Angle-resolved X-ray photoelectron spectroscopic experiments on the full series of molecular $[Au_{55}(PR_3)_{12}Cl_6]$ clusters*

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Core and valence spectra have been measured in a series of angle-resolved high-resolution X-ray photoelectron spectroscopic experiments on the molecular metal cluster compounds $[Au_{55}(PR_3)_{12}Cl_6]$ with R_3 = $Ph_2(C_6H_4SO_3Na\text{-}m)$, $(C_6H_4Me\text{-}p)_3$, $(C_6H_4OMe\text{-}p)_3$ or Ph_3 which represent all such compounds synthesized to date. Only a limited number of samples satisfies the nominal composition. In some of the samples the presence of gold particles, larger than the nominal Au_{55} clusters, is observed. Gold monomers bound to P and Cl are shown to be present in a number of samples.

The observation of phenomena associated with small metal particles,[1] such as a quantum size effect or a transition to metallic behaviour, is often severely hampered by a distribution of particle diameters. For instance, core-hole screening by conduction electrons causes the core lines in X-ray photoelectron spectroscopy (XPS) experiments to be asymmetric. Core holes in small metal particles are less effectively screened due to the limited number of conduction electrons. The asymmetry can therefore, in principle, be used as a measure of the screening response and thus of metallic behaviour. However, a far larger asymmetry of the core lines is caused by the existence of a size distribution,[2] rendering the screening asymmetry unobservable.

The distance between bare metal particles on a substrate must be kept relatively large in order to prevent coalescence of the particles. Consequently, the XPS spectrum does not depend on the escape angle of the photoelectrons because photoelectrons from a particular particle do not pass through neighbouring particles even when the angle between the substrate surface and detector is small. Bulk and surface contributions to the spectrum can therefore not be separated. Furthermore, interactions between supported metal clusters and the substrate have an appreciable influence on the photoemission spectrum.[3]

In general, a shift towards a higher binding energy of core levels and a narrowing of the valence bands are observed with decreasing particle size.[4-10] Several explanations have been offered for these findings. Most widely accepted is the one by Wertheim *et al.*[4] in which the shift to higher binding energy is attributed to a final-state positive charge on the cluster. Mason[11] favours an initial-state effect, while Cini *et al.*[12] propose that interactions with the substrate are responsible.

Monodisperse metal particles have been available for a number of years in the form of molecular metal cluster compounds consisting of a metal core of a given number of atoms surrounded and stabilized by a ligand shell formed by atoms and molecules such as Cl, PPh_3, CO (for a recent review see ref. 13). In principle, these metal clusters are ideally suited for a study of the physical properties of small metal particles. The organic ligands surrounding the metal cores insulate the clusters from each other. The clusters can therefore be close together, permitting angle-dependent XPS experiments. In addition, the electronic behaviour of the metal core is not influenced by the substrate as several layers of cluster material may be deposited on the substrate. However, the sample must be sufficiently conducting in order to prevent charging of individual clusters. Indeed, conductivity studies on a number of molecular metal cluster compounds[14] have shown a variable-range-hopping type conductivity.

Recently, there has been some debate about the actual composition and the stability of some metal cluster compounds, in particular the Au_{55} clusters, first synthesized by Schmid *et al.*[15] It was found by mass spectroscopy that samples obtained from different sources behave differently.[16] Furthermore, an influence of aging on the mass spectrum was observed. It has been posed therefore that, in fact, the Au_{55} compounds are not as monodisperse as has been claimed.[16,17] Extended X-ray absorption fine structure (EXAFS) experiments on Au_{55} did not rule out the presence of particles exhibiting a smaller or larger diameter.[18]

In a previous angle-resolved high-resolution XPS experiment on one member of the series $[Au_{55}\{P(C_6H_4OMe\text{-}p)_3\}_{12}Cl_6]$,[19] it was established that final-state charging is responsible for the binding-energy shift of the core lines and valence band. The gold 4f core line could be separated into two symmetric components assigned to the 12 apical Au atoms and the remaining 43 non-apical Au atoms, respectively. Furthermore, the valence band was observed to be narrowed with respect to bulk Au, reflecting a redistribution of the s and d electrons.

In this paper we report on an experimental XPS investigation on the four-member series of $[Au_{55}(PR_3)_{12}Cl_6]$ cluster compounds synthesized up to now. It was found that of the ten samples investigated four were consistent with the nominal formula, albeit that in two of the four a small admixture of larger particles is present. The six remaining samples exhibit a distribution of particle sizes in addition to an admixture of gold monomers.

