Chemically Induced Metal-to-Insulator Transition in Au_{55} Clusters: Effect of Stabilizing Ligands on the Electronic Properties of Nanoparticles

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The cluster compound $Au_{55}(PPh_3)_{12}Cl_6$ has been reanalyzed by photoelectron spectroscopy giving direct evidence for a nonmetallic behavior of the individual Au clusters as long as their ligand shell remains intact. The exposure to x-rays during the measurements is found to partly decompose the shell by removal of the chlorine atoms, resulting in a metallic behavior of the clusters as demonstrated by a steplike intensity at the Fermi energy. These observations resolve a long-standing controversy about the metallic behavior of ligated Au clusters emphasizing, in addition, the influence of the local environment on the electronic properties of nanoscaled materials.

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There has been a long-standing interest in the properties of nanometer sized particles since they allow to study the transition from the atomic to the solid state of a material which is of fundamental importance. One of the earliest attempts to produce nanoparticles with a monodisperse sized distribution was reported two decades ago [1], taking advantage of the increased stability of closed shell clusters corresponding to so-called magic numbers. Based on a chemical route, this method allows to prepare, e.g., Au_{55} cuboctahedrons (diameter 1.4 nm) which are covered by a $(PPh_3)_{12}Cl_6$ ligand shell consisting of 12 triphenylphosphine molecules and 6 chlorine atoms (thickness 0.45 nm). This ligand shell causes an additional chemical stabilization of the nanoparticles and helps to keep them apart from each other, thus avoiding coagulation of the individual clusters.

This method was the first to offer macroscopic amounts of size-selected nanoparticles, allowing the investigation of this type of cluster compound by a variety of different experimental methods. Among them, extended x-ray absorption fine-structure spectroscopy [2], x-ray absorption near edge spectroscopy [2], specific heat measurements [3], optical spectroscopy [4,5], scanning tunneling spectroscopy [6], atomic force microscopy [7], ac- and dc-conductivity measurements [8], impedance spectroscopy [9], Mössbauer spectroscopy [10], as well as x-ray-induced photoelectron spectroscopy (XPS) [11,12] have been used to obtain access to the structural and electronic properties of Au_{55} particles protected by a triphenylphosphine ligand shell. In addition, first principles calculations have been performed [13,14] for the naked clusters (i.e., Au_{55} without any ligands) aiming to serve as a reference system for the cluster compound. Although much work has been spent in these former studies to learn more about the properties of

$Au_{55}(PPh_3)_{12}Cl_6$ (labeled "Au_{55}-L" hereafter), one of the most fundamental questions could not yet be answered reliably, i.e., whether or not these ligand stabilized Au clusters have to be considered as metallic systems. Furthermore, the influence of the ligand shell onto the properties of the Au_{55} clusters remained unclear.

Summarizing these earlier investigations, a nonmetallic behavior of Au_{55}-L has been suggested from Mössbauer spectroscopy [10] on the basis of modified electron densities of the Au cluster core as compared to bulk material. Moreover, experimental evidence for a nonmetallic state was provided by the absence of a linear contribution to the specific heat [3], indicating a vanishing density of electronic states at the Fermi level E_F. On the other hand, XPS results clearly revealed a steplike density of states at E_F [11,12], indicating a metallic behavior of the cluster compound. Such behavior was also deduced from x-ray absorption spectroscopy studies [2] as well as from ac- and dc-conductivity measurements [8], the latter being discussed to reflect the absence of a gap in the density of states at E_F. Optical experiments [4] suggested that the situation is even more complex. Molecular spectral features as observed from triphenylphosphine-stabilized Au_{13} clusters were absent in Au_{55}-L (thereby indicating a metallic behavior), but as well, no Mie-plasmon resonances were found which are indicative for "metal" electrons in solid-state−like Au particles. The thus obvious intermediate state of Au_{55}-L has been interpreted to reflect deviations from the bulklike electronic band structure induced by interactions between the Au-6s electrons and the ligand shell [5].

Using photoelectron spectroscopy we will demonstrate for the first time, that the $(PPh_3)_{12}Cl_6$ ligand shell actually dominates the electronic properties of the 55 Au atoms

leading to a nonmetallic behavior of the cluster compound. Controlled radiation-induced damage of the ligands will allow us to systematically reduce the influence of the shell on the electronic properties of individual Au clusters. As a result, one is able to switch the Au clusters to a metallic behavior as evidenced by a finite density of states at E_F. The present experiments will explain the controversial results mentioned above as being due to modifications of the ligand shell induced by the experimental techniques themselves, a process, which has not been taken into account previously.

