

2003-2006 Final Report for DE FG02-03ER15475

The Reactivity and Structural Dynamics of Supported Metal Nanoclusters Using Electron Microscopy, *in situ* X-Ray Spectroscopy, Electronic Structure Theories, and Molecular Dynamics Simulations.

Principal Investigators: Ralph G. Nuzzo,¹ Duane Johnson,² **DE FG02-03ER15476**
Judith Yang,³ **DE FG02-03ER15475**
Anatoly Frenkel⁴ **DE FG02-03ER15477**

Collaborators: Neer Asherie,⁴ Richard Finke,⁵ Richard Crooks,⁶ Leeor Kronik,⁷ Royce Murray,⁸ Yimei Zhu,⁹ John Rehr,¹⁰ John Shapley¹, Jian-Min Zuo

Post-doctoral research associates: Joo Kang,¹ Linlin Wang,² Huiping Xu³, Fengting Xu³, Long Li³

Graduate students: Laurent Menard¹

Undergraduate students: Ariella Bram,⁴ Michelle Simpser,⁴ Nina Bursky-Tammam,⁴ Andrew Friedman⁴

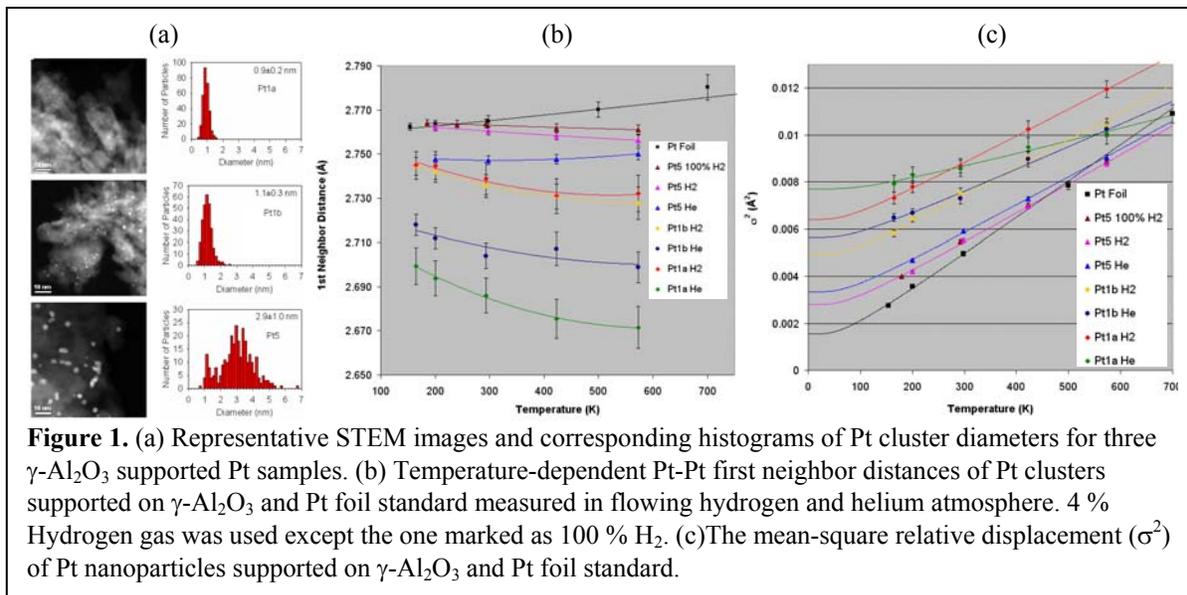
¹Dept. of Chemistry, Univ. of Illinois Urbana-Champaign, Urbana, IL 61801, ²Dept. of Mat. Science and Engineering, Univ. of Illinois Urbana-Champaign, Urbana, IL 61801, ³Dept. of Materials Science and Engineering, Univ. of Pittsburgh, Pittsburgh, PA 15261, ⁴Dept. of Physics, Yeshiva University, New York, NY 10016, ⁵Dept. of Chemistry, Colorado State University, Fort Collins, CO 80523, ⁶Dept. of Chemistry and Biochemistry, The Univ. of Texas at Austin, Austin, TX 78712, ⁷Dept. of Mat. and Interfaces, Weizmann Institute of Science, Rehovot, Israel, 76100, ⁸Dept. of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, ⁹Brookhaven National Lab., Upton, NY 11973, ¹⁰Dept. of Physics, Univ. of Washington, Seattle, WA 98195

