

# Important Aspects of Nanomaterial Description

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*[Personal perspectives and opinions of the author, prepared prior to the Workshop]*

## **Implementation Criteria - sine qua non : The Big Picture**

- Description must serve a useful function
- Language must be plain, scientifically precise, specific, un-ambiguous, and timeless.
- Must be made perfectly clear to scientists, lawyers, engineers, legislators, corporations, manufacturers, health care professionals, insurers, government agencies, and community organizations. A precise glossary of technical terms is essential.
- Must be realistic and accessible for potential users to test and implement in practice.

## **The Description: Important Items**

### Basic Definition of a Nano-Material:

*Propose:* "An object whose (one or more) small overall dimensions or small-scale surface topographic structure may cause its passive interactions with other materials (or with its environment) to differ from those of a macroscopic object of identical bulk elemental composition." [ i.e. Define by the existence of the possibility for modification of external interactions compared to those of a macro object of identical elemental composition, due to the small size of a particle or of topographic features of a surface]. i.e. Define by possible change of interactions caused by nano-dimension(s) of the particle or of surface topography.

### Activated Surfaces

Catalytic/chemical activity of surfaces or surface coatings is often maximized by imposing nano-structure to increase "effective surface area exposed". Does this count? I think it should do, since, if extrapolated, it enters the realm of interactions different from those of a bulk material surface. At the nanoscale in question, the surface becomes analogous to one coated with independent nanoparticles, whose properties might well change non-linearly with total surface area. Alternatively, we could limit the Basic Definition to cases where the external interaction scales non-linearly with net surface area exposed. However, many known metal-support interactions already scale non-linearly with net exposed surface area. I think that these appropriately fall into the category of nano-materials under these conditions.

### Agglomerated Nanoparticles

If deprived of some protective buffer coating (e.g. attached ligands acquired during particle synthesis in liquid medium), nanocrystals may cluster, without any change of structure or phase. Alternatively, at elevated temperature, ordered crystal growth may occur, creating macro particles. These processes may occur within the host medium, or by thermal diffusion on a passive support surface. Agglomeration without fusion should not change the classification of the material as a nano-material, since its components still meet the definition criteria. However, fusion/crystallite growth will eventually change the description to 'macro-material'.

## **Inorganic Nanoparticles: Inconvenient Truths**

Chemical Activity (energy and nature; reactive; catalytic) is site-specific.

- Enhanced at edge and corner sites

### Particle Shape

- determines the population of edges and corners
- depends on composition, size and temperature
- depends on process of formation

### Particle Size Distribution

- depends on elemental composition and number of atoms
- depends on process of formation
- vulnerable to particle agglomeration

### Stability of Particle Characteristics

- depends on elemental composition
- depends on size
- depends on temperature and thermal history (phase changes / agglomeration, etc.)
- depends on crystalline phase
- depends on environment (gas / liquid / support surface / neighboring particles)
- depends on any added coatings or ligands .

### Illustrative Pictorial Examples

- Fig. 1. Particle size determines the relaxed shape of the particle.
- Fig. 2. Particle shape changes with temperature. Chemical activity is highest for those atoms at corner or edge sites.
- Fig. 3. Phase diagram for a single crystallite. For a given size, the stable phase depends on temperature.
- Fig. 4. Nanoparticle size also affects layered sub-structure for diamond (carbon).
- Fig. 5. Catalytic activity is greatest for edge and corner sites. It is tunable by selection of particle size and core material.
- Fig. 6. For a compound particle, there is close correlation between exact composition and population of the surface with active atoms.
- Fig. 7. Agglomeration / coalescence event between mobile particles causes phase change.
- Fig. 8. Nanoparticle phase and shape depend on environment and support material.

## **Identifying Meaningful Descriptors for a NanoMaterial**

Inorganic nanoparticles are inherently unstable, as noted above. Although particle size, and size dispersity at the point of delivery are useful to report, it is primarily important to report the non-ephemeral properties.

