

# Chemical properties of size-selected Au clusters treated under ambient conditions

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## A B S T R A C T

Mass-selected Au clusters consisting of 5–8 atoms deposited on silica were treated with water and aqueous NaOH solution, and the change of their chemical properties upon these treatments was studied. With water, no change was observed, indicating that the clusters survive as individual entities under such realistic conditions. After immersing the samples into the NaOH solution, a change of the oxidation behaviors of the Au clusters was found to occur; the originally oxidation resistant Au<sub>5</sub> and Au<sub>7</sub> become more reactive than the other clusters towards oxidation. Non-scalable chemical behaviors can be obtained from the small clusters even under realistic conditions.

## 1. Introduction

When the size of a material is reduced to the nanometer (nm) scale, novel properties such as enhanced catalytic activity appear and, thus, extensive studies have been devoted to the chemical and physical properties of nano-materials [1–3]. Properties of clusters consisting of less than ~100 atoms depend strongly on each additional atom, and the size dependent change of the physical and chemical properties is abrupt rather than gradual [4–7]. An example of this non-scalable behavior can be found in studies of the oxygen chemisorption rates of free anionic coinage metal (Au, Ag and Cu) clusters in the gas phase: even-numbered clusters react more strongly with O<sub>2</sub> than their odd-numbered neighbors, which can be explained by an even–odd alteration of the electron affinities of these clusters [7–11].

Using deposited, mass-selected clusters, better insight into the size-selectivity of the chemical and physical properties of clusters, as well as metal-support interactions, can be gained. Previously, the strongly size-dependent variation of the electronic and chemical properties of deposited metal clusters was explored [4–6,12–15]. Au clusters were found to show superior catalytic activities to those of the Au bulk crystals. Recently, it was found that the oxidation behavior of Au clusters deposited on silica exhibits an even/odd alternation analogous to the gas phase data: for clusters consisting of less than 11 atoms, the odd-numbered clusters can readily form Au-oxide upon atomic oxygen deposition, whereas their even-numbered neighbors are more inert [15]. In particular, the pronounced resistance of Au<sub>5</sub> and Au<sub>7</sub> clusters to oxidation was observed [15].

Most of the previous studies using mass-selected clusters in the size regime of non-scalable behaviors were performed under ultra-high vacuum (UHV) conditions. Therefore, it is not clear whether the information obtained on small clusters under such ideal experimental conditions are valid in real catalysis. In the present study, we attempt to extend the results previously obtained for these clusters to more realistic experimental conditions. Samples containing mass-selected deposited Au clusters were immersed into distilled water and aqueous NaOH solution. The change of the chemical properties of the clusters after these treatments was investigated by examining their oxidation/reduction behaviors under UHV conditions. We show that the unique and non-scalable behaviors of deposited mass-selected clusters are still preserved after treating the samples under experimental conditions closer to those of real catalysis rather than UHV conditions. Hence, it is likely that the properties of these mass-selected clusters can be exploited in real catalysis. We also show that the chemical properties of the deposited clusters can be easily influenced by additional chemical treatment.

## 2. Experimental details

All the measurements were performed under UHV conditions. For X-ray photoelectron spectroscopy (XPS), a cylindrical hemispherical analyzer (CHA) and an X-ray source with an Al target ( $K_{\alpha}$ , photon energy = 1486.6 eV) were used. The upper limit of the instrumental resolution of XPS is estimated to be about 1 eV. For acquisition of each Au 4f spectrum, 1 h was required. Si wafers were chemically etched using a mixture of three different acids and water (H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, CH<sub>3</sub>COOH and H<sub>2</sub>O with a volume ratio of 3:3:23:1). The chemical etching was done in order to increase the defect density of the silica surface, thereby reducing the diffusion of the clusters on the surface, which can cause their agglom-

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eration. For the oxidation experiments, the backsides of the samples were exposed to a hot Pt-filament and, at the same time, the chamber was filled with molecular oxygen ( $8 \times 10^{-5}$  mbar). This method is known to create atomic oxygen environments, even though the existence of excited molecular oxygen species cannot be completely excluded [16]. After these atomic oxygen treatments, no Pt could be detected using XPS. The exposure time of each sample to atomic oxygen was 30 min.

