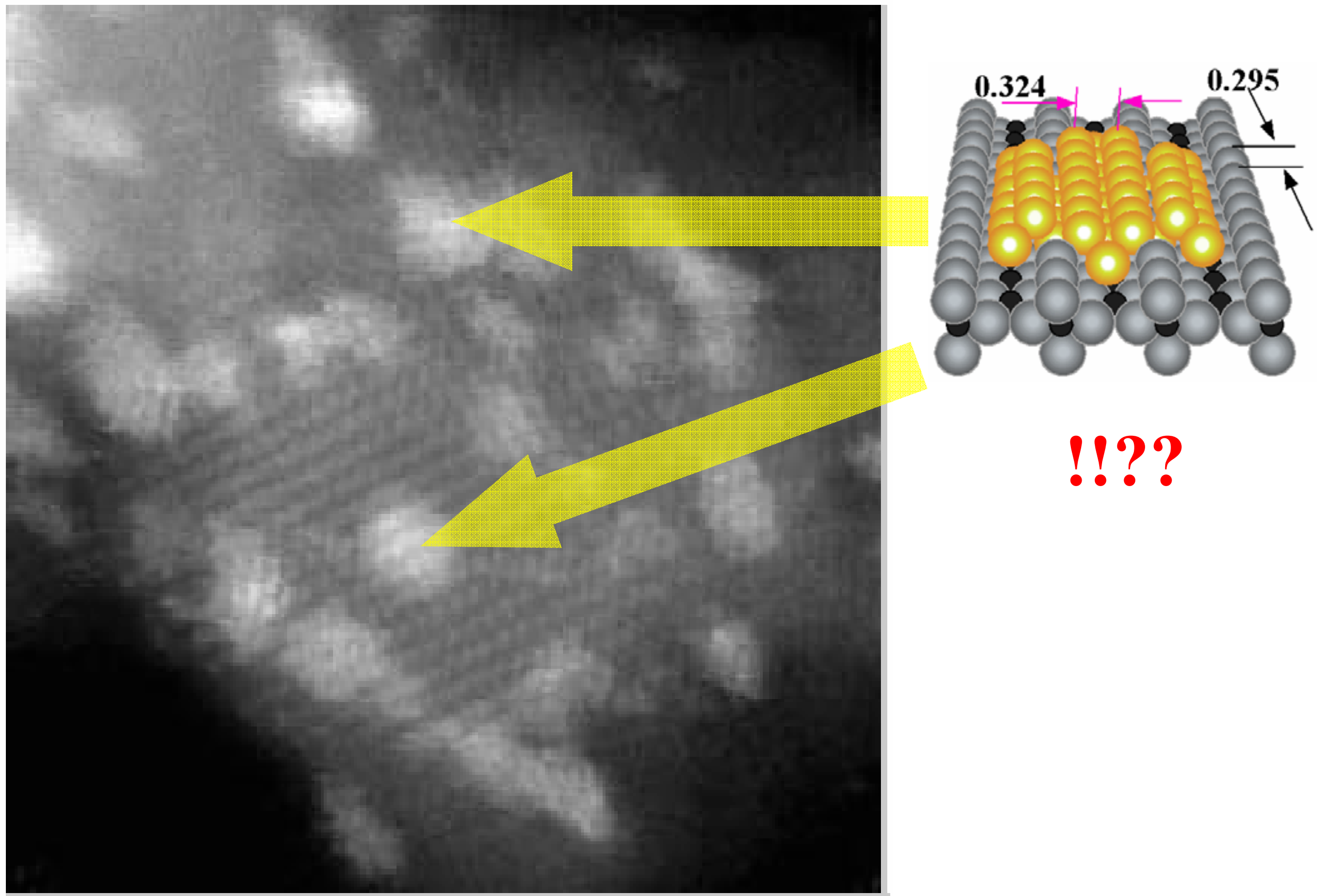
Cluster vibrational, optical, magnetic properties.

All of the above at realistic environmental conditions, i.e. operando measurements.

Tuning monodispersity and stability of limited dimensional materials

STEM: Au/TiO_2

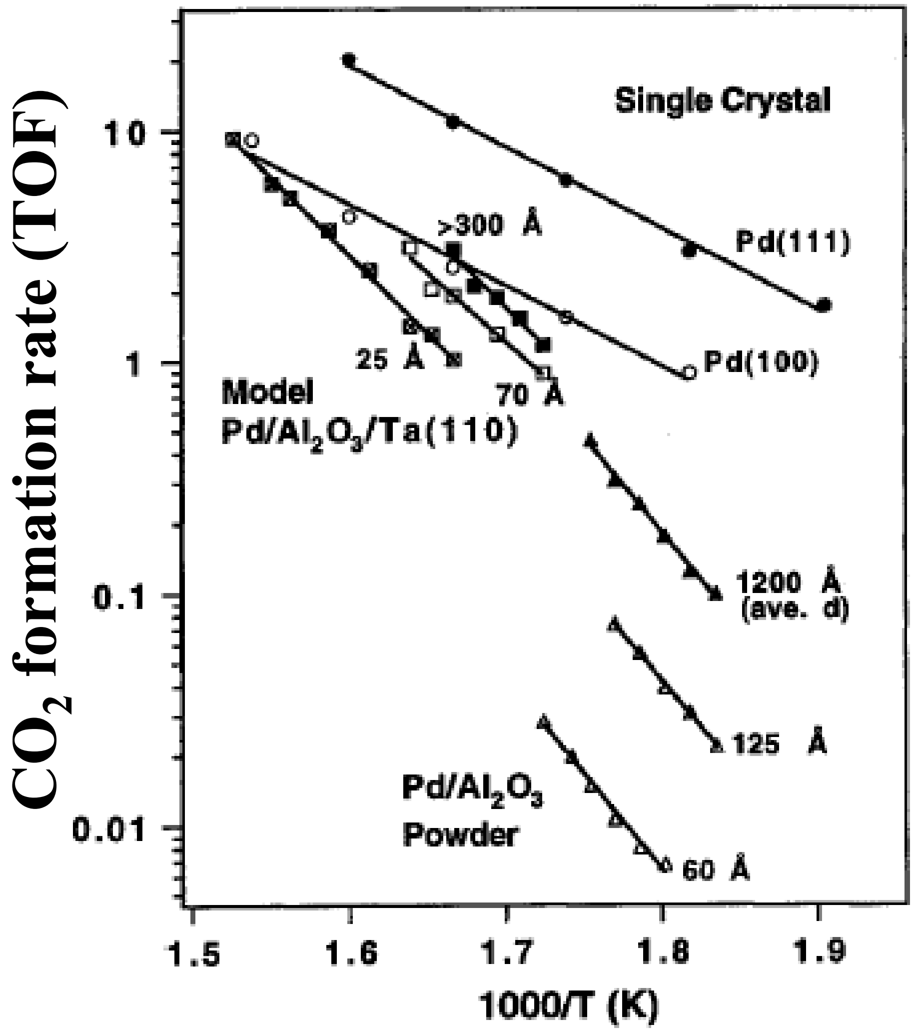
From S. Pennycook, S. Overbury, et al.



