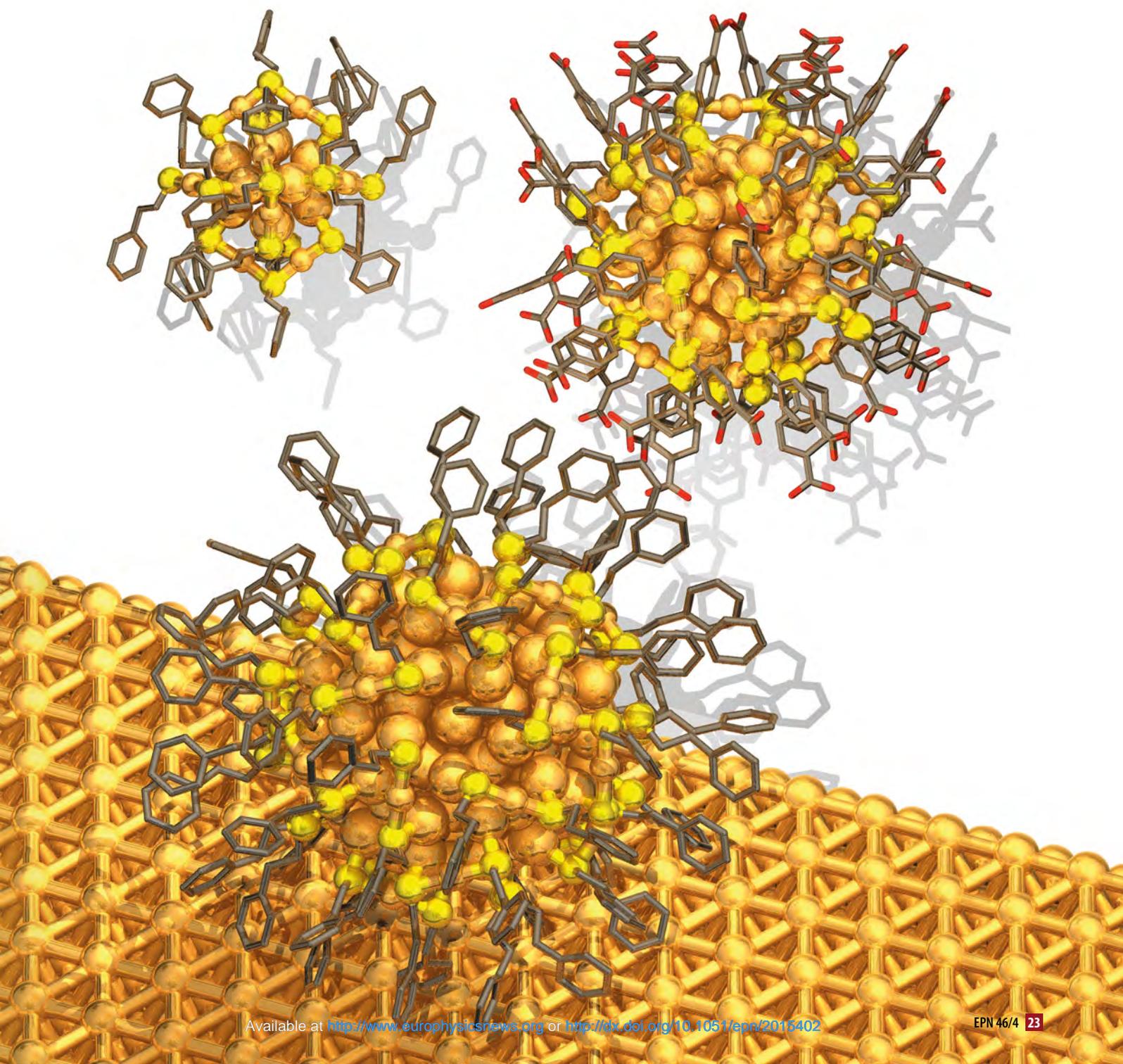


HOW MANY GOLD ATOMS MAKE GOLD METAL?

