



# Nanoparticle Reactivity

10 September 2009

TNT 2009 - Trends in NanoTechnology

**Dr. Michael R. Berman**

Aerospace, Chemical, & Material Sciences

Air Force Office of Scientific Research

DISTRIBUTION A: Approved for public release; distribution unlimited.



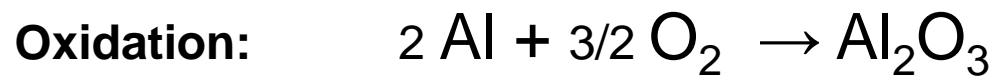
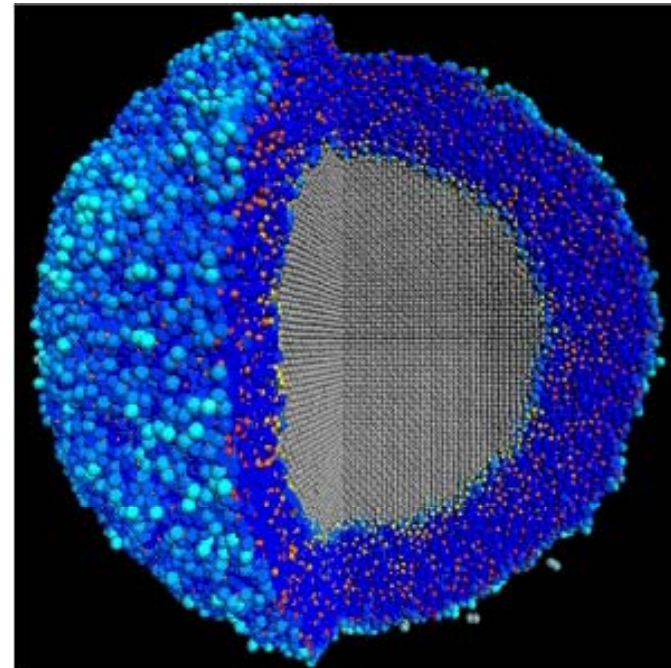
# Some Factors Affecting Nanoparticle Reactivity



- **Composition**
- **Morphology**
- **Electronic structure**
- **Geometry**
- **Spin**
- **Defects**
- **Size**
- **Fluxionality**
- **Diffusion**
- **Electric Fields**
- **Crystal Face**
- **Adsorbates**
- **Interactions with neighbors**
- **Substrate interactions**



# Aluminum Nanoparticles



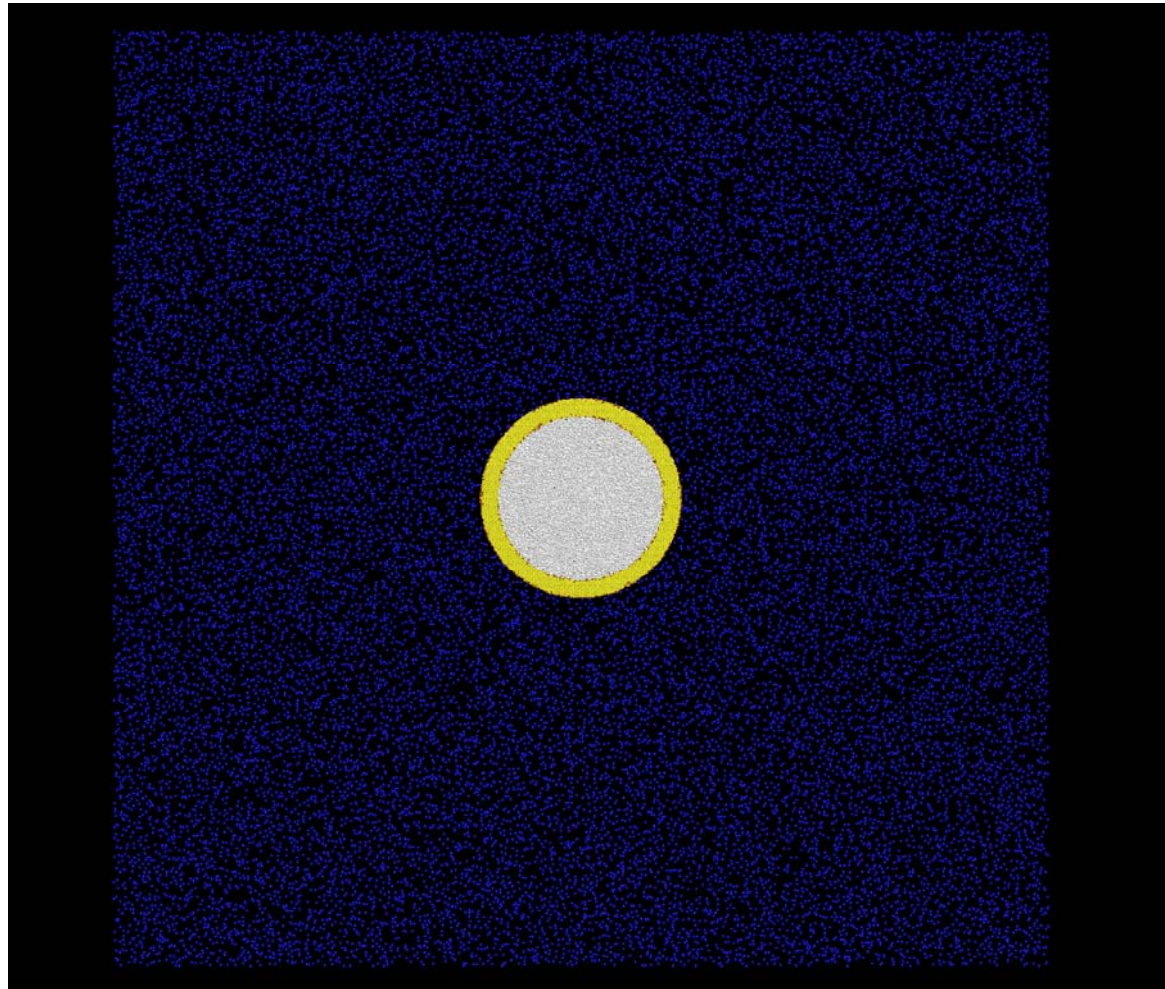
**Melting T:** 660 °C                      2054 °C



# Oxidation of Laser Heated Aluminum Nanoparticle



Crystalline  $\text{Al}_2\text{O}_3$   
shell, 4 nm thick  
48 nm Al core



Expansion  Shell Broken  Oxidation Reaction

*Vashishta, Kalia, Nakano; USC*

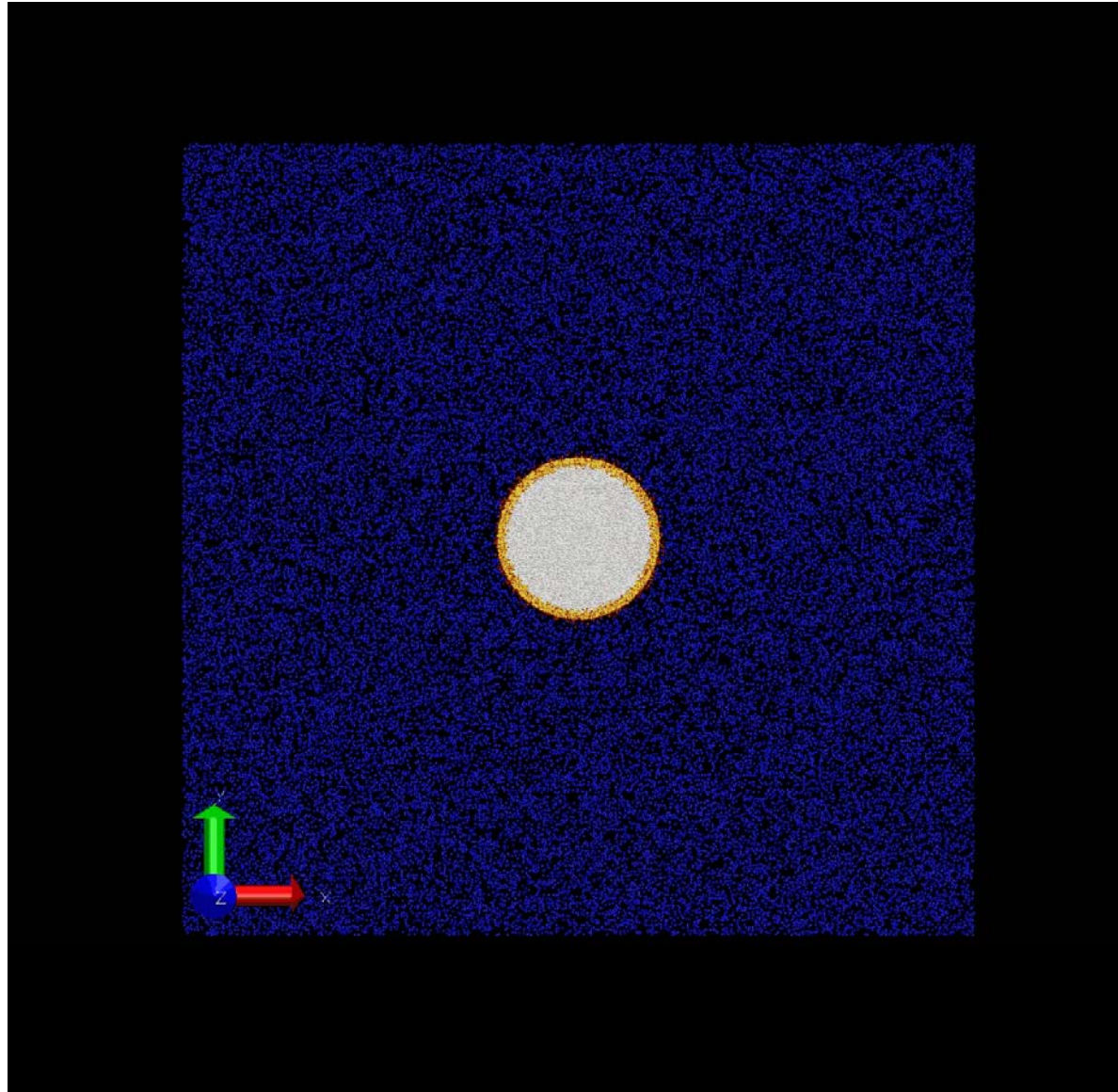




# Oxidation of Laser Heated Amorphous Aluminum Nanoparticle

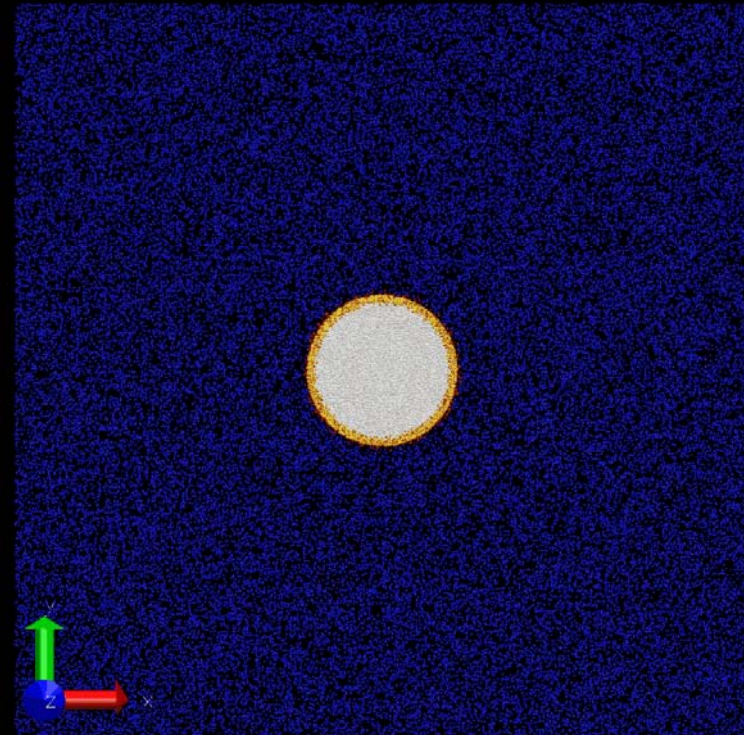
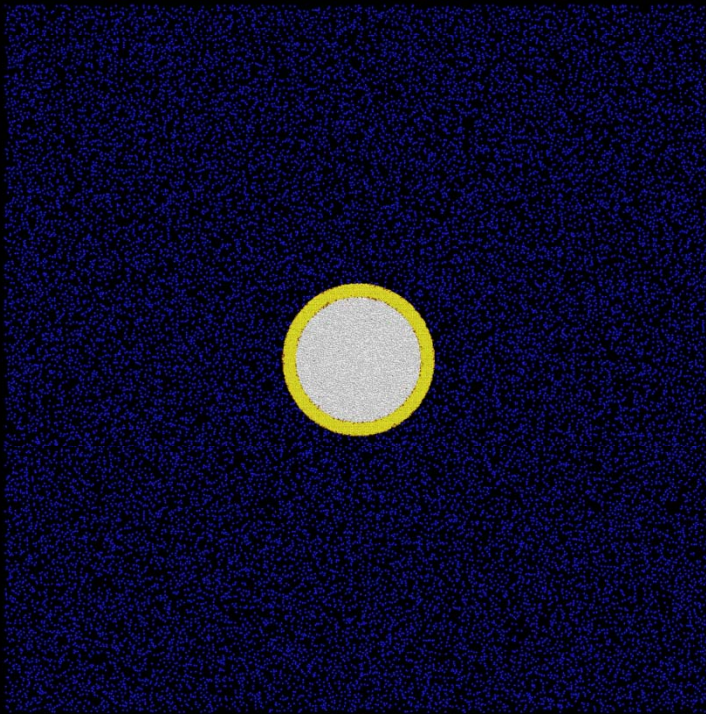


