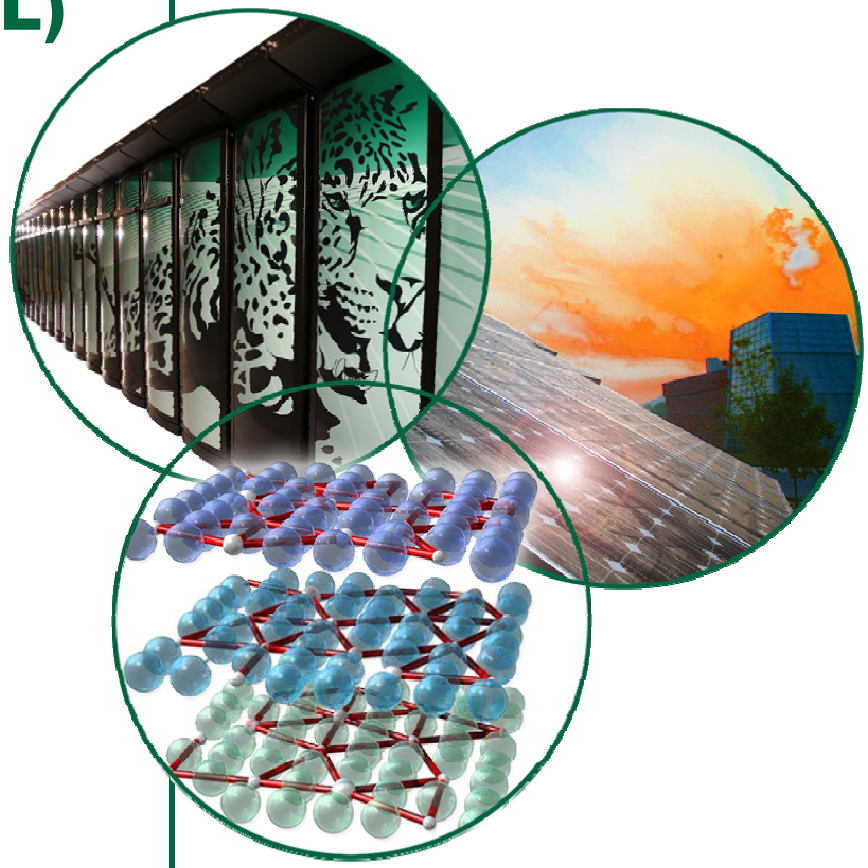
Project ID: lmp_01_allard

Electron Microscopy Catalysis Projects: Success Stories from the High Temperature Materials Laboratory (HTML) User Program



DOE 2009 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

May 21, 2009

Dr. Lawrence F. Allard, ORNL

Sponsored by
U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies Program

U.S. DEPARTMENT OF ENERGY

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OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

High Temperature Materials Laboratory
Materials Analysis User Center

Electron Microscopy Catalyst User Projects

★Prof. Jimmy Liu, UM-St. Louis: "Structural investigation of Pd/ZnO nanocatalysts for production of hydrogen and for direct-methanol fuel cell applications"

• Prof. Abhaya Datye, UNewMexico: "Characterization of supported PdZn alloy catalysts for conversion of biomass-derived reactants to fuels and chemicals"

★Prof. Paulo Ferreira, UT-Austin: "STEM analysis of surface segregation in PtxCo nanoparticles"

• Dr. Stephen Bradley, UOP Co.: "Kinetics of Bimetallic Catalyst Cluster Development on Oxide Supports"

• Prof. Howard Patterson, UMaine: "Characterization of Bimetallic Oxide Catalysts using ACEM"

• Prof. Miguel Jose-Yacaman, UT-Austin: "Structure of Bimetallic Nanoparticles"

★Dr. Charles H.F. Peden, PNNL: "High-Resolution ACEM Studies of Catalytic Phases on γ-Alumina"

• Dr. Yong Wang, PNNL: "Investigation of structure and interactive behavior of Pt-Re bimetallic clusters supported on multi-walled carbon nanotubes serving as model catalyst for aqueous phase reforming process (new)"

• Prof. Arumugam Manthiram, UT-Austin: "STEM/HAADF analysis of bi-metallic Pd-Co nanoparticles for fuel cell applications (new)"

★ Examples of User project catalyst studies utilizing JEOL 2200FS aberration-corrected electron microscope (ACEM)

Project ID:
LMP01, Allard

The HTML User Program - Background

The HTML is a National User Facility that supports the missions of DOE, EERE and the Vehicle Technologies Program in particular, by working with industry, universities and other national laboratories to develop energy efficient technologies that will enable the U.S. to use less petroleum. The HTML is organized into six user centers, which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization.

Access to the HTML is provided through the HTML User Program proposal process. Research proposals are reviewed by a committee and approved based on scientific merit, relevance of the proposed research to the mission of DOE's Vehicle Technologies Program, and feasibility. Research is completed within 24 months and normally involves one or more user visits to the HTML.

Both nonproprietary and proprietary research is conducted within the HTML User Program. There are generally no charges for nonproprietary research projects, and users conducting nonproprietary research must agree to submit research results for publication in the open, refereed literature. For proprietary research, the user owns the research data and all costs at the HTML are paid by the user based on DOE guidelines for ORNL costs. A nonproprietary project is complete when the results are published in the open literature and/or presented at a professional conference.

The HTML User Program – FY2008 Activity

During FY2008, the HTML User Program managed 76 user projects from 53 different organizations.

The FY2008 budget for the HTML was $6,072,283 and was allocated as follows:

- $1,567,500 for capital equipment purchases
- $3,879,483 to support staff participation in user projects
- $626,000 for the operation of the user program

Users cost-share user projects through:

1) their direct involvement with HTML staff members during the development of the user project;
2) funding their travel to the HTML to perform research;
3) costs of materials provided by the user or the research performed prior to the user project;
4) their subsequent collaboration with HTML staff members to analyze the data and publish the results.

The HTML also supports the education and preparation of a new generation of scientists and engineers. During FY2008, students and professors from 32 universities participated in the HTML User Program. Four of those students received their Ph.D. degree in FY2008 based in part on research performed through the HTML User Program.

JEOL 2200FS-AC
Aberration-Corrected Electron Microscope

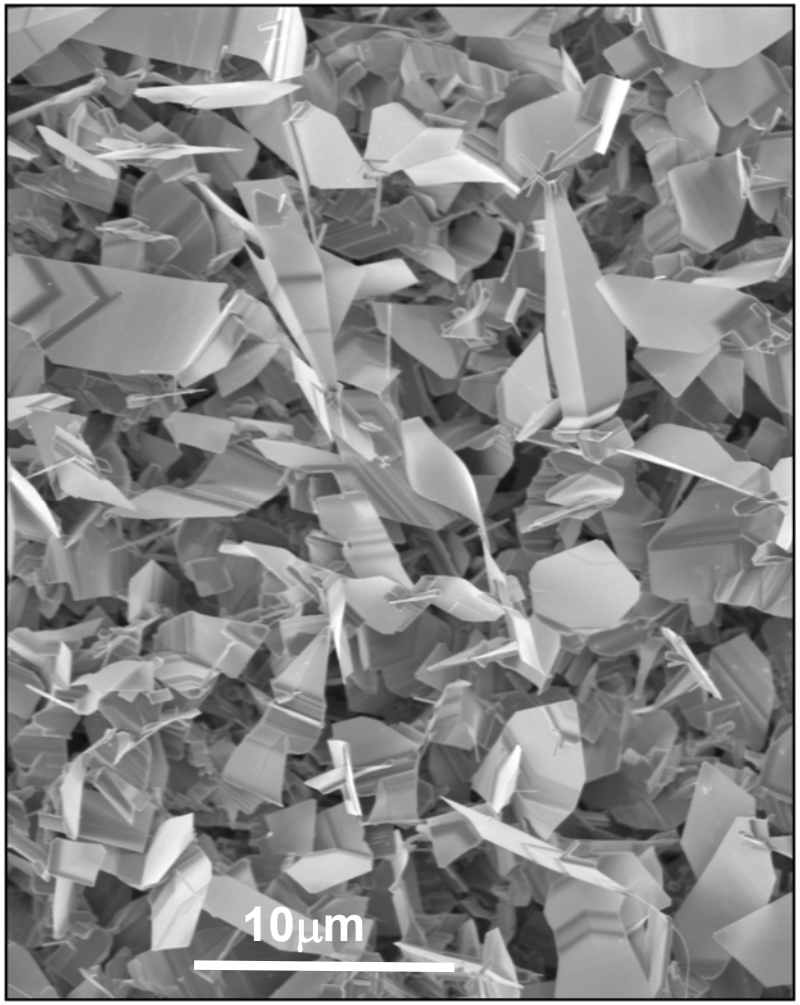
- Sub-Ångström resolution (0.7Å)
- Housed in Advanced Microscopy Laboratory
- Remotely operated (e.g. adjacent control room, London, Austin…)
- New thrust: in-situ studies with novel heating capabilities and developing "environmental cell"