(a)

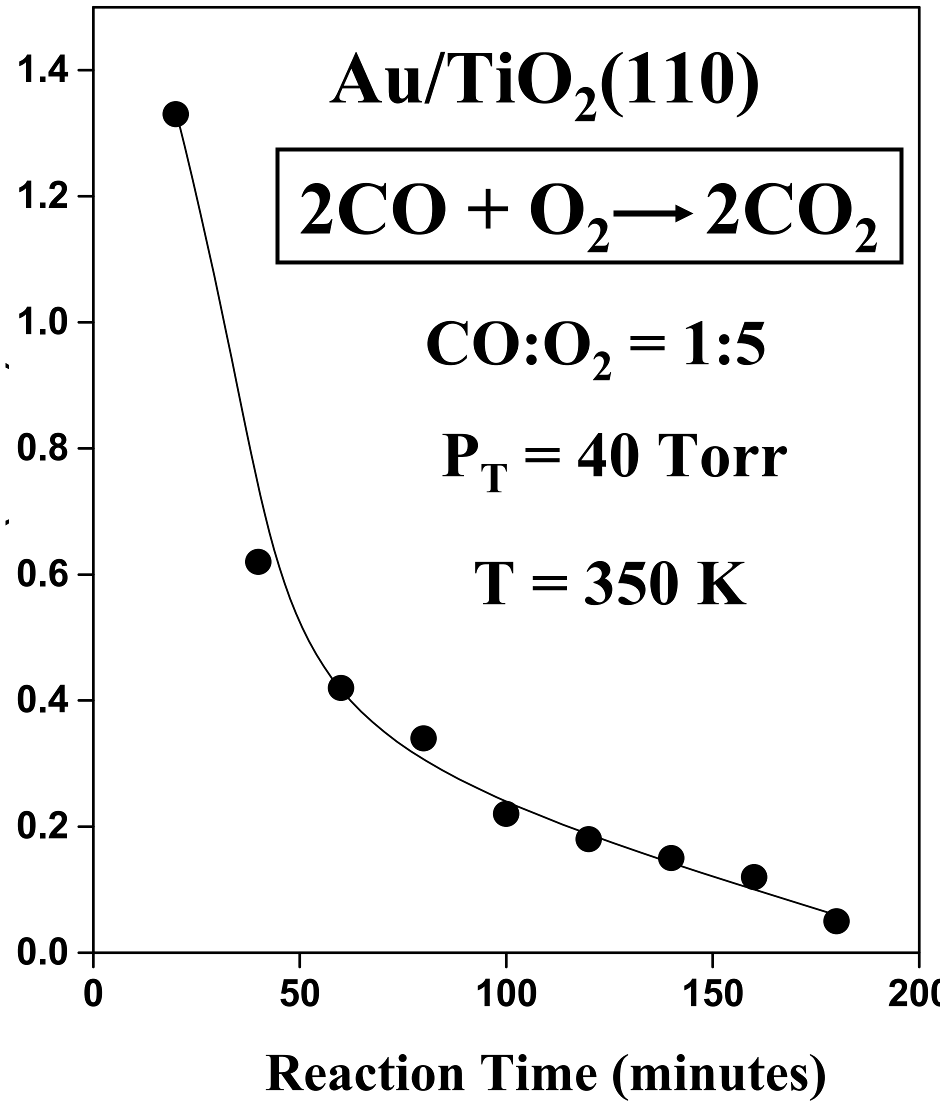
2 nm

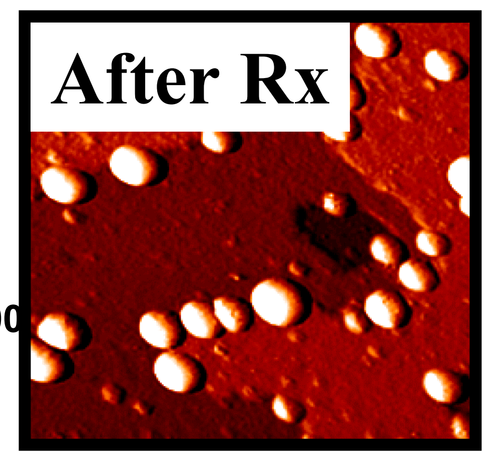
$CO + NO \rightarrow CO_2 + N_2$ over various Pd catalysts



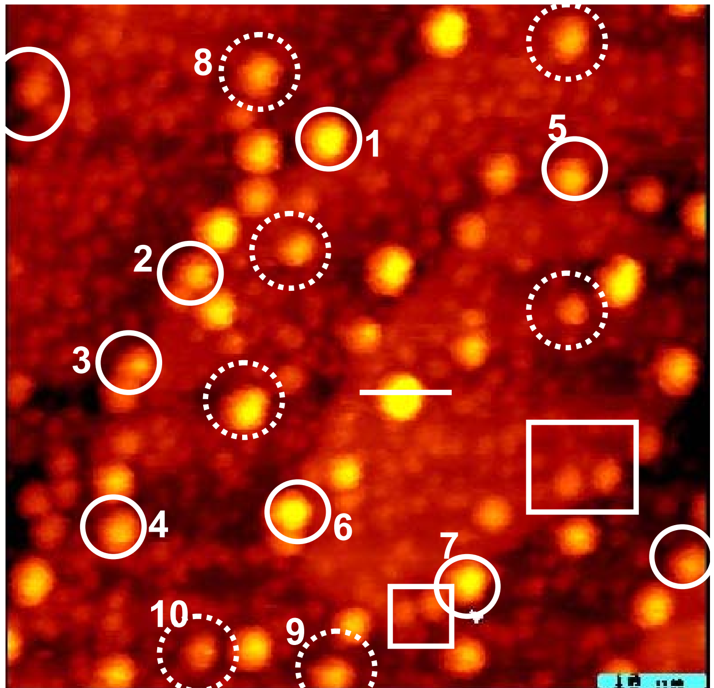
A. K. Santra, D. W. Goodman, J. Phys. C 14 (2002) R31.

