Heterogeneous Catalysis: From Imagining to Imaging a Working Surface

D. Wayne Goodman
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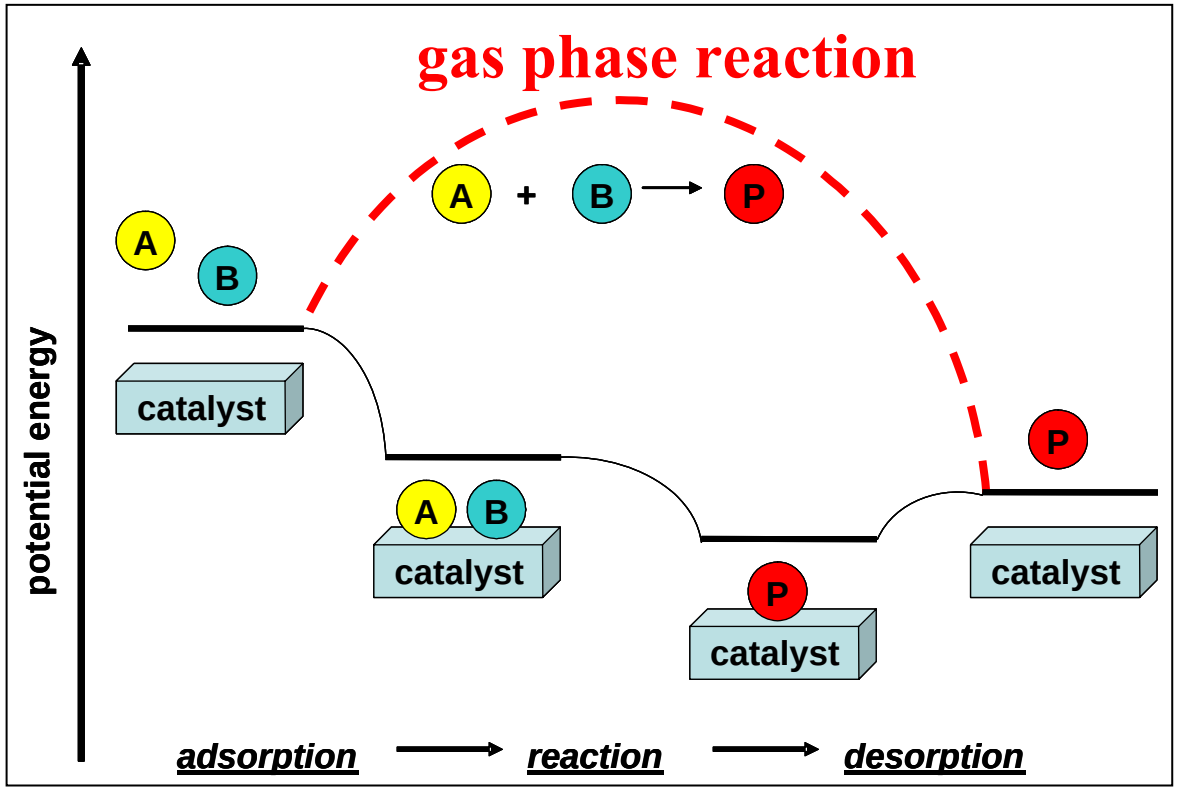
Department of Chemistry

- **Introduction to issues**
- **Studies of model catalysts with surface analytical methods: special properties of metal nanoclusters**
- **Thermal stability of metal nanoclusters**
- **Strategies for designing sinter resistant catalysts**

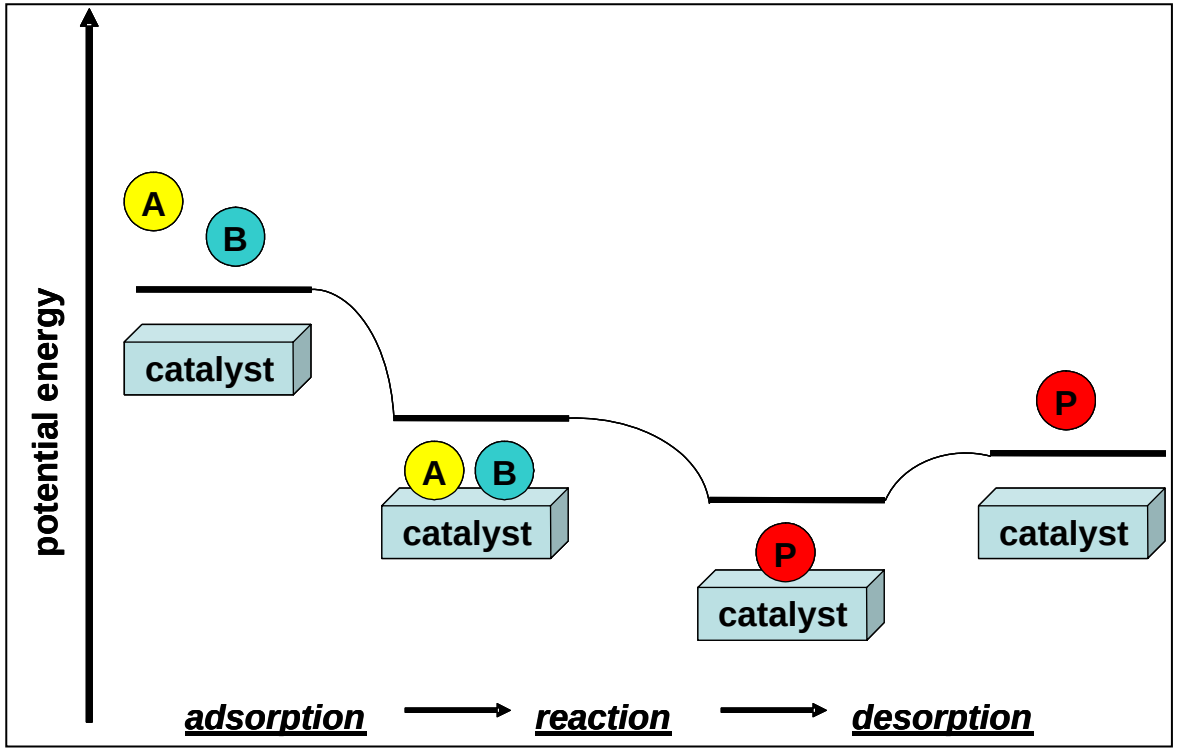
Heterogeneous Catalysis



Applications

- Production of transportation fuels (440 oil refineries)
- Production of chemicals
- Cleanup of automotive/industrial exhaust gases
- “Green” chemistry (unwanted byproducts)

Heterogeneous Catalysis



Applications

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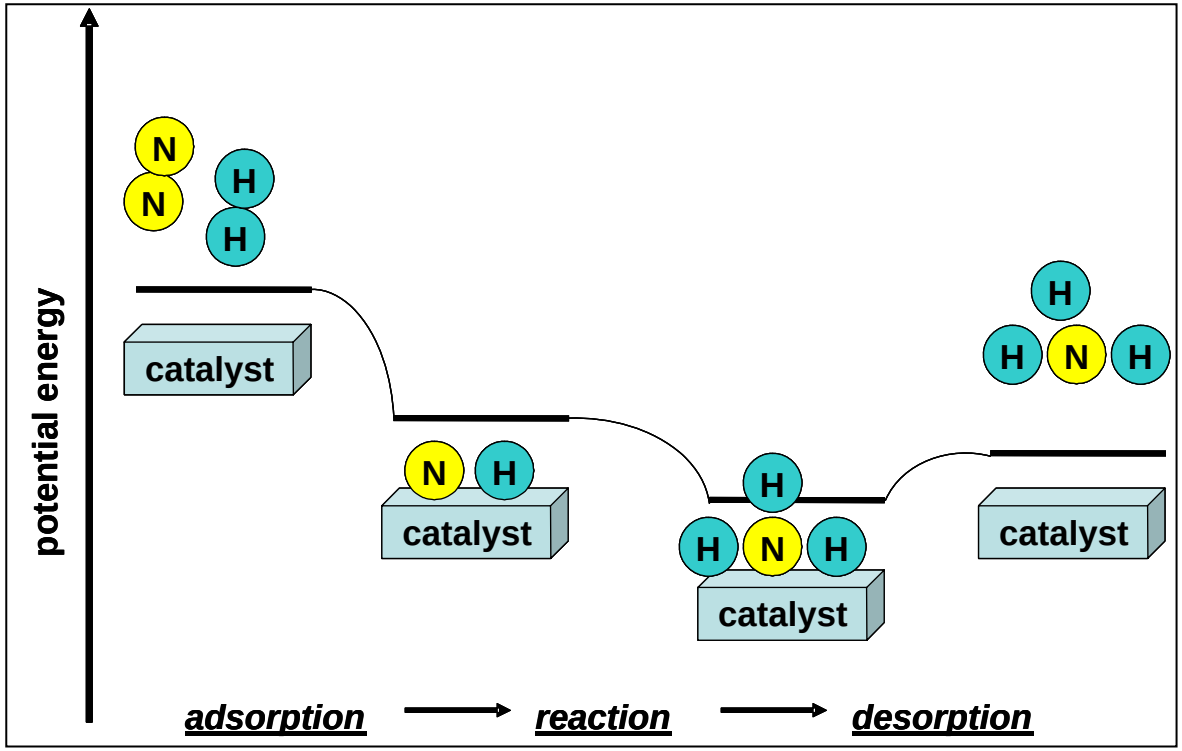
Ammonia Synthesis



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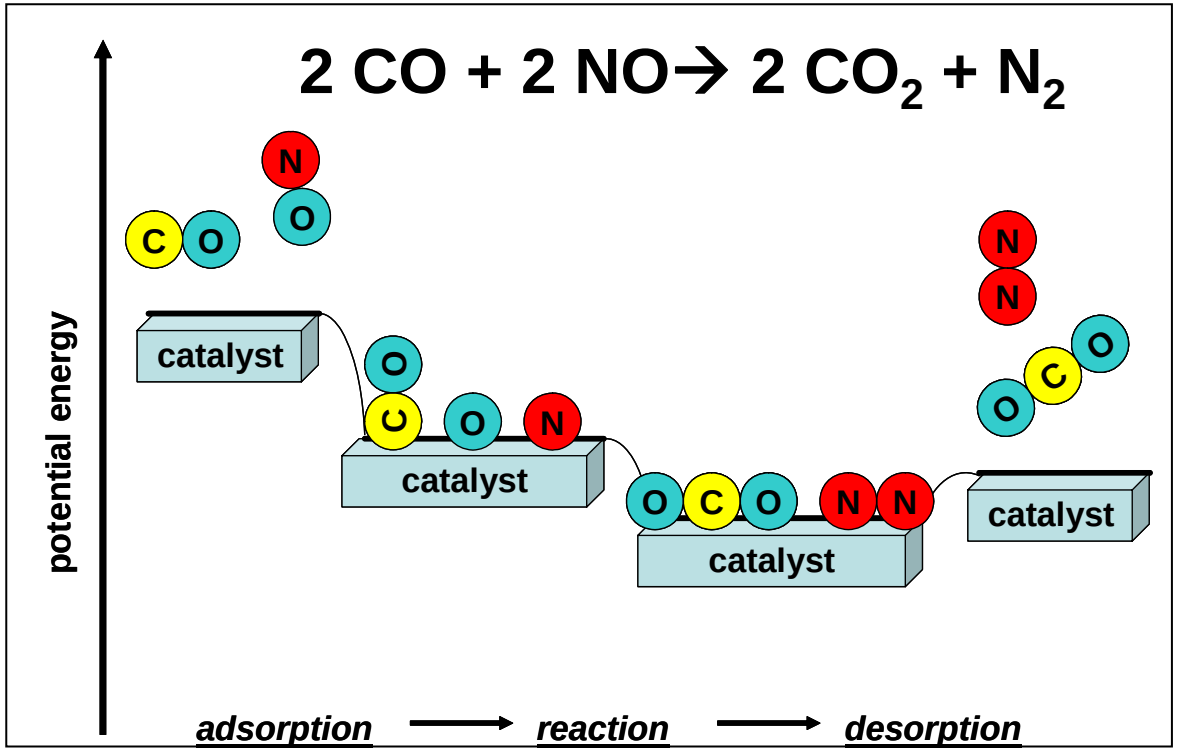
Carbon Monoxide and Nitric Oxide



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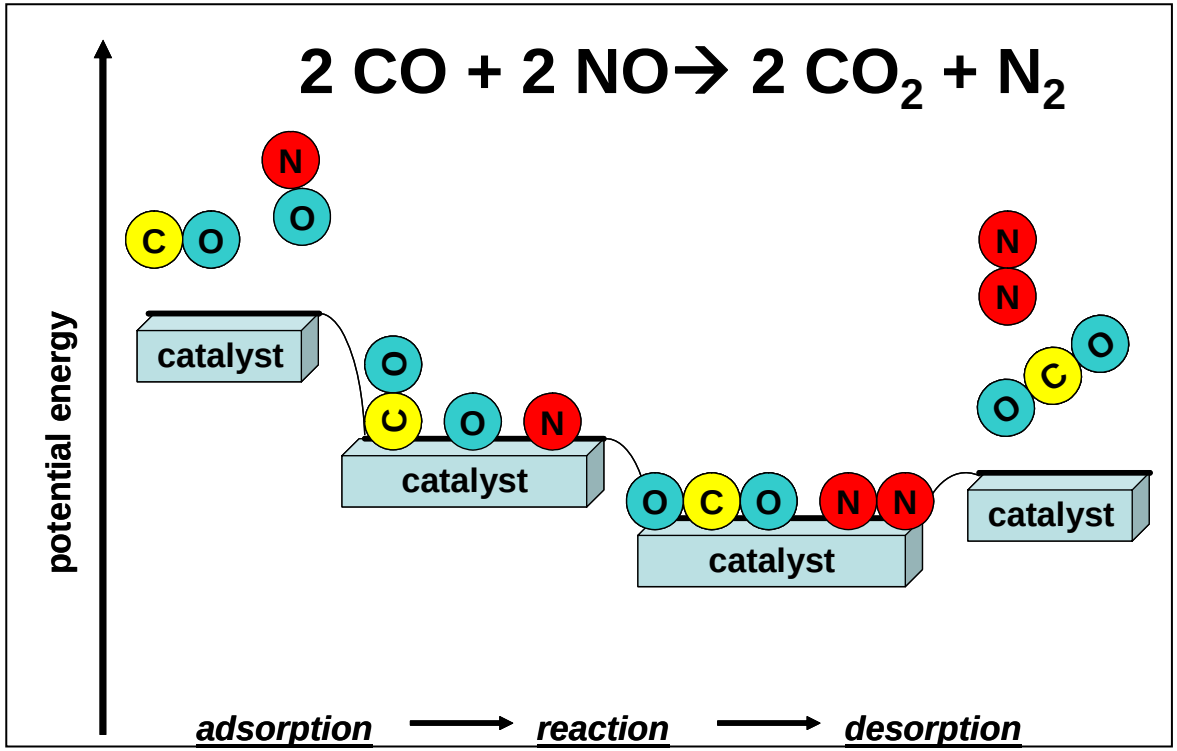


Applications

- Production of transportation fuels (440 oil refineries)
- Production of chemicals
- Cleanup of automotive/industrial exhaust gases
- "Green" chemistry (eliminate unwanted byproducts)

“Green” Chemistry with Catalysts

Example: ethylene to ethylene epoxide

$$C_2H_4 + \frac{1}{2} O_2 \rightarrow C_2H_4O$$

Old non-catalytic route (epichlorohydrine process):

Step 1: $Cl_2 + NaOH \rightarrow HOCl + NaCl$
Step 2: $C_2H_4 + HOCl \rightarrow CH_2Cl\text{-}CH_2OH$
Step 3: $CH_2Cl\text{-}CH_2OH + 1/2Ca(OH)_2 \rightarrow \frac{1}{2} CaCl_2 + C_2H_4O + H_2O$

Total: $Cl_2 + NaOH + 1/2\ Ca(OH)_2 + C_2H_4 \rightarrow C_2H_4O + 1/2\ CaCl_2 + NaCl + H_2O$

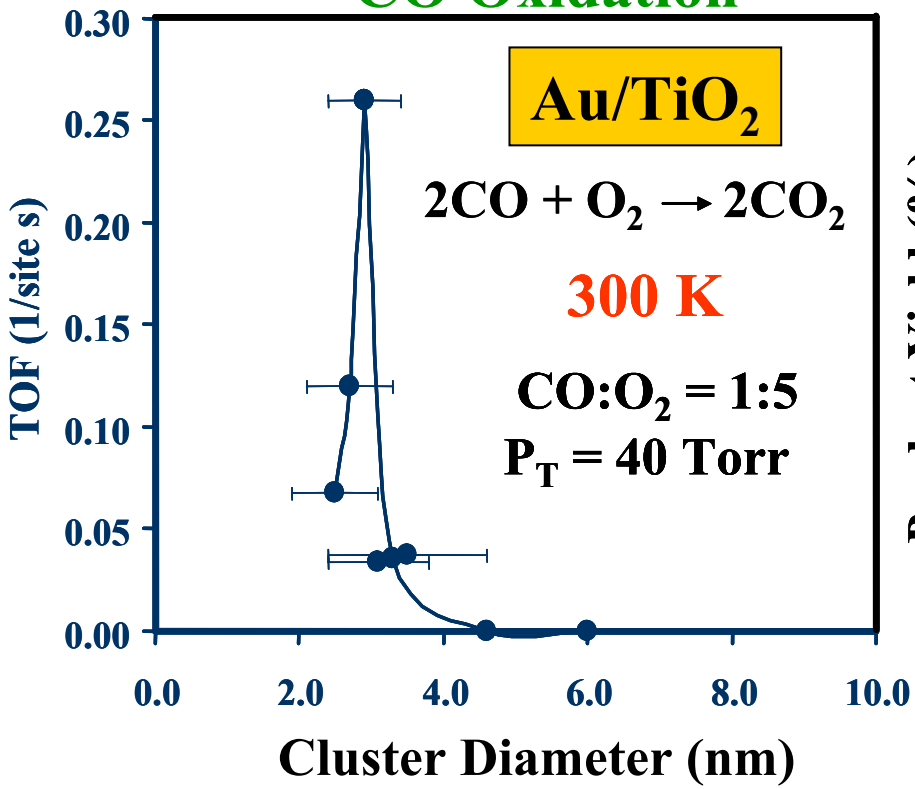
Catalytic route:

$$C_2H_4 + 1/2O_2 \xrightarrow{\text{Cl promoted Ag catalyst}} C_2H_4O$$

$$C_3H_6 + \frac{1}{2} O_2 \not\rightarrow C_3H_6O$$

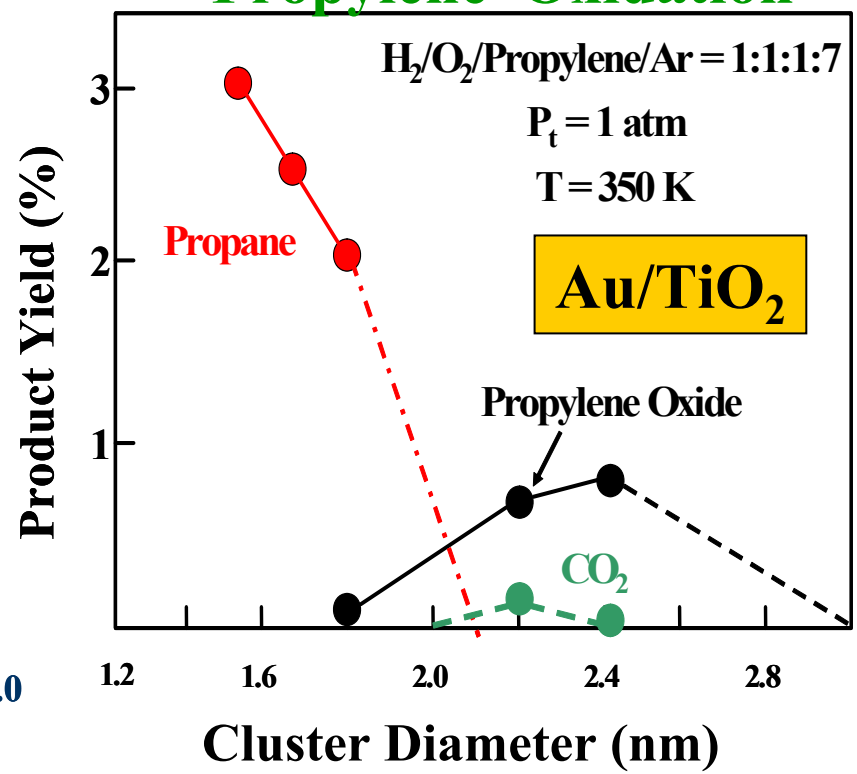
Unique Catalytic Activity of Nanosized Gold Particles