■ Sami Malola and Hannu Häkkinen – DOI: 10.1051/eprn/2015402

■ Departments of Physics and Chemistry, Nanoscience Center – University of Jyväskylä, FI-40014 Jyväskylä, Finland

It is well known that a piece of gold is an excellent metal: it conducts heat and electricity, it is malleable to work out for jewellery or thin coatings, and it has the characteristic golden colour. How do these everyday properties – familiar from our macroscopic world – change when a nanometre-size chunk of gold contains only 100, 200 or 300 atoms?



These simple but fundamental questions can now be answered due to recent developments in synthesis, characterization and theory of finely dispersed, ambient-stable gold nanoparticles with atom-precise composition and structure.

Quantum size effects

Every undergraduate textbook of solid state physics contains a discussion of a “perfect theorist’s metal”: the three-dimensional electron gas model for a monovalent metal. When electrons are confined in a small volume, the solutions of the Schrödinger equation describing their possible quantum states correspond to discrete energies (Fig. 1). The quantum states are filled according to the Pauli principle up to the highest possible energy, called the Fermi energy E_F . When the number of electrons increases, the average spacing Δ between the quantum states decreases. In the limit when Δ approaches zero (e.g., $\Delta < 25$ meV which is the thermal energy at room temperature), minute external stimuli create immediate response of the electrons and the system becomes “metallic” in nature. For a macroscopic piece of metal $\Delta = 0$ (Fig. 1) which makes the material responsive to extremely small external electromagnetic fields and/or to temperature.

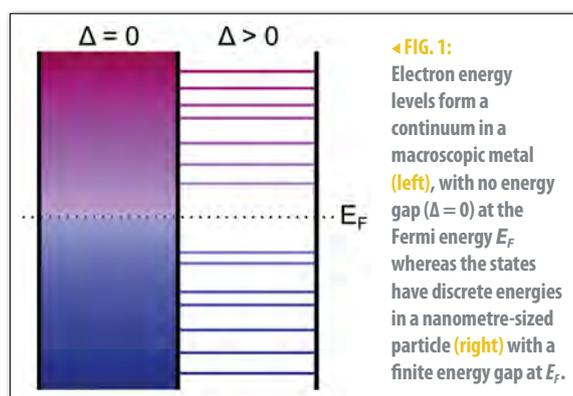
The critical nanoparticle size, where the crossover between non-metallic and metallic behaviour happens, can be estimated from the following simple consideration. The density of electron states $D(E)$ of a three-dimensional electron gas follows a square-root behaviour as a function of the electron energy E which leads to a simple estimate of D at the Fermi energy

$$D(E_F) = \frac{3N}{2E_F} \quad (1)$$

for N electrons. The mean spacing Δ of electron energy levels at E_F is then

$$\Delta = 1/D(E_F) = \frac{2E_F}{3N} \quad (2)$$

Clearly, Δ approaches zero as N grows. Plugging the Fermi energy of gold metal (about 5.5 eV) in Eq. (2) yields $N > 150$, or in terms of the nanoparticle diameter d , $d > 1.7$ nm, for the crossover where $\Delta < 25$ meV.



Breakthroughs in synthesis and structural characterization of gold nanoparticles

Small pure gold and gold-containing particles have been used in glass-making and in art since ancient times [1]. Finely-dispersed gold particles suspended in solutions (“colloidal gold”) have been known since the days of Michael Faraday, who marvelled at their beautiful ruby colour that results from their strong absorption of light around the wave length of 520 nm [2]. Faraday himself described the particles “very minute in their dimension”; later work by Turkevich concluded that Faraday’s gold particles were indeed in the nanometre-range with average diameter of 6 ± 2 nm [2], *i.e.*, well in the metallic side of the crossover region discussed above.