CO Oxidation Over Au/TiO_2 as a Function of Reaction Time



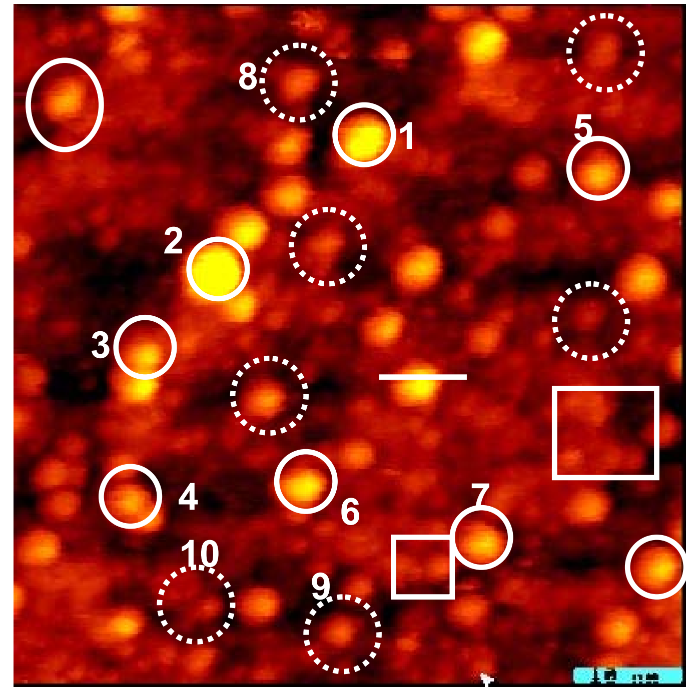


STM: 0.5 MLE Au/TiO_2 (110), CO/O_2 (1:1), 4.2 Torr @ 420K

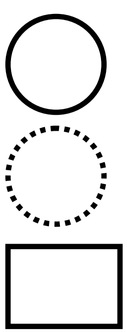


630A x 630A

+ 1 hour



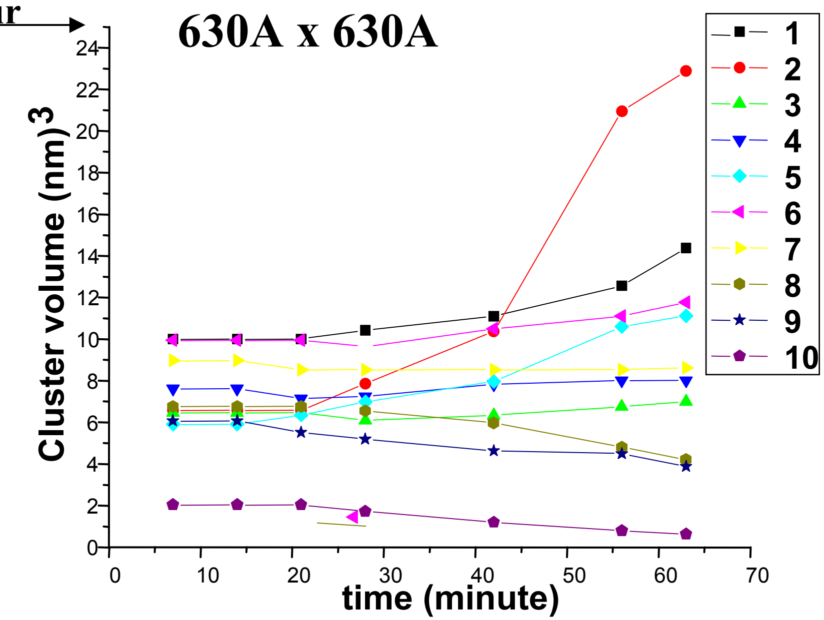
630A x 630A



Cluster size increase

Cluster size decrease

Cluster disappears

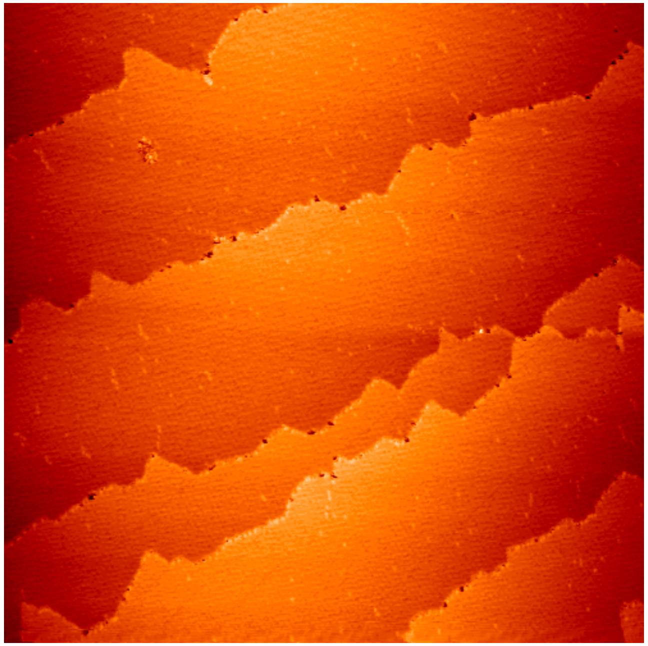


Yang and Goodman, 2004

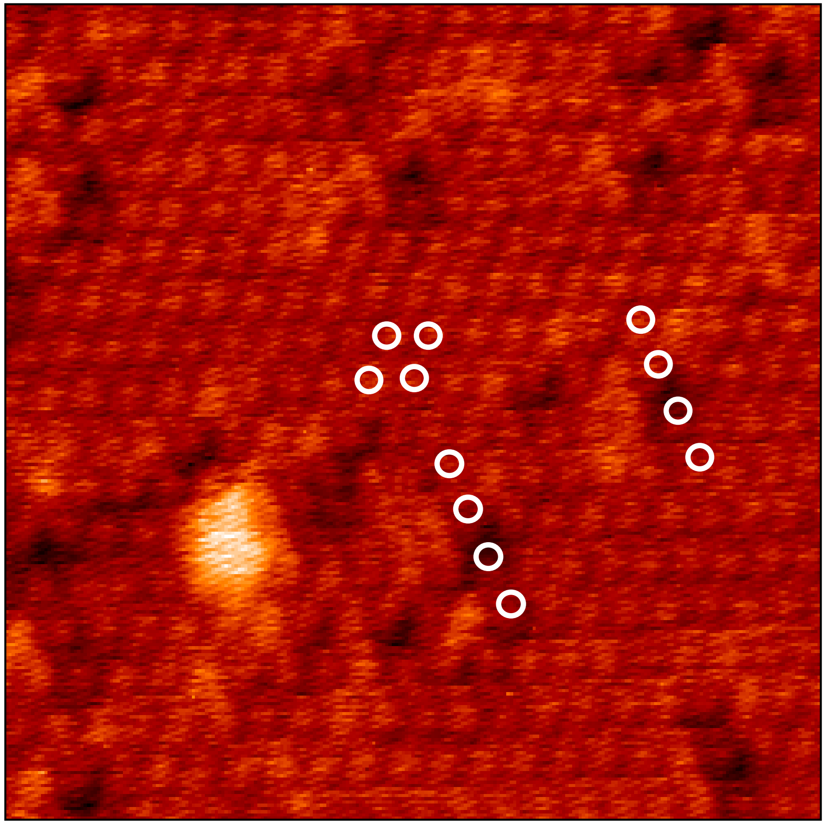
Preparation & Characterization of Ultra-thin, Well-ordered SiO_2/Mo(112)

