The role of big metal clusters in nanoscience

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The miniaturisation of a metal particle to the nanosize regime produces quantum size behavior, *i.e.* the quasi-delocalized metallic electrons begin to form discrete energy levels. This transition from bulk to molecule is frequently observed for ligand-protected clusters in the size range 1–4 nm. Tunneling spectroscopic (STS) experiments on single clusters not only prove the size dependence of the Coulomb gap, but also the temperature dependence. As the electrostatic energy $e^2/2C$ must be large compared with the thermal energy k_BT of the electron to induce Coulomb steps, very low temperatures are necessary to observe this event on larger particles. A 17 nm Pd cluster behaves like a piece of metal at room temperature, but shows a Coulomb barrier at 4.2 K. On the contrary, a ligand-stabilized 1.4 nm Au cluster shows a Coulomb step at room temperature (small C), but a series of Coulomb steps (SET processes) at 90 K. The practical use of clusters in nanoelectronics is coupled to the ability to organize them three-, two- or one-dimensionally. A quasi 3-D organization of clusters can be reached by linking them with spacer molecules, chemically fixed to the cluster surfaces. A direct relation between spacer length and activation energy for electronic inter-cluster tunneling processes is observed. Two-dimensional arrangements of different kinds of clusters have been reached by self-assembly processes on chemically modified surfaces or by using Langmuir–Blodgett (LB) films transferred onto a substrate. A deficiency of both methods is the lack of long-range order. First attempts to generate 1-D chains show good promise if nanopores in alumina membranes are used as tubes to be filled by the clusters. Electrophoretic filling has turned out to be the better method to introduce clusters compared with vacuum filling.

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1 Introduction

Since the systematic study of transition-metal carbonyl compounds by W. Hieber, the father of metal carbonyls, between the nineteen-thirties and -fifties, an enormous number of mostly organometallic cluster compounds has been discovered. However, during Hieber's time M_3, M_4 or M_6 species were more or less exclusively of academic interest. The first idea of considering clusters as parts of bulk metals arose when Chini's and later Longoni's high-nuclearity clusters, many of them structurally investigated by Dahl, became known.[1,2] This was the first time that 30 and 40 metal atoms formed individual species, structurally closely related to bulk metals, having more or less perfectly dense-packed atomic architectures. These findings initiated a tremendous development, not only in cluster science, but especially with respect to our understanding of the electronic situation in particles of a size which is located between the typical molecular state on the one hand, and the infinite bulk situation, on the other hand.

2 Observation of Quantum Size Effects

J. de Jongh was one of the pioneers who considered big ligand-stabilized metal clusters as isolated small cutouts of a bulk metal and who has foreseen the great possibilities to study the beginning (or the ending) of what we usually understand as the 'metallic state'.[3] The discovery of even larger metal clusters such as Au_{55}, Pt_{309} or a series of Pd clusters, consisting of 500–2000 atoms, in the course of the last 10–15 years enabled numerous physical investigations which clearly show that these particles in the size range 1–4 nm are electronically characterized by quantum-size effects,[4] *i.e.* classical physical laws are substituted by quantum mechanical rules. Specific heat, susceptibility, conductivity and other fundamental characteristics of a metal are going to be lost, at least at low temperatures, when the particles reach the nanoscale dimension. Electrons are no longer in a quasi-delocalized three-dimensional state, but begin to form discrete energy levels, however, still not to such an extent as is the case in molecular orbitals. The electronic situation in a nanosized cluster may best be described by Fig. 1, where the electronic density of states of three typical situations is shown: the bulk state with its electronic band structure of d and s electrons on the one hand (a), and the characteristic situation of discrete energy levels in a molecule on the other hand (c). The transition state between these two is typical for nanosized clusters (b).

From Fig. 1 it can also be concluded that the transition from bulk to molecule and *vice versa* is not a well defined situation, but develops continuously. To decide if situation (a), (b) or (c) is realized depends also on the method applied and on the temperature of investigation.