In 1994-1995 Brust, Schiffrin and collaborators published recipes [3] for a synthesis that gives a control of the size of gold nanoparticles in the important 1 – 3 nm region, and these methods have been used widely ever since. The methods produce ambient-stable particles capped at the surface by thiols, that are organic molecules containing a sulphur headgroup binding to gold.

Since late 1990’s, several stable gold nanoparticle sizes were synthesized. However, it took until 2007 before the first atomic structure of such nanoparticle was solved via X-ray diffraction. This was achieved by the group of R.D. Kornberg from a sample that contained single crystals made out of identical nanoparticles – a method completely analogous to what was used in early 1900’s to discover the atomic structures of solids made out of ordinary elements. The particle has a chemical formula of $\text{Au}_{102}(\text{pMBA})_{44}$, *i.e.*, 102 gold atoms and 44 para mercapto benzoic acid (pMBA) molecules at the surface [4]. Special to this structure and to many structures of other gold nanoparticles that have been solved since 2007 is the existence of gold atoms in two distinct parts of the nanoparticle: in the compact all-gold core and mixed with thiols in the ligand shell (Fig. 2). This chemical structure was predicted theoretically in 2006 [5]. Interestingly, a very similar mixed metal-thiol overlayer forms when thiol molecules self-assemble on a macroscopic flat gold surface and seems thus to be a universal structural feature of the gold-sulfur interface [6].

Small gold nanoparticle: Molecule or metal?

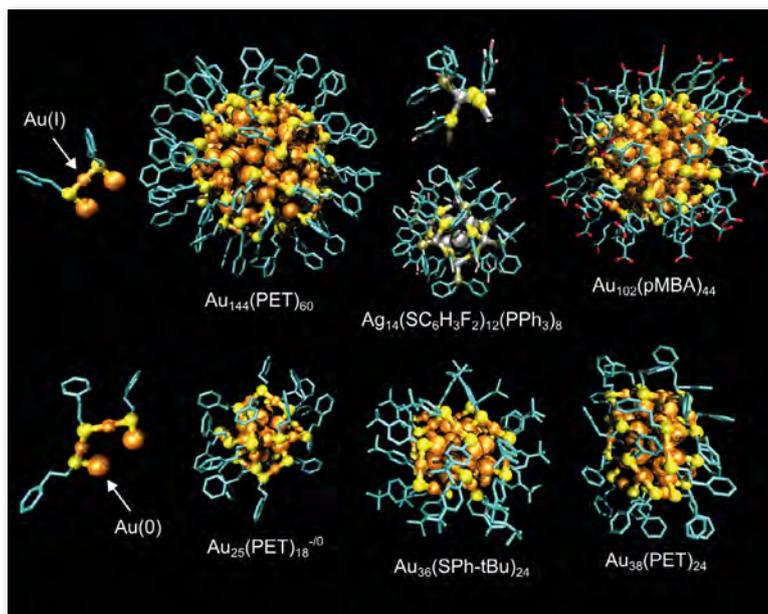
Macroscopic metals are good conductors for energy in many forms such as electricity and heat. In the nanoscale, “conducting” properties can be studied by pumping energy into a nanostructure and monitoring how it is transferred to the environment. Recent spectroscopic measurements at the Nanoscience Center in the University of Jyväskylä have shed light onto this question and shown how two different, but almost same-size nanoparticles dissipate energy in drastically different ways. One can be defined as a “molecule”, the other one as “metal” [7a,b].

Two nanoparticles, $\text{Au}_{102}(\text{pMBA})_{44}$ and $\text{Au}_{144}(\text{PET})_{60}$, that are close in size and composition (Fig. 2), were recently studied by shining visible or infrared light into the nanoparticle solution and monitoring how fast the excitation energy transfers from the particles to the solution. The energy of the photons is initially absorbed by the metal centre of the particle, and then transferred to the solution through the layer of the ligand molecules. The experiments yielded time constants for this energy transfer process by monitoring how the transient absorption by the ligand molecules changes in time. When the absorbed energy is dissipated through the ligand molecules to the surrounding solvent, shifts in typical eigenmodes for ligand vibrations take place. This generates a “hot band”, *i.e.*, shift of the vibration mode to a slightly lower frequency due to increased anharmonicity, and “bleach” of the initial frequency at the thermal equilibrium.