### Durable Basic Characteristics

- Elemental composition in bulk; known impurities
- Size and size distribution - expressed in number of atoms per particle, with approximate particle dimensions if known
- Crystalline phase and shape if known
- Temperature range for stability
- Applied protective coating, if any
- Non-interactive ambients (gases, liquids, contact surfaces)

### Handling Factors that May Affect Nanoparticle Characteristics

- Thermal history [Can readily cause shape/phase changes in a given particle]
- Ambient exposure. [ e.g., O<sub>2</sub> or H<sub>2</sub>O can passivate specific sites, activate others, promote or inhibit agglomeration]
- Support surface; containment material. [ e.g. metal-support interaction may change particle surface activity]

### Issues of Batch Description

- Size dispersity. [Mono-disperse fabrication is rare. "Mean Size" is totally inadequate specification, since batch performance can be dominated by a minority impurity population. "RMS size variance" needs to be specified.]
- Temperature range for which the 'description' is certified.
- Storage / Shipping medium.

### Known Health Hazards

- Exposure hazard levels for contact, inhalation, ingestion
- Recommended handling practices
- Responsible disposal procedure

## Some Critical Characteristics of Inorganic Nanoparticles Pictorial Examples

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Particle size determines the relaxed shape of the particle.

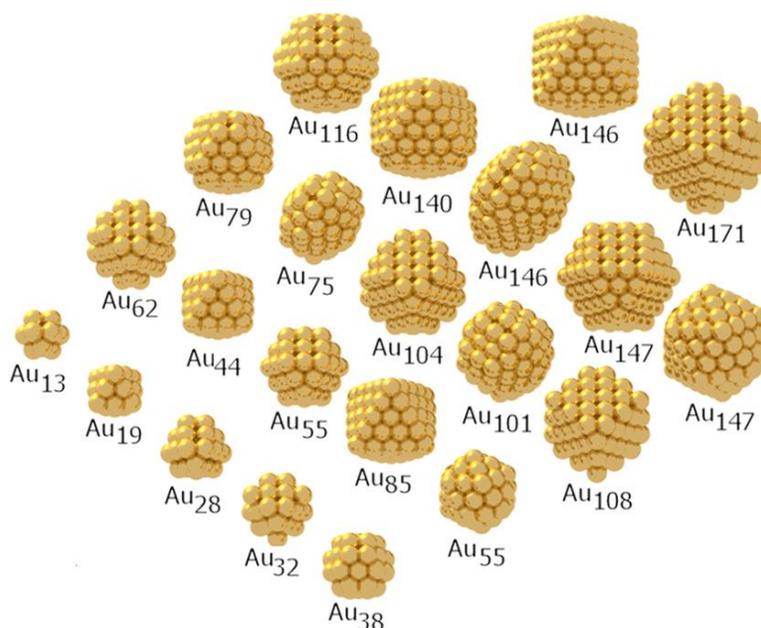


Fig. 1. Virtual sample set of relaxed gold nanoparticles of different sizes and shapes. The subscripts refer to the number of atoms. Note examples where the same number of atoms may form more than one closed-shell shape (icosahedral and cuboctahedral Au<sub>55</sub>, octahedral and decahedral Au<sub>146</sub>, icosahedral and cuboctahedral Au<sub>147</sub>).

A.S. Barnard, "Modelling of Nanoparticles: Approaches to Morphology and Evolution", Rep. Prog. Phys. **73**, 086502 (2010)

