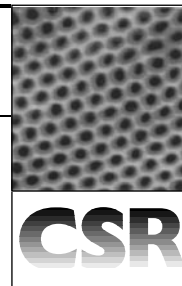


Current and future applications of nanoclusters

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Received 9th November 1998

This article deals with some recent developments in metal and in semiconducting nanocluster science. Our studies on the properties, mainly of metal nanoclusters, with respect to

future and also to current applications are reviewed, including a series of unpublished results. The general properties of metal clusters of one up to a few nanometers

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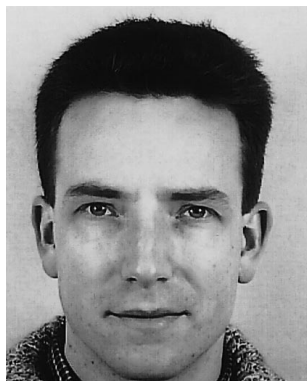
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are discussed on the basis of numerous physical investigations in the course of the last few years. Quantum size effects open the door to novel future technologies. The success of future applications of nanoclusters will strongly depend on the availability of three-, two- or one-dimensionally organized materials. Our own very recent results are promising, but also indicate that much more work will be necessary. Much more realistic is the use of metal nanoclusters in heterogeneous catalysis. Finally, novel developments in generating semiconducting nanomaterials in transparent, nanoporous alumina membranes are discussed. CdS and GaN can easily be prepared inside the pores to give photoluminescent foils of unlimited size.

1 Introduction

The term 'nanocluster' is used to name particles of any kind of matter, the size of which is greater than that of typical molecules, but which is too small to exhibit characteristic bulk properties. The special nature of such nanoclusters, whether consisting of atoms or composed of building blocks, is to be traced back to a quantum confinement of electrons leading to a change of the relevant properties compared to the bulk. Even common materials such as water or carbon change their behaviour if they become small enough: the stability of buildings at temperatures below 0 °C is guaranteed by a decisive decrease of the freezing point of water in the nanopores of cement, and the extraordinary behaviour of slices of graphite, too small to exist as a usual elementary modification, is ending up in fullerenes and nanotubes, having initiated a completely novel branch in chemistry and in material science.

Particles of metals and semiconductors in a size-regime where the wavelength of the electrons is of the same order as the particle size itself are of extraordinary interest because they behave electronically as zero-dimensional quantum dots. That means that the laws of classical physics, valuable for bulk materials, have to be substituted by quantum mechanical rules. The transition from a bulk to a nanosized material is best explained by the sketch in Fig. 1 where the electronic situation

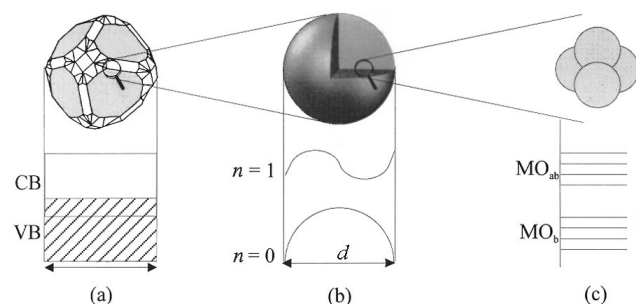


Fig. 1 Illustration of the transition of a bulk metal *via* a nanocluster to a molecule. The metallic band structure in (a) turns to a discrete electronic energy level in (b) where the particle diameter corresponds with the de Broglie wavelength. In (c) are shown bonding and antibonding molecular orbitals, occupied by electrons localized in bonds.

in three different particles of metal atoms is illustrated. The situation in (a) is that of a quasi-delocalized electronic state of overlapping valence (VB) and conductivity bands (CB) as is the case in a metallic bulk situation. In a semiconductor there exists a gap between both bands, the size of which determines the energy of electron transitions to achieve conductivity. On the way from (a) to (b) in the case of a metal the overlap of VB and CB becomes continuously smaller, finally ending up as a band gap, too. Fig. 1(b) illustrates the extreme situation where the particle diameter d corresponds with $\lambda/2$ ($\lambda =$ de Broglie

wavelength) in the ground state. This energy state can be compared with the s orbital of a giant metal atom ($n = 0$) which can be occupied by two electrons. The first excited state ($n = 1$) then corresponds to an atomic p orbital, *etc.* In (c), bonding (MO_b) and antibonding (MO_{ab}) molecular orbitals characterize the localized bonds between a few atoms in a molecular cluster.