Temporal data of the observed hot band and bleach dynamics of $\text{Au}_{102}(\text{pMBA})_{44}$ and $\text{Au}_{144}(\text{PET})_{60}$ nanoparticles is shown in Figure 3. The slightly larger nanoparticle $\text{Au}_{144}(\text{PET})_{60}$ exhibits a fast thermalization in about 50 – 60 ps timescale when both hot and bleach bands have disappeared. This agrees with the expected behaviour for a metallic system and is in fact a manifestation of rapid “heat conductance” on nanoscale. Other recent spectroscopy experiments from other laboratories agree with this result [7c]. Theoretical calculations on the electronic structure of this nanoparticle also implicate metallic behaviour, *i.e.*, rather continuous density of available electron states close to the Fermi energy.

The excitation dynamics of the smaller $\text{Au}_{102}(\text{pMBA})_{44}$ nanoparticle is drastically different. The decay dynamics has several different time scales, and particularly interesting are a medium-time scale of about 84 ps and an extremely long component with an estimated decay time of 3.5 ns for the hot band dynamics. These interesting time scales could be explained by help of theoretical calculations taking into account the electronic structure of the nanoparticle.

The excitation takes the system from its initial spin-singlet ground state S_0 to a highly excited state over the fundamental energy gap beyond the first excited singlet state S_1 (Fig. 3). The excitation can decay by rapid electronic relaxation down to the first excited singlet state or by crossing over to a manifold of magnetic states such as the lowest energy triplet state T1 on a time scale of about 1 ps. The magnetic state is transient with a decay time to the singlet ground state of about 84 ps. The long decay time, 3.5 ns, is assigned to the transition from S_1 back to S_0 over the fundamental energy gap $E(S_1) - E(S_0)$. This long decay time is a direct manifestation of the existence of a sizable fundamental gap, which has been determined to be about 0.5 eV by earlier theory and spectroscopic measurements, [7d] and thus confirms that this nanoparticle behaves like a huge gold-rich molecule. It is quite remarkable that both basic types of nanoparticle behaviour are found in these gold nanoparticles that differ just by a few tens of gold atoms.

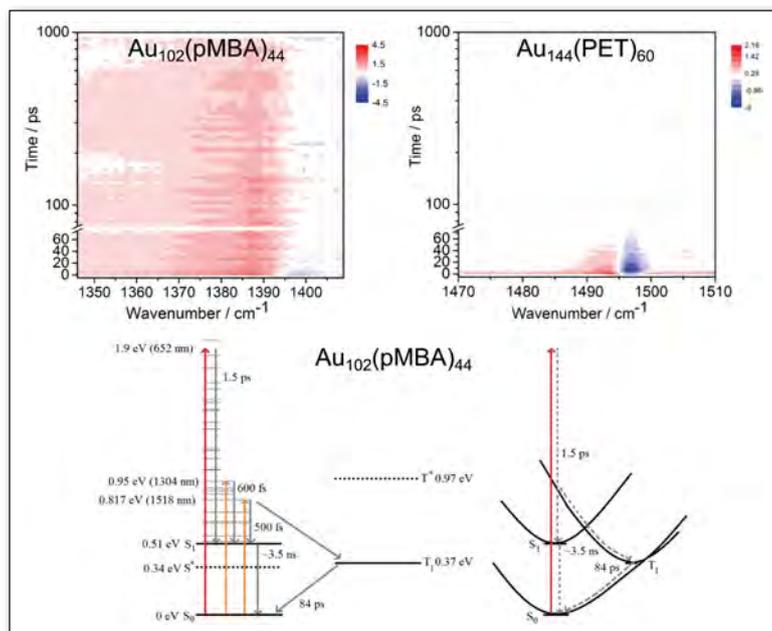


Collective electronic excitations and development of the localized surface plasmon