"Structural investigation of Pd/ZnO nanocatalysts for production of hydrogen and for direct-methanol fuel cell applications"

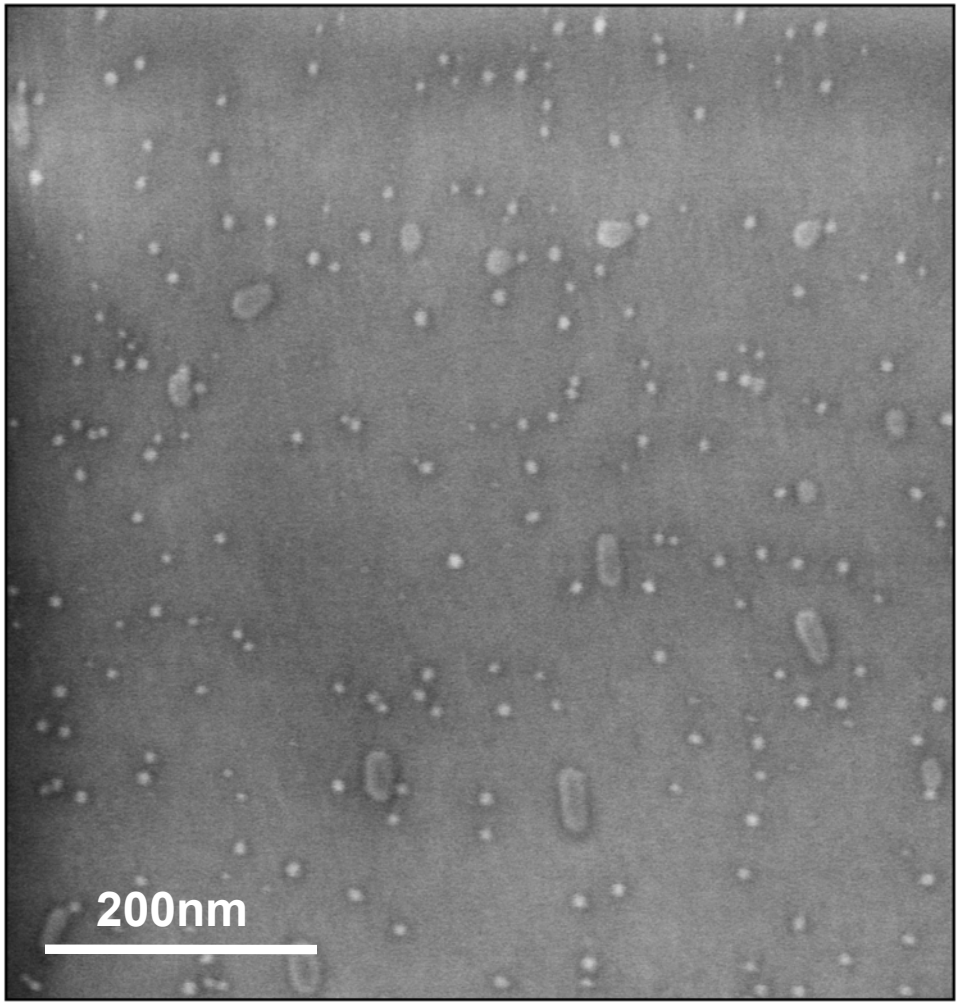
Prof. Jimmy Liu, UM-St. Louis and Dr. Larry Allard, HTML

- Alcohols, due to their easy storage and transport, have been proposed as possible sources of hydrogen via onboard reforming
- Highly active, selective and stable catalysts are required
- Pd supported on ZnO has shown promising catalytic properties.
- The formation of PdZn alloy nanoparticles has been proposed to be responsible for the improved catalytic performance of Pd/ZnO catalysts.
- The alloy formation processes and detailed surface atomic structures of the PdZn nanoparticles, however, are not well understood.
- A unique model nanocatalyst of Pd dispersed onto well-defined surfaces of ZnO nanobelts has been developed at UM-SL.
- *In situ* study of the reduction processes of the Pd/ZnO precursor materials in the ACEM has provided significant insight into the PdZn alloy formation processes, their structural evolution and the nature of the final Pd/ZnO catalysts.