This article will deal exclusively with particles of type (b), either consisting of metal atoms or semiconducting materials. The difference between both is only of quantitative, and not of principal nature. In practice, quantum size effects are to be expected even if the ultimate situation (b) is not reached, but already in larger particles where d corresponds with some multiples of the electronic wavelength. The investigations of a series of nanoclusters in the last decade showed that it is reasonable to expect quantum confinement in metal particles between 1 and 10 nm, whereas nanoclusters of semiconductors show quantum size behavior at larger sizes due to the different conditions in the bulk.

It can be predicted that the very special situation in (b) or in particles of similar size, if 'metallic' or 'semiconducting', should enable manifold applications on very different fields of science and technology. Some of them which have been the object of our own interest will be described in the following. Many others, of course, are under investigation by other groups. Before discussing possible practical aspects of nanoclusters, a first chapter will deal with the detection of quantum size effects in nanoclusters. Metal clusters are exclusively considered in connection with this, because semiconductor nanoclusters have not been so intensively studied by ourselves on the one hand and on the other hand because very good reviews have been published.¹

2 Quantum size effects in metal nanoclusters

To study quantum size behaviour of nanoclusters there is one condition to be fulfilled: the particles must be separated from each other to avoid coalescence and to keep the individual nature of the particles. The availability of numerous ligand protected metal clusters indeed enabled the systematic investigation of the properties of nanoclusters. Synthetic aspects, however, will not be considered in this article. They are described in detail in previous papers.²⁻⁶

The most frequently investigated cluster type is $Au_{55}(PPh_3)_{12}Cl_6$ and some of its derivatives. This so-called two-shell cluster (a central atom is embedded by two closely packed shells consisting of 12 and 42 atoms, respectively) is of special interest as its size of 1.4 nm (without ligands) seems to represent the borderline between the situations (a) and (c) in Fig. 1.

The generation of hot electrons in gold clusters of different size by femtosecond laser pulses allowed the observation of their relaxation behavior.⁷ The relaxation behaviour of excited electrons is determined by two opposite effects: the electron-phonon coupling on the one hand, decreasing with decreasing cluster size and, on the other hand, the collision rate on the cluster surface, increasing with decreasing cluster size. For small particles the latter process is dominating. So, on changing from *ca.* 15 nm gold particles to the 1.4 nm Au_{55} cluster the electronic relaxation increases characteristically, whereas a Au_{13} (~ 0.7 nm) cluster shows a considerable decrease of the relaxation compared with the 1.4 nm cluster. This can only mean that on changing from Au_{55} to Au_{13} , there is an expressed transition from a nanosized metal to a molecule.

Impedance measurements on $Au_{55}(PPh_3)_{12}Cl_6$ clusters in a densely pressed pelleted form gave valuable information on the intrinsic conduction behaviour of single clusters and also on that between the perfectly packed grains.⁸⁻¹⁰ Following these results

the individual cluster behavior can be understood as being caused by a doubly occupied electronic ground state, corresponding with the situation shown in Fig. 1(b). Using the formula for a three-dimensional electron gas, $d = \hbar\pi(2mE_F)^{-1/2}$ (d = lateral dimension of the quantum box, m = mass of the electron, E_F = Fermi energy) d ($= \lambda/2$) can be determined as 1.4 nm, in perfect agreement with the calculated data for a 55 atom cluster. Conductivity in the pellet is reached by exciting the electrons to the first excited state and so halving λ . In $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ there is a special geometric situation insofar as the thickness of the ligand shell is about 0.7 nm, *i.e.* half of the diameter of the cluster core itself. Two ligand shells of 1.4 nm in total separating two Au_{55} clusters from each other are of the appropriate dimensions to enable perfect tunneling of electrons through densely packed clusters. Indeed, the experiments allow us to ‘metallize’ the cluster material or to reduce conductivity to a minimum. Fig. 2 elucidates these processes in a simplified manner. As will be shown, thicker ligand shells or spacer molecules enable tunneling processes too, but under different energetic conditions.

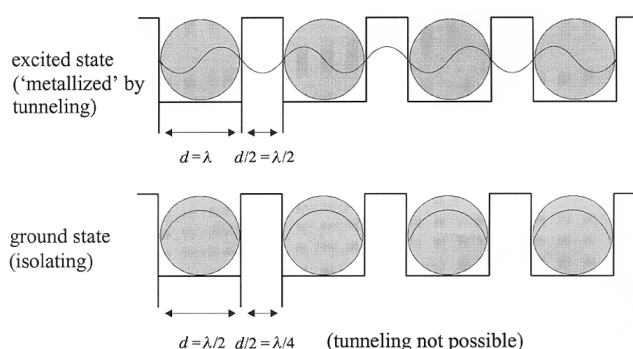


Fig. 2 Illustration of the electronic situation in a row of nanoclusters, separated by barriers (ligand shells). In the ground state electronic tunneling between the clusters is in principle not possible. In the excited state tunneling is enabled by halving the electronic wavelength.