Faraday’s liquid samples containing “very minute” gold nanoparticles had a beautiful ruby colour due to an interesting collective excitation of the nanoparticles’ electron cloud, called a surface plasmon resonance (LSPR). It forms when the energy of the incoming light photon enhances the natural oscillations of the freely moving electrons of a metal. In metal nanoparticles this leads to density changes of the electron cloud near the metal surface. The resonance energy of this oscillation is well known for gold corresponding to a wave length of light close to 520 nm. The LSPR phenomenon shows up when the electronic properties of the nanoparticle become similar to macroscopic metals and is thus considered as the sign of emergence of metallic properties when nanoparticles grow in size.

Recent theoretical work in our laboratory has established that the “birth” of the LSPR takes place when the metal core of gold nanoparticles grows from 1.5 nm to 2 nm [8]. The response of two model nanoparticles ($\text{Au}_{144}(\text{SR})_{60}$ and $\text{Au}_{314}(\text{SR})_{96}$ with metal cores of 1.5 nm and 2 nm, respectively) to light was calculated. The larger particle shows a strong absorption of light at around 540 nm, close enough to the limit for large colloidal gold particles. Analysis of the oscillations of the electron cloud (Fig. 4) shows that they are localized at the surface of the particle. The smaller particle shows a collective dipole-like oscillation as well but it is not localized at the surface. When the excitation is localized at the surface, the transition dipole moment increases, thus making the absorption stronger. These differences demonstrate for the first time a plausible mechanism of a developing surface plasmon from atomic-scale calculations.

▲ FIG. 2: Assembly of typical molecular structure found in nanometre-size gold and silver nanoparticles. Gold: orange, silver: grey, sulphur: yellow, carbon: cyan, oxygen: red. The particle fragments on the left demonstrate the existence of gold in “metallic” Au(0) and “oxidised” Au(I) forms. PET = phenylethylthiol, Ph = phenyl, pMBA = para mercapto benzoic acid and tBu = tert-butyl.



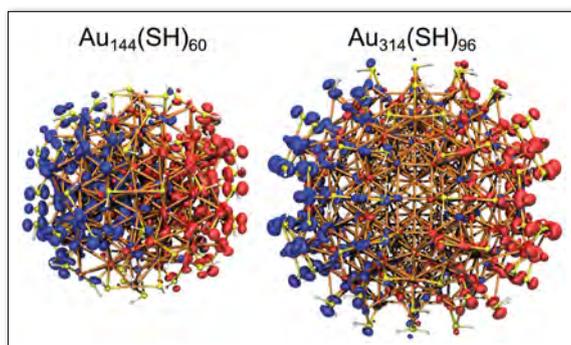
▲ FIG. 3: Top: Comparison of the transient absorption spectra of $\text{Au}_{102}(\text{pMBA})_{44}$ (left) and $\text{Au}_{144}(\text{PET})_{60}$ (right) obtained with excitation at 652 nm (visible light). The “hot bands” are shown in red and the “bleach bands” in blue. Bottom: Schematic energy diagram that explains the observed long lifetimes in $\text{Au}_{102}(\text{pMBA})_{44}$ after excitation by visible light or near-infrared radiation (for details see the text). Reproduced by permission from ref. [7a]. Copyright 2015 American Chemical Society.

Prospects

The field of molecularly precise noble metal nanoparticles is still in a discovery phase. Due to increased interest in this field, new ambient-stable particles and their atomic structures are reported several times every year, not only on gold but also on silver and intermetallic particles containing gold, silver and copper. Biological imaging techniques have yielded new recent breakthroughs for nanoparticle structural characterization [9].

► FIG. 4:

Visualisation of the response of the electron “cloud” to an excitation by light around 540 nm in two model gold nanoparticles $\text{Au}_{144}(\text{SH})_{60}$ and $\text{Au}_{314}(\text{SH})_{96}$. The metal cores of these particles have diameters of 1.5 nm and 2 nm, respectively. Red and blue areas depict the oscillatory changes in the electron density under the excitation.