ZnO “Nanobelts” as model support surfaces

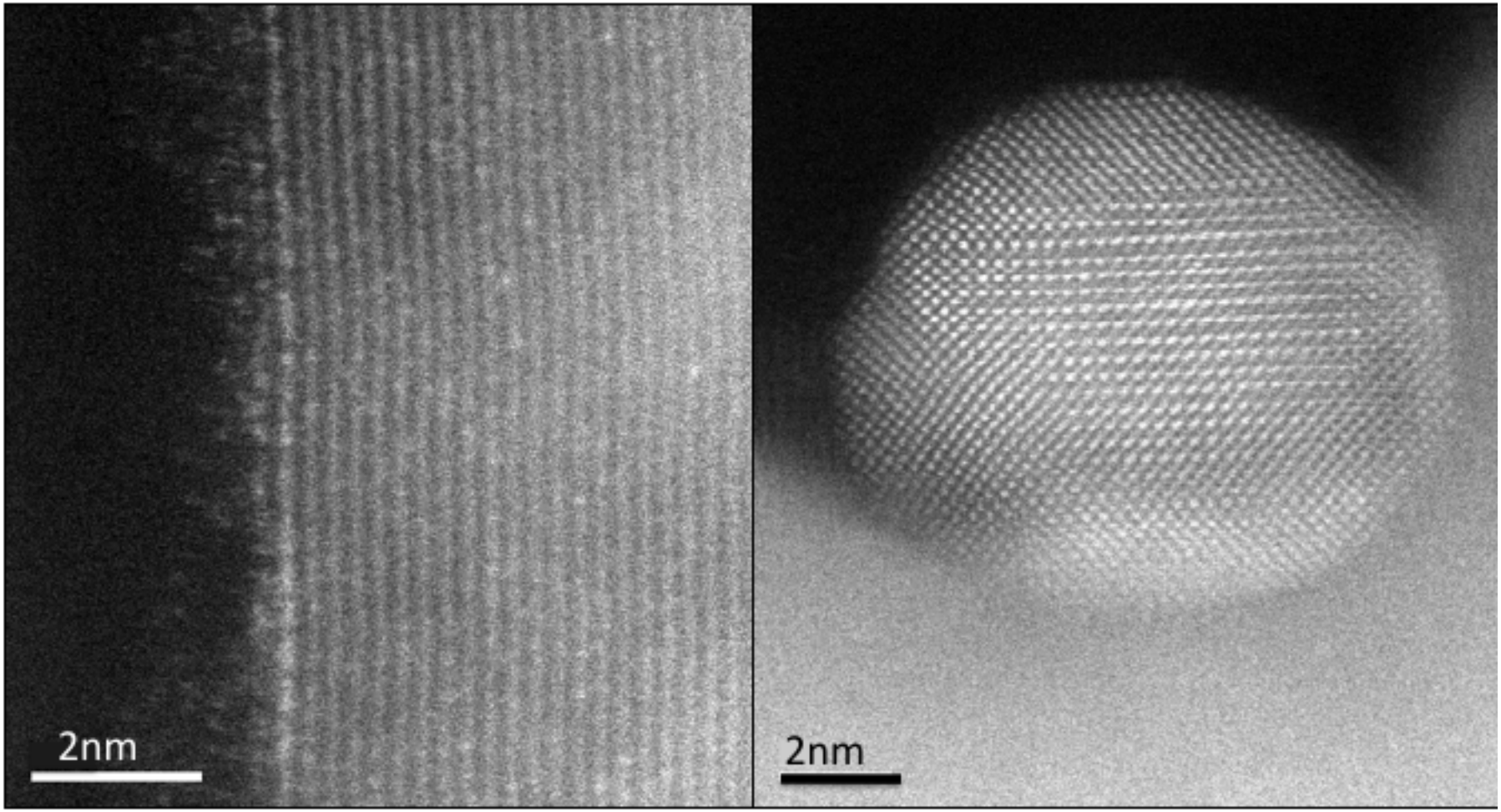


Low magnification SEM image of ZnO “nanobelts” prepared by thermal evaporation-condensation in tube furnace.



High magnification SEM image of nanobelt surface after deposition of Pd

ACEM Z-contrast images Pd/ZnO

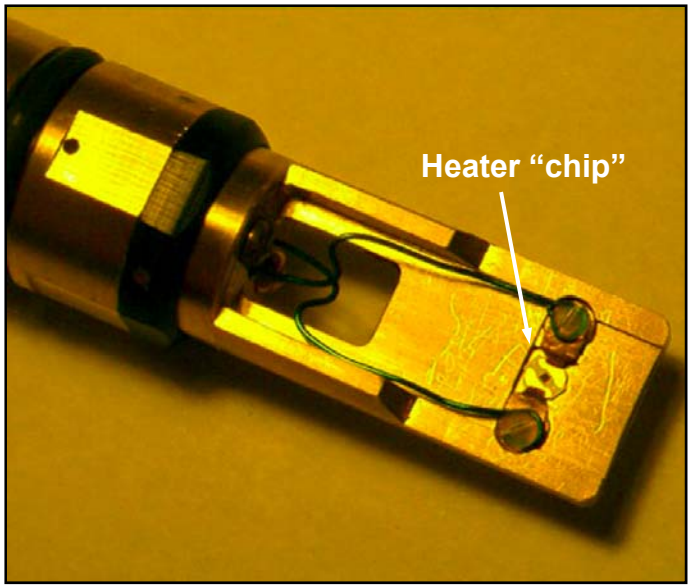


Pd atoms atomically dispersed on ZnO nanobelt, looking normal to surface

PdZn alloy nanoparticle formed by heating precursor 500°C, 30min

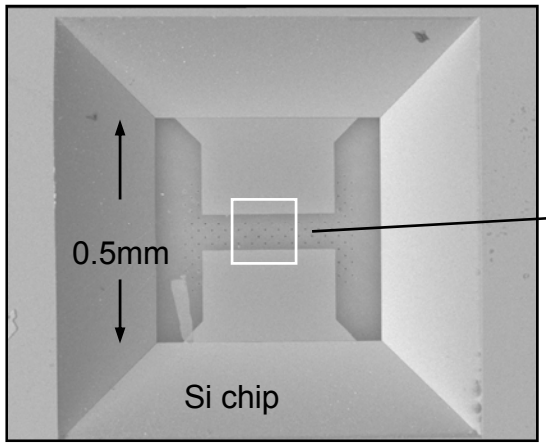
A new paradigm for in-situ microscopy…

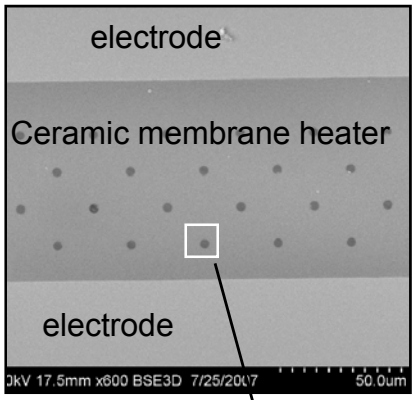
In-situ heating with Protochips MEMS heater technology

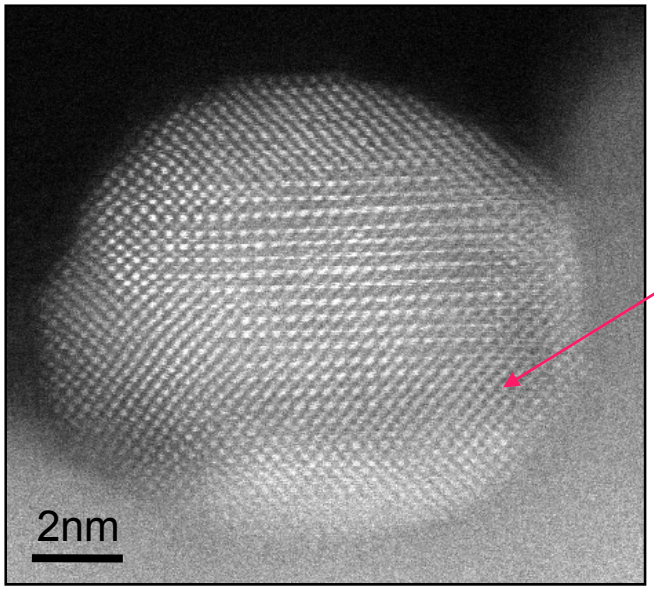


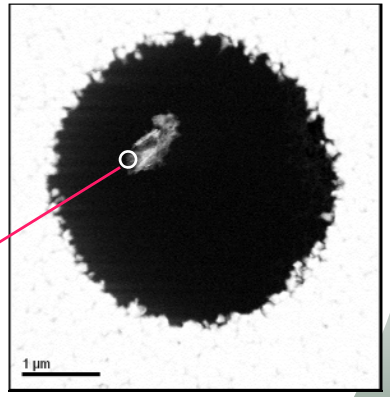
Protochips Co. provides novel heating elements fabricated using semiconductor technology. Thin ceramic membrane can be heated to >1000°C in 1 millisec!

