Nanostructured surfaces

Electronic structure of nano sized gold

Khabiboulakh Katsiev[1], Challa Kumar[2], Pavlo Galiy[3], Wai-Ning Mei[4], Wayne Goodman[5], Yaroslav Losovyj[6]

[1] *King Abdullah University of Science and Technology (KAUST), Saudi Arabia*

[2] *Friend Energy Frontier Research Center, Harvard University, Cambridge, MA 02138.*

[3] *Electronics Department, Ivan Franko Lviv National University, 50 Dragomanov Street, Lviv, 79005, Ukraine*.

[4] *Department of Physics, University of Nebraska at Omaha, Omaha, NE 68182, United States.*

5 Department of Chemistry, Texas A&M University (TAMU), College Station TX 77843, United States.

6 Department of Chemistry, Indiana University Bloomington, Bloomington, IN 47405, United States.

E-mail: ylozovyy@indiana.edu

Gold is not typically catalytically active, but gold clusters are seen to be good catalysts. When a small gold cluster is small enough to no longer be considered an inert noble metal? Although it is well established that significant quantization occurs to the electronic structure of extremely small (<2 nm in diameter) ligand-stabilized gold nanoparticles, it is unknown how precisely compact the confinement is which triggers this transition as well as how to investigate and control it.

Herein, we develop a novel approach based on photon energy dependent photoemission to explore how far down extends the size limit for metallicity in atomically precise ligand-stabilized clusters. We demonstrate that the electronic structure of the Au25 clusters can be switched between atomic like and metallic upon altering the ligand shells. While losing the ligands the cluster becomes more metal-like via increased hybridization of the states at the vicinity of the Fermi level revealing that the "naked" cluster core built of as few as 25 gold atoms is metallic. These observations are supported by DFT studies. On the other hand we demonstrate that the traditional gold film at certain condition turns into adsorption active stage which points towards a particular electronic structure responsible for catalytic activity. This particular structure could be engineered not necessary through the nano-sizing.

Our combined experimental-theoretical approach opens the avenue towards the design of nanomaterials with tunable properties as well as exploration of size dependent hybridization effects in the nanoclusters.