**Particle shape changes with temperature.  
Chemical activity is highest for those atoms at corner or edge sites.**

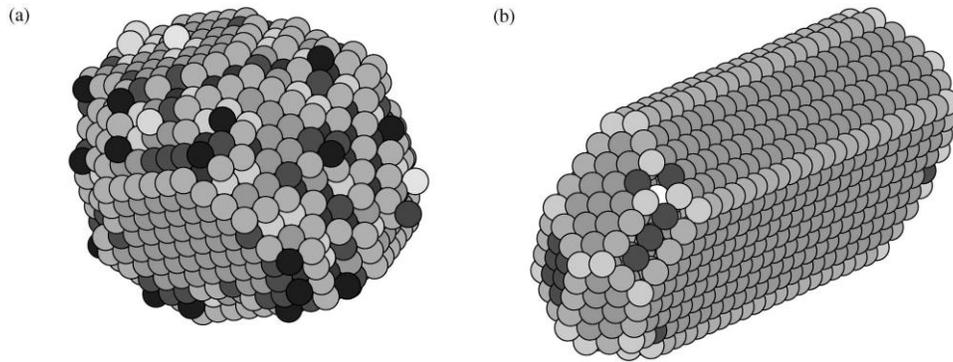


Fig. 2. Morphologies of crystallites of 1728 atoms at two different temperatures: (a) partially rough at 700 K and (b) fully faceted at 300 K. The shade of each atom depends on its number of neighbors.

N. Combe et al., "Changing Shapes in the Nanoworld", Phys. Rev. Lett. **85**, 110 (2000)

**Phase diagram for a single crystallite**  
For a given size, the stable phase depends on temperature.

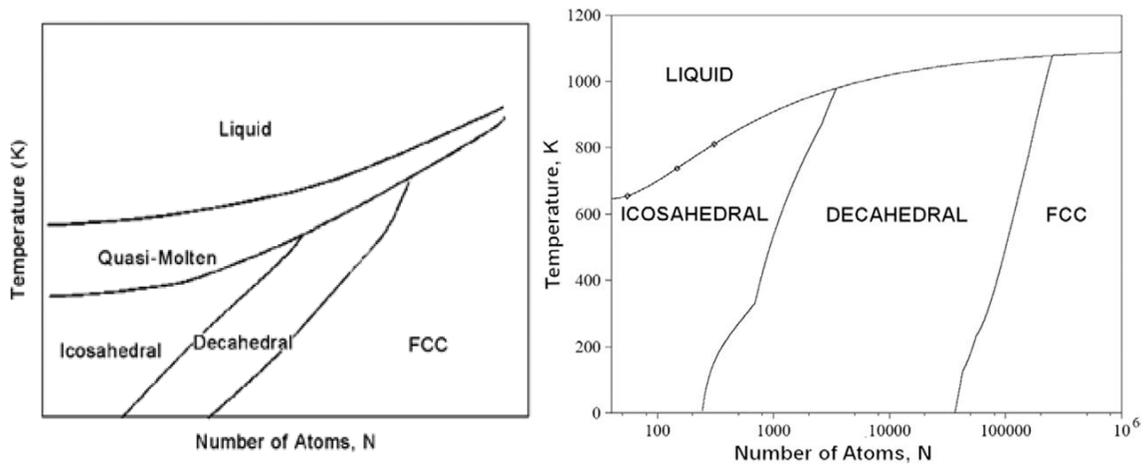


Fig. 3. The qualitative phase diagram of gold nano-crystallites computed using classical MD

C.L. Cuo and P. Clancy, J. Phys. Chem B **109**, 3743 (2005)

The calculated phase diagram of silver.

J.P.K. Doye and F. Calvo, "Entropic Effects on the Size Dependence of Cluster Structure", Phys. Rev. Lett. **86**, 3570 (2001)

