Nanoparticle size is an important parameter affecting the catalytic behavior of nanostructured metal/oxide catalysts.\(^1\)\(^-\)\(^3\) Heiz et al. showed that the catalytic activity of \(\text{Au}_n\) \((n \leq 20)\) on MgO (100) films in the oxidation of CO was highest for \(\text{Au}_1\) and that \(\text{Au}_4\) was the smallest cluster which exhibited catalytic behavior.\(^1\) A similar investigation at room temperature involving \(\text{Au}_n\) \((n = 1-4, 7)\) supported on rutile TiO\(_2\)(110) by Anderson et al. suggests a strong size dependence in the oxidation of CO, with significant reactivity for clusters as small as \(\text{Au}_4\).\(^4\) While these two studies show a strong dependence of the catalytic activity on the deposited cluster size, the eventual size (and shape) of the metal clusters once they were deposited on the substrate was not measured directly in either case. It is well-known from scanning tunneling microscopy (STM) images of evaporated Au and Ag, assumed to be monomeric in the vapor phase, that these metals sinter upon reaching the surface of TiO\(_2\) to form larger clusters \((\geq 10\) atoms\).\(^5\)\(^-\)\(^10\) Additionally, the size distribution of clusters formed by depositing size-selected metal clusters on a substrate is often not well defined due to cluster diffusion and aggregation at low landing energies (a few eV/atom) or fragmentation and implantation at higher landing energies \((>10\) eV/atom\), respectively.\(^11\)\(^-\)\(^12\) Thus, determining whether the mass-selected clusters deposited softly on a surface maintain their size after deposition is an important goal of research on catalysis by nanoclusters.\(^13\) In the experiments described here, we use ultrahigh vacuum (UHV) STM to image the shape and size of the \(\text{Au}_n^+\) \((n = 1-8)\) deposited with low kinetic energy on a single crystal rutile TiO\(_2\)(110)-\((1 \times 1)\) surface at room temperature. The atomic resolution STM images allow us to directly identify the shapes, adsorption sites, and size distributions of the adsorbed clusters.

The size-selected clusters of \(\text{Au}_{n+}\) \((n = 1-8)\) are created using laser desorption from a gold rod illuminated with a pulsed YAG laser beam (532 nm, 500 mJ/pulse max power), producing a gold plasma. Positive ion clusters are extracted and accelerated through a skimmer in an argon carrier gas. The clusters are then focused, further accelerated, and passed between the pole faces of a magnet, where the size-selection process occurs. The mass resolution is \(\sim 10\)%.

Figure 1A shows large clusters on the surface resulting from the deposition of \(\text{Au}_{1+}\). A Magnified region of this image, shown in Figure 1a, reveals that there are no small clusters on surface. These observations indicate that Au monomers are highly mobile on the rutile surface, leading to aggregation into larger clusters. Figure 2a shows a broad height distribution for the deposition of Au atoms with an average value of 4.3 Å (Figure 3) and a standard deviation of 1.7 Å. This result is similar to that observed from Au vapor deposition in the coverage range of 0.013–0.08 ML.\(^18\) These sintered clusters have an average lateral diameter of \(14.8 \pm 3.9\) Å, which indicates that an average cluster contains on the order of tens of atoms.

Figure 1B shows an STM image taken after the deposition of \(\text{Au}_{1+}\). In contrast to the monomer deposition, large, sintered clusters are rarely observed. Instead, a high density of very small clusters is seen, and most of them are located above the 5-fold coordinated titanium (5c-Ti) rows (Figure 1b). The height distribution is much narrower than that found in the case of the \(\text{Au}_1\) deposition, as shown in Figure 2b. The clusters on the surface have an average height of 1.6 Å (Figure 3) and a standard deviation of 0.5 Å, suggesting that the adsorbed \(\text{Au}_2\) clusters lay flat on the surface. The nearly uniform height and the preference for certain adsorption sites suggest that the adsorbed \(\text{Au}_2\) clusters remain intact during landing.

Only small clusters are observed for \(\text{Au}_{3+}\) (Figure 1C), and they are found mainly above the 5c-Ti rows (Figure 1c). The height distribution is narrow (Figure 2c) with an average value of 1.5 Å (Figure 3) and a standard deviation of 0.2 Å. As in the case of dimer deposition, this suggests that the adsorbed \(\text{Au}_3\) are intact and that the clusters lay flat on the surface.

Small clusters were also observed after the deposition of \(\text{Au}_{4+}\) (see Figure 1D and 1d). The height distribution for \(\text{Au}_4\) clusters is shown in Figure 2d with an average height of 1.7 Å (Figure 3) and a standard deviation of 0.2 Å, suggesting that adsorbed \(\text{Au}_4\) lays flat on the surface. The shape distribution of the \(\text{Au}_4\) clusters on the surface is also interesting. The dominant shape is the two-lobe structure shown in Figure 1d. The center of the two lobes is always observed on a bridging O row. The average distance between the two lobes is about 7 Å (given the 5c-Ti row spacing of 6.5 Å, suggesting a quasi-linear structure, possibly with an elongated central Au–Au bond). The unique shape and sharp size distribution (Figure 2d) resulting from the deposition of \(\text{Au}_4\) suggest the clusters remain intact on the surface.