The most sensitive and most valuable tool used to study the

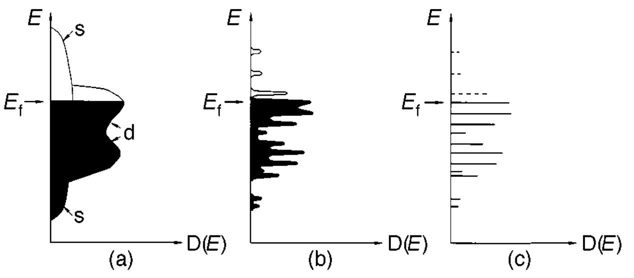

Fig. 1 Electronic situation in (a) a bulk metal particle with quasi-delocalized d and s electrons forming a band structure. In (b) the electrons begin to form discrete energy levels which are completed in the molecular state (c) with fully localized bonding electrons

electronic situation in a single nanosized particle is tunneling spectroscopy (STS), resulting in current (I)–voltage (V) characteristics. Two extreme situations illustrate the power of this method. Fig. 2(a) shows the I–V curves of a huge 17 nm Pd particle, consisting of hundreds of thousands of atoms, at room temperature and at 4.2 K. At 293 K the I–V behavior is that of the bulk: it is linear. However, at 4.2 K there is a so-called Coulomb gap to be observed, indicating a situation where the thermal energy k_BT of the electrons is small compared to the electrostatic energy $e^2/2C$ (C = capacitance of the combination cluster/tip).[5]

This situation should, however, also be realized at higher temperatures when the particles become small enough. This is indeed the case for ligand-protected Au_{55} clusters with a metal core diameter of only 1.4 nm [the I–V curve is shown in Fig. 2(b)].[6] When the cluster is cooled to 90 K a series of Coulomb steps can be observed in the I–V curve [Fig. 2(c)].[7] Single electron transitions (SET) between neighboring clusters can be initiated if they are excited.[8] Fig. 3 illustrates the electronic relation between some touching ligand-protected clusters. In the ground state the valence (metallic) electrons are localized in the cluster cores. The de Broglie wavelength corresponds with the diameter of the cluster nucleus. In the excited state the electrons become able to tunnel through the non-conducting medium between. This knowledge is of decisive importance for future applications of giant metal clusters in electronics.

3 Organization of Clusters

Before being able to use clusters for nanoelectronic devices a huge problem has to be solved: this is the organization of nanoparticles in an ordered manner, whether three-, two- or one-dimensionally. Numerous laboratories are trying to solve this problem. Chemically synthesized ligand-protected clusters, independent of their size, form solid powders which cannot directly be used for electronic purposes. On the other hand, owing to their ligand shell, even 30 nm particles become soluble in appropriate solvents. From non-polar solvents such as pentane, to water as an extremely polar medium, all kinds of solvents can in principle be used if the ligands bear appropriate substituents. This is a big advantage for the treatment of clusters, also with respect to the generation of cluster arrangements. Without having solved this 'organization problem' clusters are useless particles, even if their individual electronic conditions look ideal.

Three-dimensional arrangements

Perfect three-dimensional arrangements exist in crystals. However, from experience it is known that particles in the nanometer size regime do not tend to crystallize, although some success has recently been achieved. Whetten *et al.* reported on crystalline materials of thiol-protected gold particles, however, they are only of ≈40 μm in size.[9] The use of nanoparticles in electronics requires routine production of cluster arrangements.