Quantum size effects in nanoclusters have also been shown by studying the susceptibility of variously sized Pd particles at low temperatures.¹¹ Odd and even numbers of electrons in Pd clusters of identical size are expected to be present in a 50:50 ratio, depending on marginal deviations in geometry. Clusters with a single electron couple more intensively the smaller they are. Indeed, 2.2 nm Pd clusters show the most intensive maximum of susceptibility compared with those of 3.0, 3.6 and 15 nm.

Using the same clusters, thermodynamic properties have been shown to follow quantum size behaviour with respect to the electronic specific heat for the first time. Again 2.2 nm Pd clusters show the most significant deviations from bulk behaviour at very low temperatures.¹¹

These and several other experiments clearly indicate that quantum behaviour of metal nanoclusters is observable, and is most strongly expressed between 1 and 2 nanometers. Referring to possible applications based on the quantum confinement of electrons, particles in that size region should be of most interest.

There are also several important results concerning the electronic situation in single clusters, all indicating that they follow quantum size behaviour when the current–voltage characteristics are studied. Instead of a linear relationship, typical for the Ohm behaviour of bulk metals, so-called Coulomb blockades are observed, indicating single electron transitions (SETs) between a tip and the cluster.^{12–14} The temperature dependence of quantum size effects, based on the relation $E_{el} = e^2/2C \gg E_T = kT$ has also been demonstrated.^{12,13} This relation means that for initiating SET processes, the electrostatic energy E_{el} must be large compared with

the thermal energy E_T . As the capacity C is smaller the smaller the particle is, it becomes clear that SETs can only be observed at relevant working temperatures if C is very small. From various experiments we know C to be of the magnitude of 10^{-19} Farad for Au_{55} clusters. In other words, the use of *ca.* 1.5 nm metal clusters in principle enables switching with single electrons around room temperature. This would not be possible with semiconducting materials which lose their semiconducting properties long before being miniaturized to 1.5 nm. This knowledge prompted us and numerous other groups to look for appropriate techniques to organize clusters in a three- (3D), two- (2D) or one- (1D) dimensional manner. The use of nanoclusters in future nanoelectronics is unambiguously linked to the availability of well-ordered cluster arrangements. Indeed, some considerable progress has been made during the last five years. However, it is still difficult to make 3D, 2D or even 1D arrangements routinely and in larger amounts. Therefore, the following chapter deals with some very recent results in this field as a contribution to the development of suitable conditions for the realization of future nanoelectronic devices.

3 On the way to organized clusters

Metal and semiconductor clusters promise to substitute traditional materials in the micrometer size regime in the future. This substitution would not only be linked with the miniaturization of devices, but would especially be a big jump into a world of novel technologies. First of all, there is the above mentioned chance to work with single electrons at room temperature, a condition for the development of new computer and laser generations. Data storage capacities of orders of magnitude better than at present are to be expected and even three-dimensional neuronal networks, impossible to realize with traditional materials, become possible. However, there are numerous possible applications to be realized in shorter periods of time, *e.g.* in the field of electroluminescence, non-linear optics, surface-enhanced Raman spectroscopy, sensors or catalysis. For some of these applications organized clusters are not necessary, *e.g.* in catalysis or in sensoric. However, just for the most attractive fields of nanoelectronics ordering is an unambiguous condition.

As spheric particles in the size range of 1–10 nm do not tend to form larger crystals, this usual route to optimized 3D arrangements is in principle not possible, although some crystalline particles on the micrometer scale have been found, even consisting of relatively large nanoparticles of gold.¹⁵ Self-assembled multilayers of nanosized particles have also been observed, however, only with submicron dimensions.^{16–18}

Our own activities in this field are based on the use of bifunctional spacer molecules, linking clusters three-dimensionally. The use of simple linear molecules such as $\text{H}_2\text{N}-\text{C}_6\text{H}_4-(\text{CH}_2)_2-\text{C}_6\text{H}_4-\text{NH}_2$ and similar compounds indeed gave three-dimensional cluster arrangements, but not with ordered structures. We were not yet able to see larger cluster arrangements by high resolution tunneling electron microscopy (HRTEM).¹⁹ However, these 3D cluster materials gave another important result, namely a direct relation between cluster spacing and the activation energy needed to start electronic tunneling *via* the spacers from one cluster to the next.^{14,20}