For the creation of Au cluster anions, a magnetron-sputter-source, originally designed by Prof. Haberland's group in the University of Freiburg, Germany, was used [17]. After extracting the ion beam into a vacuum, the cluster anions were accelerated to 1.5 kV. Mass separation was done by means of a  $30^\circ$  sector magnet with a resolution of about  $m/\Delta m = 20$ . In front of the sample, the clusters were decelerated to the desired deposition energy by applying the corresponding voltage to the sample. The number of clusters deposited on the surface can be counted by measuring the sample current during deposition. Almost identical Au coverages to those of previous studies were used [15]. All the clusters were soft-landed on the surface, i.e., a kinetic energy of less than 0.6 eV per atom was used (most of the clusters had a kinetic energy less than 0.2 eV per atom during deposition). For the deposition of the Au cluster anions on the substrate, about  $\sim 30$  min were required. The measured sample current was about 0.4 nA during deposition.  $2 \times 10^{12}$  clusters were deposited on each sample. Considering that the diameter of the area of the cluster deposition is estimated to be 3 mm, the cluster density is suggested to be about  $3 \times 10^{13}$  cluster per  $\text{cm}^2$ .

After the clusters had been deposited on the surface, the samples were immersed into the distilled water or 0.1 M NaOH (purity: 99%) aqueous solution for 10 min. After these treatments, the samples were immediately inserted into the vacuum system, and oxidation/reduction experiments and XPS-analyses were performed.

### 3. Results and discussion

As has been previously reported,  $\text{Au}_5$  and  $\text{Au}_7$  clusters on silica show high inertness towards oxidation upon exposure to atomic oxygen, whereas other clusters smaller than  $\text{Au}_{11}$  partially form Au-oxide under the same conditions [15]. The formation of the Au-oxide is evidenced by the appearance of additional peaks at higher binding energies than those of Au(O) in the Au 4f level spectra (Fig. 1, data taken from Ref. [15]) [18].

In Fig. 2, the Au 4f level spectra of the NaOH-treated Au cluster samples are displayed, which were obtained after exposure to atomic oxygen. In contrast to Fig. 1., in Fig. 2, the  $\text{Au}_5$  and  $\text{Au}_7$  clusters form large amounts of Au-oxide after their exposure to atomic oxygen, whereas the  $\text{Au}_6$  and  $\text{Au}_8$  clusters are more inert. There are two conclusions to be drawn from these results:

- (i) The oxidation rates still vary dramatically with each additional atom, meaning that the mono-dispersed clusters survived the treatment.
- (ii) For the cluster sizes studied herein, the even/odd pattern seems to be inverted. For the gas phase clusters, such behavior occurs if the charge state is altered (see below).

Obviously, the properties of the mass-selected Au clusters deposited on silica are considerably altered by the NaOH-treatment. The oxidized Au clusters can be partially reduced by 10000 L (Langmuir = mbar  $\times$  s) of CO at room temperature (Fig. 3), as is evident by comparing the relative amounts of Au-oxide in Figs. 2 and 3.

It is important to mention that when the samples containing  $\text{Au}_7$  and  $\text{Au}_8$  clusters are immersed into the distilled water for 5 min each, the unique chemical properties of these clusters are preserved:  $\text{Au}_7$  is still resistant towards the formation of Au-oxide,