Figure 1E shows small clusters resulting from the deposition of \(\text{Au}_{5+}\). Most features are located over the 5c-Ti rows, as shown in Figure 1e. The height distribution is narrower than that of \(\text{Au}_1\), but wider than that of \(\text{Au}_2, \text{Au}_3, \text{and Au}_4\) (Figure 2e). The clusters have an average height of 2.6 ± 0.6 Å (Figure 3), suggesting that adsorbed \(\text{Au}_5\) unlike \(\text{Au}_2, \text{Au}_3, \text{and Au}_4\) is either strongly buckled or consists of two atomic layers.

Figure 1F and 1f shows features resulting from the deposition of \(\text{Au}_{6+}\) clusters. Most features are located over the 5c-Ti rows.
Their size distribution (Figure 2f) has an average height of 2.3 ± 0.7 Å (Figure 3) and is similar to that of Au₅, suggesting a buckled or a bilayer structure on the surface.

The result from the deposition of Au₇⁺ is shown in Figure 1G and 1g. The height distribution (Figure 2g) shows an average height of 2.8 ± 0.7 Å (Figure 3) for these clusters, which is similar to that obtained for both Au₅ and Au₆. This suggests that the Au₇ clusters adopt a three-dimensional structure on surface. Most of the Au₇ clusters are located above the bridging oxygen rows (Figure 1g), which is different from both the Au₅ and Au₆ clusters. The unique adsorption site and slightly different height suggest the presence of intact Au₇ clusters on the surface.

Figures 1H and 1h show features resulting from deposition of Au₈⁺ clusters. The height distribution (Figure 2h) gives an average height of 2.7 ± 0.9 Å (Figure 3) for these clusters. This suggests that the Au₈ clusters also adopt a three-dimensional structure on the surface with a similar average height as Au₅, Au₆, and Au₇. The high-resolution STM image of Au₈ in the inset of Figure 1H shows that a small percentage (<5% of clusters) of the deposited Au₈ clusters dissociate to pairs of the two-lobed Au₄ species, which appear particularly stable on the TiO₂(110) surface. No other cluster dissociations are observed for the systems reported here.

The results presented here are consistent with a number of earlier studies and provide some new, unexpected and important information. Soft-landing gold atoms lead to rapid sintering and formation of globules with an average height consistent with four atomic layers. Earlier STM studies on titania with larger coverages from evaporative gold sources indicated significant sintering and forma-

Figure 1. STM images 140 Å × 140 Å (uppercase letters) and 50 Å × 50 Å (lowercase letters) of the same surfaces, respectively. The bright spots are the clusters. The bright stripes are the 5-fold coordinated Ti atom (5c-Ti) rows separated by 6.5 Å by the bridging oxygen rows, which are dark. The dim spots that appear on the bridging oxygen rows are bridging oxygen vacancies. (A/a) The TiO₂ surface after the deposition of Au₁. (B/b) The same for Au₂. (C/c) The same for Au₃. (D/d) The same for Au₄. (E/e) The same for Au₅. (F/f) The same for Au₆. (G/g) The same for Au₇. (H/h) The same for Au₈. The scale of the inset in H is 65 Å × 75 Å.

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The surface can have two effects on the gold cluster. First, electron transfer can occur from the surface to the cluster. This effect would favor planar structures based on gas-phase results. Second, the surface can specifically ligate the cluster. The primary ligation sites are the bridging oxygen atoms, separated by 6.5 Å between rows. The tetramer is the smallest cluster able to span across two adjacent rows and then only if a quasi-linear structure is invoked, a structure consistent with the two-lobed image we observe for Au₄. This result suggests that surface ligation is driving cluster structure since the linear form of Au₈ is not favored by theory. Recent results on both silver and gold cluster cations indicate that gas-phase ligation can induce structural change consistent with this observation. The fact that the 2-d to 3-d transition occurs at Au₉ may reflect that the fifth gold atom is not needed for maximal ligation and begins to form a second layer in the cluster. The addition of the sixth and seventh gold atoms to the cluster continues the trend.

The importance of cluster—surface ligation is supported by the fact that the STM images observed were stable over several days and did not change with repeated scans by the STM tip. In addition, we observe a density of oxygen vacancies between clusters for all sizes studied here (see the high-resolution images in Figure 1a—1h). Generally, the density of oxygen vacancies is much higher than what would be expected if each cluster were bound to one or more oxygen vacancies. There is no direct evidence that these defects are required for binding the clusters. In fact, the lack of mobility of clusters as small as the dimer indicates that strong binding occurs with the stoichiometric surface.

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References


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