**Nanoparticle size also affects layered sub-structure for diamond (carbon).**

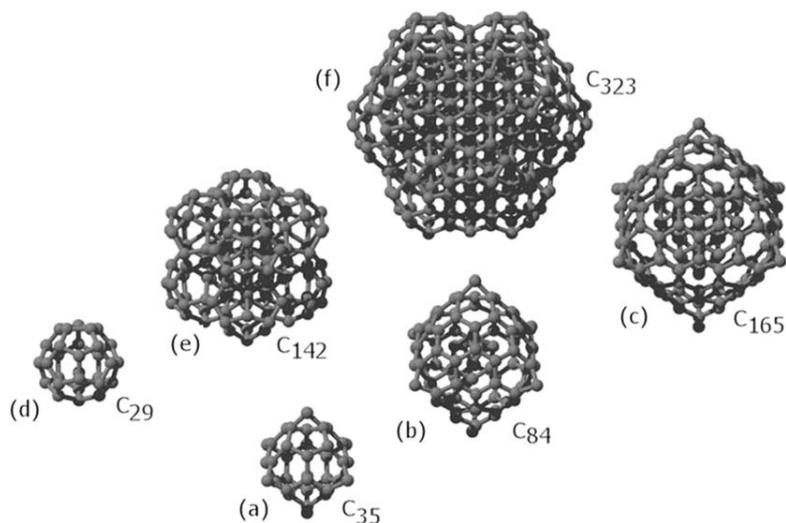


Fig. 4. Virtual sample set of relaxed diamond nanoparticles with (a)–(c) cuboctahedral and (d)–(f) octahedral morphologies. The subscripts refer to the number of atoms.

A.S. Barnard, "Modelling of Nanoparticles: Approaches to Morphology and Evolution", Rep. Prog. Phys. **73**, 086502 (2010)

**Catalytic activity is greatest for edge and corner sites. It is tunable by selection of particle size and core material (see Table)**

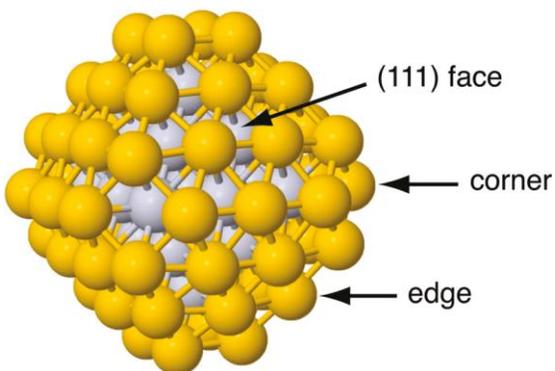


Table 1. Ethylene Binding to (111) Faces (eV)

	NP-38	NP-79	NP-140
Ni	0.94	0.73	0.77
Pd	0.65	0.74	0.75
Pt	1.35	1.24	0.99
Cu	0.11	0.29	0.14
Ag	<i>a</i>	<i>a</i>	<i>a</i>
Au	<i>b</i>	0.25	0.10

<sup>a</sup>No chemisorptive interaction >0.05 eV. <sup>b</sup> Particle deformed.

Fig. 5. A 79-atom Ag@Au core-shell nanoparticle; binding sites for ethylene are shown. The Table compares binding activity at (111) face sites, for various shell metals.

Z.D. Pozun et al., "Why Silver Nanoparticles are Effective for Olefin/Paraffin Separations", J. Phys. Chem C, **115**, 1811 (2011).

**For a compound particle, there is close correlation between exact composition and population of the surface with active atoms.**

Example: FePt, up to 4% from stoichiometry

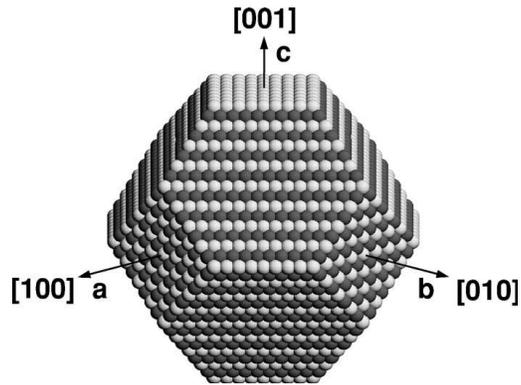


Illustration of a completely  $L1_0$  ordered regular truncated octahedron with 9201 atoms ( $d=6.3$  nm).