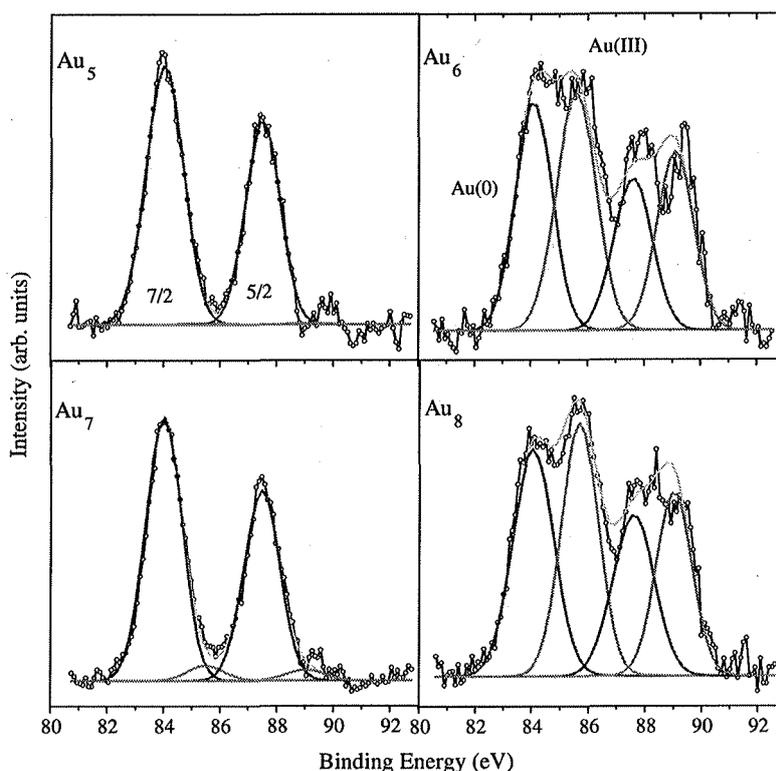


Fig. 1.  $\text{Au}_5$ – $\text{Au}_8$  clusters were deposited on Si wafers covered by native oxide layers under ultrahigh vacuum conditions, and subsequently exposed to atomic oxygen environments. After these treatments, Au 4f level spectrum of each sample was collected. The Au coverage for each sample is estimated to be less than 10%. The even/odd pattern is rather obvious here.

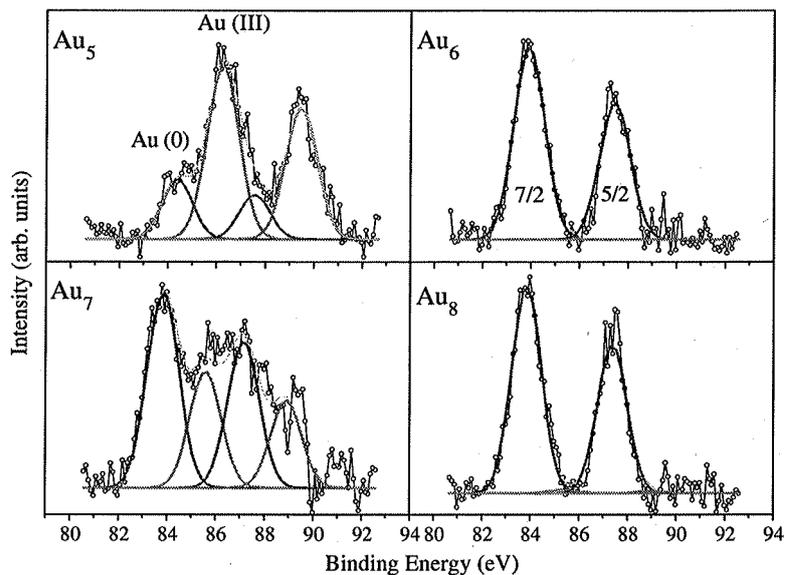


Fig. 2. The Au 4f level spectra were collected after the samples containing mass-selected and deposited Au clusters had been immersed to the 0.1 M NaOH solution and subsequently exposed to atomic oxygen under high-vacuum conditions. The even/odd pattern is inverted compared to that in Fig. 1.

