Challenges and Approaches to Nanoscale Materials Characterization at Atomic Resolution

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“Nano” is both ubiquitous and diverse in areas of impact...
A big toolbox for characterization at atomic resolution!
Advanced Analytical Electron Microscopy

- While rapidly advancing, there remain important challenges and opportunities for improvement.
- Aberrations generally limit the resolution of common microscopes.
- Over the last decade, many limitations have been addressed successfully.

Electron Microscopy: Spherical Aberration

- Arises from the curvature of lens
- Although magnetic lenses are not made of glass, the optics behave as if a glass lens system is in use
  - Electron beams not all at focal plane
    - Distorts the resolution of the image
  - $C_s$-corrector compensates for effects of aberration
    - Supplies a separate magnetic field to focus electrons farthest from the optic axis to one focal point
      - Improves resolution
- Positioning the corrector
  - Before the sample
    - Results in a finely focused electron probe capable of atomic resolution

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The intensity from HAADF detector is proportional to the:
1. number of stacked atoms
2. atomic number, Z

Single atom cross-section for scattering

\[ \frac{d\sigma(\theta)}{d\Omega} = \frac{\epsilon^4 Z^2}{16(E_0)^2 \sin^4 \frac{\theta}{2}} \]

(a) STEM image of single crystal Si along the \langle110\rangle with an intensity profile (b) and the accompanying FT (c) demonstrating ability to resolve atomic columns of Si 0.136 nm apart.

Models: Synthesis and Characterization of Pt and Pd Particles

- Hexachloroplatinic Acid
- Palladium Acetate
- Polyvinylpyrrolidone (PVP)

\[
\text{Hexachloroplatinic Acid} + \text{Polyvinylpyrrolidone (PVP)} \xrightarrow{\text{Refux @ 463K, N}_2, \text{pH}=10} \text{PVP-protected Pt Nanoparticle}
\]

- Polyvinylpyrrolidone (PVP)

\[
\text{Polyvinylpyrrolidone (PVP)} + \xrightarrow{\text{Refux @ 433K, N}_2, \text{pH}=8} \text{PVP-protected Pd Nanoparticle}
\]

Micrograph of PVP-capped Pt Nanoparticle

Micrograph of PVP-capped Pd Nanoparticle

Atom Quantification and Crystal Morphological Approximation

X-ray Diffraction Profiles

- Monometallic Pd
- Monometallic Pt

Models II: Synthesis and Characterization of Bimetallic Pt-Pd Nanostructures

CONTROLLED BIMETALLIC CORE/SHELL STRUCTURE:
Core shell motif with Pd at the core

H₂, 298K
Ethanol

H₂PtCl₆ (aq), N₂
Ethanol 298K

CONTROLLED BIMETALLIC CORE/SHELL STRUCTURE:
Core shell motif with Pt at the core

H₂, 298K
Ethanol

PdCl₂ (aq), N₂
Ethanol 298K

X-ray Diffraction Profiles

Modeling Nanoparticle Morphologies

- Pd particle modeled after icosahedron
  - Electron microscopy simulations used to replicate experimental patterns
- Theoretical core-shell structures also modeled
- Simulated scans adequately replicate intensity patterns that were found experimentally


XAS equation:

\[ \chi(k) = \sum_{j=1}^{\text{Shells}} \frac{N_j}{kR_j^2} \left( S_0 F_j(k) e^{-2k^2\sigma^2_j} e^{-2R_j/k} \right) \sin \left[ 2kR_j - \phi_j(k) \right] \]

N: Average coordination of probed element
R: Real-space distance traveled by photoelectron, combination of single and multiscattering paths
\( \sigma^2 \): Information about bond disorder

Mesoscopic Characteristics at the Nanoscale: Negative Thermal Expansion of Pt/\(\gamma\)-Al\(_2\)O\(_3\)

Different sized clusters of Pt on \(\gamma\)-Al\(_2\)O\(_3\) were examined by XAS.

Temperature-dependent measurements reveal a contraction of the first nearest neighbors bond distances with increasing temperature – negative thermal expansion (NTE).

This behavior varies with the size of the supported particle, the ambient gas, and the choice of support. XANES measurements show that NTE is correlated with changes in electronic structure.