Ultra-stable operation for sub-Ångström imaging

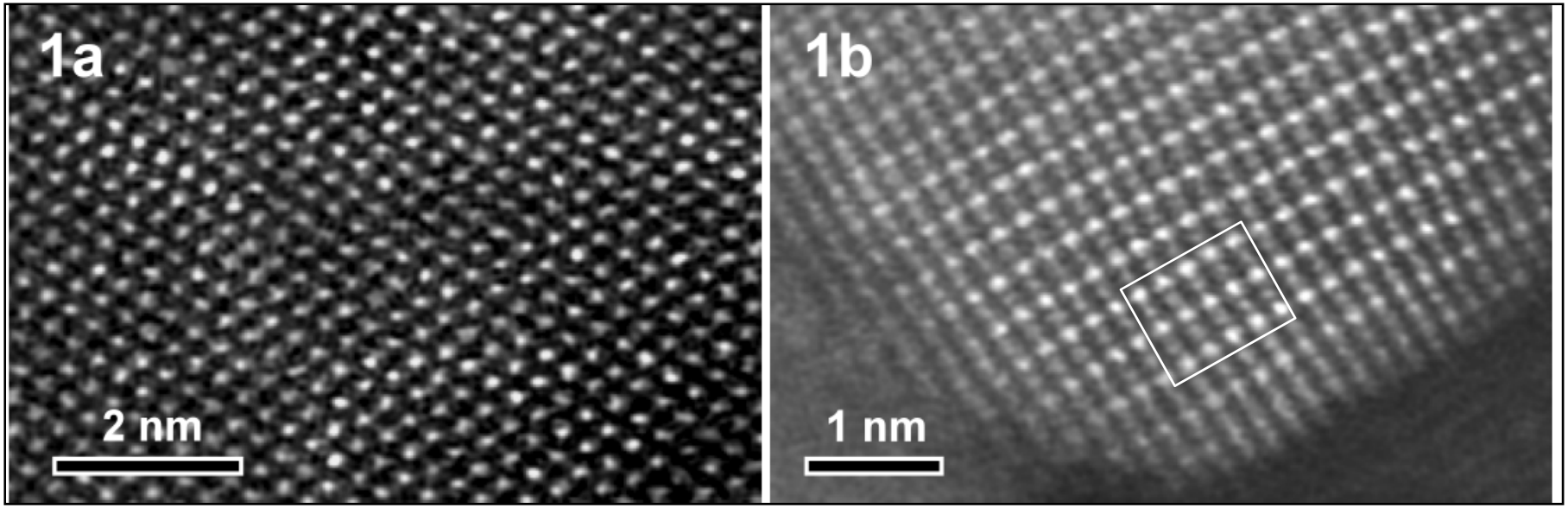






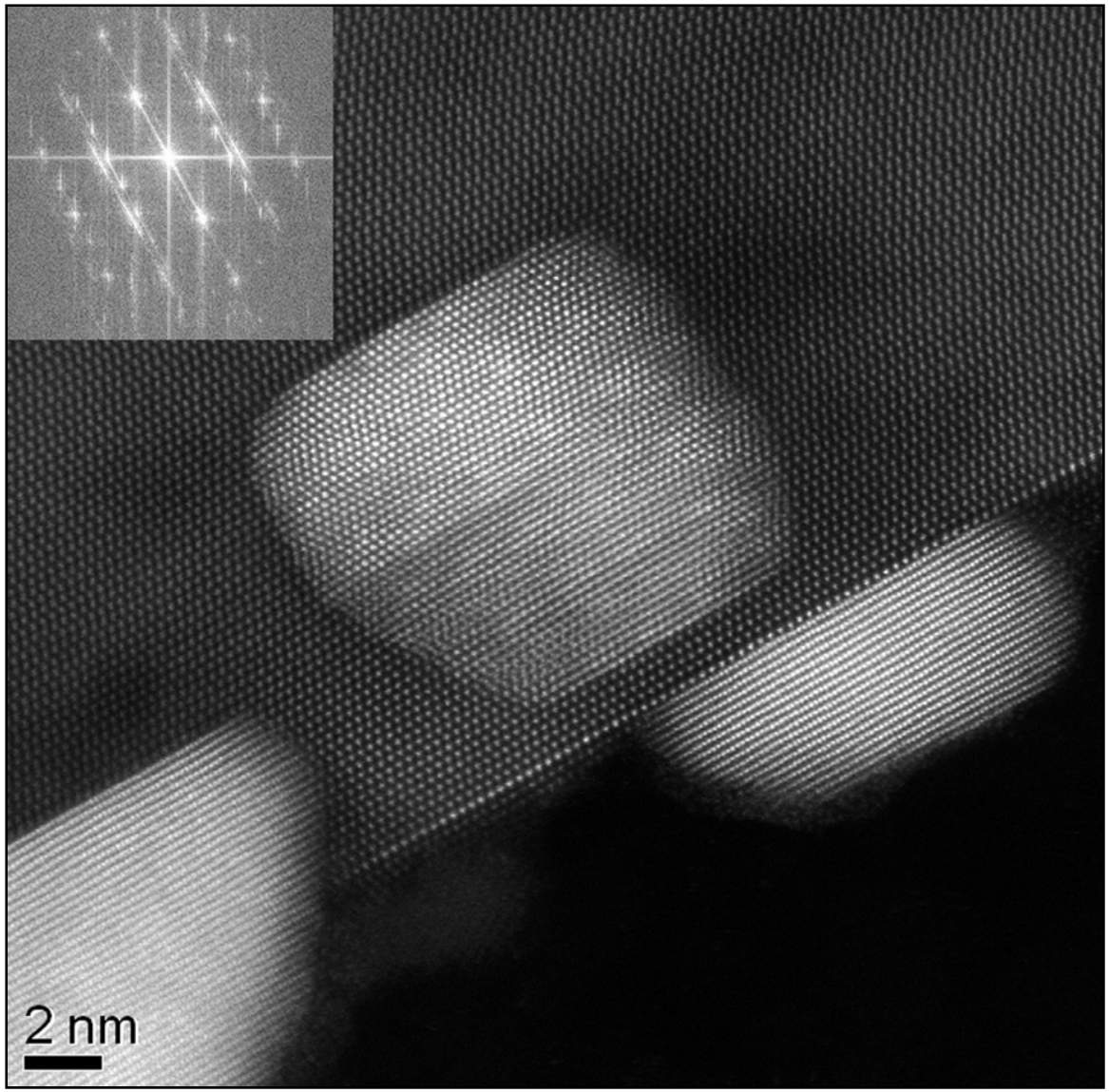


Formation of PdZn alloy nanoparticles at elevated temperatures



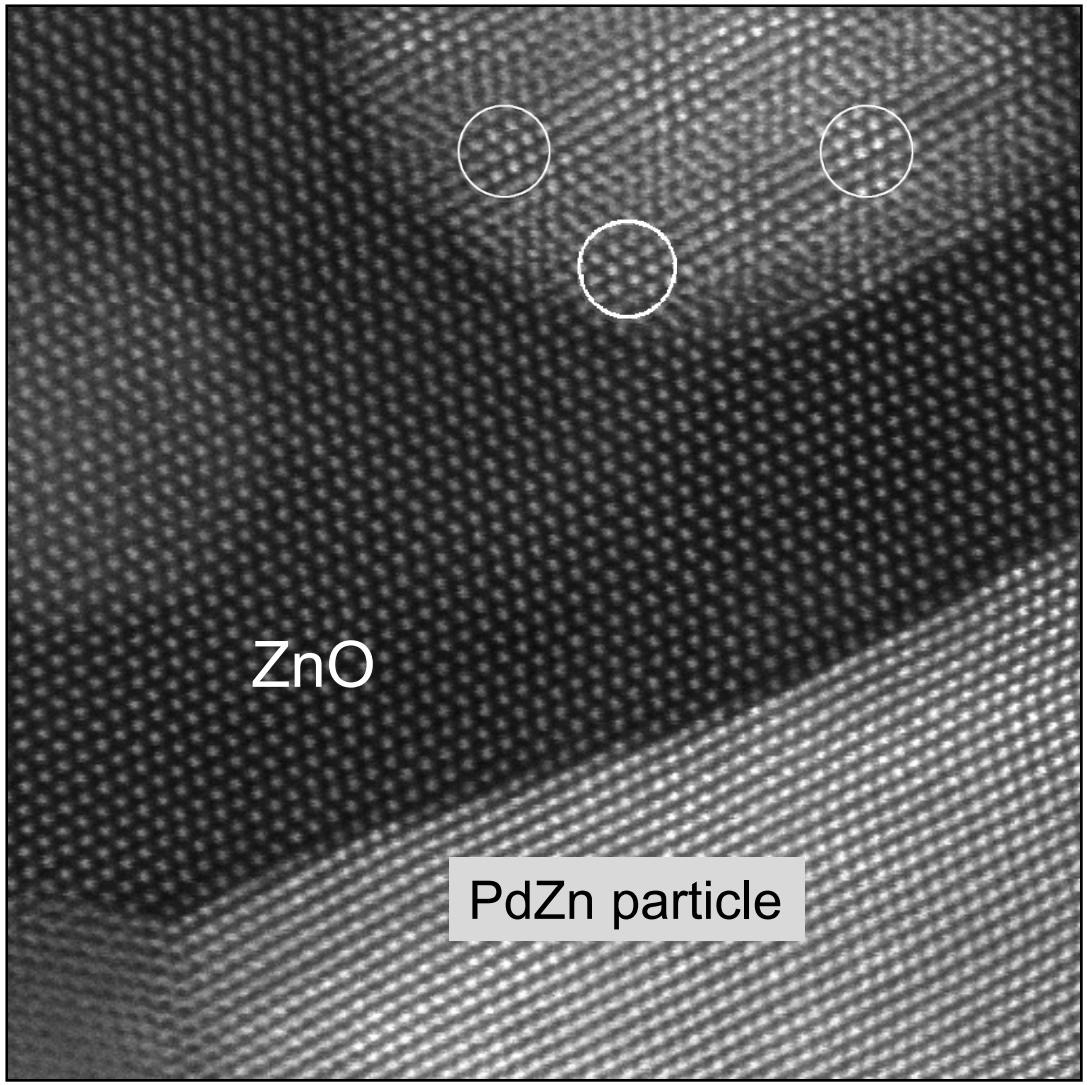
1a) Surface of precursor Pd/ZnO. Brighter columns are due to Pd atoms sitting atop columns of Zn-O.
1b) PdZn alloy nanoparticle formed after in-situ heating at 400°C for 55min. Structure is consistent with $L1_0$ tetragonal distortion of cubic FCC structure (model). Bright columns are Pd and grey columns are Zn. Note surface seems to be predominantly Zn atoms.