Experimental, Results and Discussion

Angle-resolved XPS experiments were carried out on a Scienta ESCA-300 spectrometer with an Al-Kα radiation source. The photoelectron escape angle was measured with respect to the substrate surface. The energy resolution was 0.35 eV. The experiments were performed on $[Au_{55}(PR^n{}_3)_{12}Cl_6]$ samples[15] with $R^1{}_3 = Ph_2(C_6H_4SO_3Na\text{-}m)$, $R^2{}_3 = (C_6H_4Me\text{-}p)_3$, $R^3{}_3 = (C_6H_4OMe\text{-}p)_3$ or $R^4{}_3 = Ph_3$. The amorphous powdered

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* *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

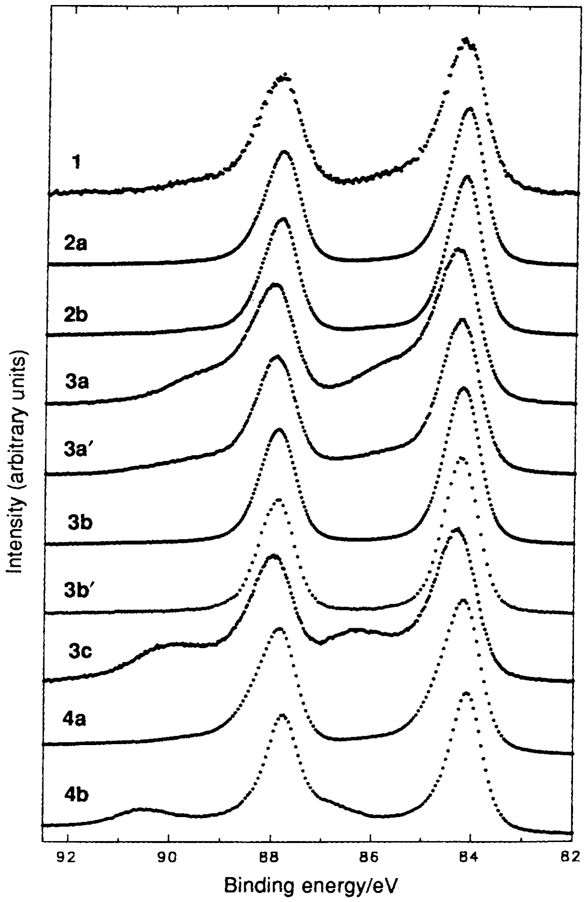

Fig. 1 Gold 4f spectra of the various samples

samples were deposited on top of a graphite substrate as homogeneously as possible in the form of a thin layer.

Figs. 1, 2 and 3 show the gold 4f, phosphorus 2p and the chlorine 2p spectra of the samples at an angle of 90° with respect to the graphite substrate. Compound **1** was measured approximately 6 months after preparation, **2a** (R''_3 = R^2_3) was measured 3 weeks after preparation, **2b** (R''_3 = R^1_3) prepared in a different batch was measured after storage for 1 year and **3a** (R''_3 = R^3_3) was measured 1 month after preparation; **3a′** is the same sample remeasured after 3 months of storage, **3b** was measured immediately after preparation, **3b′** the same sample remeasured after 1 week on a different type of graphite substrate and **3c** has been used in a number of previous experiments and stored afterwards for approximately 2 years at ambient temperatures. Sample **4a** (R''_3 = R^4_3) was measured as received, **4b** was in the form of a pressed wafer.[20] All samples were stored in air.

We checked for possible decomposition effects induced in the samples by the exposure to X-rays or vacuum. Except for a time dependence of the intensity of the shoulders present in the gold 4f spectrum of some of the samples (see below), we did not observe any decomposition.

Samples 3b, 3b′, 2a and 2b

The gold $4f_{\frac{7}{2}}$ core-level spectra of sample **3b** taken at angles of 10, 30 and 90° are shown in Fig. 4. The shift to higher binding energy and the broadening of the 10° spectra are caused by an enhancement of the contribution of Au atoms located on the surface of the clusters. By taking linear combinations of the 10 and 90° spectra, the surface contribution to the gold 4f spectrum (S_{surf}) can be separated from the contribution of the deeper-lying Au atoms (S_{bulk}):$S_{surf} \propto [S(10°) - \gamma S(90°)]$ and $S_{bulk} \propto [S(90°) - \beta S(10°)]$. The results are shown in Fig. 5 for the optimum values β_1 and γ_1, which were determined by the minimum in the standard deviation of the fits of the (normalized) bulk and surface lineshapes as a function of β and γ. We have used a mixture of a Gaussian (G) and a Lorentzian (L), $mG + (1 - m)L$. The resulting surface (84.48) and bulk (84.18 eV) lineshapes are symmetric. This is strong evidence