Schroeder, Adelt, Richter, Naschitzki, Baumer, and Freund. *Surf. Rev. Lett.* 7 (2000)

1. Si @RT
2. O_2 @ 800K
3. Anneal @1200 K



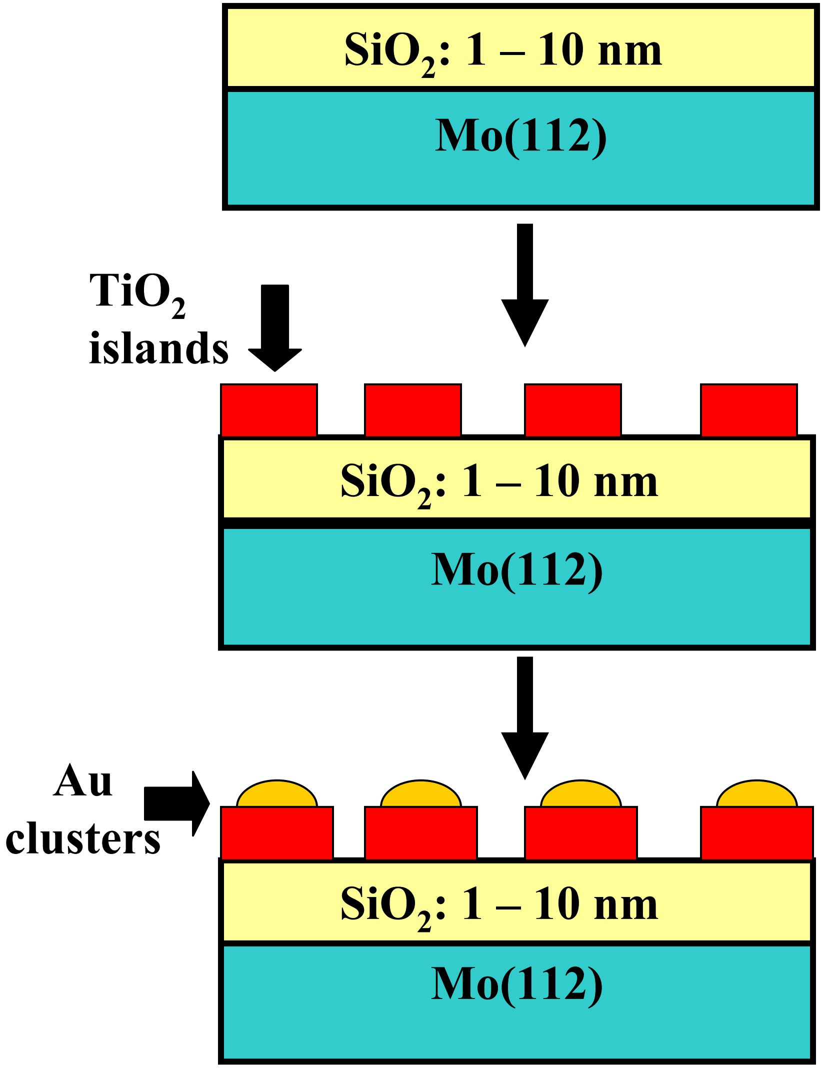
400 nm



10 nm

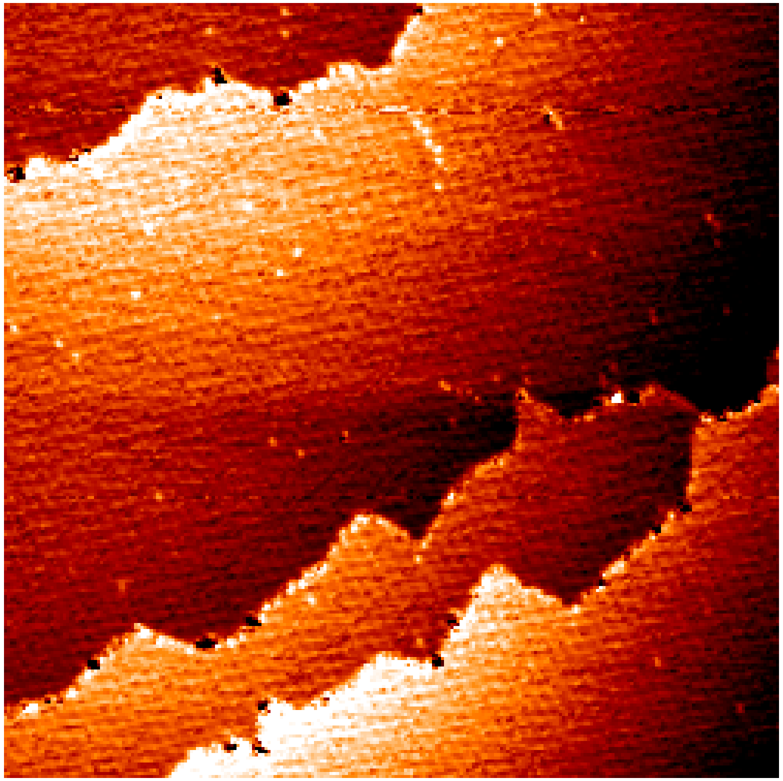
0.7 nm thick, sharp hexagonal LEED with a band gap ~8.9 eV (STS)