Well-ordered cluster assemblies can be seen in Fig. 3, where multiple layers of *ca.* 17 nm bimetallic particles can be seen, consisting of a gold core, covered by a 3–4 atom layer thick palladium shell. The very uniformly sized nanoclusters are stabilized by a ligand shell of disodium 4,7-diphenyl-1,10-phenanthroline disulfonate. This sulfonated phenanthroline derivative obviously favours ordered particle arrangements owing to strong ionic interactions between the clusters. This example demonstrates that appropriate interactions between nanoclusters

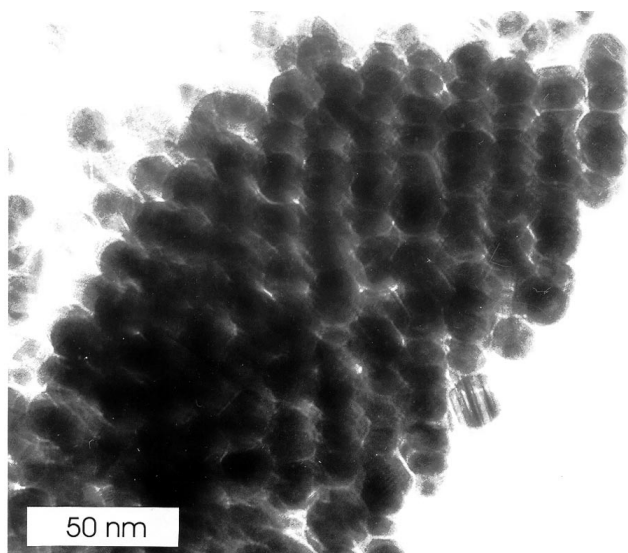


Fig. 3 A transmission electron microscopic (TEM) image of some ordered layers of shell-structured gold–palladium particles.

may lead to 3D arrangements which could be used for a regulated communication between quantum dots. However, it is to be stated that we are still at the beginning of a development which will need much more effort to get routinely 3D assemblies of nanoclusters of acceptable size.

Considering 2D nanocluster arrangements, there is some progress to be registered during the last few years. Important contributions by Shiffrin,¹⁶ Whetten,¹⁵ Andres,¹⁸ Möller,^{21,22} and others show that two-dimensionally organized nanoclusters on suitable supports are possible. But, as already mentioned for 3D assemblies, routine work is still not possible. It may be that the use of micelles in block copolymers, as used by Möller *et al.*, is one of the most promising future techniques, as the dimensions of the 2D array can be varied over a wide range and the ordering of the particles is almost perfect. Our own efforts in this field were focused on self-assembly processes between functionalized clusters and modified surfaces.^{14,19,23} However, as it turned out, strong chemical bondings between clusters and surfaces do not usually give ordered 2D layers, but instead give randomly oriented densely packed particles. It seems that good ordering is only obtained if there is no or only weak cluster–surface interactions, including the disadvantage that the structure can easily be destroyed by touching it, *e.g.* with the tip of an AFM or STM.

One-dimensional cluster arrangements (cluster wires) are of remarkable interest for several reasons: they can be used for the study of electron transitions in one direction, probably much easier to understand than those in 3D probes, and as semi-conducting nanopaths for several technical applications. 1D cluster arrangements need a template to be formed. We chose nanoporous alumina which has numerous advantages compared to other porous materials: it is easy to prepare, the pores in the transparent oxide sheets are all running parallel through the membrane, perpendicular to the surface and, most importantly, there is a broad variability of the pore width between *ca.* 5 and 200 nm.^{24–26} If special conditions during the preparation are considered, even hexagonally perfectly ordered pores can be reached. Fig. 4 shows an atomic force microscopic (AFM) image of a surface of such an ordered pore system. Filling the pores with clusters of an appropriate size leads to assemblies of cluster wires, isolated from each other by the alumina material, but open for being contacted from one or from both sides to study electronic behavior. Such measurements have not yet

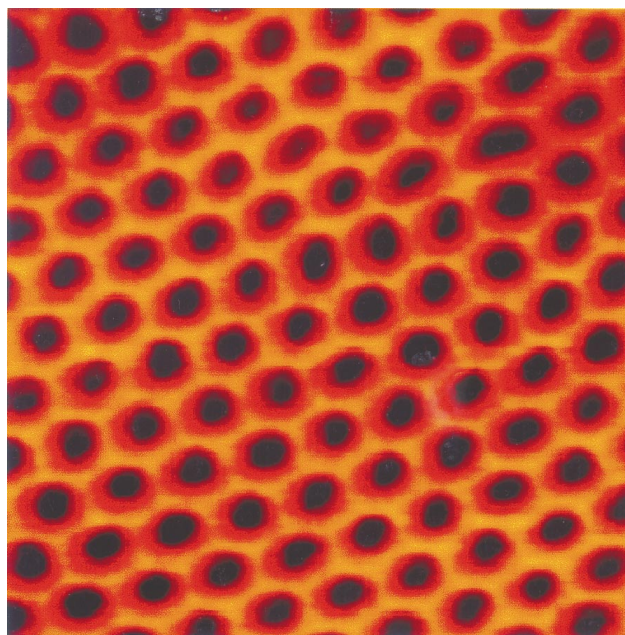


Fig. 4 Atomic force microscopic (AFM) image of the surface of a nanoporous alumina membrane. The pore diameter is ~ 40 nm. The sample has been ion-beam milled previously.

