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Chemistry of mass-selected Au clusters deposited on sputter-damaged HOPG surfaces: The unique properties of Au_8 clusters

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Abstract

Mass-selected Au clusters consisting of less than 10 atoms were deposited on sputter-damaged HOPG surfaces. Oxidation and reduction of the Au clusters were studied using X-ray photoelectron spectroscopy. Only Au_8 can be significantly oxidized by oxygen and reduced by CO, and the result is different from those for Au clusters deposited on silica. The chemical properties of mass-selected clusters are dissimilar to those of Au nanoparticles larger ~2–3 nm. STM studies on Au_7 suggest that Au_7 exists as individual clusters rather than forming larger particles on the surface.

Since the discovery of high catalytic activity of Au nanoparticles, which is known to be inert as bulk, a large number of experimental and theoretical studies has been devoted for a better understanding of the size effects in heterogeneous catalysis of supported metal nanoparticles [1,2]. Among those studies, deposition of mass-selected clusters on various substrates opened new insights into the size-selectivity of heterogeneous catalysis. Chemical properties were suggested to change with every additional atom [3,4]. Using scanning tunneling microscopy (STM), and cavity ring-down spectroscopy, deposited Au clusters on oxide surfaces were shown not to fragment or sinter [5,6].

Here, oxidation and reduction of Au clusters deposited on sputter-damaged HOPG were studied. On silica surfaces, our previous studies found Au_n with $n = 5$ and 7 to be resistant towards oxidation, whereas other clusters can readily be oxidized and reduced by O and CO [7]. In contrast, on sputtered HOPG, only Au_8 was found to be active towards the oxidation/reduction, suggesting importance of metal-support interaction for chemistry of deposited clusters [7]. Diverse chemical properties of mass-selected clusters are demonstrated, which cannot be observed from larger Au nanoparticles formed on the same substrate, addressing importance of the ability to control the cluster size on an atom-by-atom basis in order to tune catalytic activity [8].

Details of the experimental set-up and oxidation/reduction experiments can be found elsewhere [7]. The HOPG samples were outgassed at 800 K for longer than 12 h. Subsequently, the HOPG surfaces were sputtered with a kinetic energy of Ar ions of 0.5 keV for 20 s, in order to create defect sites for stabilizing Au clusters on the surface (sample current during sputtering = 1–2 μA). The defect density is estimated to be less than 2% of a monolayer based on our previous results of Au island formation on similarly sputtered HOPG surface by deposition of Au atoms at room temperature [8,9]. For oxidation of the Au clusters, the chamber was backfilled by O_2 with a pressure of 8×10^{-5} Torr, and at the same time, a hot filament was placed in the near of the sample (referred to as 'atomic oxygen') [10]. The exposure time of each sample to atomic oxygen was 30 min. This method is known to create atomic

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oxygen environments, even though existence of the excited molecular oxygen species cannot be completely excluded [10]. Our previous studies on reactions between atomic oxygen and Au nanoparticles suggest that our oxidation condition is as severe as the oxygen plasma used in other groups [11,12]. Without hot Pt-filament, no oxidation of Au clusters could be observed.

High-temperature oxygen treatment of a sputtered HOPG surface leads to the formation of large pits, resulting from etching of carbon atoms by oxygen [13]. It is not clear yet, whether the carbon surface is significantly etched by atomic oxygen at room temperature or not. We found increase of the C–O and C=O bonds upon atomic oxygen exposure [14]. The difference between our experimental conditions and those used in Ref. [13] might be that we used a lower sample temperature so that accumulation of oxygen on the sputtered HOPG surface instead of etching of surface carbon atoms by CO or CO_2 formation can be found in our case.