Strategies for a Sinter-Resistant Support: TiO_2 Dispersed onto SiO_2



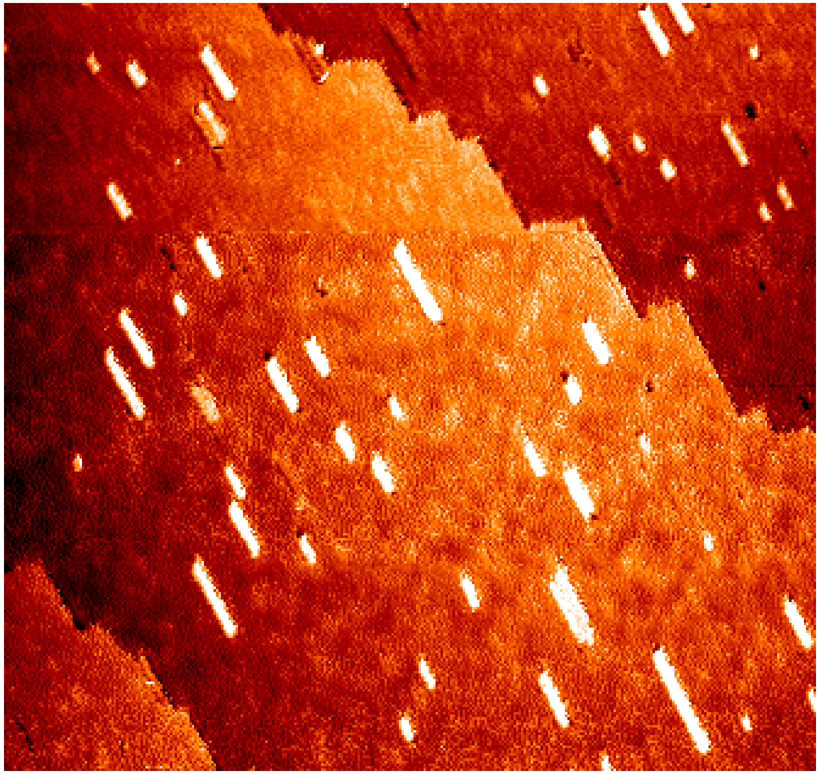
TiO_x Islands Dispersed on SiO_2

1.0 ML SiO_2/Mo(112)



100 nm

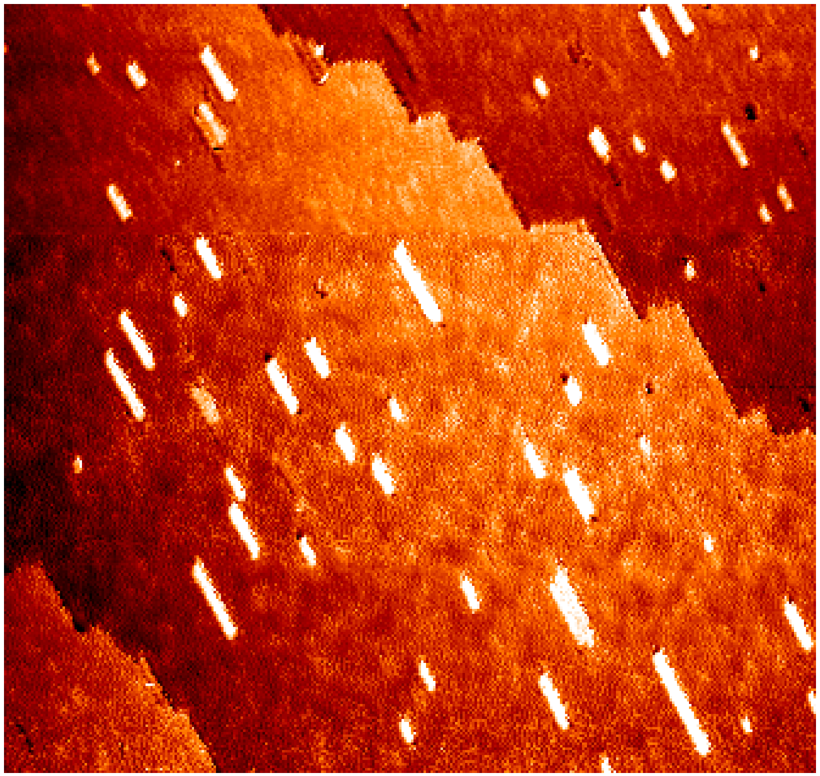
0.1 ML TiO_x/SiO_2/Mo(112)



100 nm

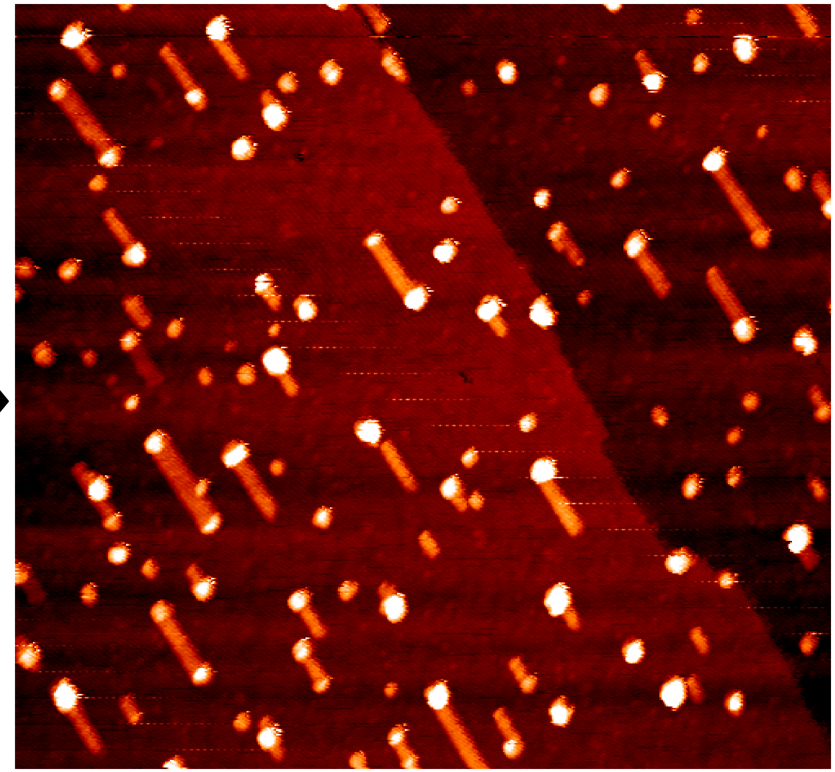
Au Particles Deposited onto TiO_x Islands Dispersed on SiO_2

0.2 ML $TiO_x/SiO_2/Mo(112)$



100 nm

0.4 ML $Au/TiO_x/SiO_2/Mo(112)$



100 nm

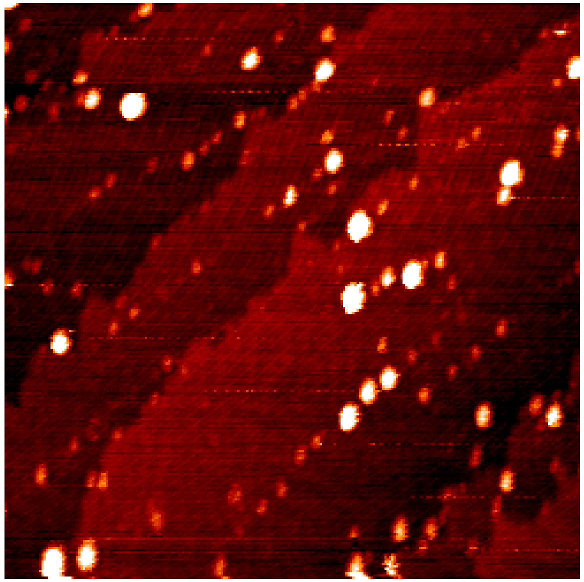
Au/SiO_2 versus $Au/TiO_x/SiO_2$: 850 K Anneal

