A study of charge quantization on ligand-stabilized Au$_{55}$ cluster monolayers

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Abstract. Low-temperature ultrahigh-vacuum scanning tunnelling microscopy and spectroscopy was employed to analyse the electronic transport through the ligand-stabilized metal cluster Au$_{55}$$[P(C_6H_5)_3]_{12}Cl_6$, prepared as a monolayer on Au(111) substrates. The current–voltage behaviour is governed by charge-quantization phenomena expected for a nanometre-sized metallic particle. The related electric capacitances of the involved tunnelling junctions have been determined from accompanying current–distance measurements. Resonant tunnelling through states of the ligands can be ruled out as a relevant process in electronic transport through the clusters.

Small metal clusters of a few up to a few hundreds of atoms have received increasing scientific and technical interest [1]–[4] because of their particular physical and chemical properties [5]. Due to the charge quantization phenomena exhibited by such clusters they are considered to be potential candidates for ‘quantum devices’ in microelectronics [6, 7].

Ligand-stabilized clusters, such as Au$_{55}$$[P(C_6H_5)_3]_{12}Cl_6$ [8], can be produced almost monodispersely in a large quantity through wet-chemical synthesis [9]. For an investigation of electron-transport properties scanning tunnelling microscopy (STM) and spectroscopy (STS) [10] provide the ideal access because the double tunnelling junction established between probe, cluster and substrate resembles a simple electronic device. In addition, the imaging ability of STM allows one to observe the neighbourhood of an individual cluster, on which current–voltage ($I$–$V$) curves are measured. This ability permits a discussion of the specific influence of the environment of a particular tunnelling junction.

Among the various clusters, Au$_{55}$$[P(C_6H_5)_3]_{12}Cl_6$ is the most intensively studied [11]–[15] because it should already exhibit charge-quantization phenomena at room temperature. Although discrete values of the conductance were observed in previous studies [14, 15] by STS, charge
quantization being the origin of this was not verified in a convincing way. One main reason for this is that the capacitances and the resistances which determine the charge-quantization phenomena were not chosen in a proper way. Furthermore, possible influences from molecular states of the ligands were not considered. Finally, in these investigations the clusters were prepared at undefined geometric packing [12]–[14], which causes difficulties in a quantitative study of individual clusters. In other studies the clusters were deposited on a substrate which was covered with other molecules [15] which again complicates the investigation of specific cluster properties.

Here we report STM/STS investigations on a locally ordered monolayer of the Au_{55} clusters, deposited on a Au(111) surface. The capacitances and resistances of the involved tunnelling junctions can be estimated from accompanying current–distance (I–z) curves. Employing the I–z data will thus permit a detailed analysis of the acquired I–V curves.

The Au_{55} cluster has a cuboctahedral structure consisting of one central atom, an inner shell of 12 atoms and an outer one of 42 atoms (figure 1(a)). The diameter is 1.4 nm. The ligand shell consists of 12 P(C_6H_5)₃ molecules and six Cl atoms and has a thickness of about 0.35 nm (figure 1(b)) [1]. The cluster compound can be dissolved in dichloromethane. For an investigation of individual clusters, it is necessary to prepare the clusters as a monolayer or submonolayer on an atomically flat metal substrate. Therefore, 50 nm thick Au films were deposited on highly oriented pyrolytic graphite (HOPG) by thermal evaporation under UHV conditions. Subsequent annealing results in large (111) terraces which are atomically flat [16]. The clusters were then ex situ deposited on the Au(111) substrate from solution by spin coating. Subsequently they were transferred again into UHV for STM/STS investigations. The employed variable-temperature UHV–STM set-up is described elsewhere [16]. The measurements were performed at 7 K. Due to the mobility of the clusters at room temperature, which makes the spectra not well reproducible [14, 15], it is necessary to work under low-temperature conditions.

The STM images confirm that cluster monolayers are produced (figure 2). Most of the Au substrate is covered by clusters. Some 120° corners of the Au(111) terraces are still visible. Only occasionally some small incompletely covered areas can be observed. STM line scans indicate...
Figure 2. STM image of a Au$_{55}$ cluster monolayer deposited on the Au(111) surface by spin coating, obtained at a bias of 2 V and a current of 150 pA. Image size: 223 nm × 170 nm.

Figure 3. STM image of a Au$_{55}$ cluster monolayer on a Au(111) substrate (a) and on an HOPG substrate (b), obtained at a bias of 2 V and a current of 100 pA. Scan range: 30 nm × 30 nm.