All this activity will provide an excellent set of realistic data revising our understanding on principles how matter, atoms and molecules, assemble from molecular to more macroscopic architectures in the nanoscale. Aside from being of great fundamental interest, ambient-stable, atomically precise noble metal nanoparticles of 1 – 3 nm size are still little-explored, but promising materials for several applications for instance in the field catalysis, biological imaging and sensing or even medical use [10,11]. ■

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About the Authors



Sami Malola (top) and **Hannu Häkkinen**

(bottom) are computational physicists working at the Nanoscience Center (NSC) in the University of Jyväskylä. Häkkinen is a professor in computational nanoscience since 2007 and the Scientific Director of the NSC since 2012. His research interests include electronic, optical, magnetic, chemical and catalytic properties of bare, supported, and ligand-stabilized metal nanoparticles, electrical conductivity of molecule-metal interfaces in nanostructures and structural and chemical properties of metal nanoparticle / bionanoparticle hybrids. Malola is a senior scientist working in the Häkkinen group.



References

- [1] C. Louis, “Gold nanoparticles in the past: Before the nanotechnology era”, in *Gold Nanoparticles for Physics, Chemistry and Biology*, edited by C. Louis and O. Pluchery (Imperial College Press, London 2012).
- [2] D. Thompson, *Gold Bulletin* **40**, 267 (2007).
- [3] (a) M. Brust, M. Walker, D. Bethell, D.J. Schiffrin and R. Whyman, *Chem. Comm.* 1994, 801; (b) M. Brust, J. Fink, D. Bethell, D.J. Schiffrin and C. Kiely, *Chem. Comm.* 1995, 1655.
- [4] P.D. Jadzinsky, G. Calero, C.J. Ackerson, D.A. Bushnell and R.D. Kornberg, *Science* **318**, 430 (2007).
- [5] H. Häkkinen, M. Walter and H. Grönbeck, *J. Phys. Chem. B* **110**, 9927 (2006).
- [6] H. Häkkinen, *Nature Chemistry* **4**, 443 (2012).
- [7] (a) S. Mustalahti, P. Myllyperkiö, S. Malola, T. Lahtinen, K. Salorinne, J. Koivisto, H. Häkkinen and M. Pettersson, *ACS Nano* **9**, 2328 (2015); (b) S. Mustalahti, P. Myllyperkiö, T. Lahtinen, K. Salorinne, S. Malola, J. Koivisto, H. Häkkinen and M. Pettersson, *J. Phys. Chem. C* **118**, 18233 (2014); (c) C.Y. Yi, M.A. Tofanelli, C.J. Ackerson and K.L. Knappenberger, *J. Am. Chem. Soc.* **135**, 18222 (2013); (d) E. Hulkko, O. Lopez-Acevedo, J. Koivisto, Y. Levi-Kalisman, R.D. Kornberg, M. Pettersson and H. Häkkinen, *J. Am. Chem. Soc.* **133**, 3752 (2011).
- [8] S. Malola, L. Lehtovaara, J. Enkovaara, H. Häkkinen, *ACS Nano* **7**, 10263 (2013).
- [9] M. Azubel, J. Koivisto, S. Malola, D. Bushnell, G.L. Hura, A.L. Koh, H. Tsunoyama, T. Tsukuda, M. Pettersson, H. Häkkinen and R.D. Kornberg, *Science* **345**, 909 (2014).
- [10] V. Marjomäki, T. Lahtinen, M. Martikainen, J. Koivisto, S. Malola, K. Salorinne, M. Pettersson and H. Häkkinen, *Proc. Natl. Acad. Sci. USA* **111**, 1277 (2014).
- [11] C. Louis and O. Pluchery (eds.) *Gold Nanoparticles for Physics, Chemistry and Biology* (Imperial College Press, London 2012).