Fig. 1 demonstrates the Au 4f core level spectra of Au_n clusters deposited on sputter-damaged HOPG surfaces. 1×10^{13} clusters were deposited on the surface (the surface area for the deposition of clusters is estimated to be $\sim 3 \times 3\ mm^2$), estimated by measuring sample current during deposition. The background pressure of the chamber was better than 1×10^{-9} mbar during deposition, and the

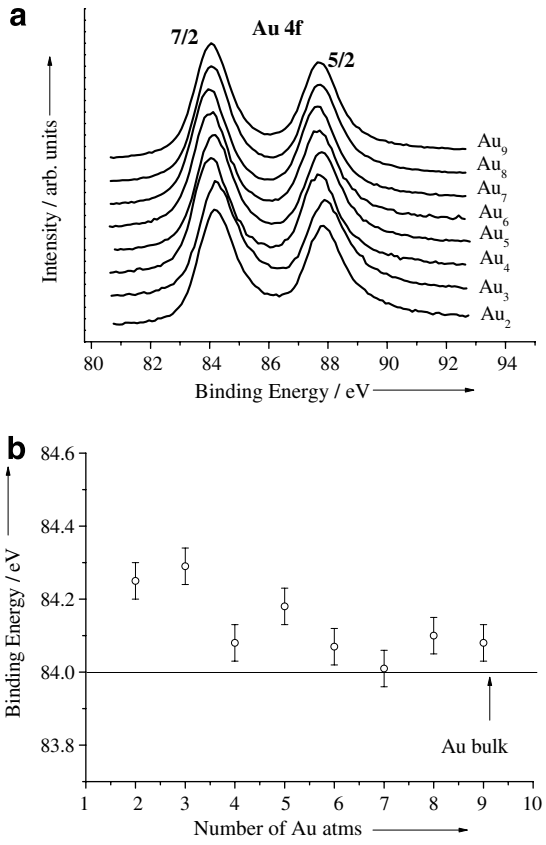

Fig. 1. Au 4f states of the deposited Au clusters on sputter-damaged HOPG. (a) Au 4f states of Au_n with $n = 2$–9. (b) Summary of the Au $4f_{7/2}$ binding energies as a function of cluster size.

kinetic energy of a cluster during deposition was lower than 0.2 eV per atom. Since no information is available for the sticking probability of Au clusters on sputter-damaged HOPG surfaces, the Au coverage cannot be precisely determined. Our XPS and also STM results are suggestive of an Au coverage of less than ~10% of a monolayer equivalent in case of Au_7. STM result also suggests that the sputtered surface is still quite flat, i.e. the surface consists of relatively flat terraces with point defects. The size dependent changes of the Au $4f_{7/2}$ binding energies are also summarized in Fig. 1, in which almost bulk-like binding energies of the Au 4f levels were observed. This result is in line with our previous data on Au nanoparticles on sputtered HOPG [9].

Au clusters on HOPG were exposed to atomic oxygen environments and subsequently, the Au 4f spectra were collected. When the Au 4f spectra of the bare Au_n/HOPG surfaces in Fig. 1 are compared to the data of the respective Au_n/HOPG samples acquired after atomic oxygen exposure in Fig. 2, the following can be found: for all clusters with one exception, only minor changes are observed after exposure to atomic oxygen. Only Au_8 clusters are strongly oxidized, evidenced by additional peaks at higher binding energies. For Au_2 and Au_3, the Au 4f peaks become slightly narrower after oxygen treatment. For Au_4, oxygen exposure induces a slight negative Au 4f level shift. For Au_n with $n = 5$–7, 9 no change in the Au 4f level can be found upon the oxygen treatment. It is important to note that no change in the metal core level does not necessarily indicate absence of Au–O formation.

When the deposited Au clusters exposed to atomic oxygen are subsequently reacted with CO (3000 L, $1\ L = 1 \times 10^{-6}\ Torr \times 1\ s$), changes of the Au 4f states can be found only for Au_4 and Au_8. For Au_4, Au 4f peaks shift to the higher binding energy side, recovering the original Au 4f binding energies. The distinct Au(III) states appeared after oxygen treatment of deposited Au_8 clusters are completely removed by CO exposure.