In contrast to pure metal clusters ligand-stabilized metal–

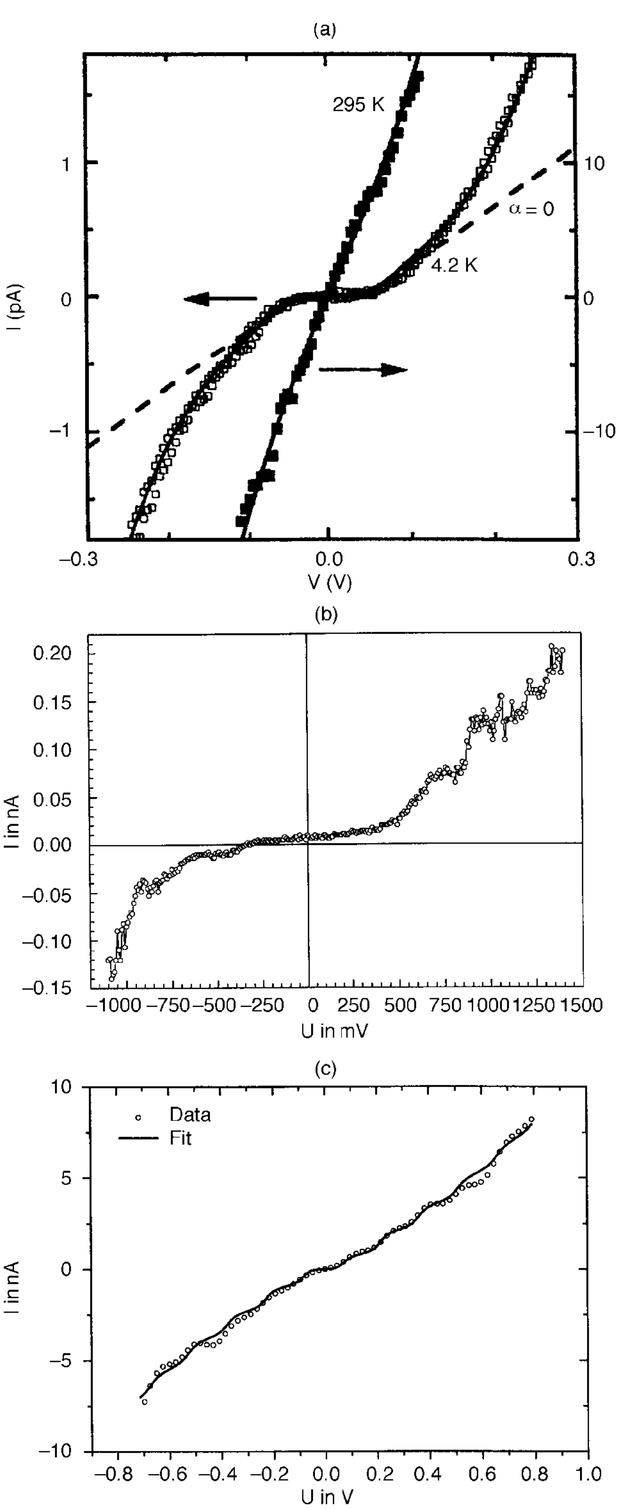

Fig. 2 (a) Current (I)–voltage (V) diagram of a single 17 nm Pd particle, enveloped in a shell of sodium sulfanilate between two Pt tips.[5] Reprinted with permission from A. Bezryadin, C. Dekker and G. Schmid, *Applied Physics Letters*, 1997, **71**, 1273. Copyright 1997 American Institute of Physics. The linear correlation between I and V indicates Ohm behavior as usual in bulk metals. At 4.2 K a Coulomb step (single electron transition) is observed showing k_BT small enough to fulfill the condition $e^2/2C \gg k_BT$ ($e^2/2C$ = electrostatic energy, k_BT = kinetic energy). In (b) the I–V characteristic of a single $Au_{55}(PPh_3)_{12}Cl_6$ cluster is shown.[6] Reprinted with permission from L. F. Chi, M. Hartig, T. Drechsler, Th. Schwaack, C. Seidel, H. Fuchs and G. Schmid, *Journal of Applied Physics* (to be published). Copyright 1997 American Institute of Physics. (The measurement has been performed using a cluster monolayer from which individual clusters have been addressed.) The particle is small enough to make $e^2/2C$ large (small C) compared to k_BT, even at room temperature. Decrease of temperature to 90 K enables even series of single electron transitions (c).[7] Reprinted with permission from G. Schmid, *Advanced Materials* (to be published). Copyright 1998 Wiley-VCH, Weinheim, Germany

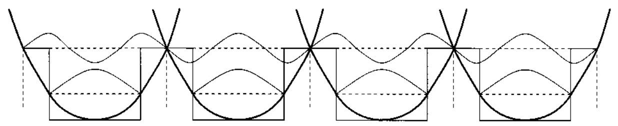

Fig. 3 Electronic situation in a row of clusters, separated by their ligand shell (energy barrier of the capacitance *C*) in the ground state and in the first excited state where electron tunneling through the ensemble becomes possible

