Structural Characterization of Nanoparticles

Nicola Pinna

Max Planck Institute of Colloids and Interfaces

e-mail: pinna@mpikg-golm.mpg.de - http://www.pinna.cx
1. Transmission Electron Microscopy
   - Selected Area Electron Diffraction
   - High Resolution Transmission Electron Microscopy
   - HRTEM Simulations

2. X-Ray Diffraction
   - Particle Size Broadening
   - Sherrer equation
   - Debye scattering equation
Transmission Electron Microscopy
Transmission Electron Microscopy
Assembly of Nanoparticles
Electron Diffraction
HRTEM & Power Spectrum

\[ d_{hk\ell} = \frac{N_{\text{pix-image}} \times P_{\text{size}}}{N_{\text{pix}}} \]  

\( N_{\text{pix-image}} \): Number of pixels along the quadratic frame (128, 256, 512 ...) of the image

\( P_{\text{size}} \): Pixel size in the HR image

\( N_{\text{pix}} \): Number of pixel between the origin and the reflection \( h\ell\ell \) studied
HCP - FCC structures*

Crystals oriented along the [110] direction

*The wurtzite structure is composed by two hcp networks, one occupied by the sulfur and the other by the cadmium, shifted by $00\frac{1}{4}$. The zinc blende structure is composed by two fcc arrays, as for the hcp occupied by the sulfur and the zinc respectively, shifted by $\frac{111}{444}$. 
Single Crystal Diffraction
Computer simulation of the HRTEM images on the basis of the structure of model particles with the multislice technique:

1. The construction of one or more atomic models of the nanocrystals
2. The calculation of the HRTEM image of these models
3. The calculation of the PS of the calculated HRTEM image
4. The comparison of the HRTEM images and the PS calculated with the data obtained from the experimental HRTEM
Multislice Technique

Electrons are assumed to scatter only in a forward direction with small diffraction angles. With this approximation the crystal can be divided in sub-slices with a thickness $\Delta z$ perpendicular to the incident beam.

1. The crystal is divided in slices perpendicular to the electron beam

2. The electrostatic potential $V(x, y)$ with in-plane coordinates $x, y$ of the sliced crystal or supercell is projected for each slice of the included atoms onto its exit surface

3. On the basis of $V_P(x, y)$ the amplitude of the electron wave function is calculated

4. Calculate the propagation of the electron wave throught all the slices

HRTEM Simulations
HRTEM Simulations

![HRTEM Simulations Diagram](image-url)

- $d^* (\text{Å}^{-1})$
HRTEM Simulations
HRTEM Simulations
Copper Nanoparticles
Copper Nanoparticles

1 nm
Tungstite
Tungstite
Tungstite
Tungstite
Oriented Attachement

Electron Energy Loss Spectroscopy

Inelastic scattering of an electron of the incident beam and the atomic electrons of the solid.

- Transition from an inner-shell \((K, L, M \ldots)\) to an unoccupied energy level (i.e. above the Fermi level)

- Transition of a valence electron across the energy gap (insulator, semiconductor) or excitation of a plasma resonance (mostly in metals metals).
Electron Energy Loss Spectroscopy
Electron Energy Loss Spectroscopy

YBa$_2$Cu$_3$O$_7$  
Carbon allotropes
Electron Energy Loss Spectrometry

α-V₂O₅

γ-V₂O₅

Counts (au)

Energy Loss (eV)
Electron Energy Loss Spectrometry

Intensity (a.u.) vs. $(E-E_p)$ (eV)

DOS (a.u.) vs. $(E-E_p)$ (eV)

- 01
- 02
- 03
- 04
- 05

01,02,05 around V2

01,03,04 around V1
TEM permits the structural characterization of a collection or isolated nanoparticles

Electron Diffraction → structure of single or many particles

HRTEM → structure, orientation, crystallinity, defaults

Image processing: fundamental tool for structural studies in electron microscopy

Spectroscopy: EELS, EDX → local structure, band structure, composition

Do not permit to study structural properties of the whole sample → Necessity to compare the results with other techniques
Particle Size Broadening

\[ I = I_e F^2 \sin^2(\pi/\lambda)(s - s_0)N_1 a_1 / \sin^2(\pi/\lambda)(s - s_0) a_1 \times \ldots N_2 a_2 \times \ldots N_3 a_3 \] (2)

\( N_1, N_2, N_3 \) Number of the unit cells along the \( a_1, a_2, a_3 \) directions

Normally \( N_1, N_2, N_3 \) are large numbers → the three quotients differs from zero only if the three Laue equations are closely satisfied. If \( N_1, N_2, N_3 \) are small, the quotients broaden.

B.E. Warren, X-Ray Diffraction, Dover
Sherrer Equation

Approximations:
1) Cubic crystal $N_1, N_2, N_3 = N$
2) Crystal free from strains and faulting $\rightarrow$ peak broadening is only due to the small crystallite size
3) Each of the three quotients of equation 2 by a Gaussian function

$$B(2\theta) = \frac{2 \left[ (\ln2)/\pi \right]^{1/2} \lambda}{N a \cos\theta} = \frac{0.94 \lambda}{L \cos\theta}$$

$B(2\theta)$: full width in radians at half maximum intensity of the powder pattern peak.

$L$: cube edge dimension

Normally valid for cubic crystal but often applied to non-cubic materials. It is not a bad approximation if for each $hkl$-reflection the L value is interpreted as an average crystal dimension perpendicular to the reflecting plane.
Debye Scattering Equation

The intensity distribution spherical averaged over the reciprocal space is described by the Debye formula:

\[ I_N(b) = \sum_{n,m \neq n}^N f_n f_m \frac{\sin(2\pi br_{nm})}{2\pi br_{nm}} \]  \hspace{1cm} (4)

\[ b = \frac{1}{d} = \frac{2\sin\theta}{\lambda} \]

\[ r_{nm} \] distance between atom \( n, m \)

\( f_n, f_m \) atomic scattering factors

- General equation valid for any form of matter in which there is a random orientation: gases, liquids, amorphous solids, and crystalline powders.
- No limitation on the number of different kinds of atoms in the sample.
- The number of terms increases proportional to the sixth order!
BaTiO$_3$ 6 nm
CeO$_2$ 2.5 nm
Final Example: HfO$_2$

Monoclinic Structure:

\[ a = 5.12 \text{ Å} \quad b = 5.18 \text{ Å} \quad c = 5.25 \text{ Å} \]

\[ \beta = 98^\circ \]
Final Example: HfO$_2$
X-Ray diffraction associated to calculations is a powerful tool to study the:

- Structure
- Crystallinity
- Particle size and size distribution
- Particle shape
- Homogeneity of the whole sample

It is the perfect tool to be associated with transmission electron microscopy study.