

PHYSICS AND CHEMISTRY OF NANOSTRUCTURES: WHY NANO IS DIFFERENT

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Contents

1. Introduction
 2. Surface effects and quantum confinement effects
 3. Learning from surface physics and chemistry
 4. The average coordination number and the stability of a particle
 5. Magic numbers: geometric and electronic closed shells
 6. Why nanoparticles and pore-confined matter melt at temperatures different from the bulk
 7. Size-induced insulator-to-metal-transitions
 8. The color of metallic and semiconducting nanoparticles
 9. Size- and dimensionality-dependent magnetic properties
 10. Catalysis by nanoparticles: dependence on size, shape and support
 11. Concluding remarks
- Glossary
Bibliography
Biographical Sketch

Summary

Properties like color, melting point, ionization potential and electron affinity, electrical conductivity, or magnetism which for bulk amounts of matter do not depend on size become size-dependent when the size of a particle falls in at least one dimension below a certain limit, which is normally taken to be about 100 nm. On this basis, the properties of matter can be tuned to their desired values by adjusting the size of nanoparticles and the thickness of thin layers or wires. For chemists this is particularly important in catalysis.

1. Introduction

Nanotechnology and nanomaterials are expressions which have received enormous publicity in recent years. In general, nanotechnology is the word used for the manipulation of individual objects on an atomic or molecular scale or for nanostructures produced by lithographic techniques, while nanomaterials are nanoscale particles which can be produced by chemical synthesis and handled in masses. In both cases it is the special properties, different from those in the bulk, which causes the excitement.

Nanomaterials are often considered to be an invention of modern science, but in fact

they have always existed, and humans have been exposed to them, for example in the smoke of open fires, or in the form of viruses. More than two millennia ago, artisans of the Roman Empire started to make use of nanoparticles by embedding colloidal metal particles into glass items to provide them with particular color. A well-known example is the Lycurgus Cup, depicting a scene of a Thracian king named Lycurgus who lived around 800 B.C. It was probably made in Rome in the 4th century B.C. The cup which is now on display in the British Museum in London changes color when held up against light. This is due to the special properties of the colloidal silver and gold nanoparticles. In the middle ages colloidal gold was also used in stained glass windows of churches.

Recognition of size effects started 1871 with William Thomson (knighted to Baron Kelvin of Largs) when he described the size-dependence of the melting point of small particles or of pore-confined matter, a relation known as the Gibbs-Thomson equation. It combines the Clausius-Clapeyron equation for the temperature-pressure relation of phase transition equilibria with the Kelvin equation that describes the dependence of the vapor pressure of a small droplet on its radius.

During the 20th century there have been two key events which have had enormous initiation effects on the development of nanotechnology and the application to nanomaterials. The first one was the famous lecture by the theoretical physicist Richard Feynman entitled “There is plenty of room at the bottom – an invitation to enter a new field of physics” in which he addressed the American Physical Society in its annual meeting on 29th December 1959. Not much happened thereafter until the second event took place, which is the development of the scanning tunneling microscope in the early 1980s by Binnig and Rohrer, and somewhat later the atomic force microscope. They provided atomic resolution, three orders of magnitude better than the diffraction limit of optical microscopes, which more than fulfilled Feynman’s request to make the electron microscope 100 times better.

Today there are many existing and planned applications which make use of nanosize effects intentionally. These range from catalysis over energy-related materials (solar cells, fuel cells, batteries, and hydrogen storage), nanomagnets and transistors (or other elements for electronics) to quantum dots where individual bits can be stored for quantum computing.

When asked about the reason for the hype for nanomaterials some people might answer that certain phenomena like for example catalysis take place at the surface, and that all catalyst atoms which are not exposed to the surface are inactive and therefore wasted, which is economically important when the catalyst is an expensive metal like platinum or rhodium. This answer is not wrong, but it misses the main point by far. The important fact is that an atom at the surface of a small catalyst particle has properties quite different from those of the same atom at the surface of a large particle. Even a corner or edge atom is chemically different from an atom embedded in the middle of a surface face or an atom sitting on top of the same crystal face.