PdZn nanoparticles after further heating at 500°C for 30min



PdZn nanoparticles on top and edge surfaces of ZnO nanobelt. No residual Pd atoms are present on nanobelt surface. Epitactical orientations (indicated by inset diffractogram) such as these makes the catalyst more resistant to further sintering. The PdZn particles display predominant {111} planar facets.

PdZn nanoparticles on ZnO nanobelt after thermal treatment



The clear bright columns on the top surface particles (typical areas circled) vs. adjacent less well-resolved columns may result from the presence of mismatch dislocations at the interface between the particle and the ZnO surface. These may also influence the further sintering of the PdZn alloy nanoparticles.

What we learned:

- ZnO “nanobelts” are a unique model structure to study fundamentals of the behavior of Pd in formation of PdZn catalysts.
- Atomically dispersed Pd atoms sit on the {100} ZnO surface at the positions of Zn atomic columns.
- Heating in vacuum at elevated temperatures causes Pd-Zn reactions that ultimate produce PdZn alloy nanoparticles in 2-10nm size range.
- The larger PdZn particles form ordered L10 structures.
- PdZn nanoparticles are epitactically oriented with the ZnO surface.
- Epitaxy results in misfit dislocations at PdZn/ZnO interface.
- These phenomena may contribute to sintering behavior in this system.

The Origin of Oxygen Reduction Reaction Activity on "Pt_3Co" Nanoparticles: Atomically Resolved Chemical Compositions and Structures

Profs. Paulo Ferreira, UT-Austin, Yang Shao-Horn, MIT and Dr. Larry Allard

- The oxygen reduction reaction (ORR) limits the efficiency of fuel cells, and thus it is of interest to discover nanocatalysts with ORR activity superior to Pt.
- Recent research efforts have been focused on understanding surface chemistry and electronic structures on Pt alloy model surfaces that exhibit ORR activity higher than Pt.
- Pt can segregate in the outermost layer on bulk Pt alloy surfaces to form a "sandwich-segregation" or "Pt-skin structure," which is shown to weaken metal-oxygen bond strength relative to Pt, and increase specific ORR activity (based on Pt surface area).
- In addition, pure Pt on the outermost surface layer can be obtained on Pt alloys by acid removal of transition metals; such surfaces also exhibit enhanced ORR activity relative to Pt.
- It is essential to examine if the ORR mechanisms established for bulk Pt alloy surfaces are applicable to tailoring the activity of Pt alloy nanoparticles.

Experimental work

- Rotating disk electrode measurements of acid-treated "Pt_3Co" nanoparticles showed specific oxygen reduction reaction (ORR) activity twice that of Pt nanoparticles.

- Upon annealing at 1000K in vacuum, the ORR activity was increased to 4 times that of Pt nanoparticles.

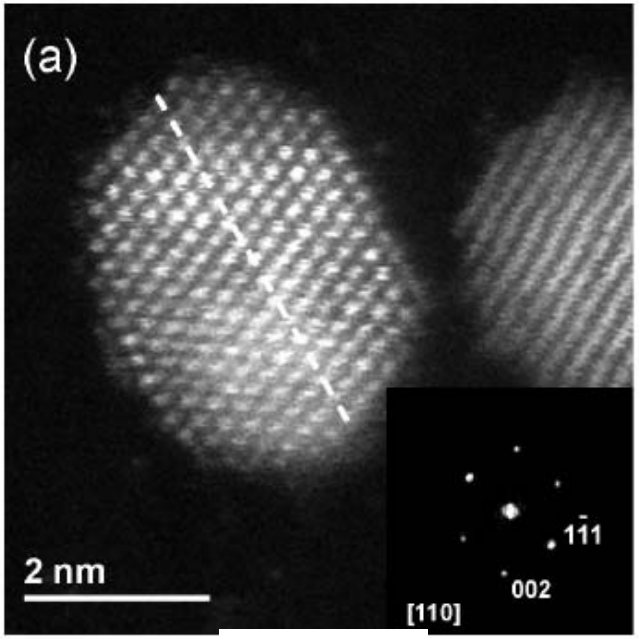
- Sub-Ångström imaging in HTML's ACEM was used to reveal surface atomic structure and chemical composition variations of Pt_3Co nanoparticles at the atomic scale.

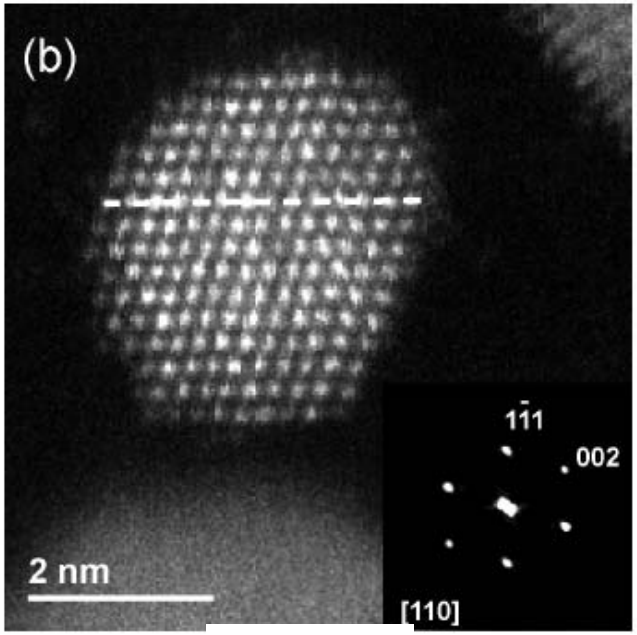
- Such information was then correlated to averaged Pt-Pt distances obtained a number of other techniques.

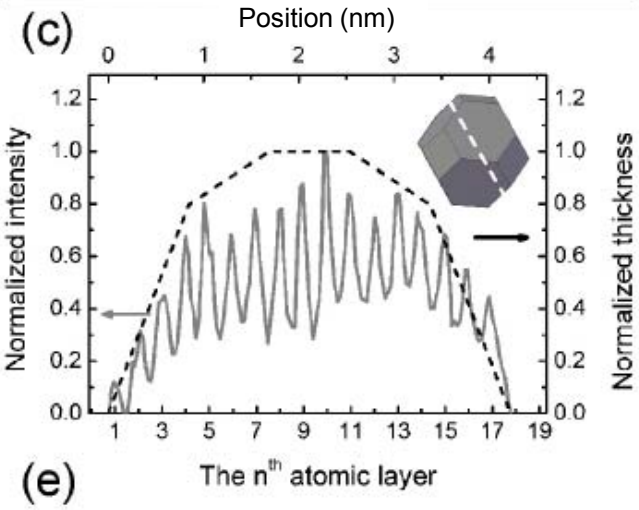
- We propose that ORR activity enhancement of acid-leached Pt_3Co relative to Pt nanoparticles is attributed to the formation of a "percolated" structure with Pt-rich and Pt-poor regions within individual particles.

