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3-DIMENSIONAL STRUCTURAL CHARACTERIZATION APPROACHES OF CARBON-SUPPORTED Au_{13} NANO-CLUSTERS

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The success of future applications of metal nano-clusters in heterogeneous catalysis depends on the full understanding of their supported three-dimensional structure [1]. Supported gold nano-cluster catalysts exhibit catalytic activities that are radically different from bulk gold [2]. The detailed atomistic structural information on these small molecular gold clusters would be particularly important, but is practically missing. By performing experimental extended x-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) studies on Au_{13} nano-clusters [3], A. Frenkel, the third author of this paper, has gained structural results of the approximate size, the near neighbor Au-Au and Au-S distances, and the disorders in these distances. In this work, we present the applications of quantitative Z-contrast imaging and high-resolution electron microscopy (HREM) techniques in confirmation of aforementioned EXAFS results as well as further insights into structural habits and the dynamics of carbon-supported Au_{13} nano-clusters.

We chose Au_{13} clusters as a model system, because a 13-atom Au cluster is a ligand-stablized one with a full shell and will not aggregate into larger particles [4-5]. A 13-atom gold cluster often exists in the form of either regular icosahedrons or cubo-octahedron geometry, as drawn schematically in Figure 1. A significant difference is observed in the edge position between XANES spectra of the Au_{13} cluster and those with a larger size, as shown in Figure 2.

This study highlights the use of the advanced Z-contrast imaging, combined with lattice imaging in high-resolution electron microscopy (HREM), as powerful tools for the studies of three-dimensional structure of these nanoscale materials. Z-contrast imaging or high angle annular dark-field (HAADF) is a novel and emerging technology in determining the number of atoms in a cluster. We have previously determined the number of atoms in very small clusters, such as Re_6 [6] and $PtRu_5$ nanoclusters [7], through quantification of absolute image intensity from very HAADF microscopy and our newly developed robust interactive computer program [8]. The HAADF image in Figure 3 shows $PtRu_5$ clusters, which was determined to be oblate with "truncated" cubo-octahedral geometry. A similar procedure is currently being performed for carbon-supported Au_{13} nanoclusters.

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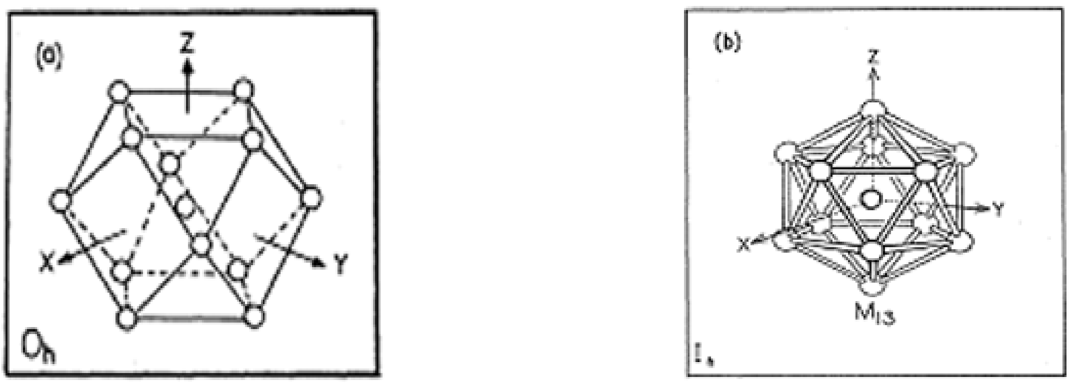

Figure 1. The cubo-octahedral (a) and icosahedral (b) Au_{13} cluster (they have a diameter of about 0.5nm.

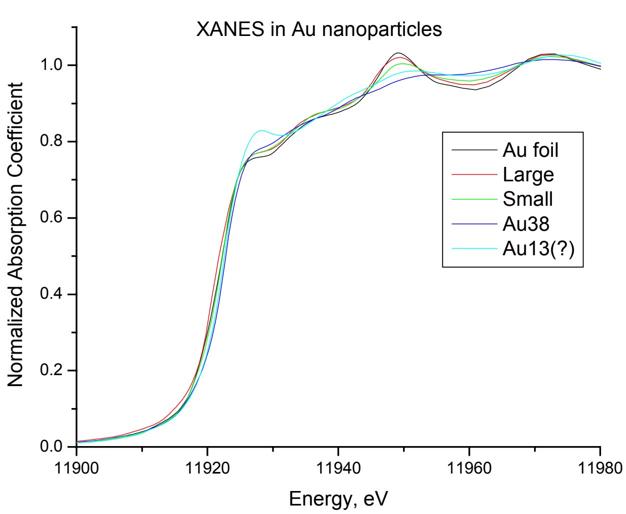

Figure 2. XANES in Au nanoparticles

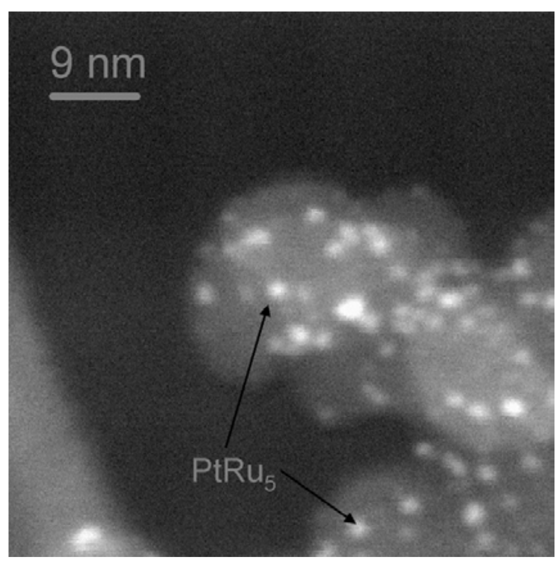

Figure 3. A HAADF image of supported $PtRu_5$ clusters