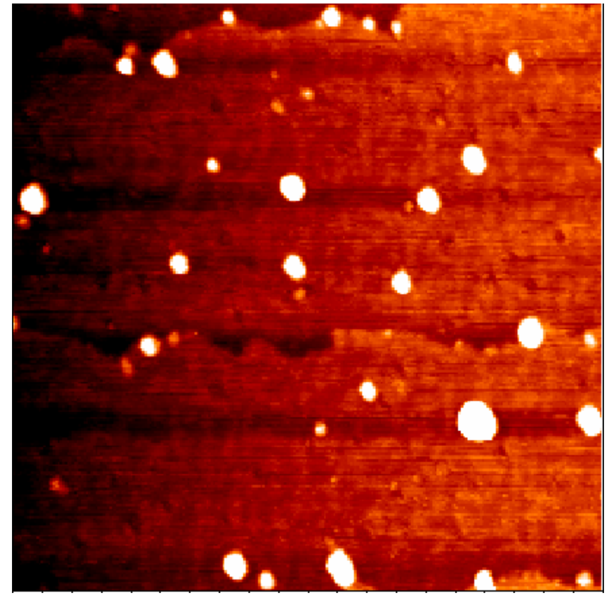
“before” **“after”**

SiO_2

+

0.4 ML Au



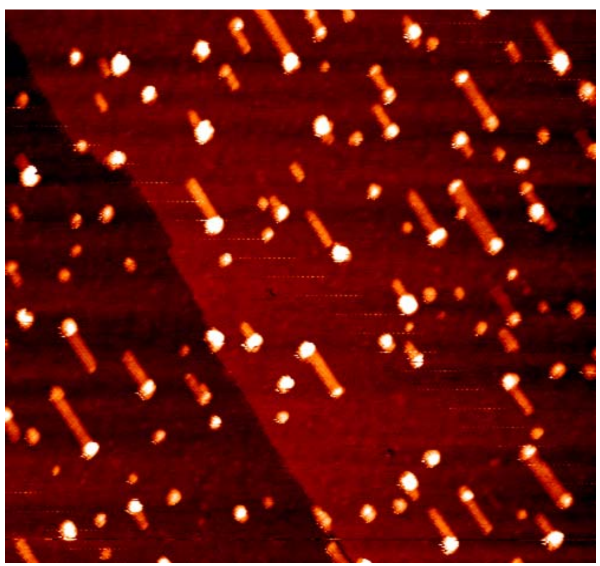


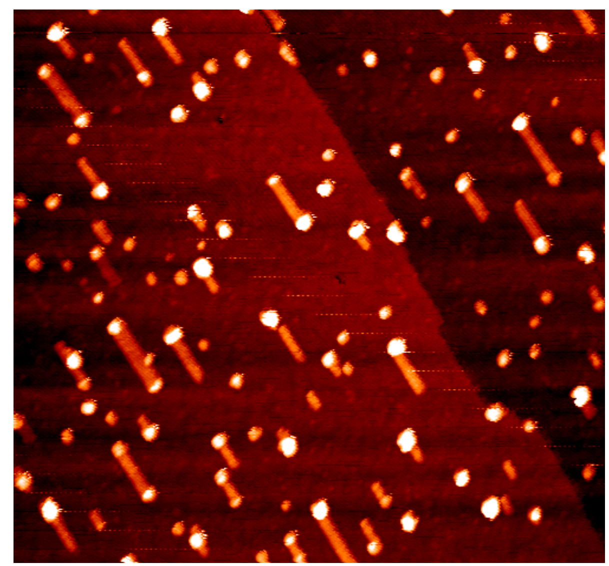
100 nm

TiO_x/SiO_2

+

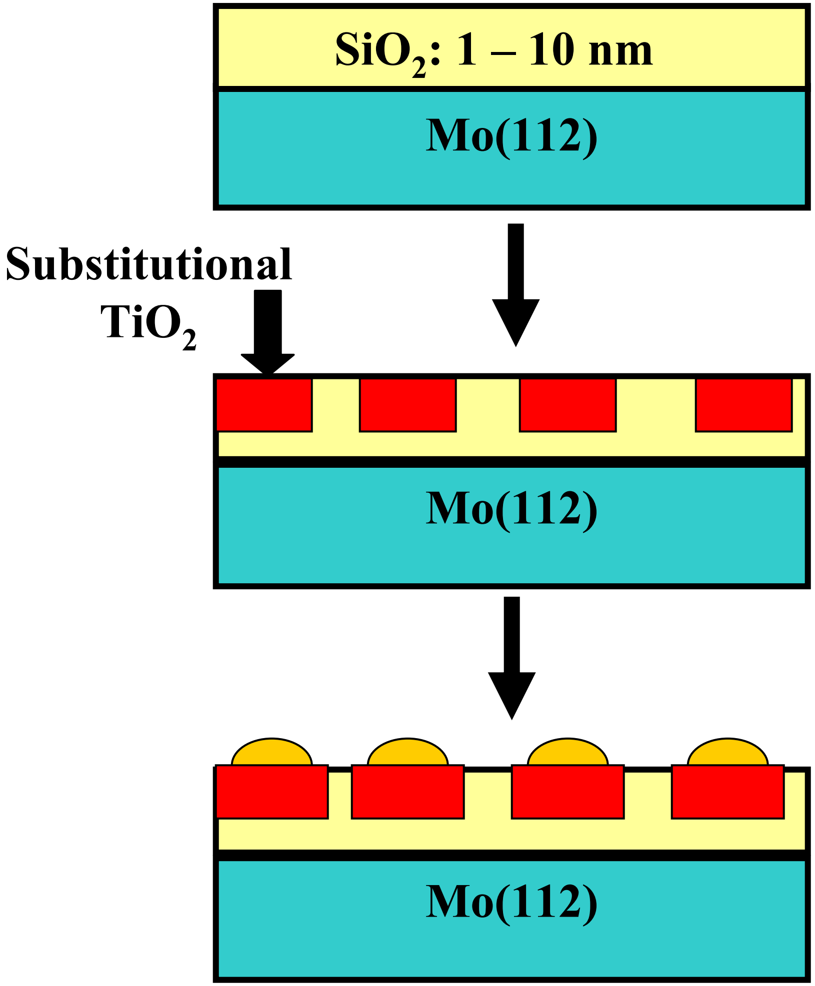
