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Ordered Two-Dimensional Monolayers of Au_{55} Clusters[**]

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Highly ordered structures of nanoparticles exhibit attractive physical properties for future nanoelectronics.[1–5] Metal particles of 1–4 nm in size are of particular interest because of their special electronic properties, as characterized by their quantum size behavior;[6] their electrons are no longer in a quasi-delocalized three-dimensional state, but are trapped in a "zero-dimensional space". Ligand-stabilized metal clusters turned out to be ideal objects for studying these effects. With its two freely mobile electrons $[Au_{55}(PPh_3)_{12}Cl_6]$ represents something like a "last metal".[7]

Ordered arrangements of such quantum dots allow correlated single electron tunneling (SET)[8, 9] at room temperature, which has been proposed as a fundamental idea of future nanoelectronics. The realization of such new systems, which require well-defined planar arrays of uniform metal clusters, might open the door to a new generation of computers with a storage capacity raised by a factor of 10^5–10^6 relative to the present state of the art.

Many research groups focus their efforts on reaching this goal.[10–14] Andres et al. reported on perfect layers of alkylthiol-protected gold particles with diameters of 3.7 nm.[15] Another method for generating ordered two-dimensional layers was described by Möller et al. who prepared gold colloids in ordered polymer micelles.[16] In the past we carried out intensive research on the preparation of monolayers by the chemical fixation of ligand-stabilized metal clusters on modified substrates,[17–20] however, we could only observe particles that were at best, densely packed, but not well ordered.

Herein we report the first successful preparation of two-dimensional (2D) hexagonal and cubic lattices of Au_{55} clusters on polymer films by self-assembly. The monolayers were prepared by dipping a poly(ethyleneimine)-covered, carbon-coated copper grid (for transmission electron microscopy) into an aqueous solution of $[Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6]$ clusters (Figure 1). Classical acid–base reactions take place because of the NH functions on the poly(ethyleneimine) (PEI). The strong interactions between clusters and the surface prevent mechanical removal, for example, by washing.

The characterization of the cluster arrangements was performed by transmission electron microscopy (TEM) at

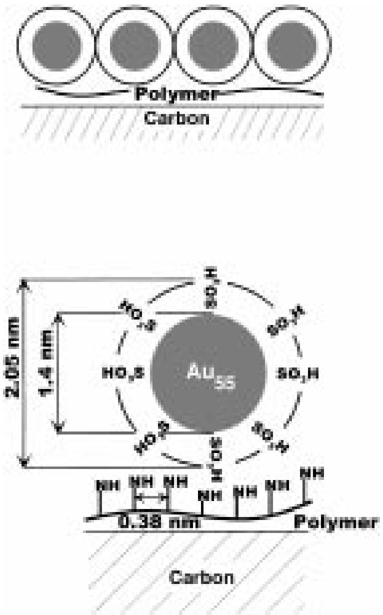

Figure 1. Schematic cross-section of a Au_{55} monolayer on a PEI-modified, carbon-coated copper grid and a magnification of the contact area with characteristic values.

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200 kV. This method allows the study of larger areas compared with scanning probe microscopy methods such as tunneling microscopy (STM) or atomic force microscopy (AFM). Most of the clusters were found in ordered arrangements of up to a few μm^2 and in two different types (Figure 2).

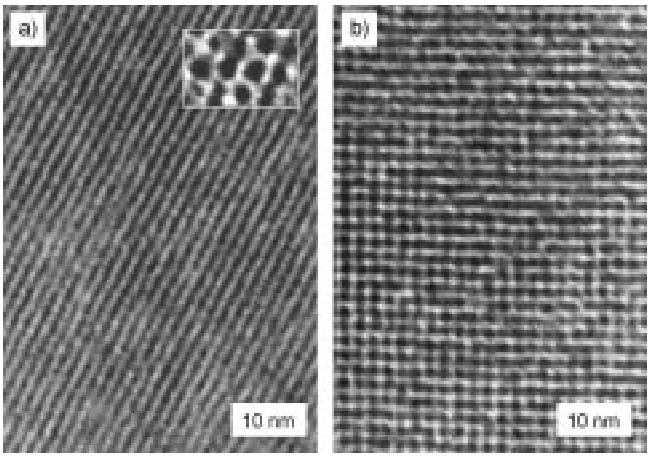

Figure 2. TEM images of Au_{55} monolayers showing a hexagonal (a) and a cubic (b) structure. The magnified insert in (a) shows single clusters in the hexagonal form.

The hexagonal form, the one most expected for an ordered monolayer, was observed, with distances between the rows of 1.87 nm along the (111) direction (Figure 2 a). The generation of hexagonal arrangements is already known for bigger colloids.[15] Unprecedentedly, there is a cubic orientation with rows 2.05 nm apart (Figure 2 b). These layers give an idea of the possibilities of future quantum dot arrangements if routine fabrication is developed. In Figures 3 a and 3 b both cases are illustrated. Both values correspond, as expected, very well with the cluster size of 2.1 nm.[21] Note, that the Au_{55} clusters have a metallic core of 1.4 nm in diameter and a ligand shell of 2×0.35 nm thickness. Consequently, both lattices are formed by Au_{55} clusters with intact ligand shells.