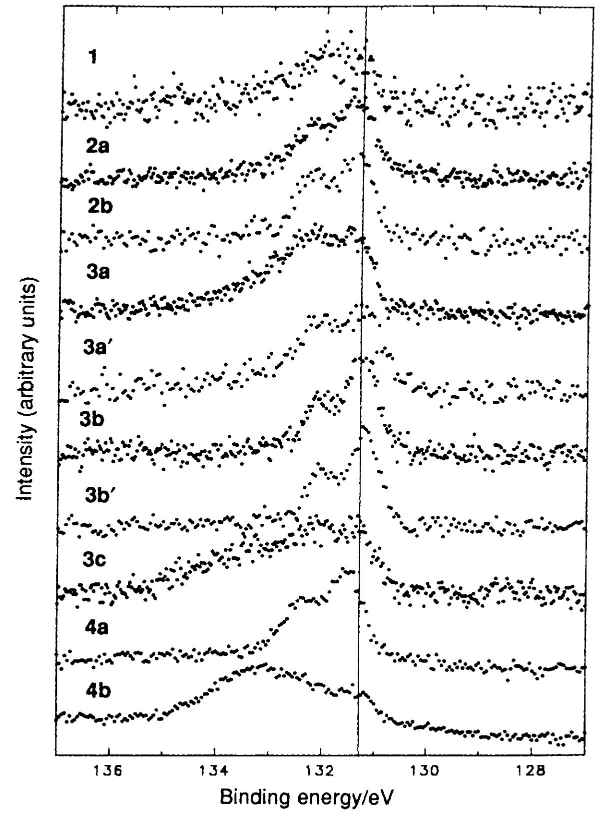

Fig. 2 Phosphorus 2p spectra of the various samples

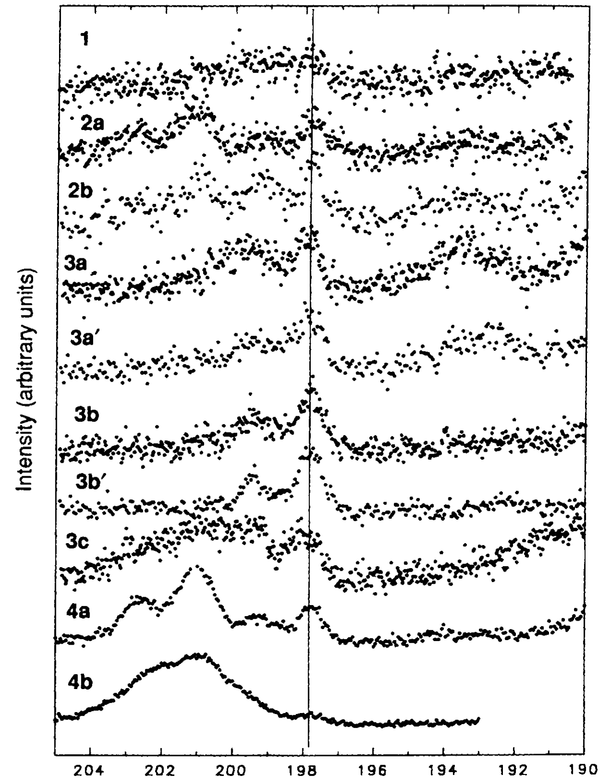

Fig. 3 Chlorine 2p spectra of the various samples

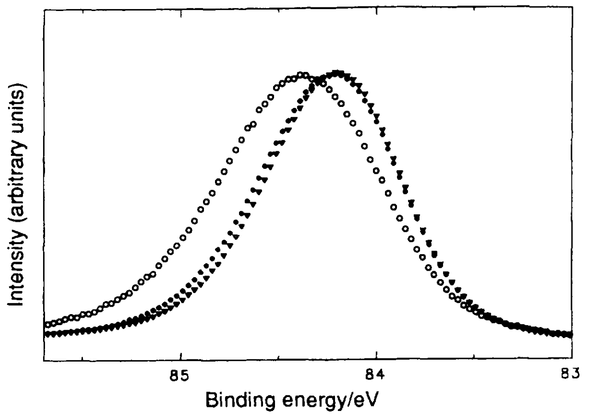

Fig. 4 Normalized gold 4f$_{\frac{7}{2}}$ spectra of sample **3b** at three angles: 10 (○), 30 (●) and 90°(▽)