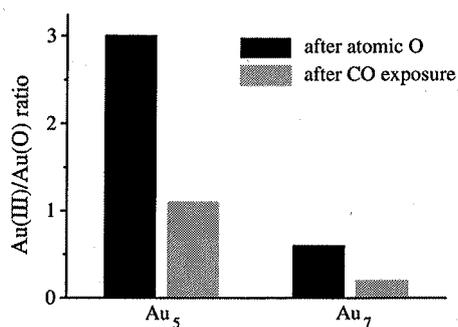
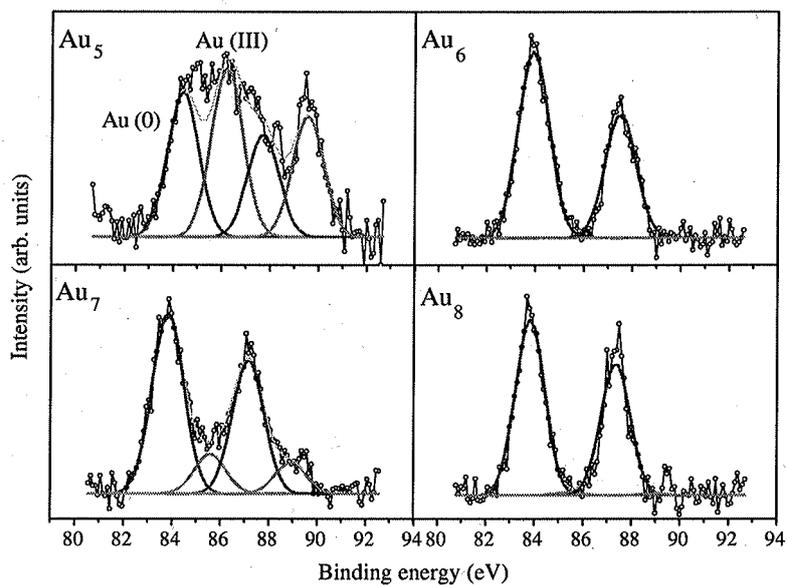
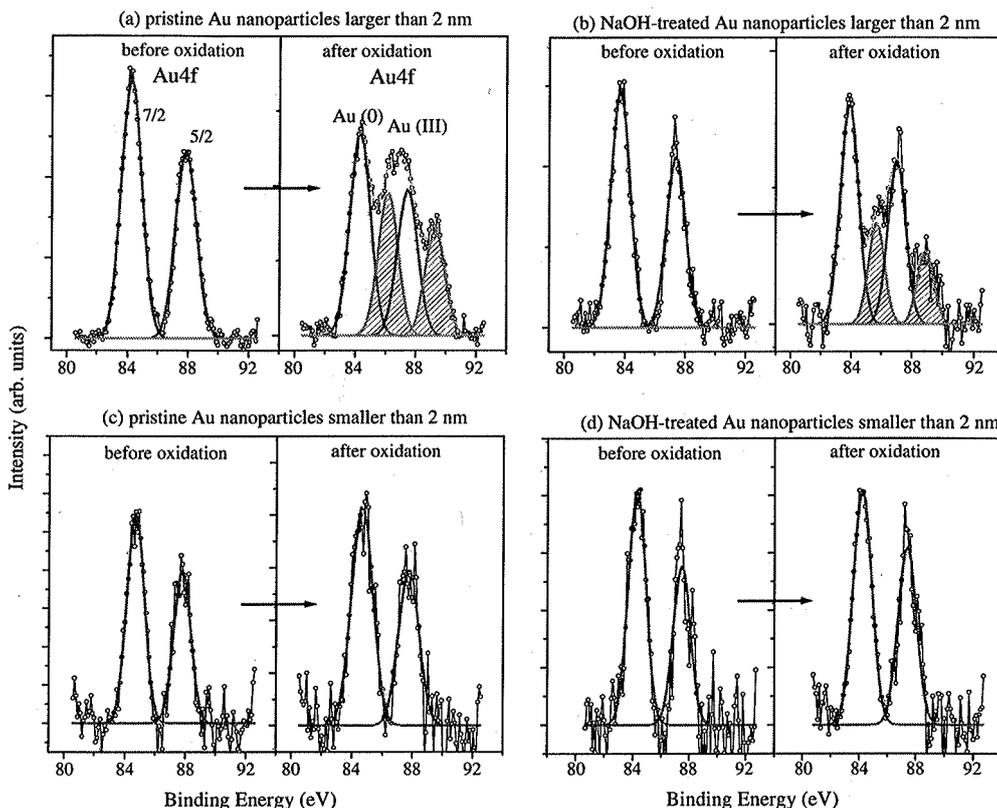


Fig. 3. The Au 4f level spectra were collected after the samples in Fig. 2 had been exposed to 3000 L of CO. In the bottom figure, the ratios of Au(III) to Au(O) of Au<sub>5</sub> and Au<sub>7</sub> before and after CO exposures are summarized. Exposure to CO results in partial reduction.