All photoemission experiments have been performed on Au_{55}-L clusters deposited on silicon substrates (covered by 1–2 nm of natural silicon oxide) by spin coating from a CH_2Cl_2 solution. Spin coating is known to allow the preparation of islands with one monolayer height after evaporation of the solvent on hydrophobic substrates such as highly oriented pyrolithic graphite or mica [15]. The specimens were introduced into the analysis chamber of the electron spectrometer (Fisons ESCALAB 210) and analyzed under ultrahigh vacuum conditions by means of XPS using monochromatized Al K_α radiation ($h\nu = 1486.6$ eV, spot size ≤ 1 mm) as well as ultraviolet photoelectron spectroscopy (UPS) using photons emitted from a gas discharge lamp (HeI, $h\nu = 21.2$ eV), respectively. XPS was exploited to perform a chemical analysis of the compound by means of core level spectroscopy and to investigate the details of the valence band of the Au particles. Data were acquired using an overall energy resolution (electrons and photons) of 0.32 eV full width at half maximum for the XPS measurements and 0.04 eV for the UPS experiments.

Since the information depth of x-ray excited photoelectrons (4–5 nm) is of the same order of magnitude as the diameter of the ligated cluster (2.3 nm), each of its 55 Au atoms will contribute to the corresponding photoemission spectrum. Additionally, core level spectroscopy on elements constituting the ligand shell (C, P, Cl) complements the analysis of the cluster compound, proving XPS an ideal tool to investigate such nanoscaled materials.

Figure 1 presents an overview of the Au-$4f$ core level region acquired after exposure to the x-ray beam for different periods of time. If irradiation is reduced to less than 30 min (top curve) the spectral shape can be described as a superposition of two well-distinguishable doublets, representing two different chemical states of the probed atoms. While the two most prominent peaks reflect, to first approximation, bulk material, the shoulders (indicated by arrows), which are shifted by about 1.5 eV towards higher binding energies, have to be attributed to a small number of Au atoms experiencing a different chemical environment. In this case, the outermost atoms of the Au particle are ligated either to phosphorous or to chlorine of the ligand shell. Among these, only the chlorine is known to lead to correspondingly large shifts of the Au binding energy [16]. Furthermore, an estimation of the relative intensities
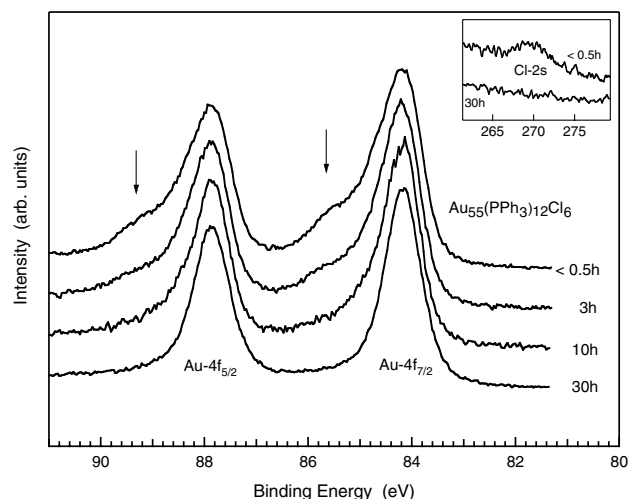

FIG. 1. Au-$4f$ core level spectra acquired from Au_{55}-L after different exposure times to the x-ray beam. The inset presents the Cl-$2s$ binding energy region, indicating a complete radiation-induced removal of the chlorine from the ligand shell.

of the high and low binding energy components by means of a least-squares fitting procedure [17] yields a fraction of roughly 7 Au atoms experiencing a different chemical environment. Thus, the shifted components are attributed to those Au atoms ligated to the chlorine atoms at the interface between the particle and the ligand shell. Bond breaking during the exposure to x-ray photons obviously leads to a continuous decrease of the Cl-bonded Au atoms with increasing time, until, after exposure times of the order of days, this contribution finally disappears. If chlorine is removed from the sample by such a bond breaking, this should also be reflected in a corresponding intensity decrease of any Cl core level. Indeed, by studying the Cl-$2s$ binding energy region which has been plotted as an inset of Fig. 1, chlorine can easily be detected in the case of short exposure times to the x-ray beam while, after long exposures, the chlorine signal is found to completely vanish. Keeping in mind the information depth of the photoelectrons (4–5 nm) and the size of the ligated cluster (2.3 nm), this observation has to be interpreted as a complete radiation-induced removal of the chlorine from the ligand shell. Additionally, it is found that the amount of phosphorus slightly decreases only by about 10%–20% under such x-ray exposures, confirming the above attribution of the shifted Au-$4f$ component to chlorine bonds. On the other hand, the amounts of the remaining elements, gold as well as carbon, are found to be conserved. Thus, effects such as x-ray-induced desorption of clusters or the linkage between individual clusters can be safely excluded. This latter point is important since it guarantees that even in case of bilayer or multilayer formation within certain areas during sample preparation the properties of monodisperse Au particles are investigated.