0.4 ML Au



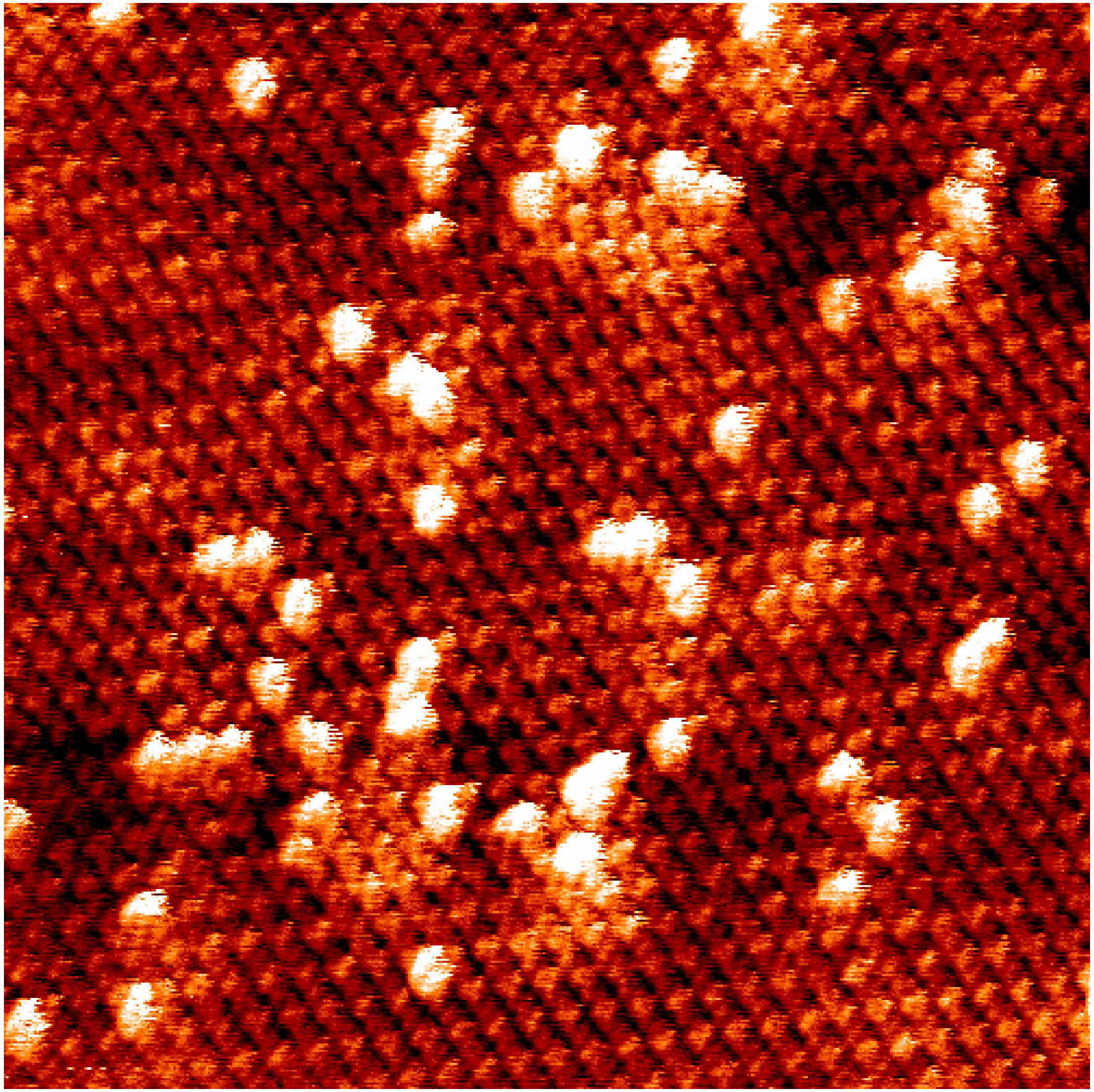


100 nm

Strategies for a Sinter-Resistant Support: TiO_2 Dispersed into SiO_2



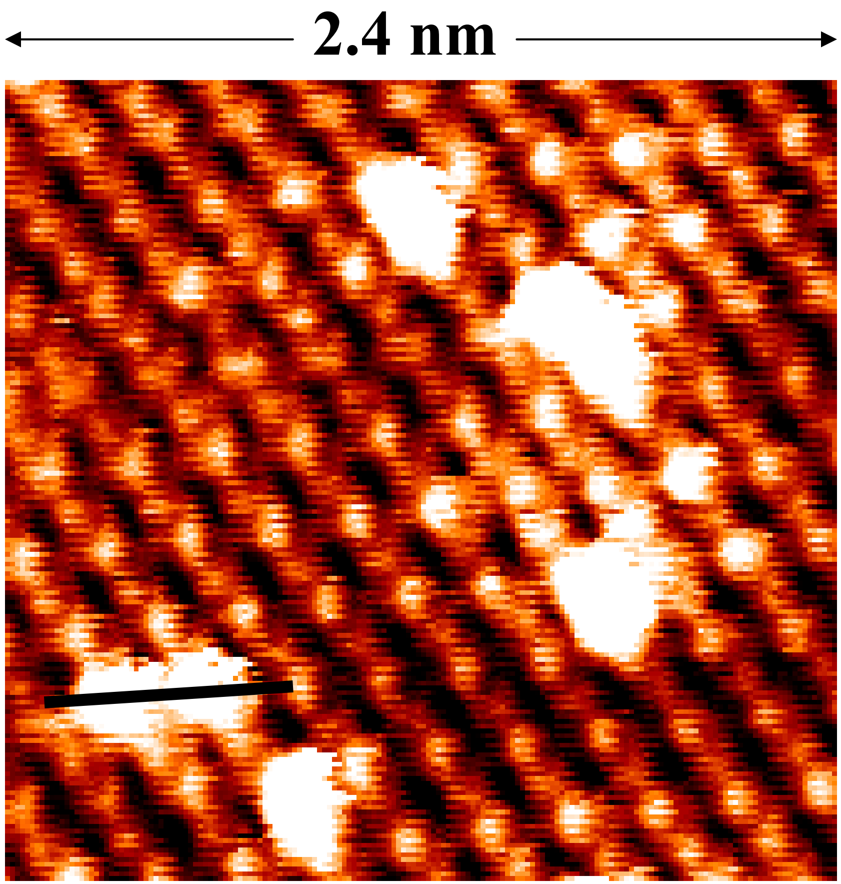
Ti Point Defects on SiO_2

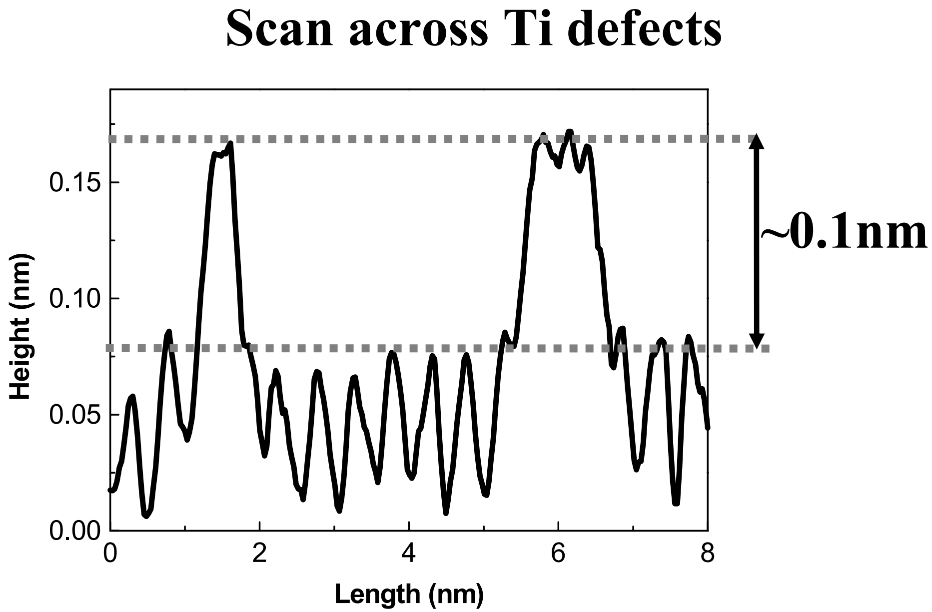