It turns out that size effects have two origins: they are either surface effects or quantum confinement effects. The surface effect reflects that the stabilization of an atom in a solid or liquid environment scales with the number of neighbors to which it can make

bonds. The temperature of melting or of any other phase transition relates to this stabilization and therefore to the average number of neighbors. This leads to a smooth scaling law of transition temperature with particle radius or thickness of a layer or wire. The second effect applies only to conducting (metallic) or semiconducting materials. It is a quantum-size effect that depends on the wavelengths of standing waves that can be matched to particles of a certain size. In the same sense as for atoms or molecules this leads to discrete (quantized) energy states, and for sufficiently small dimensions this causes non-continuous scaling. The consequence of these two effects is that many properties of nanomaterials which for macroscopic particles are independent of size can be tuned to a very significant amount by adjusting the particle size. Perhaps the most striking example is that of gold, which is essentially not catalytically active at the surface of the bulk metal, but catalysis by gold nanoparticles works very well and has become a topic of very active research. Size effects are the basis for the new chemistry that will be in the focus of the present chapter.

2. Surface Effects and Quantum Confinement Effects

The dispersion F of a sample is defined as the fraction or percentage of atoms at a surface, relative to the total number of atoms in the sample. The surface area of a sphere, $A = 4\pi r^2$, divided by its volume, $V = 4\pi r^3/3$, is $3/r$, or in terms of diameter d , $6/d$. Neglecting edge effects, the $F = A/V$ for large, thin plates of thickness d equals $1/d$, and also for long, cylindrical wires $F = 1/d$. Thus, for any body where a single narrow thickness d is defined the dispersion scales smoothly with $1/d$. This is the basis for the explanation of many observed properties which scale smoothly as $1/d$ or $1/r$, indicating that it is a surface effect.

The above scaling law extrapolates to infinity as d goes to zero, which is unphysical. When the diameter of a specimen reaches the diameter of two atoms, every atom is directly exposed to the surface, and $F = 1$. This is illustrated in Figure 1 for the example of cubic crystals with n atoms along an edge and a total number of $N = n^3$ atoms. The atoms are counted and F calculated as follows:

$$F = \frac{6n^2 - 12n + 8}{n^3} = \frac{6}{N^{1/3}} \left(1 - \frac{2}{N^{1/3}} + \frac{8}{6N^{2/3}} \right) \approx \frac{6}{N^{1/3}} \quad (1)$$

The smallest cube has 8 atoms, and each of them is at the surface, while the next larger cube has 27 atoms, one of which is at the center. For large cubes the dispersion scales as $1/N^{1/3}$, which is proportional to $1/d$ (where d is the edge length). It should be noted that this description includes only cubes with completed shells. Intermediate cases are more complicated to describe and show a somewhat higher dispersion so that the scaling law loses its smooth character.

The quantum confinement effect is a consequence of quantum mechanics and of the particle wave duality. Electrons behave at the same time as particles and as waves. As waves they explore the entire space in which they are free to move. In clusters of noble gases they remain confined to the atoms, and in clusters of molecules like water or carbon dioxide they remain confined to these molecules. Noble gases or molecular

clusters therefore do not show quantum size effects beyond the ones which they show in the isolated atoms or molecules. However, in semiconductors or metals the conduction electrons are free to move in the entire cluster or particle, and the electron waves adapt to the size of the particle in such a way that the nodes (this is where the amplitude of the oscillating wave is zero) of the waves are at the surface (Figure 2). This is exactly the same phenomenon that we know from the sound waves in music instruments. As the size of the instrument increases from the violin to the viola, the cello and the bass this allows the maximum wavelength to be excited and accommodated inside the resonance box of the instrument to increase and the sound to change. In the same way as the tones and overtones of the excited string are quantized, the energies of delocalized electrons in a cluster are quantized.