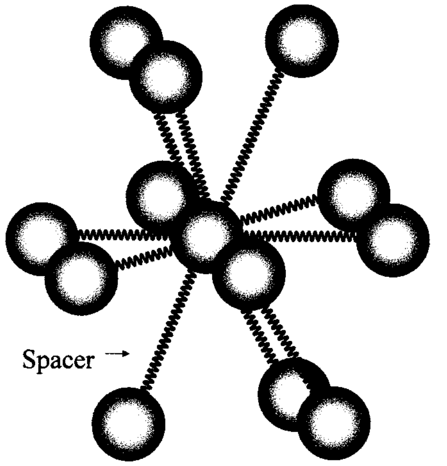

Fig. 4 Idealized three-dimensional arrangement of clusters using stiff spacer molecules to tailor the distance between the clusters

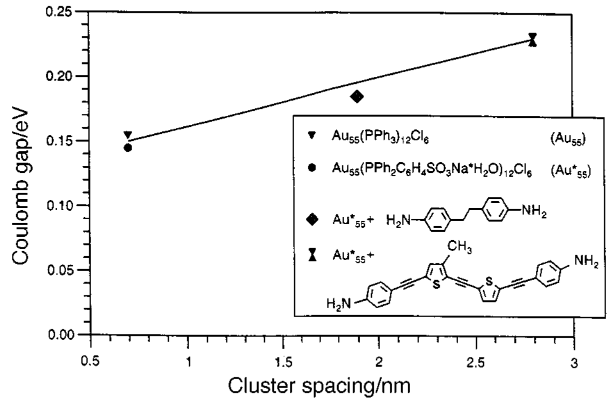

Fig. 5 Correlation between cluster distance and Coulomb gap[12]

chalcogenide clusters crystallize much better. Fenske synthesized and crystallized an impressive series of mainly copper selenide clusters, *e.g.* $Cu_{146}Se_{73}(PPh_3)_{30}$.[10] With respect to applications in electronics these particles promise to be suitable candidates for developing novel semiconductor devices.

The first successful preparation of large metal clusters three-dimensionally has recently been achieved by us when gold and palladium clusters were spontaneously linked three-dimensionally by spacer molecules.[11] As the linking process occurs rapidly, well ordered structures cannot be expected. However, due to the distinct length of the spacer molecules equidistance between the clusters is guaranteed. Fig. 4 elucidates an ideal three-dimensional arrangement of clusters *via* spacers.

The advantage of this method is the variability of spacer molecules allowing the tailoring of the energy barriers between the clusters. As can be seen from Fig. 5 the Coulomb gaps between Au_{55} clusters indeed depend directly on the spacer lengths.[12] Not only the length, but also the chemical nature of the stiff molecules can be used to influence the capacitance between single quantum dots. Such studies are currently performed in our laboratory.

The spacer–cluster interactions occur either by substitution of PPh_3, ligands by thiols or *via* simple acid–base reactions between $Ph_2PC_6H_4SO_3H$ ligands of the clusters and NH_2 groups of the diamino spacers.

Two-dimensional arrangements

Most progress in organizing metal clusters has been reached in two dimensions. Two different strategies are known by which densely packed metal particles can be arranged in monolayers: there is the self-organization of ligand-stabilized clusters on a smooth surface from solution without chemical interaction between clusters or between clusters and the surface. Andres *et al.* used this method to generate perfect layers of alkylthiol-protected gold particles.[13] The inert alkyl chains are unable to form bonds stronger than van der Waals forces within the environment. If dithiols are used instead of monothiols the gold particles will be linked to each other and also to the surface, if it has some thiophilic character as is the case for gold. As a consequence, the degree of order is not as good as in the case of the monothiols owing to a lowered mobility preventing better ordering processes.[13] Shiffrin and co-workers have used similar procedures before to generate ordered gold clusters.[14] However, two-dimensional cluster arrangements on surfaces without chemical fixation will probably not be well suited for further use due to the lack of mechanical stability. For that reason our efforts must be directed towards arrangements of strongly fixed clusters. We first attempted this some years ago by absorbing $Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6$ clusters on a mica surface which had been previously modified with a layer of polyethylenimine (PEI).[15] We observed areas with partially dense packed clusters, however, high-ordered larger faces could not be fabricated.

