A New Approach to Well-Ordered Quantum Dots

Günter Schmid*[a] and Norbert Beyer[a]

Dedicated to Professor Dr. Heinrich Vahrenkamp on the occasion of his 60th birthday

Keywords: Gold / Clusters / Quantum dots / Monolayers / Amphiphiles

Extended ordered monolayers of ligand stabilized Au_{55} clusters are formed at the phase boundary between water and dichloromethane. The water phase, containing amphiphilic molecules like per-6-deoxy-6-thio-α-cyclodextrin **(1)** or poly(vinylpyrrolidone) **(2)**, is covered by a thin film of a solution of $[Au_{55}(PPh_3)_{12}Cl_6]$ in dichloromethane. The interaction of the cluster molecules with the thiol functions of **1** or the polymer chains of **2** form perfect cluster orders of hexagonal and cubic structure. The monolayers can be transferred onto solid substrates by a simple dipping process. The use of carbon coated copper grids allows the investigation of the monolayers by transmission electron microscopy (TEM). Electron diffraction experiments under a microscope prove the hexagonal and cubic arrangements. The reason for the formation of the one or the other modification is still unknown.

Introduction

Metal particles of the size of Au_{55} clusters (1.4 nm) show quantum size effects (QSE) even at room temperature,[1a−1e] making them promising candidates for future nanoelectronic applications. The first and most important step on this way is to order the clusters in a two-dimensional lattice to become individually addressable. Recently we described the preparation of ordered monolayers of Au_{55} clusters on modified solid surfaces by a simple dip-coating process.[2] In this paper we report the first results on a more generally applicable method to generate highly ordered and extended Au_{55} monolayers at the phase boundary between two liquids.

We believe that two facts are most important for the formation of ordered monolayers. First, an absolutely flat surface is essential. Polymers like PEI as a modifier are believed to form very thin layers that can smooth small roughnesses. Second, the surface should exhibit a large number of sites that are helpful to let the clusters settle down. In the ideal case the interaction between the clusters (or their ligand shell) and the surface should show the same strength everywhere − only a small amount of energy would then be necessary to let the clusters move around to form dense packings. On the other hand, the interaction between the clusters and the anchor groups must be strong enough to adsorb the clusters from solution and to hold them during the preparation process. This very sensitive balance between mobility and fixation determines the success of the self-assembly process.

Keeping these facts in mind we found that a solid surface needs very special conditions to fulfil all these demands. As an alternative we changed from the solid support to the interface between two liquids, exhibiting atomic flatness and isotropic behaviour all over the surface except near the beaker's wall. The long known Langmuir−Blodgett (LB) technique is based on these conditions. However, previous attempts to generate ordered monolayers of clusters by using original LB techniques didn't result in high degrees of order.[1d] Our actual aim was now to find appropriate molecules to provide amphiphilic interfaces between two liquids including useful functions to trap the clusters irreversibly.

Results and Discussion

We selected the CH_2Cl_2 soluble $[Au_{55}(PPh_3)_{12}Cl_6]$ cluster and various water-soluble amphiphilic compounds. Two of them turned out to work best as modifying agents at the phase boundary: per-6-deoxy-6-thio-α-cyclodextrin **(1)** and poly(vinylpyrrolidone) PVP **(2)**. Others like cysteine, cysteamine and poly(1,4-phenylene sulfide) showed similar behaviour; however, the results were not as promising as those with **1** and **2**.

It is to be assumed that the 12 hydroxy groups in **1** function as the hydrophilic part of the basket-like molecule, whereas the six thiol groups are oriented towards the dichloromethane phase to interact with the clusters as shown in Figure 1.

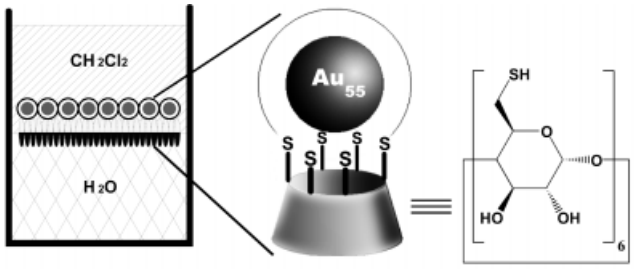

Figure 1. Sketch of the cluster-amphiphile **1** interaction at the phase boundary between water and dichloromethane solution

[a] Institut für Anorganische Chemie der Universität Essen
Universitätsstraße 5−7, D-45117 Essen, Germany
Fax: (internat.) +49-201/183-4195
E-mail: guenter.schmid@uni-essen.de

  1434−1948/00/0505−0835 $ 17.50+.50/0

The function of PVP (**2**) is not as easy to understand as that of **1**. We believe that the polyvinyl backbones form hydrophobic−hydrophobic interactions with the PPh_3 ligands of the clusters.