Amorphous  $\text{Al}_2\text{O}_3$   
shell, 4 nm thick  
48 nm Al core





# Crystalline and Amorphous Nanoshell Explosion

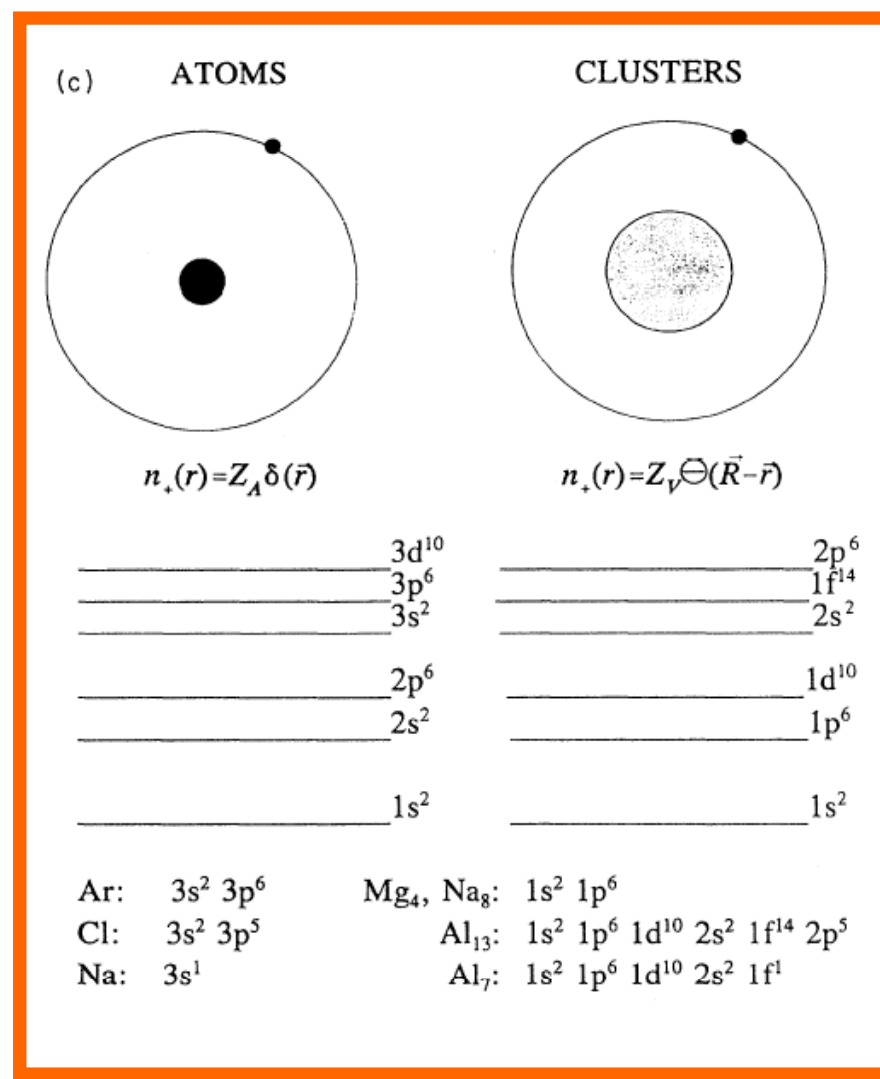
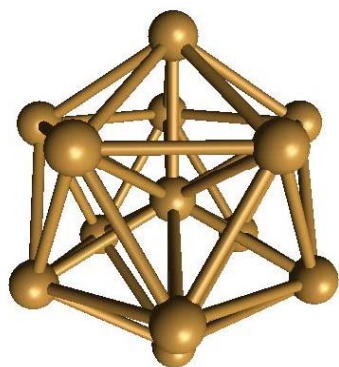
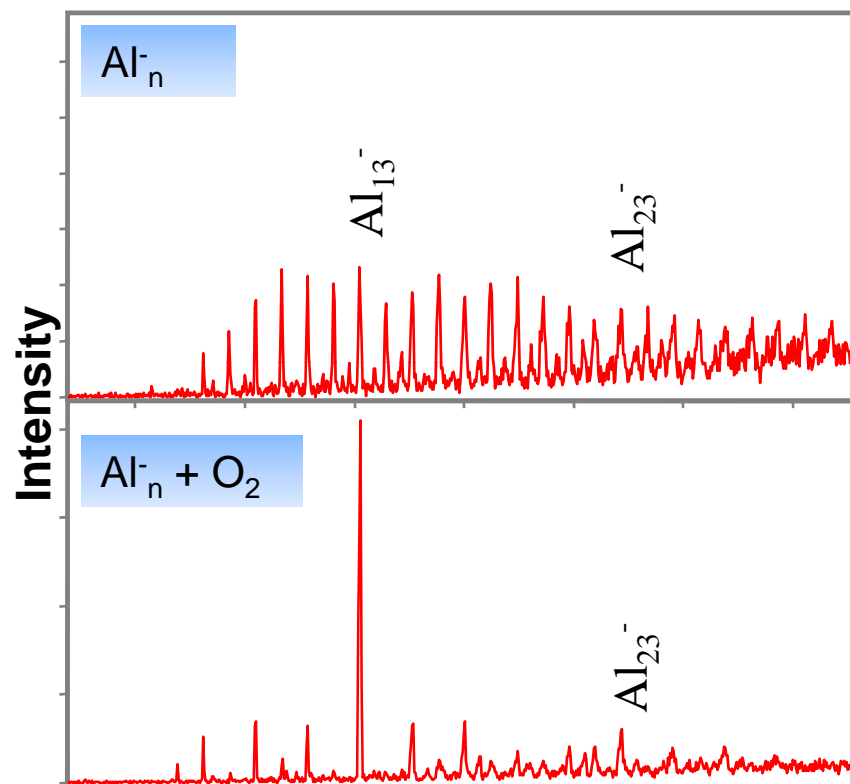


Crystalline: Expansion → Shell Broken → Oxidation Reaction  
Amorphous: Expansion → Shell Shattered → Oxidation Reaction





# Reactions of Aluminum Clusters/Nanoparticles



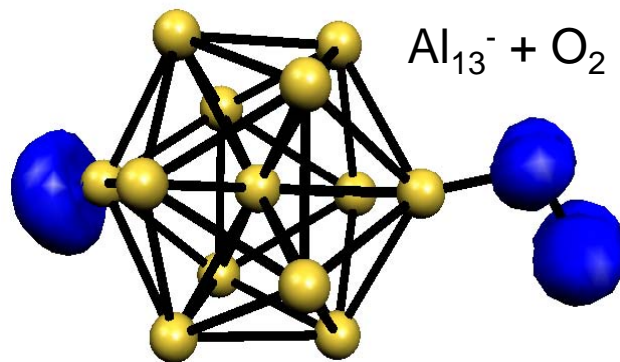
Castleman, Penn. St; Khanna, VCU



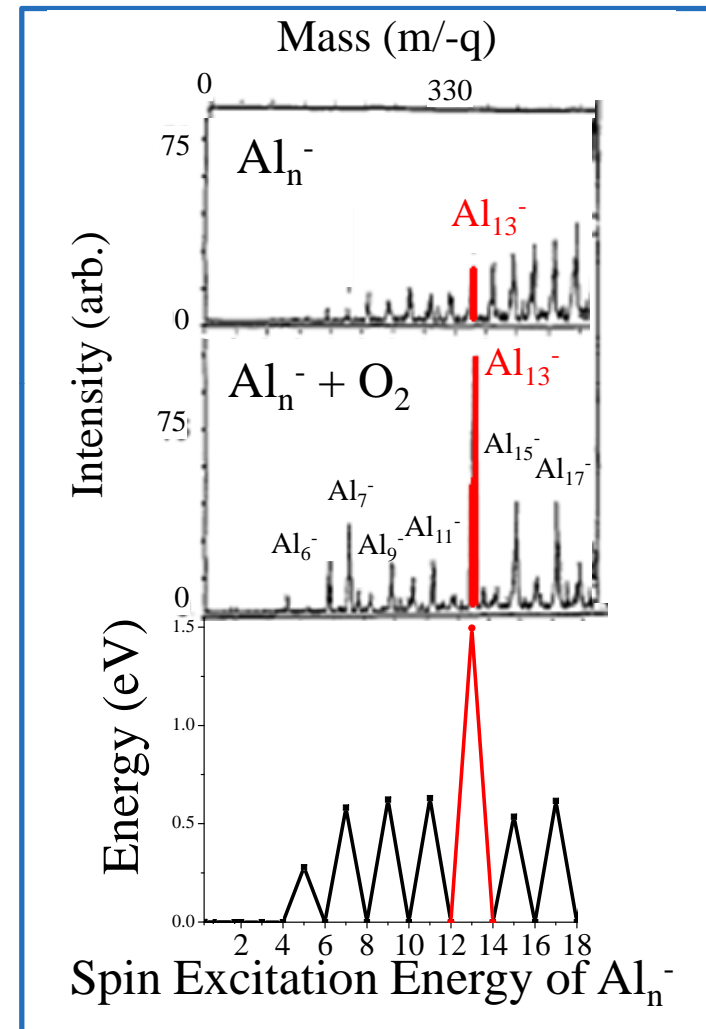
# Effect of Spin on Reactivity



- Odd electron clusters (even number of aluminum atoms) react instantaneously.
- Even electron clusters show variable reactivity with  $\text{Al}_{13}^-$  and  $\text{Al}_{23}^-$  resisting etching.
- $\text{O}_2$  is spin triplet and its **spin** must transfer to metal cluster for strong reaction
- Spin Accommodation Energy affects reactivity; energy required to excite even electron clusters to spin triplet to accommodate **spin**



$\text{Al}_{13}^-$  has high spin excitation energy.  
Spin (blue region) remains on  $\text{O}_2$ ;  
Etching resistant.



Khanna, Castleman and co-workers;  
*J. Amer. Chem. Soc.* **129** 16098 (2007); 8  
*PNAS* **104** 14565 (2007)

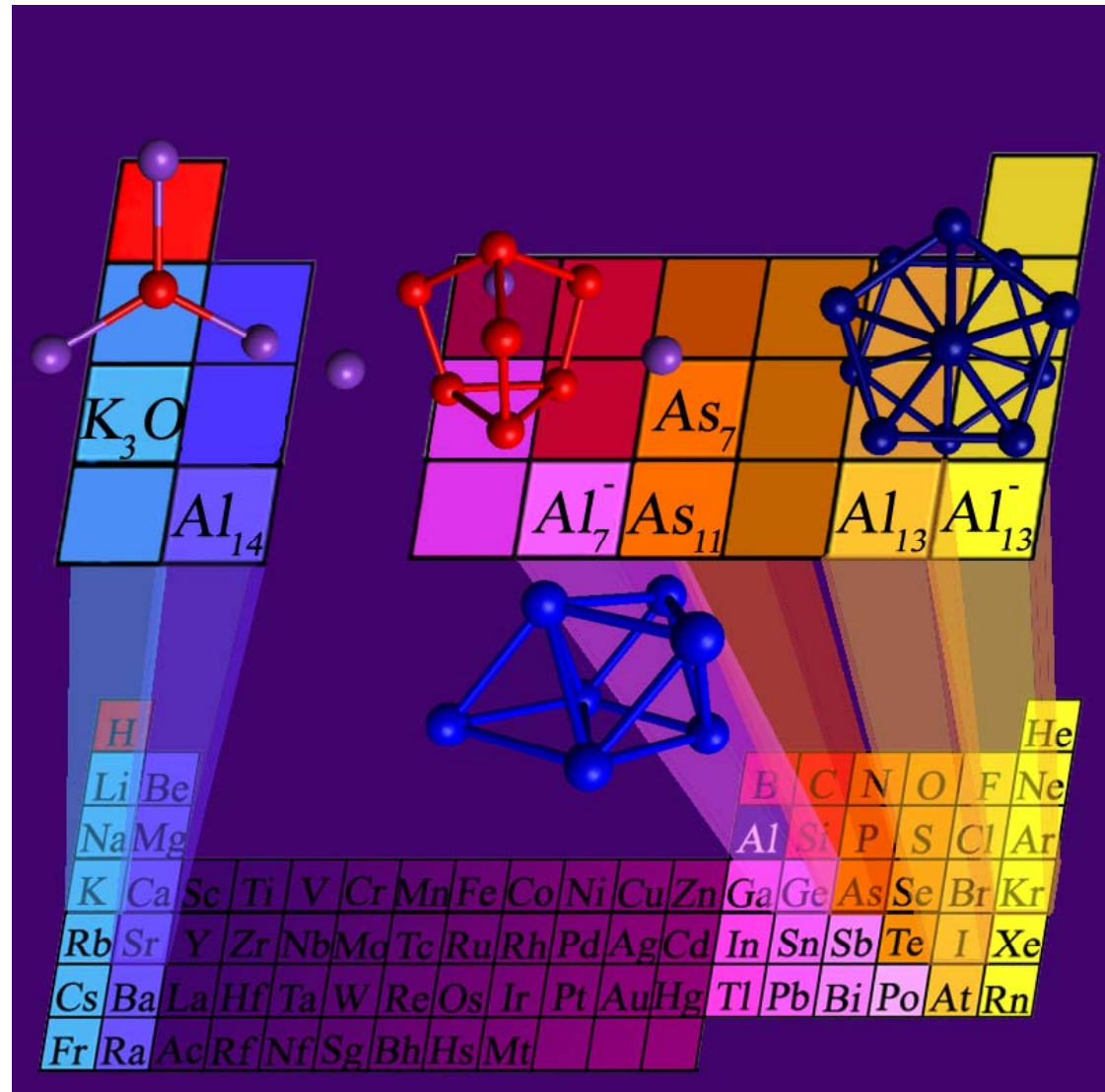




# Superatoms and Periodicity



- Various clusters or “superatoms” display properties similar to those of elements in the periodic table.
- Stability is achieved by filling shells of electrons (in jellium model or other descriptions).
- Analogy provides model for how cluster-assembled materials can be developed
- First cluster-assembled material prepared,  $K_3As_7$