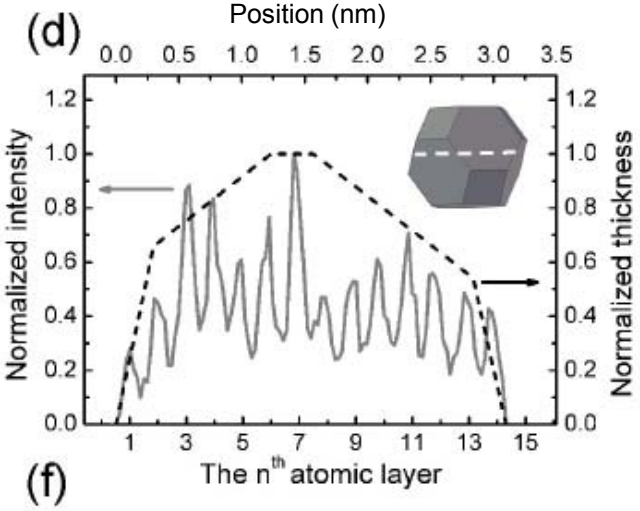
- The subsequent increase in the specific ORR activity of annealed Pt_3Co nanoparticles relative to Pt can be attributed to the presence of surface Pt segregation.

Effects of acid-leaching on nanoparticles





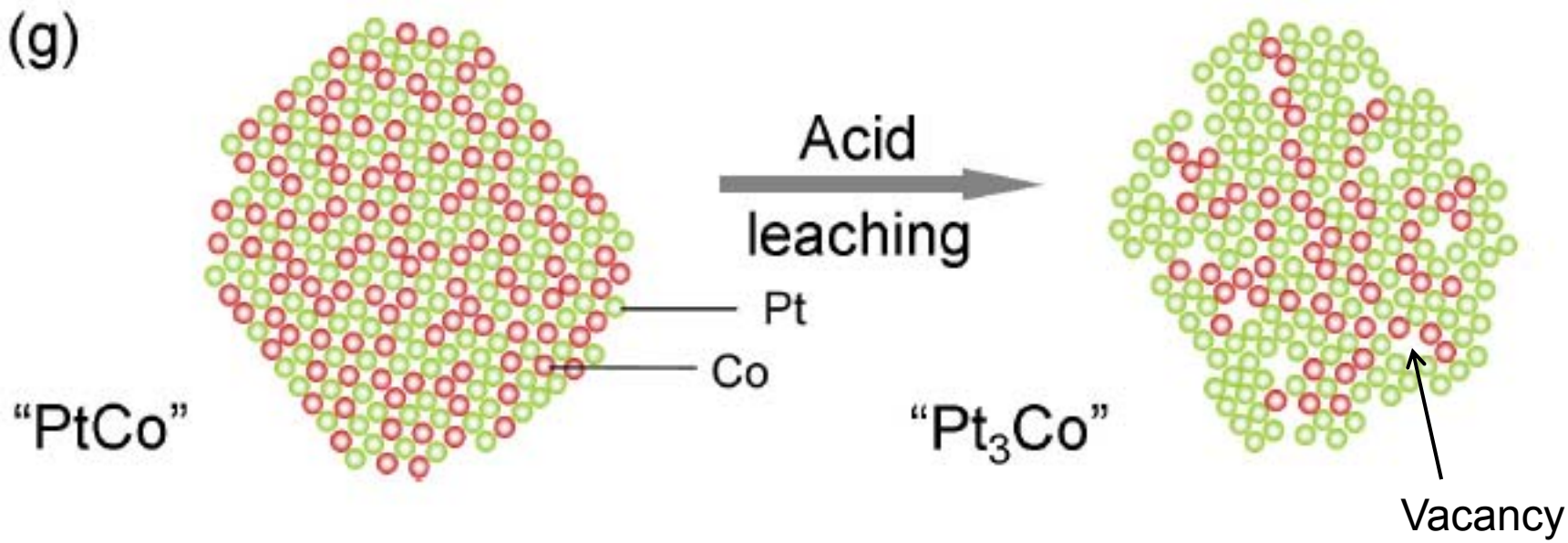




Acid-Leached "Pt_3Co" nanoparticles have reduced Co at surface

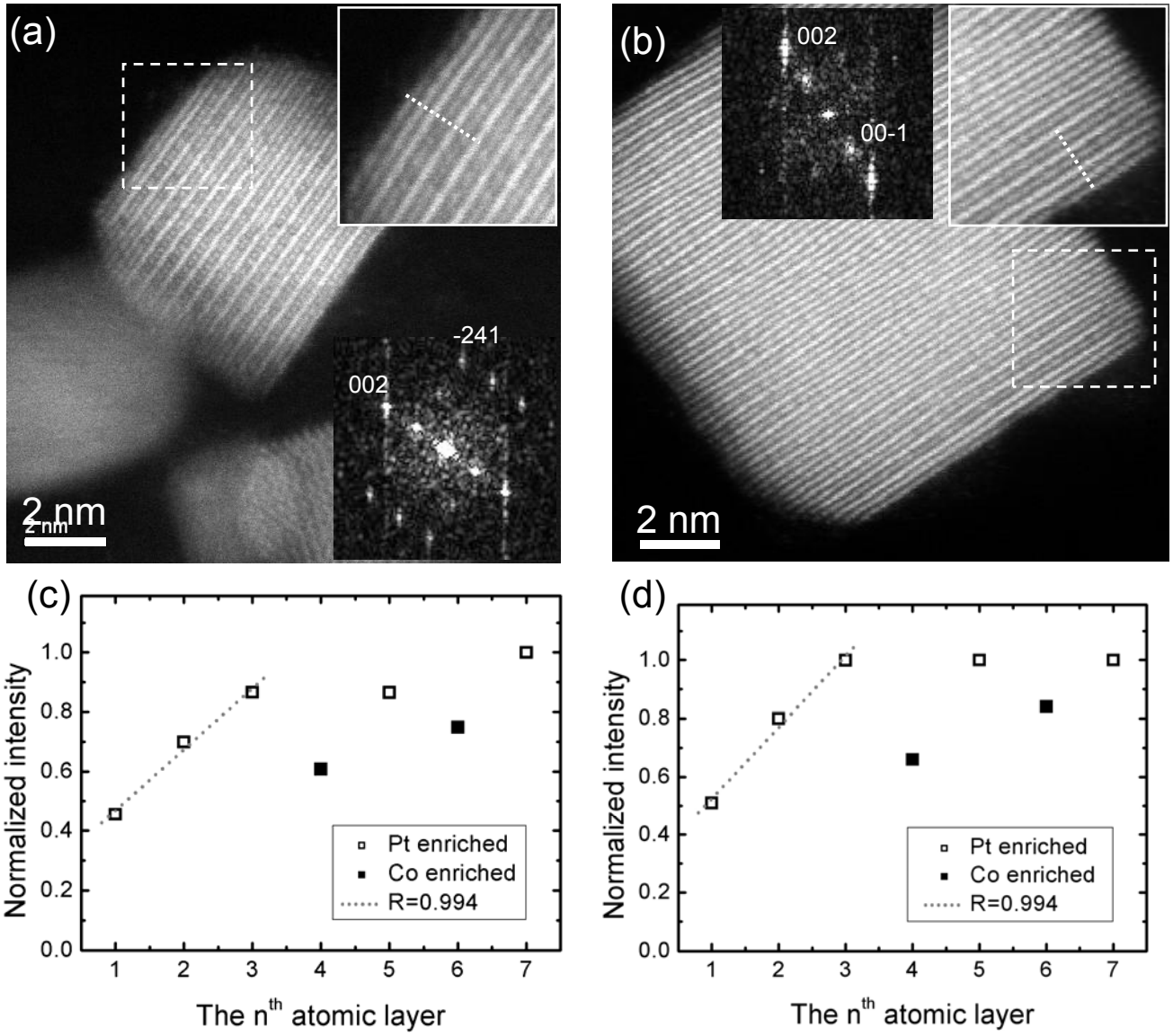
Dotted line represents true projected intensity profile for particles with the inset orientations

