

# Size matters: why nanomaterials are different

Emil Roduner\*

Received 16th March 2006

First published as an Advance Article on the web 4th May 2006

DOI: 10.1039/b502142c

Gold is known as a shiny, yellow noble metal that does not tarnish, has a face centred cubic structure, is non-magnetic and melts at 1336 K. However, a small sample of the same gold is quite different, providing it is tiny enough: 10 nm particles absorb green light and thus appear red. The *melting temperature* decreases dramatically as the size goes down. Moreover, gold ceases to be noble, and 2–3 nm nanoparticles are excellent *catalysts* which also exhibit considerable *magnetism*. At this size they are still *metallic*, but smaller ones turn into insulators. Their *equilibrium structure* changes to icosahedral symmetry, or they are even hollow or planar, depending on size. The present *tutorial review* intends to explain the origin of this special behaviour of nanomaterials.

## 1. Introduction

We have long accepted that diamond and graphite are different allotropic forms of carbon which have distinctly different structures, bonding characteristics and therefore grossly different chemical and physical properties. However, only a little more than a decade ago new forms were discovered: fullerenes (C<sub>60</sub>, C<sub>70</sub>, and others) and carbon nanotubes which can be regarded as rolled-up graphite sheets of cylindrical shape with single or multiple layer walls, exhibiting amazing properties. We are thus getting used to the fact that carbon is not equal carbon. We might still want to think, though, that gold is gold, platinum is platinum and CdS is CdS, but we slowly have to get used to the fact that this is also not true and depends on size when the specimen is small

*Institute of Physical Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany. E-mail: e.roduner@ipc.uni-stuttgart.de; Fax: +49 711 6856 4495; Tel: +49 711 6856 4490*



Emil Roduner

*Emil Roduner obtained an MSc in physical chemistry at the Rensselaer Polytechnic Institute in Troy, NY, and his PhD in the field of Muonium Chemistry at the University of Zürich. In 1995 he was appointed to a chair of Physical Chemistry at the University of Stuttgart. 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 behaviour of pore-confined matter and of well-defined noble metal nanoclusters in zeolites. He has written a textbook on Nanoscopic Materials: Size-Dependent Phenomena (Ref. 1).*

enough. We have to learn that bonding in a small metal or semiconductor cluster is different from that in the bulk. We have to accept that an atom at the surface of a large hunk of material is different from an atom of the same element inside that hunk. Moreover, an atom at the smooth surface of a sizable single crystal is different from an atom at the surface of a small cluster of the same element. Furthermore, the properties of a surface atom of a small metal cluster depend on the type of support on which it sits or whether the cluster is doped with one or a few atoms of a different element.

Evidence for such effects has been available for some time, but only over the last one or two decades have the experimental methods become available which allow chemists to synthesize nanomaterials in a controlled and reproducible way and to investigate their properties by direct observation of individual clusters or by electrically contacting them using techniques like scanning tunnelling or atomic force microscopy. The availability of size as a new parameter that permits the tuning of chemical properties has tremendously extended the potential of chemistry. There is no doubt that this will be an exciting major focus in research of an entire generation that is leaving universities now.

There are basically two types of size-dependent effects:<sup>1,2</sup> smoothly scalable ones which are related to the fraction of atoms at the surface, and quantum effects which show discontinuous behaviour due to completion of shells in systems with delocalised electrons.

## 2. Surface effects

### 2.1. The fraction of atoms at the surface

The surface of a sphere scales with the square of its radius  $r$ , but its volume scales with  $r^3$ . The total number of atoms  $N$  in this sphere scales linearly with volume. The fraction of atoms at the surface is called *dispersion*  $F$ , and it scales with surface area divided by volume, *i.e.* with the inverse radius or diameter, and thus also with  $N^{-1/3}$ . Basically the same relation holds for long cylinders of radius  $r$  and for thin plates of thickness  $d$ . The size dependence of dispersion is illustrated in

Fig. 1 for cubes of  $n$  atoms along an edge and a total of  $N = n^3$  atoms, where the number of atoms at the surface is  $6n$  corrected for double counts at the 12 edges and for reinstalling the 8 corners. For large  $N$  the edge and corner corrections become negligible, leading to the  $N^{-1/3}$  scaling:<sup>1</sup>

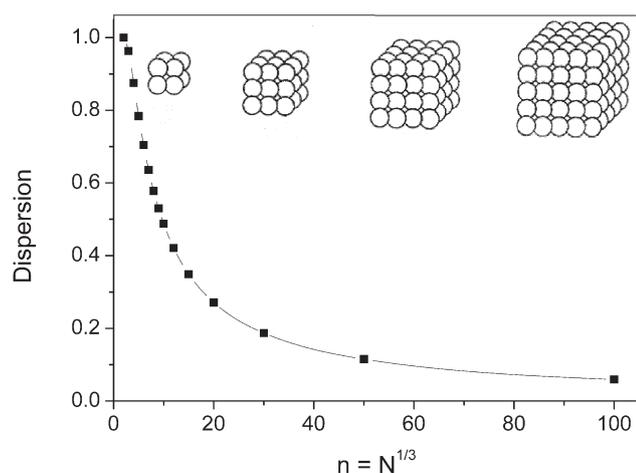
$$F = \frac{6n^2 - 12n + 8}{n^3} = \frac{6}{N^{1/3}} \left( 1 - \frac{2}{N^{1/3}} + \frac{8}{6N^{2/3}} \right) \approx \frac{6}{N^{1/3}} \quad (1)$$

All properties which depend on the dispersion of a particle lead to a straight line when plotted against  $r^{-1}$ ,  $d^{-1}$ , or  $N^{-1/3}$ .