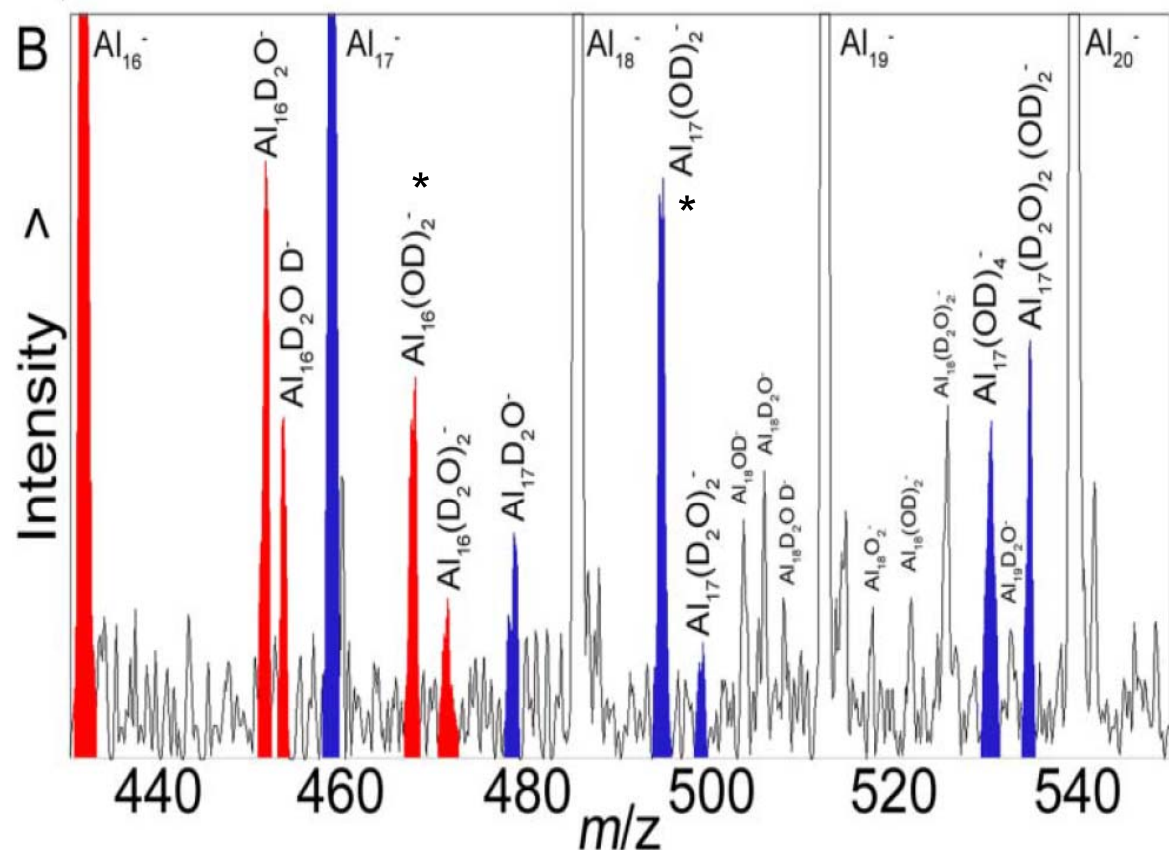


# Reactivity of Aluminum with Water



- Aluminum + ice propellant – Yetter et al., others
- Selective reactivity of aluminum clusters

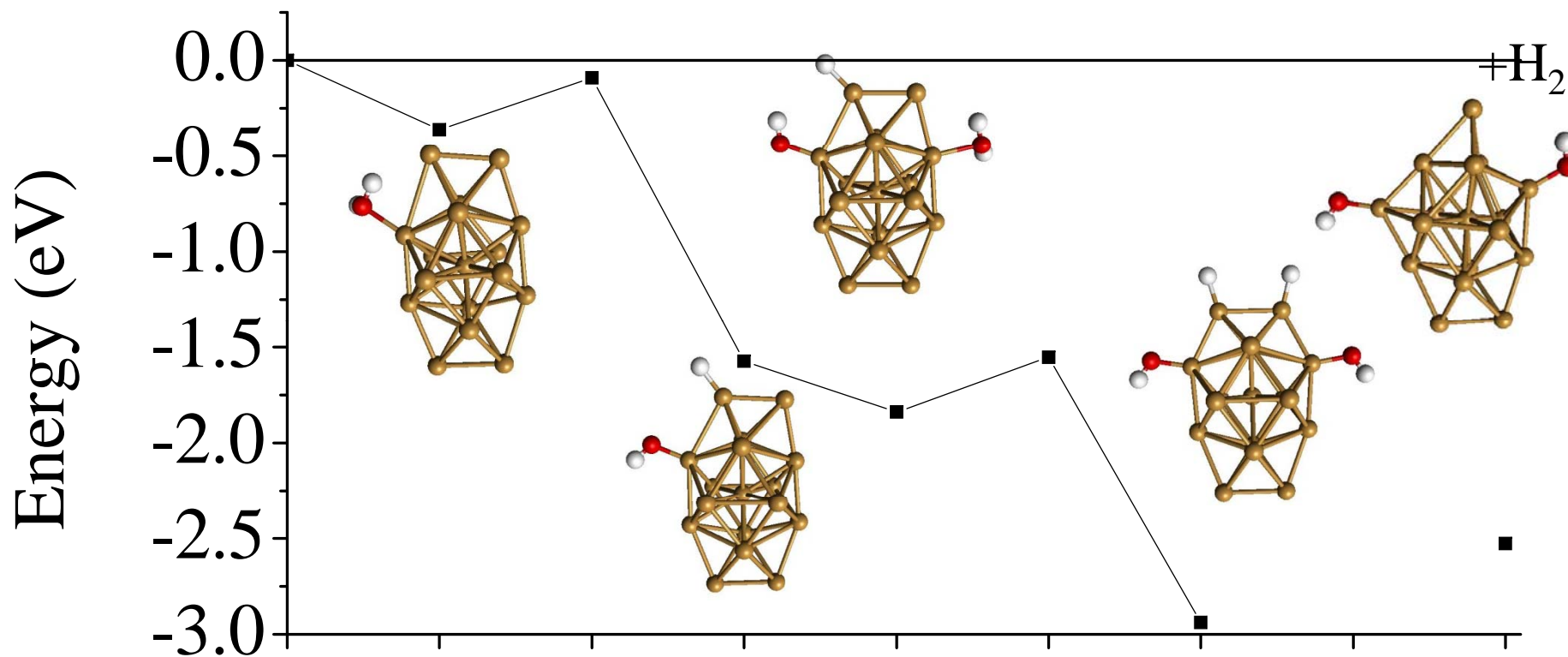
- Dissociative adsorption of water on aluminum cluster anions
- Loss of  $H_2$  for  $Al_n^-$  with  $n = 16-18$



Castleman, Penn St.



# Some Aluminum Nanoparticles React with Water to Produce H<sub>2</sub>



*Reactivity (loss of H<sub>2</sub>) seen for Al<sub>n</sub><sup>-</sup> with n = 12, 16-18.*

*LUMO energies predict other clusters would react*

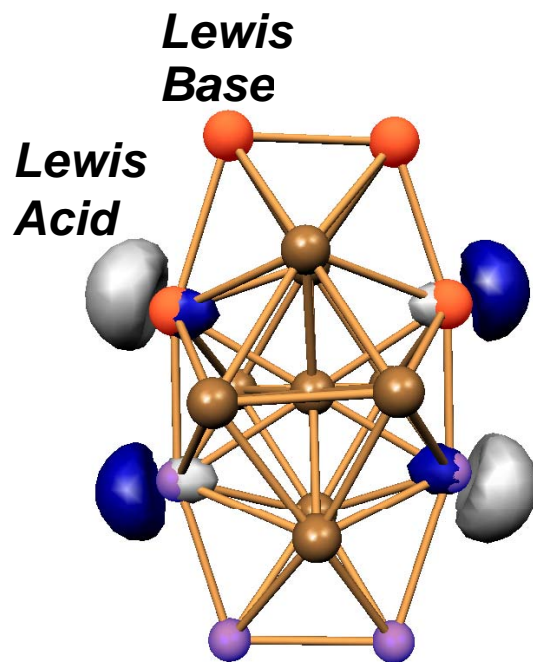
*Castleman, Penn St.  
Khanna, VCU*

*Science* **323**, 492 (2009)

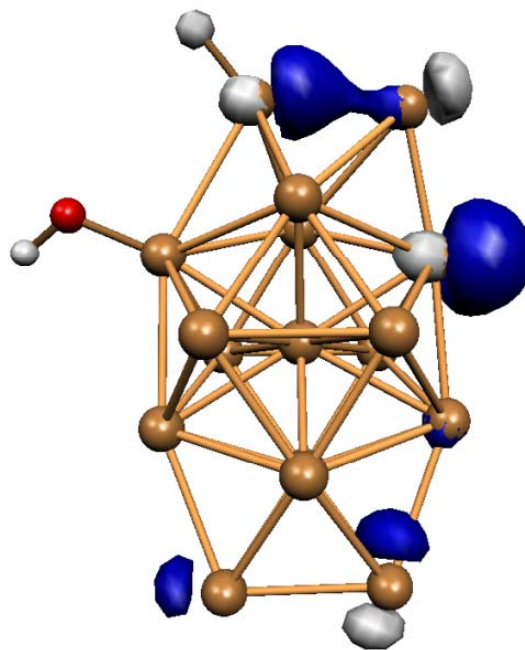




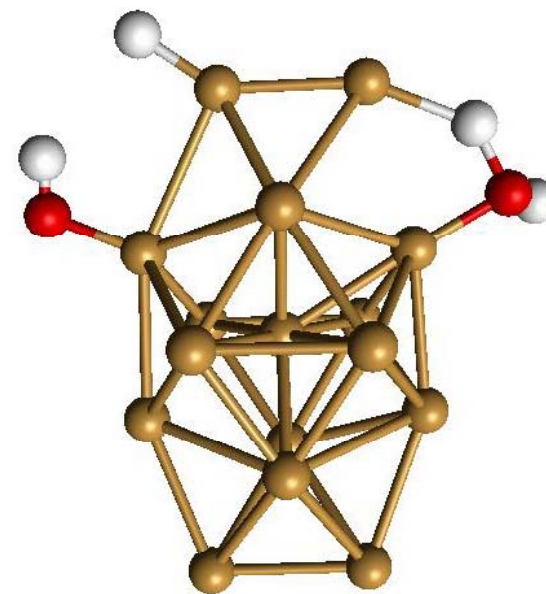
# Water Adds to Specific Sites of the $\text{Al}_{17}^-$ Cluster



$\text{Al}_{17}^-$   
(showing  
LUMO)



$\text{Al}_{17}^- + \text{H}_2\text{O}$   
(dissociative  
adsorption)



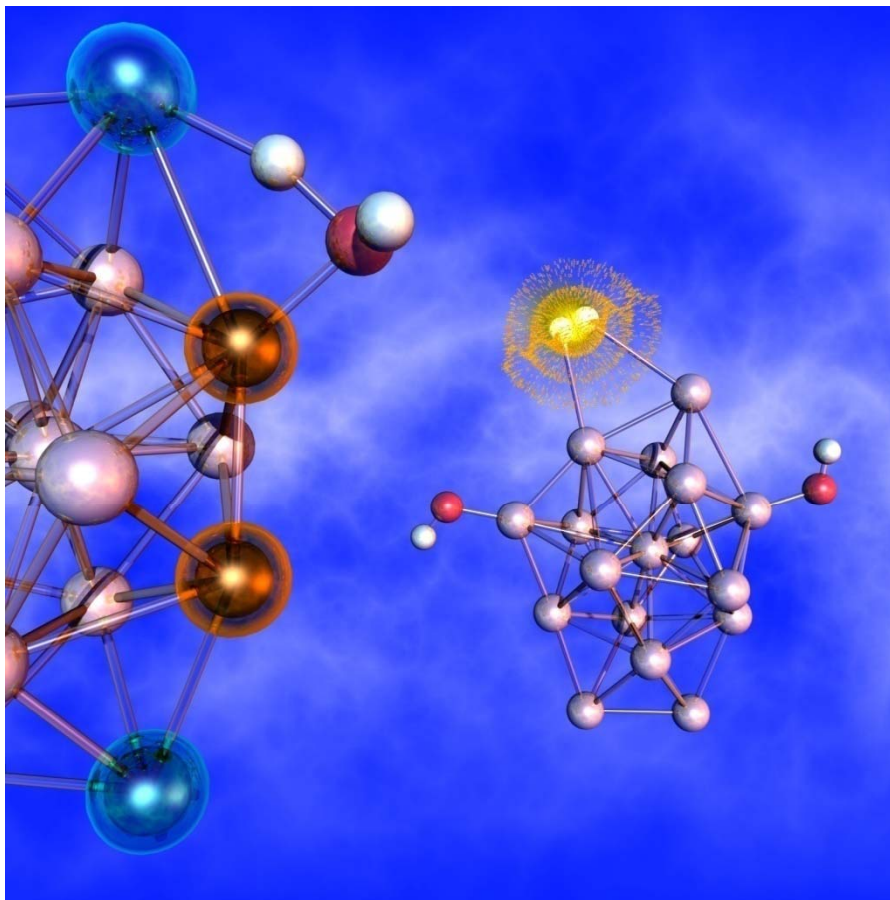
$\text{Al}_{17}^- + 2\text{H}_2\text{O}$   
(transition  
state)



# New Lessons Learned about Cluster Reactivity



- Complementary active sites cause size-selective reactivity
  - *Proximate Lewis acid and Lewis base sites*
- Geometric factors are critical in determining reactivity
- Water split on Al clusters to form molecular hydrogen
  - *Can the active cluster easily be regenerated?*
- Do other OH-containing molecules react with  $Al_n$ ?