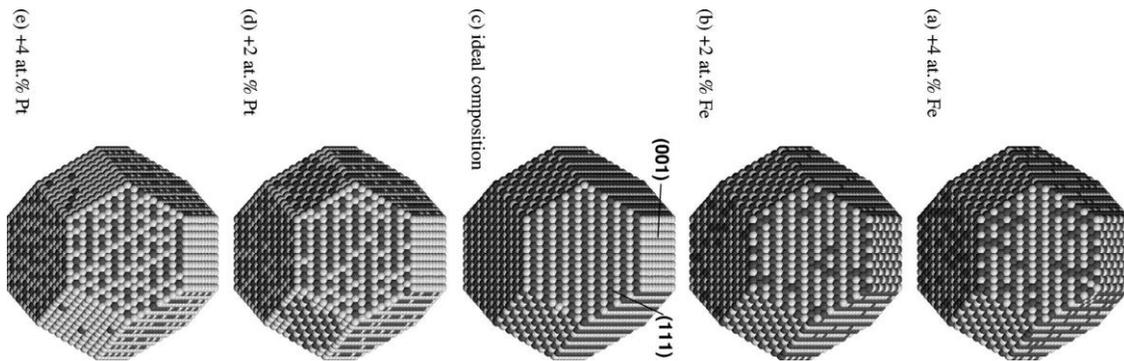


Fig. 6. Structure of particles with  $d=7.0$  nm (12 934 atoms) after simulation at 300 K. The particle concentration varies from +4 at. % Fe to +4 at. % Pt relative to the concentration of an ideally ordered TO. Pt atoms are displayed light gray, Fe atoms dark gray.

M. Muller and K. Albe, "Lattice Monte Carlo Simulations of FePt Nanoparticles: Influence of size, composition and surface segregation on order-disorder phenomena", Phys. Rev. B **72**, 094203 (2005)

## Agglomeration / Coalescence Event between Mobile Particles Causes Phase Change

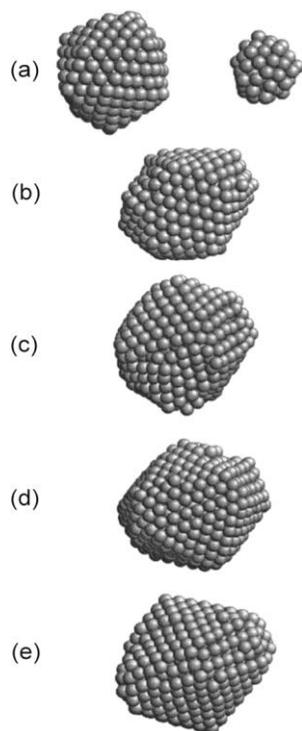


Fig. 7. A sequence of images of a coalescence event transforming small icosahedral nanoparticles into a larger decahedral structure (a)–(e). (a) Approaching small nanoparticles, (b) an ‘egg’ elongated polymorphic icosahedral nanoparticle forms after the initial coalescence, (c) the (1 0 0) facet emerging on top of the elongation, (d) a complete transformation to a decahedral motif with  $(1 \times 5) - (1 0 0)$  surface reconstructions and (e) the final decahedral nanoparticle without  $(1 \times 5) - (1 0 0)$  reconstructions.

G. Grochola et al., "On Morphologies of Gold Nanoparticles Grown from Molecular Dynamics Simulation", *J. Chem. Phys.* **126**, 164707 (2007)