Time Period: September 15, 2003- October 31, 2006

Abstract: The distinguishing feature of our collaborative program of study is the focus it brings to emergent phenomena originating from the unique structural/electronic environments found in nanoscale materials. We exploit and develop frontier methods of atomic-scale materials characterization based on electron microscopy (Yang) and synchrotron X-ray absorption spectroscopy (Frenkel) that are in turn coupled innately with advanced first principles theory and methods of computational modeling (Johnson). In the past year we have made significant experimental advances that have led to important new understandings of the structural dynamics of what are unquestionably the most important classes of heterogeneous catalysts—the materials used to both produce and mitigate the consequences of the use of liquid hydrocarbon fuels.

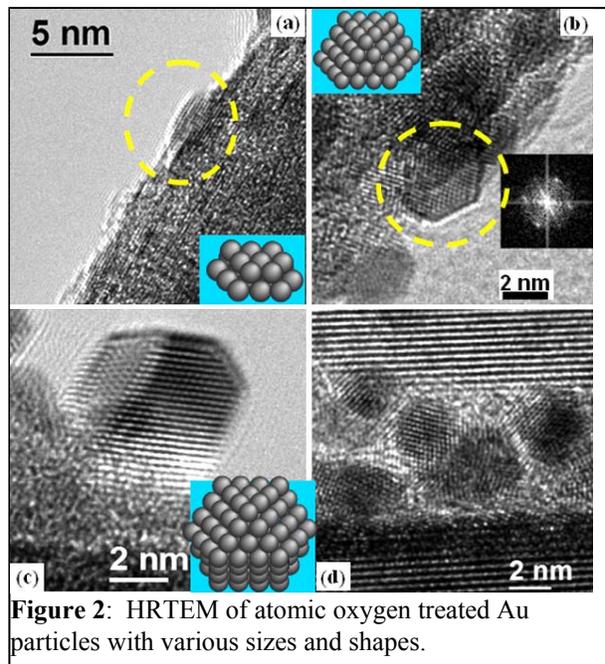
Recent Progress Highlights (due to the collaborative nature of this program, individual PI award numbers are indicated next to each highlight)

1) **Combined EXAFS, TEM and theoretical investigation of the Negative Thermal Expansion (NTE) in supported metal particles ((DE FG02-03ER15475, DE FG02-03ER15476, DE FG02-03ER15477): Fig. 1.** These experiments allowed us to separately study the effects of the atmosphere (H₂ or He) on Pt-Pt first nearest neighbor distances. As a result, we identified two driving forces responsible for the particle



contraction at high temperature: a) the temperature-dependent charge transfer between the support and the particle (responsible for the 0.9 and 1.1 nm particle behavior in He, Fig. 1b) and b) the competing electronic consequences that follow from H₂ chemisorption. The results of more recent and far more extensive studies using state of the art methods of electron microscopy and synchrotron XAS are summarized in the data of Figure 1. One notes significant impacts of cluster size—in any environment—on the atomic relaxations seen in the M-M bonding. In all cases, though, the thermal dependences are vastly atypical—demonstrating the emergence of new electronic effects that have origins related to both the adsorbate bonding and, most importantly, the metal support interactions. The nature of these effects, related to a charge sensitive stiffening of the M-M bonds, exceeds the current descriptive capacities of theory. This work highlights an important need for future research, namely to provide atomically precise descriptions of the bonding present at the metal support interface—a task that will form a dominating goal for work conducted in the next program year..