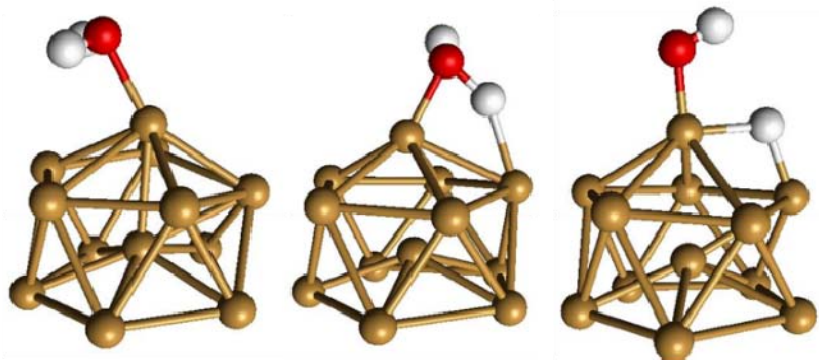
Castleman, Penn St., Khanna, VCU; *Science* **323**, 492 (2009)



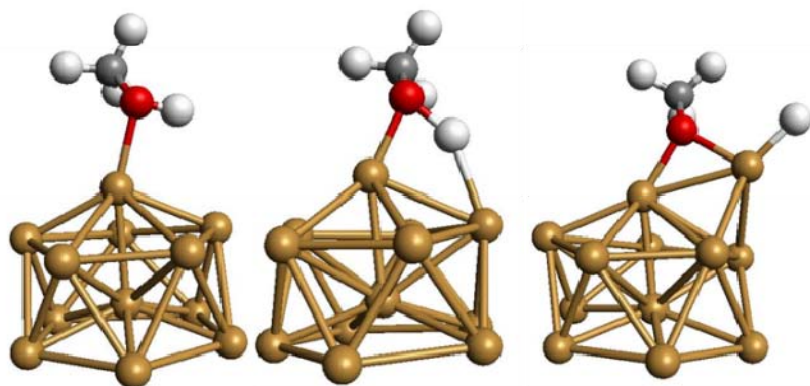
# Reactions of Methanol with Aluminum Clusters



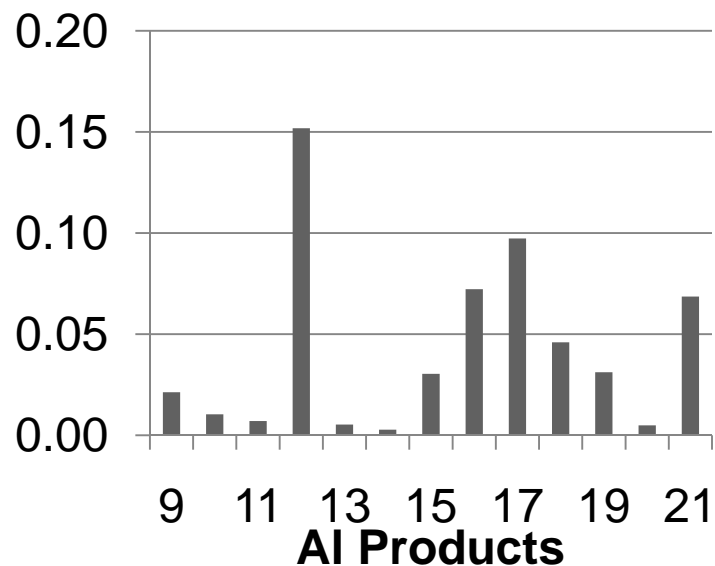
Water



Methanol



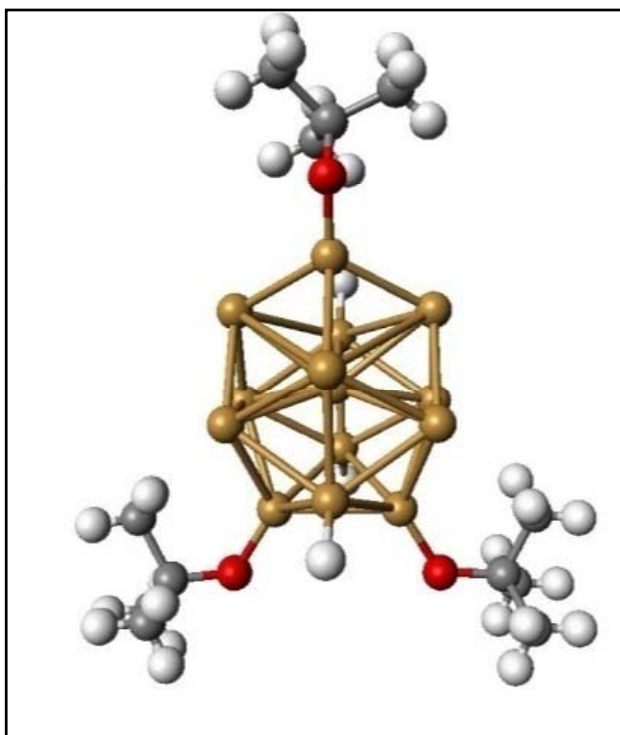
- Methanol reactivity energetics very similar to water
- $n = 12, 16, 17, 18$  most reactive
- $n = 11, 13, 20$  least reactive
- Energetically favorable
- Adsorption of several methanol molecules seen



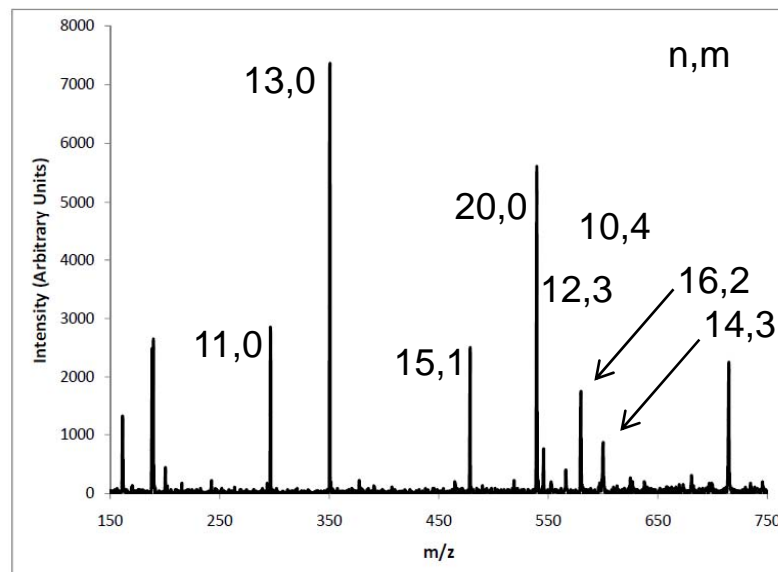




# Reactions of Butanol with Aluminum Clusters



- Passivates aluminum sites and tethers organic molecules to Al
- Future work: preserve aluminum clusters through steric hindrance of the surface active sites





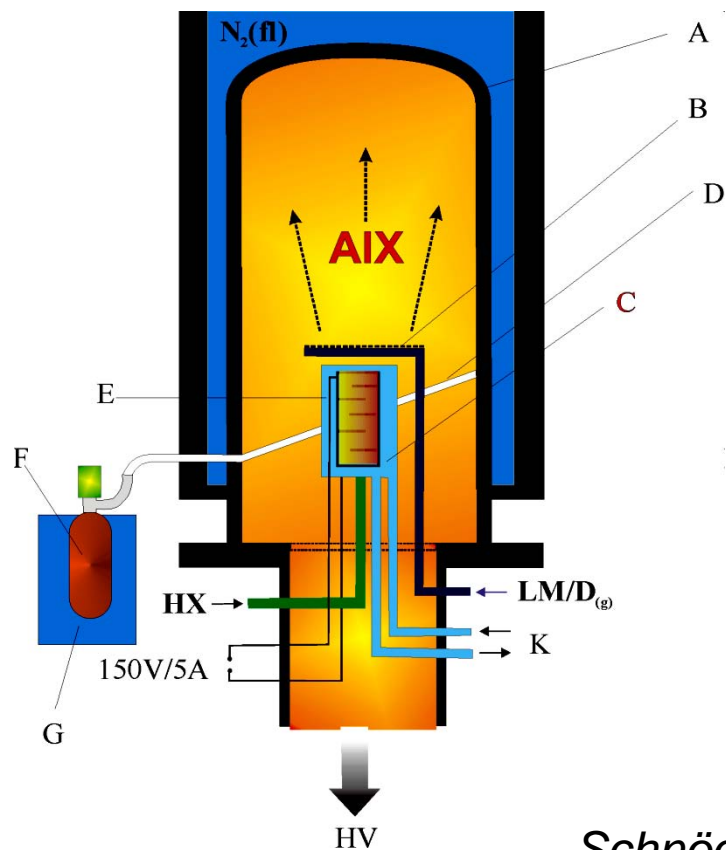
# Bulk Synthesis of Al-based Clusters



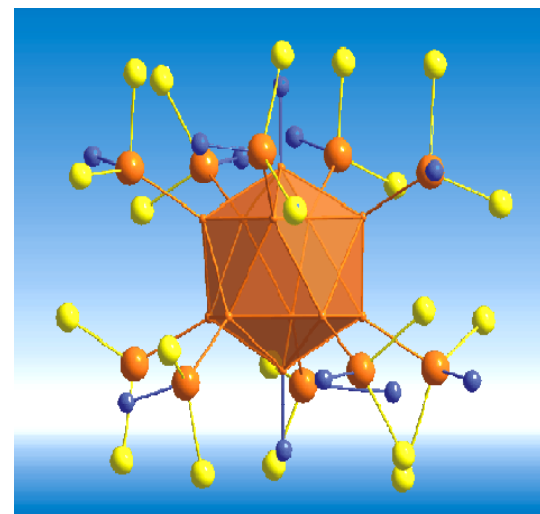
$\text{Al (vapor)} + \text{HCl} \rightarrow \text{AlCl (vapor, then frozen)}$

$\text{Li}[\text{P}(\text{t-Bu})_2] + \text{AlCl} \rightarrow \text{Al}_4[\text{P}(\text{t-Bu})_2]_6$

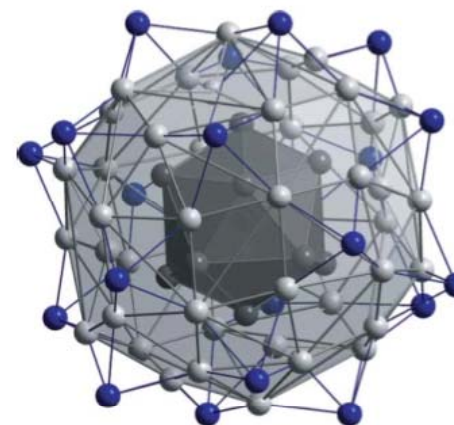
Structure determined by X-Ray crystallography