A thickness difference of about 2 nm between covered and uncovered areas. By zooming into a covered region (figure 3(a)) the clusters appear to be arranged within many local areas in a 2D closest packing. For comparison, an image of clusters which were deposited directly on HOPG substrates (as used in early approaches [12, 14]) is displayed in figure 3(b). In this case no homogeneous monolayer is formed. The image suffers from the mobility of the clusters. This increased mobility is probably due to the weaker van der Waals interaction between the clusters and HOPG in comparison to Au. The cluster–cluster interaction seems to be stronger than the cluster–substrate interaction.

We performed STS on individual clusters. A typical $I$–$V$ curve is shown in figure 4. Prior to the spectral measurements the tip–cluster distance was set by a tunnelling current of 0.7 nA and a bias voltage of 2 V. All curves acquired on the same position were identical. Around zero bias the spectrum exhibits a Coulomb blockade [17] with a total width of about 1.2 V in which the current is largely suppressed. The Coulomb blockade occurs due to the large charging energy of tunnelling junctions with small capacitances. Upon increasing the bias the current increases stepwise. The step width changes, however, gradually. The curve is strongly asymmetric with respect to zero bias. This asymmetry could have been caused by both the charge quantization (Coulomb staircase) [17] of the metal core and the electronic structure of the ligand molecules. Discrete energy levels of the cluster due to the quantum size effect [18] can be excluded here.
Figure 4. $I-V$ curve acquired on top of a cluster. Inset: modelling curve for the bias range from 0.4 to 2.0 V (red curve) in comparison with the measured curve (black curve). The bias refers to the substrate potential.

Figure 5. $I-z$ curve acquired on top of a cluster at a bias of 1 V.

because the level spacings are expected to be much smaller than the step width [19].

The molecular states of $P(C_6H_5)_3$ should for reasons of symmetry more or less equal those of $C_6H_6$ which have been investigated to some extent [20]. Due to the reduced symmetry, however, $P(C_6H_5)_3$ should exhibit some splitting of energy levels which are degenerate for $C_6H_6$. In order to experimentally analyse the situation we have carried out STM/STS measurements on $P(C_6H_5)_3$ molecules adsorbed to a Au(111) surface. As a result, the minimum level spacing of the molecular states amounts to about 0.5 V. Following a rough estimation, these states can only influence the $I-V$ curve in figure 4 at a bias above 1 V since the electric potential of the ligands is somewhere in between that of the substrate and that of the tip. Thus the voltage applied across them should be less than one-half of the whole tunnelling bias. The step widths in figure 4 are however about 0.4–0.7 V. Hence the molecular electronic states of the $P(C_6H_5)_3$ ligand are not responsible for the predominant features in the $I-V$ curves.

To study the charge-quantization effect it is required to know the capacitances ($C$) and
the resistances ($R$) of the double tunnelling junction (substrate–cluster and cluster–tip), which strongly depend on the distance of the interfaces. The substrate–cluster distance should approximately be equal to the thickness of the ligand molecule (3.5 Å), whereas the cluster–tip distance is unknown during the $I–V$ measurements. For a determination of the latter, we have performed measurements of the tunnelling current as a function of distance ($I–z$) on top of a cluster (figure 5). Prior to the measurement ($z = 0$), the tip was retracted from the cluster ($I → 0$) at a bias of 1 V. The tip was then driven to approach to the cluster by 6.5 Å at open feedback and the resulting current was recorded. The current increases exponentially with decreasing distance according to usual $I–z$ behaviour until a distance, marked by ‘$X$’ in figure 5, is reached, where the slope reduces to a minimum. We attribute this reduction in slope by touching the ligand molecule with the tip, i.e., by a strong interaction between the tip outermost atoms and the phenyl ring. This interaction gives rise to a repulsive force between tip and cluster. Further approach of the tip causes then a bending of the phenyl ring toward the cluster surface (see the inset in figure 5). It had been observed before that the tunnelling resistance is bigger in tunnelling through a lying phenyl molecule than through one which stands upright [21]. Since the distance between the tip and the cluster is continuously reduced at the same time leading to a smaller tunnelling resistance, the resulting current remains almost constant. From the position ‘$X$’, one can estimate the distance between the tip and the cluster in the previous $I–V$ measurement (figure 4).