CO Oxidation



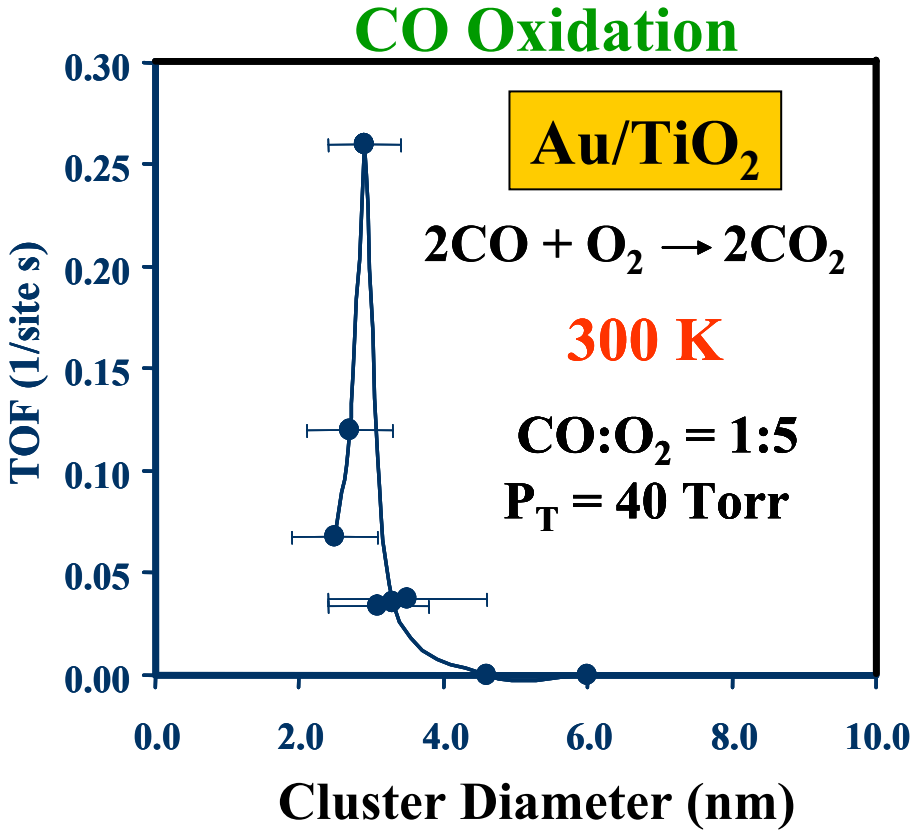
from Haruta, et al., Catalysis Letters (1997)

Propylene Oxidation

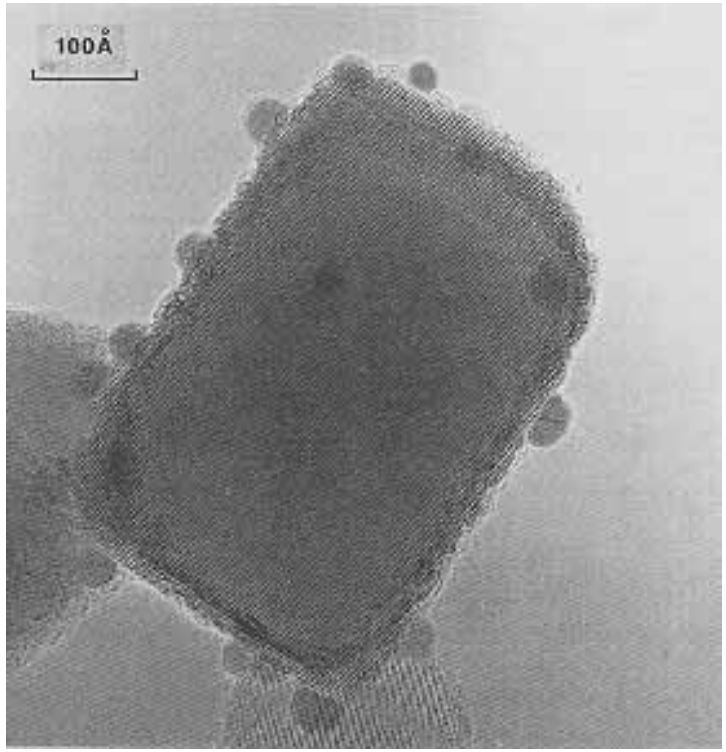


from Haruta, et al., Shokubai, Catalysts and Catalysis (1995)

Unique Catalytic Activity of Nanosized Gold Particles



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

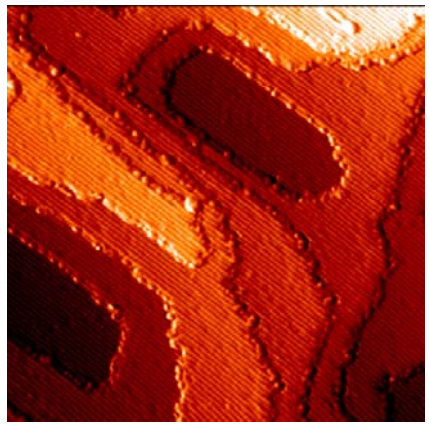


TEM Image of Gold Supported on Titania (from M. Date, ONRI)

Model Oxide-Supported Metal Catalysts

e.g.
TiO_2

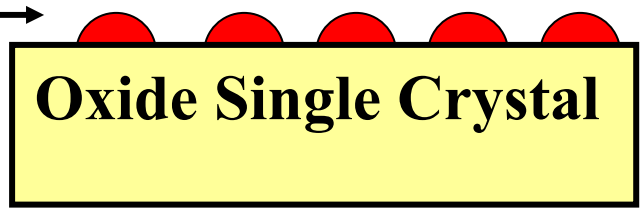
Oxide Single Crystal

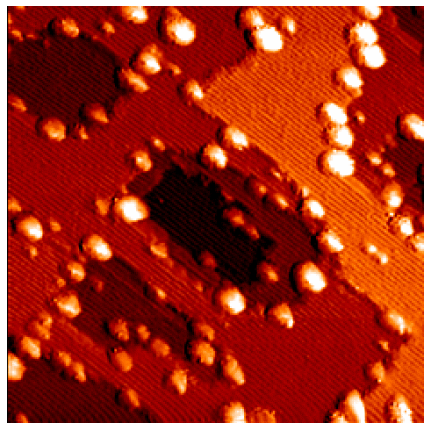


50 nm

$TiO_2(110)$

Metal Clusters
1.0-50 nm

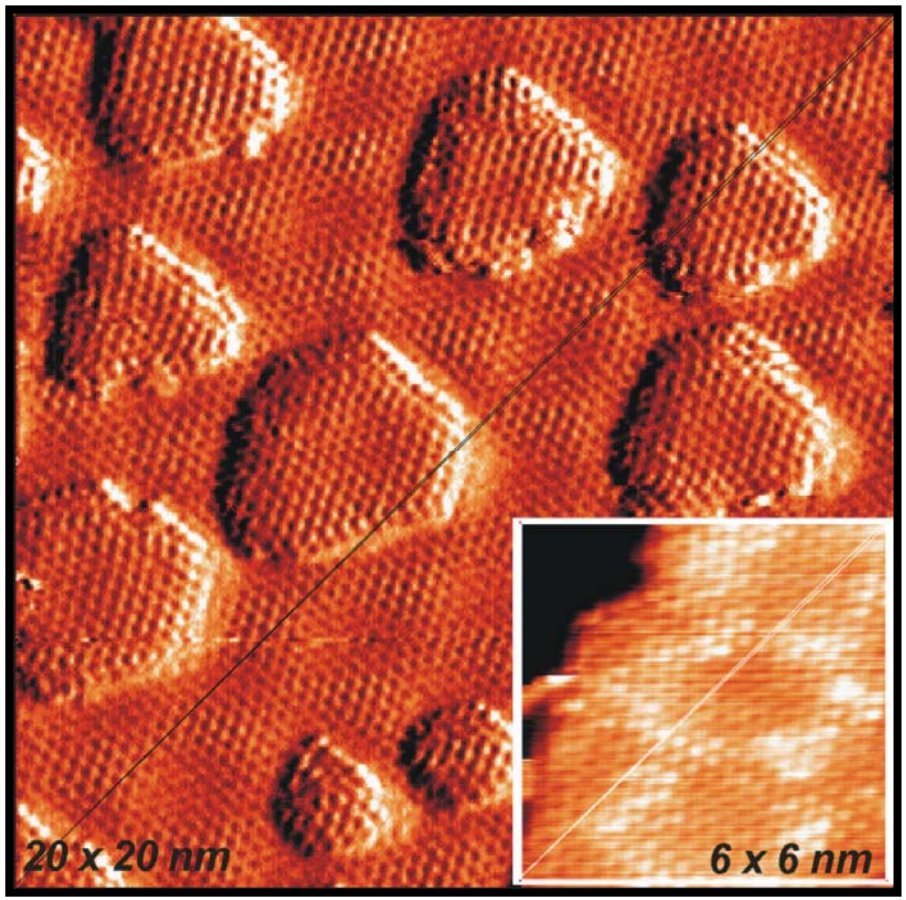


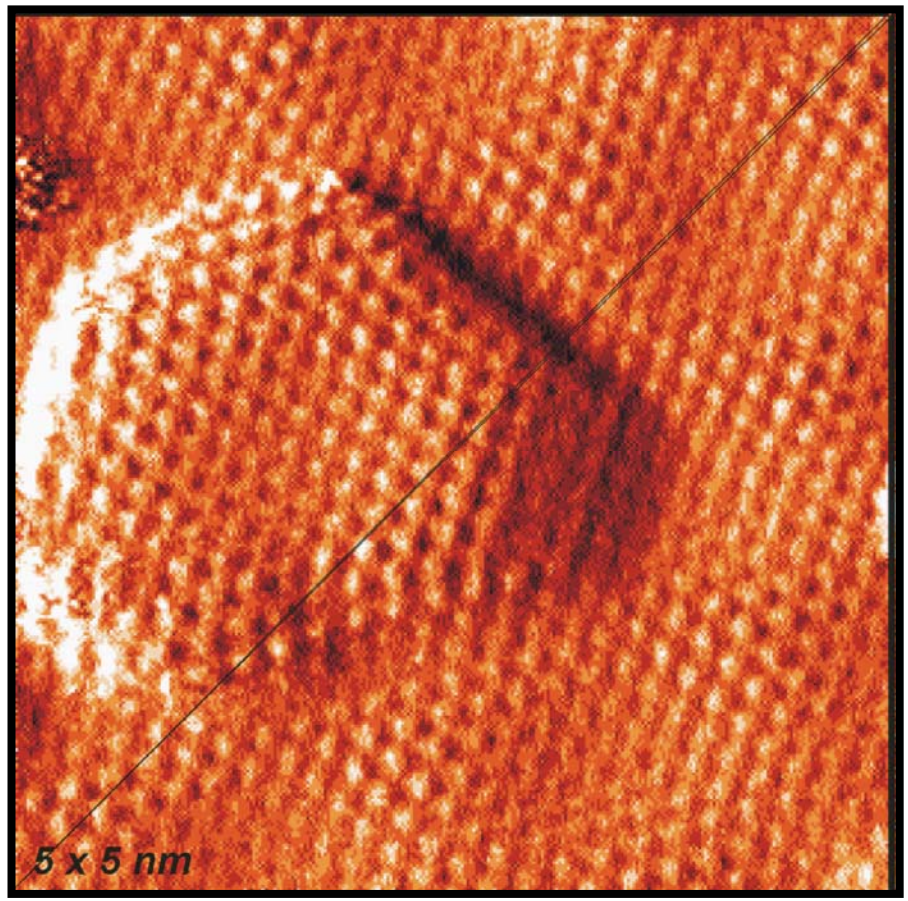


50 nm

$TiO_2(110)$
+
0.25 Au

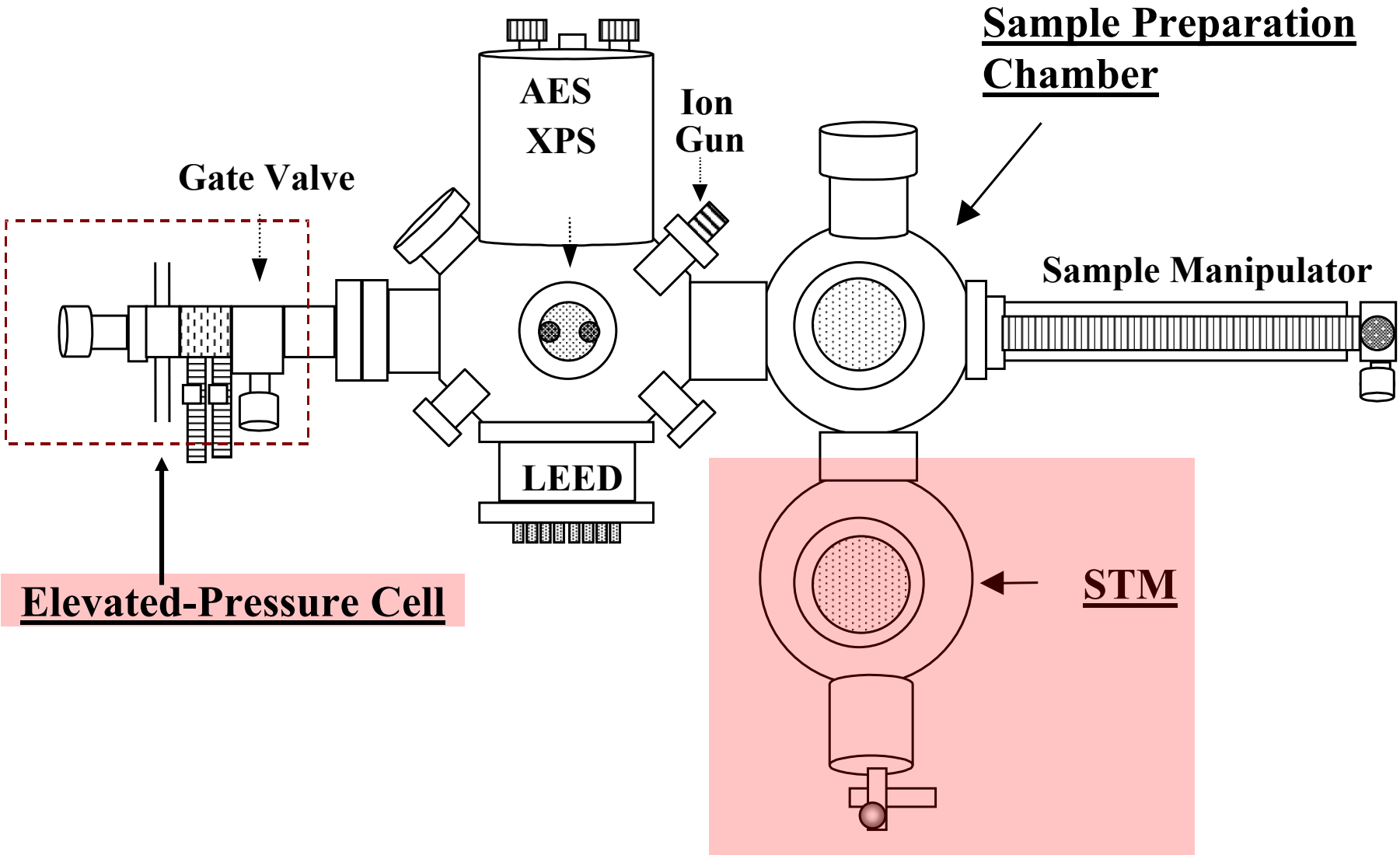
Pd on FeO(111)/Pt(111)



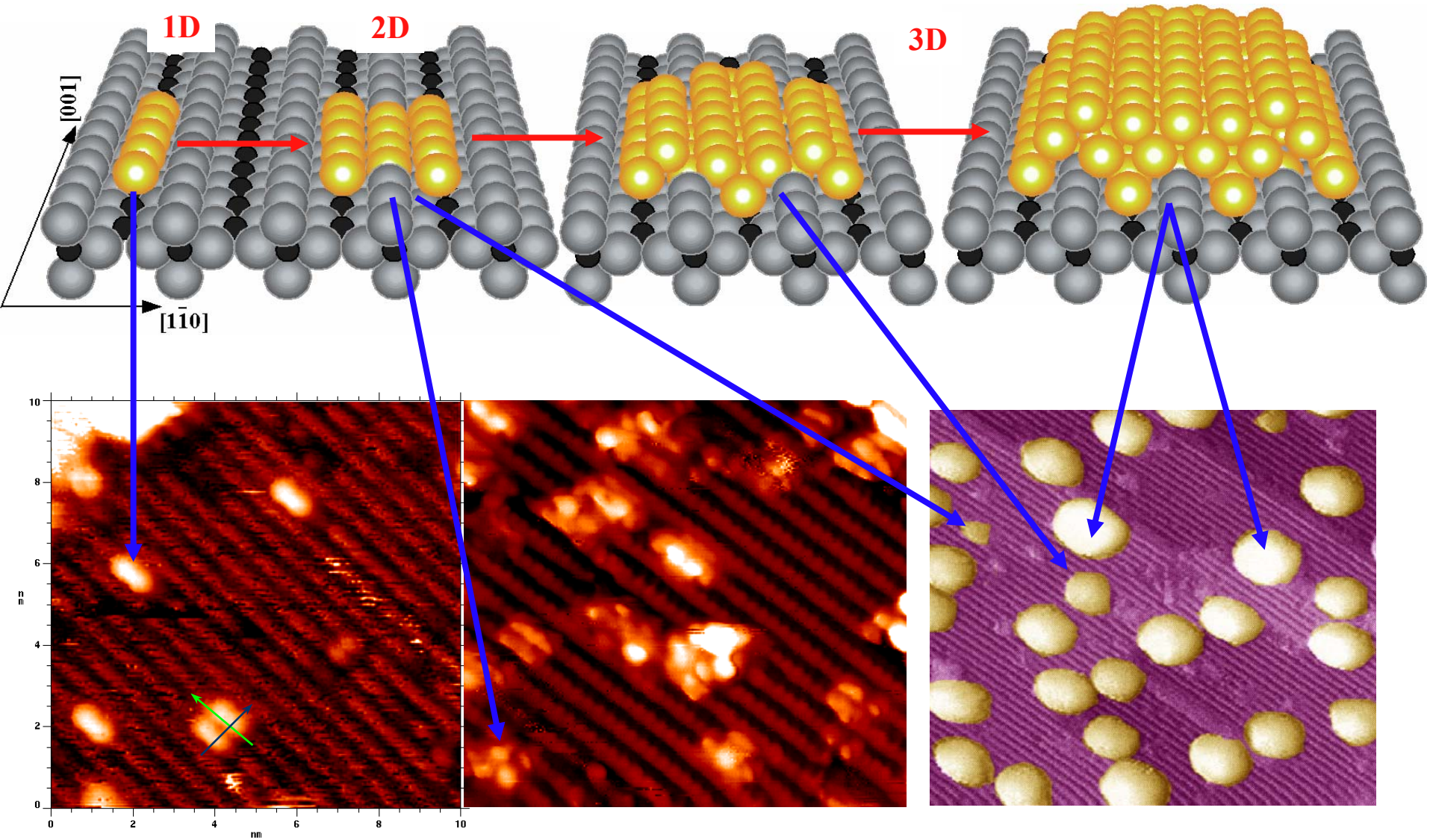


S. Shaikhutdinov, R. Meyer, D. Lahav, M. Baeumer, T. Kluener, H.-J. Freund
Phys. Rev. Lett. (2003)

Apparatus

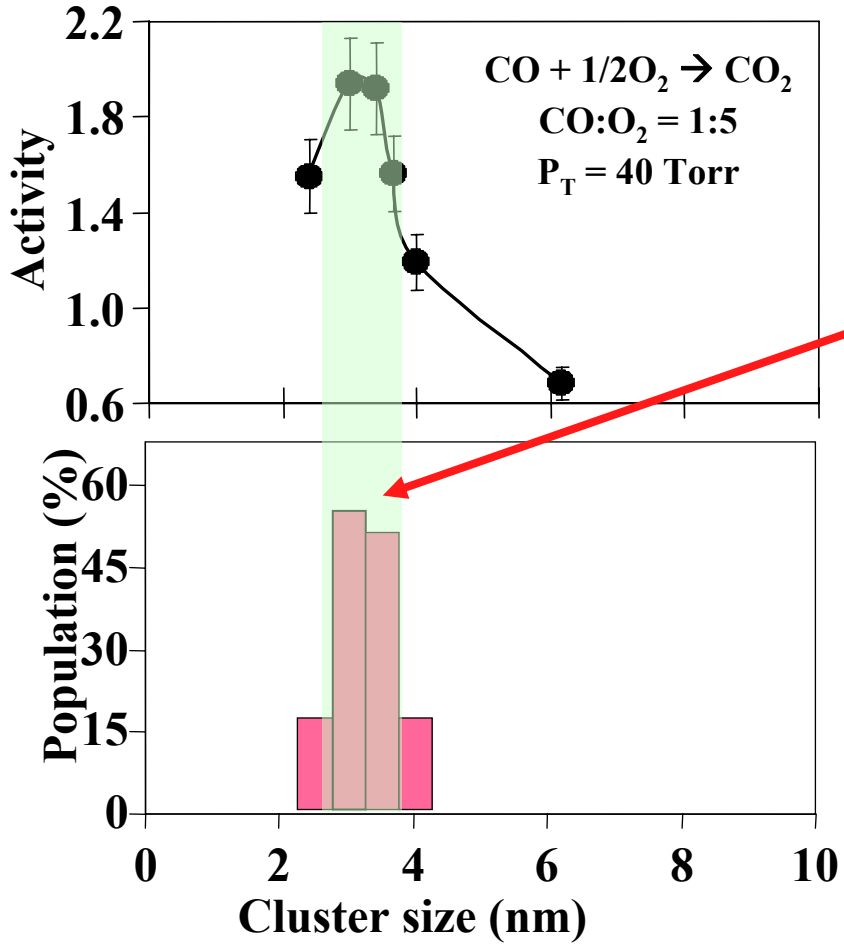

Sample Preparation Chamber
AES
XPS
Ion Gun
Gate Valve
Sample Manipulator
LEED
Elevated-Pressure Cell
STM