been performed, but promising success has been achieved in making cluster wires.²⁷

Fig. 5 shows a TEM image of a cluster wire containing membrane, sectioned along the pores. The clusters consist of 1.4 nm Au₅₅ cores, enlarged to 4.2 nm by a ligand shell of thiol-functionalized silsequioxanes.²⁸ The difficulty is to fill the pores without interruptions. This is obviously not possible if the pores are longer than ten nanometers. Such thin alumina films

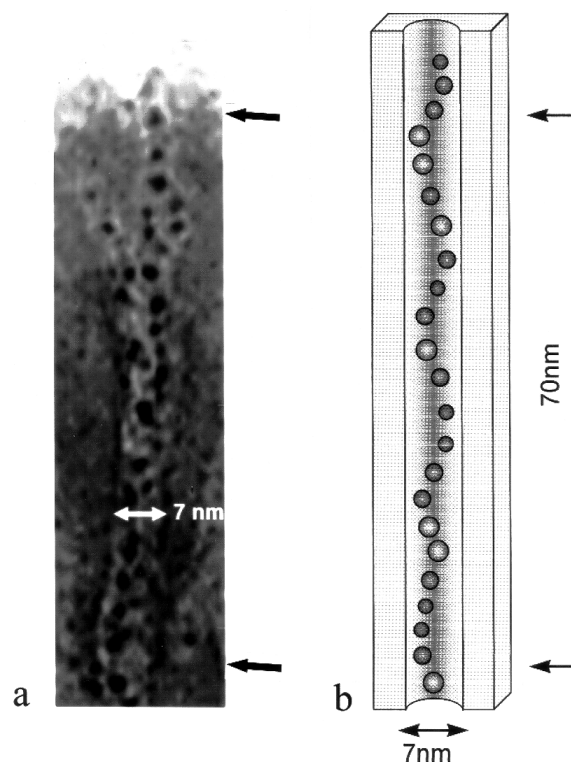


Fig. 5 TEM image of a single 1.4 nm Au cluster wire in a nanoporous alumina membrane (a), (b) is a schematic representation of the helical situation in the 7 nm pore. Reproduced with permission from *Chem. Eur. J.*, 1997, 3, 1951. Copyright 1997 Wiley-VCH.

are obtained by ion beam milling processes. Electronic measurements are just at the beginning.

4 Catalysis

The use of ligand stabilized transition metal clusters on the one hand and of unprotected, bare nanoparticles on the other hand as homogenous and heterogeneous catalysts, respectively, is extensively described in the literature.²⁹ In particular, supported metal particles are traditionally applied in industrial catalysis for many purposes. The catalytic behavior of bare particles on supports has been studied as a function of size and shape in a huge number of papers in the course of the last decades, whereas ligand protected clusters are much less investigated as immobilized catalysts. The main interest was focused on the function of the ligands. Indeed, they can increase or reduce activity, however, it has also been shown that the influence of ligands with respect to selectivity may also be of some interest. We have been able to show that ligand stabilized Pd clusters in the size range of 3–4 nm show very good activities and selectivities on various supports when they are used for the semihydrogenation of hex-2-yne to *cis*-hex-2-ene.^{30,31} The ligands consisted of variously substituted phenanthrolines. It could be observed that, depending on the kind of substituent, e.g. alkyl groups of various lengths, the activities changed considerably, whereas the selectivity was in any case close to 100%.

Here, we report for the first time on the use of very small Pd nanoparticles (1.5 nm) in a supported form with and without ligands to semihydrogenate hex-2-yne. This comparison of protected and bare clusters for the same catalytic reaction is important since there is, to our knowledge, no information on comparable reactions. This type of cluster is formed when palladium acetate and 1,10-phenanthroline in a 1.3:10 molar ratio are dissolved in 3-methylbutanol and heated to 60 °C for 7 days. The clusters, which can be isolated from solution by centrifugation as a black powder, can be redissolved in a 1:1 water-pyridine mixture. Immobilization occurs from solution by the addition of supports such as active carbon, TiO₂, Al₂O₃ or various zeolites. Catalysis was performed with 1 wt.% Pd on support. The ligands were removed by heating the immobilized clusters to 100–130 °C for 4–5 hours in high vacuum. Transmission electron microscopy was used to prove that the particle size was the same before and after heating. The hydrogenation reactions were carried out in ethanol at room temperature and with hydrogen gas at 1 atm. Figs. 6(a) and 6(b) show the results.