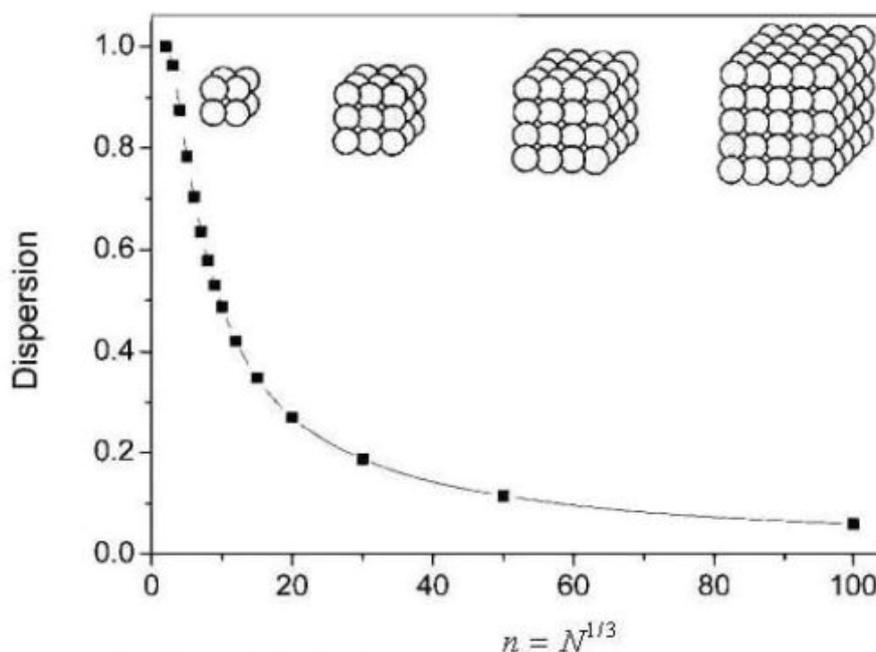


Figure 1. Size-dependence of the dispersion for cubic particles with $n = N^{1/3}$ atoms along an edge. (Roduner E. (2006), *Nanoscopic Materials: Size-Dependent Phenomena*, Cambridge, UK: RSC Publishing. Reproduced with permission of the Royal Society of Chemistry).

There are music instruments in which the excited waves are mostly inside a resonance body, for example in guitars or in organ pipes, but in others it is primarily the surface which is excited, such as in drums, where there are two-dimensional waves of the excited skin. In the same way there are not only volume waves of the conduction electrons but also collective excitations of surface electrons. The latter are called surface plasmon resonances, and they play an important role in gold or silver nanoparticles.

An additional requirement that comes in from quantum mechanics is the Pauli principle, which states that at most two electrons (when they have opposite spin) can occupy a quantum state. Thus, when we fill electrons into the level scheme it happens that the level gets filled, and the next electron will have to occupy the next higher level, in

exactly the same way as we know it from atoms as we move through the periodic table. This has the consequence that the electron energy jumps when a new series of levels (called a shell) starts to be occupied. Therefore, quantum size effects lead to non-continuous size scaling behavior, which is in contrast to that of surface effects. In fact, the behavior of spherical clusters is so closely analogous to that of atoms that clusters containing delocalized conduction electrons (this is an essential requirement) are best regarded as pseudo-atoms or super-atoms, a fact that will be discussed further in chapter 5 below.