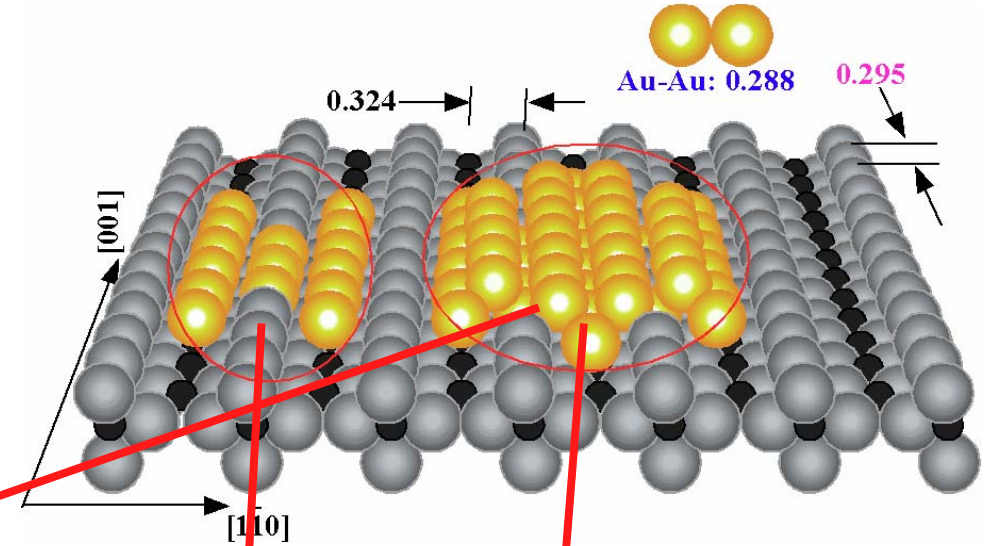
$Au/TiO_2(110)$:1D→2D→3D

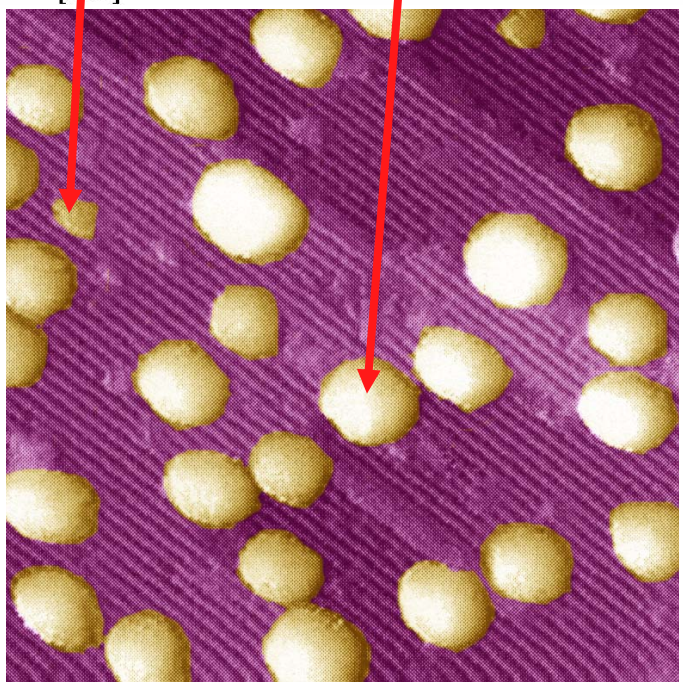


M. Valden, X. Lai, and D. W. Goodman, Science 281, 1647 (1998)

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



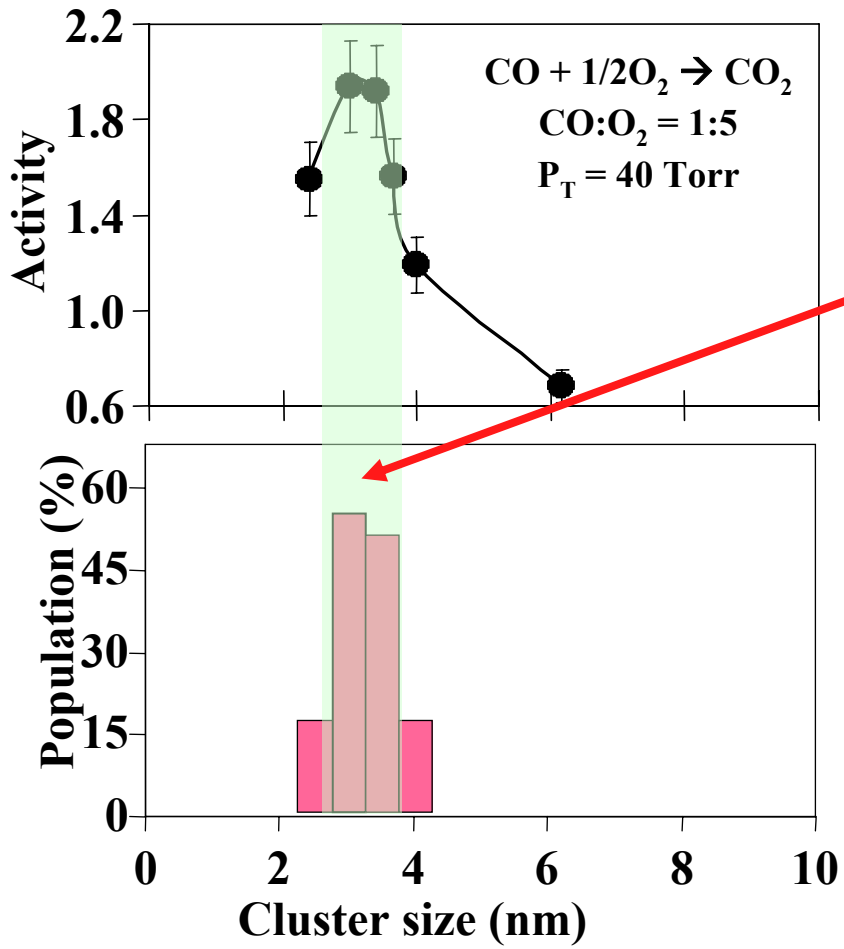


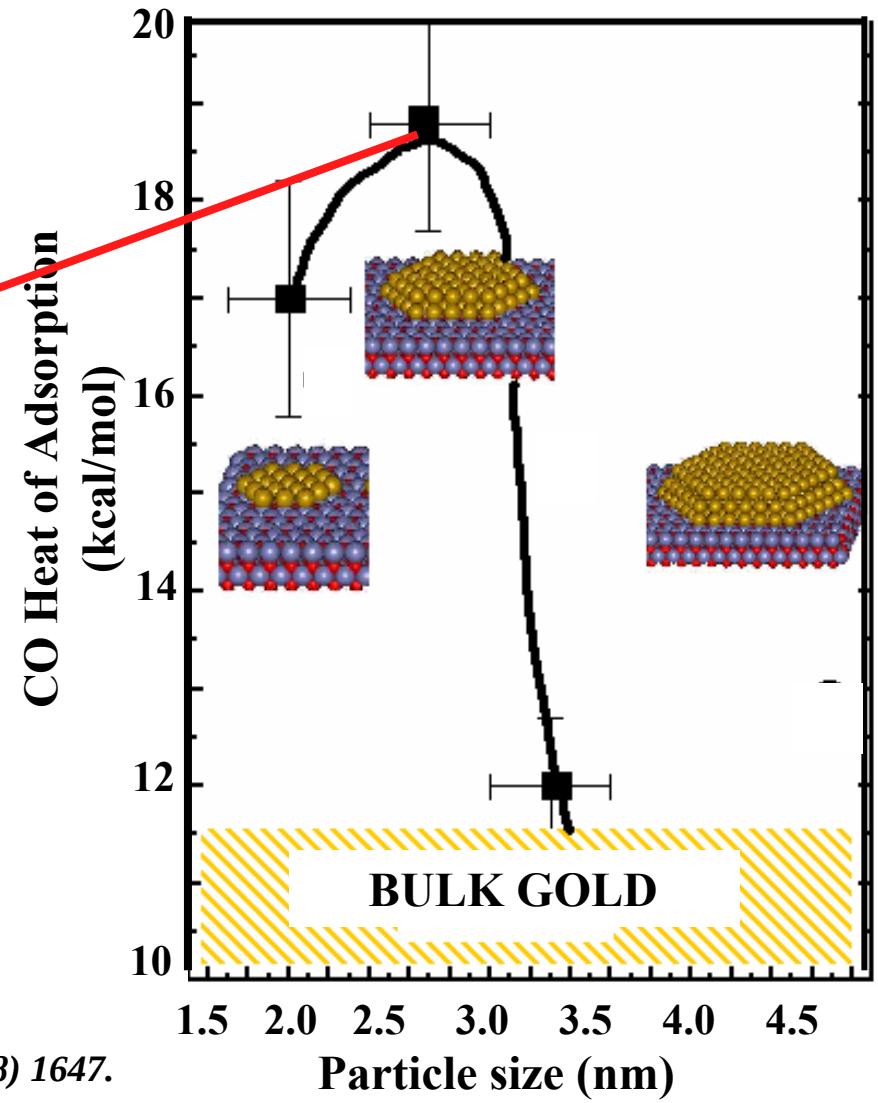


30nm x 30nm

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

Unique properties of $Au/TiO_2(110)$

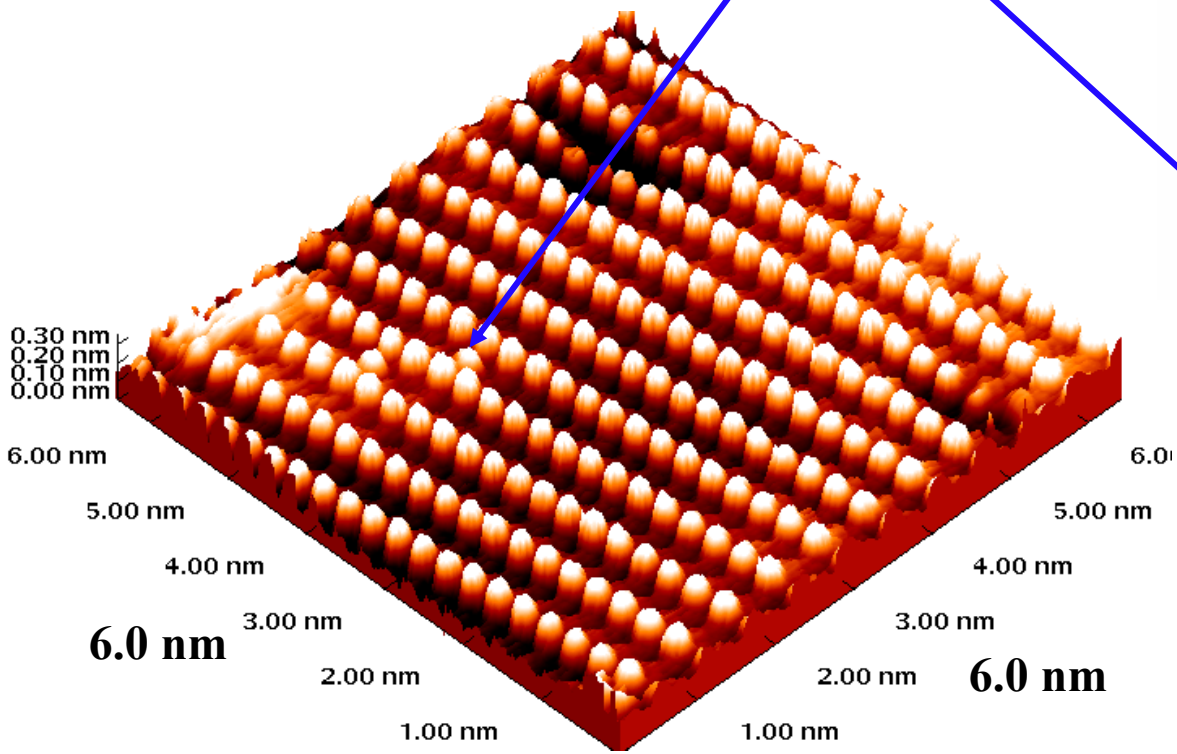


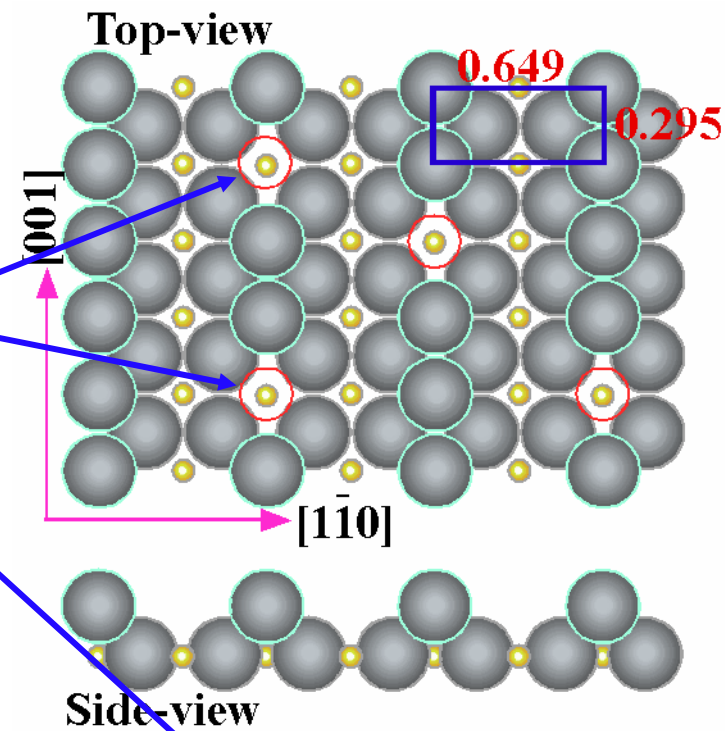


M. Valden, X. Lai, and D. W. Goodman, Science 281 (1998) 1647.

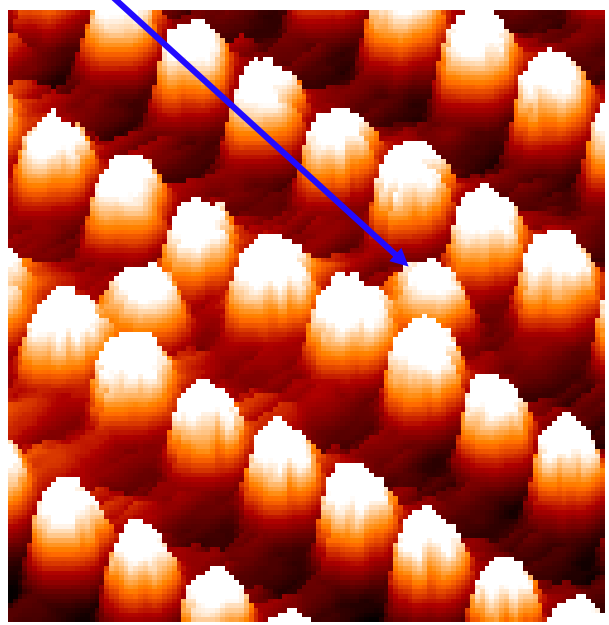
D. C. Meier, D. W. Goodman, J. Am. Chem. Soc. 126 (2004) 1892.