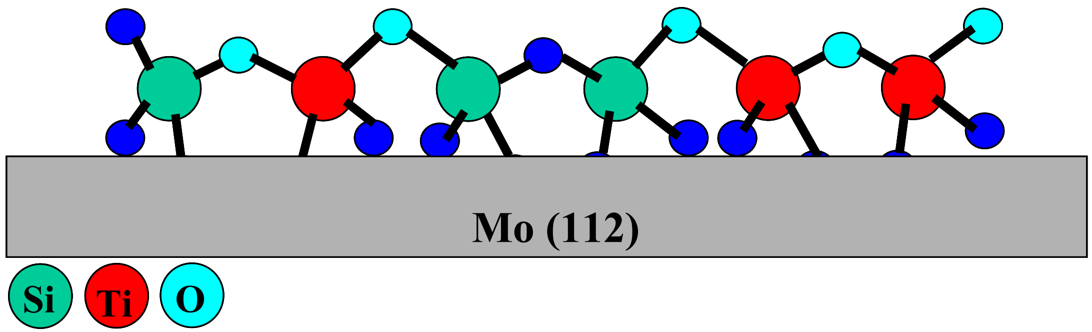
15 nm

15 nm

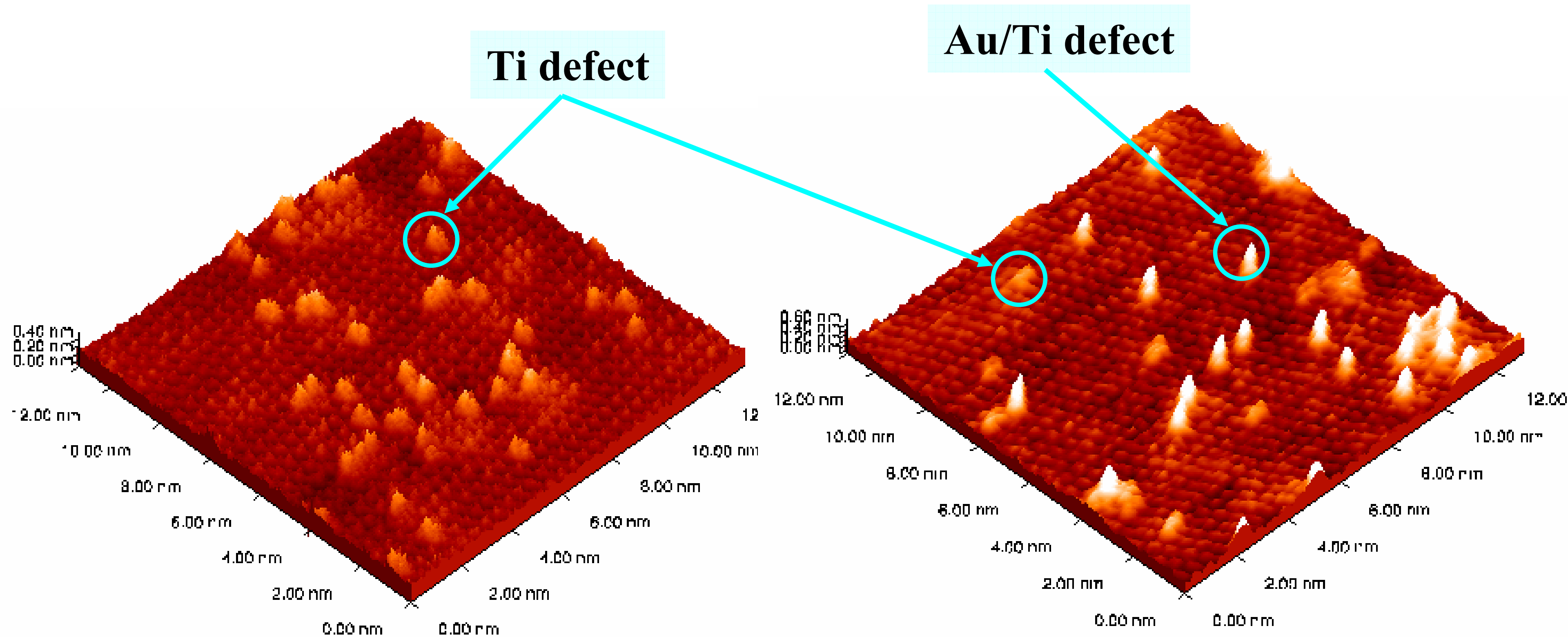
STM: TiO_x-SiO_2 Thin Film with 2% Ti







Decoration of Ti Point Defects with Gold



+ 0.04 ML Au

$Ti/SiO_2/Mo(112)$ → $Au/Ti/SiO_2/Mo(112)$