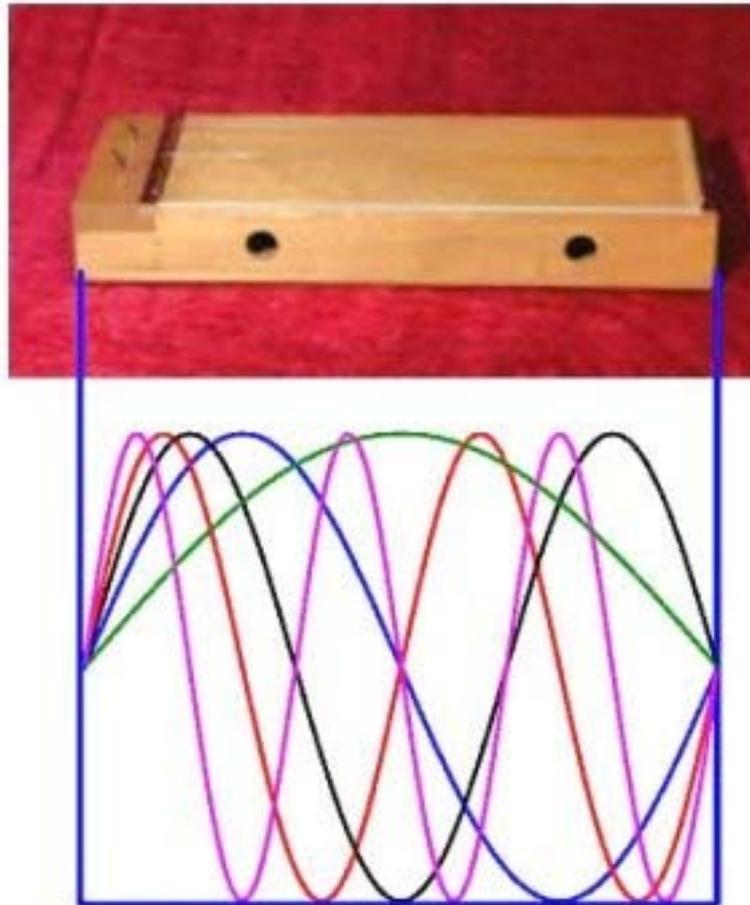


Figure 2: “Quantum confinement” of standing waves that fit into a simple instruments resonance box with zero (green), one (blue), two (black), three (red) and four (pink) nodes. Intermediate wavelengths are not permitted.

3. Learning from Surface Physics and Chemistry

Surface physics and chemistry is a discipline which is several decades older than nanochemistry. Since the dispersion of nanomaterials is high it is important to understand surface effects, and much of this knowledge can be taken from surface science – except that surface science is done on larger specimens, where nano-size effects do not occur.

Splitting a crystal along one of the crystal planes creates two new surfaces, and the work

spent to do the splitting is directly the initial surface energy of the fresh surface. Thus, the surface energy is calculated from the sum of bond energies of all the covalent, ionic and van der Waals bonds across the splitting plane which were broken when the crystal was split.

Breaking the crystal also breaks the local symmetry at the new surface. Atoms or molecules which previously occupied a site with a symmetry corresponding to their position in the bulk lattice are now found near the surface where the translational periodicity stops at the surface, while it is still there towards the inside of the crystal.

Breaking the crystal also creates an imbalance of forces at the surface which calls for a new equilibrium. The dangling bonds of a fresh diamond surface want to be satisfied, and they achieve this by forming chemical bonds to molecules which are available in the environment. In humid air they will be terminated after a short time with surface hydroxyl groups. Many metals will form a thin oxide layer that lowers the surface energy. Both these effects occur by forming chemical bonds, a process that is called chemisorption. Lower energy surfaces tend to further lower their energy by physisorption, i.e. by forming weaker adsorptive bonds. Such processes are extremely important in nanochemistry and serve to stabilize small particles by capping their surface but also to steer the morphology of crystallites of a given crystal structure to a wide variety of shapes. The basis of the latter process is the different adsorption energy of an adsorbate at different crystal facets. An adsorbate that adsorbs strongly on a given surface essentially blocks this surface from growing. At other facets adsorption may be weak and dynamic, so that further atoms or molecules may be added whenever the adsorbate has left a surface site free for a moment.

However, even in vacuum a freshly created surface will react to the imbalance of forces. For example, the dangling bonds of a fresh silicon (100) surface will satisfy themselves by forming a through-surface “banana bond” to a neighboring atom. This leads to the formation of dimers parallel to the surface, which results in dimer rows and grooves at the surface. The process is called surface restructuring. Also the surface of a sodium chloride crystal will restructure under the formation of surface dimers, but these are oriented perpendicularly to the surface: the surface sodium cations move towards the neighboring chloride anion in the second layer, while the sodium ions in the second layer move toward the surface and make a shorter bond to the surface chloride ion.