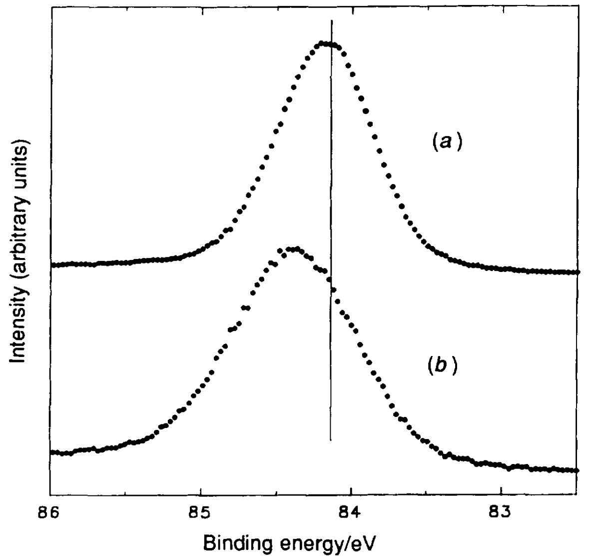

Fig. 5 Normalized gold 4f$_{\frac{7}{2}}$ spectra of the non-apical (*a*) and apical atoms (*b*) of sample **3b** obtained from linear combinations of the 10 and 90° spectra of Fig. 4

that only two components constitute the gold 4f spectra. If three or more components were present in the spectrum this procedure would yield asymmetric lineshapes. We note in passing that in bulk metals the conduction-electron screening process results in an asymmetry of the core line, tailing out to higher binding energy. A measure for the asymmetry is provided by the singularity index α in the Doniach–Šunjić line shape.[21] In small metal particles α is expected to decrease due to the reduced screening efficiency of the conduction electrons. Bulk Au has one of the lowest values for α.[22] It is therefore not surprising that in small gold particles a screening-response asymmetry of the core line is not observed.

The surface peak is assigned to the 12 apical Au atoms of the cuboctahedral Au_{55} cluster and the bulk peak to the remaining 43 Au atoms.[19] This assignment was corroborated by the fact that both surface and bulk atoms exhibit similar valence-band spectra, with a Fermi level, ruling out an assignment of one of the two peaks to gold monomers which could be present in the sample due to degradation of the Au_{55} clusters or to the presence of reaction residues. Another source of contamination could be the existence of particles larger or smaller than the nominal Au_{55} clusters. A distribution of particle diameters, however, would result in asymmetric lineshapes.[2]

It can also be argued that the peak with the highest binding energy is the result of the presence of smaller particles of a unique size in addition to Au_{55}. However, the relative intensity ratios $I_{\text{bulk}}/I_{\text{surf}}$ of the two components is independent of the angle in a range between 90 and 50°, with a value of 3.5, in excellent agreement with the ratio of non-apical to apical atoms (43/12). A dramatic decrease in relative intensity ratio is observed only at angles below 50°. Such behaviour would be at odds with the assumption that two types of gold clusters with different diameters are present in the sample.

It was shown[19] that a final-state charge is responsible for the positive core-line shifts of both apical and non-apical Au atoms of the Au_{55} clusters. This mechanism was proposed by Wertheim *et al.*[4] in 1983 to explain the positive binding energy (b.e.) shift of small supported gold particles. The poorly conducting substrate on which the bare gold particles are deposited is not able to neutralize the cluster in the relevant time of the photoemission process. An excess charge of $+e$ resides on the surface of the cluster. Definite evidence for a final-state charge was obtained from the fact that the valence bands of the two types of Au atoms were shifted by the same values as the corresponding gold 4f levels.