The experiments were carried out by generating a thin film of a dichloromethane solution of $[Au_{55}(PPh_3)_{12}Cl_6]$ clusters on the aqueous phase containing the amphiphilic compound. Because transmission electron microscopy (TEM) is the most suitable method for examining the success of the experiments, the self-assembled cluster monolayers were transferred onto a carbon-coated copper grid. For good results it is important that the two-phase system does not invert, which may easily happen due to the higher density of the CH_2Cl_2 solution than that of water. This fact presently limits the extension of the monolayers to no more than a few square centimetres. If the CH_2Cl_2 layer becomes too large, it can drop down to the bottom of the flask. If the cluster layer is fished out through the organic phase only a thin, volatile film is covering the surface. If water covers the monolayer it is destroyed during drying.

Following this procedure we were able to generate highly ordered cluster areas in two different structures. A hexagonal and a cubic structure were found beside one another in a sample independent of the surfactant used in the water phase; however, usually the hexagonal structure dominated. The structures were formed in an approximate ratio of 1 to 20 in a number of areas although the cubic arrangements were usually twice as large in extension as the hexagonal ones. Hexagonally structured cluster monolayers, combined with the cyclodextrin **1** and PVP **2**, are shown in Figure 2 and Figure 3, respectively. The insert in Figure 3 shows the electron diffraction pattern, proving the predominately perfect hexagonal architecture.

Figure 4 shows a cut-out of a cubically organized surface, consisting of more than 20,000 clusters. Compound **2** was used as a modifier, as in Figure 3. Here the inserted diffraction pattern was calculated afterwards from the recorded image. The total area is slightly tilted so that the cubic structure is not that easily recognized. This can also be deduced from the diffraction pattern, where the spots show two different distances perpendicular to each other.

It can be assumed that the original areas of ordered clusters at the phase boundary are much larger than those observed under the microscope due to the not yet well developed transfer process from the liquid onto a solid surface. However, we started experiments to improve the procedure by automation.

As reference experiments we tested pure water and, in addition, a water phase containing sodium dodecyl sulfate (SDS). There was absolutely no evidence of cluster assembly in either case. Neither the alkyl chains of the SDS nor the water surface itself showed any attraction for the clusters.

The TEM images of the hexagonal and of the cubic structures showed cluster−cluster distances of 2.3 ± 0.1 nm. This agrees fully with the observed distances in three-dimensional cluster crystals.[3] The value of 2.3 nm seems to be completely independent of the surfactant used. Obviously there is no influence on the clusters if a 40,000 g/mol polymer like **2** or a small molecule like cysteine is used, indicating that the model of the phase boundary as a perfect flat, dense packed support with appropriate anchor groups works pretty well.

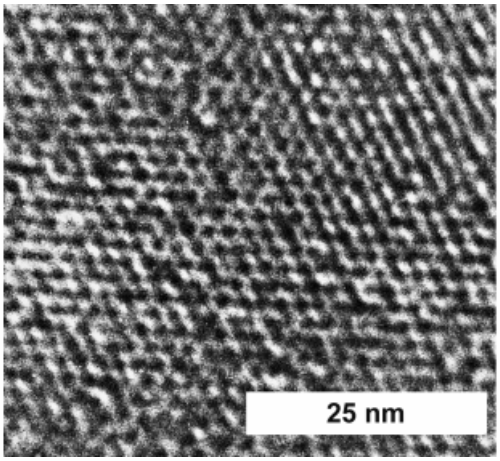

Figure 2. TEM image of a hexagonally ordered area of Au_{55} clusters with a thiol-modified cyclodextrin **1** as amphiphile

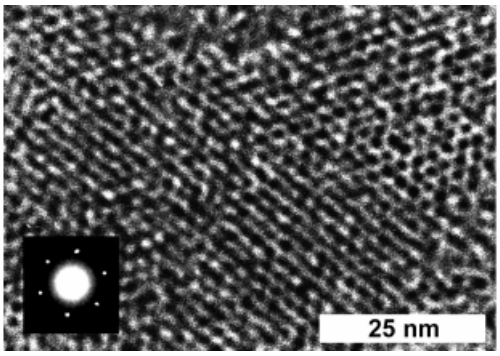

Figure 3. TEM image of a PVP **(2)** supported Au_{55} monolayer; the insert shows the electron diffraction pattern, recorded at a camera length of 4700 mm, proving the hexagonal structure