Recent detailed studies with gold and palladium clusters on various substrates showed that chemical fixations are easily reached, but perfectly organized and routinely realizable two-dimensional arrays have not been reached until now.[16] A possible reason for the lack of formation of ordered 2-D arrays is to be seen in the strong bonds formed between the functionalized surface and the arriving clusters. Ordering processes demand mobility of the building blocks in order for them to be well arranged. This is not possible if the first interactions are too strong. As has been shown by Andres *et al.*[13] non-fixed clusters can form perfect 2-D arrays, in contrast to those which are linked to the surface. The disadvantage of non-fixed clusters, however, is the easy dislocation of the clusters by mechanical contact. Processes to reach both goals are in progress.

Fig. 6(a) shows a tunneling microscopic (STM) image of a 250 × 250 nm area of a monolayer of *ca.* 13 nm gold particles which are roughly dense packed, but not well ordered.[17] Such arrays are formed when a surface such as quartz glass, silicon or mica is first modified by appropriate molecules forming a monolayer attractive to clusters or colloids. For instance, 2-aminoethanethiol reacts with a Au(111) surface by its aurophilic SH functions. The NH_2 groups then chemisorb colloids from aqueous solution by simple acid–base reactions. This procedure is schematically shown in Fig. 6(b).

The chemical fixation of the particles prevents mechanical dislocations *e.g.* by the tip of the microscope. In a continuation of the monolayer formation of Au_{55} clusters on PEI-covered mica,[15] which is a less smooth surface and furthermore requires atomic force microscopy rather than the better resolving scanning tunneling microscopy (STM), we changed from mica to monocrystalline Au(111) surfaces. The Au(111) areas can simply be generated when thin gold layers on flat chromium are heated and spontaneously cooled down by a stream of nitrogen. Treatment of such surfaces with aminothiols $H_2N(CH_2)_nSH$ gives modified surfaces with strong S–Au bonds. The NH_2 functions form a kind of basic carpet which chemisorbs acidified clusters eagerly. As acidified clusters we used

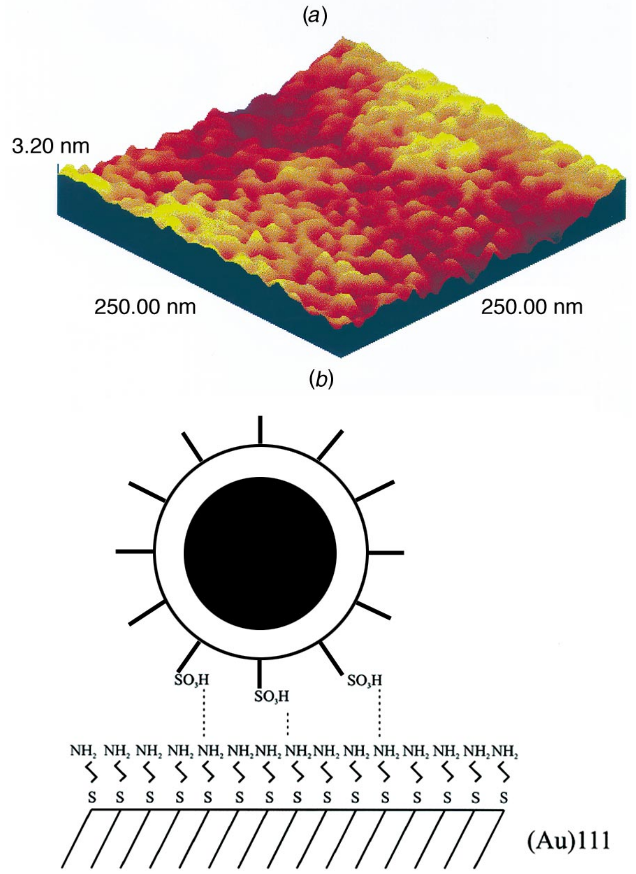

Fig. 6 (a) An STM image of a monolayer of ≈13 nm gold colloids, fixed on a Au(111) layer which has been modified by 2-aminoethanethiol.[17] (b) Illustration of a cluster–linker–substrate combination, resulting in monolayers as shown in (a)