2) **Reduced sintering of Au₁₃ nanoclusters using reactive oxygen (DE FG02-03ER15475, DE FG02-03ER15476, DE FG02-03ER15477).** We compared the effects of reactive oxygen (ozone and atomic oxygen) exposure to calcination on ligand-protected Au₁₃ clusters deposited onto anatase TiO₂. All three treatments: calcinations, ozone, and atomic oxygen successfully removed the ligands from the Au



particles and provide bulk-scale access to this most important example of a system displaying rate sensitivities arising due to the consequences of strong metal support interactions. Both reactive oxygen species, ozone and atomic oxygen, significantly reduced the amount of agglomeration of the Au clusters as compared to annealing at 400°C (2.7 ± 0.6 nm, 324 ± 264 atoms), where ozone produced the smallest clusters (1.2 ± 0.5 nm, 40 ± 49 atoms). The Au particles formed after 5 eV atomic oxygen exposure revealed a broad size distribution (2.1 ± 0.7 nm, 72 ± 98 atoms) with an average size in between those produced by the two prior treatments. Fig.1 shows the HRTEM images from different Au particles on

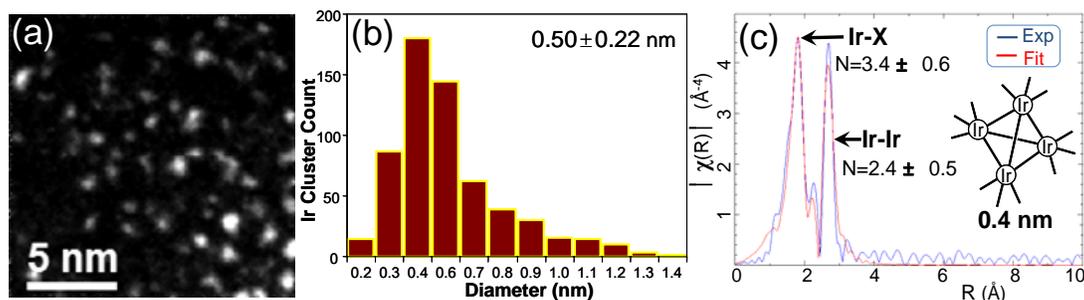


Figure 3: (a) A HAADF (Z-contrast) image of Ir nanoclusters with diameters less than 1 nm diameters mostly; the size distribution of Ir clusters in (b) is, to a good approximation, monodisperse. It is a central assumption made in EXAFS analysis in (c) which showed good agreement with the STEM results for the cluster diameter.

TiO₂ after atomic oxygen exposure, revealing a variety of structures including bilayer rafts (a), faceted hemispheres (b) and spherical shapes (c).

3) Combined HREM, STEM and EXAFS structural characterization of ultra-small Ir and Ni hydrogenation catalysts. (DE FG02-03ER15475, DE FG02-03ER15477)

“Ziegler-type hydrogenation catalysts”, such as Ni and Co, are used for polymer hydrogenation in industry to hydrogenate 100 million pounds of polymer per year, and Ir is a model for these industrial catalysts. Recently, very small Ir, Ni and Co nanoparticles containing approximately 4-6 atoms, were synthesized by Prof. Richard Finke’s group at Colorado State University. All of the samples were characterized by HREM, STEM and EXAFS, where very small sizes were noted for both the Ir and Ni, but the observed Co particle sizes were larger probably due to coalescence. Most of the Ni and Ir particles had diameters less than 0.5 nm, corresponding to clusters with 4-6 atoms, but some particles were close to 1 nm in size. Figure 3 is a HAADF image from Ir sample, which (a) shows Ir clusters with less than 0.5 nm; (b) with around 0.7 nm;

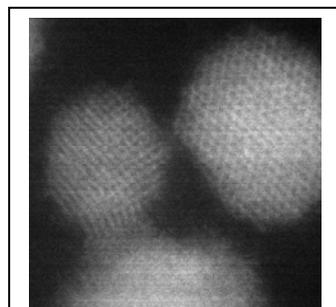


Figure 4: Atomic resolution Z-contrast image of a Pd-rich:Cu nanoparticle. Courtesy of M. Ghass (SuperSTEM, Daresbury, UK)

(c) some clusters as large as about 1 nm in diameters. EXAFS analysis was performed, guided by TEM information about cluster monodispersity. The EXAFS results allowed us to develop a 3D model of the Ir clusters.