Corrected for the final-state charge, the gold 4f b.e. is 83.84 eV, in excellent agreement with the expected value based on the surface- and bulk-b.e. values of metallic Au (83.60 and 84.00 eV, respectively). From the fact that no b.e. shift is observed for the surface Au atoms bound to P and Cl, we may conclude that the amount of charge transfer between Au atoms and P and Cl atoms is small. This observation is in contrast with results on small ligated Au_{11} clusters[23] where the large positive b.e. shift of the Au atoms was attributed to a charge transfer of gold 6s electrons to the ligands. However, in a recent discussion on the nature of the bonding between metals and alkali-metal adsorbates[24,25] it was argued that there is little or no charge transfer between the alkali-metal atoms and the metal. A very small charge transfer was also observed in iodine adsorbed on copper.[26] A discussion on the nature of the Au–P and Au–Cl bonds in Au_{55} is beyond the scope of the present article. However, contrary to Au_{11}, the valence-band spectrum of Au_{55} resembles that of metallic Au with a 6s band and a Fermi cut-off.[19] Thus it can be argued that the absence of a b.e. shift of the Au atoms bound to P or Cl in Au_{55} has its origin in the same mechanism as proposed for the adsorbate–metal systems.

In order to prevent charging of the sample the clusters must be neutralized in the time between successive photoemission events. This charge is provided by the conductivity of the sample.[14] However, owing to the variable-range-hopping type of conduction the conductivity decreases exponentially with temperature. Consequently, a static charging of the sample is expected at low temperatures. Indeed, this was observed by Quinten *et al.*[27] in an angle-integrated XPS experiment on $[Au_{55}(PPh_3)_{12}Cl_6]$ at temperatures below 100 K.

The phosphorus 2p (Fig. 2) and chlorine 2p (Fig. 3) spectra of samples **3b** and **3b′** at 131.3 (P 2p$_{\frac{3}{2}}$) and 197.8 eV (Cl 2p$_{\frac{3}{2}}$) are relatively sharp and well resolved in their spin-orbit components. Their b.e. values support the view that there is little charge transfer from the gold core to the ligands.[28]

At first sight the gold 4f spectra of samples **2a** and **2b** do not differ from those of **3b** and **3b′**, although the phosphorus 2p and the chlorine 2p spectra are slightly broader. However, linear combinations of spectra at different angles always produced slightly asymmetric line shapes, tailing out to higher binding energy (Fig. 6). Moreover, the non-apical line shape is shifted by 0.1 eV to higher binding energy as compared to the (symmetric) non-apical line shape of **3b** and **3b′**. We attribute this slightly smaller shift and the asymmetry of the line shape to the presence of larger gold particles than the nominal Au_{55} clusters.

Samples 1, 3a, 3a′, 3c, 4a and 4b

These samples exhibit pronounced shoulders in the gold 4f (Fig. 1) spectra at higher binding energy, as well as large broadening of the phosphorus 2p (Fig. 2) and chlorine 2p (Fig. 3) spectra.

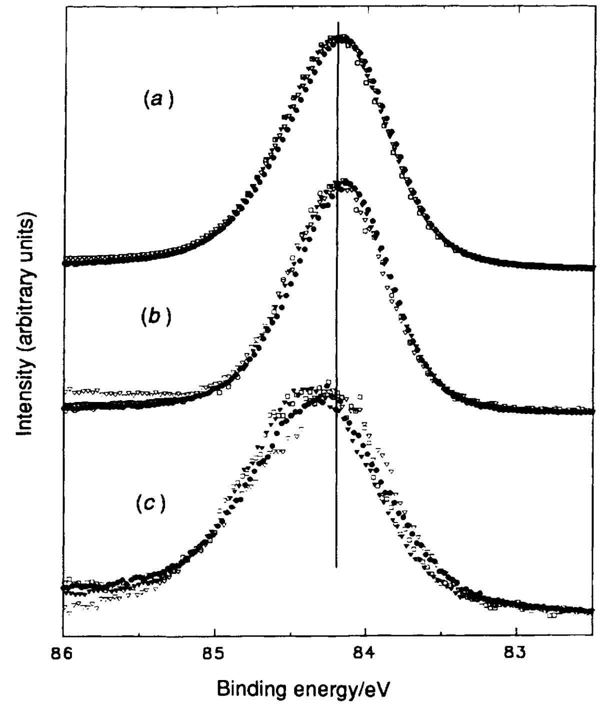

Fig. 6 Normalized gold 4f$_{7/2}$ spectra of samples **2a** (●), **2b** (▽), **3b** (▼) and **3b′** (□): (*a*) angle 90°, (*b*) non-apical atoms, (*c*) apical atoms

We attribute the shoulder and the broadening to the existence of gold monomers bound to P and Cl. Clearly, this is inferred by employing a flood-gun (used to prevent static charging of non-conducting samples) on *e.g.* sample **4b** (Fig. 7). Whereas the main peaks of the gold 4f spectrum are not sensitive to the flood-gun, the shoulders shift to lower b.e. by about 1 eV. The observed b.e. shift depends on the operating parameters of the flood-gun, *e.g.* power, kinetic energy. It is therefore not possible to obtain quantitative b.e. values for the monomers.