Comparison of theoretical and experimental XANES data for a 10-atom Pt cluster supported on \( \gamma \)-Al\(_2\)O\(_3\). The theoretical spectra are obtained from a configurational average of 32 random conformations extracted from a 5.5 ps MD simulation.

Molecular Dynamics simulation of the cluster determined that the bonding between the cluster and the support was dynamic in nature. In the simulation the gold atoms represent Pt atoms bonded directly to the \( \gamma \)-Al\(_2\)O\(_3\) whereas purple atoms denote Pt atoms free from the interface.

*Phys. Rev. B 2008, 78, 121404(R).*
Anomalous/Mesoscopic Bond Disorder: Quantification Using XAS

Disorder can be characterized for these clusters via Debye-Waller factor ($\sigma^2$) measurements obtained using XAS.

The level of disorder is highly sensitive to nanoparticle size, the presence of a reactive gas, and the choice of the support.

The nature of the disorder requires analytical models. To definitively determine whether the enhanced disorder is strictly coordination dependent or more randomized requires direct observations.

$$\sigma^2 = \sigma_s^2 + \sigma_d^2$$

$$\sigma_d^2 = \frac{\hbar}{2\omega\mu} \frac{1 + \exp(-\Theta_E/T)}{1 - \exp(-\Theta_E/T)}$$

Nano-Area Coherent Electron Diffraction and Modeling of Surface Relaxation in Au Clusters

Contraction model based on distance to cluster center and coordination

\[ \Delta r = \alpha \cdot \kappa(h, k, l) \cdot r \cdot \ln(12/\hat{n}) / r_0 \]

r=distance to center, \( r_0 \)=average cluster diameter, \( n \)=coordination, \( \alpha \)=scaling parameter, \( \kappa(h, k, l) \)=ratio describing facet-dependent contraction


Dashed white arrow in (a) is the <002> direction in reciprocal space and the solid white arrow points toward the central beam.

Vectors representing surface atom displacements. The magnitudes of the displacements are rendered using colors.
Metal-Support Interactions and Atomic Strains

- Impregnation of and reduction of $[\text{Ir}_3\text{Pt}_3(\mu-\text{CO})_3(\text{CO})_3(\eta-\text{C}_5\text{Me}_5)_3]$ on $\gamma-\text{Al}_2\text{O}_3$
- Stoichiometry of precursor retained
- Hemispherical cubeoctahedral structures
- Lattice of support observable - and identifiable - near clusters with aligned zone axes

To be submitted.
Characterization of Interfacial Charge Transfer

- Electron energy loss spectroscopy (EELS)
  - Can be used to characterize the electronic structure of a material
  - Elucidate oxidation states of atomic columns when using an aberration-corrected microscope

Arrows A and C are represented by the EELS spectra “Outside Nanocrystal.” The shifts in the red and black spectra correlate with Ti$^{3+}$ and Ti$^{4+}$, populations for surface and bulk TiO$_2$ sites, respectively. Arrow B represents the EELS spectrum collected “At Nanocrystal”.  

Coherent Diffractive Imaging

- Diffractive imaging provides atomic resolution structural determinations even when an atomic-resolution imaging lens is not available—radiation damage lessened
- Synergistic information from electron diffraction and low resolution images
- Micrograph of CdS quantum dot (with inset electron diffraction pattern) prior to refinement by diffractive imaging
  - Only shows lattice planes but no atomic detail
- After integrating with the electron diffraction data atomic details are revealed
  - Resolution improved to subangstrom resolution
    - 0.84 Å separation between Cd and S atoms
- This technique has also been implemented to provide the structure of carbon nanotubes
  - Chirality and presence of double walls clearly visible

*Science* 2003, 300, 5624.
Some Important Limitations for Analysis and Future Directions

- Current methods can reveal
  - Atomic structure
  - Speciation of elements at the nanoscale
  - Electronic structure

- Challenges
  - Structural dynamics
    - Limited (or no) temporal resolution to monitor processes
  - Atomic level characterization of adsorbate-interface bonding
  - In situ studies
  - Theory vs. experiment (“too many” atoms, excited electronic states, chemistry.....)