It is clearly to be seen that the selectivity in the case of phenanthroline protected clusters (a) is only ca. 80–90%, whereas in the case of the bare clusters (b) it is 100%. From our experience this result could not be expected. Whatever the reason for that behavior may be, it becomes clear that catalytic studies with clusters of definite size and environment are valuable materials to work out principles.

5 Luminescence of semiconducting nanoclusters

The well-defined nanoporous alumina membranes, briefly described in Chapter 3, can not only be used to fill in clusters which have been prepared before, but they offer the unique chance to synthesize nanoparticles inside tubes of defined length and width. The advantage of that system is the absolute transparency in the visible range so that the generation of optically interesting materials in the membrane can directly lead to useful materials.

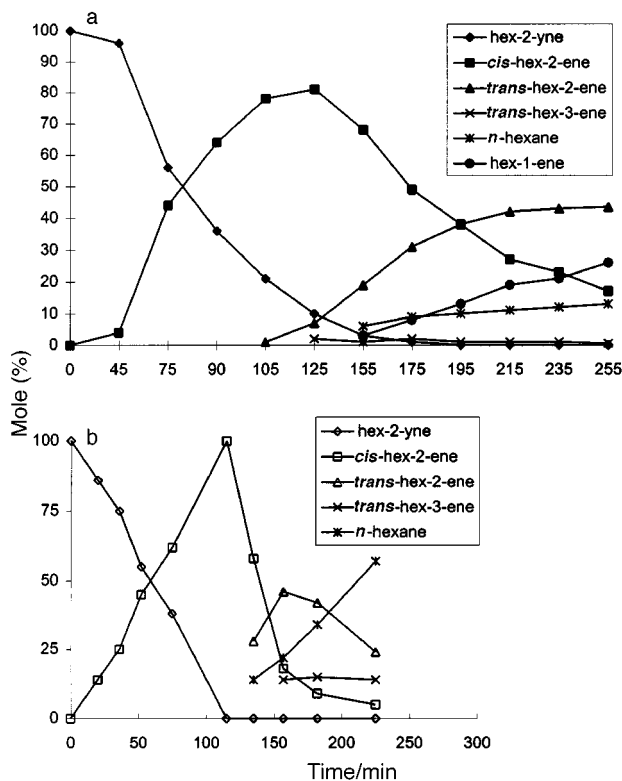
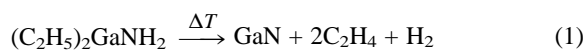


Fig. 6 Semihydrogenation of hex-2-yne to *cis*-hex-2-ene by ligand protected (a) and bare (b) 1.5 nm Pd clusters on active carbon in ethanol at room temperature and 1 atm of hydrogen pressure.

Among the possible candidates to form photoluminescent nanoclusters inside the pores, the compounds CdS and GaN have been selected, owing to their large band gaps of 2.38³² and 3.40³³ eV, respectively.

To generate crystalline CdS nanoclusters in the pores, membranes which are open on both sides have been used, and aqueous solutions of CdCl₂, beginning with 5 wt.% up to saturated ones have been filled in by vacuum induction, followed by the reaction with gaseous H₂S which diffuses rapidly into the pores to precipitate CdS. GaN was produced by the ligand precursor compound (C₂H₅)₂GaNH₂³⁴ which, after its transfer into the pores, was decomposed at 350–550 °C in an atmosphere of nitrogen, corresponding to eqn. (1). The gaseous



products ethene and hydrogen leave the pores and GaN is deposited. In contrast to the CdS nanoclusters, the size and structure of the GaN particles has not yet been determined.

The luminescence of CdS monocystals was observed between 2.08 eV (595 nm) and 2.05 eV (605 nm).³⁵ The luminescence of the CdS in the pores was found between 1.94 eV (640 nm) and 1.70 eV (730 nm), depending on the conditions to be discussed in the following. Fig. 7 shows the photoluminescence spectrum of a 25 nm pore-containing membrane, filled and dried at room temperature. Besides the broad peak at ca. 650 nm there is a high-energetic excitonic fluorescence at 2.84 eV (437 nm).