Schematic illustrating acid-leaching effects

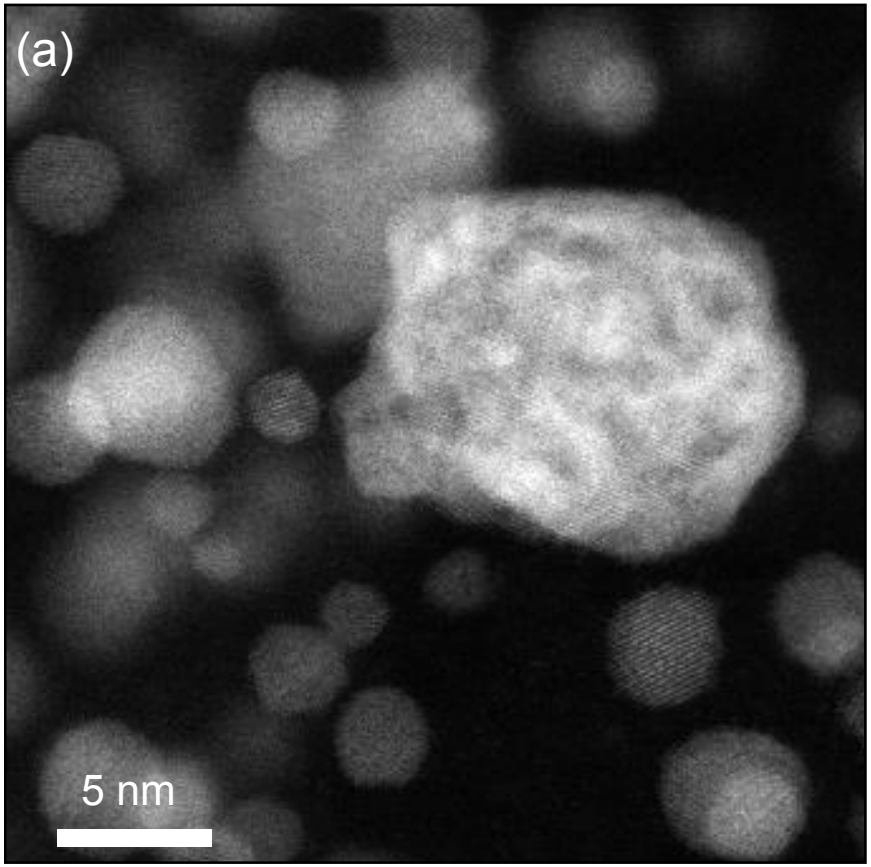


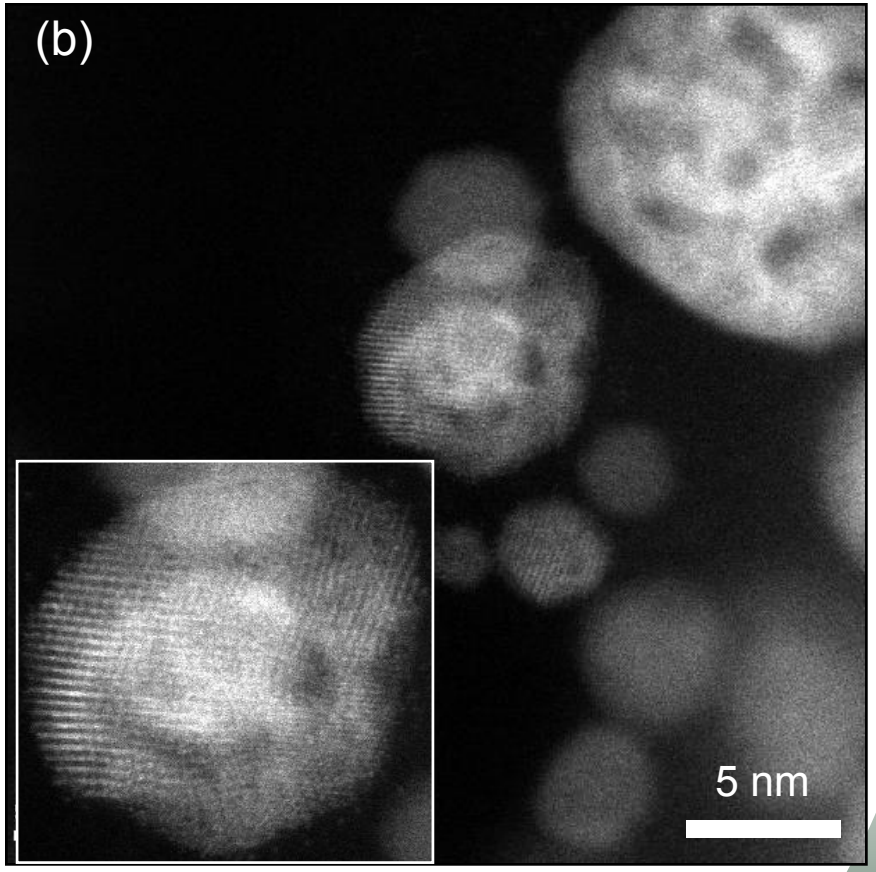
Leaching removes Co atoms from surface, leaving surface vacancies

Heat-treated AT particles show Pt enrichment of outer layers



Larger (≥7nm) particles often show intensity variations consistent with a porous (skeleton) structure with surfaces enriched in Pt





The dark regions inside the particles corresponds to volumes of relatively low average atomic number.

What we learned

- With no direct evidence, several previous studies have proposed a core-shell structure (unleached regions in the core, and Co-removed, Pt-enriched surface regions for the shell) for acid-treated Pt alloy nanoparticles.

- The percolated structure proposed for AT-"Pt_3Co" nanoparticles in this study is different from the previously proposed core-shell structure.

- Pt-enriched regions can extend from surface regions into particle core.

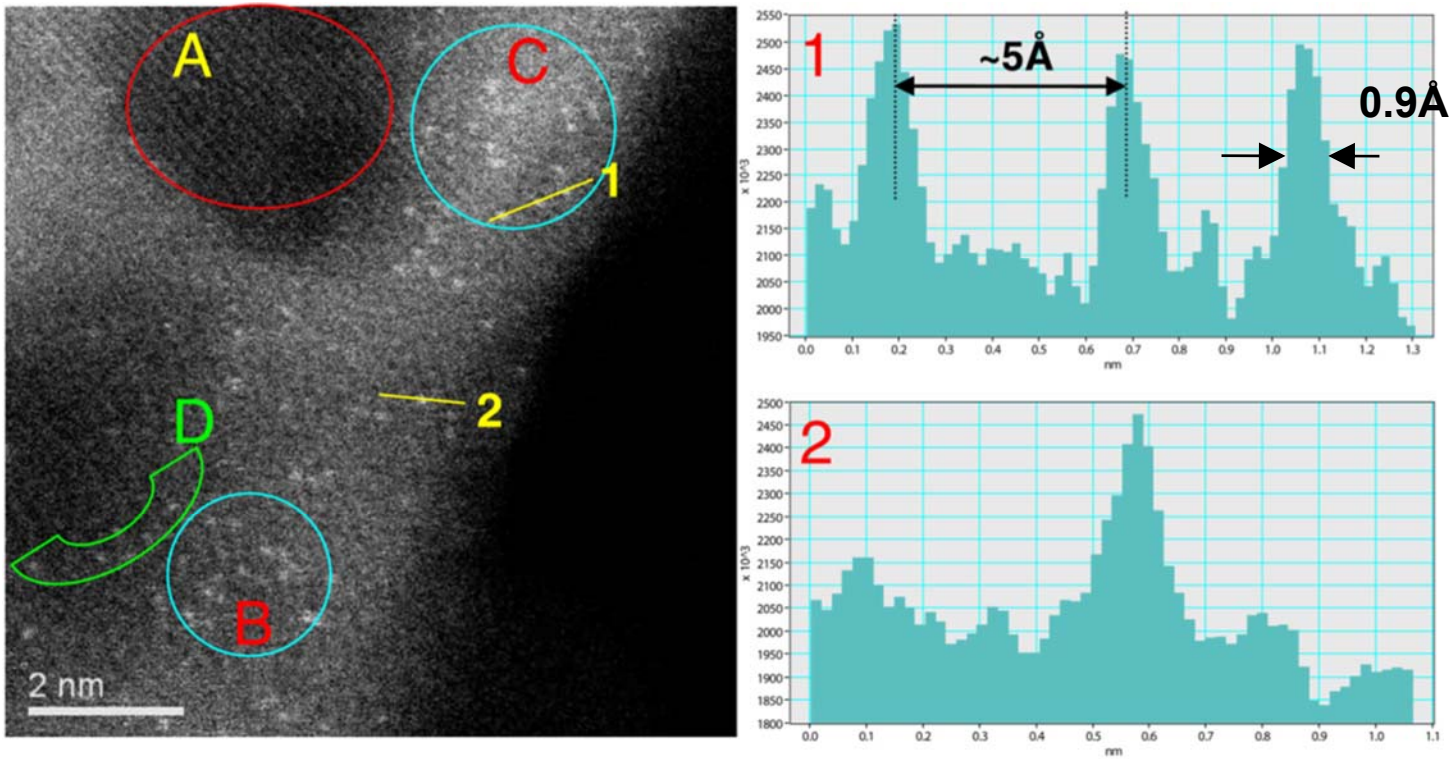
- These acid-treated Pt alloy nanoparticles were obtained under very different treatment conditions and from very different Pt alloy compositions, where different leached structures might form.