## Nanoparticle Phase and Shape Depend on Environment and Support Material

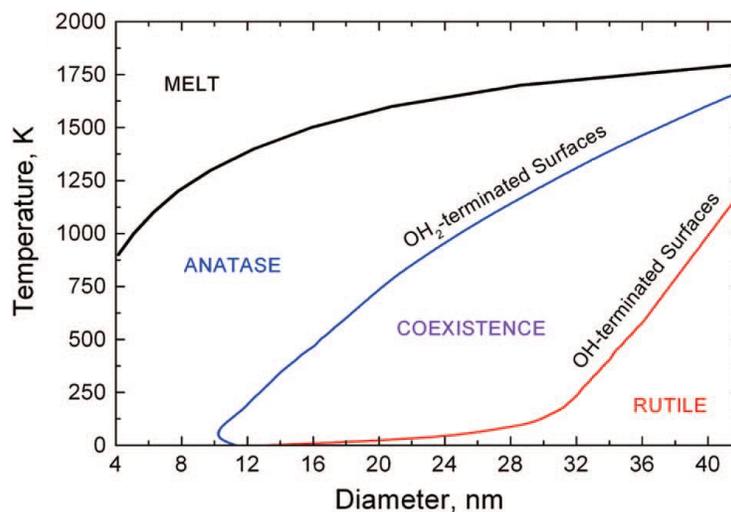


Fig. 8. The  $(D, T)$  phase map of titania, based on first principles calculations and melting enthalpies from experiment. The solid–solid phase transition lines for nanocrystals with  $\text{OH}_2$ - and  $\text{OH}$ -terminated surfaces, (due to moisture exposure) and the coexistence region where the relative stability depends on the type of adsorbed groups. The diameter refers to the anatase phase.

A.S. Barnard and H. Xu, "An Environmentally Sensitive Phase Map of Titania Nanocrystals", *ACS Nano* **2**, 2237 (2008)

## Au Nanoparticle Activity vs. Particle Size, for Various Support Materials

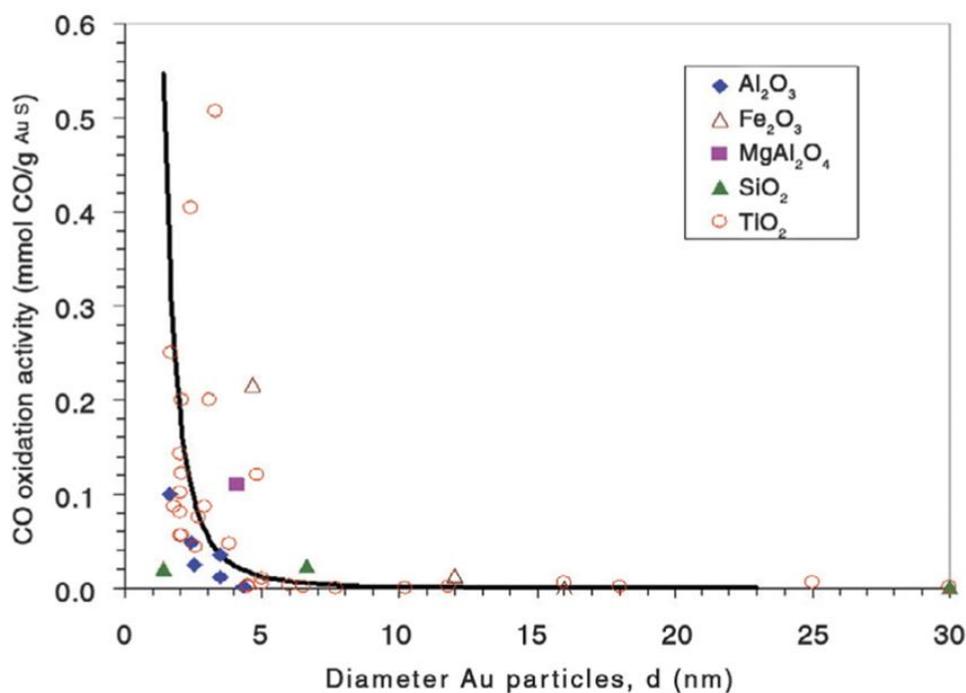


Fig. 9. Reported catalytic activities (in  $\text{mmol/g}_{\text{Au}}\text{s}$ , left axis) for CO oxidation at 273 K as a function of Au particle size ( $d$ , in nanometers) for different support materials. The supports are indicated by the symbol shape: open symbols correspond to reducible supports, closed symbols to irreducible supports. The solid curve shows the calculated fraction of atoms located at the corners of nanoparticles as a function of particle diameter for uniform particles shaped as the top half of a regular cuboctahedron

B. Hvolbaek et al., "Catalytic Activity of Au Nanoparticles", *nanotoday* 2, 14 (2007)