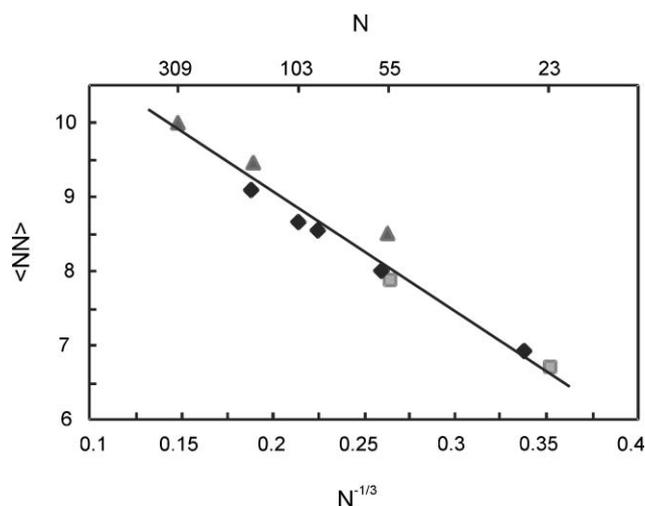
Atoms at the surface have fewer direct neighbours than atoms in the bulk. Therefore, particles with a large fraction of atoms at the surface have a low mean coordination number (which is the number of nearest neighbours). In fact, the dispersion and the mean coordination number  $\langle NN \rangle$  obey the same scaling law and are equivalent measures of surface effects. The linearity of a plot of  $\langle NN \rangle$  against  $N^{-1/3}$  is shown in Fig. 2 for small clusters of Mg atoms in various packing symmetries. In the limit of infinitely large clusters the line extrapolates to  $\langle NN \rangle = 12$ , the coordination number of close packed spheres in the bulk.<sup>1</sup>

## 2.2 Typical smoothly scaling properties due to surface effects

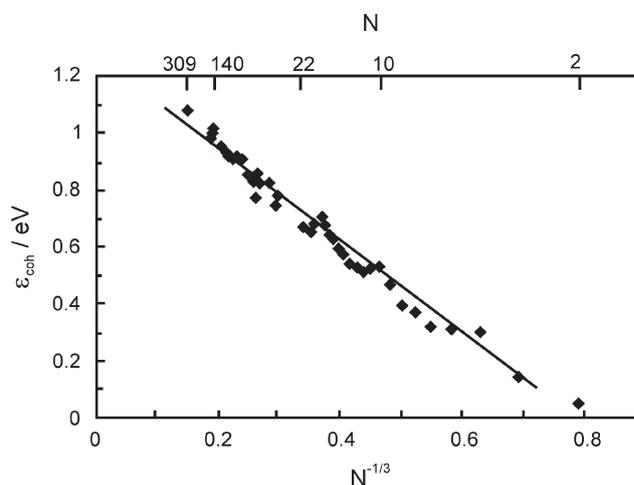
An example for the above  $N^{-1/3}$  scaling law is given by the calculated cohesive energy for magnesium clusters,<sup>3</sup> which is the bond energy per atom, as shown in Fig. 3. Extrapolation yields a bulk binding energy per atom of 1.39(1) eV, which is close to the experimental value of 1.51 eV. It is plausible that the cohesive energy scales the same way as the coordination number, since each neighbouring atom forms one bond. It should be noted that the cohesive energy in Fig. 3 represents an average value. In reality, however, the atoms in the interior of the cluster are more highly coordinated, form more bonds and are therefore more stable than those at the cluster surface. For cubic crystals as those drawn in Fig. 1 the corner atoms are the least saturated ones, followed by the edge, the in-plane surface



**Fig. 1** Evolution of the dispersion  $F$  as a function of  $n$  for cubic clusters up to  $n = 100$  ( $N = 10^6$ ). The structure of the first four clusters is displayed (Ref. 1 – Reprinted with permission of the PCCP Owner Societies.)



**Fig. 2** Calculated mean coordination number  $\langle NN \rangle$  as a function of inverse radius, represented by  $N^{-1/3}$ , for magnesium clusters of different symmetries (triangles: icosahedra, squares: decahedra, diamonds: hexagonal close packing). (Ref. 1, based on data in Ref. 3. Reprinted with permission of the PCCP Owner Societies.)



**Fig. 3** Calculated cohesive energies of various size magnesium clusters in their most stable geometry as a function of  $N^{-1/3}$ . (Ref. 3 – Reprinted with permission of the PCCP Owner Societies.)

and then the atoms in the interior. For this reason, the corner atoms normally exhibit the highest affinity to form bonds to adsorbate molecules, followed by the edge and the in-plane surface atoms, a fact that is of utmost importance for the catalytic activity. Alternatively, because of their low stabilisation due to low coordination, edge and in particular corner atoms are often missing on single crystals even in thermodynamic equilibrium.

A further consequence of the lower stabilisation of atoms or molecules at the surface is the lower melting point of surface layers. Ice, for example, is covered by a liquid-like layer down to below  $-10$  °C. This, besides the pressure exerted by the weight of the skater on the sharp edge of his skates, is another factor that facilitates skating. Furthermore, this has been known since 1871 when W. Thomson<sup>4</sup> described that the

melting point scales inversely with the radius of a particle according to eqn (2),

$$\frac{T_m - T_m^*}{T_m^*} = \frac{\Delta T_m}{T_m^*} = - \frac{2V_m(\ell)\gamma_{sl}}{\Delta H_m r} \quad (2)$$

which is known today as the Gibbs–Thomson equation. In this equation  $T_m$  is the melting point of the cluster with radius  $r$ ,  $T_m^*$  that of the bulk,  $V_m(\ell)$  the molar volume of the liquid,  $\gamma_{sl}$  the interfacial tension between the solid and the liquid surface layer, and  $\Delta H_m$  the bulk latent heat of melting. This behaviour is illustrated in Fig. 4 for indium confined in controlled-pore glass and in Vycor of various pore diameters.<sup>5</sup> In agreement with eqn. (2) the melting point plotted against the inverse pore diameter gives a straight line that extrapolates to the bulk melting point. The melting endotherms show a behaviour that is very characteristic for nanomaterials: The sharp peak at 430 K represents melting of bulk indium between the grains. It is clearly seen that there is a second peak which shifts to lower temperatures as the pore diameter decreases. It belongs to indium inside the pores. Furthermore it broadens, which is another characteristic of small particles. Since the pore size is well defined this broadening cannot be ascribed to a pore-size distribution. Rather, it reflects that melting is a cooperative phenomenon which is not well defined for a small number of members of the ensemble. A sharp melting point is only

obtained in the thermodynamic limit of an infinite number of particles.