The O 1s spectra collected from the samples of Fig. 2 are displayed in Fig. 3. The interpretation of the O 1s spectra is rather complicated: the sputter-damaged HOPG takes some oxygen, forming C–O and C=O species. These two different oxygen species bound to carbon show the O 1s states at 531 and 533 eV, respectively [8,15]. An O 1s spectrum obtained from an oxygen-treated sputtered HOPG surface is displayed in Fig. 3 (squares in the frame of Au_8) for comparison. In addition, various Au–O species may exist, which are electronically and also chemically different. We have previously shown that oxygen treatment of Au nanoparticles on sputtered HOPG surfaces results in formation of at least two electronically and chemically different oxygen species bound to Au [8,12]. Although the assignment of the O 1s spectra is complicated, the data in Fig. 3 clearly show that the chemical properties of the Au_n/HOPG surfaces are very sensitive to the size of the clusters deposited. Only for $n = 8$ a pronounced change indicating oxidation of Au is clearly observed. The results in Fig. 3 can be summarized as below:

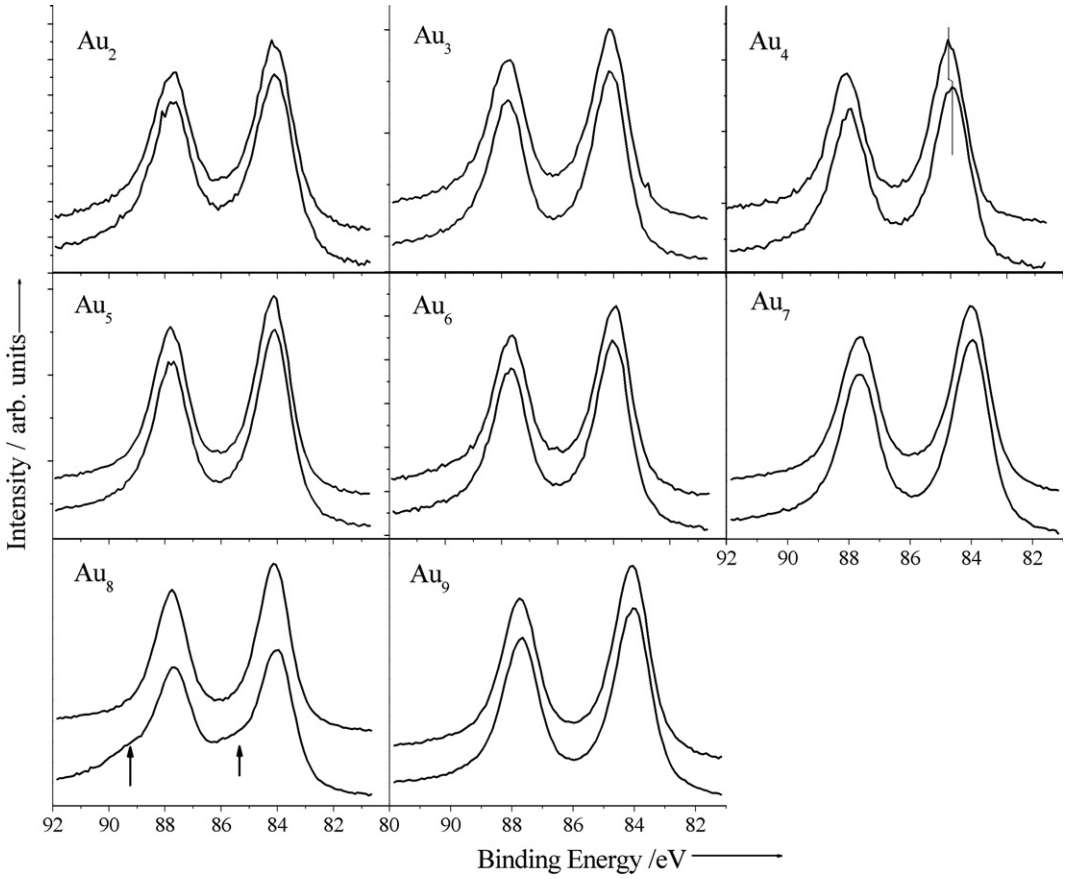

Fig. 2. The Au 4f spectra of the deposited Au_n clusters with $n = 2$–9 after atomic oxygen exposure (first spectrum of each graph from the bottom), and after subsequent CO exposure are displayed.