4) Development of self-consistent methods of structural investigation (size, structure, degree of alloying) of bimetallic catalysts by combined STEM and EXAFS. (DE FG02-03ER15475, DE FG02-03ER15476, DE FG02-03ER15477).

The distribution of elements within a single nanoparticle is critical to determine, such as homogeneous distribution or core-shell. We have examined Pd-Cu bimetallic catalysts with varying relative amounts of Pd:Cu (100% Pd to 50% Pd:Cu), as a promising catalyst to reduce nitrates from drinking water. Figure 4 is a HAADF image from an aberration-corrected STEM (where one now exists at

UIUC) of Pd-rich Cu nanoparticle, where a core-shell structure is not observed.

EXAFS measurements of coordination numbers in nanoclusters contain size- and shape-specific information. For bare metal clusters, a number of different minimum-energy, regular polyhedral

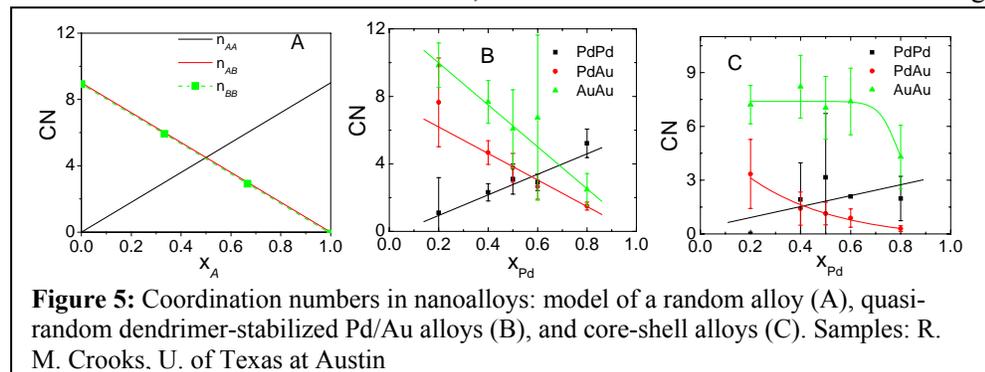


Figure 5: Coordination numbers in nanoalloys: model of a random alloy (A), quasi-random dendrimer-stabilized Pd/Au alloys (B), and core-shell alloys (C). Samples: R. M. Crooks. U. of Texas at Austin

geometries are often proposed as structural motives. We have developed a suite of computer programs for cluster geometry generation for most regular polyhedra, as well as a data analysis package to process cluster

coordinates and obtain radial distribution function information that can be directly compared with experiment. For bimetallic alloys, our methods of multiple-edge, constrained fits can discriminate between quasi-random and core-shell structures (Fig. 5).

5) DFT modeling of ligand-stabilized Au₁₃ nanoclusters (DE FG02-03ER15475, DE FG02-03ER15476, DE FG02-03ER15477):

We simulated thiol/phosphine-stabilized Au₁₃ nanoclusters via DFT (collaborator: L. Kronik, Weizmann Inst.), and compared structure/ligand placement patterns with recent EXAFS/TEM measurements of these clusters. The structural model that is in a good quantitative agreement with experiments corresponds to a distorted icosahedral structure by on-top phosphine ligands and a combination of on-top and bridging thiol ligands (Fig. 6). The ligand-induced bond-length disorder is predominantly tangential, not affecting radial Au-Au distances.