It must be stressed that the chemically shifted Au-$4f$ components observed in our study in the case of short

exposures to the x rays have not been detected in previous photoemission experiments [11,12]. Thus, one has to conclude that in these earlier studies decomposition of the ligand shell must have taken place, preventing the study of the electronic properties of the original cluster compound. In order to avoid such a decomposition in our investigation, advantage was taken of the small spot x-ray source capability of the electron spectrometer (spot size ≤1 mm) allowing us to probe a certain sample position (sample size 5 × 10 mm) for times less than 30 min and then to move to a new position. This procedure enables us to analyze, for the first time, the electronic properties of Au_{55}-L using photoemission techniques.

Because of their higher electronegativity, Cl atoms ligated to Au at the periphery of the Au core are expected to detract charge. This should result in significantly changed electronic properties as compared to the situation of a partially decomposed ligand shell which, however, still protects the individual Au clusters from coagulation due to the conserved amount of carbon atoms. In this state with the Au-Cl bonds broken and the Cl removed, the electronic properties of the cluster compound may resemble those of a hypothetical naked Au_{55} particle since carbon is generally believed to exhibit only weak interactions with a noble metal such as gold (carbon-based supports are used in most investigations of the electronic properties of Au nanoparticles by electron spectroscopy).

In Fig. 2 the XPS valence bands are presented for the cluster compound *with* (assigned as Au_{55}-L, lowest curve) and *without* (assigned as Au_{55}-C, second curve from the bottom) chlorine atoms in the ligand shell in comparison to photoemission results from well-defined, well-separated Au particles (size 1.6 nm) prepared by a micellar technique [18] together with the results obtained from a gold reference film. Starting with the electronic structure of the original compound (lowest curve), two pronounced maxima with approximately symmetrical shape can be recognized at binding energies of about 4.3 and 6.2 eV, reflecting the Au-$5d$ contribution to the electronic structure of the Au particles. By analyzing the electron distribution in the vicinity of the Fermi energy (indicated by the dotted line), one concludes on an insulating behavior, which resembles very much the band shape observed for size-selected Au_{33} clusters (not shown here) deposited onto amorphous carbon in an earlier investigation [19]. The spectral shape drastically changes by removing the chlorine atoms from the ligand shell, now exhibiting a different shape of the Au-$5d_{5/2}$ subband, which is shifted towards the Fermi energy by about 1 eV, and a steplike intensity at E_F, providing experimental evidence for a metallic behavior of the 1.4 nm sized Au_{55} particles. This spectrum nearly coincides with that acquired from naked 1.6 nm sized Au particles on top of diamond [18]. By comparing the latter two spectra with the results obtained from the bulk metal (top curve), good overall agreement is found with respect to the position of the characteristic Au-$5d$
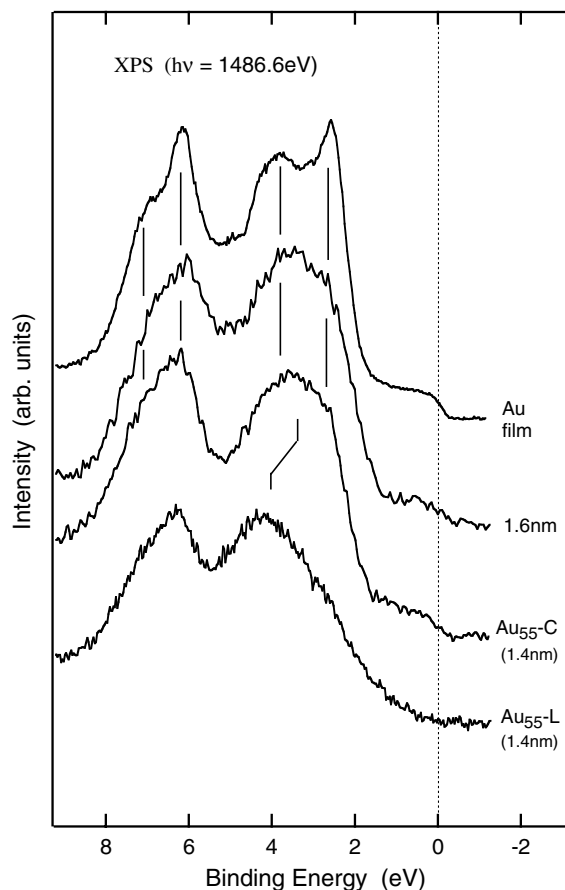