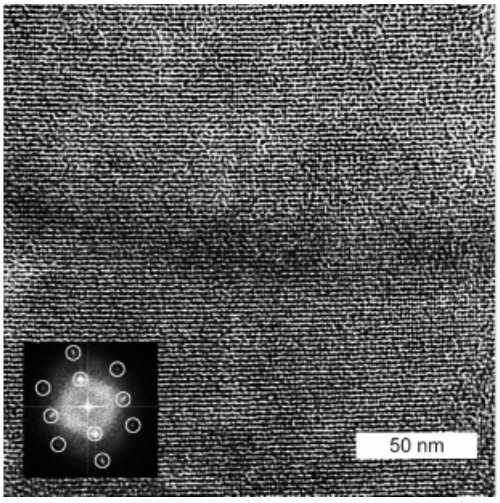

Figure 4. TEM image of a large cubic cluster arrangement; the insert shows the diffraction pattern calculated from the recorded image; the faint spots are marked with circles; the two different distances indicate that the total area was somewhat tilted

Further investigations are still in process. The formation of densely packed cluster layers should have an effect on the surface tension which could be revealed by rheological measurements. There must be strong interactions between the clusters, otherwise these nanometre-thick layers at the phase boundary would not survive under the rough conditions of the sample preparation for the TEM. We also plan to image the interface in situ by means of cryo-TEM. This technique needs very special conditions; however, it will allow snapshots of the formation process itself. Finally we have to use solid supports other than carbon-coated copper grids. First experiments with thin films of silicon carbide gave very promising results which will be reported elsewhere together with further results.

Experimental Section

The synthesis of $[Au_{55}(PPh_3)_{12}Cl_6]$ has been described elsewhere.[4a,4b] Per-6-deoxy-α-cyclodextrin (**1**) was synthezised by G. von Kiedrowski et al., University of Bochum, following published procedures.[5a,5b]. Poly(vinylpyrrolidone) (**2**) K30 (Fluka 81420) was used as received. The ordered $[Au_{55}(PPh_3)_{12}Cl_6]$ monolayers were prepared by adding a small droplet (0.5 mL) of a solution of 0.1 mg/L $[Au_{55}(PPh_3)_{12}Cl_6]$ in CH_2Cl_2 onto the aqueous phase (10 mL) in a tube of 1 cm in diameter, containing 1 mg/L of the amphiphilic compound. This has to be done very carefully to avoid the organic phase falling to the bottom of the tube. After 5−10 minutes the monolayer was formed between the two phases. This film was transferred onto a carbon-coated copper grid (Plano) by dipping it carefully under the surface and then pulling it back slowly, followed by drying in air. The characterization of the samples was carried out by transmission electron microscopy, using a Philips CM 200 FEG at 200 kV.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 452) and the Fonds der Chemischen Industrie. The authors acknowledge financial support by the MSWWF, Nordrhein-Westfalen. We also thank Prof. G. von Kiedrowski and Dipl. Chem. M. Pankau, both Ruhr-Universität Bochum, for providing us with the thiol-modified cyclodextrin.

[1] [1a] U. Simon, G. Schön, G. Schmid, *Angew. Chem.* **1993**, *105*, 264−269; Angew. Chem. Int. Ed. Engl. **1993**, *32*, 250−254. − [1b] G. Schön, U. Simon, Coll. *Polym. Sci.* **1995**, *273*, 101−117. − [1c] G. Schön, U. Simon, Coll. *Polym. Sci.* **1995**, *273*, 202−218. − [1d] L. F. Chi, S. Rakers, M. Hartig, H. Fuchs, G. Schmid, *Thin Solid Films* **1998**, *327−329*, 520−523. − [1e] G. Schmid, L. F. Chi, *Adv. Mater.* **1998**, *10*, 515−526.

[2] G. Schmid, M. Bäumle, N. Beyer. *Angew. Chem*. **2000**, *112*, 187; *Angew. Chem. Int. Ed.* **2000**, *39*, 181−183.

[3] G. Schmid, R. Pugin, Th. Sawitowski, U. Simon, B. Marler, *Chem. Commun.* **1999**, 1303−1304.

[4] [4a] G. Schmid, R. Boese, R. Pfeil, F. Bandermann, S. Meyer, G. H. Calis, J. W. van der Velden, *Chem. Ber.* **1981**, *114*, 3634−3642. − [4b] G. Schmid, *Inorg. Synth.* **1990**, *27*, 214−218.

[5] [5a] M. T. Rojas, R. Königer, J. F. Stoddard, A. E. Kaifer, *J. Am. Chem*. Soc. **1995**, *117*, 336−343. − [5b] G. R. J. Thatcher, *Tetrahedron Lett*. **1196**, *37*, 4647−4650.

Received January 11, 2000
[I00004]