Surface defects on $TiO_2(110)$

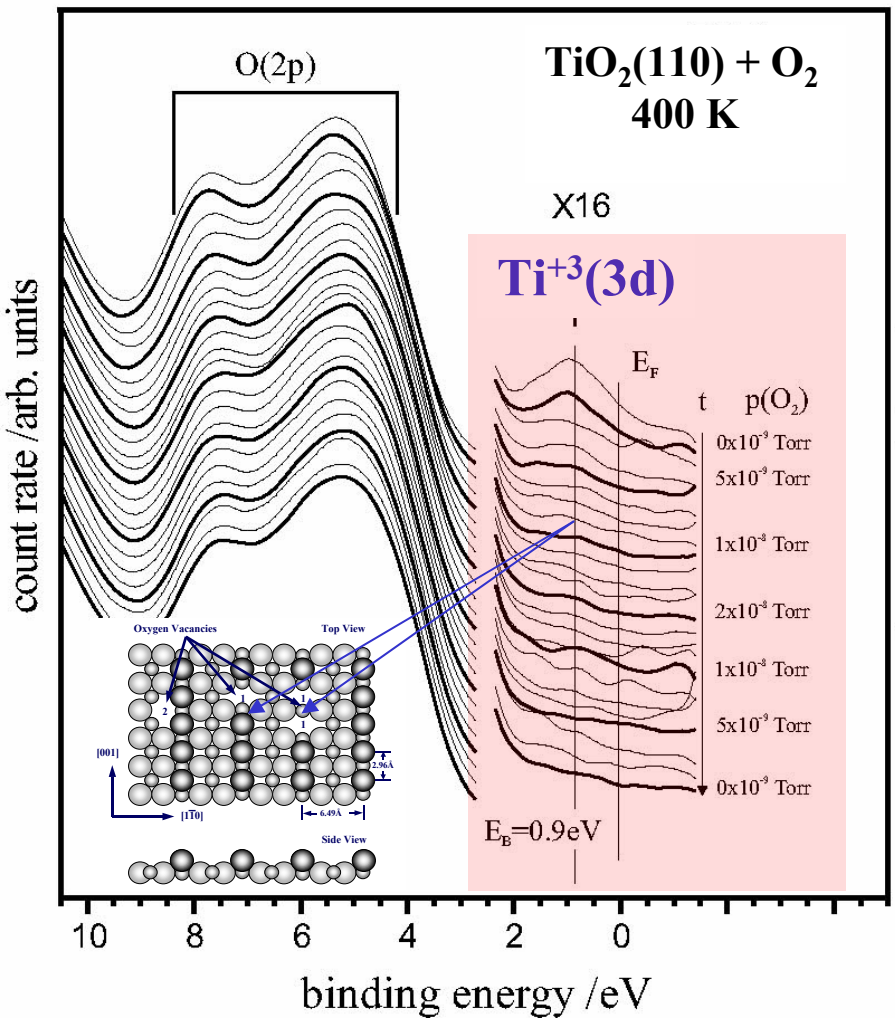


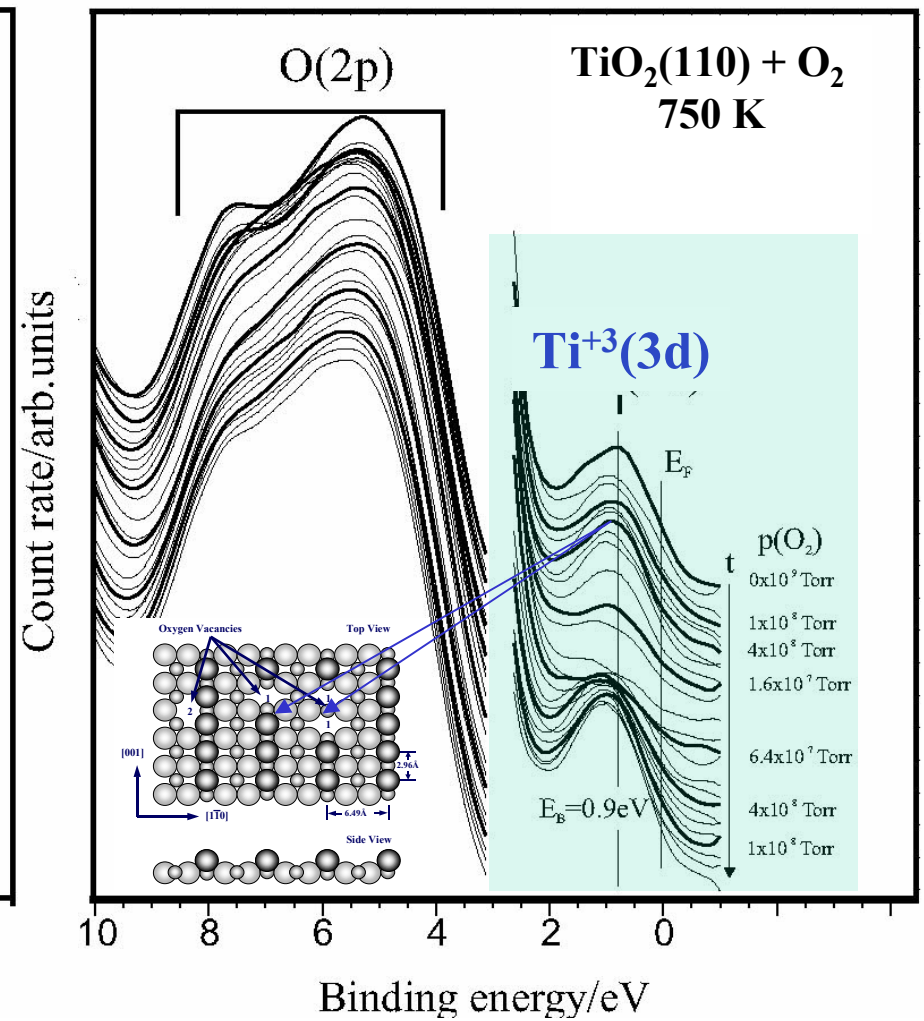


Oxygen vacancies



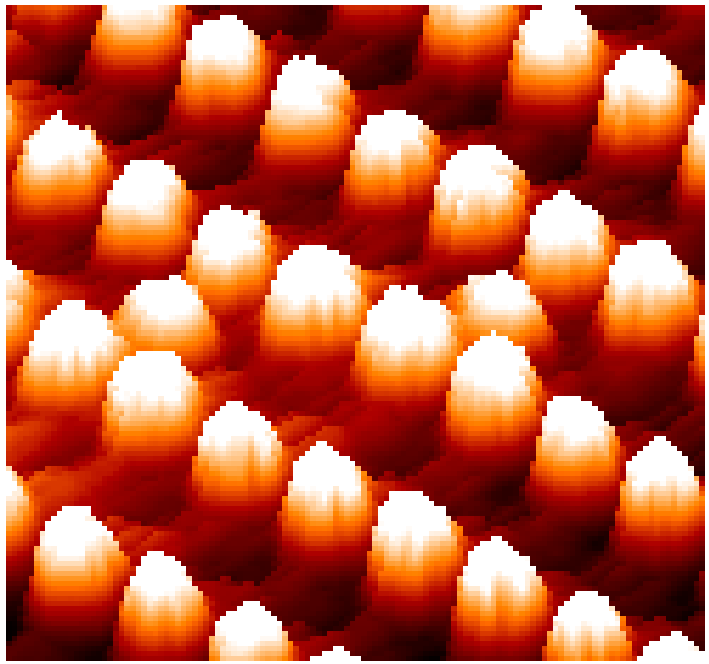
Ultraviolet Photoelectron Spectroscopy (UPS): Defects on $TiO_2(110)$





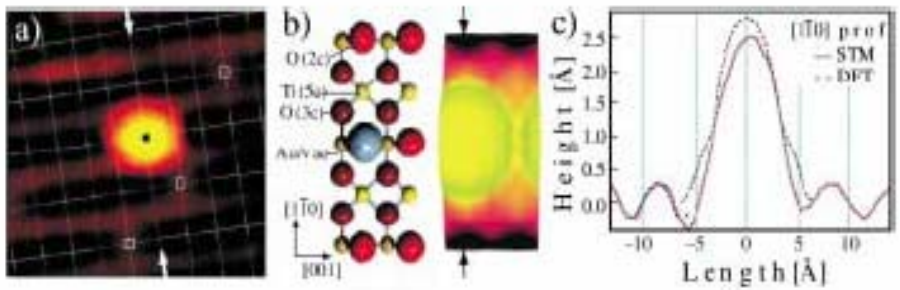
Krischok, Guenster, Goodman, Hoefft, and Kempter, submitted for publication

Role of Oxygen Defects in Metal Cluster Nucleation and Growth on $TiO_2(110)$



oxygen vacancies

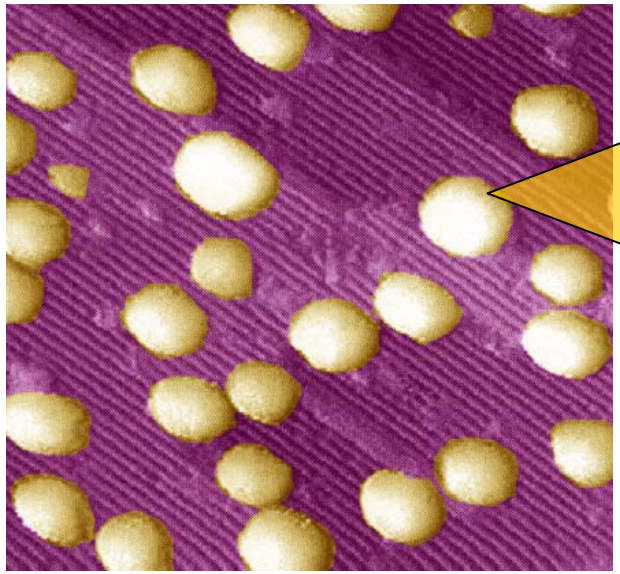
Bridging oxygen vacancies are the active nucleation sites for Au clusters



a) STM image of a small Au clusters on TiO_2 . Vacancies are marked with squares. b) Simulated STM image of a single Au atom trapped in a oxygen vacancy. c) Line profiles comparing DFT theoretical results and experiment.

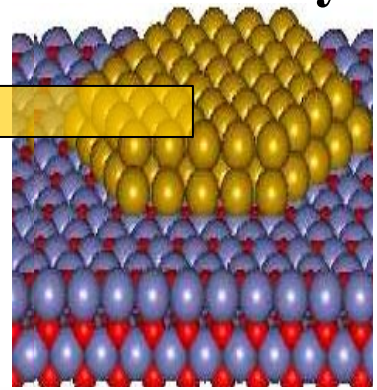
E. Wahlstroem, N. Lopez, R. Schaub, P. Thostrup, A. Ronnau, C. Africh, E. Laegsgaard, J. K. Norskov, and F. Besenbacher, Phys. Rev. Lett. 90, 101 (2003)

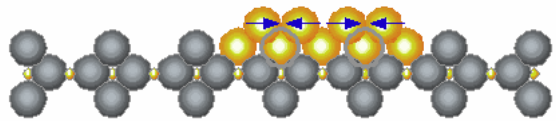
Au on TiO_2(110): Cluster Anchored via Reduced Titania



30 nm

Au bilayer





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

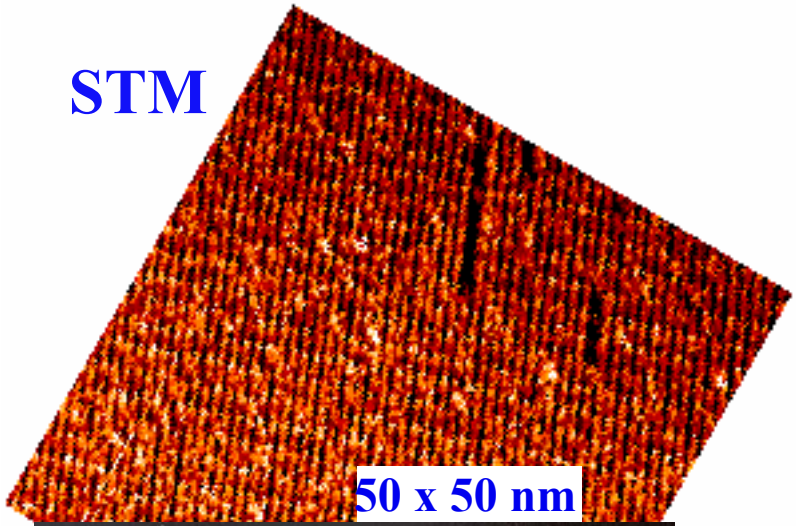
Rodriguez et al, J. Am. Chem. Soc., 124 (2002) 5242

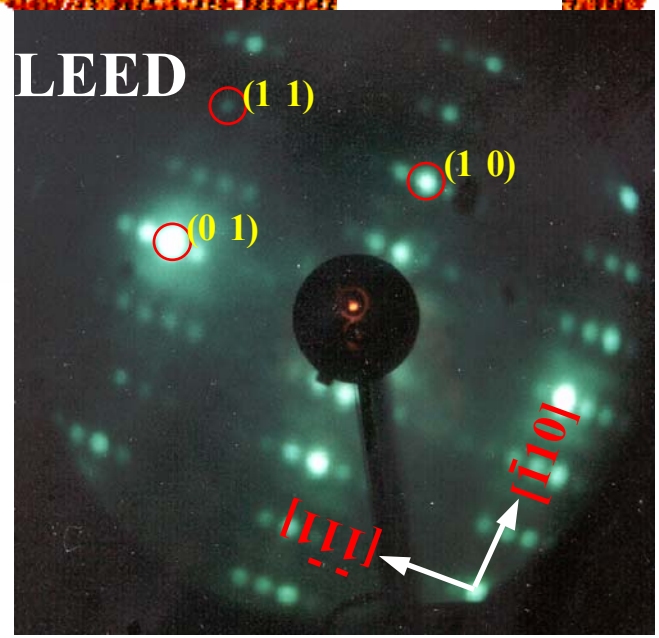
and

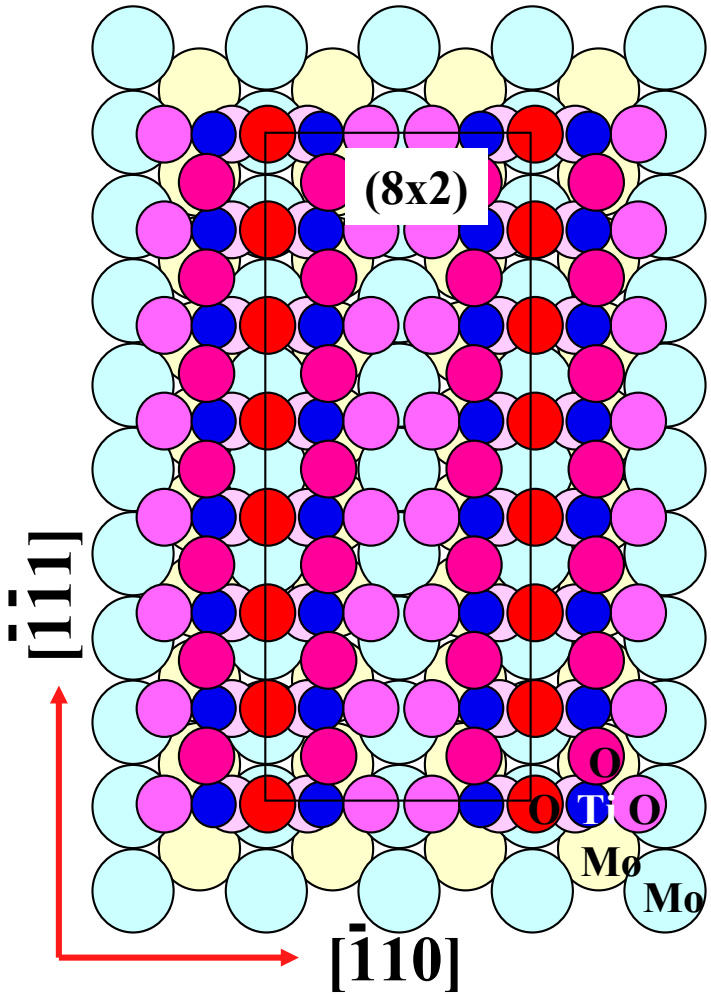
Single oxygen vacancy can bind 3 Au atoms on average

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)

Reduced Titania Surface: TiO_x/Mo(112)





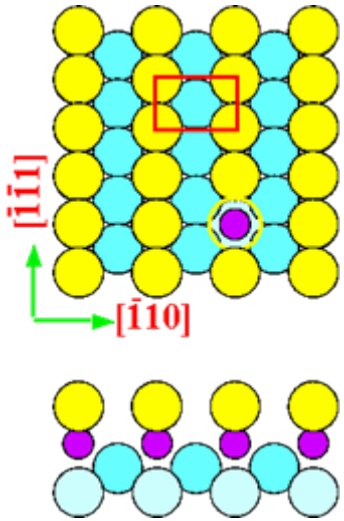


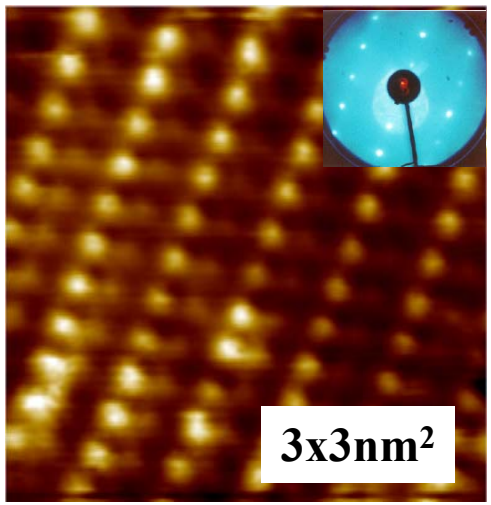
Full-1ML-Ti^{3+}!!

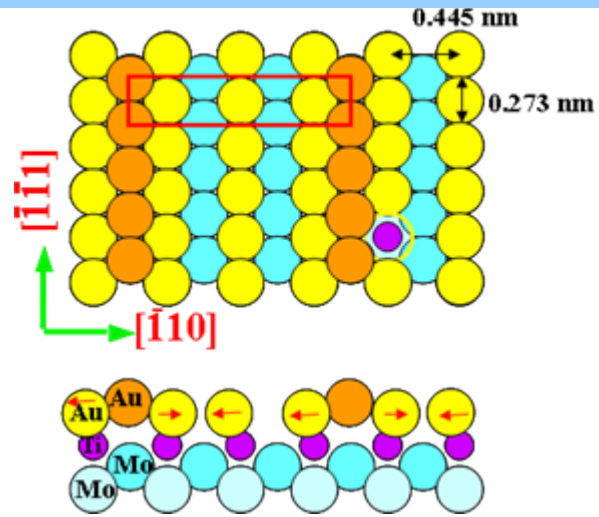
Chen et al., Surf. Sci. Lett. (2005), & Science 306 (2004) 252.

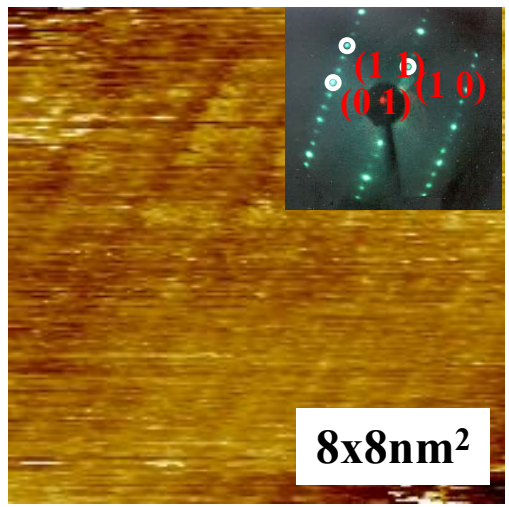
1.0 monolayers Au: (1x1)-Au/TiO_x/Mo(112)

1.33 monolayers Au: (1x3)-Au/TiO_x/Mo(112)



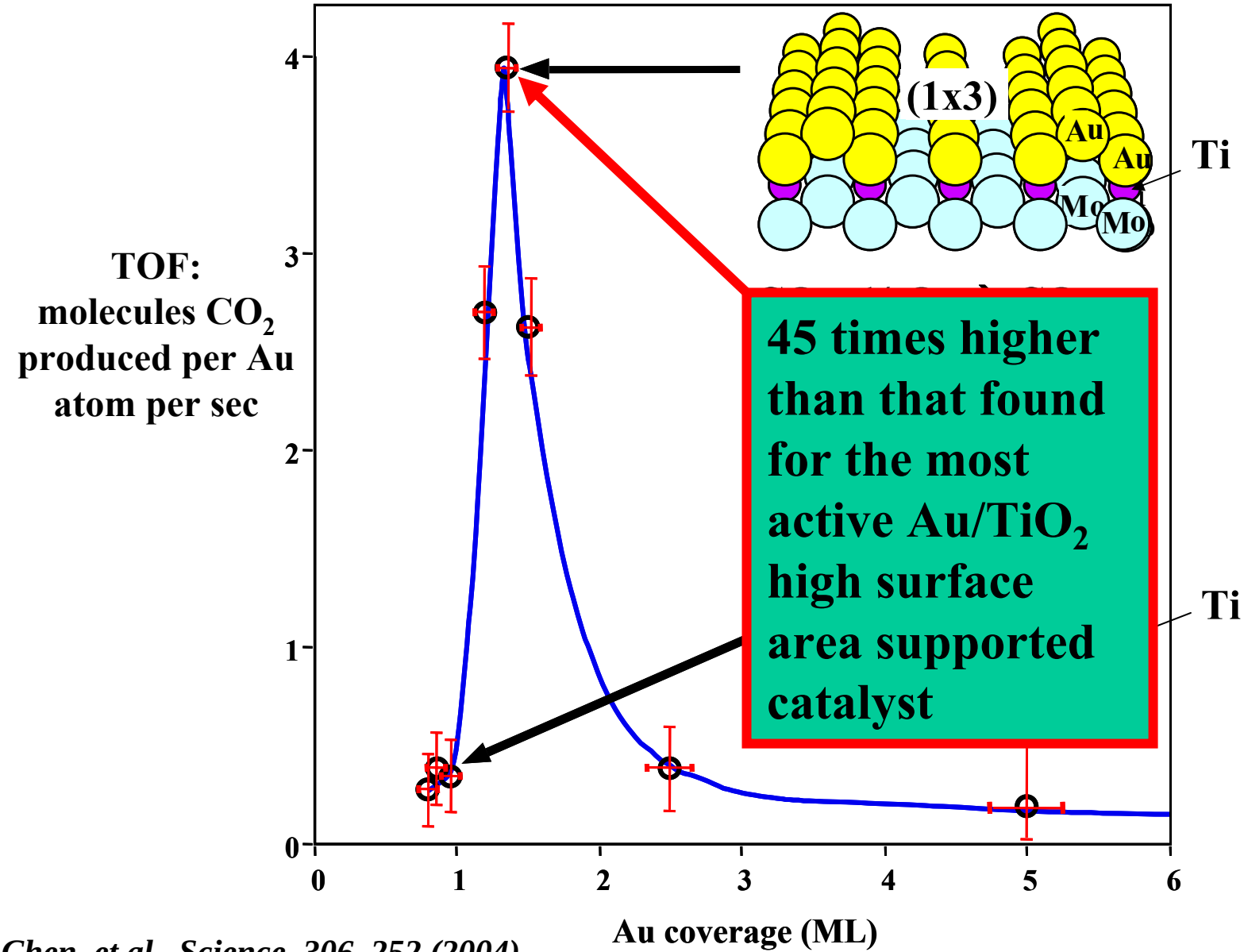






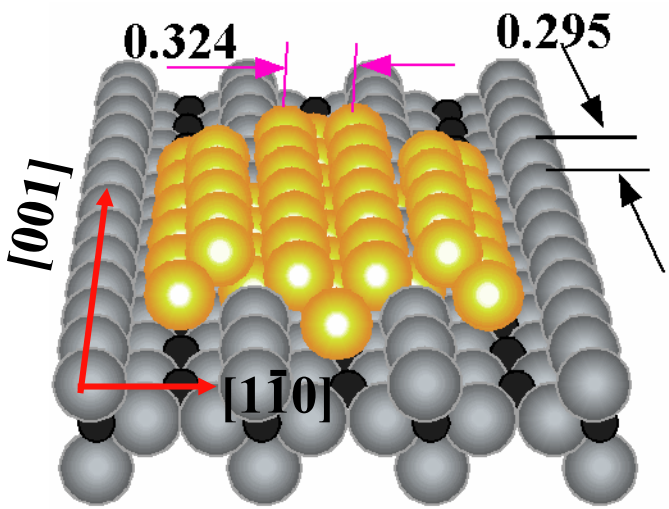
M. S. Chen and D. W. Goodman, Science 306 (2004) 252;
STM: Chen et al. (2006)

