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Outlook of application of aberration corrected-electron microscopy in the ligand-protected metal clusters

HUIPING XU*, RAY D. TWESTEN**, LAURENT MENARD***, ANATOLY FRENKEL****, RALPH NUZZO***, DUANE JOHNSON*****, JUDITH C. YANG *

* Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA 15261.
** Center for Microanalysis of Materials, University of Illinois at Urbana-Champaign, Urbana, IL 61801.
*** Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.
**** Department of Physics, Yeshiva University, New York, NY 10016.
***** Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

Significant improvement on activity/selectivity of catalysts would be achieved, when their scale is reduced to small size, specifically, the subnanometer regime (<1nm), such as gold[1]. 3-dimensional structural characterization of metal nanoparticles would be required to understand the mechanism of catalysts. However, it is difficult to determine accurately important required parameters (size, crystal structure, polyhedral shape, and bond information) of individual subnano-clusters at atomic level by the conventional high-resolution electron microscopy(HREM) and high angle annular dark field (HAADF) -scanning transmission EM (STEM) imaging. The detrimental effect of lens aberration on the conventional HREM and HAADF imaging for subnanometer metal clusters has been observed. For example, both Fresnel fringes around the particles and strong phase contrast from the carbon films occur in a HREM image (Figure 1) and the obscured edges of the particles in a HAADF image (Figure 2) and these images are taken from our newly synthesized ligand-protected Au_{13} clusters having small size (~0.82nm) and narrow distribution (Figure 3). In this work, we will present our current efforts regarding atomistic structural characterization of our Au_{13} clusters and discuss challenges, limitations of methods currently used and the possibly expected results achieved by incorporating emerging aberration corrected both HREM and Z contrast STEM techniques into the study of metal subnano-clusters.

Newly developed aberration correction [2-3] is an emerging technique providing sub-angstrom resolution and reduced probe size when it is applied to electron microscopes. With the enhanced resolution and reduced probe size, the aforementioned problems in the HREM and HAADF images will be completely suppressed. Specifically, our recently developed STEM-based quantitative mass spectroscopic method [4-6] will be applied to these aberration-free HAADF images with expected much improvement in accuracy in determination of number of atoms per cluster. In addition to this, with aid of aberration correction, acquisition of subnano-diffraction and EELS spectra in STEM from individual subnanometer clusters becomes possible due to reduced probe size. They will provide precisely complementary information in crystal structure, polyhedral shape and bond information.

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References:
1. G. Schmid et. al, Chem. Soc. Rev., 28 (1999) 179.
2. J.L. Huchison, et.al, Jeol News, 37E (2002) 2.
3. ORNL Review, Vol. 35, No. 3, 2002.
4. A. Singhal et al, Ultramicroscopy 67 (1997) 191.
5. J.C.Yang et al, Materials Characterization 51(2003) 101.
6. J.C.Yang et al, Microsc. Microanal. 6 (2000) 353.

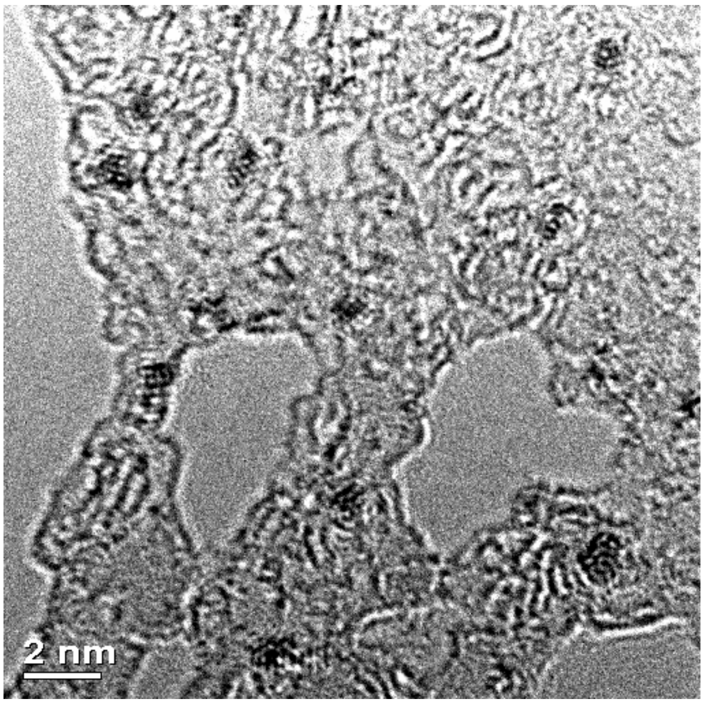

Figure 1. A HREM image (Jeol 2010F) of Au clusters. The clusters shown here are of size less than 1nm

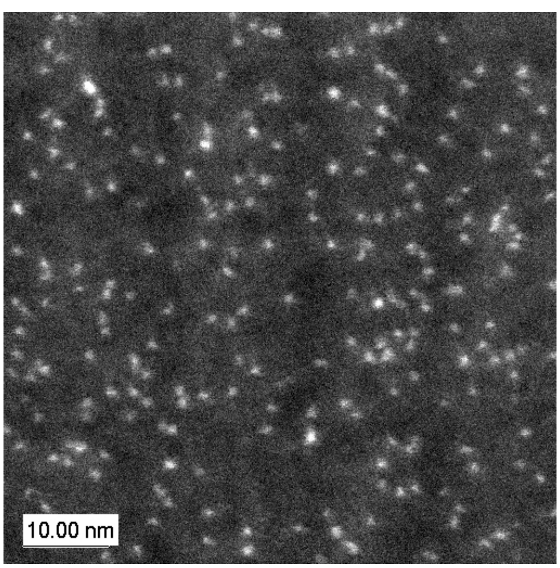

Figure 2. A representative STEM-HAADF image (VG HB 501) of Au clusters in the same sample in Figure 1, under conditions of 100kv, inner angle: 96mgrad and outer angle: 343mgrad.

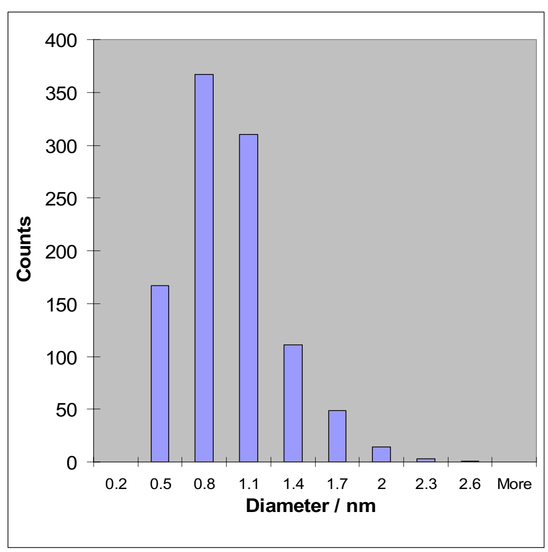

Figure 3. A histogram of the particle size distribution of the same Au samples measured from HAADF images taken in different sample regions, where 1025 Au nanoparticles are counted and of average size of 0.82±0.34 (nm).

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