High-Resolution ACEM Studies of Catalytic Phases on ©-Alumina, in NOx-trap catalyst studies

Drs. C.H.F. Peden and J.H. Kwak, PNNL and Dr. Larry Allard

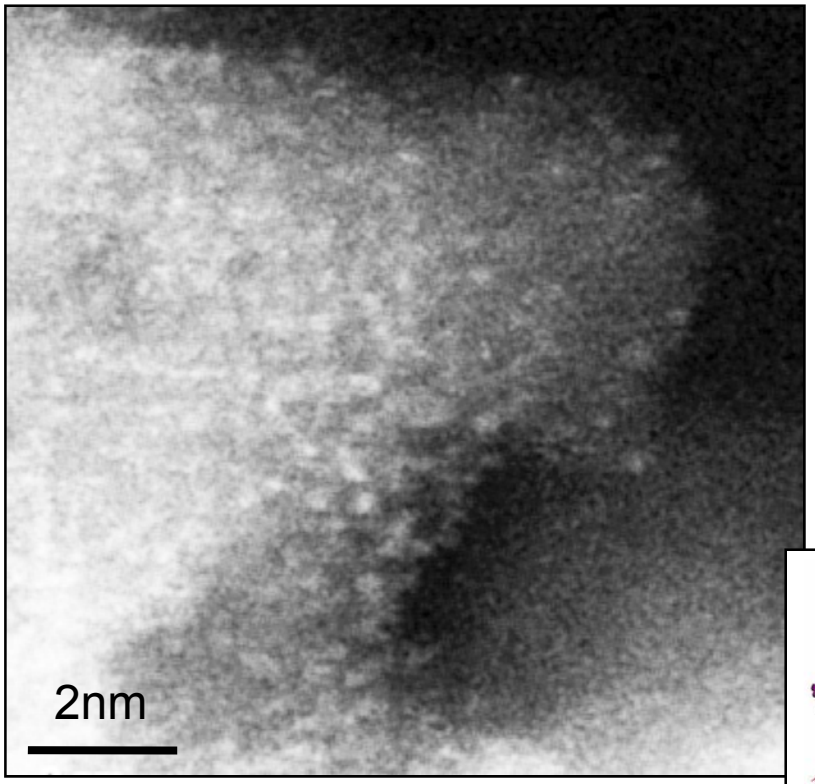
- Magic-angle spinning NMR experiments at PNNL have clearly shown penta-coordinated Al^{3+} sites are located on the surface of γ-alumina support material.
- BaO deposition onto this ©-alumina surface resulted in the loss of peak intensities that strongly suggested that, at least for BaO, these penta-coordinated Al^{3+} ions are the nucleation sites for BaO species.
- To establish the generality of this observation, we included impregnation of other catalytically interesting metal and metal oxide particles onto ©-alumina into the study .
- If this correlation holds for all active phase/©-alumina systems, it could have profound implications for the preparation of catalyst materials.
- For example, systematically varying the number of penta-coordinated Al^{3+} sites could improve control of dispersion of catalytically active phases on this important catalyst support material.
- For BaO (and perhaps other catalytically active phases as well), we expect the complex to consist of a monomeric species on the ©-alumina support surface, at low loading.
- Sub-Ångström resolution high-angle annular dark-field imaging (HA-ADF) on the HTML's aberration-corrected JEOL 2200FS electron microscope (ACEM) was used to study alumina impregnated with BaO and Pt species.

ACEM imaging of 2% BaO/alumina

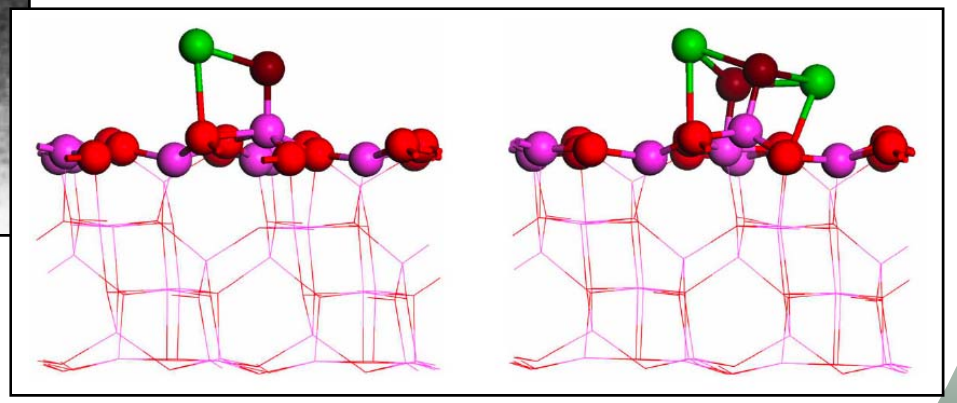


The high resolution HA-ADF image differentiates regions on the ©–Al_2O_3 *support that have significantly different BaO populations.* In A, no BaO units are seen, in accord with the prediction of DFT calculations that suggest the complete absence of pentacoordinated Al^{3+} sites on some facets that would serve as anchoring points for BaO. In regions B and C the BaO units are uniformly dispersed; intensity profiles1 and 2 are consistent with single BaO units. Region D may show decoration of a step. These observations are all consistent with the results of our recent high resolution solid state NMR study that showed preferential anchoring of BaO monomers onto Al^{3+} penta sites formed by the dehydroxylation of the ©–Al_2O_3 *(100) surface.*

ACEM imaging of 8% BaO/alumina



NMR results showed that to saturate all the Al3+ penta sites a loading of 4% BaO was required. At 8% loading, each site should have a dimer of BaO. Comparing the Z-contrast image of an area of the 8% loaded sample to the preceding 2% loaded sample suggests that this area comprises BaO dimers to a large extent, validating the NMR results.



Model structures of BaO monomer and BaO dimer on alumina

What we learned

- Sub-Ångström imaging with the ACEM provided direct visual evidence to support the NMR observations of BaO species on γ-alumina.

- At 2% loading, approximately ½ the Al^{3+} pentacoordinated sites in the γ-alumina are filled with BaO monomers.

- At 8% loading, all the Al^{3+} penta sites should be filled, with BaO dimers. ACEM images were consistent with this observation.