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

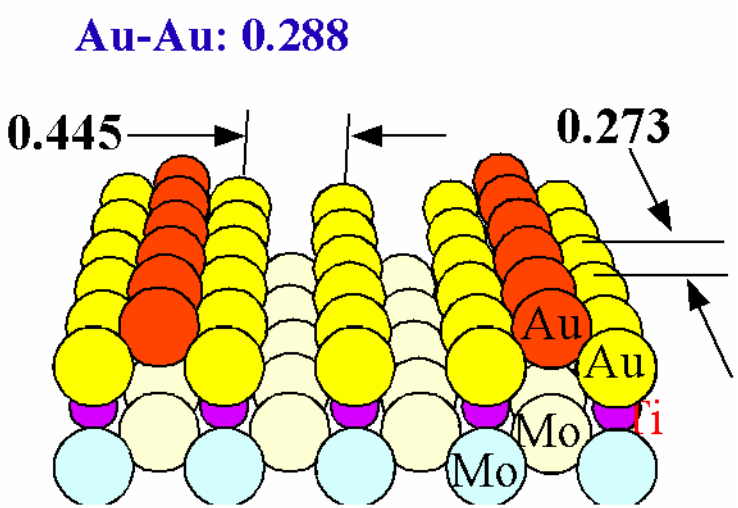


Chen, et al., Science, 306, 252 (2004)

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



Au(2~3 nm)/TiO_2(110)



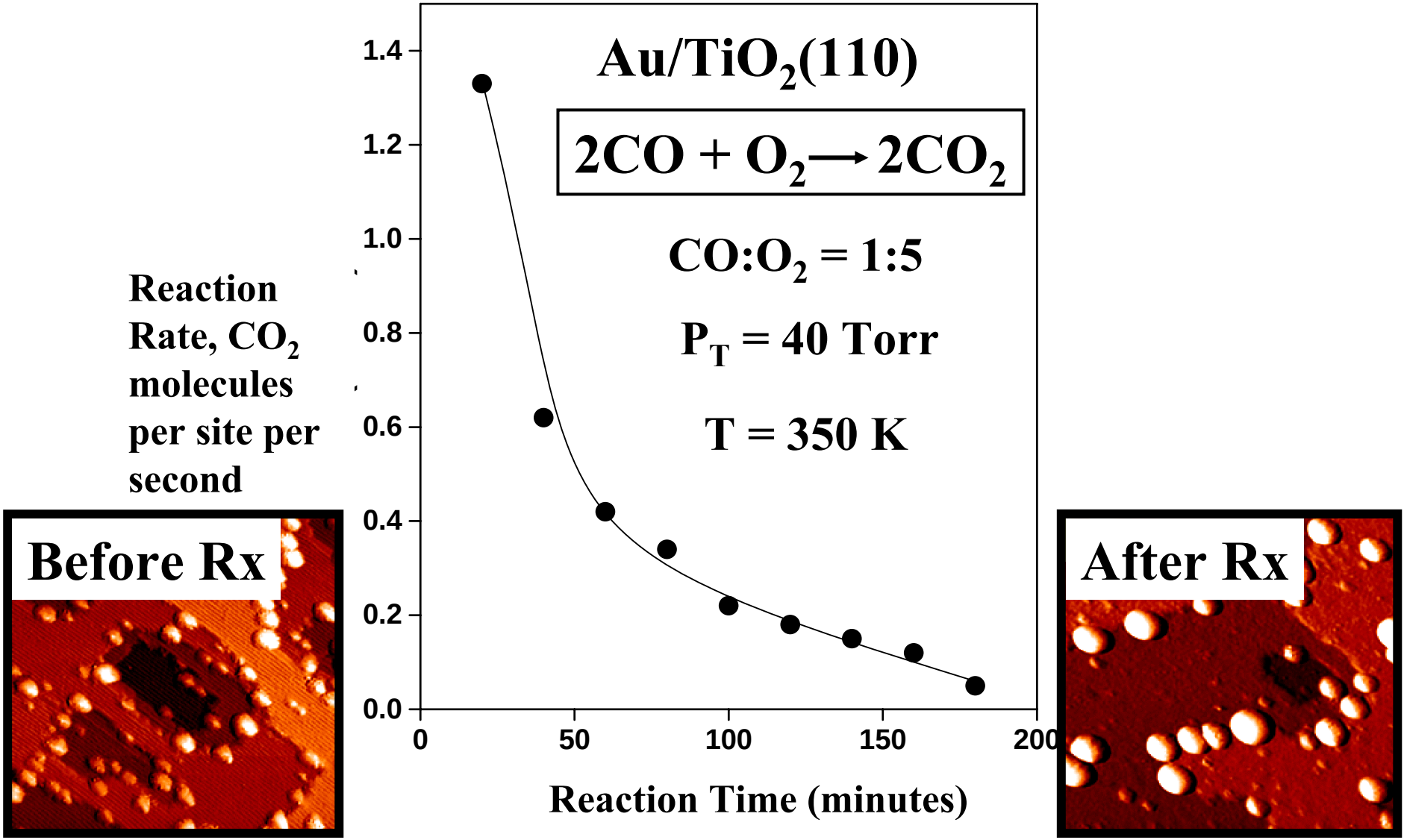
Mo(112)-(1x3)-(Au,TiO_x)

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

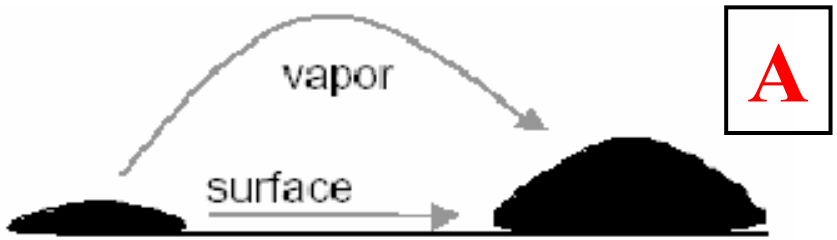
Summary: Properties of Supported Au Nanoclusters

- Adsorbate binding energies, e.g. CO and O_2, change significantly from the bulk values for clusters < 3.0 nm.
- DFT calculations show center of Au d-band significantly destabilized for Au/TiO_2 compared to Au.
- Core-level shifts are markedly non-bulk-like at <ca. 3.0 nm.
- Surface plasmon not observed for clusters <ca. 3.0 nm.
- **Sublimation energies of clusters < 3.0 nm are markedly lower than the corresponding bulk value.**
- **Nanoclusters are generally unstable to reaction conditions, i.e., understanding and maintaining stability is a key to technological break-throughs.**

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



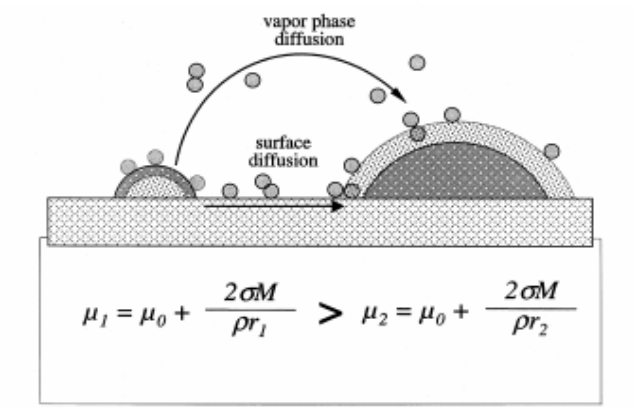
Sintering Mechanisms



P. Wynblatt and N. A. Gjostein,
Acta Metallurgica, 24, 1165 (1976)

interparticle transport

Atom Migration (Ostwald Ripening) : atoms/atom ensembles migrate to adjacent clusters to form larger clusters

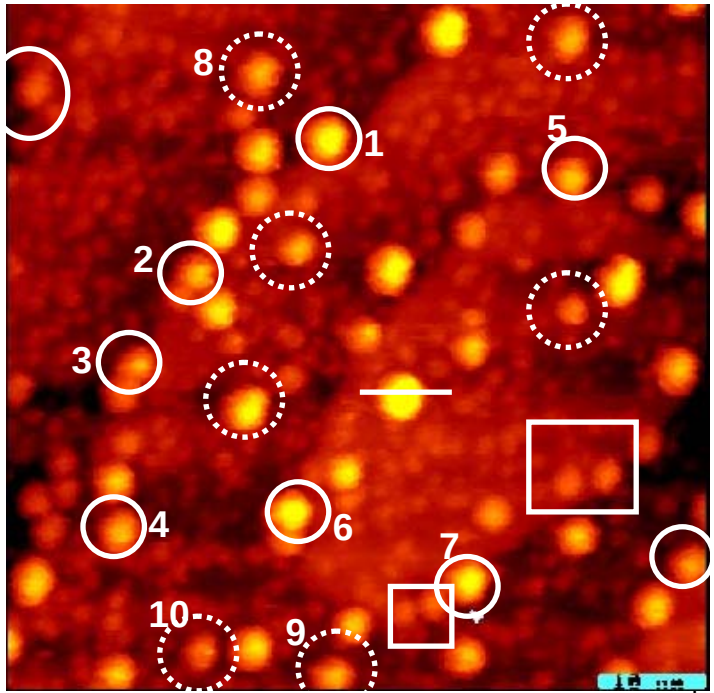


$$\mu_1 = \mu_0 + \frac{2\sigma M}{\rho r_1} > \mu_2 = \mu_0 + \frac{2\sigma M}{\rho r_2}$$

μ – chemical potential; σ – surface free energy
M/ρ – atom volume; r – cluster radius

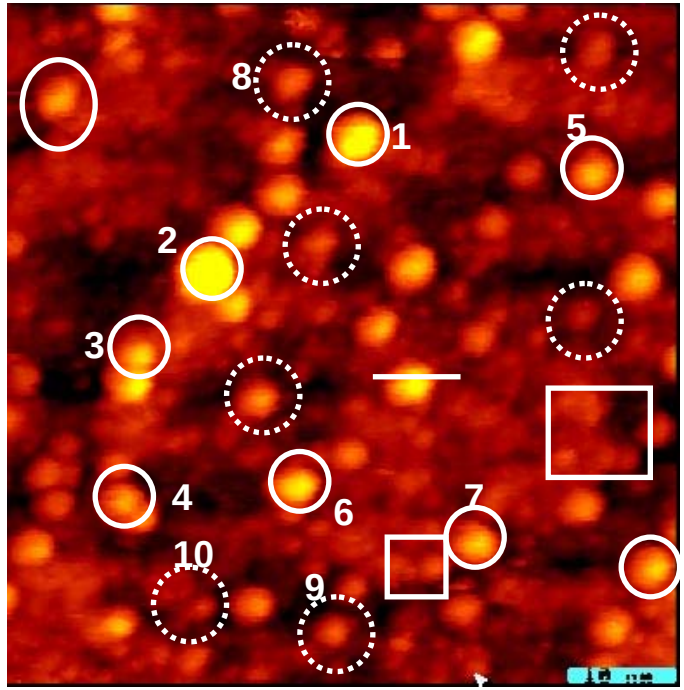
Gibbs-Thompson relationship

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

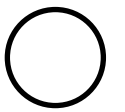


630A x 630A

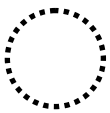
+ 1 hour



630A x 630A

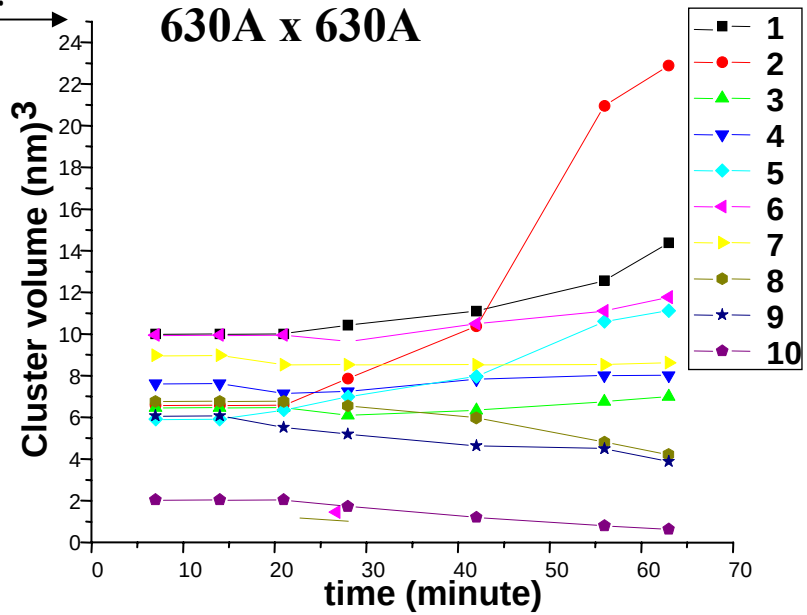


Cluster size increase



Cluster size decrease

Cluster disappears



Yang and Goodman, 2004

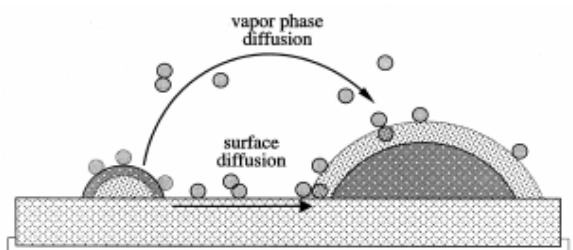
Sintering Mechanisms

A

P. Wynblatt and N. A. Gjostein,
Acta Metallurgica, 24, 1165 (1976)

interparticle transport

Atom Migration (Ostwald Ripening) : atoms/atom ensembles migrate to adjacent clusters to form larger clusters



$$\mu_1 = \mu_0 + \frac{2\sigma M}{\rho r_1} > \mu_2 = \mu_0 + \frac{2\sigma M}{\rho r_2}$$

μ – chemical potential; σ – surface free energy
M/ρ – atom volume; r – cluster radius

Gibbs-Thompson relationship

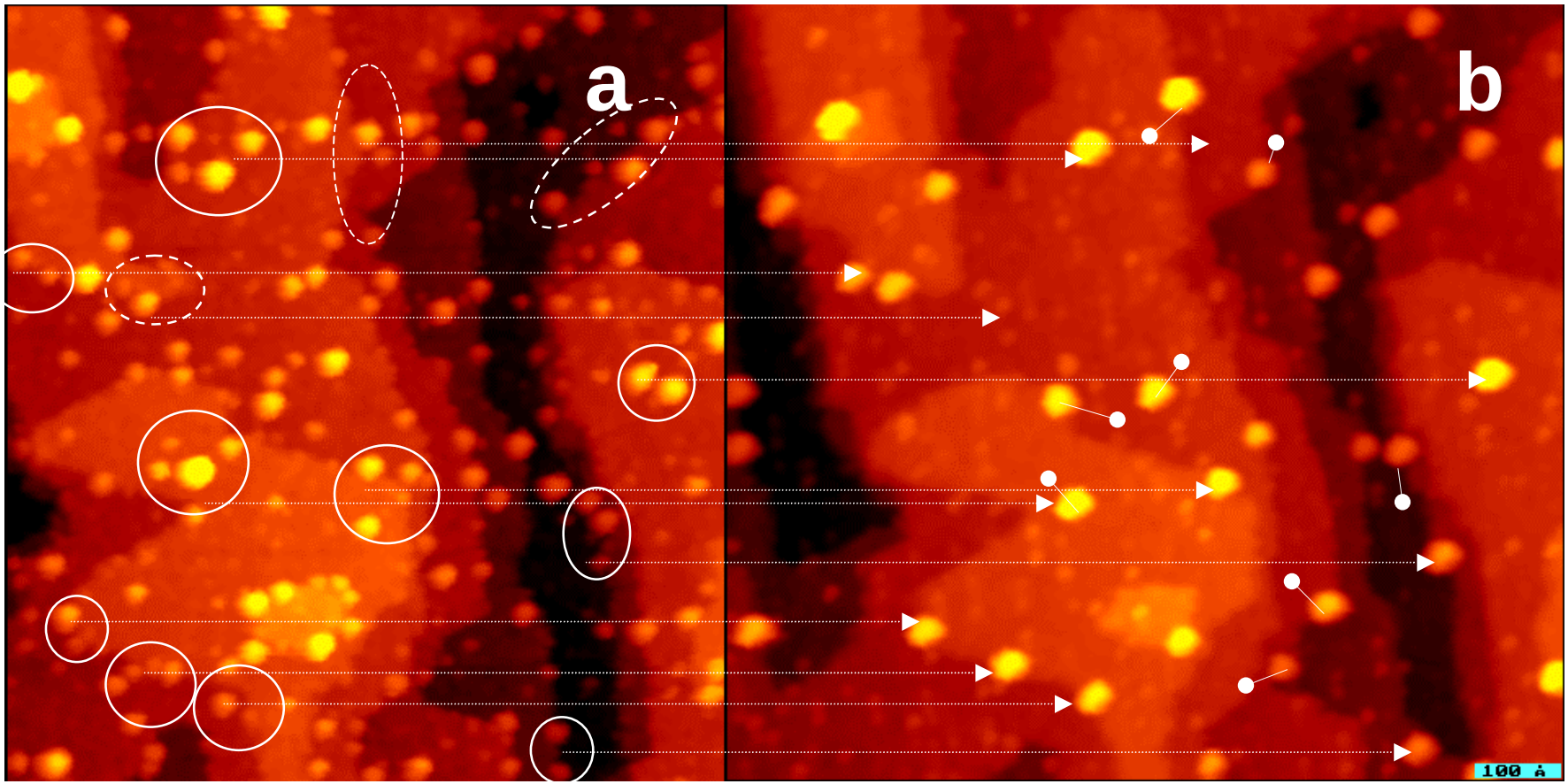
B

particle migration/coalescence

Cluster Migration : Clusters migrate along the surface, collide with others and coalescence

$Au/TiO_2(110)$ Before and After Annealing to 950K

As deposited **After a 950K x 30 min. anneal**



100 nm **100 nm**

Kolmakov and Goodman, Chem. Rev., 2003

Role of support in metal activation & cluster sintering:

SiO_2 versus TiO_2?