The question is how deep this surface restructuring is effective. It depends on the range of the forces, and in general this is only a few to very few atomic layers. For more or less spherical particles there is a net force towards the inside. This is readily understood if one realizes that the surface free energy which is the same as the surface tension leads to a pressure, as in a soap bubble or in a small balloon, that compresses the particle. It has the effect that in small particles below 10 nm radius the density increases, and larger particles have a density gradient near the surface with up to a few percent shorter bonds compared with the bulk. Even if it is only a few percent, it has significant consequences, as shorter interatomic bonds between the atoms of a transition metal particle increase the binding energy of adsorbates and therefore affects catalysis.

4. The Average Coordination Number and the Stability of a Particle

In face-centered and hexagonal close packed cubic crystal structures an atom in the bulk is in direct contact with 12 neighbors, i.e. its coordination number is 12. A fragment of such a structure is shown in Figure 3, and the coordination number of several atoms at the surface is indicated. The highest value that is shown is 9 for an atom inside a surface layer of a (111) crystal face. It is readily seen that it is surrounded with six atoms of the same plane, and from below it is in contact with three further atoms. If one would place another layer on top this would give the atom three more direct neighbors and the full bulk coordination number of 12. An atom on the (110) surface has only four direct neighbors in the same plane, four more make contact from below, giving it a total of 8. Corner atoms have rather low coordination numbers.

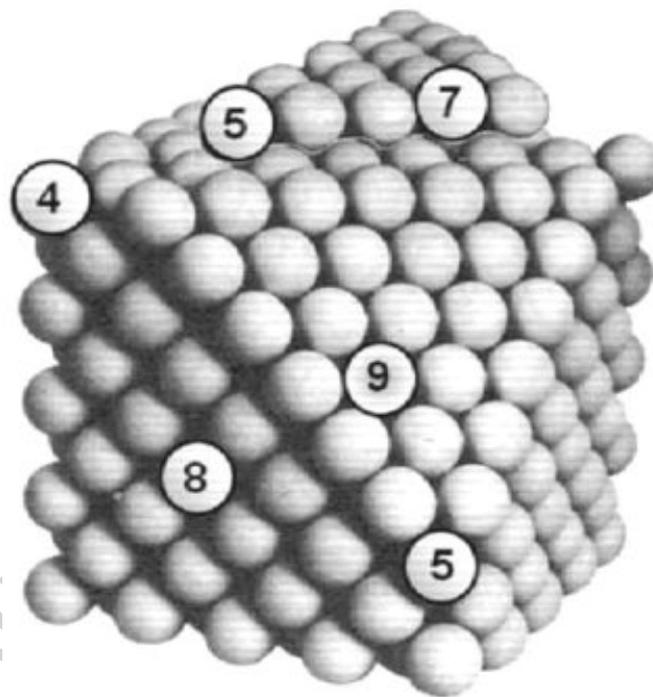


Figure 3. Fragment of a face-centered cubic crystal indicating the coordination numbers of various surface atoms.

To first order, if we neglect the interactions with the second and higher shells, each direct neighbor contributes with one bond to the binding energy or cohesive energy of an atom in the lattice. The total cohesive energy of a crystallite is the sum of all atomic contributions (without counting the interaction of a pair of atoms A–B and B–A twice). Obviously the smaller the crystallite the higher the dispersion and therefore the fraction of atoms with a lower coordination number, which results in a decrease of the average cohesive energy per atom. This is shown in Figure 4. Plotted as a function of the number of atoms $N^{-1/3}$ this gives a linear scaling, showing convincingly that the origin is a surface effect.

The extrapolated coordination number for the bulk is 12, and the calculated cohesive

energy per bond is 0.23 eV (experimental value: 0.25 eV, one-sixth of the bulk binding energy per atom). The large change in cohesive energy per atom is impressive. It is plausible that this will have consequences for the melting or sublimation temperature of a cluster.