*Schnöckel, Karlsruhe*



$\text{Al}_{12}(\text{AIBr}_2)_{10} \times 12 \text{ THF}$



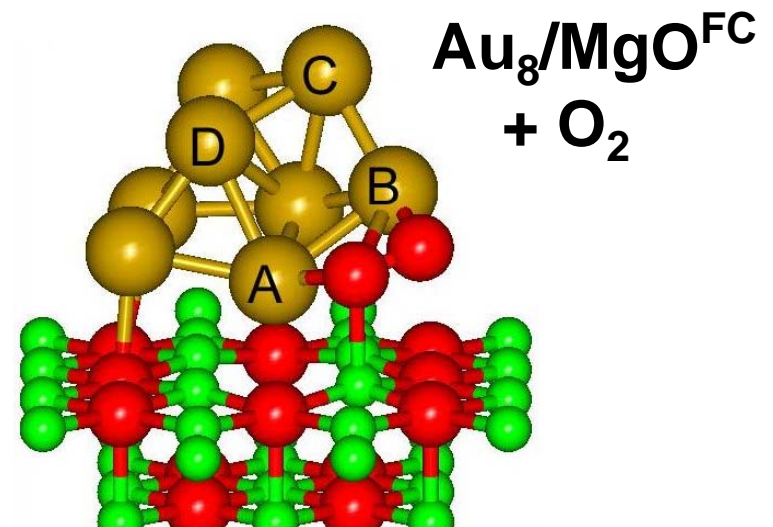
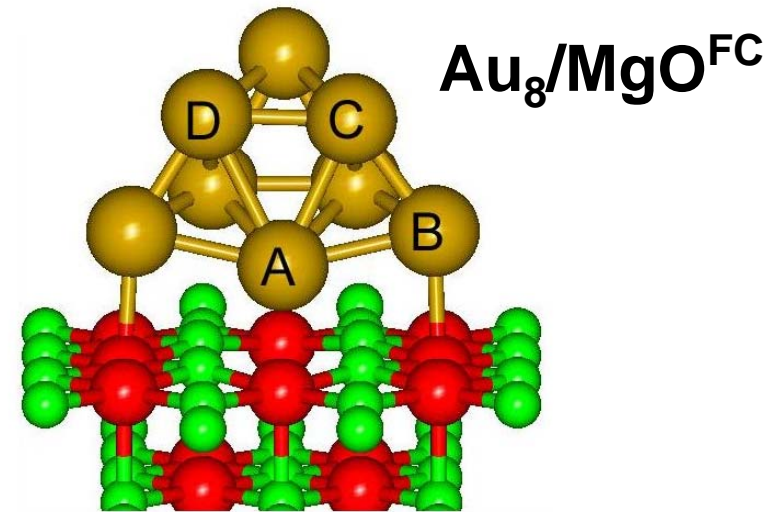
$\text{Al}_{77}$  Cluster



# Principles of Nanocatalysis



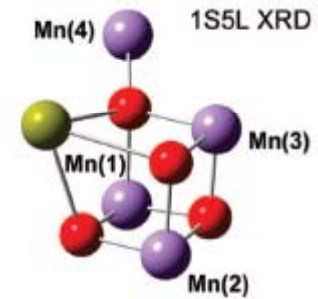
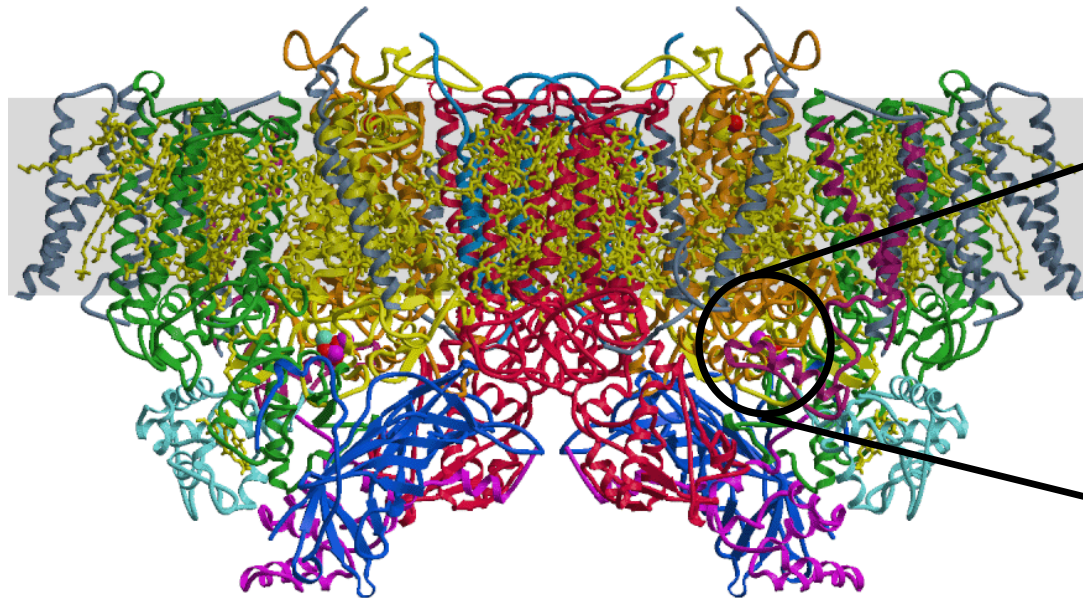
- **Dynamic Structural Fluxionality**
  - Rearrangement of cluster permits adsorption of  $O_2$
- **Spectral Quantum Size Effect**
  - Cluster size affects energy levels
  - Position of HOMO, LUMO, Fermi level
  - Antibonding orbitals of  $O_2$  below Fermi level and resonant with Au orbitals can weaken or bonding in adsorbate
- **Impurity-Doping Modifications and Control**
  - Control of position of orbitals with respect to Fermi level