As was also observed for the main peaks of the gold 4f spectrum, the phosphorus 2p and chlorine 2p peaks, visible at 131.3 and 197.8 eV, respectively, are not sensitive to the flood-gun. These peaks were previously assigned to phosphorus and chlorine atoms bound to the Au_{55} cluster. The broad shoulders, however, do change when the flood-gun is switched on. The shoulders in the gold 4f, the phosphorus 2p and the chlorine 2p spectra can therefore be attributed to the presence of gold monomers, bound to P and Cl.

Fig. 8 represents the gold 4f spectra of sample **4b** at angles of 90 and 15°. The intensity of the shoulders is much higher at the smaller angle, which means that the gold monomers bound to P and Cl are preferentially located on the surface of the sampled material.

Sample **3a** was remeasured after 3 months (**3a′**), *i.e.* powder from the same batch was deposited on a clean substrate. From Fig. 1 it is seen that the intensity of the shoulder is reduced. In order to check the origin of the intensity change the experiment was repeated on different locations on the sample. We observed a pronounced dependence of the shoulder intensity on the spatial location of the surface spot exposed to the X-rays, indicative of sample inhomogeneity.

A reduction of the shoulder intensity was observed in sample **4b** in the course of the experiment. These intensity changes are caused by prolonged exposure of the gold monomers to X-rays. Indeed, in order to verify this we measured a sample of $[Au(PPh_3)Cl]$ and found that it was very unstable under X-rays.

Conclusion

Angle-resolved XPS experiments on a number of molecular metal cluster compounds $[Au_{55}(PR_3)_{12}Cl_6]$ show that interactions between the organic ligands and the metal core are small. Core-level shifts of Au atoms on the surface of the cluster bound to different organic ligands could not be observed. Moreover, no distinction exists between fully co-ordinated Au atoms, unbound surface Au atoms and surface Au atoms bound to P or Cl. Instead, a simple model invoking final-state charge effects accounts for the experimental results.

We have also shown that, although it is possible to obtain pure molecular metal cluster Au_{55} compounds, the inclusion of differently sized particles and, in some cases gold monomers, does occur. The mechanism responsible for these unwanted by-products is unclear. Thus, samples with the same nominal compositions and roughly the same temporal history behave completely differently (*e.g.* **3a** and **3b**). Moreover, samples with the same nominal compositions but with different temporal histories behave in the same way (*e.g.* **2a** and **2b**).

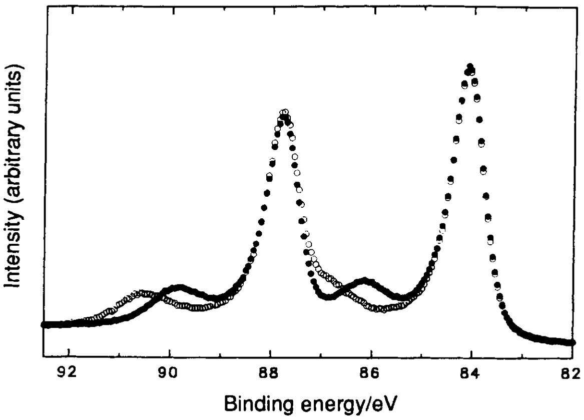

Fig. 7 Normalized gold 4f spectra of sample **4b** with the flood-gun off (○) and on (●)

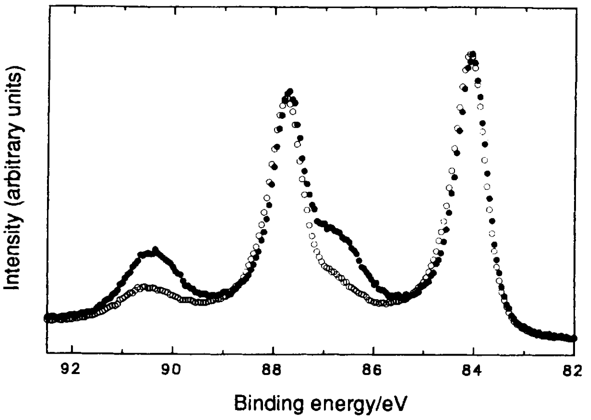

Fig. 8 Normalized gold 4f spectra of sample **4b** at angles of 90 (○) and 15° (●)

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