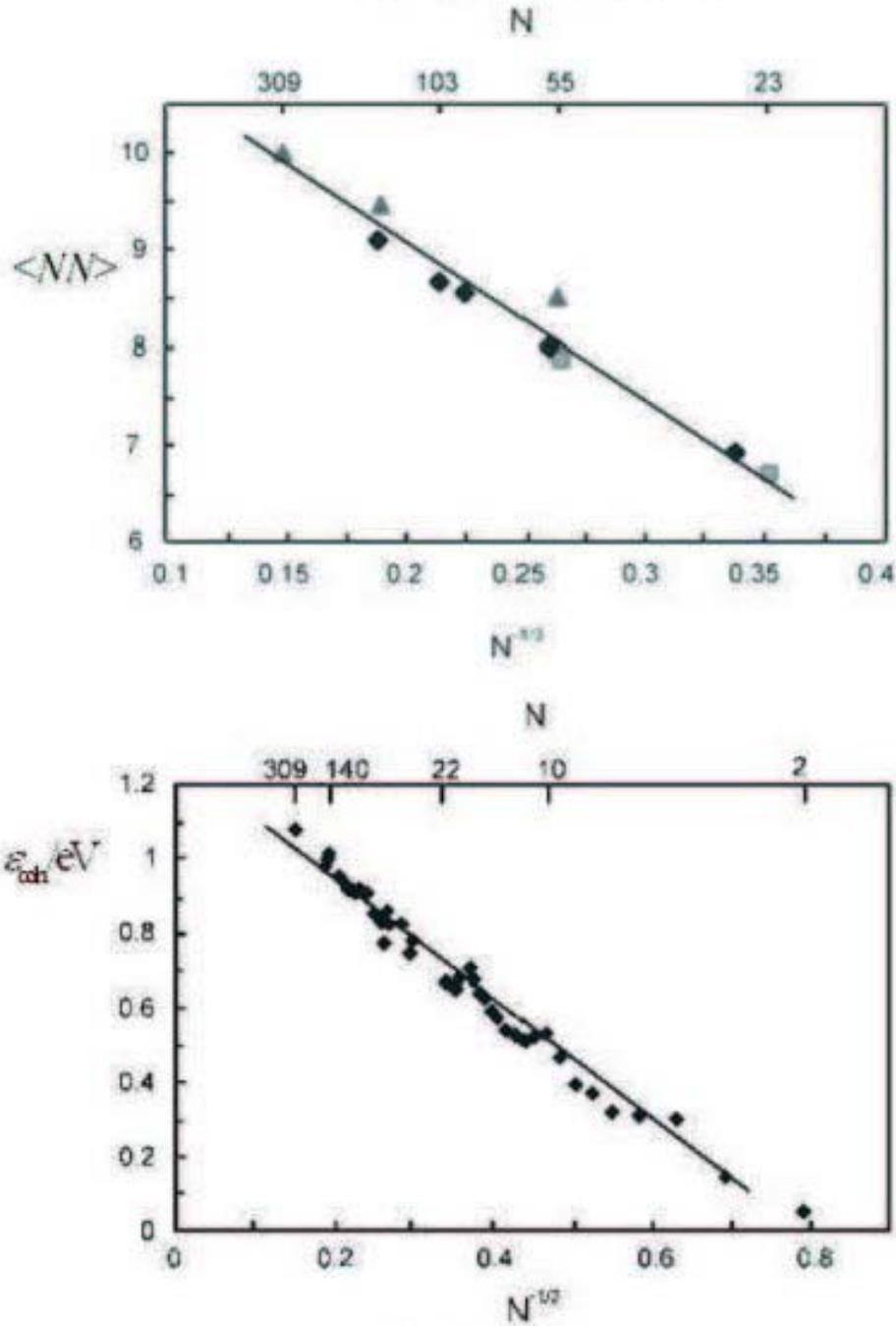


Figure 4: Average coordination number $\langle NN \rangle$ (upper entry) and cohesive energy per atom, ϵ_{coh} (lower entry) calculated for small magnesium clusters of up to 309 atoms. The different symbols in the upper entry relate to different structural isomers (Köhn A., Weigend F., Ahlrichs R. (2001) *Phys. Chem. Chem. Phys.* 3, 711. Reproduced with permission from the PCCP Owner Societies).