(i) For $n = 3, 7, 9$, a broad peak centered at ~533 eV can be observed in the O 1s spectra after exposing the surfaces to atomic oxygen environments. For these clusters, a subsequent CO exposure does not result in any change of the O 1s and Au 4f spectra. Since the O 1s state at 533 eV is more pronounced than in the case of the oxygen-treated bare sputtered HOPG surface, the 533 eV peak for these samples should mostly be related to the oxygen species attached to Au, which is inert towards CO-oxidation. The nature of this inactive oxygen species is not clear. Oxygen species can be inert towards CO-oxidation either due to the fact that oxygen occupies the same adsorption site as CO, inhibiting the Langmuir–Hinshelwood type CO-oxidation, or oxygen has a too high binding energy [11]. Formation of carbonate species by the reaction between Au, oxygen and carbon from substrate may be also one possible explanation for the existence of inert oxygen species of Au [14]. Since this oxygen species does not lead to the core level shift, the Au–O bond nature should be rather covalent than highly ionic.

(ii) For $n = 2, 6$, a peak centered at 533 eV with a shoulder at 531 eV can be found in the O 1s spectra. The absolute intensities of the O 1s spectra of these samples are larger than that of the bare sputtered HOPG surface after the same oxygen treatment. No CO-oxidation takes place in this case.

(iii) For Au_5, the relative intensity of the shoulder at 531 eV with respect to other peaks becomes larger than in other cases mentioned above. Here again, no indication for CO-oxidation can be observed.

(iv) For Au_4, formation of Au–O species upon oxygen treatment and removal of some oxygen (characterized by the O 1s state at 530 eV) by CO can be observed in the O 1s spectrum, even though most of oxygen remains unreacted. The Au 4f spectra in Fig. 2 also show negative and positive shifts by O and CO treatments, in line with the O 1s data in Fig. 3.

(v) For Au_8, the shoulder at 530 eV is more pronounced, which is reduced by CO. The O 1s peak at 530 eV can be assigned to oxygen atoms attached to Au(III). After exposing the oxidized Au_8 clusters to CO, the O 1s spectrum becomes identical to that of the bare substrate.

We have shown that Au_5 and Au_7 on silica are inert towards oxidation, whereas other Au clusters smaller than Au_{11} are able to be oxidized and reduced by O/CO [7]. In the present work, Au_8 was found to be the only cluster,