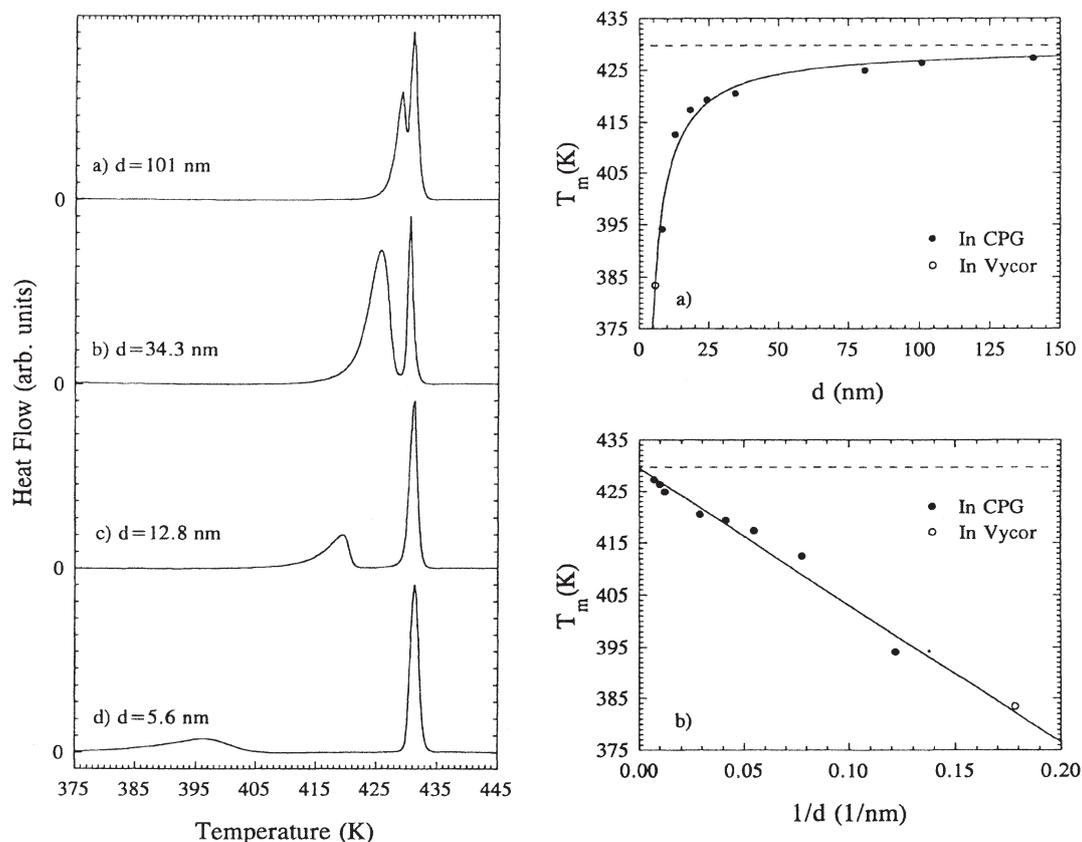
As a second example: the melting point of 2.5 nm gold particles was reported to be about 930 K,<sup>6</sup> much lower than its bulk value of 1336 K but revising an even lower value from an earlier determination.

The average latent heat of melting shows a size-scaling behaviour similar to that of the melting point,<sup>7</sup> and some experiments have also determined a significant size dependence of the interfacial tension.<sup>8,9</sup>

It should be noted that also the critical point of pore-confined matter shifts to lower temperatures. Condensation of a fluid to a liquid state requires stabilising interaction with a sufficient number of neighbours. However, the maximum coordination number in pores is limited due to spatial constraints, providing lower stabilisation, a fact that has to be compensated by a lower phase transition temperature.

### 2.3 Break-down of thermodynamics

Phase transitions are collective phenomena. With a lower number of atoms in a cluster a phase transition is less well defined, *it is therefore no longer sharp*. Small clusters behave more like molecules than as bulk matter. Rather than of phases it may be more useful to think of different structural isomers which *coexist over a range of temperatures*.<sup>10</sup> For



**Fig. 4** Left: Background-subtracted differential scanning calorimetry melting endotherms for indium confined in controlled pore glass (a–c) and in Vycor samples (d) with different pore diameters. Note that the melting feature of the pore-confined material moves to lower temperatures and broadens as the pores get narrower. Right: Melting temperature as a function of pore diameter and inverse diameter. The broken line represents the bulk melting point (Reprinted with permission from ref. 5. Copyright (1993) by the American Physical Society.)

example, part of a cluster may look frozen since its atoms do not exchange, while another part exhibits liquid-like dynamic behaviour. At a given temperature, the solid-like regime may fluctuate in position and in size. When phases are no longer well defined the Gibbs phase rule loses its meaning.<sup>10</sup>

In narrow pores the conventional fluid-liquid critical point may shift to very low temperature, it may even vanish. However, new phases may appear which are characterised by discrete chemical potentials and separated by so-called *layering transitions*.<sup>11</sup>

Particular phenomena that can occur with isolated clusters are *negative heat capacities*.<sup>12</sup> This means that the temperature of a cluster drops over a certain range when it is heated. It is understood in the following way: temperature relates to kinetic energy, heat capacity to total energy; thus, temperature drops when a fraction of kinetic energy is converted to potential energy. For example, when more and more energy is deposited on an isolated  $S_8$  ring this corresponds to heating and is seen by higher amplitudes of vibrational and rotational motion. At some point, sufficient energy may be localised in a single bond so that this bond breaks, converting a hot  $S_8$  ring into a colder linear  $S_8$  chain. This also means that temperature fluctuates at constant energy and is no longer well defined for small isolated species. It may impose a principal limit to certain applications of nanotechnology.<sup>13</sup>

### 3. Quantum confinement effects in materials with delocalised electron states

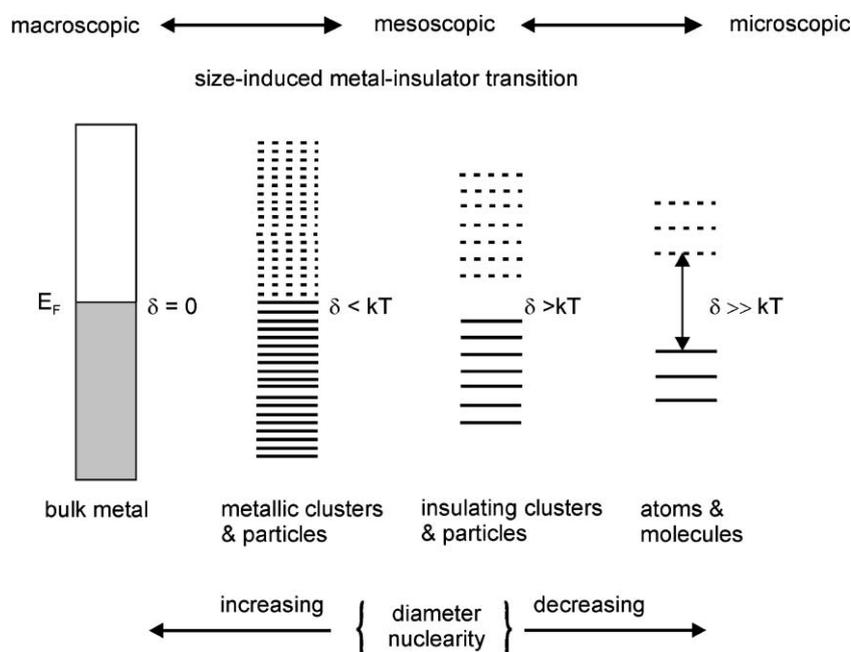
#### 3.1. The density of states

Atoms have their well known atomic orbitals. Depending on the extent of overlap in a solid they remain mostly unperturbed, as in noble gases, or they combine to extended