Since the $I–z$ curve is measured at a bias of 1 V, and the $I–V$ curve shows a current of 0.14 nA at this bias (figure 4), the tip position during the $I–V$ measurement can be deduced to correspond to position ‘A’ in figure 5. This is about 1.7 Å away from the ligand molecule. It is then possible to calculate the capacitance between tip and cluster, $C_1$, by assuming two metal spheres [22] with radius of 10 nm (tip) and 0.7 nm (cluster), respectively, separated by a dielectric layer (ligand, 3.5 Å) and a vacuum gap of 1.7 Å. The capacitance between cluster and substrate, $C_2$, can be calculated by assuming a sphere and a slab [22] separated by a dielectric layer of 3.5 Å. We thus found $C_1 = 0.05 \text{ aF}$ and $C_2 = 0.13 \text{ aF}$. The relative dielectric constant of the ligand layer is taken to be 1.1 and derived from the polarizability of benzene molecules [23].

According to the analytical solution describing single-electron tunnelling through a double tunnelling junction [24], the Coulomb blockade range is determined by the dominating capacitance of the two junctions, i.e., $\Delta V_C = e/\max\{C_1, C_2\}$. In the present case we find $\Delta V_C = e/C_2 ≈ 1.2 \text{ V}$. This value is in very good agreement with the experimental result shown in figure 4. The asymmetry of the gap with respect to zero bias (−0.8–0.4 V) is likely to result from the misalignment of the Fermi energies of the cluster and the electrodes at zero bias [25]. The latter was treated in many works as a ‘fractional charge’ [26], which is in our case equal to 0.17 $e$.

In the simplest situation, the width of the Coulomb stairs should be $\Delta V_C$. The step width in the $I–V$ curve is, however, narrower and varies with the bias voltage. A reasonable explanation is a change of the gap widths of the junctions due to a motion of the cluster between tip and substrate during the $I–V$ measurement. Experimental results from scanning force microscopy [27] indicate that the clusters are likely to be negatively charged. A possible origin of this residual charge is the lower Fermi energy of the cluster compared to that of bulk Au. In general, the Fermi energy of metal clusters decreases with decreasing cluster radius [28, 29]. This is a result of the increasing surface potential. For a cluster with a radius of 0.7 nm, the Fermi energy is 0.7 eV lower than that of the bulk [29]. This energy difference is big enough to permit an electron in the substrate (Au film), in the absence of any bias voltage, to overcome the charging energy of the
Figure 6. Monte Carlo simulation of the $I-V$ curve with (red curve) and without (black curve) consideration of the neighbouring clusters. The resistance between the clusters is taken to be 10 GΩ and the capacity to be 0.03 aF.

cluster and to tunnel towards the latter. The negatively charged cluster will be attracted by the substrate at positive bias (with respect to the substrate) and by the tip at negative bias. We have observed while taking the STM images (figures 2 and 3) that the clusters were not stable enough at negative bias to be imaged in an unperturbed way. The clusters could be shifted laterally during the tip scanning. The step width in the $I-V$ curve in figure 4 should then consequently decrease with increasing bias voltage. This is indeed observed in the experiments. At negative bias, the step width is even determined by $C_1$ since in this case $C_1$ becomes the dominating capacitance.

Upon considering the cluster motion during the $I-V$ measurement, we have chosen $C_2 = 0.22$ aF and $C_1 = 0.05$ aF for modelling the curve within the bias range of 0.4–2.0 V (see the inset in figure 4). The other relevant parameters are $R_1 = 1.6 \, \text{GΩ}$, $R_2 = 930 \, \text{MΩ}$ and $T = 10$ K. The $R$-values were estimated from measuring the tunnelling resistance through a P(C$_6$H$_5$)$_3$ molecule which was adsorbed to a Au(111) surface. The modelling was carried out using a Monte Carlo simulation [30] based on the orthodox theory of single-electron tunnelling [17]. The step width of the theoretical curve matches very well the experimental values. The current increases, however, more strongly with increasing bias for the measured curve in comparison to the simulation. This can be explained by the fact that the transmission probability of the tunnelling electrons increases with increasing bias, whereas it is assumed to be constant in the calculation. The small step at about 0.4–0.6 V in the measured curve occurs due to the energy quantization of the cluster [19].

A Monte Carlo simulation which considers as well the neighbouring clusters in the 2D closest packing results in almost the same $I-V$ behaviour as that discussed above (figure 6).

In conclusion, we have demonstrated that well ordered monolayers of ligand-stabilized Au$_{55}$ clusters can be produced on Au(111) surfaces by spin coating. Tunnelling spectra acquired on top of a cluster show charge-quantization phenomena typical for a metallic particle. The ligand shell of the clusters acts solely as a dielectric tunnelling barrier in the applied bias range. The capacitances of the double-junction arrangement were determined from accompanying $I$–$z$ measurements. The varying step width in $I-V$ curves could be explained by cluster motion during the measurements caused by a negative residual charge on the clusters.
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