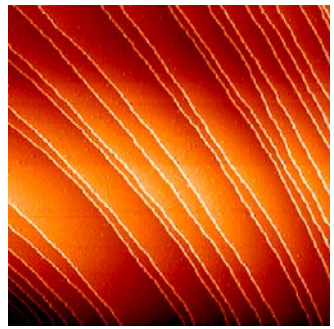
Model Oxide-Supported Metal Catalysts

Thin Oxide Film Support + Metal Clusters

e.g. Mo, Re
Ta, W

Refractory Single Crystal

400 nm

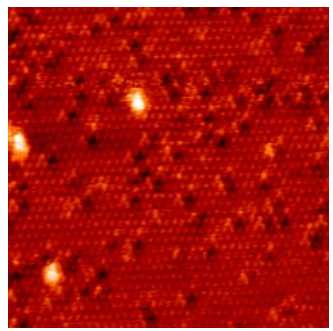


Mo(112)

e.g. SiO_2, Al_2O_3,
MgO, TiO_2
1-10 nm

Oxide Thin Film
Refractory Single Crystal

50 nm

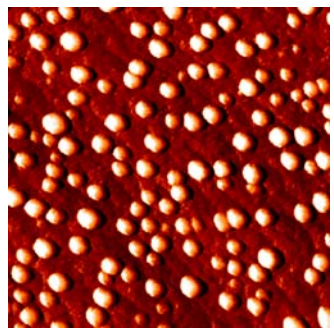


SiO_2/
Mo(112)

Metal Clusters
1.0 - 50 nm

Oxide Thin Film
Refractory Single Crystal

50 nm

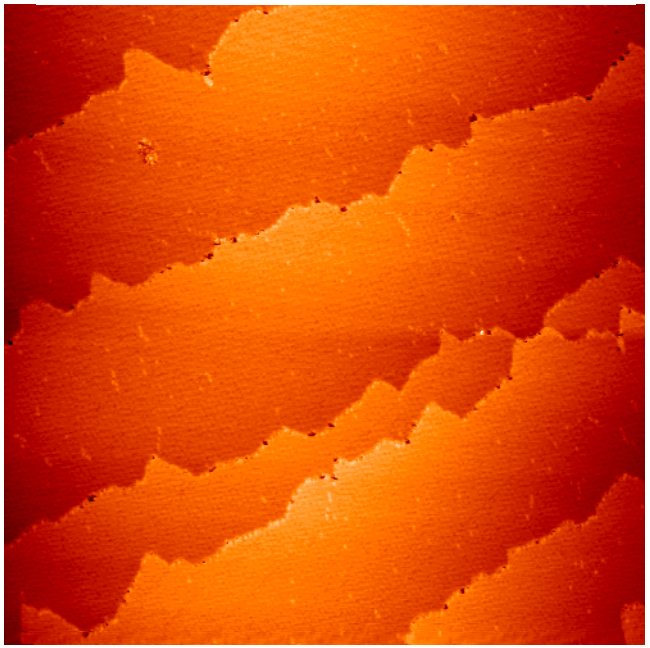


0.5 ML Au
SiO_2/
Mo(112)

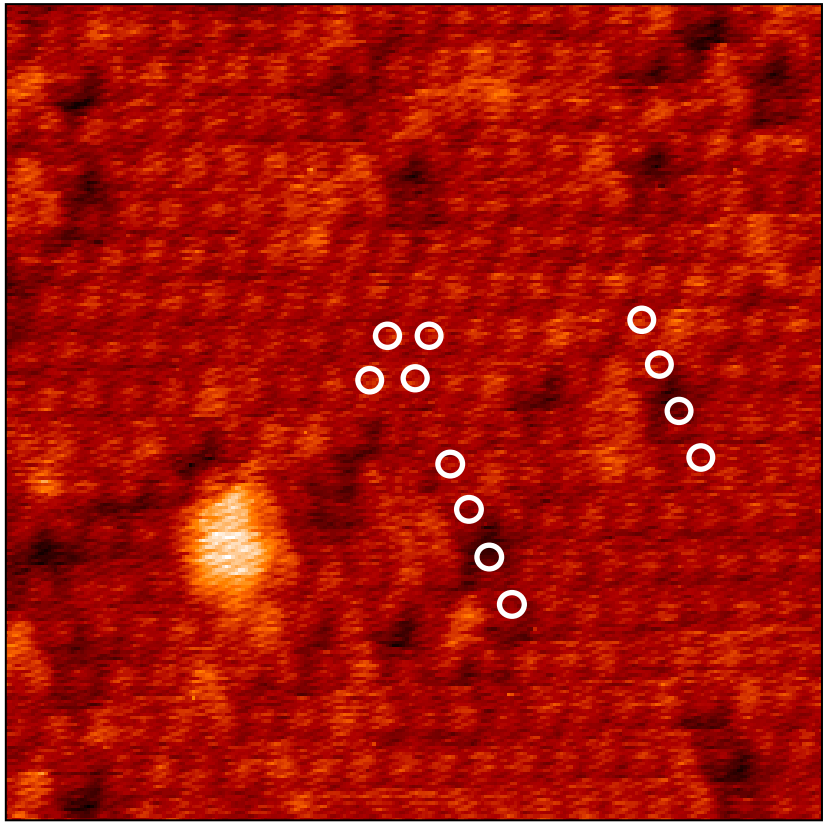
Preparation & Characterization of Ultra-thin, Well-ordered SiO_2/Mo(112)

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

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



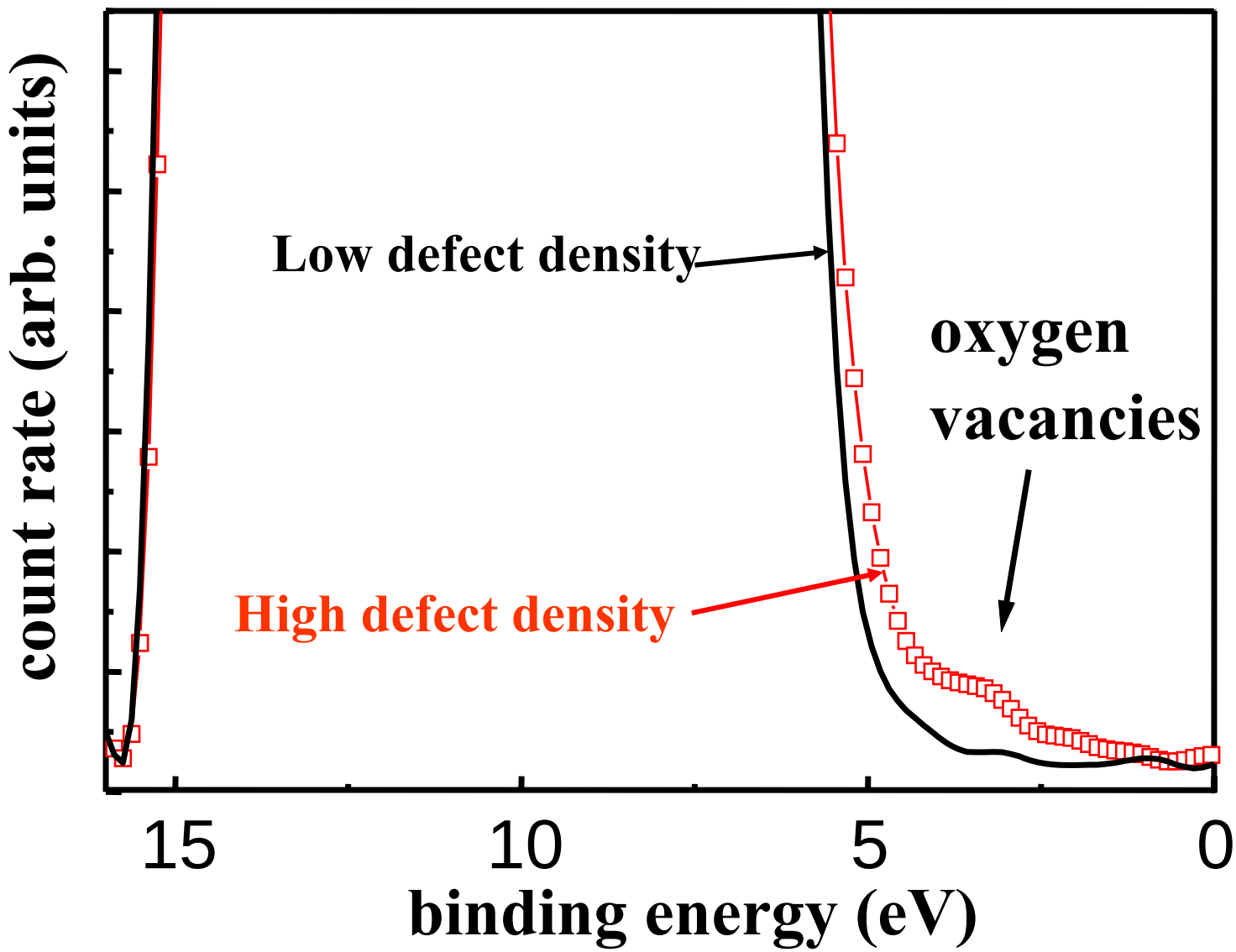
400 nm



10 nm

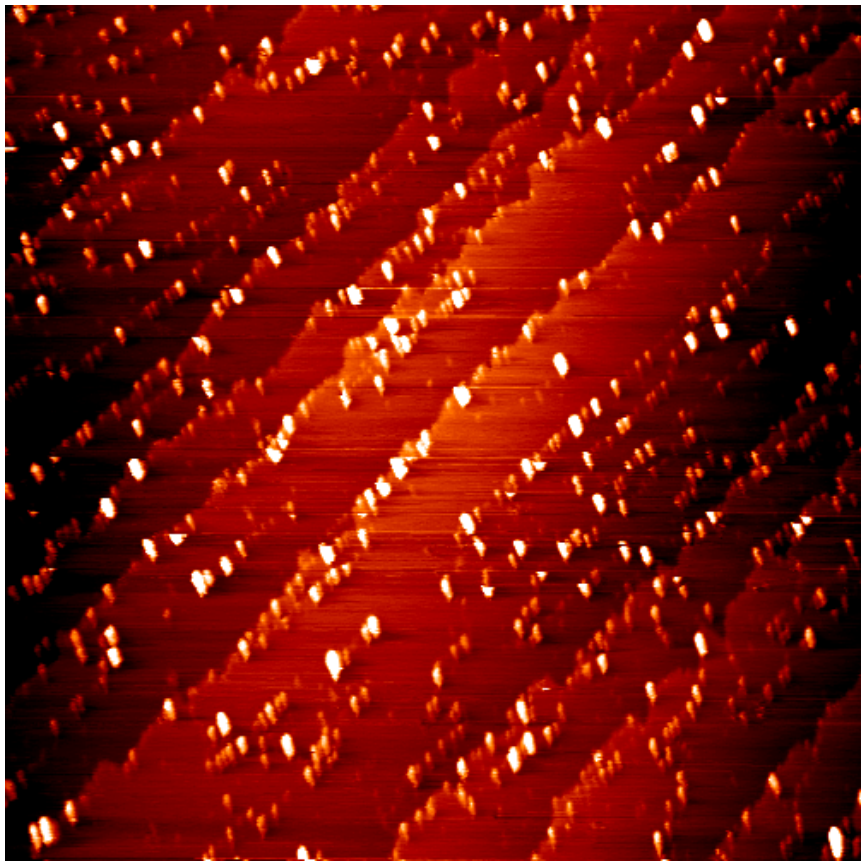
0.7 nm thick, sharp hexagonal LEED with a band gap ~8.9 eV (STS)

Defects on SiO_2 Surfaces Studied by Metastable Electron Impact Spectroscopy: MIES



Au Cluster Nucleation on Low-Defect Versus High-Defect SiO_2

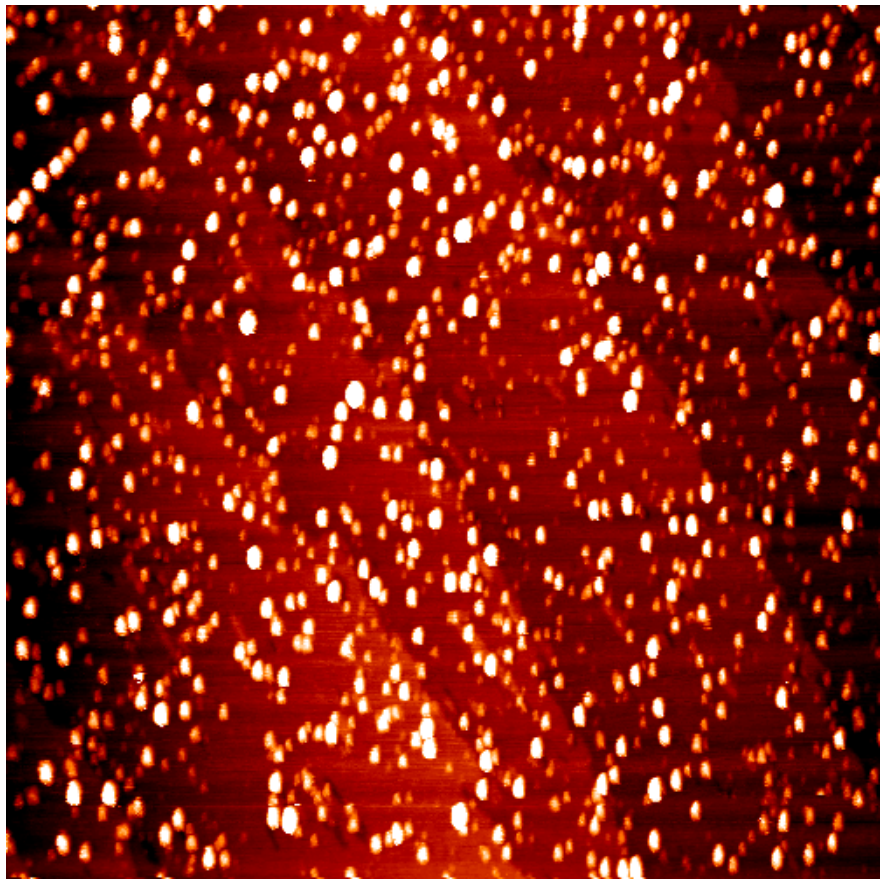
"Au + Low Defect SiO_2"



200 nm

0.40 ML of Au
0.033 ML/min
300 K

"Au + High Defect SiO_2"

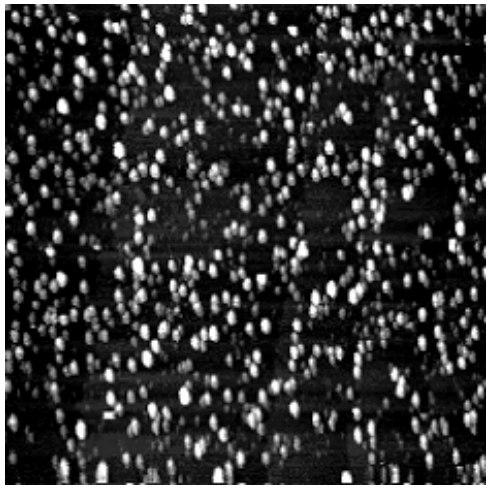


200 nm

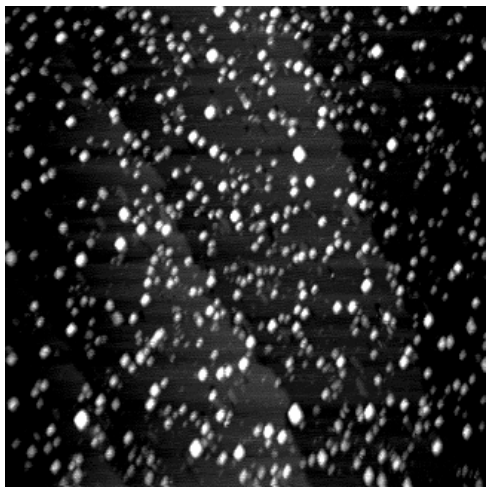
0.40 ML of Au
0.033 ML/min
300 K

Au Cluster Nucleation on Defective SiO_2

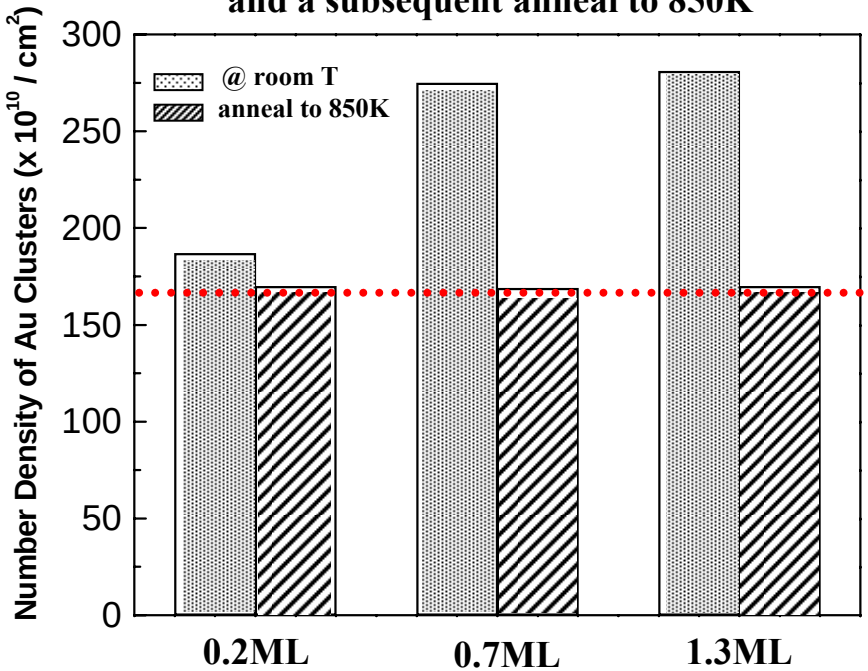
0.7 ML Au at room T

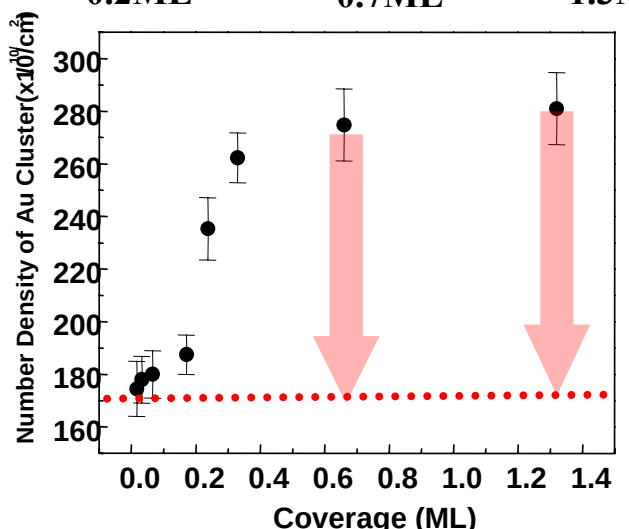


0.7 ML Au after a 850 K anneal

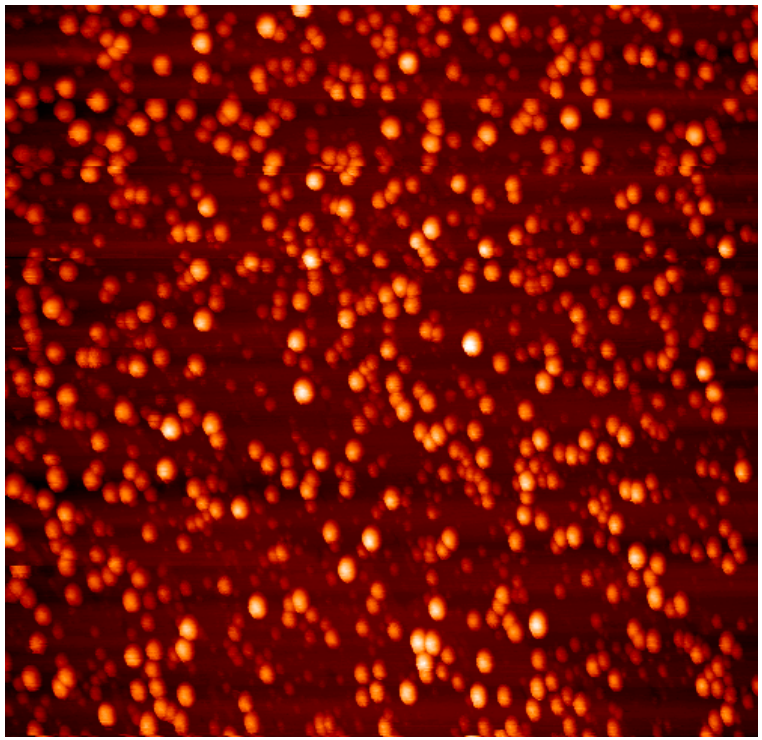


A comparison of Au cluster density after deposition at RT and a subsequent anneal to 850K