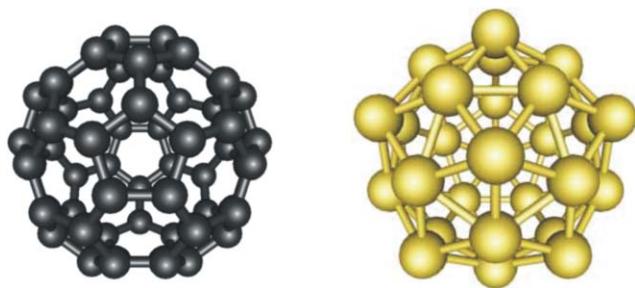
band structures, as in metals or semiconductors. The core orbitals are confined to a relatively small volume and remain localised (atom-like). Each of  $N$  atoms contributes with its atomic states to a band so that, although the width of a band increases slightly when more atoms are added, the density of states (DOS) within a band is basically proportional to the number of atoms of an ensemble with an extended band-like state. The band width amounts typically to a few eV. Thus, the DOS is on the order of  $N$  per eV, which is very large for a bulk amount of matter ( $N \approx$  Avogadro's number,  $N_A$ ) but low for small clusters.

The DOS basically scales smoothly with size, but with a scaling law that is different from that found from surface effects. It is described to a first approximation by the 'particle in a box' model in which the size of the box is given by the size of the particle. Discontinuities come in when the states are populated with electrons: for highly symmetric systems there are degenerate states, and when one of these is filled the next electron has to go into the next state of higher energy. These discontinuities are often somewhat blurred since the symmetry is normally lowered when an additional atom is added to a highly symmetric system. Thus, the discontinuities are typically superimposed on a smooth size-dependent slope, as will be detailed in Section 3.3.

An important threshold is reached when the gap between the highest occupied and the lowest unoccupied state (called the *Kubo gap*  $\delta$ ) equals thermal energy.<sup>14</sup> When electrons get thermally excited across the Kubo gap, a low temperature insulator becomes a semiconductor and at higher temperatures a metal; and also magnetic properties of small clusters can change dramatically. This non-metal-to-metal transition can take place within a single incompletely filled band, or when two bands begin to overlap because of band broadening. The development of the DOS with cluster size is illustrated in Fig. 5.



**Fig. 5** Evolution of the band gap and the density of states as the number of atoms in a system increases (from right to left).  $\delta$  is the so-called Kubo gap. (Redrawn with permission from ref. 14.)



**Fig. 6** Calculated structures of the fullerene  $C_{60}$  (left) and of the  $Au_{32}$  (right) nanoclusters which are both hollow. The colour of  $Au_{32}$  may be different from the typical appearance of gold as suggested in the figure. (Reprinted with permission from ref. 15.)

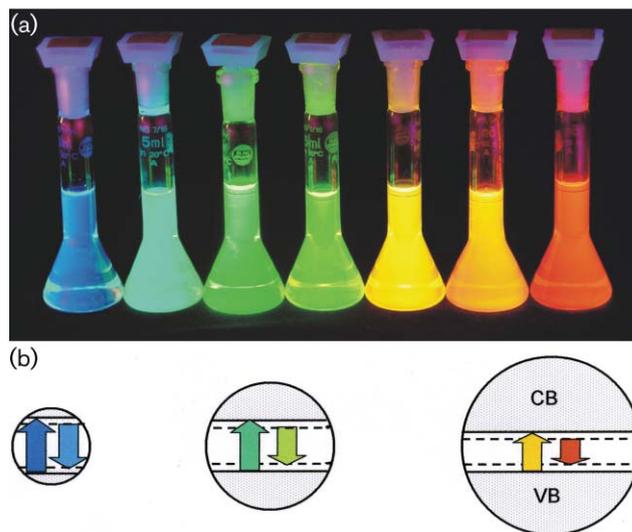
Chemists may prefer to think of small clusters as molecules. Instead of bands they talk of delocalised molecular orbitals, and the Kubo gap becomes the HOMO–LUMO gap. In such a view it is obvious that high cluster symmetry leads to correspondingly degenerate molecular orbitals.<sup>1</sup> Incompletely filled degenerate HOMO lead to magnetism, but often also to symmetry lowering by Jahn–Teller distortion.

### 3.2. Examples of delocalised clusters

Two interesting delocalised systems of high symmetry are those of  $C_{60}$  fullerene and  $Au_{32}$  gold (Fig. 6). Both are cage-like hollow clusters.<sup>15</sup>  $Au_{32}$  has been predicted from high level quantum chemical calculations, and its hollow structure was ascribed to the relativistic character of its electrons. For the same reason  $Au_N^-$  clusters up to probably  $N = 13$  are planar,<sup>16</sup> in contrast to most other elements which form icosahedral or cuboctahedral minimum energy structures.  $C_{60}$  is meanwhile well known both from experiment and theory. As a consequence of its icosahedral symmetry its HOMO is five-fold degenerate. Since it is fully occupied by 10 electrons it is not prone to Jahn–Teller distortion.

The size dependence of the HOMO–LUMO band gap introduced in Fig. 5 is best seen in the luminescence properties of semiconductor nanoparticles.<sup>17</sup> It is illustrated in Fig. 7a for the fluorescence of colloidal CdSe–CdS core–shell nanoparticles. By adjusting the particle size the fluorescence can be tuned between blue for particles of 1.7 nm diameter and red at 6 nm.<sup>18</sup> A similar size effect but shifted to higher energy relative to fluorescence applies to the absorbed light. The difference in wavelengths between absorption and fluorescence occurs because after absorption the system relaxes to adapt to the new charge distribution, initiated by creation of the electron–hole pair that is also called *exciton*.