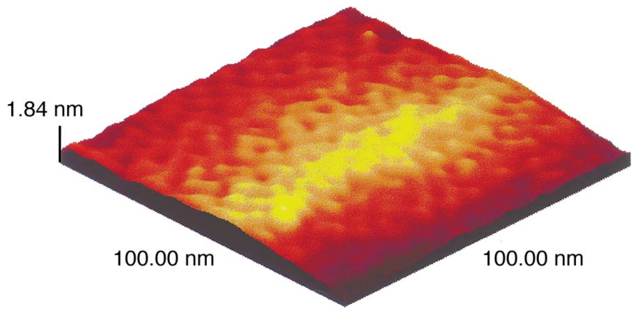

Fig. 7 An STM image of a monolayer of $Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6$ clusters on Au(111), modified as shown in Fig. 6(b). Some ordered rows of clusters can be observed, however, an overall close-packed structure is not realized[17]

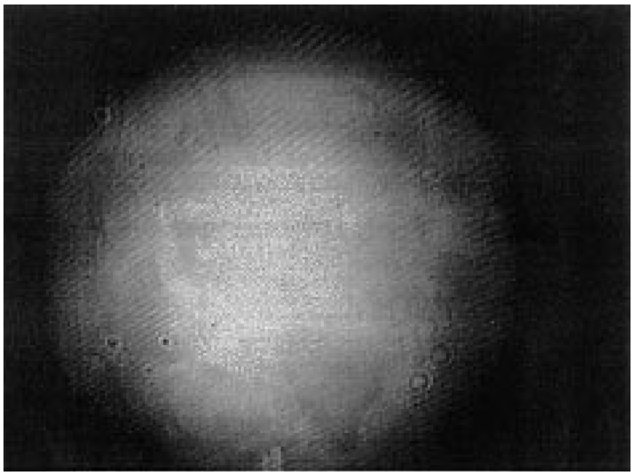

Fig. 8 A Brewster–Angle microscopic image of a Langmuir–Blodgett film of macroscopically well ordered $Au_{55}(PPh_3)_{12}Cl_6$ clusters on a water surface.[18,19] Reprinted with permission from L. F. Chi, S. Rakers, T. Drechsler, M. Hartig, H. Fuchs and G. Schmid, *Langmuir* (to be published). Copyright 1998 American Chemical Society

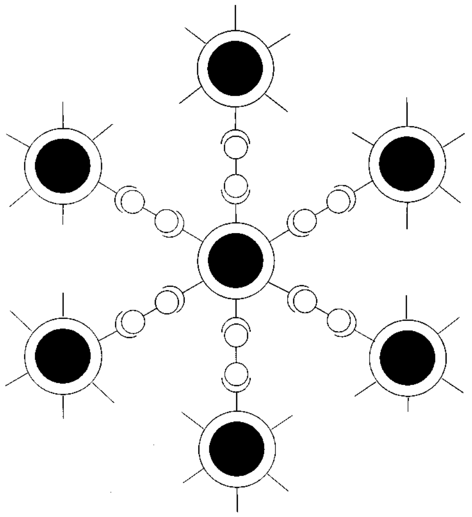

Fig. 9 Sketch of a two-dimensional cluster arrangement linked by spacers with functional groups complementary to those on the cluster surface

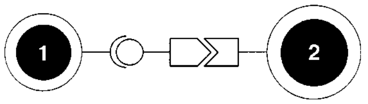

Fig. 10 Combination of two different clusters *via* a spacer with two different functions

$Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6$, dissolved in water and transferred to the substrate by a simple dipping process. The STM result of an as-prepared monolayer is shown in Fig. 7.[17] Although the imaged 100 × 100 nm cutout is still not perfectly ordered, areas of organized clusters can be observed.