Excitonic fluorescence of CdS nanoclusters is normally only observed after modification of the particle surface.^{1,36} The modification consists of a substitution of free valences on the surface by Cd ions blocking the S and SH radicals. These are responsible for the non-radiative recombination by trapping holes and preventing activation of fluorescence. Excess Cd ions on the surface allow radiative deactivation of electrons from the conductivity band and holes from the valence band to give the high-energetic emission. The excitonic emission of CdS nanoclusters in the alumina pores is obviously caused by the

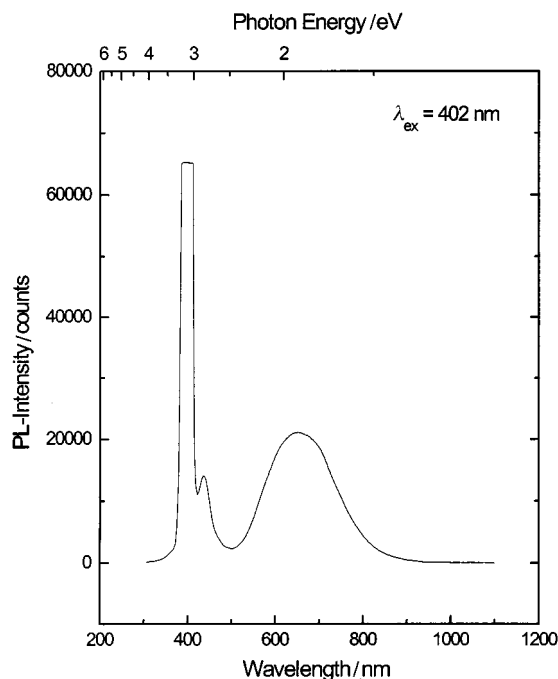


Fig. 7 Photoluminescence spectrum at 300 K of a CdS filled nanoporous alumina membrane with 25 nm pores.

interaction of the particle surface with the pore walls, consisting of reactive Al-OH functional groups, and by excess Cd ions blocking the hole-trapping by free reactive valences of the clusters.

We also studied the effect of repeated CdS precipitation in the pores and observed that the luminescence intensity increased considerably by a second CdS formation in 20 nm pores, but decreased with further CdS depositions. Fig. 8 shows this behavior. As can also be seen, there is no significant effect on the wavenumbers. We interpret the intensity maximum after the

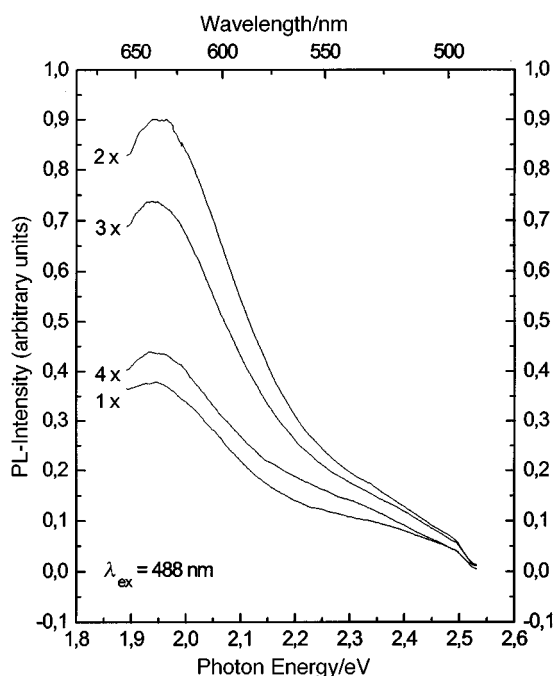


Fig. 8 Dependence of the photoluminescence intensity of CdS containing alumina membranes on the number of CdS precipitations.

second filling by the formation of additional active particles, the decrease of intensity after three- or four-fold precipitations is to be traced back to the progressive formation of bulk-like larger and inactive particles. This agrees with the fact that membranes

with larger pores, e.g. 30 nm, show the maximum of luminescence only after the fourth filling, followed by an intensity decrease with further CdS formations.

The situation in the CdS-containing pores is best seen from TEM images of ion-beam milled, very thin membranes. In Fig. 9(a), a larger cutout of an ion-beam milled membrane is shown. The pores have been filled by CdS, precipitated from a concentrated CdCl₂ solution, leading to a relatively high particle loading. Most of the pores at the distinct positions, accidentally reached by the milling process, are completely or partially filled, depending on the local situation. In Fig. 9(b) a single pore is shown, filled with polycrystalline CdS matter.