The size dependence is shown schematically in Fig. 7b where the valence and conduction bands are drawn inside a circle that represents particle size. It is analogous to the well-known shift of colour of conjugated polyenes with increasing chain length. It can be understood on the basis of the fundamental model of electrons confined in a spherical square well potential ('particles in a box').<sup>19</sup> It should be noted that already at a size of a few nanometers a system contains several hundred atoms so that discontinuities are no longer observed and the wavelength shift with size appears smooth. It is nevertheless



**Fig. 7** a) Fluorescence of CdSe–CdS core–shell nanoparticles with a diameter of 1.7 nm (blue) up to 6 nm (red), giving evidence of the scaling of the semiconductor band gap with particle size. (Figure courtesy of H. Weller, University of Hamburg). b) Schematic representation of the size effect on the gap between the valence band (VB) and the conduction band (CB) and the absorption (up arrow) and fluorescence (down arrow). Smaller particles have a wider band gap.

a quantum effect since it is governed by the nature of standing waves of a confined system rather than by the fraction of atoms at the surface.

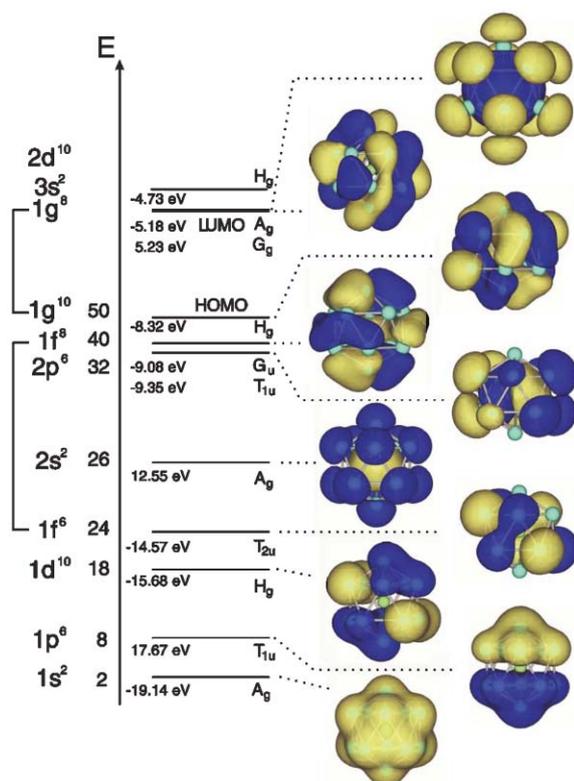
Colloidal gold nanoparticles were already well known in the middle ages. They were used as dyes in stained glass windows of cathedrals and palaces. 10 nm particles absorb green light and thus appear red, smaller ones would even fluoresce. In contrast to the above semiconductor particles this absorption of metallic particles is due to *surface plasmons*, a collective excitation of electrons near the surface that represents standing waves on a surface. Their interaction with light is well described by Mie theory.<sup>20</sup> Surface plasmons obey somewhat complex rules, and their wavelength in some cases increases and in others decreases with size.<sup>20</sup>

### 3.3 The concept of pseudo-atoms

Because of the quantised states of electrons and holes these nanocrystallites are often called *quantum dots*, *pseudo-atoms* or *superatoms*. The core–shell structure serves to control the potential that confines the electrons and determines the lifetime of excited states. Applications range from light emitting diodes (LEDs) and novel solid state lasers to potential future devices for quantum electronics<sup>21</sup> and quantum information processing (quantum computing).

Experimental and theoretical support for the pseudo-atom character of small metal clusters comes from properties such as ionisation potentials and electron affinities which reveal shell structures akin to those of conventional elements. Two examples are given to illustrate this behaviour: Fig. 8 compares the electron affinities of gold clusters  $Au_N$  ( $1 \leq N \leq 70$ ) with those of the elements as a function of their atomic number  $Z$ . The analogy of the periodicity due to their shell structures is obvious. Fig. 9 derives a periodic table for sodium clusters and



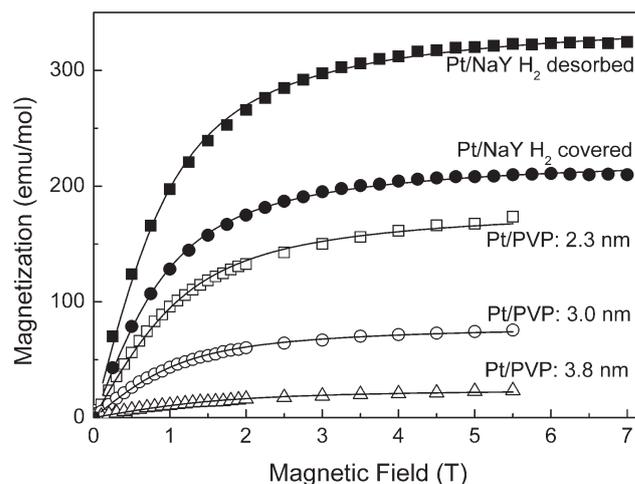


**Fig. 10** Calculated electronic orbitals for the core-shell icosahedral cluster  $\text{AlPt}_{12}^+$ . Note that there is a HOMO–LUMO gap of *ca.* 3 eV, indicating the large band-gap semiconductor nature of this species. The orbitals of this super-atom resemble the s-, p-, d- and higher hydrogen-like orbitals and show basically the energetic sequence which is also obtained from the three-dimensional ‘particle-in-a-box’ model. (Reprinted with permission from ref. 22. Copyright (2004) American Physical Society.)

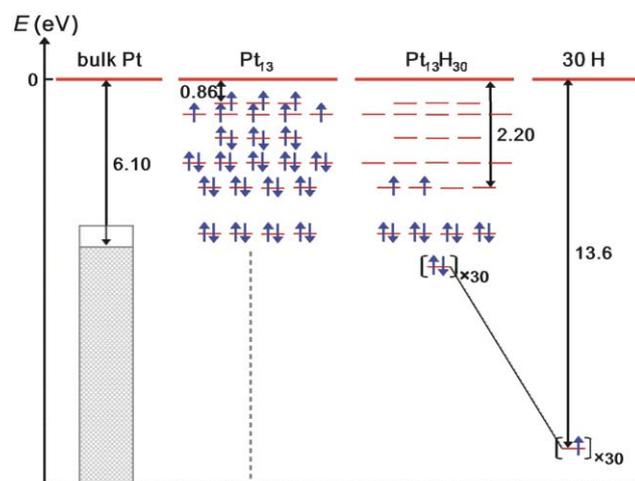
magnetic polarisation with up to 8 unpaired electrons on a cluster, corresponding to a magnetic moment of  $0.65 \mu_B$  per atom (Fig. 11).