**Fig. 4.** Top: The Au 4f level spectra of pristine Au particles larger than 2 nm in width before and after atomic oxygen exposure. The same sample was immersed into the NaOH solution and then the Au 4f level spectra were taken before and after the atomic oxygen exposure. Bottom: The Au 4f level spectra of pristine Au particles smaller than 2 nm in width before and after atomic oxygen exposure. The same sample was immersed into the NaOH solution and then the Au 4f level spectra were taken before and after the atomic oxygen exposure.

whereas  $\text{Au}_8$  readily forms Au-oxide by reacting with atomic oxygen even after the water-treatment. Air exposures without water treatment showed the same results as those of the water treatments. This result shows that the chemical properties of Au are modified by the solutes of the solution, rather than by water. According to recent theoretical studies, water does only weakly adsorb on Au nanoparticles without dissociation [19].

For comparison, Au islands grown by evaporating Au atoms on the same substrate were exposed to atomic oxygen, and subsequently, the Au 4f level spectra were collected (Fig. 4). We have previously shown that Au islands larger than  $\sim 2$  nm in lateral size can be readily oxidized by exposure to atomic oxygen, whereas smaller ones are more inert towards oxidation (Fig. 4) [20]. After immersing the samples containing larger and smaller Au islands into the aqueous NaOH-solution, the larger islands were still able to be oxidized by atomic oxygen, whereas the smaller islands remained inert, i.e., after the NaOH-treatment, no significant change of the chemical properties of the Au islands was detected. Our result show that the chemical properties of the mass-selected Au clusters smaller than nine atoms deposited on silica surfaces are unique and much different from those of the larger particles. Moreover, we also show that the chemical properties of clusters smaller than 9 atoms can be modified more easily by additional treatment than those of larger particles.

The origin of the modification of the oxidation behaviors of Au clusters by NaOH is not well understood yet. The reason for the  $\text{Au}_5$  and  $\text{Au}_7$  clusters being more inert towards oxidation before the NaOH-treatment is still questionable as well. In the gas phase studies, a similar inversion of the even-odd pattern in the chemical

behavior caused by the attachment of a single OH group to an Au cluster was found [21]. This phenomenon was attributed to a single electron transfer from an Au cluster to an OH group. One can imagine that the attachment of a single OH or Na to an Au cluster on silica can result in an opposite even-odd pattern in the oxidation behavior; however, it is not likely that our samples experienced a one-electron change of the valence electronic structure by simply immersing them into NaOH solution. It is possible that silica, NaOH (possibly contaminated by  $\text{Na}_2\text{CO}_3$ ) and Au form a mixed complex. It can also be postulated that the deposition of Na, -OH groups, NaOH or  $\text{Na}_2\text{CO}_3$  on the silica surface alters the work function of the surface significantly, modifying the metal-support charge transfer and, thus, changing the electronic structure of the deposited clusters. In addition, modification of the morphology by OH groups can also come into play. The origin of the alteration of the chemical properties of Au by NaOH is a subject of future studies.

#### 4. Conclusion

We demonstrate that the chemical properties of individual tiny clusters consisting of 5–8 Au atoms are preserved upon exposing to ambient conditions and immersing into distilled water. In addition, properties of these clusters can be modified more easily by additional treatment, as compared to those of larger particles. The Au clusters deposited on silica surfaces are immersed into water and aqueous NaOH solutions and, after these treatments under realistic conditions, the chemical properties of the clusters remain unique, non-scalable and size-selective. The control of the cluster size on

an atom-by-atom basis can be important for obtaining high activity in heterogeneous catalysis, not only in UHV, but also under realistic conditions. Tuning the catalytic properties of metal clusters by adding or abstracting a single atom from a cluster in various reactions will be studied in the future.

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