For equilibrium conditions the size-dependence of stability is given in terms of the chemical potential μ , which for one-component systems is a molar Gibbs free energy

$$\mu_{\text{nano}} = \mu_{\text{bulk}} + \frac{4\gamma}{V_m d} \quad (2)$$

As expected, μ_{nano} is higher than μ_{bulk} , and the difference is related to the surface or interfacial tension γ (for non-isotropic materials the average over the different crystal faces should be taken), the molar volume V_m and the particle diameter d . Experimental evidence for this has long been known in terms of Ostwald ripening: when a saturated solution of a soluble substance is stirred it is observed that the crystallites coarsen with time, which means that the large crystallites grow at cost of the smaller ones. It is also possible to verify this relation quantitatively, for example for electrochemically active substances. In a cell where the two half cells are identical except that one half-cell works with sufficiently large crystallites to represent bulk conditions while the other half-cell works with the nanomaterial, the electromotive force (emf) is related in a first approximation to the Gibbs free energy via the Nernst equation by

$$\frac{4\gamma}{V_m d} = -nF \Delta E \quad (3)$$

F is the Faraday constant ($96485 \text{ C} \cdot \text{mol}^{-1}$), n the number of electrons transferred per mol turnover in the oxidation and reduction reactions of the two half-cells, and ΔE is the measured emf of the cell. Figure 5 shows the result of such measurements for the example of nanocrystalline TiO_2 (anatase), and it reveals that 5 nm particles are less stable by ca. 50 kJ mol^{-1} than bulk material. The figure confirms the expected linear dependence in a $1/d$ -plot, except for a small offset for the bulk reference values.

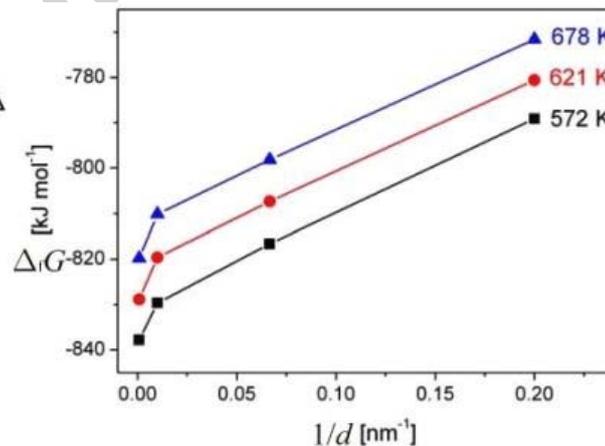


Figure 5: Size-dependence of the Gibbs free energy of formation of nanocrystalline TiO_2 (anatase) particles at temperatures where thermal equilibrium is granted. (Drawn based on data by Balaya P. (2008), *Energy Environm. Sci.* 1, 645.).

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Biographical Sketch

Emil Roduner was born in Teufen, Switzerland, in 1947. He first finished education as an elementary school teacher (1968). He studied chemistry at the University of Zürich and then obtained an MSc in chemistry at the Rensselaer Polytechnic Institute in Troy, NY, U.S.A. (1974). He was awarded his PhD in the field of muonium chemistry at the University of Zürich, Switzerland (1979), then pursued an academic career and obtained his Habilitation and *venia legendi* at the University of Zürich, Switzerland (1989).

He first worked as a Teacher in the elementary school of the small town of Hundwil in Switzerland (1968-1971). During his PhD work he served as a Teaching Assistant. In 1981 he was promoted to Oberassistent. In 1995 he was appointed to a Chair of Physical Chemistry at the University of Stuttgart in Germany, which is his current position. His research interests cover all aspects of physical chemistry of free radicals, in particular their role in the degradation of fuel cell membranes, and the dynamics of their reorientation in solids and adsorbed on surfaces. Of special interest to him is also the behavior of pore-confined matter and of well-defined noble metal nanoclusters in zeolites. He has written a textbook on *Nanosopic Materials: Size-Dependent Phenomena*.

Prof. Roduner is a member of the Deutsche Bunsengesellschaft für Physikalische Chemie and of the Gesellschaft Deutscher Chemiker. For his fundamental work that established using spin polarized positive muons as probes in free radical chemistry he was awarded the Werner Price with medal by the Schweizerische Chemische Gesellschaft (1988).