The magnetization is partly quenched by hydrogen chemisorption, because each adsorbed hydrogen atom binds one of the unpaired electrons. Fig. 12 gives a schematic view of the situation: Bulk Pt metal has an incompletely filled d-band corresponding to a  $5d^96s^1$  electronic configuration and a Fermi level of 6.10 eV. In the  $\text{Pt}_{13}$  cluster the Fermi level rises considerably because of the shorter interatomic distances and concomitant higher orbital overlap. Density functional calculations of the discrete energy level diagram predict near-degenerate frontier orbitals with 8 unpaired electrons.<sup>24</sup> The levels of atomic hydrogen come in at much lower energy, leading to extensive electron transfer under formation of  $\text{Pt}_{13}\text{H}_x$  ( $x \leq 30$ ) hydrides.<sup>27</sup> Each surface H takes one electron out of the frontier orbital so that the magnetization should be expected to be zero for  $\text{Pt}_{13}\text{H}_8$ , then increase and decrease again for each set of degenerate orbitals which is depleted. This should lead to an oscillating magnetization as a function of decreasing hydrogen coverage, a prediction that awaits experimental verification.

Such studies provide insight into the electronic and magnetic structure of clusters and are fundamental for an understanding



**Fig. 11** Magnetization at 1.8 K of the  $\text{Pt}_{13}\text{NaY}$  before (solid dots, lower curve) and after hydrogen desorption (solid dots, upper curve), compared with literature data for analogous measurements of Pt nanoparticles embedded in a PVP polymer.<sup>26</sup> The particles have diameters of 2.3 nm (*ca.* 420 atoms), 3.0 nm (940 atoms) and 3.8 nm (1900 atoms).



**Fig. 12** Schematic representation of the d-band in bulk Pt metal and of the energy level structures and populations in  $\text{Pt}_{13}$ , and  $\text{Pt}_{13}\text{H}_{30}$  (lower levels are omitted). Note the depletion of the highest energy levels when electrons are used to form bonds to the surface hydrogen atoms.

of how magnetism develops in non-magnetic elements. Again, clusters may have to be regarded as pseudo-atoms, with the important difference that the cluster orbital momentum should be expected to be much larger than for atoms, because it scales with the square of the radius.<sup>28</sup> It is quite likely that the orbital momentum has important implications for the magnetic character of the cluster.

### 3.5 Catalysis at the surface of small particles

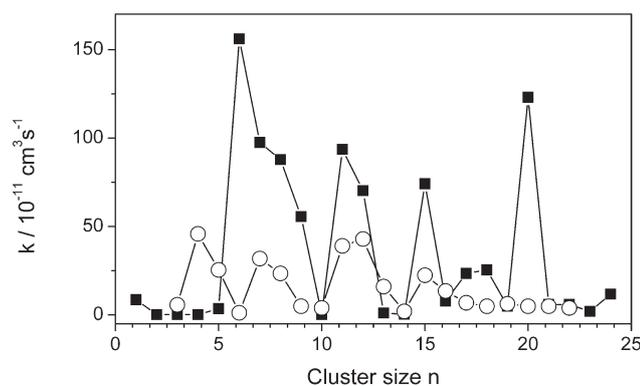
Small transition metal clusters exhibit strong variations as a function of size not only in their physical and electronic properties but also in their chemical behaviour as catalysts. Obviously, the ability to accept or donate charge plays a key

role. As shown in Fig. 8, the electron affinity of gold clusters changes by *ca.* 2 eV as a function of the cluster size. This holds also for the ionisation potential, and it may even be more pronounced for other elements.<sup>1</sup> For example, for platinum it varies between its value of 9.0 eV for a single atom and the work function of the bulk metal which amounts to 5.3 eV. This demonstrates that *chemical properties can be tuned over a very large range by variation of the cluster size.* This variation is not smooth since it reflects both the geometric and delocalised electronic shell structures of the cluster.<sup>1</sup> Often, a pronounced odd–even effect is observed, as seen in Fig. 8. This is ascribed to the filling of subsequent orbitals with a single or with two paired electrons.

An example which demonstrates that pronounced oscillations are found in the catalytic activity is shown in Fig. 13 for the decomposition reaction of N<sub>2</sub>O on Pt<sub>N</sub> clusters (1 ≤ N ≤ 24).<sup>29</sup> Of the cationic clusters, Pt<sub>N</sub><sup>+</sup>, N = 6–9, 11, 12, 15, and 20 are very reactive, while N = 10, 13, 14, 19, and 21–24 show very little reactivity. The reactivity of anionic clusters is clearly lower and the size dependence is considerably different.

Gold is extremely noble and does not tarnish. This is not only the reason for its popular application for jewellery but also for its inactivity as a catalyst. However, in the early 90's, Haruta *et al.* discovered that small gold particles have excellent catalytic properties.<sup>30</sup> Since then, nanogold has become a subject of high interest for fundamental investigations and has already found first practical applications in catalysis, for example as 'odour eaters' in bathrooms or for the low-temperature oxidation of CO to CO<sub>2</sub>.

It is well known that the catalytic activity of transition metal nanoparticles depends on the support on which they are dispersed. The interface between the metal and the semiconducting or insulating support can be regarded as a *Schottky contact* which is polarised due to partial charge transfer between the metal and the support.<sup>1</sup> Defect states in the support and in particular near its surface may play an important role for this charge transfer. For large particles, the effect of polarisation is minute because the Fermi level of the metal is almost unchanged and the partial charges remain located near the interface, remote from the adsorption site of



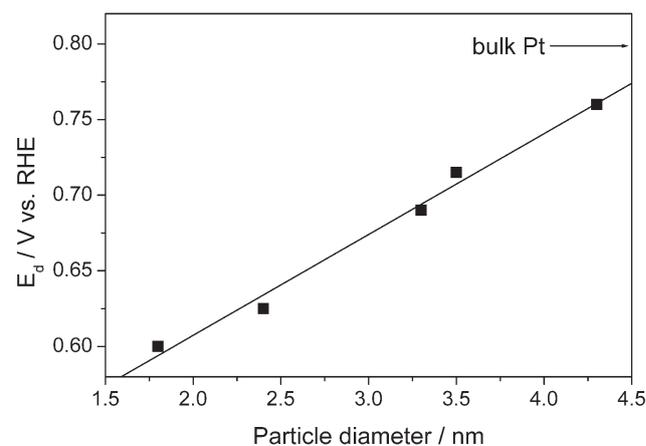
**Fig. 13** Absolute rate constants for the reaction with N<sub>2</sub>O of cationic (squares) and anionic (open circles) Pt<sub>n</sub> clusters. Some of the lowest values represent upper limits of the rate constant for unreactive cluster sizes. (Ref. 1, drawn using data from ref. 29 – Reprinted with permission of the PCCP Owner Societies.)