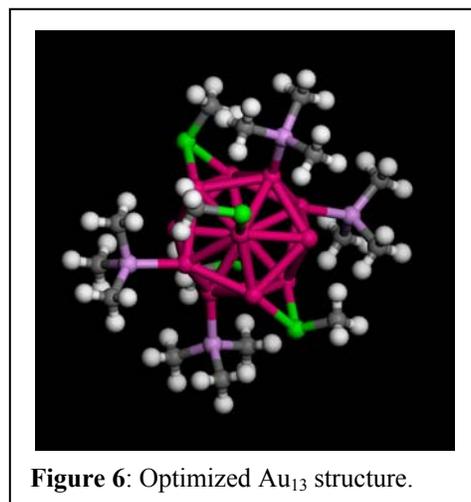
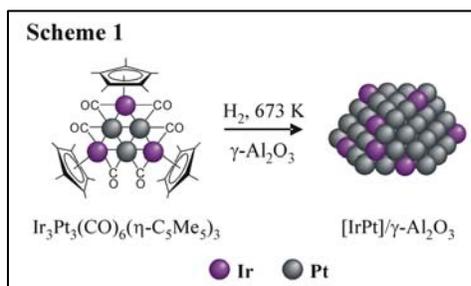


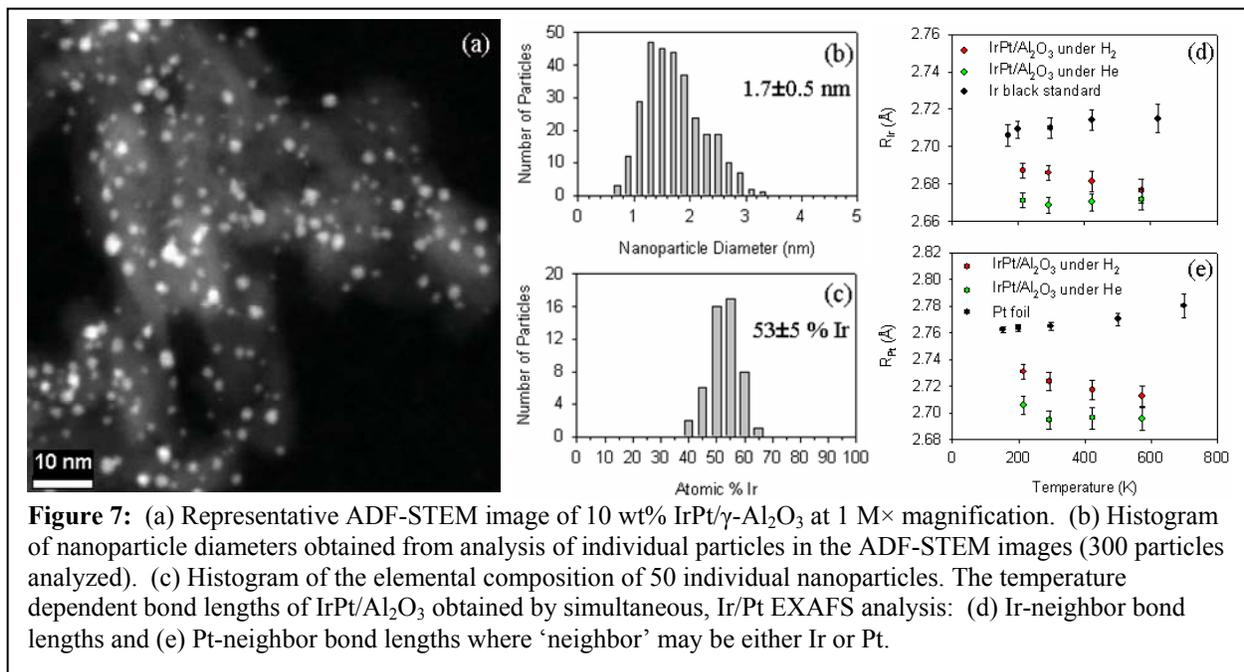
Figure 6: Optimized Au₁₃ structure.