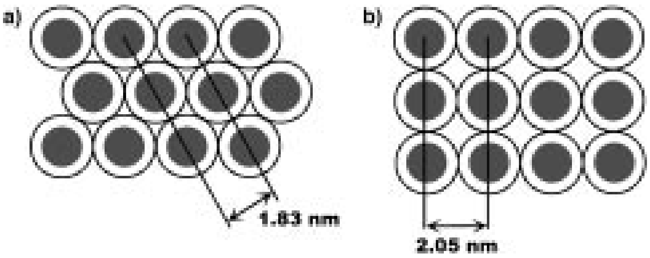

Figure 3. Sketch of both observed cluster superstructures: hexagonal (a) and cubic (b)

Although we have made many attempts in the past few years to assemble two dimensional clusters on PEI-modified substrates, we never observed such perfect structures.[18] Both STM and AFM imaging only showed areas of metal particles that were partially densely packed, but not well ordered. We attributed the lack of perfect assembling to the strong chemical bonds between the functionalized surface and the clusters. It is assumed that a two-dimensional ordering process only takes place if the particles are at least slightly movable on the surface so that they can rearrange. Andres et al. have shown that nonfixed colloids are able to build perfect two-dimensional structures, which is in contrast to those that are chemically absorbed to the surface.[15] Two important questions arise from this observation: why is there a two-dimensional crystallization in spite of the strong chemical fixation, and why is there a hexagonal as well as a cubic pattern of particles?

The reason for this behavior must be attributable to the influence of the polymer, since numerous cluster samples on substrates without this polymer have been investigated by TEM before, but such large ordered domains have never been observed. In the current experiment we used a PEI with the lower molecular weight of 60000 instead of the 600000 used in former experiments, so as to avoid the coiling of the polymer on the surface.

Although polymer monolayers are irregular it is known that under special conditions some polymers are partially crystalline.[22, 23] Decher et al. have demonstrated by X-ray scattering experiments that after drying the polymer multilayers up to four Bragg peaks could be observed, which could be traced back to crystalline areas. An X-ray structure analysis of linear PEI with a low molecular weight (3000) by Chatani et al. also confirmed the presence of crystalline structures. This PEI exists in two distinct crystalline phases, depending on the water content. In both hydrates the polymer chains are planar zigzag and hydrogen bonds seem to have an important influence on the stabilization of the crystal lattices. The phase with the higher water content (12 water molecules per unit cell) offers a more "open structure" with a change in the position of the NH groups. If the existence of crystalline islands in a monolayer of PEI is assumed, then the hypothesis that these two phases act as a template that might direct clusters arising in certain positions seems justified. Such effects have been confirmed by epitaxy experiments.[24–26] Blaadred et al. have demonstrated a template-directed crystallization of colloids that leads to an epitaxial growth of thin crystalline layers.[27]

Another observation supports the hypothesis that the polymer acts as structure-determining template: during current investigations of the interactions between various rodlike polymers and clusters we combined poly(1,4-phenyleneethynylene) derivatives and PPh_3-stabilized palladium clusters. TEM investigations showed small ordered areas of Pd_{55} clusters. Although 80 % of the cluster material we used consisted of larger particles, only the 1.2 nm fraction formed hexagonally ordered structures from very dilute solutions.[28] Assuming that the polymer forms lamellar aggregates, described as a concentration dependent behaviour,[29] these prestructures probably forced the clusters to crystallize.

In conclusion, the results can be considered as a successful first step in two dimensional arrangements of metal quantum dots by chemical fixation of ligand-stabilized Au_{55} clusters on a polymer-modified surface. The transmission electron micrographs exhibited highly ordered hexagonal and cubic orientations, which could be attributed to the influence of the polymers. Although further investigations are necessary to optimize these procedures to generate well-defined systems over long range, these preliminary results are promising for applications in nanoelectronics. The investigation of the electronic properties of the novel monolayers need much effort and has just been started.

Experimental Section

$[Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6]$ monolayers: the synthesis of $[Au_{55}(Ph_2PC_6H_4SO_3Na)_{12}Cl_6]$ has been described elsewere.[30] To replace the Na^+ ions by protons the clusters were dissolved in desalinated water and treated with an ion exchanger for 30 min. The polymer monolayer was prepared by dipping a carbon-coated copper grid (Plano) into a 10^{-5} M aqueous solution of PEI (60000) for 1 h. After washing the coated grid with 10 mL desalinated water and drying in air the monolayer of the gold clusters was prepared by immersing the grid into a 2.6×10^{-6} M aqueous solution of $[Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6]$ for 24 h. Careful cleaning with 10 mL desalinated water and drying in air yielded the monolayers. The the samples were characterized by transmission electron micoscopy (Philips CM200FEG) at 200 kV.

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