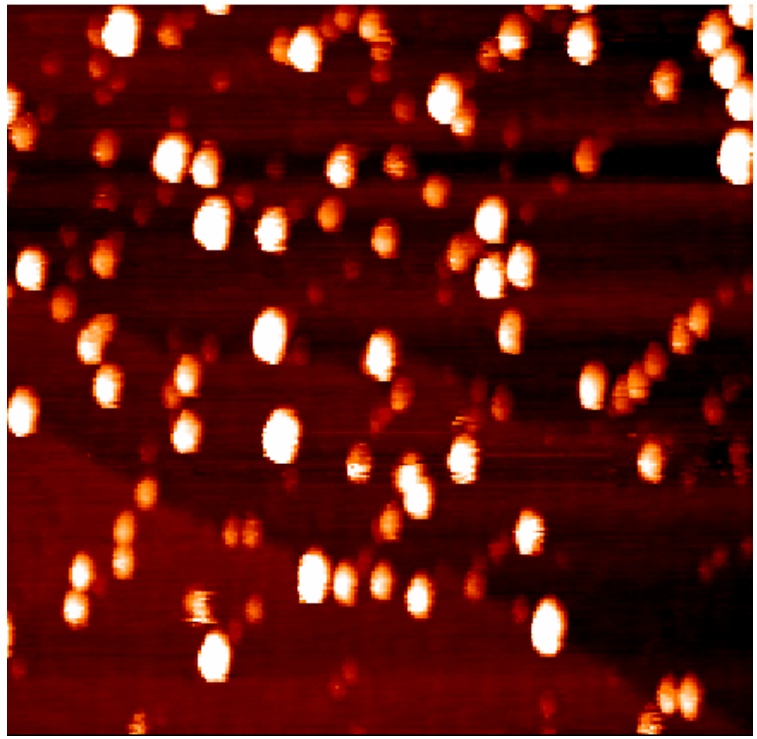


Sintering of Au Clusters on SiO_2



200 nm

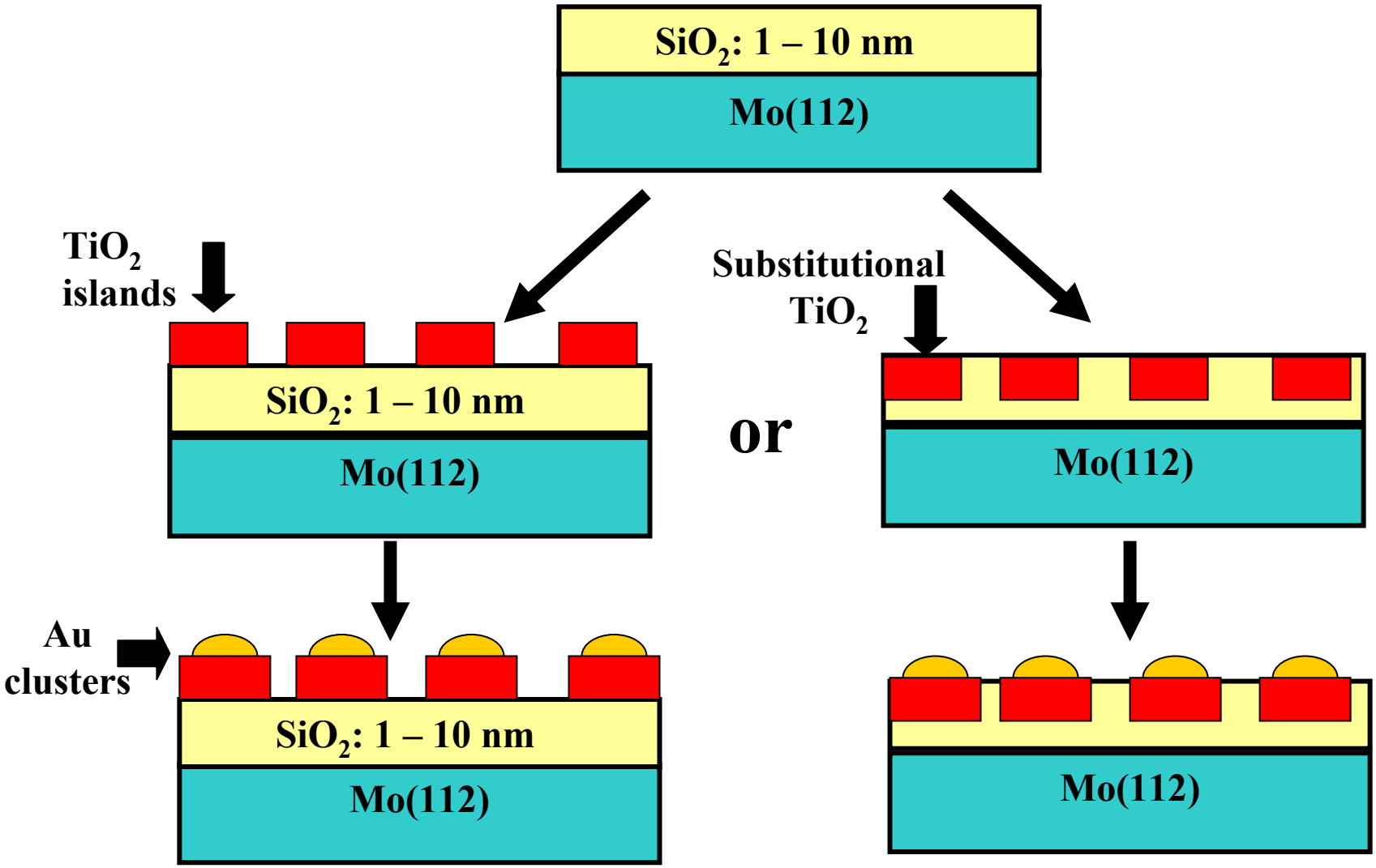
850 K
anneal



200 nm

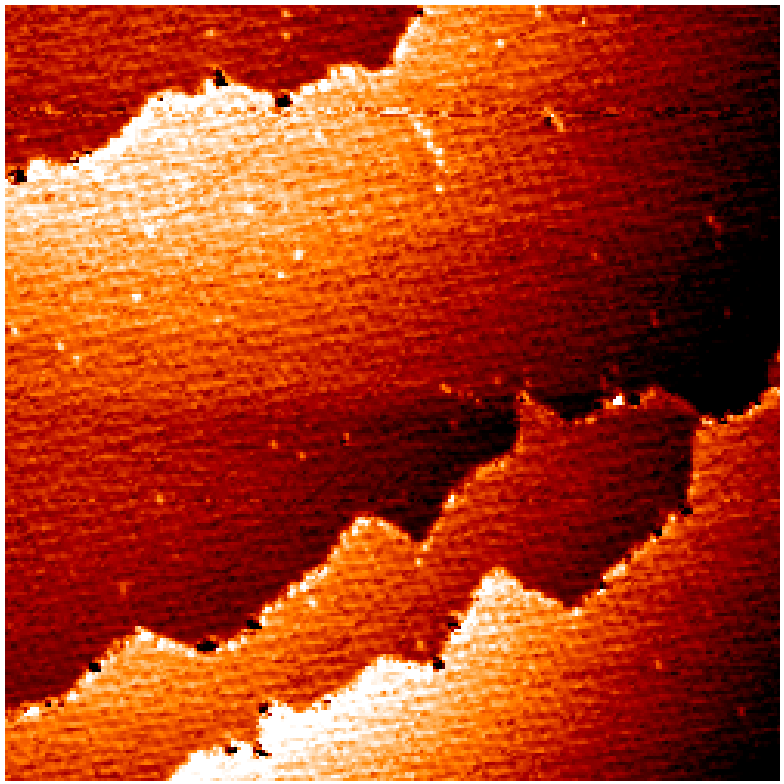
- Sintering of Au on SiO_2 more facile than on TiO_2
  i.e, Au binds less strongly to SiO_2 than to TiO_2

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



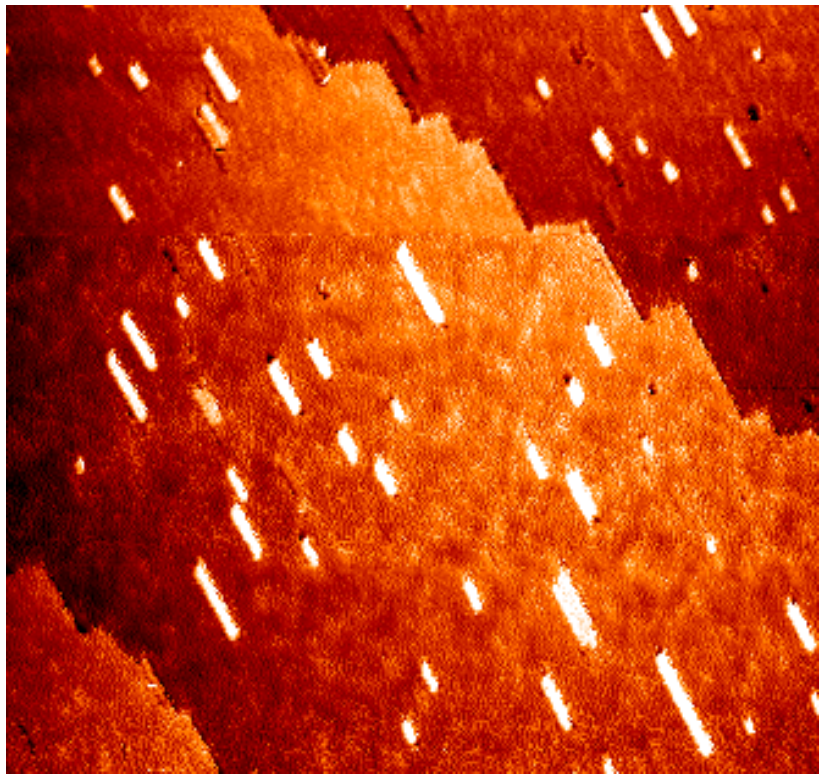
TiO_x Islands Dispersed on SiO_2

1.0 ML SiO_2/Mo(112)



100 nm

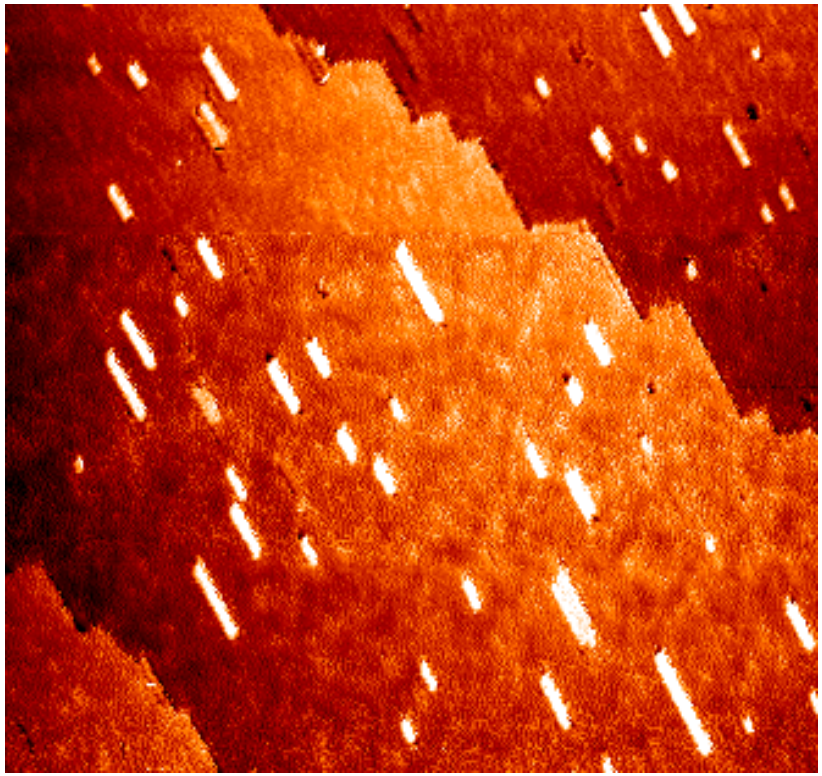
0.2 ML TiO_x/SiO_2/Mo(112)



100 nm

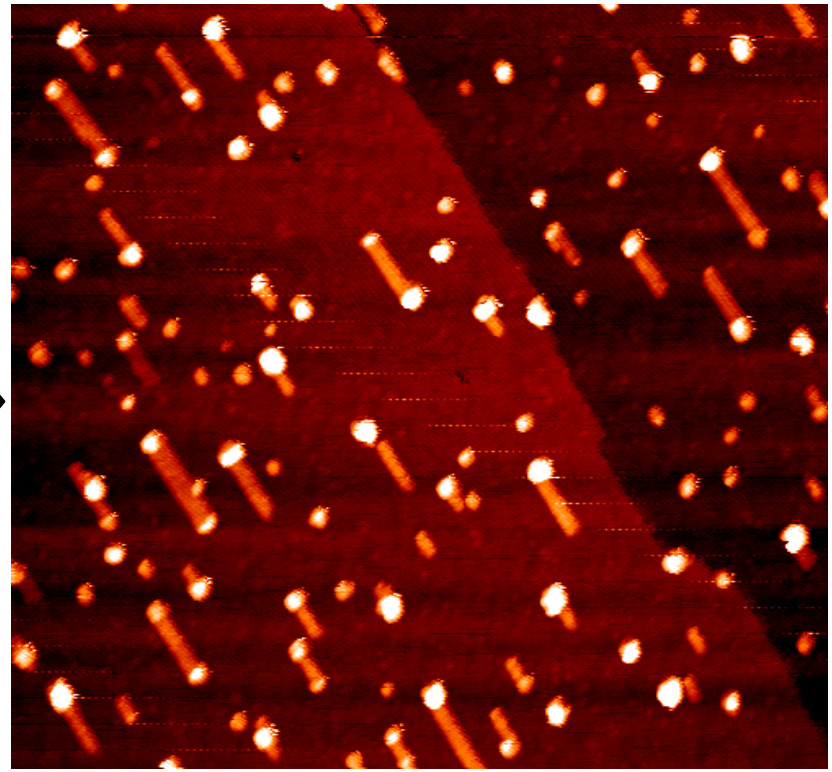
Au Particles Deposited onto TiO_x Islands Dispersed on SiO_2

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



100 nm

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



100 nm

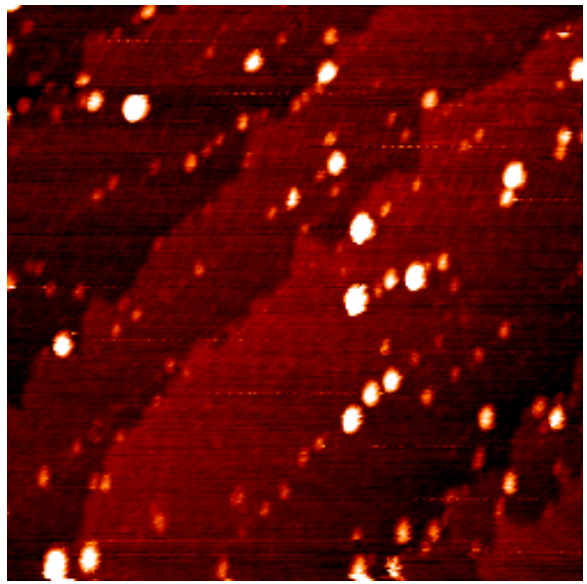
Au/SiO_2 versus $Au/TiO_x/SiO_2$: 850 K Anneal

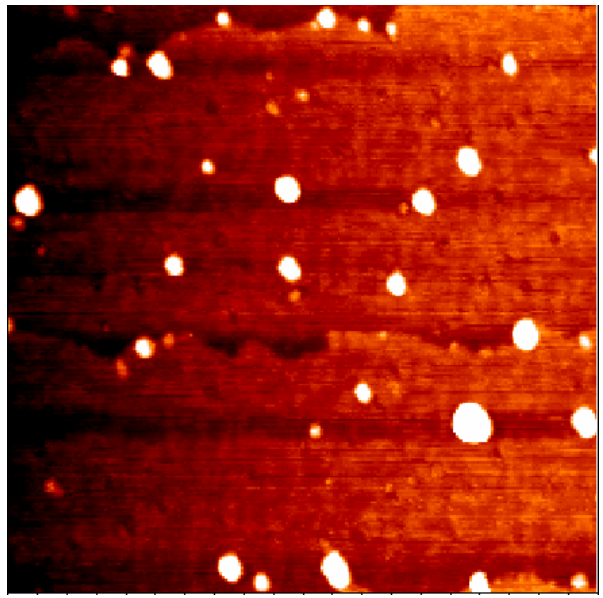
"before" "after"