the reactants. For small particles, however, any polarisation changes the bond to the adsorbate significantly. This has also been shown for the Au<sub>8</sub> cluster on a single crystal MgO support.<sup>31</sup> The gold clusters are bound strongly on negatively charged *F* centre vacancies, and there is a charge transfer of *ca.* 0.5 *e* from the vacancy into the cluster.<sup>32</sup> This anchors and localises them at the defect site, preventing their agglomeration and concomitant deactivation. It is interesting also that there is a minimum of 8 Au or 15 Pt atoms in the particle for efficient catalysis of CO oxidation to CO<sub>2</sub>.

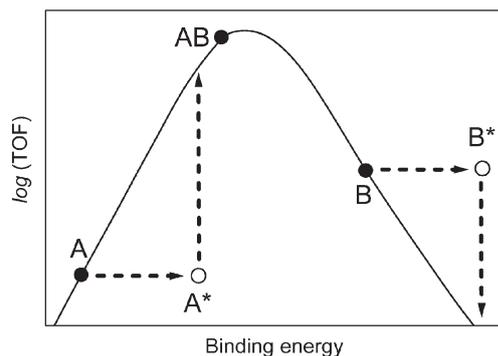
Early investigations of molecular oxygen adsorption on free gold clusters occurred only for even-numbered anionic clusters (Au<sub>2n</sub>, 2 ≤ n ≤ 10), and the reactivity correlated with the size-dependent pattern of the neutral gold clusters. This demonstrates that charging is essential, and it suggests that the neutral gold clusters deposited on MgO act as mediators of electron transfer from the surface to the adsorbed substrate.

It is often believed that decrease of specific catalytic surface area is the only consequence of particle agglomeration. Such views neglect any quantum size effects. Indeed, it has recently been demonstrated that peak potentials in cyclic voltammetry for CO oxidation on carbon supported Pt nanoparticles depend on the average particle size, which is a clear proof that it is not only the surface area but the electrochemical potential which changes.<sup>33</sup> The peak potential begins to shift away from its value observed for bulk polycrystalline Pt foils as the particle size decreases below *ca.* 4 nm (Fig. 14).

It has long been known and more recently been confirmed in high-level quantum chemical calculations that the turnover frequency of a heterogeneously catalysed reaction as a function of binding energy of the reactants onto the catalyst surface yields a *volcano-shaped plot*,<sup>34</sup> as shown schematically in Fig. 15. The effect is explained as follows: at low binding energies the reactant is not adsorbed at all or not sufficiently perturbed towards the transition state of the reaction. At too high adsorption energies the product does not desorb, and the surface is blocked ('poisoned'). The optimum activity is obtained with an intermediate adsorption energy which represents a compromise between a catalyst with a small



**Fig. 14** Potential of the surface oxide reduction peak *E<sub>d</sub>* of glassy carbon-supported Pt nanoparticles as a function of particle size. (Ref. 1, prepared using data from ref. 33 – Reprinted with permission of the PCCP Owner Societies.)



**Fig. 15** Schematic logarithmic volcano plot of turnover frequencies (TOF) as a function of the adsorption energy. The point denoted “AB” represents the predicted 1 : 1 alloy between A (which binds weakly) and B (which binds strongly). The arrows indicate the increasing binding energy of a substrate to the nanoparticle, which results in a higher TOF for A but in a lower one for B. (Adapted from ref. 34.)

activation barrier for the reaction which leads to a product blocked surface and a surface with low reactant coverage.<sup>34,35</sup>

So far, this volcano plot has nothing to do with nanomaterials. However, since adsorption energies on the surface of small particles which have many edges and corners, the turnover frequency of a low-activity catalyst can be tuned towards the maximum of the volcano plot by reducing the particle size (arrow A in Fig. 15). This may be the reason for the much higher activity of nanogold as compared with bulk gold. It may also be the explanation for much less successful efforts to further increase the activity of platinum, which is already an excellent catalyst as a bulk metal. For a reaction that is very efficiently catalysed by a certain bulk material the nano-size-effect would shift the turnover frequency away from the maximum to lower values (arrow B in Fig. 15).

It was furthermore predicted that the adsorption energy of a 1 : 1 alloy catalyst particle AB is to a first approximation simply the average between the adsorption energies of the two individual components A and B.<sup>34</sup> If A is located on one side and B on the other side of the volcano plot, the alloy AB may show close to the maximum turnover frequency (see Fig. 15). This offers a way for catalyst design by interpolation in the periodic table.

#### 4. Summary

The main reasons why nanomaterials show properties so different from those of the bulk are:

- *Surface effects:* atoms at surfaces have fewer neighbours than atoms in the bulk. Because of this lower coordination and unsatisfied bonds, surface atoms are less stabilised than bulk atoms. The smaller a particle the larger the fraction of atoms at the surface, and the higher the average binding energy per atom. The surface-to-volume ratio scales with the inverse size, and therefore there are numerous properties which obey the same *scaling law*. Among them are the melting and other *phase transition temperatures*. Edge and corner atoms have an even lower coordination and bind foreign atoms and molecules more tightly.

The *coordination number* is also limited in narrow pores. The solubility of salts in pore-confined water, the melting point and even the critical point of a fluid are therefore greatly reduced. Phase transitions are collective phenomena. With fewer atoms *a phase transition is less well defined*, it is therefore no longer sharp. The Gibbs phase rule loses its meaning because phases and components are no longer properly distinguishable. Small clusters behave more like molecules than as bulk matter. It is therefore useful to think of different isomers which coexist over a temperature range rather than of different phases. There are numerous other *concepts of thermodynamics which can break down*, in particular when the system of interest consists of a single isolated cluster with a small number of atoms.<sup>1</sup>

- *Quantum size effects:* In metals and semiconductors the electronic wave functions of conduction electrons are delocalised over the entire particle. Electrons can therefore be described as ‘particles in a box’, and the densities of state and the energies of the particles depend crucially on the size of the box, which at first leads to a smooth size-dependence. However, when more atoms are added the shells are filled up, and discontinuities occur when a new shell at higher energy starts to be populated. Because of these discontinuities there is no simple scaling. Instead, one finds behaviour akin to that of atoms, with filled shells of extra stability. Therefore, such clusters are often called ‘*pseudo-atoms*’. The HOMO–LUMO band gap of semiconductor particles and therefore their *absorption and fluorescence wavelengths* become size dependent. *Ionisation potentials* and *electron affinities* are *tuned* between the atomic values and the work function of the bulk material by variation of the cluster size. These same properties relate to the availability of electrons for forming bonds or getting involved in redox reactions. Therefore, the *catalytic activity* and *selectivity* become functions of size.