# Nanoparticle Catalyst in Photosystem II

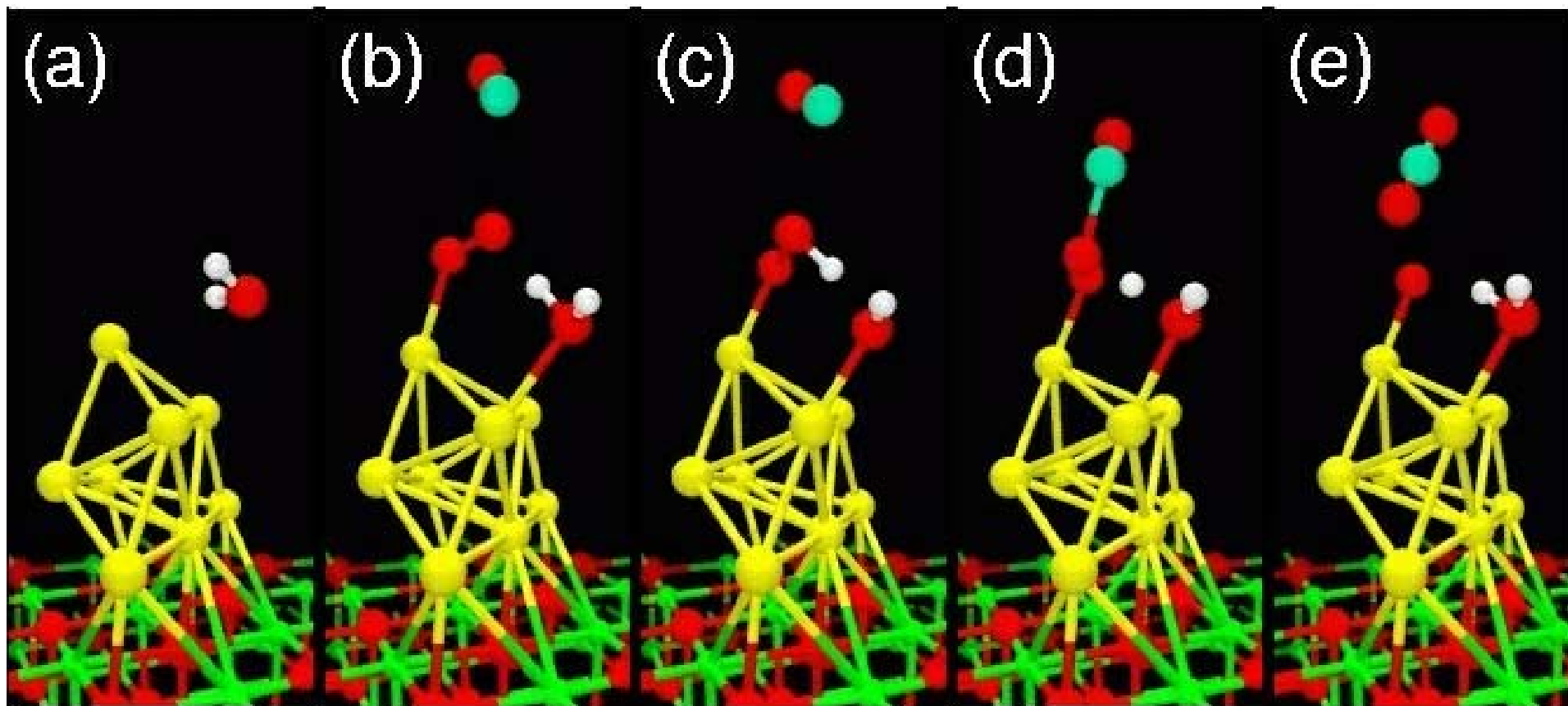


Oxygen Evolving Complex  
Active site in PSII

*Photosystem II oxidizes water in plants to produce molecular oxygen*



# Enhancement of Nanocatalysis by Water and Substrates



Effects of adsorbates: weakening bonds

Effects of substrates: charge donation

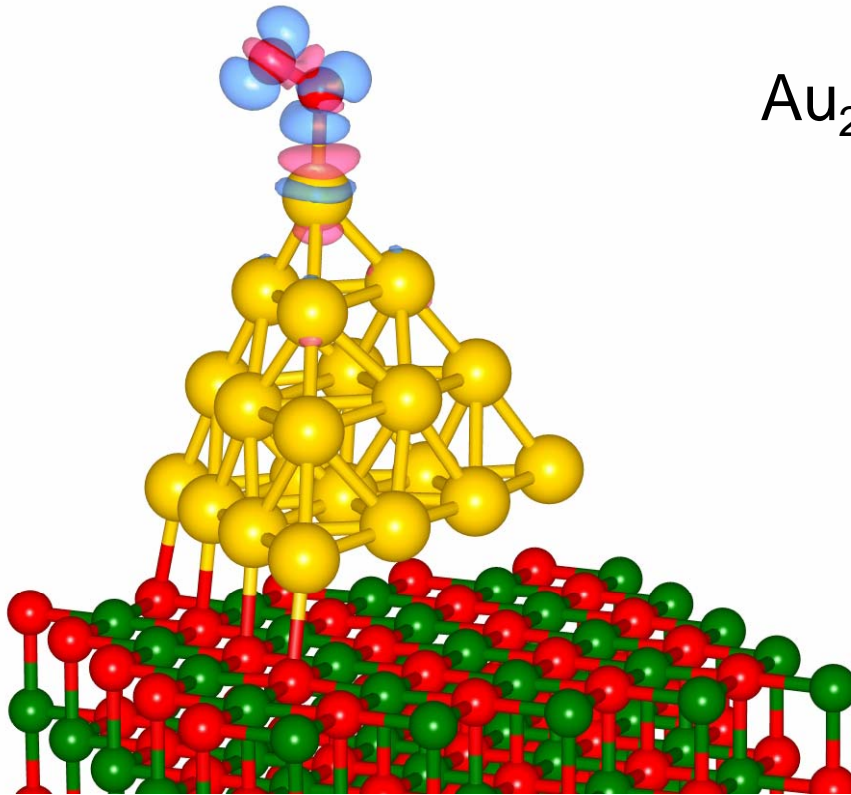


# Electric Field Induced Nanocatalytic Activation of O<sub>2</sub>



Landman, Georgia Tech

Au<sub>20</sub> on MgO

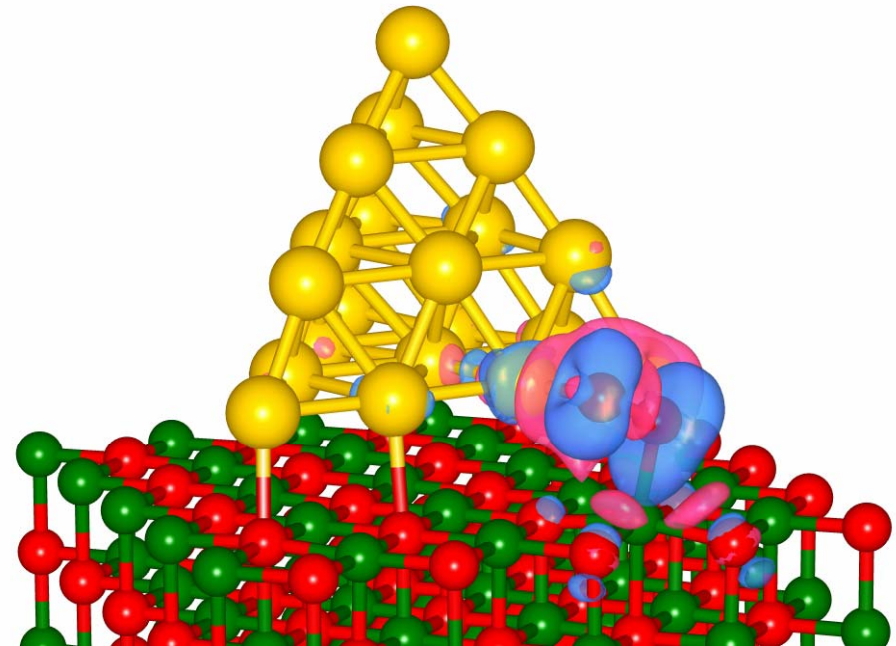


→  $E_z = 0.0 \text{ eV/\AA}$

$d_{\text{oo}} = 1.275 \text{ \AA}$  *non-activated*

$\text{BE}[\text{O}_2] = 0.19 \text{ eV}$

$\Delta Q(\text{O}_2) = 0.159e$



→  $E_z = 0.2 \text{ eV/\AA}$

\*  $d_{\text{oo}} = 1.41 \text{ \AA}$  *activated*

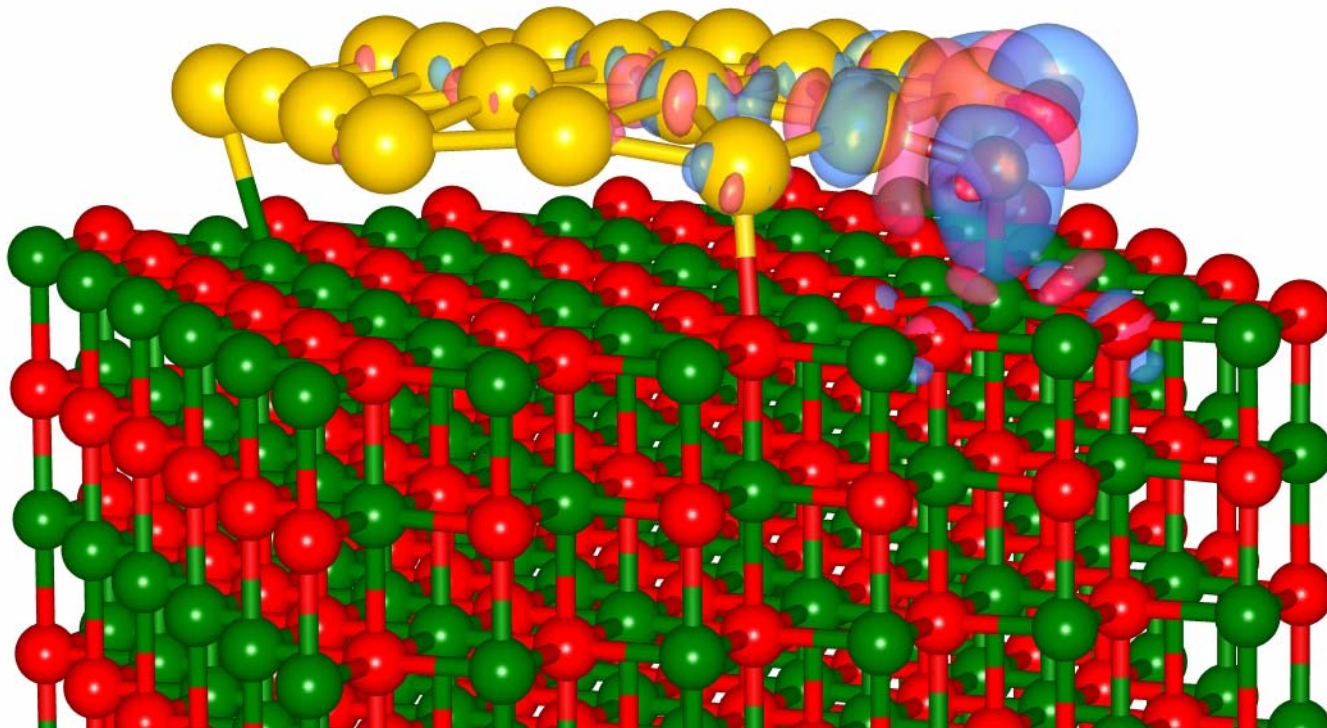
$\text{BE}[\text{O}_2] = 0.37 \text{ eV}$

$\Delta Q(\text{O}_2) = 0.421e$





# Electric Field Activation of Planar Gold Nanocatalyst



$$E_z = 0.2 \text{ eV/\AA}$$

$$d_{\text{oo}} = 1.44 \text{ \AA}$$

$$\text{BE}[\text{O}_2] = 0.98 \text{ eV}$$

$$\Delta Q(\text{O}_2) = 0.413 \text{ e}$$

*activated  
O<sub>2</sub>*

Landman, Georgia Tech  
Phys. Rev. Lett. **100**, 056102 (2008)

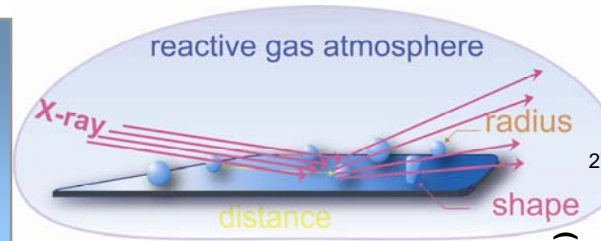




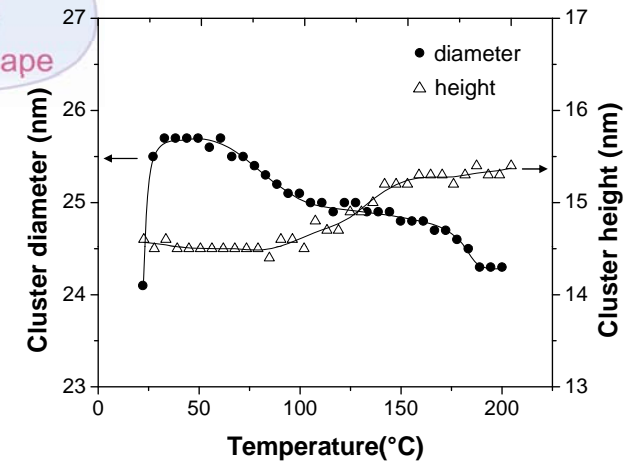
# Probing the Catalyst/Support Interface Using GISAXS



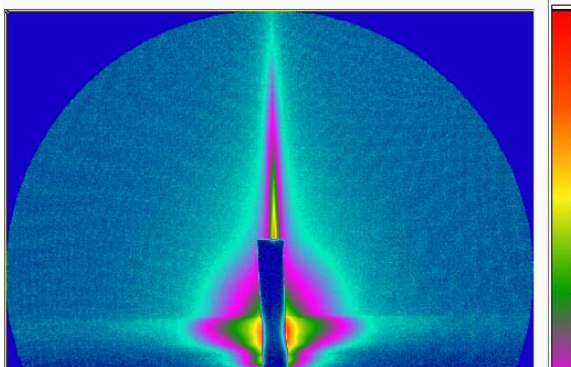
- *In situ* Grazing Incidence Small Angle X-ray Scattering
- Size-selected Ag clusters (few nm) catalyzing rxn of propylene + O<sub>2</sub>
- New capability to probe catalyst/support interactions



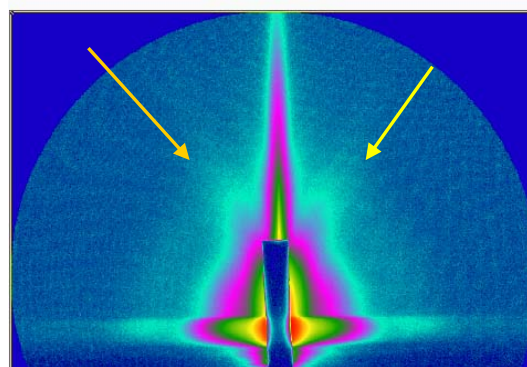
Exp'ts performed at Argonne Advanced Photon Source



reaction time



spherical particle



- flattening (decrease in height)

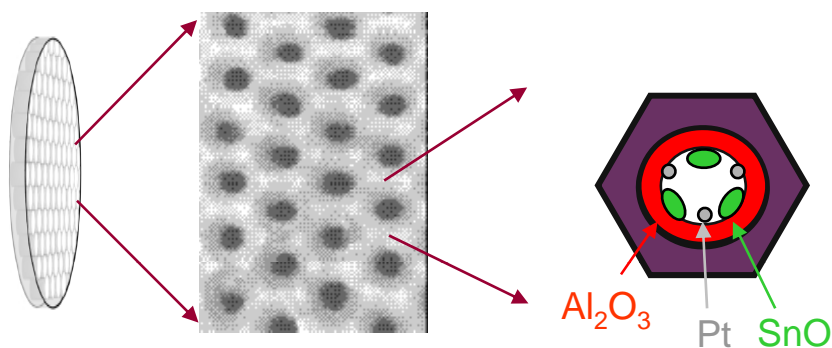
- change of wetting angle at the nanoparticle/support interface



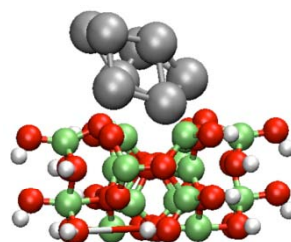
# Platinum Nanoclusters Catalyze Dehydrogenation of Propane



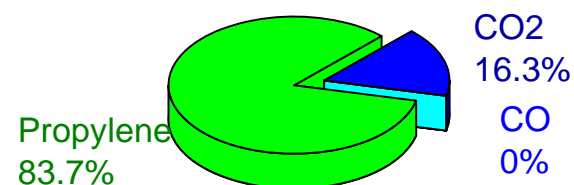
Pt<sub>8-10</sub> clusters on nanoporous anodized aluminum oxide membranes (AAO)



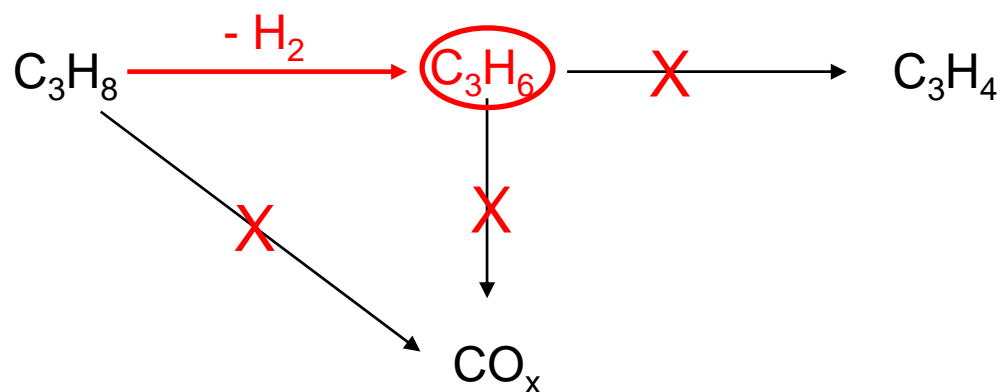
~10<sup>11</sup> nanoreactors/cm<sup>2</sup>



## Catalytic Performance



- Conversion rate: up to 23%
- Turn over freq: 0.8 - 2.9 s<sup>-1</sup>  
(x40-100 higher than prev.)

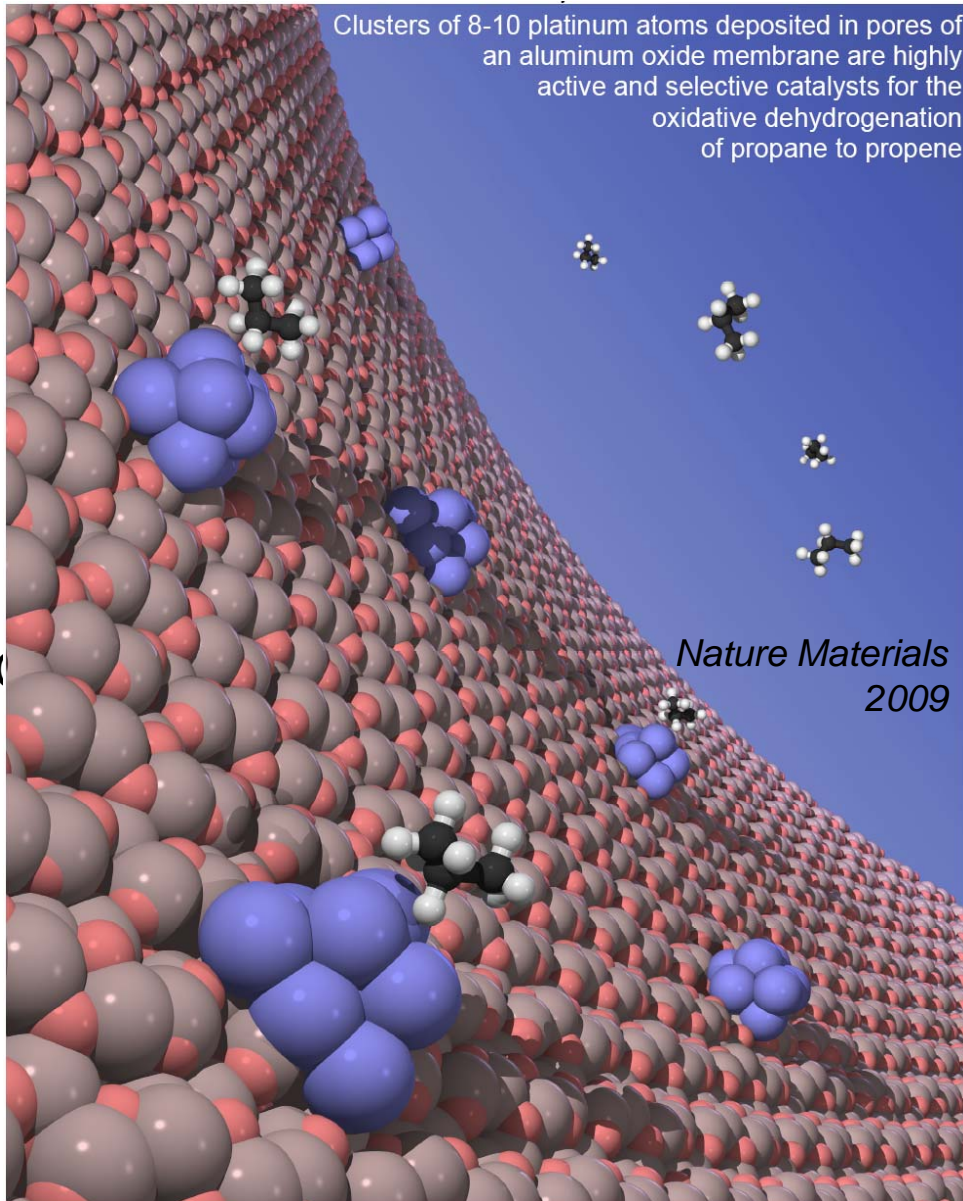


Vajda, Argonne/Yale;  
*Nature Materials*, 2009

- First highly active and selective catalyst for oxidative propane dehydrogenation
- Stable catalyst; no sintering
- Calculations on Pt<sub>4</sub> and Pt<sub>8</sub> indicate preferential breaking of the C-H bond
- Endothermic fuels applications

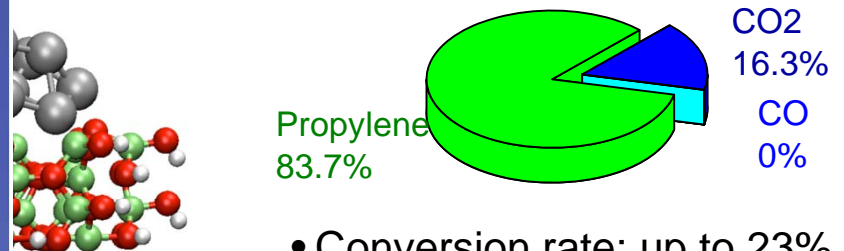


# Platinum Nanoclusters Catalyze Dehydrogenation of Propane



aluminum oxide membranes (AAO)

## Catalytic Performance



- Conversion rate: up to 23%
- Turn over freq: 0.8 - 2.9 s<sup>-1</sup>  
(x40-100 higher than prev.)