SiO_2

+

0.4 ML Au



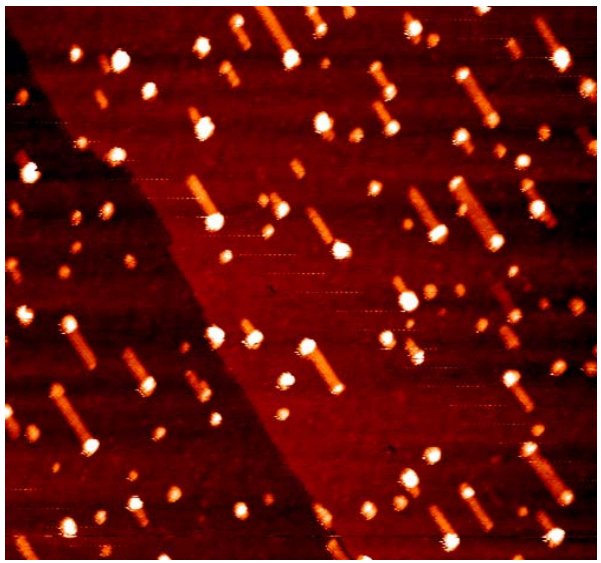


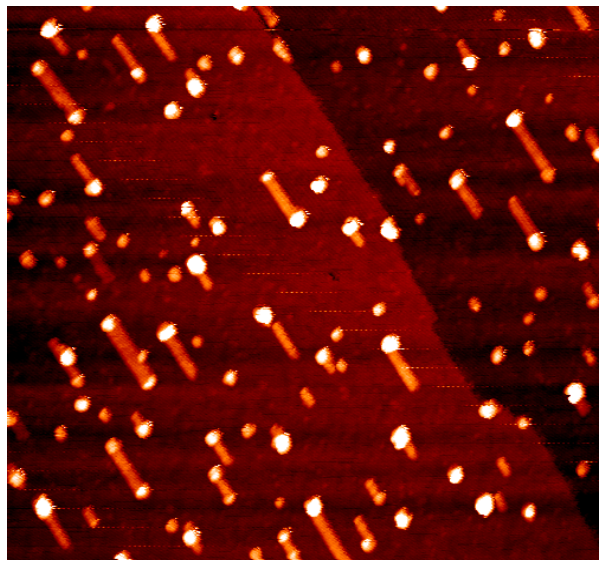
100 nm

TiO_x/SiO_2

+

0.4 ML Au

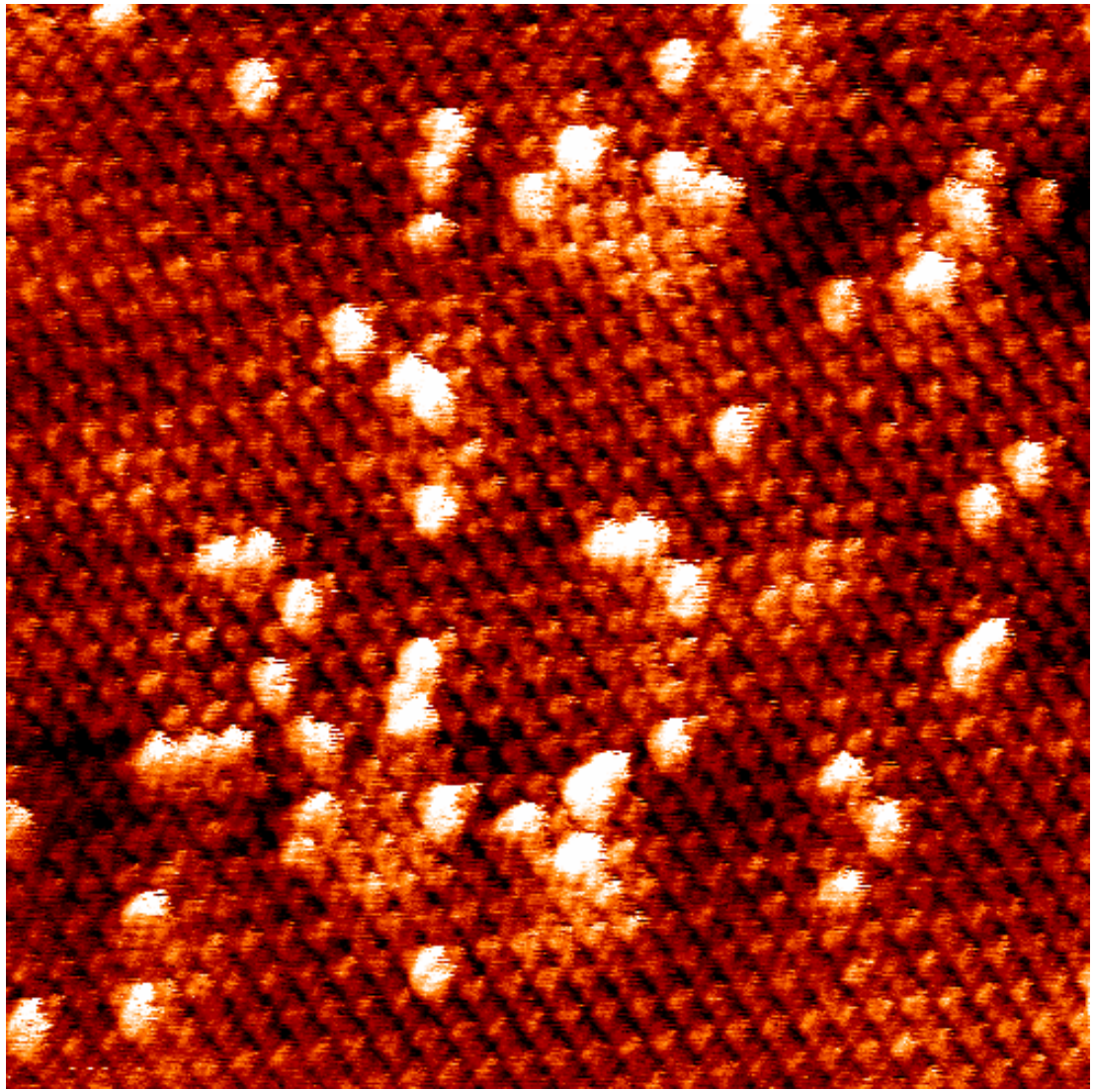




100 nm

Ti Point Defects on SiO_2

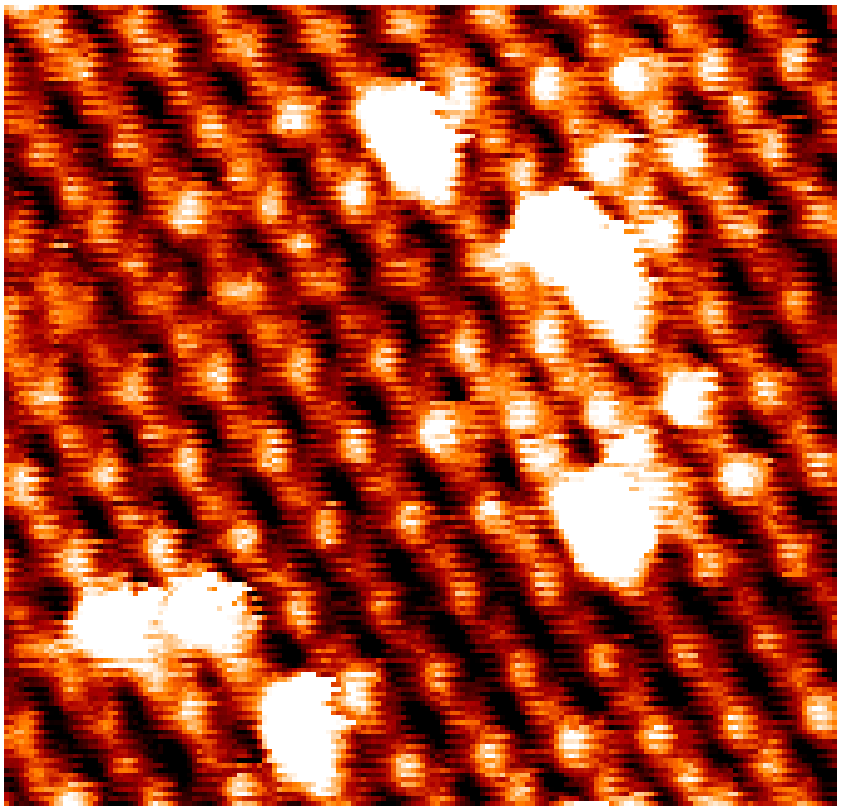
15 nm



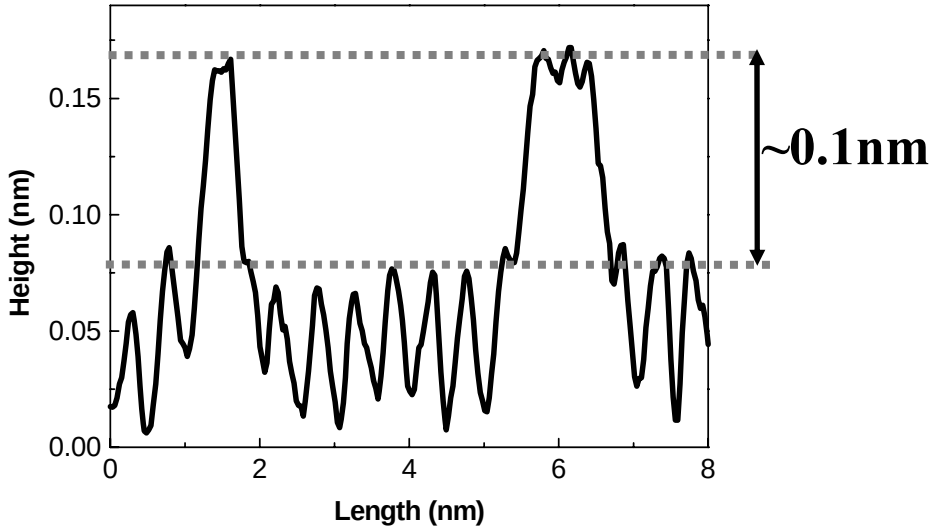
15 nm

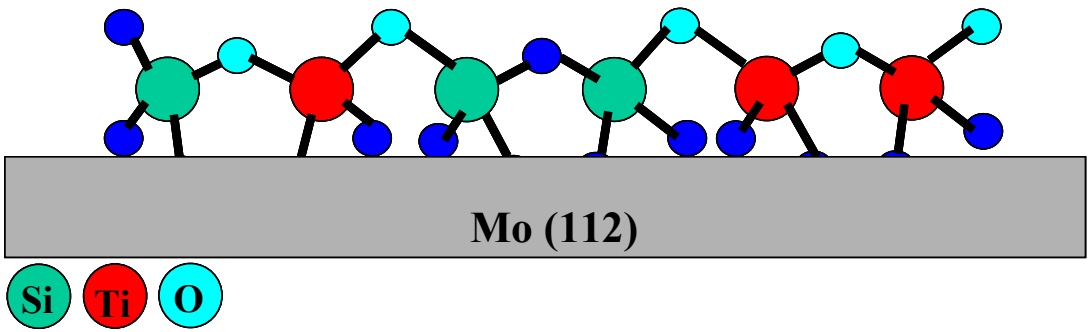
STM: TiO_x-SiO_2 Thin Film with 8% Ti

2.4 nm

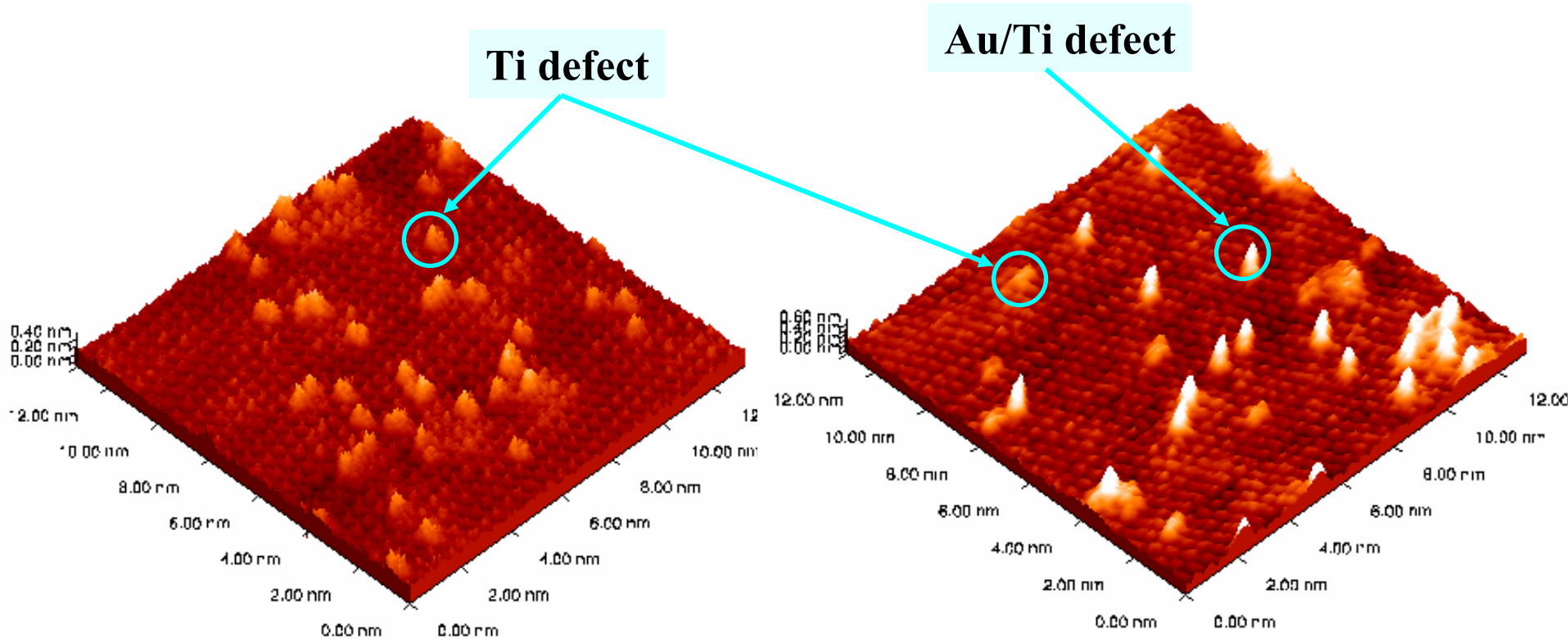


Scan across Ti defects





Decoration of Ti Point Defects with Gold



$Ti/SiO_2/Mo(112)$ → + 0.04 ML Au → $Au/Ti/SiO_2/Mo(112)$

Conclusions

- Catalytic reactivity and selectivity are markedly different for clusters < ~3.0 nm.
- Core-level shifts, valence band structure, sublimation energies, and adsorbate binding energies are unique for clusters < ~3.0 nm.
- Nanoclusters are generally unstable to reaction conditions, i.e., understanding and maintaining stability are the keys to technological break-throughs.

Coworkers

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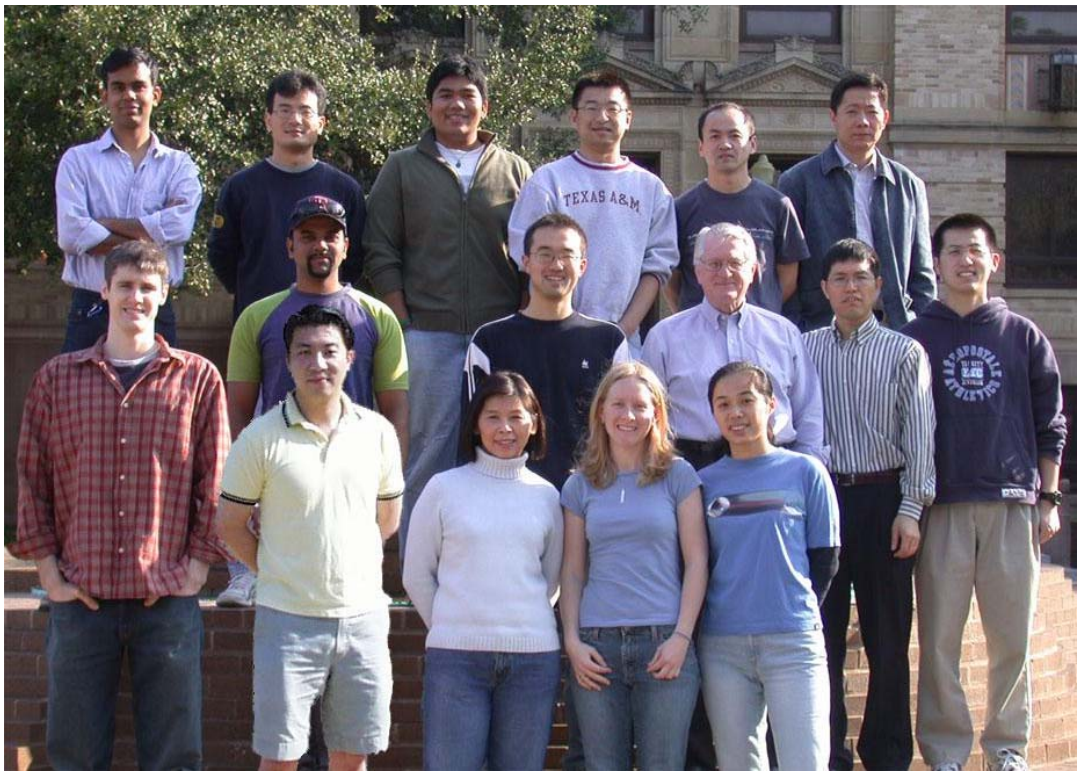
Tao Wei
Matt Lundwall

STM
Mingshu Chen

ISS
Kai Luo
Stepahnus Axnanda



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Ming-shu Chen

Rx-XPS
Dheeraj Kumar
Mingshu Chen

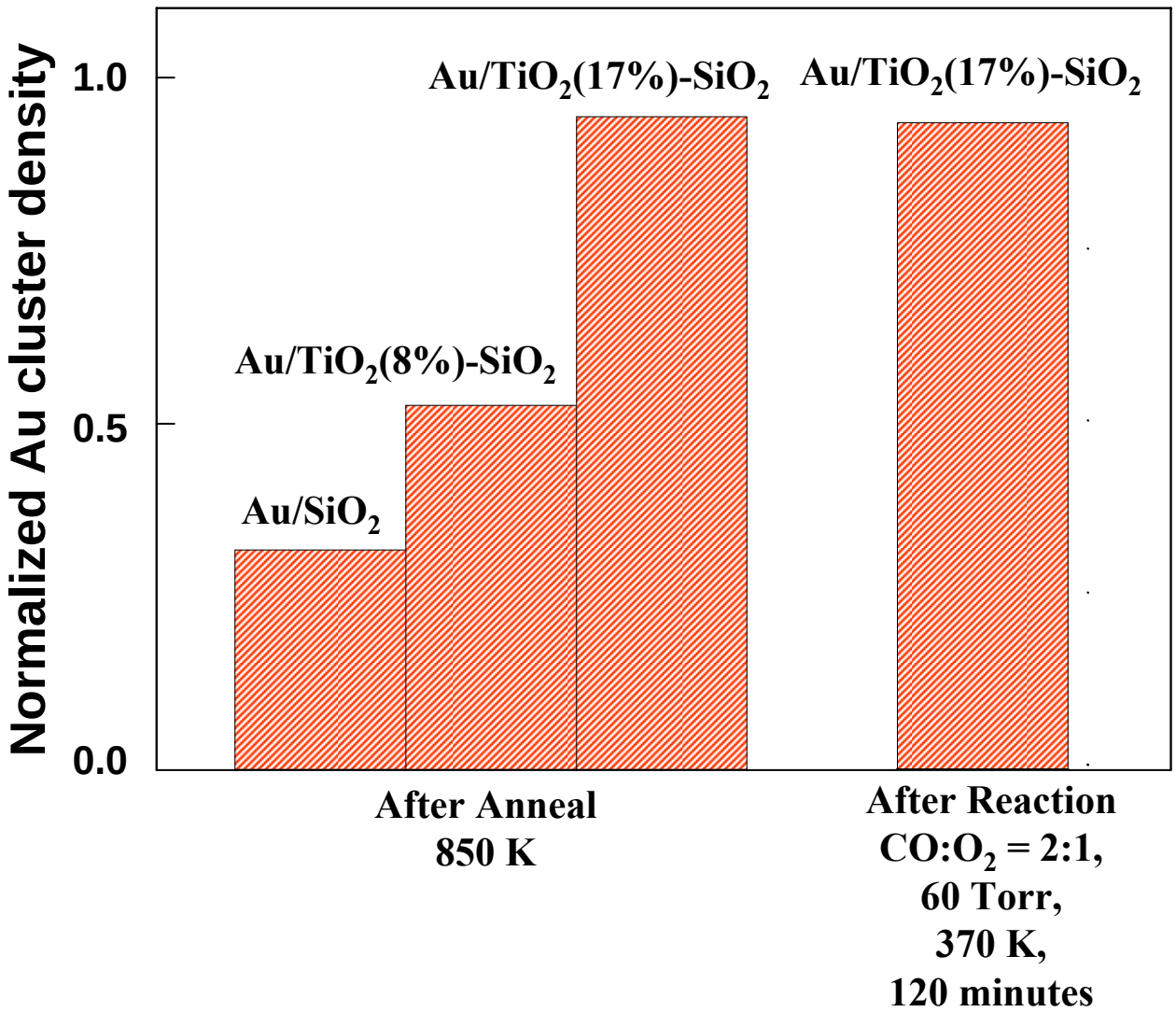
PM-IRAS
Yun Cai

Lo-T IRAS
Cheol-Woo Yi

MIES
Sungsik Lee

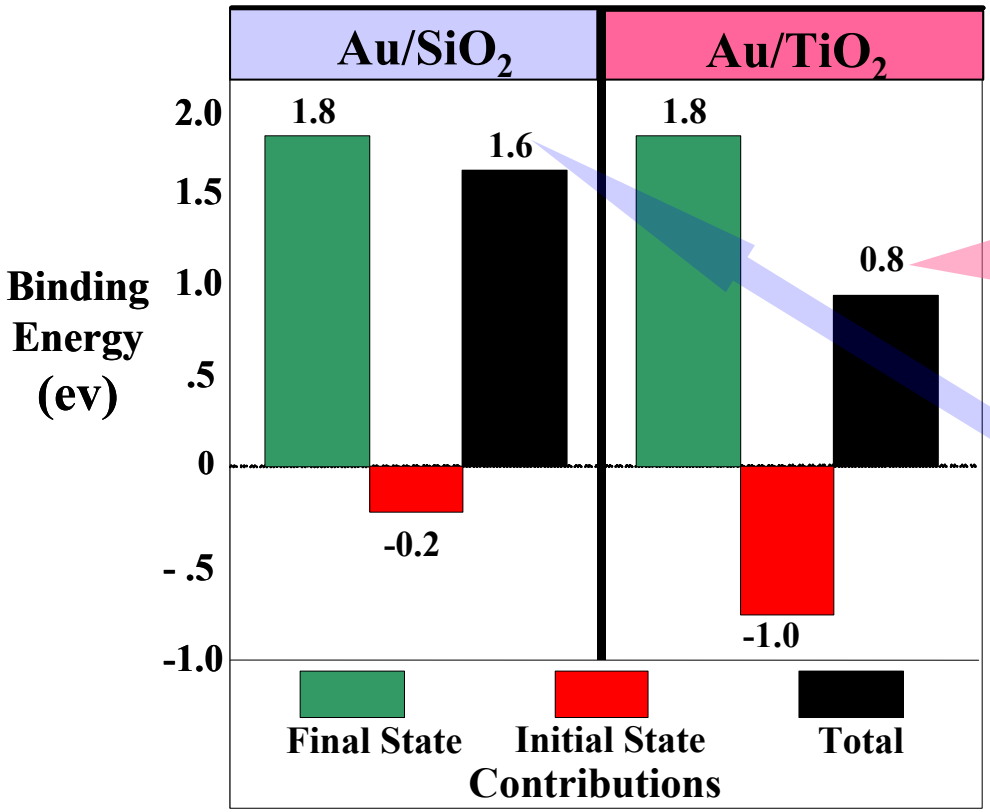
Hi-SA Supported Catalysts
Zhen Yan
Bo Wang

Au Cluster Density After The Indicated Treatment Normalized To The Cluster Density After Nucleation At Room Temperature

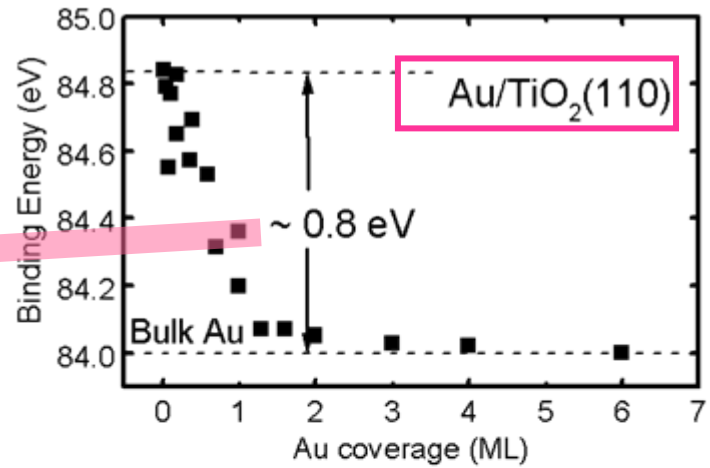


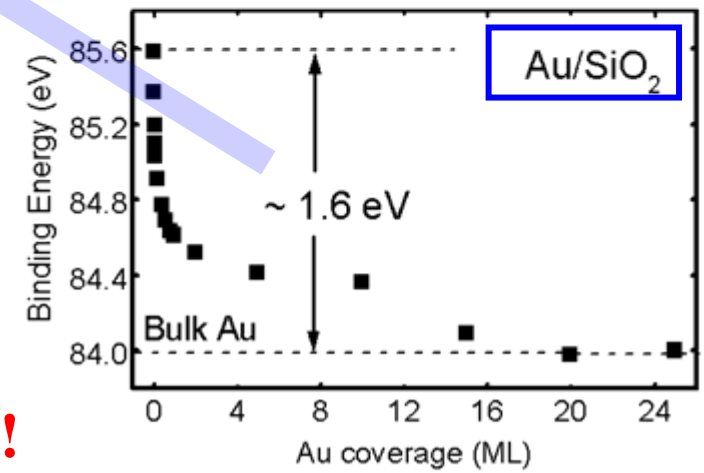
XPS Core Level Shifts: Au/SiO_2 vs. Au/TiO_2

Core Level Shift: Bulk – Small Cluster Limit



XPS Core Level Shifts





Implications: electron-rich Au on TiO_2!

DFT Calculations for Au and Au/TiO_2(110)

Yang, Wu, Goodman, PRB (2000)