Quite often, the discontinuous behaviour of quantum size effects is superimposed on a smoothly scaling slope which also reflects the size of a quantised system. It may be difficult to distinguish it from the smoothly scaling surface effect.

#### References

- 1 E. Roduner, *Nanoscope Materials: Size-Dependent Phenomena*. The Royal Society of Chemistry, Cambridge, 2006.
- 2 J. Jortner, *Z. Phys. D: At., Mol. Clusters*, 1992, **24**, 247.
- 3 A. Köhn, F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2001, **3**, 711.
- 4 W. Thomson, *Philos. Mag.*, 1871, **42**, 448.
- 5 K. M. Unruh, T. E. Huber and C. A. Huber, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 9021.
- 6 K. Koga, T. Ikeshoji and K. Sugawara, *Phys. Rev. Lett.*, 2004, **92**, 115507.
- 7 S. L. Lai, J. Y. Guo, V. Petrova, G. Ramanath and L. H. Allen, *Phys. Rev. Lett.*, 1996, **77**, 99.
- 8 C. Soliari and M. Fluehli, *Surf. Sci.*, 1985, **156**, 487.
- 9 J. Weissmüller, *J. Phys. Chem. B*, 2002, **106**, 889.
- 10 R. S. Berry, *Phases and Phase Changes of Small Systems*, in *Theory of Atomic and Molecular Clusters*, ed. J. Jellinek, Springer, Berlin, 1999.
- 11 L. D. Gelb, K. E. Gubbins, R. Radhakrishnan and M. Sliwinski-Bartkowiak, *Rep. Prog. Phys.*, 1999, **62**, 1573.
- 12 M. Schmidt, R. Kusche, T. Hippler, J. Donges, W. Kronmüller, B. von Issendorff and H. Haberland, *Phys. Rev. Lett.*, 2001, **86**, 1191.
- 13 M. Hartmann, G. Mahler and O. Hess, *Phys. Rev. Lett.*, 2004, **93**, 080402.

- 14 P. P. Edwards, R. L. Johnston and C. N. R. Rao, *On the Size-Induced Metal-Insulator Transition in Clusters and Small Particles*, in *Metal Clusters in Chemistry*, Vol. 3, ed. P. Braunstein, L. A. Oro, P. R. Raithby, Wiley, Weinheim, 1999.
- 15 M. P. Johansson, D. Sundholm and J. Vaara, *Angew. Chem.*, 2004, **116**, 2732.
- 16 H. Häkkinen, M. Moseler and U. Landman, *Phys. Rev. Lett.*, 2002, **89**, 033401.
- 17 A. D. Yoffe, *Adv. Phys.*, 1993, **42**, 173.
- 18 A. Eychemüller, *J. Phys. Chem. B*, 2000, **104**, 6514.
- 19 J. Lüning, J. Rockenberger, S. Eisebitt, J.-E. Rubensson, A. Karl, A. Kornowski, H. Weller and W. Eberhardt, *Solid State Commun.*, 1999, **112**, 5.
- 20 U. Kreibig and M. Volmer, *Optical Properties of Metal Clusters*, Springer Series in Materials Science, Springer, Berlin, 1995, vol. 25.
- 21 L. P. Kouwenhoven, D. G. Austing and S. Tarucha, *Rep. Prog. Phys.*, 2001, **64**, 701.
- 22 S. Neukermans, E. Janssens, Z. F. Chen, R. E. Silverans, P. v. R. Schleyer and P. Lievens, *Phys. Rev. Lett.*, 2004, **92**, 163401.
- 23 D. E. Bergeron, A. W. Castleman Jr., T. Morisato and S. N. Khanna, *Science*, 2004, **304**, 84.
- 24 N. Watari and S. Ohnishi, *Phys. Rev. B: Condens. Matter*, 1998, **58**, 1665.
- 25 Y. Nakae, Y. Seino, T. Teranishi, M. Miyake, S. Yamada and H. Hori, *Physica B*, 2000, **284–288**, 1758.
- 26 Y. Yamamoto, T. Miura, Y. Nakae, T. Teranishi, M. Miyake and H. Hori, *Physica B*, 2003, **329–333**, 1183.
- 27 X. Liu, H. Dilger, R. A. Eichel, J. Kunstmann and E. Roduner, *J. Phys. Chem. B*, 2006, **110**, 2013.
- 28 V. Kresin, *Phys. Rev. B: Condens. Matter*, 1988, **38**, 3741.
- 29 I. Balteanu, O. P. Balaj, M. K. Beyer and V. E. Bondybey, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2910.
- 30 M. Haruta, *Catal. Today*, 1997, **36**, 153.
- 31 B. Yoon, H. Häkkinen, U. Landman, A. S. Wörz, J.-M. Antonietti, S. Abbet, K. Judai and U. Heiz, *Science*, 2005, **307**, 403.
- 32 A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Häkkinen, R. N. Barnett and U. Landman, *J. Phys. Chem. A*, 1999, **103**, 9573.
- 33 F. Maillard, S. Schreier, M. Hanzlik, E. R. Savinova, S. Weinkauff and U. Stimming, *Phys. Chem. Phys.*, 2005, **7**, 385.
- 34 C. J. H. Jacobsen, S. Dahl, B. S. Clausen, S. Bahn, A. Logadottir and J. K. Nørskov, *J. Am. Chem. Soc.*, 2001, **123**, 8404.
- 35 B. Hammer and J. K. Nørskov, *Adv. Catal.*, 2000, **45**, 71.

# Chemical Biology

An exciting news supplement providing a snapshot of the latest developments in chemical biology



Free online and in print issues of selected RSC journals!\*

**Research Highlights** – newsworthy articles and significant scientific advances

**Essential Elements** – latest developments from RSC publications

**Free links** to the full research paper from every online article during month of publication

\*A separately issued print subscription is also available

RSC Publishing

[www.rsc.org/chemicalbiology](http://www.rsc.org/chemicalbiology)