- First highly active and selective catalyst for oxidative propane dehydrogenation
- Stable catalyst; no sintering
- Calculations on Pt<sub>4</sub> and Pt<sub>8</sub> indicate preferential breaking of the C-H bond
- Endothermic fuels applications





# Fischer-Tropsch Synthesis on Size-Selected Ni and Co Clusters



## Motivation:

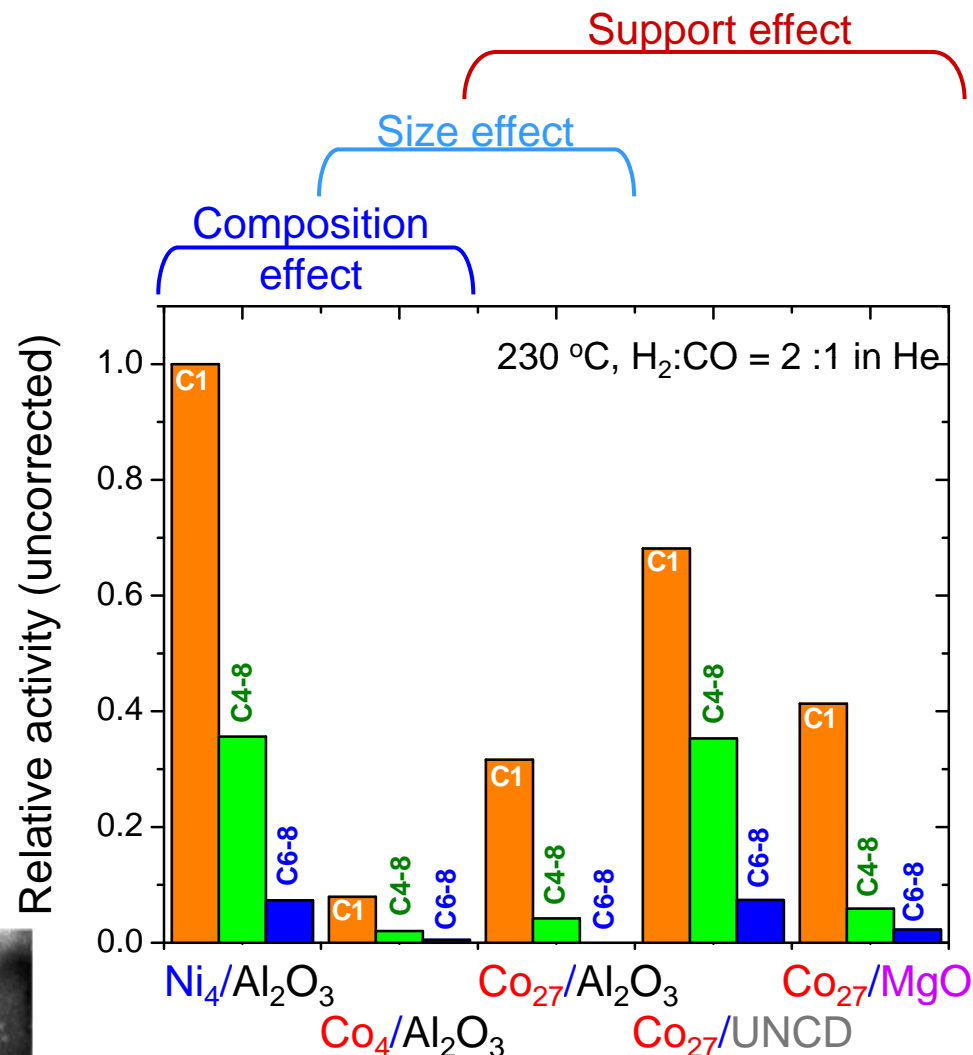
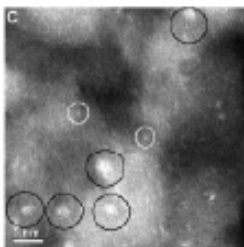
- $(2n+1)H_2 + nCO \rightarrow C_nH(2n+2) + nH_2O$
- Primary catalyst: Co
- Particle size effect unclear (<2 nm)
- Design new class of catalytic mat'ls

## Results:

- Small clusters are effective catalysts
- Composition: Ni > Co
- Size:  $Co_{27} > Co_4$
- Support:  $Co_{27}$  on MgO >  $Co_{27}$  on  $Al_2O_3$

***A few very active sites dominate the process***

Vajda, Argonne/Yale

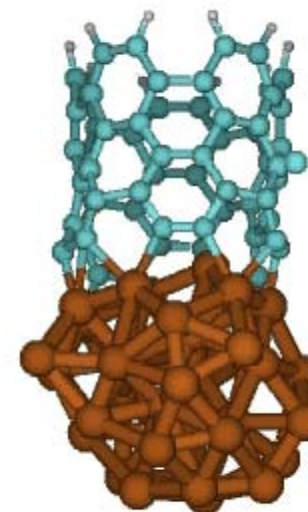
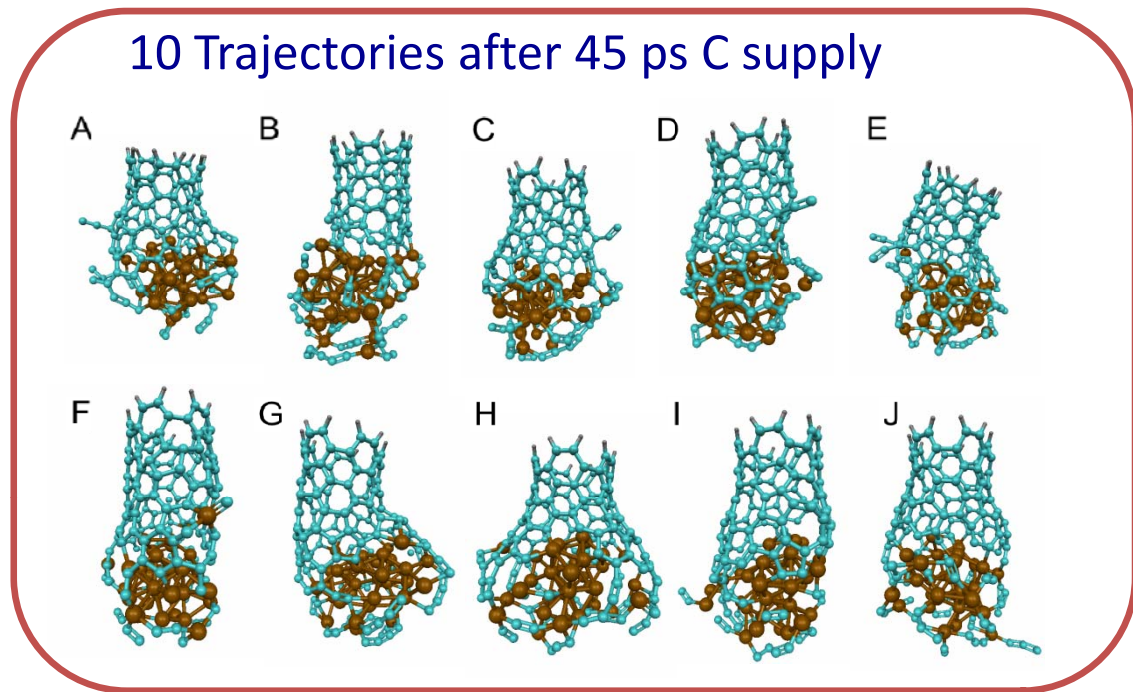


Hutchings and co-workers,  
*Science* **321**, 1332 (2008)

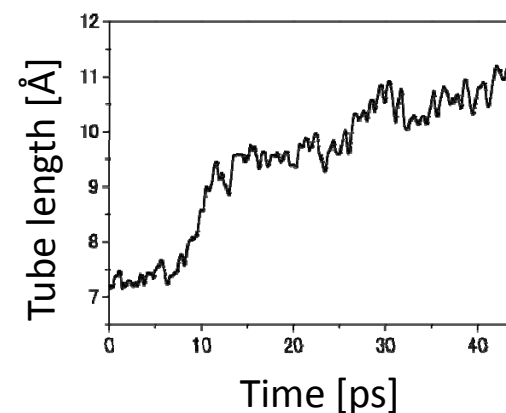


ACS Nano 2, 1437 (2008)  
Morokuma, Emory Univ.

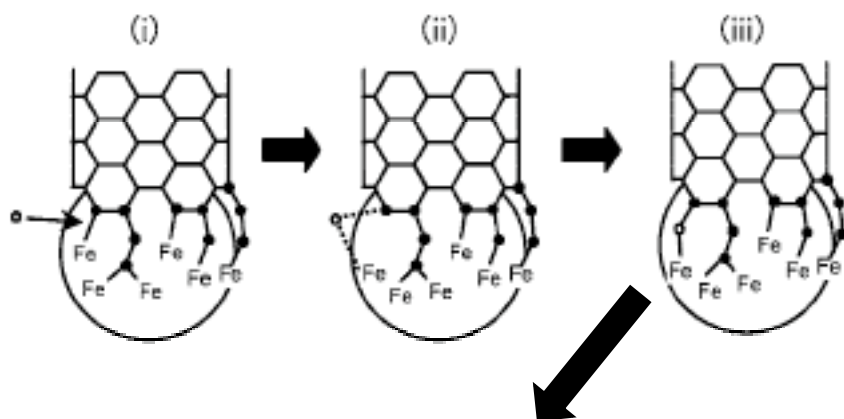
## 10 Trajectories after 45 ps C supply



Trajectory F



## Schematic depiction of C atom insertion events



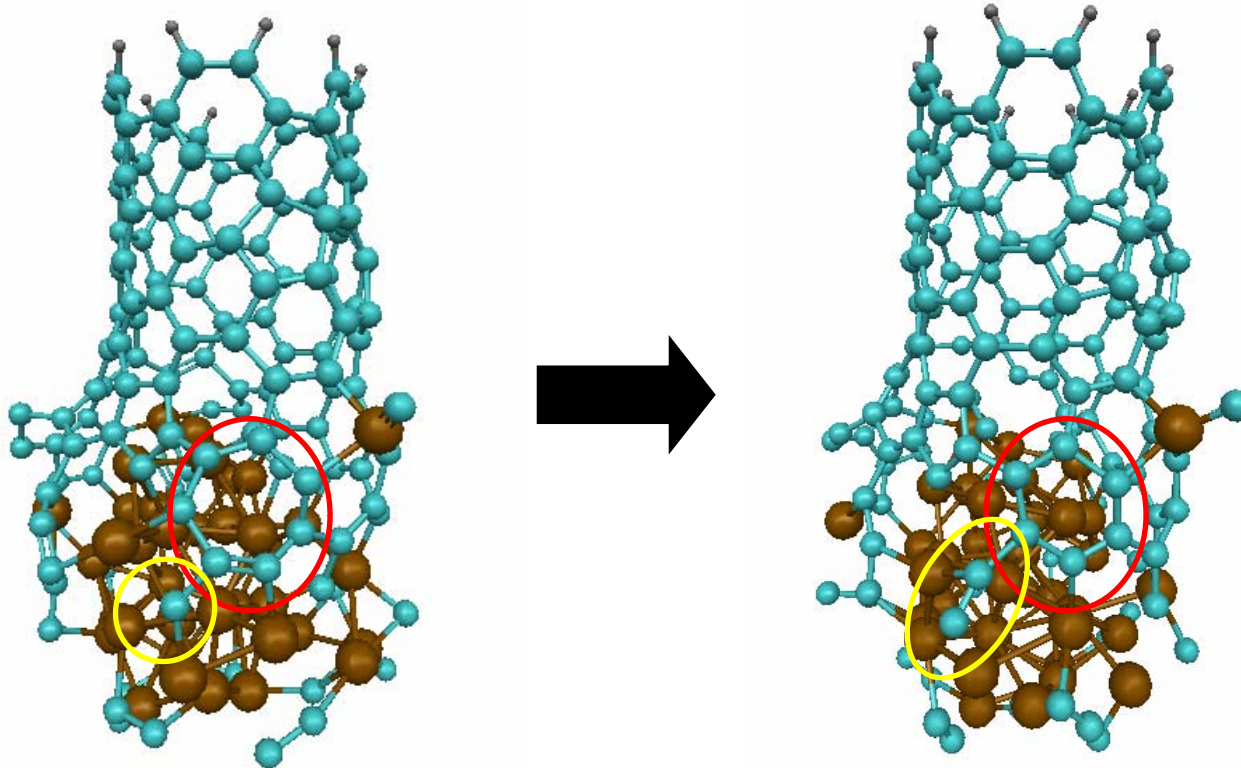
new 5-, 6-, 7-membered rings

Growth rate: ~10 pm/ps

# Self-healing process of sidewall (annealing)

**Fe-Carbon mobility at interface important!**

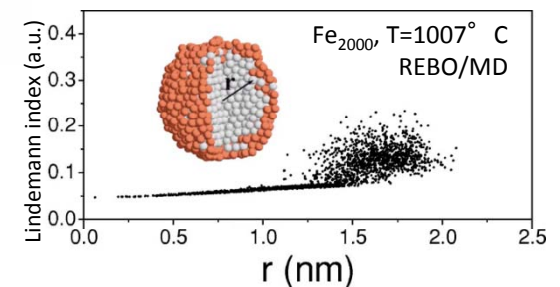
Trajectory 6:  $T_n = 1500$  K,  $T_e = 10k$  K,  $C_{int} = 1500$  K