FIG. 2.   XPS valence band spectra of bulk gold, "naked" gold nanoparticles (1.6 nm) on top of diamond [18], the original cluster compound, and the compound after two days of x-ray exposure.

features as well as to the existence of a Fermi edge. Thus, we conclude that particles formed by 55 Au atoms can still be interpreted as reflecting the prominent features of the bulk material as long as there is no strong chemical interaction with the surrounding material. This situation dramatically changes, if the outer atoms of the Au particle are ligated to a chemically active species such as chlorine. In that case, the system undergoes a metal-to-insulator transition (MIT) accompanied by a significant change of the Au-$5d$ band properties.

In order to substantiate this main result, additional UPS experiments were performed on both types of cluster compounds (Au_{55}-L, Au_{55}-C), allowing to critically test the idea of a ligand-induced MIT transition due to a strongly improved energy resolution. The corresponding data are presented in Fig. 3, where the photoelectron distribution in the vicinity of the Fermi energy is shown on an enlarged scale for both compounds together with results acquired under identical conditions from the gold reference sample. While the density of states, in the case of the original compound, is found to vanish at E_F, the modified cluster compound clearly exhibits a distinct intensity step as in the case of the bulk metal, thus corroborating
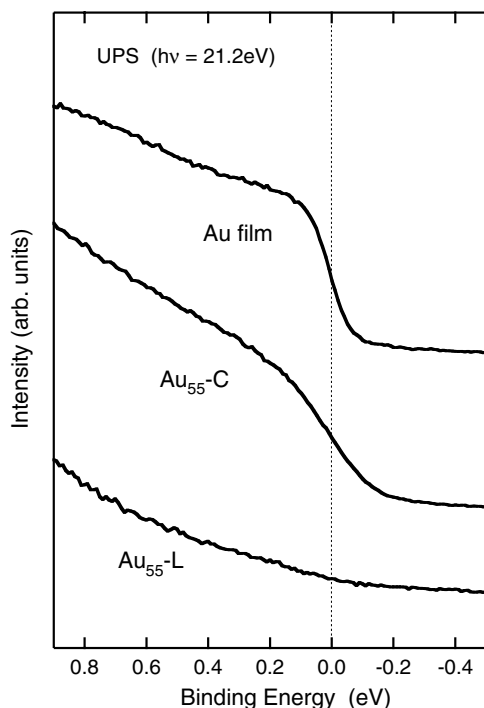
FIG. 3. UPS valence band spectra in the vicinity of the Fermi energy of bulk gold, the original cluster compound, and the compound after two days of x-ray bombardment.

the results obtained by XPS. It should be noted that the slightly increased smearing of the steplike intensity in the case of the Au_{55}-C compound is due to a final-state effect induced by the photoionization process itself due to a temporal charging of the Au particle, which can be modeled as an extremely small capacitor [20]. However, this process leads only to an additional smearing of the spectroscopic features by about 0.1 eV which does not influence the conclusions drawn so far.

As a final remark, the removal of the chlorine atoms and, consistently, the MIT transition could also be achieved by applying a short oxygen plasma treatment [21]. This also suggests that experimental conditions which provide oxygen radicals near the sample surface, such as optical experiments within the UV range performed under ambient conditions, may remove part of the chlorine from the cluster surface. As a result, the Au particles will act metallic after some time.

In conclusion, it has been experimentally demonstrated that Au_{55} clusters can be switched from a metallic into an insulating state by ligating the outer atoms to the structure-stabilizing triphenylphosphine ligand shell via chlorine. This MIT proves the strong influence of chemical bonding on the electronic properties of even relatively large clusters with a well-defined inner core, emphasizing that the environment of nanoparticles must always be taken into account when discussing their fascinating properties.

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