Assuming that still better organized cluster-monolayers could be made in the near future, there is still another big problem to be solved: the distance between ordered clusters must be variable in order to separate them from each other depending on the electronic demands. In other words, we need spacer molecules which act only in two dimensions. There is only one recent result which gives an idea as to how this challenge might be conquered. The water insoluble cluster $Au_{55}(PPh_3)_{12}Cl_6$ has been used to generate Langmuir–Blodgett (LB) films on water.[18,19] Such films can be transferred onto various substrates where they may be chemically fixed by methods corresponding to those mentioned above. Fig. 8 shows a Brewster angle (BAM) microscopic image of a well ordered cluster LB film. The AFM investigations (not shown here) confirm the existence of monolayers.

In current experiments we try to 'dilute' such cluster LB films by appropriate spacer molecules which can act only two-dimensionally due to the conditions on the surface. The situation is explained in Fig. 9. The cluster ligands and the spacer molecules must be equipped with complementary substituents, as is formally shown in the image. As both functions must have hydrophobic properties, the condition is not easy to reach, but solutions appear in outline.

Another interesting perspective can be foreseen if clusters of different metals and of different size can be combined *via* spacers. If the two types are charged by appropriate functions, corresponding spacers will interact only with the complementary cluster sites and so build up novel kinds of monolayers as indicated in Fig. 10.

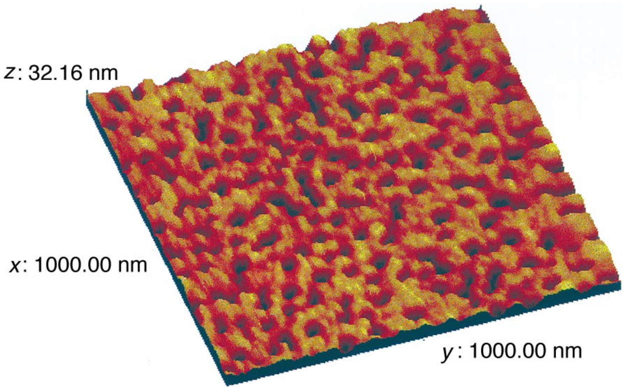

Fig. 11 An AFM image of a 1000 × 1000 nm^2 surface of a porous alumina membrane. Pore size 67 ± 9 nm

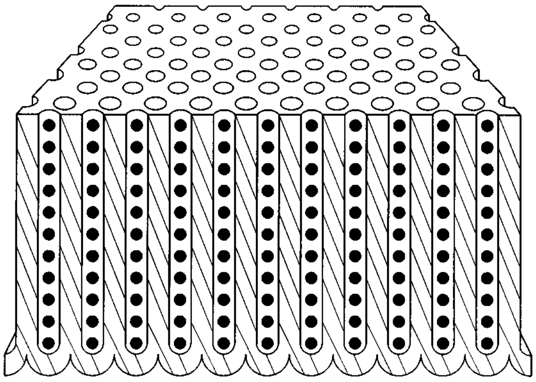

Fig. 12 Illustration of an ideally cluster-filled nanoporous alumina membrane

One-dimensional arrangements

A scientific as well as a technological first-rate goal is the generation of one-dimensional arrays of quantum dots. Several groups try to fabricate cluster wires by using atomic steps on crystalline surfaces where the particles are preferably absorbed. Indeed, this route works quite well in some cases, however, the preparation of distinct steps on ordered surfaces requires complicated nanotechnological procedures, especially if numerous parallel quantum dot rows are to be made. We decided to follow another technique, namely to fill parallel running pores in alumina membranes with clusters. The technique used to generate nanoporous alumina by anodizing aluminium metal is well known and allows the control of the pore width as well as the pore length.[20,21] Perfect filling of such pores would result in 10^9–10^{11} wires per cm^2, all separated from each other by walls of non-conducting Al_2O_3.

