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Chemical tailoring of the charging energy in metal cluster arrangements by use of bifunctional spacer molecules

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The insertion of bifunctional spacer molecules into a three-dimensional arrangement of $Pd_{561}phen_{36}O_{200}$ clusters leads to an increase of the charging energy from 0.02 eV to 0.05 eV, which was determined from the temperature dependence of the conductivity.

Recent progress in chemistry allows the synthesis of well defined nanoscaled metal or semiconductor particles with uniform size and high reproducibility.[1] With respect to possible applications in microelectronics we illustrated recently[2] that some of these materials have potential uses resulting from their electronic inter-particle interactions. If metallic particles with a size of a few nanometers are arranged in a small spatial distance of *ca.* 1 nm, they build tunnel junctions with electrical capacitances down to 10^{-19} F. This allows controlled charge transport between the particles by single electron tunneling (SET) up to around room temperature, which has been recognized to be a fundamental concept for ultimate miniaturisation in electronics.[3] Inspired by this fascinating idea, many efforts have been made to tailor one-, two- and three-dimensional metal nanoparticle arrangements and to examine experimentally[4,5] and theoretically[6] the electrical properties of these materials. Most recently a single electron transistor has been constructed using alkanedithiol stabilized gold nanoparticles as tunnel junctions.[5]

The family of ligand stabilized metal clusters like $Au_{55}(PPh_3)_{12}Cl_6$, $Pt_{309}phen^*_{36}O_{30}$ or $Pd_{561}phen_{36}O_{200}$ (phen* = *batho*-phenanthroline, phen = 1,10-phenanthroline) are uniform, chemically tailored metallic nanoparticles in the size range 1.4–2.4 nm. They consist of a metal core with a well defined number of atoms, which is surrounded or 'dressed' by a protecting ligand shell. If these particles are attached to each other the ligand shell acts like a dielectric spacer between the metal cores. The electrical capacitance which is built up between them determines the charging energy for inter-particle electron transitions and it depends on the size of the metal core as well as on the thickness and chemical nature of the ligand shell.

In this work we report the chemical tailoring of the charging energy by insertion of bifunctional dielectric spacer molecules into a three-dimensional arrangement of $Pd_{561}phen_{36}O_{200}$ clusters. The basic idea is to stretch the cluster package in comparison to densest sphere packing and by this to increase the inter-particle spacing, which denotes the spatial distance between the surface of neighboring clusters (see Fig. 1). This should lead to an increase of the charging energy, *i.e.* a decrease of the electrical capacitance between the clusters.

The spacing of the $Pd_{561}phen_{36}O_{200}$ cluster, the synthesis of which is described elsewhere,[7] starts with its deoxygenation by hydrogen in a water–pyridine solution at room temperature with the formation of H_2O_2. The oxygen-free cluster $Pd_{561}phen_{36}$ now provides very active surface sites which can be coordinated by the NH_2 groups of 4,4′-diamino-1,2-diphenylethane, the spacer molecule. Generally, the reaction described here is suitable for every bifunctional molecule with terminal NH_2 groups. This particular spacer molecule was chosen, since (i) it is large enough to lead to sufficient stretching of the packing, and (ii) steric hinderance rules out folding of the molecule as well as the possibility to bind to the same cluster with both termini. The latter could be the case if α,ω-diaminoalkanes are used. This means that the spacer may be regarded to be quasi-stiff with respect to the purpose discussed here. As the naked cluster surface places are oriented in all directions the spacing procedure leads to an insoluble precipitate with three-dimensional cluster linkage. This network exhibits an increased inter-particle spacing with respect to the closest sphere packing of the non-modified cluster, like in a pressed pellet or a layer deposited from solution.

The charging energy, E_C, *i.e.* the energy barrier that has to be overcome to transfer a single electron from an initially neutral cluster to a neutral nearest neighboring cluster, is dependent of the inter-particle capacitance C, as follows from $E_C = e^2/2C$ where e is the charge of the electron. It can be determined directly from the temperature dependence of the dc conductivity $[\sigma(T)]$ of the cluster arrangements, which were investigated in this work on pressed pellets by means of a Keithley 6517 electrometer. Earlier investigations on the electrical properties of these ligand stabilized metal clusters have shown that even at high temperatures thermally activated electron hops between nearest neighbors, instead of hops of variable range, dominate the charge transport, giving a temperature dependence according to the Arrhenius relation $\ln\sigma(T) \approx E_A/k_BT$, where E_A is the activation energy.[8] This is confirmed by this work, as we found the simple activated behavior over the temperature range 80–300 K. Fig. 2 shows the Arrhenius plot, in which the slopes of the straight lines correspond to the activation energy of the charge transport, *i.e.* the charging energy of the particles in the three-dimensional arrangement.

While the close packing of the cluster material shows an activation energy of 0.02 eV the insertion of the spacer molecules increases the value to 0.05 eV. Correspondingly the capacitance decreased from initially 4.0×10^{-18} F down to 1.6×10^{-18} F. The specific conductivity follows the same trend,

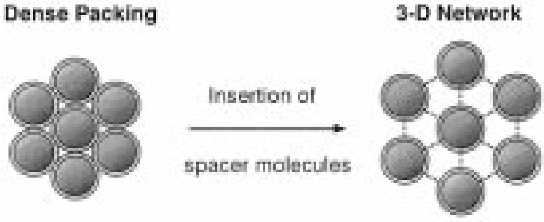

Fig. 1 Schematic illustration of the insertion of spacer molecules into a three-dimensional arrangement of clusters, which leads to an increase of the spatial distance of the cluster surfaces

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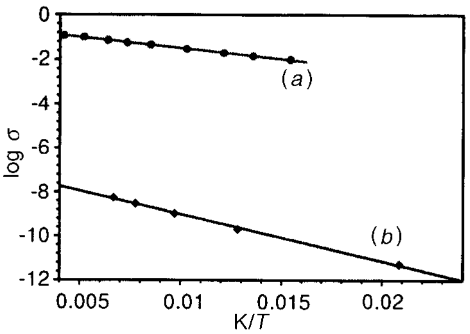

Fig. 2 Arrhenius plot of the Pd_{561} cluster (*a*) in dense packing ($E_a = 0.02$ eV) and (*b*) with inserted spacer molecules (3-D network; $E_a = 0.05$ eV)

as might be expected due to the decrease of the volume fraction of the metal in the volume of the sample. Thus, the trend observed is in agreement with the results found by Schiffrin *et al.*[9] who investigated 2.2 nm and 8.8 nm colloidal gold nanoparticles with interconnecting alkanedithiols.

In conclusion, this work provides one example of electrical capacitance between metal clusters in a three-dimensional arrangement; by this the charging energy can be chemically tailored by use of bifunctional spacer molecules. The decrease of E_C, which was determined by the temperature dependence of the conductivity, proved that chemical control of the physical properties of cluster arrangements is possible, which contributes to an understanding of the structure–property relationship in these nanomaterials. The power of this strategy will be examined in future works, where we will extend our investigations to even smaller clusters like $Au_{55}(PPh_3)_{12}Cl_6$ with a variety of spacer molecules with variable length, and a rigid backbone, *e.g.* due to π-conjugation, to determine the spacing definitely by the molecule length.

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