6) Supported core-shell Ir-Pt nanoparticles on Al₂O₃ prepared from a molecular cluster precursor: structure and dynamics determined using STEM, HRTEM and EXAFS (DE FG02-03ER15475, DE FG02-03ER15476, DE FG02-03ER15477):

Addition of Re or Ir to Pt/Al₂O₃ petroleum reforming catalysts enhances catalytic activity, increases the octane rating of the fuel product, and reduces deactivation of the catalyst due to coking. In many systems, the properties that emerge exceed those expected from an additive combination of the behavior of the monometallic components, and this synergistic enhancement of catalyst performance has been attributed to a combination of geometrical and electronic effects. The presence of both metals on the surface provides a variety of chemically and geometrically different binding sites for reactant adsorption and consequent reaction. Additionally, strain induced by lattice mismatches of the component metals can modify the intermetallic distances and affect adsorption energetics. Lastly, charge transfer from one metal to another and orbital rehybridizations induced by bimetallic bonding can impact the electronic structure of the bimetallic system and alter the energetics of catalysis. In some systems, the addition of the second metal dramatically inhibits sintering of the nanoparticles under reactive conditions. The deposition of the bimetallic cluster [Ir₃Pt₃(μ-CO)₃(CO)₃(η-C₅Me₅)₃] on γ-Al₂O₃, followed by reduction with hydrogen, results in highly-dispersed supported bimetallic Ir-Pt



nanoparticles with exceptional structural and compositional qualities. The composition of the cluster precursor is retained as revealed by energy dispersive x-ray (EDX) spectra collected from individual, isolated nanoparticles (Fig. 7). The narrow size distributions (typically 1.7 ± 0.5 nm) and compositional distributions ($53 \pm 5\%$ Ir) obtained from this preparation allow an unambiguous structural characterization



by x-ray absorption spectroscopy. The EXAFS data indicate that the nanoparticles assume an Ir-Pt core-shell structure with the Pt preferentially present on the cluster surface and the Ir preferentially segregated to the cluster interior and support interface. The EXAFS analysis for this system is exceptionally challenging for technical reasons related to the close proximity of the Pt and Ir adsorption edges. This work provided a powerful new protocol—a computational model developed by a then graduate student L. Menard (UIUC) that enables a full treatment of complex spectra of this type for the first time. This advance will be communicated in a detailed publication shortly.

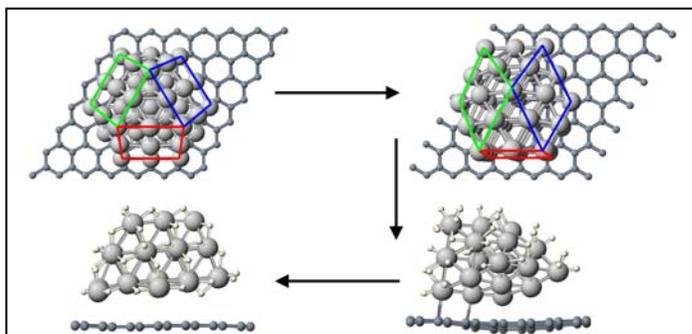


Figure 8: Morphological changes of a Pt₃₇ cluster with/without H passivation supported on graphene. Following the arrows, first, truncated cuboctahedral (TC) structure with three (100) facets highlighted in red, green and blue. Next, structure is derived by shearing of two of the (100) facets, green and blue, to (111) facets. Then the sheared structure is passivated by 54 H atoms. Lastly passivating Pt₃₇ restores the TC structure with Pt-Pt bond length increase by 3%, agreeing with experiments.

Summary:

- The Yang group effort at U. Pittsburgh has complemented this team’s efforts in determining the 3-dimensional structures of supported nanoparticles in relevant heterogeneous catalysis systems, such as Au on titania. This work is being continued as a subcontract through the University of Illinois (PI: R. Nuzzo).