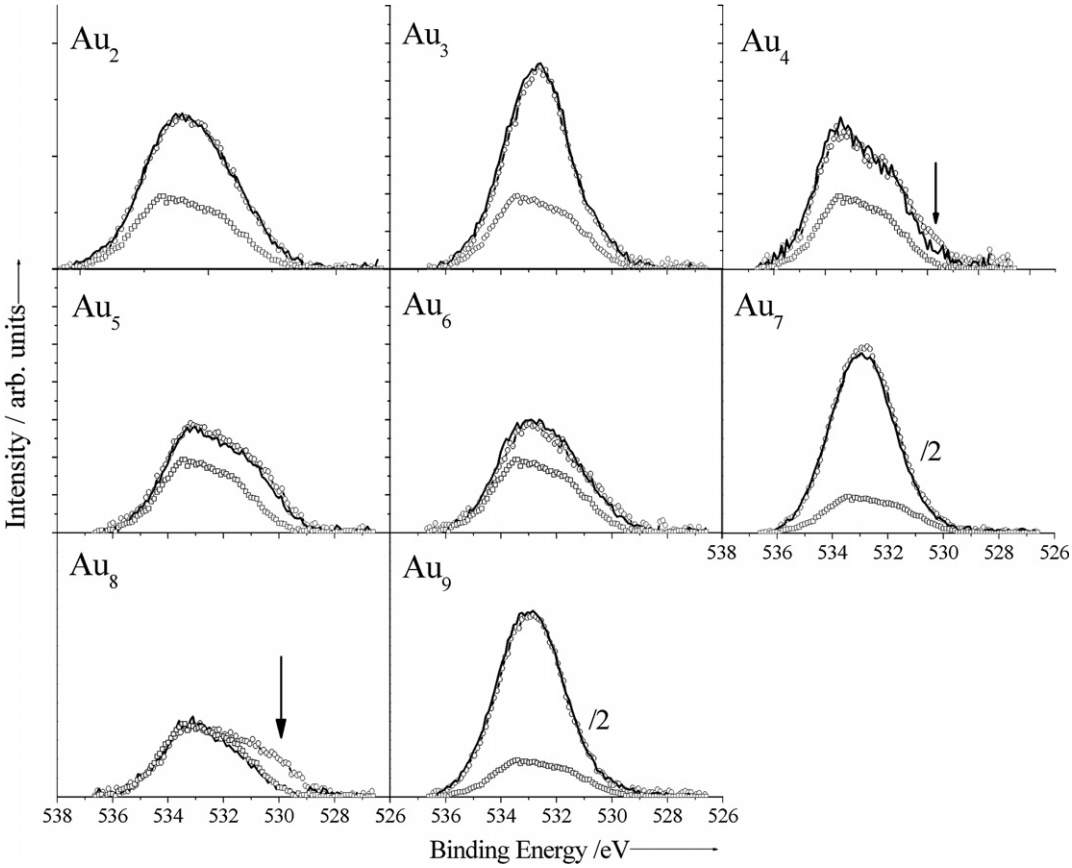

Fig. 3. O 1s spectra of the deposited Au_n clusters with $n = 2$–9 after atomic oxygen exposure (line with circles), and after subsequent CO exposure (solid) are displayed. A O 1s spectrum collected from a bare sputtered HOPG exposed to the same amount of atomic oxygen is shown for comparison (line with squares). After exposing the oxidized Au_8/HOPG to CO, the O 1s spectrum becomes nearly identical to that of O/HOPG. Absolute intensities of all the O 1s spectra shown here were normalized based on the C 1s spectrum of each sample. The *y*-scale of each spectrum has been normalized, so that the absolute intensities of different spectra can be directly compared. The intensities of the O 1s spectra of Au_7 and Au_9 and the respective spectra from bare O/HOPG were divided by 2.

showing a significant activity for the oxidation and reduction. We have shown that the chemical properties of deposited clusters are very sensitive to the substrate. Since Au nanoparticles on HOPG larger than 2–3 nm can form Au-oxide by the same oxygen treatment as used in the present work, which can be reduced by CO, one may argue that the Au_8 clusters sinter significantly forming larger particles instead of existing as individual clusters [8]. However, our O 1s spectra unambiguously show that the chemical properties of the mass-selected deposited clusters are very unique and much different from the larger Au nanoparticles: when larger Au nanoparticles are oxidized, two different oxygen species form, one of which is active towards CO-oxidation, and the other one is not [8]. In contrast, Au_8 forms exclusively active oxygen species as shown in Fig. 3. Accumulation of catalytically inactive oxygen species can poison the catalysts, and Au_8 on carbon may not experience this problem, which is different from other Au clusters and larger nanoparticles. This result shows that optimization of catalytic activity can be achieved by the control of the cluster size on an atomic-by-atom basis.