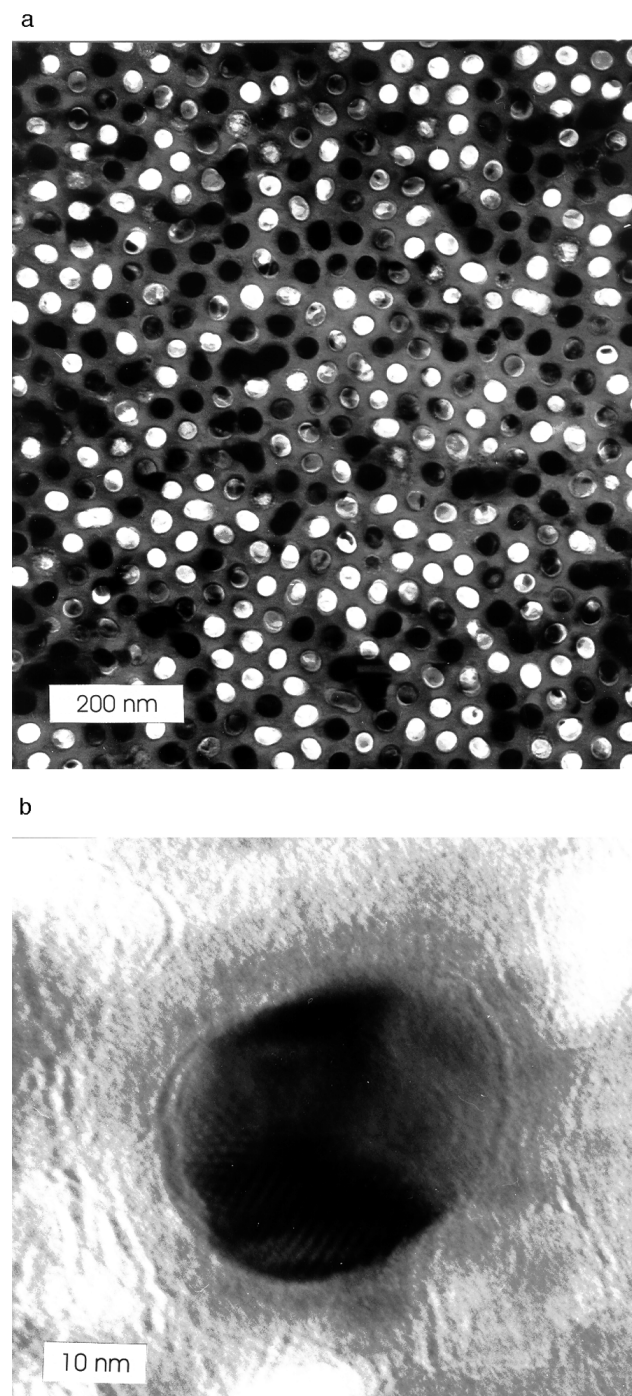


Fig. 9 Transmission electron microscopic images of CdS filled alumina membranes. (a) shows the surface of an ion-beam milled, very thin membrane. Most of the pores show the presence of CdS; (b) shows a magnified pore filled with crystalline CdS.

Finally we studied the temperature dependence of the luminescence. It was found that tempering of the filled

membranes leads to a continuous decrease of luminescence, completely ending at *ca.* 350 °C. The disappearance of the orange luminescence by thermal treatment is known from literature and is caused by the phase transition from the cubic to the hexagonal modification.³⁷

The GaN loaded membranes showed a luminescence signal at 3.62 eV (341 nm). Compared with literature data of cubic or hexagonal GaN, this is a short-wave shift of 41 and 21 nm, respectively.³⁸ A relationship between the photoluminescence intensity, the time of tempering and the number of GaN depositions can not yet be confirmed. However, as mentioned above, these results are still preliminary and should just show that photoluminescent foils of unlimited size can be produced in a very simple way, if appropriate reactions can be performed in the pores or if suitable precursors are available. In this connection it should be mentioned that luminescent silicon, probably in the form of a siloxene, has also been generated in the pores by us recently.³⁹

6 Outlook

Nanoclusters of metals or semiconductors can more and more be considered as the building blocks of future modern technologies. This is due to the size dependant electronic properties of these particles. Nanoclusters of transition metals become semiconductors if small enough. If the more technological problems such as organization and addressing of these quantum dots can be solved, there is an almost unlimited field of applications to be foreseen. The properties of nanosized semiconductors have long been known to depend very sensitively on the particle size. There are numerous and important applications which become possible considering these facts. The use of transparent alumina membranes (and of course other comparable materials) gives an additional chance to prepare and to apply semiconducting nanoclusters in new fields in the near future.

7 Acknowledgements

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We also wish to thank the BASF AG, Ludwigshafen, for their support of the catalytic work.

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Review 8/01153B