Fig. 11 shows an AFM image of a nanoporous alumina membrane and Fig. 12 illustrates the situation in a perfectly filled membrane. In practice a big problem has emerged in the course of our running experiments. It is the uninterrupted filling of the channels. Two techniques have been found to work best: vacuum filling and electrophoretic filling.[22] Vacuum filling means that a solution of the cluster is used to penetrate into the evacuated membrane. Dense filling is difficult as solvent molecules claim a part of the pore volume which becomes empty when the solvent is evaporated. Electrophoresis has turned out to be the better alternative. The membrane is in contact on one side with a metallic layer, *e.g.* gold or the original aluminium which serves as a cathode during electrophoresis. Small clusters and even large colloids can thus be transported into the pores growing from the bottom up to the open surface. However, even using this method, interruptions in the cluster chains are always observed. This is not surprising considering that, for instance, a 10 µm thick membrane, having pores of the same length, must be filled by *ca.* 4000 clusters of 2.5 nm diameter each. This is not very realistic. On the other hand membranes much thinner than a few microns are very difficult to handle. For that reason we now prepare thicker membranes and reduce a small part of them to *ca.* 100 nm using ion-milling techniques. By this method we are able to fabricate a relatively stable device of cluster wires the length of which is appropriate to make their filling predominantly undisturbed, as shown in Fig. 13.

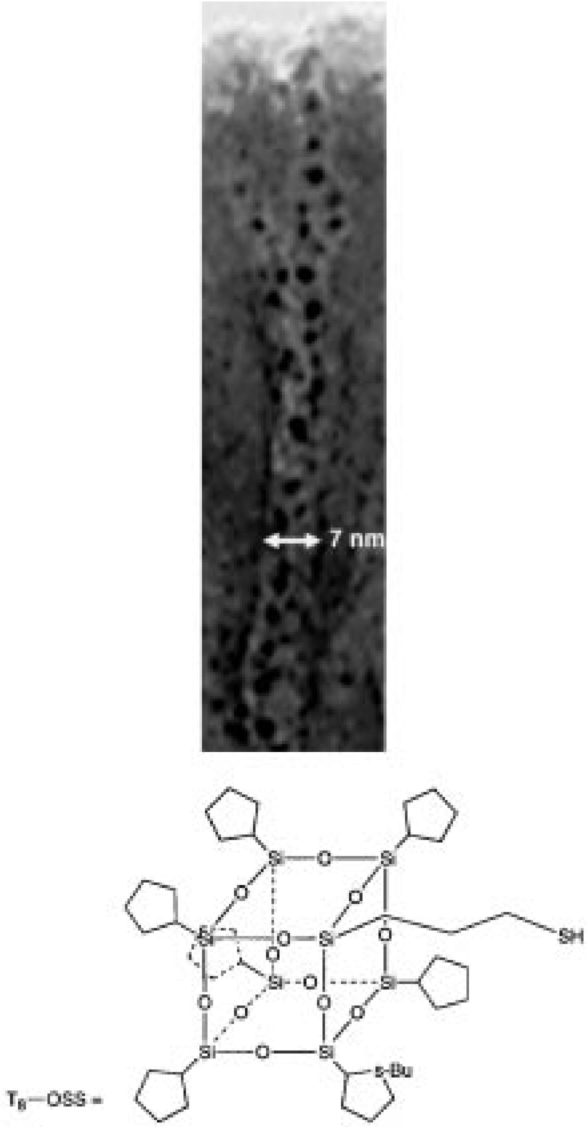

Fig. 13 High resolution transmission electron microscope image of a 7 nm channel in alumina, filled with $Au_{55}(T_8\text{-}OSS)_{12}Cl_6$ clusters.[22] Reprinted with permission from G. Hornyak, M. Kröll, R. Pugin, Th. Sawitowski, G. Schmid, J.-O. Bovin, G. Karsson, H. Hofmeister and S. Hopfe, *Chemistry European Journal*, 1997, **3**, 1951. Copyright 1998 Wiley-VCH, Weinheim, Germany

4 Conclusion

In retrospect, ligand-stabilized transition-metal clusters turned out to be promising candidates to act as model quantum dots. Although technical applications, *e.g.* in nanoelectronics, are far from being realized, it is to be stated that the electronic properties of clusters, if small enough, offer ideal conditions. The appearance of quantum size properties not only at very low temperatures but even at room temperature makes clusters in principle superior to traditional techniques which still end up with structures of a factor 10–100 times bigger. An important conclusion, however, overviewing the state of the art, is that the future of 'cluster technology' is definitely linked with the ability to organize these diminutive particles into suitable arrangements. Our and many other scientists interest is presently therefore focused on this goal. Other huge problems can be foreseen, *e.g.* addressing single clusters. However, we should not try to put the cart before the horse.

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