CO absorption of Au and Pt nanoclusters on h-BN

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Abstract

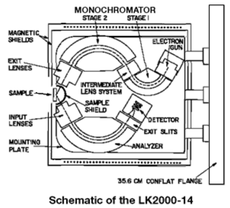
The Au and Pt nanoclusters are studied on an oxygen-free thin film, hexagonal boron nitride (h-BN), to isolate the metal clusters from the underlying substrate. In this way, measurements can be taken of chemical absorption only from the metal being tested. The h-BN thin film is also chosen for its hexagonal pores that provide locations for controlled metal nanocluster growth. In this experiment we will use EELS to examine CO adsorption of these nanoclusters to learn more about their catalytic/electronic properties and compare them to the DFT calculations.

Methods

- All experiments were performed under ultrahigh vacuum (UHV).
- The Rh(111) was cleaned by repeated cycles of Ne sputtering and flashing to about 900ºC.
- The borazine was purified by repeated cycles of pumping and freezing in liquid nitrogen [1].
- 100L of borazine (1L = 1s of dosing at 10^{-6} torr) was dosed with the sample heated to 750ºC in order to create the h-BN monolayer.
- Pt was deposited using an e-beam evaporator.
- The Au evaporator was built in the lab using a thin tungsten wire wrapped with high purity Au wire surrounded by a stainless steel collimator.
- Au was deposited at -185ºC and the temperature was maintained throughout the experiment.
- The periodic density functional theory (DFT) computations were performed using the PBE functional as implemented in the Vienna *Ab Initio* Simulations package (VASP) [2] [3] [4].

Equipment

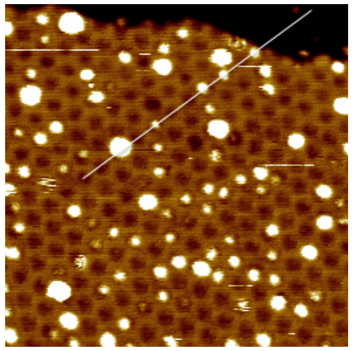
High Resolution Electron Energy Loss Spectroscopy (HREELS)



Schematic of the LK2000-14

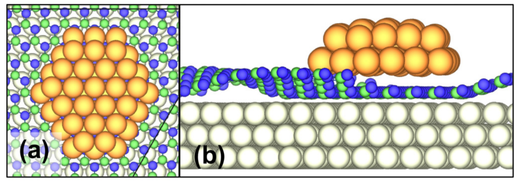
- Sends a monochromatic beam of electrons onto the sample
- The detector measures the energy lost of scattered electrons after interacting with the sample
- Low energy incident e- (~ 7eV) used for vibrational modes
- Higher energy e- (~30 eV) used for electronic excitations.

Results

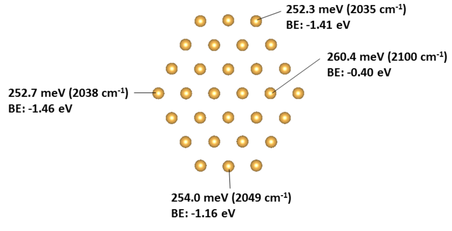


STM Image (50 x 50 nm) of 0.16 ML Au on h-BN nanomesh on Rh(1110) [5]. You can see the distinct pores and wires of the nanomesh that support the Au clusters of various sizes.

Density Functional Theory Calculations



(a) Top and (b) side view of bilayer Au51 clusters inside the nanomesh pore [5]

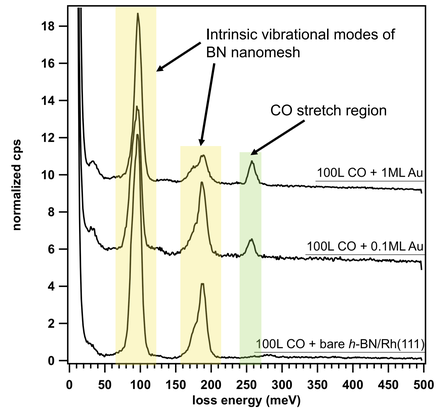


Cluster	Avg. Charge per Au Atom
Au_1	-0.462
Au_7	-0.187
Au_{19}	-0.116
Au_{30}	-0.085
Au_{51}	-0.042

Average charge per Au atom changes inversely to the size of the cluster. This can be attributed to the fact that Au atoms along the edge of the cluster have a larger negative charge than the central atoms. As the cluster gets larger, a smaller percentage of the total Au atoms are on the edge of the cluster.

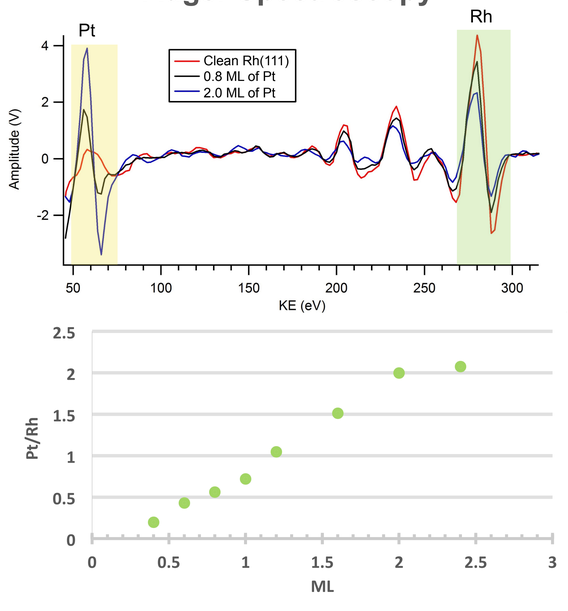
Results

Electron Energy Loss Spectroscopy



The EELS results for the bare h-BN dosed with 100L CO at -180C shows only the two peaks intrinsic to the h-BN (phonons) and no discernable CO peak. This shows that not only does CO not absorb to the bare h-BN layer, but that the h-BN layer completely covers the Rh(111). Because of this the CO peaks shown in the other scans must be associated only with CO absorbed onto the Au. On the scans with Au present, CO shows a peak energy of around 257 eV, which is a lower binding energy than gaseous CO but agrees with the DFT results.

Auger Spectroscopy



Auger shows a piecewise linear increase in the ratio of Pt to Rh peaks indicating a layer by layer growth pattern.

Summary

- DFT calculations show that the average charge per atom in Au clusters decreases as the size of the cluster increases
  - Tentatively this is caused by higher negative charge of atoms on the edge of a cluster
- EELS shows no CO vibrational peak for bare h-BN meaning:
  - CO does not bind to bare h-BN supported on Rh(111)
  - h-BN layer completely covers the Rh(111)
- CO peak energy of about 257 eV
  - Agrees with DFT calculations
  - Redshifted from gaseous CO
- Auger shows a layer by layer growth of Pt

Further Studies

- EELS of CO absorbed on Pt on h-BN
- STM images of Pt nanoclusters on h-BN
- Same experiments done with Ni, Co, Pd, Ag

References

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