24.5 ps - 27.5 ps

**Heptagon** + **C** changes into **hexagon** + **C<sub>2</sub>**

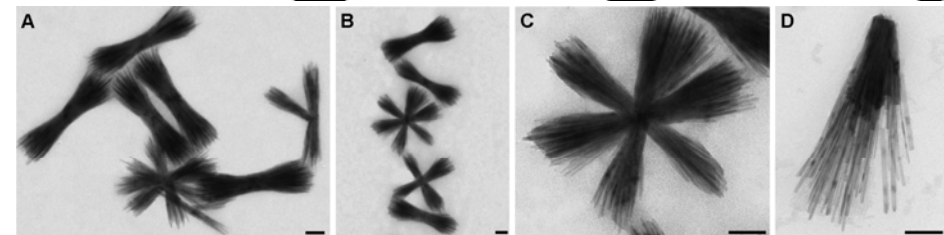
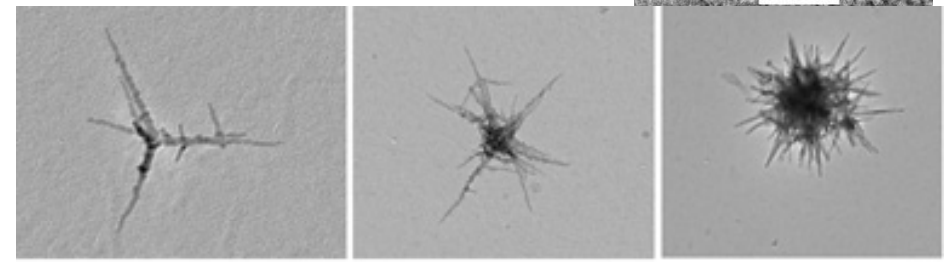
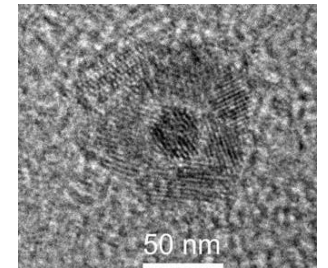
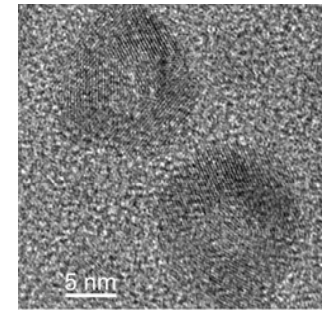
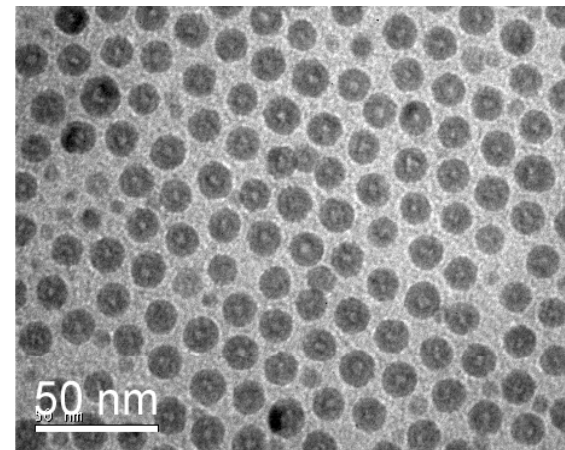
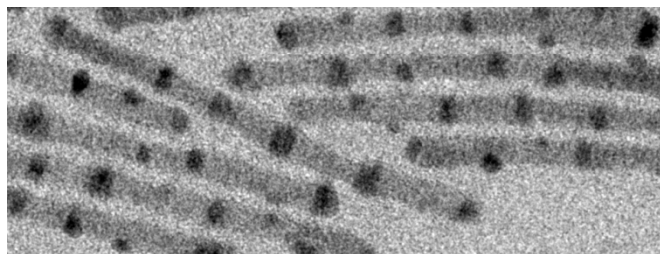
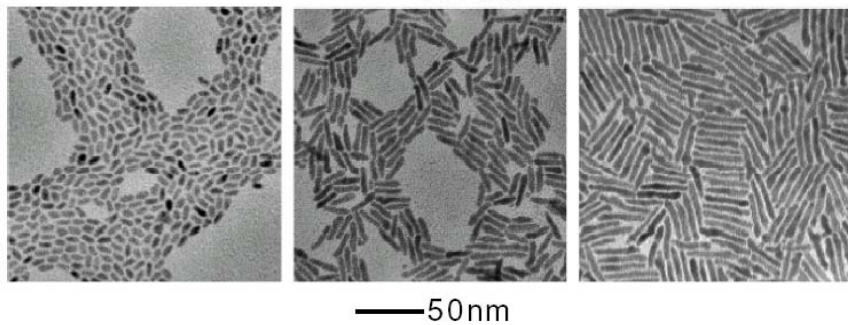
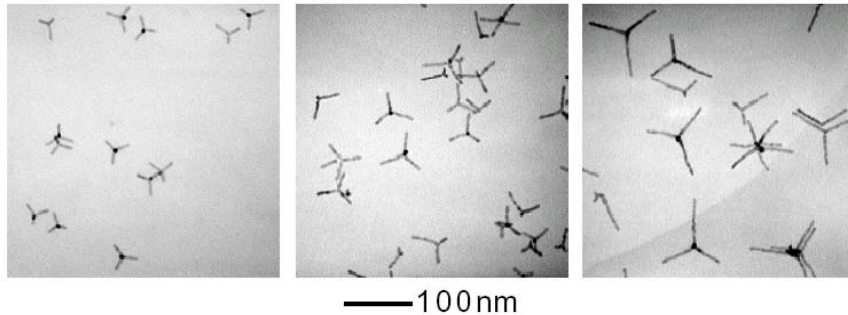
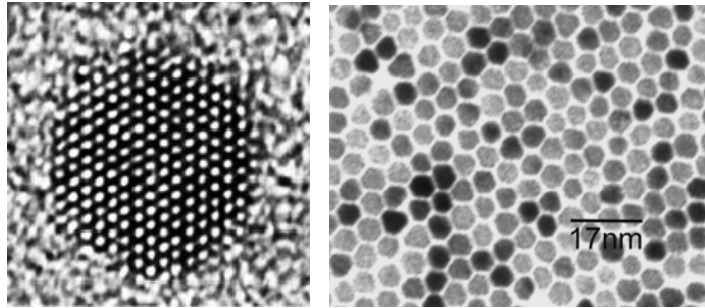
F. Ding, *et al. Appl. Phys. Lett.* **88**, 133110 (2006)







# Colloidal Inorganic Nanocrystals: Building Blocks for New Materials



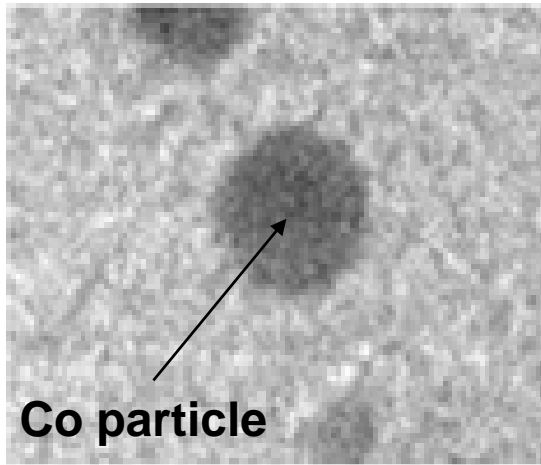
Symmetry, topology, connectivity...<sup>8</sup>



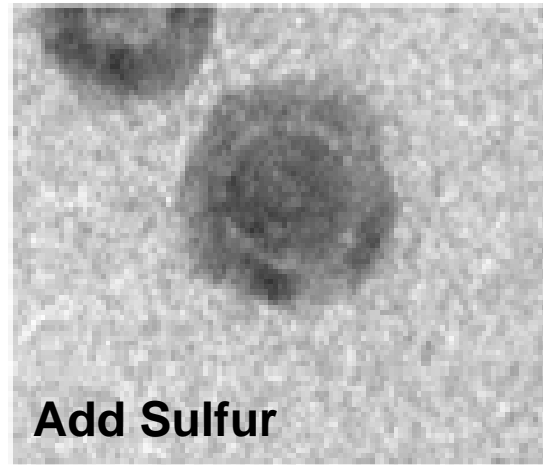
# Evolution of the Pore Structure: Cobalt Sulfide



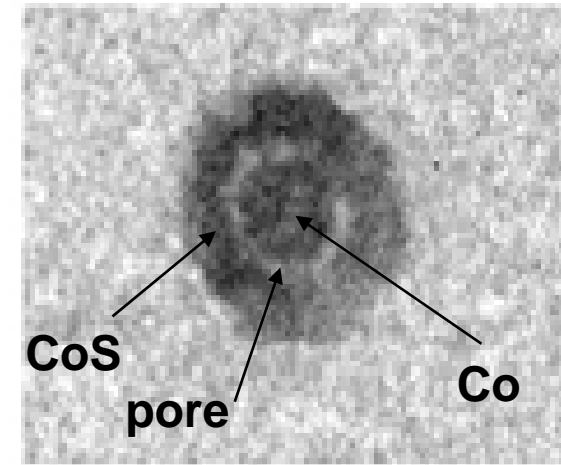
0 sec



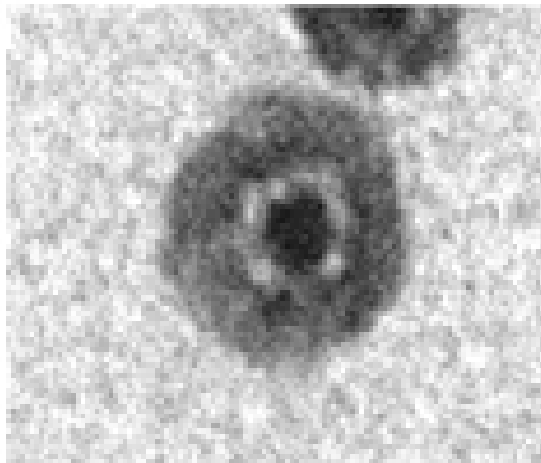
10 sec



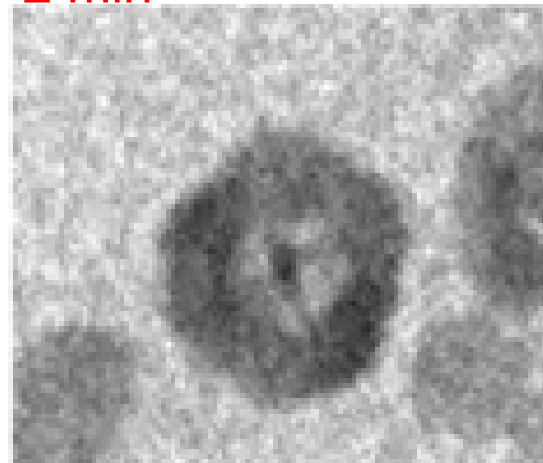
20 sec



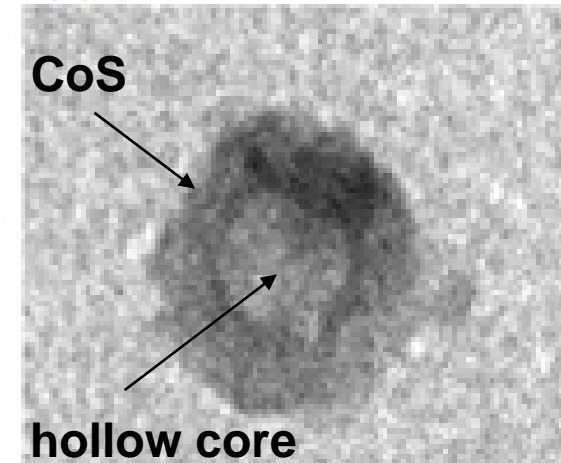
1 min



2 min



30 min



*Alivisatos, UC Berkeley*

20 nm





# Some Factors Affecting Nanoparticle Reactivity



- **Composition**
- **Morphology**
- **Electronic structure**
- **Geometry**
- **Spin**
- **Defects**
- **Size**
- **Fluxionality**
- **Diffusion**
- **Electric Fields**
- **Crystal Face**
- **Adsorbates**
- **Interactions with neighbors**
- **Substrate interactions**