Besides Au_8, other clusters studied here also show chemical properties different from those of larger Au nanoparticles [8]. Au_4 clusters show negative and positive shifts of the Au 4f states without Au(III) species formation upon O/CO exposure, which has never been observed for larger Au nanoparticles on HOPG. Note that relatively small Au nanoparticles show a negative core level shift upon oxygen treatment, yet no positive shift upon CO exposure [12]. Furthermore, the O 1s spectra of Au_n with $n = 2$, 3, 6, 7, 9 showing a pronounced feature centered at 533 eV, are much dissimilar to the respective data from larger Au nanoparticles (Fig. 3) [8]. For Au_5, the O 1s state centered at 530–531 eV is not reduced by CO, whereas for larger Au nanoparticles, the O 1s state at the same binding energy range is essentially removed by CO at room temperature. All these results demonstrate unique chemical properties of the mass-selected deposited Au clusters, and indicative of the mass-selected clusters not sintering but rather surviving as individual clusters on the surface after deposition on the sputter-damaged HOPG surfaces.

The idea of an Au cluster surviving as an individual entity is also supported by our STM results. As shown in

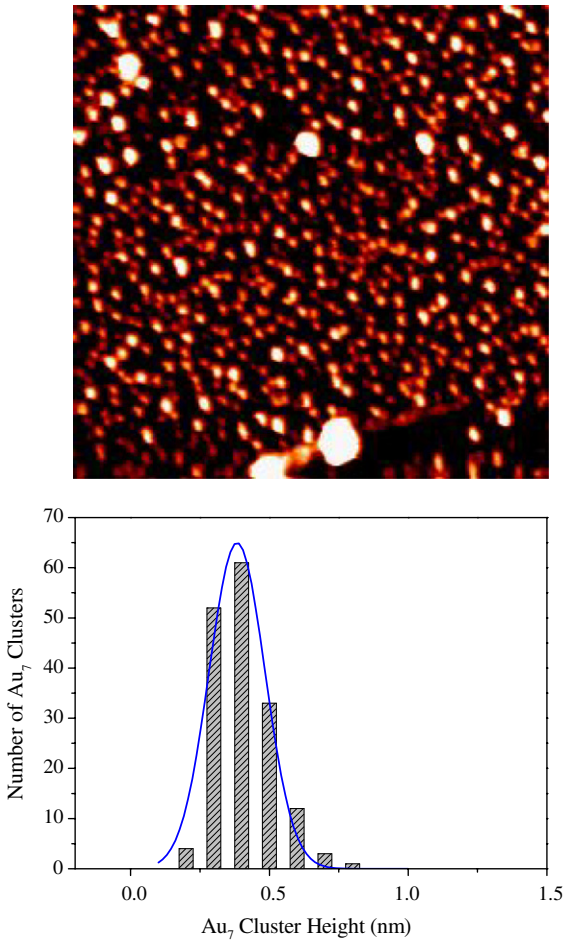

Fig. 4. STM images of Au_7 deposited on sputter-damaged HOPG (150 nm × 150 nm, 1.61 V, 0.7 nA). Statistics of the cluster height is shown in the bottom image. The cluster height is 0.38 ± 0.1 nm.

Fig. 4, the STM image of Au_7 clusters deposited on sputtered HOPG exhibits many particles distributed on the surface with a very narrow size distribution. The average particle height is about 0.4 nm, corresponding to two atomic layers. The particle diameter is subject to the particle-tip convolution and therefore cannot be determined precisely; one may roughly suggest that the cluster diameter in Fig. 4 should be smaller than 2 nm. In the STM image of Fig. 4, a few larger particles can be found near to vacant areas, which we tentatively suggest to be due to the agglomeration of the clusters induced by the STM tip.

In summary, we found a significant size-dependent change of the chemical properties of mass-selected Au clusters deposited on sputtered HOPG. The chemical properties of mass-selected clusters consisting of less than 10 atoms are found to be much different from those of larger nanoparticles. Results from Au clusters deposited on carbon and silica demonstrate importance of metal-support interactions for tuning chemical activity of metal clusters.

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