Significant Honors Received

R. G. Nuzzo: Fellow of the American Academy of Arts and Sciences; Fellow of the World Innovation Foundation; Wall

Street Journal Technology Innovation Award; Adamson Award of the American Chemical Society, ISI Selection for Citations in Chemistry; Senior Editor of Langmuir; National Research Council MRSEC Evaluation Committee; Advisory Boards: Semprius Corporation (co-founder), Intermolecular Corporation, Surface Logix Corporation, Masters Nanotechnology LLC, Dreyfus Foundation, Petroleum Research Fund, Pacific Northwest National Laboratory, Los Alamos National Laboratory, Lawrence Livermore National Laboratory, Singapore Agency for Science, Technology, and Research.

J. C. Yang: Chancellor's Distinguished Faculty Research Award, B.P. America Faculty Fellow, NSF Career Award, Promotion to associate professor (with tenure) 2004.

D. D. Johnson: Computational Physics Division Fellow of the American Physical Society, UIUC Bliss Faculty Scholar

A. I. Frenkel: Promotion to full professor at YU

Recent publications (since the 2006 progress report) from J.C. Yang on this grant

1. J. H. Kang, L. D. Menard, A. I. Frenkel, R. G. Nuzzo, *Negative Thermal Expansion of γ -Alumina-Supported Pt Catalysts*, J. Am. Chem. Soc. (Communications) 128, 12068-12069 (2006).
2. L. Li, L.D. Menard, F. Xu, J. Kang, R. G. Nuzzo, and J.C. Yang, *Quantitative Studies on Au Nano-Catalysts by STEM and HRTEM*, Microscopy and Microanalysis Supplement, in press (2007).
3. L. D. Menard, F. Xu, R. G. Nuzzo, and J. C. Yang, *Preparation of TiO₂-supported Au nanoparticle catalysts from a Au₁₃ cluster precursor: Ligand removal using ozone exposure versus a rapid thermal treatment*, J. Catal. 243, 64-73 (2006).
4. J. Yang, F. Xu, H. Xu, L. Menard, L.-L. Wang, D. D. Johnson, R. Nuzzo, and A. Frenkel, *Three-dimensional Structures of Supported Metal Nanoparticles*, Proceedings of the 16th International Microscopy Congress, IMC-16, Sapporo, Japan, 1572 (2006).
5. (*) Y. Sun, A. I. Frenkel, L. Zhang, Y. Zhu, H. Xu, J. C. Yang, M. H. Rafailovich, J. C. Sokolov, *Comparison of decanethiolate gold nanoparticles synthesized by one-phase and two-phase methods*, J. Phys. Chem. B 110, 23022-23030 (2006).
6. (*) L. D. Menard, H. Xu, S. Gao, R. D. Twisten, A. S. Harper, Y. Song, G. Wang, A. D. Douglas, J. C. Yang, A. I. Frenkel, R. W. Murray, R. G. Nuzzo, *Structural dynamics of ultrasmall monolayer protected clusters: metal core bonding motifs of monodisperse icosahedral Au₁₃ and larger Au nanoparticles as revealed by x-ray absorption spectroscopy and scanning transmission electron microscopy*, J. Phys. Chem. B 110, 14564-14573 (2006).
7. (*) L. D. Menard, S. Gao, H. Xu, R. D. Twisten, A. S. Harper, Y. Song, G. Wang, A. D. Douglas, J. C. Yang, A. I. Frenkel, R. G. Nuzzo, R. W. Murray, *Sub-nanometer Au monolayer protected clusters exhibiting molecule-like electronic behavior: quantitative HAADF-STEM and electrochemical characterization of clusters with precise atomic stoichiometry*, J. Phys. Chem. B 110, 12874-12883 (2006).
8. (*) J. Yang, H. Xu, K. Guy, Z. Liu, and J. Shapley, *Development of Bimetallic Catalysts for Nitrate Removal from Drinking Water*, Proceedings of the 16th International Microscopy Congress, IMC-16, Sapporo, Japan 1566 (2006).
9. (*) K.A. Guy, H. Xu, J. Yang, C. Werth, and J. Shapley, *Catalytic Nitrate and Nitrite Reduction with Pd-Cu Colloids: Composition, Structure and Reactivity Correlations*, in preparation for J. Phys. Chem. C.